Chapter 10
Biosorption of Dye and Heavy Metal Pollutants by Fungal Biomass: A Sustainable Approach

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10.1 Introduction

Dye and heavy metal pollutants present in the aquatic and terrestrial ecosystem are hazardous to the environment as well as the human health due to their toxicity even at the lower concentration. Industrial effluents produced from printing, food colorant, textile, dyes (Patel 2016), gold mining, cement production, and coal industry production (Rahman and Singh 2016) released directly into the environment at large scale magnify the pollution level and cause harmful effects on the human health as well as reduce the quality of ecosystem.

10.2 Dyes and Heavy Metals

Dyes are aromatic compound which can be divided into two major groups based on their synthesis, i.e., natural and synthetic dye (Tahir et al. 2016). Natural dyes are mainly used to dye leather and natural proteins. Synthetic dyes have advantage over the natural dyes as its color fastness and brightness. Synthetic dyes are produced by complex process of chemical synthesis, having aromatic structure with delocalized electron which possesses various functional groups (Tahir et al. 2016) contributes to its recalcitrant property (Kristanti et al. 2016).

Synthetic dyes are subdivided into auxochromic ($–SO_3H$, $–OH$, $–NH_2$, and $–COOH$) and chromophoric dyes ($–N=N–$, $–NO_2$, $–C=O$) including quinonoid rings.

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The broad range of dyes depends on two main parameters: (i) the presence of chromophore group in the aromatic ring and (ii) anionic (direct, acid, and reactive dyes), cationic (basic dyes), and nonionic (disperse dyes) based on dissociation while interacting with water molecules (Tahir et al. 2016).

10.2.1 Anionic Dyes

Textile industries and printing industries are the major source for the azo dye pollution and responsible for severe health issues, i.e., provoking allergic reactions, cancer, and mutations. Azo dyes are electron-deficient xenobiotic components with chromophore group –N=N–, which have been released in the environment (Patel 2016) by loading dangerous organic pollutants, potential toxicants (Corso and Almeida 2009), and hazardous pollutants (He et al. 2016). Azo dyes contain sulfonate functional group, with high molecular weight which restricts its entry into the cells (Solis et al. 2012).

Acid Magenta, Acid Navy Blue, Fast Red A and Acid Sulfone Blue, Orange-HF (diazo dye) (Kaushik and Malik 2010), Direct Blue 151 and Direct Red 31 (Lalnunhlimi and Krishnaswamy 2016), and Acid Orange 7 [*p*-(2-hydroxy-1-naphthylazo) benzene sulfonic acid] are azo dyes specially used in cosmetics as well as detergent, silk, and wool industries for dyeing. Their high toxicity leads to allergic reactions like upper respiratory tract, skin and eye irritation, dermatitis, and anemia in humans. Azo chromophore donates electron and reduced to generate toxic form, responsible for the carcinogenic nature. 1-Amino-2-naphthol, the reduced form, is well known for inducing bladder tumors. Enzymatic degradation causes aromatic amines production and responsible for mutagenic activity (Gupta et al. 2006). The microbial degradation initiates with cleavage of azo linkages which involves an anaerobic azoreductase and redox mediator to shuttle the electron, the intracellular reductase, and the extracellular dye which requires cofactors such as NADH, NADPH, and FADH (Solis et al. 2012).

Acidic dyes also known as anionic dyes with anionic group in their chemical structure include direct, mordant, reactive dyes. Acidic dyes are more problematic than basic or disperse dyes due to their water solubility and high reactivity (Laszlo 1994). Congo red is a well-known brownish red crystal, anionic dye with high water solubility and stability. The benzidine- and napthoic-derived Congo red are mainly used in clinical laboratories as pH indicator for diagnosis and histological studies for amyloidosis and to check the free HCl presence into gastric contents. It affects blood clotting factors and enhances allergic reactions (Gupta et al. 2006). Anionic dyes like Reactive Black 5 (Huanga et al. 2016), Reactive orange 16, Brilliant Red HE 3B (Chander et al. 2004) and Remazol Blue, Reactive textile dye (Tastan et al. 2009), and some direct dyes Blue 71 and Red 31 (He et al. 2016) which are widely used into textile industry are hazardous to human health. The anionic dyes are unable to degrade due to presence of complex aromatic structure (Huanga et al. 2016).

10.2.2 Cationic Dyes

Cationic dyes are water soluble and well known as basic dyes. Crystal Violet can cause bladder cancer in human and is harmful to fish if it is absorbed into the fish skin and metabolized into leucocrystal violet form. The leuco form can also induce hepatic and lung tumor (Smitha et al. 2017). The other cationic dye Rhodamine B also has carcinogenic effects (Maurya et al. 2006). Methylene blue (Maurya et al. 2006) is a cationic dye which is able to cause breathing problem and skin and eye irritation if inhaled or swallowed (Priac et al. 2014).

Other aromatic synthetic dyes are triphenylmethane which includes methyl violet, cotton blue, and malachite green that contribute 10–15% (Chen and Ting 2015) annual dye release into the environment through pharmaceuticals, acrylic (Asfaram et al. 2016), leather, and paper industries. Malachite green an N-methylated diaminotriphenylmethane dye is a highly recommended component for fish farming industry due to antifungal (Asfaram et al. 2016), antibacterial, and antiprotozoan nature. These toxic components are recalcitrant and can cause mutation and cancer (Chen and Ting 2015). It is harmful to aquatic animals as it blocks direct penetration of sunlight (Chowdhury et al. 2011) and enhances malignant cell formation (Jasinska et al. 2012).

10.2.3 Heavy Metals

Heavy metal pollutants generated through various industrial practices, i.e., combustion, extraction (Jarup 2003), mineral processing, and metallurgical process, and released liquid effluents, etc. are highly toxic to human health and atmosphere. Due to their nondegradable nature, it can accumulate into living system and cause potential irreversible health effects even at small quantity (Ahluwalia and Goyal 2007). Lead released through paint industry, photographic materials, battery manufacturing, and pigments poses a huge danger for the environment and humans. Lead poisoning causes severe health problem, i.e., hemolytic anemia (Faryal et al. 2007). Chromium highly present in industrial effluents is released from leather tanning and metal finishing. It is a carcinogenic metal, exists in oxidative states Cr III and Cr VI, and causes kidney failure, diarrhea, stomach ulcers, and allergic reactions (Ata et al. 2012). Mercury commonly found as methylmercury (MeHg) is able to enter the human blood and can cross placenta through the barriers. MeHg has toxic effects on neurological and cardiovascular system and gastrointestinal tract (Taylor and Williamson 2017). Cadmium and arsenic both present in natural form due to its anthropogenic activity. Cadmium and arsenic are found in aquatic environment having detrimental effect on the aquatic entity (Tan et al. 2016). The combination of zinc with acids or oxygen can cause extreme harm to biological systems. Copper affects human health by causing chronic diseases and leads to kidney and liver failure if consumed at high amount. Nickel metal mainly found in volatile form as $Ni(CO)_4$ causes death if inhaled (Siddiquee et al. 2015).

10.3 Traditional Methods

10.3.1 Adsorption

The mechanism involved the adsorption of soluble organic dyes from the waste water to highly porous, solid surface. It should be high surface capacity to adsorb the maximum amount of the pollutant and can be reusable (Veglio and Beolchini 1997).

10.3.2 Membrane Processes

Membrane process involves filtration of the polluted effluent to clarify the dye or metal and concentrate to recover the particular for reuse. The common membrane filtration processes are ultrafiltration, nano-filtration, and reverse osmosis (Gunatilake 2015). According to Gunatilake (2015), ultrafiltration requires membrane filter with pore size of 5–20 which allows the segregation of the molecules based on their weight ranging from 1000 to 100,000 Da. Reverse osmosis applies pressure to transfer the molecules through the membrane; it blocks the passage of solutes and separates solvent.

10.3.3 Oxidative Processes

Conversion of hazardous compounds into less toxic organic material using chemical agents, i.e., sodium hypochlorite, comes under the chemical oxidative processes. It involves ozonation process, photochemical oxidation process, and electrochemical oxidation process (Holkar et al. 2016).

10.3.4 Coagulation-Flocculation and Precipitation

The mechanism of coagulation-flocculation and precipitation requires electrostatic attraction between the oppositely charged soluble dye and polymer molecules to remove toxic dyes and heavy metals from the industrial effluents (Holkar et al. 2016).

10.3.5 Electrocoagulation

Electrocoagulation involves several mechanisms such as electrolytic reactions at electrodes, formation of coagulants in aqueous effluent and adsorption of soluble or colloidal pollutants on coagulants, and removal by sedimentation and flotation.

Electrocoagulation technique is easy to employ and does not require chemical treatment with production of less sludge amount (Gunatilake 2015).

10.3.6 Ionic Exchange

The ionic exchange is mainly based on the ionic interaction between functional group on ionic species and an adsorptive solid material (Veglio and Beolchini 1997).

10.4 Advantage Over Traditional Method

Rapid increase in industrialization and anthropogenic activity leads to increased production of toxic effluents accommodating various organic pollutants, toxic metals, and their metalloids. At industrial level effluent discharge demands increasing expenditure (Fomina and Gadd 2014). These physiochemical techniques are costly and may not always be practicable and non-ecofriendly, and also their metal-binding properties are nonspecific. Biosorption involves both physiological, biochemical, and metabolically independent processes based on surface complexation, ion exchange, precipitation, and absorption (Fomina and Gadd 2014). Fungal biosorption depends on various parameters, i.e., metal ion or dye concentration, biomass concentration, pH, temperature, and pretreatment of the biomass (Kapoor and Viraraghavan 1997). The ability to solubilize complex metal compounds, environmental adaption capability at various physiochemical conditions, and high surface area-volume ratio are important factor that increases fungal usage over other microorganisms (Leitao 2009).

10.5 Fungal Biosorbent

Biosorption is a versatile mechanism with combined adsorption and absorption process that mediate the adhesion of any substance on biological material. Adsorption mechanism involves the attachment of organic or inorganic matter onto biological subsistence surface or coupling of ions onto surface of biological entity in removal process from aqueous solution. Biosorption diverges the process into bioadsorption, bioabsorption, or bioaccumulation (Fomina and Gadd 2014).

Biosorbent manifests higher compatibility for metal ions as well as for the organic or inorganic pollutants and beneficiary for organic pollutant degradation, metal recovery, and recycling. Microbial origin, i.e., bacteria, cyanobacteria, algae, and fungi, can be utilized as biosorbent. Fungi cell composed of thick cell wall contains prominent structures like mannan, chitin, glucans, extracellular proteins, polysaccharides, and pigment which assist the metal binding at various peculiar binding sites (Gadd 2008). Fungi can familiarize with any bionomic condition and survive in any habitat. Fungal species, i.e., *Trichoderma*, are easy to cultivate due to fast-growing nature and able to produce spore (Siddiquee et al. 2015).

Both live and dead fungal biomasses are applicable to eliminate dyes/heavy metals from the contaminated terrestrial and aquatic ecosystem. Madani et al. (2015) analyzed the biosorption capacity of the fungal biomass of *Pleurotus mutilus* for biosorption of Fe^{+3} and Mn^{+2}. FTIR data showed the presence of alcohol (–C–O), hydroxyl (–OH), amino ($–NH_2$), and carboxyl group (–C=O) on biosorbent which are responsible for biosorption of positively charged metal ions (Fe^{+3} and Mn^{+2}) with negatively charged functional group. *Trichoderma versicolor* fungal biomass analyzed for biosorption of chromium (VI) and Remazol Black B reactive dye in the study conducted by Aksu et al. (2007). Chromium (VI) biosorption was observed at initial concentration of 15–30 mg l^{-1}, and chromium uptake was found to be in the range of 2.34–4.04 mg/g^{-1}. The biosorption of Remazol Black B reactive dye also estimated with *Trichoderma versicolor*, but the biosorption process was slow compared to the chromium (VI). Dye biosorption was found to be 92.4% with the incubation time of 5–8 days with initial dye concentration of 58.4 mg l^{-1}.

Kuhar and Papinutti (2013) reported that due to overpressure during dye/heavy metal degradation, fungi do not outlast. They analyzed the effect of vanilloids on *Ganoderma lucidum* while removing the gentian violet (GV) and malachite green (MG) dyes, clotrimazole, and cadmium metal. They are added into culture medium and observed high adsorption capacity into fungi after vanilloids addition. Recently report shows that modification of fungal biomass increases the activity. *Aspergillus versicolor* modified by using cetyl trimethyl ammonium bromide (CTAB) enhances the fungal biosorption of Reactive Black 5 at various physiochemical conditions compared to the unmodified (Huanga et al. 2016). White rot fungi *Coriolopsis* sp. (1c3), known for decolorizing anthraquinone and heterocyclic and azo dyes, were analyzed for triphenylmethane (TPM) dye biosorption and found able to reduce TPM dyes. Akar and Divriklioglu (2010) reported the increased fungal biosorption of *Agaricus bisporus* with small modification using CTAB for Reactive Red dye biosorption. Fungal biomass can accumulate dyes into cell wall and internal space. *Candida tropicalis* proficiently bioaccumulate the dyes, i.e., Remazol Blue, Reactive Black, and Reactive Red. *Candida albicans* isolated from industrial discharge are found to degrade the azo dye Direct Violet 51 at lower pH conditions (Vitor and Corso 2008). Living fungal biomass equally degrades the heavy metal pollutant as dyes based on their interaction. Metal resistance developed by organisms involves particular mechanism, i.e., cell membrane metal efflux, intracellular chelation, and phytochelatins and metal compartmentalization (Errasqun and Vazquez 2003).

Mucor indicus avowed as fermenting agent which convert hexose and pentose into volatile solvent ethanol. The dimorphic fungus is also known for the metal-binding affinity due to the presence of chitin and chitosan. Javanbakht et al. (2011) conducted the study using *M. indicus* of different morphology and analyzed as biosorbent for lead removal from the contaminated solution. Fungal biomass has great prospective to produce extracellular enzymes during whole life cycle. Fungal enzyme mediated metal binding and acts as feasible biosorbent agents (Sharma and Malaviya 2016). Srivastava and Thakur (2006) performed detoxification of heavy metal chromium (Cr) based on the enzyme-mediated process using *Aspergillus niger* fungi isolated from tannery effluents. Sewage sludge-isolated nonpathogenic *Trichoderma atroviride* was analyzed for metal tolerance and uptake capacity and effectively removed copper, zinc (Errasqun and Vazquez 2003), and cadmium (Mohsenzadeh and Shahrokhi 2014). Nongmaithem et al. (2016) assessed *Trichoderma* isolates MT-4, UBT-18, and IBT-I biosorption capacity to remove nickel and cadmium at higher metal concentration. *Rhizopus arrhizus* established with great potential to uptake 18.5% thorium among microorganisms, i.e., *Penicillium* spp., *Aspergillus* spp., *Mycobacterium smegmatis*, *Citrobacter* spp., and *Pseudomonas* spp. Bhainsa and D'Souza (2009) reported the *Aspergillus fumigatus* for metal uptake capacity, which was higher compared to the *Rhizopus arrhizus* with 37% (Errasqun and Vazquez 2003).

Dead cells execute more number of favors over the live cells such as no special media requirement for growth, easy to desorption and recovery, facile regeneration process, and no lethal effects of toxicants (Kabbout and Taha 2014; Kapoor and Viraraghavan 1997). Sanghi et al. (2009) found that dead white rot fungus *Coriolus versicolor* is able to remove chromium (Cr^{6+}) by forming complex with its polysaccharide component of the cell wall. Immobilization processes provide protection to the cell from physical damage, minimize the medium viscosity, procure protease activity, supply sufficient amount of oxygen, and increase mass transfer between media and cells (Daassi et al. 2013). Goyal et al. (2014) examined the bioreductant activity of immobilized white rot fungus *Coriolus versicolor* for decolorization at various parameters, i.e., pH, nutrient, and oxygen. Daassi et al. (2013) embedded the fungal biomass *Coriolopsis gallica*, *Bjerkandera adusta*, *Trametes versicolor*, and *Trametes trogii* onto Ca-alginate beads. The beads were further used for the removal of Lanaset Grey (LG), a metal textile dye comprising of organometal complexes (chromium III and cobalt).

Tannery dye Black Dycem TTO decolorization by white rot fungi *Trametes versicolor*, *Ganoderma lucidum*, and *Irpex lacteus* was evaluated and suggested adsorption and biodegradation as key mechanism (Baccar et al. 2011). Yang et al. (2011) compared the biosorption capacity of unmodified and CDAB-modified nonviable *Aspergillus oryzae* biomass for removal of Acid Blue 25 and Acid Red 337 using single and binary system and found that modified fungal biomass was more efficient than the unmodified. Maurya et al. (2006) formulated biosorbent from *Fomes fomentarius* and *Phellinus igniarius* for biosorption of methylene blue and Rhodamine B. Dead *Aspergillus niger* was pretreated with $NaHCO_3$ which improved the biosorption capacity and enhanced Congo red removal from the solution (Fu and Viraraghavan 2002).

10.6 Biosorption Mechanism

Heavy metal affects fungal growth, and metabolism results in uptake of metals through various processes (Kapoor and Viraraghavan 1997) including chemisorption, adsorption-coupled reduction process, ion exchange, precipitation (Pundir et al. 2016), and electrostatic interaction as shown in Fig. 10.1.

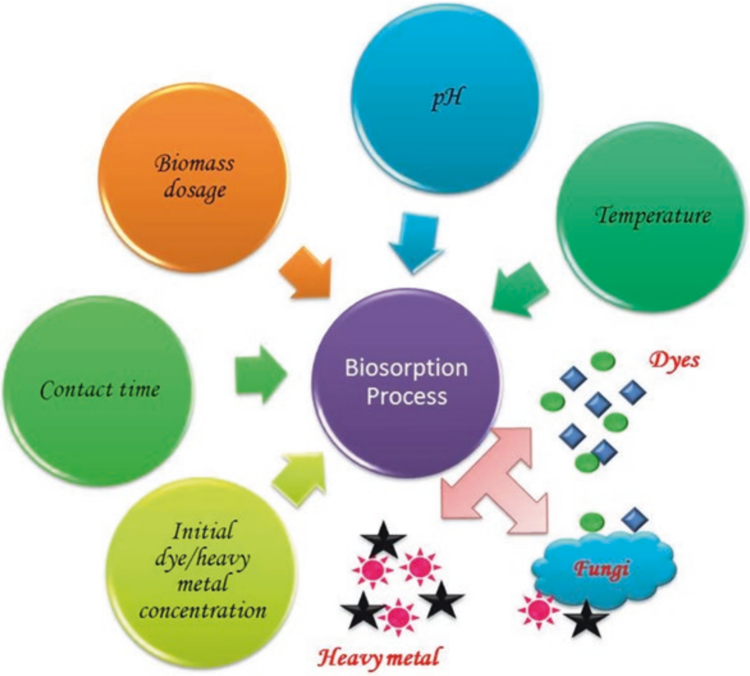

Fig. 10.1 Factors affecting fungal biosorption for dye/heavy metal

10.6.1 *Molecules Translocation Through Cell Membrane*

Transportation of dye/heavy metal ions into the cell from the extracellular environment using active/passive transport mechanism through the cell membrane is required for removal of dye/heavy metal ions from the environment. Two type of transportation are present in cell metabolism-dependent mechanism which require energy and allow dye/heavy removal from the aqueous solution (Veglio and Beolchini 1997).

10.6.2 *Chemisorption/Electrostatic Interaction*

Chemisorption involves bonding formation in chemical group (hydroxyl, amine, phosphoryl, thiol, etc.) present on fungal cell wall/surface and substrate to be adsorbed. Chemisorption excludes dependency on metabolic reaction within fungal cell (Bhainsa and D'Souza 2009) and forms strong bonding than ion exchange (Sheoran and Sheoran 2006). Bhainsa and D'Souza (2009) analyzed thorium (IV) uptake mechanism of *Aspergillus niger* using Temkin isotherm and first- and second-order Lagergren equations which clearly indicate that it involves chemisorption mechanism.

10.6.3 Ion Exchange

The functional groups present on cell surface interact with the metal ion known as ion exchange mechanism, for the uptake of metal ions from the surrounding environment and decontaminated (Kapoor and Viraraghavan 1997). Cationic ion exchange relied on environmental condition, metal concentration, and presence of other metals.

10.6.4 Precipitation

Condensation of dye/heavy metal concentration in the absence of water molecules known as precipitation that hepls in removal of contaminants in bulk amount. Gibert et al. (2005) removed Zn metal as merging of two chemical reaction metal (oxy) hydroxides and carbonates precipitation and sorption onto surface of municipal compost. This process depends on metal solubility, metal ion concentration, and presence of relevant anions and wetland pH (Sheoran and Sheoran 2006).

10.7 Factors Affecting Biosorption Mechanism

Biosorption process depends on various factors that influence the biosorption mechanism, i.e., pH, biosorption rate, initial dye/heavy metal concentration, metal speciation, solubility of metal ions, temperature, contact time, and binding site present on fungi for biosorption of dye/heavy metals (Veglio and Beolchini 1997).

10.7.1 pH

pH is one of the major factors that affect dye/heavy metals uptake from the environment. Change in pH enhances the biosorption rate as decreasing pH provides large number of free binding site and hence increases metal uptake (Dwivedi 2012). Maximum Cd removal capacity was higher at pH 9.0 compared to pH 5.0 and pH 7.0 by *Trichoderma* sp. (Mohsenzadeh and Shahrokhi 2014). Thorium removal by *Aspergillus fumigatus* was found to be at pH 4.0 with maximum metal ion removal capacity (Bhainsa and D'Souza 2009). Excess H^+ ions provide positive charge to *Coriolus versicolor*, and surface positive charges interact with $HCrO_4$– with higher affinity at pH 2.0 (Sanghi et al. 2009).

10.7.2 Initial Concentration of Dye/Heavy Metal

Initial dye concentration plays an important part that determine molecules mass transfer resistance between the medium and sorbent (Khataee et al. 2013). Methylene blue biosorption increased from 0.8 to 9 mg/g *Aspergillus fumigatus* fungal biomass with the initial dye concentration of 2–24 mg/g (Kabbout and Taha 2014). The effect of initial concentration on metal ion biosorption is analyzed by using initial concentration of chromium [Cr(III)/ Cr(VI)] ranging from 0 to 500 mg/L. Reduction of Cr (IV) to Cr (III) by microalga *Nannochloris oculata* was observed over 200 mg/L initial concentration which proves that initial concentration also matters along with fungal biomass and contact time (Kim et al. 2011).

10.7.3 Metal Speciation

Solubility and mobility of metal ions depend on metal speciation which refers to the quantification of metal ions into solution as hydroxides, organometallic compounds, and other biomolecule form.

10.7.4 Temperature

Temperature between 25 and 30 °C is the most favorable condition for the optimum fungal growth. Temperature also affects the enzymatic degradation of the dye by fungi (Kabbout and Taha 2014). Iqbal and Saeed (2007) studied the influence of physiochemical parameters on dye biosorption capacity, i.e., pH, contact time, initial dye concentration, and temperature on loofa sponge-immobilized fungal biomass and free fungal biomass *Phanerochaete chrysosporium* on Remazol Brilliant Blue R. The biosorption equilibrium was analyzed at different temperature ranging from 20 to 50 °C with initial concentration of 100 mg l^{-1}. The biosorption of Remazol Brilliant Blue R increased till 30 °C and decreased with increasing temperature.

10.7.5 Contact Time

Contact time also plays an effective role in fungal biosorption indicating the efficiency of biosorbent to remove pollutant from the environment. Yousefi et al. (2015) evaluated the metal adsorption efficacy of dead mass of *Aspergillus niger*. Quick removal of metal ions depends on the interchange between the functional groups present on fungal cell surface at initial reaction period and further reduction into metal ions adsorption due to intracellular aggregation of the metal particles. Adsorption rate at initial 5 min for metal ions (zinc (II), cobalt (II), and cadmium (III)) was quick until it reaches equilibrium condition.

10.7.6 Biomass Dosage

Biomass dosage has its own importance in enhancing the decolorization by increasing dosage. The efficiency of decolorization rapidly increased in dose-dependent manner, as 0.1 mg/ml Congo red dye was found to be 90.58% at 3 g of white rot fungus, *Ceriporia lacerate*. Sometimes rapid increase in adsorption surface area and biosorption sites can hinder the adsorption rate of biomass dosage (Wang et al. 2017). Akar and Divriklioglu (2010) explained that later constant biosorption is possessed due to binding site superabundance of dyes particles which occupied the biosorbent surface. List of fungal biomass used as biosorbent for dye/heavy metal biosorption is given below in the (Table 10.1).

10.8 Biosorption Isotherms Models

The association that materialize between adsorbate concentration and adsorbed compound per biosorbent biomass designate as biosorption equilibrium isotherm. Indulgement of various parameters which explains the compatibility with adsorbent and the surface properties of the biosorbent and analyzes the biosorption capacity for individual toxic/hazardous compounds (Abdel-Ghani and El-Chaghaby 2014). The isotherm equilibrium generates an equation that is helpful to compare the diverse biosorbent and to optimize the process for future experiment (Ata et al. 2012). Gadd (2008) explains that the parameters, viz., pH, biomass dosage, presence of metal ions, and their cationic opposites, are applicable in single-batch system. Many scientists prefer breakthrough curves to calculate sorbent efficiency due to complexity of flow/continuous system. The equilibrium data can be explained by plotting the sorbent uptake value (q_e) against the end sorbent concentration (C).

$$q_e = \frac{V\left(C_i - C\right)}{S} \tag{10.1}$$

Solution volume contacted with the sorbent (V), sorbate initial and end concentration (C_i and C), and biosorbent amount (S) affirm as dry weight.

A wide range of models are present from simple to complex multidimensional models, i.e., *Langmuir*, *Freundlich*, *Temkin*, *Dubinin-Radushkevich*, *Flory-Huggins*, *Sip*, *Khan*, *Toth*, *Redlich-Peterson*, and *Radke-Prausnitz*, to explain the equilibrium isotherm for biosorption of dye/heavy metal.

Table 10.1 List of fungal biomass used as biosorbent for dye/heavy metals biosorption

S. No.	Live/dead fungal biomass	Biosorbed dye/heavy metal	References
1	*Trametes versicolor*, *Ganoderma lucidum*, *Irpex lacteus*	Black Dycem	Baccar et al. (2011)
2	*Coriolopsis gallica*, *Bjerkandera adusta, Trametes versicolor, Trametes trogii*	Lanaset Grey (LG)	Daassi et al. (2013)
3	*Aspergillus oryzae*	Acid Blue 25; Acid Red 337	Yang et al. (2011)
4	*Fomes fomentarius Phellinus igniarius*	Methylene Blue, Rhodamine B	Maurya et al. 2006)
5	*Aspergillus niger*	Congo red	Fu and Viraraghavan (2002)
6	*Agaricus bisporus*	Reactive Red dye	Akar and Divriklioglu (2010)
7	*Candida tropicalis, Candida albicans*	Remazol Blue, Reactive Black, Reactive Red, Direct Violet 51	Vitor and Corso (2008)
8	*Mucor indicus*	Lead (Pb^+)	Javanbakht et al. (2011)
9	*Aspergillus niger*	Chromium (Cr)	Srivastava and Thakur (2006)
10	*Trichoderma atroviride*	Copper, zinc	Errasqun and Vazquez (2003)
11	*Aspergillus fumigatus*	Thorium	Bhainsa and D’Souza (2009)
12	*Coriolus versicolor*	Chromium (Cr^{6+})	Sanghi et al. (2009)
13	*Pleurotus mutilus*	Fe^{+3} and Mn^{+2}	Madani et al. (2015)
14	*Ganoderma lucidum*	Gentian violet, malachite green, clotrimazole cadmium	Kuhar et al. (2013)
15	*Trichoderma versicolor*	Chromium (VI) Remazol Black B	Aksu et al. (2007)

10.8.1 Langmuir Equilibrium Model

Hypothesis proposed by Langmuir model describes the consistency of energies adsorption without adsorbent renascence on the plane of the surface. Accuracy of the *Langmuir* model defines uniform distribution of adsorbent on the specific position situated on the biosorbent surface as monolayer, and the saturation of the sites blocks the excess adsorbate’s adhesion. The isotherm can be represented as

$$q_e = \frac{Q_0 b C_e}{1 + b C_e} \tag{10.2}$$

C_e represents the equilibrium concentration (mg/L), qe represents the amount adsorbed per specified amount of adsorbent (mg/g), and Q_0 represents the amount of adsorbate required to form a monolayer.

Bhainsa and D'Souza (2009) observed maximum loading capacity of filamentous fungal biomass *Aspergillus fumigatus* for biosorption of thorium (Th) metal ions by *Langmuir* model. The statistical data showed that the maximum loading capacity (*Q0*) per gram biosorbent was 99, 143, and 455 mg thorium at initial pH 2, 3, and 4. The uptake of thorium was pH dependent which enhances with increase in pH range from 2.0 to 4.0. Maximum intake was noticed as 455 mg of thorium per gram biosorbent at pH 4.0 with estimated value of 370 mg Th/g fungal biomass. Increased pH allows binding of bivalent $Th(OH)_2^{2+}$ to the biomass due to thorium's lower solubility. According to Eq. (10.2), biosorption process is convenient when the *R*L value is less than 1, where 50 mg Th/L showed *R*L values of 0.59, 0.53, and 0.83 at the pH 2, 3, and 4, respectively. This demonstrates the suitability of the biosorption process for the thorium removal.

Tan et al. (2010) calculated biosorption capacity for biosorption of basic orange dye by dried fungal biomass *Azolla filiculoides*. *Langmuir* isotherm model determined the maximum biosorption capacity of *Azolla filiculoides* as 833.33 mg/g biosorbent and 3.67×10^{-3} L/mg of the K_L (consumed energy for biosorption). Correlation coefficient (R2) 0.996 also showed the favorability of the isotherm. This study indicates the basic orange dye biosorption by dried *Azolla filiculoides* which supports the formation of monolayer onto binding sites present on biomass surface.

10.8.2 Freundlich Equilibrium Model

Freundlich model suggests (Saha and Orvig 2010) the multilayer formation of adsorbate over a heterogeneous surface with different energies as a result of uneven dispersion of the adsorbate and is independent of biosorbent saturation. Mathematical representation for the *Freundlich* models is expressed as

$$q = kC_f^{(1/n)} \tag{10.3}$$

k and *n* (nondimensional) represents Freundlich constants, based on the estimation using the slope and the intercept of the plot drawn between 1n *q* and 1n C_f.Linear form of the *Freundlich* equation can be expressed as

$$1\text{n}\,q = 1/n\,1\text{n}\,C_f + 1\text{n}\,k$$

The model can be considerable to design biosorption process if the *n* follows the range between 1 and 10. This represents the higher affinity in between biosorbent and adsorbate which increases the biosorption rate.

Patel and Suresh (2008) analyzed the equilibrium data using *Freundlich* model for the biosorption of Reactive Black 5 dye by *Aspergillus foetidus*. Fungal biomass of

Aspergillus foetidus was pretreated with 0.1 M sodium hydroxide (NaOH) and compared the biosorption capacity with untreated fungal biomass. The K_f values for *Freundlich* isotherm increased with the elevated temperature (30–50 °C) signified the endoergic nature of the biosorption of Reactive Red 5 dye by pretreated *Aspergillus foetidus* biomass with 0.1 M NaOH. The studies showed that *Freundlich* isotherm model was fitted for anticipation of the isotherm for lesser dye concentration. Analytical data proposed the heterogenic nature of the *Aspergillus foetidus* mediated biosorption and pretreatment with 0.1 M NaOH enhanced the biosorption capacity.

10.8.3 Temkin Equilibrium Model

Temkin isotherm assumes the concomitant interaction of adsorbate-adsorbate on adsorption isotherm which produces heat energies that decrease with increasing coverage (Smitha et al. 2017).

$$q_{\mathrm{e}} = \mathrm{RT} / b 1\mathrm{n}\left(\mathrm{AC}_e\right) \tag{10.4}$$

The equation can be expressed in a linear form

$$q_{\mathrm{e}} = \beta 1 n \alpha + \beta 1 n C_{\mathrm{e}}$$

Constant β represents the adsorption heat generated by the interaction, where β is equal to (RT)/b.

Madani et al. (2015) observed biosorption of Fe^{+3} and Mn^{+2} by *Pleurotus mutilus* fungal biomass and used different isotherm to explain simple biosorption equilibrium data. The pH varied from range 1 to 8.5 and biosorption was executed for Mn^{2+} and Fe^{3+} ions. The biosorption of ions depends on the ionic form of the metal and electrical charge present on biomass mainly concerned with pH of the solution. The pH preferred for biosorption studies of Mn^{2+} and Fe^{3+} ions were 2.6 and 8, respectively. The Temkin isotherm found b constant as 684.383 and K_T as 34.982 with R2 value of 0.955 for Fe^{3+} and for Mn^{2+} b constant as 0.002 and K_T 1 and R2 value of 0.841.

10.8.4 Dubinin-Radushkevich Equilibrium Model

Dubinin and Radushkevich (1947) proposed an isotherm model which explains the effects of porous structure of biosorbent that indirectly affects biosorption capacity. The Dubinin-Radushkevich avoids the existence of constant sorption potential and heterogeneous surface of the biosorbent. The isotherm can be represented as

$$q = q_{\max} \exp\left(-B\varepsilon^2\right) \tag{10.5}$$

$q_{\max}$ stands for the monolayer saturation capacity (mol g^{-1}), constant B is correlated with biosorption energy, and ε represents Polanyi potential.

$$\varepsilon = \mathrm{RT}\ln\left(1 + 1/C_{\mathrm{f}}\right) \tag{10.6}$$

where R characterized as gas constant (8.314 J mol^{-1} K^{-1}) and T represents absolute temperature (K). The linearized form can be expressed as

$$\ln q = -B\varepsilon^2 + \ln q_{\max} \tag{10.7}$$

Dubinin-Radushkevich describes mean biosorption energy and determined chemical or physical nature of biosorption process. Biosorption energy (E) can be measured as

$$E = \frac{1}{\sqrt{2B}} \tag{10.8}$$

The biosorption energy ranges from 8 to 16 kJ mol^{-1} for chemical ion exchange, and biosorption energy less than 8 kJ mol^{-1} describes physical nature of the process.

Ahmad et al. (2013) studied the biosorption of zinc ions (Zn^{2+}) by *Candida utilis* and *Candida tropicalis*. The biosorption energy calculated from the *Dubinin-Radushkevich* isotherm describes the chemical ion exchange nature as the values fall under 9.81–11.16 kJ mol^{-1} for *Candida utilis* and 10.15–12.33 kJ mol^{-1} for *Candida tropicalis*. Akar et al. (2013) examined the biosorption potential of the filamentous fungal *Thamnidium elegans* for the removal of Reactive Red 198 dye. They studied the effect of various parameters such as contact time, temperature, initial dye concentration, and pH. The biosorption energy observed 18.39 kJ mol^{-1} for batch system and 16.09 kJ mol^{-1} for continuous column system. These energy values show the chemical ion exchange nature of the biosorption process.

10.9 Desorption and Reuse

Desorption process is the major part of the biosorption process which relieves the adsorbed molecule attached to the biosorbent using different kind of elution solution. It permits the recovery and reuse of the particular adsorbate. Biosorbent loses the biosorption capacity after elution, so the elution system should not harm the biosorbent properties while eluting the adsorbate. For the purpose organic solvents as desorbing agents, i.e., ethanol and surfactants chemical like NaOH and $\mathrm{CaCl_2}$, are available for regeneration and elution of the adsorbate (Fomina and Gadd 2014).

Patel and Suresh (2008) performed the desorption process for the recovery of Reactive Black 5 dye by exposing the fungus *Aspergillus foetidus* with pH range from 3 to 10 with 0.1 M and 1 M NaOH. At higher pH due to electrostatic repulsion between cationic fungal cell surface and anionic reactive dye, so desorption was observed at higher pH condition. The desorption percentage at 0.1 M NaOH was 90%, whereas in case of 1 M NaOH, 32% was observed.

Bhainsa and D'Souza (2009) desorbed thorium (Th) bound with *Aspergillus fumigatus* biomass. They compared different desorbing agents: ethylenediaminetetraacetic acid (EDTA), calcium carbonate ($CaCO_3$), sodium carbonate (Na_2CO_3), and sodium bicarbonate ($NaHCO_3$). The 97% and 99% desorption was observed in 1 M Na_2CO_3 and 1 M $NaHCO_3$ eluting agents, respectively. At 0.1 M EDTA concentration, 91% thorium desorption was found where as in 1 M $CaCO_3$ maximum desorption found was 93%.

Javanbakht et al. (2011) treated the *Mucor indicus* used for biosorption of lead with 0.05 M HNO_3 for 1 h to perform desorption of the ions. Acidic elution is one of the important approaches for desorption process. Nitric acid (HNO_3) and hydrochloric acid (HCl) are found to be the favorable desorbing agents due to their proton exchange properties, where HNO_3 eluted 80% lead from the fungal biomass of *M. indicus.*

10.10 Conclusion

Fungal biosorption can be considered as feasible biological approach that is eco-friendly as well as cost-effective. The biosorption capacity of the fungal biomass can be enhanced by pretreatment of the biomass or immobilization onto immobilizing agents that protects fungal biomass from the harsh conditions during biosorption process. Biosorption process can be enhanced by optimization of various physiochemical parameters, i.e., pH, incubation time, temperature, biomass dosage, and monitoring the initial dye/heavy metal concentration. Further we can use biosorption process for the recovery of organics removal, recovery of pharmaceuticals and precious metal and elements.

References

Abdel-Ghani NT, El-Chaghaby GA (2014) Biosorption for metal ions removal from aqueous solutions: a review of recent studies. IJLRST:2278–5299

Ahluwalia SS, Goyal D (2007) Microbial and plant derived biomass for removal of heavy metals from wastewater. Bioresour Technol 98:2243–2257

Ahmad MF, Haydar S, Quraishi TA (2013) Enhancement of biosorption of zinc ions from aqueous solution by immobilized *Candida utilis* and *Candida tropicalis* cells. Int Biodeterior Biodegrad 83:119–128

Akar T, Divriklioglu M (2010) Biosorption applications of modified fungal biomass for decolorization of Reactive Red 2 contaminated solutions: batch and dynamic flow mode studies. Bioresour Technol 101:7271–7277

Akar T, Arslan S, Akar ST (2013) Utilization of *Thamnidium elegans* fungal culture in environmental cleanup: a reactive dye biosorption study. Ecol Eng 58:363–370

Aksu Z, Kilic NK, Ertugrul S, Donmez G (2007) Inhibitory effects of chromium(VI) and Remazol Black B on chromium(VI) and dyestuff removals by *Trametes versicolor*. Enzym Microb Technol 40:1167–1174

Asfaram A, Ghaedi M, Ghezelbash GR, Dil EA, Tyagi I, Agarwal S, Gupta VK (2016) Biosorption of malachite green by novel biosorbent *Yarrowia lipolytica* isf7: application of response surface methodology. J Mol Liq 214:249–258

Ata A, Nalcaci OO, Ovez B (2012) Macro algae *Gracilaria verrucosa* as a biosorbent: a study of sorption mechanisms. Algal Res 1:194–204

Baccar R, Blanquez P, Bouzid J, Feki M, Attiya H, Sarra M (2011) Decolorization of a tannery dye: from fungal screening to bioreactor application. Biochem Eng J 56:84–189

Bhainsa KC, D'Souza SF (2009) Thorium biosorption by *Aspergillus fumigatus,* a filamentous fungal biomass. J Hazard Mater 165:670–676

Chander M, Arora DS, Bath HK (2004) Biodecolourisation of some industrial dyes by white-rot fungi. J Ind Microbiol Biotechnol 31:94–97

Chen SH, Ting ASY (2015) Biodecolorization and biodegradation potential of recalcitrant triphenylmethane dyes by *Coriolopsis* sp. isolated from compost. J Environ Manag 150:274–280

Chowdhury S, Chakraborty S, Saha P (2011) Biosorption of basic green 4 from aqueous solution by *Ananas comosus* (pineapple) leaf powder. Colloids Surf B Biointerfaces 84:520–527

Corso CR, Almeida ACM (2009) Bioremediation of dyes in textile effluents by *Aspergillus oryzae*. Microb Ecol 57:384–390

Daassi MT, Nasri M, Rodriguez-Couto S (2013) Decolorization of the metal textile dye Lanaset Grey G by immobilized white-rot fungi. J Environ Manag 129:324–332

Dwivedi S (2012) Bioremediation of heavy metal by algae: current and future perspective. J Adv Lab Res Biol 3(3):195–199

Errasqun EL, Vazquez C (2003) Tolerance and uptake of heavy metals by *Trichoderma atroviride* isolated from sludge. Chemosphere 50:137–143

Faryal R, Sultan A, Tahir F, Ahmed S, Hameed A (2007) Biosorption of lead by indigenous fungal strains. Pak J Bot 39(2):615–622

Fomina M, Gadd GM (2014) Biosorption: current perspectives on concept, definition and application. Bioresour Technol 160:3–14

Fu Y, Viraraghavan T (2002) Removal of Congo red from an aqueous solution by fungus *Aspergillus niger*. Adv Environ Res 7:239–247

Gadd GM (2008) Biosorption: critical review of scientific rationale, environmental importance and significance for pollution treatment. J Chem Technol Biotechnol 84:13–28

Gibert O, Pablo J, Cortina JL, Ayora C (2005) Municipal compost-based mixture for acid mine drainage bioremediation: metal retention mechanisms. Appl Geochem 20:1648–1657

Goyal A, Sanghi R, Misra AK, Shukla JB (2014) Modeling and analysis of the removal of an organic pollutant from a water body using fungi. Appl Math Model 38:4863–4871

Gunatilake S (2015) Methods of removing heavy metals from industrial wastewater. JMESS 1:12–18

Gupta VK, Mittal A, Gajbe V, Mittal J (2006) Removal and recovery of the hazardous azo dye acid orange 7 through adsorption over waste materials: bottom ash and de-oiled soya. Ind Eng Chem Res 45:1446–1453

He X, Du M, Li H, Zhou T (2016) Removal of direct dyes from aqueous solution by oxidized starch cross-linked chitosan/silica hybrid membrane. Int J Biol Macromol 82:174–181

Holkar CR, Jadhav AJ, Pinjari DV, Mahamuni NM, Pandit AB (2016) A critical review on textile wastewater treatments: possible approaches. J Environ Manag 182:351–366

Huanga J, Liua D, Lub J, Wanga H, Weia X, Liua J (2016) Biosorption of reactive black 5 by modified *Aspergillus versicolor* biomass: kinetics, capacity and mechanism studies. Colloids Surf A Physicochem Eng Asp 492:242–248

Iqbal M, Saeed A (2007) Biosorption of reactive dye by loofa sponge-immobilized fungal biomass of *Phanerochaete chrysosporium*. Process Biochem 42:1160–1164

Jarup L (2003) Hazards of heavy metal contamination. Br Med Bull 68:167–182

Jasinska A, Rozalska S, Bernat P, Paraszkiewicz K, Dlugonski J (2012) Malachite green decolorization by non-basidiomycete filamentous fungi of *Penicillium pinophilum* and *Myrothecium roridum*. Int Biodeterior Biodegrad 73(2012):33–40

Javanbakht V, Zilouei H, Karimi K (2011) Lead biosorption by different morphologies of fungus Mucor indicus. Int Biodeterior Biodegrad 65:294–300

Kabbout R, Taha S (2014) Biodecolorization of textile dye effluent by biosorption on fungal biomass materials. Phys Procedia 55:437–444

Kapoor A, Viraraghavan T (1997) Biosorption of heavy metals on *Aspergillus niger*: effect of pretreatment. Bioresour Technol 63:109–113

Kaushik P, Malik A (2010) Alkali, thermo and halo tolerant fungal isolate for the removal of textile dyes. Colloids Surf B Biointerfaces 81:321–328

Khataee A, Vafaei F, Jannatkhah M (2013) Biosorption of three textile dyes from contaminated water by filamentous green algal Spirogyra sp.: kinetic, isotherm and thermodynamic studies. Int Biodeterior Biodegrad 83:33–40

Kim EJ, Park S, Hong HY, Choi YE, Yang JW (2011) Biosorption of chromium (Cr(III)/Cr(VI)) on the residual microalga *Nannochloris oculata* after lipid extraction for biodiesel production. Bioresour Technol 102:11155–11160

Kristanti RA, Zubir MMFA, Hadibarata T (2016) Biotransformation studies of cresol red by *Absidia spinosa* M15. J Environ Manag 172:107–111

Kuhar F, Papinutti L (2013) Protective effect of vanilloids against chemical stress on the white-rot fungus *Ganoderma lucidum*. J Environ Manag 124:1–7

Lalnunhlimi S, Krishnaswamy V (2016) Decolorization of azo dyes (Direct Blue 151 and Direct Red 31) by moderately alkaliphilic bacterial consortium. Braz J Microbiol 47:39–46

Laszlo JA (1994) Removing acid dyes from textile wastewater using biomass for decolorization. Am Dyest Rep 83(8):17–21

Leitao AL (2009) Potential of *Penicillium* species in the bioremediation field. Int J Environ Res Public Health 6:1393–1417

Madani A, Chergui A, Selatnia A (2015) Biosorption of Fe+3 and Mn+2 ions from aqueous solution by a *Pleurotus mutilus* fungal biomass. J Chem Pharm Res 7(7):19–26

Maurya NS, Mittal AK, Cornel P, Rother E (2006) Biosorption of dyes using dead macro fungi: effect of dye structure, ionic strength and pH. Bioresour Technol 97:512–521

Mohsenzadeh F, Shahrokhi F (2014) Biological removing of cadmium from contaminated media by fungal biomass of *Trichoderma* species. Iranian J Environ Health Sci Eng 12:102

Nongmaithem N, Roy A, Bhattacharya PM (2016) Screening of *Trichoderma* isolates for their potential of biosorption of nickel and cadmium. Braz J Microbiol 47:305–313

Patel SJ (2016) Review on biosorption of dyes by fungi. IJIRSET 5(1):2347–6710

Patel R, Suresh S (2008) Kinetic and equilibrium studies on the biosorption of reactive black 5 dye by *Aspergillus foetidus*. Bioresour Technol 99:51–58

Priac A, Morin-Crini N, Gavoille CDS, Bradu C, Lagarrigue C, Torri G, Winterton P, Crini G (2014) Alkylphenol and alkylphenol polyethoxylates in water and wastewater: a review of options for their elimination. Arab J Chem. https://doi.org/10.1016/j.arabjc.2014.05.011

Pundir R, Chary GHVC, Dastidar MG (2016) Application of Taguchi method for optimizing the process parameters for the removal of copper and nickel by growing *Aspergillus* sp. Water Resour Res. https://doi.org/10.1016/j.wri.2016.05.001

Rahman Z, Singh VP (2016) Assessment of heavy metal contamination and Hg-resistant bacteria in surface water from different regions of Delhi, India. Saudi J Biol Sci. https://doi.org/10.1016/j.sjbs.2016.09.018

Saha B, Orvig C (2010) Biosorbents for hexavalent chromium elimination from industrial and municipal effluents. Coord Chem Rev 254:2959–2972

Sanghi R, Sankararamakrishnan N, Dave BC (2009) Fungal bioremediation of chromates: conformational changes of biomass during sequestration, binding, and reduction of hexavalent chromium ions. J Hazard Mater 169:1074–1080

Sharma S, Malaviya P (2016) Bioremediation of tannery wastewater by chromium resistant novel fungal consortium. Ecol Eng 91:419–425

Sheoran AS, Sheoran V (2006) Heavy metal removal mechanism of acid mine drainage in wetlands: a critical review. Miner Eng 19:105–116

Siddiquee S, Rovina K, Al Azad S, Naher L, Suryanil S, Chaikaew P (2015) Heavy metal contaminants removal from wastewater using the potential filamentous fungi biomass: a review. J Microb Biochem Technol 7:6

Smitha T, Santhi T, Prasad AL, Manonmani S (2017) *Cucumis sativus* used as adsorbent for the removal of dyes from aqueous solution. Arab J Chem 10:S244–S251

Solis M, Solis A, Perez HI, Manjarrez N, Flores M (2012) Microbial decolouration of azo dyes: a review. Process Biochem 47:1723–1748

Srivastava S, Thakur IS (2006) Evaluation of bioremediation and detoxification potentiality of *Aspergillus niger* for removal of hexavalent chromium in soil microcosm. Soil Biol Biochem 38:1904–1911

Tahir U, Yasmin A, Khan UH (2016) Phytoremediation: potential flora for synthetic dyestuff metabolism. JKSUS 28:119–130

Tan CY, Li G, Lu XQ, Chen ZL (2010) Biosorption of basic orange using dried *A. filiculoides*. Ecol Eng 36:1333–1340

Tan LC, Nancharaiah YV, Hullebusch EDV, Lens (2016) Selenium: environmental significance, pollution, and biological treatment technologies. Biotechnol Adv 34:886–907

Tastan BE, Ertugrul S, Donmez G (2009) Effective bioremoval of reactive dye and heavy metals by *Aspergillus versicolor*. Bioresour Technol 101:870–876

Taylor DL, Williamson PR (2017) Mercury contamination in Southern New England coastal fisheries and dietary habits of recreational anglers and their families: implications to human health and issuance of consumption advisories. Marine Poll Bull 114:144–156

Veglio F, Beolchini F (1997) Removal of metals by biosorption: a review. Hydrometallurgy 44:301–316

Vitor V, Corso CR (2008) Decolorization of textile dye by *Candida albicans* isolated from industrial effluents. J Ind Microbiol Biotechnol 35:1353–1357

Wang N, Chu Y, Wu F, Zhao Z, Xu X (2017) Decolorization and degradation of Congo red by a newly isolated white rot fungus, *Ceriporia lacerata*, from decayed mulberry branches. Int Biodeterior Biodegrad 117:236–244

Yang Y, Jin D, Wang G, Wang S, Jia X, Zhao Y (2011) Competitive biosorption of Acid Blue 25 and Acid Red 337 onto unmodified and CDAB-modified biomass of *Aspergillus oryzae*. Bioresour Technol 102:7429–7436

Yousefi J, Shahram S, Zadeh N (2015) The effect of contact time and temperature on biosorption of heavy metals from aqueous solution. Int J Rev Life Sci 5(2):1406–1411