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Security of Industrial Water Supply and Management

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Security of Industrial Water Supply and Management

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Series C: Environmental Security

Security of Industrial Water Supply and Management

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Preface

The United Nations Secretariat predicts that by 2050, 5.5 billion of a projected 9–10 billion people worldwide will live in urban areas, an increase from three billion today. This tremendous increase in urban population will bring with it corresponding increase in various water needs of urban living. The agricultural activity that would be needed to support this additional population will also enhance water needs for irrigation, cleaning, and processing. Additionally the tremendous volumes of wastewater that will be generated both in urban and rural areas will create challenging pollution abatement issues. As it stands today, poor people from many parts of the world don't have access to clean water, causing widespread diseases that are avoidable. Even developed countries, in which most of the citizens live in an urban setting anyway, are experiencing water scarcity. For instance, in the western United States, restrictions on water use are frequently enforced. With the advent of advanced semiconductor processing and nanotechnology, in which water use is not only huge but the purity requirement is stiffer than potable drinking water, we see public outcry against such industry siting. Chemistry Nobelist Smalley[1] stated that safe water availability is the second most important sustainability issue of the twenty-first century, the foremost being energy. The UN Millennium Development Goals[2] also cited water as a top priority. Thus the security of water supply for industry is intertwined with needs of potable and agricultural use, and in its totality is an environmental security issue of great magnitude.

Clean and safe water is already in short supply in much of the world. Water-stressed areas are beginning to appear in developed nations as well, such as the desert southwest of the United States. U.S. EPA[3] predicts that by 2025 two-third of the world population will experience moderate to high water stress and half of the world population will face real constraints in their water supplies. Several of the NATO and

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[1] R. Smalley, Future Global Energy Prosperity. The Terawatt Challenge, Symposium X – Frontiers of Materials Research, Materials Research Society Fall Meeting, Boston, MA, Dec 2, 2004. http://cohesion.rice.edu/NaturalSciences/Smalley/emplibrary/120204%20MRS%20

[2] UN Millennium Development Goals, 2000, http://www.un.org/millenniumgoals/

[3] U.S. Environmental Protection Agency, Guidelines for Water Reuse, Report number EPA/625/R-04/108, September 2004, Washington, DC.

Mediterranean partnership countries are water-stressed, such as France, Spain, Italy, Germany, Ukraine, Belgium, the Netherlands, Hungary, Israel, Tunisia, Morocco, and Jordan. Water stress is defined as per capita renewable freshwater availability of less than 1,700 m^3 $year^{-1}$. In the future the number of countries experiencing water stress will surely increase owing to economic development that has accelerated everywhere, bringing with it the increasing demand for potable water for the urbanites as well as clean water for increasing industrial uses. Overall use of fresh water is highest in the agricultural sector and accounts for about two-thirds of world consumption,[4] the rest being consumed by industry and the domestic sectors. Much of this water, especially in arid areas, is fossil water, typically found in underground aquifers. The withdrawal of fossil water, which takes thousands of years to form, is much like the extraction of fossil fuels, in the sense that this water withdrawal rate is higher than recharge, and hence the level in most aquifers is dropping fast. The "renewable" water on the other hand is readily available from surface sources, such as lakes and rivers, but they mostly require treatment the costs of which are not insignificant. This cost consists mostly of capital cost of equipment and the cost of energy to remove unwanted impurities or pollutants from raw water. There is thus a water-energy nexus that presents a barrier to affordable fresh water production. The need for affordable technologies thus cannot be over-emphasized in this context.

Industrial Water

Some industry sectors use large amounts of fresh water in their production processes. For instance 0.375 m^3 water is used to produce paper of $1 value, 2650 U.S. gallons to produce one pound of coffee, and 400 gal to produce one pound of sugar. For decades non-agricultural industries have been a major source of polluted wastewater discharges into receiving water streams and lakes. Even though this industry is not the major consumer of fresh water and it represents point sources, it gets most of the public scrutiny and hence is subject to regulatory actions. Point sources are easy to identify, are transparent to the public eye, and treatment solutions depend primarily on innovative technologies. In contrast, non-point sources, such as agricultural practices, are more difficult to control technologically. Worldwide 300 million tons of synthetic chemical products, equivalent to 50 kg per person, are annually discharged to water from industrial activities.[5] This discharge represents threats to aquatic life as well as human health. Water shortage not only poses environmental and disease proliferation threats but also can lead to international and intra-national frictions causing security threats. For instance, in early February 2007, the State of Montana in the U.S. sued the State of Wyoming in a Federal Court seeking restraint on excessive withdrawal by the latter from a river used by both states.

Water shortages, increase of salinity in aquifer water, and other pressing demands create problems for industrial growth. There are some specific drivers for restoring

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[4] Science, v313, 25 August 2006, p 1067.

[5] Science, 313, 2006, August 2006, p.1072.

industrial wastewater for reuse. First, water demands are increasing with increasing industrialization and urbanization. Second, discharging polluted industrial wastewater creates public health and environmental protection concerns. Many times these polluted wastewaters contain highly toxic chemicals such as complex organics, heavy metals, and pathogens, which threaten human health and the ecosystems. In many countries, environmental laws and regulations have forced industries to treat wastewaters before they can be discharged. In the future the net fresh water intake by industry will fall because of the constraints on water availability, making it mandatory for industry to adopt recycle/reuse programs. This is beginning to happen already, for instance, the Japanese industries recycle an estimated 80% of their water requirement.[6] Much more progress is required overall and this progress needs to be geographically well distributed. Exchange of best practices and results of current research in industrial wastewater recycle/reuse is therefore of utmost importance for facilitating such knowledge sharing and transfer.

Scope of Industrial Wastewater Recycle and Reuse

These waters, depending on industry, do have specific requirements. Cooling water for power plants and chemical plants, for instance, require soft water that would not cause scaling of the heat transfer surfaces and therefore cannot have those inorganic chemicals, which can be tolerated in drinking water. Technologies for assuring the appropriate levels of impurities can be different for different applications in industry. Because of this feature, each industrial sector can improve its water efficiency by being nearly independent of other sources.

Decoupling much of the industrial need for cooling and processing from municipal water infrastructure goes a long way in making water secure and sustainable for industry while boosting economic development for the welfare of people. The ideal solution is zero industrial water discharge based on wastewater treatment directed to reuse.

There are many industry sectors with large needs for fresh water. The ones with the most importance are power industry with boiler water needs, chemical plants and petroleum refineries with cooling water needs; pulp and paper, chemicals, textiles, automotive, electronic, food and beverage, metal processing, and mining industries. Currently wastewaters from many of these industries in the developed world cannot be discharged into receiving water streams without treatment. Many industrial plants are already practicing recycling wastewater after treatment, for environmental and economic reasons, although not always for the original uses. In the future, for an industrial plant to be self-sufficient in water, wastewater needs to be treated to the standards for reuse, and not merely recycled to uses for which the water quality requirements are lower. This is the biggest technological challenge for a sustainable industrial water reuse.

The eco-industrial park concept of consolidating disparate industries in one location for the purpose of waste minimization and waste exchange (the so-called

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[6] Science, 313, 2006, August 2006, p.1071.

industrial ecology) has a natural fit for an industrial wastewater infrastructure in which water need for each plant can be met with inter-plant transfer with or without treatment, resulting in no polluted water discharge to the environment from the park as a whole. The technological challenge for intra-park water management is new and is of interest to several such parks that have been developed in some countries, such as Singapore, Denmark, and Israel.

Technology Considerations

The task that technology designers face to meet the industrial wastewater challenge is to affordably produce clean water for recycling and reusing in manufacturing processes. There are various technologies that can technically handle the purity standards of a specific industry. The cost requirement however puts additional constraints on technologies. Thus not all technologies shown to work in the laboratory will either be scalable to large applications or be cost effective. Typical pollutants in industrial wastewater are salinity, inorganic ions such as sodium, trace elements, chlorine residuals, nutrients, dissolved organics, particulates, nitrogenous chemicals, and microbials. Removal of all pollutants to predetermined levels is not a necessity for each specific application, but all of these waters that will come in contact with humans either directly or in aerosol form must be free of toxic substances and pathogens. Each successful application of a recycle/reuse water technology at the same time, however, needs to assure that the residuals do not become a significant environmental problem.

Although the specifications for water needs are different for different industry, spanning from inexpensive cooling water for power plants to very expensive ultrapure water for semiconductor processing, there are general technology trends that are of interest. This is where the water-energy nexus plays out. Large multi-national companies such as General Electric, Siemens Water Technology, Lyonnaise, Veolia, Mekorot, and Suez realize the importance of this nexus and have heavily invested in technology development for exploiting economic opportunities to meet the ensuing demands and satisfy a need. Distillation and evaporation are thermal approaches that are attractive for certain geographical locations where energy is inexpensive. Even here much development in heat integration has made it possible to increase thermal efficiency by recycling thermal energy. Conventional filtration can be useful in certain applications, specifically to remove particulates. Solar thermal energy has also been researched for evaporative water purification in areas where solar exposure is high. Membrane technologies are also coming on strong for a variety of industrial water applications for producing cleaner water from sources contaminated by inorganics (reverse osmosis and membrane distillation), by particulates (microfiltration), by larger organic molecules and polymers (ultrafiltration), and by volatile and semivolatile organic compounds (pervaporation). Membranes are generally recognized as low-energy approaches. Sorption technologies may be particularly attractive in situations where the impurity or pollutant level is very low (in parts per million range). Sorption includes absorption as well as adsorption.

Typically sorption is carried out in packed beds, and when pollutant breakthrough occurs, the beds are regenerated for reuse. Packed beds suffer from potential channeling, i.e. the water flows preferentially through low resistance channels formed in the bed and consequently all parts of the bed are not used. There could also be high pressure drop developed leading to bed malfunction or to increased pumping costs. There can be alternate designs that exploit the benefits of the best features of sorption without the ill effects of pressure drop or channeling. The state-of-the-art of these new sorption designs is of great interest in water industrial recycle/reuse. In addition to these known approaches, there may be other innovative technologies, such as biological treatment processes, that may be potentially useful.

This book, "**Security of Industrial Water Supply and Management**" is a **select** collection of chapters chosen from presentations made at a NATO-SPS Advanced Research Workshop held in Ankara, Turkey, September 2010 focused on "industrial water reuse and recycle". All the chapters have been reviewed by referees and revised. The book is organized to contain the chapters on "Water Integration for Recycling and Recovery in Process Industry", "Water Networks in Theory and Practice", "Water Conservation by Mass Integration Approach", "Technological Advances in Industrial Water Safety and Security", and how to do "Water Footprinting". Then in the following chapters "Water Reuse Strategies" in textile, paper, sugar, iron and steel industries are covered. In the last part of the book "Industrial Wastewater Reuse Applications" in several countries are discussed. The total number of chapters in the book is 16.

This published book containing the proceedings will be a reference work useful to academicians, Government and industry professionals alike. In addition, the process designers will find the book useful for devising specific solutions in the context of the overall water picture in the human community.

We would like to thank the authors of the chapters who generously shared their knowledge with the readers of this book. Special thanks are due to reviewers of the chapters. The support and the funding provided by the NATO Science for Peace and Security are greatly appreciated.

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Contents

Chapter 1
Water Integration for Recycling and Recovery in Process Industry

Jiří Jaromír Klemeš, Hon Loong Lam, and Dominic Chwan Yee Foo

Abstract Water is widely used in the process industries as an important raw material. It is also frequently used in the heating and cooling utility systems. Strict requirements for the products quality and the associated safety issues in manufacturing contribute to large amounts of high-quality water being consumed by the process industry. Environmental regulations as well as the growing human population with improved quality of life have led to the growing demand of good quality water. These changes have increased the need for improved water management and wastewater minimisation. The adoption of water minimisation techniques can effectively reduce both the fresh water demand and subsequently the effluent generation in the process industry. This results in the reduced cost for fresh water acquisition and effluent treatment. This paper presents a graphical water integration method based on Water Pinch Analysis. This method locates various network targets prior to detailed design. A case study is given to demonstrate how to synthesise a water network for maximum water recovery with this method.

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Keywords Water minimisation • Water recycling and recovery • Water Pinch analysis • Process industry

1.1 Introduction

Water is used in most process industries for a wide range of applications. Industrial processes and systems using water are today being subjected to increasingly stringent environmental regulations relating to the discharge of effluents. As a result of growing population and its quality of life there is a growing demand for fresh water. The changes are taking place fast and the pace of these changes has increased the need for improved water management and wastewater minimisation. The adoption of water minimisation techniques can effectively reduce the fresh water demand of water-using processes considerably and subsequently reduce the amount of effluent generated. These results in reduced both the cost incurred in the acquisition of fresh water and the cost involved in the treatment of effluent streams.

Important methodologies that have been applied to the minimisation of water use and effluent generation have been listed by Klemeš and Perry [12]:

- The minimisation of water consumption by the efficient management and control of process operations.
- The optimisation of material and energy balances of processes by the application of advanced optimisation strategies aiming at waste reduction.
- The integration of optimisation and production planning techniques in conjunction with real-time plant measurements and control for product quality and minimisation of losses.
- The use of Process Integration techniques based on Pinch Analysis and Mathematical Optimisation.

In the processing industry, with its specific features, it is considered advisable to progress from the simplest measures – such as good housekeeping based on efficient management, control and maintenance – to more advanced methodologies. Food processing is not, in many cases, a continuous process running 7 days a week for the whole year, but one that is intermittent and highly dependent on the availability of the feed stock. Typical production campaigns occur in sugar, fruit juice or cereal processing plants. On the other hand, breweries are in operation on a continuous basis, but are batch processed. These features influence the investment in the processing plants and technologies adopted, including those involving water and waste minimisation and processing.

A summary of the main water use as well as water and wastewater minimisation, which are relevant for the processing industry was presented by Smith [20]:

1. *Process changes.* These include increasing the number of stages in an extraction processes that use water, changing from wet cooling towers to air coolers, improving energy efficiency to reduce steam demand, increasing condensate return from steam systems, etc. Under ‘process changes’ we can also add good housekeeping, which includes analysing and measuring water use and wastage,

reducing water wastage, cleaning operations, maintenance of equipment and daily work practices. It is also possible to decrease water consumption or replace some of the water-consuming operations, such as hazardous cleaning agents, chemicals and additives. Additionally, 'process changes' also include technology and topology alterations driven either by inspection findings or by the process optimisation, resulting from some modern process analysis methodologies and techniques – e.g. Process Integration/Pinch Technology. It is possible to adopt new technologies or replace equipment in order to reduce the generation of waste and increase the efficiency of the process.

2. *Reuse/Recycle.* This can occur when waste water is used directly in other operations or is recirculated, but only if the existing pollutants do not disturb the process. Maximum water reuse/recycle methodologies and methods to recycle water are discussed elsewhere in details [15], together with the opportunities to use recycled water used in processing.

Hoekstra [10] defined the water footprint (WFP) as an indicator of direct and indirect water use, which is measured in terms of water volumes, consumed, evaporated and/or polluted. The WFP includes consumptive use of virtual green, blue and grey water. The virtual green water content of a product is the volume of rainwater that evaporated during the production process. For the process industry, it is mainly consumed by agricultural products, where it refers to the total rainwater evaporation from the field during the growing period of a crop. The virtual blue water content of a product is the volume of surface water or groundwater that evaporates as a result of production. An example includes the evaporation of irrigation water from a field, irrigation canals and storage reservoirs. The virtual grey water content of a product is the volume of water required to dilute pollutants to meet the water quality standards for reuse or discharge to the environment.

A water footprint (WFP) [11] can be calculated for any product or activity as long as the group of consumers and producers are well-defined. The WFP is a geographically and temporally explicit indicator. It shows volumes of water consumption and pollution and also referring specifically to the type of water use, as well as where and when the water was used.

The idea of water LCA (Life Cycle Assessment) has gained more interest after the introduction of the WFP [10, 11]. Considering water use along supply chains, the real water content of the product is generally negligible if compared to the virtual water content, which is the total fresh water being used at the various steps of product supply/production chains. Apart from being used as an ingredient in process preparation, most of the water use in processing industry is categorised as virtual water [15]. The most commonly found water-using operations include the following:

1. Heating – boiler, heat exchangers, etc.
2. Process water – cooling towers
3. Potable uses – offices, canteens, etc.
4. Washing – equipment, bottles, floor, vehicles, etc.
5. Rinsing – equipment, bottles, food materials, final products
6. Fire fighting
7. Transport medium

Table 1.1 Average virtual water content of some selected food products [10, 11]

Product	Virtual water (L)
1 glass of beer (250 mL)	75
1 glass of milk (200 mL)	200
1 cup of coffee (125 mL)	140
1 cup of tea (250 mL)	35
1 slice of bread (30 g)	40
1 slice of bread (30 g) with cheese (10 g)	90
1 potato (100 g)	25
1 apple (100 g)	70
1 glass of wine (125 mL)	120
1 glass of apple juice (200 mL)	190
1 glass of orange juice (200 mL)	170
1 bag of potato crisps (200 g)	185
1 egg (40 g)	135
1 hamburger (150 g)	2,400

The process industry is characterised as a high water consumer. For example, the annual total water consumption for the processing industry was estimated as 347.2 Mm^3 in Canada [4] and 455 Mm^3 in Germany [7]. Several studies [2, 23] have reported the virtual water for the production of some common products. The findings are summarised in Table 1.1.

In the industry, it is advisable to approach water recovery from the simplest measures based on efficient management (e.g. good housekeeping) to more advanced methodologies (e.g. process integration techniques). Process is not always operated in continuous mode, as it is intermittent and highly dependent on the availability of the feed stock.

A more comprehensive summary of water and wastewater minimisation application for the processing industry can be found in the books of Klemeš et al. [14], Smith [20] and most recently Klemeš et al. [15]:

1. *Process changes*. This enables the fundamental changes on unit operations that consume fresh water. This includes the increase of the number of stages in an extraction process to reduce its inherent water use, changing from wet cooling towers to air coolers, improved energy efficiency to reduce steam demand, increased condensate return from steam systems, as well as good housekeeping. For the latter, analysing and measuring water use and wastage, reducing water wastage, cleaning operations, maintenance of equipment and daily work practices are some good practices.
2. *Reuse/recycle/regeneration*. These options enable the recovery of wastewater in water-consuming operations. However, the presence of pollutants in the wastewater streams needs to be taken into consideration in order not to affect the water-using processes. This aspect will be discussed in greater detail in the following section.

Important methodologies for water minimisation are listed by Klemeš and Perry [12]:

1. The use of Water Pinch analysis techniques.
2. The use of mathematical optimisation techniques.
3. Minimisation of water consumption by efficient management and control of process operations.
4. The integration of optimisation and production planning techniques in conjunction with real-time plant measurements and control for product quality and minimisation of losses.

1.2 Water Minimisation with Water Pinch Analysis Technique

1.2.1 Introduction to Water Pinch Analysis

Pinch analysis was initiated for heat exchanger network synthesis, and subsequently has been extended into other energy integration works [5, 13, 16, 20]. Based on the analogy of heat and mass transfer, it was then extended for the synthesis of mass exchange network and a series of other mass integration applications [21]. Water Pinch analysis then emerged as a special case of mass integration, following the work of Wang and Smith [22]. This targeting technique was limited to the fixed load problem where water-using processes are modeled as mass transfer operations. Later work on water pinch analysis has been mainly dedicated to the fixed flow rate problem where flow rate requirement is the taken as the primary concern for water-using processes [3, 6, 9, 17, 19].

In the context of Water Pinch analysis, reuse means that the effluent from one unit is used in another unit and does not re-enter the unit where it has been previously used. On the other hand, recycle allows the effluent to re-enter the unit where it has been previously used. Besides, one may also utilise a regeneration unit (e.g. filter, stripper, etc.) to partially purify the water stream prior to reuse/recycle [22].

A typical Pinch analysis study consists of two stages, i.e. setting minimum fresh water and wastewater flow rates (often termed as targeting), followed by network design to achieve the targeted flow rates. It is worth mentioning that the focus on Water Pinch analysis is the targeting step. With targeting, we are able to set a baseline target to determine how well a reuse/recycle system can actually perform based on first principle. Knowing the targets ahead of design is possible to eliminate the query of "will there be a better design?" during any design exercise. Once the minimum flow-rate targets are established, a water network can be designed using any network design tools. An example of this approach demonstrated by Thevendiraraj et al. [21]. Various examples are published elsewhere [15].

To set the flow rate targets for water reuse/recycle, various graphical and tabulated targeting techniques may be employed. These include the Limiting Composite

Curves [22], Water Surplus Diagram [9], Material Recovery Pinch Diagram (MRPD) [6, 19], Cascade Analysis technique [17] and Source Composite Curve [1]. After the flow rate targets are identified, numerous techniques can be used to design a water network that achieves the flow rate targets, e.g. Water Grid Diagram [22] Nearest Neighbour Algorithm (NNA) [19]. In the following sections, the targeting technique of MRPD [6, 19] and NNA [19] is illustrated.

1.2.2 Flow Rate Targeting with Material Recovery Pinch Diagram

To construct a MRPD, material flow rates and loads of the individual process sink and source are to be considered. The steps required to construct the MRPD are given as follows [6, 19]:

1. Arrange water sinks (SKj) in descending order of quality level (concentration for mass-based water or property operator for property integration). Calculate the limiting load for each sink ($m_{\mathrm{SK}j}$) by multiplying its flow rate ($F_{\mathrm{SK}j}$) with its limiting quality level ($C_{\mathrm{SK}j}$).
2. Repeat step 1 for all water sources (SRi). In this case, the product of its flow rate ($F_{\mathrm{SR}i}$) with quality ($q_{\mathrm{SR}i}$) gives the load possessed by the source.
3. Plot the water sinks and sources on a load-versus-flow rate diagram with an descending order of their quality levels (given by the slope of the segment). Connect the tail of the individual sink/source segments to the arrowhead of another water sink/source to form a Composite Curve.
4. For pure fresh water source (i.e. with highest quality level), the Sink and Source Composite Curves are shifted horizontally until they just touch, with the Source Composite Curve lying below and to the right of the Sink Composite Curve, as shown Fig. 1.1a.
5. For impure fresh water source, the Source Composite Curve is shifted along an impure fresh locus (with slope correspond to its quality level) until it lies below and to the right of the Sink Composite Curve, as shown Fig. 1.1b.

The overlap area of the Sink and Source Composite Curves represents the maximum water recovery among all sinks and sources. The point where the two Composite Curves touch is termed as the material recovery pinch, which is the bottleneck for maximum recovery. The segment where the Sink Composite Curve extends to the left of the Source Composite Curve represents the minimum fresh water (F_{FW}) needed for the water network (to be purchased from external source); while region where the Source Composite Curve extends to the right of the Sink Composite Curve represents the minimum wastewater discharge (F_{WW}) from the network (for waste treatment before discharging to the environment). The minimum fresh water needed and the minimum wastewater generated by the network constitute the flow rate targets of the network, and are determined ahead of detailed design of the water network.

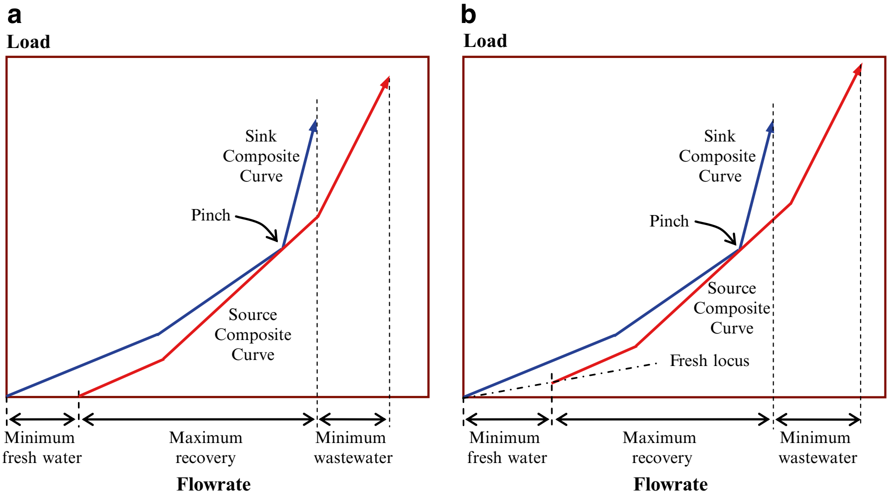

Fig. 1.1 MRPD for: (**a**) Pure fresh water source (no impurity); (**b**) Impure fresh water source [6]

1.2.3 Network Synthesis with Nearest Neighbor Algorithm

The basic principle of NNA in its simplest form may be stated as: "To satisfy a sink, the sources to be chosen are the nearest available neighbors to the sink in terms of its quality level" [19]. In other words, two sources that are having quality level just higher and just lower than the sink are mixed to satisfy the flow rate and load requirements of the latter. In this case, the required amounts of the two neighbor sources are dictated by the material balance equations. If the required flow rate of a source is not sufficient, then the total flow rate of that source is used completely and the next neighbor source is considered to satisfy the sink.

Steps for synthesising a maximum recovery network using NNA are summarised as follows [19]:

1. Arrange all water sinks and the sources (including fresh water) in a descending order of quality levels, respectively. Start the design process from candidates with highest quality level (i.e. lowest impurity concentration).
2. Match each sink with source(s) of the same quality level, if any are available.
3. Mix two sources i (with flow rate $F_{\mathrm{SR}i}$ and quality $q_{\mathrm{SR}i}$) and $i+1$ (with flow rate $F_{\mathrm{SR}i+1}$ and quality $q_{\mathrm{SR}i+1}$) to fulfil flow rate and load requirement of sink j (with flow rate $F_{\mathrm{SK}j}$ and quality $q_{\mathrm{SK}j}$). Note that the two sources have to possess quality level of just lower and just higher than that of the sink, i.e. *i.e.* $q_{\mathrm{SR}i} > q_{\mathrm{SK}j} > q_{\mathrm{SR}i+1}$. Note also that the available source candidates include the fresh resource, with its

flow rate F_{FW} obtained in the targeting stage. The flow rate for each source is calculated via the mass balance Eqs. 1.1 and 1.2:

$$F_{\mathrm{SR}i,\ \mathrm{SK}j} + F_{\mathrm{SR}i+1,\ \mathrm{SK}j} = F_{\mathrm{SK}j} \tag{1.1}$$

$$F_{\mathrm{SR}i,\ \mathrm{SK}j} q_i + F_{\mathrm{SR}i+1,\ \mathrm{SK}j} q_{i+1} = F_{\mathrm{SK}j} q_{\mathrm{SK}j} \tag{1.2}$$

Unutilised source(s) will be discharged as wastewater.

In the following section, MRPD is used to determine the minimum fresh water and wastewater flow rate targets for an industrial case study; while NNA is used to synthesise the water network that achieves that flow rate targets.

1.3 Industrial Case Study: Tyre-to-Fuel Process

Figure 1.2 shows a tyre-to-fuel process, where scrap tyres are converted into energy [5, 18]. Scrap tyres are shredded by high-pressure water-jet before they are fed to the pyrolysis reactor. The spent water from the shredding unit is then filtered, re-compressed and recycled. Wet cake from the filtration unit is sent to the solid waste handling section. To compensate water loss in the filter wet cake, fresh water is added to the recycled water loop at the water-jet compression station.

In the pyrolysis reactor, the shredded tyres are turned into oils and gaseous fuels. The oils are sent for separation and finishing to produce liquid transportation fuels. Off-gases from the reactor are sent to a condenser to separate its light oils content from the gaseous fuel. The condensate is sent to a decanter where a two-phase liquid is produced. The organic layer from the decanter is mixed with the liquid oil from the reactor for separation and finishing; while the aqueous layer forms the wastewater effluent. On the other hand, a waste gas emits from the finishing section and is sent

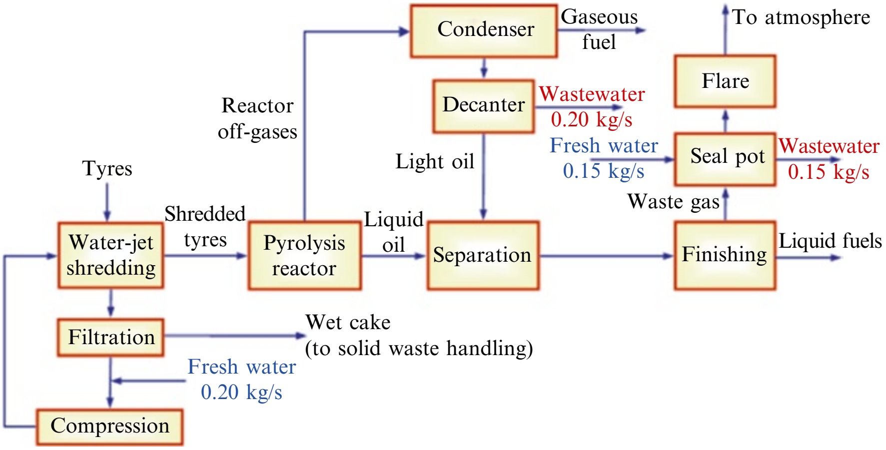

Fig. 1.2 Tyre-to-fuel process [18]

Table 1.2 Limiting water data for tyre-to-fuel case study

SKj	Sinks	F_{SKj} (kg s^{-1})	C_{SKj} (ppm)	m_{SKj} (mg s^{-1})
SK1	Seal-pot feed water	0.1	500	50
SK2	Water jet makeup	0.18	50	9
SRi	**Sources**	F_{SRi} (kg s^{-1})	C_{SRi} (ppm)	m_{SRi} (mg s^{-1})
SR1	Decanter wastewater	0.2	500	100
SR2	Seal-pot WW	0.1	200	20

for flare. A seal pot is used to prevent the back-propagation of fire from the flare, by passing through a water stream to form a buffer zone between the fire and the source of the flare gas.

Two wastewater streams are observed in the process, i.e. effluent from decanter and seal pot. These sources may be recovered to the process water sinks, i.e. seal pot and water-jet compression station, in order to reduce fresh water consumption. To evaluate the potential of water recovery, heavy organic content of the wastewater streams is the main impurity in concern. For the water sinks, the following constraints on feed flow rate and impurity concentration should be satisfied:

1. Seal pot:

$0.10 \leq$ Flow rate of feed water (kg s^{-1}) ≤ 0.20
$0 \leq$ Impurity concentration of feed water (ppm) ≤ 500

2. Make-up to water-jet compression station:

$0.18 \leq$ Flow rate of feed water (kg s^{-1}) ≤ 0.20
$0 \leq$ Impurity concentration of makeup water (ppm) ≤ 50

On the other hand, the water sources have the following operating condition:

1. Decanter:

Wastewater flow rate = 0.20 kg s^{-1}
Impurity concentration = 500 ppm

2. Seal pot:

Wastewater flow rate = flow rate of its water sink
Impurity concentration = 200 ppm

Following the appropriate data extraction principle [8], the limiting data for this process is summarised in Table 1.2. The third column of the table gives the impurity loads correspond to each water sinks and sources, given by the product of their flow rate and concentration. Following the above described procedure, the MRPD for the case study is shown in Fig. 1.3. For the Sink Composite Curve, segment for SK2 is first plotted, since it has lower concentration as compared to SK1. The vertical and horizontal distances of each segment correspond to its limiting load and flow rate. Similar steps are followed to generate the Source Composite Curve. As shown in Fig. 1.3, the minimum fresh water flow rate (F_{FW}) is determined as 0.135 kg s^{-1}; while the wastewater flow rate (F_{WW}) is 0.155 kg s^{-1}.

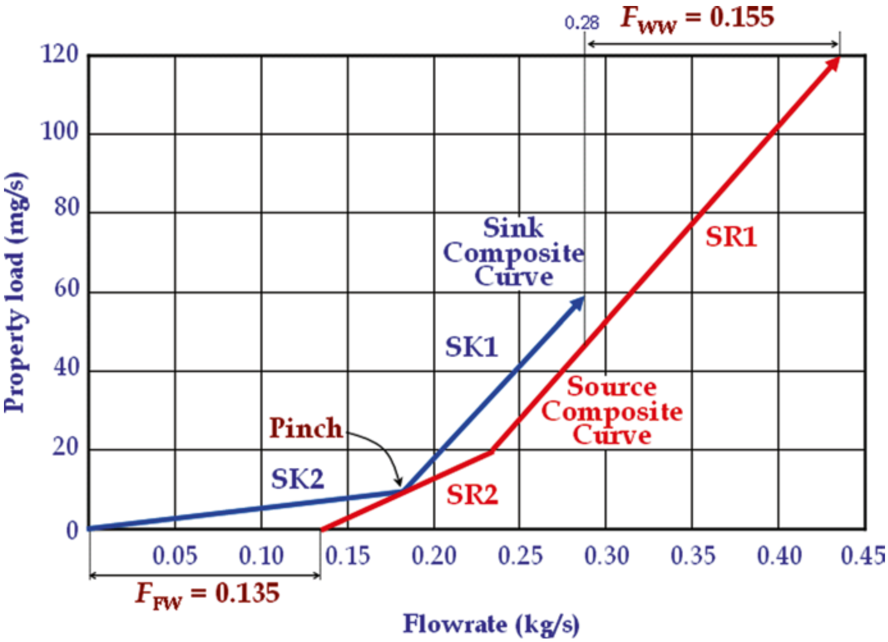

Fig. 1.3 MRPD for tyre-to-fuel process

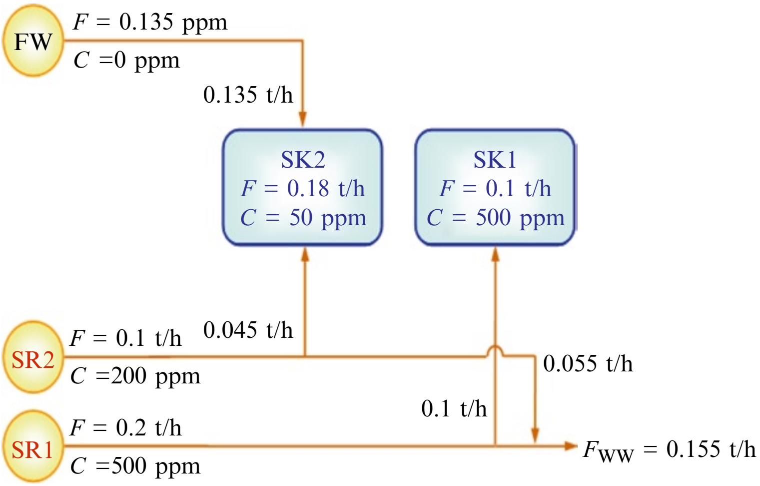

Fig. 1.4 Network design with NNA

A water network that achieves the flow rate targets is next synthesised using the NNA. This is shown in Fig. 1.4. As shown, the water sinks and sources are arranged in descending order of quality, i.e. from lowest to highest impurity concentration. We then start the design from the lowest concentration sink, i.e. SK2.

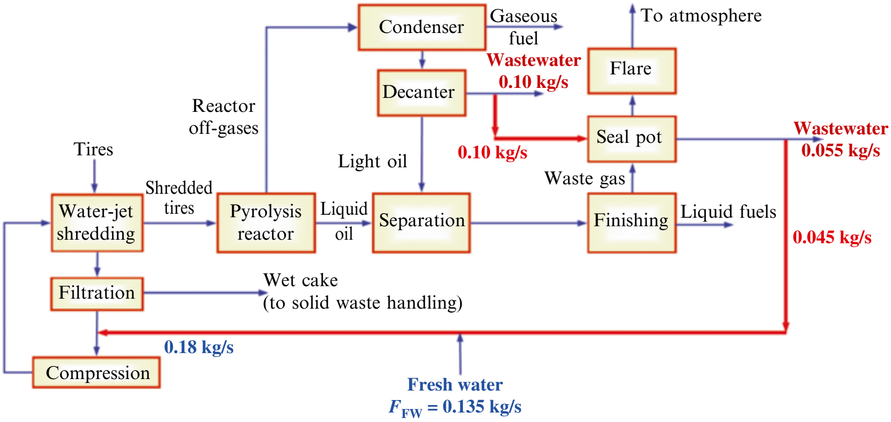

Fig. 1.5 Water network for tyre-to-fuel process

Since no source of the same concentration is found, fresh water and source SR2 are the neighbor candidates identified. Their allocation flow rates are calculated using Eqs. 1.1 and 1.2. On the other hand, since water SR1 has the same concentration as sink SK1, it may be recovered to SK1 directly. The water recovery scheme is displayed in the conventional process flow diagram as in Fig. 1.5. Note that the water recovery streams are indicated with thinker line. As shown, effluent from decanter is sent for reuse in the seal pot; while effluent of the latter is recycled to the water-jet compression station. Compared to the total water flow prior to water recovery, this represents a significant flow rate reduction of 51.8 and 48.3% for fresh water and wastewater.

1.4 Conclusion

This Chapter has been dealing with the methodology for water and wastewater minimisation by reuse, recovery and recycling. The methodology base on mass integration has been implemented. The mass integration, in this special case water integration has been base on Pich Technology. This field has been developing fast and every year some even more efficient approaches have been developed. The methodologies reviewed in this Chapter have been applied in the minimisation of water use and effluent generation in the process industry on many various industrial and agricultural applications.

One of these case studies – Tyre-to-Fuel Process – has been at least in shortened version included in this Chapter. The variety of the others is available it the referenced literature.

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Chapter 2
Water Networks – Theory and Practice

Peter Glavič and Miloš Bogataj

Abstract In this chapter, an extended strategy for efficient and applicable water minimization in process industries is presented. The strategy effectively incorporates environmental, organizational and economic aspects accompanying the water minimization issue. The strategy was tested and applied in several water minimization projects involving chemical and process industries. Four case studies are presented for illustration purpose. The results obtained indicate that in most cases water efficiency can be greatly improved by using technologically, environmentally and economically viable solutions.

Keywords Water networks • Heuristic rules • Water minimization strategies • Textile industry • Refineries • Petrochemical complex • Sugar beet plant • Brewery • Sankey diagram

2.1 Introduction

Covering over 70% of the Earth's surface, water is unquestionably the most precious natural resource that exists on our planet, as it is essential for everything that grows and prospers on our planet. Although recognizing this fact, we are slowly but persistently headed towards water scarcity/unavailability on a global level. There are several factors, which contribute to lowering the water availability, but we point out two of them, which in combination accelerate the dynamics of fresh water reduction.

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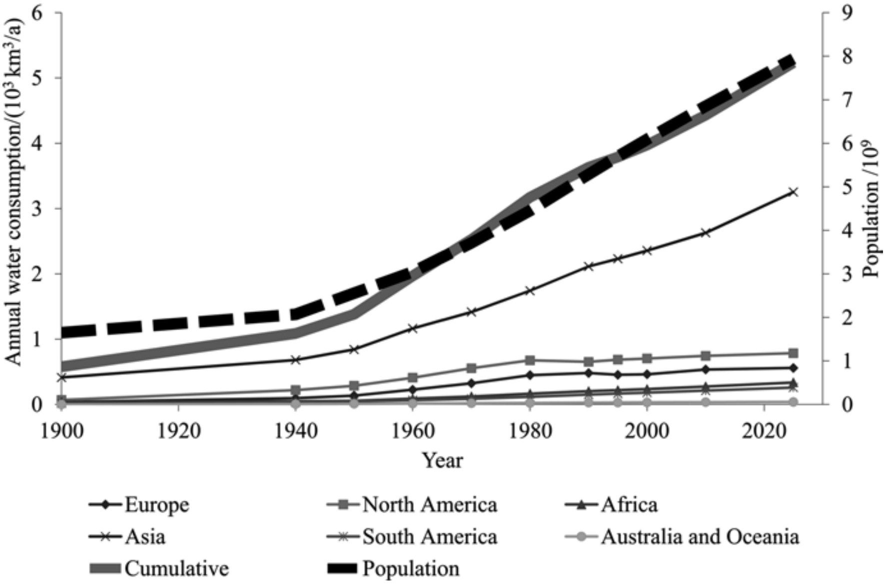


Fig. 2.1 Water consumption and population growths (Source: UNESCO [17]; US Census Bureau [18])

The first one is that we are dealing with constant volume of usable Earth's water; however, its consumption is constantly increasing (Fig. 2.1) mainly due to population growth. Taking into account the prognosis of Earth's population reaching some 9.3 billion by 2050 [18] the water availability per capita is expected to drop severely.

The second is the industrial pollution. Water is an important resource for industrial activity. For example, water is used extensively in petrochemical plants, refineries, in food, textile and pharmaceutical industry. It is needed for various purposes, e.g. product formulation, washing, cooling, high-purity water makeup systems, general plant service water, waste conveyance/transfer, potable/sanitary service, and fire protection.

After being used in these processes, the water is commonly polluted with various contaminants, making it unsuitable for release into the environment without an efficient and often expensive treatment.

It is estimated that approximately 22% of water resources are being consumed by the industry (Fig. 2.2a). Currently, approximately 59% of these are being utilized by the industry in high-income countries (Fig. 2.2b). In contrast, industrial water use contributes 10% to the total water use in low-to-middle income countries (Fig. 2.2c). These numbers will rise with industrial production. It is expected that industrial water consumption will increase from estimated 870 $(km)^3\ a^{-1}$ in the year 2010 to 1,170 $(km)^3\ a^{-1}$ in the year 2025, which equates to 25% increase over the period of just 15 a (years) [17].

These trends clearly indicate that in order to provide sufficient volume of quality water for the future generations, efficient actions focusing on minimizing the industrial water consumption and pollution need to be taken now.

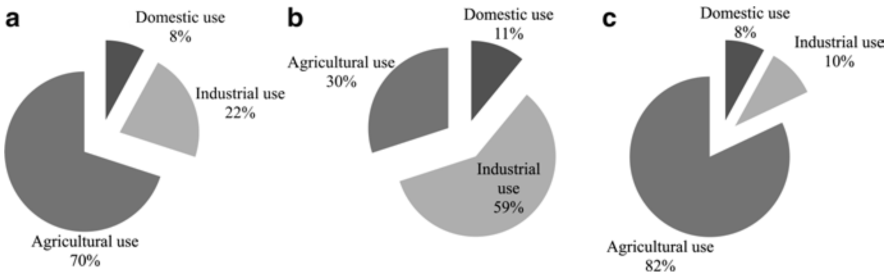


Fig. 2.2 Competing water users (**a**) World (**b**) High-income countries (**c**) Low- and middle-income countries (Source: UNESCO [16])

2.2 Why and How to Reduce Water Consumption?

Water scarcity and economic consideration are perhaps the most obvious reasons or in other words, the most powerful driving forces to push the profit-oriented process industry into considering and implementing the steps towards reducing the water consumption. However, there are also other reasons, such as wastewater discharge permit compliance, priority of legislation banning, "good neighbour" policy, etc. which certainly motivate the water-using industries towards improving their water efficiency.

At the beginning of the second decade of the twenty-first century, several methodologies for minimizing water consumption in process industries are readily available. Reduction in water usage can be achieved by implementing the solutions obtained by either one or a combination of the following methods:

- Good water management practice
- Heuristic rules
- Various techniques based on systematic approaches:
  - Conceptual design methodology based on Pinch Analysis, commonly considered as the Water Pinch methodology and/or
  - Mathematical programming.

2.2.1 Good Water Management Practice

Good water management practice is based on collecting process data by constant monitoring. Water flow rate (especially the inlet and discharge streams) should be constantly measured, thus providing the data for water mass balances. In addition, the quality of water streams should be monitored in order to assess the contamination of water. It is only through the comprehensive monitoring that the real *status-quo* regarding the water consumption can be evaluated. In addition, by carefully analyzing the mass balances, process failures, such as water leakages, spill-overs, underground water irruptions, etc. can be easily identified and prevented. Nonetheless, for achieving step-change improvements in water efficiency of a given process it is often needed to tackle the "water problem" with more elaborate methods.

2.2.2 Heuristic Rules

Heuristic rules are commonly obtained through experiences, testing and analysis of process data. These rules are valuable for *ad hoc* collection of potentially promising solutions and are often utilized in practical applications. An example of such a rule is to use a multistage (preferably counter-current) washing operation instead of a single stage one. Multistage washing operation utilizes the concept of water reuse, thus reducing the fresh water consumption, i.e. low quality water can be used in the initial stages, while high quality water can be used in the final stages. This rule can be generalized to: use water of the lowest allowable quality for any given operation. Other examples are replacing water cooling with air cooling, using lightly contaminated water to partially reduce fresh makeup water flow rate, improving control of boiler and cooling tower blow down, etc. [12].

2.2.3 Systematic Methodologies for Water Minimization

The water pinch methodology [9, 19, 20] is a graphical technique for reducing water consumption and wastewater generation through integration of water-using activities, or processes. It originates from mass exchanger network (MEN) synthesis method [4], which is analogous to that proposed by Linnhoff and co-workers for the design of heat exchanger networks [10, 11]. Similar to the latter it provides targets (minimum water consumption) ahead of the actual water network design. Once the targets are obtained, the water network is designed by a matching procedure.

The water pinch methodology is straightforward, simple and intuitive. Besides, it offers good insights into the problem itself as long as the problem is simple, i.e. water streams contain one contaminant at most. While sometimes there truly exists a water network with a single contaminant, or multiple contaminants can be lumped under certain circumstances into a single pseudo-contaminant, this is rarely the general case. When the assumption of a single contaminant does not apply, the water pinch methodology turns out to be somewhat cumbrous and impractical.

To avoid the above limitations we resort to approaches based on mathematical programming. The first systematic approach reported for water management problem was addressed as a water/wastewater allocation problem and formulated as a nonlinear optimization problem [13]. It took more than 10 years for the scientific/engineering community to recognize the potential and implications of this work. However, in the past two decades several methodologies and approaches based on mathematical programming, addressing various water minimization problems in

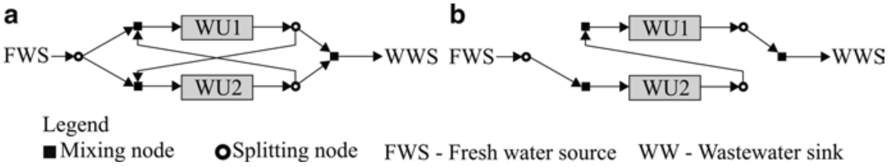


Fig. 2.3 Water network superstructure (**a**) Simple two-water-using unit superstructure (**b**) Potential solution, embedded in the superstructure

numerous ways were developed. For a comprehensive review and discussion on the pros and cons of these approaches, the reader is referred to Bagajewicz [1], Dunn and El-Halwagi [3], Foo [5] and Jeżowski [6]. Nonetheless, we present and outline some basic features.

Common to these approaches is a superstructural representation of the water network (Fig. 2.3). In the simplest case, water from a single fresh water source (FWS) is fed to each water-using unit (WU). These are interconnected with streams via mixing and splitting nodes. In addition, each water-using unit is connected to a wastewater sink (WWS). The superstructure of a given problem is than coded into a mathematical program.

Depending on how the water minimization problem is postulated, the mathematical program takes a form of:

(a) *Linear program*, e.g. single-contaminant network, simple linear models of water-using units
(b) *Nonlinear program*, e.g. multi-contaminant network, detailed nonlinear models of water-using units
(c) *Mixed-integer linear program*, in general the same as (a), but with a possibility of handling continuous (e.g. water flow rates) and discrete decisions (e.g. cost, associated with existing connections) simultaneously
(d) *Mixed-integer nonlinear program*, the most general approach, it can handle all of the above.

The major advantage of the approaches based on the mathematical programming is that the objectives such as water consumption, water cost, wastewater treatment cost, and capital investment can be taken into account simultaneously. It was proven that the solutions obtained using these approaches were often superior to the ones obtained by heuristic rules or the conceptual approach. However, a profound knowledge of advanced mathematics, modeling and computer programming is usually a necessity.

2.2.4 Beyond Water Minimization

In the previous section, we presented the approaches for water minimization. However, in many cases the picture is broader than the water minimization alone. Besides water, energy is among the most important utilities used in the process

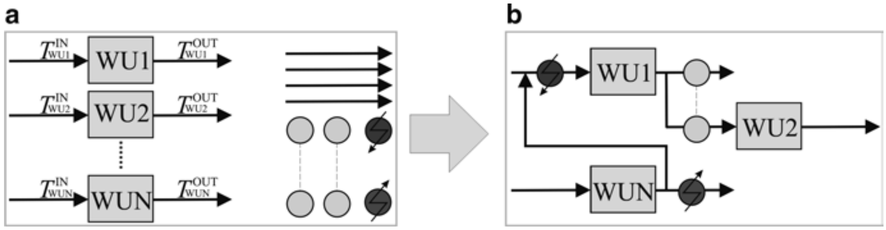


Fig. 2.4 Task of designing a heat-integrated water network

industries. Moreover, in certain situations significant volumes of water need to be heated up or cooled down to meet process operating conditions. Consequently, high energy consumption in the form of cooling and heating utilities is needed. In such cases, when both the quality and temperature of water are important, water and energy management need to be considered simultaneously. Surprisingly, despite all the enabling technologies simultaneous consideration of water allocation planning for generalized, multi-contaminant water networks and heat integration has been scarcely addressed.

The problem of heat-integrated water networks can be stated as follows (Fig. 2.4). Given is a set of water using processes, which require water of adequate quality (contaminant concentrations) and temperature. The inlet and outlet temperatures generally are different for each process using water. Also, given is a set of heat exchangers, coolers, heaters and a set of process streams (Fig. 2.4a). The task is to determine the optimal network of water stream interconnections among the processes and the corresponding heat exchanger network (Fig. 2.4b) by simultaneously optimizing annual operating costs (fresh water, regeneration, and utility costs), and depreciation (of e.g. heat exchangers).

Bogataj and Bagajewicz [2] presented the approach based on mathematical programming. The problem was formulated as a mixed-integer nonlinear program on a basis of a superstructure, which comprises a water network, and a heat exchanger network superstructure. The key concept of their approach is that the target temperatures of water streams can be achieved either by direct heat transfer (mixing of streams) or by indirect heat transfer (heat exchangers) or both. Their method can be used in synthesis of single- and multi-contaminant heat integrated water networks. The designs are obtained in a single step, and show fairly low topological complexity. The latter is highly desirable for industrial application.

With the methods presented, economic and environmental aspects of the sustainable development can be addressed in a sufficient way. By using the above approaches, we tend to produce solutions with minimal negative impacts on the environment and solutions, which are at the same time economically efficient. However, to comply fully with the sustainable development paradigm, the next milestone in the development of water minimization approaches should be the inclusion of the third – societal aspect (e.g. process safety, health hazards). The latter can be achieved by using indicators of sustainable development [7, 8].

2.2.5 Water Minimization Strategy

Evidently, many approaches can be used to tackle the water minimization problem, and there are many ways to address it. Each of the approaches has arguments in favor or against using them. Overall, water minimization is a challenging task, especially because criteria like technical ability, reliability, control, uncertainty, impact on process/product quality, secondary waste generation have to be considered in the final design. Based on our experiences we propose the strategy shown in Fig. 2.5.

After the need for water minimization is recognized, goals and working schedule are set. In addition, for the project to be successful a support from company's management team is vital even at this early stage.

Next, the assessment stage follows. It is crucial to obtain the most current, accurate, and overall representative data (i.e. water/wastewater quality, process demands, flow rates, etc.). The data are needed for calculating the water balances and for the subsequent design stage.

In the design stage, alternative solutions of the problem are generated. For this purpose, either an approach based on heuristics, or a systematic approach can be used. Preferably, the approaches should complement each other. After the alternatives (preliminary designs) are obtained, detailed technical and economical evaluations, as well as evaluations considering reliability, control, uncertainty, etc., are carried out.

Finally, the most promising alternative is selected and implemented.

2.3 Case Studies

Four case studies are presented in this section, all based on real, large-scale industrial processes. The approach used in all the case studies follows the flowchart given in Fig. 2.5 (see Sect. 2.2.5).

2.3.1 Textile Dyeing Mill

Textile industry is one of the largest water pollutants. Among various process operations common to textile industry, the dyeing processes and accompanying washing/rinsing operations are especially problematic, as vast volumes of water are utilized, mainly in a function of a solvent. What alarms the most is that the water needs to be of relatively high quality as it enters the dyeing mill, but is generally heavily loaded with organic and inorganic pollutants as it is being discharged to an on-site or municipal wastewater treatment facility. In this case study, various opportunities are proposed for reducing the water consumption in a textile dyeing mill.

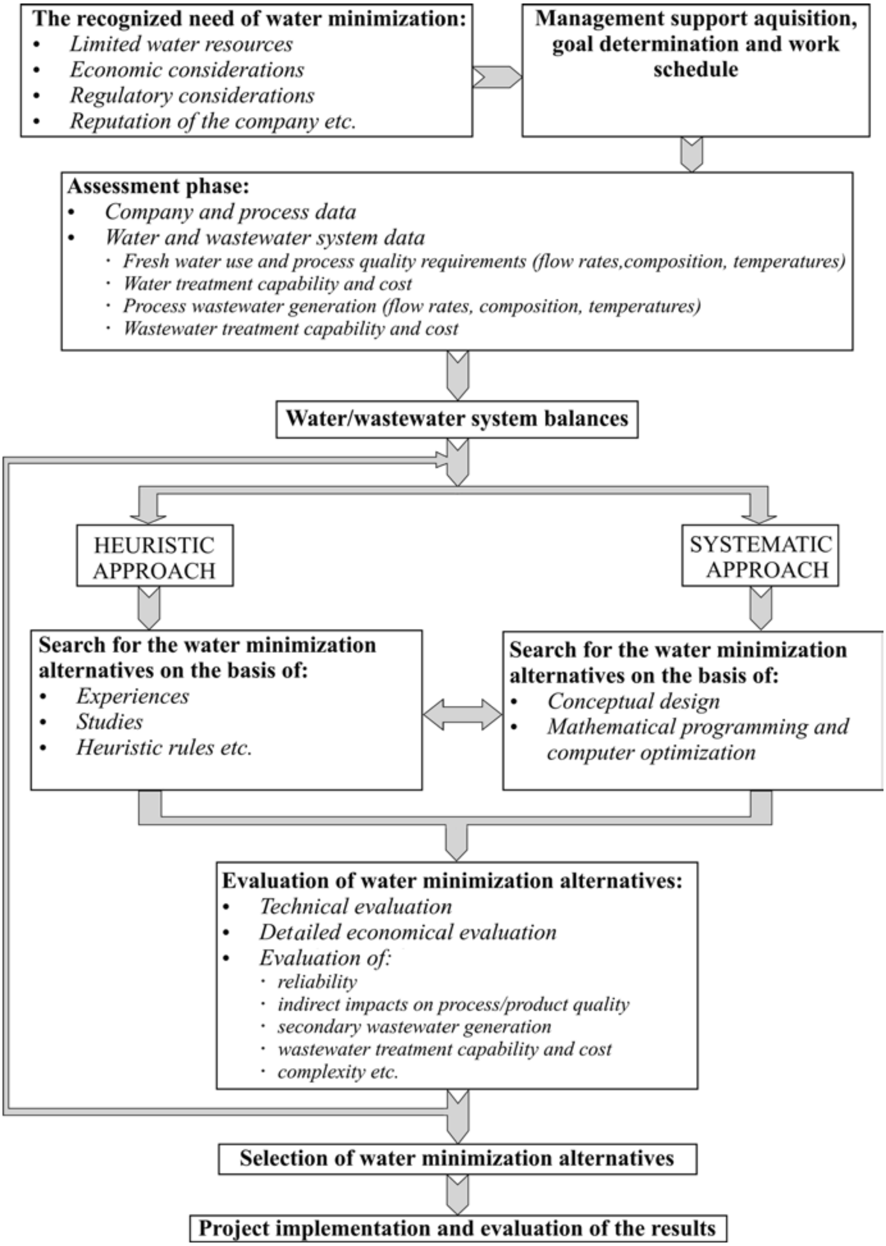


Fig. 2.5 Flowchart of water minimization strategy

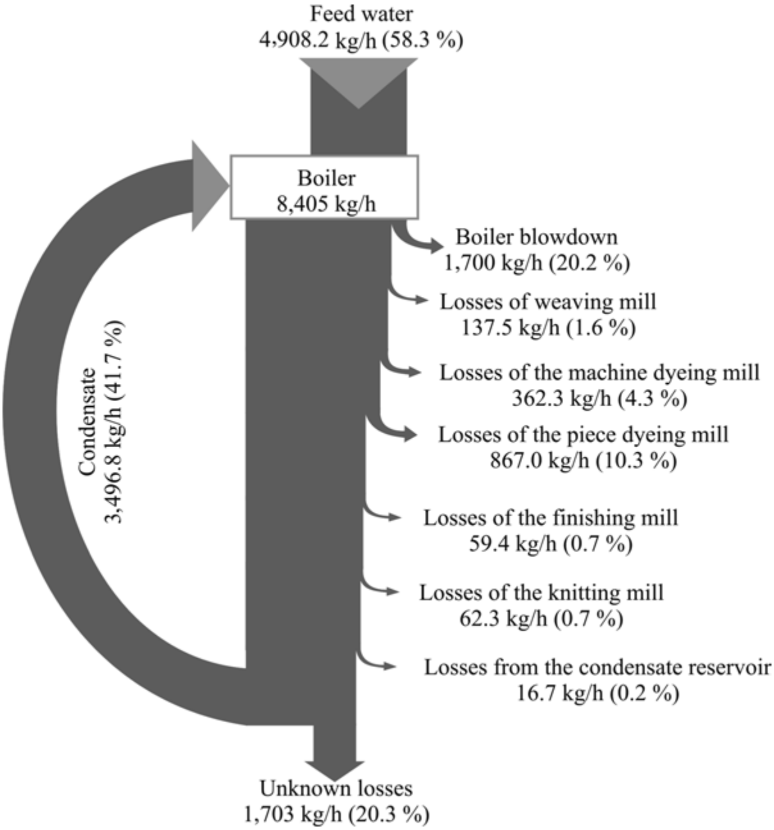


Fig. 2.6 Material flow rates of steam losses and condensate return in textile dyeing mill presented in the form of a Sankey diagram

2.3.1.1 Water Minimization Options Proposed

For keeping the water consumption of any given water using process as low as possible – be it state of the art or somewhat out-dated technology – good housekeeping and regular maintenance are of crucial importance. Based on detailed analysis of the water flow rates and the existing process equipment in the textile dyeing mill, the following improvements were proposed [23]:

- After-washing in machine dyeing mill can be shortened, and pre-washing in piece dyeing mill can be banned without a negative impact on the quality of the product
- New dye kitchen installation
- Cooling water can be reused for dyeing and rinsing
- Condensate can be reused as a boiler feed water (Fig. 2.6)
- Boiler blow down can be reused for heating of buildings
- Steam losses can be reduced by substituting steam traps with more efficient ones.

2.3.1.2 Economical and Environmental Benefits

Implementation of the proposed solutions could cause 21% reduction in wastewater flow rate produced (153,000 m^3 a^{-1}), and 15% reduction in soft water demand (78,300 m^3 a^{-1}). Furthermore, substantial savings in dyes consumption (7,300 t a^{-1}) and consumption of other chemicals (73,800 t a^{-1}) were proposed. Steam demand can be decreased by 25% (8,100 t a^{-1}), causing the 15% (342,000 m^3 a^{-1}) decrease in consumption of natural gas utilized as a fuel in the boiler house. Investment was estimated to 67,000 €. With annual savings of 237,600 € a^{-1}, the payback time was approximately 0.25 a.

2.3.2 Refinery and Petrochemical Complex

The petrochemical complex comprises formaldehyde, methanol and synthetic resin production processes. Formaldehyde is produced in two lines that differ in capacity. Some of the wastewater produced in the two lines is reused; however, 2.3 m^3 h^{-1} (hour) of wastewater still ends in the sewer. Methanol is produced by a catalytic conversion of synthesis gas in a Lurgi low-pressure process, consisting of three main steps:

- Production of synthesis gas
- Catalytic conversion of methanol
- Processing of crude methanol.

In the methanol production process, cooling water is being used for cooling samples and condensate. In total 6.5 m^3 h^{-1} of cooling water is needed, which after being used, ends as a wastewater. Urea-formaldehyde and phenol-formaldehyde synthetic resins are produced in two synthetic resin plants. Their operation requires 16.9 m^3 h^{-1} of surface water for vacuum pumps. In addition to this, other users consume 2.3 m^3 h^{-1} of potable and cooling water. The refinery comprises three atmospheric distillation columns for oil refinement. Out of 9.2 m^3 h^{-1} of wastewater produced, 2.2 m^3 h^{-1} of that is unpolluted wastewater.

In total, the refinery and petrochemical complex produce 37.2 m^3 h^{-1}, or roughly 268,000 t a^{-1} of wastewater.

2.3.2.1 Water Minimization Options Proposed

On the basis of technological wastewater analysis and after the characteristics of the individual water streams were established, new interconnections of water outflows from the processes or process units, and potential water consuming processes were identified [21].

The first proposal addresses the concept of wastewater regeneration reuse. Acidic wastewater from the storage tank of the formaldehyde production process can be

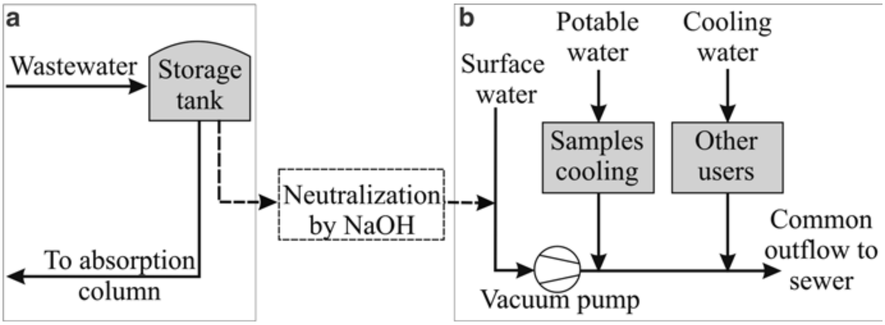


Fig. 2.7 Possible wastewater regeneration reuse (Adapted from [21]) (**a**) Formaldehyde production process (**b**) Synthetic resin production process

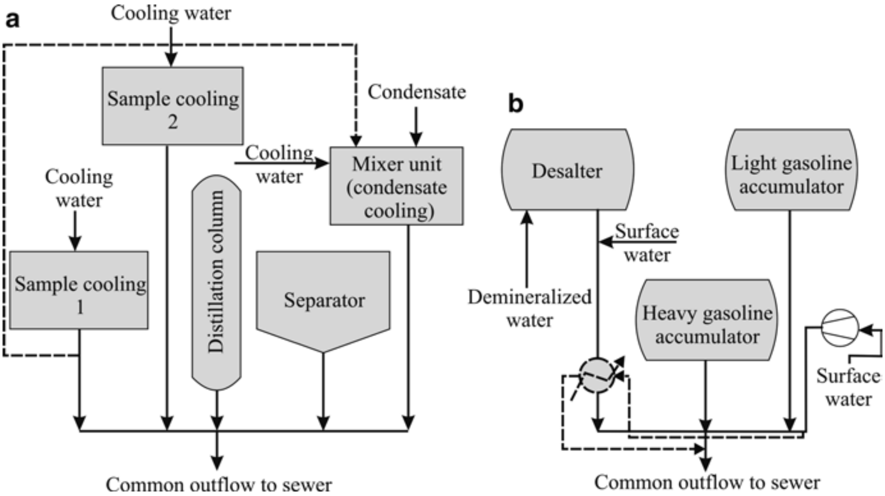


Fig. 2.8 Water-flow diagram including the proposed improvements (Adapted from [21]) (**a**) Methanol production process (**b**) Atmospheric distillation

regenerated (neutralized by alkali) and then reused in the synthetic resin production process to reduce the surface water intake for the vacuum pumps up to 60% (Fig. 2.7).

A direct water reuse within a process was found to be a feasible option in the case of the methanol production process. A fraction of cooling water used from sample 1 cooling stage can be reused for direct cooling of condensate by mixing of streams. The solution is graphically represented in Fig. 2.8a.

The third proposal refers to the refinery and deals with the reduction of water needed for cooling the desalter outlet stream (Fig. 2.8b). It was feasible to use pump outlets for desalter outflow cooling.

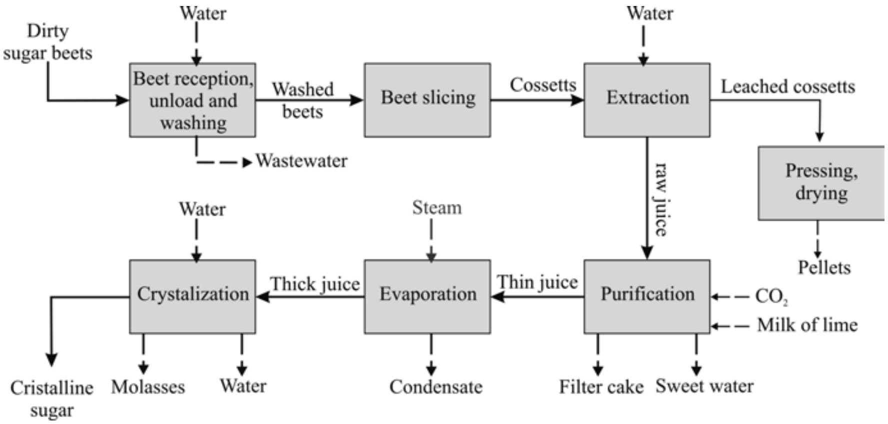


Fig. 2.9 Process flow sheet of a sugar beet extraction process (Adapted from [22])

2.3.2.2 Economical and Environmental Benefits

The three proposals could result in total savings of 43,100 € a^{-1}, 24% reduction in total volume of water used in the petrochemical process, and 14% reduction of the total volume of water used in the refinery. The payback time for the investments into the improvements of petrochemical complex was estimated to 0.5 a. As for the refinery, the payback time was estimated to 11 days only. It should be mentioned that 1 year after this study was performed; the increased water tax would double the above reported savings.

2.3.3 Sugar Beet Extraction Plant

The objective of sugar beet processing is to extract pure sugar from the beet while separating pulp and non-sugars such as minerals and water. A typical sugar beet contains (in mass fractions): 76.0% water, 17.0% sugar, 3.0% soluble non-sugar materials, and 4% fibres. Beside the main product, sugar, two valuable by-products, molasses and pulp proceed from the sugar beet processing. Processing 4,200 t day^{-1} of sugar beets requires 2,000 t day^{-1} of fresh water and produces roughly 4,600 t day^{-1} of wastewater. The latter is in part a consequence of high water content in sugar beet.

A simplified process flow sheet of sugar manufacturing process is given in Fig. 2.9. The main stages are:

- Beet reception, unloading, washing and storing/transporting
- Beet slicing and cossettes (cut up beets) extraction, leached cossettes drying and pelleting
- Raw sugar purification (liming, carbonation, filtration)
- Thin juice evaporation
- Thick juice crystallization (boiling and centrifugation).

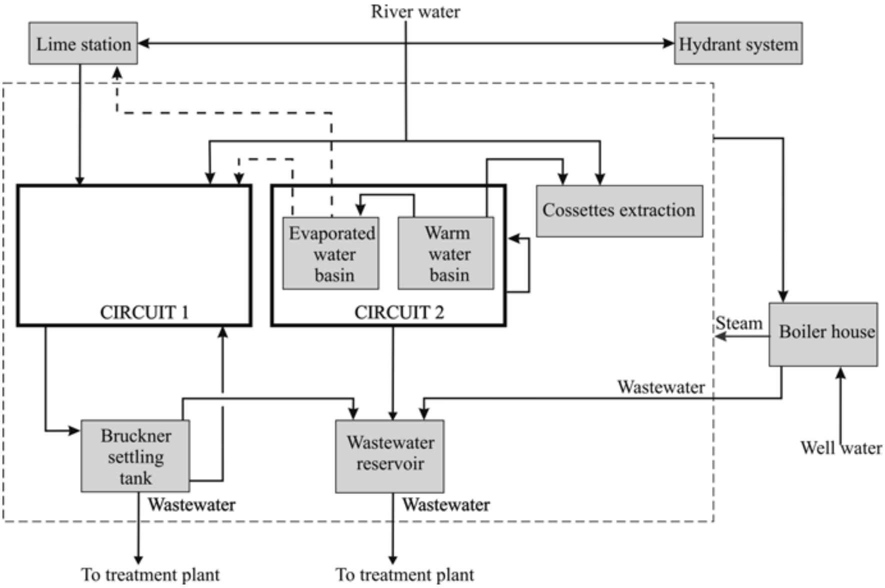


Fig. 2.10 Fresh water/wastewater flow sheet in a sugar beet extraction process (Adapted from [22])

There are several water and wastewater streams used or generated in various operations of the sugar plant. The streams have specific characteristics and require different handling or treatment. In the sugar plant studied, there are four qualitatively dissimilar water streams and circuits, respectively (schematically shown in Fig. 2.10):

- Fresh water (well water, river water)
- Wastewater
- Water recycle used for unloading, transporting, and washing of beet (circuit I)
- Condensate, warm water, cooling water, and evaporated water recycles from the crystallization stage (circuit II).

2.3.3.1 Water Minimization Options Proposed

After a detailed survey of water and wastewater streams was carried out, several options for water minimization were established using a heuristic approach and considering the selection criteria like costs, technical ability, reliability, complexity, impact on process/product quality, secondary waste generation, etc.:

- Water in the evaporated water basin can be disinfected, and reused partially in the lime station and partially in circuit 1 (dashed lines in Fig. 2.10);
- Condensate from the evaporation stage can be recovered and used as a feed water for the boiler;

- Irruptive water flow into the flume system must be limited, thereby reducing the expenses for water tax;
- River water intake can be reduced by replacing a part of it with water from the warm water basin.

2.3.3.2 Economical and Environmental Benefits

Assuming that all the proposed improvements are implemented, the fresh water intake is to be reduced by 69% (216,000 m^3 a^{-1}). Total savings per season are estimated to 42,500 €. Payback time for the required investment is planned to be approximately 5 d.

2.3.4 Brewery

The brewery considered in this case study has a production capacity of approximately 1,000,000 hL a^{-1}. The volume ratio of water consumed to beer sold is 6.04 L L^{-1}, which totals to fresh water consumption of 653,300 m^3 a^{-1}. According to the ratio specified by the Reference document on best available techniques (BREF), the fresh water consumption exceeded the upper limit by 144,900 m^3 a^{-1}.

First, the most critical departments were identified. These were:

- Brew house to worth cooling (the water balance is represented in Fig. 2.11)
- Fermentation and maturation
- Packaging
- Energy system.

In Fig. 2.12, the volume ratio of water consumed to beer sold is compared to BREF limits, good practice limits, and best practice limits. It can be seen that in all the departments the ratio is well within the BREF limits, the exception being the energy system for which the BREF limits were not given and which was also superior in terms of good and best practice limits. On the other hand, the fermentation and maturation department, as well as packaging department are considerably more troubling. Although the volume ratio of water consumption to beer sold is within the BREF limits for both the departments, it is well above the good and best practice limits.

2.3.4.1 Water Minimization Opportunities Proposed

To improve the water efficiency in the brewery, the possibilities of water reuse in the packaging area were analyzed. It was established that several continuous water streams with low concentrations of contaminant were available.

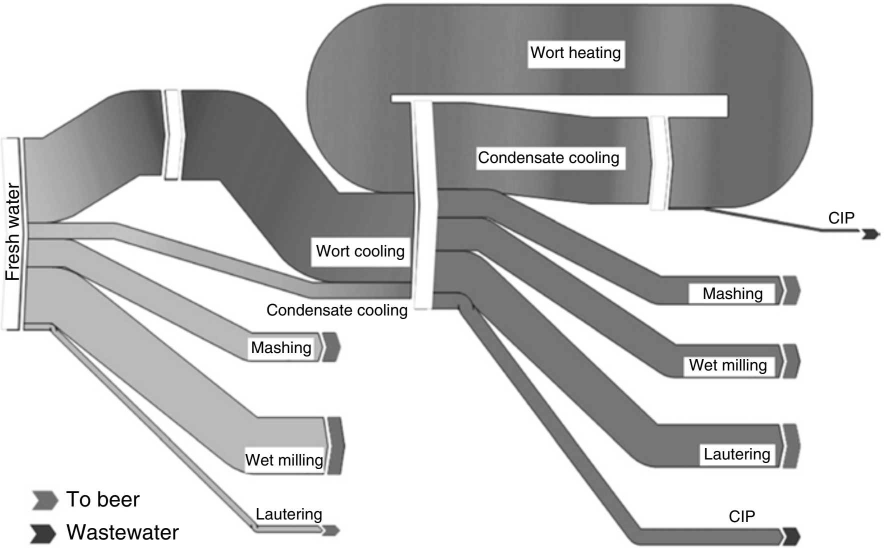
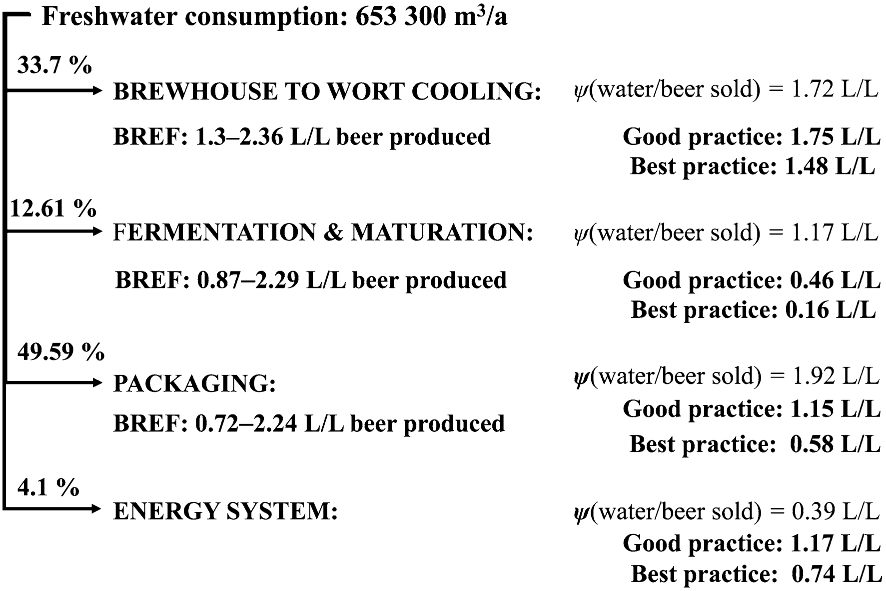


Fig. 2.11 Sankey diagram of water balance in the brew house (Adapted from [14])



Freshwater consumption: 653 300 m^3/a

33.7 %
BREWHOUSE TO WORT COOLING: ψ(water/beer sold) = 1.72 L/L
BREF: 1.3–2.36 L/L beer produced
Good practice: 1.75 L/L
Best practice: 1.48 L/L

12.61 %
FERMENTATION & MATURATION: ψ(water/beer sold) = 1.17 L/L
BREF: 0.87–2.29 L/L beer produced
Good practice: 0.46 L/L
Best practice: 0.16 L/L

49.59 %
PACKAGING: ψ(water/beer sold) = 1.92 L/L
BREF: 0.72–2.24 L/L beer produced
Good practice: 1.15 L/L
Best practice: 0.58 L/L

4.1 %
ENERGY SYSTEM: ψ(water/beer sold) = 0.39 L/L
Good practice: 1.17 L/L
Best practice: 0.74 L/L

Fig. 2.12 Identification of the most critical departments

Furthermore, the possibilities of water regeneration reuse in the brew house and the cellar were analyzed, where the direct reuse was unacceptable due to relatively high concentrations of contaminants.

The first opportunity to reduce the water consumption is to treat the wort boiling condensate with high chemical oxygen demand (COD) value. Electrolytic process based on hypo-chlorous acid and a suitable membrane separation process could be applied for the task. The treated condensate could then be reused as a rinsing water in packaging department or as a floor wash.

The second opportunity is to treat the "clean-in-place" (CIP) rinsing water (low COD value, but high conductivity value) with a suitable membrane process and reuse it in the same way as the treated wort boiling condensate.

The third opportunity was identified in the cellar, where the filter rinsing water (acceptable COD), is directly usable as a floor wash.

Finally, the fourth opportunity, if implemented, would boost the water efficiency of the already efficient energy system even further. Problem arises from the fact, that the wastewater produced needs to be cooled down before being released to the environment. At the time, this is achieved by mixing hot wastewater with cold fresh water. To satisfy the environmental temperature constraint, approximately 20,000 $m^3\ a^{-1}$ of fresh water is being used for this purpose. Clearly, either mixing of the hot wastewater with a cold one, or prolonged air-cooling is the solution to this problem.

2.3.4.2 Economical and Environmental Benefits

By realizing the proposed solutions, the brewery could reduce its water consumption by 25% (163,300 $m^3\ a^{-1}$) causing total savings of 121,600 € a^{-1}. All the proposed solutions are economically viable, with payback times ranging from 0.3 a to 1.4 a [14].

In addition to the water minimization, the opportunities of heat integration between batch operations were analyzed by using a mixed integer linear programming approach. The feasibilities of combined electricity, heating and cooling production were studied. The results indicate that it is possible to improve company's economic performance and reduce its environmental impact even further [15].

In the case of a trigeneration system, the highest electricity production is estimated to cover approximately 60% of the current electricity consumption. Nevertheless, due to high investment (1,173,600 €) the optimal solution selected is the cogeneration (combined heat and power) system with a back-pressure steam turbine at the pressure level of 42.4 bar. During the heating season, heat production should increase by 50% above the current level. Electricity production would cover 42% of the company's requirements. The net present value is estimated to 934,467 € and the payback period to 3.2 a.

2.4 Conclusion

Water is becoming more valuable and more expensive in the last years, and the forecast is even worse for the future. Some experts are talking about its comparison with oil availability and price. Therefore, much effort needs to be put into research and development of water usage minimization in industry and in other fields of application.

The results presented in the four case studies were obtained by using the proposed water minimization strategy in conjunction with strong collaboration of experts from individual companies. The latter is always desired (read – necessary), as they possess profound and the most up-to-date knowledge for a given process. It is through this knowledge that company's process constraints can be successfully integrated in the workflow. Consequently, because the solutions obtained are tailored to the needs and demands of companies willing to improve the water efficiency, their chances of being implemented are even higher.

The results also indicate that in many cases a significant reduction in water consumption and thereby a reduction in wastewater volume can be achieved with only minor investments compared to the savings caused by a more rational water usage. The key concept for achieving this is to recognize the possibilities of direct water reuse. If such a possibility existed, it should be exploited, as this is often economically, technologically, and environmentally the most effective way for improving the water efficiency.

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Chapter 3
Water Conservation in the Chemical Process Industry – Mass Integration Approach

Predrag Rašković

Abstract The chapter provides a simple, *Mass Integration* (MI) method for design and optimization of water-using system in *Chemical Process Industry* (CPI). In the first part of the chapter the major problems, drivers and solution strategies, that govern the development of efficient water system in CPI, are analyzed. The short review of *Process Integration* (PI) technology and *Mass Integration* (MI) approach are presented to vindicate their recognition as one of the most successful tools for energy and water savings in CPI. The theoretical background of MI approach summarizes the most important strategies, measures and rules, necessary for proper and effective design of *Water Network* (WN). Special attention is being given to the *No/Low cost* strategy that has been explained by the set of graphical illustrations and diagrams. In the second part of the chapter, MI approach is demonstrated in the case study from literature, Acronylate plant, where single contaminant WN was analyzed and improved by the MI solving procedure.

Keywords Chemical process industry • Water conservation • Mass integration

3.1 Introduction

The *Chemical Processing Industry* (CPI) is one of the most significant users of water and also one of the largest sources of environmental pollution by wastewater. The limited availability of water and hence, the higher industrial water tariffs, today have become one of the most restrictive elements for CPI progress. On the one hand

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the accessibility of good quality industrial water determines the locations of new plants, and on the other, its absence usually relates to the closure of the existing plants. All of this is followed by rapid increase of the effluent discharge costs, primarily raised by more and more restrictive environmental regulations.

Over the past decade, CPI companies have been constantly prompted to look for solutions that optimize, subject to the amount and quality, freshwater usage in the plant, and wastewater discharge into the environment. Hereafter this task will be denoted as the *water-using problem*. During that period of time, several strategies have been developed to solve the water-using problem, but two of them the most significant ones: *modification of individual process/utility units,* and *optimal design and operation of Water Network* (WN) within the plant. The former strategy is accomplished by the replacement and/or improvement of the existing process/utility units, whiles the latter, employs the system-oriented methods, primary targeting the global minimization of water use in the plant.

Within the scope of the second strategy, which will be of primary interest in this chapter, the WN is presented by the set of four basic elements: *Fresh water resources*; *Water-using units*; *Water cleaning units (regeneration and/or treatment units)*; and *Auxiliary equipment* [16, 20]. Next, the WN is determined by flow rate (in the following text G, kg/s) and composition of all water/wastewater streams, where the composition of stream refers to the *concentration* (y, ppm) or *mass load* (M, 10^{-6} kg s^{-1}) of contaminant in it. Depending on the number of contaminants in the stream, the WN problem can be considered either as *single contaminant*, or *multiply contaminant*. From conceptual point of view WN is commonly represented by two different models [13]. The first model decomposes the global WN system into two subsystems: *Water-Using Network* (WUN) – network of water-using units, and, *Wastewater Treatment Network* (WTN) – network of water-cleaning units. The second model considers three subsystems by distinguishing the regeneration from similar treatment processes [18]. In the case of the first model (far more utilized in literature) optimal design of WN is accomplished either by simultaneous consideration of both subsystems [23] or by separate optimization of each subsystem [25]. Most of the methods for optimal design and operation of WN fall under the broad classification of *Process Integration* (PI): "holistic approach to process design, retrofitting, and operation which emphasizes the unity of the process" [7]. PI methods were originally developed toward energy dimension of a process [15, 19, 24] referred to as *Energy Integration* (EI). Later, inspired by the success of EI, the PI has been expanded into new areas, mainly by using various analogies. The most obvious analogy, between heat transfer and mass transfer, was first utilized in the paper related to the synthesis of *Mass Exchanger Network* (MEN) [9]. This paper initiated the development of a new system-oriented methodology and indirectly introduced the WN design (and some other environmental issues) into area of PI.

From that time two major PI approaches were employed to address the optimal WN design in CPI. In the early years the optimal WN design was primarily performed by *conceptual (graphical) approach*, associated with *pinch analysis* [22]. Later, *mathematical optimization-based approach*, supplemented the conceptual approach by including other design constrains, e.g. forbidden match, safety, controllability, fluctuating mass load, etc. Conceptual and mathematical optimization methods have been presented, applied and evaluated in numerous scientific papers and books, and for further details the readers are referred to the comprehensive reviews [5, 12, 16] and books [17, 20].

In the mid 1990s El-Halwagi and Spriggs initiated the new approach to the WN design through a *source* (supply)-*sink* (demand) representation [10]. Previous MEN methods, based on network synthesis of process units with mass transfer-based operations, were upgraded to a more general concept, which involved process units with non-mass transfer-based operations in WN research space. New approach, commonly named as Mass Integration (MI), addressed the global flow of mass within the processes in order to optimize the allocation, separation, generation and routing of streams and species (including water and contaminants) throughout the plant. The MI approach has only given attention to the WUN design, in the literature also referred to as the *Water/Wastewater Allocation Planning* [2]. The main difference between them and the other conceptual and mathematical programming approaches lies in the fact that MI neither has a distinct targeting and design stage like conceptual methods, nor relies on mathematical programming technique. Instead the design of WN evolves simultaneously through the implementation of a systematic procedure which will be explained in the rest of the chapter. The main contributions in this field include books and papers published by El-Halwagi [8] and Dunn et al. [4, 6].

3.2 Overview of Mass Integration Approach

The WUN design task in the scope of MI approach can be simply described by the following statement: For a known set of water-using units, it is desired to determine a network of interconnections of water streams among the units so that the overall fresh water consumption is minimized while the processes receive water of adequate quality. Operation mode of WUN is assumed to be steady-state, and its configuration should enable the reuse (wastewater streams can be used as a feed in the other units but without reentering possibilities) and/or recycling (reuse with reentering option) of the streams leaving the water-using units. The design of WUN may optionally include regeneration processes which are employed to increase the potential for wastewater reuse, and also to enable recycling.

The MI approach relies on three phases to accomplish the WUN task. The first phase studies the global mass flow in the processes and addresses the strategy goals which will be used for improvement of the existing water system in the plant. The design tool utilized in this phase is *Source-sink stream representation diagram* [4] or *Global mass allocation diagram* [8] (Fig. 3.1). In some cases, after this phase, the graphical technique of *Material recycled pinch diagram* [11], illustrated on Fig. 3.2, can be employed to identify the maximum extent of MI applied for WUN design.

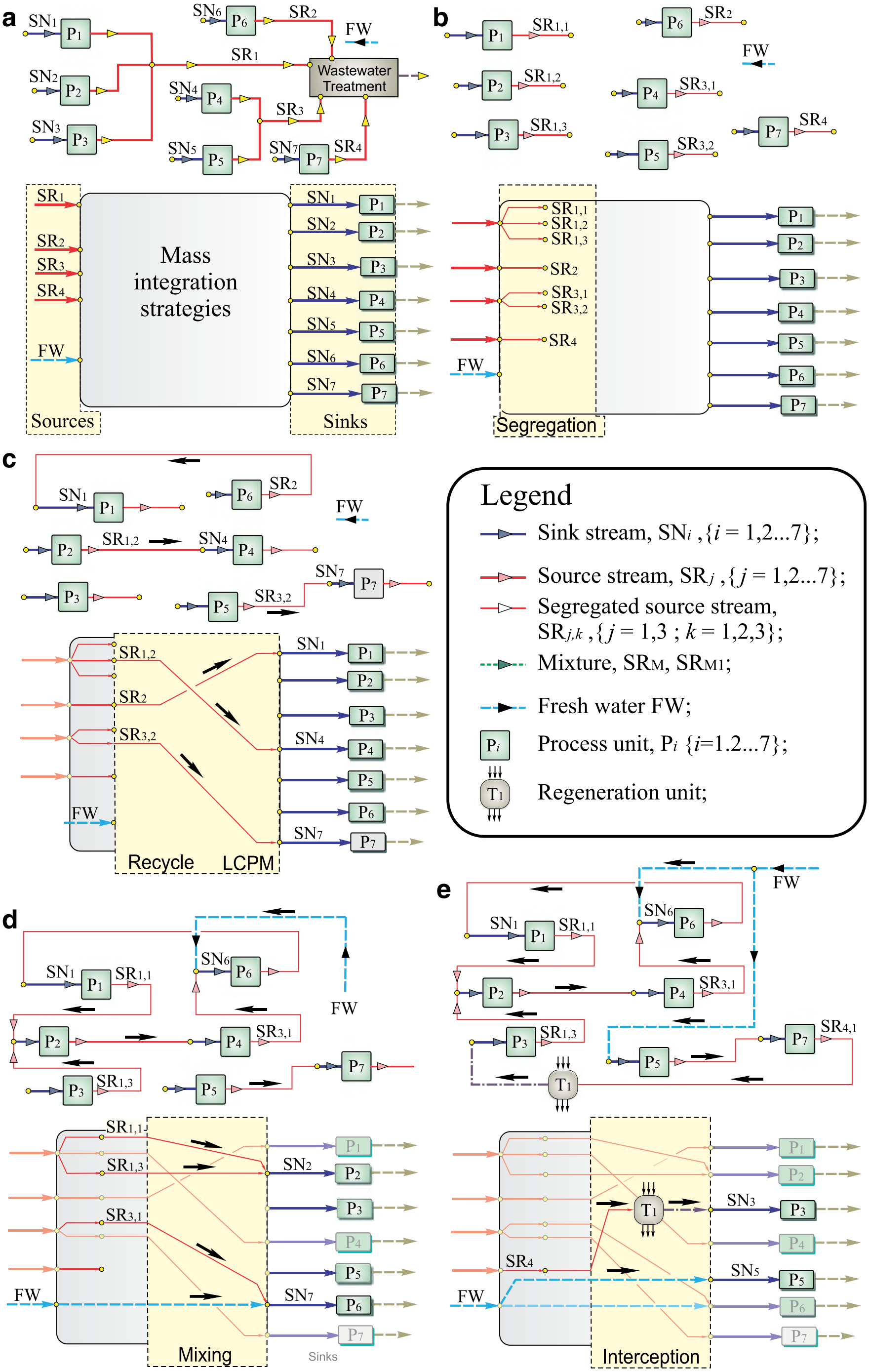

Fig. 3.1 Graphical presentation of MI analysis in source-sink stream representation diagram, based on process flow sheet from a species viewpoint [10]

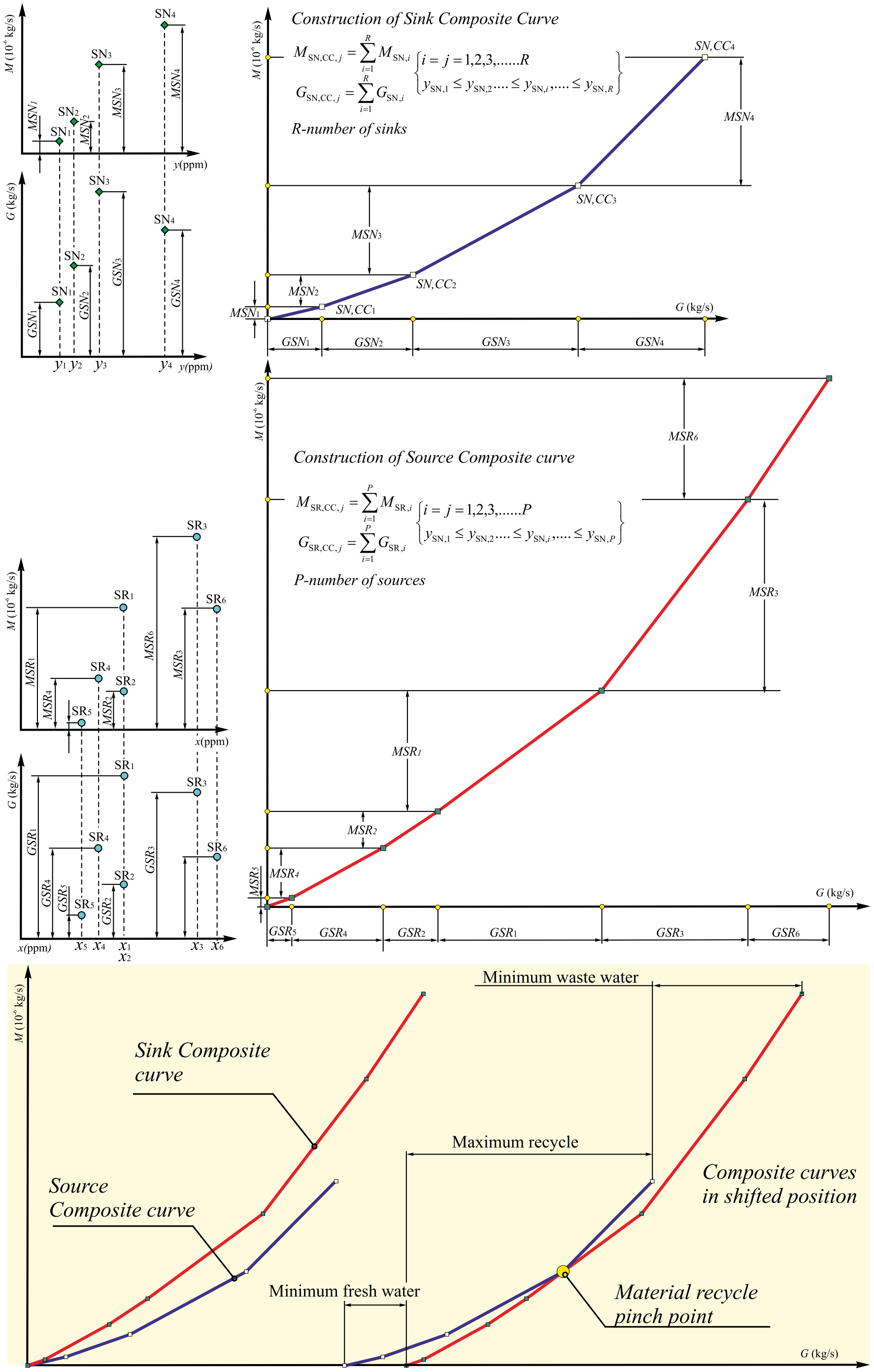

Fig. 3.2 Material recycled pinch diagram [11]

In the second phase, different measures and rules are applied on appointed streams and units in accordance with the goals defined in the analysis phase. The application of measures can be visualized by few graphical design tools; among them the main focus in this chapter will be on *Mass mapping diagram* [4] or *Source-sink mapping diagram* [8]. Finally, in the third phase, the results obtained in the previous phases are implemented in the plant. Explanation of the third phase strongly depends on the specific plant configuration and therefore it will be demonstrated by a case study.

The MI approach is commonly classified in the hierarchy of three strategies: *No/Low-cost*, *Medium-cost* and *High-cost strategy* [8]. The hierarchical order is set up pursuant to the cost, but their potential for use is also evaluated due to its efficiency and its ability to be implemented in the plant. Looking above, the strategies are in ascending order seeing the cost or efficiency and in descending order concerning the implementation possibilities.

No/Low-cost strategy includes two options: *Structure-based modifications* and *Parametric-based modification*. Structure-based modification explores the possibilities for reconfiguration of water system, and can be applied by the set of three measures: *stream segregation*, *stream mixing* and *recycling of streams*. Here the term recycle is used in a general sense that includes reuse option. The segregation measure refers to the separation of streams (not splitting of streams); this means that some wastewater streams could be recycled within the WUN instead of being mixed with the other effluent sources and sent to the treatment facility. As a consequence, the terminal wastewater stream from the WUN could have a lower G and higher y, and can be treated in more cost-effective manner. Mixing of streams (or their parts) is carried out to adjust the G and y of the wastewater streams to the level which is acceptable for recycling. The mixing measure can include fresh water as one of the mixing components. The recycling of streams is performed when some wastewater stream fulfills the conditions to be used as feed in one unit. The parametric-based modification includes *Low-Cost Process Modifications* (LCPM) like changes of temperature, pressure, flow rate and similar operating conditions of water-using units [14]. The cost associated with No/Low-cost strategy includes piping, pumping and the use of cheap auxiliary equipment like mixing tanks, control, pumps etc. In the literature No/Low-cost strategy is also named as *Direct recycle strategy* [8], since the network solution does not include the installation of new devices.

The Medium-cost strategy considers the addition or replacement of equipment, and substitution of materials such as solvent, catalyst, etc. Additional equipment is commonly separation unit, necessary to *intercept* selectively the targeted contaminants from wastewater streams. In case of large group of process options (multiple streams. technologies and/or the use of different separating agents), Medium-cost strategy can be accomplished by one of the network synthesis techniques [22]. The last, High-cost strategy, considers the implementation of new technologies, use of environment benign chemistry, new processing technology, etc.

3.3 Mass Integration Approach – Analysis by Source-Sink Stream Representation Diagram

The solving procedure of MI approach starts with the generation of source-sink stream representation diagram (Fig. 3.1). This diagram considers the water system in the plant by mapping only the water-using units-*process sinks* (reactors, separators, heaters, pumps, pollution-control facilities, and the like) and water/waste-water streams which connect them.

Process sinks and water/wastewater streams of interest are typically identified from the plant *Process Flow Diagram* (PFD) or *Block Flow Diagram* (BFD). In the Fig. 3.1a, simplified, hypothetical BFD, illustrates the existence of seven process sinks (P_i). Water/wastewater streams which are involved in the WUN design are the streams which enter or exit the process sinks. Among them, "source" stream (SR_i) refers to stream that exits, either the single P_i (SR_2 and SR_4), or the subsystem consisting of a few P_i (terminal streams SR_1 and SR_3). Source streams, which should be considered for possible recycling or regenerating, are presented on the left side of the diagram in Fig. 3.1a. The "sink" streams (SN_i), presented on the right side of the diagram Fig. 3.1a, refer to any stream that enters the P_i. These streams should be replaced with SR_i streams after the application of MI measures. *Fresh Water* (FW) resources are presented in the same part of the diagram as other SR_i. It should be noted that stream leaving the P_i become, in turn, the SR_i stream.

A gap, made in the diagram between the SR_i and SN_i streams (Fig. 3.1a), symbolically presents the research space which should be "filled" by utilization of MI strategy and the most important measures: segregation, LCPM, mixing, recycling, and interception. These measures are illustrated in the following parts of Fig. 3.1. In Fig. 3.1b source streams $SR_{1,1}$, $SR_{1,2}$, and $SR_{1,3}$ are segregated from terminal source stream SR_1, while $SR_{3,1}$, $SR_{3,2}$, are segregated from terminal source stream SR_3. Next, in Fig. 3.1c*,* stream SR_2 is directly recycled in sink SN_1; stream $SR_{1,2}$ is recycled in SN_4, while the stream $SR_{3,2}$ is recycled in SN_7, after the LPCM of process sink P_7 (different color of process sink in presentation).Mixing measures are illustrated in the Fig. 3.1d where the mixture of $SR_{1,1}$ & $SR_{1,3}$ is recycled in SN_2, while the $SR_{3,1}$ is recycled in SN_6, after having been mixed with FW. In Fig. 3.1e the $SR_{4,1}$ is intercepted in regeneration unit T_1 and then recycled in SN_3. If more source streams need to be intercepted, the framework of interception task has to be presented as *Species Interception Network* (SPIN) [8]. The inevitable use of FW resources for some process sinks is illustrated by feed in SN_5.

In practice the analysis phase in source-sink stream representation diagram includes the segregation measure and collection of G_i and *yi* of all SR_i and SN_i streams. In particular, the parameters of SN_i streams should be defined under the acceptable range. The flow rate and composition bonds of P_i are determined according to the technical, physical and historical (overlook of process data) limitations of that sink [7]. From this point the MI solving procedure should be transferred to the next phase-practical application of MI measures. The following discussion will be primarily focused on the application of No/Low cost strategy on single contaminant WUN problem.

3.4 Practical Application of Mass Integration Approach – Mass Mapping Diagram

The most important tool for practical application of MI measures, mass mapping diagram (Fig. 3.3), is generated from the SR_i and SN_i stream data, previously extracted in phase of analysis. In the case of single contaminant problem, the diagram is two dimensional showing the streams *y* on horizontal axis and the corresponding *G* on vertical axis. In Fig. 3.3a, SR_i and SN_i streams are presented as single points, but with different shapes and colors. Source streams include only the streams obtained after the segregation measure. In order to denote the sink's acceptable range of *G* and *y*, the shaded area is added to SN_i points.

For the purpose of better explanation, it is assumed that the streams data are obtained from a hypothetical plant, presented as simplified PFD in the Fig. 3.3b. Hypothetical plant is composed of separate (non-interconnected) units to bypass the segregation measure in WN, unnecessary for theoretical discussion in this section. The positions of SR_i and SN_i points in diagram determine the kind of measure which will be used inside the No/Low cost strategy. The opportunity for direct recycling of source stream appears when the *y* in that stream is less or equal to maximal acceptable in the targeting sink. Depending on the relation between the SR_i flow rate and the flow rate determined as maximum acceptable in the targeting sink, the SR_i can be completely (Fig. 3.4a) or partially recycled (Fig. 3.4b). In the second case only a portion of SR_i can be recycled, while the rest of it can be utilized by other measures or discharged in the environment. In a hypothetical plant, Fig. 3.4a, three SR_i (SR_5, SR_2 and SR_3) can be completely recycled in the two process sinks (replace of SN_3, SN_4), while in Fig. 3.4b the source stream SR_1 can be partially recycled in one sink (replace of SN_4).

Mixing measure considers the possibility for recycling of SR*i* whose *y* exceeds the acceptable level of targeting process sink. The second component of the mixing process has to be the source stream with the *y* less than maximum acceptable in that sink. The

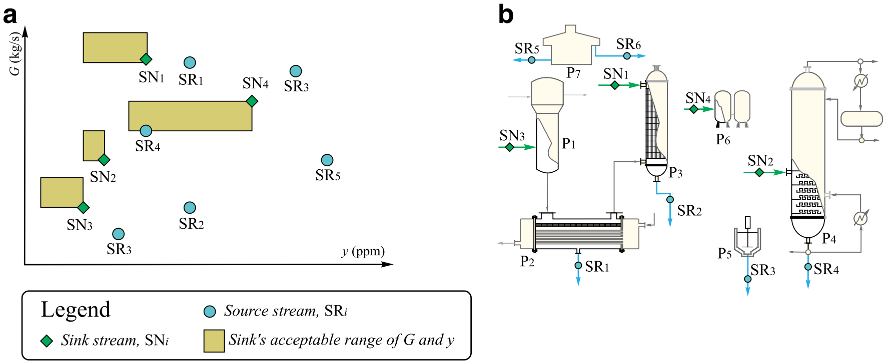

Fig. 3.3 (**a**) Mass mapping diagram, *G* (kg s^{-1}) – flow rate, *y*(ppm) – concentration of contaminate [4, 8]; (**b**) simplified PFD of hypothetical plant

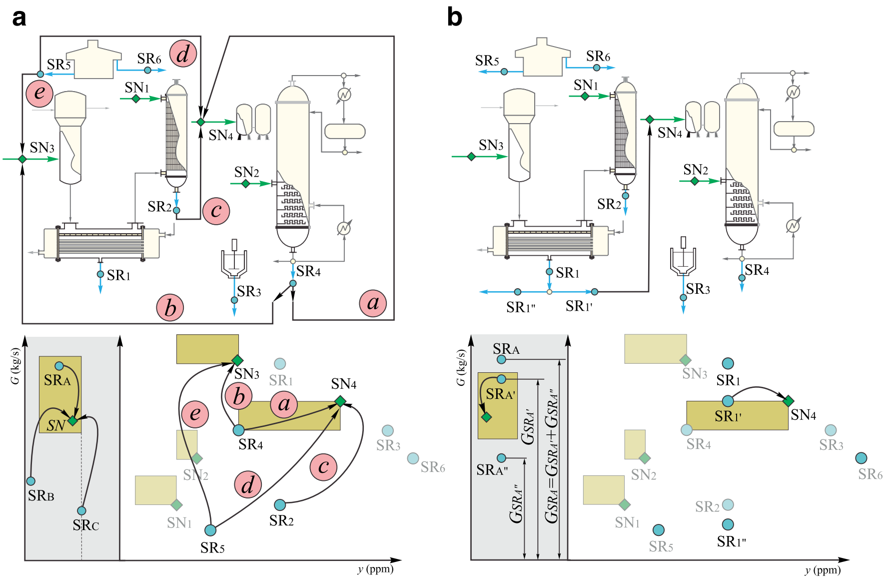

Fig. 3.4 Mass mapping diagram- direct recycle measure [4, 8]

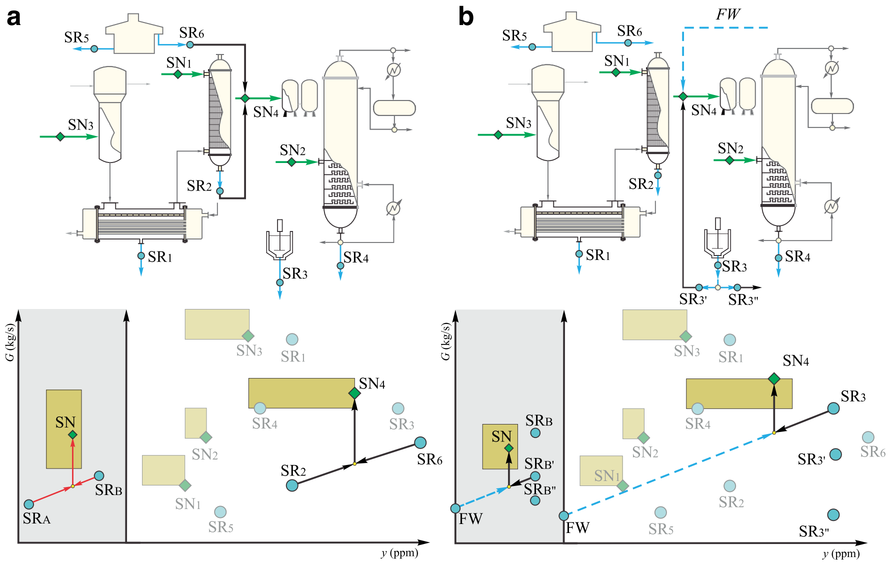

Fig. 3.5 Mass mapping diagram – mixing measures [4, 8]

final *G* and *y* of the mixture are calculated by the lever-arm rule [7]. The mixing measure is visualized within the hypothetical plant for two sources (SR_2 and SR_5) which are mixed and recycled in the process sinks to replace SN_4 (Fig. 3.5a). Similar considerations can be used in the case when SR_i mixes with fresh water, as in Fig. 3.5.

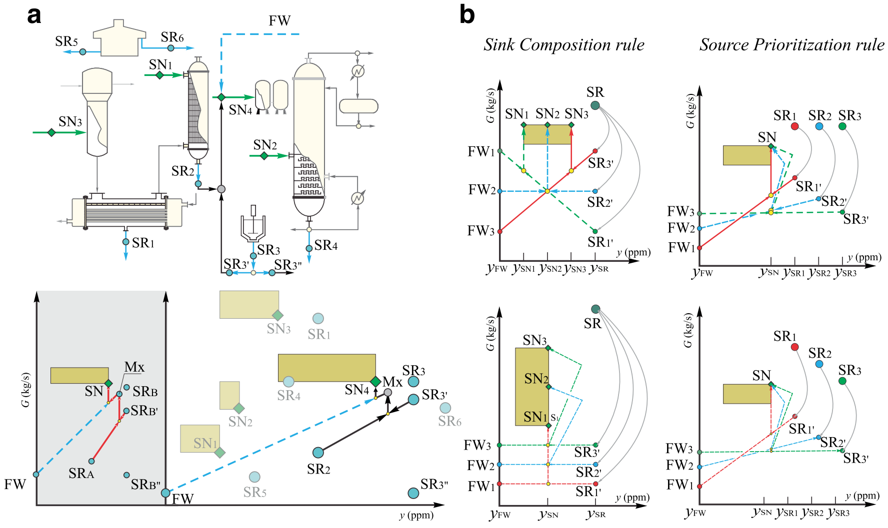

Fig. 3.6 (**a**) Mass mapping diagram- combine mixing measure, (**b**) Sink composition rule and source prioritization rule [4, 8]

In some cases two previous possibilities of mixing can be combined in one, as in Fig. 3.6a. The calculation procedure in the first step determines the portion of source stream SR$_3$ which can be recycled regarding the prescribed parameters of SN$_4$, SR$_2$ and FW. In the next step of calculation, minimum flow rate of fresh water, necessary to adjust the composition of new formed mixture, is obtained.

Mixing of the source stream with fresh water may be used for the definition of two important rules [7] illustrated in Fig. 3.6b. The first rule, *Sink Composition rule,* assign the maximum *y* and minimum *G* inside the process sink's acceptable range, as the one which should be target when mixing measure is used. In other words, the composition of the mixture should be set to those parameters of sink.

The second rule, *Source Prioritization rule* appoint that the source with minimal concentration of contaminant is the first that should be mixed with fresh water and recycled in the targeting process sink.

3.5 Design of Water-Using Network by Mass Integration Approach – Case Study

The previous sections in chapter provided the theoretical background of MI approach and appointed its most important phases for design of efficient WUN. In the following sections the Acronylate (ACN, C_3H_3N) production process [1, 7], one typical CPI plant, was used as a case study to demonstrate MI solving procedure. Acrylonitrile (ACN) is an intermediate monomer, used world-wide as an important material for the manufacture of plastics. Most industrial C_3H_3N is produced by catalytic ammoxidation of propylene, sometimes called the SOHIO process, acknowledging that ammoxidation was commercialized by Standard Oil of Ohio. More detailed description of SOHIO process can be found in the open literature [3]. ACN plant is simplified and partially readjusted, to address only the components which are important for clear explanation of WUN design. After brief description of the reference plant, followed by WUN design problem statement, the opportunities for water system improvements are first analyzed in source-sink stream representation diagram. In addition, material recycled pinch diagram is generated to display the attainable WUN performance target for the proposed No/Law cost strategy. Next, solving procedure employed segregation, LCPM, mixing and recycle measures to enable the reduction of fresh water demand in the system. Finally, parameters of the new WUN are established by material balance revision. The whole procedure is also embedded in the simple sequentially-oriented spreadsheet software which is used to simulate the influence of LCPM strategy on final WUN performances.

The ACN production process, presented in Fig. 3.7a, consists of four interconnected subsystems, whereby every subsystem accomplishes one of the important technology operations. The subsystem comprises a set of process units, but sometimes, as a result of process simplification, a set includes only the one, main water-using unit. The existing WUN in the plant involves pure fresh water (H_2O) resource, and wastewater streams, containing only C_3H_3N and one contaminant of interest-ammonia (NH_3).

The production process starts in *Reaction subsystem*, in *fluidized-bed reactor*, where oxygen, ammonia, and propylene react in the presence of a catalyst (typically bismuth-molybdenum based). The vaporous reactor off-gas, made up of H_2O, C_3H_3N and NH_3, is transferred to *Quench subsystem*, and rapidly cooled, in the indirect-contact cooler/*condenser.* The condensed liquid, built in *condensate stream* (CN) is sent to a wastewater collector. The remaining part, *gaseous stream* (GS), is introduced in *Recovery subsystem*, first in the *scrubber*, which utilizes the *fresh scrubbing water* (SW) for cleaning operation. Outputs from scrubber are *liquid effluent stream* (SS), which is fed to the *decanter* and *off-gas stream*, containing a negligible amount of H_2O, C_3H_3N, and NH_3, which is discharged into the environment.

In the decanter, SS stream is separated into an *aqueous layer form* (ALF) and an *organic layer form* (OLF). It is assumed that OLF contains a negligible amount of H_2O and 4.3 times higher concentration of NH_3 than ALF, also that mass fraction of C_3H_3N in ALF is 0.068. The output stream from the decanter are the *aqueous layer stream* (ALS), which contain only ALF, and the *distillation column stream* (DC), which is built from 1 kg s^{-1} of ALF and whole amount of OFL. The ALS flows to the wastewater collector, while the DC stream proceeds to the *Purification subsystem.* Purification of DC stream is conducted by a vacuum distillation column. Vacuum in the column is produced by a *steam-jet ejector* which utilizes the high pressure steam generated from the *fresh boiler water* (BW) in the *boiler. Condensate* from steam-jet ejector (SJ), which pulls off C_3H_3N, $NH_3$and negligible amount of H_2O from the distillation column, is transferred to the wastewater collector. Concentration of NH_3 in SJ stream is 34 times higher than in the *final product stream* (PS). The *mixture of*

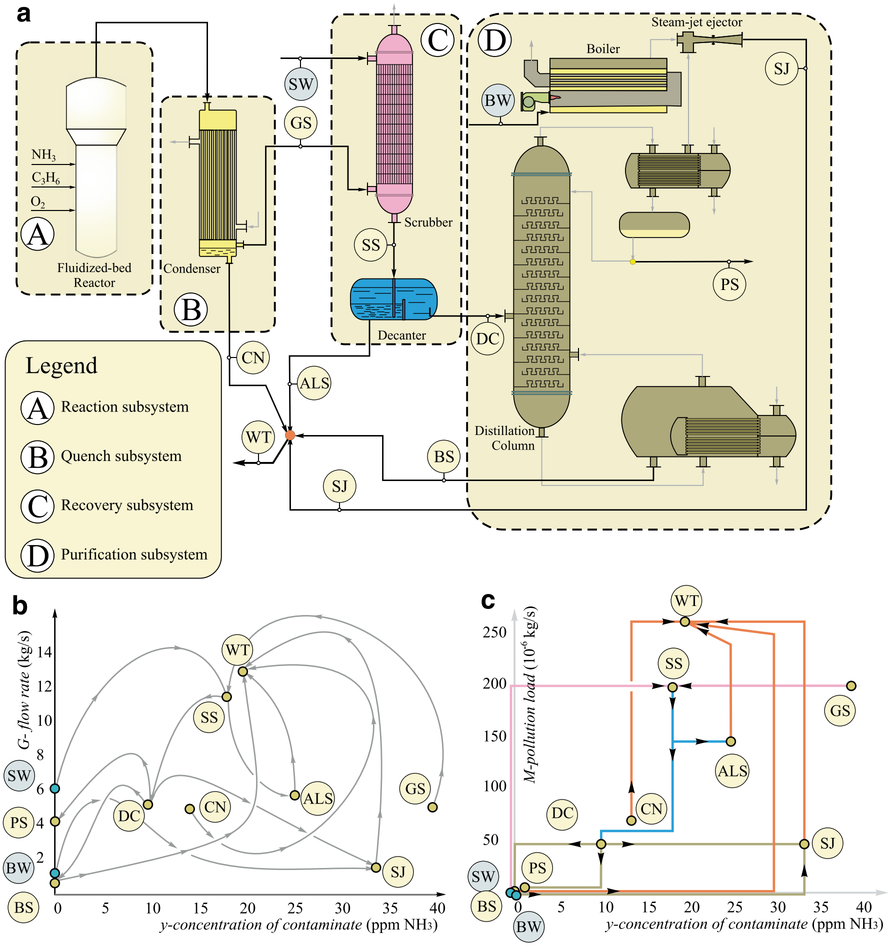

Fig. 3.7 (**a**) Flow sheet of acronylate plant; (**b**) Stream mapping diagram; (**c**) Path diagram

wastewater streams (WT), composed from BS, SJ, AL and CN, from wastewater collector goes to the wastewater treatment facility.

Other material balance data of streams necessary for WUN design are presented in Table 3.1. The global mass flow and global mass load of contaminant (NH_3) throughout the production process are also visualized by Stream mapping diagram (Fig. 3.7b) and *Path diagram* (Fig. 3.7c) [7].

The design task which considers the WUN problem by MI approach in ACN plant may be stated briefly as follows:

For a given ACN production process, with known overall material balances (*Table* 3.1) *and the known process/environmental constraints* (*Table* 3.2)*, the No/Law-cost strategy for single contaminant problem and non-mass transfer based operations, should be applied to minimize the fresh water use and wastewater generation in the*

Table 3.1 Stream parameters of WUN in ACN plant

Stream	C_3H_3N (kg s^{-1})	H_2O (kg s^{-1})	Total (kg s^{-1})	y_{NH3} (ppm NH_3)	M_{NH3} (10^{-6} kg s^{-1})
BW	0	1.2	1.2	0	0
SW	0	6.0	6.0	0	0
CN	0.4	4.6	5	14	70
GC	4.6	0.5	5.1	39	198.9
SS	4.6	6.5	11.1	18	199.8
ALS	0.4	5.5	5.9	25	147.5
DC	4.2	1	5.2	10	52
SJ	0.2	1.2	1.4	34	47.6
BS	0.1	0.7	0.8	0	0
PS	3.9	0.3	4.2	1	4.2
WT	1.1	12	13.1	20	262

Table 3.2 Process and environmental constraints of some streams in ACN plant

	Feed flow rate (kg s^{-1})		NH_3 content (ppm NH_3)		C_3H_3N content (wt% C_3H_3N)	
Stream	min	max	min	max	min	max
Scrubber feed stream	5.8	6.2	0	10	0	0
Boiler feed stream	–	–	0	0	0	0
Scrubber outlet	10.6	11.1	–	–	–	–
Distillation column inlet	5.2	5.7	0	30	80	100

plant. It is assumed that water-using units in the network operate under steady-state and non-reacting conditions.

Mass integration analysis starts by identification of the SR_i and SN_i streams which should be included in the WUN task. The relevant SR_i is only the WT stream, since the other candidates like PS, DC and SS streams are excluded from the task from technology limitations. WT stream is terminal-wastewater mixture, composed of four individual streams prior to its transfer to wastewater treatment facility. Therefore, the segregation measure renders four SR_i streams (OG, AL, BS and SJ) which should be considered in the rest of the task instead of the WT stream. Relevant sink streams are streams which feed the scrubber (SN_S) and boiler (SN_B). Inside the acceptable range (Table 3.2), the specific parameters of SN_S are determined subject to minimization of fresh water usage, as the one with maximal concentration of contaminant, $y = 10$ ppm NH_3, and minimum flow rate $G_{SNS} = 5.8$ kg s^{-1}. This can be accomplished by LCPM measure, which involves setting the flow control valve. FW resource, necessary to supplement the recycle of source streams in this process sink is denoted as FW_S – fresh water source.

Rigorous limitations for SN_B (cannot contain any NH_3 or C_3H_3N) restricted the recycle possibilities for that process sink. This means that the boiler water demand can be covered only by fresh water resources, more specifically by FW_B fresh water stream. This situation relatively simplified the problem by excluding FW_B and SN_B streams from the task in the following design stages.

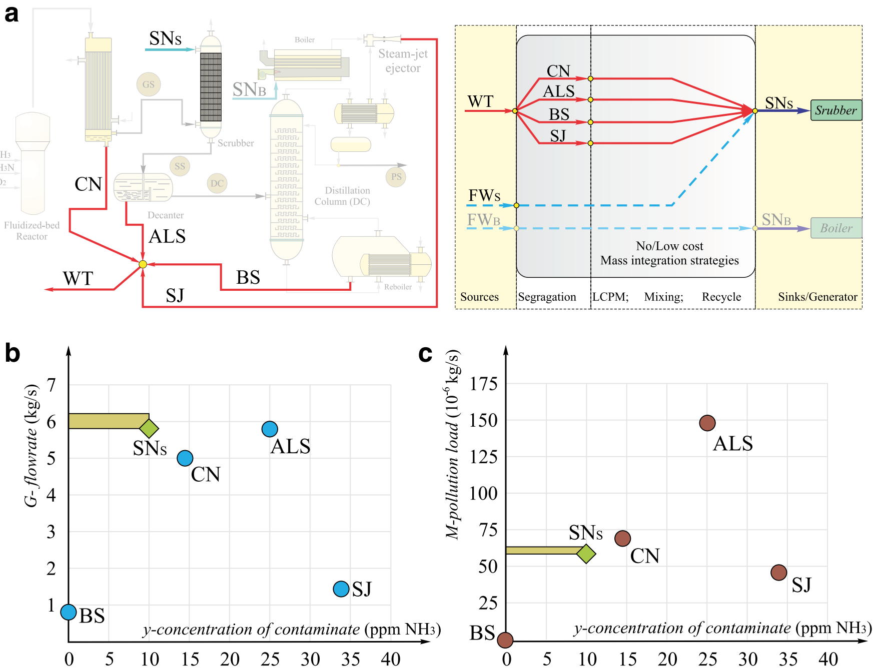

Fig. 3.8 (**a**) Source-sink stream representation diagram; (**b**) Mass mapping diagram; (**c**) Diagram of NH_3 mass load throughout the process as a function of its composition in carrying streams

The results of analysis reduced the WUN task to five SR_i streams (four process streams and one fresh water stream) and one SN_i stream. These results are visualized in Source-sink stream representation diagram in Fig. 3.8a. The SR_i and SN_i streams are also presented in the mass mapping diagram (Fig. 3.8b) and diagram which analyzes the mass load of NH_3 throughout the process as a function of streams composition (Fig. 3.8c). The streams data extracted in the phase of MI analysis are presented in Table 3.3.

The performance targets of WUN were established via construction of material recycled pinch diagram (Fig. 3.9). As can be seen from Fig. 3.9c, when direct recycle strategy is used, maximum flow rate of all SR_i streams (OG, AL, BS and SJ) which can be recycled is 4.9 kg s^{-1}; minimum flow rate of fresh water necessary to supplement the recycle of SR_i streams in the one sink is 0.85 kg s^{-1}; and minimal flow rate of all SR_i streams which have to be sent to the treatment plant is 7.95 kg s^{-1}. Last value will be different after revised material balance since the flow rate and composition of ALS and SJ stream will be changed.

Examination of the mass mapping diagram in Fig. 3.8b reveals two design possibilities for application of the second No/Low cost strategy measure: direct recycling of BS stream or mixing of source streams, followed by recycling of the mixture(s). Direct recycle of BS is possible but not preferred option since its concentration of contaminant ($y = 0$ ppm NH_3) is far less than one required for the process sink ($y = 10$ ppm NH_3). Such measure also opposes the *Sink composition*

Table 3.3 Streams data extracted in the phase of MI analysis for ACN plant

Stream	G (kg/s)	y_{NH3} (ppm NH_3)	M_{NH3} (10^{-6} kg/s)
SN_S	5.8	10	58
CN	5.0	14	70
ALS	5.9	25	147.5
SJ	1.4	34	47.6
BS	0.8	0	0

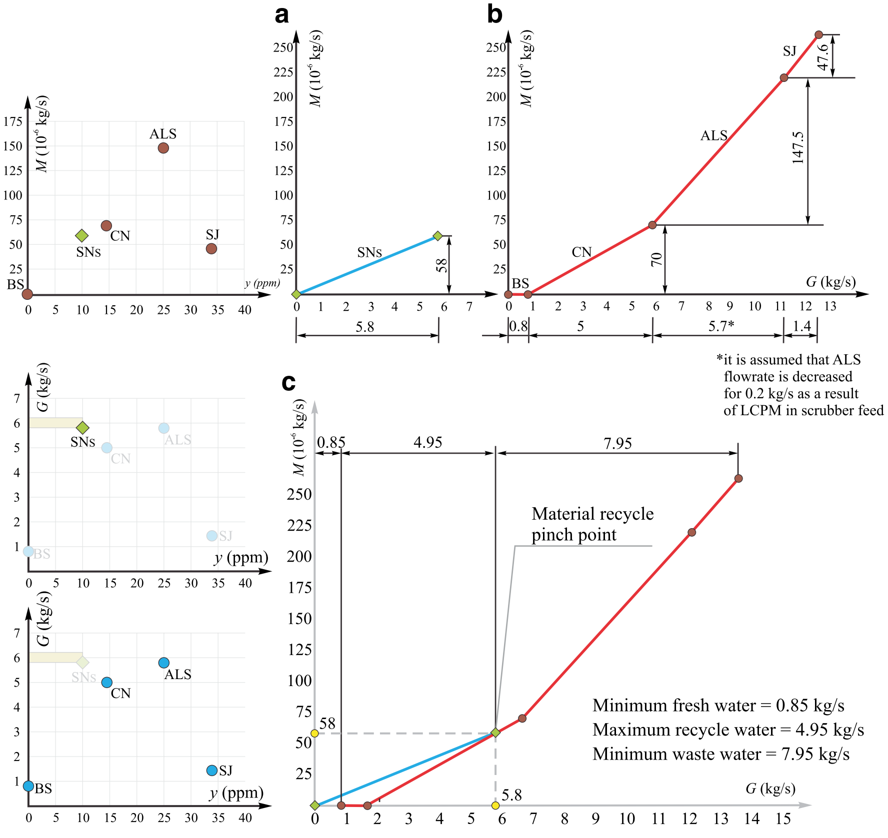

Fig. 3.9 (**a**) Sink composite curve; (**b**) Source composite curve (**c**) Material recycle pinch diagram

rule. The next possibility considers (according to the *Source prioritization rule*) the mixing of the streams with the least concentrations of contaminant: BS and CN. The flow rate of such mixture, $G_{mixture} = 5.8$ kg s^{-1}, meets the scrubber's demand ($G_{SNs} = 5.8$ kg s^{-1}), but its concentration of contaminant, $y_{mixture} = 12.1$ ppm NH_3, exceeds the maximum acceptable value for the process sink ($y_{SNS} = 10$ ppm NH_3). The problem can be overcome by the use of another appropriate source stream (in this case only FW_S stream), which will replace a part of CN in the mixture. In this way the scrubber should be fed by mixture made up of three components:

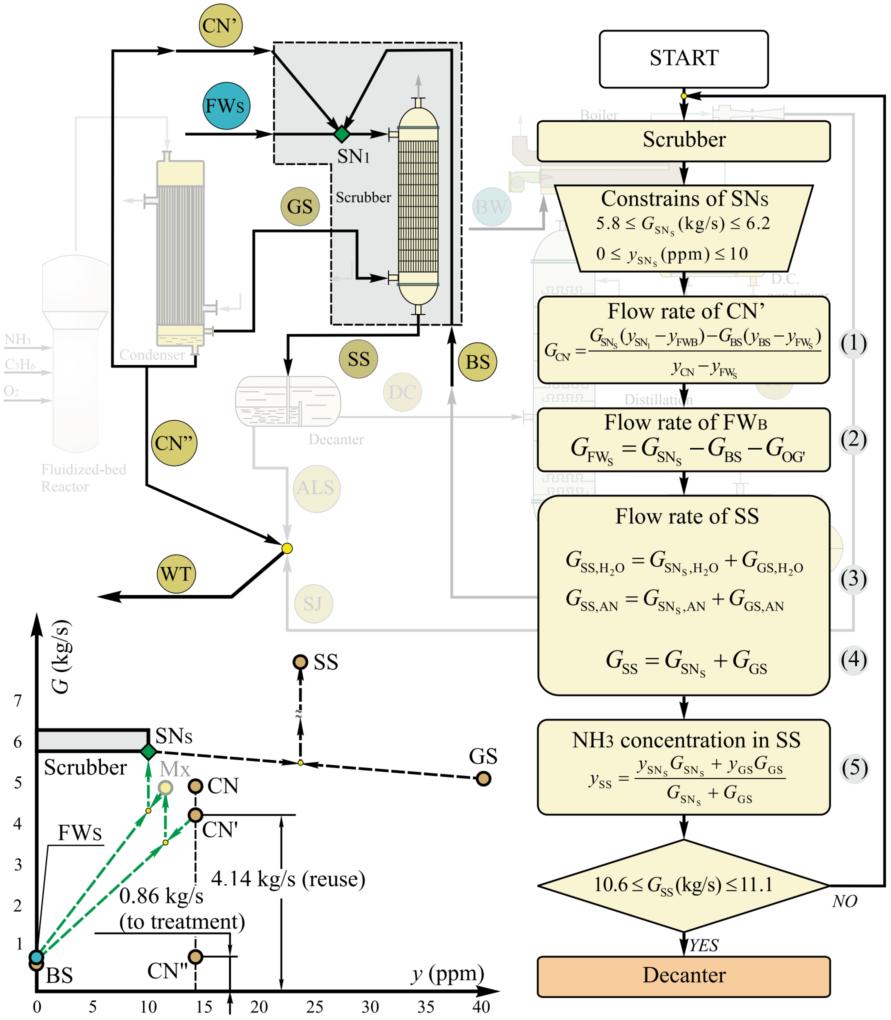

Fig. 3.10 Physical model, mass mapping diagram, and calculation flowchart of scrubber model

complete BS, the part of CN and certain amount of FW_S stream; FW_S stream flow rate should be high enough to adjust the characteristic of mixture to the level which satisfies the scrubber constrains. Graphically, this procedure is presented by three steps on the mass mapping diagram in Fig. 3.10:

- In the first step source stream CN is divided into two parts: CN', which will be used for mixing with BS and FW_S streams and CN" which will be sent to the wastewater collector. The flow rate of CN' is determined by (1) in the algorithm presented in flowchart in Fig. 3.10.
- In the second step, BC and CN' are combined in the mixture (Mx). The flow rate of Mx presents the maximum amount of source streams which could be recycled

by this operation, but it is insufficient to satisfy the scrubber demand. Also, the Mx composition is still outside the acceptable range.

- In the last step, the Mx is mixed with FW_S to accomplish the required characteristic to be used in the scrubber. The flow rate of FW_S (the same as the flow rate of CN") is obtained by (2).

Since the amount of recycled streams (BC + CN') reaches the value of performance target (4.95 kg s^{-1}) it is obvious that the possibilities for recycling, based on No/Low cost strategies, have been exhausted. The other reason for that conclusion indirectly lies in the source prioritization rule. The CN stream, despite being the second priority option, cannot be completely recycled, and as a consequence there is no need to consider the recycle possibility from any remaining "worse" source stream.

The application of No/Low cost strategy enables the recycling of two source streams in appointed process sink-scrubber, and whereby changes the composition of its feed. As a consequence the material balances of the scrubber and all consecutive water-using units (subsystems) have to be revised on two levels: material balances by flow of H_2O and C_3H_3N (kg s^{-1}), and material balance of contaminant- NH_3 (10^{-6} kg s^{-1}); both around the units/subsystems.

The material balance revision starts in the scrubber whose simplified model involved two input streams: SN_S and GC, and only one output stream, SS. According to the adopted assumptions, SS can be presented as the mixture (Mx) made up of SN_S and GC (Fig. 3.10). The flow rate of H_2O and C_3H_3N inside SS is obtained using (3) and (4), while the concentration of NH_3 of SS (y_{SS}) is calculated by lever-arm rule (5). The results are then checked over the scrubber output constrains.

Next, the material balance is performed around the decanter model. The process in the decanter can be explained by few operations presented in mass mapping diagram in Fig. 3.11. The SS – single input stream in simplified model, can be represented either as the mixture ($Mx_{OLF,ALF}$) made up of OLF and ALF or a mixture ($Mx_{DC,ALS}$) of output streams DC and ALS. On the other side, output stream DC, which is transferred to the distillation column, is a mixture of OLF and 1 kg s^{-1} of ALF, while the ALS stream is a residue of aqueous layer form (ALF–1 kg s^{-1}), which is sent to the wastewater collector.

The material balance by flow is first employed to define the water content in the output streams. The overall water flow rate of DC is obtained by (6), assuming that OLF form does not contain the water. The rest of the water from SS is built in the ALS. The flow rate of C_3H_3N in ALS is determined by predefined composition of ALF (7), while the overall flow rate of ALF and OLF (as parts of SS) are obtained by (8). Finally the flow rate of decanter output streams, ALS and DC, are calculated by (9). The concentration of NH_3 in OLF is obtained by lever-arm rule, and by assuming that ALF has 4.3 times higher concentration of NH_3 than OLF (11). The flow rate of C_3H_3N in OLF, necessary for (11) is obtained from material balance by flow in (10). The concentration of NH_3 in output streams are calculated by (12) and (13). The results are checked over constraints of input in the distillation column.

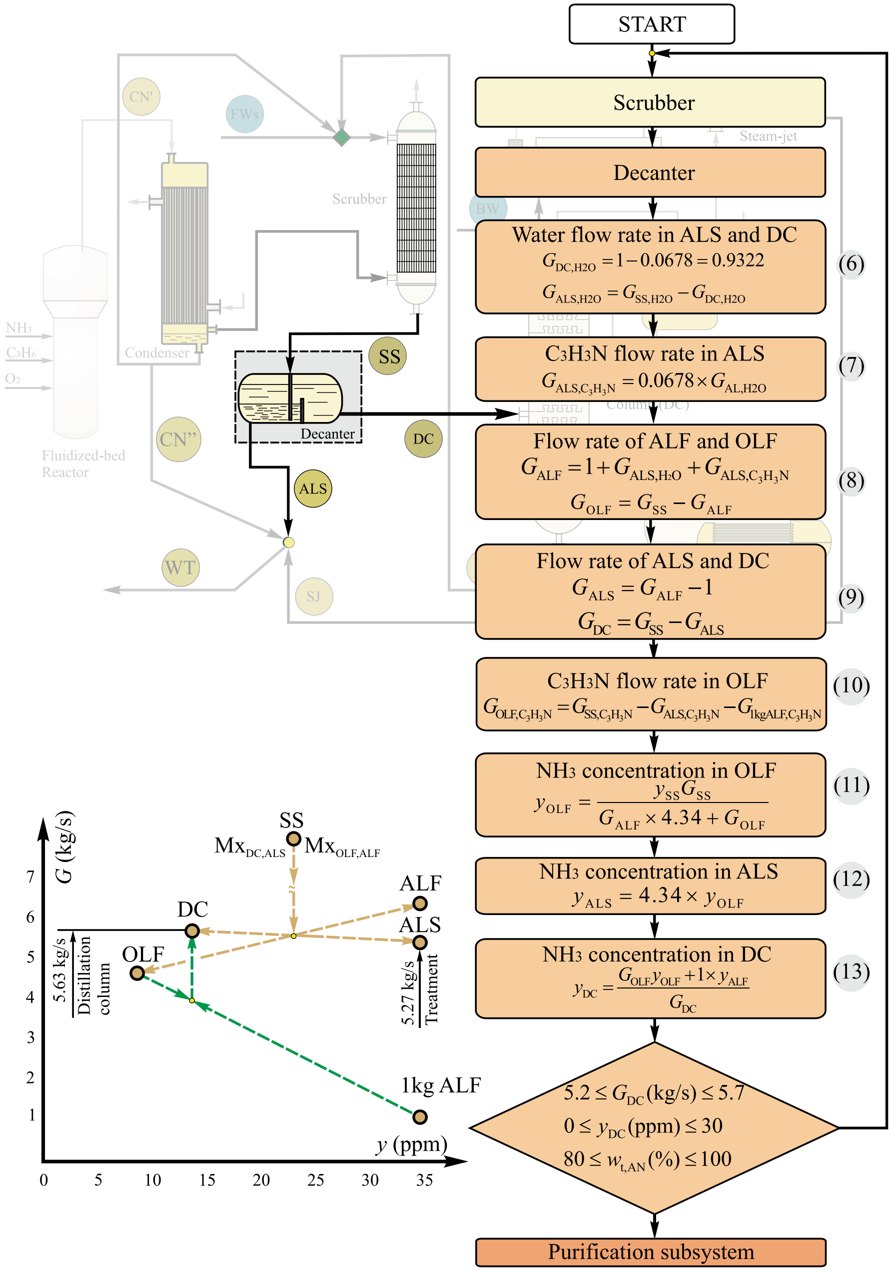

Fig. 3.11 Physical model, mass mapping diagram, and calculation flowchart of decanter model

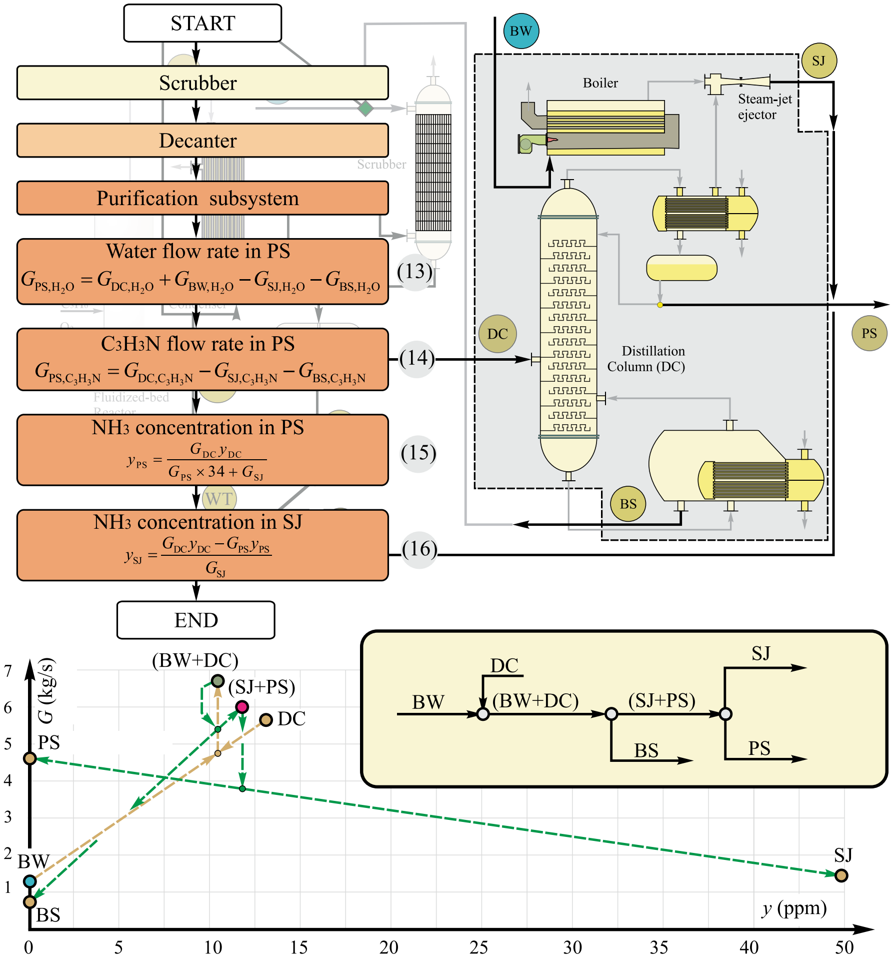

Fig. 3.12 Calculation flowchart, physical model and mass mapping diagram of purification subsystem

In the third step of the procedure the material balance is performed around the purification section (Fig. 3.12). For the purpose of better process explanation BW stream is involved in the model. The purification section includes two input streams (DC and BW) and three output streams (BS, SJ, PS). BS is recycled in the scrubber; therefore its characteristic should not be changed in the revised material balance. Different flow rate of input in the purification section will affect only *final product stream* (PS), since SJ retains the same flow rate of water and C_3H_3N as in the starting balance. The new flow rates of water and C_3H_3N in PS are obtained from (14) and (15) respectively. Ammonia concentration in PS is calculated by (15) accounting that NH_3 content in SJ is 34 times higher than in PS. The configuration of the final WUN is presented in Fig. 3.13, while its water/wastewater

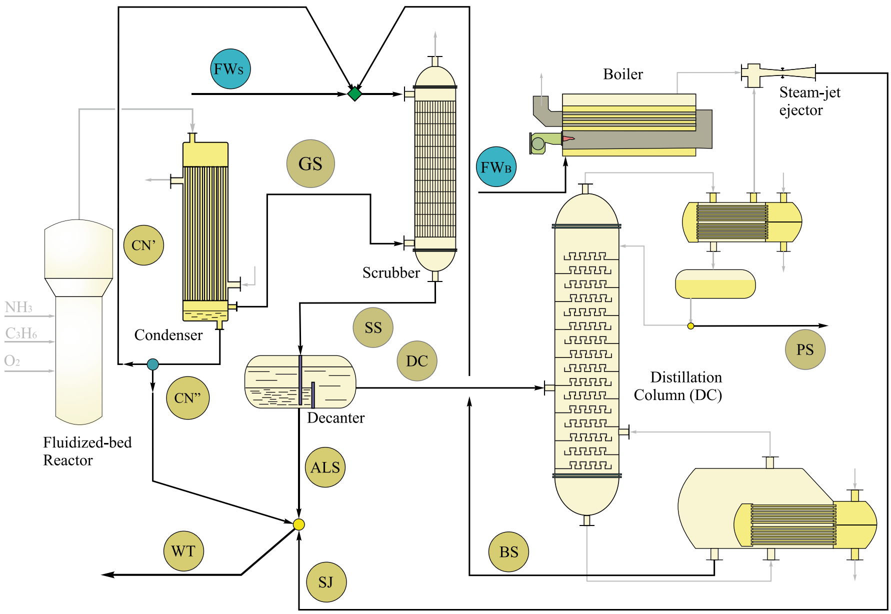

Fig. 3.13 Final flow sheet of WUN in ACN plant

Table 3.4 Stream parameters of water-using network in final flow sheet of ACN plant

Stream	C_3H_3N (kg s^{-1})	H_2O (kg s^{-1})	Total (kg s^{-1})	y_{NH3} (ppm NH_3)	M_{NH3} (10^{-6} kg s^{-1})
SN_B	0	1.2	1.2	0	0
SN_S	0.43	5.37	5.80	10.00	58.00
CN'	0.33	3.81	4.14	14.00	58.00
CN"	0.07	0.79	0.86	14.00	12.00
GC	4.60	0.50	5.10	39.00	198.90
Mx	0.43	4.51	4.94	11.73	58.00
SS	5.03	5.87	10.90	23.57	256.90
OLF	4.63	0.00	4.63	8.07	37.34
ALF	0.40	5.87	6.27	35.01	219.56
ALS	0.33	4.94	5.27	35.01	184.55
DC	4.70	0.93	5.63	12.85	72.35
SJ	0.20	1.20	1.40	50.17	70.24
BS	0.10	0.70	0.80	0.00	0.00
PS	4.40	0.23	4.63	0.46	2.11
WT	0.60	6.92	7.53	35.44	266.79

stream parameters are summarized in Table 3.4. The difference between the amount of fresh water demand and wastewater discharge in the starting and final WUN are presented in Fig. 3.14a. Fresh water demand is decreased for about 70% and the flow rate of WTS is reduced by about 42%.

Next, sequential spreadsheet software enabled automatic calculation of all WUN parameters in relation to different flow rates of scrubber feed (SN_S). The calculation

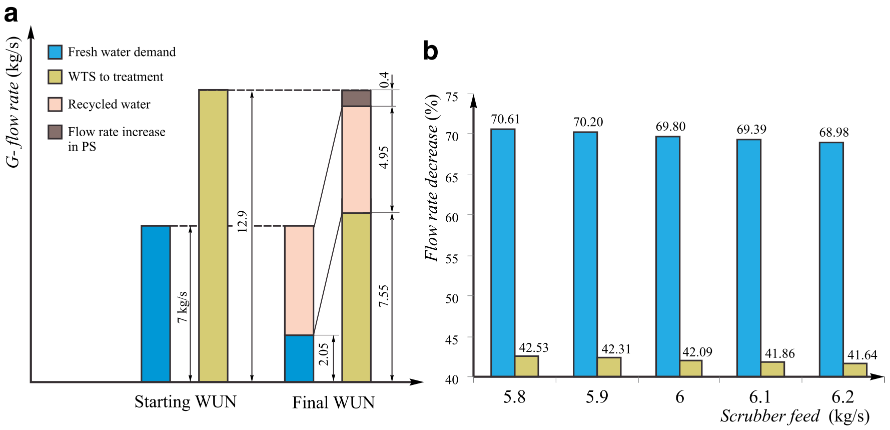

Fig. 3.14 Differences of water demand and waste-water discharge in starting and final WUN

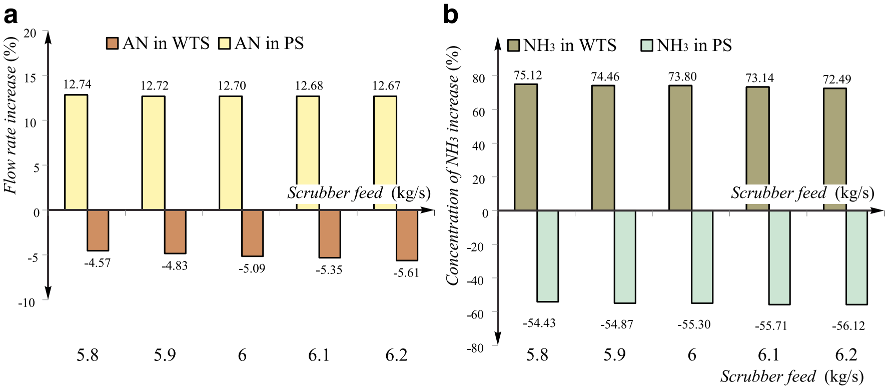

Fig. 3.15 Flow rate and composition analysis of PS and WTS stream in starting and final WUN

results are presented in the form of percentage difference between stream flow rates and compositions in starting and final WUN. In Fig. 3.14b the results approved the proper selection of minimal scrubber feed ($G_{\mathrm{SNS}} = 5.8\ \mathrm{kg\ s^{-1}}$), since it enables the most efficient WUN solution subject to amount of recycled water and discharged wastewater.

Diagram in Fig. 3.15a exposes the recovery potential of the plant by analyzing the variations of C_3H_3N flow rate in WTS and PS stream. The redesign of WUN provides the recovery of almost 13% of C_3H_3N built in PS stream, and 5% decrease of C_3H_3N loss which is sent to the water treatment facility. The recovery potential of the WUN does not change considerably with different scrubber feeds, but maximal scrubber feed provides additional loss of AN, which is transferred by WTS stream. The composition of WTS and PS streams due to the concentration of NH_3 is analyzed in Fig. 3.15b. Final WUN decreases the NH_3 concentration in the PS and also increases NH_3 concentration in WTS, making the valuable economical benefits of the new design.

3.6 Conclusion

During the last 40 years measures undertaken by many CPI companies for resolving the water-using problem in the plants across the world are already beginning to have an impact. In Europe, in the period 2003–2006, in chemical plants water demand was reduced by 8%; nitrogen/phosphorus emissions is decreased by 16/32%, while emissions measured in terms of chemical oxygen demand (COD) – have been decreased by over 25%. In particular, Swiss company Ciba reduced its water consumption by 22% in 2006, while BASF, decreased the process water consumption by 14%, COD levels by 66% and heavy metal emissions by 44% in 2002–2007. In the US, water emissions of chemicals classified as hazardous or potentially harmful were halved in the 10 years from 1995. They are now only around 10% of what they were in the late 1980s [21].

All of these results are provided by wide range of measures and approaches, among them one of the most successful is PI approach, presented in this chapter. The water-using problem was considered by the MI approach and practical application of No/Low-cost strategies in design of efficient and cost-effective WUN. The solutions presented on the case study, obtained by simulation spreadsheet software, revealed a great potential of proposed methodology by improving the plant sustainability performance and its ability to remain competitive on the global market.

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Chapter 4
Technological Advances in Industrial Water Safety and Security

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Abstract Assessment of contaminants in source water systems with inputs from industrial discharge, sewage treatment plants, storm water systems and runoff from urban and agricultural land is critical to formulating remediation of contaminants strategies for specific application. Generally, materials approaching nanoscale dimensions exhibit characteristics with numerous unique and previously unexploited applications. Hence, to develop application-specific uniform standards for water quality critical for different applications, advances in nanoscale materials devices and systems are reviewed to evaluate chemical, biological, and physical characteristics and integrity of water. Certain characteristics of nanoscale materials are exploited to remove, remediate, and even neutralize contaminants in water supply, as needed for a specific industrial application. A water quality management system is proposed based on region specific contaminants. The approach is proposed to be extrapolated for portable water purification systems. Water quality is a rather complex subject and is intrinsically tied to the regional ecology, application, and point-of-use, hence standards vary accordingly. Thus, it is extremely important to monitor, control, and maintain water quality – typically defined as physical, chemical and biological characteristics of water in relationship to a set of standards. An overview of latest advances in point and stand-off sensors/detectors from industrial water safety and security standpoint as a tool for better preparedness is described.

Keywords Nanomaterials • Industrial water quality • Detection • Security

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4.1 Introduction

Water is fundamental to sustaining life. Notwithstanding use of water for drinking -safe, secure, and functional water supplies that support industry, irrigation and agriculture, aquatic systems for fisheries and recreation, processing and cleaning, thermal management, etc. are indispensable to sustaining modern urban living. A growth in human population and associated increased demands on water poses a significant challenge in maintaining adequate yet acceptable water quality in various sectors. It is estimated that worldwide, approximately 1.2 billion people lack access to clean drinking water (WHO 2004 [9]). Water experts believe that to meet the soaring demand, humankind must find smarter ways of using its water supply. The demand for clean water extends beyond residential and municipal needs. High volumes of high purity water are critical for most industries and laboratories, e.g., environmental remediation, hydrocarbon processing, catalysis and chemical processing, food and beverage, mining and hydrometallurgy, pharmaceuticals, power generation and semi-conductors. For example, microelectronic facilities require approximately 2,000 gal of water to manufacture one 200 mm wafer [3]. Ultrapure water is generally considered to be >18.2 MΩ-cm resistivity at 25°C, less than 50 ppt in inorganic anions and ammonia, less than 0.2 ppb in organic anions, and below 1 ppb total organic carbon and silica, and is essential for semi-conductor plants and microelectronic manufacturers and is the primary solvent used to remove contaminants from semiconductor wafers [5]. The high volume of water required for such manufacturing processes can make businesses unsustainable in areas with limited water availability. At the same time, these industries also have stringent requirements to control wastewater discharge in the environment, for which the same innovative solutions for water purification for manufacturing processes are necessary to the remove contaminants from discharge and wastewater reclamation. As industries grow incorporating recently developed more advanced technologies, pure water will become ever more critical to advance these operations and increasing the demand for the limited water resources. Furthermore, by a survey conducted by the International Council for Science, environmental experts ranked freshwater scarcity as a twenty-first century issue second only to global warming.

For many years, most developed countries have had easy access to high-quality, fresh water that was relatively easy to obtain, treat and transport. However, global water shortage problems are becoming more widespread with population growth, drought, and industrial expansion. There are increasing concerns about the availability of usable water, and many communities and industries alike are faced with dramatic reductions in traditional fresh water supplies and deteriorating water quality in the form of contaminated wells, runoffs, and other ground supplies. Global water scarcities increase the urgency for the preservation of fresh water resources and increased water reclamation efforts (i.e., wastewater treatment, remediation, water reuse, and desalinization); management of global water resources is critical to creating sustainable water supplies for residential, agricultural, and industrial purposes, energy conservation, and improved quality of life. High volumes of wastewater are generated daily from residential and industrial discharge.

For geographic locations with water scarcity, the primary use of reclaimed water has been for agricultural and landscape irrigation, but the push for alternative, sustainable water sources to meet the ever increasing demand for clean water, has propelled more innovative, advanced water treatment technologies to efficiently and safely convert wastewater into high quality product water for reuse in such applications as industrial processes and groundwater replenishment.

It is critical to observe the association between the basic need for clean drinking water and water resources, and national security concerns and policy. There are numerous national threats emanating from the growing crisis of global freshwater scarcity. Many of the earth's freshwater ecosystems are being critically depleted and used unsustainably to support growing residential and industrial demands; thereby increasing ecological destabilization, creating a greater regional divide thus directly impacting current political, economical and social landscapes.

In view of the above scenario, it is important to use the latest state-of-the-art technological advances for detection of contaminants in water sources. Since composition of contaminants varies from region to region, it is technological and economically beneficial to develop a remediation strategy that is region specific and removes only those contaminants that are present for a specific region and also sector specific application. Such a distributed water purification system is likely to be more technologically efficient, economical, and serve a better purpose.

4.2 Materials in Reduced Dimensions

Reduced dimensional systems, in which one or more dimensions are reduced (in nanometers) such that material begins to display quantifiable novel characteristics, hold tremendous unique potential [6, 8]. For solids, typically reduced dimensions amount to reduction of the coordination number; hence the electrons have less opportunity to hop from site to site; thus reducing kinetic energy of electrons or their bandwidth. A higher Coulomb interaction/bandwidth ratio at a site enhances electron correlation and Mott-transition. Furthermore, the symmetries of the system are lowered and the appearance of new boundary conditions leads to surface and interface states. A change of the quantization conditions alters the Eigenvalue spectrum and transport properties of the solid. A high surface area/volume ratio in nanoscale materials alters mechanical and other physical properties. One critical impact is that surface stresses existing in nanomaterials have a different bonding configuration as compared to bulk atoms. The effects of the difference between surface and bulk elastic properties thus become magnified as the surface area/volume ratio increases with decreasing structural dimension. Studies to calculate surface elastic constants using MD simulations, curvature effect using the Cauchy-Born rule, and electronic effects via effective nuclei-nuclei interaction using DFT calculations provide better understanding of surface and interface effects in reduced dimensions. Size and surface collectively control characteristics of nanoscale materials due to the existence of large boundaries adjoining its surrounding medium and interplay of physicochemical interactions. The surface free-energy is size-dependent and hence increases almost inversely with the decreasing feature sizes of the material. Collective response of a nanomaterials-medium system that is attributable to reduced dimensions, viz. size, surface structure, physical, and chemical is vital to developing a scientific model that predicts its response and interaction.

4.2.1 Chemical-Biological Sensors/Detectors

Nanomaterials, such as carbon nanotubes (CNTs), nanoparticles, nanowires, nanocones, quantum dots (QDs), nanoporous materials, etc. are commonly used for chem.-bio sensors/detectors. CNTs are conducting, can act as electrodes, generate electro-chemiluminescence (ECL) in aqueous solutions, and can be derivatized with a functional group that allows immobilization of biomolecules. The uniform chemical functionalization of CNTs is critical to the formation of biosensors. Oxidation of CNTs leads to high concentrations of carboxylic, carbonyl, and hydroxyl groups on the surface and removal of the tip to expose the tube interior. Carboxyl groups can readily be derivatized by a variety of reactions allowing linking of biomolecules such as proteins, enzymes, DNA, or even metal nanoparticles. The covalent modification of CNTs facilitates the creation of well-defined probes, which are sensitive to specific intermolecular interactions of many chemical and biological systems. Integration of the transducer and probe enables quick, accurate, and reversible measurement of target analytes without the use of reagents. Covalent modification of single wall CNTs (SWNTs) offers mapping of functional groups at a molecular resolution. Furthermore, chemical processes to link catalysts, such as transition-metal complexes, to the ends of CNTs are useful in creating or modifying the structures at a molecular scale, creating interconnections for electronic devices, and even developing new classes of materials. Covalent functionalization of the sidewalls of SWNTs provides stability and best accessibility, but at the expense of damaging the sidewalls, thereby changing their electronic characteristics. Noncovalent functionalization on the contrary, offers ease of synthesis and minimum disruption of the tubular structure. During interaction with the polymer coatings, the electrical properties of NTs are altered, enabling detection of the molecules leading to a very sensitive sensing mechanism. In addition to NTs, novel materials such as porous silicon and porous carbon, with porosities of comparable dimensions to those of the biomolecules are used for biosensor applications. The mesoporous carbon matrix is used for stable immobilization of the biological molecule, and C60 serves as an electron mediator. Both C60 and NTs are good electron mediators when used with a mesoporous carbon matrix or modified metal electrodes. CNT-based transducers, however, show a significant advantage over porous silicon due to the well-defined, defect free structures, and also because the NTs promote homogenous electron transfer reactions [1].

Self-assembled monolayers (SAM) based Surface Plasmon Resonance (SPR) is used to detect several pathogens. The SPR detection technique is rapid, real-time, requires no labeling, and involves immobilizing antibodies by a coupling matrix on the surface of a thin film of precious metal [2]. A main response is the refractive index of the metal film, to which target molecules are immobilized using specific capture molecules or receptors along the surface, that cause a change in the SPR angle. This can be monitored in real-time by detecting changes in the intensity of the reflected light, producing a sensorgram. The rates of change of the SPR signal can be analyzed to yield apparent rate constants for the association and dissociation phases of the reaction. Surface enhanced Raman Spectroscopy (SERS) has been used for chemical-biological detection. One possible mechanism of the enhancement of the signal is due to excitation of localized surface plasmons primarily due to physisorbtion, while the other chemical theory explanation rationalizes the effect through the formation of charge-transfer complexes.

Nucleic acids offer a powerful tool for recognition and monitoring of many important compounds. Recent advances in molecular biology aid investigation of the effects of proteins and drugs on gene expression, viz. gel mobility shift, filter binding, DNA footprinting and fluorescence-based assays. Most of these methods, however, are indirect and require various labeling strategies. Electrochemical DNA biosensors play an important role for clinical, pharmaceutical, environmental and forensic applications, because they provide rapid, simple and low-cost point-of-care detection of specific nucleic acid sequences. Binding of small molecules to DNA primarily occurs in three modes: electrostatic interactions with the negative-charged nucleic sugar-phosphate structure, binding interactions with two grooves of DNA double helix, and intercalation between the stacked base pairs of native DNA. Most electrochemical sensors use different chemistries, and employ interactions between the target, the recognition layer and an electrode. In direct electrochemical DNA sensors, the analysis is based on a guanine signal where a base-pairing interaction recruits a target molecule to the sensor, allowing monitoring of drug/biological molecule-DNA interactions, which are related to the differences in the electrochemical signals of DNA binding molecules. It is vital to develop sensing strategies to maintain critical dynamics of target capture to generate a sufficient recognition signal.

Recent progress in nanostructured materials based sensor platforms has significantly contributed to data collection, processing, and recognition to enable the direct detection of biological and chemical agents in a label-free, parallel, multiplexed, broadly dynamic range, allowing fast and accurate detection of chemical and biological agents with high sensitivity and specificity [7].

4.3 Advanced Sciences Convergence

To meet the future water demands for the growing global population, it is imperative that we seek technological advances for water and wastewater treatment and process systems that provide long term solutions for creating a sustainable source of water supply. Advanced Sciences Convergence (ASC) refers to the early monitoring and identification of emerging scientific advances across multiple disciplines that create revolutionary, integrated and cross-cutting technologies to break through existing solution paradigms. The process of ASC is to understand how different disciplines, focusing on discrete problems and applications, can coalesce into an integrated system to solve a seemingly intractable problem. It requires understanding of far-reaching end goal that is not yet defined, but can be described in terms of desired actions or qualities of the eventual system. Multiple approaches, some of which may be high risk research, can be pursued simultaneously to create components of the system. A patchwork of emerging scientific advances is constructed through a strategic planning process to create a fully integrated system.

The first step in this high-level analysis is to understand the challenge vectors, identify the specific requirements of the stakeholders, and design a strategic approach based on the intersection of global cutting edge scientific advances with the most critical operational requirements identified in collaboration with the user community. The convergence process requires monitoring domestic and international developments in multiple disciplines. These data mining operations are focused in areas identified through the strategic planning process as having a high potential for meeting some desired characteristic of the solution system. Constant cross pollination among multiple disciplines is required to identify emerging patterns within the larger scientific community. The overall process starts with strategic planning to describe the solution system supported by data mining and investigation of emerging science. It is an ongoing iterative process which includes greater understanding of the science, research entity, eventual technology, and system integration. Advances are supported by tapping into multiple databases to develop not only individual science but also the nature of the integrated solution system and are applied at the Institute for Advanced Sciences Convergence and International Clean Water Institute to develop sustainable, clean water production strategies.

4.4 Contamination Identification and Remediation

Scientists and engineers use a combination of conventional to state-of-the-art detection, disinfection, remediation and filtration technologies to produces safe, energy-efficient, and cost-saving water purification and wastewater reclamation facilities. Ideally, the technology must be portable, amenable to both field and laboratory analysis, and provide fast, reliable, and real-time detection and differentiation of biological system (e.g., bacteria, virus, pathogens) that enable service providers to take corrective action immediately before any infection or further contamination can occur.

4.4.1 Detection and Disinfection

Disinfection of wastewater is to reduce the number of microorganisms in holding tanks. Common methods of disinfection include ozone, UV light, and sodium hypochlorite. However, the most common and inexpensive disinfection methods involve some form of chlorine (e.g., chlorination, chloramines, chlorine dioxide) and although highly effective in killing most bacteria, viruses and protozoa, the process exhibits limited effectiveness against certain pathogens, such as cryptosporidium. The eradication of waterborne diseases is an overwhelming challenge. However, the devastating effects of infectious microorganisms may be minimized and controlled through efficient methods of monitoring and detection. Direct pathogen identification and isolation is difficult, if not impossible. Indirect "indicator organism" based inferences have been used for decades as indicators of contaminated water. Traditional and standard bacterial detection methods for identifying waterborne pathogens are often not suitable for routine monitoring due to their high cost, inadequate sensitivity, or lengthy processing time (up to 7–8 days to yield an answer). Moreover, all conventional methods require *a priori* knowledge of the pathogen. There is a growing global public health concern, within the scientific community and amongst the public, about the emergence and re-emergence of waterborne microbial pathogens that is occurring through a complex interaction of social, economic, and ecological factors. Currently, indicators for water quality do not take into account new and emerging microbes. Interestingly, only ~1% of microorganisms have actually been characterized; the spectrum of new disease is expanding, antimicrobial resistance is increasing, and waterborne diseases once believed to have been done away with are re-emerging. Clearly, there calls for a greater need for more appropriate methodologies, both for routine monitoring and detection.

The advancement of molecular biology and its application in environmental microbiology has represented significant advancement in the ability to rapidly detect waterborne microbial pathogens. Molecular biology-based alternative methods have improved the speed of detection from several days down to a few hours. The advent of new technologies, as mentioned earlier, has provided new and promising methodologies. The nano-enabled biosensors can specifically interact with cells (bacteria, viruses, and protozoa), however, only a small percentage have focused on the detection of waterborne pathogens. Metal ion pollution is a major challenge and attempts to getter by metal-binding ligands are currently in progress. Roots of some plants have known to sequester Arsenic ions and are currently in use as test pilot project [4]. In yet other effort, iron getters are employed in holding tanks and absence of iron in water lines will reduce bacterial growth. Such innovative concepts, in conjunction with modeling that specifically address fluid flow and movement of chemicals in rock formations near aquifers. This research may lead to improved management of freshwater resources along the coast or underground sources of salinity.

4.4.2 Wastewater Remediation and Contaminant Removal

Remediation and contamination removal systems span the range from reverse osmosis and nano-filtration, electro-deionization, ultra/micro filtration membrane technology, ion exchange resins (ion exchange is a well-proven technology for the removal of a wide variety of trace metal contaminants, including chromium,

Table 4.1 Wastewater treatment processes

	Conventional sand filtration	Membrane micro-filtration	Membrane ultra-filtration	Membrane nano-filtration	Membrane reverse osmosis
Operating pressure (bar)	0.1–2.0	0.2–2.0	1.0–5.0	5.0–20.0	20.0–80.0
Contaminant removal	Large suspended matter	Colloids bacteria	Large organic molecules, viruses	Small organic molecules, divalent ions	All dissolved species
Water treatment application	Filtration, clarification	Purification, filtration	Purification, filtration	Color, natural organic matter, micro-pollutant removal	Desalination

cadmium, nickel, copper, lead and zinc) to chelating resins and adsorption media. However, membrane filtration, semi-permeable thin barrier sheets used in water treatment processing for less than 50 years, is the leading technology for the specific removal of pollutants and wastewater treatment to high purity standards. Membranes are considered an ideal tool for recycling water due to their extensive abatement range. Advanced wastewater treatment processes often incorporate a high-pressure reverse osmosis system, among the most effective technologies for removing PFCs, trace pharmaceuticals, and disease-causing bacteria and viruses from water, with lower pressure membrane filtration pretreatment (Table 4.1). The integrated membrane system possesses the capability to remove salts, volatile organic and inorganic chemicals, nitrates, radio-nuclides, etc., and reduce pathogen exposure to produce a customized solution for meeting localized clean water needs.

4.5 Water Quality Management Methodology

Providing for abundant fresh water for human use is among one of the most pressing priorities facing the international community for the reasons stated earlier in the introduction section. Unfortunately, the problem set of water purification is rather diverse and becomes rather complicated due to different geographic locations and also complex issues requiring individual, local, regional, national, and even international solution platforms. Despite advances in large scale, conventional purification and disinfectant systems for both ground and surface water sources employing chlorine dioxide, ozone, and ultraviolet irradiation, there are reports of disease outbreaks from waterborne infections. In addition to microbial contamination from bacteria, protozoans, and viruses, the water supply contains previously undiscovered pathogens and pharmaceuticals – viz. antibiotics, steroids, and common over-the-counter (OTC) painkillers causing adverse affects in younger generations. Hence, a number of disinfection technologies, including both point of use (POU) and point-of-entry (POE) have been deployed to address the contamination issues.

The opportunity nexus for water purification consists of (i) Environment – decontamination technologies to minimize environmental impact, globalization, urbanization, and other emerging issues to ensure adequate clean supply of potable water. (ii) Energy generation – as the energy demand continues to increase, water consumption for such plants is expected to increase between 30% and 50% (depending upon efforts to reduce consumption of fossil fuels). (iii) Agriculture – increase in population will require greater water supplies for irrigation and livestock and new mechanisms for enhanced agricultural water conservation and increased recovery and reuse of irrigation runoffs; (iv) Health – as the water supply continues to be excessively strained, production and access to clean potable water is closely related to human health. In addition, several regions worldwide have increased amount of arsenic in water supplies leading to toxicity. Pathophysiology of arsenic includes disruption of ATP production; inhibits pyruvate dehydrogenase and energy-linked reduction of NAD^+, mitochondrial respiration, increased hydrogen peroxide production leading to oxidative stress; and metabolic interferences leading to death from multi-system organ failure. Several studies have linked long-term exposure to small concentrations of As with cancer and cardiovascular, pulmonary, immunological, neurological and endocrine effects; thus necessitating studies for developing efficient methods for removing As from drinking water. (v) Security – Maintaining water supply chain integrity has been a major challenge for military. Water supply chain has emerged as one of the main targets for terrorism. Mechanisms are intentionally omitted here for security reasons; needless to mention that maintaining water security is one of the primary areas of the author. Furthermore, U.S. EPA has initiated a Water-Sentinel program for the design, development, and deployment of a robust, integrated water surveillance system to provide real-time system wide water quality monitoring, critical contaminants sampling and analysis, and public health surveillance. The complexity of the Water-Sentinel program is expected to be modified using nanomaterials based sensors, improvised signal distribution and transmission, and decision support technology. (vi) Economy – The congressional budget office in the U.S. estimated in late 1990s that the average cost of water and wastewater services represented ~0.5% of household income and it is anticipated that by 2020 the cost are projected to be ~0.6–0.9% of national household income. With increasing population, pollution, energy consumption, and associated health impact, dependence of economy of water becomes a rather complex issue impacting country's potential for prosperity. To enhance economic prosperity, the issue of abundant clean water has emerged to quintessential for international community for economic prosperity and maintaining quality of life index for its citizens.

4.5.1 Water Quality Definition

Water quality is typically defined as physical, chemical and biological characteristics of water in relationship to a set of standards. Water quality is a rather complex subject and is intrinsically tied to the regional ecology, application, and point-of-use, hence standards vary accordingly.

Figure 4.1 shows a water quality definition model based on application and point of use. As pointed earlier, based on regional ecology, a more efficient water treatment can be designed which is likely to be more efficient, economical, and practical. The processing of water is proposed to be distributed and even at point of use, as described in the following sections.

4.5.2 Management System

A conceptual schematic of proposed water management system is presented in Table 4.2 and Figs. 4.2 and 4.3. The methodology consists of conducting a thorough detection of chemical and biological contaminants in water derived from a specific source and comparing with an inventory of acceptable maximum contaminants acceptable quantities according to local regulations or the U.S. Environmental Protection Agency (EPA).

The water derived from aquifers, rivers, water shed, and other available sources will have different contaminants. In designing water purification strategies specific to an application, the limits of contaminants will be different for different applications. As for example, the water for drinking and cooking will have different standards as for potable water and for gardening. Likewise, for industrial applications, water for medical, pharmaceutical and semiconductor processing applications have different level of acceptable contaminants than power generation, and aquatics and leisure. Based on regional ecology and associated water contaminants, an efficient water purification scheme and process flowchart is provided in Fig. 4.2 and an overview of the methodology is shown in Fig. 4.3. It is anticipated that such a scheme is likely to produce economical, more efficient, and distributed purification scheme at the point of use.

It is intended that a similar approach is to be utilized for water purification system for hand-held portable units (similar to Life-Straw, Life-Saver, and other portable water filtration systems) however with a striking difference that the unit is designed for contaminants specific to a region and is rendered more efficient. The approach is more effective as not all sources of water may contain all contaminants and hence by selecting remediation strategy, the unit will be more cost effective.

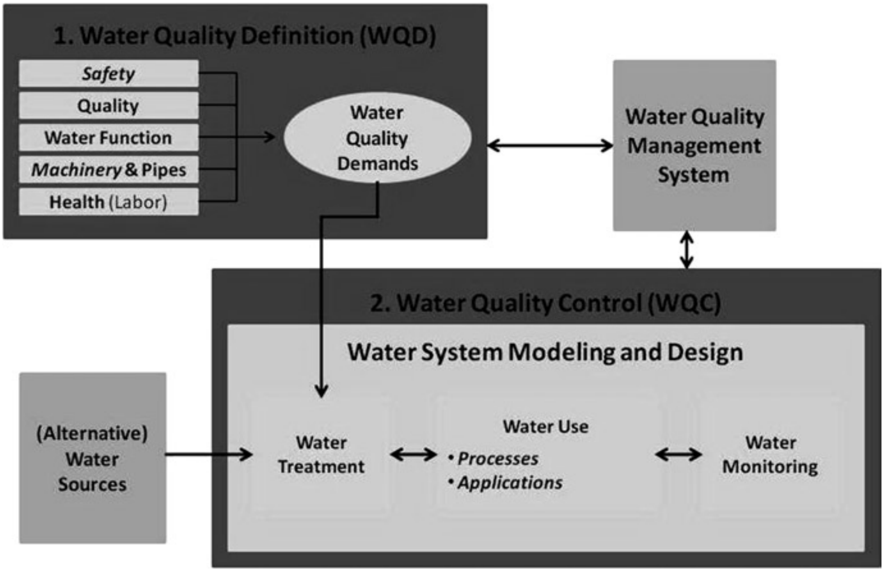

Fig. 4.1 Water quality definition model

Table 4.2 Inventory of maximum allowable contaminants for process water function as per regulatory guidelines

Region	Industry/sector	PWF	Compound and corresponding range
Region 1	Residential	Drinking	Compound 1[..,..]; Compound 2 [..,..]; Compound n [..,..]
		Cooking	Compound 1[..,..]; Compound 2 [..,..]; Compound n [..,..]
		Bathing	Compound 1[..,..]; Compound 2 [..,..]; Compound n [..,..]
		Gardening	Compound 1[..,..]; Compound 2 [..,..]; Compound n [..,..]
	Commercial	Restaurants and food service	Compound 1[..,..]; Compound 2 [..,..]; Compound n [..,..]
		Hospitals, labs and clinics	Compound 1[..,..]; Compound 2 [..,..]; Compound n [..,..]
		Aquatics and leisure	Compound 1[..,..]; Compound 2 [..,..]; Compound n [..,..]
		Hotels and resorts	Compound 1[..,..]; Compound 2 [..,..]; Compound n [..,..]
	Industrial	Semiconductor	Compound 1[..,..]; Compound 2 [..,..]; Compound n [..,..]
		Power generation	Compound 1[..,..]; Compound 2 [..,..]; Compound n [..,..]
		Agriculture	Compound 1[..,..]; Compound 2 [..,..]; Compound n [..,..]
		Pharmaceutical	Compound 1[..,..]; Compound 2 [..,..]; Compound n [..,..]

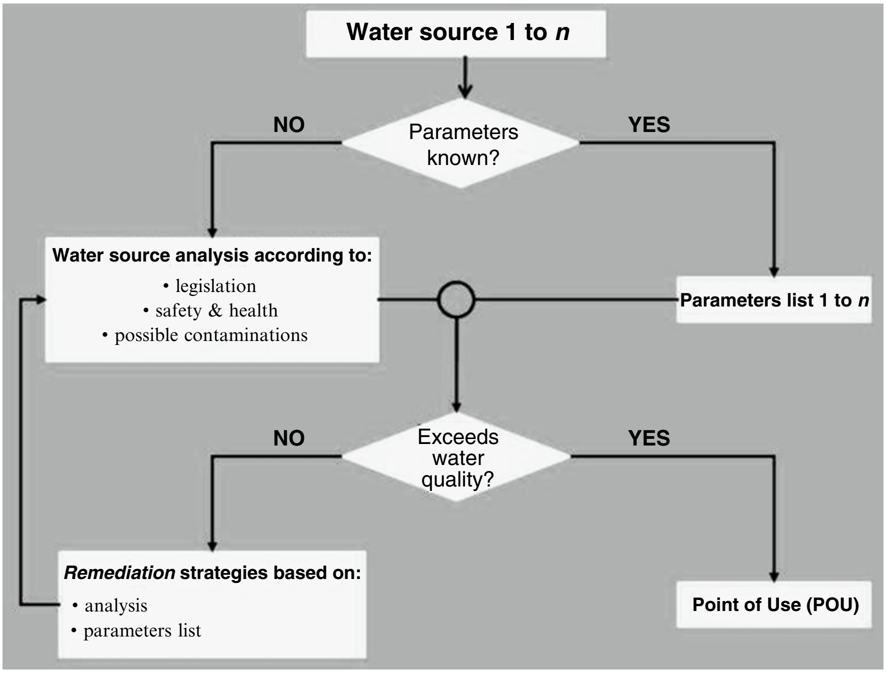

Fig. 4.2 Water purification decision flow chart

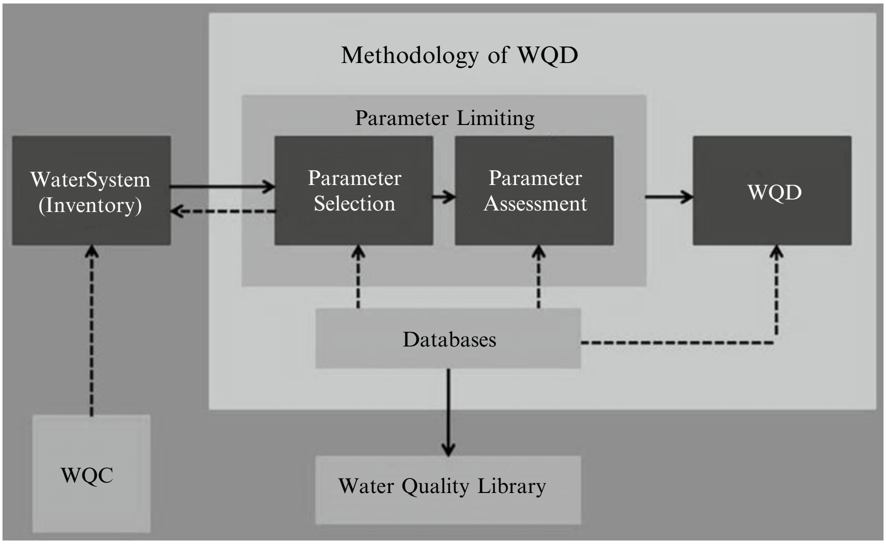

Fig. 4.3 A region specific contamination detection and remediation methodology

4.6 Conclusion

Using technological advances, more specifically using nanomaterials and convergence of advanced sciences, identification, prioritizing, and remediation of contaminants specific to regional ecology is proposed in this investigation. The methodology is equally applicable to assess water source systems that receive inputs from industrial waste and sewage treatment plants, storm water systems and runoff from urban and agricultural lands. It is extremely important to monitor, control, and maintain water quality – typically defined as physical, chemical and biological characteristics of water in relationship to a set of standards. To maintain water quality in an efficient manner, a methodology is proposed which is based on remediation of regional contaminants specific to point of use. Such an approach is likely to be economical and more efficient. It is to be further noted that not all countries have uniform set of guidelines for water quality. Such methodology is likely to bring uniformity in standards of water purification across the globe.

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Chapter 5
Water Footprinting: A Tool to Develop and Manage Water Stewardship for Business

Alistair J. Wyness

Abstract With increasing pressures on water resources throughout the world, the role of business in managing water resources is increasingly important. Corporately, the management of water resources is changing from one of compliance with local regulations to corporate water stewardship, where industry not only conserves water use within its direct control, "inside the facility fenceline" but also acts responsibly and seeks to influence water managed within the supply chain, the local communities and the wider regional, national and international watersheds, "beyond the fence line". Understanding the risks and opportunities at these different scales can be developed through water footprinting. The water footprint is a measure of freshwater use and impacts, a more comprehensive measure of freshwater resources appropriation than traditional water abstraction and discharge measures. The water footprint calculates the total water consumption and impact on water resources of a product or service. The footprint, when mapped against water availability, allows businesses to understand where the pressures may lie, so that appropriate strategies can be developed. This chapter presents the method, developed from its implementation across different products, and highlights how the results of the water footprint can help develop and manage appropriate water stewardship strategies.

Keywords Water footprint • Virtual water • Stewardship • Life cycle analysis

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5.1 Introduction

Global water resource availability, already at critical levels in many parts of the world, is expected to worsen in the coming years as a result of population growth, urbanization and industrialization, increased water pollution and the effects of a changing climate. The world's population is expected to rise from the current 6.9 billion to between 9.15 and 9.51 billion by 2050 [14]. Much of the demographic change up to 2050 is predicted to take place in the less developed regions. Collectively, the less developed regions will grow 58% over 50 years, as opposed to 2% for more developed. Similarly the growth rate in urban areas is likely to be significantly greater than in rural areas. By 2030, almost 60% of the people in developing countries will live in cities [17, 18].

This growth in population will result in a significant increase in the demand for clean water for water supply and sanitation, for agriculture to support the increased demand for food, for energy as the energy demands increase with the rising population and for industry. Adding to the pressures, climate change from greenhouse house gases will impact the distribution of precipitation and evaporation across the world, changing the water resource availability in many, if not all, locations.

Over the next 20 years, these pressures will result in a global deficit in supply over demand. It is estimated that by 2030 that this deficit will be around 40% based on the current estimate of sustainable resource availability, as shown in Fig. 5.1.

Significant investment in irrigation, water supply and sanitation infrastructure is required throughout the world, an area that international lending institutions will be focusing on in the coming years (e.g. IFC [13]). Governments will need to invest in harnessing sustainable water resources for agriculture and water supply and sanitation.

For industry, all these pressures threaten the long-term viability of businesses and pose serious financial and operational risks for companies that rely on large amounts of water for processes and/or manufacturing or food and agricultural based raw materials. At the same time investors in these businesses are now seeking an understanding from companies on the risks that companies may be facing in relation to water resource availability and the actions being taken [5, 6].

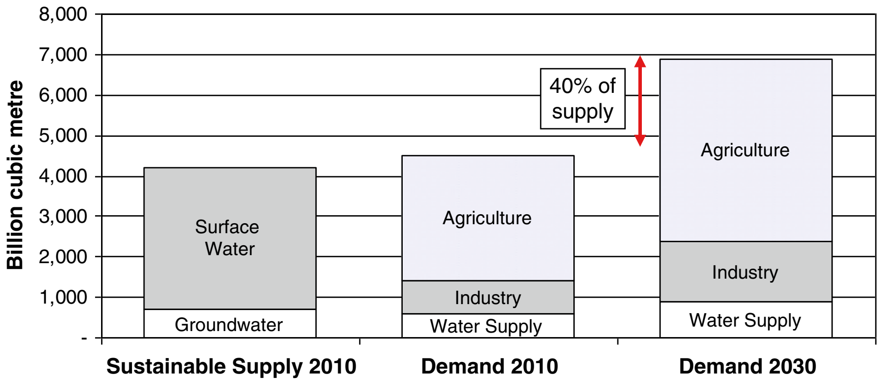


Fig. 5.1 Global water supply and demand 2010–2030 [1]

It is now important that industries understand their consumption of freshwater and the impact that their operations may have on freshwater resource availability and quality, not only in their direct control (direct use), but also across the full life cycle of the product development, from raw materials to customer use (indirect use). One emerging technique to quantify water use is through water footprinting, the subject of this chapter.

5.2 The Concept of Water Footprinting

The *water footprint* has been defined by Hoekstra [10] as:

> An indicator of water use that looks at both direct and indirect water use of a consumer or producer. The water footprint of an individual, community or business is defined as the total volume of freshwater that is used to produce the goods and services consumed by the individual or community or produced by the business. Water use is measured in terms of water volumes consumed (evaporated) and/or polluted per unit of time. A water footprint can be calculated for any well-defined group of consumers (e.g. an individual, family, village, city, province, state or nation) or producers (e.g. a public organization, private enterprise or economic sector). The water footprint is a geographically explicit indicator, not only showing volumes of water use and pollution, but also the locations.

The water footprint concept was introduced as a consumption-based indicator of water use for products and services. The concept of a water footprint is closely linked to the virtual water concept, introduced by Allen JA [2, 3]. Virtual water is defined as the volume of water required to produce a commodity or service. Allen developed this concept as a tool to manage water scarcity in regions, for example, importing the virtual water in food production to conserve scare resources in country.

A water footprint can be applied at different scales, an individual, a product, a business and a nation. For example, Hoekstra and Chapagain [11] develop a method for calculating the water footprint of nations on the basis of the consumption pattern of its people, Chapagain et al. [7] developed the global water footprint for cotton consumption from crop growth through garment production, import and export patterns and waste disposal and many organisations have developed an estimate of the water footprinting for individual household items.

The water footprint is calculated for three different types of water: green water, blue water and grey water. The most up to date definitions were developed by Hoekstra et al. [12] as follows:

- The **green** water footprint refers to the volume of precipitation evaporated during the production process. This is mainly relevant to agricultural products. Green water refers to the precipitation on land that does not runoff or recharge groundwater but is stored in the soil and evapotranspires during crop growth. The evaporative loss is included as a component part of the water footprint because a significant proportion of the water would be available to other water users (e.g. groundwater reserves, ecological features) if the crops were not, in fact, grown. Although the evaporation may be an available resource to other users, it has been assumed that such a loss is not available to the area on immediately downstream of the area in which the crops are grown and is, therefore, considered a water use.

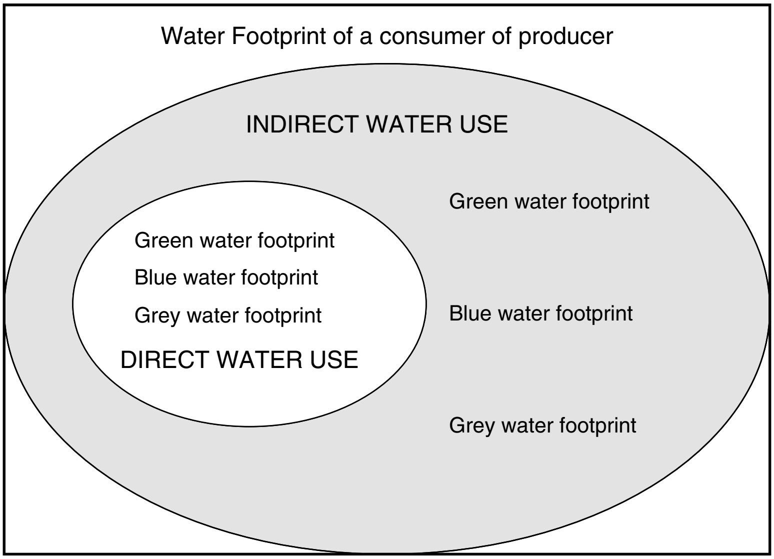


Fig. 5.2 Components of a water footprint

- The **blue** water footprint refers to the volume of surface and groundwater "consumed" as a result of the production of the product or service. The consumptive water use covers four cases: the evaporation of water, the water incorporated in the product, the water that is not returned to the same catchment from which it was withdrawn (e.g. to another catchment or the sea) and the water is not returned in the same period in which it was withdrawn. For example in the production of crops, the blue water in irrigation can include the additional evaporation rated to irrigating an area larger than the cropped area, the additional evaporation from impounding the irrigation water, the losses from the conveyance facilities etc. For the manufacture of a product this is defined as the amount of water withdrawn from groundwater and surface water that does not return to the system in which it came.
- The **grey** water footprint refers to the volume of polluted water associated with the production of goods and services, quantified as the volume of water that is required to dilute pollutants to such an extent that the quality of the ambient water quality remains above agreed water quality standards. For example, in crop production this could be taken as the volume of dilution to reduce nitrate and phosphate (fertilizer) levels and pesticide levels leaching from soils to agreed standards. For industrial production, the grey water is the dilution of effluent quality to agreed standards.

The water footprint is further split between **direct water use**, water consumption within the direct control of the business or consumer, often termed as "within the fenceline" [19], and **indirect water use,** consumption within the supply chain and customers, "beyond the fenceline". The components of a water footprint are described in Fig. 5.2.

A water footprint is a geographically explicit indicator, not only showing volumes of water use and pollution, but also the locations. It is, therefore, important that when calculating all the components of the water footprint, the locations of each component is noted. A water footprinting study should have two components: the calculation of the water footprint in each catchment and an impact assessment of the water use within each catchment. This way the footprint can be compared with the available water resources, quality and constraints of the individual watershed to understand the localised impacts. A water footprint calculation without reference to the location in which the water is consumed or impacted has significantly less value.

5.3 Methods of Assessment

In calculating a water footprint the different components of direct and indirect water consumption are assessed separately. For direct use, the water footprint is primarily blue water with the effluent grey water. In the case of a manufacturing process, the data required to calculate the blue and grey water direct uses is traditionally measured and reported by business and is therefore more readily available. However, to define green, blue and grey water for the supply chain and the consumer use, the data sets generally become less prevalent and less available to the industry concerned.

In developing the green, blue and grey water footprints, it is important that the boundaries of the footprint are defined (i.e. start point and end point in the development, production and consumption of the commodity). It is best that a full life cycle type approach is adopted so that all components of water use and impacts are mapped and quantified. Most importantly, though, it is essential that the locations of water use and impact are maintained throughout the assessment process. In effect the process is to calculate direct and indirect water use and impact, split according to green, blue and grey water, for all the locations in which the water is used or impacted through the full life cycle of the product or service.

The calculation methods will vary according to the process that is being undertaken. Table 5.1 defines the process and data requirements to calculate the different components according to a generic manufacturing process, which involves a supply chain, the manufacturing process and a consumer.

Two examples of a water footprint are presented in the next section in order to demonstrate the methods and uncertainties for two different consumer products: beer production in South Africa, where the water footprint is primarily related to crop cultivation; and, washing products across the world, where the water footprint could potentially include significant grey water impacts from domestic use. The two examples also demonstrate the different ways a water footprint can help influence corporate water stewardship and decision making to progress from simply focusing on reducing water consumption ‘within the fenceline’.

Table 5.1 Water footprint assessment methods

Process	Water type	Method	Data
Supply chain – crop cultivation	Green water	Use of standards crop water requirement calculation methods such as Allen et al. [4] and model CROPWAT [16]	Climate data: rainfall, evapotranspiration. Crop growing season Soil information
	Blue water	Assessed directly from data OR Calculated as $V_{bw} = \left(V_{th} - V_{er}\right) / \eta_{irr}$ where V_{bw} = volume of blue water V_{er} = volume of effective rainfall V_{th} = theoretical crop water requirement η_{irr} = irrigation efficiency, dependent upon irrigation type	Irrigation methods, schedules and application rates
	Grey water	Various techniques depending upon availability of data. Aim is to calculate the quality of the leachate percolating past the root zone to impact groundwater quality. The grey water is calculated from the equation: $V_{gr} = \frac{L}{c_{\max} - c_{nat}} = \frac{V_{effl}\left(c_{effl} - c_{nat}\right)}{\left(c_{\max} - c_{nat}\right)}$ Where L = pollutant load C_{nat} = natural concentration of contaminant of receiving water $C_{\max}$ = maximum allowable concentration of contaminant in the receiving water V_{effl} = volume of leachate C_{effl} = concentration of contaminant in the leachate	Fertilizer and pesticide application rates Soil types Water quality standards and natural quality of contaminants within the receiving water body

Supply chain – none agricultural products	Green	Not applicable	
	Blue	Assessed directly from data from supplier (if available) OR Assessed from data obtained from Life Cycle Assessment Tools	Packaging volumes
	Grey	Assessed directly from data from supplier (if available)	
Manufacturing of a product (not including raw materials assessed elsewhere)	Green water	Evaporation of water lost in factory grounds (e.g. grassed areas) calculated as in the crop assessment above	Climate data: rainfall, evapotranspiration.
	Blue water	Losses from the production process, including water incorporated into the product. $V_{bw} = V_{in} - V_{effl}$ V_{bw} = volume of blue water V_{effl} = volume of effluent V_{in} = volume of water from surface and groundwater sources Energy can be converted into an embedded water component depending upon primary source of energy e.g.: • Oil based – 1.06 m^3 GJ^{-1} • Gas based – 0.11 m^3 GJ^{-1} • Hydropower – 22 m^3 GJ^{-1} Gerbens-Leenes et al. [9]	Inflowing volumes Factory water balances Effluent volumes Energy consumption and source of energy Transportation distances and means of raw materials to factories and from factory to consumers

(continued)

Table 5.1 (continued)

Process	Water type	Method	Data
	Grey water	Dependent upon whether the effluent is treated	Treatment and receiving water course standards for all the contaminants of concern
		Also dependent upon whether the effluent is treated at an offsite municipal treatment works and location of water footprint boundary	
		Uses same formulae as for crop growth use	Volumes treated
Consumer use	Blue water	Water used to consume the product	Consumer locations and practices
	Grey water	Assessment of effluent concentrations and discharges from consumer use. Possible that the impact of a single product will be embedded within the overall impacts from a number of products, particularly if a domestic product	Treatment and receiving water course standards for all the contaminants of concern

5.4 Water Footprint of Beer in South Africa

The overall water footprint for beer in South Africa has been calculated from a variety of data sources. This footprint was calculated on behalf of the brewery initially to understand the total water consumption and subsequently to aid the development of an appropriate water stewardship strategy that considered water beyond the breweries.

The primary data was derived from the barley and hops suppliers, from published climatic data in the areas where the crops are grown and from confidential brewery data supplied on water and energy use, packaging, waste and recycling quantities and an assessment of the transportation of raw materials and products. Table 5.2 presents the volume of green, blue and grey water per unit of beer.

In Table 5.2, the green water footprint has been split into two separate components, natural and net green. The natural green component is the volume of rainfall stored in the root zone and transpired by natural vegetation in the same location as the crops. The net green is the difference between the total and the natural green, effectively a measure of the additional evapotranspiration caused by the crops grown specifically for beer. However, there are two significant issues in assessing the natural green water footprint: defining natural vegetation and assign an appropriate level of evapotranspiration to the natural vegetation. In many areas, the land will have been used for agriculture for many centuries. In some areas, it is possible for the natural evapotranspiration rates to exceed the cropped rates (e.g. deforestation for agriculture). In Table 5.2, the natural vegetation has been defined as semi-desert scrub or tropical grasslands dependent upon location. Although uncertain, the net green is considered a valuable consideration in the water footprint as it is a better

Table 5.2 Estimated water footprint for beer in South Africa (liters of water for each liter of beer produced)

Item	Total green water	Natural green water	Net green water	Blue water	Grey water	Total	% of total
Crop growth in SA (Maize, Hops, Barley)	157.37	84.78	72.60	44.93	14.01	216.32	77.1%
Fertilizer use	0.00	0.00	0.00	0.04	0.00	0.04	0.0%
Crop processing (e.g. Malting) in SA	0.00	0.00	0.00	0.13	0.00	0.13	0.0%
Imported crops (Argentina, USA, France, Austrialia)	25.71	22.34	3.37	22.37	7.74	55.82	19.9%
Direct water use in brewing and bottling	0.00	0.00	0.00	3.59	0.00	3.59	1.3%
Energy use through full life cycle	0.00	0.00	0.00	0.55	0.00	0.55	0.2%
Packaging	3.08	0.00	3.08	0.42	0.00	3.50	1.2%
Domestic consumption and waste disposal	0.00	0.00	0.00	0.56	0.00	0.56	0.2%
Total	186.17	107.12	79.04	72.60	21.75	280.51	

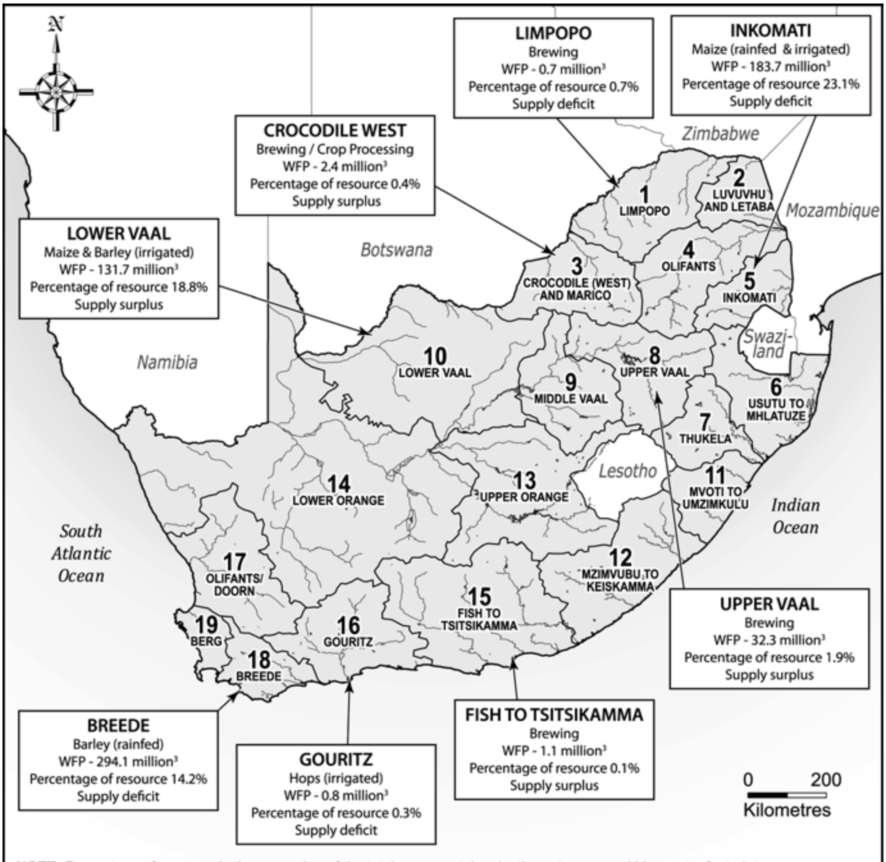
measure of anthropogenic influences. Potentially more valuable is to compare green water footprints of different crops in the same location to establish the different impacts of the crop: the greater the green water footprint the lower the infiltration to groundwater and the reduction in base flow.

There are many key points that should be noted from this overall footprint:

- The dominant component of the water footprint is in the crop cultivation, both in South Africa and imported.
- Only 1.3% (or 3.6 units of water) of the footprint is related to the use of water in the brewing and bottling process. This has been traditionally the key metric in assessing the efficiency of water consumption in beer production.
- The water embedded in packaging (aluminum cans, labeling and cardboard packaging) is a similar to that of the water consumed in the brewing process.
- Based on the imported volumes of crops, for every unit of beer consumed in South Africa, around 56 units of water have been imported.
- There are many uncertainties in this footprint. The key uncertainties relate to the crop production. Real irrigation application rates and schedules were not available for the calculations and so a theoretical calculation was adopted. Similarly, actual fertilizer application rates and measureable impacts on the groundwater quality were not available. Consequently the grey water footprint was estimated from a lumped leachate dilution model, focused solely on nitrogen based fertilizers.

The total water footprint has a characteristic “shape”, where the supply chain dominates and the domestic consumption is minimal. This suggests that potentially more significant savings in water consumption can be made at the farm level than within the brewery productions. Economically the situation is very different, with price of water for industry approximately 50 times the cost of water for irrigation.

As noted earlier, the water footprint calculations need to be location-specific. Water resources should be considered at catchment or regional level, as scarcity and water quality issues are localized. In South Africa water is known to be relatively scarce. In 2008 water resource availability was around 1,007 m^3 $person^{-1}$, below the 1,700 m^3 $person^{-1}$ threshold set by the Revenga et al. [15] which defines potential water stress and scarcity conditions. In some watersheds of South Africa, the water resource availability is below 500 m^3 $person^{-1}$, considered an extremely scarce water environment. Consequently it is important that the water footprint is mapped against water resource constraints and availability. This is shown in Fig. 5.3, where the total water footprint has been superimposed on a map of the water management areas of South Africa. In four of the water management areas (WMA), there are currently deficits [8] where water is consumed. In two of these areas, the water footprint is very high: in the Breede WMA where rainfed barley is grown (294 million m^3) and the Inkomati WMA where maize is grown from rainfall and supplementary irrigation. Therefore in these areas, investment by the brewery in farming practices could from a component of a water stewardship strategy for the brewery, focused on influencing and improving yields per unit of water and minimizing grey water impacts from fertilizer and pesticide use. This could result in a significant reduction in water use compared with investments in water conservation related to the brewing processes alone.



NOTE: Percentage of resource is the proportion of the total resource taken by the net green and blue water footprints

Fig. 5.3 Water footprint of beer across South Africa

5.5 Water Footprint of Domestic Washing Products

Washing products (laundry, personal hygiene, dishwashers) are manufactured and used the world over. They use a variety of raw materials (natural and synthetic) and are used by consumers in a variety of different economic settings. An estimate of the water footprint of a kilogram of manufactured washing materials (solid or liquid) is presented in Table 5.3. Two economic conditions have been adopted: a developed country with comprehensive municipal treatment facilities and a developing country where surfactants and other residues from the washing process impact the watercourses. In this example the water footprint is primarily related the blue water in the raw materials and potentially grey water in the use of the products, depending upon the availability and standard of municipal treatment facilities. The component of water footprint related to the direct use of water and energy in the manufacture of the washing products is very small (0.1–0.3%).

Table 5.3 Water footprint of washing products (liters per kilogram)

Item – developed country with municipal treatment and energy and water saving washing equipment	Total green water	Blue water	Grey water	Total water footprint	Percentage of total
Raw materials (zeolite, sodium hydroxide, sodium tripolyphosphate, surfactants plus many others)	0.0	2,571.5	Not available	2,571.5	90.9%
Packaging materials and production	208.4	23.2	0.0	231.6	8.2%
Direct use of water and energy to manufacture the products	0.0	2.2	0.0	2.2	0.1%
Domestic use	0.0	23.8	0.0	23.8	0.8%
Total	208.4	2,620.6	0.0	2,829.0	100%
Item – less developed country with limited municipal treatment and manual washing	**Total green water**	**Blue water**	**Grey water**	**Total water footprint**	**Percentage of total**
Raw materials (zeolite, sodium hydroxide, sodium tripolyphosphate, surfactants plus many others)	0.0	2,571.5	Not available	2,571.5	40.1%
Packaging materials and production	208.4	23.2	57.9	289.5	4.5%
Direct use of water and energy to manufacture the products (partial treatment of effluent)	0.0	2.2	19.8	22.0	0.3%
Domestic use	0.0	14.3	3,508.8	3,523.0	55.0%
Total	208.4	2,611.1	3,586.5	6,406.0	100%

This is used purely as a theoretical example to demonstrate the influence of the grey water footprint. In reality the standards of treatment will vary in developed and developing countries, ranging from very high treatment standards and the treated effluent is effectively blue water to the washing of clothes directly in a river where the effluent immediately impacts river water quality.

In a developing country, the shape of the water footprint is similar to beer, with the majority of the footprint embedded in the supply chain. Consequently, for a manufacturer of washing product, a key response to this "shape" of water footprint would be to focus corporate water stewardship on where the water is consumed and impacted within the raw material supply chain. There may be raw materials being manufactured in areas where there are significant water resource constraints. Therefore, in this case the corporate water strategy could include engaging with and influencing key suppliers regarding water management practices and impacts on business continuity.

The potential impact of the use of washing products in an area where there is limited treatment of the washing effluent can be clearly seen. The shape of the footprint changes, with two significant elements: the supply chain and the grey water impacts from the domestic use. In this example the focus of the water stewardship strategy and investment would also include where water is consumed by the end user. This could include focusing business investment in product innovation to reduce blue and grey water in consumer use.

Influencing the municipal authorities to invest in treatment facilities is often outside the scope of a manufacturer of domestic goods. However, investing in understanding the pressures on water resources (quantity and quality) in catchments through the coming together of all the stakeholders of the water environment is something that businesses can invest in to help develop and manage water resources for all.

5.6 Conclusion

A water footprint provides a better indication of water demands and impacts than suggested by national and regional statistics on water use as these normally only focuses on the total withdrawals from surface water bodies and groundwater aquifers.

Water footprinting builds on the excellent work and initiatives driven by businesses in life cycle analysis and carbon footprinting. It is an effective tool to provide business with an understanding of water consumption and impacts of different products. Unlike the carbon footprint, however, it is not the magnitude of the water footprint that is the most important feature but it is the locations of the green, blue and grey components mapped against the water resource and pollution impacts that provide the true value of the footprint. With a full life cycle analysis, the environmental, social and economic sustainability of each component of the footprint can be evaluated and appropriate corporate decisions can be made.

In areas of water scarcity, businesses are quite rightly focussing on saving water within its direct operations. However, such a business may be exposed to much greater risks within the supply chain or its customers. A water footprint which combines the calculated water footprint with an understanding of the freshwater availability and constraints in the areas in which green, blue and grey water is used, can highlight where the greatest risk lies and therefore provides the information to develop appropriate water stewardship strategies covering suppliers, direct use and consumers.

The water footprint can then be used to report progress on the water stewardship strategies, where the aim is to reduce the footprint in the areas where resources are constrained and continued consumption unsustainable.

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Chapter 6
Color Removal with Natural Materials for Reuse of Wastewater in Textile Industry

Aysel T. Atimtay and Bahadir Duygulu

Abstract The water consumption in textile industry, especially in dyeing and washing processes is too high. Therefore, large amount of wastewater is produced and discharged to the receiving environment during textile production process. Discharge of colored effluents without decoloration originated from textile industries may cause serious problems in the receiving environments. Besides water resources are limited. The textile industry should look for recycling and reusing this water. The objective of this chapter is to explain the use of various natural materials like basaltic tephra and clinoptilolite to remove basic, acidic and reactive types of dyes from textile wastewater. The determination of dye removing capacities and adsorption isotherms of these adsorbents are among the objectives of this study.

The second objective is to modify the surface properties of these adsorbents by using a surfactant chemical and then determine their equilibrium sorbent capacities again with basic, acidic and reactive dyes. The results showed that removal efficiencies for cationic basic dyes are higher than those for anionic acidic and reactive dyes with the natural materials. Therefore, modification of surface properties of natural materials with a cationic surfactant was considered to increase the removal efficiencies of those for anionic dyes. After modification of the surface properties, adsorption capacities of adsorbents for anionic dyes were higher than those of natural materials. The results showed that the adsorption of dyes on adsorbents used in this study fitted nicely to the Langmuir Isotherm Equations.

Keywords Color removal • Adsorption • Basaltic tephra • Clinoptilolite • Freundlich and Langmuir isotherms

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6.1 Introduction

Textile industry is one of the most important industries in almost all developing countries. The water consumption in textile industry, especially in dyeing and washing processes, is too high. Therefore, large amount of wastewater is produced and discharged to the receiving environment during textile production process. According to a study performed in Germany 30–120 L of water is used in preparing 1 kg of cotton textile for dyeing process. Also, 50–120 L of water is consumed for each kg of cotton textile for dyeing. Therefore, totally 80–240 L of water is required for dyeing 1 kg of cotton textile. Marzinkowski [8] has reported that for 1 kg of textile consisting of 55% polyester and 45% of cotton, 9–14 L of water is consumed for washing and 75–96 L of water is consumed for dyeing process.

As one can see from these water consumption data given in the literature, the amount of water consumed per unit amount of textile produced is quite high. Besides, wastewater from textile industry contains various colorants due to printing or dyeing process. For example the amount of yarn, textile and carpet production in Turkey for the year 2007 is given in Table 6.1.

Assuming very roughly that 100 L of water is used on the average in Turkey for 1 kg of cotton textile production, the amount of water necessary will be about 55 million tons for 542,935 ton per year of cotton yarn. When we look at textile production values given in Table 6.1, we can have an idea about how much water is consumed in textile industry in Turkey per year. We know that much of the water used in various processes in Turkish textile industry in the past was discharged to a receiving environment without treatment. Therefore, there is a large burden on the receiving water bodies. Besides water resources are limited. The textile industry should look for recycling and reusing this water before it is too late. There are a large number of studies going on this subject and also there are many success stories.

In textile industry the use of organic dyes has increased dramatically. In the world, the consumption of various dyestuffs is more than 700,000 ton for an annual production of 30 million tons of textile [2]. About 90% of this dyestuff ends up on fabrics. Therefore, approximately 70,000 ton of dyestuffs are discharged into waste streams each year. Dyestuff producers and users are interested in stability and fastness of dyes on the fabric and they are continually producing dyestuffs which

Table 6.1 Yarn, textile and carpet production in 2007 in Turkey [14]

Production type	Amount[a]
Yarn (ton)	
Cotton	542,935
Wool	37,997
Textiles (m) (*1,000)	
Cotton	649,378
Woolen	34,078
Carpets (m^2)	64,206,620

[a] Sum of production by private and public firms

are more difficult to degrade after use [4]. Therefore, this also poses a problem on the degradation of dyestuffs in the environment by natural processes.

Although, many of dyes are not normally toxic, discharge of colored effluents to environment without removing the color may cause several problems in water. They can be listed as follows:

1. Depending on the exposure time and dye concentration, dyes may have acute and/or chronic effects on exposed organisms.
2. Dyes may absorb and reflect sunlight entering the water so the growth of bacteria, to levels sufficient to degrade impurities in the water and to start the food chain, may be interfered.
3. Abnormal coloration of surface waters captures the attention of both the public and the authorities [11].

The removal of dyestuffs from effluents is of great importance for many countries in the world, both from environmental and economical aspects. Because water consumption in the textile industry is too high and water is very costly in many developed countries, such as Germany, advanced treatment methods are considered for re-use of wastewaters generated from textile industries. For example, in Germany, the cost of 1 m^3 of fresh water is about 1 Euro and the cost of 1 m^3 wastewater is about 2.5 Euro. The total cost of 1 m^3 water used in the textile industry is 3.5 Euro [8].

The treatment of colored wastewaters (mostly resulting from finishing plants) should not be restricted to the reduction of ecological parameters only, such as chemical oxygen demand (COD), biological oxygen demand (BOD), total organic carbon (TOC), adsorbable organic halide (AOX), temperature and pH, but also reduction of dye concentrations in the wastewaters should be considered [11]. In Turkey, for example, the control of related parameters in textile effluents required in the Water Pollution Control Regulation (1988) is almost achieved. However, there is no limit in Turkey in the regulations for the control of "color" in effluents originated from textile industry. This limit has to be defined in the nearest future in order to protect the water receiving bodies from discharge of colored wastewaters.

In the past, municipal wastewater treatment systems were used for the treatment of textile dye effluent, but because of the xenobiotic and recalcitrant nature of many dyes, those systems were found to be ineffective. In addition, when dyes are released into aquatic systems anaerobic bacteria in the sediment are unable to mineralize dyes completely. Therefore, the result is the formation of toxic amines [10]. It is therefore necessary for dye-containing effluents to be treated in an effective manner before being discharged into natural waterways [10]. Many physical and chemical processes for color removal have been applied including coagulation and flocculation, biosorption, photo-decomposition, and ultrafiltration [1]. Textile, tannery, pulp, and paper industries seldom apply these processes to treat their effluents due to relatively high operation costs and low removal efficiencies in using the above-mentioned processes [1].

Among those methods, adsorption techniques have gained favour in recent years because of their proven efficiency in the removal of pollutants from effluents [4]. The removal of dyes and organics in an economic way remains as an important problem although a number of systems have been developed with adsorption techniques.

Adsorption has been found to be superior to other techniques for water re-use in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances [9].

Activated carbon is the most widely used adsorbent for adsorption method because it has a high capacity for the adsorption of organics, but its use is limited due to its high cost. This has led to a search for cheaper and more effective substitutions, such as coal, fly ash, wood, silica gel, bentonite clay, bagasse pit, maize cob, coconut shell, rice husk, and cotton waste have been tried with varying success for color removal [5].

In Turkey, adsorptive capacities of several materials for color removal were investigated. Especially, natural zeolite, sepiolite and bentonite and their modified forms were used for the removal of some dyestuffs [2, 12, 13]. In order to improve the color removal capacities of adsorbants, modified processes were applied by increasing their surface area or by changing their surface properties.

The objective of this chapter is to explain the use of various natural materials like basaltic tephra and clinoptilolite to remove basic, acidic and reactive types of dyes from textile wastewater. The determination of dye removing capacities and adsorption isotherms of these adsorbents are among the objectives of this study. The second objective is to modify the surface properties of these adsorbents by using a surfactant chemical and then determine their equilibrium sorbent capacities again with basic, acidic and reactive dyes.

6.2 Materials and Method

The use of natural materials as low cost adsorbents has found an important application for the adsorption of various dyestuffs from wastewater of textile industry. In this chapter, the adsorbents and dyestuffs used in the adsorption process, their physical and chemical properties are explained.

6.2.1 Adsorbents

“Basaltic tephra” and “clinoptilolite” were used as adsorbents in this study. They are naturally occurring minerals. In addition to these minerals, “activated carbon” in powdered form (PAC) was also used to compare adsorption capacities of the adsorbents for the dyestuffs used in this study.

“Basaltic tephra” is a kind of volcanic stone that contains large amount of gas space formed by dissociation of evolved gases due to rapid cooling of magma. Its apparent density is less than 1.0 g cm^{-3} and its hardness is about 5–6 according to mohs scale (TSI, 6918, 1989) [7]. Bayraktar [3] studied the characterization of “basaltic tephra” in the particle size of 0.5–30 mm and reported that the density and porosity of “basaltic tephra” is 0.87 g cm^{-3} and 40%, respectively. It can adsorb water in the

Table 6.2 Dyestuffs used in the experiments

Commercial name	Color index	Chemical class	Abbreviations
Setacryl Golden –Yellow GL	Basic yellow 28	Methine	BY
Setacryl Blue – FGRL	Basic blue mix	Mix	BB
Nyloset Yellow – SN6G	Acidic yellow 95	Azo	AY
Nyloset Red – EBL	Acidic red 57	Monoazo	AR
Setazol Yellow – 3RS	Reactive yellow 145	Monoazo	RY
Setazol Red – 3BS	Reactive red 195	Monoazo	RR

amount of 1/3 of its volume due to open pores in its structure [3]. "Basaltic tephra" used in this study was obtained from Osmaniye-Adana region.

"Clinoptilolite" is a natural zeolite mineral and is a natural Aluminum Silicate. The typical unit cell formula is given as $Na_6[(AlO_2)_6(SiO_2)_{30}] \cdot 24H_2O$. "Clinoptilolite", like most of the zeolites, has a three-dimensional crystal structure and it contains two-dimensional channels in it. Therefore, some exchangeable cations like Na^+, K^+, Ca^{2+} and Mg^{2+} can be exchanged with organic and inorganic cations, like NH_4^+, metal ions [2]. Some dye molecules can also be exchanged like cations. "Clinoptilolite" used in this study was obtained from Gördes-Manisa region.

6.2.2 *Dyestuffs*

The dyestuffs used in this study were obtained from Setas Chemistry Co. (Bursa). Name and color index numbers of the six different dyestuffs are presented in Table 6.2.

6.2.3 *Physical and Chemical Properties of Adsorbents*

The chemical composition of the "tephra" and "clinoptilolite" is given in Table 6.3. As can be seen from this table SiO_2 and Al_2O_3 are the main constituents in the structure of "basaltic tephra" and "clinoptilolite".

The other oxides found in "basaltic tephra" are also present in "clinoptilolite" in various quantities. The amount of SiO_2 in the clinoptilolite is approximately 70–76% and that of Al_2O_3 is about 14–15% by weight. SiO_2/Al_2O_3 ratio in the structure is about 5 [2, 15]. Tephra is classified as acidic, neutral and basic according to its SiO_2 content. Tephra used in this study is "basaltic tephra" since the SiO_2 content is 47%.

Particle sizes of "basaltic tephra" and "clinoptilolite" used in this study are given in Table 6.4. The **surface areas** of the adsorbents used in the experiments was determined by the BET method by using Micromeritics ASAP 2000. The results are given in Table 6.5.

As seen from Table 6.5, surface area of "basaltic tephra" is smaller than that of "clinoptilolite" for all particle sizes. Also, surface areas of the adsorbents increase if particle sizes decrease, i.e. the smallest particle size has the largest surface area.

Table 6.3 Chemical composition of basaltic tephra and clinoptilolite

Constituent	Basaltic tephra, % by weight	Clinoptilolite, % by weight
SiO_2	47.35	76.86
Al_2O_3	19.99	14.61
CaO	9.23	2.11
Fe_2O_3	12.26	1.24
MgO	4.03	0.76
Na_2O	2.97	0.65
K_2O	2.56	3.77
TiO_2	1.61	–

Table 6.4 Particle sizes of basaltic tephra and clinoptilolite used in the experiments

Material	Particle size, mm
Basaltic tephra	$d_p < 0.60$
Basaltic tephra	$0.60 < d_p < 1.00$
Clinoptilolite	$d_p < 0.50$
Clinoptilolite, powdered form	$d_p < 0.063$

Table 6.5 Surface areas of the adsorbents

Material	BET surface area, $m^2\ g^{-1}$
Basaltic tephra, <0.60 mm	6.4
Basaltic tephra, 0.60–1.00 mm	4.2
Clinoptilolite, <0.50 mm	28.4
Clinoptilolite, powdered form	36.7
Powdered activated carbon	598.4

Table 6.6 Average pore diameters and total pore volumes of the adsorbents

Material	Average pore diameter, Å	Total pore volume, mL g^{-1}
Basaltic tephra, 0–0.60 mm	92.6	0.0184
Basaltic tephra, 0.60–1.00 mm	83.9	0.0087
Clinoptilolite, 0–0.50 mm	91.3	0.0647
Clinoptilolite, powdered form	96.5	0.0884
Powdered activated carbon	22.0	0.4498

In addition “powdered activated carbon” has much higher BET surface area than other adsorbents.

Average pore diameters and **total pore volumes** of the adsorbents used in this study are given in Table 6.6. These parameters were measured by using Micromeritics ASAP 2000.

The average pore diameters of “basaltic tephra” and “clinoptilolite” are very similar, approximately 85–95 Å. The total pore volume of “basaltic tephra” is about 3.5 times smaller than “clinoptilolite” for almost the same particle sizes.

The **Scanning Electron Microscope (SEM)** photographs of basaltic tephra were taken in the Department of Metallurgical and Materials Engineering at METU. The instrument is Jeol, JSM-6400 Scanning Microscope. SEM photographs of the basaltic tephra and clinoptilolite are given in Figs. 6.1 and 6.2, respectively.

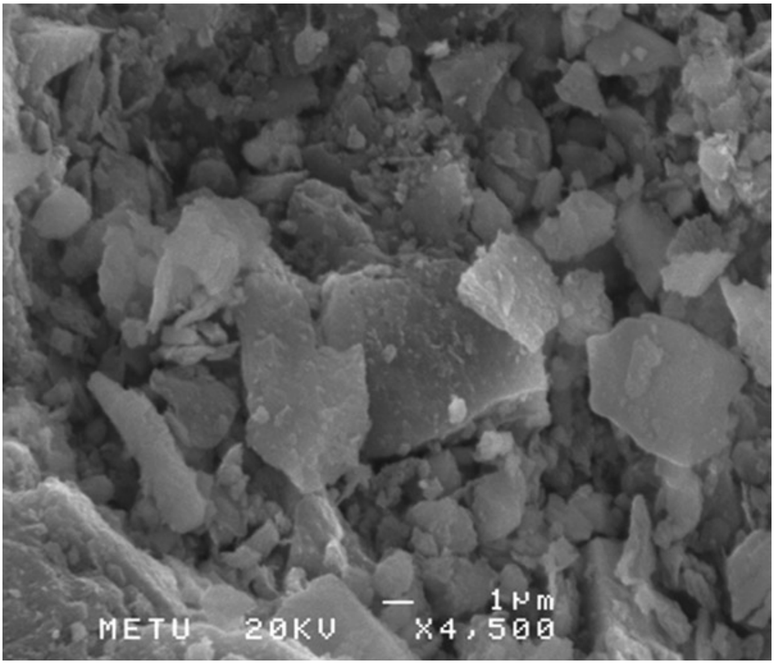

Fig. 6.1 SEM photograph of basaltic tephra for $d_p < 0.60$ mm (×4,500)

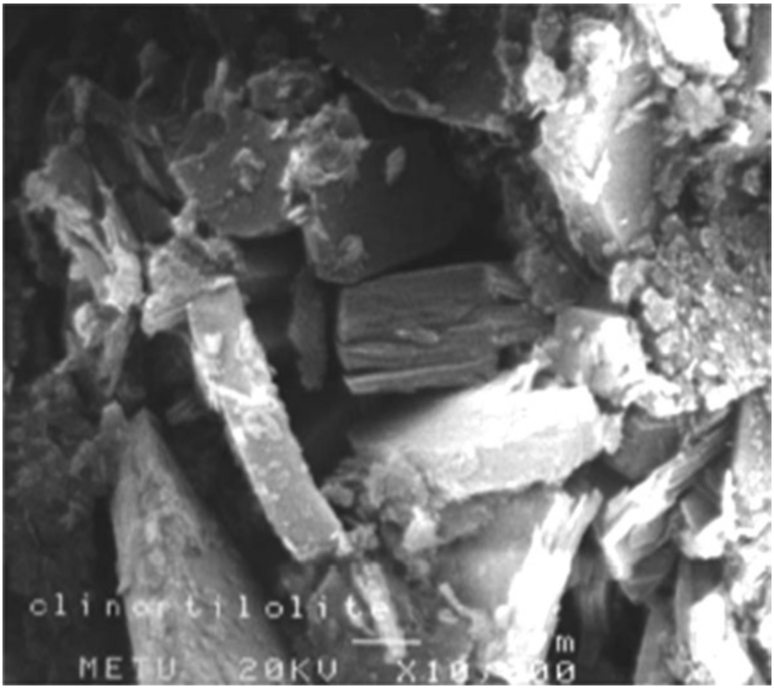

Fig. 6.2 SEM photograph of clinoptilolite for $d_p < 0.25$ mm (×10,000) [15]

Table 6.7 Zeta potentials of the adsorbents at pH = 7

Material	Zeta potential, mV
Natural basaltic tephra	−20
Natural clinoptilolite	−28

Table 6.8 Wavelengths corresponding to maximum absorbance

Dyestuffs	Wavelengths, nm
Basic blue	600
Basic yellow	445
Acidic yellow	420
Acidic red	515
Reactive yellow	420
Reactive red	540

The **electrokinetic properties** of “basaltic tephra” and “clinoptilolite” were determined by using Zeta Sizer (Nano-ZS90) in the Central Laboratory of METU. In the preparation of the samples to measure zeta potentials, 1 g of material was conditioned in 250 mL of distilled water for 10 min. The suspension was kept still for 5 min to allow the larger particles to settle. Each data point is an average of 30 measurements. As all adsorption experiments were conducted at neutral potential state, zeta potentials of “basaltic tephra” and “clinoptilolite” were determined at the pH of 7 and the results are given in Table 6.7.

6.3 Experimental Setup

The setup consists of a shaker, a filter system and a visible spectrophotometer. The shaker used in this study is Gallenkamp Orbital Incubator. Samples were filtered through 0.45 μm filter system. Absorbance of the samples was measured with a DR/2000 model Direct Reading Visible Spectrophotometer. The range of wavelength and absorbance for the spectrophotometer is 325–900 nm and −0.3 to 3.0, respectively.

6.3.1 Calibration Curves

Calibration curves were prepared by plotting known concentrations of each dyestuff versus corresponding absorbance values. The concentrations of dyestuffs in the solutions were measured with the spectrophotometer at appropriate wavelengths corresponding to the maximum absorbency for each dye listed in Table 6.8.

6.4 Experimental Procedure

First of all, duration of the experiments was determined. Determination of equilibrium time is very important and should be decided in order to define agitation period during adsorption experiments. Therefore, for each set of experiment 5–8 Erlenmeyer flasks of 500 mL volume were taken and 100 mL of dye solution with a concentration of 100 mg L^{-1} was placed into each flask. An adsorbent of 0.1 g per 100 mL for *basic dyes*, and 0.5 g per 100 mL for *acid* and *reactive dyes* was added to the solution. The top of the flasks was closed and they were placed in the shaker. The Erlenmeyer flasks were agitated in the shaker at 200 rpm and at a temperature of 25 ± 2°C. After the start of the experiment, one flask was taken out of the shaker at a time in order to see how much of the dye in the solution was adsorbed by the adsorbent during the time elapsed between the start of the experiment and the time at which the flask was taken out, while the adsorption of dyes continued in the other flasks. From each flask about 20 mL of the solution was filtered through a 0.45 μm filter system to avoid turbidity interference during color determination. Then, dye concentration of the filtered solution was measured by the spectrophotometer with a 1 cm path length and concentration of the dye solution was determined by using the calibration curves. Finally, percent removal versus time graphs were plotted to determine the equilibrium time.

After the determination of the equilibrium time, adsorption experiments were conducted by mixing a fixed amount of dry adsorbent (0.1 g) with 100 mL dye solutions at eight different concentrations, which were varied from 25 to 500 mg L^{-1}, in 500 mL Erlenmeyer flasks which were shaken at 200 rpm and 25 ± 2°C for 2 days. Then, at the end of the experiment approximately 20 mL of a sample from each flask was filtered through 0.45 μm filter system and dye concentrations of the filtered solutions was measured by using the spectrophotometer with a 1 cm path length. If the absorbance value measured was higher than 0.6, dilution of the solution was applied. Finally, adsorption isotherms were plotted to see the relationship between adsorption capacity of the adsorbent and equilibrium concentration of the adsorbate.

It was noted during the filtration of solutions through 0.45 μm filter system that filter paper adsorbs the dye to a small extent for various dyes. In order to determine the amount of adsorption by filter paper, solutions with various dyes used in this study at various concentrations were prepared, filtered through the paper and the concentration of the dye solutions before and after filtration were measured. The concentration measurements for all adsorption experiments were corrected for the adsorption of filter paper.

6.4.1 Modification of Surface Properties

At the end of the adsorption experiments, adsorption capacities of the natural adsorbents were determined. *Basic dyes* were adsorbed better due to electrostatic interactions between the adsorbate and adsorbent. *Basic dyes* are cationic dyes and the surface charges of both “basaltic tephra” and “clinoptilolite” are negative.

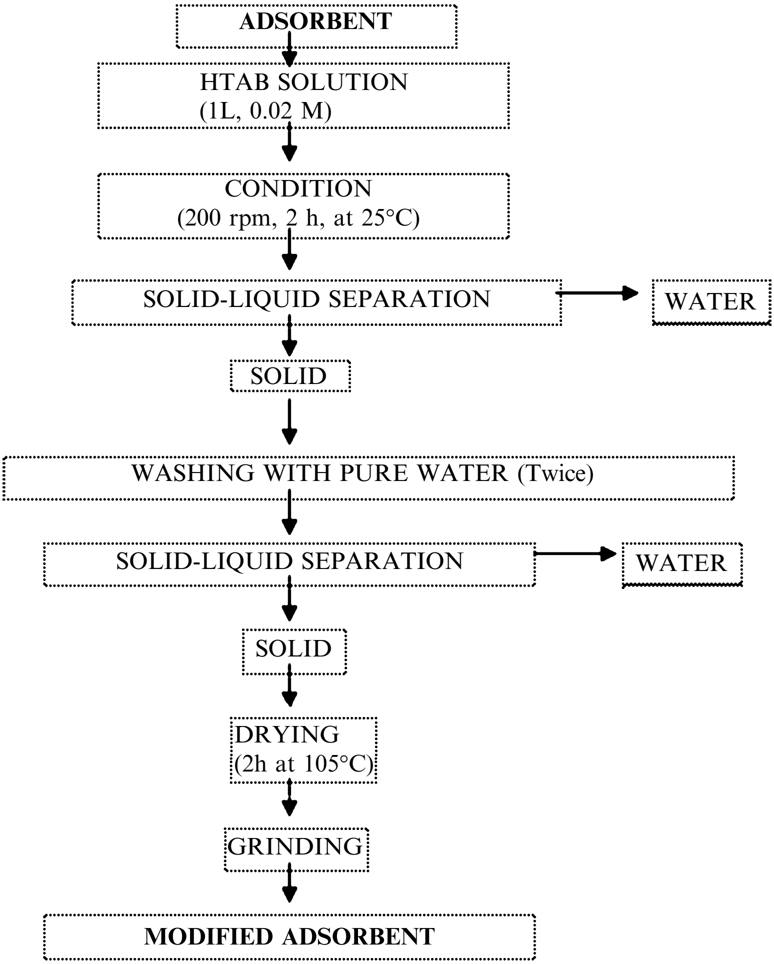

Fig. 6.3 Flow sheet for preparing modified adsorbents

However, little or no adsorption for *acid dyes* and *reactive dyes* were obtained because they are anionic dyes. Therefore, modification of surface properties of the natural materials was considered. Surface modification of “basaltic tephra” and “clinoptilolite” was made by using a quaternary amine, hexadecyltrimethlyammonium bromide (HTAB, $C_{19}H_{42}BrN$) that is a cationic surfactant purchased from Sigma. The molecular weight of HTAB is 346.46 g mol^{-1}. The procedure of modification is given in Fig. 6.3 [2]. The experiments were conducted again under the same conditions by using modified adsorbents. It should be noted that 0.02 M of the HTAB is approximately 7.5 g and that amount was used to modify 50 g of the natural adsorbent. After agitation of natural adsorbents in HTAB solution, the solids were washed with distilled water twice until no HTAB is present. Therefore, it is safe to assume that no HTAB was released to dye solutions during adsorption experiments.

6.5 Results and Discussion

6.5.1 *Effect of Particle Size on Adsorption*

Two particle sizes of natural “basaltic tephra” were used in the adsorption of *basic blue* dyestuffs from aqueous solution in order to see the effect of particle size on the adsorption process. Adsorption isotherms for two particle sizes of “basaltic tephra” are presented in Fig. 6.4. It can be seen from the figure that the smaller size particles ($d_p < 0.60$ mm) have the higher adsorption capacity as expected due to higher surface area available for adsorption.

Two different particle sizes of “clinoptilolite” (0–0.5 mm and powdered form) were compared in their adsorption capacities for *basic blue* dyestuffs under the same experimental conditions. Figure 6.5 shows that smaller particles have much higher

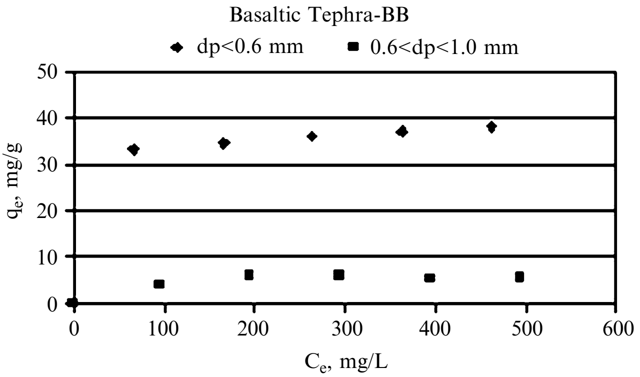

Fig. 6.4 Adsorption isotherms for basic blue on two particle sizes of basaltic tephra

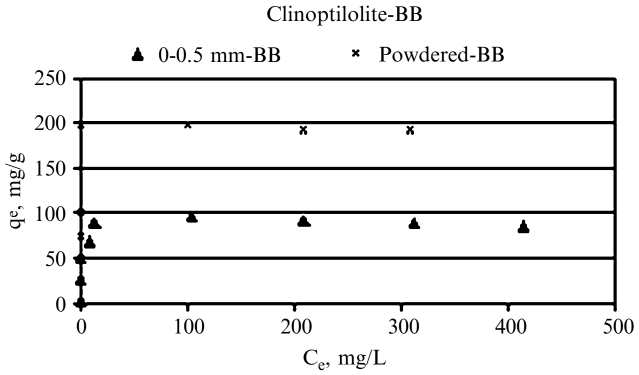

Fig. 6.5 Adsorption of basic blue dyestuff onto natural clinoptilolite

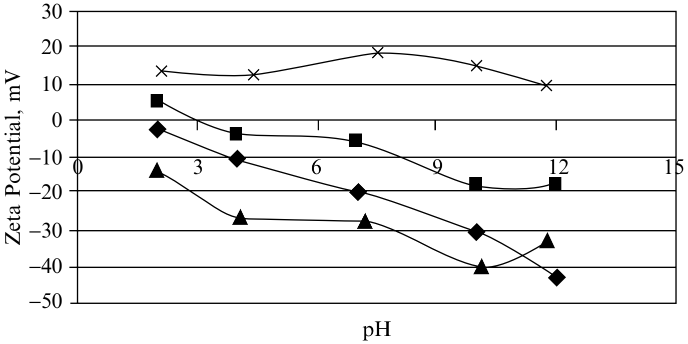

Fig. 6.6 Zeta potential vs pH profiles of natural and modified adsorbents (♦ Natural Tephra, ■ Modified Tephra, ▲Natural Clinoptilolite, **x** Modified Clinoptilolite)

adsorption capacity than that of larger particles. Since the particle size $d_p < 63$ μm gave better results than the other size, powdered form of the “clinoptilolite” was used in other experiments.

6.5.2 Effect of Surface Modification on Zeta Potential

After modification of the surface properties of “basaltic tephra” and “clinoptilolite” by using HTAB, some changes in the properties of the adsorbents were observed. The most interesting change was observed in the electrokinetic properties of the adsorbents. Zeta potentials for natural and modified “basaltic tephra” and “clinoptilolite” were measured at different pH values and zeta potential versus pH profiles are plotted in Fig. 6.6.

The zeta potential curve for the “modified basaltic tephra” lies above the curve for the “natural basaltic tephra”. The zeta potentials of “natural basaltic tephra” after the surface modification increased for all pH range. This figure shows that HTAB has been effective in changing the surface charge of “basaltic tephra”. The surface charge of the “clinoptilolite” changed from anionic state to cationic state with the modification. The effect of the modification process on “basaltic tephra” and “clinoptilolite” was different from each other probably due to different surface structures of the materials.

6.5.3 Effect of Surface Modification on BET Surface Area

Surface areas of “basaltic tephra” and “clinoptilolite” were determined after the modification. The results have shown that surface areas of the “basaltic tephra” and “clinoptilolite” were changed after surface modification with HTAB. The results are

Table 6.9 Surface areas of the adsorbents before and after surface modification

Material	BET surface area, m^2 g^{-1}
Basaltic tephra, <0.60 mm	6.44
Modified tephra	2.73
Clinoptilolite, <0.063 mm	36.65
Modified clinoptilolite	19.14

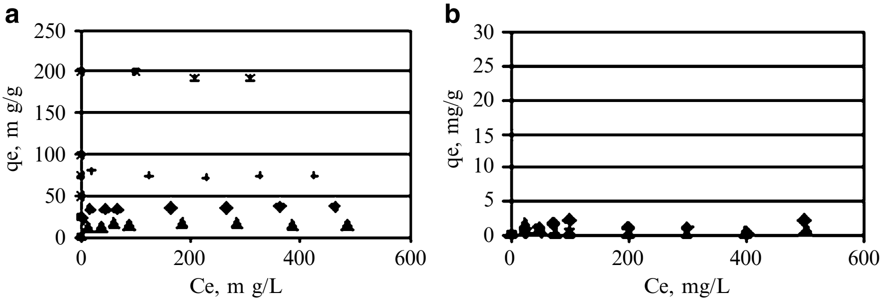

Fig. 6.7 Adsorption isotherms for (**a**) basic dyes (♦ Tephra-BB, ▲ Tephra-BY, ж Clinoptilolite-BB, + Clinoptilolite-BY), (**b**) acidic dyes (♦ Tephra-AY, ▲ Tephra-AR, ж Clinoptilolite-AY, + Clinoptilolite-AR)

given in Table 6.9. As can be seen from the table, surface areas of natural materials decreased after modification, most probably due to the closure of the pores with bigger HTAB molecules.

6.5.4 Equilibrium Adsorption vs Equilibrium Concentration Data

Adsorption capacities of natural and modified "basaltic tephra" for *basic (A), acidic (B) and reactive* (*C*) *dyestuffs* were determined before and after surface modification. Adsorption isotherms are given in Figs. 6.7 and 6.8.

- *Before modification*

  Before modification the adsorption capacity of clinoptilolite for BB and BY are about 200 and 75 mg g^{-1}, respectively. But for basic tephra adsorption capacity for BB and BY are low (about 25–40 mg g^{-1}). For acidic dyes the adsorption capacity of both tephra and clinoptilolite for AY and AR are very low.
- *After modification*

  After modification the adsorption capacity of clinoptilolite for BB and BY has decreased down to 15–20 mg g^{-1}. But for acidic dye, the capacity increased to 70 mg g^{-1}. For basic tephra the capacity for BB and BY are low (about 15–20 mg g^{-1}). For acidic dyes the adsorption capacity of tephra for AY and AR did not change much (Figs. 6.9 and 6.10).

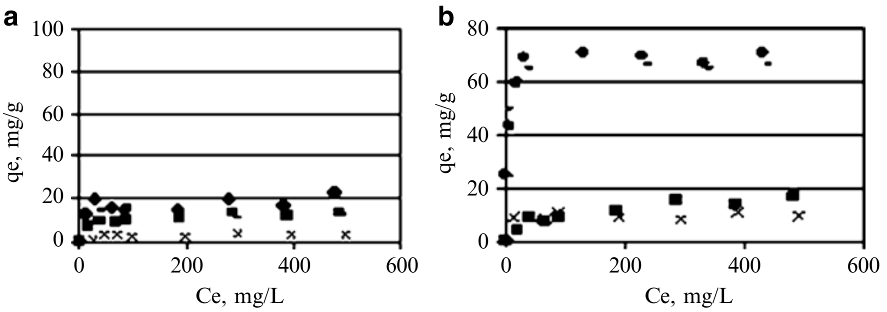

Fig. 6.8 Adsorption isotherms for (**a**) **basic dyes** (■ Tephra-BB, x Tephra-BY, • Clinoptilolite-BB, – Clinoptilolite-BY), (**b**) **acidic dyes** (■ Tephra-AY, x Tephra-AR, • Clinoptilolite-AY, – Clinoptilolite-AR)

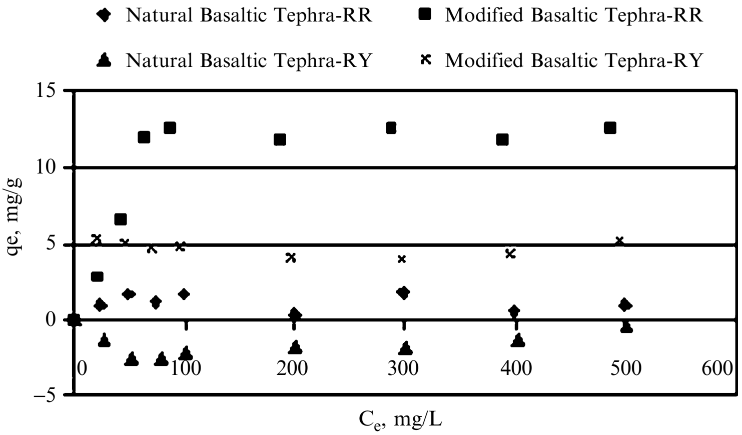

Fig. 6.9 Adsorption isotherms for reactive dyes on natural and modified basaltic tephra **(C-reactive dyes)**

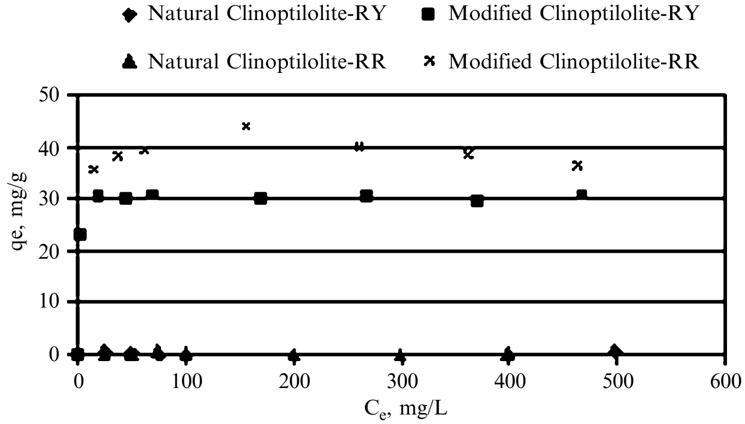

Fig. 6.10 Adsorption isotherms for reactive dyes on natural and modified clinoptilolite **(C- reactive dyes)**

6.5.5 *Adsorption Capacities of the Adsorbents Used in This Study*

The adsorption capacities of the "basaltic tephra" and "clinoptilolite" in their natural and modified forms and "powdered activated carbon (PAC)" for the dyestuffs used in this study are summarized in Table 6.10.

As can be seen from the table, adsorption capacities of "natural basaltic tephra" and "natural clinoptilolite" for *cationic dyes* that are *basic blue* and *basic yellow* are much higher than that of *anionic dyes* because electrostatic interactions between the negatively charged surface of the natural adsorbents and positively charged dye molecules result in "attractive forces". Also, adsorption capacity of "clinoptilolite" for *basic dyes* is approximately five times more of "basaltic tephra".

For *anionic dyes*, "natural basaltic tephra" and "clinoptilolite" has limited adsorption capacities. The negatively charged adsorbent surface repels the dye molecules that have also negative ions. The dispersion force is small as compared to repulsive forces. As a net result of repulsion and dispersion forces, very small adsorption of *anionic dyes* was obtained for the natural adsorbents.

Also, a negative capacity was observed in the case of the adsorption of *reactive yellow* dyestuff on "basaltic tephra" because pores of "basaltic tephra" are not big enough for the penetration of bigger dye molecules. Therefore, smaller molecules like water molecules penetrated through those pores and therefore water amount decreased in the solution so apparent dye concentration increased. This caused a negative capacity value.

With the modification of surface properties of "basaltic tephra" and "clinoptilolite", their surface charges and surface areas were changed. Surface charge of "basaltic tephra" was still in anionic state but it was not strong as in the case before modification. Therefore, the magnitude of attraction forces between *cationic dyes* and the "basaltic tephra" was decreased. Also, magnitude of dispersion forces were decreased due to smaller surface area of "modified basaltic tephra".

Similar results were obtained for "clinoptilolite". Surface charge of "clinoptilolite" was changed from anionic state to cationic state with HTAB modification. Also, surface area of "clinoptilolite" was decreased. Therefore, electrostatic forces

Table 6.10 Adsorption capacities of the adsorbents used in this study

	Basaltic tephra, mg g^{-1}		Clinoptilolite, mg g^{-1}		
Dyestuff	Natural	Modified	Natural	Modified	PAC, mg g^{-1}
Basic blue	38.1	13.6	192.3	21.3	625.0
Basic yellow	14.1	3.8	74.1	11.9	243.9
Acid yellow	0–1	18.4	0–1	69.9	294.1
Acid red	0–1	9.7	0–1	66.2	312.5
Reactive yellow	−3.0	4.7	0–1	30.2	145.9
Reactive red	0–1	13.5	0–1	37.2	164.3

between *basic dyes* and “clinoptilolite” became repulsion forces and dispersion forces were decreased due to smaller surface area. As a result, adsorption capacities of two adsorbents for *basic dyes* decreased significantly with the modification. On the contrary, adsorption of *anionic dyes* onto “basaltic tephra” and “clinoptilolite” were improved significantly after the surface modification with HTAB. Because the effect of repulsion forces between the *anionic dyes* and “basaltic tephra” was decreased with modification, adsorption of those dyes onto “basaltic tephra” increased significantly.

For “clinoptilolite”, repulsive forces were changed to attractive forces with surface modification and consequently, important adsorption of *anionic dyes* onto “clinoptilolite” surface was achieved. This is a very important achievement in this study.

“Powdered activated carbon” has highest capacity for all dyestuffs used because its surface area is much higher than that of other adsorbents. In the neutral potential state the zeta potential is nearly zero and therefore, the electrostatic interactions between the carbon surface and the dyes are negligible. The adsorption forces are mainly dispersion forces. Adsorption capacity of “powdered activated carbon” for *basic dyes* is approximately 3 times higher than that of “clinoptilolite” and 15 times greater than that of “basaltic tephra”.

In order to compare results of this study with results obtained from the literature, results of some studies taken from the literature are summarized in Table 6.11.

As can be seen from the table various types of adsorbents were used to adsorb various dyestuffs from aqueous solutions. The best adsorption capacities of the adsorbents were obtained for *basic dyes* similar to this study.

“Basaltic tephra” used in this study has much smaller capacity for *basic dyes* than adsorbents used in the literature. However, the adsorption capacity of “clinoptilolite” compared very well with the other adsorbents. Considering the low cost factor for natural materials, they can be very attractive for color removal for *cationic dyes*.

Also, “modified basaltic tephra” used in this study has much less capacity for *acid* and *reactive dyes* than the adsorbents used in the literature. However, the adsorption capacity of “modified clinoptilolite” is comparable, especially for *acid dyes*, with the other adsorbents.

6.6 Adsorption Isotherms

Langmuir and Freundlich isotherm equations were tried to fit the equilibrium data obtained from experiments. Langmuir isotherm equations are given in Eqs. 6.1 and 6.2. Here:

$$\theta = q_e / q_{mon} = K_L C_e / (1 + K_L C_e) \tag{6.1}$$

$$C_e / q_e = (1 / K_L q_{mon}) + (1 / q_{mon}) Ce \tag{6.2}$$

Table 6.11 Summary of results of some studies from literature

			Dye used		
Reference	Adsorbent	Adsorbent form	Type	Name	q_{mon}, mg g^{-1}
Armağan et al. [2]	Sepiolite	Natural	Reactive	Black 5	0.5–1
	Zeolite				Neg. values
	Sepiolite	Modified with HTAB		Red 239	120
					108
					169
	Zeolite			Yellow 176	111
					61
					89
Turabik and Kumbur [13]	Bentonite	Natural	Basic	Red 46	312
		Acid activated			476
				Blue 41	263
					270
Turabik [12]	Bentonite	Natural	Basic	Blue 3	75
Choy et al. [4]	Granular Activated Carbon	Natural	Acid	Red 114	101
				Polar yellow	129
				Polar blue	101
Juang et al. [6]	Chitosan	Natural	Reactive	Red 222	379
				Yellow 145	179
				Blue 222	87
Juang et al. [5]	Clay	Acid activated	Basic	Blue 69	394
				Red 62	406
			Acid	Blue 25	256
			Direct	Blue 183	49
				Red 227	37
			Reactive	Red 123	36

where;

q_e = the amount of dyes adsorbed per unit mass of adsorbent
C_e = final concentrations of dyes in the aqueous phase
q_{mon} = the amount of dye adsorbed corresponding to monolayer coverage
K_L and q_{mon} can be found from the graph of (C_e/q_e) versus C_e.

The Freundlich isotherm equation is given in Eq. 6.3.

$$q_e = K_F C_e^{b_F} \tag{6.3}$$

The correlation coefficients obtained for various adsorbents are given in Tables 6.12 and 6.13.

Correlation coefficients for Langmuir Equation for natural and modified adsorbents give a very good fit with Langmuir Isotherm Equation.

Table 6.12 Langmuir isotherm constants for natural and modified adsorbents

Adsorbent	Dye	q_{mon} (mg g^{-1})	K_L (L g^{-1})	R_L (–)	R^2 (–)
Natural tephra	BB	38.1	0.13	0.015	0.998
Modified tephra	BB	13.6	0.04	0.045	0.992
Natural tephra	BY	14.1	0.17	0.012	0.992
Modified tephra	BY	3.8	0.02	0.106	0.934
Natural clinopt.	BY	74.1	5.19	0.001	0.999
Modified clinopt.	BY	11.9	0.09	0.023	0.985
Natural clinopt.	BB	192.3	2.60	0.001	0.999
Modified clinopt.	BB	21.3	0.04	0.050	0.943
Modified tephra	AY	18.4	0.01	0.129	0.975
Modified tephra	AR	9.7	0.23	0.009	0.980
Modified clinopt.	AY	69.9	0.52	0.003	0.998
Modified clinopt.	AR	66.2	1.31	0.001	0.999

Table 6.13 Freundlich isotherm constants for natural and modified adsorbents

Adsorbent	Dye	K_F (–)	b_F (–)	R^2 (–)
Natural tephra	BB	23.06	0.083	0.877
Modified tephra	BB	4.84	0.165	0.873
Natural tephra	BY	11.78	0.041	0.202
Modified tephra	BY	0.37	0.388	0.478
Natural clinopt.	BY	52.88	0.068	0.489
Modified clinopt.	BY	16.85	0.043	0.118
Natural clinopt.	BB	72.23	0.172	0.378
Modified clinopt.	BB	11.93	0.078	0.288
Modified tephra	AY	1.88	0.356	0.904
Modified tephra	AR	8.91	0.011	0.018
Modified clinopt.	AY	37.22	0.121	0.904
Modified clinopt.	AR	41.31	0.095	0.650

6.7 Conclusion

- Basaltic tephra and clinoptilolite in their natural forms can be used for the adsorption of basic dyes (cationic dyes). Clinoptilolite gives about five times better adsorption capacity than “basaltic tephra”.
- The adsorption capacities of basaltic tephra and clinoptilolite in their natural form for the adsorption of acidic (anionic dyes) are not high enough.
- The adsorption capacities of basaltic tephra and clinoptilolite in their natural form for the adsorption of reactive dyes are not good enough.
- If surface modifications of these adsorbents are done with a surfactant, like HTAB, the adsorption capacities of basaltic tephra and clinoptilolite for anionic dyes are

increased several times based on the type of the dye. Modified clinoptilolite 3–7 times has higher adsorption capacity for acidic dyes than modified basaltic tephra.
- Surface modification helps reactive dyes to a certain extent.
- Langmuir Isotherm Equation represents the adsorption of all dyestuffs on the adsorbents used in this study better than Freundlich Isotherm Equation.

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Chapter 7
Reuse of Biologically Treated Process Water: Industrial Water Management in the Paper and Sugar Industry

Otto Nowak and Peter Enderle

Abstract Internal process water cycles have been installed in many industries throughout the last decades. Closing the water cycle is advantageous from the ecological as well as from the economic point of view, mainly because of savings of water and energy. However, closed water cycles may lead to serious operational problems in the production process, such as biofouling and encrustations of limescale. These problems can be avoided by implementing biological wastewater treatment in the internal water cycles. Moreover, energy can be recovered by biological wastewater treatment, particularly if the first treatment step is anaerobic. Examples of heat recovery in the paper industry are presented as well as an example of reuse of biologically treated wastewater in a beet sugar factory. Trends in the application of biological process water treatment for reuse are discussed.

Keywords Paper industry • Closing the water cycle • Biofouling and encrustations of limescale • Biological wastewater treatment • Heat recovery in the paper industry • Beet sugar factory

7.1 Introduction

Stricter environmental regulations, increasing wastewater treatment and discharge costs, and greater environmental awareness are some of the forces leading to development of innovative technologies and strategies to optimize industrial water management. To improve ecological and economic performance, internal process water cycles are installed in many industries. The implementation of process water

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reuse measures are nowadays widely considered the primary step for efficient water use within industrial branches that consume high amounts of water.

One of the first internationally known examples of reuse of biologically treated process water was the sugar mill *Leopoldsdorf* near Vienna [2]. In this mill, the process water has been treated in a single-stage activated sludge plant and reused as flushing and washing water since the 1980s.

More recently, two examples of reuse of biologically treated process water within the paper industry have become known. One of these was operated as a "zero emissions" plant prior to inclusion of biological treatment but increasing difficulties forced integration of a biological treatment plant in order to maintain a closed water cycle [3]. The second company decided to close the water cycle with an integrated process water treatment plant, as increasing wastewater disposal costs were resulting in a steady increase of environmental costs [1]. Meanwhile, additional examples, particularly within the paper industry, become known which at least partially reuse biologically treated process water.

This chapter gives an overview on the state of the art of reuse of biologically treated process water. Advantages and further possible applications are discussed.

7.2 Advantages and Problems in the Case of Process Water Reuse

Reuse of process water has been considered desirable for a long time as part of the general goal of "Cleaner Production". Even in central Europe there are many good reasons for companies to minimize their freshwater demand although in this region water saving measures are only of limited use from the economic point of view and from the perspective of water quantity management. Nevertheless, for many industries there are other good reasons to minimize fresh water consumption, as far-reaching ecological and economic advantages can be achieved. The ecological advantages can be summarized as followed:

- Less organic matter (COD) in the effluent
- Conservation of thermal energy

COD (Chemical Oxygen Demand) characterizes the amount of organic matter in the wastewater. The effluent of low-loaded biological wastewater treatment plants (WWTPs) consists of non-degradable ("inert") organic matter which is not degraded during the biological wastewater treatment process and of very slowly biodegradable COD ("recalcitrant COD"). In regard to the very slowly biodegradable COD, increased concentrations often lead to a higher removal rate and therefore to a reduced COD load in the effluent. Although not fully validated whether this enhanced removal is due to improved degradation or enhanced adsorption, there is evidence that it is due to improved biological degradation.

Conservation of thermal energy derives from the lower heating demand. Generally – e.g. in the paper industry – a higher water temperature is desired for production processes than temperatures characteristic of raw water entering the plant.

In addition to reductions in energy costs, economic advantages result from water supply and wastewater disposal fee structures. Significant cost savings may result from:

- Lower water supply costs
- Reduced wastewater charges for both indirect and direct dischargers (e.g. in Germany)

However, the reuse of organically polluted process water normally leads to significant production problems in both the paper industry and sugar industries. Within the paper and cardboard industry some companies known to the authors have abandoned their zero-emissions approach and reopened their closed water cycle to solve accrued production problems. All production problems that occur when reusing high organically-polluted process water result from the formation of organic layers, i.e. on biofouling.

Biofouling leads to significant production problems and necessitates the application of biocides. An immediate consequence of biofouling is the formation of organic acids out of glucose and starch, i.e. the formation of organic layers leads to an acidification of the process water. Due to this reaction, dissolution of calcium carbonate may occur if lime enters the production process, e.g. via raw materials such as waste paper. A subsequent increase of the pH in the process water cycle leads to the formation of limescales ("encrustations"). Lime hydrate ($Ca(OH)_2$) is often applied to increase the pH and reduce acidification. However, in doing so, the lime content in the process water will be increased accompanied by a higher risk of lime precipitation.

Furthermore, acidification itself can lead to corrosion problems. This problem is exacerbated by the anaerobic processes under the organic layer. In these anaerobic zones, sulfate reducing bacteria (SRB) reduce sulfate (SO_4^{-2}) to hydrogen sulfide (H_2S), causing odor problems and leading to an enhancement of the corrosion affects when H_2S gets into the condensate and is oxidized to sulfuric acids. Finally, the accumulation of organic matter in combination with biofouling can lead to a decline of the product quality, e.g. within the paper and cardboard industry.

To avoid biofouling effects and the accompanying undesirable consequences, biological treatment of organically polluted process water before reuse has turned out to be advantageous. Industries in which biological treatment in the process water cycle can be usefully applied include: paper and pulp; sugar and starch; textile (usually only after filtration); and food industry (only after membrane filtration). Four examples from the paper and sugar industries are presented in detail in the following chapters.

7.3 Process Water Reuse After Biological Treatment Within the Paper Industry

Within the paper industry, producers of high quality papers are confronted with biofouling and its side effects, especially if the production process includes almost closed process water cycles designed to achieve close to zero-emissions and if waste

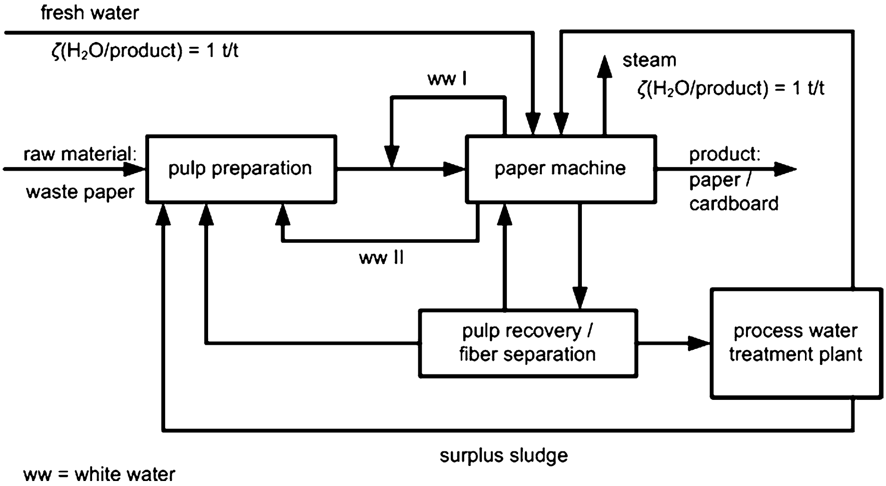

Fig. 7.1 Process water cycle of paper mill 1 and 2 closed over a process water treatment plant

paper is used as a raw material for the production process. To avoid negative effects on the production process and product quality, the input of biocides is required to inhibit biological conversion processes in the process water cycle. As mentioned in the previous chapter, acidification in the process water cycle is accompanied by the release of calcium ions out of the lime introduced with the waste paper and, as a consequence, by the formation of limescales ("encrustations").

Due to these operational problems and a planned expansion in production, the first paper mill discussed ("paper mill 1") decided to integrate a process water treatment plant into the closed process-water cycle [3].

The second paper mill discussed ("paper mill 2") had not originally operated under a completely closed process-water cycle. Due to high wastewater charges, the operators decided to integrate a process-water treatment plant accompanied by closure of the process water cycle [1].

Figure 7.1 shows the more or less identical process-water cycles of paper mills 1 and 2 after the integration of a process water treatment plant ("paper mill 1") and after closure of the process-water cycle and introduction of a process-water treatment plant ("paper mill 2"). In the paper industry, water is inevitable consumed due to the necessary drying processes, whereby approximately one cubic meter of fresh water is needed per produced ton of paper.

At both of these paper mills the excess sludge from the process-water treatment is returned to the production process and inserted into the product. However, this is not possible at all paper and cardboard mills.

The process-water treatment plants of both paper mills consist of an anaerobic and a downstream aerobic stage. In both cases the process water is cooled down from 55°C to a temperature of 37°C before entering the anaerobic stage. This is necessary to adjust mesophilic conditions in the anaerobic stage (Fig. 7.2). However, there is also experience with an anaerobic-thermophilic treatment of

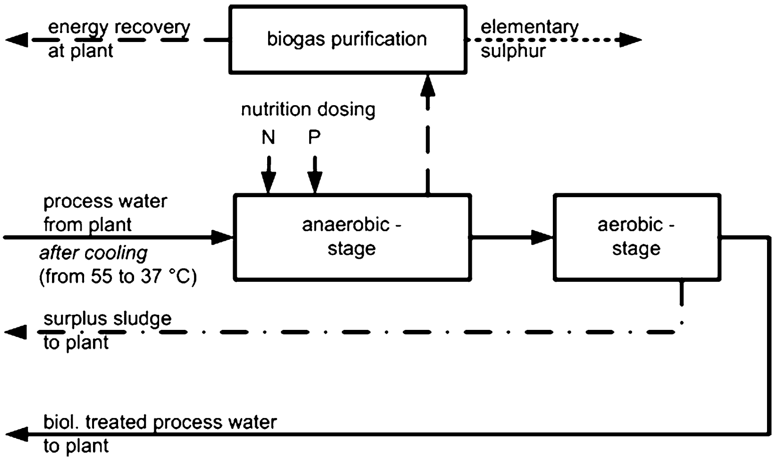

Fig. 7.2 Block diagram of the process water treatment plant of paper mill 1 and 2

process water from paper production followed by the reuse of the biologically treated process water [4, 5].

The aerobic treatment stages are an activated sludge plant at paper mill 1 and an aeration reactor without sludge retention at paper mill 2. Besides the aerobic treatment and the further degradation of the organic matter, the purpose of the aerobic stage is to achieve systematic precipitation of calcium carbonate in a fine crystalline form. This enables the calcium carbonate to be removed from the water cycle together with the excess sludge. This systematic precipitation was reached at paper mill 1 due to use of a shallow aeration tank aerated by surface aeration. This solution achieves a much better stripping of CO_2 compared to the high aerobic reactor with air diffuser used in paper mill 2 where a high amount of CO_2 and therefore calcium remains in solution.

Both paper mills combine purification of the biogas resulting from anaerobic digestion with sulfur recovery (Fig. 7.2). Consequently, the anaerobic process significantly reduces the sulfate concentration in the process water as a significant amount of sulfur is removed as sulfide from the digester gas.

Integration of an anaerobic-aerobic process water treatment plant enhanced the product quality at paper mill 1. The concentration of organic acids in the product was reduced significantly and the product output could be slightly increased. Furthermore, the concentration of calcium ions was considerably decreased by the significant increase of the pH-value in the process water. In contrast, the chloride concentration remained unchanged as expected.

Summarizing the results of the adapted production process, in comparison to the closed operation without an integrated process-water treatment plant at paper mill:

- the COD, calcium and sulfate concentration in the process water was decreased by 80%,
- the odor problem was reduced and
- the product quality improved [3].

In summarizing the advantages achieved by the integration of a process-water treatment plant in comparison to the operation without integrated process-water treatment with a wastewater flow of 3.2 $m^3\ t^{-1}$ paper at paper mill 2:

- the COD concentration, especially the content of organic acids, was reduced,
- the calcium and sulfate concentrations in the process water remained approximately at the same levels,
- the chloride concentration in the process water and in the product increased and
- the integration of the process water treatment has been worth the investment [1].

In general, there is no cost-effective way to remove chloride in the course of wastewater treatment. The same applies for sulfate, if no anaerobic stage is integrated into the wastewater treatment process. Consequently, managers need to first clarify acceptable process water salt concentrations. Based on these decisions, the extent to which the process-water cycle can be closed by integrating a biological treatment plant [8] can be assessed.

Concerning the tendency of biofouling (organic layers) after the integration of an aerobic biological treatment within the water cycle, studies of Malmqvist et al. [7] have shown that this could be a critical issue. Although the investigations have revealed that the problem can be handled, an overdose of the nutrients nitrogen and phosphor can lead to increased growth of biofilms in the process water system.

It should be noted that, a partial recycle of biological treated process water to the production process is carried out even at paper mills where a closed process-water cycle seems not to be suitable because of the required product quality.

7.4 Process Water Reuse After Biological Treatment Within the Sugar Industry

As mentioned in the introduction, the first internationally known example of reusing biologically treated process water was at the sugar mill *Leopoldsdorf* near Vienna [2],

The production processes of this sugar mill (“sugar mill 1”) and the second discussed Austrian sugar mill (“sugar mill 2”) although not identical are quite similar. However, the water and wastewater process flows (Figs. 7.3 and 7.4) differ significantly as these sugar mills have been built taking specific local situations into consideration [6].

Most beet sugar mills nowadays, have two main wastewater flows within the production process:

- Vapor condensate from the cooling water circuit (ca. 4 $m^3\ t^{-1}$ beet) with a temperature of 25–40°C: $\gamma_{COD} < 30\ mg\ L^{-1}$, $\gamma_{NH4\text{-}N} < 200\ mg\ L^{-1}$
- Flume and washing water (ca. 4 $m^3\ t^{-1}$ beet) including 70–90% of the organic matter (mainly sugar, parts of beets) and adherent soil (50–100 kg dry matter per t beet) which gets eliminated in the sedimentation tank [6].

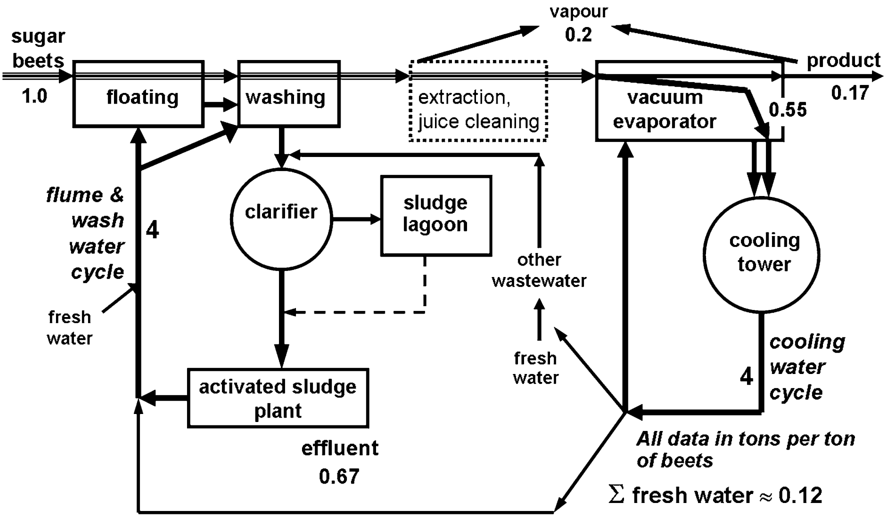

Fig. 7.3 Process flow diagram of sugar mill 1 (= sugar mill *Leopoldsdorf*)

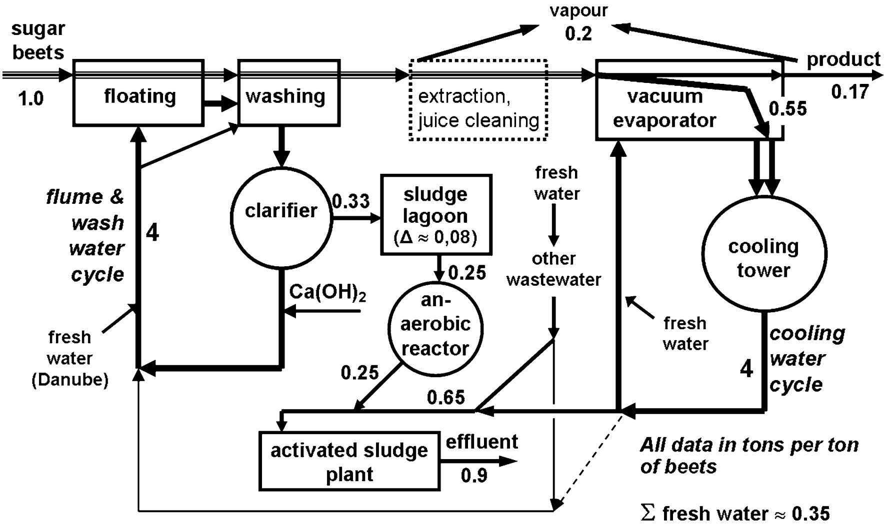

Fig. 7.4 Process flow diagram of sugar mill 2

Accordingly, at both Austrian sugar mills the internal water management is designed with two water cycles: cooling water circuit, where the vapor condensate accrues; and the organically highly polluted washing- and flume-water cycle (compare Figs. 7.3 and 7.4).

At both sugar mills the water cycles are predominantly closed. The difference between the water cycle systems at the two mills is that sugar mill 1 has integrated an aerobic wastewater treatment plant within the highly polluted wash- and flume-water cycle.

In contrast to sugar mill 1, in sugar mill 2 the organically highly polluted wash and flume water only passes through a sedimentation tank with the consequence that organic matter accumulates in the water cycle. To avoid excessive biofouling, lime hydrate is dosed into the wash- and flume-water cycle (Fig. 7.4).

The sludge from the sedimentation tank, basically soil, gets extracted into so called sludge lagoons. The supernatant of these lagoons is fed into an anaerobic biological treatment stage (anaerobic reactor). The effluent of this anaerobic stage is treated at an activated sludge plant together with the excess vapor condensate and other wastewater streams. While at sugar mill 1, nitrogen has to be added to the aerobic treatment to avoid nitrogen deficiency, at sugar mill 2, nitrogen is present in excess in the influent to the aerobic stage due to the removal of COD, but not of nitrogen in the anaerobic reactor. Accordingly, at sugar mill 2 the aerobic treatment has to be operated with nitrification and denitrification.

Sugar beets contain approximately 75% water and 17% sugar. During the production process about 0.2 m^3 water evaporates and 0.55 m^3 of wastewater are produced per ton of sugar beets processed, even without freshwater input.

Within sugar mill 1 only a small amount of fresh water is used for supplying the wash- and flume-water cycle, the water primarily being supplied by the cooling water cycle, i.e. by the surplus water from the sugar beets resulting from processing. Altogether, sugar mill 1 has had a water demand of 0.12 $m^3\ t^{-1}$ sugar beets over the recent years.

At sugar mill 2, a small amount of fresh water is used within the production process as well as to supply the wash- and flume-water cycle. In addition, some fresh water is used for the cooling water cycle. The water consumption at sugar mill 2 is around 0.35 $m^3\ t^{-1}$ sugar beet.

Regarding these two sugar mills, it turns out that the process water treatment at sugar mill 1 shows advantages compared to the process performance of sugar mill 2. At sugar mill 1 there is:

- almost no biofouling; therefore less organic layers and hardly any organic acids in the process water (wash and flume water) and therefore no corrosion problems in the piping system,
- no need to add calcium hydroxide to the wash and flume cycle to avoid biofouling; therefore no limescales,
- significantly lower investment costs for the process water treatment compared to sugar mill 2 and
- much easier operation of the process water treatment plant than at sugar mill 2.

The disadvantage of the process-water treatment at sugar mill 1 compared to sugar mill 2 is that as a result of the aerobic degradation more nutrients (nitrogen and phosphor) have to be added and more energy is needed. However, the electricity demand is covered by means of cogeneration.

7.5 Conclusion

The integration of a biological treatment stage in a process water cycle can lead to significant operational and energetic advantages. Within this paper, examples of the paper and the sugar industry have been presented and discussed.

Currently the focus of efforts to integrate biological treatment into industrial operations seems the paper and cardboard industry, industries with relatively low water demand and high COD concentrations in the process water, which makes anaerobic treatment together with biogas production feasible.

However, energy can also be gained from the biogenic heat produced in aerobic systems, where the amount of energy is in the same range as the amount of calorific energy in the methane formed during anaerobic degradation. In this case, energy is needed for the aeration system in the aerobic wastewater treatment plant. However, the gain of thermal energy is larger than the energy demand for suitable aeration systems, even when calculated as primary energy. Consequently, in cases where process water needs to be warmed up, it may be advantageous to integrate an aerobic treatment stage into the process water cycle, especially as the energy demand for the drying process (paper and cardboard) declines with the reduction of the COD concentration in the process water. This is particularly applicable for small companies, where an anaerobic stage including gas purification and utilization would lead to high investment and operating costs.

Finally it should be mentioned that combinations of biological and chemo-physical treatment systems are gradually becoming more important in both wastewater treatment and in process-water treatment. An important step in the reuse of biologically treated process water in industry is the application of membrane activated sludge systems, so-called "membrane bio-reactors" (MBR).

On the one hand, these systems are sensible for economic reasons in particular for wastewaters with high organic concentrations. On the other hand the main advantage of these systems is the bacteria-free effluent that can be expected. Moreover, as the effluent of an MBR is free of particles, it can be directly fed into reverse osmosis (RO) systems and the filtrate from RO can be used instead of desalinated or softened fresh water.

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Chapter 8
Water Consumption in Paper Industry – Reduction Capabilities and the Consequences

Konrad Olejnik

Abstract Water is particularly important substance in papermaking. It plays essential role in fibers transportation, equipment cleaning, lubrication, cooling and in development of a product quality. A tendency to reduce the fresh water consumption in paper production is economically and environmentally justifiable but it must be emphasized that strict closing of water system in paper mill has significant negative impact on several technological operations. High water temperature, as well as increased content of suspended and dissolved solids in water system of a paper machine is examples of major consequences of closing the water loop. As a result, serious problems may cause e.g. paper defects, loss of product quality and problems with run ability of a paper machine. Situation becomes even worse when recycled raw materials are used. Hence, methods of fresh water usage reduction in papermaking are very complex issues and usually depend on the degree of closure. Equilibrium between the advantages and the disadvantages relevant to water consumption restrictions should be established. The acceptable level of water loop closure will depend on the several factors e.g. paper quality required, raw materials used, chemical additives, equipment and staff education.

The objective of this chapter is to present main problems related with reduced water consumption in paper industry, to describe the further possibilities of water usage reduction and consequences of this operation for the technological process and for the environment.

Keywords Paper • Papermaking • Balance • Equilibrium • Water consumption • Reduction • ZLE (Zero Liquid Effluent)

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Abbreviations

AOX	Adsorbable Organic Halogens
BAT	Best Available Technology
BATNEEC	Best Available Technology Not Entailing Excessive Costs
BATEA	Best Available Technology Economically Achievable
BPEO	Best Practicable Environmental Option
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
DAF	Dissolved Air Flotation
TDS	Total Dissolved Solids
EGSB	Expanded Granular Sludge Bed reactor
IPPC	Integrated Pollution and Prevention Control
MBBR	Moving Bed Bio Reactor
NF	Nanofiltration
RO	Reverse Osmosis
UF	Ultrafiltration
NZLE	Near Zero Liquid Effluent

8.1 Introduction

Paper is one of the most eco-friendly products manufactured by humans. It is made from natural, renewable raw material; it is relatively cheap, commonly accessible and biodegradable.

In the twentieth century, paper production had doubled every 20 years. At present, the global paper industry produces around 400 million tons of paper yearly [5]. It is worth mentioning that the annual consumption of paper products (expressed in kg per capita) is often considered as a level of economic development of a country. For example, in 2008 the average paper consumption in highly developed countries amounted to 180–340 kg per capita per year. However, the average global paper consumption was around 58 kg per capita per year [6]. Paper products are generally well perceived by people as it was proved by the poll conducted by CEPI (the Confederation of European Paper Industries). The results showed that 93% of consumers in Europe agree with the opinion that manufacturers should use more paper packaging due to the environmental friendliness of paper. Growing human's population and constant development of our civilization show that, at least in coming years, the global paper production is also expected to continue to grow.

The paradox is that while the paper itself contains mainly positive connotations, the pulp and paper industry is still, in some regions, perceived as highly harmful and dangerous to the environment. This opinion is mainly created by such factors as: wood collection (logging), high water consumption in paper industry, discharge of large quantities of effluents and solid wastes.

Nowadays, the growing awareness of the hazards related to uncontrolled emissions and disposal of industrial waste, supported by legislation changes, forces to monitor and limit and process all types of waste (gas, liquid and solids). In many countries, the industry and trade are required by new legal regulations to take full responsibility for the product life cycle "from cradle to grave". Paper industry is also forced by various legal and economic requirements to modify and optimize its production process in terms of industrial waste and consumer goods recycling. New production plants have to be designed according to the guidelines of the BAT, BATNEEC, BATEA and BPEO [2, 3, 22].

Due to economic and environmental requirements, present production of paper products is a very complex industrial process. Paper is a mass product, thus the production equipment is required to work with high precision and at maximal capacity. The largest paper machines have manufacturing capacities exceeding 3,000 t day^{-1}. The paper web produced on these machines runs with speed over 100 km h^{-1}. As a result of growing capacities, the unit operations last shorter and shorter. For example, presently, over 90% of water from formed paper web is removed in less than 1–2 s. It is very difficult to control the proper run ability of the process and simultaneously maintain the high product quality. Therefore, the most sophisticated control algorithms and systems are used for this purpose including multivariable model predictive control, statistical process control, fuzzy logic, neural networks, etc. This still does not guarantee the trouble-free operation.

Properties of the raw material are one of the most important factors still causing some difficulties and production limitations. Papermaking pulp is a heterogeneous medium of natural origin with specific properties (e.g. flocculation, swelling, high sorption ability). The reasons mentioned above make it difficult to maintain pulp as homogeneous and stable fibrous suspension. It is very complicated to control the proper pulp processing in order to get a final product of required properties.

Apart from the raw material quality, water is a key factor affecting the production cycle.

8.2 Water Consumption in Papermaking Process

In paper technology, water is used in the following operations:

- Preparation of raw materials and chemicals,
- Development of fibers papermaking properties,
- Transportation and dilution of pulp,
- Formation and consolidation of paper web,
- Cleaning of parts of paper machines and accompanying equipment.

Additionally, water is used for:

- Cooling,
- Sealing,
- Lubrication,
- Heating (in the form of steam).

Table 8.1 Examples of specific water consumption range per sector [11]

Paper grade	Fresh water consumption (m^3 t^{-1} of paper)	Liquid effluent (m^3 t^{-1} of paper)
Tissue	5–30	5–27
Printing and writing	10–50	8–45
Specialty	20–80	15–74
Newsprint	15–30	12–25
Packaging (virgin and recycled pulps)	6–45	5–40
Corrugated boards	6–40	4–35

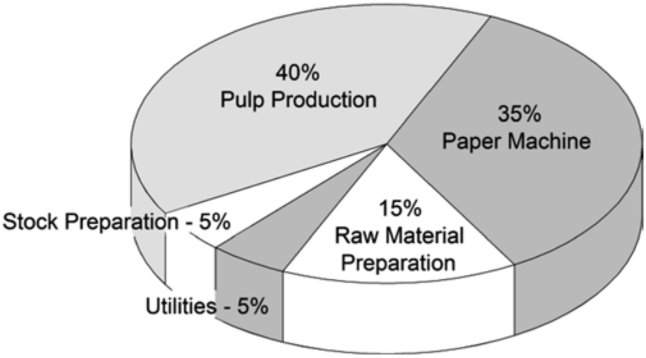


Fig. 8.1 Consumption of fresh water in each stage of pulp and paper production

It must be strongly pointed out that it is impossible to produce paper in conventional way without water because of the nature and properties of cellulose fibers.

Productions of different paper grades have different water requirements (see Table 8.1). However, considering absolute water needs, it can be stated that an average paper mill needs approx. 10–20 m^3 of fresh water and 100–150 m^3 of process water in order to produce 1 ton of paper. Depending on its application, each type of water has to meet specific quality requirements. For this reason, not always the most available water can be directly used. The analysis of demand for fresh water in each stage of pulp and paper production shows that the highest amount of water is consumed during the pulp manufacture and on the paper machine (Fig. 8.1).

A characteristic feature of paper production is its internal, high demand for water, which cannot be easily reduced in practice. It can be illustrated by the fact that there are unit operations in the technological line which locally require pulp dilution levels corresponding to water consumption amounts ranging from 200 to 400 m^3 t^{-1} of paper. In practice, such a high water consumption is unacceptable, therefore some water saving solutions are used, including buffer tanks, circulating water systems, etc. [14, 17, 18].

Figure 8.2 presents a flow diagram of water and pulp production system in a paper mill. The typical system consists of three basic water cycles: a short (white water) loop, fibre recovery loop and waste water treatment plant loop. In the middle of the

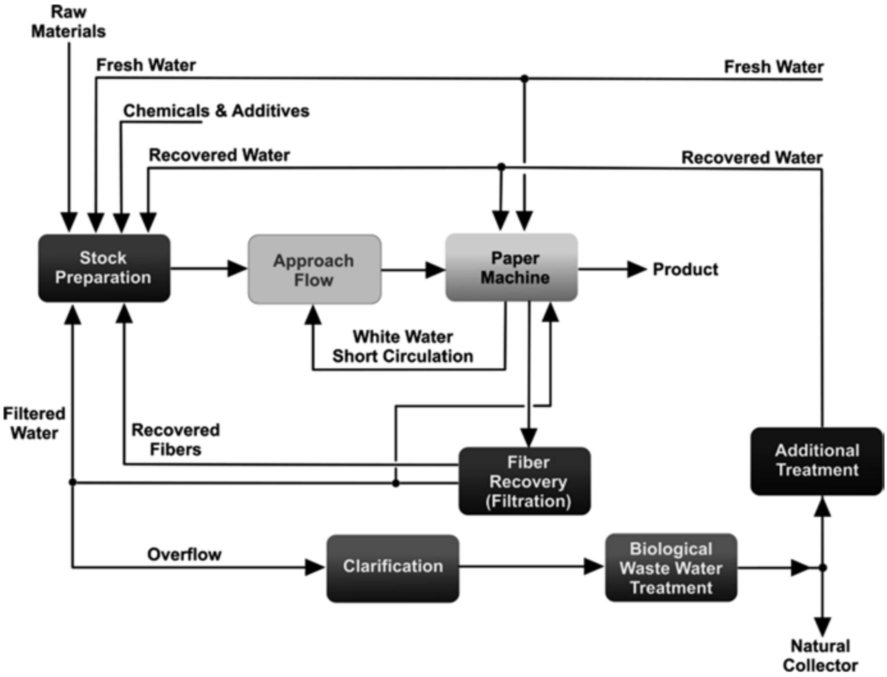


Fig. 8.2 Block diagram of water and pulp system in paper mill

twentieth century, many, especially small paper mills did not have the waste water treatment loop. For this reason, water circulating in the technological line could not be treated and re-used effectively. It resulted in excessive consumption of fresh water. It should be noticed that the structure of water system complicates considerably the technological process and makes the system periodically unstable. In order to keep the production process running smoothly, the water and pulp system of the paper machine has to be maintained in a state of specific dynamic technological balance consisted of the following partial equilibriums:

- Water,
- Mass,
- Physicochemical,
- Thermal,
- Microbiological.

All partial equilibriums are linked together. Any change in one of the partial equilibriums affects the other partial equilibriums and has a direct impact on the balance of the whole system. That is why disturbance of one may destabilize the whole production process in a short period of time. For example, reduction in fresh water consumption (water equilibrium) increases the content of pulp particles in circulating water (mass equilibrium), increases the concentration of solutes

Table 8.2 Substances contained in papermaking stock

Basic components of papermaking pulp	Auxiliary substances added to pulp	Impurities and other unwanted substances
Cellulose	Flocculants	Black liquor residues
Hemicellulose	Coagulants	Bleaching substances residues
Lignin	Biocides	Acidic compounds
Extraction substances	Aluminum compounds	Substances contained in fresh water
Sizing substances	Antifoaming agents	
Fillers (e.g. clay, TiO_2, $CaCO_3$, talc)	De-inking substances	Iron compounds (corrosion)
Modified starches	Semi-bleaching substances	Unidentified, non-paper soluble substances from recovered paper processing
Dyes, pigments, optical brighteners		

(physicochemical equilibrium) and increases the temperature of circulating water (thermal equilibrium). Factors that are mentioned above have also an effect on the amount and the type of microorganisms in the system (microbiological equilibrium). Additionally, the temperature increase makes the paper web easier to dewater. This subsequently influences retention in the wire section and quality of the product. Finally, it results in further changes in the pulp and physicochemical equilibrium (change in concentration of pulp particles and substances dissolved in circulating water) [15, 18, 19]. Another difficulty is connected with the fact that each paper mill has its unique chemistry resulting from the type and the origin of used raw materials, pulp additives or chemical aids (Table 8.2). Due to differences among paper mills, in practice each operation aiming at optimization of technological system should be developed individually [24, 25]. Success in optimization of paper mill water system depends on proper understanding of interactions between all major variables.

8.3 Consequences of Reduction in Fresh Water Consumption in Paper Mills

Further reduction of fresh water consumption in the papermaking process is both economically and environmentally justified. The most important advantages resulting from reduced water consumption in the paper mills include [9]:

- Lower energy consumption,
- Lower consumption of raw materials,
- Higher production efficiency,
- Lower costs of fresh water use,
- Lower waste water effluent.

However, the reduction of water consumption involves the occurance of some unwanted phenomena.

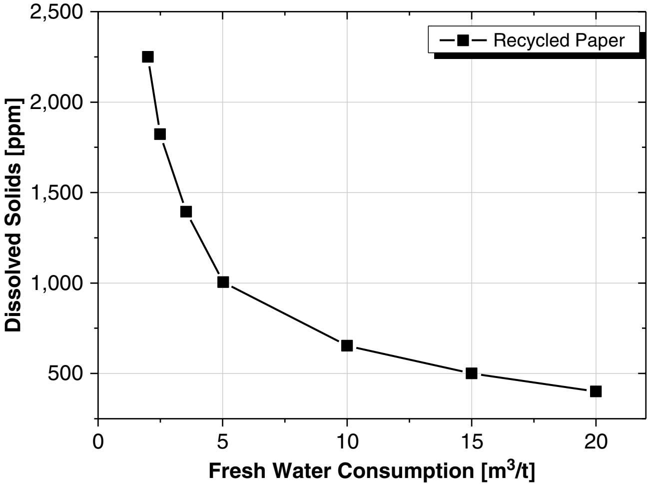


Fig. 8.3 Example of accumulation of substances dissolved in paper mill circulating water

It should be emphasized that soluble, colloidal substances and the smallest solid particles (the fines fraction), which did not retain in the formed paper web, pass through the wire together with discharge water to circulating water loop of a paper machine [15, 19]. Repeated recirculation and utilization of the same water increase concentration of those substances (Fig. 8.3). The highest increase in the concentration of unwanted substances is observed in the usage of water below the level of about 5–7 m^3 t^{-1}.

The resulting changes in the technological equilibrium have a direct effect on the production process, water management and the quality of effluents discharged from the mill. As a consequence, it may lead to:

- Reduction in retention of the furnish on the paper machine wire,
- Higher corrosion of equipment,
- Precipitation of deposits,
- Pulp foaming,
- Significant increase in temperature of circulating water (even up to 60–70°C).
- Faster growth of microorganisms in the technological system,
- Threats to health (occurance of irritating properties of circulating water, which even with neutral pH may cause a threat to eyes and skin),
- Problems with paper machine runnability (web breaks, decline in dewatering of formed paper web),
- Lower efficiency of chemical aids,
- Negative impact on further waste water treatment processes,
- Lower product quality (lower brightness, lower strength, spots, holes, micro- and macrostructural inhomogeneity, etc.).

Destabilization of the entire production process may be the most serious problem resulting from the above difficulties.

Despite those risks, the industry continues to work on the reduction of fresh water consumption. It should be stressed that the most considerable savings in water consumption were made at the turn of the 80-ties and 90-ties. At that time, the water consumption was reduced from 150 to 100 m^3 t^{-1} of paper to 15–50 m^3 t^{-1}.

Presently, in accordance with the EU guidelines with regard to the BAT, each paper mill should consume around 10–20 m^3 of fresh water per 1 t of manufactured paper [5, 22]. Nevertheless, the average water consumption in the European paper industry is still high and reaches about 40 m^3 t^{-1}.

In majority of cases, reduction in water consumption to the level of around 40–60 m^3 t^{-1} usually requires reorganisation of the technological line and personnel training. Further reduction can only be achieved by application of new and more advanced technological solutions, such as:

- Complex assessment of circulating water through multidimensional control of the physical and physicochemical state (electrokinetic potential, cationic demand, redox potential, pH, TDS, COD, BOD, AOX, turbidity, color, etc.),
- Advanced process chemization (application of coagulants, flocculants, antifoaming agents, biocides, etc.),
- More efficient fiber and fines recovery processing.

At the moment, it seems particularly difficult to reduce permanently the water consumption below the level of around 5–10 m^3 t^{-1} of paper (it should be remembered that 1–1.5 m^3 of water per ton of manufactured paper is evaporated during paper web drying). Such a significant closure of water and pulp circulation in the paper mill, especially with deteriorating quality of raw materials used for paper production (recycled pulps), is connected with a real risk of serious loss of technological balance of the entire production line.

Evolution of environmental impacts of the European pulp and paper industry is illustrated by Fig. 8.4. This figure shows relative changes in basic indices such as production, total consumption of fresh water and waste water pollution in the pulp and paper industry in the countries associated in CEPI from 1990 to 2008 [5].

When analyzing presented curves, continuous production increase and considerable declines in number of compounds of the COD and BOD discharge can be observed. The curve for the consumption of fresh water after 2000 is basically maintained at the same level. Taking into account the rising production, it shows that, in the discussed period, the demand for fresh water had been reduced, however not to such an extent as up to 2000. Provided that the tendency in the production increase is maintained, in the future the absolute demand for the fresh water is not expected to be reduced dramatically, it may even grow. It proves that without new technologies and more restrictive water management there are not any real possibilities of further reduction in the consumption of fresh water.

In order to understand better the scale of the problem, it should be remembered that, even with a relatively low rate of specific consumption of fresh water, an absolute consumption will still be considerably high. Assuming the average global specific consumption of fresh water amounts to 50 m^3 t^{-1} of paper it can be easily calculated that the paper industry itself needs around 2×10^{10} m^3 of fresh water yearly. This is the average amount of water discharged by the Nile River within 2 months.

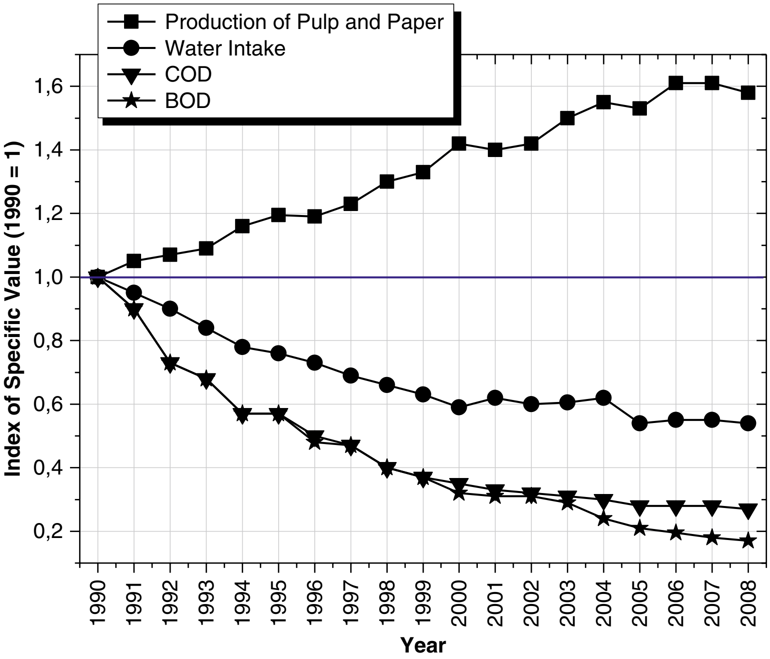


Fig. 8.4 Changes in production and consumption of fresh water and waste water pollution in pulp and paper industry in CEPI countries from 1990 to 2008 [5]

Additionally, taking into account the production of chemical pulp, the demand will be even higher. The largest amount of the water is removed from the technological unit in the form of effluents. It can be easily calculated that the reduction in the specific water consumption only by 1 m^3 t^{-1} helps to save approximately 400 mln. m^3 of water yearly, whereas the reduction in the consumption to the level recommended by the EU (15 m^3 t^{-1}) allows to save 1.4×10^{10} m^3 of water annually.

8.4 Possibilities of Further Reduction of Fresh Water Consumption in Paper Mills

Reduction of fresh water consumption in paper industry is mainly imposed by economic factors. Among others, the most important factors are prices of:

- Fresh water inlet,
- Waste water outlet,
- Solid waste storage and/or utilization and,
- Technological water treatment,
- Waste water treatment,
- Sludge thickening and disposal.

It is obvious that every investment including activities related to water and waste management must always take into consideration profits and sacrifices referred to actual tax levels and process operational costs. Large number of different variables which should be taken into account causes that reduction of fresh water consumption in paper industry is a very complex problem that always must be solved individually. For already existing paper mill, successful accomplishment of this task is rather a matter of “evolution” than “revolution”. Several major and minor steps (e.g. recognising system limitations, proper water management planning, trials, etc.) should be done for this purpose [8, 9].

Due to shrinking resources of clean water in the natural environment, further reduction in fresh water consumption is necessary, including final, total closure of the paper mill water system (ZLE – Zero Liquid Effluent or ZLD – Zero Liquid Discharge System). To obtain this goal the following, primary actions should be taken:

- Application of advanced water management and treatment technologies,
- Personnel training,
- Introduction of more restrictive raw materials management and control,
- Implementation of new legislation,
- Scientific research.

8.4.1 Application of Advanced Water Management and Treatment Technologies

In the paper mill, water treatment is connected with effective solution to removal of suspended solids (including colloidal particles) and dissolved substances. The following actions and unit operations are recommended or already used for the treatment of water discharged from paper production process:

- Reduction of the internal volume of pulp and water system in paper mill,
- Separation of solid waste (supported by precipitation or coagulation),
- Membrane filtration,
- Advanced and intensified biological treatment,
- Oxidation,
- Evaporation.

High internal volume of pulp and water system in paper mill can be nowadays considered as a legacy of pre-computer control age. At that time, high capacity buffer tanks were disturbance suppressors installed in certain points of technological line. Excessive consumption of chemical aids, problems with process control, fiber loss during grade change and startup, and higher water demand are the main side effects of that situation. As a response to a present tendency, in 1993 so called POM system was invented and introduced for strict water management [12].

The main idea of this sophisticated technology is to simplify the papermaking pulp and paper system and to reduce its volume as much as possible. This is achieved by using special devices (POMix stock processor, POM Header, POMp Degasser, POMlock) in order to significantly increase flow rates and eliminate high capacity vessels. Fast flows enable to reduce dead time and maintain process equipment clean. As a result, better stability, controllability, lower consumption of fiber, chemical aids and water are obtained. Nowadays, POM system has been installed in several paper mills worldwide. Of course, this technology cannot be considered as a stand-alone. Water treatment technologies must be used as well for permanent reduction of fresh water consumption.

Currently, used basic solutions usually include unit operations which mainly remove the suspension (the fines). They are usually carried out in the second and third water loop in the paper mill. For this purpose, in the second loop, disc filters or bow screens are used, whereas in the third loop – gravitational sedimentation tanks and microflotators (regular DAF systems) are installed. Application of chemical aids (coagulants and flocculants, activators, surface active agents, dissolvents, oxidizers) makes it possible to intensify the process [17–19].

In case of occurrence of excess amount of colloidal and dissolved substances, membrane filtration is the most effective method. Depending on the size of the particles removed there are four basic types of this process: microfiltration, ultrafiltration, nanofiltration and reverse osmosis. Considering the water from paper production, the application of ultrafiltration enables to remove totally dissolved poly- and oligosaccharides, some of lignin-based substances, substances responsible for micro-stickies as well as bacteria. Water treated in this way shows significantly lower cationic and biocides demand. The disadvantage of ultrafiltration is its minor impact on the reduction of the COD and the TDS [9, 20]. However, water treated in this process may be used for high pressure cleaning showers and dilution of chemical aids (Fig. 8.5). Reduction in the COD and TDS values requires other methods for water treatment, e.g. nanofiltration or reverse osmosis [20]. These techniques have been already well known in many other industrial areas but they are relatively new to the pulp and paper industry. Currently ultrafiltration is considered as an optimal solution for circulating water treatment in papermaking.

Figure 8.6 shows the example of the distribution of the operational costs for UF plant installed in a paper mill. This plant produces constantly 10 $dm^3\ s^{-1}$ of ultrapure water, 350 days $year^{-1}$. Total operational costs of the mentioned UF plant are approx. 300 Euro for every 1,000 m^3 of water produced [20]. One has to remember that membrane technology has also certain disadvantages. UF, NF and RO are high pressure systems; therefore, special feed units must be installed (however UF units which can operate under pressure below 1 bar are also available). Membranes are very sensitive to excess of impurities thus pre-filters must be used, too. Finally, membrane technology itself is not a pollutant-free. Membranes must be periodically (every 7–14 days) washed with alkali and acid agents.

Biological filtration will be probably always used in papermaking as an optimal, all-purpose water treatment method. Both aerobic and anaerobic systems are used today, as well as activated sludge technologies, EGSB, MBBR, trickling filter plants, etc. Progress in the methods for industrial water treatment is a continuous process. Many suppliers offer very efficient equipment consisted of several unit operations.

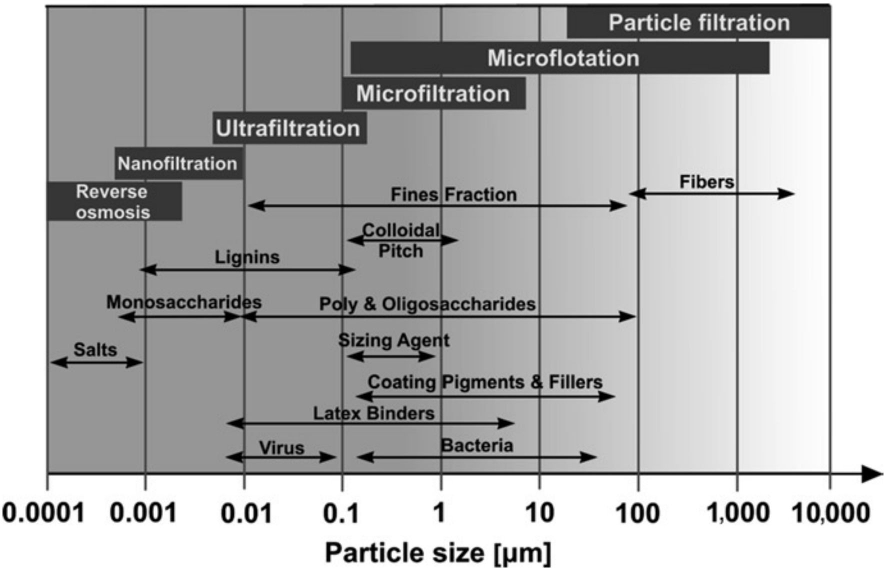
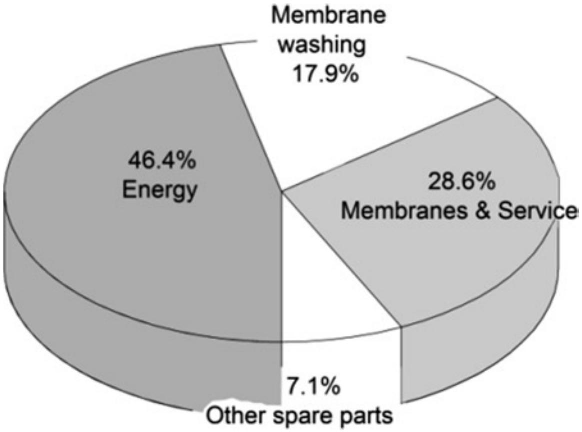


Fig. 8.5 Comparison of effectiveness of various filtration methods [13]

Fig. 8.6 Example of the distribution of the operational costs of UF plant in paper mill [20]



For example, MBR (Membrane BioReactor) combines biological treatment (nitrification – denitrification) and membrane filtration. When biological filtration itself is not able to reduce effectively the COD and AOX parameters, an inter-stage oxidation of waste water can be used. Oxidizing chemical substances (often with catalyst) or energy consuming radiation (including UV) is used in those processes. The basic aim is to force oxidation of substances which are difficult to biodegrade. As a result of this process, they become fully biodegradable. The AOP (Advanced Oxidation Process) is a good example. It uses ozonization combined with biological treatment in the biofilm reactor. Carried out tests proved that the method enables to reduce efficiently the COD by over 60% and the AOX by 70% as well as the color resulting from the presence of lignin-based compounds by 85% [16]. In the past, the main AOX load came from the pulp bleaching process where chlorine and chlorine compounds were used (e.g. chlorine dioxide, hypochlorite). Today's bleaching process is usually TCF (Total Chlorine Free) and, as a result, AOX load in pulp mill's effluent has been significantly decreased.

The last years witnessed the application of evaporation as an efficient method for water treatment. The Thermal Vapor Recompression (TVR) and the Mechanical Vapor Recompression (MVR) can be used by the industry now. These are the technologies which bring good results, however they are still very expensive and for this reason they are not very popular [16].

Apart from the development of the control and testing equipment, the research is carried out on chemical aids that support water treatment processes.

Finally, temperature increase in the circulation water systems as a result from lower water consumption in the paper mill have to be mentioned. While slight increase in temperature brings positive effects, the range of 60–70°C is however too high. It seems rational to introduce additional water cooling. For this purpose, open cooling lagoons, cooling towers or cogeneration (also combined heat and power, CHP) can be used.

Nowadays, the growing amount of solid waste from the paper mill technological line becomes the most serious problem for the paper industry. If the situation does not change, the industry may use minimal amount of fresh water in the future, but instead of this it may produce large amounts of hazardous waste, which – if not managed properly – can be a reason for serious pollution of underground water and water reservoirs. This aspect should be analyzed in more detail when assessing the effects of reduction in consumption of fresh water in the paper mill.

In the conclusion of discussing the methods of water treatment in paper industry it can be stated that suitable technologies are already well known. In most cases, they are sufficient. However, one has to remember that effective and long term reduction of fresh water consumption always depends on successful combination of the technology and several other actions.

8.4.2 Personnel Training

Efficient water management has been always a socio-technical matter. Rising ecological awareness among those who can influence reduction in consumption of fresh water is one of the most important factors, however often underestimated. In industrial conditions even minor actions such as less often using of hoses for cleaning, turning off or repair of leaking valves, proper shower adjustment, reduction of unwanted or excessive flows may have surprisingly good impact on reduction in total water consumption. These are the measures which may and should be taken without an official order. However, it requires well-motivated and committed personnel. That is why the education in a form of seminars, conferences, specialist literature is so important. Good relationships between staff, management and administration are also crucial. It should be stressed, that these are a long term actions and their positive effects will be noticeable throughout many years.

8.4.3 Introduction of More Restrictive Raw Materials Management and Control

The need of much more attention to waste paper sorting starting from households and more restrictive inspection of purity of materials delivered to the paper mill is discussed here. First of all, it is estimated that replacement of virgin pulp by recycled pulp can save about 40% of water in pulp and paper industry [21]. Furthermore, smaller amount of pollutants in the production line will contribute to more efficient equipment running, relief to the water and pulp system, improvement of parameters of discharged effluents and reduction in the amount of solid waste.

Efficient management of raw materials is particularly important for lower grades of recovered paper which usually have very low papermaking potential and contain various pollutants (inorganic, organic and biological, heavy metals, etc.). Such a material not only overloads the technological line and may have a negative impact on the product quality, but, apart from that, it is a source of large quantities of solid waste which finally have to be removed and utilized. Therefore, the separation of the lowest and the most polluted grades of recovered paper and their usage for non-papermaking purposes or direct utilization are worth to be considered.

Recently, we may hear about the efforts of adding to paper various substances which in fact are residues from other industrial sectors. Despite some efforts to attribute such steps to eco-friendly aspects, in many cases, it is nothing else but shifting the responsibility for generating the waste. Obviously, such initiatives will not improve the quality of product and process water in the paper mill. From the environmental point of view, the improvement of general quality of raw materials rather than rising their amount seems to be the most effective solution. Better quality means higher purity, slower wear of production equipment, lower demand for chemical aids and lower volume of generated waste.

8.4.4 Implementation of New Legislation

Profit increase is the main aim of almost all industrial activities therefore legislative actions and uniform, clear rules are very important for the process of reduction of fresh water consumption and pulp and paper industry is not an exception. For example, in some EU countries (e.g. Netherlands, Germany) taxes for discharge of waste waters have to be paid. In some other countries (e.g. Poland) general taxes for water use are paid. Those differences affect the different approach to fresh water consumption and waste management.

In Europe, the IPPC Bureau works on an amendment of BREF rules. There are reference documents regarding the Best Available Technologies (BAT) in the pulp and paper industry included. Another important document is the Water Framework Directive (more formally – the Directive 2000/60/EC of the European Parliament establishing a framework for Community action in the field of water policy) (BREF Document; [7, 16, 22]).

Similar actions are taken by the AFPA (American Forest and Paper Association). In each case, the attention is paid to sustainable use of renewable resources, reducing the overall environmental impact and conserving energy and materials [1]. Nowadays, several companies are registering in EMAS (Eco-Management and Audit Scheme). As a result, they are obligate to public environmental reporting. It is also worth mentioning that more and more companies, including paper producers, now also disclose their Water Footprint [22, 23] and Carbon Footprint [4]. In several situations it is imposed by the customers. It seems to be the right direction, since revealing such information will contribute to the more effective environmental protection. However, it should be noticed that Water Footprint and Carbon Footprint are not perfect yet as they do not contain all data on the environmental impact. Currently, the Industrial Footprint seems to be the most reliable index to be universally used in the future. It takes into consideration a comprehensive impact of a given product (as a total operation effect of an industrial operator) on the environment. The index combines both indices typical for water and carbon footprint, includes the impact of any other waste emissions, and additionally it introduces economic and social factors (e.g. human rights, relations at workplace, personnel healthcare, etc.) [10].

8.5 Conclusion

The consumption of fresh water and the volume of discharged effluents in the pulp and paper industry have been reduced significantly over the last 20 years. The development of modern technologies, rising environmental awareness and legislation changes have contributed to this trend. Small amounts of fresh water probably will be always needed as a supplement to water loss during production process (e.g. evaporation during drying). Therefore, probably it is not possible to introduce ZWI (Zero Water Influent) system in papermaking. Nevertheless, it should be emphasized that there are the technological possibilities of complete or almost complete closure of the water cycle and creation of ZLE or NZLE system in a paper mill, however the cost of such operation is still significantly high.

One can assume that maintaining the attractiveness of paper as a product will require the Zero Liquid Effluent system in the future. In order to achieve it, further coordinated initiatives and research embracing technology, biology and economics are required. Trainings in this area are also of great importance. They should be aimed not only at those who manage and control the industrial processes but also at the whole of the human community.

Real sustained development and success in water sources preservation mainly depend on our sensibility and self-responsibility for the natural environment. As a result, the evaluation of effectiveness of all activities related to water conservation will be fully reliable only if considered together with the impact of other waste emissions. International, clear and uniform guidelines in the area of all emissions and natural resources management as well as in the area of responsibility for taken actions would be of vital support.

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Chapter 9
Wastewater Reuse in Textile Industry

Fatoş Germirli Babuna

Abstract Current understanding of industrial pollution control attributes significant attention to in-plant control measures targeting mainly waste minimization at source. Accordingly only after realizing front-of-pipe prevention measures by the help of in-plant control activities, end-of-pipe treatment alternatives can be adopted. Wastewater reuse which is considered as an important part of in-plant control efforts gains special significance in textile industry due to the intense usage of water in the sector. While evaluating a textile plant for wastewater use alternatives a rational methodology covering technical and economical feasibility studies must be followed. Issues such as possible adverse effects on product quality or the end-of-pipe wastewater characterization must be addressed.

Keywords Wastewater • Reuse • Textile industry • In-plant control • End-of-pipe treatment

9.1 Introduction

According to the up to date understanding of industrial pollution control two issues come forward: The first one is about the scale of protection dictating the coverage of the entire environment rather than concentrating on a single media. Hence emissions to air, land and water must be controlled within an integrated industrial waste management policy. The second issue addresses the importance of manufacturing processes in pollution control efforts. Accordingly an industrial facility must adopt

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a stage-wise approach that tackles in-plant control measures prior to coping with an end-of-pipe treatment. European Council Integrated Pollution Prevention and Control (IPPC) Directive; and the US Pollution Prevention Act (PPA) [9, 19] are among the examples of legislation underlining the significance of in-plant control measures. Besides, environmental and ethical issues attract public attention nowadays. Therefore, the manufacturers are tending to improve their images through avoiding wasteful practices and applying reuse. Briefly a sound industrial waste management strategy requires the prevention of multimedia pollution via in-plant control measures followed by end-of-pipe treatment. In order to do so the following steps must be adopted in a stage-wise manner:

1. in-plant control

   water conservation
   wastewater reclamation and reuse
   material reclamation and reuse
   substitution of chemicals
   modifications and/or changes in processes and/or technologies

2. end-of-pipe treatment

When applying an in-plant control measure case specific issues must be considered. For example, the cost of fresh water in the region where the plant is located gains importance while evaluating a plant in terms of wastewater reclamation and reuse. A feasibility study covering both technical and economical issues must be conducted before adopting any kind of in-plant control measure. It should be kept in mind that not only many environmental benefits but also some financial inputs can be obtained by following such a management strategy.

Textile industry is among the most wide-spread manufacturing sectors in the world. The sector generates many products (carpet, knit fabric, yarn, hosiery, woven fabric, denim fabric, etc.) from a variety of raw materials (cotton, wool, natural polymers, jute, silk, linen, synthetic polymers such as polyester etc. and their blends) with the help of various types of equipment (jig, beck, package, thermosol, skein, pad-roll, jet, pad-steam etc.) operating under different modes (batch, semi-continuous or continuous). During the production an array of dyes from direct, disperse, acid, mordant, metal-complex to sulphur, basic, reactive together with a huge number of auxiliary chemicals (biocides, anti foaming agents, surfactants, carriers, flame retardants, leveling agents, softeners, lubricants etc.) can be used. Small and medium scale production facilities, some operating very dynamically to meet the immediate demands of market; as well as integrated large scale premises are manufacturing within textile wet processing sector. Such a variable and complex picture necessitates a case by case evaluation for the application of environmental measures.

Poor housekeeping practices leading to unnecessary water usage, missing the opportunities of valuable by-product recovery, inefficient operations causing the loss of expensive chemicals are the common pitfalls observed in textile mills. All of these examples can be solved by applying case specific in-plant control measures.

Textile wet processing can be characterized with high water usage that consequently leads to high wastewater generation. Although water consumption and wastewater generation levels as low as 20 m^3 ton^{-1} textile products are also reported in literature, the typical values are stated to be within a range of 200–400 m^3 ton^{-1} textile product [14, 16]. Such a high water requirement highlights the significance of wastewater reclamation and reuse applications among other in-plant control measures. Possible economical benefits triggers the efforts to adopt wastewater reuse in textile sector.

In the context given above the objective of this chapter is to present a wastewater reuse methodology applicable to textile wet processing industry.

9.2 Methodology to Achieve Wastewater Reuse in Textile Wet Processing

Industrial wastewater reuse is an in-plant control measure. Hence it requires a lot more effort devoted to the details of the production processes. In order to evaluate the applicability of wastewater reuse in an industrial premise a comprehensive analysis including a wide range of items from the auxiliary chemicals added during each step of the processes to the detailed characterization of the segregated wastewater streams must be performed. A stage-wise methodology for wastewater reuse is presented below:

9.2.1 Establishing Production Flowcharts

Production flowcharts developed to illustrate every step of the production processes with the help of boxes and arrows can be used as an information rich tool. An example production flowchart dealing with knit fabric finishing is illustrated in Fig. 9.1. All sorts of material movements i.e. inputs (from auxiliary chemicals to raw materials) and outputs (from products and by-products to wastes) must be tabulated in production flowcharts. If available the quantities related to the inputs and outputs have to be presented. Especially the quantities of water inputs and wastewater discharges must be inserted to production flowcharts. The reliability of the gathered data must be checked by conducting a simple materials balance. After such a check, the production flowcharts can be used as a solid source of information.

9.2.2 Assessment of Water Usage

The quantities of process water inputs are obtained from the production flowcharts. Apart from these inputs all other water requirements (i.e. for domestic purposes, cooling water make-up, boiler make-up etc.) must be tabulated. The quality requirements for these water usages must also be defined. For this purpose reuse criteria given in literature and/or the specific quality requirements of the manufacturer can be used. Due to the complex and variable nature of textile industry there is no

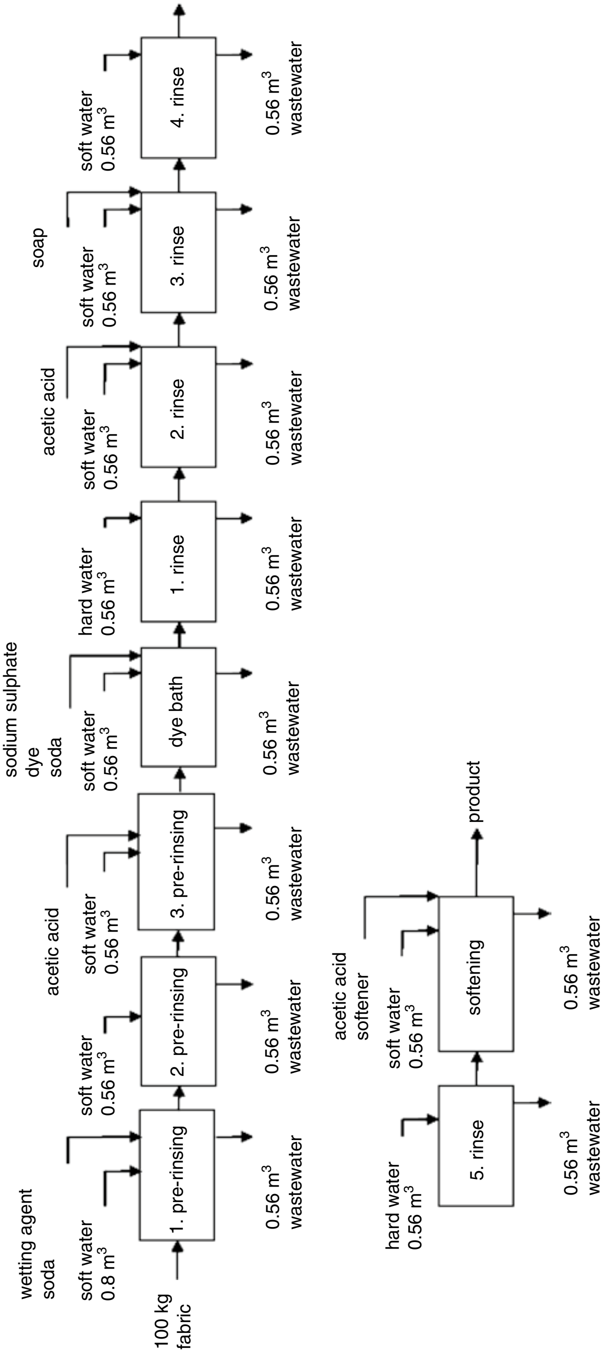

Fig. 9.1 Knit fabric finishing in overflow equipment [7]

Table 9.1 Reuse criteria applicable to textile process waters

Parameter	Li and Zhao [12]	Hoehn [11]	De Florio et al. [3]	Van der Bruggen et al. [20]	Unlu et al. [18]	Lu et al. [13]
Total COD (mg L^{-1})	0–160	<50	80	60	80	50
TSS (mg L^{-1})	0–50	<500	5	–	–	0
TDS (mg L^{-1})	100–1,000	–	–	–	–	–
Total hardness (mg $CaCO_3$ L^{-1})	0–100	90	2.5 (°F)	5 (°F)	–	–
Chloride (mg L^{-1})	100–300	<150	–	–	–	–
Total Chromium (mg L^{-1})	–	0.1	–	–	–	–
Iron (mg L^{-1})	0–0.3	0.1	–	0.1	–	–
Manganese (mg L^{-1})	<0.05	0.05	–	0.1	–	–
Conductivity (μS cm^{-1})	800–2,200	–	1,000	–	1,000	–
Alkalinity (mg $CaCO_3$ L^{-1})	50–200	–	–	–	–	–
TKN (mg L^{-1})	–	–	20	–	–	–
Turbidity (NTU)	–	–	1	–	–	2
TOC (mg L^{-1})	–	–	30	–	–	–
Color (Pt-Co)	–	–	–	–	20	10
pH	6.5–8.0	6.5–7.5	6–8	6.5–8	–	–

agreed upon reuse criteria applicable to process waters. Table 9.1 gathers reuse criteria given in literature. In some textile plants process waters having two different qualities (hard and relatively soft) are used as a feed for different processes. An example of such textile process is given in Fig. 9.1 [7].

9.2.3 Characterization of Segregated Effluent Streams

By referring to the established production flowcharts some of the segregated effluent steams must be selected for characterization. As the relatively clean discharges (effluent streams obtained from the process stages where no or very small amounts of auxiliaries are added; i.e. rinsings) have a reuse potential, such streams have to be characterized for pollutants.

Table 9.2 outlines reusable wastewater characterization obtained from three different textile plants. Plant 1 and 2 deal with cotton knit fabric manufacturing. In both of the textile mills optical brightening, peroxide bleaching and dyeing operations are performed by adding auxiliaries such as H_2O_2 and reactive dye. Plant 3 applies wool, polyester and wool/polyester blends woven fabric finishing operations. Softeners and crease proofing agents are used during processes.

9.2.4 Evaluation of Segregated Wastewaters

Segregated effluent quality and quantities must be evaluated by checking the quality and quantities of water requirements. In some cases segregated effluents are reused only after passing through a specific treatment to improve the quality.

The most commonly applied wastewater reuse measures adopted in textile mills can be discussed under two headings [21]: The first one involves the reuse of uncontaminated non-contact cooling water obtained from condensers, heat exchangers, yarn dryers,

Table 9.2 Characterization of untreated reusable wastewater streams

	Dogruel [4]	Orhon et al. [15]	Dulkadiroglu et al. [5]
Reference	Plant 1	Plant 2	Plant 3
Total COD (mg L^{-1})	315	350	180
Soluble COD (mg L^{-1})	190	200	120
TSS (mg L^{-1})	60	80	15
VSS (mg L^{-1})	60	80	ND
Color (Pt-Co)	30	25	20
Cl^- (mg L^{-1})	275	320	ND
TDS (g L^{-1})	1.18	1.1	0.34
pH	7.4	5.2	7.1
% Flow rate	52	22	34

Table 9.3 Characterization of end-of-pipe effluents before (B) and after (A) wastewater reuse

Reference	Plant 1[a]		Plant 2[b]		Plant 3[c]	
(mg L^{-1})	B	A	B	A	B	A
Total COD	955	1,220	1,180	1,475	690	1,460
Soluble COD	675	850	890	1,215	455	970
TSS	105	125	100	115	88	190
VSS	85	95	90	94	80	180
TKN	ND	ND	14	ND	20	ND
T-P	ND	ND	13	ND	0.8	ND
pH	6.5	9.7	10.3	10.6	7.1	6.2

[a] Dogruel [4]
[b] Orhon et al. [15]
[c] Dulkadiroglu et al. [5]

pressure dyeing machines, air compressors etc. in processes requiring hot water. The second one on the other hand is the reuse of process wastewater originating from one operation in another unrelated operation. The most common examples are [14, 21]:

1. reuse of wash water from bleaching operations in caustic washing and scouring;
2. direct reuse of cooling water;
3. reuse of mercerizing wash water for scouring, bleaching operations and for wetting the fabric;
4. reuse of scouring rinses for desizing;
5. reuse of final rinsing waters in bleaching for bath make up or primary rinsing baths.

The approval of the workers is needed if the reclaimed wastewater is going to be used for domestic purposes i.e. in toilet flushing. On the other hand if a part of the generated wastewater is used in production processes (as it is or after passing through a specific treatment defined for reusable effluent streams), an approval from the manufacturer is required. The key term at this stage is the product quality. The product quality has to be checked after reusing the segregated effluents in production. The possible negative effects detected can be avoided by improving the reused wastewater quality.

9.2.5 Technical and Economical Feasibility

By segregating the relatively less polluted wastewater streams as reusable effluents, a much stronger end-of-pipe effluent likely to cause troubles in treatment plant can be generated. The treatability of end-of-pipe wastewaters before and after the application of reuse must be compared with each other. Characterization of end-of-pipe effluent streams before and after wastewater reuse for the Plant 1, 2 and 3 are tabulated in Table 9.3. As expected a stronger end-of-pipe wastewater is obtained after reuse application. The important issue at this point is to assess the impact of reuse

Table 9.4 Biodegradability of end-of-pipe effluent before (B) and after (A) wastewater reuse

		Total COD (mg L^{-1})	Soluble inert COD (mg L^{-1})	Particulate inert COD (mg L^{-1})	Biodeg. COD/Total COD (%)
Plant 1[a]	A	955	320	ND	ND
	B	1,220	365	ND	ND
Plant 2[b]	A	1,180	247	63	74
	B	1,475	307	78	74
Plant 3[c]	A	690	32	72	85
	B	1,460	67	149	85

[a] Dogruel [4]
[b] Orhon et al. [15]
[c] Dulkadiroglu et al. [5]

on the biodegradability of the end-of-pipe effluent. The results of this investigation presented in Table 9.4 indicated that reuse application does not affect the biodegradability of the effluents originating from the plants under evaluation.

Furthermore segregated effluent streams might require a specific treatment prior to be reused. Treatability of reusable wastewater streams must be evaluated. A wide range of treatment schemes from activated carbon applications, ozonation to electrolysis and nanofiltration can be used for reclaimed textile effluents [1, 2, 6, 8, 10, 17].

An evaluation based on:

1. the savings obtained from lowering the freshwater input;
2. the additional investment and operation costs related to the installation and operation of new pipelines, pumping facilities etc.;
3. investment and operational costs arising from the possible pre-treatment requirement of the reclaimed wastewater before reuse;
4. possible elevation of the end-of-pipe treatment costs due to dealing with a more concentrated effluent can be used to get economical feasibility.

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Chapter 10
Water Reuse Strategies: Iron and Steel Industry Case Study

Volkan Çağin and Ülkü Yetiş

Abstract Water reuse by industry is a vital part of reducing the pressure on our water. With appropriate water management that requires a comprehensive understanding of process design; industrial water can be reused for a wide range of purposes.

Iron and steel manufacturing is one of the oldest industrial sectors using water in nearly every step of the process chain at large quantities. In the present study, a comprehensive effort has been allocated in a large integrated iron and steel plant in Turkey, with the goal of developing the best available options for water and wastewater management practices. Considering the need for well grasping the processes and water use in the facility, detailed water block diagrams of each process were developed and the characteristics of each flow were studied. Based on detailed mass balances, specific water consumption for each process unit was determined and alternative techniques/technologies for the most effective water and wastewater management practices were developed.

Keywords Reuse • Iron and steel industry • Specific water consumption • Best available techniques

10.1 Introduction

Iron and steel industry is in evolution from large, integrated, multiple-product plants to smaller facilities focused on specific products or markets. Among those, integrated iron and steel plants, which employ a series of individual industrial processes to produce principally steel products from iron ore, consumes vast amounts of water.

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Increasing demand for reliable, abundant, economic and predictable water resources and diminishing quality of water supplies, along with more stringent wastewater discharge limits have pushed iron and steel industry to seek for water conservation in applied processes. Since 1950, water use intensity of the steel industry has been decreasing as a result of increasing amounts of water being recycled and/or reused [5]. Water recovery rates as high as 95% have been reached by several iron and steel plants using advanced water treatment technologies. In such plants, daily industrial water-input per ton of crude steel produced is calculated between 7.3 and14.6 m^3 t^{-1} crude steel [7].

In the present study, a comprehensive effort has been allocated in a large integrated iron and steel plant in Turkey, with the goal of developing the best available options for water and wastewater management practices. This, in turn, will result in an improvement of water reuse towards minimal discharge and in optimization of incoming fresh water use by integration of water management practices in the entire production processes.

To this end; the way of water use, types of process wastewaters and fate of the wastewater management outputs within each process, specific water consumption and best available techniques arising as the promising alternatives were studied.

10.2 Overview on Water Use in the Iron and Steel Facility

The iron and steel plant of concern is an integrated one with a production capacity of about 2.5 million tons of liquid iron. The main products of the plant consist of hot rolled coil and sheet, billet, wire rod, slab, deformed reinforcing steel bar and pig iron. The plant consumes water at large quantities either as untreated raw water or as treated water.

The amount and type of treatment applied varies with the required water quality. But, the treated waters used in the plant are classified as: softened water, demineralized water, mixed water (mixing of raw fresh water, demineralized water, softened water and distilled water), and softened mixed water.

In iron and steel production, water use patterns also vary considerably, depending on the process requirements. In the iron and steel plant considered, water is used for a number of purposes such as:

1. *material conditioning*: controlling dust in sinter feeds, slurrying or quenching dust and slag in blast furnaces, quenching of coke and removing mill scale in hot- rolling operations and in continuous casting,
2. *air pollution control*: scrubbing for air pollution abatement and recovery of COG, BF Gas and BOF gas, which possess substantial calorific values, and
3. *heat transfer*: cooling (used as a coolant) to protect the equipment and the refractory material used in processes [5].

As in all integrated iron and steel plants, [5] among the water use purposes; heat transfer applications account for the largest use of water in the plant.

This brings the fact that, the techniques, equipment, technologies and efficiency of technologies used and the incoming water quality in water recirculation systems are key factors affecting water demand and water conservation potential in iron and steel production [6]. Means of process-based water use and types of water (raw or treated) within the integrated iron and steel facility in the present study are as follows.

10.2.1 Sinter Plant

In sintering plant, water is used as;

1. Material conditioning agent – water supplied for material conditioning remains on the material and thus no wastewater is generated. 150 m^3 h^{-1} of raw fresh water (as make-up water) is supplied on average for this purpose.
2. Coolant for the ignition hoods and the fans as well as for the sinter machines – 350 m^3 h^{-1} of raw fresh water (as make-up water) is supplied on average. The cooling water is recycled via a closed recirculation system and reused for cooling purposes.

10.2.2 Coke Plant

In coke plant, water is used for cooling;

1. Cokes (wet quenching) – There exists four active coke ovens in the facility of concern and two of them employ wet quenching method for quenching of coke. Following transport of hot coke to the wet quenching towers, coke is quenched directly by large volumes of water. Most of the water used in wet quenching evaporates and the remaining portion is collected to be used in the next batch rather than being treated as wastewater. Reuse of quenching water thus results in preventing from wastewater emissions. Fresh water is currently used as make-up water for substituting the evaporating portion.
2. Coke oven gas (direct and indirect cooling) – Hot crude oven gas collected from the coke batteries are directed to the ascension pipes at a temperature of approximately 800°C. First, it is directly cooled by an ammonia liquor spray to a steam saturation temperature of around 80–85°C and separated into a liquid phase and a gas phase. The liquid phase (the condensate) is fed to the tar/water separator, while the gas phase is led to the primary coolers where gas phase is indirectly cooled to below 25°C by raw fresh water within heat exchangers. Below 25°C, most of the higher boiling point compounds and the water from the steam fraction of the incoming gas to the heat exchangers condenses and droplets and particles within this condensate are precipitated in the down-stream electrostatic tar precipitators prior to be led to the tar/water separator.

The liquid phases separated respectively in direct cooling and indirect cooling of the crude oven gas are further separated off in tar/water separator and then led to ammonia liquor storage tank. Here, ammonia liquor is recycled to the point where direct cooling of crude oven gas is achieved and the surplus ammonia liquor that results from the coal moisture and from thermal decomposition of coal during coking process is eventually directed to the ammonia stripper/still to remove the ammonia prior to wastewater treatment. Since there is no need for raw fresh water addition for direct cooling of crude oven gas due to the exceeding amount of excess water resulting from the coal moisture and from thermal decomposition of coal compared to the losses, almost whole make-up water employed for cooling purposes is used for indirect cooling. This water is re-circulated around the circuit and approximately 200 m^3 h^{-1} of raw fresh water is necessary to replace evaporation and blow down losses from cooling towers and mechanical losses within the recirculation system.

10.2.3 Blast Furnace

In the iron making process, water is used for;

1. Indirectly cooling the blast furnace body, tuyere and hot blast valves - in order to protect these equipments from overheating. There exist three blast furnaces within the facility of concern that are numbered as BF1, BF2 and BF3. BF3 is recently constructed and employs newer technology than BF1 and BF2. While cooling of furnace body, tuyere and hot blast valves within BF1 and BF2 are achieved using raw fresh water as make-up water in a semi-closed re-circulation system employing cooling towers, demineralized water is used as the coolant within BF3. Since demineralized water is used in a closed re-circulation system, negligible amounts of make-up water is required that is 1 m^3 h^{-1}.

   Cooling of demineralized water that is exposed to temperature increase within BF3 is achieved via heat exchangers using the mixed water. While demineralized water is cooled within a closed circuit, a semi-closed re-circulation system is used to achieve mixed water cooling in cooling towers. Approximately 200 m^3 h^{-1} of mixed water is required to compensate for the water losses in cooling towers due to mechanical losses, evaporation and blow downs.
2. Directly cooling the blast furnace slag – Slag granulation and slag pit processes are currently used to treat the blast furnace slag within the facility of concern. Slag pit process is employed within BF1 and BF 2, while slag granulation is employed within BF3.

   The slag pit process involves collection of slag in ladles and leave the molten slag be slowly cooled and crystallized in open air.

   Slag granulation process involves pouring the molten slag through a high-pressure water spray in a granulation head, located in close proximity to BF3. After granulation, the slag/water slurry is transported to a recirculation system, consisting of a separation tank prior to cooling operations. By this way, water is largely collected and reused and very small amounts of wastewater are generated.

3. Cleaning the blast furnace gas (BF Gas) – BF Gas arise as one of the significant outputs of the blast furnace operations and possesses high calorific values which make it a promising energy source in iron and steel facilities. Accordingly, blast furnace gas from all three blast furnaces in the facility of concern are collected and treated prior to be used in energy supply within the facility.

The need for treatment arises from the fact that raw BF Gas contains particulate matter (including heavy metals and carbon), carbon monoxide, carbon dioxide, sulphur compounds, ammonia, cyanide compounds, HCs and PAH [1].

Electro-filters are used as the pre-treatment for the removal of coarse particulate matter from raw BF Gas and subsequently wet scrubbers using approximately 500 $m^3 h^{-1}$ of raw fresh water as make-up source for the removal of fine particulate matter accomplish the secondary treatment. In wet scrubbers, raw fresh water contacts with the fine particulates and becomes rich in a number of pollutants. Since the liquid phase (mixing of raw fresh water and fine particles) leaving the wet scrubbers contains a large quantity of suspended solids and high in temperature, the water is recycled following the solid-liquid separation in circular settling tanks and cooled in semi-closed recirculation systems employing cooling towers.

10.2.4 Basic Oxygen Furnace

In the steel making process, water is used for;

1. Indirectly cooling the oxygen blowing lances, side tuyere and the hoods - in order to protect these equipments from overheating. A semi-closed circuit is used for re-circulation of cooling water and raw fresh water is used as the coolant.
2. Cleaning the converter gas (BOF gas) as scrubbing water – BOF Gas can be treated either wet or dry. In the facility of concern, wet scrubbers are employed in BOF Gas cleaning and 180 $m^3 h^{-1}$ of mixed water is used as the cleansing agent within the system. In wet scrubbers, mixed water contacts with the pollutants within the raw BOF Gas and further directed to a two phase wastewater treatment unit prior to be cooled and eventually to be recycled.

10.2.5 Continuous Casting

In continuous casting plant, water is used for;

1. Indirectly cooling the casting moulds, machinery and the inner part of the rollers in a closed circuit – in order to protect these equipments from overheating. A closed circuit is used for recirculation of cooling water that is demineralized water and 6 $m^3 h^{-1}$ of demineralized water is necessary for compensating the mechanical losses within the re-circulation system.

Cooling of demineralized water that is exposed to temperature increase in indirectly cooling of casting moulds, machinery and inner part of the rollers is achieved via heat exchangers using the mixed water. While demineralized water is cooled within a closed circuit, a semi-closed re-circulation system is used to achieve mixed water cooling in cooling towers. Approximately 300 m^3 h^{-1} of mixed water is required to compensate for the water losses in cooling towers due to mechanical losses, evaporation and blow downs.

2. Directly cooling the continuous casting machines (direct cooling slabs, blooms, billets and the machines) – In the facility of concern, approximately 150 m^3 h^{-1} of pressurized mixed water is sprayed on slabs, blooms, billets and the machines for direct cooling and surface cleaning purposes. The mixed water becomes rich in metal oxides (scales) and hydrocarbons (oils) following the contact and therefore directed to sedimentation treatment for phase separation and cooling towers for cooling purposes prior to be recycled.

10.2.6 Hot Rolling Mill

At hot rolling mill, water is used for;

1. Indirectly cooling the furnace in order to protect the furnace from overheating.

   A closed circuit is used for recirculation of cooling water that is softened mixed water and 5 m^3 h^{-1} of softened mixed water is necessary for compensating the mechanical losses within the re-circulation system.

   Cooling of softened mixed-water that is exposed to temperature increase in indirectly cooling of the furnace is achieved via heat exchangers using the mixed water. While softened mixed water is cooled within a closed circuit, a semi-closed re-circulation system is used to achieve mixed water cooling in cooling towers. Approximately 100 m^3 h^{-1} of mixed water is required to compensate for the water losses in cooling towers due to mechanical losses, evaporation and blow downs.
2. Indirectly cooling various equipment (electric motors, control rooms and power systems, instruments and process control devices, oil exchangers and blow pumps) in order to protect these equipment from overheating.

   A semi-closed circuit is used for recirculation of cooling water that is mixed water and approximately 70 m^3 h^{-1} of mixed water is necessary for compensating the water losses in cooling towers.
3. Directly cooling the rolls, saws, cropped ends, coilers, hot run out tables and steel products and scale breaking, flushing scale and scale transport.

   Descaling is achieved via breaking and spraying off the scale by means of high-pressure mixed water. Accordingly, cooling is also performed via contacting the cooling water with the equipment. A semi-closed circuit is implemented for recirculation of cooling/descaling water and approximately 1,000 m^3 h^{-1} of mixed water is necessary for compensating the water losses in cooling towers due to mechanical losses, evaporation and blow downs.

As the mixed water is in contact with steel products and rolling equipment, it becomes contaminated with scale and oil. Therefore, prior to be recycled in the circuit, wastewater from direct cooling is directed to treatment for phase separation.

To sum up, water is mostly used as make-up water in re-circulation systems by which direct cooling, indirect cooling and cleaning of the machinery, equipments, devices, products and semi-products are achieved along with material conditioning such as the case in sinter process. Apart from the aforementioned purposes, approximately 800 m^3 h^{-1} of raw fresh water is utilized in deionized water production some of which is utilized as make-up water in particularly closed re-circulation systems. Also, minimal water consumption is necessary other activities within the premises of the facility of concern such as cleaning agent in administrative buildings, in irrigation and in chemical preparation.

10.3 Overview on Wastewaters in the Iron and Steel Facility

In iron and steel production, wastewater generation patterns also vary considerably as water use, depending on the process conditions. In the iron and steel plant facility of concern, types of wastewaters are mainly divided into four groups such as:

1. *Cooling water*: In order to operate closed and semi-closed cooling water cycles the cooling water is re-cooled and treated. Cooling is carried out by evaporation in cooling towers in semi-closed systems and by heat exchangers in closed systems.

   In semi-closed water re-circulation systems, desalting is controlled via measurement of the electrical conductivity. An increase in the conductivity above the performance limits results in wasting some portion of the circulating water and replacement is achieved with fresh water namely make-up water. Necessary amount of dispersants, sodium hypochlorite and biocide (prevention of growth of bacteria and fungi) and acid or alkali (pH-value) is added when required whether automatically or manually depending on the continuous monitoring of water quality parameters.
2. *Wastewater from COG gas treatment*: the surplus ammonia liquor resulting from coal moisture and from thermal decomposition of coal during coking operation is processed for separation of “COG gas by products” such as tar. Following separation of the by-products, the remaining wastewater effluent containing various organic (such as phenols) and inorganic compounds (such as residual ammonia and cyanides) are directed to wastewater treatment plant in which an aerobic biological system with activated sludge is employed for this purpose.
3. *Overflow water from BF Gas and BOF Gas treatment*: Wastewater from wet scrubbing of BF gas and BOF Gas results in overflows rich in contaminants and are treated prior to be cooled in cooling towers.

Wastewater emissions from blast furnace gas (BF gas) treatment
Wet scrubbing of pretreated raw BF gas generates a contaminated wastewater flow that is rich in suspended solids.

Treatment of this wastewater flow involves sedimentation of suspended particles in radial sedimentation tanks and the overflow is directed to cooling towers and further subjected to cooling water treatment. Generated sludge in the radial sedimentation tanks is recycled to the sinter plant following a dewatering process. The overflow from the dewatering process is also treated in the radial sedimentation tanks.

Wastewater emissions from Basic Oxygen Furnace Gas treatment
Apart from the BF Gas wet scrubbing wastewater, overflow of the BOF Gas wet scrubbing system contains heavy metals such as zinc and lead along with the suspended solids.

Treatment of BOF Gas wet scrubbing wastewater involves two steps: (1) separation of readily settleable coarse particles in relatively small high rate circular sedimentation tanks followed by (2) separation of fine particles in radial sedimentation tanks. Flocculating agents are added to improve sedimentation and accumulating sludge at the bottom of the sedimentation tanks is recycled to the sinter process.

4. *Wastewaters from direct cooling and cleaning applications in continuous casting and hot rolling mills*

Wastewater from continuous casting
Emissions to water from continuous casting machines are generated by the direct cooling of slabs, blooms, billets and the machines. Since cooling water is in contact with the machinery and the materials, the discharge water is contaminated with metal oxides and with hydrocarbons (oil). This wastewater is treated by physicochemical means in order to remove the scale and oil prior to be re-circulated.

Firstly, wastewater is led to a scale pit where the scale is removed by crane and oil is removed by skimmers. Following separation of the phases, suspension is directed to the sand filters for removal of fine particles and eventually to the cooling towers for cooling water treatment.

While removed scale at the scale pit is recycled to the sinter process due to its low oil content, waste oil is directed to storage prior to be delivery to the licensed disposal authority.

Wastewater from hot rolling mills
Wastewaters from directly cooling of the rolls, saws, cropped ends, coilers, hot run out tables and steel products and from scale breaking, scale flushing and scale transport contain oil and suspended solids along with coarse scale and treated prior to be directed to the cooling towers where cooling water treatment is achieved for recycling.

Scale and oil bearing waste water from hot rolling is treated by a sequence of cleaning steps. The first step is the scale pit where the coarse scale is removed by sedimentation. At the scale pit, settled scale at the bottom of the pit is removed by cranes and then recycled to the sinter process. Overflow of the scale pit that is rich in suspended solids is further treated in laminar flow rectangular tanks where fine scale particles suspended in the water flow are settled at the bottom of the tank and directed to another unit namely, radial settling tanks. While overflow of the laminar flow rectangular tanks are supplied through pipes to the sand filters, further treatment of scale sludge is achieved in radial settling tanks. Treatment of scale sludge results in a fine scale sludge consisting mainly of very small scale particles which absorb oil to a very high degree. This fine scale sludge is then directed to the belt filters and the sludge cake is treated as hazardous waste and disposed according to the legal constraints while overflow of the belt filter process enters laminar flow rectangular sedimentation tanks along with the overflow of the scale pit. Overflow of the sand filters are eventually recycled to the cooling towers for cooling water treatment.

Apart from the main types of wastewaters and their management expressed above, brine water from water demineralization process, wastewaters from administrative buildings and run-off water contaminated with leachable compounds such as hydrocarbons from scale, sludge and scrap deposition, and deposition of raw materials such as coal and ore.

Considering the need for well grasping the processes and water use and wastewater management in the facility, detailed water block diagrams of each process were developed. Information is obtained on site via interviews and data are collected from an extensive review of process performance reports of water and wastewater management system, process diagrams and technical specifications of the water and wastewater management systems. They all were used to develop the water block diagrams. Characteristics of each flow and quantity of water flow needed in each individual operation within production processes (e.g. sinter process) or support processes (e.g. lime production and power plant) and/or sub processes (e.g. scale removal in hot rolling operations) were primarily studied. Representative examples of water block diagrams demonstrating various recirculation systems implemented for water and wastewater management within different operations are given in Figs. 10.1–10.6.

10.4 Specific Water Consumption in the Facility

There is a significant variation in the per-production-unit water consumption among different enterprises. In the literature, it is stated that the typical fresh water use of similar iron and steel facilities range typically between 4 and 15 m^3 t^{-1} of crude liquid steel [4]. Considering the specific industrial water consumption obtained through analyzing the existing water management system of the facility of concern is compared to the specific water consumption of 10.12 m^3 t^{-1} of crude liquid steel in 2009, it is revealed that the facility is almost at the high end of the range. There are a lot of opportunities for further savings in water consumption and decreasing specific water use.

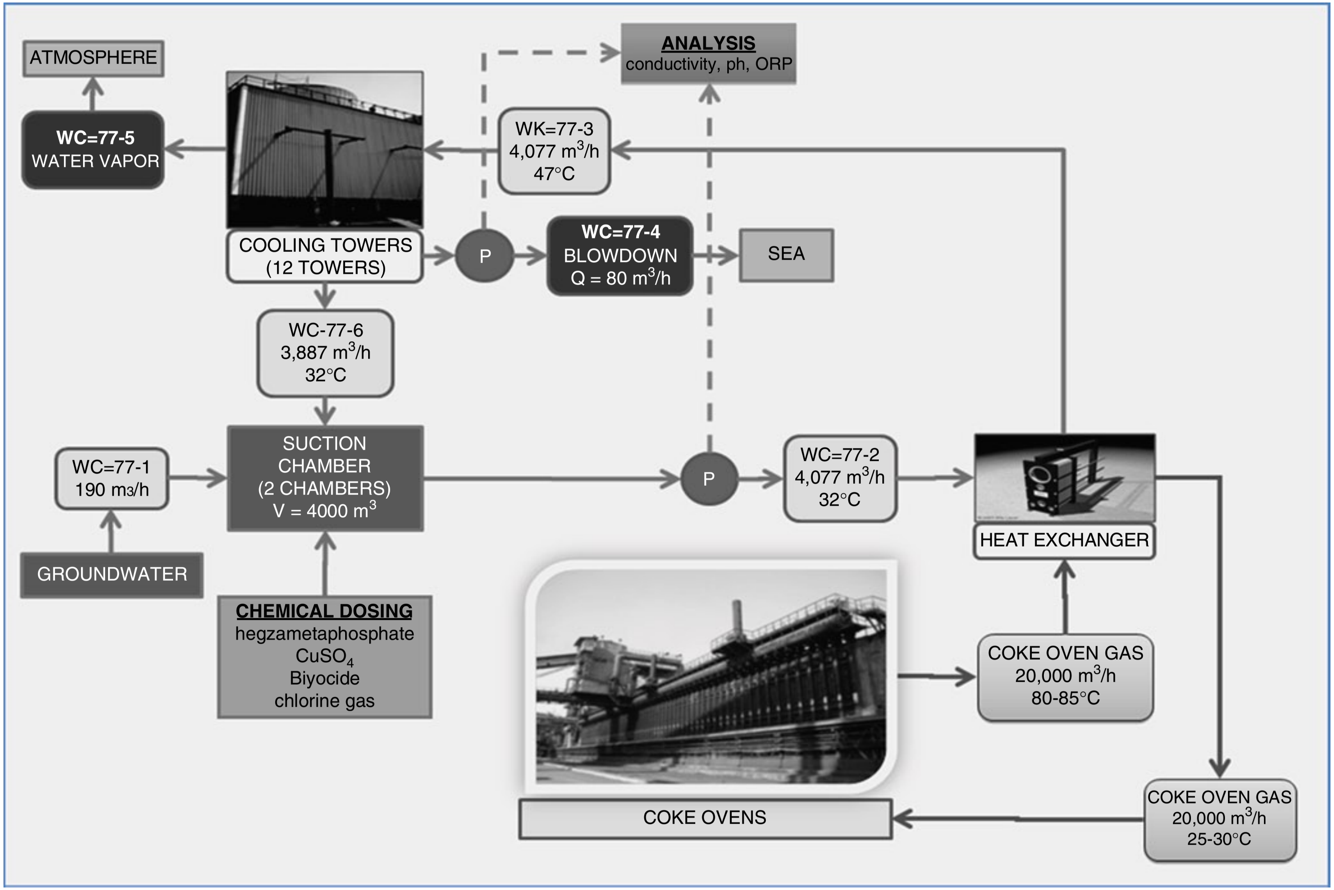

Fig. 10.1 Indirect cooling of coke oven gas

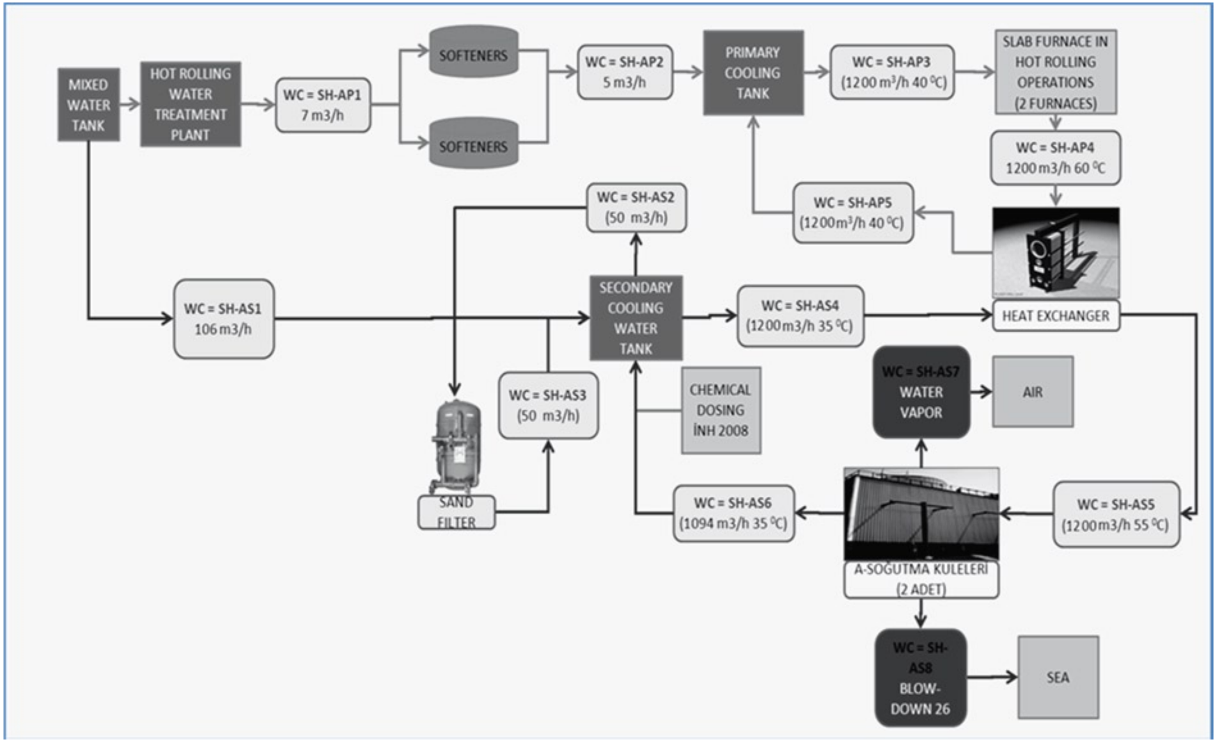

Fig. 10.2 Indirect cooling of slab furnace in hot rolling operations

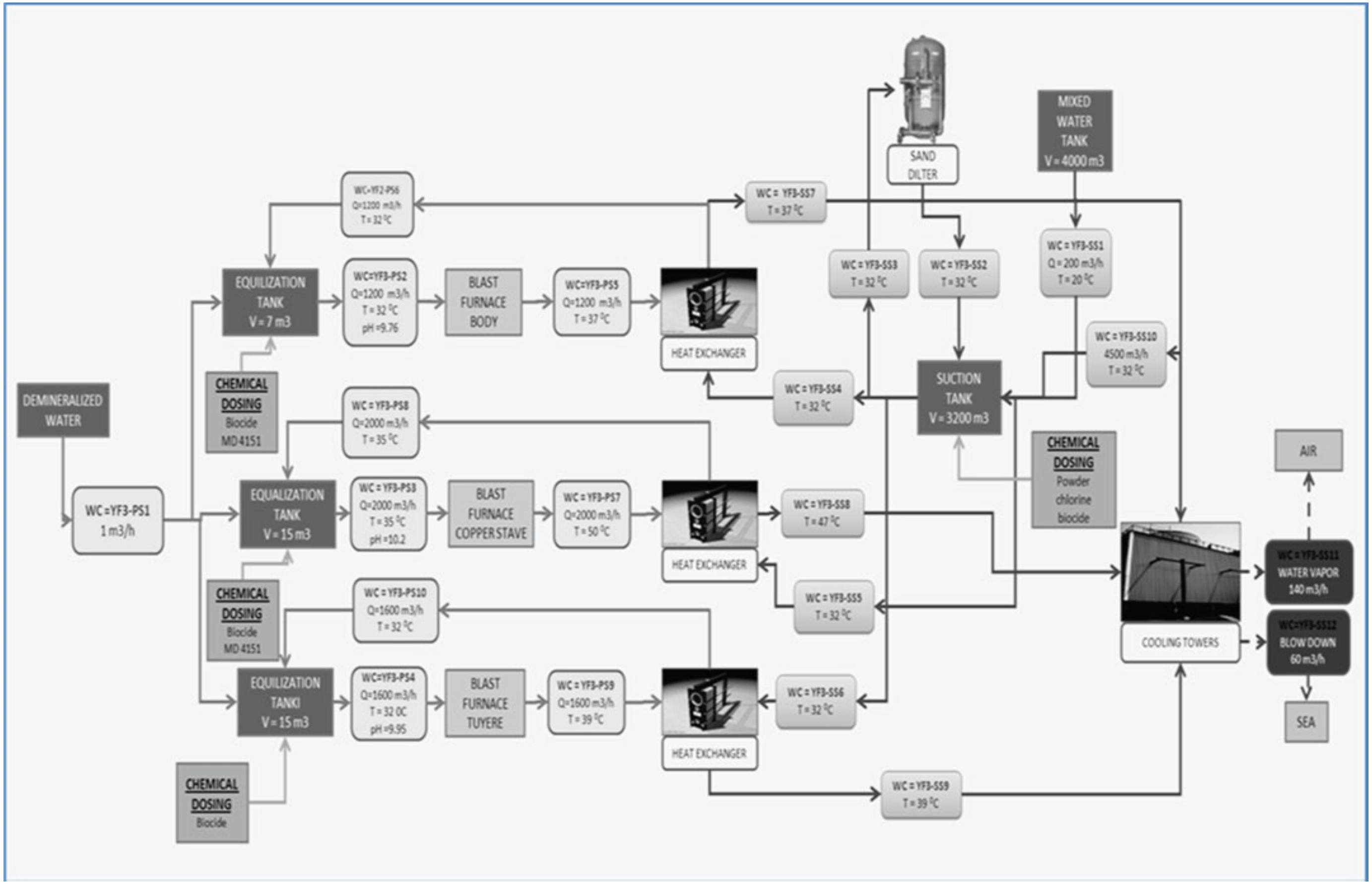

Fig. 10.3 Indirect cooling of BF3

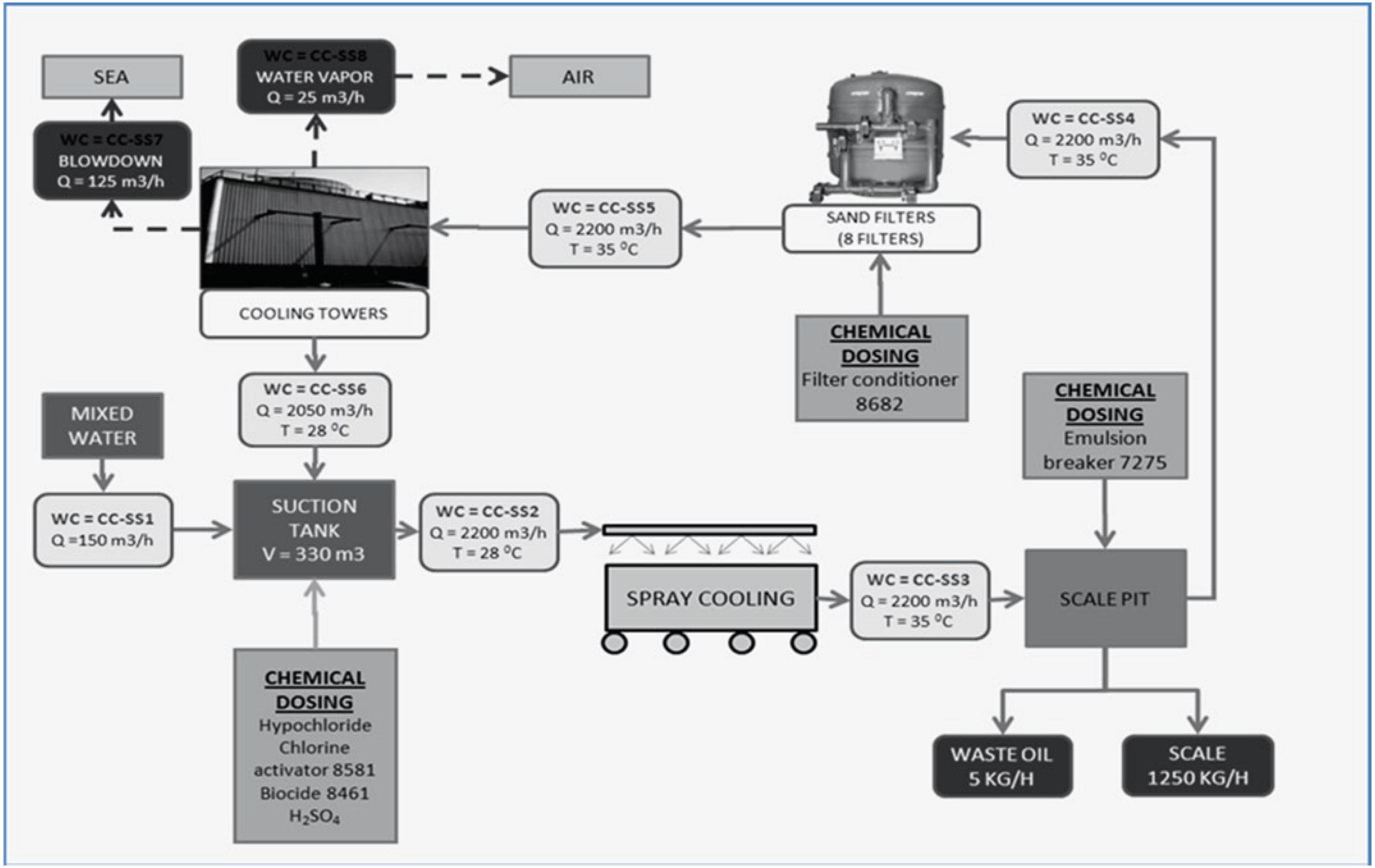

Fig. 10.4 Directly cooling the continuous casting machines (direct cooling slabs, blooms, billets and the machines)

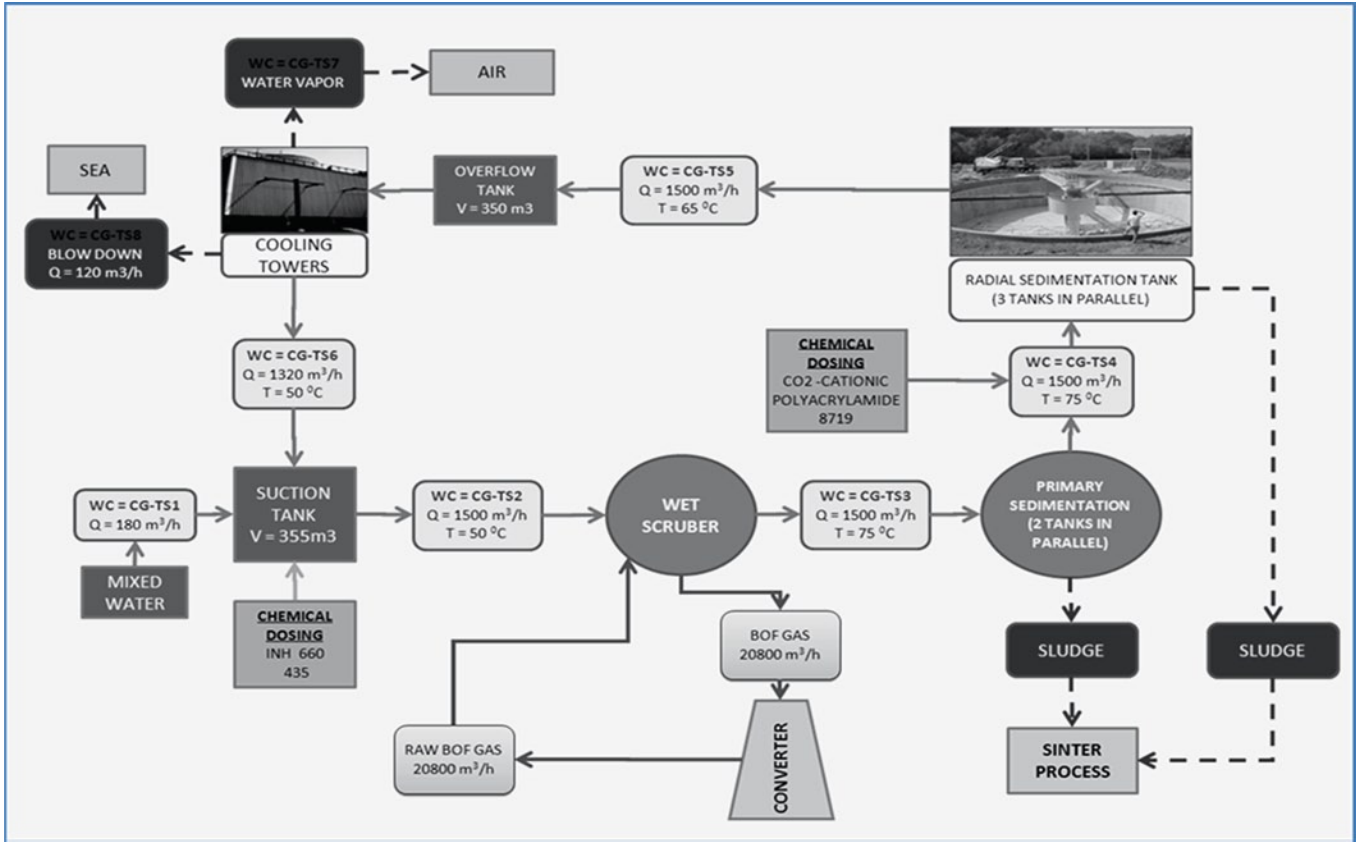

Fig. 10.5 Cleaning and directly cooling the converter gas (BOF gas)

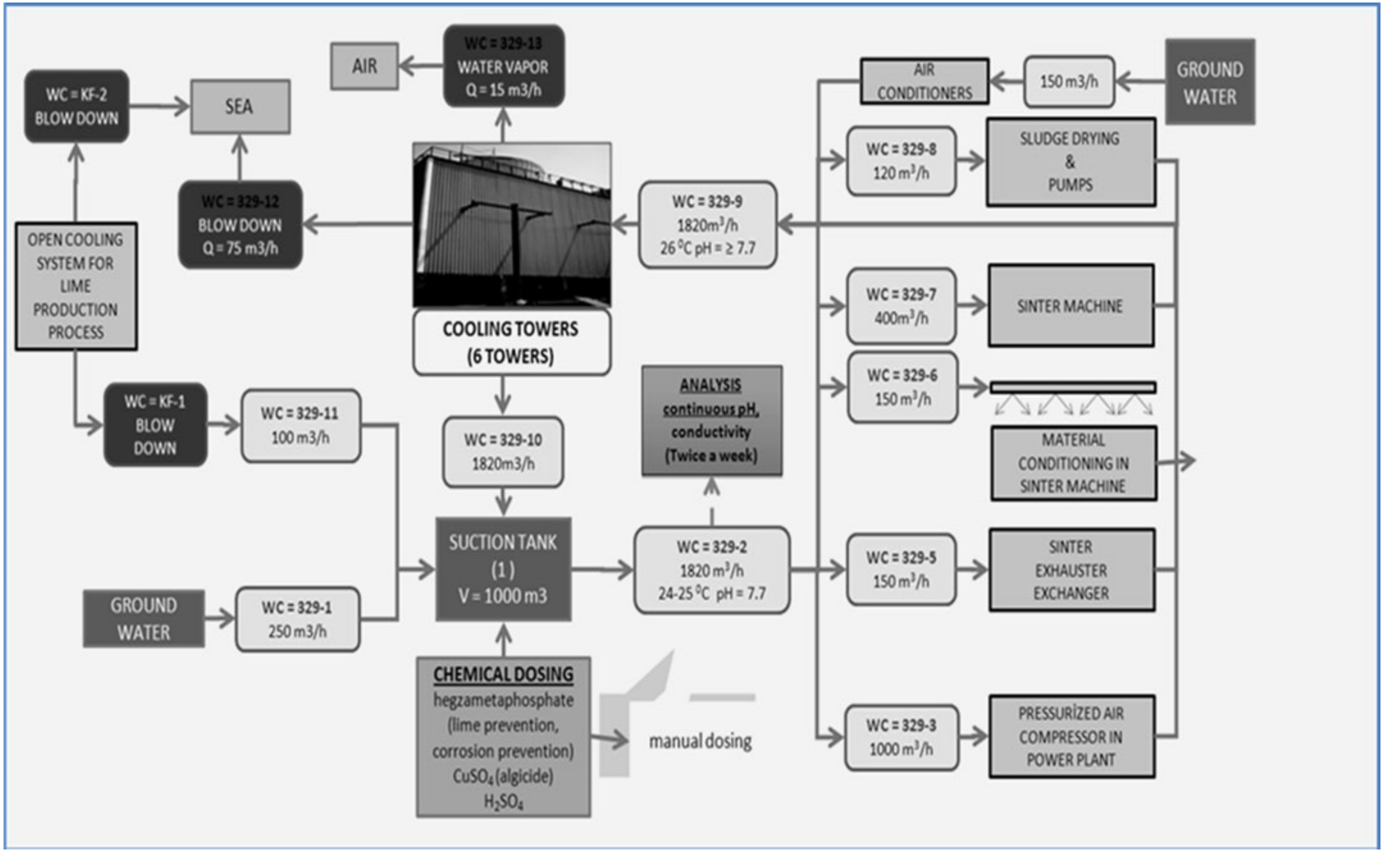

Fig. 10.6 Cooling water supply system for indirect cooling in sinter process and in power plants along with material conditioning

Table 10.1 Water consumption in 2009 with respect to processes

Process	Specific make-up water consumption ($m^3\ t^{-1}$ product)
Coke making	0.562
Sinter plants	0.138
Blast furnace	1.462
Basic oxygen furnace	1.487
Continuous casting	0.456
Hot rolling mills	0.935
Support processes	5.070
Total	10.12

Water consumption with respect to processes differs considerably due to the nature of each process. Specific water consumption of each process was obtained from detailed water block diagrams that are developed at the beginning of the study. Table 10.1 illustrates specific water consumption of each process.

After collecting all necessary data and information and conducting the analysis on all aspects and effectiveness of existing water and wastewater management systems, the next steps of the study were planned to be as follows;

- Development of alternative techniques/technologies for the most effective water and wastewater management practices (Use of Waste Management Hierarchy, BAT Options),
- Evaluation of the options (on lab-scale if necessary),
- Comparison of evaluated alternatives – Use of Cross Media Methodology and Costing Methodology [3],
- Application of the selected alternatives on pilot scale/on site.

10.5 Suggested BAT Options

After the current situation in the facility is well grasped and the mass balance for water is constructed, BAT options which are promising alternatives have been inspected. Some of these alternatives are summarized as follows:

- Rehabilitation of existing make-up water pre-treatment systems and performing pretreatment where applicable (to increase quality of incoming water via decreasing the salt contents) which will increase recovery rate and decrease amount of make-up water.
- Diversion from the utilization of certain water types (i.e. diverting from mixed water use to a surface water supply in sensitive processes such as new technology blast furnaces).
- Reuse of blow down water from the flow through cooling systems as make-up water for semi-closed and closed circuits.

- Chemical substitution or redesigning of the parameters in chemical dosing operations for water conditioning and modernization of water supply equipments and systems, i.e. addition of formaldehyde during blow downs when cyanide treatment arises to be necessary.
- Recovery of blow-down waters prior to be discharged to the sea using membrane systems.
- Review of design parameters of chemical dosing operations and physical treatment units in which cooling waters are directly in contact with process gases, scale and slag for better separation of phases, i.e. application of hydrocyclonage to separate the sludge flow from wet scrubbing of BF Gas into two flows; one with a low zinc content, which can be recycled to the sinter plant, and a second with a high zinc content, which can be stored or disposed of European Commission [1].
- Implementation of advanced treatment for wastewater, which is rich in phenol and ammonium, originating from by-product management operations of coke oven processes in order to prevent the receiving environment from eutrophication phenomena and even to reuse the water within the facility.
- Monitoring the make-up water consumptions via online systems.
- Prevention of Hydrocarbon Contamination in hot rolling operations. Reduction of oil and lubricant losses is a preventive measure against the contamination of process waters and the included scale. The use of modern design bearings and bearing seals for work-up and back-up rolls and the installation of leakage indicators in the lubricant lines (pressure monitoring equipment e.g. at hydrostatic bearings) can reduce the hydrocarbon content (oil) of scale and waste water and reduces the oil consumption by 50–70% [1].
- Pretreatment of fine scale sludge in order to enable the fine scale sludge be recycled to the sinter process- treatment of scale sludge from laminar flow horizontal sedimentation tanks in radial sedimentation units results in a fine scale sludge consisting mainly of very small scale particles which absorb oil to a very high degree. This hampers the recycle of fine scale sludge to the sinter process due the potential risk of increased emissions of VOC and potentially dioxins and problems in waste gas purification systems [2].
- Use of blow down waters that do not contact directly with gases and materials in coke wet quenching process.

Water recovery rates as high as 95% have been reached by several iron and steel plants using advanced water treatment technologies [7]. Water recovery rate in the facility of concern was calculated as 94% that is almost the same with the typical reference value. However, there are opportunities for further decrease in specific water consumption and in turn increase in the recovery rate. The formula of water recovery rate is given below:

$$\text{recovery rate }(\%) = \frac{\text{Total amount of water in recirculation} - \text{total make up}}{\text{Total amount of water in recirculation system}} \tag{10.1}$$

Subsequent to the development and examination of the BAT options, the following practices are planned to be the further steps of the study;

- Evaluation of the BAT options environmentally and economically,
- Comparison of the BAT options environmentally and economically, application of the environmentally and economically promising alternative(s) in pilot scale/on site.

10.6 Conclusion

The fresh water use in the factory was determined as 10.12 m^3 t^{-1} of crude liquid steel which is at the high end of the typical range.

Having a comprehensive understanding of the mass balance of water and the constituents in water is a first step for water reuse in a complicated industrial plant such as steel manufacturing or processing. The contaminants and the chemistries applied can have significant interaction so they should be carefully selected and evaluated for each particular situation.

A number of BAT options are studied and a lot of opportunities for further savings in water consumption, decreasing specific water use and accordingly increasing recovery rates arise.

Evaluating the BAT options economically and environmentally and their comparison will lead the study to its final stage. Application/implementation of the promising alternative(s) will eventually result in more cost effective and more environmentally friendly water and wastewater management practices.

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Chapter 11
Environmental Friendly Technologies for Wastewater Treatment: Biosorption of Heavy Metals Using Low Cost Materials and Solar Photocatalysis

Vítor J.P. Vilar, Cidália M.S. Botelho, and Rui A.R. Boaventura

Abstract As globalization continues, and the earth's natural processes transform local problems into international issues, few societies are being left untouched by major environmental problems. Water-our most precious natural resource-is being threatened by a multitude of contaminants (toxic metals, recalcitrant organic compounds, pathogenic microorganisms), resulting in an unprecedented water contamination crisis with local and national implications. The research community proposes different solutions for this problem, some of them have been applied successfully for different environmental water/wastewaters problems, considered as the Best Available Technologies. However, the concept of best available technologies must be considered in addition to technical feasibility and costs, potential trade-offs between environmental issues, in order to avoid creating a new and more serious environmental problem when solving another. Therefore, research of Environmental Friendly Technologies, considering a complete environment assessment, will be the future of the water/wastewater treatment technologies. Under these circumstances, during the last 6 years, the environmental research group from Laboratory of Separation and Reaction Engineering (LSRE) has been focused on bring other perspectives to best available technologies for wastewater treatment and reuse, including the use of low cost materials, e.g. algal biomass and industrial wastes for toxic metal ions removal, and the use of solar radiation, as UV photon source, for disinfection of water by photocatalytic processes or detoxification of wastewaters using the combination of these processes with biological oxidation ones.

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Keywords Biosorption • Heavy metals • Solar photocatalysis • Water disinfection • Compound parabolic collectors • Environmental friendly technologies • Detoxification of wastewaters

11.1 Introduction

Nowadays it is well known that heavy metals escaping into the environment pose a serious health hazard because they accumulate in living tissues throughout the food chain. The Decision No 2455/2001/EC of the European Parliament and of the Council of 20 November 2001 established a list of priority substances in the field of water policy, where toxic metals are included. The main metal pollution sources of emissions in Portugal are the metal plating and battery industries and oil refineries and smelters. Conventional treatment technologies of metal bearing industrial effluents are precipitation, oxidation/reduction, adsorption onto activated carbon, ion-exchange, evaporation and electrochemical treatment [16]. As these processes generate high volumes of toxic sludge or are expensive (high energy consumption, operation and investment costs) or not effective enough, there has been an increasing demand for efficient, particularly cost-effective and ecofriendly alternatives. Biosorption promises to fulfill the requirements, principally for the treatment of dilute metal solutions, in the range of low hundreds of mg L^{-1} or less. Biosorption is a passive process of metal uptake whereby the metal is sequestered by chemical sites naturally present and functional even when the biomass is dead [75]. A unique and ubiquitous type of macroscopic biomass known for its metal-sorbing potential is seaweeds. Seaweed biomass has a certain rigid macro-structure of its own and, in some instances, it has been revealed to offer excellent metal-sorbing properties [15]. At certain ocean locations, seaweeds are plentiful and very fast growing, as for example in the 1,230 km of the Portuguese coast, with different species of algae. At some locations, they threaten the tourism industry by spoiling pristine environments and fouling beaches. For example, the invasion of Ria Formosa (Faro, South of Portugal) by macro-algae *Sargassum muticum* has been causing a serious problem to the ecosystem. Turning seaweeds into a resource can be quite beneficial to some local economies. The renewable character of the macro-algae makes it an inexhaustible resource for the biosorption application in full-scale.

Different brown macro-algae, *Pelvetia c.*, *Laminaria h.*, *Ascophyllum n.*, *Fucus s.*, *Sargassum m.* and *Gelidium s.* harvested in the north coast of Portugal were used as biosorbents for Cu(II), Pb(II), Zn(II), Cd(II), Ni(II) and Cr(III) removal [21, 66] (Fig. 11.1).The maximum biosorption capacities found for *Pelvetia c.,* at pH 5.0 without pre-treatment, were 1.24 (Cu), 0.96 (Pb), 0.91 (Zn), 0.79 (Cd) and 0.71 (Ni) mmol g^{-1} [21]. However, after a pre-treatment with an acid solution followed by a calcium solution (Fig. 11.1), the Ca-biomass was able to accumulate up to 1.45 mmol of lead per gram of biosorbent (more than 50%) [14].

Different kinds of equilibrium models have been used to describe biosorption equilibrium data, as Langmuir [36], Freundlich [22], Langmuir-Freundlich combination [60],

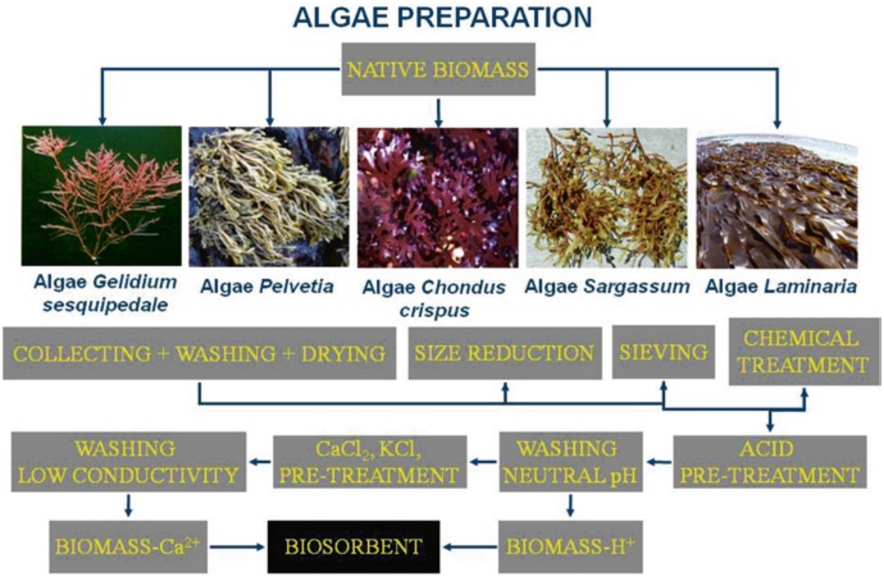

Fig. 11.1 Scheme of algae preparation procedure

Redlich-Petterson [53], Brunauer et al. [12], Radke and Prausnitz [52], and others. As these equilibrium models, in their simple form, do not consider the heterogeneity of the binding sites, the influence of pH on the biosorption process and hardly reflect the sorption mechanism, continuous affinity distribution equilibrium models, considering a complexation mechanism and non ideal competitive adsorption (NICA) have been used successfully to describe biosorption of Cu(II), Pb(II) and Cd(II) by raw algae *Gelidium s.* [66, 68, 71], showing that Cu(II) presents a narrow distribution of the affinity constant, while Pb(II) and Cd(II) present a wider distribution of the same constant. Metal ions act as Lewis acids by accepting electron pairs from ligands. Class A metal ions, also called hard or nonpolarizable, preferentially form complexes with similar nonpolarizable ligands, particularly oxygen donors, and the binding is mainly ionic. Class B or soft metal ions preferentially bind to polarizable soft ligands (S), to give a rather more covalent bonding [49]. Lead, copper and cadmium ions are considered as borderline metals. The affinity increases in the following order Cd(II) < Cu(II) < Pb(II) for algae *Gelidium s.* [69]. The covalent index (product of the electronegativity square by the sum ionic radius + 0.85, which is an appropriate constant assumed to reflect the radius of O and N donor atoms) also increases in the order: Cd(II) (5.20) < Cu(II) (6.32) < Pb(II) (6.61) [47]. In general, the greater the covalent index of a metal ion, the greater its Class B character, and consequently its potential to form covalent bonds with biological ligands.

The biosorption mechanism for lead uptake in algae *Pelvetia c.* loaded with calcium was identified as ion exchange between calcium, lead and hydrogen ions, with a stoichiometry 1:1 (Ca:Pb) and 2:1 (H:Ca or H:Pb). Lead ions showed higher

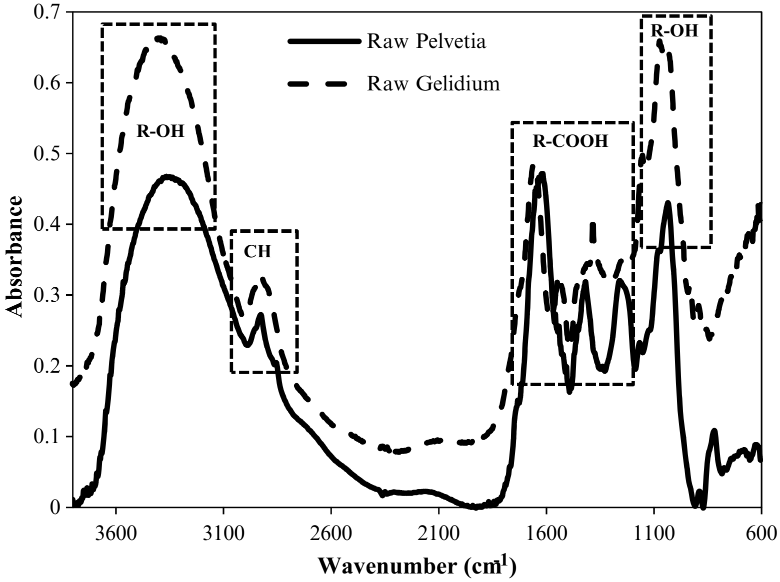

Fig. 11.2 Infrared spectroscopy of algae *Gelidium s.* and *Pelvetia c.*

affinity than hydrogen and calcium ions to the carboxylic groups, as indicated by the respective selectivity constants of the mass action law ($\alpha_{Ca}^{Pb} = 44 \pm 5$, $\alpha_{Ca}^{H} = 9 \pm 1$ and $\alpha_{H}^{Pb} = 5 \pm 1$) [14]. These values also shows that lead ions bind more easily to the biomass pre-treated with calcium ions than hydrogen ions, since the last ones bind more strongly to the carboxylic groups present in the surface of the biosorbent. Similar results were also obtained by other authors [58, 82]. A mathematical model using the Nernst-Planck approximation for the ionic flux of counter-ions, taking into account the intraparticle diffusion resistance and the influence of the electric field in the biosorbent was able to predict the kinetic behavior in batch and column systems [14]. Fourier Transform Infrared Spectroscopy (FTIR) analyses have shown a complex nature of the biomass and provided information about predominant binding groups present on the surface of the algae, as carboxylic groups (*Pelvetia c.*-alginic acid: mannuronic and guluronic acids; *Gelidium s.*-agaropectin: D-glucuronic acid, Pyruvic acid), hydroxyl groups (*Pelvetia c.* -mannitol, laminaran and cellulose; *Gelidium s.*-agarose, Floriden starch, cellulose) and sulphate ester groups (*Pelvetia c.*-fucoidan; *Gelidium s.*-sulfated galactans) (Figs. 11.2 and 11.3).

Potentiometric acid-base titrations showed a heterogeneous distribution of the two major binding groups, carboxyl and hydroxyl, following a Quasi-Gaussian affinity constant distribution [60], which permitted to estimate the maximum amount of acid functional groups (2.8 and 0.36 mmol carboxylic groups/g respectively for algae *Pelvetia c.* and *Gelidium s.*) and proton binding parameter ($pK_{\text{carboxylic groups}} = 3.5$ and 5.0, respectively for algae *Pelvetia c.* and *Gelidium s.*) [14, 72].

The adsorption capacity of the brown algal material is directly related to the presence of the carboxylic sites on the alginate polymer (up to 40% of dry weight, [50]

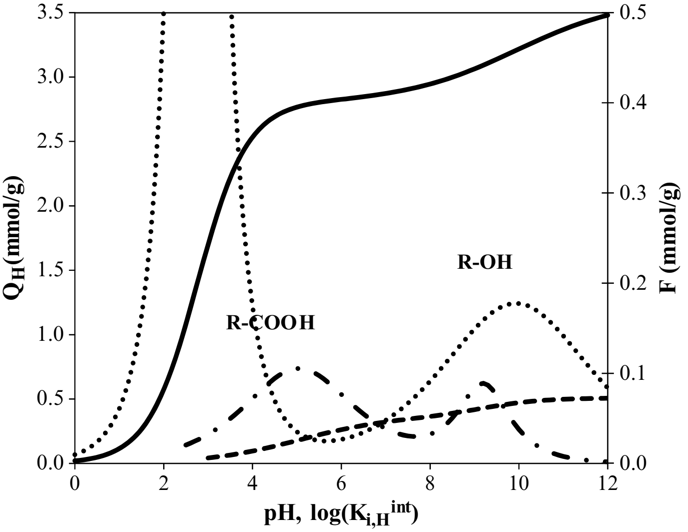

Fig. 11.3 Experimental data and model curves for biosorbent potentiometric titrations and affinity distribution function for hydrogen ions. —, — — Continuous model; …, — — • — — Sips distribution for a IS = 0.1 M. respectively for Algae *Pelvetia c.* and Algae *Gelidium s.*

of the dried seaweed biomass). Furthermore, the majority of metals of interest (i.e. Cd(II), Cu(II), Ni(II), Pb(II)) show maximal, or near maximal, sequestration at pH near the apparent dissociation constant of the carboxylic acids observed in algal biomass (pK_a around 4–5), although for low pH values (<2.5), the biosorbents reveal competitive adsorption capacities when compared with the ion exchange resins, which are in the same way affected by the pH, but has a price ten times higher than the biosorbents. Moreover, the biosorption technology is normally used as a polishing step in wastewater treatment with a metal concentration between 1 and 100 mg L^{-1}. As the majority of metal contaminated effluents present high metal concentrations, it's necessary to carry out a pre-treatment, normally chemical precipitation, after which the pH of the effluent is neutralized. So, the subsequent treatment, using the biosorption process, will be not affected by the alkaline precipitation pH. The role of carboxylic groups in the adsorption process has been clearly demonstrated by a reduction in cadmium and lead uptake by dried *Sargassum* biomass following partial or complete esterification of the carboxylic sites [20]. FTIR spectral analyses have shown that after Pb biosorption onto algae *Pelvetia c.*, the peak related to C-O stretch of COOH disappeared (Fig. 11.4) [14] and Cd biosorption to *Sargassum* arises from bridging or bidentate complex formation with the carboxylate groups of the alginate [20].

The second most abundant acidic functional group is the sulfonic acid of fucoidan. Sulfonic acid groups typically play a secondary role, except when metal binding takes place at low pH. Hydroxyl groups are also present in all polysaccharides but they are less abundant, and only become negatively charged at pH > 10, so, they are

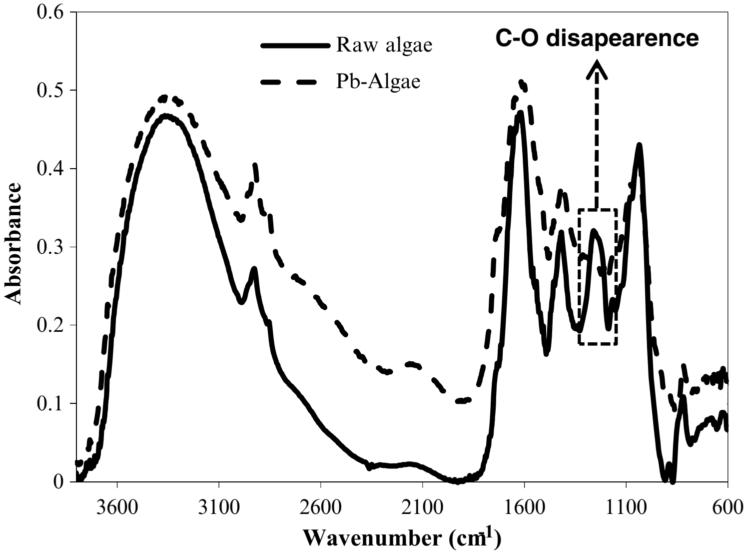

Fig. 11.4 Infrared spectroscopy of algae raw *Pelvetia c.* and saturated with Pb

less relevant for metal binding at low pH. The titration curves are not affected significantly by the salinity for ionic strengths between 0.005 and 0.1 M, which are usual in the majority of the industrial effluents [14, 72]. This result reveals that the polyelectrolyte effect is small leading to the conclusion that the charges are well spaced (distance larger than the Bjerrum length) [10].

If the biosorption process is to be used as an alternative in wastewater treatment, the biosorbent regeneration is important to keep low processing costs and open the possibility to recover the extracted metal(s). The desorption process should yield metals in a concentrated form, which facilitates disposal and restores biosorbent for effective reuse [77, 78]. The desorption mechanism is similar to ion exchange. The biomass stripping can be achieved with inexpensive acids such as HCl, HNO_3 and H_2SO_4 [2, 35, 65] and EDTA as metal chelating agent [62, 64, 81, 84]. Desorption of different metal ions from different brown algae has been completely achieved at pH 1 [21, 67]. An intermediate conditioning step is normally used after desorption and before the next adsorption cycle, whereby the protons binding to the active sites (after acidic desorption) are replaced by Ca^{2+}. Multiple reuses of the active sorbent particles in consecutive adsorption/desorption cycles have been performed without any loss in the uptake capacity, which greatly increases the process economy [70]. Although different kinds of biosorbents have been tested to remove several metals [5, 8] only few have been commercialized [4, 24, 75, 76, 78]. Despite the simplicity of the biosorption process, the technology is not yet established and it requires continued Research and Development (R and D) efforts at pilot-scale, using real metal bearing effluents.

11.2 Solar Photocatalysis

Nowadays, the elimination of recalcitrant, non-biodegradable organic chemical compounds is one of the most important problems in the treatment of effluents deriving from industrial applications (textile, winery, cork, etc.) and also as a result of the agricultural exploration and domestic use (pesticides, fertilizers, detergents, etc.). On the other hand, the reuse of wastewater after adequate polishing step constitutes a potential water resource, which could be of great interest to several activities, such as agriculture, especially in countries suffering from a deficiency in water resources. More than 200 different chemical compounds – many of which may be acutely or chronically toxic to aquatic organisms and may pose a health risk to man and animals alike, since they are not easily degraded – have been identified in secondary effluents of municipal Wastewater Treatment Plants (WWTP). Additionally, environmental regulations are getting stringent and with the introduction of EU Water Framework Directive in 2000 [48], secondary sewage effluent (SSE) was no longer a guarantee for discharge [33]. Advanced tertiary treatment is therefore required for further removal of the residual constituents in SSE, especially near sensitive areas. The search of effective methods to remove these compounds is of global interest in order to fulfill the discharge regulations and, particularly, to allow water recycling.

Advanced Oxidation Processes (AOPs) are an emergent and promising methodology for the degradation of persistent environmental pollutants, refractory to other decontamination/remediation treatment processes. In the near future, AOPs may become the most widely used water/wastewater treatment technologies for organic pollutants which cannot be removed by conventional techniques, due to their high chemical stability and/or low biodegradability [26, 27]. AOPs involve generation and subsequent reaction of hydroxyl radicals ($HO^{\bullet}$), which are one of the most powerful oxidizing species. Their attack is not very selective, which is a useful attribute for use in pollution treatment. Many oxidation processes, such as TiO_2/UV, H_2O_2/UV, photo-Fenton and ozone (O_3, O_3/UV, O_3/H_2O_2) are currently employed for this purpose and their versatility is enhanced by the fact that there are many different $HO^{\bullet}$ radical production possibilities. The use of AOPs for wastewater treatment has been studied extensively, but ozone production or UV radiation generation by lamps are expensive processes [46], and, in the latter case, future applications can only be economically envisaged through the use of solar energy. So, research is focusing more and more on those AOPs which can be driven by solar irradiation, such as photo-Fenton and heterogeneous catalysis with TiO_2. Several photocatalysis reviews have been published during the last years [7, 30, 38]. It has been demonstrated that the photo-Fenton reaction is more efficient for the treatment of different recalcitrant pollutants [17, 37] than TiO_2, since the reaction rate is much higher and very low iron concentrations are enough for promoting wastewater treatment. This is very helpful because removal of iron at low concentrations will not be necessary before disposal. The advantage of the photo-Fenton process is the higher light sensitivity up to 580 nm, corresponding to 35% of solar radiation spectrum, when compared with ≈ 5% for TiO_2 photocatalysis.

Apart from developments increasing the reaction rate, the most important progress in solar photocatalysis in recent years has been related to its combination with biological treatment techniques, which proved to be successful in decreasing treatment time (i.e. plant size) and consequently increasing the overall process efficiency [19, 39, 57].

The southern European countries, due to their high average number of sun hours are very prone to the application of solar photocatalytic technologies. Besides, Spain has been the first country that has built a commercial photocatalytic solar plant (Albaida) where, in a field of 150 m^2 of compound parabolic collectors (CPCs), is performed the wastewater treatment from a pesticide containers plastic recovery facility (treatment capacity: 21,600 ton $year^{-1}$). In Spain is also found, at DSM-Deretil company, a demonstration plant for the treatment of wastewaters containing pharmaceuticals in a sequential chemical-biological process using photo-Fenton photocatalytic technology in a field of 100 m^2 of CPC (treatment capacity: 6.3 m^3 day^{-1} in the solar field).

Portugal is the world leader in cork production and manufacturing, harboring about 800 industrial facilities and employing 12,000 people in 2009 [3]. The cork production process (*Quercus suber L.*) follows a series of steps: preparation of the cork barks (stabilization, boiling and flattening), production of the cork stoppers (cutting into strips, punching out the stoppers), and their final treatment for launching in the market (disinfection, drying, sorting and packing). This process creates two types of wastewaters: the cork boiling wastewater (CBW) and the cork bleaching wastewater (CLW) [73].

The CBW consists of a dark liquor, of around 400 L per ton of prepared cork, that is produced after the repeated boiling of cork in water (around 20–30 times for the same batch of water) [44]. This wastewater has a high non-biodegradable organic load and is rich in phenolic acids and polyphenols [31]. The CLW is produced in the disinfection of the cork stoppers in a volume of around 400 L per 50,000 stoppers (and 1 ton of cork = 75,000 stoppers, approximately). The most common reactant used in the bleaching process is hydrogen peroxide, which concentration can range from 0.7 to 7.7 g L^{-1} in the final wastewater, depending on the industrial process. CLW has a lower organic load than CBW but is equally non-biodegradable [73].

Previous studies from Silva et al. [59] and Vilar et al. [73] have concluded that heterogeneous photocatalysis with TiO_2 is inefficient in treating CBW in a short period of time. However, photo-Fenton and solar-photo-Fenton showed improved results from Fenton alone. Moreover, photo-Fenton can make use of the high concentration of hydrogen peroxide of CLW for its treatment. Pintor et al. [51] showed that is possible to perform the decontamination of CBW and CLW simultaneously, using CLW as a H_2O_2 source in solar-photo-Fenton treatment of CBW, modeling the AOP as a pre-oxidation step before a traditional biological treatment. This method proved to be efficient, achieving mineralization rates higher than 90% for different iron concentrations. Lower energy consumption was achieved for higher iron concentrations, and 60 mg L^{-1} was selected as the optimum (16.6 kJ_{UV} L^{-1} for

91% mineralization) and used for biodegradability studies. According to the Zahn-Wellens test, the optimum phototreatment energy to achieve a biodegradable effluent is 13.6 kJ_{UV} L^{-1} (65% mineralization), which corresponds to a hydrogen peroxide consumption of 76.1 mM (approximately 8.5 L of CLW (at 7.7 g H_2O_2 L^{-1}) for 15 L of CBW).

Sanitary landfill leachates resulting from the rainwater percolation through the landfill layers and waste material decomposition is a complex mixture of high-strength organic and inorganic compounds that constitutes a serious environmental problem [13]. The photo-Fenton process is much more efficient in leachates treatment than heterogeneous (TiO_2, $TiO_2/H_2O_2/UV$) or homogeneous (H_2O_2/UV) photocatalysis, showing an initial reaction rate more than 20 times higher, and leading to almost complete mineralization of the wastewater. However, when compared with $TiO_2/H_2O_2/UV$ with acidification, the photo-Fenton reaction is only two times faster [56]. The optimal energy dose estimated for the photo-treatment to reach a biodegradable effluent, considering the Zahn-Wellens test, respirometry test, and biological oxidation tests at pilot plant scale, is 29.2 kJ_{UV} L^{-1} (3.3 h of photo-Fenton at a constant solar UV power of 30 W m^{-2}), consuming 90 mM of H_2O_2 when used in excess, which means almost 57% mineralization of the leachate, 57% reduction of polyphenols concentration and 86% reduction of aromatic content [74].

The high concentration of nitrogen in landfill leachates constitutes, beyond the presence of recalcitrant carbon content, a big environmental concern that must be solved. Complete removal of ammonium, nitrates and nitrites of the photo-pre-treated leachate was achieved by biological denitrification and nitrification, after a previous neutralization/sedimentation of iron sludge (40 mL of iron sludge per liter of photo-treated leachate after 3 h of sedimentation). The optimum C/N ratio obtained for the denitrification reaction was 2.8 mg CH_3OH per mg $N{-}NO_3^-$, consuming 7.9 g per 8.2 mL of commercial methanol per liter of leachate. The best nitrification ratio obtained was 68 mg $N{-}NH_4^+$ per day, consuming 33 mmol of NaOH per liter (1.3 g NaOH per liter) during nitrification and 27.5 mmol of H_2SO_4 per liter during denitrification [74].

11.3 Solar Photocatalytic Disinfection

Due to the lack of available on-site disinfection technologies in many rural areas, water supply is not widely treated and the risk of transmission of many diseases is very high and has been largely responsible for several large epidemics such as typhoid and cholera throughout the world [79]. The most commonly used techniques for water disinfection are chlorination and ozonation. However, the overall water service coverage in rural areas is rather low, because of many factors (technological, cost, maintenance, social, cultural, logistics, education, etc.) responsible of present situation. In addition, there is the risk caused by the chlorinated by-products such as trihalomethanes (THMs) and other organohalides resulting from the reaction of chlorine with organic matter. Other existing technologies, such as ozone and UV disinfection, are clearly of very difficult implementations in rural areas [45], often among the sunniest in the world. This is why solar water disinfection methods, such as the solar drinking-water disinfection process called SODIS [http://www.sodis.ch/], have gained relevance in recent years, mainly in rural areas [61]. Nevertheless, the disinfection efficiency of the SODIS treatment can easily be affected by water turbidity, low irradiation intensity and regrowth of bacteria after the solar treatment, probably due to photo-repair mechanisms [55].

The combination of sunlight and a photocatalyst may be a promising option for disinfection/decontamination of natural waters for human consumption, in areas with insufficient infrastructures but high yearly sunshine. The reactive oxygen species produced can destroy a large variety of co-adsorbed chemical pollutants and inactivate waterborne microorganisms [6, 80].

Application of TiO_2 to water treatment has been reviewed by Fujishima et al. [23] and more recently by Herrmann [34]. Some authors suggest that the cell membrane is the primary site of attack by the reactive hydroxyl radicals [40, 63], which can be explained by peroxidation of the polyunsaturated phospholipid component of the lipid cell membrane leading to a loss of essential cell functions, e.g., respiratory activity, and in the end, to cell death [11, 83]. Disinfection with supported TiO_2 or Fe reduces the need of a post-treatment not only in the laboratory, but also in large solar reactors [18, 25, 41, 54]. On the other hand, the immobilization of iron avoids also the initial acidification procedure, in order to prevent iron precipitation [9]. Fe-ions deposited onto chemically treated carbon fabrics or encapsulated in Nafion thin films cast directly onto the carbon fabrics are efficient in decomposing H_2O_2 used as an oxidant in the photo-assisted abatement of non-biodegradable azo-dyes used in textiles even at neutral pH [32]. The supported catalyst was firmly attached around an inner glass tube closed at the bottoms before being placed in two of the CPCs tubes. Tedlar polyvinyl fluoride (PVF) film has also been tested as the inert support for TiO_2 deposition followed by a subsequently coating with iron oxides by means of forced hydrolysis of solution of $FeCl_3$ [42].

McLoughlin et al. [43] studied the use of three types of static solar collectors, with aluminum reflectors consisting of compound parabolic, parabolic, and V-groove profiles and all enhance the effect of the natural solar radiation, for the disinfection of water containing *Escherichia coli*, although the CPC was found more efficient. As a result, they suggest that the disinfection mechanism in the reactor configuration is either a synergistic effect between UV radiation and the mechanical stress of recirculation, or a stroboscopic shock effect in which bacteria are intermittently exposed to radiation and dark in the reactor, which is in agreement with the results presented by other authors Fernandez et al. [18].

The majority of work in this field uses artificially contaminated samples that are prepared with standard microorganisms in distilled water. Very little work has been done with real water sources, such as rivers, lakes and wells as reported by Rincón and Pulgarín [55] and Wist et al. [80].

Solar disinfection of synthetic and natural waters from the Douro River, northern Portugal was studied in a pilot plant with CPCs [28, 29]. Inactivation of *Enterococcus faecalis* (*E. faecalis*) was slower than of *Escherichia coli* (*E. coli*) possibly due to the cell wall composition of the gram positive and negative bacteria, respectively.

The high content of peptidoglycan, teichoic acids, polysaccharides, and peptidoglycolipids, in *E. faecalis* cell wall, when compared with *E. coli*, acts as a protective coating. The obtained results revealed that *E. coli* inactivation can be achieved by photolysis; however, the presence of TiO_2 in suspension accelerates the reaction. The Degussa P25 TiO_2 coated on a paper matrix Type NW10 "Ahlstrom paper" [1], was tested and showed low efficiency for bacteria inactivation. A non-empirical model (Langmuir-Hinshelwood), considering a simplified reaction mechanism, was successfully used to describe the *E. coli* inactivation. The interaction between the bacteria and the supported TiO_2 is the reaction constraint, reducing significantly the bacteria inactivation. The release of organic matter from the support (paper matrix NW10) is also responsible by the absorption of UV light, radical scavenging and inhibition of the catalyst and, furthermore, may act as a nutrient supply for bacteria. No bacterial regrowth was observed for *E. faecalis* in synthetic waters. Oppositely, regrowth occurred in natural waters. This behavior can be due to the natural water chemical composition, with the presence of various organic and inorganic species.

11.4 Conclusion

Environmental Friendly Technologies are the new trend for water and wastewater treatment. The strict environmental regulations and the world concern about environment issues became a high priority of all governments around the world. Funds for environment research are continuously rising, increasing the number of researchers and environmental research infrastructures. Under these circumstances, this chapter brings other perspectives to best available technologies for water/wastewater treatment, as the use of low cost materials, e.g. algal biomass, for toxic metal ions removal, and the use of solar radiation, as photon source. Solar-driven photocatalysis alone or combined with biological oxidation is a "green" technology for detoxification of different recalcitrant wastewaters and disinfection of water.

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Chapter 12
Closing Water Cycles in Industry: Theory and Implementation

Jurgis K. Staniškis

Abstract Sustainable development calls for processes with a closed loop philosophy and recycling becomes thus a normal, rather than exceptional solution. Water reuse and recycling in industry is one of the most important ways enabling absolute and relative decoupling of environmental impact from economic growth. There are more and more corporations focusing development efforts on Cleaner Production (CP) and Pinch analysis methods, i.e. systematic approach to using resource more efficiently, and avoiding the use of hazardous substances where substitutes are available.

Paper deals with water saving, reuse and recycling in industrial companies by preventive strategies, which are achieved by applying know-how, by improving technology and/or by changing attitudes. Preventive strategies included the following prevention methods: good housekeeping, input substitution, better process control, equipment modification, technology change, product modification and on-site recovery/reuse. The key idea is to remove the reasons of problems rather than their symptoms.

Keywords Water saving • Water reuse and recycle in industry • Preventive strategies • Cleaner production • Water pinch study

12.1 Introduction

Natural resources include both the raw materials necessary for most human activities and the different environmental media, such as air, water and soil, which sustain life on our planet. Therefore, careful management of the use of these resources is a basis

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for sustainable development. In contrast with raw material, it is their declining quality that causes concern. It is not question of how much there is, but what state they are in.

Resource efficiency or resource productivity can be defined as the efficiency with which we use energy and materials throughout the economy, i.e. the value added per unit of resource input. An example of resource productivity calculation on a national level is total material (water) use divided by the total economic activity by the country, expressed in GDP.

There are many difficulties facing those who have interests both in the natural environment and in the man-made environment together with the problems of their interfacing. The industrial system is the collection of physical, chemical, and technological processes developed by man for the restructuring of materials. The biosystem involves the collection of natural ecosystems in the landscape. There are two main types of interaction between physico-ecological and socio-economical systems. Firstly, there is environmental intervention in which socio-economic systems operate apart from physico-ecological systems to cause them to react in the pre-determined and in advantageous manner. Such intervention systems involve a considerable amount of monitoring and tend to take a rather analytical view of environmental systems. Three main types of intervention could be considered [1]:

1. prediction of outputs,
2. manipulation of storages and
3. control of inputs.

Prediction of outputs may be viewed in a purely passive sense where expected outputs are predicted by the use of forecasting techniques. The classical example of this type of intervention is the model for the Nemunas River which is one dimensional quasi-dynamic, based on the differential equations of the first order with the possibility to analyze conservative materials transport and to predict transport and transformation of non-conservative materials, for instance dissolved oxygen, organics, nutrients [13].

Manipulation of storages is very important method of environmental system interfacing which involves the manipulation of physico-ecological storages by the socio-economic system. Using this method, water quality problem at the hot spot could be solved instead of controlling inputs by spatial distribution of pollution along rivers and estuaries. This creates the ability of the natural processes of stream channels to renew and dissipate pollution. As usual, regional treatment plants are fixed in their location as a result of political and engineering considerations. Using second method of intervention, the problem instead could be solved by means of non-linear programming.

The potentially most important approach is the *control of inputs*. This is very difficult to achieve except over small scales of space and time and requires a considerable input of energy and sophistication of time space application to make such control effective. The simple and very practical case of this type of intervention was designed as a decision support system for the waste management [2].

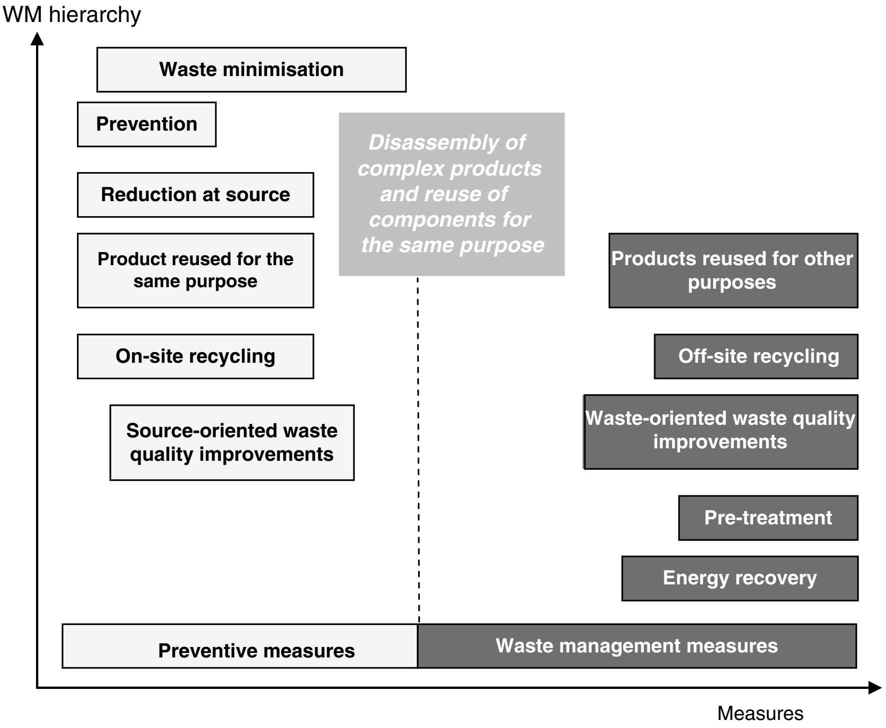

Fig. 12.1 Simple presentation of waste minimization (WM) concept defined by European topic centre on waste

However, it has been widely recognized and practically proved that waste prevention is the most important tool for resource efficiency and for sustainable waste management. The acceptance that waste is there, it always will be and we have just to deal with, it will not lead to waste prevention. To be able to prevent, we need to know the reasons of waste generation. Only after understanding the causes of waste generation we can prevent it. The definition for waste minimization was declared at the task meeting of the European Topic Centre on Waste in 1999 (see Fig. 12.1). Waste preventive measures include [4]:

- reduction of waste by application of more efficient production technologies,
- internal recycling of production waste,
- substitution of hazardous substances,
- more efficient process optimization and control, and
- re-use of products, or parts of products, for the same purpose.

The measures require a proactive attitude and the producer has to implement waste management decisions long before the holder is to dispose an item.

It should be stressed that environmental performance improvement measured through the adoption of waste minimization innovations is regarded as an indicator of business health. Good waste management reflects good management in general. There is also good indicator for financial institution to avoid companies that may face the costs associated with environmental liability [16].

12.2 Waste Prevention and Management: Theory

It has been assumed up to this point that the structure of the system of interest is known together with its inputs and outputs. In most practical environmental instances, however, one or more of the three system elements (input, output, and transformation) may be unknown, or only partially known. The structural properties of a system input, output and transformation, which determine whether all elements of system response can be observed, are usually termed observability and controllability criteria.

Controllability implies the ability of control input to affect any state of the system and observability implies the ability of each state to influence the system output. Figure 12.2 presents four possible system configurations, where system S_1 is controllable and observable, S_2 – controllable but unobservable, S_3 – uncontrollable but observable, and S_4 – uncontrollable and unobservable [1, 5].

The model is an accurate representation of the environmental system if, and only if, the system is controllable and observable. It means:

- A system is to be said to be state controllable if any initial state Y_0 can be transformed to any final state Y_{tf} in a finite time $t_f \geq 0$ for some input X_t.
- A system is set to be observable if every state Y_0 can be exactly determined from measurements on the output Y_t over a finite interval of time $0 \leq t \leq t_f$.

The overall type of control system required in any environment, is dependent not only on the control instruments available, but also upon the nature of the

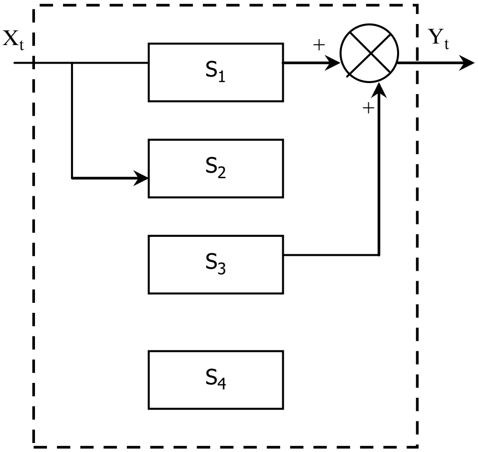

Fig. 12.2 A simple flowchart representing the four possible system configurations

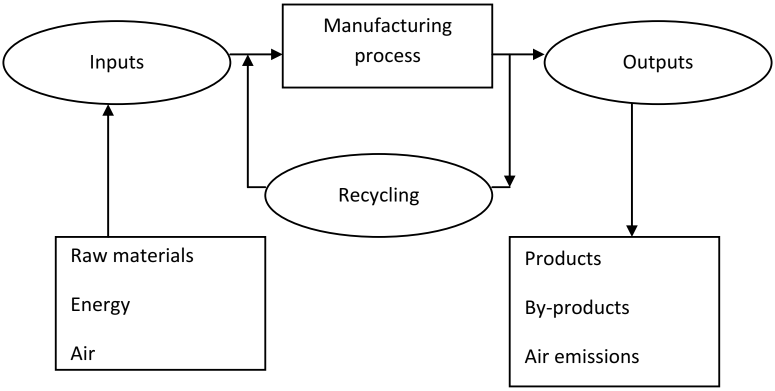

Fig. 12.3 Block flow diagram of typical industrial process

disturbances entering the system. The most common environmental control systems structures are [6]:

- open-loop control systems,
- active closed-loop feedback control systems,
- feedforward control systems, and
- feedback-feedforward control systems.

In practical systems control, it is usually necessary to build up a complex set of feedback, feedforward adaptive and environment control systems capable of representing the whole range of system disturbances and changes, which may occur. This requires the development of hierarchical and nested control systems.

The industrial waste (gas, liquid and solid) is generated in many different processes. The amount and toxicity of waste releases vary with specific industrial processes. Figure 12.3 shows typical industrial processes that produce waste containing different types of pollutants, depending on the input materials and process designs. Thus, process information is critical to make accurate and reliable assessment of the potential for different environmental strategy.

Environmental management has, until recently, developed under the assumption that environmental effects of anthropogenic activities should be addressed by carrying on the "normal" ways of production and adding on control technologies later as needed. This principle has led to attempts to protect the environment by isolation of contaminants from the environment or the use of end-of-pipe technologies. Although these kinds of solutions have undoubtedly led to short term improvements in local pollution problems, there are some significant problems associated with this approach:

- end-of-pipe approach is in one medium risks transferring pollution from that medium to another, where it may either cause equally series environmental problems or even end up as an indirect source of pollution to the same medium,
- end-of-pipe at the abatement contributes significantly to the cost of production processes and products,

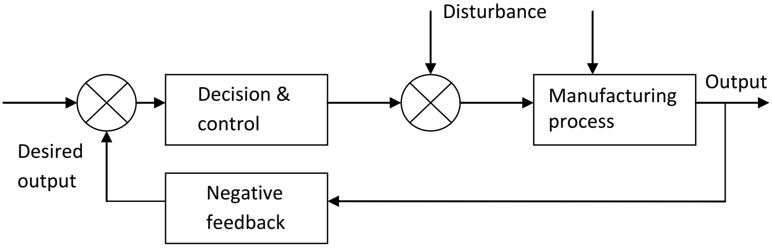

Fig. 12.4 Block diagram representing the structure of environmental control paradigm

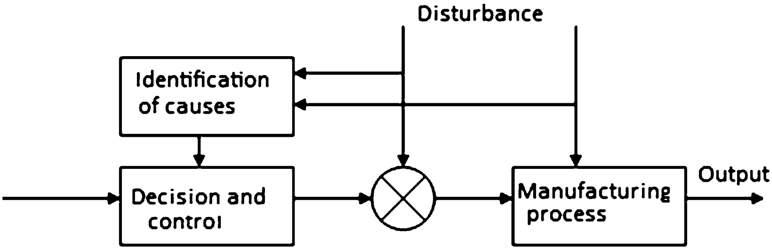

Fig. 12.5 Block diagram representing the structure of preventive paradigm

- end-of-pipe abatement of pollution requires regulation through control legislation which is often costly and cumbersome, leading to potentially inefficient regulatory structures and problems of non-compliance,
- end-of-pipe abatement technology represents a significant technological market with an associated economic inertia which encourages the continued generation of waste and works against any attempt to reduce pollution at the source.

From the systems' theory point of view, this approach is reactive and could be presented as a closed loop feedback control system (Fig. 12.4). Taking corrective measures at the input, when deviations from the standard are recorded in measuring the output is called feedback control.

The structure of environmental control approach shows that this strategy is reactive which refers to actions taken "after the fact" in response to effects. Reactive actions focus on negative impacts and risk reduction through acting on a waste or pollutant, and thus there is an opportunity in space and time to act on what is already a waste or pollutant [6].

The precautionary principle, which is clearly related closely to the concept of prevention, calls for reduction in anthropogenic emissions of potentially hazardous substances in two environmental medium. Preventive actions focus on identification and reduction or elimination of use of materials that could cause harm or damage to the environment. That is, preventive actions are anticipatory by definition, and act not on waste but on conditions and circumstances that have the potential to generate waste. Anticipation and prevention of waste generation is an example of feedforward control in the system development (Fig. 12.5).

The most interesting level, and also the most important in relation to the preventive paradigm, is the internationalization of environmental stewardship thinking and action. The main elements are the following:

- the recognition of the good quality of environment as an integral factor of sustainable industrial activities;
- the recognition of good environmental management as an important factor for the continuity of a company;
- the integration of environmental compatibility within the quality concept of products.

The extensive research and experience from the implementation of cleaner production (CP) proposals in Lithuania and other countries have confirmed the possibility to decrease waste generation by 30% without any investments or with very low cost investments. The further decrease of wastes up to 70% could be achieved by economically viable CP proposals with medium size investments [8, 9].

Currently, company's attitude towards the environment could be characterized by three different levels:

- compliance with regulations,
- anticipation of increasingly stringent regulations, and
- internationalization of environmental stewardship thinking.

The compliance with regulations in most cases is reactive, because measures are taken on an ad-hoc basis after regulations have been developed by the authorities, which is usually done after environmental damages have occurred. The anticipation of increasingly stringent regulations attitude goes further in the pollution control efforts than those strictly required by law. Such approach becomes a corporate strategy since corporate leadership perceives that such activities are positive for their relationship with the authorities and for the environment. The level were preventive paradigm could play extremely important role is internationalization of environmental stewardship thinking.

Therefore, the most effective environmental management should combine both preventive and end-of-pipe strategies (see Fig. 12.6).

Reactive actions focus on explicit use of technology that is manifested as equipment. But preventive actions can be implemented completely through the application of knowledge and changed behavior, or technology that has no apparent linkage to an environmental objective. Prevention means, doing something differently so, that waste is reduced and eliminated.

At the same time, the profitability of pollution prevention measures is clearly critical to the successful implementation. Unless profitability is demonstrable at the level of investment and industrial management decisions, companies will have little incentive to pursue the preventive path. Our broad experience have showed that total cost assessment (TCA) offers an alternative to conventional project analysis approaches by enlarging the inventory of costs and benefits, allocating such costs and benefits more closely to specific processes and products, using multiple profitability indicators to capture indirect, less tangible and longer term pay-offs. Therefore, TCA

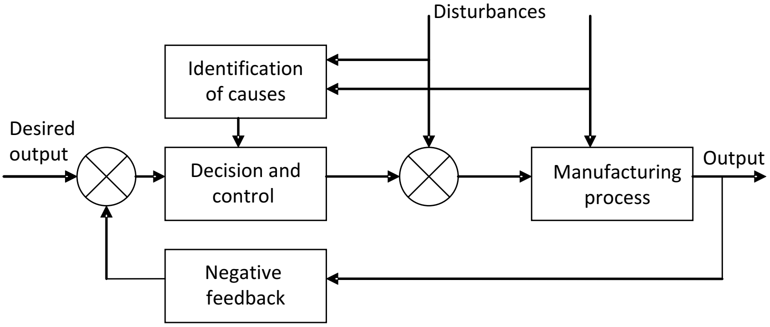

Fig. 12.6 Block diagram representing the structure of closed-loop feedback- feedforward control

is an approach for refining project financial analysis such that prevention investments are treated on the same level in relation to other competing investments [11].

In the early approaches to cleaner production, attention has tended to focus on waste generated during the production processes, and on the need for recycling of raw materials to reduce the environmental burden of product disposal. Developments of the earlier concepts have emphasized the need for attention to be paid both to the general use of materials and to the importance of the design and of the life cycle concept in minimizing subsequent environmental impact.

The life of any product can be divided into five more or less distinct phases as follows:

- conception, design and testing,
- production involving the extraction and transformation of natural resources,
- distribution including packaging, transformation, and marketing,
- the utilization period during which the product provides some useful service, and
- post-utilization period, which involves either the recycling or the treatment and disposal.

The concepts and practices of waste prevention and clean production need to be applied at every stage of the product life-cycle in order to minimize environmental input.

By integrating product life-cycle planning into all product and production considerations, companies could drastically reduce their environmental impacts and increase their efficiency / profits simultaneously [10, 14].

12.3 Implementation

There are two main practical preventive methods for the closing waste and water cycles in industry:

1. Cleaner Production [14],
2. Pinch analysis [17].

The concept of CP was introduced by UNEP in 1989 as a response to the question of how industry could work towards sustainable development.

CP means a continuous application of an integrated preventive environmental strategy to processes, products and services to increase overall efficiency. This leads to improved environmental performance, cost savings, and the reduction of risks to humans and the environment.

- *In production processes*, CP includes conserving raw materials and energy, eliminating toxic raw materials, and reducing the quantity and toxicity of all emissions and waste before they leave the process.
- *In products*, CP focuses on reducing impacts along the entire life cycle of the product – from raw material extraction to the final disposal of the product.
- *In services*, using a preventive approach CP involves design issues, housekeeping improvement, and a better selection of material inputs (in the form of products).

Other concepts such as eco-efficiency, waste minimization and pollution prevention share a common emphasis on pollution/waste elimination/reduction at the source where it is generated. However, CP strategy includes a well-developed procedure for systematic assessment of pollution/waste generation causes and development of practical options aimed at the solution of concrete problems. Additionally, CP strategy includes a clearly defined CP management system, which ensures continuous improvement of environmental and economic performance [7].

CP should not be considered only as an environmental strategy, because it also relates to economic considerations. In this context, waste is considered as a "product" with negative economic value. Each action to reduce consumption of raw materials and energy, and prevent or reduce generation of waste increases productivity and brings financial benefits to the enterprise.

A preventive approach means that environmental problems are addressed before they arise when choices are made concerning processes, raw materials, design, transportation, services, etc. Such approach effectively addresses the wasting of natural resources since pollution not only leads to environmental degradation but it is also a sign of inefficient production processes or management. In practice, CP means the following:

- avoiding or reducing the amount of the waste produced,
- using energy and resources more efficiently,
- producing environmentally sounder products and services, and
- generating less waste, reducing costs and increasing profits.

Cleaner production is achieved by applying know-how, by improving technology, and/or by changing attitudes. CP strategy includes the following prevention practices: good housekeeping, input substitution, better process control, equipment modification, technology change, product modification, energy efficiency/reuse.

The method of Cleaner production assessment was developed by the Institute of environmental engineering (APINI) together with World Cleaner Production Society (WCPS, Norway). CP assessment procedure is a closed loop system, consisting of: preparation phase, preliminary assessment, planning and organization,

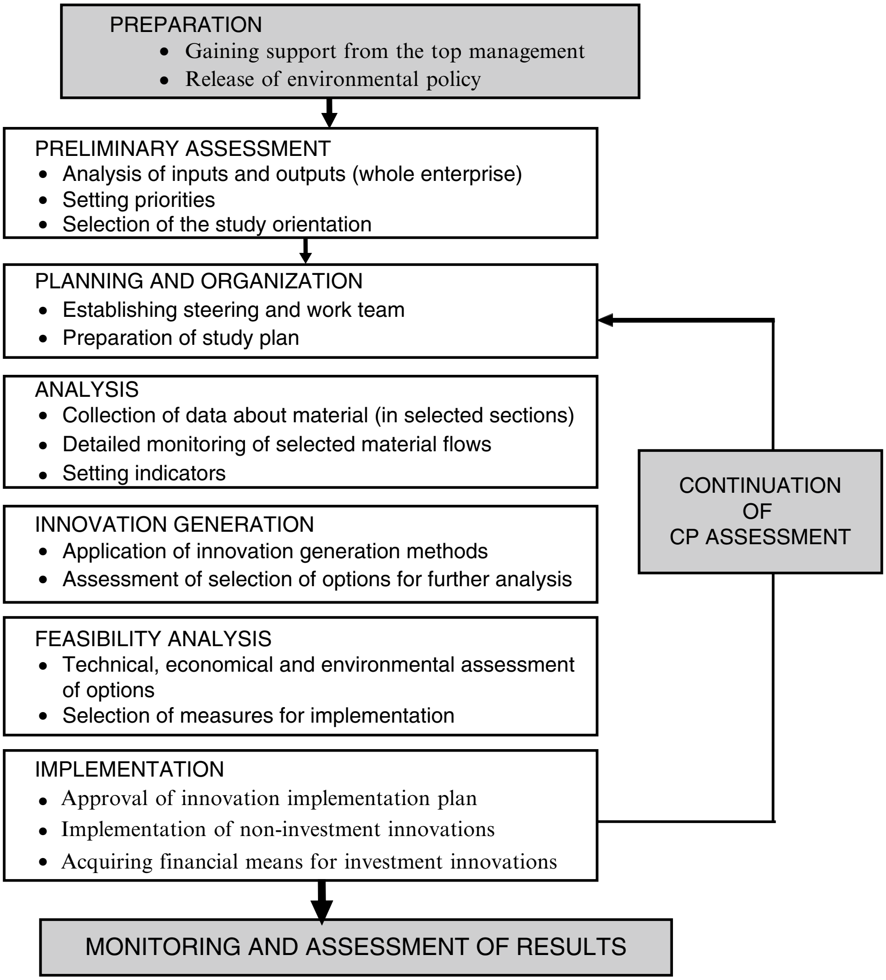

Fig. 12.7 Flowchart of Cleaner production assessment procedure

analysis, innovation generation, feasibility analysis, implementation and monitoring (see Fig. 12.7) [10, 15].

For a number of years, process integration techniques based on pinch analysis have been successfully applied to improving energy efficiency in the process industries. Analogous techniques have been developed for water conservation and wastewater minimization [15].

Water pinch is a systematic technique for analyzing water networks and identifying innovations to increase the efficient use of water in industrial processes. Pinch applications help to identify and to optimize the water system in the plant by application of reuse, recycle and regeneration strategy [17].

During the water pinch study in an industrial facility, several types of water reuse solutions, with or without water treatment, are possible [3]:

1. A water pinch study starts with the assumption that existing input concentrations are at their maximum acceptable limits for all processes and equipment. This shows the minimum acceptable usage under currently imposed constraints on the inlet concentrations. Innovations, identified at this stage will be low-cost proposal, generally allowing only small water reuse possibilities.
2. Larger water savings are possible by increasing upper concentration limits to selected inputs. This type of innovation should be carefully discussed between plant operators and engineers in order to evaluate the risk of quality. In most cases external process experts, data from manufacturers and feasibility studies are required.
3. The next water reuse potential is different combinations of regeneration and reuse. These innovations comprise partially treated some process water streams before their reuse. First, the key streams for possible treatment in regeneration are identified. Then existing and new treatment units are evaluated in terms of reducing overall water consumption. Innovations identified at this stage usually involve capital investments for local treatment facilities.
4. The final possibility is the assessment of distributed effluent treatment options. Instead of mixing all waste streams together and treating them in a single treatment plant, streams are segregated according contaminants they contain and appropriately treated. In this case, several small-scale treatments units will operate on undiluted effluent streams. Distributed treatment systems are interesting innovations as they often offer better removal efficiency at reduced cost.

Water pinch typical assessment procedure consists of three main phases:

1. *Planning and water balance.* It is essential to construct water and pollutant balance, as well as industrial company future plans and objectives for the site. The balances should be validated and conflicts in available data should be resolved. If required, additional measurements for water flows and contaminant concentrations should be performed. The location of main effluent streams should be identified together with their associated problems and key contaminants.
2. *Water pinch analysis*. The main objective is to identify the areas for water savings and innovations. For this freshwater target for fixed operating conditions, the maximum acceptable input concentrations, water stream regeneration and distributed wastewater treatment possibilities have to be identified. Besides that, detailed analysis of wastewater treatment options and appropriate technologies, such as membranes or biological treatment has to be performed.
3. *Innovation identification and implementation.* The objective of this phase is full evaluation (technical, economical, environmental) of innovations identified in the previous phases, and the development of an investment projects with their associated costs.

The structure of the typical water pinch assessment procedure is very close to cleaner production assessment (see Fig. 12.7). Therefore, it looks rational to combine both procedures into one model, especially when it comes to low-cost innovations (see Fig. 12.8).

The integrated Cleaner Production and Process integration assessment scheme was successfully used for many innovations identification, financing and implementation in different industrial sectors. One of real and simple case is presented below.

First of all, the Cleaner production assessment method was used for the wastewater recirculation in sheep skins tannery. Initially, all water used in beamhouse operations was fresh water supplied directly from the river Nemunas. All waste water from the beamhouse (663 m^3 per day) became sewage. This waste water contained detergents and other chemicals (formalin, sodium carbonate). The working temperature was about 35°C. Great losses of water, steam energy and chemicals occurred because of inefficient technology and operations [12].

The following improvement steps based on the detailed assessment of process material balance have been made in the tannery:

Step 1: Wastewater from degreasing and rinsing (60 m^3) operations is used in the soaking operation.
Step 2: Wastewater from squeezing operations after first and second washings (140 m^3) is used for squeezing after soaking.
Step 3: Wastewater from degreasing and rinsing operations (70 m^3) is used for squeezing after the first washing.
Step 4: Wastewater from the second washing (53 m^3) is used for the first washing. Wastewater from a degreasing operation (17 m^3) is used for the first washing.
Step 5: Wastewater from degreasing and rinsing operations (53 m^3) is used for the second washing (Fig. 12.9).

Main advantage of the innovation
This innovation enabled recirculation of the wastewater and has clear economic and environmental benefits.

Environmental benefit:

- reduction in water consumption,
- reduction in chemicals consumption,
- energy savings, and
- decrease in pollution load to wastewater.

Economic benefit
Investment in the modification of production processes (reuse of waste water) – 50 000 USD. Because of reduced costs for chemicals and more efficient use of water, the annual savings at this facility – 100 000 USD. Pay-back of the investment – 6 months.

It is important to mention, that very close results of economical and environmental benefits have been achieved by pinch analysis method too.

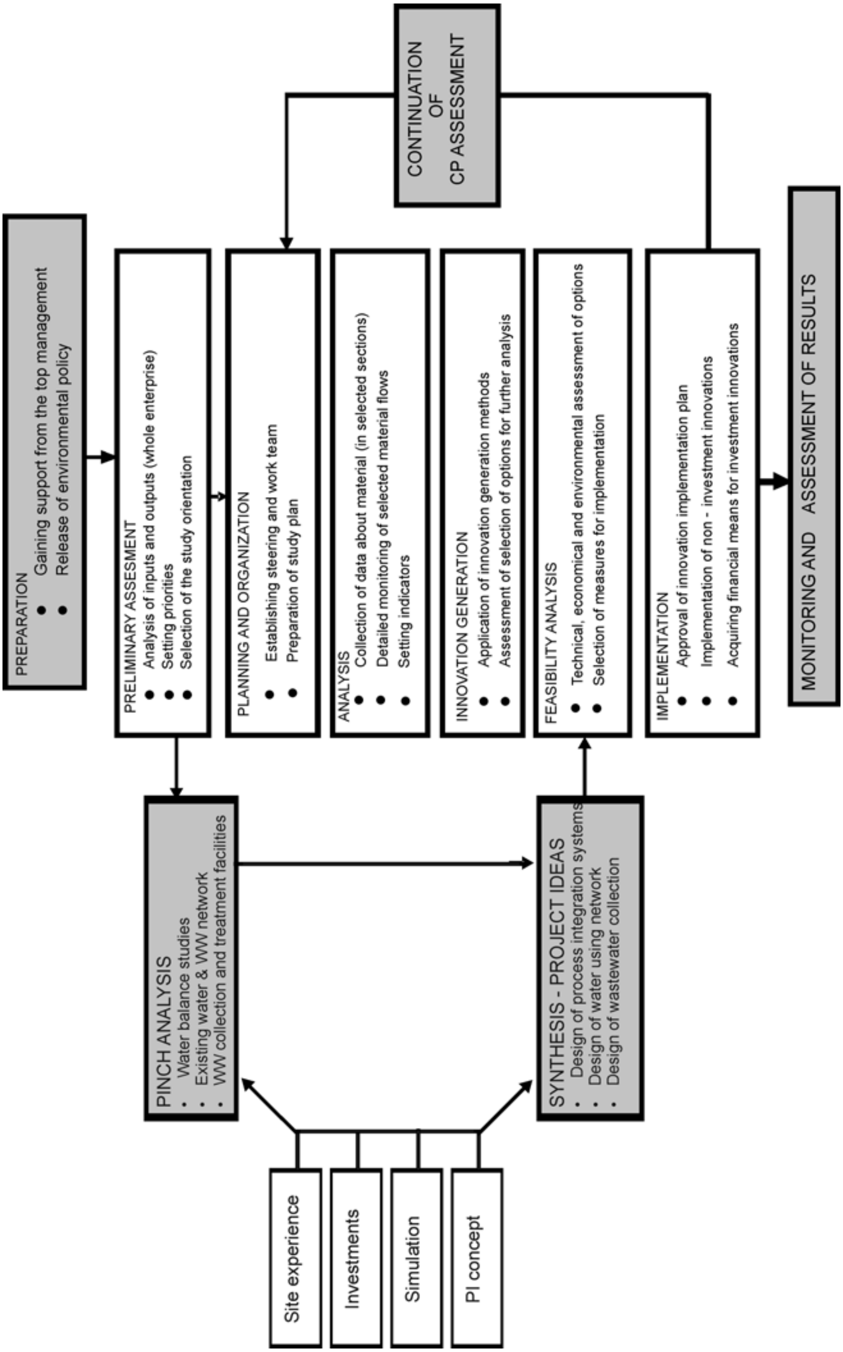

Fig. 12.8 Flowchart of integrated CP and water pinch assessment scheme

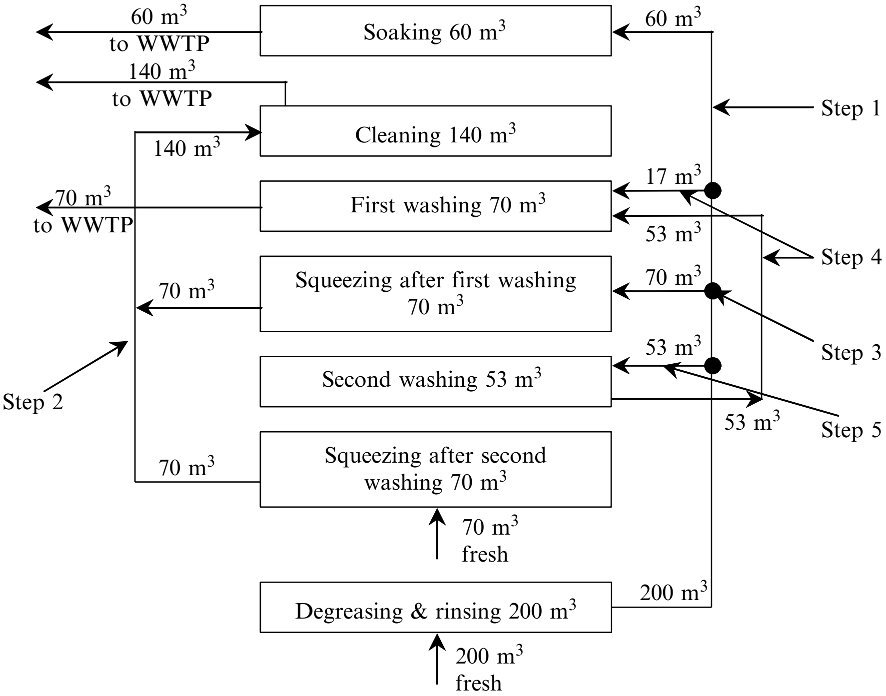

Fig. 12.9 Flow sheet presentation of water recycling in beamhouse operations (WWTP – wastewater treatment plant)

The Cleaner Production and Process Integration concept has been widely implemented in Lithuanian industries during the last decade. The experts of the Institute of Environmental Engineering (APINI) have played the crucial role in waste minimization innovations identification, evaluation, implementation and reporting. 85 industrial companies have implemented 177 waste minimization innovations. The impact of implemented waste minimization methods to the environmental performance improvement is summarized in Table 12.1.

12.4 Conclusion

As it was mentioned in the article, in most case of environmental systems there is incomplete and partial knowledge of the system, which has to be understood and controlled. The nature of knowledge is often incremental and greater insight is gained as analysis and control continues. The consequence of the way we view a system, and hence of the way we observe and measure it, is that our understanding of the system is limited by that view of measurement. In this paper it was demonstrated how systems analysis method can be applied to environmental problems to push

Table 12.1 Environmental benefits from preventive innovations implemented in 1994–2010 in different sectors of Lithuanian economy

	Environmental areas	Environmental benefits	Unit per year
1	Reduction in resource consumption/losses:		
1.1	Electricity	29,940	MWh
1.2	Heat energy	237,205	MWh
1.3	Chemicals and additives	2,289	t
1.4	Water	811.1	1,000 m^3
1.5	Oil	89.9	t
1.6	Fuel	448.1	t
1.7	Fuel consumption, etc. from heat energy saving or from reduction in heat energy losses in production and supply	22,071.61	toe
2	Reduced impact on the environment:		
2.1	Emissions to the atmosphere from stationary pollution sources	3,093.95	t
2.2	Emissions of greenhouse gasses (CO2)	79,759.53	t
2.3	Emissions to the atmosphere from mobile pollution sources	183.98	t
2.4	Wastewater volume	774	1,000 m^3
2.5	Wastewater pollution	521.21	t
2.6	Hazardous waste	621.5	t
2.7	Non-hazardous waste (or waste transformed into raw material for production of other products)	116,108	t
3	Indirect impact on the environment from electricity and heat energy saving (energy produced elsewhere):		
	Reduction in greenhouse gas emissions (CO2): In accordance to natural gas emission factor (in accordance to fuel oil emission factor)	7,107.46 (22,616.36)	t

back information accuracy constraints, to increase the degree of understanding of environmental systems and increase the possibilities of management. It could be concluded:

1. The most environmental problems dealing with interface between physico-ecological and socio-economic systems can be formulated from the systems theory point of view. This allows using modern systems theory methods to solve environmental problems. At the same time, two points must be clearly grasped. Firstly, that the understanding of the system does not necessarily imply that we can control it, and, secondly, that control has a meaning in terms of some stated goal.
2. The structured environmental management clearly shows, that emerging preventive environmental management paradigm differs significantly from the control paradigm of earlier management strategies and calls for new attitudes, not only to the development of production processes and the design of products, but also

to the relationships between consumer and the environment. It must be stated, that for sustainable economic growth and development, the environmental prevention paradigm as a technological and cultural means to achieve the desired compatibility between environmental and economical goals should be used.

3. As long as the material components of products are largely based on the use of virgin resources (including water), while energy is derived from fossil fuels, there is no way to reduce the output of wastes and pollutants below a certain minimum point using preventive management. Unless, the product cycle and materials cycle are (very nearly) closed, the system as a whole will continue to be unsustainable. In this case, preventive and reactive environmental strategies have to be used as a feedforward – feedback management structure.
4. The systems approach relies heavily on large amounts of accurate data, i.e. material and energy balances, which are used both to construct and test environmental models and in their manipulation. The more complex the system, the more data is required, both in space and time. At the same time, in most cases, there is a lack of basic environmental data, existing administrative fragmentation resulting in interfacing and compatibility difficulties, lack of interdisciplinary integration and well defined social goals. One of the main problems is the divorce of the data collector and the systems modeller.
5. Cleaner Production and Pinch analysis proved to be appropriate proactive methods to source/water consumption reduction and has to be included into corporate decision making process. Unlike the command and control regulations to ensure proper management of waste already created, the role of authorities and top management in promoting prevention might therefore be more appropriately viewed as catalytic – pressing manufacturing companies to identify prevention innovations that serve their own and public interest.
6. The integrated assessment model, comprising cleaner production and Pinch analysis methods, allows optimizing the environmental review, material and energy balance construction and feasibility analysis procedures. At the same time, integrated model opens more possibilities for closing water cycles in industry by preventive innovations, including their generation, financing and implementation.

The systems approach and modern systems theory provides a powerful vehicle for the estimation of environmental situation of ever-growing temporal and spatial magnitude and for reducing the areas of uncertainty in our increasingly complex decision-making and management situations based on feedforward – feedback closed loop systems.

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Chapter 13
An Energy Saving Process for the Reactivation of Activated Carbon Saturated with Organic Contaminants

Raymond A. Sierka

Abstract Activated carbon is the best broad-spectrum adsorbent available for the removal of dissolved organic material in aqueous solution. Granular activated carbon (GAC) has been commonly used to adsorb molecules that cause taste and odor, mutagenicity and toxicity. Synthetic organics, natural organic matter (humic and fulvic acids) pharmaceuticals, personal care products and disinfection by-products (chloroform) are well removed from domestic and industrial wastewaters. Physical adsorption efficiency of GAC is due to extensive surface area within the adsorbent deposited in a large range of pore sizes and volumes while the adsorbent surface chemistry affects chemisorption of adsorbates. Activated carbons have finite adsorption capacity that when exceeded, the adsorbent must be reactivated before reuse.

Off-site thermal regeneration of GAC, at temperatures in excess of 700°C, is currently the only viable technology employed for large amounts of spent carbon. Thermal processes have a large carbon footprint, requires high-energy inputs and result in adsorbent mass losses as well as changes in pore size distributions. These factors limit utilization of GAC particularly in developing countries.

A carbon regeneration process is described in which, contaminants adsorbed to activated carbon containing fixed iron oxides, are exposed to hydrogen peroxide (H_2O_2). The reaction of H_2O_2 and Fe (II) (Fenton's Mechanism) generate hydroxyl radicals ($^*OH$) that oxidize the adsorbates. The adsorbent is regenerated with minimum mass loss or alteration of the original pore size and volume distribution and adsorption capacity is restored. This process is conducted in situ at ambient tem-

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perature with low energy inputs and low carbon footprint. Research results for the chemical regeneration of methyl *tert*-butyl ether–spent GAC will be presented to demonstrate the application and feasibility of the Fenton based process.

Keywords Reactivation of GAC • Oxidation of organic contaminants • Fenton reaction • Fenton based regeneration of GAC

13.1 Introduction

The introduction of man synthesized organic matter (SOCs) and natural organic matter (NOMs) into the world's supply of fresh water require that these compounds must be removed before safe water reuse ensues. Activated carbon (AC), specifically granular activated carbon (GAC), has been shown to be the best broad-spectrum adsorbent available for this task. The economics of the GAC adsorption process is dependent upon the reactivation of the adsorbent saturated with dissolved organic matter.

The objective of this chapter is to detail a low energy, on-site, in-situ GAC reactivation process based on the use of two, time-tested technologies; adsorption onto GAC followed by chemical reactivation based on Fenton chemistry principles.

13.2 Organic Contaminants in Fresh Water

The available freshwater supply on Earth is estimated to be only 1% of the total water covering the planet. The current human population exceeds six billion and is growing at an exponential rate and therefore there is a parallel demand for fresh water. Protection of our water resources is of paramount importance in the twenty-first century.

The growth of SOCs in both type and amount from industries, agriculture, pharmaceuticals and personal care products (PPCPs) discharged into our water supplies has precipitated concern because of potential adverse ecological and human effects.

Research has demonstrated these chemicals enter the aquatic system in both regulated and unregulated fashion, disperse and in many cases persist in the environment. Conventional wastewater and potable water treatment plants are not capable of removing all SOCs to levels where harm will not be inflicted.

The U.S. Geological Survey [1] performed a comprehensive study of 95 organic compounds in 139 streams across 30 of the United States of America during 1999 and 2000. The sampling sites were downstream of urbanized and agricultural centers where contamination was most likely. The most frequently measured compounds were coprostanol (fecal steroid), cholesterol (human and animal), N,N-diethyltoluamide (insect repellent), caffeine (stimulant), Triclosan (antimicrobial disinfectant), tri (2-chloroethyl) phosphate (fire retardant), and 4-nonylphenol (nonionic detergent metabolite).

Pharmaceuticals and personal care products (PPCPs) enter the aquatic environment through daily domestic use either as unused products or as partially metabolized entities. The problem is immense. For example, the European Union (EU) [2] estimates that over 3,000 chemicals are employed in producing pharmaceutical medicines including painkillers, antibiotics, contraceptives, impotence drugs and tranquilizers. The production of personal care products (PCP) includes a vast array of compounds including skin and dental care products, sunscreen ointments and hair products. In Germany alone, the production of PCP's exceeded 550,000 metric ton year^{-1} during the 1990s. Specific chemical additions to PCPs include fragrances (nitro-and polycyclic-musks), UV blockers (methylbenzylidene camphor) and preservatives (parabenes and isothiazolin derivatives). These chemicals do not pass through human bodies but are directly added to sewers and septic systems and thus contaminate water bodies.

Sewage treatment plant effluents (STPE) and surface waters have been extensively studied [3] to identify trace organic compounds. The analytical emphasis has been on PPCPs and plasticizers. Studies conducted in Southern California [4] on reclaimed wastewater found 14 of the 19 target compounds that included hormones and metabolites, antioxidants and various pharmaceuticals.

Source water [1, 5–15] and finished potable water quality has also been the subject of considerable research. Stackelberg et al. [16] analyzed for organic compounds found in wastewater upstream, and through each unit process (coagulation-flocculation-sedimentation) of a conventional water treatment plant. Forty contaminants were identified in the source water and 17 were present in the finished water. Phthalate plasticizers have been reported present in bottled drinking water [17, 18]. A wide variety of contaminants have been identified with a large number emanating from prescription and non-prescription drugs as well as their metabolites, plant and animal steroids.

In utility produced potable water, measured concentration of organic matter was found to be low ($<1\ \mu g\ L^{-1}$) and rarely exceeded drinking water standards, drinking water advisories or aquatic life criteria. Primary Drinking Water Standards are based on the toxicity of individual compounds and not mixtures and therefore their combined presence in source water effect on human health and the environment is not currently known.

13.3 Contaminant Adsorption by Activated Carbon

Ternes et al. [19] studied the adsorption of 4 pharmaceutical compounds, bezafibrate, carbamazepine, ciofibric acid and diclofenac by a coal based pulverized activated carbon. Freundlich isotherms were employed to characterize the responses that provided evidence of their potential removal in water treatment plants. In pilot scale experiments Carbamazepine showed the highest adsorption of the 4 selected pharmaceuticals, as predicted by Freundlich isotherms. Clofibric acid was not well removed in flow-through carbon column experiments.

Adsorption is the accumulation of a substance at an interface between two phases (e.g. liquid–solid). The material being accumulated is the ***adsorbate*** while the accumulating medium is the ***adsorbent***. The surface area, pore size and volume distribution and surface chemistry of the adsorbent affect adsorption efficiency. Maximum adsorption is proportional to the amount of adsorbent surface area within the pores that are accessible to a given adsorbate. Commercially available GACs contain as much as 1,500 m^2 g^{-1} of total surface area. Distribution of the surface area is in micropores (<2 nm in diameter, d), mesopores ($2 < d < 50$ nm) and macropores (d >50 nm). Surface chemistry of GACs also plays a role in adsorption efficiency.

13.4 Thermal Reactivation of Spent Activated Carbon

Once activated carbon has been saturated or exhausted of capacity, the adsorbates must be removed to reactivate the spent activated carbon before reuse. Thermal reactivation of spent adsorbent has been employed for a considerable period of time in developed countries. The types of thermal furnaces include multiple hearth, rotary kilns and fluidized beds. Multiple hearth furnaces (MHF) are most commonly used to reactivate spent GAC.

The reactivation process involves four steps [20]. *Drying* is the first step where transport water for the spent GAC is volatilized together with highly volatile organic adsorbates at temperatures to 200°C. The second process is conducted between 200°C and 500°C, resulting in *vaporization* of volatile adsorbates and the partial decomposition of unstable adsorbates. Step three is the *pyrolysis* of non-volatile adsorbates and adsorbate fragments that leads to chars on the GAC surface. Pyrolysis occurs at temperatures ranging from 500°C to 700°C. In step four, the pyrolyzed chars are *oxidized* using steam or carbon dioxide as the oxidizing agent, normally at temperatures in excess of 700°C.

A MHF normally is configured with 5–8 hearths. Spent carbon enters the top hearth through a dewatering screw. The water content of the carbon slurry is approximately 50%. A rotating center shaft supporting arm with rabble blades conveys the carbon in a spiral path through each of the hearths and exits the furnace to a quench tank for cooling. MHF residence time is a function of rotation of the center shaft and the angle of the rabble arms. The furnace temperature profile is controlled by the amount of energy added, generally through burners located at the bottom of the furnace and the oxidation gas concentration. Table 13.1 [21] lists the typical overall parameters for an MHF.

MHF off-gases contain particulates and volatile organic matter not combusted to CO_2 in the reactivation process. Particulates are removed by water-scrubbers. Organic matter is passed through after-burner maintained at between 750°C and 1,000°C by burning fuel in excess oxygen.

Table 13.1 Typical overall parameters for multiple hearth furnaces (MHF)

Parameter	Value
Furnace loading (kg m^2 day^{-1})	195–561
Residence time (min)	120–240
Natural gas fuel (Nm^3 kg^{-1} C)	0.178–0.326
Steam (kg kg^{-1} C)	1.0–3.0
Heat Loss (%)	15.0
Carbon Losses (%)	5.7

13.4.1 MHF Reactivation Studies

Few large size GAC reactivation studies have been conducted and reported in the literature. A full-scale on-site GAC reactivation study [22] began in 1992 in the Richard Miller Water Treatment Plant in Cincinnati, Ohio that has a design capacity of 220 MGD (0.86×10^6 m^3 day^{-1}). During the study, the average flow was 112 MGD (0.42×10^6 m^3 day^{-1}). The plant has 12 GAC beds each containing approximately 21,000 ft^3 (595 m^3) of Calgon F-400 adsorbent. The GAC progressed through 6 cycles (adsorption/thermal reactivation) before the study was terminated.

The GAC volume losses noted were between 6% and 11% per reactivation. Pore size distributions were considerably different for the virgin and reactivated. While the surface area of the virgin F-400 was mostly found in the micropores and less in the mesopores, reactivated GAC was mostly mesoporous, with less micropores. Adsorption by the virgin GAC significantly altered the volume of pore below 50A in width with minor changes in pores larger than 50A. By comparison, the reactivated GAC produced the greatest volumetric change in the pore size range 100–500 Å in width. Surface chemistry of virgin and reactivated GAC was not addressed in this study.

13.5 A Low Energy Process for the Reactivation of Spent GAC

Chemical reactivation of spent GAC employs two well understood treatment technologies: *adsorption* onto GAC and *Fenton driven oxidation* in a synergistic scenario. Adsorbates are transformed by hydroxyl radicals (*OH) and other reactive species during the reaction of H_2O_2 and iron (Fe) immobilized on GAC surfaces prior to the initiation of wastewater treatment. The treatment process objectives include transformation of adsorbed contaminants into less toxic by-products, the re-establishment of sorptive capacity of spent GAC for the target chemicals, the increase in treatment life of the GAC and reduction of costs associated with adsorbent reactivation and pollution emissions, for both air and water phases. Chemical reactivation is carried out ***on-site***, eliminating the need for off-site transport and thermal reactivation and ***in-situ*** that is, in the vessel that contains process activated carbon. GAC reactivation is performed at ***ambient temperature*** or at slightly elevated temperatures if desired, thus achieving a ***green***, ***low carbon footprint*** with ***minimal energy inputs*** for the process. Figure 13.1 is a process schematic.

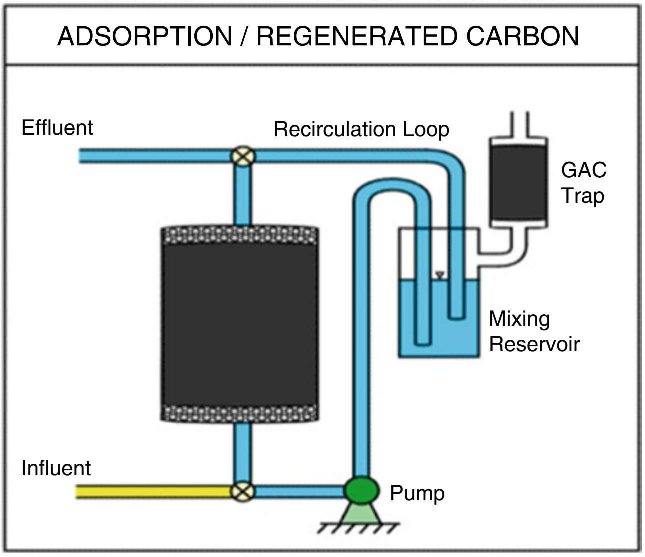

Fig. 13.1 A low energy process for the reactivation of spent GAC

13.5.1 Process Parameters

The classic Fenton driven oxidation mechanism for the continuous production of radicals ($^{*}OH$) (reaction 13.1) and side reactions, where Fe (II) is regenerated from Fe (III) (reactions 13.2 and 13.3), is depicted below [23]. While $^{*}OH$ reacts rapidly [24, 25] with virtually all organics including MTBE (1.6×10^9 L mol^{-1} s^{-1}), it is non-selective and therefore reactants (in this case the adsorbates, Fe and oxidant) must in close proximity to optimize reaction conditions.

$$\text{Fe }(\text{II}) + H_2O_2 \rightarrow \text{Fe }(\text{III}) + {}^{*}OH + O \tag{13.1}$$

$$\text{Fe }(\text{III}) + H_2O_2 \rightarrow \text{Fe }(\text{II}) + {}^{*}O \tag{13.2}$$

$$\text{Fe }(\text{III}) + {}^{*}O_2^{-} \rightarrow \text{Fe }(\text{II}) + C \tag{13.3}$$

In commercial reactivation systems, non-ideal reactions occur. The first are reactions that proceed when H_2O_2 is consumed without the production of $^{*}OH$ and the second is the scavenging of $^{*}OH$ by H_2O_2 and other non-target reactions.

Commercially available activated carbons produced from various starting raw materials (e.g. coal, wood natural fibers) vary considerably in iron content. GAC produced from coal has the highest associated iron concentrations while wood based carbons have considerably less metal concentration.

Experimental and field studies have been conducted by the University of Arizona and the United States Environmental Protection Agency (USEPA) [please see Appendix for a specific list of references for this research] to demonstrate chemical reactivation concept viability and to optimize process parameters including; (1) GAC type, (2) amended iron concentration, (3) H_2O_2 concentration, (4) GAC pretreatment prior to iron amendment (5) reaction temperature and (6) contaminant type. The focus of this paper will be on the results obtained with methyl *tert-butyl ether* (MTBE) as the adsorbed specie in single substrate laboratory experiments. Experimental protocols are detailed [29] elsewhere.

MTBE is a gasoline additive and according to the USEPA there may be as many as 250,000 releases associated with leaking underground fuel tanks in the United States [26]. Because MTBE has high water solubility, a low Henry's constant and bio-recalcitrance, it is mobile and persists in the environment [27, 28]. Adsorption by GAC is a technology capable of removing MTBE, albeit a costly one. For these reasons MTBE was chosen for in-depth study.

13.5.2 GAC Type

For all the studies reported below a single GAC type URV, obtained from the Calgon Carbon Corporation, was employed. URV is produced from a bituminous coal, however it is steam activated by a special technique to produce an adsorbent that has minimal H_2O_2 reactivity (Hayden R, 2001, Calgon corporation, Pittsburgh, personal communication). The iron concentration of URV ranges between 980 and 1,070 mg kg^{-1}. The surface area is 1,190 $m^2\ g^{-1}$ (95% C.I. 1,110–1,270 $m^2\ g^{-1}$) while the total pore volume is 0.59 mL g^{-1} (C.I. 0.53–0.66 mL g^{-1}). Micropore volume is 0.39 mL g^{-1} and the mesopore plus macropore volume is 0.26 mL gm^{-1}.

13.5.3 Amended Iron Concentrations

While all GAC's contain some iron, the concentration is insufficient for Fenton chemistry purposes. Experiments have been conducted [29] to investigate external additions of iron to UVR. One major concern about iron addition to an adsorbent is the potential for reduction of micropore area and pore blockage. The optimum iron concentration for adsorption and Fenton oxidations requires further investigation.

Shown in Table 13.2 are the various concentrations of Fe amended to UVR and the fraction of Fe retained on the GAC. The Fe concentration on the GAC ranged from background to over 25 times the background UVR concentration. Three basic reactions types, precipitation, ion exchange and complexation, all contribute to iron amendment on the adsorbent. Retained iron was shown to be proportional to the initial iron solution concentration indicating a saturation effect. Approximately 31 $m^2\ g^{-1}$ in N_2 BET surface area and 0.015 mL g^{-1} of pore volume loss were experienced per 5,000 mg L^{-1} of Fe amended. This represents about 2–3% loss of original surface area (1,250 $m^2\ g^{-1}$) and pore volume of (0.64 mL g^{-1}) of the URV adsorbent (Fig. 13.2).

Table 13.2 Pre-oxidation results of Fe to the GAC[a]

Reactor	Final $[Fe]_{Gac}$[b] (mg kg^{-1})	Fraction retained[c] (%)
A	1,020 (background)	–
B	4,270	97
C	6,710	98
D	9,640	98
E	12,630	98
F	15,760	95
G	16,900	89
H	18,520	81
I	23,500	68
J	25,660	97

[a] Background (Fe) = 1,020 mg kg^{-1}

[b] 95% C.I. in parenthesis (n = 3)

[c] Mass fraction of Fe retained after treatment ((Initial $[Fe]_{AQ}$ – Final $[Fe]_{AQ}$)/ Initial $[Fe\}_{AQ}$) × 100

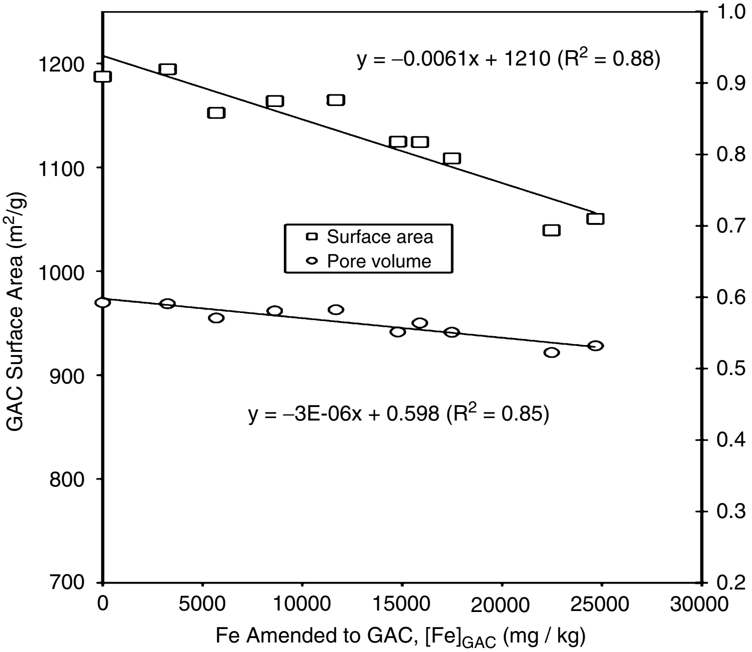

Fig. 13.2 Inverse correlation between the quantities of iron added to the GAC and the GAC surface area and pore volume

13.5.4 MTBE Adsorption and Oxidation

Batch adsorption and reactivation experiments were conducted [29] to determine the effect of Fe concentration (see Table 13.2) amended to UVR. Oxidation of MTBE is increased by a factor of ten over background from the amendment of Fe. The apparent optimal iron loading was approximately 6,710 mg kg^{-1} (reactor C)

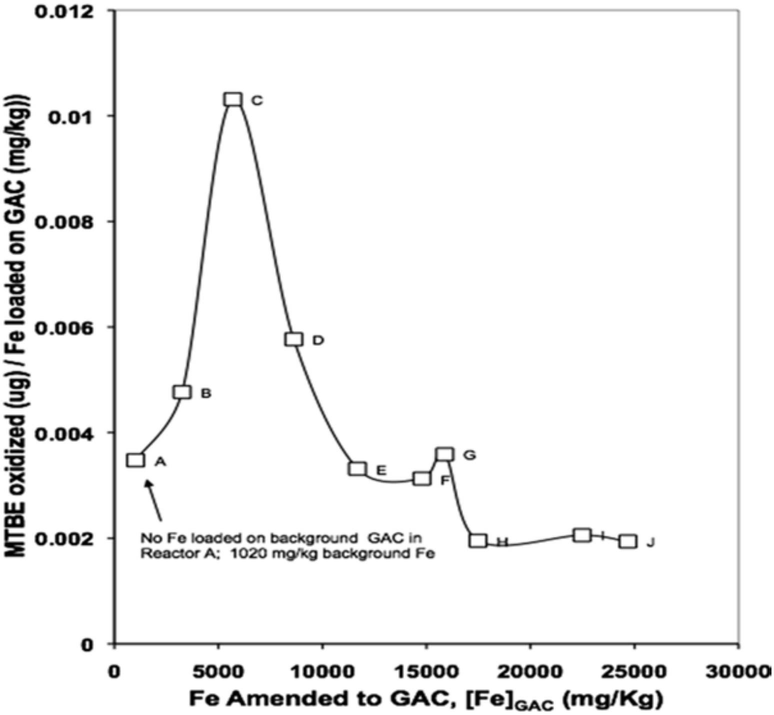

Fig. 13.3 MTBE degraded in the GAC is functionally dependent on the Fe concentration in the GAC. Amended Fe was calculated as the difference between background (1,020 mg kg^{-1}) and the final iron concentration in the GAC

where the highest MTBE removal was noted relative to the background reactor (reactor A) and where the highest Fe loading efficiency was measured (Fig. 13.3).

13.5.5 H_2O_2 Concentration

Shown in Fig. 13.4 is the non-linear relationship between total Fe and pseudo first order H_2O_2 degradation rate constant. These data indicate that H_2O_2 was somewhat limited by Fe concentration at higher concentrations and other mechanisms affect H_2O_2 reaction. Three mechanisms have been cited as possibly responsible for this response; (1) Fe blockage of H_2O_2 transport in the GAC, (2) unavailable Fe, and (3) the effect of fast H_2O_2 reaction rates on H_2O_2 diffusive transport. Essentially the mechanisms limited the contact of GAC surface area, H_2O_2, Fe and MTBE.

13.5.6 Acid Pretreatment and Temperature Effects

Acidic iron solutions amended to GAC deposit between 18 and 20 μm from the adsorbent periphery [29]. The effect of acid pretreatment was investigated to

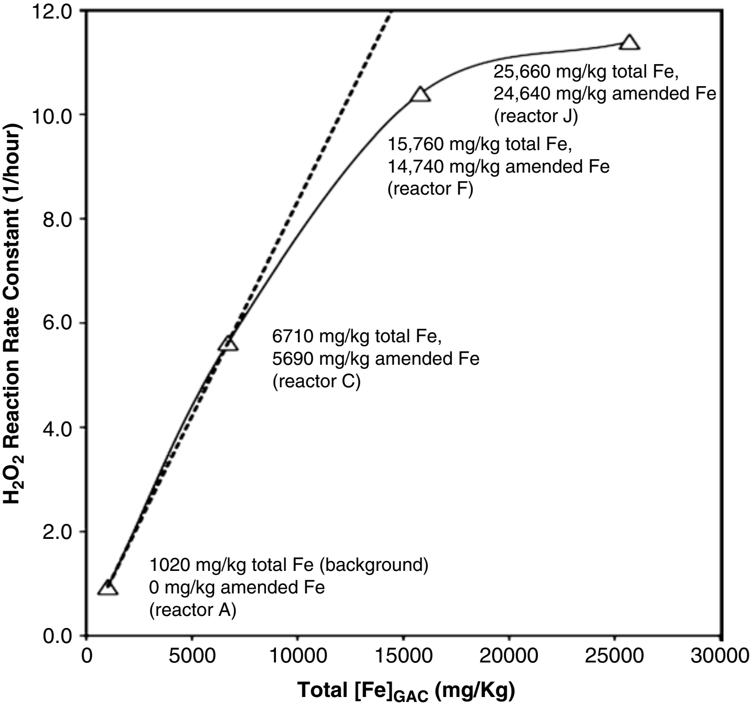

Fig. 13.4 Non linear relationship between total Fe (background plus amended) and the pseudo first order H_2O_2 degradation rate constant

reduce electronic repulsive forces between Fe^{3+} of Fe^{2+} in solution and the positively charged carbon surface that could hinder penetration and deposition of iron deep within the GAC pore structure. Acidic pretreatment basically alters the surface chemistry of the adsorbent by increasing carboxylic and lactonic acid surface oxide groups, increasing the cation exchange capacity [31] and Fe sorption lowers the pH_{ZPC} [32] of the GAC. Application of the iron solution at a pH above pH_{ZPC} of the GAC reduces electronic repulsion and permit greater penetration and dispersion in the adsorbent. Extension of the iron rich zone within the adsorbent promotes Fenton oxidation of the adsorbate. Positive impacts on intra-particle desorption and diffusion were observed. The roles of temperature on MTBE desorption and diffusion, H_2O_2 diffusion and reaction, and subsequent effects on MTBE oxidation and UVR reactivation have likewise been studied.

Examination of the data in Fig. 13.5 indicates that MTBE oxidation and removal increased as a result of UVR acid pretreatment and an increase in reaction temperature. Under all experimental conditions, the H_2O_2 reaction rate constant also increased (Fig. 13.6).

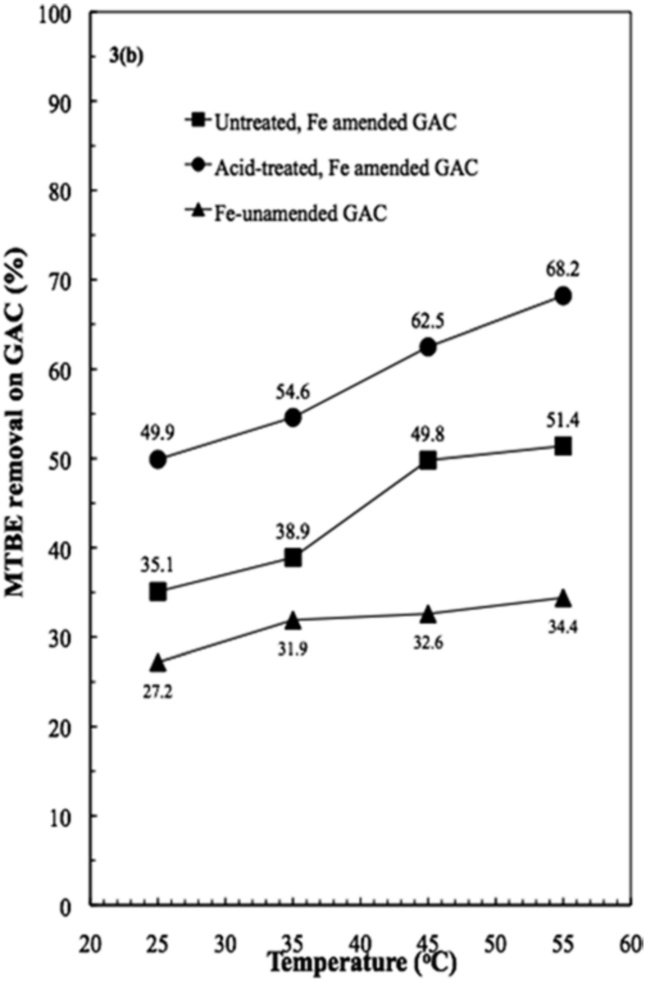

Fig. 13.5 Temperature dependent MTBE removal in the GAC

13.5.7 Other Contaminant Studies

Adsorption plus Fenton oxidation reactivation experiments have been conducted on a wide range of environmental contaminants with success. The contaminants chosen represent industrial contaminants that significantly impact water resources. The chemicals studied, and the reactivation levels achieved are listed in Table 13.3.

These oxidation-reactivation experiments demonstrate the viability of the concept. However, the questions of GAC degradation and performance after reactivation as well as the stoichiometry and kinetics of H_2O_2 in adsorbent reactivation have been addressed.

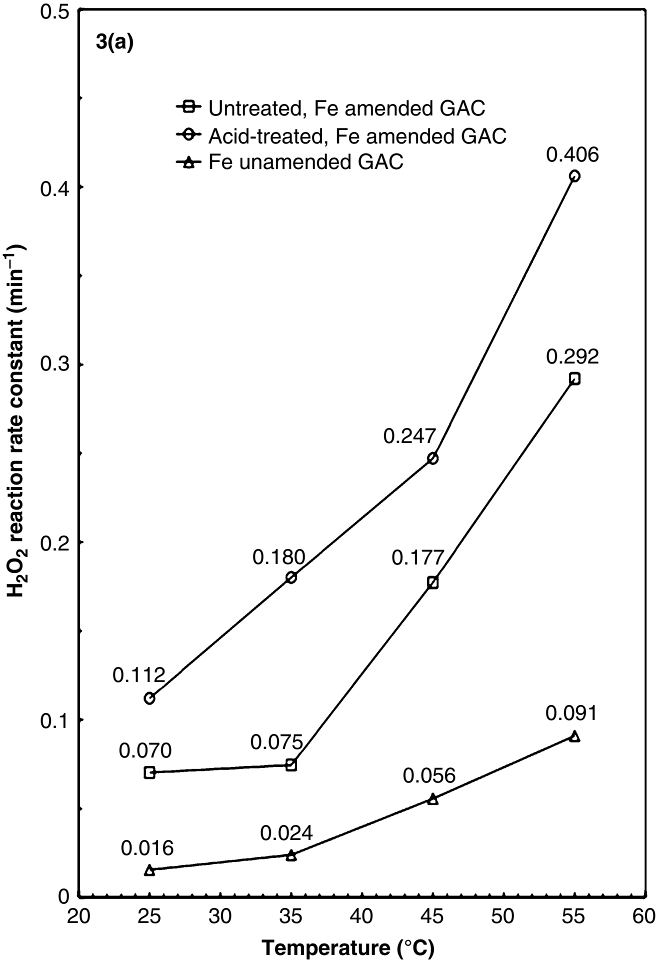

Fig. 13.6 Pseudo first-order H_2O_2 reaction rate constants for acid-treated and untreated Fe-amended and Fe-unamended GAC at 25°C, 35°C, 45°C, and 55°C

Table 13.3 Fenton based reactivation of Gac's saturated with various industrial chemicals

Chemical tested	Gac reactivation level	References
Trichlororthylene	73–95%	[33]
Methylene chloride	100%	[33]
Chloroform	94%	[33]
N-nitrosodimethylamine	99%	[34]
MTBE	91%	[35]
Di-isomethyl phosphate	97–98%	[36]

In the study of Huling et al. [37] repeated H_2O_2 treatment in Fe-amended adsorbate-free GAC was performed. After 15-sequential applications of H_2O_2, there was a 4% mass loss of GAC, 15% loss in total surface area, a 30% reduction in Iodine Number, a 37% loss in micropore volume with a concomitant increase in meso plus macropore volume. Losses in sorption capacity for 2CP, TCE, and MTBE were observed.

A companion study [35], employing the identical GAC and chemical treatment conditions discussed above, however for these experiments an MTBE-spent GAC was employed. The differentiating factor between the experiments was the presence of an adsorbate, MTBE. Two full reactivation cycles (adsorption followed by oxidation) were twice carried out followed by an adsorption step. Comparing the data from the two experiments, differentiated only by the presence or absence of adsorbate (MTBE), there was no GAC mass loss, a 5 times less loss in surface area and pore volume and no loss in adsorption capacity for MTBE. Reactivation of the GAC was limited to 91%. It is postulated that the residual adsorbate protected the adsorbent from oxidation by $^{*}OH$ and reaction by-products.

It is apparent from the experience derived from these experiments that an optimal balance needs to be established between the GAC reactivation level and the amount and application methodology for $H_2O_{2.}$

13.6 Conclusion

The Earth's population is growing exponentially, with a parallel demand for fresh and safe water. Chemical inputs from industry, agriculture, pharmaceuticals and personal care products of SOC's portend the potential for adverse ecological and human effects. Current water and wastewater treatment facilities are not designed to remove SOC's.

The best broad spectrum adsorbent for the removal of deleterious contaminants in water is GAC. The economics of GAC treatment is dependent upon reactivation. Reactivation of spent GAC at low cost, with minimal adsorbent mass loss and without substantial changes in the adsorption properties of the adsorbent must be achieved.

Off site thermal (temperatures to 700°C) reactivation of spent GAC is the currently employed procedure although this process (MHF) has large carbon footprints. Full scale testing has established that large GAC mass losses and substantial changes in pore size and volume distributions occur after each reactivation. Large energy inputs and costly post reaction control of emissions are also required.

An energy saving process for the reactivation of spent activated carbon has been developed. The process employs adsorption onto GAC followed by Fenton driven oxidation. Adsorbates are transformed by hydroxyl radicals and other by-products of the reaction between iron amended to the GAC and H_2O_2. Chemical reaction is carried out on-site and in the adsorber columns at ambient temperature, resulting in a low carbon footprint minimal energy process. This GAC reactivation protocol is applicable to a wide variety of adsorbed contaminants. This Green Technology extends the potential for activated carbon treatment systems to protect potable water supplies at an acceptable cost.

Acknowledgements Dr. Scott Huling of the United States Environmental Kerr Research Laboratory is responsible for initial and on-going research on the topic presented in this paper. Professor Robert G. Arnold of the University of Arizona likewise contributed to these studies and together with the author were the inventors of the activated carbon regeneration process described herein.

Appendix A: Chemical Regeneration of Granular Activated Carbon (GAC)

Numerous publications and patents have been published involving the fundamental mechanisms in chemical regeneration of GAC. These studies include the investigation of key parameters, and optimization of the treatment process. Studies involving the field-scale deployment of the technology involving MTBE-contaminated ground water, and persulfate-driven chemical regeneration of GAC have been completed and publication is imminent.

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Chapter 14
Industrial Wastewater Treatment Systems in Egypt: Difficulties and Proposed Solutions

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Abstract The industrial wastewater disposal into surface water and/or land has become a vital issue to consider especially when it becomes a threat to the aquatic life and surrounding environment. Consequently, thorough studies and analyses should be done for the quality of wastewater being discharged from the different industries to determine and implement the most suitable method of treatment at feasible costs. In Egypt, this has been done for 10th of Ramadan City, New Nubaria City, New Borg El Arab City, and Industrial Area of Mubarak – Quesnna. It was found that the optimum treatment facility to be used for the first was oxidation ponds for the availability of vast areas; for the second city best results for treating combined domestic and industrial WW was to construct an anaerobic pond at the inlet of the existing WWTP with a retention time of over 6 h, which can be considered as flow equalization basin; for the third city, studies showed that best results could be attained when domestic and industrial WW are mixed and treated using an activated sludge process but replacing the primary tanks with anaerobic ponds; as for the fourth and last city, it was recommended to install additional units to enhance the treatment of industrial WW before combining it with the received domestic WW to proceed with the treatment process.

Keywords Anaerobic ponds • Chemical treatment • Cost • Industrial WW • Organic load • UASB

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14.1 Introduction

The effluent constituent of wastewater released from industries varies depending on the type of production of the industry. Organic loads in terms of BOD and TSS could alter along the day causing high short-term loadings, in other words "shock loadings"; this becomes a prime problem in the operation of treatment plants with limited capacities [5]. Moreover, various hazardous materials such as heavy metals, organic micro-pollutants, solvents, paints and other chemical are produced from different industries with various activities [3]. Consequently, it is necessary that industries don't drain their effluent wastewater nor to collections systems, nor to treatment facilities before being analyzed and determining their constituents and mass loadings before disposal. About 50% of the industries in Egypt, on statistical analyses done for 37 industries in Egypt, violate the Egyptian environmental law and discharge their effluents into the public sewage network [2] leading to deterioration problems in the sewage pipe network, the biological activity during treatment in WWTPs and threatening the aquatic life in streams and rivers; specially that industrial WW could contain massive loads of toxic materials and increase the cost and environmental risks of sludge treatment and disposal [1].

Hence, the properties of industrial wastewater should be studied in terms of its physical characteristics (which include: solid material, odor, temperature degree, color, and turbidity), chemical characteristics (which include: organic material, industrial detergent, phenol, volatile organic material, organic components indicator, inorganic material), and biological characteristics before discharging the effluent to the sewage network.

This research includes studies done for the combined domestic and industrial WW produced from four Egyptian cities which include: 10th of Ramadan city, New Nubaria city, New Borg El Arab city, and Mubarak industrial zone in Quesnna and shows the different proposed treatment facilities to enhance the final effluent treated quality of the combined domestic and industrial wastewater before discharging it to surface waters.

14.2 Materials and Methods

In order to determine the most suitable type of treatment for each of the above mentioned city, industrial wastewater samples were taken to be analyzed at the Egyptian labs to identify its constituents and loads to be treated. Tests were done to measure pH, COD, BOD_5, TSS, TDS, precipitated solids in 10 min, precipitated solids in 30 min, oil and grease, and phenol using the American Standards Methods. Results are presented in Table 14.1 below. It is worth mentioning that some of the cities don't include separate networks to receive the industrial and domestic wastewater produced but they depend on common networks as those networks of 10th of

Table 14.1 Available characteristics of industrial wastewater for some Egyptian countries compared to the allowable limits determined by the Egyptian environmental law

Type of test	Unit	10th of Ramadan	New Nubaria	New Borg El Arab	Mubarak industrial zone	Allowable limits[a]
pH	–	5.2–6.6	4.9–6.3	5.5–8.1	4.8–8.9	6–9.5
COD	mgO_2L^{-1}	760–1,646	953–7,600	945–1,454	1,790–9,680	1,100
BOD5	mgO_2L^{-1}	420–900	389–2,390	319–417	1,050–3,900	600
TSS	mg L^{-1}	220–610	250–1,200	400–504	1,153–2,750	800
TDS	mg L^{-1}	1,122–1,200	1,700–7,800	–	–	2,000
Precipitated solids in 10 min	mg L^{-1}	15.0	7.0	25	2.0	8.0
Precipitated solids in 30 min	mg L^{-1}	17.0	11	27.0	12.0	15.0
Oil and grease	mg L^{-1}	81–112	20–50	25–385	32–304	100
Phenol	mg L^{-1}	0.7	–	0.74	0.2	0.05

[a] Allowable limits to be discharged to the sewerage system are set according to Law no. 44/2000 in Egypt

Ramadan city. Some cities include separate networks for industrial and sanitary wastewater, which combine in pump stations (PS) before treatment such as in New Nubaria city. Other countries contain separate networks and PSs to the treatment plant such as New Borg El Arab city and Mubarak industrial zone.

As a means to protect WWTPs and its treatment systems, the Egyptian authorities had set up standards and limits for the allowable concentrations of pollutants in the industrial wastewater discharged by the different industries to the sewage network system. This part of the study includes different systems used at current for treating these types of WW and suggested methods for enhancing the treatment efficiency of industrial wastewater whether the waste produced from industrial areas or those combined with sanitary wastewater for the different cities.

14.3 Case Study I: 10th of Ramadan City

Main Problem: As illustrated in Fig. 14.1, there are currently two sources for industrial wastewater at 10th of Ramadan: the first source includes industrial waste only (treated and untreated) with a flow rate of about 130,000 m^3 day^{-1} coming from heavy industrial zone at south of the city; the second source includes the industrial waste coming from the boundaries of the residential area combined with domestic sewage. Despite the presence of independent networks for wastewater for every area, the industrial and sanitary wastewaters are combined in the main common lines to be discharged to the treatment plant. The flow rate of the combined industrial and sanitary wastewater is estimated to be approximately 90,000 m^3 day^{-1}, 55.5% of which represents industrial wastewater.

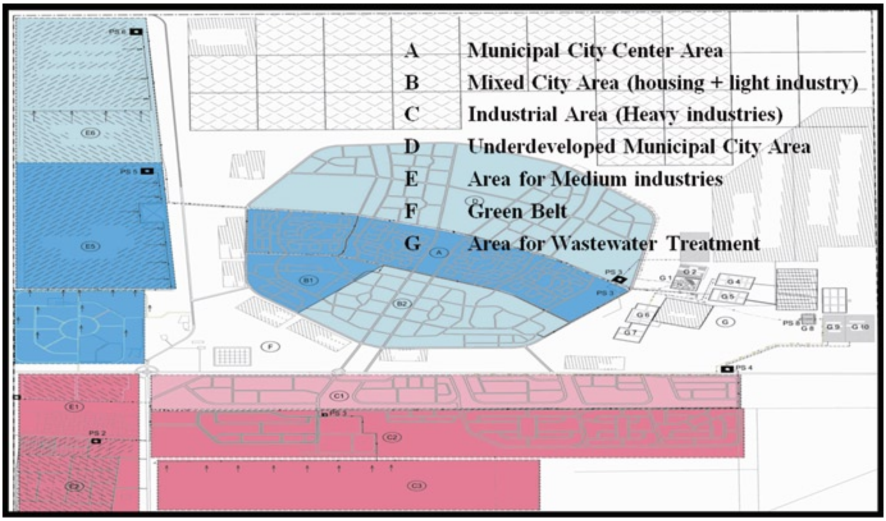

Fig. 14.1 Project area at 10th of Ramadan city

14.3.1 First Source: Raw Industrial Wastewater Treatment

Industrial wastewater received from the south of the city is discharged into oxidation ponds number 3 as shown in Fig. 14.2. These ponds were established in the eastern boundaries in the 10th of Ramadan with a design capacity of 60,000 m^3 day^{-1}, including (anaerobic, facultative and maturation ponds). Currently, the efficiency of these three ponds is deteriorating due to hydraulic over loads and the lack of purification and maintenance ever since they have been established. In addition, these ponds are not coated and they had turned into forests full of trees, grass and ditch reed with high densities affecting the efficiency of treatment in these ponds. Table 14.2 displays the characteristics of influent and effluent WW from these ponds by samples taken and analyzed by the city authorities at year 2007. Results clearly show that these ponds are unable to treat industrial wastewater to reach the allowed standards.

14.3.2 Second Source: Combined Domestic and Industrial Wastewaters

Combined domestic and industrial wastewaters are gathered from the networks to the main PS which directs all wastewater of about 90,000 m^3 day^{-1} to the mechanical WWTP (primary treatment), then to the aerated lagoons to continue secondary treatment; yet the effluent concentrations as displayed in Table 14.3 don't comply with the allowable standards.

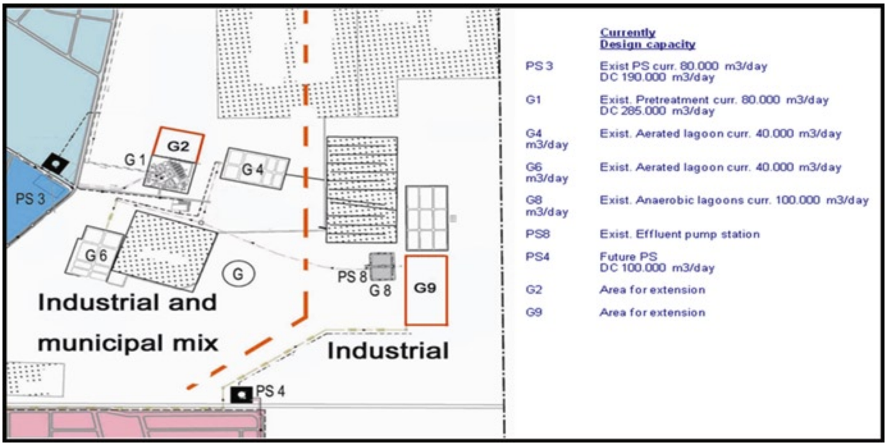

Fig. 14.2 Schematic diagram showing all the existing WWT facilities in 10th of Ramadan city and the suggested solution for enhancement of all facilities

Table 14.2 Result of analyzed samples taken from the influent and effluent of oxidation ponds no:3

		Concentration from ponds no:3 (mg L^{-1})	
Item	Unit	Influent	Effluent
TSS	mg L^{-1}	447–610	120–394
COD	mg L^{-1}	760–1,646	341–698
BOD_5	mg L^{-1}	635–900	240–380

Table 14.3 The characteristics of raw, primary, and secondary treated combined domestic and industrial wastewater

Item (ppm)	Characteristics of raw industrial WW	Results of primary treated WW (from mechanical WWTP)	Results of secondary treated WW (from aerated lagoons)	Required WW characteristics according to law 48/1982
COD	814–1,542	650–1,033	340–676	80
BOD	420–780	260–620	190–300	60
TSS	220–440	154–220	160–290	50

14.3.3 Suggested Solutions for Enhancing Industrial Wastewater Treatment in the 10th of Ramadan City

Aiming to reach the effluent allowable standards, it is suggested that industrial wastewater be separated from residential wastewater; this would allow better treatment of the domestic wastewater and the ability to use treated effluent in irrigating green areas inside the population mass as well as irrigating some crops. As for the industrial wastewater treatment, three different alternatives are proposed in the following lines:

- First alternative: Using chemical treatment
  Chemical treatment is the most suitable ways in treating industrial wastewater. A study was conducted to experiment a number of curdled chemical substances (lime, Alum, H_2O_2 and Ferric chloride) for raw and combined industrial WW. Ferric chloride was chosen for combined domestic and industrial wastewater resulting from the 10th of Ramadan city because of the small dose required (300 mg L^{-1}) in addition to the minimized amount of sludge produced compared to other chemical substances. However, the cost of using ferric chloride in treatment would reach 725,000 £ wk^{-1}, the number of required sludge concentrating tanks would increase from 4 to 20 tanks, and the number of required sludge drying tanks would increase from 29 to 285 tanks.

  This study concluded that it is difficult to use chemical treatment from the practical and economical aspect despite of its success from the practical aspect. According to what was previously mentioned, it is not recommended to use chemical treatment for industrial wastewater in the 10th of Ramadan city.
- Second alternative: Using UASB reactors
  UASB system is one of the modern treatment methods and is ideal for treating industrial wastewater which contains high proportions of COD that may exceed 10,000 mg L^{-1}. Its efficiency in removing COD could vary from 60% to 80%. However, this system is more expensive either in establishing, operating or maintenance from natural oxidation ponds. It also faces a lot of difficulties in implementation and requires well trained technicians and automatic controlling devices in all operation sections of the plant. Thus, it wouldn't be advised to use such a system in this case, especially at high industrial flow rates (about 180,000 m^3 day^{-1} currently and approximately 570,000 m^3 day^{-1} by the year 2050).
- Third alternative: Using anaerobic ponds followed by activated sludge system
  The most suitable and preferred method for treating industrial wastewater (180,000 m^3 day^{-1}) is to use anaerobic oxidation ponds to primary treat the industrial wastewater in order to reduce the concentration of COD and TSS followed by an activated sludge system. This can be achieved using the new established anaerobic ponds (180,000 m^3 day^{-1} total design capacity), not working yet, followed by the existing aerated lagoons (190,000 m^3 day^{-1} total design capacity) as illustrated in Figs. 14.2 and 14.3. For the domestic WWTP, it is proposed to construct secondary treatment (Biolak system) along with the existing primary tanks to treat all the domestic wastewater produced at 10th of Ramadan (which is about 286,000 m^3 day^{-1}) as illustrated in Figs. 14.2 and 14.4. It is proposed to implement a Biolak system (aeration and sedimentation occur in the tank) to follow the existing primary tanks, then allow the effluent wastewater to flow through sand filters for tertiary treatment.

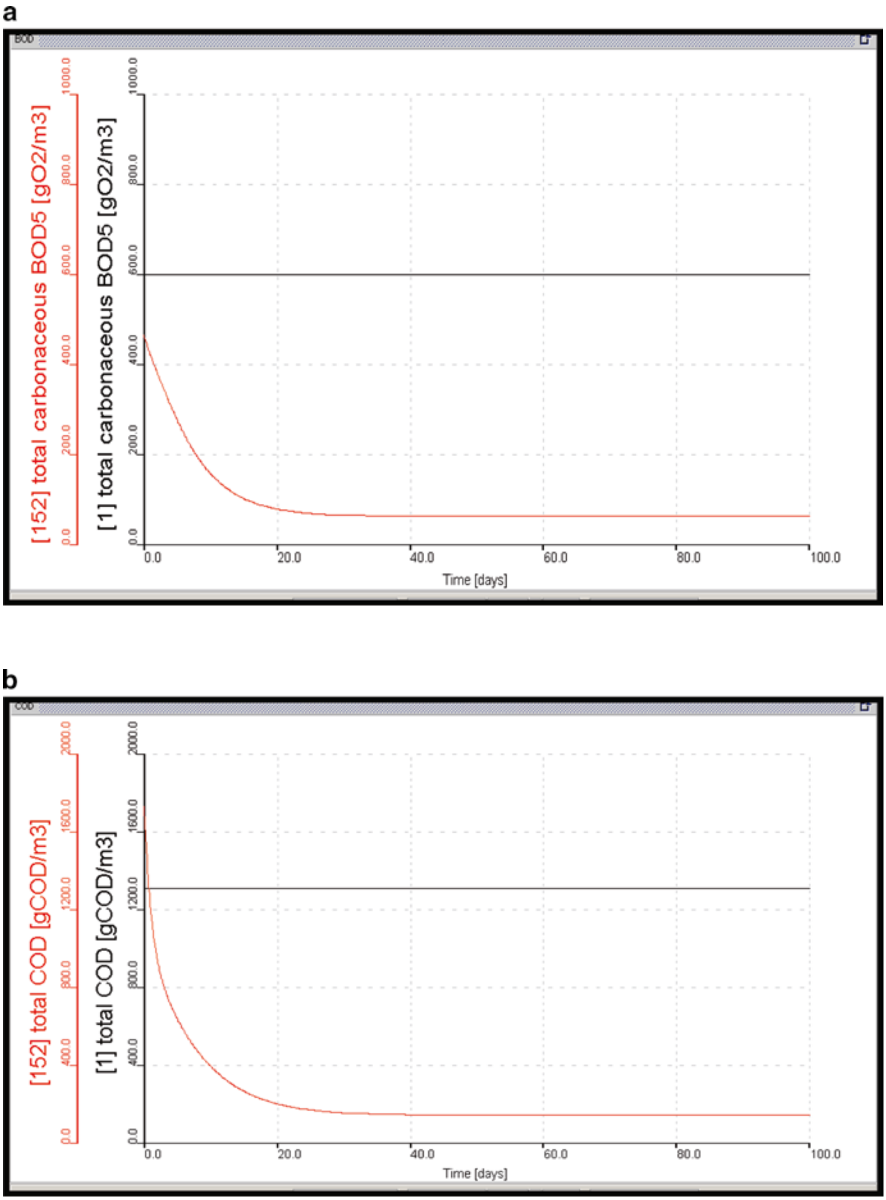

Fig. 14.3 Proposed connection between the new established anaerobic ponds and the existing aerated lagoons to treat all discharged industrial wastewater from 10th of Ramadan industries. (**a**) BOD5 inlet and outlet concentrations in the proposed system ($BOD_{in} = 600$ g O_2 m^{-3}, $BOD_{out} = 60$ g O_2 m^{-3}). (**b**) COD inlet and outlet concentrations in the proposed system ($COD_{in} = 1{,}400$ mg L^{-1}, $COD_{out} = 180$ mg L^{-1}).

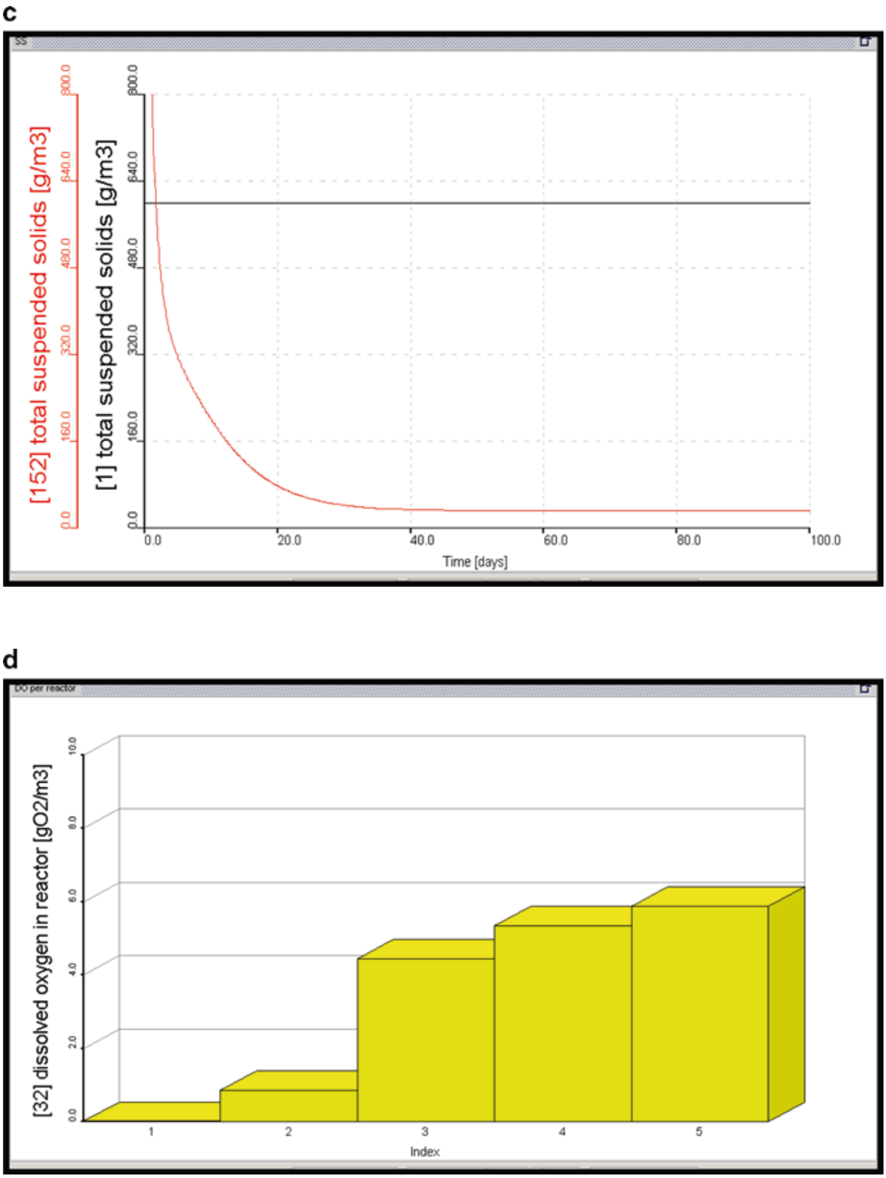

Fig. 14.3 (continued) (**c**) Suspended solids inlet and outlet concentrations in the proposed system ($SS_{in}=600$ mg L^{-1}, $SS_{out}=33$ mg L^{-1}). (**d**) Dissolved oxygen effluent concentration in the proposed system (Effluent DO = 5.8 mg L^{-1})

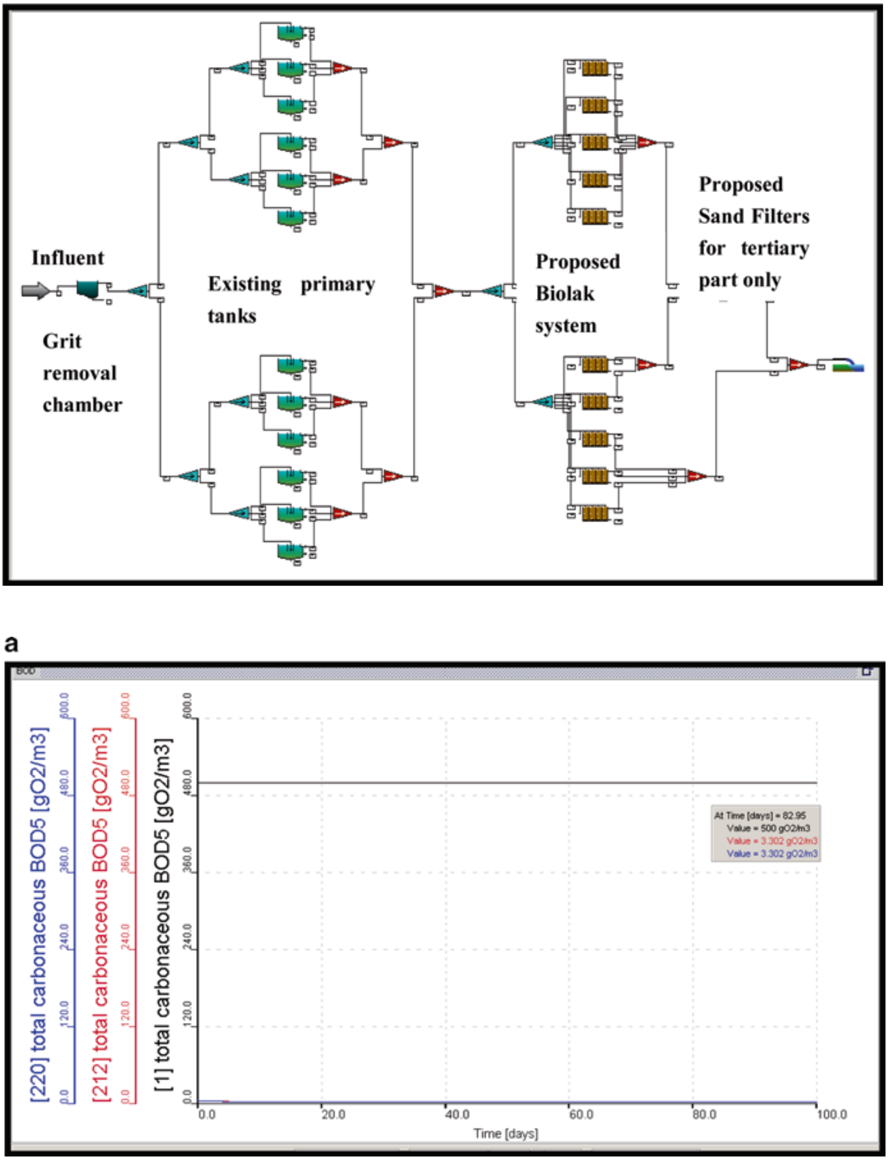

Fig. 14.4 Proposed extensions of mechanical WWTP using the existing PSTs followed by Biolak basins and slow sand filters to treat the domestic wastewater discharged by the city. (**a**) Total carbonaceous BOD5 concentrations in the proposed system.

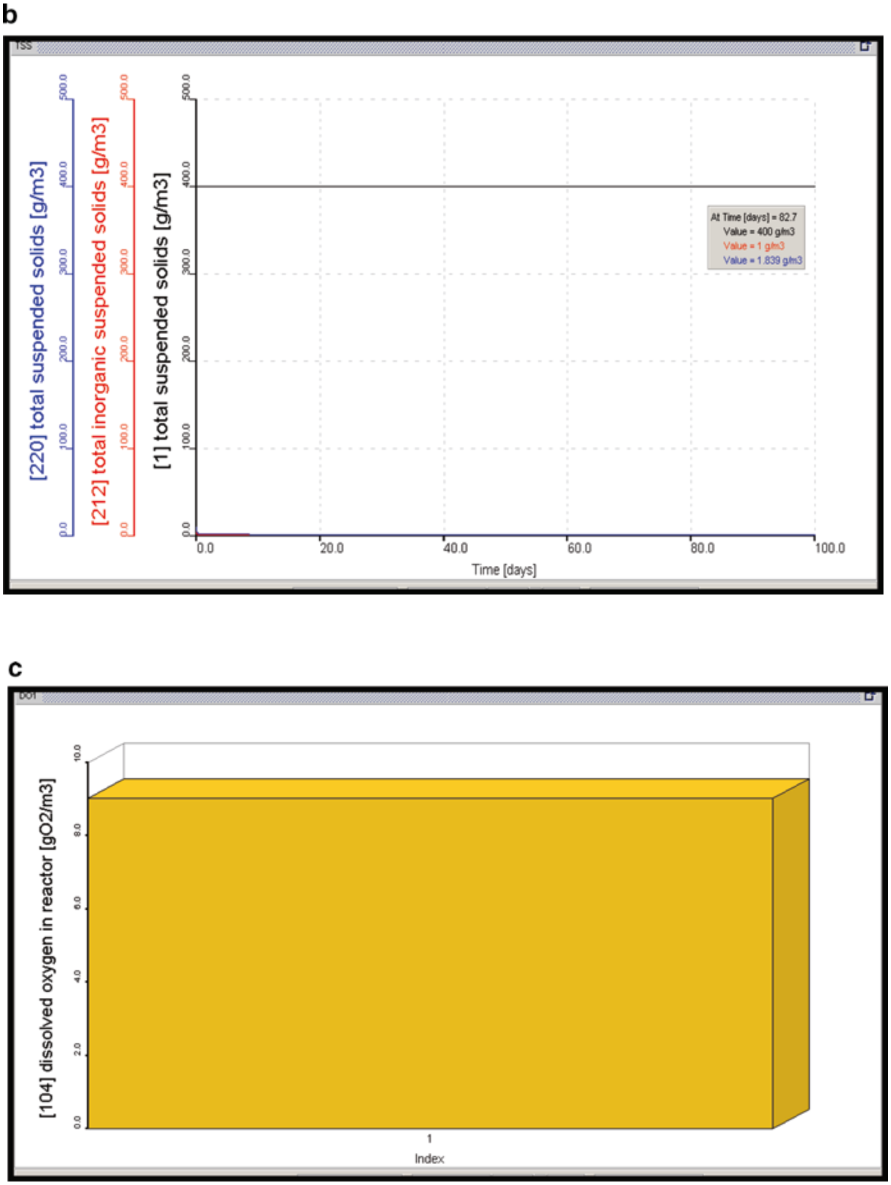

Fig. 14.4 (continued) (**b**) Total suspended solids concentrations in the proposed system. (**c**) Dissolved oxygen concentration in reactor in the proposed system (DO = 9 mg L^{-1})

14.4 Case Study II: New Nubaria City

The New Nubaria city is a small city and was designed to include two residential districts and two industrial areas. There are two sources of industrial wastewater in the city: raw industrial wastewater and combined domestic and industrial wastewater.

Main Problem: There is an existing mechanical WWTP that is designed to receive a 6,800 m^3 day^{-1} total flow pumped at different timings from 3 pump stations that work alternatively. Thus the influent characteristics of wastewater change as it being pumped from each PS. The mechanical treatment plant consists of two aeration tanks followed by two final clarifiers followed by a chlorine tank. After that the treated WW is transported to the nearest drain outside the city. Table 14.4 presents the characteristics of combined domestic and industrial wastewater and the current removal efficiency of pollutants.

From these facts it is clear that the effluent quality of WW doesn't comply with the required standard. This is due to the continual variation of high influent levels of COD and BOD, especially that the current WWTP was designed to treat domestic wastewater only. Also the plant is hydraulically over loaded, since the incoming flow rates exceeding the design capacity.

Before suggesting the best treatment method for industrial wastewater in New Nubaria city, a study of level of efficiency for the current plant was performed. One of the computer programs has been used (GPS-X) to evaluate the performance level of the current condition of the plant. The influent flow rate, concentration of pollutants over the day, dimensions of the units and their operating conditions have been used. The program gave the various pollutants concentrations expected under different conditions. Figures 14.5–14.7 show some of the expected output results from the program representing the expected results to be discharged from the current WWTP under the current operation conditions.

Figures 14.6 and 14.7 illustrate the high effluent concentrations of COD and SS which may reach 6,000 mg $L^{-1}$and 1,200 mg L^{-1}, respectively, indicating the poor level of treatment efficiency of the plant due to the high influent organic load resulting from industrial wastewater and flow over loading.

Table 14.4 Characteristics of sanitary and industrial wastewater in the treatment plant of New Nubaria city

Item	Unit	Influent	Effluent	Acceptable range
pH	–	4.8	5.6	6–9
COD	mg O_2 L^{-1}	7,600	5,500	80
BOD	mg O_2 L^{-1}	2,400	1,400	60
TSS	mg L^{-1}	1,200	1,100	50
Oil and grease	mg L^{-1}	50	38	10

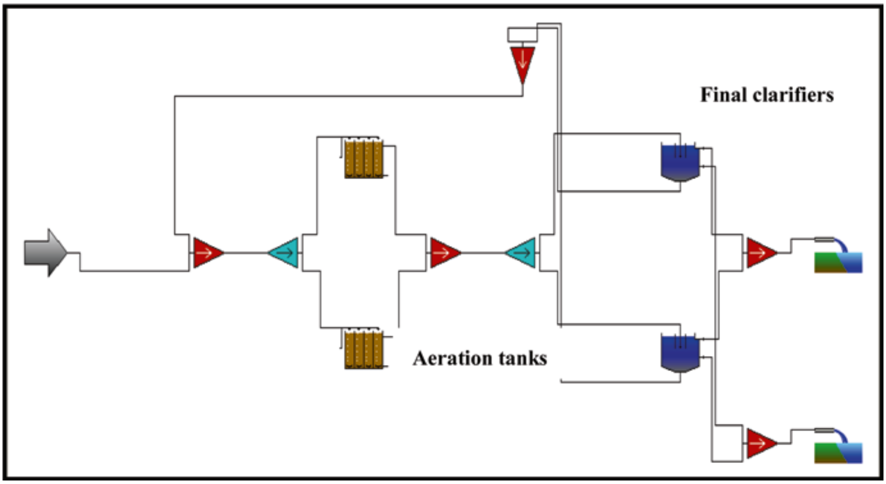

Fig. 14.5 Schematic diagram shows layout of Noubaria WWTP (existing facilities)

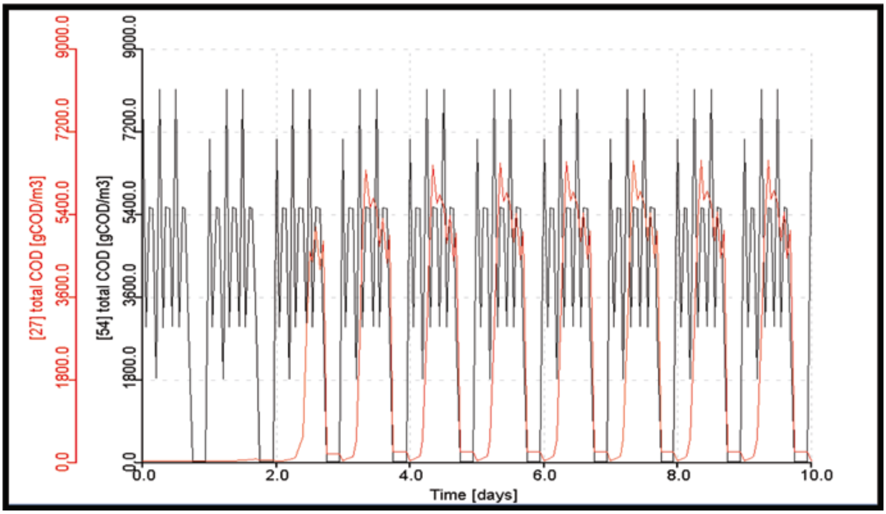

Fig. 14.6 Influent and effluent COD concentrations

14.4.1 Suggested Solution for the Industrial Wastewater Produced at New Nubaria City

Two suggestions could be proposed to enhance the performance level of the existing WWTP. The first solution suggests treating the organic load being released from the factories to acceptable standards according to law no. 44/2000 before being disposed to the plant and which would most likely be difficult to implement.

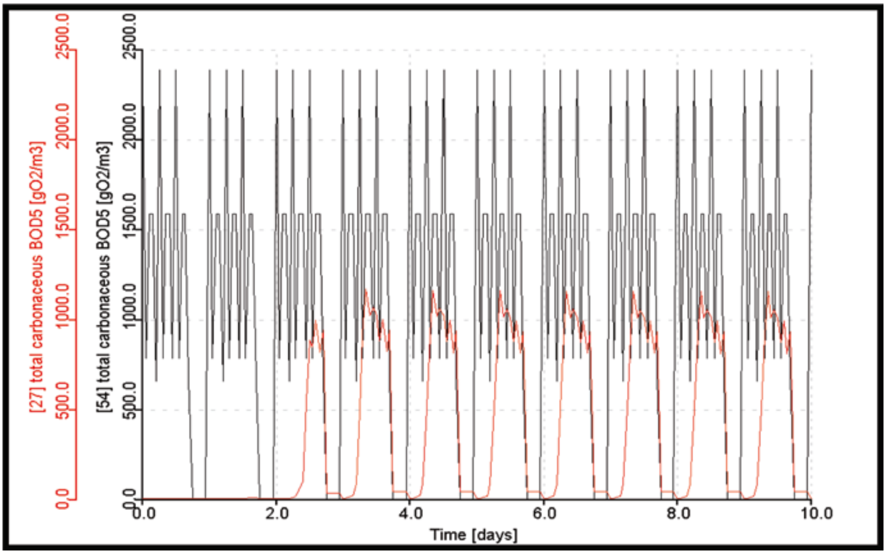

Fig. 14.7 Influent and effluent SS concentrations

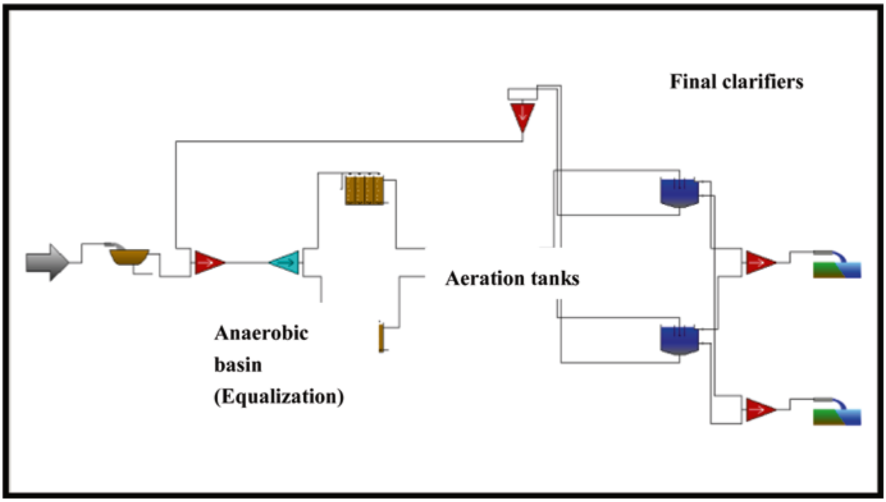

Fig. 14.8 Schematic diagram shows the modifications suggested for Noubaria WWTP

The second suggests constructing anaerobic basin at the inlet of the plant to decrease concentrations of BOD and COD, and more importantly, it would act as a flow equalization tank which would decrease the continual variation in the levels of COD and BOD in the aeration tanks; hence improve the efficiency of the treatment process inside the plant. The second proposal has been studied using GPS-X and the results are illustrated in Fig. 14.8.

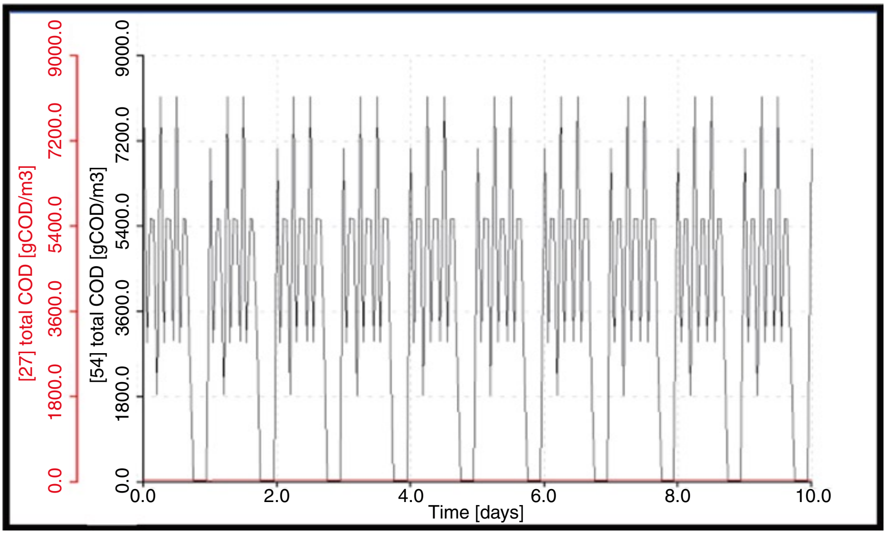

Fig. 14.9 Influent and effluent COD concentrations

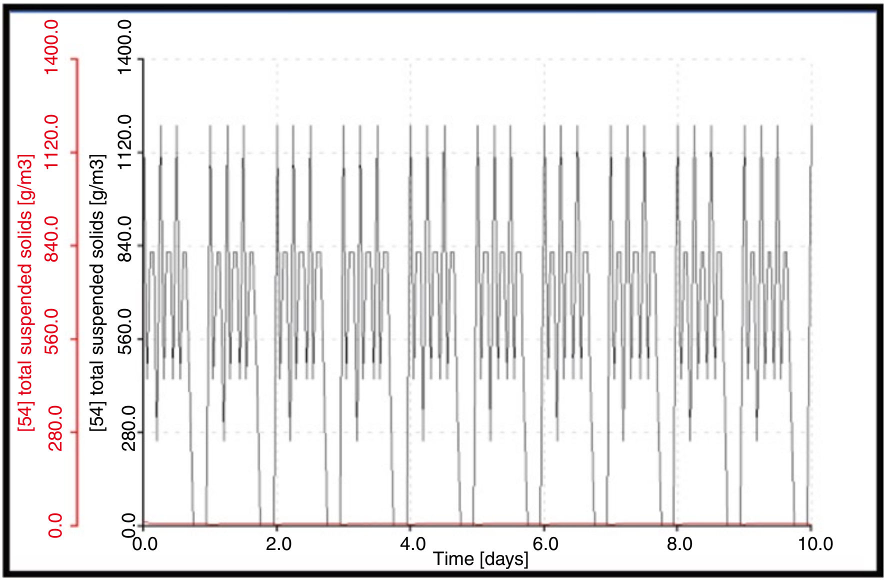

Fig. 14.10 Influent and effluent SS concentrations

Figures 14.9 and 14.10 illustrate the enhanced and steady effluent concentrations of COD and SS, 70 ppm and 30 ppm respectively, showing the vital importance of constructing anaerobic basin before proceeding with the treatment process.

14.5 Case Study III: New Borg El Arab City

New Borg El Arab, with an aimed population of 535,000 is characterized with its various industrial activities which play a major role in the development of the city. The amount of domestic wastewater is estimated to reach 136,000 m^3 day^{-1} at the saturation level, while the amount of industrial WW is estimates to reach 162,000 m^3 day^{-1} by 2017 according to the modified general layout of Borg el Arab city.

Main Problem: In the present, the domestic WW produced from the city (30,000 m^3 day^{-1}) in addition to about 45,000 m^3 day^{-1} industrial WW are treated through a WWTP located east of the city using 6 batteries of oxidation ponds (include aerobic, facultative and maturation ponds). The other portion of industrial WW received from another area is being disposed into a pond or lake located at El Mahager area west of the city with an area of 55 acres.

Table 14.5 illustrates the characteristics of domestic and industrial wastewater produced from the city. It is clear that the concentration of pollutants is moderate and close to the allowable standards, which in turn signifies the adherence of most of the factories to treat their waste before disposing it into stream water or sewage networks. Table 14.5 displays the characteristics of influent and effluent WW from the treatment plant with the oxidation pond system. It is clear that the treatment plant is inefficient in decreasing the amount of organic load for the industrial wastewater to the allowable standards. The other portion of the received industrial wastewater is disposed in the lake where part of the water is allowed to leak into the ground and the remaining water is vaporized. Recently the high level of ground water was noticed in the neighboring areas near to this pond in addition to the over flooding of the wastewater above the embankments leading to environmental problems in the surrounding area.

14.5.1 Suggested Solution for Industrial Wastewater in New Borg El Arab City

According to the improved general layout of Borg El Arab city, it is suggested to establish a WWTP west of the city at El Mahager area to treat all domestic WW conveyed from the city till the level of saturation. Because New Borg El Arab is distinguished, most factories primarily treat their wastes before discharging it into the sewerage system. Hence, it is suggested to combine domestic and industrial WW which is free of any poisonous material and treat them together to dilute the concentration of organic load present in the industrial wastewater.

For primary treatment, two alternatives were suggested: the first depends on the use of primary sedimentation tanks that remove about 40–60% of SS and about 30–40% of organic substances. The second alternative depends on the use of anaerobic ponds. GPS-X program was used to simulate both alternatives and has proven to use the second alternative as shown in Figs. 14.11–14.13. Simulation results showed the possibility of reaching the allowable effluent concentration limits using the above proposed system.

Table 14.5 Characteristics of domestic and industrial WW for New Borg El Arab WWTP (oxidation ponds)

Item	Unit	Domestic and industrial wastewater (3 batteries)		Industrial wastewater (3 batteries)		Acceptable ranges of effluent
		Influent	Effluent	Influent	Effluent	
pH	–	5.5	6.5	7.1	7.3	6–9
COD	$mgO_2\,L^{-1}$	748	422	1,454	621	80
BOD	$mgO_2\,L^{-1}$	289	104	417	189	60
TSS	$mg\,L^{-1}$	134	26	504	172	50
Oil and grease	$mg\,L^{-1}$	315	65	385	230	10

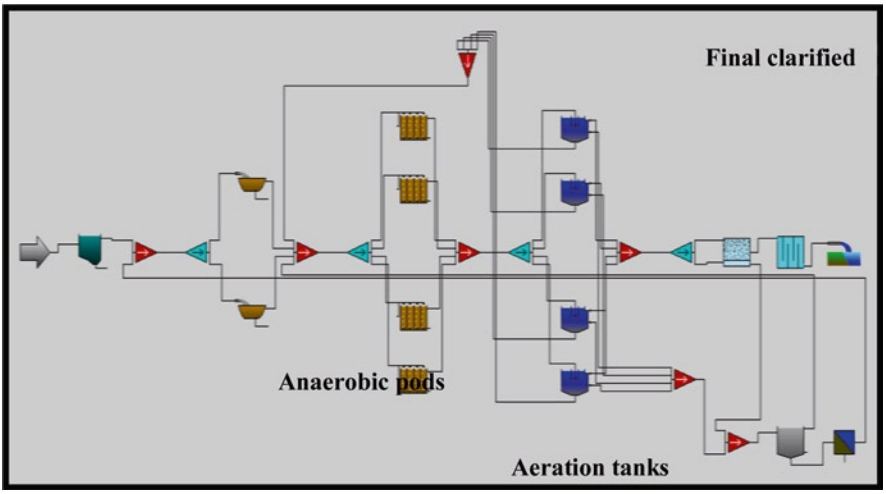

Fig. 14.11 Layout of Borg El Arab WWTP (using anaerobic ponds)

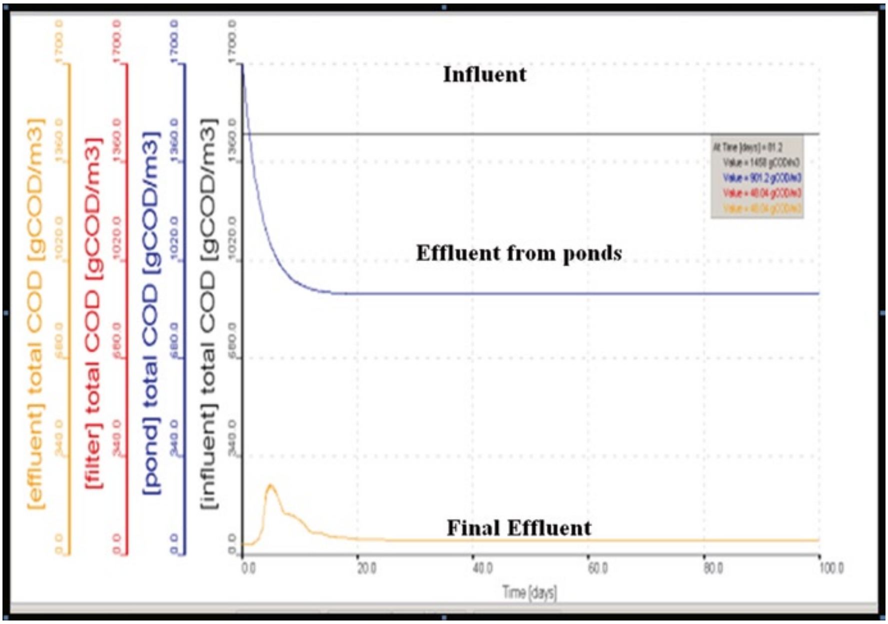

Fig. 14.12 Concentration of COD at different locations

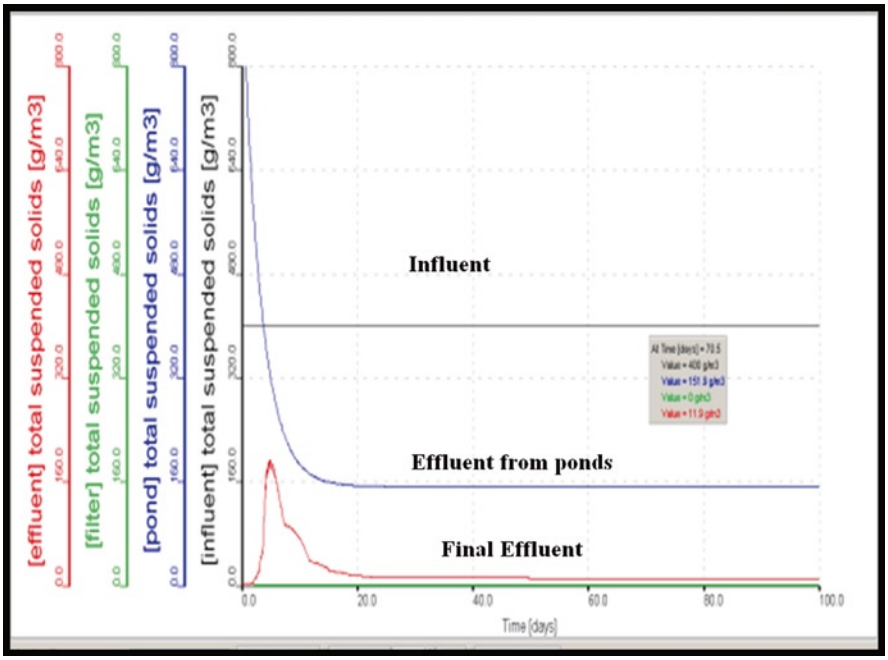

Fig. 14.13 Concentration of SS at different locations

14.6 Case Study IV: Mubarak Industrial Zone-Quesnna

The industrial zone of Mubarak belongs to Quesnna district in Monofia governorate. This area was planned and divided into four industrial zones; each includes a number of factories with different activities. There is a common wastewater network for these areas to gather industrial wastewater and domestic sewage from labors which end with three pump stations. Table 14.1 shows the characteristics of combined wastewater in Mubarak industrial zone. Results show the high levels of organic load indicating that most of the factories avoid primary treating their wastewater before discharging them into the network system.

Main Problem: The expected total discharge from Mubarak industrial zone is about 42,000 m^3 day^{-1} at the level of saturation, 32,000 m^3 day^{-1} of this shall represent the raw industrial wastewater. At present, a mechanical treatment plant is under construction with a design capacity of 62,000 m^3 day^{-1}. 42,000 m^3 day^{-1} of this capacity is from Mubarak zone and the rest 20,000 m^3 day^{-1} is from the neighboring villages. However, this plant is designed to receive and treat domestic wastewater only based on a 500 mg L^{-1} organic load and suspended solids concentration of 450 mg L^{-1}. Table 14.1 illustrated the great difference in the concentrations of organic loads in both domestic and industrial wastewater, signifying the necessity of an equalization tank to be implemented at the inlet of the existing WWTP. Results also show the decreased ratio of BOD/COD resulting from the increase of untreated industrial wastewater compared to domestic wastewater. Moreover, a high level of chrome was found to be present in the wastewater discharged from the first industrial region (55.3 mg L^{-1}), requiring treating chrome to the allowable standards. Chrome is produced from some industries such as leather, paper, coating and dyes industries. Chrome composition represents a real danger on public health as they infect the lungs, kidneys, liver, digestive system, and may cause skin cancer. They also have a direct effect on the biological process inside treatment plants. Consequently, it is preferred to mix domestic and industrial wastewater influents to the treatment plant to decrease the concentration of the organic loads.

Currently, raw wastewater is disposed temporarily in a drain near by the city till the treatment plant is implemented and operated.

14.6.1 Suggested Solution for Industrial WWT in Mubarak Industrial Zone

It is well known that the quality of industrial wastewater differs and varies according to the types of industries and the amount of production. Industrial wastewater may contain high levels of dissolved organic substances in addition to poisonous substances which may harm the biological treatment process; hence, a nontraditional treatment process including the following units is being suggested:

1. Chromium removal unit (for WW received from 1st PS only)
2. Flow equalization tank (for received industrial and domestic WW)
3. A removal and/or a decrease COD unit.

Due to the high levels of COD in influent WW to the plant, it is recommended to use anaerobic biological treatment (anaerobic oxidation ponds or UASB system) to decrease the concentration of COD, followed by aerated biological treatment (Biolak system) to make treated WW achieve the aimed characteristics.

Anaerobic oxidation ponds system is not preferred in this case for it requires vast areas of land which is not available here because removal units of COD must be put inside the currently implemented treatment plant so it could be connected to the remaining treatment units (aeration tanks – final sedimentation). However these ponds are known for their low costs of establishment, operation and maintenance but their efficiency may not exceed 45%.

As for the UASB system, it is considered as one of the modern treatment methods and it is perfect for industrial wastewater treatment with high levels of COD which may exceed 10,000 mg L^{-1}. They are preferred compared to anaerobic oxidation ponds system as they don't require vast areas of land and their efficiency in removing COD may vary between 60% and 80%. This system is expensive in operation, establishment and maintenance. It must be mentioned that the sponsoring and financing organization for the costs of implementing, operating and maintaining the industrial wastewater treatment station is the Investors Institution in Mubarak industrial zone. Consequently there will be no obstacles in implementing and operating these units.

Extended aeration shall be followed by the anaerobic process where a high proportion of the organic load (COD) is expected to be removed until reaching the allowable limits (80 mg L^{-1}). This system is known for its low costs of implementation and low energy needed for aeration. However it requires vast areas of land compared to traditional treatment.

Figure 14.14 illustrates currently implemented WWTP units while Fig. 14.15 displays the suggested modifications for primary treatment of industrial wastewater to reach the allowable standards that could make it treatable combined with domestic wastewater.

14.7 Conclusion

From the above research, it could be concluded that:

- Industrial wastewater could be a threat to the surrounding community and environment if not handled cautiously.
- Wastewater analyses should be regularly done, especially for industrial WW to be able to determine the required type of treatment in case a treatment plant is to be constructed and to maintain the level of efficiency of an operating plant, mainly the biological process.
- The process to be selected depends on several factors, such as characteristics of the incoming wastewater, land availability and costs
- In case of 10th of Ramadan city, vast areas were available which encouraged the use of anaerobic oxidation ponds followed by aerated lagoons.
- In case of New Nubaria city, a combination between anaerobic basin (working as equalization tank) and the existing secondary treatment was suggested due to the continual variation in the influent organic load.
- In case of New Borg EL Arab, a combined system was also suggested between anaerobic ponds and activated sludge system.
- Mubarak industrial zone also had a problem with the industrial WW produced from the factories due to the high percentage of Chrome found. Because limited area is available, the investors responsible for the development of the city could propose constructing UASB units followed by the establishment of a Biolak system.

Acknowledgement The authors of this paper would like to express their gratitude to the Environmental Civil Engineering Consulting Firm (Enviro Civec), located in Cairo, Egypt, for its technical help and support via its profound experienced team in studying the above mentioned industrial cities and helping reaching the optimum solutions for each case. They would also like to thank the authorities of each city for providing us with the information and data needed to support the study done in this paper.

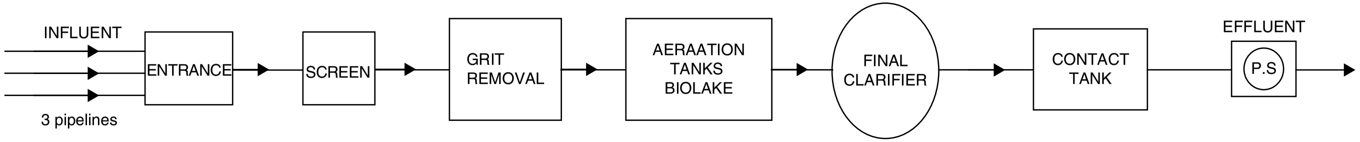

Fig. 14.14 Schematic diagram shows treatment units in the current WWTP

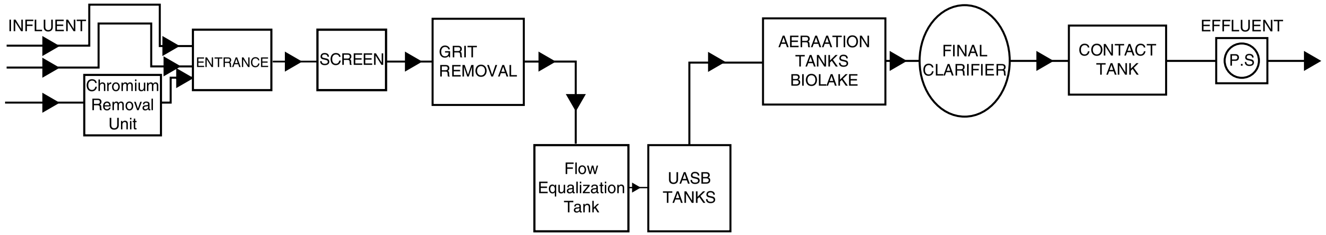

Fig. 14.15 Schematic diagram shows the additional treatment units for industrial wastewater

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Chapter 15
Industrial Wastewater Reuse Applications in Romania

Liviu-Daniel Galatchi

Abstract In order to promote industrial wastewater reuse in Romania on a sustainable basis and for wider applications, some key factors should be addressed. Firstly, planning for industrial wastewater reuse is important with reference to meeting specific needs and conditions. This could be facilitated by incorporating industrial wastewater reuse into local plans for water management. Planning process needs to take care of all the sensitive issues including public health, the role of stakeholders, and the viability of operation and maintenance. Secondly, economic and financial requirements are crucial, as less viable schemes for industrial wastewater reuse will only create a social burden and will not last for long. Cost-effectiveness should be given high priority. Partnerships with the private sector and the community may help to improve the level of investment and also to improve efficiency during operation and maintenance, thus reducing the overall cost and making it economically and financially viable. Thirdly, local capacity, including human resources, policy and legal framework, and institutions are very important in achieving sustainable targets of wastewater reuse plans. Capacity building should be an integrated part of the overall plan, and national and international agencies can actively assist in this.

Keywords Romania • Industrial wastewater • Reuse • Advantages • Potential concerns • Recycling • Implementing factors

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15.1 Introduction

In Romania, industrial water use accounts for approximately 20% of the freshwater withdrawals (Fig. 15.1).

Power generation constitutes a large share of this water usage, with 60–70% of total industrial water used for hydropower, nuclear, and thermal power generation, and 30–40% used for other, non-power generation processes (Fig. 15.2). Industrial water reuse has the potential for significant applications, as industrial water demand is expected to increase by 1.5 times by 2025 [4].

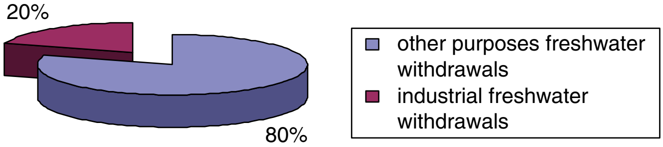


Fig. 15.1 Freshwater withdrawals in Romania

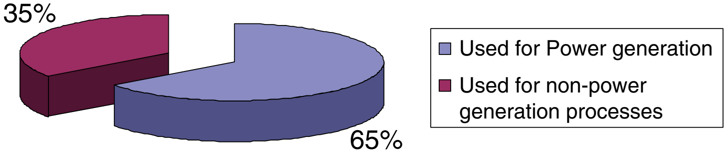


Fig. 15.2 Uses of industrial freshwater in Romania

15.2 Advantages of Reusing Industrial Water

Industrial water reuse has the following specific benefits (in addition to other general environmental benefits):

- potential reduction of the production costs from the recovery of raw materials in the wastewater and reduced water usage
- heat recovery
- potential reduction in costs associated with wastewater treatment and discharge (Fig. 15.3).

Water reuse and recycling for industrial applications in Romania have many potential applications, ranging from simple housekeeping options to advanced technology implementation. Wastewater reuse for industry can be implemented through the reuse of municipal wastewater in industrial processes, internal recycling and cascading use of industrial process water, and non-industrial reuse of industrial plant effluent, as summarized below (Fig. 15.4).

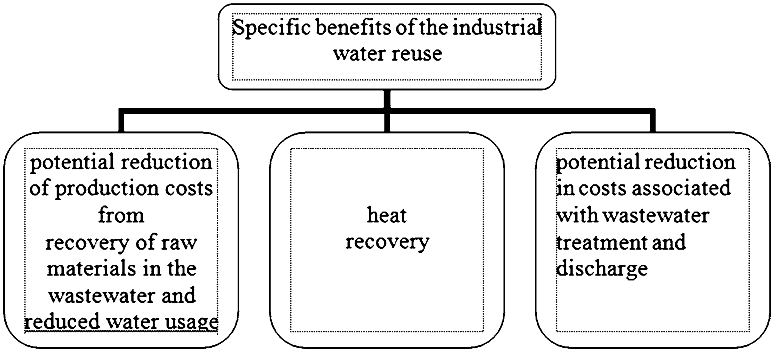


Fig. 15.3 Benefits of the industrial water reuse

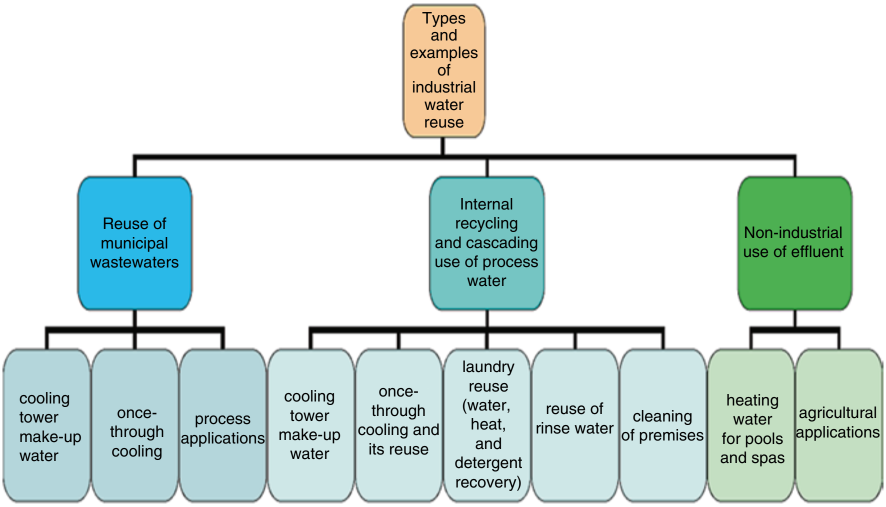


Fig. 15.4 Types and examples of industrial water reuse

Some types and examples of industrial water reuse are shown below:

Reuse of municipal wastewaters:

- cooling tower make-up water,
- once-through cooling,
- process applications.

Internal recycling and cascading use of process water:

- cooling tower make-up water,
- once-through cooling and its reuse,
- laundry reuse (water, heat, and detergent recovery),
- reuse of rinse water,
- cleaning of premises.

Non-industrial use of effluent:

- heating water for pools and spas,
- agricultural applications.

In particular, cooling systems may consume 20–50% of a facility's water usage, and also present a significant potential for reuse. Cooling systems remove heat from air-conditioning systems, power stations, oil refining, and other various industrial processes. Many facilities operate cooling towers, in which warm water is circulated and cooled continuously. Water (commonly referred to as make-up water), is added to replace evaporative loss and pollutant discharge. Some facilities also use once-through water to cool heat-generating equipment and discharge water after heat transfer. In both systems, adequately treated wastewater can be used as cooling water or make-up water, with or without mixing with tap water. Once-through cooling systems also present additional opportunities for water reuse, such as connection to a re-circulating cooling system to reuse water, and cascading use of cooling water in other applications.

In Romania, water quality requirements for industry reuse differ according to application types. Obtaining the necessary quality may require secondary treatment, tertiary treatment, or specific methods to meet individual needs. For example, rinsing and cleaning for semi-conductor wafer manufacturing requires ultra-pure water, which can be supplied from municipal wastewater that has undergone reverse osmosis and ultraviolet treatment. Almost all well-managed cooling towers use a water treatment scheme such as sulphuric acid treatment, side stream filtration and ozonation to inhibit corrosion and scaling. The cascading of process water of non-potable quality without treatment may be sufficient for general office cleaning and rinse water. In the steel industry, the effluent from wet scrubbers of blast furnaces can be recycled after treatment to remove iron oxide, silica, carbon lime and magnesium by coagulation or high-gradient magnetic separation. In the pulp and paper industry, water reuse is an important strategy for recovering fibers, chemicals and heat from process effluent, as well as for reducing freshwater consumption and wastewater production. Wastewater treatment, with respect to the industrial use, depends on the effluent, i.e. if the effluent is coming from somewhere other than the industry that is reusing it, or if the industry is recycling its effluent reusing within the same industry.

Cleaner production assessment is an analytical method of particular relevance for evaluating options for industrial water reuse. It has been promoted by Romania since the late 1990s, and is defined as the "*continuous application of an integrated, preventive environmental strategy to processes, products, and services to increase overall efficiency, and reduce risks to humans and the environment*", as stated by UNEP. Cleaner production can be implemented to improve industrial processes, product performance and various services provided in society. The assessment methodology is used for systematic identification and evaluation of cleaner production opportunities, thereby facilitating their implementation.

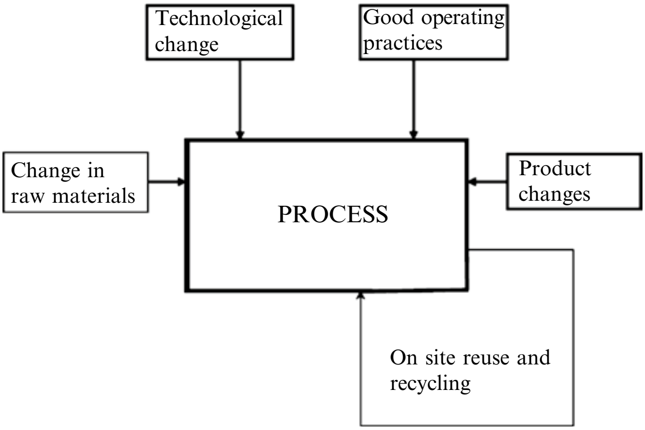


Fig. 15.5 Areas of cleaner production opportunities (Based on UNEP [5])

Figure 15.5 shows five areas of cleaner production opportunities to be identified through cleaner production assessment [5]:

- changes in raw materials,
- technological change,
- good operating practices,
- product changes,
- on-site reuse and recycling.

Water reuse and recycling in the process can be achieved by implementing good operating practices, changing to technologies that require less process water and on-site reuse and recycling. In addition, cleaner production assessment can be applied to reformulate industrial products to use less water.

15.3 Potential Concerns for Industrial Water Reuse

Potential concerns for industrial water reuse include:

- scaling
- corrosion
- biological growth
- fouling

which may impact industrial process integrity and efficacy, as well as product quality (Fig. 15.6).

These concerns are often interrelated. The scaling concern is caused by inorganic compounds and salts, having treatment options as scaling inhibitor, carbon adsorption, filtration, ion exchange, and the blow down rate control.

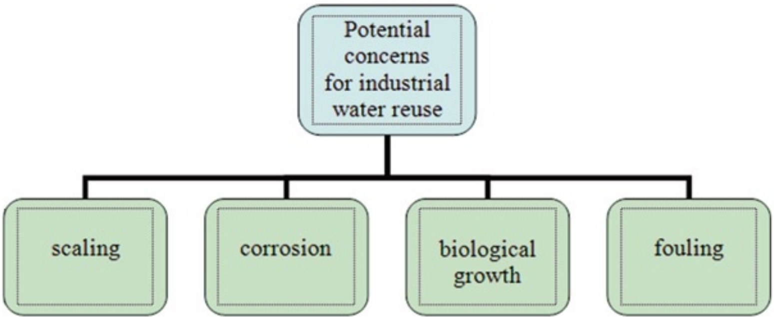


Fig. 15.6 Potential concerns for industrial water reuse (Based on Asano and Levine [2])

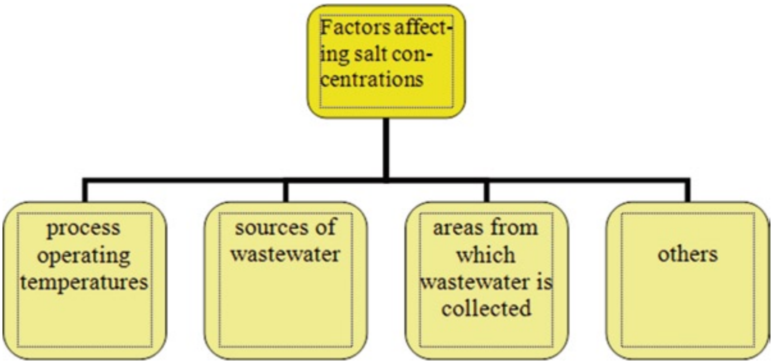


Fig. 15.7 Factors affecting salt concentrations

As about corrosion, its causes are related mainly to dissolved and suspended solids and the pH imbalance. The treatment options include corrosion inhibitor and reverse osmosis.

The biological growth concern relates to residual organics, ammonia and phosphorous concentrations etc. The problem could be solved using biocides, dispersants or filtration.

The microbial growth, phosphates, dissolved and suspended solids are causes for the fouling deposition. The treatment of fouling deposition is usually done by the control of scaling, corrosion, microbial growth, filtration, and chemical and physical dispersants.

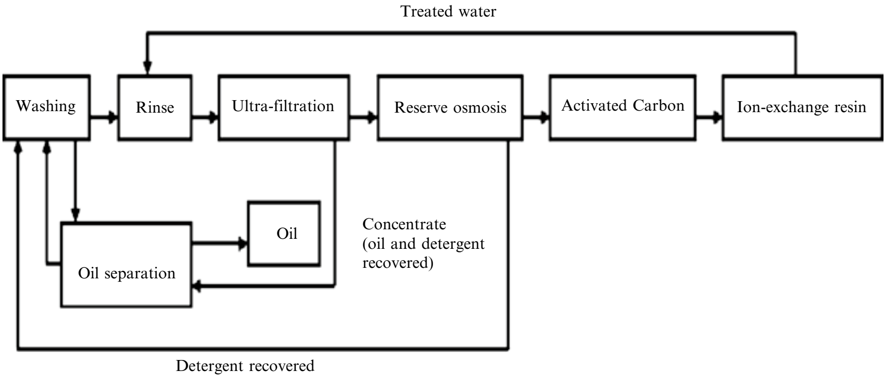
Salt concentrations can be affected by various factors, including:

- process operating temperatures,
- sources of wastewater,
- areas from which wastewater is collected (e.g. coastal areas may have higher concentrations) (Fig. 15.7).

15.4 Recycling Industrial Water

A Romanian chemical engineering company refined a cleaning process for parts washing, coupled with membrane technologies to recycle rinse water to minimize process cost. The need for wastewater treatment arose with the conversion to non-chlorofluorocarbons based detergents in connection with the phase-out of ozone-depleting substances under the Montreal Protocol in the mid 1990s. The automated process utilizes various membrane technologies, as shown in the flow diagram below, after a Japanese model (Fig. 15.8) [1]. For example, oil and dirt are separated from rinse water by an ultra filtration membrane. The detergent is then removed from the water by reverse osmosis, and reused in the washing process. The ion-exchange resin can be used to treat water, to be recycled as rinse water as needed.

The environmental and economic benefits of this process are significant. For example, the volume of water usage and discharge is 0.5% of the previous process. The running cost is one-tenth of an alternative adsorption treatment that uses activated carbon and ion-exchange resin. The maintenance requirement is once a month or less. The key to successful implementation is the selection of appropriate types of membranes and their combinations, management of temperature and flow rate, and a suitable cleaning agent used in appropriate amounts.



	Oil separation	**Rinse**	**Reverse osmosis**	**Ion-exchange resin**
COD (ppm)	3,00	250	5	1
Oil (ppm)	500	400	< 1	< 1
Conductivity ($\mu S\ cm^{-1}$)	1,200	200	15	1

Fig. 15.8 Diagram of the washing process

Occupational health concerns include exposure to aerosols that contain toxic volatile organic compounds and bacteria, such as *Legionella sp.*, which causes Legionnaire's disease.

Some of the important and practical aspects for industrial wastewater reuse are:

- Usually, the industry itself decides the needs and extent of wastewater treatment for its reuse. The government does not decide how to reuse/recycle water in the industry; it only motivates industry through incentives such as the price of water or subsidies for the technology.

Most industries select types of wastewater treatment processes that have a great level of reliability. This differs from wastewater reuse projects in municipalities, where the cost is a crucial factor to decide both the type of reuse and the type of treatment.

15.5 Factors Needed for Implementing Industrial Wastewater Reuse

Launching an industrial wastewater reuse initiative requires careful consideration of the local conditions, and must be based on the sufficient and well-integrated analysis of technology options, financial implications, health risks mitigation, and other factors (Fig. 15.9).

Planning to meet specific needs and conditions: During a planning process, the appropriateness of water and wastewater reuse applications needs to be carefully evaluated against the volume of available wastewater, degree of water scarcity, availability of existing infrastructure, and receptivity of potential users. The purpose of the application, such as irrigation, industrial use, landscape, and household use needs to be evaluated together with the water quality requirements and associated health risk. Such evaluation is useful in identifying necessary treatment and disposal technologies, as well as operational and maintenance requirements. The public should be recognized as legitimate stakeholders, and their roles and responsibilities should be clearly defined in the planning process.

Analyzing economic and financial requirements: Economic and financial analyses are also needed to identify viable solutions and to access financial assistance when necessary. While industrial wastewater reuse programs have many benefits and long-term cost effectiveness, they may have a high initial cost associated with additional treatment and infrastructure needs, such as additional treatment, pumps, pipes, reservoirs, and so on. Alternatives to address this impediment, such as public assistance, incentives, and preferential private sector financing, must be explored. The decision-makers and the users should be aware of the impact on water prices resulting from wastewater reuse projects.

Selecting options to minimize risk: One of the most important factors in water and industrial wastewater reclamation projects is complying with water quality standards

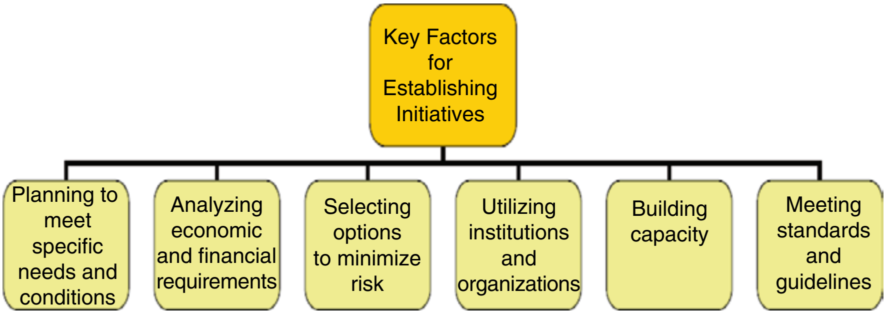


Fig. 15.9 Important factors for establishing initiatives

to minimize health risks, or establishing them if they do not exist. While the WHO guidelines for agricultural applications of wastewater are available, there are no international guidelines or criteria for other types of wastewater reuse, including industrial wastewater. Therefore, guidelines and standards need to be developed, with health risks as well as technical and economic feasibility being taken into account. Technological options should be selected to meet such guidelines and standards and ensure the protection of human health and the environment.

Utilizing institutions and organizations: Industrial wastewater reuse involves many stakeholder institutions, such as utilities and private users that implement the initiative, local environmental authorities for permits and enforcement, financial institutions for provision of funding, the national environmental ministry for setting national standards and supporting local authorities, and so on. Their responsibilities and roles for facilitating reuse programs need to be identified and understood clearly.

Building capacity: Capacity is needed to successfully plan and implement wastewater reuse initiatives. Such capacity encompasses human resources, policy and legal frameworks, institutional and organizational management and financing, as well as public awareness and participation.

Meeting standards and guidelines: Standards and criteria for water reuse need to be complied with in order to protect human health and the environment. Applications need to be monitored to ensure that industrial wastewater is being reused in a manner consistent with the intended applications and practice.

15.6 Conclusion

In conclusion, water is a limited resource. Increasingly, society no longer has the luxury of using water only once. Wastewater reuse more appropriately matches water use application with water resource quality resulting in more effective and efficient use of water. The goal of water resource sustainability is more attainable when wastewater reuse option is implemented.

Potential benefits of wastewater reuse are related to the fact that it:

- conserves freshwater supplies;
- is environmentally responsible;
- makes economic sense;
- can save resources.

So, industrial wastewater reuse increases the total available water supply. High-quality water supplies can be conserved by substituting reclaimed water where appropriate. The reuse can preserve the health of waterways, wetlands, flora and fauna. It can reduce the level of nutrients and other pollutants entering waterways and sensitive marine environments by reducing wastewater discharges.

In the mean time, reclaimed water is available near urban development where water supply reliability is most crucial and water is priced the highest. Industrial wastewater contains sometimes nutrients; if this water is used to irrigate agricultural land, less fertilizer is required for crop growth. By reducing nutrient (and resulting pollution) flows into waterways, tourism and fishing industries are also helped.

As about the factors driving further implementation of industrial wastewater reuse, they are as below:

- *Proximity*: Reclaimed water is readily available in the vicinity of the industrial environment, where water resources are needed (and are highly priced).
- *Dependability:* Reclaimed water provides a reliable water source, even in drought years, as production of industrial wastewater remains nearly constant.
- *Versatility*: Technically and economically proven wastewater treatment processes are available now that can provide water for not potable use (and sometimes even for potable reuse).
- *Safety*: Non-potable water reuse systems have been in operation for over five decades with no documented adverse health impacts.
- *Competing demands for water resources*: Increasing pressure on existing water resources due to population growth and increased agricultural demand.
- *Fiscal responsibility*: Growing recognition among water and industrial wastewater managers of the economic and environmental benefits of using reclaimed water.
- *Public interest*: Increasing awareness of the environmental impacts associated with overuse of water supplies, and community enthusiasm for the concept of wastewater reuse.
- *Environmental and economic impacts of traditional water resources approaches*: Greater recognition of the environmental and economic costs of water storage facilities such as dams and reservoirs.
- *Proven track record*: The growing number of successful industrial wastewater reuses projects all over the world.
- *A more accurate cost of water*: The introduction of new water charging arrangements (such as full cost pricing) that more accurately reflect the full cost of delivering water, and the growing use of these charging arrangements.

- *More stringent water quality standards*: Increased costs associated with upgrading industrial wastewater treatment facilities to meet higher water quality requirements for effluent disposal.
- *Necessity and opportunity*: Introduction of motivating factors for development of industrial wastewater reuse projects such as droughts, water shortages, prevention of sea water intrusion and restrictions on wastewater effluent discharges, plus economic, political, and technical conditions favorable to industrial wastewater reuse (based on Asano et al. [3]).

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Chapter 16
Opportunities and Experiences in Implementing the Recycling Methods for Industrial Water Supply in Bulgaria

Plamen Stoychev

Abstract In this chapter, the importance of recycling of industrial wastewater in general and in Bulgaria is explained. The necessary preconditions for water recycling, i.e. environmental, technical and economical conditions are overviewed. The present opportunities for use of technologies for recycling of water are analyzed according to the requirements of the Bulgarian environmental legislation. A brief overview of implementing the recycling methods in Bulgaria in the past is given. Examples of successful wastewater treatment systems with recycling the treated water in Bulgaria are presented. The historical review gives the opportunities for implementing the recycling methods for water supply for the future investments.

Keywords Applications in Bulgaria • Industrial wastewater reuse • Water sources • Water usage • Water discharge • Preconditions

Abbreviations

BOD	Biochemical Oxygen Demand
BSI	Bulgarian Statistics Institute
COD	Chemical Oxygen Demand
EU	European Union
NGO	Non–Governmental Organization
pH	Negative Logarithm of Hydrogen Ion Activity

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SS	Suspended Solids
TPP	Thermal Power Plants
UN	United Nations
WPP	Water Power Plants
WWTP	Wastewater Treatment Plant
WWT	Wastewater Treatment

16.1 Introduction

Bulgaria is a country poor in water resources. Water resources are formed mainly from the annual precipitations for which average value is 703 mm (range 413–1,095 mm), depending on the region and the altitude. This is the main water source for the country and it forms the flow of the surface water sources and feeds the underground ones. There are no surface water bodies which form their flow outside the country boundaries (except Danube, but it is a boundary river), so the flow rate of the rivers at the country boundaries or in their discharge points give the real value of the water sources of the country (Fig. 16.1).

The main parameters of the water sources in the country, according the data from the Bulgarian Statistics Institute, are given in Table 16.1.

According to the statistical data collected from the Bulgarian Statistics Institute (BSI) from the last 5 years, the gross amount of fresh water received from the surface sources is between 4,500 and 4,800 × 10^6 m^3 a^{-1}, while the same received from underground sources is between 620 and 650 × 10^6 m^3 a^{-1} [4]. The total gross quantity of fresh water received from the nature is 5,100–5,400 × 10^6 m^3 a^{-1}. The gross amount of fresh water received from natural sources, is given in Table 16.2.

According the same statistical sources [4] the water usage for different purposes is the Bulgarian economy is given in Table 16.3.

The domestic needs are 16.4% of the water usage in Bulgaria, which is approximately the average value in different countries. The amount of the water used for industrial purposes seems to be high but this is because other uses are low. For example, the agricultural needs are extremely small considering that now only 10–15% of the irrigation systems are in use. As a consequence, the amount of water needed for industry is 68.7% of the total annual water usage.

The water discharge into the natural water bodies shows that the main sources are the domestic and the industrial sewage systems [4]. The quantities discharged into the natural water bodies are given in Table 16.4.

From the industrial sewage water, 30 × 10^6 m^3 a^{-1} are discharged through the common sewerage systems, while the rest –174 × 10^6 m^3 a^{-1} is discharged directly into the natural water bodies. From those, which discharge directly, about 99.7 × 10^6 m^3 a^{-1} or 57% is treated, while the rest –74 × 10^6 m^3 a^{-1} is discharged without treatment.

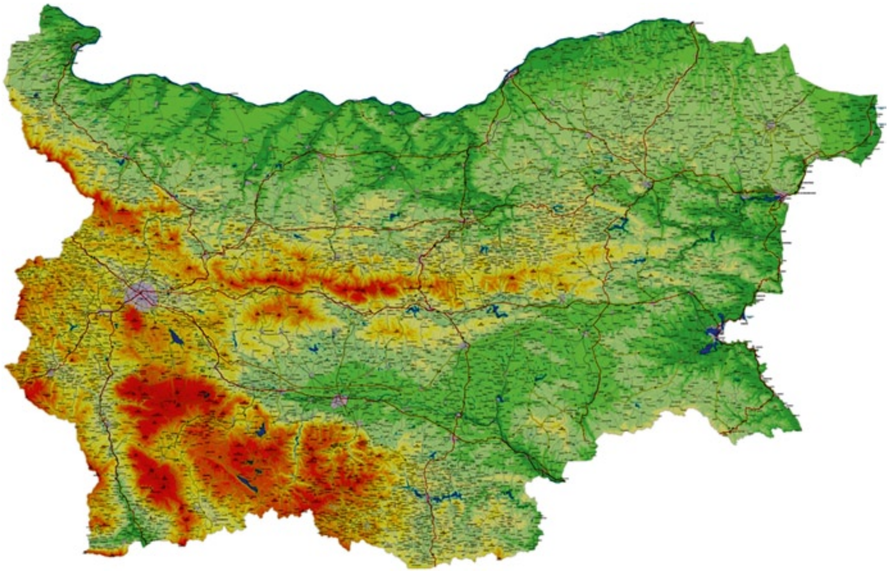

Fig. 16.1 Map of Bulgaria

Table 16.1 Main parameters of the water sources in Bulgaria

Area of Bulgaria	110,000 km^2
Annual average precipitation	703 (413–1,095) mm
Annual fresh water resources	68,600 mil. m^3
Evaporation	50,500 mil. m^3
Internal flow from the country	18,100 mil. m^3

Table 16.2 Gross amount of fresh water received from natural sources

Gross value of fresh water received from the nature/(10^6 m^3 a^{-1})		
	Minimum	Maximum
From surface sources	4,500	4,800
From underground sources	620	650
Total	5,100	5,400

NB: The volume of water which is only passing through (used) in Water Power Plants (WPP) without subsequent usage, is not included in that quantity, concerning that it is not used in further processes

Table 16.3 Annual water usage in Bulgaria

Annual water usage /(10^6 m^3 a^{-1}) /average values for the last 5 years	
For domestic needs	430
For industrial needs	1,800
• Cooling systems in the industry	1,100
• Energy production thermal power plants/TPP	200
• Other industrial needs	500
For agriculture needs	290
For other needs	100
Total	2,620

Table 16.4 Water discharge into the water bodies

Water discharging in the natural water bodies /(10^6 m^3 a^{-1})/average values for the last 5 years/;	
Domestic sewage systems	244
Industrial sewage systems	204
Agriculture needs	10
Other	32

NB: The water used for the cooling systems is not specified, because either that this is water only passing through the cooling system which returns back to the nature, or is used until it evaporates

16.2 Preconditions for Using Recycling Methods in the Industrial Water Supply

The industry is the main consumer of fresh water with enlarging amounts used each year. On other hand, the used water sometimes with unacceptable content of pollutants is the other problem that the industry has to solve. Recycling the part of the used water from one hand decreases the usage of the natural water sources, and on the other hand protects the environment from discharging the polluted water. Outside the ecological problems, there are objective preconditions, which can ensure or make unacceptable recirculation of the water in an industrial item. They can be specified as:

- Technical – economical preconditions
- Societal preconditions
- Legal preconditions

Normally the companies proceed to apply recycling methods for water supply combining all three preconditions.

16.2.1 Technical – Economical Preconditions

They are focused on the objective limits, which presume or reject the recycling of water supply.

- Lack of enough fresh water resources
- The price of fresh water resources
- Lack of appropriate discharge point for sewage water or high taxes for discharging in common sewerage systems
- Technological option for waste water treatment on affordable price
- Additional economical result due to the catchments of valuable impurities in the contaminated outlet water

16.2.1.1 Lack of Enough Fresh Water Sources

Definitely of primary importance is the quantity of the fresh water, the quantity stability of the source, the technical equipment price for water extraction and treatment

Table 16.5 Taxes for extracting water from natural water bodies

Water tax for extracting from a water body for purpose: (in Euro per 1,000 m^3)	Category of the water body according Ordinance N 7 taking account the concentration of BOD, COD, SS and pH		
	1	2	3
For domestic water supply	10.00	5.000	3.00
For agriculture	1.25	0.375	0.25
For cooling systems	0.20	0.100	0.05
For industrial purposes	20.00	6.000	4.00

of the raw water. This must be compared with the eventual expenses (investment and operating) necessary for a water treatment process to treat the sewage water to a level, which makes it suitable to be used again. So normally, when huge water quantities are used, the treatment of the foul water is not too difficult, and the quality of the treated water not very high, recirculation is the only way out to ensure the necessary water quantities. Such examples can be the Thermal Power Plants, the mining and concentrating ore plants, metallurgical plants, where water is used to transport the raw materials or the waste materials to the depots such as slime tailings, cinder damps where the used water settles down, and after additional simple treatment can be used again.

The situation is nearly the same with the process water used for transport or for the first (rough) washing of the materials in the canning factories. Here the water can be used again after it is cleared from the impurities but sometimes the main process requires treatment to higher quality, then additional disinfection of the recycled water is necessary.

16.2.1.2 The Price for the Use of Fresh Water Resources

This is the second important indicator and it includes the governmental taxes which are paid for water extraction from or discharge into the water bodies [3]. Those taxes added to the costs for the extraction and transport of the raw water, costs for the raw water treatment, compared with the costs for the suitable water treatment necessary for recycling the foul water before discharging, give the answer should open or closed (recycling) water supply system be used.

In Bulgaria, the taxes for using natural water resources (so called Water Extract Tax) or for discharging into a natural water body vary according to the purpose of use. They are associated with the impact on the water and water bodies as a natural resource. Their values are symbolic, and definitely are not a stimulus for preservation of the natural water resources or for implementing the recycling water supply systems.

The taxes for water extraction depend on the reason the water is used for, and the category of the water resource (the category depends on the concentration of the impurities). Table 16.5 gives the costs that the users of fresh water are charged.

The taxes for discharging polluted water into natural water bodies depend on the concentration of the impurities in the discharged water as compared with the same

Table 16.6 Water tax for discharging polluted water into natural water bodies

Water tax for discharging polluted water in natural water bodies. The category of the polluted water is defined by Ordinance N 7 (in Euro per 1,000 m^3)	Category of the water body according Ordinance N 7 taking account the concentration of BOD, COD, SS and pH		
	1	2	3
Discharging water with category up to or equal to first category	0.50	0.25	0.10
Discharging water with category up to or equal to second category	1.00	1.00	0.50
Discharging water with category up to third category or higher	1.50	1.50	1.50

in the water body. The taxes paid by the industrial units for discharge of foul water into the natural water bodies are given in Table 16.6.

When the water extraction is done through the medium of intermediate supplier such as water extraction from:

- a dam
- irrigation system
- an industrial water main

then water taxes are included in the total water price. The price depends on the pricing policy of the intermediate supplier. That is why they are much higher but more or less, it is not so high to stimulate the recirculation of the water.

When discharging into a common sewerage in or near the settlements, the taxes that have to be paid depend on the owner or the operator of the sewage system. Usually one of the reasons that the managers of the industrial units to look for independent discharge possibilities after treatment or to implement recycling methods of water supply is taxes. Definitely, in the long term a recycling system is economically more efficient than other methods of removing the polluted water.

The penalties that have to be paid for discharging foul water with concentration exceeding the permitted ones are not considered, although they are the main stimulus for both the purification of wastewater and implementation of recycling technologies. Missing sources for fresh water or the existing sources are with variable (insecure) flow, or the underground sources are with unsteady water flow. Normally this can result from varying parameters of the source, or the capacities of the permitted water intakes are much bigger than the source can bear.

This case partially overlaps with the case of high price of fresh water, considering the fact to find the necessary quantities of water depend mainly on the investigation and exploitation prices. This is maybe the most serious argument for implementing recycling methods for water supply especially when the location of the industrial unit has other arguments.

16.2.1.3 Lack of Appropriate Discharge Point for Sewage Water or High Taxes for Discharging in Common Sewerage Systems

Normally this case is when the industrial unit is outside the settlement's boundaries where natural water receivers or common sewerage network are missing. Then the methods for water recycling are not just alternatives but the only way to solve the problem.

16.2.1.4 Technological Options for Wastewater Treatment for Affordable Prices

Considering technologically there is no limit to purify a quantity of water, the necessary investments and the running costs are those items for which the price has to be paid. Beside the technical opportunities, this can be defined as the main economical factor. It depends on the:

- pollution level of the wastewater,
- requirements for the quality of the fresh water used in the manufacturing process,
- technical possibility to treat the polluted water to the required quality,
- necessary investment and operating costs for the treatment equipment.

16.2.1.5 Additional Economic Value Owing to The Recovery of Valuable Impurities in the Contaminated Outlet Water

The next precondition can be considered both for normal treatment of waste water before its discharging, and for treatment of water for recycling in the same industrial unit. As it was explained above, the taxes for discharge of wastewater depend on its contamination. Therefore, if the impurities are of such kind that they are valuable for some industrial units, there is an additional reason the wastewater to be treated and the received materials to decrease the overall costs for the water supply of the industrial unit. As far as it was found during some feasibility studies in firms whose production is lead acid batteries, the declared interest of implementing recycling water supply was the reuse of the lead contaminations back in the main manufacture. The same result was found during the examination the wastewater coming from the main producer of sanitary tiles in Bulgaria. Here the interest was the reuse of the coloring agents used for the tiles.

All of the mentioned preconditions separately or in conjunction, form the technological and economical reasons for implementing the recycling methods of water supply in the industrial world.

16.2.2 Societal Preconditions for Implementing Recycling Water Supply

To this group of prerequisites belong all the conditions, which reflect to the society as a whole. The sensibility of the society normally is to those problems, which affect it exactly, while for the other troubles, it is quite indifferent.

The problems with the water usage are the same. The society reflects to such problems like lack of water, frequent accidents with the network and other poor water quality, – when the treatment process of the raw water is not sufficient, but only in the regions where they occur. The society seems not to react to the real reasons, as such problems result on missing water sources, illegal, or incorrect discharges of foul water and so on.

The recycled water usage in the industry, due to its nature, seems to be imperceptible by the surrounding people, and as result, they cannot have a direct impact to its implementation. The effect in the right direction usually is mediated, through the ecological NGO's or the media. Sometimes the needed effect can result from governmental restrictions, through its departments but this is not a regular affect.

Highlighting the problems and the achieved results can only help to take the right decision, but insuring the necessary investments, and implementing the tasks can be done only by the industrial site.

Therefore, this can only be welcomed when an industrial site takes an engagement to provide environmental protection much higher than the governmental requirements. More or less such policy becomes more popular especially when the environmental protection is defined as a part of the principles of sustainable development, which were defined by the Commission on Sustainable Development at UN in 1993 [2]. Those principles related to the protection and conservation of the water sources can be defined as:

- Frugal usage of the water resources – Although the water is a renewable source, when some restrictions of the water usage apply the outcome is a safer environment,
- The economical analysis for effectiveness of each activity must take into account the necessary expenses needed to recover the water resources to their initial values,
- To recover promptly the disturbed ecological balance,
- The expenses for protecting the water resources from cross–boundary pollution must be shared equally by the parties.

These principles are usually presented in the firm's policy as "Widespread Corporate Social Responsibility" initiatives, especially among the large companies aiming at reducing their environmental footprint.

16.2.3 Legal Preconditions

The legal preconditions for implementation of the recycling technologies can be mentioned in two main groups:

- Legal requirements regarding water use and wastewater discharges
- Legal stimuli for wastewater treatment and wastewater recycling

Starting with the second item it can definitely be said that there are no legal stimuli for safe usage of the water resources in the Bulgarian state policy and legislation, neither for implementing recycling technologies.

The environmental protection is based only on the restrictions of the present legislation, whose main item is the Environment Protection Act [1]. As a main part of the Environment, a special act for the water is issued – The Water Act [11], where the water usage is examined in details.

As part of the European Union (EU) the Bulgarian legislation harmonization, was achieved with the corresponding units of the European legislation. For the environmental legislation can be said that it is already fully harmonized with the EU directives. In the water sector that reflects to the Water Act and its subordinate regulations. As a result, a National strategy for management and development of the water sector was issued. This gives to the society socially responsible, planned, open and predictable policy on water management; rational, effective, and economical use of the water resources, and their fair distribution to the population and economy. It gives protection and guarantee to the restoration of the water resources quality.

16.2.3.1 The Main Principles of the Water Act and Its Subordinate Regulations

- The establishment of the river basins as a basic unit for integrated water management

As can be seen on the map (Fig. 16.2), Bulgaria is divided into four River Basin Directorates. Their responsibilities are the management of these Directorates.

- Total water usage
- Employment of the “polluter pays” principle
- Recovery of the costs for water services, including resource costs and environmental costs
- Prevent or reduce water pollution by adequate treatment at the source
- Application of economic regulators to achieve sustainable water use and conservation

Fig. 16.2 Map of Bulgaria with boundaries of river basins

The Water Act gives the framework, while the details are given in a number of regulations and orders. Here, the more important of them are referred, whose objects reflect to the water treatment and reuse, and wastewater discharge and so, affect partly the water usage recirculation.

- **Regulation** on the exploration, use and protection of groundwater [5]
- **Regulation** on water monitoring [6]
- **Regulation** on the limit values for admissible contents of dangerous and harmful substances in the waste water discharged into the water bodies [7]
- **Regulation** on the terms and procedure for discharge of industrial waste waters into settlement sewer systems (Regulation No. 7) [8]
- **Regulation** on issuing permits for waste water discharge into water bodies and setting individual emission limit values for point sources of pollution (Regulation No. 10) [9]
- **Regulation** on characterization of surface water [10]

As can be seen from the titles, these items cover the state requirements about the water circle, but there are no special items for implementing the recycling methods of water usage. It is left to the initiative of the respective owners and technical persons.

Of course, there are many more laws, ordinances, regulations and orders in the Bulgarian legislation, which regulate the examination, design, construction, supervision and exploitation of the facilities connected with the water usage. They cannot be fully explained here due to shortage of space.

16.3 Examples of Industrial Wastewater Recycling in Bulgaria

The recycling in the industrial water supply in Bulgaria can be roughly divided in two periods:

- During the regime before 1989
- The period after 1989

Excluding the recycling systems, which were implemented in our Thermal Power Plants for production of soft water, the recycling in the industrial water supply during the regime before 1989 started in the eighties, when the main environmental laws were fact and the environmental protection somehow started to be implemented. Such facilities were our metallurgical industry, metalworking industry, chemical industry and food industry. Generally, the recycling systems were started first with industrial units with huge water usage, where the quality of the reused water was not so important. Some of the recycled water was used for the cooling systems, some other as a transport medium and only in some very small facilities recycled water were used in the main processes. In some cases the foul water from the main units was not treated, but discharged in the recycling systems used for transportation of materials, where the quality of the water was not so important.

The technologies used in the main processes were old, non–concurrent energy–intensive and that is the reason why several years after 1989 the industry in Bulgaria collapsed. Many industrial facilities were closed and for that reason their Waste Water Treatment Plants (WWTP) were stopped, which means that the existing recycling systems were also lost. The equipments were not protected and only the concrete basements were left from many WWTPs.

In the next years, some of the industrial units started again, with new technologies, but with decreased capacity or proceedings related to non–waste technologies. It is very difficult to find information about the existing WWT technologies that are applied in Bulgaria now. For that reason, only information published in specialized magazines or technical manuals, can be presented here.

- **Thermal Power Plants** – almost everyone uses circulating systems for transport the cinder to tilling ponds.
- **Metallurgical plant – Kremikovtsi** – now it is shut down. When it was in charge used approximately 2.5 mil m^3 $month^{-1}$ fresh water. The main consumption was in the cooling systems of the plant and for transporting raw materials and the solid wastes to a tailing pond.
- **Copper Ore Concentrating Plant – Asarel Medet-** It continues to operate. The contaminated water from the floating process is sent to tailing pond where after sedimentation is used back in the main manufacture as well as for preparing the technological solutions. That stream also contains the acid water from the so called “dump pile” which are neutralized to the necessary stage.

- **Some projects** for recycling the wastewater are ready but still not implemented in the:
- paper industry in towns of Belowo and Pazardjik
- ore concentrating plant in Plovdiv, for lead and zinc
- oil processing plant nearby Bourgas.

In some industrial facilities, some small units for water recycling are reported, but their capacity is small and does not affect the water consumption of the whole industrial unit. Mainly they are orientated not to save water but to extract valuable impurities from the wastewater.

16.4 Conclusion

- Bulgaria is not rich in water resources,
- There is a price for the use of water, but the cost charged is not stimulating the reuse of the water,
- The critical pollution level in many water resources is still not reached, but in some regions it is hard to find suitable water sources,
- Implementing water recycling technologies in particular cases is left to the initiative of the owner (user) of the water source,
- Governmental policy for water reuse and recycling is not adequate.

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