Remediation of Dyes from Aquatic Ecosystems by Biosorption Method Using Algae

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1 Introduction

1.1 Aquatic Pollution

Water, the elixir of life, is subjected to contamination and pollution in the hands of man. The aquatic ecosystem around the globe is facing a major threat by anthropogenic activities. Although 70 % of the Earth's crust is covered by water, only less than 1 % of that is fresh water and is used by all for consumption as well as nonconsumptive purposes. Industries around the world consume a major share of fresh water for processing, washing and cooling of industrial products. Apart from the direct usage of water in the production of materials, the industries also foul the water bodies by discharging effluents in them. The toxic and hazardous effluents released from industries create havoc in the aquatic ecosystem and also affect organisms on terrestrial ecosystems when water is consumed directly or used for irrigation. The dye industry poses a major threat to the aquatic ecosystem as the colours from the dyes not only reduce the aesthetic value of the water but also increase toxicity in the water body which can hamper the normal growth of aquatic organisms as well as terrestrial organisms when it reaches the higher trophic levels. The water usage in textile industry alone is about 9 trillion gallons annually around the world (Blacksmith Institute Annual Report 2012). An estimate by World Bank suggests that the textile industries contribute around 17-20 % of the total industrial water pollution globally (Blacksmith Institute Annual Report 2012). The world population will be about 9.3 billion in the year 2060 (UN Report 2011). The ever-increasing population will create stress on the existing

resources, and fresh water will be amongst the scarcest natural resources.

1.2 Dyes

Unfortunate are those men who cannot see the beauty of the Earth in its vibrant hues. This statement has perfect truth as we cannot imagine this world without colours. A substance having an affinity towards the substrate on which it is applied is described as a dye. The dyes are of a certain colour as they absorb visible rays of the electromagnetic spectrum at a particular wavelength (Pereira and Alves 2012). Natural dyes are known to be used by man since 3500 BC according to the historical records (Kant 2012). Organic colours were also used by Egyptians 4000 years back in the wraps for the mummies in the form of blue dye, indigo (Gordon and Gregorn 1983). The first synthetic dye was accidentally discovered by W.H. Perkins in the year 1856 which paved the way for modern day dye industry. More than one lakh commercial dyes are present today, and over 700,000 tonnes of dyes are produced annually (McMullan et al. 2001; Pearce et al. 2003).

Dyes are used in textile, paper, leather, pharmaceuticals, cosmetics, agricultural, wood staining, food and many other industries. Natural dyes were used earlier which had a drawback of low colour fastness. The natural dyes are less bright in colour also the dyes fade away with time. Therefore, the use of synthetic dyes has increased at present times which are polluting in nature. The natural dyes can also harm the environment as substances known as mordants have to be used with them to fix or bind the colour on fibres. Chromium is an example of such mordant which is a potentially toxic heavy metal for all living organisms (Kant 2012).

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1.2.1 Types of Dyes

The dye molecules comprise of two major components the chromophore group and the auxochrome group. Chromophores are electron acceptors, and they are responsible for the light absorption in molecules of the dye. Auxochromes are the electron donors, and they are the colour enhancers in the dye molecules (Gomes 2001; Pereira and Alves 2012). The dyes can be classified on the basis of application and on the basis of chemical structure. The anionic dyes are of three types: reactive, direct and acid dyes (Fu and Viraraghavan 2001). Reactive dyes are used in textile industries, and these dyes show a fast colour even after washing and exposure to light. Direct dyes are used for colouring cellulose fibres without the application of mordants. Acid dves are mostly used in colouring of protein fibres; azo dyes come under the category of acid dyes. Basic dyes fall in the category of cationic dyes; these dyes are bright in colour but are not fast to light and water. These dyes are usually used in textile industries for silk fibres. Disperse dyes are nonionic in nature, mostly used in synthetic fibres in paper or textile. Disperse dyes are insoluble in water; therefore, their colour is fast and bright (Fu and Viraraghavan 2001).

1.2.2 Toxicity of Dyes

Synthetic dyes are complex compounds in nature, manufactured in a way to increase the longevity of the coloured product. Dyes are xenobiotic in nature and thus resist degradation by traditional wastewater treatments and reach the aquatic ecosystem (Crini 2006). The undesirability of the presence of dyes in water increases because of the toxic and carcinogenic nature of majority of dyes and the breakdown products released by them, for example, benzidine, naphthalene and other aromatic compounds (Alves de Lima et al. 2007; Tsuboy et al. 2007; Suteu et al. 2009a, b; Zaharia et al. 2009; Oplatowska et al. 2011; Li et al. 2012; Punzi et al. 2015). The usage of water in the dye industry is also very high where almost 90-94 % of water is used in processing and the rest of the water is used for cooling purposes in case of textile industries. The amount of textile dyes lost during dying process itself is 10-25 %, and 2-25 % of dyes are directly released as effluents into water bodies (Zaharia and Suteu 2012). According to the annual report of Blacksmith Institute of 2012, the dye industry contributes around 400,000 DALYs (disability-adjusted life years) out of the total 17,147,600 DALYs which is the total burden of disease in the 49 countries which were assessed. The DALY is a measurement of life expectancy adjusted according to several health hazards caused due to pollution and other factors. The first basic problem with the effluents released from dye industry is that it gives the water an unnatural hue which ruins the aesthetic value of that water body. Figure 8.1 depicts the impacts of effluents discharged by dye industries on the aquatic and terrestrial ecosystem. The coloured dyes on reaching the water body obstruct solar radiation penetration and thus consequently reduce the photosynthesis rate of phytoplanktons and other macrophytes present in water. The pH and salinity of the water are affected by the presence of dye effluents as the dye effluents are high in pH and salinity; thus, these factors in turn disturb the maintenance of the equilibrium in the water bodies (Chia and Musa 2014).

The homeostasis of aquatic organisms is adversely affected by toxicity and water quality degradation by dye effluents. The effluents from dye industry are organic in nature; they tend to lower the dissolved oxygen level of water bodies which affects the overall ecological balance of the water body (Ratna and Padhi 2012). The lowering of DO leads to increase in biological oxygen demand (BOD) and chemical oxygen demand (COD) which leads to death of aquatic organisms and increase in anaerobic bacteria (Khopkar 2004). When the water polluted by effluent is used for irrigation, it leads to clogging of pores in the soil, hardening of soil particles and prevention of root penetration in soil which further results in reduction in soil productivity (Kant 2012). Effluents discharged from industries usually do not stay fixed at the point of release. Explanation about the impact of dyes on agricultural crops is given in Fig. 8.2. The effluents if discharged into water bodies may enter the terrestrial ecosystem in form of irrigation water. The effluents from the dye industries are found to have an inhibitory effect on the germination of seeds (Nirmalarani and Janardhanan 1988). The effluents may also bring about alterations in the biological and chemical status of water and soil which affects the overall development and productivity of plants. When the concentration of solids present in the effluent is higher, it reduces the DO level and restricts the development of seedlings (Saxena et al. 1986). The chlorophyll content in leaves of such plants is also lowered because of the presence of dissolved solids (Gadallah 1996). These toxic effluents may also lower the tolerance of the plants towards abiotic and biotic stresses.

Several of the dyes are found to be mutagenic and carcinogenic in nature specially the azo dyes and the anthraquinone dyes (Rochat et al. 1978; Kornbrust and Barfknecht 1985; IARC 1987; Moghaddam et al. 2004; Puvaneswari et al. 2006; Mathur and Bhatnagar 2007; Jayaraj et al. 2011; Mayson and Suad 2012; Kousha et al. 2012; Chia and Musa 2014). A detailed explanation on the dyes and their toxic impact on health of organisms are given in Table 8.1. Organically bound chlorine is found in 40 % of the dyes found globally which is found to be a carcinogen (Kant 2012).

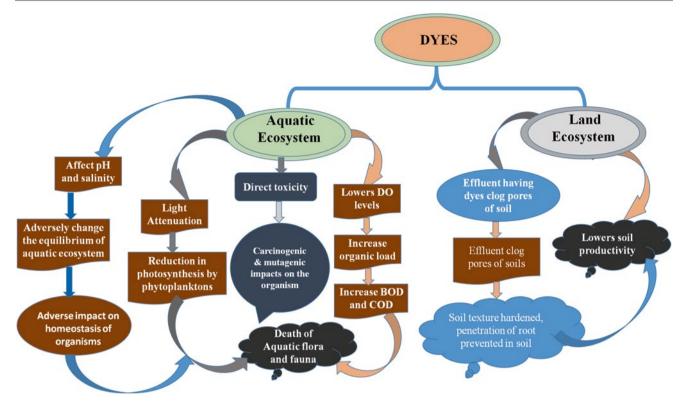
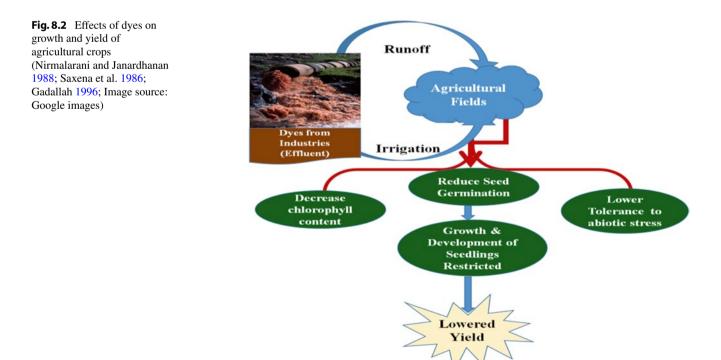


Fig. 8.1 Effects of dyes on aquatic and land ecosystems (Khopkar 2004; Kant 2012; Ratna and Padhi 2012; Chia and Musa 2014; deLuna et al. 2014)



Dye	Class	Application	Toxicity impact	Reference	
Azo dyes (general)	Azo	Textile industries	Bladder cancer in workers handling dyes	Puvaneswari et al. (2006)	
Rhodamine B	Xanthene	Textile and food industry, used as water tracer	Irritation to skin, eyes, respiratory tract Carcinogenic, reproductive and development toxicity, neurotoxicity	Rochat et al. (1978), Kornbrust and Barfknecht (1985), Jain et al. (2007) and IARC (1987)	
Acid black	Diazo	Paints, inks, plastics, leather	Irritation to eyes, skin and respiratory system	Daneshvar et al. (2012)	
Acid orange ll	Azo	Textile, paper	Carcinogenic	Kousha et al. (2012)	
Acid green (3)	Triphenylmethane	Textile	Animal carcinogens, tumour growth observed in fish species	Hazrat and Shah (2008)	
Methylene blue	Phenothiazine	Textile	Vomiting, shock, increased heart rate, tissue necrosis in humans, Heinz body formation	Hameed et al. (2007)	
Malachite Green	Triphenylmethane	Textile, biological stain	Carcinogenic and mutagenic	Moghaddam et al. (2004)	
Congo Red	Diazo	Textile, paper and pulp industry, biological stain	Carcinogenic and mutagenic	Jayaraj et al. (2011), Mayson and Suad (2012)	
Indigo dye	Azo	Textiles, paper, leather, plastic, food, drug,	Mutagenic effect on bacterium Salmonella typhimurium	Mathur and Bhatnagar (2007)	
		cosmetics	Acute toxicity effect seen on S. quadricauda	Chia and Musa (2014)	

 Table 8.1
 Effects of dyes on human health

2 Removal of Dyes from Aquatic Ecosystem

Presence of dyes in the water bodies is a nuisance at present times due to toxic and polluting nature of dyes. Removal of colour is a must from all effluent as it ruins the aesthetic appearance of water bodies and reduces light penetration. The laws are stringent regarding organic content in effluents; therefore, it is necessary to remove dyes from the effluents before their release into the water bodies (Crini 2006). Since the popularisation of synthetic dyes in the modern world, several techniques have been employed for removal of dyes. Very few methods have been successful considering the holistic view (Ghoreishi and Haghighi 2003).

2.1 Traditional Methods

The technologies for removal of dyes can be categorised into physical, chemical and biological techniques as described in Fig. 8.3 (Robinson et al. 2001). Physical treatment methods include membrane filtration techniques such as reverse osmosis, electrodialysis, nanofiltration, adsorption processes, etc. Membrane filtration techniques are not economically feasible because of low life span of the membranes which requires periodic replacement (Crini 2006). Adsorption is considered as one of the most feasible and effective techniques for removal of dyes (Dabrowski 2001; Crini 2006). Adsorption by activated carbon is referred to as one of the most efficient dye removal techniques of current by US EPA (Derbyshire et al. 2001). The activated carbon adsorption method is not very cost-effective, nonselective and considered ineffective for vat and disperse dyes (Babel and Kurniawan 2003). Chemical treatment methods for removal of dyes from waste-

waters include coagulation and flocculation followed by filtration, precipitation using Fe(II)/Ca(OH)₂ followed by flocculation, electrokinetic coagulation, oxidation using ozone and irradiation. These methods are expensive and contain toxic sludge which poses a problem for disposal, and excess chemical usage may add to the burden of existing pollution problem (Crini 2006). Biological treatment processes are the most cost-effective alternatives for treatment of dye effluents in comparison to traditional physical and chemical methods. Microbial degradation, fungal decolourization, biosorption by microbes and macro-organisms and bioremediation techniques fall under the category of biological treatment processes. Bacteria, algae, fungi and yeasts are known to accumulate or degrade effluents (Banat et al. 1996; Fu and Viraraghavan 2001; McMullan et al. 2001; Crini 2006). Biological treatment processes also have some constraints in terms of application and technology. The disadvantages of biological treatment processes are as follows: they require a larger area (Bhattarcharyya and Sharma 2003); complete colour elimination is not possible (Robinson et al. 2001); and some complex compounds being xenobiotic in nature cannot be completely degraded (Ravi Kumar et al. 1998). Nonconventional methods are now being developed to combat the problem of pollution resulting from dyes.

2.2 Nonconventional Methods of Dye Removal

2.2.1 Adsorption

Adsorption techniques can be considered as one of the most environmental friendly technologies for the successful elimination of dyes from the wastewater. The use of activated carbon made from waste materials from agriculture, industries

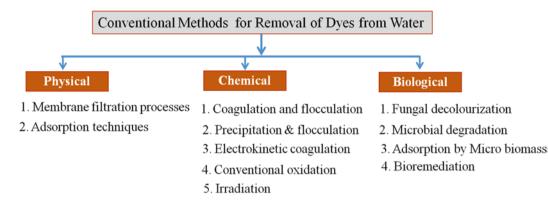


Fig. 8.3 Methods for removal of dyes from water (Source: Crini 2006)

 Table 8.2
 Adsorption efficiency of some conventional and nonconventional adsorbents

Adsorbent	Dye	Class	Adsorption capacity (mg g ⁻¹)	Reference
Chitosan	Reactive blue 2	Anthraquinone	2498	Chiou et al. (2004)
Activated carbon Taipei Chemical corp. (Taiwan)	Acid yellow	Azo	1179	Chern and Wu (2011)
Chemviron Carbon (UK)	Remazol yellow	Anthraquinone	1111	Al-Degs et al. (2000)
Pinewood	Acid blue 264	Anthraquinone	1176	Tseng et al. (2003)
Biomass	Reactive black 5	Azo	588.2	Aksu and Tezer (2000)
Tree fern	Basic red 13	Methine	408	Ho et al. (2005) and Gupta et al. (2003)
Peat	Basic violet 14	Triarylmethane	400	Sun and Xang (2003)
Activated sludge	Reactive yellow 2	Azo	333.3	Aksu (2001)
Clay	Basic blue 9	Triarylmethane	256.41	Gulnaz et al. (2004)
Yeasts	Remazol blue	Anthraquinone	173.1	Aksu and Donmez (2003)
Zeolite	Reactive red 239	Diazo	111.1	Ozdemir et al. (2004)

and municipal solid wastes is becoming popular nowadays as they are cost-effective; also it makes use of the materials which are polluting in nature and thus are beneficial in all respects. Natural materials such as clays, zeolites and silicates also are used as nonconventional adsorbents (Crini 2006). Table 8.2 shows the adsorption capacities of different conventional and nonconventional adsorbents (Cardoso et al. 2011). Chitosan is observed to have the maximum adsorption capacity followed by AC Taipei Chemical Corp (Chiou et al. 2004; Chern and Wu 2011).

2.2.2 Biosorption

The use of biomass for the accumulation of pollutants from effluents or other aqueous solutions can be termed as biosorption. The biosorbents are effective in removal of dyes due to their complex nature and chelating properties (Crini 2006). According to Aksu and Tezer (2005), biosorption consists of several processes independent of metabolism such as chemical and physical adsorption, chelation, microprecipitation, complexation and ion exchange; these take place within the cell wall. The process of biosorption includes two phases: one is a solid phase involving biosorbent that is the biological material and the second one is the liquid phase consisting of a solvent usually water which has a dissolved adsorbate (dyes) that needs to be sorbed (Ramachandra et al. 2005). Biosorption is a lucrative technique for dye removal because of its costeffectiveness, high efficiency and selectivity and abundance of biosorbents found in nature or present in waste materials which can be effectively used (Aksu and Tezer 2005).

2.2.3 Phycoremediation

Algae have the potential to become suitable biosorbent because of their abundance in nature, very fast growth in a simple medium and cost-effectiveness (Aksu and Tezer 2005; Rawat et al. 2011; Olguín and Sánchez-Galván 2012; Prajapati et al. 2013; Malla et al. 2015). Phycoremediation can be defined as the use of microalgae and macroalage to transform contaminants with potential hazards present in water or soil into nonhazardous materials. The use of algae is being popularised nowadays for treatment of wastewater instead of using conventional bacteria. Algae are considered as a better option for the treatment processes because some of the pollutants have nutritional value for the algae; thus, it is efficiently taken up (Rawat et al. 2011; Olguín and Sánchez-Galván 2012; Singh et al. 2012; Prajapati et al. 2013; Sode et al. 2013; Laffont-Schwob et al. 2015). Heavy metals such as iron and chromium are essential for the photosynthetic process and metabolism of the algae; thus, these heavy metals are effectively removed from the environment by them. Algae, which live in such conditions where there is a lack of these metals, develop special mechanisms to collect the essential nutrients. This feature of algae can be successfully used to treat effluent laden with heavy metals, toxic materials and dyes (Kumar et al. 2007; Gomes and Asaeda 2009; Olguín and Sánchez-Galván 2012; Kumar et al. 2015; Machida and Horizoe 2015). One of the advantages of using algae over bacteria is that algae do not require oxygen to remove pollutants instead they release oxygen and gather carbon dioxide. The additional advantage of carbon sequestration can be obtained from the process of detoxification (Dwivedi 2012). Treatment of coloured water by algae is proving to be highly beneficial because of several factors such as abundance nature of algae, cost-effectiveness, efficiency, no competition with other aquatic species, etc. (Chisti 2007; Kumar et al. 2014). In some instances where nonliving algal biomass is used for biosorption, the de-oiled algal biomass is used for biosorption of dyes. This provides double benefit as biofuel is obtained by algae and same biomass is used for waste water treatment. Microspora sp. (ATCC PTA-12197) was first de-oiled, and then the biomass was used for biosorption of methylene blue dye by Maurya et al. (2014).

Algae have been found to cleanse toxic effluents and wastewater by the processes of bioaccumulation, biosorption and biodegradation. The biosorption capability of macroalgae and microalgae can be attributed to the porous cell walls which allow movement of ions and molecules in aqueous solutions (Sheng 2004; Wang and Chen 2009; Fakhry 2013). The functional groups such as carboxyl, hydroxyl, phosphate, amino and other charged groups that are present on the cell surface of algae are responsible for binding of dye molecules and separation of pollutants from water (Srinivasan and Viraraghavan 2010; Celekli and Geyik 2011; Celekli and Bozkurt 2011; Fang et al. 2011). The extracellular biopolymers comprise mostly of alginate in Phaeophyta which are permeable to small ions (Vieira and Volesky 2000). Agar, porphyran and carregeenan which are sulphated galactans are found in Rhodophyta (Davis et al. 2003). These extracellular biopolymers which have long-chain structure are responsible for the adsorption of dyes and heavy metals (Fakhry 2013). The adsorption of contaminants or heavy metals in live microalgae is carried out in two steps: first step takes place rapidly where the adsorption is onto the cell surface and the second step is absorption which is lengthy and takes place within the cell and is dependent on cell metabolism (Dwivedi 2012). The macroscopic structure and rigidity in shape makes some macroalgae such as Azolla filiculoides very efficient in biosorption column applications (Padmesh et al. 2005). Some algae are capable to convert complex toxic compounds and dyes into simple compounds like Chlorella vulgaris which is capable of removing about 63-69 % of colour from water in mono-azo dye tectilon yellow 2G by breaking it up into aniline (Acuner and Dilek 2004). The use

of immobilised algae for removal of colour is being studied with positive results. In a study by Chu et al. (2009), it was found that alginate-immobilised *Chlorella vulgaris* is capable of removing more colour than the suspension culture.

3 Biosorption Studies and Adsorption Kinetics

3.1 Biosorption by Macroalgae

Macroalgae have been reported to eliminate dyes successfully from aqueous solution in laboratory experiments (Khataee and Dehghan 2011; Khataee et al. 2010, 2011; Daneshvar et al. 2012; Kousha et al. 2012; Salima et al. 2013). Acid black 1 which is a diazo dye was efficiently removed from the solution using macroalgae S. glaucescens and S. marginatum where adsorption by S. marginatum and by S. glaucescens was found to be 30.9 mg g^{-1} (Table 8.3.) and 27.0 mg g^{-1} , respectively (Daneshvar et al. 2012). Kousha et al. (2012) found that C₃H₉N-treated S. margin*atum* was capable of 71.05 mg g⁻¹ biosorption of acid orange dye, whereas untreated S. marginatum removed 35.62 mg g⁻¹ of same dve. Padina pavonica removed 11.72 mg g⁻¹ of acidfast yellow dye (Fakhry 2013). Jayaraj et al. (2011) found that Valoria bryopsis could remove 10.5 mg g⁻¹ of Congo red dye. Chara aspera has been found to remove 60-81 % methylene blue dye with pH ranging from 2.40 to 11-16. Basic blue 3 was removed by Chara aspera with an efficiency of 17.36-27.33 % at pH of 2.17-9.43 (Low et al. 1994).

3.2 Biosorption by Microalgae

Acutodesmus obliquus efficiently removed 44.24 mg g⁻¹ of acid red 66 dye (Sarwa et al. 2014). *Microspora* sp. (ATCC PTA-12197) was capable of removing 86 % of methylene blue dye (Maurya et al. 2014). Aksu and Tezer (2005) found that *Chlorella vulgaris* effectively removed remazol black B, remazol red R and remazol golden yellow with accumulation rate of 368.8 mg g⁻¹, 181.9 mg g⁻¹ and 52.8 mg g⁻¹, respectively (Table 8.4).

The treatment process where algae are used is highly pH dependent. The pH of the solution influences the dye chemistry in water as well as the dye binding sites at the cell surface. When the pH is low, the biomass has a net positive charge; it is assumed that in this case, amines or imidazoles present in the biomass will be protonated when pH has acidic values. The lower the pH, the higher the adsorption can be caused due to negative dye anions and positive cell surface. When the pH increases, the sites with positive charge decrease and sites with negative charge increase causing electrostatic repulsion between dyes and cell surface; thus, the adsorption capacity decreases (Crist et al. 1981; Gardea-

Algae	Dye	Class	Concentration of dye (mg L ⁻¹)	Rate of accumulation (mg g ⁻¹)/efficiency	рН	Biosorbent dosage (g L ⁻¹)	Time (h)	Adsorption isotherms	Reference
S. glaucescens	Acid black 1	Diazo	10–50	27.0	2	1–9	1.5	Temkin and Freundlich	Daneshvar et al. (2012)
S. marginatum	Acid black 1	Diazo	10–50	30.9	2	1–9	1.5	Temkin and Freundlich	Daneshvar et al. (2012)
S. marginatum	Acid orange	Azo	30–90	35.62	2	1	1	Langmuir	Kousha et al. (2012)
C ₃ H ₉ N-treated <i>S. marginatum</i>	Acid orange	Azo	30–90	71.05	2	1	1	Langmuir	Kousha et al. (2012)
CH ₃ OH treated <i>S. marginatum</i>	Acid orange	Azo	30–90	29.08	2	1	1	Langmuir	Kousha et al. (2012)
HCHO treated S. Marginatum	Acid orange	Azo	30–90	34.06	2	1	1	Langmuir	Kousha et al. (2012)
HCHO/HCOOH treated S. marginatum	Acid orange	Azo	30–90	14.95	2	1	1	Langmuir	Kousha et al. (2012)
Padina pavonica	Acid-fast yellow	Azo	5-160	11.72		2	1.5	Pseudo second-order model	Fakhry (2013)
Valoria bryopsis	Congo red	Diazo	5–25	10.5	5	50–250 mg		Langmuir, Freundlich, DKR adsorption isotherm	Jayaraj (2011)
Chara aspera	Methylene blue	Basic	100	60.0-81.25 %	2.40–11.16	0.05–0.5	2	Langmuir	Low et al. (1994)
Chara aspera	Basic blue 3	Triaryl– methane	100	17.36–27.33 %	2.17–9.43	0.25–1	2	Langmuir	Low et al. (1994)

Table 8.3 Biosorption efficiency of macroalgae for different dye	Table 8.3	Biosorption efficiency of macroalgae for different dyes
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 Table 8.4
 Biosorption efficiency of microalgae for different dyes

Algae	Dye	Class	Concentration of dye (mg L ⁻¹)	Rate of accumulation (mg g ⁻¹)/efficiency	pН	Biosorbent dosage (g L ⁻¹)	Time (h)	Adsorption isotherms	Reference
Acutodesmus obliquus	Acid red 66	Azo	10–50	44.24 (max)	2	0.1	1	Langmuir	Sarwa et al. (2014)
<i>Microspora</i> sp. (ATCC PTA-12197)	Methylene blue	Basic	50	86 %	7	10		Pseudo second- order model	Maurya et al. (2014)
Chlorella vulgaris	Remazol black B	Azo	20-800	368.8	2	1	-	Freundlich, Redlich-Peterson, Kolbe-Worigan	Z.Aksu and Tezer (2005)
C. vulgaris	Remazol red R	Azo	20-800	181.9	2	1	-	Langmuir	Z.Aksu and Tezer (2005)
C. vulgaris	Remazol golden yellow	Azo	10–200	52.8	2	1	-	Langmuir	Z.Aksu and Tezer (2005)

Torresdey et al. 1990; Aksu 1998; Aksu and Tezer 2005; Tam et al. 2002; Tien 2002). Most of the studies indicated that the optimum pH of 2 was most suitable for biosorption of dyes from the aqueous solution.

The dye removal efficiency of macro- and microalgae is calculated by the following formula:

Removal efficiency (%) =
$$(C_0 - C_f) * 100 / C_0$$
 (8.1)

where C_o is the initial dye concentration and C_f is the equilibrium dye concentration in the solution (mg/l)

$$q_e = V(C_0 - C_f) / m$$
 (8.2)

where V is the volume of the solution, M is the mass of biosorbent (g), and q_e is the dye biosorption.

3.3 Adsorption Isotherms

Adsorption models are used to investigate and study the adsorption mechanisms and surface properties of the biosorbents. The maximum adsorption capacity of any adsorbent is determined by the adsorption equilibrium measurements. Langmuir, Freundlich, Redlich-Peterson and Temkin isotherms are commonly used. Freundlich isotherm was developed in 1906 by Freundlich which described the heterogeneous surface equilibrium, and monolayer capacity is not assumed in this case (Lin and Juang 2009). The surface is considered as homogeneous in Langmuir isotherm where all adsorption sites exhibit equal affinity for solute particles (Langmuir 1918). Redlich-Peterson isotherm combined the elements from Langmuir and Freundlich isotherms (Redlich and Peterson 1959). The initial dye concentration also determines the adsorption capacity of biosorbent; when the initial concentration is high, the adsorption increases as more driving force is provided to overcome resistance from mass transfer between the solid and aqueous phases (Aksu and Tezer 2005). Similarly, the amount of biosorbent dosage when increased increases the rate of adsorption.

4 Conclusions

Algal biosorption can prove to be a boon for the people who are suffering from the adverse impacts of dyes present in the effluents releasing from different industries like textile, paper and pulp, tanning and pharmaceuticals. The algal biomass can have multipurpose use in extraction of oil, waste water treatment and carbon fixation. Marine and freshwater algae have both been made use of to detoxify the dye from wastewater. Algae being cosmopolitan and cost-effective can be used at even community level for the removal of dyes contamination. Some technical interventions like application of genetic engineering can be engaged which may further enhance the rate of phycoremediation of dyes with accelerated amount of lipid content.

References

- Acuner E, Dilek FB (2004) Treatment of tectilon yellow 2G by *Chlorella vulgaris*. Process Biochem 39:623–631
- Aksu Z (1998) Biosorption of heavy metals by microalgae in batch and continuous systems. Springer/Landes Bioscience, Berlin
- Aksu Z (2001) Equilibrium and kinetic modelling of Cadmium (II) biosorption by C. vulgaris in a batch system: effect of temperature. Sep Purif Technol 21:285–294

- Aksu Z, Donmez G (2003) A comparative study on the biosorption characteristics of some yeasts for Remozal Blue reactive dye. Chemosphere 50:1075–1083
- Aksu Z, Tezer S (2000) Equilibrium and kinetic modeling of biosorption of Remazol Black B by Rhizopus arrhizus in a batch system: effect of temperature. Proc Biochem 36:431–439
- Aksu Z, Tezer S (2005) Biosorption of reactive dyes on the green alga Chlorella vulgaris. Process Biochem 40:1347–1361
- Al-Degs Y, Kharaisheh MAM, Allen SJ, Ahmad MN (2000) Effect of carbon surface chemistry on the removal of reactive dyes from textile effluent. Water Res 34:927–935
- Al-Taee MMS, Al-Ahmad SGK (2012), Biological decolorization of malachite green dye from aqueous solution by algae. J Babylon Univ/Pure Appl Sci 2(20):542–550
- Alves de Lima RO, Bazo AP, Salvadori DMF, Rech CM, de Oliveira Palma D, Umbuzeiro GA (2007) Mutagenic and carcinogenic potential of a textile azo dye processing plant effluent that impacts a drinking water source. Mut Res/Gen Toxicol Environ Mutagen 626:53–60
- Babel S, Kurniawan TA (2003) Low-cost adsorbents for heavy metals uptake from contaminated water: a review. J Hazard Mater B97:219–243
- Banat IM, Nigam P, Singh D, Marchant R (1996) Microbial decolorization of textile-dye-containing effluents: a review. Bioresour Technol 58:217–227
- Bhattarcharyya GK, Sharma A (2003) Adsorption characteristics of the dye, brilliant green on neem leaf powder. Dyes Pigm 57:211–222
- Blacksmith Institute Annual Report: 2012 report: the top ten sources by global burden of disease. http://en.wikipedia.org/wiki/ Blacksmith_Institute#2012_report:_The_Top_Ten_Sources_by_ Global_Burden_of_Disease
- Cardoso NF, Lima EC, Pinto IS, Amavisca CV, Royer B, Pinto RB, Alencar WS, Pereira SFP (2011) Application of *cupuassu* shell as biosorbent for the removal of textile dyes from aqueous solution. J Environ Manag 92:1237–1247
- Çelekli A, Bozkurt H (2011) Bio-sorption of cadmium and nickel ions using *Spirulina platensis*: kinetic and equilibrium studies. Desalination 275:141–147
- Çelekli A, Geyik F (2011) Artificial Neural Networks (ANN) approach for modeling of removal of lanaset red G on *Chara contraria*: application of isotherm and kinetic model. Bioresour Technol 102:5634–5638
- Chern JM, Wu CH (2001) Desorption of dye from activated carbon beds: effects of temperature, pH and alcohol. Water Res 35:4159–4165
- Chia MA, Musa RI (2014) Effect of indigo dye effluent on the growth, biomass production and phenotype plasticity of Scenedesmus quadricauda (Chlorococcales). An Acad Bras Cienc 86(1):419–428
- Chiou MS, Ho PY, Li HY (2004) Adsorption of anionic dyes in acid solutions using chemically cross-linked chitosan beads. Dyes Pigments 60:69–84
- Chisti Y (2007) Biodiesel from microalgae. Biotechnol Adv 25:294–306
- Chu WL, See YC, Phang SM (2009) Use of immobilised *Chlorella vulgaris* for the removal of colour from textile dyes. J Appl Phycol 2:61–648
- Crini G (2006) Non-conventional low-cost adsorbents for dye removal: a review. Bioresour Technol 97:1061–1085
- Crist HR, Oberholser K, Shank N, Nguyen M (1981) Nature of bonding between metallic ions and algal cell walls. Environ Sci Technol 15:1212–1217
- Dabrowski A (2001) Adsorption, from theory to practice. Adv Colloid Int Sci 93:135–224
- Daneshvar E, Kousha M, Jokar M, Koutahzadeh N, Guibal E (2012) Acidic dye biosorption onto marine brown macroalgae: isotherms, kinetic and thermodynamic studies. Chem Eng 204–206:225–234

- Davis TA, Volesky B, Vieira RHSF (2003) A review of the biochemistry of heavy metal biosorption by brown algae. Water Res 37:4311–4330
- deLuna LAV, da Silva THG, Nogueira RFP, Kummrow F, Umbuzeiro GA (2014) Aquatic toxicity of dyes before and after photo-Fenton treatment. J Hazard Mater 276:332–338
- Derbyshire F, Jagtoyen M, Andrews R, Rao A, Martin-Gullon I, Grulke E (2001) Carbon materials in environmental applications. In: Radovic LR (ed) Chemistry and physics of carbon, vol 27. Marcel Dekker, New York, pp 1–66
- Dwivedi S (2012) Bioremediation of heavy metal by algae: current and future perspective. J Adv Lab Res Biol 3:229–233
- Fakhry EM (2013) *Padina pavonica* for the removal of dye from polluted water. Am J Plant Sci 4:1983–1989
- Fang L, Zhou C, Cai P, Chen W, Rong X, Dai K, Liang W, GuJ D, Huang Q (2011) Binding characteristics of copper and cadmium by cvanobacterium *Spirulina platensis*. J Hazard Mater 190:810–815
- Fu Y, Viraraghavan T (2001) Fungal decolorization of dye wastewaters: a review. Bioresour Technol 79:251–262
- Gadallah MAA (1996) Phytotoxic effects of industrial and sewage wastewaters on growth, chlorophyll content, transpiration rate and relative water content of potted sunflower plants. Water Air Soil Pollut 89:33–47
- Gardea-Torresdey JL, Becker-Hapak MK, Hosea JM, Darnall DW (1990) Effect of chemical modification of algal carboxyl groups on metal ion binding. Environ Sci Technol 24:1372–1378
- Ghoreishi SM, Haghighi R (2003) Chemical catalytic reaction and biological oxidation for treatment of non-biodegradable textile effluent. Chem Eng J 95:163–169
- Gomes JR (2001) Estrutura e Propriedades dos Corantes. Barbosa e Xavier Lda, Braga
- Gomes PIA, Asaeda T (2009) Phycoremediation of Chromium (VI) by Nitella and impact of calcium encrustation. J Hazard Mater 166:1332–1338
- Gordon P, Gregorn P (1983) Organic chemistry in colour. Springer, Berlin, pp 208–211
- Gulnaz O, Kaya A, Matyar F, Arikan B (2004) Sorption of basic dyes from aqueous solution by activated sludge. J Hazard Mater B108:183–188
- Gupta VK, Ali I, Suhas Mohan D (2003) Equilibrium uptake and sorption dynamics for the removal of a basic dye (basic red) using lowcost adsorbents. J Colloid Int Sci 265:257–264
- Hameed BH, Ahmad AL, Latiff KN (2007) Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust. Dyes Pigments 75:143–149
- Hazrat A, Shah KM (2008) Biosorption of crystal violet from water on leaf biomass of *Calotropis procera*. J Environ Sci Technol 1:143–150
- Ho YS, Chiang TH, Hsueh YM (2005) Removal of basic dye from aqueous solution using tree fern as a biosorbent. Process Biochem 40:119–124
- IARC (1987) Overall evaluations of carcinogenicity: an updating of IARC monographs, vol. 1–42. Supplement 7. IARC, Lyon
- Jain R, Mathur M, Sikarwar S, Mittal A (2007) Removal of the hazardous dye rhodamine B through photocatalytic and adsorption treatments. J Environ Manag 85:956–964
- Jayaraj R, Chandramohan M, Prasath MD, Khan TH (2011) Malachite Green dye removal using seaweed Enteromorpha. J Chem 8(2):649–656
- Jayaraj R, Thanaraj PJ, Natarajan ST, Deva Prasath PM (2011) Removal of Congo red dye from aqueous solution using acid activated ecofriendly low cost carbon prepared from marine algae Valoria bryopsis. J Chem Pharm Res 3(3):389–396
- Kant R (2012) Textile dyeing industry and environmental hazard. Nat Sci 4:22–26

- Khataee AR, Dehghan G (2011) Optimization of biological treatment of a dye solution by macroalgae *Cladophora* sp. using response surface methodology. J Taiwan Institute Chem Eng 42:26–33
- Khataee AR, Dehghan G, Ebadi A, Zarei M, Pourhassan M (2010) Biological treatment of a dye solution by Macroalgae Chara sp.: effect of operational parameters, intermediates identification and artificial neural network modeling. Bioresour Technol 101:2252–2258
- Khataee AR, Dehghan G, Zarei M, Ebadi E, Pourhassan M (2011) Neural network modeling of biotreatment of triphenylmethane dye solution by a green macroalgae. Chem Eng Res Des 89:172–178
- Khopkar SM (2004) Environmental pollution-monitoring and control. New Age International (P) Limited Publisher, New Delhi, p 224
- Kornbrust D, Barfknecht T (1985) Testing of 24 food, drug, cosmetic and fabric dyes in the in vitro and the in vivo/in vitro rat hepatocyte primary culture/DNA repair assays. Environ Mutagen 7:101–120
- Kousha M, Daneshvar E, Sohrabi MS, Jokar M, Bhatnagar A (2012) Adsorption of acid orange II dye by raw and chemically modified brown macroalgae *Stoechospermum marginatum*. Chem Eng J 192:67–76
- Kumar KS, Ganesan K, Subba Rao PV (2007) Phycoremediation of heavy metals by the three-color forms of Kappaphycus alvarezii. J Hazard Mater 143:590–592
- Kumar PS, Pavithra J, Suriya S, Ramesh M, Kumar KA (2014) Sargassum wightii, a marine alga is the source for the production of algal oil, bio-oil, and application in the dye wastewater treatment. Desalin Water Treat. doi:10.1080/19443994.2014.924032
- Kumar KS, Dahms HU, Won EJ, Lee JS, Shin KH (2015) Microalgae a promising tool for heavy metal remediation. Ecotoxicol Environ Saf 113:329–352
- Laffont-Schwob I, Triboit F, Prudent P, Soulié-Märsche I, Rabier J, Despréaux M, Thiéry A (2015) Trace metal extraction and biomass production by spontaneous vegetation in temporary Mediterranean stormwater highway retention ponds: freshwater macroalgae (Chara spp.) vs. cattails (Typha spp.). Ecol Eng 81:173–181
- Langmuir I (1918) The adsorption of gases on plane surfaces of glass, mica and platinum. J Am Chem Soc 40:1361–1367
- Li Y, Shi JQ, Qu RJ, Feng MB, Liu F, Wang F, Wang ZY (2012) Toxicity assessment on three direct dyes (D-BLL, D-GLN, D-3RNL) using oxidative stress bioassay and quantum parameter calculation. Ecotoxicol Environ Saf 86:132–140
- Lin SH, Juang RS (2009) Adsorption of phenol and its derivatives from water using synthetic resins and low-cost natural adsorbents: a review. J Environ Manag 90:1336–1349
- Low KS, Lee CK, Toh BL (1994) Binding of basic dyes by the algae, *Chara aspera*. Pertanika J Sci Technol 2(1):85–92
- Machida H, Horizoe H (2015) High efficiency metal removal from hexane-extracted algae oil using super and subcritical propane. Energ Conv Manage 95:90–93
- Malla FA, Khan SA, Rashmi SGK, Gupta N, Abraham G (2015) Phycoremediation potential of Chlorella minutissima on primary and tertiary treated wastewater for nutrient removal and biodiesel production. Ecol Eng 75:343–349
- Mathur N, Bhatnagar P (2007) Mutagenicity assessment of textile dyes from Sanganer (Rajasthan). J Environ Biol 28(1):123–126
- Maurya R, Ghosh T, Paliwal C, Shrivastav A, Chokshi K, Pancha I, Ghosh A, Mishra S (2014) Biosorption of methylene blue by deoiled algal biomass: equilibrium, kinetics and artificial neural network modelling. PLoS One 9(10), e109545. doi:10.1371/journal. pone.0109545
- Mayson MS Al-Taee and Suad GK Al-Ahmad (2012), Biological Decolorization of Malachite Green Dye from Aqueous Solution by Algae Journal of Babylon University/Pure and Applied Sciences/2(20): 542–550

- McMullan G, Meehan C, Conneely A, Kirby N, Robinson T, Nigam P, Banat IM, Marchant R, Smyth WF (2001) Microbial decolourisation and degradation of textile dyes. Appl Microbiol Biotechnol 56:81–87
- Moghaddam LS, Emtyazjoo M, Emadi H (2004) Alvita as alternative of malachite green in cold water fish systems. J Environ Sci 21
- Nirmalarani J, Janardhanan K (1988) Effect of South India Viscose factory effluent on seed germination seedling growth and chloroplast pigments content in five varieties of maize (Zea mays I) Madras. Agriculture 75:41
- Olguín EJ, Sánchez-Galván G (2012) Heavy metal removal in phytofiltration and phycoremediation: the need to differentiate between bioadsorption and bioaccumulation. New Biotechnol 30:3–8
- Oplatowska M, Donnelly RF, Majithiya RJ, Kennedy DG, Elliott CT (2011) The potential for human exposure, direct and indirect, to the suspected carcinogenic triphenylmethane dye Brilliant Green from green paper towels. Food Chem Toxicol 49:1870–1876
- Ozdemir O, Armagan B, Turan M, Celik MS (2004) Comparison of the adsorption characteristics of azo-reactive dyes on mesoporous minerals. Dyes Pigments 62:49–60
- Padmesh TVN, Vijayaraghavan K, Sekaran G, Velan M (2005) Batch and column studies on biosorption of acid dyes on fresh water macro alga *Azolla filiculoides*. J Hazard Mater B125:121–129
- Pearce CI, Lloyd JR, Guthrie JT (2003) The removal of colour from textile wastewater using whole bacterial cells: a review. Dyes Pigments 58:179–196
- Pereira L, Alves M (2012) Dyes-environmental impact and remediation. In: Malik A, Grohmann E (eds) Environmental protection strategies for sustainable development- strategies for sustainability. Springer, New York, pp 111–162
- Prajapati SK, Kaushik P, Malik A, Vijay VK (2013) Phycoremediation and biogas potential of native algal isolates from soil and wastewater. Bioresour Technol 135:232–238
- Punzi M, Anbalagan A, Aragão Börner R, Svensson BM, Jonstrup M, Mattiasson B (2015) Degradation of a textile azo dye using biological treatment followed by photo-Fenton oxidation: evaluation of toxicity and microbial community structure. Chem Eng J 270:290–299
- Puvaneswari N, Muthukrishnan J, Gunasekaran P (2006) Toxicity assessment and microbial degradation of azo dyes. Indian J Exp Biol 44:618–626
- Ramachandra T, Ahalya N, Kanamadi R (2005) Biosorption: techniques and mechanisms, CES technical report 110. Centre for Ecological Sciences/Indian Institute of Science, Bangalore
- Ratna, Padhi BS (2012) Pollution due to synthetic dyes toxicity & carcinogenicity studies and remediation. Int J Environ Sci 3:3
- Ravi Kumar MNV, Sridhari TR, Bhavani KD, Dutta PK (1998) Trends in color removal from textile mill effluents. Colourage 40:25–34
- Rawat I, Kumar RR, Mutanda T, Bux F (2011) Dual role of microalgae: phycoremediation of domestic wastewater and biomass production for sustainable biofuels production. Appl Energy 88:3411–3424
- Redlich O, Peterson DL (1959) A useful adsorption isotherm. J Phys Chem 63:1024–1026
- Robinson T, McMullan G, Marchant R, Nigam P (2001) Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. Bioresour Technol 77:247–255
- Rochat J, Demenge P, Rerat JC (1978) Toxicologic study of a fluorescent tracer: rhodamine B. Toxicol Eur Res 1:23–26

- Salima A, Benaouda B, Noureddine B, Duclaux L (2013) Application of Ulva lactuca and Systoceira stricta algae-based activated carbons to hazardous cationic dyes removal from industrial effluents. Water Res 47:3375–3388
- Sarwa P, Vijayakumar R, Verma SK (2014) Adsorption of acid red 66 dye from aqueous solution by green microalgae Acutodesmus obliquus strain PSV2 isolated from an industrial polluted site. Open Access Library J 1:e712. http://dx.doi.org/10.4236/oalib.1100712
- Saxena RM, Kewa PF, Yadav RS, Bhatnagar AK (1986) Impact of tannery effluents on some pulse crops. Indian J Environ Health 2(196):345
- Sheng PX (2004) Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms. J Coll Int Sci 275:131–141
- Singh SK, Bansal A, Jha MK, Dey A (2012) An integrated approach to remove Cr(VI) using immobilized Chlorella minutissima grown in nutrient rich sewage wastewater. Bioresour Technol 104:257–265
- Sode S, Bruhn A, Balsby TJS, Larsen MM, Gotfredsen A, Rasmussen MB (2013) Bioremediation of reject water from anaerobically digested waste water sludge with macroalgae (Ulva lactuca, Chlorophyta). Bioresour Technol 146:426–435
- Srinivasan A, Viraraghavan T (2010) Decolorization of dye wastewaters by biosorbents: a review. J Environ Manag 91:1915–1929
- Sun Q, Yang L (2003) The adsorption of basic dyes from aqueous solution on modified peat-resin particle. Water Res 37:1535–1544
- Suteu D, Zaharia C, Bilba D, Muresan A, Muresan R, Popescu A (2009a) Decolorization wastewaters from the textile industry – physical methods, chemical methods. Ind Text 60:254–263
- Suteu D, Zaharia C, Muresan A, Muresan R, Popescu A (2009b) Using of industrial waste materials for textile wastewater treatment. Environ Eng Manag J 8:1097–1102
- Tam NFY, Chong AMY, Wong YS (2002) Removal of tributyltin (TBT) by live and dead microalgal cells. Marine Pollut Bull 45:362–371
- Tien C-J (2002) Biosorption of metal ions by freshwater algae with different surface characteristics. Process Biochem 38:605–613
- Tseng CH, Chong CK, Tseng CP, Hsueh YM, Chiou HY, Tseng CC, Chen CJ (2003) Long term arsenic exposure and ischemic heart disease in arseniasis-hyperendemic villages in Taiwan. Toxicol Lett 137:15–21
- Tsuboy MS, Angeli JPF, Mantovani MS, Knasmüller S, Umbuzeiro GA, Ribeiro LR (2007) Genotoxic, mutagenic and cytotoxic effects of the commercial dye CI Disperse Blue 291 in the human hepatic cell line HepG2. Toxicol Vitro 21:1650–1655
- United Nations, Department of economic and Social Affairs, Population Division (2011) World Population Prospects: the 2010 Revision, Highlights and Advance Tables. ESA/P/WP.220
- Vieira RHS, Volesky B (2000) Biosorption: a solution to pollution. Int Microbiol 3:17–24
- Wang J, Chen C (2009) Biosorbents for heavy metals removal and their future. Biotechnol Adv 27:195–226
- Zaharia C, Suteu D (2012) Textile organic dyes characteristics, polluting effects and separation/elimination procedures from industrial effluents – a critical overview. In: Puzyn T, Mostrag-Szlichtyng A (eds) Organic pollutants ten years after the Stockholm Convention – environmental and analytical update, 1st edn. InTech, Croatia, pp 55–86
- Zaharia C, Suteu D, Muresan A, Muresan R, Popescu A (2009) Textile waste water treatment by homogenous oxidation with hydrogen peroxide. Environ Eng Manag J 8:1359–1369