Asian Journal of Chemistry Vol. 22, No. 9 (2010), 6625-6639

REVIEW

Factors Affecting Biosorption of Direct Dyes from Aqueous Solution

YUSRA SAFA and HAQ NAWAZ BHATTI*
Department of Chemistry and Biochemistry, University of Agriculture, Faisalabad-38040, Pakistan
Tel: (92)(41)9200161/3309; Fax: (92)(41)9200764; E-mail: hnbhatti2005@yahoo.com

Dyes contamination in ground and aquatic environment has become a serious menace today. Removal of dyes from wastewater before discharging to environment is necessary for the safety of living beings. Dyes are difficult to degrade due to complex structures. Different techniques are used to remove the dyes from wastewater. Among these techniques, biosorption has emerged as an effective and ecofriendly technique. Biosorption of dyes using different biomaterials has been investigated by different researchers. This review article gives an insight into the removal of different synthetic direct dyes using different biomaterials from aqueous solution. The effect of various process parameters such as pH, biosorbent dose, initial dye concentration, sorbent particle size, agitation time, temperature, ionic strength *etc.* has been discussed.

Key Words: Biosorption, Contamination, Synthetic dyes, Colour removal.

INTRODUCTION

Pollution of water, air and soil is a major environmental problem since decades[1]. Synthetic dyes are one of the most problematic organic pollutants[2,3]. Dyes are extensively used in the textile, rubber, pulp and paper, plastics, cosmetics, pharmaceutical, food, tanneries, paint and electroplating industries[4-9]. Approximately 10,000 different types of dyes are in use and nearly 7.105 metric tones dyes are produced annually[10]. It is estimated that about 10-15 % of dyes are discharged in the industrial wastes and cause pollution[11,12].

The presence of dyes in effluents causes damage to ecosystem[10] and also affects the ground water system due to leaching from the soil[13]. Dyes reduce light penetration[14] and prevent the photosynthetic activity of aquatic flora[15]. In addition, dyes are toxic, mutagenic and carcinogenic. Some skin diseases such as irritation and allergic dermatitis are also caused by dyes[16]. Dyes are not degraded easily due to complex aromatic molecular structures and xenobiotic properties[17]. Dyes can be classified into different groups such as: anionic (direct, acid and reactive dyes), cationic (basic dyes) and non-ionic (disperse dyes)[17,18].

In direct dyes ionic groups (mostly sulphonic acid) are present which facilitate solubility in water. Direct dyes containing aromatic rings are highly toxic[15,19]. Due to conjugated structure, these dyes are carcinogenic[20]. In reactive dyes, dye-fiber bond is of covalent nature[21]. In reactive dyes, azo-based chromophores combined with reactive groups such as vinyl sulfone, trichloropyrimidine and chlorotriazine[22]. Fast colour of basic dyes makes them visible at low concentration[23,24]. Acid and reactive dyes are soluble in water and bright in colour. So, they can not be removed easily from industrial effluents[2,25]. Fibers which contain nitrogen are dyed by acid dyes[26]. Ionization of disperse dyes in aqueous solution does not take place and some are decolourized by bioaccumulation[27]. Removal of dye concentration from waste water is necessary to reduce/remove toxicity[28,29]. Many treatment processes have been applied for the removal of dyes from waste water such as physical, chemical and biological treatments[30]. The physical and chemical treatment methods include ozonization, adsorption, chemical precipitation, flocculation[30] coagulation, chemical oxidation, photocatalysis, dilution, ion-exchange, reverse osmosis, ultra-filtration[27] membrane filtration, irradiation and electro-chemical destruction[1]. But these methods have certain disadvantages such as inefficient dye removal, costly, sludge formation and not applicable to a wide range of dye wastewaters[29]. Most important drawback of chemical treatments is production of secondary pollutants due to excessive utilization of chemicals[31].

Biological methods like biodegradation, bioaccumulation and biosorption are also employed for dye removal[2,7]. However, the use of biodegradation and bioaccumulation could not be accomplished because different conditions such as aeration level, pH, temperature and nutrient concentrations should be optimized for effective dye elimination. The major drawback of bioaccumulation is the inhibition of cell growth at elevated dye concentrations[2]. Among these techniques adsorption is considered to be more promising technique due to its efficiency, less cost, capacity and capability to eliminate non- biodegradable dyes from industrial effluents on a large scale[32].

Physical adsorption by activated carbon has been found to be superior to other techniques because it has good capacity for the adsorption of dyes[33]. Due to its spongy structure and large surface area, activated carbon has good capacity for dyes. Accessibility of functional groups on the surface helps in the dye adsorption[9]. But its high price, high operating costs and regeneration problems do not favour its application on extensive scale[34]. The most important attractions of biosorption are high selectivity and efficiency, fewer expenditure, design simplicity, high removal performance and regeneration of biosorbent[35]. Biosorption is the passive uptake of contaminants and pollutants through different physical and chemical processes such as ion-exchange, adsorption, complex formation, chelation and micro precipitation *etc.*, by non-living/non-growing biomass[2].

A wide variety of low cost adsorbents have been reported in literature such as orange peel[2], cassava peel[36], banana pith[37], plum kernels[38], apple pomace, wheat

straw[17], cotton waste, rice husk, tea wood bark[39], sawdust[40], baggasse pith, maize cob[41], palm fruit bunch[42,43], coir pith[44], oil palm trunk fiber[45], fly ash[46], guava leaf powder[47], almond shells[3], treated parthenium biomass[48] and broad bean peels[49]. However exploration for cost effective, efficient adsorbent is continuing.

Different methods are present to make the efficient biosorbent material. One of them is cross-linked and entrapment immobilization of biosorbent[50,51]. Immobilization in a polymeric matrix shows great performance, controlled particle size, biosorbent regeneration and facilitate separation of biomass from contaminated solution[52]. Several matrices used in biomass immobilization include polysulfone[51,53,54], polyacrylamide[50], polyurethane[52], sodium alginate[50,54], cellulose[55] and polyvinyl alcohol[56]. Actually, immobilized biomass has many restrictions including high cost of pre-treated biosorbent and blocking of many binding sites of biosorbent[57].

Biosorption of direct dyes: Direct dyes are water-soluble containing one or more ionic groups (mostly sulfonic acid and amino groups). These are complex molecules and almost soluble in water. Benzidine based dyes are highly toxic and carcinogenic. Different process parameters such as pH, biosorbent dose, initial dye concentration, temperature, contact time *etc.* affect the removal of dyes from the wastewater streams.

Effect of pH: The initial pH of solution appreciably influences biosorption of dyes due to change in the surface properties of the adsorbent. Dye colour and solubility are mainly affected by changing the pH of solution. Namasivayam *et al.*[13] investigated the effect of pH on the removal of direct dye (Congo red) by orange peel. The percentage uptake of Congo red was maximum (76.6 %) at pH 5.0 and minimum (49 %) at pH 12. The study showed that acidic pH was favourable for sorptive removal of the direct dye. Namasivayam and Kavitha[58] discussed the effect of pH on the removal of Congo red from aqueous media onto activated carbon prepared from coir pith. At pH 2 (20-40 mg/L dye concentration), the maximum uptake percentage was about 70 and 50 %, respectively which then decreased at pH 4.0. The uptake percentage remained constant up to pH 10.0. Adsorption of dye on the biosorbent might be due to electrostatic attraction between the positively charged biosorbent and acidic dye. The other possibility of adsorption of dye is due to chemical reaction between biomass and dye. At the basic pH, the binding sites of the adsorbent become negatively charged which did not allow the adsorption of dye due to repulsion.

Bhattacharyya and Sharma[59] reported that pH of the solution showed a little effect on Congo red removal by neem leaf powder (NLP). They demonstrated that the adsorption of the dye increased between pH 4.0 and 6.0 and after that the pH showed no effect on the adsorption of dye. In this study, it was concluded that the neem leaf powder surface showed maximum interaction with the dye molecule at or near pH 7.0. Gong *et al.*[8] demonstrated the effect of pH on biosorption of three dyes Amaranth, Sunset yellow and Fast green FCF by the powdered peanut hull.

They studied the effect of pH ranging from 2 to 11 and found that the removal of dye decreased by increasing the pH of solution from 2 to 11.

Mall *et al.*[60] observed the effect of pH on uptake of Congo red from aqueous solution by bagasse fly ash (BFA). They reported that in the absence of bagasse fly ash, pH decreases the colour below pH 6.0. At pH 3 and 13, colour decline was the highest. Colour decline without bagasse fly ash only with change in pH was due to change in structure of dye molecule. In the presence of bagasse fly ash, about 80 % dye uptake was observed at pH 4-10. In the aqueous media, the dye is ionized and negative charge developed on it. Alumina, calcium and silica oxides present on the bagasse fly ash produced positive charge. The negatively charged silica sites are counter balanced by H^+ ions. So, in the acidic pH, a strong electrostatic attraction between biosorbent and dye anion enhanced the colour removal from aqueous solution. In the basic pH range 7-10, electrostatic repulsion between negatively charged biomass and dye reduced the dye uptake from the aqueous solution.

Akhtar *et al.*[34] attempted to study the effect of pH on % sorption of 2,4-dichlorophenol (DCP) onto rice husk. At lower pH, the per cent sorption of 2,4-dichlorophenol onto rice husk was found higher. The highest % sorption (*ca.* 76 %) at pH 1.0 was due to strong chemical interaction between the lone pair of electrons on the -OH group in phenols and the Si^{4+} of the rice husk. There is strong binding between biosorbent and the polar resonance contributing phenolic structure. Arami *et al.*[32] observed the effect of pH on the adsorption of direct dyes from aqueous solution by Soy meal hull. They examined that the sorptive removal of dye increased by lowering the pH value. The highest uptake occurred at pH 2.0. Soy meal hull (SMH) biosorbent contains large number of functional groups (amine, hydroxyl and carbonyl groups). At pH 2.0 the biosorbent surface turned out to be positively charged and electrostatic attraction develops between positively charged biomass and negatively charged anionic dye. However, at basic pH, adsorption decreased due to presence of hydroxyl ions which showed competition with dye anions for binding sites. In another study of Bayramoglu and Arica[15], the effect of pH on the benzidine based textile dyes (direct blue 1 and direct red 128) removal capability of heat treated fungal biomass was observed. The maximum uptake value of direct blue-1 was determined to be 24.80 mg/g for native and 60.88 mg/g for heat treated biomass at pH 6.0. On the other side, the enhanced uptake removal of direct red-128 was found to be 76.3 mg/g for native and 98.9 mg/g for inactive fungal biomass by increase in pH from 2.0 to 3.0. The results suggested that the higher uptakes occurred at low pH values due to electrostatic interactions between negatively charged dye and positively charged biomass surface.

Bulut *et al.*[29] studied the effect of initial pH on biosorption of direct blue 71 from aqueous solution using wheat shells as biosorbent. The dye removal efficiency increased from 74.15 % at pH 2 to 98.95 % at pH 7.0. At higher pH, the surface of wheat shells carries negative charge, as a result, the positively charged direct blue 71 adsorbed through electrostatic forces of attraction. Ardejani *et al.*[3]

also studied the effect of initial pH on adsorption of direct red 80 from aqueous solution onto almond shells. As pH increased from 2 to 12, the adsorption capacity decreased from 20.5 to 18.8 mg/g. The results indicated that maximum uptake of dye was observed at pH 2.0. Han *et al.*[61] reported the pH effect on the breakthrough curves. They examined the breakthrough curves moved from right to left by increasing the pH value, which showed that less dye was adsorbed. At acidic pH the uptake of Congo red from aqueous media was high. There would be many reasons which facilitated the removal of Congo red at lower pH value. A large number of binding sites present on the surface of rice husk, an electrostatic interaction developed between positively charged surfaces of the biosorbent and anionic dye at lower initial pH value. At basic pH, the surface of the biosorbent becomes negatively charged which does not facilitate the adsorption of dye anions due to the repulsive hindrance.

In a study performed by Jain and Sikarwar[62], the effect of pH on the adsorption of Congo red by activated carbon and activated sawdust was observed. The results showed that at pH 6.5, the highest adsorption of about 99 and 88 % for activated carbon and activated sawdust was observed. Mohan *et al.*[10] investigated the effect of pH on the uptake of direct azo dye from aqueous solution onto *Spirogyra* sp.102. There was a decrease in the sorption capacity as the pH of the aqueous solution increased from 2.0 to 10.0. At pH 2.0, the maximum adsorption (80 %) was occurred. The surface of algal biosorbent contains many functional groups such as amino, carboxyl, thiosulfhydryl and phosphate groups. At low pH, the biomass surface became positively charged due to protonated effect of functional groups. This positively charged surface of the biomass helped the biosorption of dye by anionic exchange mechanism. At basic pH, less dye sorption showed due to formation of complexes, as the number of hydroxyl ion increased therefore inhibited the sorption phenomenon.

Dulman and Cucu-Man[63] studied the pH effect on the uptake of direct dyes by beech wood sawdust. The per cent removal of brown 2 was the higher (98.6 %) at pH 3.0. The biosorption on agricultural wastes is a complicated process and it is affected by the nature of biosorbent and dye molecule. Khaled *et al.*[1] tested the effect of pH on the removal efficiency of direct yellow 12 by orange peel carbon. The highest adsorption occurred at pH 1.5 with percentage removal of 11.1 %. At basic pH, adsorption decreases due to excess of OH^- ions which show competition with dye anions for the binding sites. At the acidic pH, the number of positively charged sites increase which help in adsorption of dye anions through electrostatic attraction mechanism. Khaled *et al.*[14] also presented the effect of pH on the uptake of direct N Blue-106 from aqueous solution. The maximum removal was found at pH 2 was about 93.5 %. Then there was considerable decrease in dye uptake when pH increased up to 12.75. At low pH, there is an electrostatic attraction between positively charged binding sites of sorbent and negatively charged dye molecule.

EI-Nemr *et al.*[64] used orange peel biosorbent for removal of direct blue-86 from aqueous solutions. At pH 2, the removal of direct blue-86 was the maximum. An increase in H^+ ion concentration occurs at low pH (1.0-3.0) and the surface of activated carbon from orange peel gets positive charge by taking H^+ ions. A strong electrostatic attraction develops between positively charged biomass surface and negatively charged dye molecule. At high pH value electrostatic repulsion appears due to number of negatively charged sites on the biosorbent. The highest adsorption took place at pH 2.0 and the lowest adsorption took place at pH 8.0.

EI-Sayed and EI-Ashtoukhy[65] reported that maximum sorption of direct blue 106 by *Loofa egyptiaca* biomass occurred at pH 2.0. A net negative charge was present on the surface of activated carbon in aqueous solutions. By decreasing the pH of dye solution, the dissociation of acid groups of the dye is also decreased. As a result, the number of negative charged dye molecules which are repelled by negatively charged activated carbon also decreases.

Effect of biosorbent dose: Biosorbent dose is the most significant factor because it describes the capability of biosorbent for a particular dye concentration. Namasivayam *et al.*[13] used Congo red direct dye to see the effect of biomass dose. The results show that per cent uptake of dye increased with increase in the biosorbent dose. Maximum uptake (92 %) of Congo red was observed with 0.5 g of biosorbent dose. This might be attributed to the presence of large surface area of the biosorbent for the given mass. On the other hand Namasivayam and Kavitha[58] also reported removal of Congo red by coir pith carbon using different biosorbent doses (100-900 mg/50 mL) and different dye concentrations (20, 40, 60 and 80 mg/L). Maximum percentage removal was observed with the high biosorbent dose.

In another study Bhattacharyya and Sharma[59] reported the effect of the biosorbent dose on the removal of Congo red dye. With low biosorbent dose of neem leaf powder, the dye removal was maximum because the minute amount of neem leaf powder biosorbent dose showed good interaction with Congo red dye. Gong *et al.*[8] determined the effect of adsorbent dose on the elimination of dyes from aqueous solution. The per cent uptake of dyes increased with increase in the biosorbent dose. At high biosorbent dose (10 g/L), the per cent removal of Amaranth, Sunset yellow and Fast green was 98.64, 98.26 and 99.12 %, respectively. With high dose of biosorbent, more exchanging sites are present which cause more removal of dyes.

Mall *et al.*[60] studied the effect of biosorbent dose on the sorptive uptake of Congo red. The results indicated that dye uptake increased and then remained constant. Maximum removal for bagasse fly ash, commercial activated carbon and laboratory grade activated carbon was observed with 1, 20 and 2 g/L of biosorbent dose, respectively. By increasing biosorbent dose, the per cent removal also increased due to large surface area of biosorbent and large number of exchanging sites. Akhtar *et al.*[34] tried to explain the effect of adsorbent dose on the uptake of 2,4-dichlorophenol. By increasing the biosorbent dose from 0.025 to 0.1g, the percentage adsorption increased rapidly up to 66 % and then remained constant.

Arami *et al.*[32] reported the effect of various doses of Soy meal hull (0.2-0.36 g) for direct red 80, (0.04-0.6 g) for direct red 81, (0.2-0.6 g) for Acid blue 92 and (0.2-0.7 g) for Acid red 14. They observed that the per cent dye uptake increased with increase in the biosorbent dose. This might be due to increase number of sorptive sites. Bulut *et al.*[29] demonstrated the effect of the biosorbent dose of wheat shell on the removal of direct blue 71 dye. They used various amount of biomasses (0.25. 0.5, 1.0 and 2.0 g/100 mL). The dye removal capacity decreased with an increase in biosorbent concentration. This might be due to the unsaturation of binding sites at large amount of biosorbent dose. Jain and Sikarwar[62] determined the effect of the biomass dose of activated carbon and activated sawdust on the Congo red dye removal. There was an increase in per cent dye removal with the increase in biosorbent dose. It is known that availability of binding sites increases with biomass dose. The results indicated that the percentage of dye removal was maximum with more biosorbent doses, both for activated carbon and activated sawdust.

Mohan *et al.*[10] reported that adsorbent dose imparted significant influence on the biosorption of direct azo dye from aqueous media. They investigated that at the highest biosorbent dose (0.5 g), the dye removal was maximum (*ca.* 85 %). Khaled *et al.*[1] described the uptake of direct yellow-12 on orange peel carbon at different biosorbent doses (0.10, 0.25, 0.50, 0.75 and 1.0 g/100 mL) keeping the other parameters such as temperature, dye concentration and pH constant. By increasing the biosorbent dose from 0.1-1.0 g/100 mL, the per cent uptake also increased from 63.5 to 100 %. On the other side, the amount of dye sorbed, q_e decreased by increasing the orange peel carbon dose.

Khaled *et al.*[14] also investigated the effect of the biosorbent dose on the sorption of direct N blue-106. They used different doses (0.2, 0.4, 0.6, 0.8 and 1.0 g/100 mL) of orange peel carbon. Maximum sorption (nearly 100 %) was observed with biosorbent dose of 1.0 g/100 mL. The increase in adsorption with increasing amount of biomass dose was due to large surface area of orange peel carbon.

EI-Nemr *et al.*[64] examined the percentage removal of direct blue-86 by activated carbon from orange peel at different biomass doses (0.2, 0.4, 0.6, 0.8 and 1.0 g/100 mL). The per cent removal increased from 64 to 100 % when biomass dose was increased from 0.2 g to 1.0 g/100 mL.

In another study conducted by EI-Sayed and EI-Ashtoukhy[65], the effect of adsorbent dosage on per cent dye uptake was investigated. The results indicated high uptake of dye with high biosorbent dose due to availability of more binding sites.

Effect of sorbent particle size: Sorbent particle size is also one of the most important parameters because adsorption is directly related with surface area of biomass. Biosorption capability is also influenced by particle size of adsorbent. Gong *et al.*[8] indicated the effect of biosorbent particle size on the per cent removal of direct dyes. They observed that biosorption capacity of biomass increased with decrease in particle size. Jain and Sikarwar *et al.*[62] characterized the effect of various particle sizes of biomass on the removal of Congo red dye. For both activated carbon

and activated sawdust biomass, biosorption reduced with an increase in biosorbent particle size. The highest adsorption (94.5 % for activated carbon and 76.6 % for activated sawdust) obtained at the smallest particle size (< 106 BSS mesh). This might be attributed to large surface area of the smallest particle size biosorbent.

Effect of initial dye concentration: An increase in the biosorption of dyes with increase in concentration is generally observed. Hence removal of dyes from aqueous streams is generally affected by the concentrations of the dyes. Namasivayam *et al.*[13] reported that the amount of dye sorbed per unit mass of the adsorbent increased by increasing the initial dye concentration. This showed the dependence of the dye uptake on the initial concentration of the dye. Namasivayam and Kavitha[58] observed maximum biosorption capacity (mg/g) with the highest dye concentration. But the percentage dye uptake decreased from 66.5 to 30.5 % with an increase in dye concentration from 20-80 mg/L. From this study, it was concluded that dye uptake was affected by initial dye concentration.

In a study performed by Bhattacharyya and Arunima[59], it was observed that the biosorption process was affected by changing the initial dye concentration. The percentage removal of dye was decreased from 100.0 to 68.3 % with increase in the dye concentration from 2.87×10^{-2} to 8.61×10^{-2} mmol/L.

Gong *et al.*[8] conducted an experiment to show the effect of initial dye concentration on the per cent removal of three direct dyes. The per cent removal decreased from 98.7 to 72.83 % for Amaranth, from 99.57 to 70.42 % for Sunset yellow and from 98.2 to 74.31 % for Fast green with the increase in initial dye concentration. This might be due to accumulation of dye ions at higher dye concentration. Such accumulation decreased the availability of the total surface area of the biosorbent particles for biosorption. Mall *et al.*[60] reported the effect of initial concentration of Congo red dye onto bagasse fly ash and activated carbon. They concluded that the percentage uptake of Congo red dye decreased with the increase in the dye concentration. However, the amount of dye sorbed increased with the increase in the initial dye concentration. This might be attributed to increase in the driving forces to overcome mass transfer resistances of the dye between the aquatic and solid phases.

Akhtar *et al.*[34] demonstrated the effect of initial concentration of 2,4-dichlorophenol on its adsorption onto rice husk. The initial concentration used was from $0.61\text{-}6.1 \times 10^{-4}$ mol/dm^3. They suggested that the distribution coefficient decreased with the increase in concentration of 2,4-dichlorophenol up to 4×10^{-4} mol/dm^3 and then remained constant. This might be attributed due to small number of binding sites which are inadequate to adsorb large number of 2,4-dichlorophenol molecules. Ahmad *et al.*[66] observed the effect of initial dye concentration on the amount adsorbed. The biosorption capacity also increased from 32 to 321 mg/g with increase in dye concentration. In the start, the dye molecules adsorbed externally and the biosorption rate increased rapidly. When the external surface was saturated, the dye molecules began to adsorb internally.

Bayramoglu and Arica[15] estimated that the amount of dyes (direct blue-1 and direct red-128) adsorbed per unit mass of the biomass and observed that the dyes uptake increased with increase in the initial concentration of dyes. The highest adsorption capabilities of the native and heat treated fungal biosorbent were observed to be 101.1 and 152.3 mg/g for direct blue-1 and 189.7 and 225.4 mg/g for direct red-128 dyes, respectively. The heat treated biomass showed more adsorption due to excess number of biosorption sites through cell wall proteins destruction. From this study, it was concluded that dye uptake was also depended upon the molecular mass of dye molecules. The molecular mass of direct blue-1 is greater than direct red-128. So, removal capacity of direct blue-1 is lower than other dye. This is due to large molecules of direct blue-1 dye that can not pass through the minute pores of the biomass. Bulut *et al.*[29] observed that the amount of dye sorbed per unit mass of biosorbent increased with increase in initial dye concentration from 50 to 250 mg/L. It is estimated that the binding sites of biosorbent stays unsaturated during the biosorption mechanism.

Ardejani *et al.*[3] investigated the effect of initial dye concentration of direct red 80 biosorption by almond shells. They showed that the per cent uptake of direct red 80 decreased from 94 to 83.9 % with increase in initial dye concentration from 50 to 150 mg/L. Jain and Shikarwar[62] tried to explain the effect of initial dye concentration. They concluded that amount of dye sorbed per unit mass of the biomass increased with increase in the dye concentration. The per cent uptake was the highest about 99 % at the lowest dye concentration (1.0×10^{-5} M) for activated carbon biomass and 80 % for activated sawdust.

Khaled *et al.*[14] investigated the effect of initial direct N blue-106 on the biosorption of orange peel carbon. They used various concentrations of direct N blue-106 (50, 75, 100, 125 and 150 mg/L) on three biosorbent doses (0.2, 0.4 and 0.6/100 mL). The amount of dye adsorb, q_e, increased from 20.42 to 54.39, 11.36 to 28.34 and 7.99 to 23.09 mg/g with increase in the dye concentration from 50 to 150 mg/L at biosorbent doses 2, 4 and 6 g/L, respectively. But the per cent removal of dye was decreased with increase in dye concentration. In the biosorption mechanism of dye, first, the dye ions adsorbed on the outer surface and then finally, adsorbed into the spongy structure of the biosorbent. This process would take more time. Khaled *et al.*[1] studied the effect of initial dye concentration on the biosorption capacity onto the orange peel carbon. They used various dye concentrations of direct yellow-12 (25, 50, 75, 100 and 125 mg/L) and three biosorbent dosages (0.25, 0.50 and 7.50 g/100 mL) of biomass. The amount of dye adsorbed was found to be the maximum at the highest dye concentration (125 mg/L). The dye ions adsorb on the outer surface of biomass and then pass into the pores of biosorbent particles. On the other side, the per cent uptake of dye was greater at less initial dye concentration, which shows that the biosorption of direct yellow-12 was affected by initial dye concentration.

In another study conducted by Dulman and Cucu-Man[63] the effect of initial dye concentration on the amount of dye adsorbed was investigated. They used different concentrations of direct brown and direct brown 2 dyes. They observed that the amount of dye adsorbed increased with increase in the initial dye concentration. EI-Nemr *et al.*[64] used orange peel activated carbon to determine the effect of various concentrations of direct blue-86 on it. They used various initial concentrations of direct blue-86 (25, 50, 75, 100 and 125 mg/L). It was determined that the per cent removal of dye was the maximum at the smallest concentration of dye. But the amount of dye adsorbed was the maximum at high concentration of dye. The dye uptake was increased from 10.84 to 39.98 mg/g with the increase in concentration of dye from 25 to 125 mg/L. In the biosorption mechanism of dye, first, the dye ions adsorbed on the outer surface and then finally, absorbed onto the spongy structure of the biosorbent. EI-Sayed and EI-Ashtouky[65] expressed the effect of initial concentration of the direct blue dye on the biosorption process. They observed that the per cent dye uptake was the maximum at the low concentration of dye. This is due to agglomeration of dye ions at high dye concentration.

Effect of contact time: The contact time has been found to affect the sorption process significantly. Namasivayam *et al.*[13] investigated the effect of contact time on the biosorption of Congo red dye onto orange peel. Initially the rate of dye sorption was higher and then this rate decreased. The equilibrium was attained after 1.5 h. Mall *et al.*[60] studied the effect of agitation time on the uptake of Congo red. The biosorption rate was fast in the starting 15 min and the equilibrium was attained after 4 h. Akhtar *et al.*[34] reported the effect of contact time on the biosorption of 2,4-dichlorophenol onto rice husk. The results showed that percentage removal increased from 26 to 97 % up to 10 minute. The equilibrium was achieved within 10 to 20 min.

Ahmad *et al.*[66] also reported the effect of contact time on the uptake of direct dye by palm ash. The biosorption capacity increased with increase in contact time. The equilibrium was established after 1 h of contact time. The different dye concentration ranging from 50 to 600 mg/L were used. The dye uptake increased from 32 to 321 mg/g with increase in dye concentration. In the start, the biosorption rate was rapid due to adsorption of dye molecules on the upper surface of biosorbent. Then it became slow due to passing of dye molecules into the inner porous structure of the biosorbent.

Bulut *et al.*[29] reported the effect of agitation time on the biosorption capacity of direct blue-71 by wheat shells. The biosorption capacity (mg/g) increased with increase in agitation time. The equilibrium was achieved after 36 h. In the beginning, the biosorption capacity improved quickly. It was observed that *ca.* 50 % biosorption occurred within 12 h. Ardejani *et al.*[3] determined the effect of shaking time on the biosorption capacity of direct red-80 dye onto almond shells. The per cent uptake was rapid initially and then slowed down with time. The equilibrium was maintained after 5 h. The per cent uptake of dye was 94 % at the equilibrium.

Mohan *et al.*[10] investigated the effect of agitation time on biosorption of direct azo dye onto *Spirogyra* sp.102. They discussed that dye uptake was fast in the start and then became constant at equilibrium. A large amount of dye was adsorbed in 2 h of the agitation time. They used dye concentration from 5-15 mg/L and percentage uptake of dye was 64.0-35.3 %, respectively. The fast uptake of dye was due to involvement of binding sites on the biomass and may be chemisorptions. Khaled *et al.*[1] attempted to study the effect of agitation time on the uptake of direct yellow 12 onto orange peel carbon. They used various concentrations from 25 to 125 mg/L. About 75 % biosorption took place in the starting 19 min and then biosorption capacity began to slow. In the beginning, the high-speed biosorption might be attributed due to presence of positive charge on the biosorbent which developed an interaction with negatively charged direct yellow-12. Then the biosorption began to slowdown after 20 min due to slow movement of dye molecule into the interior of bulk of the biosorbent. The equilibrium was reached after 2 h.

Khaled *et al.*[14] used the direct N-blue-106 dye to study the effect of agitation time. The dye uptake increased with increase in the agitation time. About 70 % dye was eliminated within 10 min. The equilibrium was reached after 3 h. Dulman and Cucu-Man[63] studied the effect of contact time on the biosorption of dye. They used direct brown and direct brown 2 dyes with initial dye concentration from 330 to 900 mg/L and from 320 to 600 mg/L, respectively. The biosorption capacity (mg/g) of direct brown dye remained constant after 2 h up to 3 h. And for direct brown 2, the biosorption capacity remained constant after 3 h up to 5 h. The biosorption is increased rapidly in the initial time.

EI-Nemr *et al.*[64] reported the effect of agitation time on the biosorption of direct blue-86 onto orange peel carbon. The per cent sorption (*ca.* 64 %) occurred in the initial 5 min and then biosorption rate became slow. The fast biosorption rate is attributed due to presence of positive ions on the surface of the orange peel carbon for biosorption of negative charged direct brown-86 dye. The decreased biosorption rate was due to repulsion between negatively charged direct brown-86 dye on the orange peel carbon surface. The equilibrium had achieved after 3 h. EI-Sayed and EI-Ashtoukhy[65] tested the shaking time effect on the biosorption of direct blue dye by *Loofa egyptiaca*. With the increase in shaking time, the per cent uptake of dye also increased. The equilibrium was maintained after 2 h of shaking time.

Effect of temperature: Temperature is also an important factor which affects the dye removal process. Because the industrial dye effluents are produced into the water, their temperature are very high *ca.* 60-70 ºC. In a study performed by Namasivayam and Kavitha[58], the effect of temperature on the biosorption capacity of Congo red dye was investigated. The biosorption capacity (mg/g) increased with increase in temperature. They used following van't Hoff equation to study the temperature effect.

$$\log Kc = \Delta S^{\circ}/2.303R - \Delta H^{\circ}/2.303RT$$

The positive values of ΔH° show that the biosorption process was endothermic. The value of ΔG° is positive at 35, 40 and 50 °C which represent that biosorption process was unfavourable at low temperatures. But at high temperature 60 °C, the negative value of ΔG° shows that biosorption was favourable at high temperature.

Bhattacharyya and Sharma[59] expressed the effect of temperature on the Congo red dye removal by *Azadirachda indica* leaf powder. They used four different temperatures (303, 308, 313 and 323 K). The biosorption capacity decreased with increase in temperature. So, the process was exothermic in nature. The values of enthalpy changes were negative. The negative values of ΔG° indicated that the process was spontaneous. The negative values of ΔS° show the less randomness of dye molecules on the solid surface than liquid surface. With increasing the temperature, the movement of the dye molecules also increases and departs from the solid surface to liquid surface and decrease the biosorption capacity (mg/g).

Bayramoglu and Arica[15] studied the temperature effect on the removal of direct dyes by *Trametes versicolor* biosorbent. They studied the temperature effect from 5 to 35 °C. They demonstrated that dye removal capacity increased with increase in temperature. This might be due to increase in the motion of dye molecules. The process was endothermic in nature. Akhtar *et al.*[34] investigated the effect of temperature on the biosorption of 2,4-dichlorophenol. In the start the percentage sorption was increased *ca.* 98 % by rise in temperature from 273 to 573 K. Then again rise in temperature up to 873 K, the percentage biosorption began to decrease. This might be attributed due to change in the structure of the biomass. The value of ΔH° and ΔG° was negative which indicated that the process was exothermic and spontaneous in nature.

Bulut *et al.*[29] observed the effect of temperature on the uptake of direct blue-71 by wheat shells. They used various temperatures (293, 303 and 313 K). The biosorption capacity (mg/g) increased with increase in temperature. The process was endothermic in nature. The negative values of ΔG°, showed that the biosorption process was spontaneous in nature. The value of ΔS° was positive which showed the attraction of biosorbent for dye.

Mohan *et al.*[10] described the effect of direct dye removal from aqueous solution. They studied various temperature ranges (10, 20, 30, 40 and 50 °C). The percentage removal increased with increase in temperature. This shows that process was endothermic. This might be attributed to increase in the number of molecules attaining sufficient energy to undergo chemical reaction which shows chemisorption.

Effect of ionic strength: Ionic strength is the most important parameter that affects sorption of dyes. Because salts are used in the dyeing procedure and their concentration affect the removal efficiency of dye from the aqueous solution. Gong *et al.*[8] studied the effect of ionic strength on the biosorption of direct dyes by peanut hull. They took different concentrations of sodium chloride (0.0-0.5 M). The per cent removal was decreased with increase in the concentration of salt. This was due to screening effect of salt which decrease the electrostatic interactions between dye molecules and biosorbent surface.

Bayramoglu and Arica[15] observed the effect of ionic strength on the uptake of direct blue and direct red dyes by *Trametes versicolor* biosorbent. They used different concentrations of sodium chloride salt (0.0-0.5 M). They noted that the changing concentrations of salt were not influenced the uptake of dye. So, the results showed that the *Trametes versicolor* biosorbent was good for elimination of direct dyes from salted water. Grabowska and Gryglewicz[16] also investigated the effect of salt concentrations on the biosorption of Congo red onto activated carbon. The ionic strength governed the electrostatic and non-electrostatic attractions between the dye and biosorbent. When there was no salt, the biosorption capacity (mg/g) was high because more attraction between dye molecule and the biosorbent. The biosorption capacity decreased with an increase in the amount of salt added. This might be attributed due to the fact that addition of salt minimizes the electrostatic attractions.

Conclusion

This review presents the effect of various process parameters affecting the biosorption of direct dyes. The dye removal/biosorption process is highly affected by the process parameters. The pH not only influences the dye colour but also affects the structure of the dye molecules. Biosorbent size, dose and number of exchanging sites play an important role in the biosorption capability of different biosorbents. Most important parameters are dye concentration and temperature because highly concentrated and hot dye solution is discharged by industries. Several investigators showed that the biosorption process is the most advance and environmental friendly technique but the question is that still biosorption is not a popular wastewater treatment technique. Industrialists have no facilities to treat the discharging polluted water. They only remove the coarse particles from effluents and discharge the dangerous wastewater into the water streams. It is our duty to aware the whole population about the deleterious effects of dye contaminated water.

ACKNOWLEDGEMENTS

This work is a part of Ph.D. degree of Miss Yusra Safa. The authors are thankful to Higher Education Commission (HEC) of Pakistan for providing funds to accomplish this work.

REFERENCES

1. A. Khaled, A. El-Nemr, A. EI-Sikaily and O. Abdelwahab, *Desalination*, **238**, 210 (2009).
2. Z. Aksu, *Process Biochem.*, **40**, 997 (2005).
3. F.D. Ardejani, K. Badii, N.Y. Limaee, S.Z. Shafaei and A.R. Mirhabibi, *J. Hazard. Mater.*, **151**, 730 (2008).
4. G. McKay, *Chem. Eng. J.*, **27**, 187 (1983).
5. Y.M. Slokar and A.M.L. Marechal, *Dyes Pigments*, **37**, 335 (1997).
6. T. Robinson, G. McMullan, R. Marchant and P. Nigam, *Bioresour. Technol.*, **77**, 247 (2001).
7. Y. Fu and T. Viraraghavan, *Bioresour. Technol.*, **79**, 251 (2001).
8. R. Gong, Y. Ding, M. Li, C. Yang, H. Liu and Y. Sun, *Dyes Pigments*, **64**, 187 (2005).

9. Z. Aksu, A.I. Tatli and O. Tunc, *Chem. Eng. J.*, **142**, 23 (2008).
10. S.V. Mohan, S.V. Ramanaiah and P.N. Sarma, *J. Chem. Eng.*, **38**, 61 (2008).
11. M.A. Al Ghouti, M.A.M. Khraisheh, S.J. Allen and M.N. Ahmad, *J. Environ. Manage.*, **69**, 229 (2003).
12. N. Hoda, E. Bayram and E. Ayranci, *J. Hazard. Mater.*, **137**, 344 (2006).
13. C. Namasivayam, N. Muniasamy, K. Gayatri, M. Rani and K. Ranganathan, *Bioresour. Technol.*, **57**, 37 (1996).
14. A. Khaled, A. EI-Nemr, A. EI-Sikaily and O. Abdelwahab, *J. Hazard. Mater.*, **165**, 100 (2009).
15. G. Bayramoglu and M.Y. Arica, *J. Hazard. Mater.*, **143**, 135 (2007).
16. E.L. Grabowska and G. Gryglewicz, *Dyes Pigments*, **74**, 34 (2007).
17. T. Robinson, T.B. Chandran and P. Nigam, *Water Res.*, **36**, 2824 (2002).
18. G. Mishra and M. Tripathy, *Colourage*, **40**, 35 (1933).
19. G. Bayramoglu, G. Celik and M.Y. Arica, *J. Hazard. Mater.*, **137**, 1597 (2001).
20. E. Rinde and W. Troll, *J. Natl. Cancer Inst.*, **55**, 181 (1975).
21. S. Karcher, A. Kornmuller and M. Jekel, *Dyes Pigments*, **51**, 111 (2001).
22. Z. Eren and F. N. Acar, *Desalination*, **194**, 01 (2006).
23. A.K. Mittal and S.K. Gupta, *Water Sci. Technol.*, **34**, 157 (1996).
24. H.C. Chu and K.M. Chen, *Process Biochem.*, **37**, 595 (2002).
25. S.W. Won, S.B. Choi and Y.S. Yun, *Colloid Surf.*, **262**, 175 (2005).
26. T.V.N. Padmesh, K. Vijayaraghavan, G. Sekaran and M. Velan, *Chem. Eng. J.*, **122**, 55 (2006).
27. I.M. Banat, P. Nigam, D. Singh and R. Marchant, *Bioresour. Technol.*, **58**, 217 (1996).
28. S. Wang, Y. Boyjoo and A. Choueib, *Chemosphere*, **60**, 1401 (2005).
29. Y. Bulut, N. Gozubenli and H. Aydin, *J. Hazard. Mater.*, **144**, 300 (2007).
30. K. Vijayaraghavan and Y.S. Yun, *Dyes Pigments*, **76**, 726 (2008).
31. G. Crini, *Bioresour. Technol.*, **97**, 1061 (2006).
32. M. Arami, N.Y. Limaee, N.M. Mahmoodi and N.S. Tabrizi, *J. Hazard. Mater.*, **135**, 171 (2006).
33. V. K. Garg, M. Amita, R. Kumar and R. Gupta, *Dyes Pigments*, **63**, 243 (2004).
34. M, Akhtar, M.I. Bhanger, S. Iqbal and S.M. Hasany, *J. Hazard. Mater.*, **128**, 44 (2006).
35. B. Volesky, *Hydrometallurgy*, **59**, 203 (2001).
36. Rajeshwarisivaraj, S. Sivakumar, P. Senthilkumar and V. Subburam, *Bioresour. Technol.*, **80**, 233 (2001).
37. C. Namasivayam, D. Prabha and M. Kumutha, *Bioresour. Tehnol.*, **64**, 77 (1998).
38. R. Juang, F. Wu and R. Tseng, *J. Colloid. Interf. Sci.*, **227**, 437 (2000).
39. G. McKay, G. Ramprasand and P. Pratapamowli, *Water Air Soil Pollut.*, **29**, 273 (1986).
40. V.K. Garg, R. Gupta, A.B. Yadar and R. Kumar, *Bioresour. Technol.*, **89**, 121 (2003).
41. M.M. Nassar and S.M. EI-Geundi, *J. Chem. Technol. Biotechnol.*, **50**, 257 (1991).
42. M.M. Nassar, M.F. Hamoda and G. H. Radwan, *Water. Sci. Technol.*, **32**, 27 (1995).
43. M.M. Nassar, *Water. Sci. Technol.*, **40**, 133 (1999).
44. C. Namasivayam and K. Kadirvelu, *Bioresour. Technol.*, **48**, 79 (1994).
45. B.H. Hameed and M.I. EI-Khaiary, *J. Hazard. Mater.*, **154**, 237 (2008).
46. P. Pengthamkeerati, T. Satapanajaru and O. Singchan, *J. Hazard. Mater.*, **153**, 1149 (2008).
47. V. Ponnusami, S. Vikram and S.N. Srivastava, *J. Hazard. Mater.*, **152**, 276 (2008).
48. H. Lata, S. Mor, V.K. Garg and R.K. Gupta, *J. Hazard. Mater.*, **153**, 213 (2008).
49. B.H. Hameed and M.I. EI-Khaiary, *J. Hazard. Mater.*, **154**, 639 (2008).
50. R.S. Bai and T.E. Abraham, *Bioresour. Technol.*, **87**, 17 (2003).
51. F. Beolchini, F. Pagnanelli, L. Toro and F. Veglio, *Hydrometallurgy*, **70**, 101 (2003).
52. M.Z.C. Hu and M. Reeves, *Biotechnol. Prog.*, **13**, 60 (1997).
53. P.R. Puranik and K.M. Paknikar, *Biotechnol. Prog.*, **15**, 228 (1999).
54. K. Vijayaraghavan, M.H. Han, S.C. Choi and Y.S. Yun, *Chemosphere*, **68**, 1838 (2007).
55. B.E. Wang, Y.Y. Hu, L. Xie and K. Peng, *Bioresour. Technol.*, **99**, 794 (2008).

56. K.C. Chen, J.Y. Wu, G.C. Huang, Y.M. Liang and S.C.J. Hwang, *J. Biotechnol.*, **101**, 241 (2003).
57. Z. Aksu and F. Gonen, *Process. Biochem.*, **39**, 599 (2004).
58. C. Namasivayam and D. Kavitha, *Dyes Pigments*, **54**, 47 (2002).
59. K.G. Bhattacharyya and A. Sharma, *J. Environ. Manage.*, **71**, 217 (2004).
60. I.D. Mall, V.C. Srivastava, N.K. Agarwal and I.M. Mishra, *Chemosphere*, **61**, 492 (2005).
61. R. Han, D. Ding, Y. Xu, W. Zou, Y. Wang, Y. Li and L. Zou, *Bioresour. Technol.*, **99**, 2938 (2008).
62. R. Jain and S. Sikarwar, *J. Hazard. Mater.*, **152**, 942 (2009).
63. V. Dulman and S.M. Cucu-Man, *J. Hazard. Mater.*, **162**, 1457 (2009).
64. A. EI-Nemr, O. Abdelwahab, A. EI-Sikaily and A Khaled, *J. Hazard. Mater.*, **161**, 102 (2009).
65. EI-Sayed and Z. EI-Ashtoukhy, *J. Environ. Manage.*, **90**, 2755 (2009).
66. A.A. Ahmad, B H. Hameed and N. Aziz, *J. Hazard. Mater.*, **141**, 70 (2007).

(*Received*: 1 February 2010; *Accepted*: 24 May 2010) AJC-8743