Chapter 9
Wastewater Treatment of a Denim Washing Plant by Using Waste Pumice Stones to Recycle Wastewater and Reuse

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Abstract In this study, the removal of pollutants from the wastewater of a denim washing plant by using the waste pumice stones and reuse of treated water were targeted. The trials were carried out through a continuous adsorption system. For this aim, the waste pumice stones were placed into an adsorption column, and the wastewater was allowed to pass through the column in different flow rates. The treated water was mixed with freshwater in certain ratios in order to be reused in laundry. The result of the studies revealed that the treated water has the potential to be used as denim washing input water.

Keywords Denim · Stone washing · Indigo · Pumice stone · Adsorption · Waste water · Waste water treatment

9.1 Introduction

In general, the textile industry consumes enormous amount of water and auxiliary chemicals primarily in the dyeing and finishing operations (Lin and Chen 1997; O'Neill et al. 1999; Veliev et al. 2006; Wambuguh 2009). Because the chemicals are not fixed on the fibre, they are removed during the washing and ending up in wastewater. About 12% of synthetic dyes used each year in the textile industry are lost, and 20% of these lost dyes released the environment through effluents. The effluent from denim industry containing 5–20% of the indigo dye used causes

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A. Matthes et al. (eds.), *Sustainable Textile and Fashion Value Chains*,
https://doi.org/10.1007/978-3-030-22018-1_9

wastewater with colour, suspended solids (salts) and dissolved organics (O'Neill et al. 1999). Some of those contents cause main toxicity in the wastewater, effect the aesthetic look, harm the quality of receipt streams and could be toxic for the treatment processes. Discharged effluent containing dyestuffs decreases the light conductivity which is necessary for the life cycle of the primary photosynthesis producers that live in water. Therefore, it seriously damages ecosystems (Veliev et al. 2006).

Miscellaneous processes have been applied to remove the colloidal compounds and suspended solids to decrease the higher biological oxygen demand (BOD). However, there is no single treatment available to decompose the dyestuffs in the effluent. The main disadvantage of the existing processes is the high investment, operating and maintenance costs (Wambuguh 2009).

In contrast, the adsorption method is now becoming an appropriate method for treating the effluents and has been widely used in various industrial processes in separation and removal purposes, mostly in the removal of organic pollutants particularly in textile industry (Al-Qoda 2000; Zaharia and Suteu 2012). The well-known industrial adsorption processes are nano-filtration and reverse osmosis systems. Their biggest disadvantages are the high costs of the investments and periodical refreshment of the expensive adsorption materials (medium) (Bagiran 2018). Even though the contaminants are moved from liquid to solid medium, adsorption process is a very efficient solution to protect the environment due to the ability of capturing and keeping apart the treated effluent in small volumes. The contaminants which are loaded onto the adsorbents can be removed by using various methods like chemical and thermal treatments (Sabbas et al. 2003; Toraman and Topal 2003). Some opportunities exist to use up these materials like in house construction, public roads and buildings so that waste can be recycled (Sabbas et al. 2003; Sivrikaya et al. 2014).

Pumice is a very interesting adsorbent. It is a volcanic rock which has a porous structure resulting in having high porosity and large amorphous areas inside. It is mainly composed of SiO_2 with lower density (0.35–0.65 g/cm^3) in aggregate form. Thanks to high porosity/surface area of pumice, the use of various pumice types (natural, modified, etc.) to be used as an adsorbent to remove the inorganic and organic substances that pollute the wastewater is still under research (Akbal 2005; Veliev et al. 2006; Kitis et al. 2007; Samarghandi et al. 2012a, b; Derakhshan et al. 2013; Samarghandi et al. 2013; Sepehr et al. 2013; Çifçi and Meriç 2015; Heibati et al. 2015; Asadia et al. 2016; Kocadağıstan and Kocadağıstan 2016).

Denim is pure cotton or cotton blend twill fabric. Cotton can be blended with lycra, polyester, regenerated cellulose fibres, etc. Denim fabric consists of dyed and undyed yarn. Undyed weft yarn is nearly white in colour. In jeans manufacturing, warp yarns are dyed with indigo-based dyestuffs that enable to obtain dark blue colour on the fabric (Wambuguh 2009; Paul 2015). Nowadays, synthetic indigo has almost taken the place of natural indigo. On the other hand, non-indigo dyes like sulphur dyes are also alternative to indigo. Sulphur dyes are commonly used for bottoming and topping of indigo due to reduce the overall cost (Chavan 2015; Paul 2015). Manufacturing of denim fabric is generally similar to that of grey fabric. However, sizing process in denim manufacturing is different from conventional sizing. Warp yarns of denim fabric are dyed at the stage of sizing. Therefore, weaving has important effect on

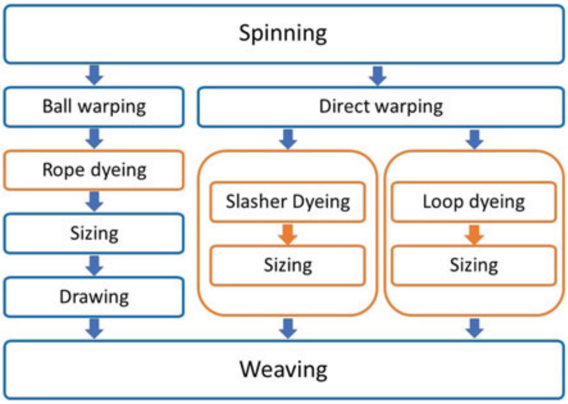


Fig. 9.1 Warp yarns dyeing methods in denim manufacturing (Illustration by S. Jonas)

the quality of the final garment (Paul 2015). Warp yarns are dyed continuously in three major methods. They are rope dyeing, slasher dyeing and loop dyeing (Fig. 9.1) (Meksi and Mhenni 2015).

In rope dyeing, 350–400 warp yarns make very thick cable of 10,000–15,000 m in length. Usually, 12–36 cables are first scoured and rinsed. Then, cables are dipped into a bath of leuco indigo. The wet pickup value is about 70–80%. After each dip, the cables are oxidized in air. At the end of the process, the cables are washed (Meksi and Mhenni 2015).

Instead of ball warping, direct warping is the stage of slasher dyeing. The warp yarns are in the form of sheet. It consists of about 4000 yarns. The sheet is first scoured and rinsed as in rope dyeing. Then, the sheet passes through the multi-dip/nip indigo dyeing section. The oxidation time is shorter than that of rope dyeing. The oxidation time takes at least 45 s. After dyeing, the sheet is washed and dried. The dyed sheet is dipped into size box, and the warp yarns pick up the required quantity of size solution (Meksi and Mhenni 2015).

Loop dyeing process is known as "Loopdye one for six". After pre-treatment process, the warp yarns are dyed in only a single bath with one squeezing unit. The yarns exit the dyeing bath. However, they do not move forward. Warp yarns are borne rear of the machine and come back to dyeing bath for another dye passage. Then, the dyed yarns are washed and dried. Sizing process follows drying directly (Meksi and Mhenni 2015).

Final stage is the weaving in the manufacturing of denim fabric. It is used for jeans, skirts, dresses, jackets, shorts, etc. Finishing of denim garments is very important for different look such as worn-out appearance. In order to get "the washed/aged look" on blue jeans, it is required to wash the raw garments in the wash baths that include pumice stones and/or various enzymes like cellulase and/or laccase so called "stonewashing". Following stonewashing, local or all over bleach steps are applied to obtain used look and faded colour that neutralization and many rinsing steps follow for ensuring to remove the leftovers of oxidative bleach agents (Wambuguh 2009).

Starting generally with the “stonewashing” process, the complete washing processes cause high amount of indigo to be removed from the denim fabrics into the discharged effluent. The effluent colour is highly visible even in very low concentrations for most dyestuffs, receiving complaints from an environmentally sensitive public and often failing to meet minimum requirements of the regulations valid for wastewater discharge (Wambuguh 2009). Effluent that contains indigo dyestuff is characterised by a certain amount of chemical oxygen demand (COD), organic and inorganic content, pH, suspended and dissolved solids and colour. Even though colour and COD are one of the main parameters monitored to meet wastewater discharge standards, some companies avoid treating the waste dyestuff present in the effluent due to extra operating cost (Wambuguh and Chianelli 2008).

9.2 The Washing Processes of Denim Garments and Their Basic Effects on Effluents

Finishing processes in textile industry are applied not only in yarn or fabric form but also in garment form. In denim washing processes, the treated materials so-called *jeans* are in garment form. Thanks to treating in garment form, denim washing processes are specialized to remove the indigo partially and create natural fade out effect on the garments. Denim washing processes consist of two separate sub processes: “*wet processes*” and “*dry processes*”. The main denim wet processes are desizing, rinsing, stone washing, enzyme washing, local and/or complete bleaching and tinting. The main denim dry processes are scraping, tagging, oxidative agent spraying, 3D look application and resin application. The main pollutant of denim washing effluents is the denim wet processes (Bağıran 2011).

In desizing process, the stiffener chemicals which are applied onto warp yarns to protect the breakages during weaving are removed. The main sizing agents are starch, carboxylmethilcellulose (CMC) and polyvinylalcohol (PVA). These chemicals are difficult to degrade in effluent systems that cause higher COD and BOD (Bağıran 2011; Periyasamy et al. 2017; Periyasamy and Militky 2017).

In stone washing process, denim garments are treated with pumice stones in short liquor ratios to remove the indigo dyestuff on the garments so that natural fade out effect along seams and on the panels is obtained. In this process, high amount of surface indigo dyestuff is removed from the garments and dosed to the effluent. Because the indigo dyestuff is difficult to degrade, both the COD and BOD figures become too high that causes difficulty to clean the effluent effectively, and the colour degree of the effluent increases (Bağıran 2011; Amutha 2017; Periyasamy et al. 2017; Periyasamy and Militky 2017).

In enzyme washing processes, several types of enzymes like amylase, cellulase and laccase are used. Amylase is used in desizing processes to degrade starch molecules (Bağıran 2011). Cellulase is used in stone washing and biopolishing processes to remove fuzziness and create seam and panel abrasion on the garments (Sefer 2009;

Bağıran 2011; Periyasamy et al. 2017; Periyasamy and Militky 2017; Amutha 2017). Laccase is used to generate radical groups to catalyse the bleaching processes and remove indigo dyestuffs (Rodríguez-Couto 2012). As all the enzymes have abrasion effects on the garments, they cause to increase the pollution in the effluent in toxicity, COD, BOD and colour wise.

In bleach processes, oxidative agents like chlorine derivatives, hydrogen peroxide and potassium permanganate are widely used. Reductive agents are not preferred in denim bleaching due to low reaction speed. Bleach agents are used for fading the colour on denim garments to create wide variety of colour options. As the main bleach agents are oxidative, they are the main responsible chemicals to generate adsorbable organic halogen compounds (AOX) in the effluent (Sefer 2009; Bağıran 2011; Amutha 2017; Periyasamy et al. 2017; Periyasamy and Militky 2017).

In tinting process, denim garments are dyed mostly with direct dyestuffs. This process shall not be considered as a real dyeing process. Instead, it is for colour the garments in diverse shades. During tinting processes, salts are used to enhance the exhaustion, whereas they cause to increase the total suspended solid (TSS) figures. Direct dyestuffs and fixing agent do cause the effluent pollution in terms of colour, total dissolved solid (TDS) and TSS (Sefer 2009; Bağıran 2011; Amutha 2017; Periyasamy et al. 2017; Periyasamy and Militky 2017; Bağıran 2018).

9.3 The Characteristics of Denim Washing Effluents

Effluents are dirty wastewater and are supposed to be treated prior to discharging to the environment. Although they look dirty and contain suspended and dissolved solids which cause pollution in the water, more than 99% percent of the effluents are only water. The main issue is to treat the effluents by basic and/or special effluent treatment processes efficiently and discharge the properly cleaned water back to the environment (Eltem 2008).

The characteristics of denim washing effluents are categorized under three sub titles:

- Physical characteristics
- Chemical characteristics
- Biological characteristics

9.3.1 Physical Characteristics of Denim Washing Effluents

The most important physical characteristics of denim washing effluents are "*total suspended and dissolved solids, odour, temperature, density, colour and turbidity*".

9.3.1.1 Total Dissolved and Suspended Solids

The total solids in the effluents consist of suspended and dissolved solids. The total solid in the effluent, analytically, can be calculated by the remaining solids after heating and evaporating the effluent at 103–105 °C. The total solids effect turbidity and the proper delivery of dissolved oxygen in the water. They also effect the sludge amount that will be generated during effluent treatments. If the effluent has higher solid concentration, it consumes more oxygen to decompose the solid matters and causes to reduce the treatment efficiency with gas release with unpleasant odour (Eckenfelder 2000; Eltem 2008).

9.3.1.2 Odour

Odour in the effluents is mostly generated by the degradation of the organic compounds or by the chemicals added during denim washing processes. Besides, dissolved phenols and chlorophenols do cause the unpleasant odour, too. The most unpleasant odour from the effluent is caused by hydrogen sulphur which is generated by anaerobic microorganisms during the reduction reaction of sulphate to sulphite (Eltem 2008; Spellman 2009; Yerli 2011).

9.3.1.3 Temperature

The increase in the effluent temperature effect two main parameters: "*rapid oxygen exhaustion*" and "*fast breeding of microorganisms*".

Oxygen that provides to sustain the aerobic reactions in the effluents dissolves in cold/warm water rather than hot water. Moreover, the increase in the temperate boosts the biochemical reactions in the effluents which causes to consume the oxygen content in the effluents.

Furthermore, the increase in the effluent temperature will fast breed some microorganisms which they are supposed to be at lower concentrations to keep the balance (Eltem 2008; Spellman 2009; Yerli 2011).

9.3.1.4 Density

A certain density value is needed for proper flow of the effluents in the tanks and through the pipes. Density is linked with the content of the total solids in the effluent and the effluent temperature (Eltem 2008).

9.3.1.5 Colour

Normally, water is colourless. But the industrial waste contains colourful chemical substances which turn the effluent colour to diverse shades.

Furthermore, the increase in the effluent temperature will fast breed some microorganisms which they are supposed to be at lower concentrations to keep the effluent environment in balance (Eckenfelder 2000; Gönder 2004; Spellman 2009; Yerli 2011).

9.3.1.6 Turbidity

Turbidity, a measurable characteristic of the light permeability of water, is used for stating the quality of effluents based on included suspended and dissolved solids.

If the suspended and dissolved solid concentrations are high in the effluents, they cause to have lower light permeability which lessens photosynthesis reactions and to have less degradation of the chemical substances. Furthermore, the increase in the effluent temperature will fast breed some microorganisms which they are supposed to be at lower concentrations to keep the effluent environment in balance (Eckenfelder 2000; Eltem 2008; Spellman 2009; Yerli 2011).

9.3.2 Chemical Characteristics of Denim Washing Effluents

The most important chemical characteristics of denim washing effluents are "*organic substances and inorganic substances*".

9.3.2.1 Organic Substances

Organic substances contain carbon, hydrogen and oxygen atoms which sometimes have the combination of nitrogen and phosphor. A denim washing effluent contains proteins, carbohydrates, oils and synthetic organic substances. In mid-degree polluted effluents, approximately 75% of total suspended solids and approximately 40% of total separable solids have organic chemical structure (Eltem 2008).

Synthetic organic substances carry the most complex molecule structure that complicate the removal out of the effluent. They are the most polluting substances in the effluents. The most preferred types of them are "*surface-active substances*" which reduce the surface tension of the water, meaning that they reduce the free energy of the medium. Alkylbenzensulphonates (ABS) are widely used in surface-active substances which cause to have foaming on effluent surface thanks to their indecomposable structure (Eckenfelder 2000; Eltem 2008).

The amount of the organic substances in effluents is considered as the basic pollution measuring parameter in denim washing effluents. However, the composition of the organic substances in the effluents is so complex that it is impossible to define the concentration of each organic substance. To define the organic substance quantity in the effluent, two individual approaches have been set: "*biological oxygen demand* (*BOD*)" and "*chemical oxygen demand* (*COD*)" (Eckenfelder 2000; Eltem 2008; Yerli 2011).

9.3.2.2 Inorganic Substances

The inorganic substances of the effluent identify the water quality. The most common inorganic substances presented in the effluents are hydrogen, chlorine and ammonium anions, nitrogen, phosphor, sulphur and heavy metal ions.

Each inorganic substance mentioned has individual effect on effluent quality. Individually, they have the effects like determining the pH value, causing AOX and toxicity, acting as a nutrient for microorganisms and playing a role in vital reactions (Eckenfelder 2000; Eltem 2008; Spellman 2009; Yerli 2011).

9.3.3 Biological Characteristics of Denim Washing Effluents

Biological treatment activities in the effluents are as important as chemical treatment activities. In biological treatments, bacteria lead the reactions to degrade the unwanted substances such as organic and inorganic compounds. For effective biological treatments, the following parameters are needed to be considered:

- The type and the quantity of the bacteria in treatment areas and in the effluent.
- The optimal living conditions of the bacteria (Eltem 2008).

9.4 The Basic Effluent Treatment Processes

In denim washing plants, the main effluent treatment processes are performed in three individual steps: "*physical treatment, chemical treatment and biological treatment*".

9.4.1 Physical Effluent Treatments

Physical effluent treatments are the first step in the wastewater treatment. This step generally consists of screening to remove large floating objects, rags and other things that could damage plant equipment of the system. Additionally, grit removal is applied to take out the large gravel, stones and other mostly inorganic components.

Primary treatment consists of a sedimentation basin in which relatively heavy objects settle out and buoyant materials, such as plastic, as well as fats, greases and oil, float to the top. These are mostly organics at this stage, but there may be a few inorganics mixed in with them, as well (Hopcroft 2015).

9.4.2 Chemical Effluent Treatments

In this step, chemical reactions are benefitted to remove the pollutants from the effluents by using some special chemicals. The most important chemical treatment methods are "*chemical oxidation*", "*neutralization*", "*coagulation*" and "*flocculation*".

In chemical oxidation step, either the pollutants are provided to have harmless compound structures by increasing their oxidizing level or they are prepared for the next effluent treatment processes by the impact of oxidizing reactions. This process is used to remove colour, unpleasant odour, iron, manganese and organic substances from the effluent. Most common oxidizing agents used in this step are oxygen, ozone, chlorine anions and potassium permanganate (Eltem 2008).

In neutralization step, the pH figure of the effluent is set to the required value for bacteria activation during biological treatments, proper coagulation in the following chemical effluent processes and obtaining suitable discharge requirements after biological treatments. Acidic (citric acid, sulphuric acid) or basic (caustic soda, lime) chemical can be used to adjust the pH (Eckenfelder 2000; Eltem 2008).

In coagulation step, the individual colloidal substances in the effluents are prepared to form aggregates by adding some specific salts like aluminium sulphate and copperas. After the reaction, the colloidal substances tend to form the aggregates called flocs which will coagulate in the effluent.

In flocculation step, the coagulated colloidal substances attract each other to form the flocs by the impact of special chemicals called "polyelectrolytes". They form large aggregates, lose the ability to suspend in the effluent and sink in the effluent that helps form the effluent sludge (Eckenfelder 2000; Eltem 2008).

9.4.3 Biological Effluent Treatments

Biological wastewater treatment is often applied as a secondary treatment process, used to remove any material remaining after primary treatment. During the primary water treatment process, sediments or substances such as oil are removed from the wastewater, and then, the suspended and dissolved substances in the effluent left from the chemical effluent treatments are decomposed by bacteria, and they are converted to biological flocs, inorganic substances and gases.

There are three types of bacteria that perform the decomposing: "*aerobic, anaerobic and facultative*". Aerobic bacteria perform the reactions in the presence of oxygen as they need it to survive. In contrast to aerobic bacteria, anaerobic bacteria do not need oxygen in their life cycles and can decompose the organic substances in the lack of oxygen molecule. Facultative bacteria can both live in the mediums with or without oxygen molecules (Hopcroft 2015).

Aerobic wastewater treatment systems involve activated sludge process, oxidation ditches, trickling filters, lagoon-based treatments and aerobic digestion. During the treatment, aeration is applied to provide oxygen to the bacteria as they decompose organic substance in the wastewater.

In the case of anaerobic treatment, the organic residues are deteriorated by anaerobic bacteria in an oxygen-free environment.

9.5 Adsorption

Adsorption known to mankind for a very long time is increasingly used to perform desired bulk separation or purification purposes. Adsorption has two components an adsorbate that is the compounds attached to the solid surface and an adsorbent the solid itself. The heart of an adsorption process is usually a porous solid providing a very high surface area, and thus, a high adsorption capacity is achieved. However, the porous medium is usually associated with very small pores causing an increase in the resistance to the mass transfer. Understanding of the adsorptive capacity is within the domain of equilibria, and understanding of the diffusional resistance is within the domain of kinetics (Duong 1998).

The term *adsorption* is universally understood to mean the enrichment of one or more of the components in the interface between the bulk fluid (gas or liquid) and a solid surface. Because the adsorption process is accompanied by *absorption,* i.e. the penetration of the fluid into the solid phase in certain systems (e.g. some metals exposed to hydrogen, oxygen or water), the term *sorption* is also used to define the process. The term sorption is sometimes used to denote the uptake of a gas or liquid by a molecular sieve. The removal of the adsorbed substances from the surface is called as *desorption,* and the equilibrium is established when the adsorption and desorption rates are equal. The relation showing how the adsorbed amount changes with the equilibrium pressure, or concentration at constant temperature is known as the *adsorption isotherm* (Rouquerol et al. 1999).

Adsorbent to be used in a certain adsorption process is a critical variable because the success or failure of the process depends on how the solid performs in both equilibria and kinetics. A solid with good capacity but slow kinetics requiring too long time to reach the equilibrium is not an appropriate choice, since the slow kinetics means a high residence time in a column, hence a low throughput. On the other hand, a solid with fast kinetics but low capacity is not good either as a large amount of solid is required for a given throughput. Thus, a good adsorbent means a solid that provides good adsorption capacity as well as good kinetics. To satisfy these two requirements, the adsorbent must have a reasonably high surface area, reactive groups on the surface and relatively large pore network for the transport of molecules to the interior.

To satisfy the first requirement, the porous solid must have small pore size with a reasonable porosity. This suggests that a good solid must have a combination of two pore ranges: the micropore range and the macro pore range. The classification of pore size as recommended by IUPAC (Rouquerol et al. 1999) is often used to delineate the range of pore size:

Micropores $d < 2$ nm.
Mesopores $2 < d < 50$ nm.
Macropores $d > 50$ nm.

This classification is arbitrary and was developed based on the adsorption of nitrogen at its normal boiling point on a wide range of porous solids. The adsorbents such as activated carbon, zeolite, alumina and silica gel that are commonly used in industries do satisfy these two criteria (Duong 1998).

9.6 Pumice Stone

Pumice stone is a volcanic, light density rock which is formed following the volcanic eruptions. The stone has high porous structure thanks to the immediate cooling of lava by the impact of wind and cooler weather. The pore sizes and size of the pumice stone are variable. The pore sizes can be in nano, micro, meso and macro scale. The pores are generally not connected with each other, and they are covered by a glassy film layer (Sapçı and Üstün 2003).

Physically, pumice stones can have beige, dirty white and brown colour. Their density varies between 0.5–2 gr/cm^3. Their hardness varies between 5–6 in Mohs scale.

Chemically, the main component of pumice stones is "*sillicium mono oxide* (*SiO*)". The content of it varies between 45–80%. Thanks to the high content of sillicium, pumice stones both have a light density and good abrasion ability. The second main component is "*Di aluminium tri oxide* (Al_2O_3)". The content of it varies between 10–15%, and it provides good thermal resistance (Gündüz et al. 2001; Özkan and Tuncer 2001).

Due to the variable volcanic eruptions in the nature, pumice stones gain either acidic or basic characters based on their silica content. Acidic pumice stones have white or dirty white colour which are less in density and hardness compared to the basic pumice stones (Özkan and Tuncer 2001).

In denim garment stone washing processes, acidic pumice stones are preferable thanks to their lightweight structure which does not damage the garments and provide smooth abrasion effects along seams and on the garment panels.

9.7 Experimental

In this study, the removal of pollutants from the effluent of a denim washing plant by using the waste pumice stones used in stonewashing process was targeted. The reuse of the treated water in laundry was investigated. Thanks to their porous structures, the waste pumice stones should have a high adsorption capacity for the treatment of the effluent of a denim washing plant. The pollutants in the effluent of the denim plant were targeted to be removed through the adsorption, and the experimental studies were carried out in a pilot scale adsorption column installed at the exit of the biological effluent treatment unit of the industrial effluent treatment facility of the denim washing plant. The change in wastewater parameters like colour, COD, etc., determined by taking the samples at predetermined time intervals from the inlet and the outlet streams of the column. In addition to colour and COD, the parameters like TDS, turbidity, the amount of chloride anion, etc., were also measured.

The treated effluent was mixed with freshwater in 1:1 ratio for reusing purpose in denim washing processes determined as rinsing, stonewashing, stone bleaching and tinting. Two sets of garments were prepared, and the first set was washed with freshwater, whereas the second set was washed with the water mixture prepared. Following this, physical tests like crocking, tear/tensile strength, etc., and subjective evaluations like change in all over look were performed.

9.7.1 Materials

During the study, the waste pumice stones that were extracted from the denim washing plant were used as the adsorption material. The pumice stones were grinded into smaller sizes, and the size "*100–595* μm" was selected based on older studies as reference.

The effluent selected for the tests was taken from the exit of the biological treatment area.

For adsorption process, a special adsorption colon was manufactured with inlet and outlet points and pre-filtering area. The waste grinded pumice stones were placed into the adsorption colon.

A special pressure adjustable pump was used to pump the effluent to the inlet of the adsorption colon.

For effluent reuse tests, one type of denim fabric was used to form the denim garments. The fabric composition is 98% cotton + 2% elastane, and woven type is 3/1 right twill.

9.7.2 Method

During the study, the method was set to identify three main points as seen in the following:

1. The waste pumice stone adsorption of the effluent
2. Identifying the waste pumice stone characteristics
3. Reuse the recycled water in basic denim washing processes

In the first stage, the waste pumice stones were put into the adsorption colon. The effluent was pumped into the colon with constant temperature/pressure and specimens were taken at predetermined intervals. On specimens, the water quality parameters were tested.

In the second stage, on waste pumice stones after the adsorption, the material characteristics like scanning electron microscopy (SEM), energy dispersive X-ray (EDX) and Brunauer–Emmett–Teller (BET) analyses were investigated and parameters were tested.

In the third stage, the characteristics of the denim garments washed with the recycled water were investigated and parameters were tested.

9.7.3 Findings

9.7.3.1 The Waste Pumice Stone Adsorption of the Effluent

During the experimental that took two weeks in total, 55 treated effluent specimens were taken from the outlet of the adsorption colon. The change in the colour of the samples taken from inlet and exit of column are given in Fig. 9.2. As shown in

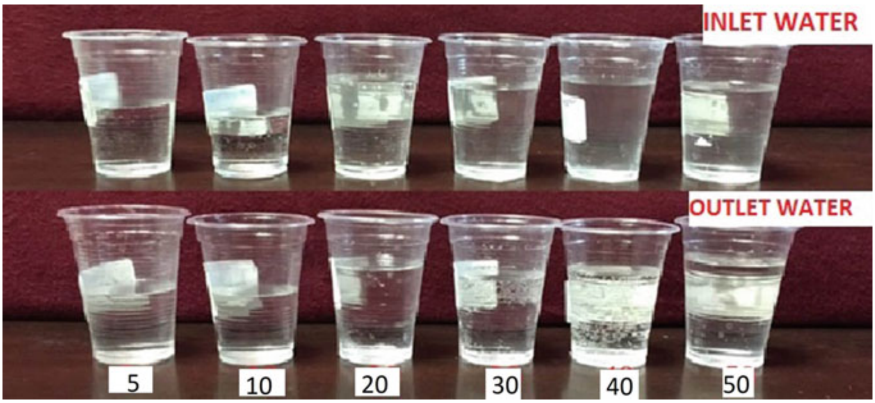


Fig. 9.2 The visuality of the change in the colour after adsorption (Author's own illustration)

the figure treated water is clearer than the untreated one. Fresh oxygen bubbles can clearly be observed.

In addition to visual observations, the samples were tested in terms of colour, and other water quality parameters. For colour wise, it has been observed that 59.09% of the effluent colour (in Pt–Co unit) has been removed after pumice stone adsorption.

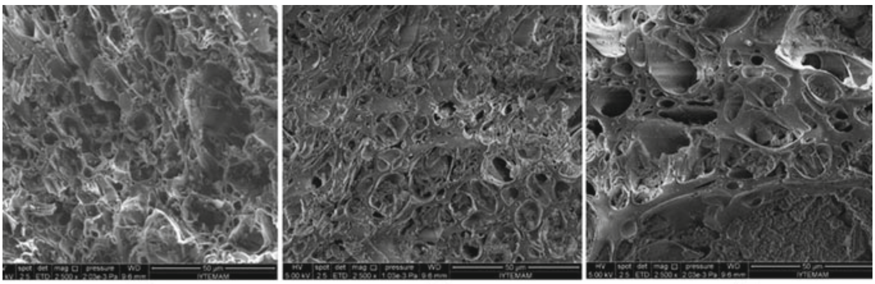
COD wise, it has been observed that adsorption reduced the COD value by 25.88%. For total suspended solid wise, the reduction value is 46.66%. For turbidity wise, the reduction value is 79.15% and for AOX wise, the reduction value is 46.23%. All the results show that adsorption by waste pumice on denim washing effluent has reduced the pollution and colour drastically and prepared a suitable medium for reusing the wastewater in denim washing processes.

9.7.3.2 Identifying the Waste Pumice Stone Characteristics

The waste pumice stone that was used in the adsorption was subjected to SEM, BET and EDX tests to see how the adsorption affected the structure of the material adsorbent.

For the comparison purposes, three different samples (raw pumice stone, waste pumice stone used in stone washing and waste pumice stone used in both stone washing and in adsorption) were subjected to SEM analysis. The images magnified by 2500 × were given in Fig. 9.3.

A close examination of the figure revealed that the samples have almost the same surface morphologies with non-uniform sized pores. However, the pores on the surface of raw pumice stone have sharper edges in the entrance than the other samples. The edges of the pores are smoothed and become more open in waste pumice stone used in stonewashing. This structure forms an advantage for the adsorption of dye molecules because this makes easy the penetration of the molecule to the active sites. In the case of waste pumice stones used in stonewashing and adsorption, the



(a) (b) (c)

Fig. 9.3 SEM images of specimens: **a** shows raw pumice stone, **b** shows the waste pumice stone used in denim washing, and **c** shows the waste pumice stone used in stonewashing and adsorption (Author's own illustration) surface seems to be more compact. This compactness will probably be the result of the filling of the pores with polluting materials.

The surface area and pore volumes of the pumice stones were determined by using the data obtained from adsorption isotherms. In Fig. 9.4, the adsorption isotherm of waste pumice stone used in denim washing and adsorption is given as an example.

When the figure is analysed, based on the guided graphics (Rouquerol et al. 1999), it is observed that the pumice stone used here has macro pores. The adsorption occurred on the surface of the stones and around the edges of the macro pores, and it continued both on single and multi-layers.

The surface area of the waste pumice used in denim washing and adsorption is calculated as 2.739 m^2/g, and the cumulative pore volume is calculated as 0.005910 cm^3/g. The surface area of the waste pumice used in only denim washing is calculated as 1.0806 m^2/g, and the cumulative pore volume is calculated as 0.002321 cm^3/g. Adsorption is a surface phenomenon, and therefore, the higher surface area means higher adsorbed amounts. However, the pore size plays

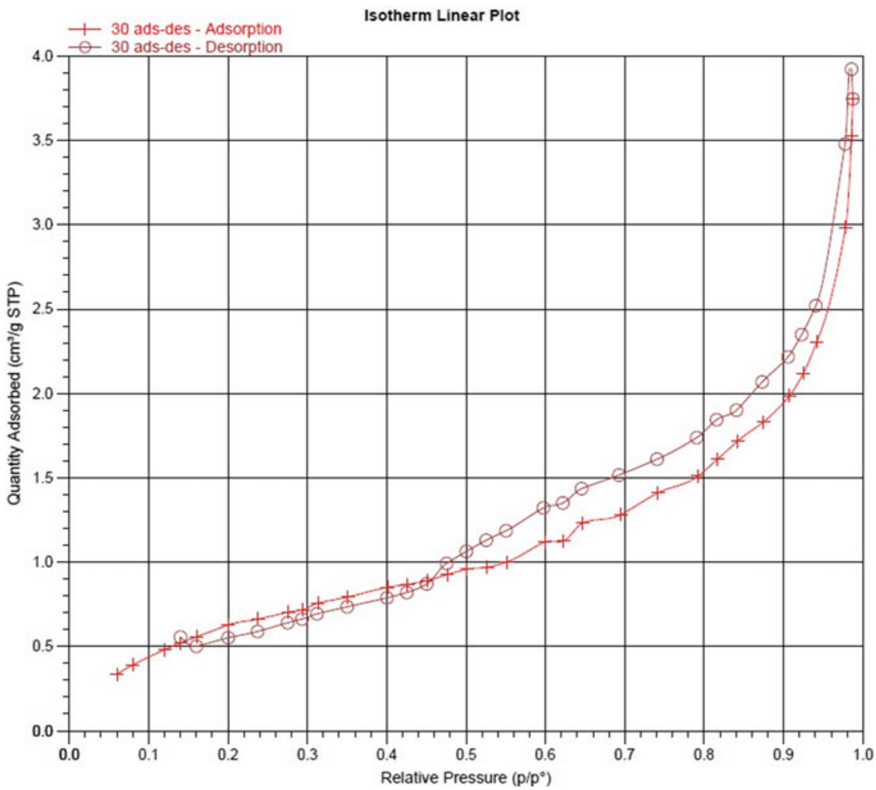


Fig. 9.4 Adsorption isotherm of waste pumice stones used in denim washing and adsorption (Author's own illustration)

an important role because if the pore size is less than the size of compounds to be adsorbed, adsorption does not occur.

In EDX analysis, the atom contents in the “waste pumice stone used in denim washing”, and “the waste pumice stone used in denim washing and adsorption” were calculated and compared to each other. Based on the results, it has been observed that the amount of carbon atoms has increased from 3.56 to 10.54% (in weight basis). The sulphur and chlorine atoms were observed at 0.05% and 0.36, respectively, whereas they were not observed in the pumice stone which was not used in adsorption. These increases proof that pumice stones have adsorbed the pollutants such as surface-active inorganic substances.

9.7.3.3 Reuse the Recycled Water in Basic Denim Washing Processes

After the adsorption, the treated water was mixed with freshwater in 1:1 ratio. The prepared water was used as input water in denim washing processes selected as rinse, stonewashing, chlorine bleaching and tinting. In order to get comparable results, another set of garments were washed with freshwater, and both results were compared.

The selected test parameters to compare the results are colour value, tear and tensile strength, crocking fastness and yellowing degree.

Colour wise, both specimens have very similar shades in all washing types according to objective and subjective evaluations. It has been observed that the garments washed with recycled water have slightly lighter shades. This could be due to the inclusion of chlorine and surface-active substances in recycled water which cannot be 100% removed.

Tear and tensile strength and crocking fastness wise, all specimens with all washes have close values to each other. No significant differences are noticed.

Yellowing degree wise, the garments washed with recycled water in rinsing have half degree less grade than the ones washed with the fresh water. Similar to lightness in the colour, this could be due to the chemical residues of chlorine and surface-active substance. In the other washing processes, all the yellowing values are the same.

9.8 Conclusion

In this study, the removal of pollutants from the textile effluent by waste pumice stone from a denim factory was studied. The results of COD and other parameters’ measurements indicated that the dyestuffs and other organic impurities were removed by adsorbent. It was observed that there were not significant changes on the garments that were washed in separate sets. The results show that the waste pumice stones can be used as adsorbents for the treatment of wastewater of a denim plant. It is recommended that the adsorption system of pumice stones can be used as a helping effluent treatment unit in addition to main treatment units, and through this way, an economic value can be added to the solid waste.

Acknowledgements The authors gratefully acknowledge the support of Ege University Scientific Research Project Dept. (BAP) with the project number "13-MÜH-50" and Turkish Scientific Research Council (TÜBİTAK) with the project number "114M883".

References

Akbal, F. (2005). Adsorption of basic dyes from aqueous solution onto pumice powder. *Journal of Colloid and Interface Science, 286*(2), 455–458.

Al-Qodah, Z. (2000). Adsorption of dyes using shale oil ash. *Water Research, 34*(17), 4295–4303.

Amutha, K. (2017). Environmental impacts of denim hazards. In S. S. Muthu (Ed.), *Sustainability in denim* (pp. 37–40). Cambridge: Woodhead Publishing.

Asadia, F., Dargahib, A., Almasic, A., & Moghofea, E. (2016). Red reactive 2 dye removal from aqueous solutions by pumice as a low-cost and available adsorbent. *Arch Hyg. Sci., 5*(3), 145–152.

Bağıran, İ. C. (2011). Denim yıkamada karşılaşılan sorunlar ve bunlara yönelik cözüm onerileri. *Dissertation*, Ege University.

Bağıran, İ. C. (2018). Denim yıkamada kullanılmış ponza taşlarının atık su arıtmada kullanımı ve geri kazanılan suyun tekrar denim yıkamada kullanım olanakları. *Dissertation*, Ege University.

Chavan, R. B. (2015). Indigo dye and reduction techniques. In R. Paul (Ed.), *Denim manufacture, finishing and applications* (pp. 37–39). Cambridge: Woodhead Publishing.

Çifçi, D. İ, & Meriç, S. (2015). A review on pumice for water and wastewater treatment. *Desalination and Water Treatment, 57*(39), 1–13.

Derakhshan, Z., Baghapour, M. A., Ranjbar, M., & Faramarzian, M. (2013). Adsorption of methylene blue dye from aqueous solutions by modified pumice stone kinetics and equilibrium studies. *Health Scope, 2*(3), 136–144.

Duong, D. D. (1998). *Adsorption analysis: Equilibria and kinetics*. London: Imperial College Press.

Eckenfelder, W. W., Jr. (2000). *Industrial water pollution control*. Boston: McGraw-Hill.

Eltem, R. (2008). *Atık sular ve arıtım*. Izmir: Ege Üniversitesi Fen Fakültesi Yayınları.

Gönder, Z. B. (2004). Fenton prosesi ve iyon değişimi kombinasyonu ile renkli atıksuların arıtımı. *Dissertation*, İstanbul University.

Gündüz, L., Rota, A., & Hüseyin, A. (2001). *Türkiye ve dünyadaki ponza oluşumlarının malzeme karakteristiği analizi*. In H. Köse, V. Arslan., & V. Tanrıverdi (Eds.), Izmir: 4. Endüstriyel Hammaddeler Sempozyumu.

Heibati, B., Rodriguez-Couto, S., Turan, N. G., Ozgonenel, O., Albadarin, A. B., Asif, M., et al. (2015). Removal of noxious dye-Acid orange 7 from aqueous solution using natural pumice and Fe-coated pumice stone. *Journal of Industrial and Engineering Chemistry, 31,* 124–131.

Hopcroft, F. J. (2015). *Wastewater treatment concepts and practices*. New York: Momentum Press.

Kitis, M., Kaplan, S. S., Karakaya, E., Yiğit, N. O., & Civelekoğlu, G. (2007). Adsorption of natural organic matter from waters by iron coated pumice. *Chemosphere, 66*(1), 130–138.

Kocadağıstan, B., & Kocadağıstan, E. (2016). Batch and column removal of the dye blue 3R over pumice. *Desalination and Water Treatment, 57*(58), 1–14.

Lin, S. H., & Chen, M. L. (1997). Treatment of textile wastewater by chemical methods for reuse. *Water Research, 31*(4), 868–876.

Meksi, N., & Mhenni, M. F. (2015). Indigo dyeing technology for denim yarns. In R. Paul (Ed.), *Denim manufacture, finishing and applications* (pp. 69–79). Cambridge: Woodhead Publishing.

O'Neill, C., Hawkes, F. R., Hawkes, D. L., Lourenco, N. D., Pinheiro, H. M., & Delee, W. (1999). Colour in textile effluents—sources, measurement, discharge consents and simulation: A review. *Journal of Chemical Technology and Biotechnology, 74*(11), 1009–1018.

Özkan, Ş. G., & Tuncer, G. (2001). Ponza madenciliğine genel bir bakış. In H. Köse, V. Arslan, & V. Tanrıverdi (Eds.), 4. Izmir: Endüstriyel Hammaddeler Sempozyumu.

Paul, R. (2015). Denims and jeans: An overview. In R. Paul (Ed.), *Denim manufacture, finishing and applications* (pp. 1–4). Cambridge: Woodhead Publishing.
Periyasamy, A. P., & Militky, J. (2017). Denim processing and health hazards. In S. S. Muthu (Ed.), *Sustainability in denim* (pp. 163–167). Cambridge: Woodhead Publishing.
Periyasamy, A. P., Wiener, J., & Militky, J. (2017). Life-cycle assessment of denim. In S. S. Muthu (Ed.), *Sustainability in denim* (pp. 87–88). Cambridge: Woodhead Publishing.
Rodríguez-Couto, S. (2012). Laccases for denim bleaching: An eco-friendly alternative. *The Open Textile Journal, 5,* 1–7.
Rouquerol, F., Rouquerol, J., & Sing, K. (1999). *Adsorption by powders and porous solids*. London: Academic Press.
Sabbas, T., Polettinib, A., Pomi, R., Astrup, T., et al. (2003). Management of municipal solid waste incineration residues. *Waste Management, 23*(1), 61–88.
Samarghandi, M. R., Zarrabi, M., Amrane, A., Soori, M. M., & Sepehr, M. N. (2013). Removal of acid black dye by pumice stone as a low-cost adsorbent: Kinetic, thermodynamic and equilibrium studies. *Environmental Engineering and Management Journal, 12*(11), 2137–2147.
Samarghandi, M. R., Zarrabi, M., Sepehr, N. M., Amrane, A., Safari, G. H., & Bashiri, S. (2012). Application of acidic treated pumice as an adsorbent for the removal of azo dye from aqueous solutions: Kinetic, equilibrium and thermodynamic studies. *Iranian Journal of Environmental Health Sciences and Engineering, 9*(9), 1–10.
Samarghandi, M. R., Zarrabi, M., Sepehr, N. M., Panahi, R., & Foroghi, M. B. (2012). Removal of acid red 14 by pumice stone as a low-cost adsorbent: Kinetic and equilibrium Study. *Iranian Journal of Chemistry and Chemical Engineering, 31*(3), 19–27.
Sapçı, Z., & Üstün, B. (2003). The removal of color and COD from textile wastewater by using pumice stones. *Electronic Journal of Environmental, Agricultural and Food Chemistry, 2,* 286–290.
Sefer, O. (2009). *Çevre dostu organik denim terbiyesinin klasik denim terbiyesiyle karşılaştırılması. Dissertation.* Izmir: Ege University.
Sepehr, M. N., Zarrabi, M., Kazemian, H., Amrane, A., Yaghmaian, K., & Ghaffari, H. R. (2013). Removal of hardness agents, calcium and magnesium, by natural and alkaline modified pumice stones in single and binary systems. *Applied Surface Science, 274,* 295–305.
Sivrikaya, O., Kıyıldı, K. R., & Karaca, Z. (2014). Recycling waste from natural stone processing plants to stabilise clayey soil. *Environmental Earth Science, 71*(10), 4397–4407.
Spellman, F. R. (2009). *Handbook of water and wastewater treatment plant operations.* Boca Raton: Taylor & Francis Group.
Toraman, ÖY., & Topal, H. (2003). Katı atık teknolojiler ve uygulamaları. *Journal of Factor Engineering Arch Gazi University*, *18*(1), 19–33.
Veliev, E. V., Öztürk, T., Veli, S., & Fatullayev, A. G. (2006). Application of diffusion model for adsorption of azo reactive dye on pumice. *Polish Journal Environmental Studies, 15*(2), 347–353.
Wambuguh, D. (2009). *By-product synergy in the textile industry: Indigo waste recovery in the denim finishing process. Dissertation.* Texas: The University of Texas.
Wambuguh, D., & Chianelli, R. R. (2008). Indigo dye waste recovery from blue denim textile effluent: A by-product synergy approach. *New Journal of Chemistry, 32*(12), 2189–2194.
Yerli, S. V. (2011). *Su kalitesi ders notları.* Ankara: Hacettepe Üniversitesi Yayınları.
Zaharia, C., & Suteu, D. (2012). Textile organic dyes—Characteristics, polluting effects and separation/elimination procedures from industrial effluents—A critical overview. In T. Puzyn & A. Mostrag (Eds.), *Organic pollutants ten years after the stockholm convention—Environmental and analytical update* (pp. 55–86). Rijeka: InTech.