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Adsorptive removal of direct dyes by low cost rice husk: Effect of treatments and modifications

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In the present study, free, carboxymethyl cellulose (CMC)-immobilized, polyvinyl alcohol (PVA)-alginate immobilized and chemically treated rice husk biomass was used for the biosorption of Everdirect Orange-3GL and Direct Blue-67 dyes. Maximum biosorption capacity of free, immobilized and hydrochloric acid treated biomass was observed for both dyes at low pH. Comparative study of free, immobilized and HCl treated biomass showed that, the HCl treated biomass exhibited more biosorption capacity (29.98 and 37.92 mg/g) for Everdirect Orange-3GL and Direct Blue-67, respectively. Equilibrium time was less for HCl treated biomass when compared with immobilized biomass. The Langmuir type 1 and 2 models were best fitted to experimental data for free, CMC, polyvinyl alcohol-alginate immobilized and HCl treated biomass in case of Everdirect Orange-3GL, while the equilibrium data of Direct Blue-67 followed the Langmuir type 2 isotherm. Pseudo-second-order and Elovich kinetic models illustrated good fitness to all types of biomasses showing chemisorption nature of biosorption. The amount of dyes sorbed (mg/g) increased with increase in temperature. The values of Gibbs free energy (ΔG°) showed that reaction was spontaneous at high temperature.

Key words: Biosorption, kinetics, thermodynamics, direct dyes, immobilization, pretreatments.

INTRODUCTION

The recent leap in industrial and technological advancement at the global level brought the introduction of different pollutants into water bodies. Dyes and other organic compounds are among such pollutants. The discharge of dye wastewaters into aqueous bodies adversely affect aquatic environment by reducing light penetration and photosynthesis (Aksu and Tezer, 2000). Moreover, dyes are dangerous, mutagenic and carcinogenic in nature (Chen et al., 2003). The removal of dyes and organic compounds in an economic fashion remains an important problem, although a number of successive systems have been developed with the adsorptive

technique. The conventional methods for removal of dyes and other pollutants from aqueous solution such as ozonation, adsorption, coagulation, chemical oxidation, catalysis, membrane separation and advanced oxidation are difficult, ineffective and not eco-friendly (Mondal, 2008; Gadd, 2009). Biosorption is considered as an alternative and promising technique for the removal of pollutants due to its cost effectiveness and efficiency (Volesky, 2001). Activated carbon is generally used commercially but high cost limits its use (Gong et al., 2005).

Rice husk is easily available low cost agricultural waste biomass. Approximately 80 million tones of rice husk are obtained annually (Armesto et al., 2002). Rice husk is composed of silica, cellulose, hemi cellulose and lignin. It is an efficient biosorbent material for metals cation and dyes (Suemitsu et al., 1986; Low and Lee, 1997). Advantages of the immobilization of biosorbent include excellent reuse of the biosorbent, controlling of biosorbent particle, increasing mechanical strength and less flocculation in the continuous system (Bayramoğlu et al., 2003). Immobilization of dead biomass is more effective

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Abbreviations: CMC, Carboxy methyl cellulose; **PVA,** polyvinyl alcohol; **Na-CMC,** carboxy methyl cellulose sodium salt; **CTAB,** cetyl trimethyl ammonium bromide; **TVFB,** free biomass; **TVIS,** immobilized loofa sponge.

than living biomass because complication in biosorbent kinetics due to cell growth can be eliminated (Benyahra and Polomarkaki, 2005). Different polymeric matrix are used in the immobilization process such as, polysulfone (Puranik and Paknikar, 1999; Beolchini et al., 2003), poly-acrylamide and alginate (Bai and Abraham, 2003; Asghar and Bhatti, 2010), polyurethane (Hu and Reeves, 1997), carboxy methyl cellulose (CMC) (Wang et al., 2008), etc.

CMC is soluble in water. Carboxylic groups are present on the cellulose for immobilization. CMC is biodegra-dable, naturally present and large number of functional groups is present on its surface (Arica and Bayramoğlu, 2005). Polyvinyl alcohol (PVA) is an efficient, less costly and non-toxic polymer. Physical modifications such as boiling, heating, autoclaving and chemical treatments with acids, alkali, salts, surfactants and some organic compounds enhanced or decreased the biosorption capacities of pollutants such as metals and dyes (Selatnia et al., 2004; Janos et al., 2009; Asgher and Bhatti, 2010). The pretreatments or modifications of the biomass may increase the surface area of the biomass and enhanced the amount of pollutant sorbed from aqueous solution (Oei et al., 2009; Bhatti et al., 2010).

This study examines the effect of physical (heating and boiling) and chemical modifications (acids, alkali, salts, surfactants, ethanol, methanol and glutaraldehyde) of biosorption capacity of rice husk. In order to investigate the effect of immobilization, the rice husk biomass was immobilized with CMC and PVA-alginate matrices. Comparison of native rice husk was done with the CMC and PVA-alginate and HCl-treated biomass for the biosorption of two direct dyes. Moreover, the effect of pH, initial dye concentration, contact time and temperature on the biosorption of direct dyes was also investigated.

MATERIALS AND METHODS

Chemicals

All the chemicals and reagents used in the present investigation were of analytical grade and mainly purchased from Sigma-Aldrich (USA) and Merck (Germany).

Preparation of rice milling waste biomass

Fresh rice (*Oryza sativa*) milling waste biomass of super basmati variety was procured from local rice mills. The biomass was washed several times with distilled water to remove dust and other foreign particles. The cleaned biomass was dried in sunlight and then in oven at 70°C for 24 h. The washed materials was ground with food processor (Moulinex, France) and sieved using Octagon sieve (OCT-DIGITAL 4527-01) to various mesh sizes from < 0.250, 0.250 - 0.355, 0.355 - 0.500, .500 - 0.710 and 0.710-1.000 mm. The biosorbent material was stored in plastic bottles for further use.

Preparation of aqueous dye solutions

In the present investigation, two direct dyes, Everdirect orange-3GL and Direct blue-67 (obtained from local market, Faisalabad, Pakistan) were used without further purification. Stock solutions of both dyes were prepared by dissolving 0.1 g of each dye in 1000 ml of double distilled water. The experimental solutions of different concentrations ranging from 25 to 150 mg/l for Everdirect orange-2GL and from 25 to 300 mg/l for Direct Blue-67 were made by further dilutions. Standard curves were developed through the mea-surement of the dye solution absorbance by UV/visible spectrophotometer (Hitachi U-2001). The general characteristics of these dyes are shown in Table 2.

Batch biosorption experimental studies

Optimization of various process parameters such as pH, initial dye concentration, contact time and temperature for enhanced removal of Everdirect Orange-3GL and Direct Blue-67, was carried out by using classical approach. The 250 ml conical flasks containing 50 ml of dyes solution of known pH, concentration and biosorbent dose were shaken in orbital shaking incubator (PA250/25H) at 100 rpm. Blank solutions were run using same conditions except the addition of biosorbent material. After certain time, the samples were taken out and centrifugation was performed at 2000 pm for 20 min. The amount of biosorbed dye per unit mass was calculated using following equation:

$$q = (C_o - C_e) \, V/W \tag{1}$$

Where, q is the amount of dye biosorbed on the biosorbent (mg/g), C_o and C_e are the initial and equilibrium concentration of dye solution, respectively. V is the volume of dye solution (ml) and W is the amount of the rice husk (g). The % sorption was measured by the following equation:

$$\% \text{ sorption} = C_o - C_e/ \, C_o \times 100 \tag{2}$$

The experiments were conducted in triplicate.

Immobilization of biomass

PVA 10 g (10 % W/V) and sodium-alginate 1.0 g (1 %w/v) were dissolved in 100 ml of water by heating and then, the solution was cooled to 40°C; rice husk (2 g/100 ml) was added to each of mentioned mixture and mixed to form a homogeneous mixture. Then, the mixture was dropped into a solution of 50% sodium nitrate (w/v) and 1% $CaCl_2$ (w/v) to form uniform beads of immo-bilized biomass. After 1 h, the beads were washed and stored at 4°C in distilled water (Li-Sheng et al., 2007).

Rice husk biosorbent was also immobilized into carboxy methyl cellulose sodium salt (Na-CMC). Carboxy methyl cellulose sodium salt (2 g) was dissolved into 100 ml of distilled water and then, 4 g/100 ml of biosorbent was mixed in this Na-CMC solution. The mixture was extruded into 0.1 M $FeCl_3$ solution to form beads. The aggregation of beads was inhibited by continuous stirring of solution. After 15 min, the beads were washed with distilled water and stored at 4°C (Arica and Bayramoĝlu, 2005). Blank beads of PVA and Na-CMC were also formed without biomass.

The biomass concentrations, 0.09 g for Everdirect Orange-3GL (with bead dosage of 1.8 g/50 ml) and (bead dosage 2.1 g/50 ml) in case of CMC and PVA-alginate immobilized beads, respectively, were used. But in case of Direct Blue-67, the biomass concen-tration, 0.01 g (with bead dosage of 1.85 g/50 ml) and (bead dosage 2.32 g/50 ml) in case of CMC and PVA-alginate immo-bilized beads, were used, respectively.

Modifications of rice husk biomass

Rice husk biosorbent was treated physically and chemically.

Physical treatments was mentioned as heat-treated (the rice husk biomass was heated at 100°C for 24 h) and boiling (5 g of biomass/100 ml of H_2O and boiled for 30 min). To study the effect of pH, various pH (1-8 for Everdirect Orange-3GL and 3-8 for Direct Blue-67) were adjusted using 0.1 M HCl and NaOH solutions. In chemical modifications, 5 g of the biosorbent was treated with 0.1 N HCl, H_2SO_4 and HNO_3 (acids), 0.1 N NaOH and NH_4OH (alkali), 0.1 N $CaCl_2$, NaCl and $MgSO_4$ (salts), 1% cetyl trimethyl ammonium bromide (CTAB) and 1% Triton-X100 (surfactants), 0.1 N ethanol, 0.1 N methanol and glutaraldehyde (50 ml) for 1 h at 30°C. Then, all the modified biomasses were washed with double distilled water and filtered. The modified biosorbent were dried in oven at 60°C for 24 h and it was ground (Bhatti et al., 2009).

RESULTS AND DISCUSSION

Effect of modifications/treatments

Rice husk biomass was modified/treated physically and chemically. The amount of dyes sorbed (mg/g) onto free and treated rice husk increased in the following order after various treatments: Glutradehyde < methanol < ethanol < NaOH < NH_4OH < boiling < native < Triton X-100 < heat treated < CTAB < $MgSO_4$ < $CaCl_2.H_2O$ < NaCl < HNO_3 < H_2SO_4 < HCl. The results indicated that, the boiling of rice husk showed no effect on the biosorption capacity of the biomass. Heating the biomass at 100°C slightly increased the biosorption capacity due to denaturation of lignin on the surface of rice husk (Bhatti et al., 2009). The sorption capacity enhanced after modification of biomass with HCl, H_2SO_4 and HNO_3 acids. This might be due to protonation of the biosorbent surface that became positively charged and electrostatic attraction developed between positively charged biomass and negatively charged dye molecule and increased the amount of dye sorbed (Yazici et al., 2008).

Alkali (NaOH, NH_4OH) treatments decreased the biosorption capability of rice husk biomass due to deprotonation of functional groups on the biosorbent surface creating a negative charge on the biomass. This might be attributed to electrostatic repulsion between negatively charged dye and biomass surface. Modification of biomass with certain salts (NaCl, $CaCl_2$ and $MgSO_4$) increased the amount of dye sorbed (mg/g). This might be due to activation of interior biosorbent surface and production of more binding sites for dyes (Batzias and Sidiras, 2007). Cationic surfactant (CTAB) increased the biosorbent capacity due to impregnation of positive charge on the rice husk surface and produced an electrostatic attraction with negative dye molecules (Baskaralingam et al., 2006). Non-ionic surfactants showed no effect on the biosorbent capacity of rice husk biomass.

By treating the rice husk with ethanol and methanol, the biosorption capacity decreased significantly as a result of formation of esters. The carboxylate functional groups on the surface of biomass formed the esters by reacting with ethanol and methanol (Jianlong, 2002)

$$RCOOH + CH_3OH \rightarrow RCOOCH_3 + H_2O$$

$$RCOOH + CH_3CH_2OH \rightarrow RCOOCH_2CH_3 + H_2O$$
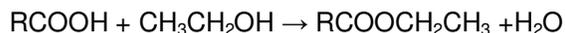
Modification of biosorbent with glutaraldehyde also decreased the biosorbent capacity. This might be due to cross-linking of the functional groups on the biomass surface (Zhou et al., 2005). HCl treatment of biomass showed the highest biosorbent capacity among all modifications, due to protonation of functional groups and increased the amount of dyes sorbed (Vijayaraghavan and Yun, 2008). Janos et al. (2009) treated the wood with HCl, Na_2CO_3 and Na_2HPO_4. The results indicated that the biosorption capacity increased after treating with Na_2CO_3 in case of methylene blue while in case of egacid orange, the biosorption capacity increased when the wood was treated with HCl.
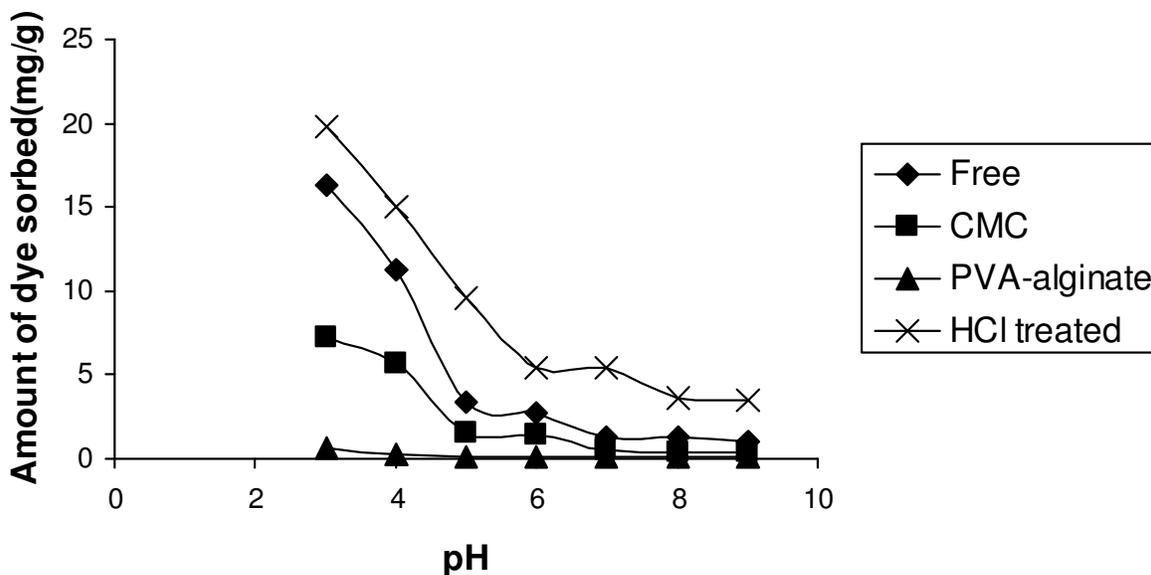
Effect of pH

With the free, immobilized and HCl treated biomass, the effect of pH on the biosorption of direct dyes was investigated over a range from 1.0 to 8.0 for Everdirect Orange-3GL and from 3 to 8 for Direct Blue-67. The results show that, maximum biosorption was recorded at pH 1.0 and 3.0 for Everdirect Orange-3GL and Direct Blue-67, respectively. At higher pH value, the biosorption of both direct dyes was not effective. The optimum uptake of Everdirect Orange-3GL and Direct Blue-67 dye by free, CMC, PVA-alginate immobilized and HCl treated biomass was investigated at low acidic pH and results are depicted in Figures 1 and 2. A maximum uptake value of 25.69 and 19.85 mg/g was observed for Everdirect Orange-3GL and Direct Blue-67, respectively, at the optimum pH with free biomass.

At low pH, the concentration of H^+ ions increased and the surface of the biomass become positively charged. A strong electrostatic interaction develops between positively charged biomass surface and negatively charged dye molecule. While at high pH value, electrostatic repulsion occurs due to number of negatively charged sites on the biosorbent (El-Nemr et al., 2009). A similar behavior was observed earlier for the biosorption of acidic dyes by *Paenibacillus macerans* (Colak et al., 2009).

CMC and PVA-alginate immobilized biosorbent also showed the maximum removal of Everdirect Orange-3GL and Direct Blue-67 at low pH. The biosorption capacity of CMC and PVA-alginate immobilized biomass is less than free biomass. This may be due to the blocking of exchanging sites through immobilization and dyes can not reach the binding sites easily (Vijayaraghavan et al., 2008). Saeed et al. (2009) investigated the biosorption of methyle blue onto the immobilized *Trichoderma viride*. The results showed that the amount of dye sorbed (155.06 mg/g) by free biomass (TVFB) is less than the
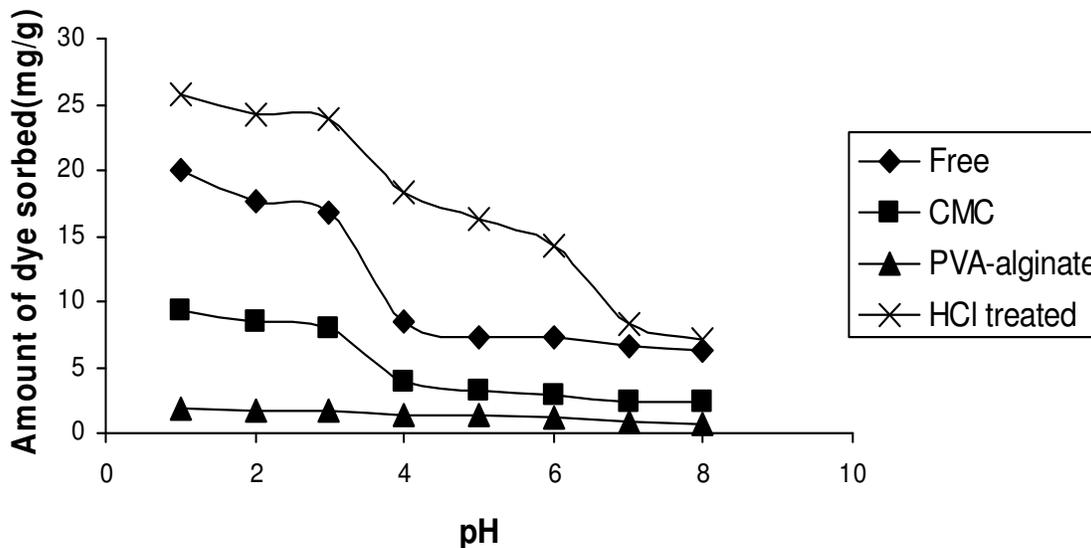
Figure 1. Effect of pH on the biosorption of Everdirect orange-3GL dye (biosorbent dose: 0.09 g/50 ml, C_o: 50 mg/l, Temp: 30°C, shaking speed: 100 rpm, particle size: 0.255 mm).

Figure 2. Effect of pH on the biosorption of Direct blue-67 dye (biosorbent dose: 0.1g/50 ml for Direct blue-67, C_o: 50 mg/l, Temp: 30°C, shaking speed: 100 rpm, particle size: 0.255 mm).

amount of dye sorbed (201.52 mg/g) by immobilized loofa sponge (TVIS).
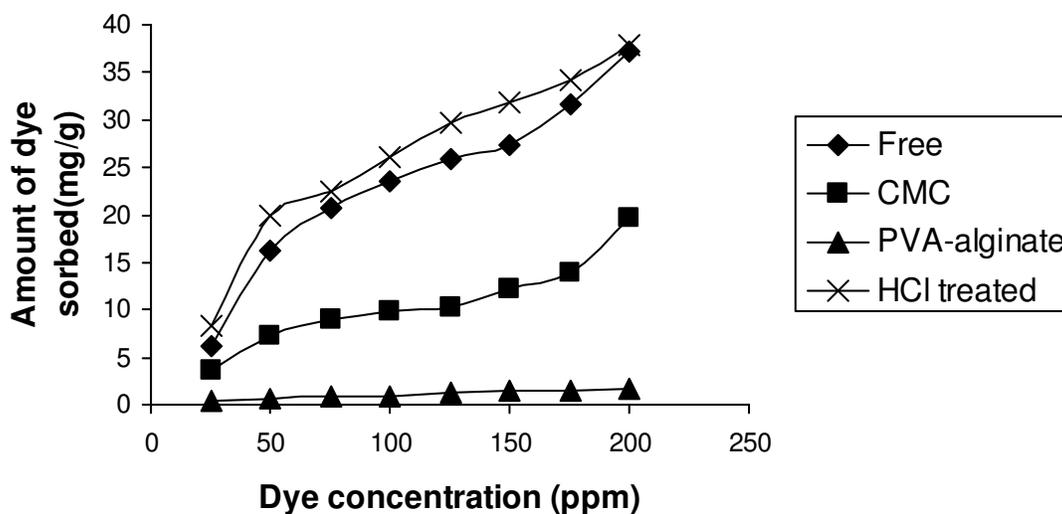
Effect of initial dye concentration

The effect of initial concentration of Everdirect Orange-3GL and Direct Blue-67 onto the biosorption capacity of rice biomass was investigated by varying the initial concentrations of Everdirect Orange-3GL (25 to 150 mg/l) and Direct Blue-67 (25 to 200 mg/l). The results

regarding the effects of initial concentration of dyes on the biosorption capacity of rice husk for free, immobilized and HCl treated biomass are given in Figures 3 and 4.

The uptake capacity of biomass increased from 12.95 to 25.59 mg/g (free), 4.42 to 16.42 mg/g (CMC immobilized), 0.571 to 3.67 mg/g (PVA-alginate immobilized) and 17.081 to 29.98 (HCl treated) for Everdirect Orange-3GL and 6.18 to 37.16 mg/g (free), 3.58 to 19.60 mg/g (CMC immobilized), 0.423 to 1.64 mg/g (PVA-alginate immobilized), and 8.29 to 37.92 mg/g (HCl treated) for of Direct Blue-67 with increase in the initial dye concentration.
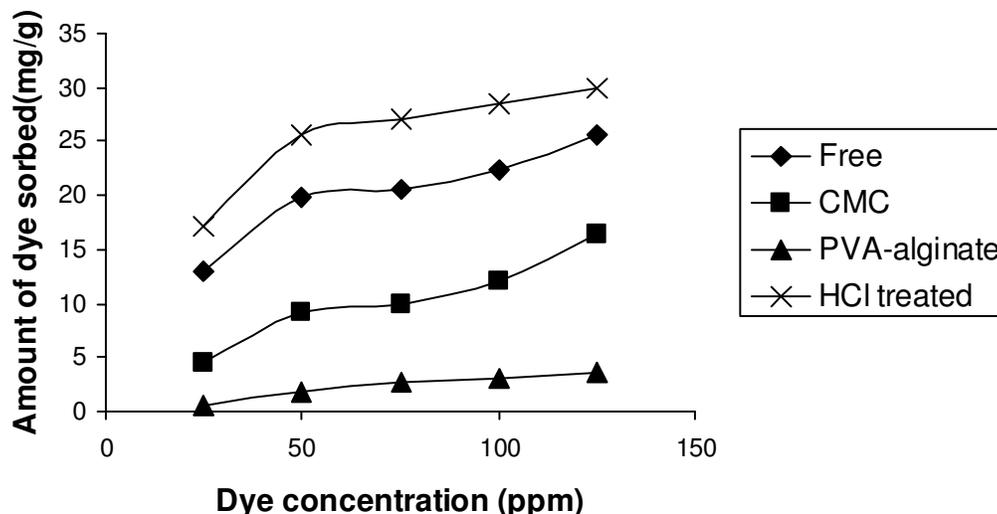
Figure 3. Effect of initial dye concentration on the biosorption of Everdirect orange-3GL dye at t biosorbent dose, 0.1g/50 ml (C_o: 25, 50, 75, 100 and 125 mg/l, Temp: 30°C, shaking speed: 100 rpm, particle size: 0.255 mm, pH: 1).


Figure 4. Effect of initial dye concentration on the biosorption of Direct blue-67 dye at biosorbent dose, 0.1g/50 ml (C_o: 25, 50, 75,100, 125,150,175 and 200 mg/l, Temp: 30°C, shaking speed: 100 rpm, particle size: 0.255 mm, pH: 3).

The percentage of biosorption showed opposite trend.

The amount of dye sorbed increased because the dye ions adsorbed on the outer surface of the biomass and then, finally began to adsorb internally (Ahmad et al., 2007). Vijayaraghavan et al. (2007) reported that the biosorption of reactive black 5 by the *Corynebacterium glutamicum* immobilized biosorbent. They observed that the biosorption capacity decreased from 19.89 to 17.33% after immobilization. In another study, Prakasham et al. (1999) used free and immobilized *Rhizopus arrhizus* for the biosorption of dye. Immobilization decreased the amount of dye sorbed (mg/g).

Effect of contact time

The biosorption efficiency of rice husk for Everdirect Orange-3GL and Direct Blue-67 was evaluated as a function of time and results are depicted in Figures 5 and 6. The amount biosorbed (mg/g) by the biosorbent increased rapidly with increase in contact time for both dyes. When the agitation time was further increased, there was no drastic increase in the biosorption capacity of the biosorbent. The equilibrium time for the Everdirect Orange-3GL and Direct Blue-67 was 180 and 240 min, respectively for free biomass. For CMC immobilized rice
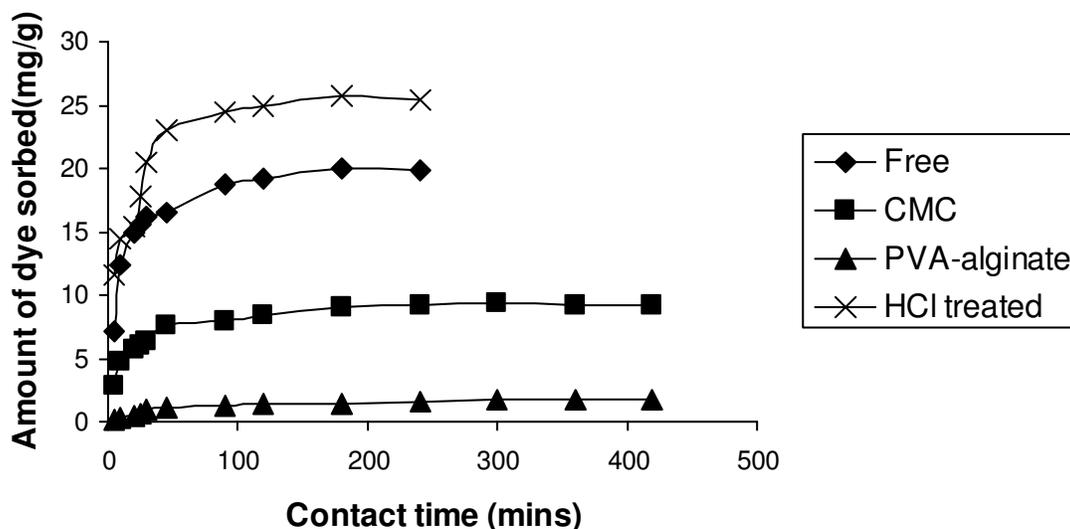
Figure 5. Effect of contact time on the biosorption of Everdirect orange-3GL dye at dye conc, 50 mg/l (biosorbent dose0.09g/50 ml, Temp: 30°C, shaking speed: 100 rpm, particle size: 0.255 mm, pH: 1).
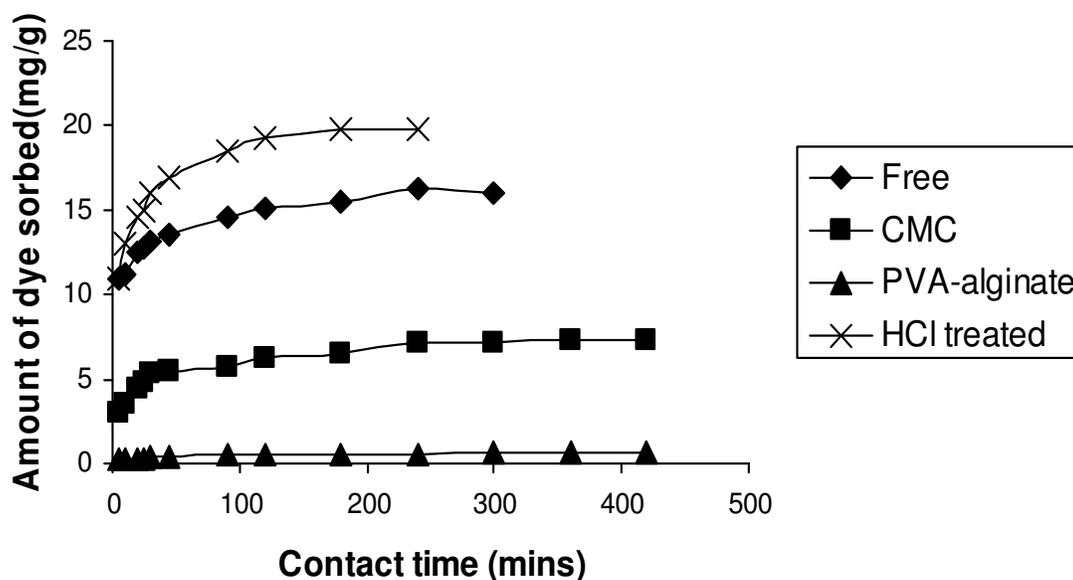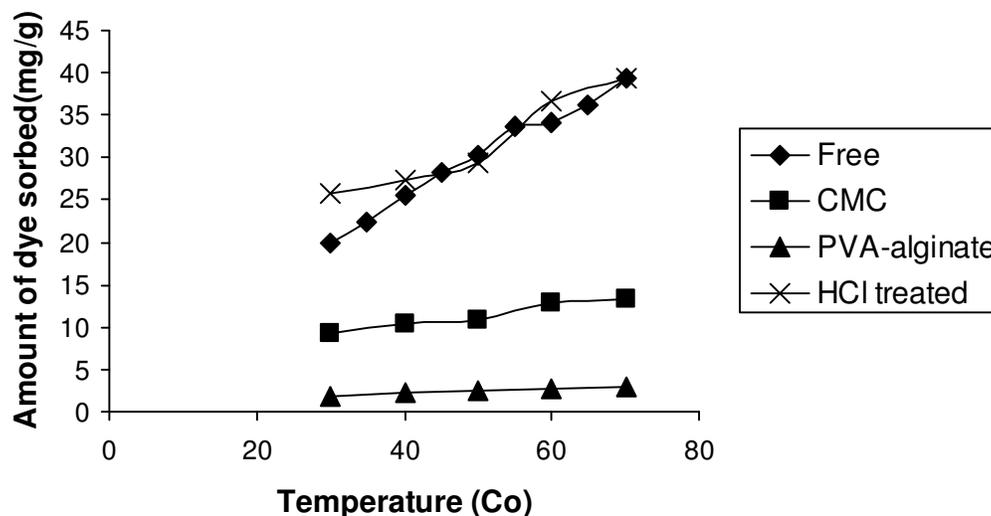

Figure 6. Effect of contact time on the biosorption of Direct blue-67dye at initial dye conc. 50 mg/l (biosorbent dose 0.1 g/50 ml, Temp: 30°C, shaking speed: 100 rpm, particle size: 0.255 mm, pH: 3).

husk, the equilibrium time for the Everdirect Orange-3GL was 300 but 360 min for Direct Blue-67. By using PVA-alginate immobilized biomass, the equilibrium was established after 360 min for Everdirect Orange-3GL and Direct Blue-67 dyes. The equilibrium time after using HCl treated biomass was less when compared with free and immobilized biomass. The equilibrium was attained for both dyes after 180 min by using HCl treated biomass.

The fast biosorption might be attributed to the presence of positive charge on the rice husk biosorbent surface which developed an interaction with negatively charged

dye molecules. Then, the biosorption began to slow down due to slow movement of dye molecule into the interior bulk of the biosorbent (Khaled et al., 2009). Akar et al. (2008) observed that, the amount of acid blue 40 dye sorbed (mg/g) by cone biomass *Thuja orientalis* increased with increase in the contact time. To attain the equilibrium, the immobilized CMC and PVA-alginate beads took more time because the rice husk biosorbent existed inside the immobilized biomass; the exposure of binding sites on the outer surface of biomass enhanced the biosorption capacity and less time is required to reach

Figure 7. Effect of temperature on the biosorption of Everdirect orange-3GL dye (pH:1, biosorbent dose:0.09 g/50 ml, C_o: 50 mg/l, shaking speed:100 rpm, dyes respectively, particle size: 0.255 mm).
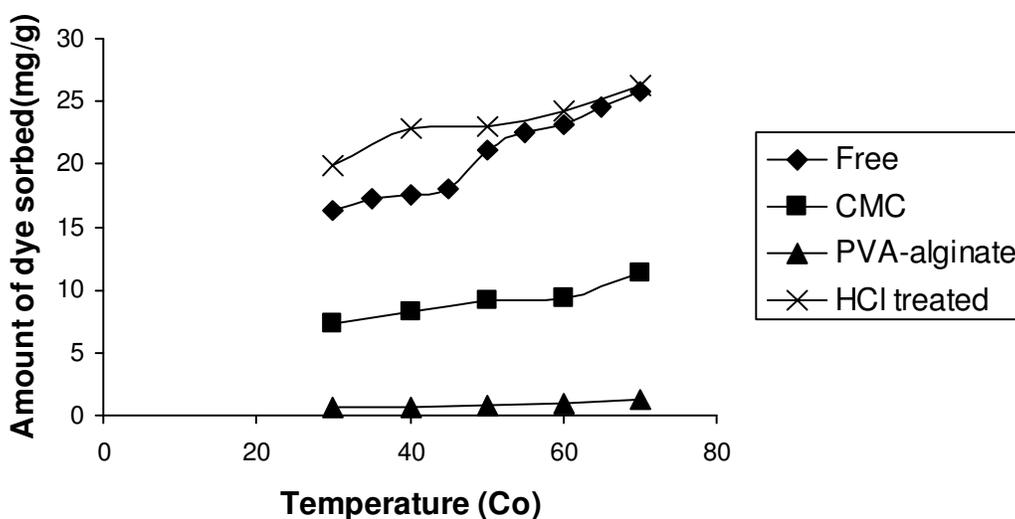
Figure 8. Effect of temperature on the biosorption of Direct blue-67 dyes (pH:1, biosorbent dose: 0.1 g/50 ml for Direct blue-67, C_o: 50 mg/l, shaking speed: 100 rpm, particle size: 0.255 mm.

the equilibrium (Guo et al., 2003).

Effect of temperature

The results regarding the effect of temperature on the biosorption of Everdirect Orange-3GL and Direct Blue-67 by rice husk are shown in Figures 7 and 8. The results indicated that, biosorption of both the dyes increase with an increase in temperature from 30 to 70°C. The biosorption capacity of the biomass for Everdirect Orange-3GL was found to be 19.92 mg/g (free biomass), 9.29 mg/g (CMC immobilized), 1.80 mg/g (PVA-alginate

immobilized) and 25.69 mg/g (HCl treated) at 30°C and 39.27 mg/g (free), 13.39 mg/g (CMC immobilized), 2.89 mg/g (PVA-alginate immobilized) and 39.27 mg/g (HCl treated) at 70°C. Similarly, for Direct Blue-67, the amount of dye sorbed increased from 16.27 and 25.82 mg/g (free), 7.251 to 11.33 mg/g (CMC immobilized), 0.619 to 1.29 mg/g (PVA-alginate immobilized) and 19.85 to 26.29 mg/g (HCl treated) at 30 and 70°C, respectively.

The biosorption of both dyes was favorable at high temperatures indicating the endothermic nature of the process. This might be due to the increase in the number of pores on the biomass surface at high temperature. High temperature reduced the thickness of outer surface

Table 1. R_L values

R_L value	Nature of biosorption mechanism
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

Table 2. General characteristics of direct dyes.

Dyes	Color index number	λmax (nm)	Type
Everdirect orange-3GL	Orange-39	415	Anionic
Direct blue-67	27925	570	Anionic

of the biosorbent and increased the kinetic energy of dye molecules, as a result, the dye molecules biosorbed easily into the surface of the biomass (Aksu et al., 2008). Aksu and Tezer (2005) investigated that, the rate of biosorption of reactive dyes on the green algae *Chlorella vulgaris* increased with increase in the temperature.

Biosorption equilibrium modeling

Equilibrium data commonly known as biosorption isotherm are basic requirements for the design of adsorption systems. Seven different models like Langmuir (Four linear expressions), Freundlich and Temkin isotherm were used to test or estimate the equilibrium data obtained in this research work. The comparison of the correlation coefficients (R^2) of all models suggests whether the isotherm equation is applicable or not.

Langmuir isotherm

The Langmuir adsorption isotherm (Langmuir, 2000) is frequently applied for the biosorption of organic and inorganic pollutants (dyes and heavy metals) from aqueous solution. This model suggests that the biosorption onto the adsorbent surface is homogeneous in nature. According to Langmuir isotherm, the biosorption of solute from aqueous solution onto the biosorbent surface occurred as monolayer biosorption on the homogeneous number of exchanging sites. This phenomenon describes the uniform biosorption energy on the biosorbent surface. The non-linear Langmuir isotherm equation can be presented in the following equation:

$$q_e = Q_m K_a C_e / 1 + K_a C_e \tag{3}$$

Where, q_e is the amount of dye biosorbed on the biomass (mg/g) at equilibrium, Ce is the equilibrium concentration of dye solution, Q_m is the maximum biosorption capacity

describing a complete monolayer adsorption (mg/g) and K_a is adsorption equilibrium constant (L/mg) that is related to the free energy of biosorption. The four linear Langmuir isotherms are shown in Table 3.

The values of various Langmuir constants for Everdirect Orange-3GL and Direct Blue-67 dyes are described in Tables 4 and 5, respectively. The value of correlation coefficients showed that, Langmuir type 1 and 2 were the best fitted for free, immobilized and HCl-treated biomass in case of Everdirect Orange-3GL and correlation coefficients of free, immobilized and HCl-treated biomass; this described that the Langmuir type 2 was the highest for Direct Blue-67. The important features of the Langmuir isotherm model can be defined by the dimensionless constant separation factor R_L which is expressed by the following equation (Aksu and Donmez, 2003):

$$R_L = 1/1 + K_a C_o \tag{4}$$

Where, C_o is the initial dye concentration (mg/l) and K_a is the Langmuir constant (L/mg). R_L shows the nature of biosorption mechanism. The value of R_L obtained in the present study was in the range of 0 to 1, describing that the biosorption process was favorable for both direct dyes (Table 1).

Freundlich isotherm

The Freundlich isotherm is the earliest known equation explaining the biosorption mechanism (Freundlich, 1906). This model is based on the assumption that the biosorption process takes place by interaction of the dye molecules on the heterogeneous surfaces. There is a logarithmic decline in the energy of biosorption with increase in the occupied binding sites. The non-linear equation is expressed as follows:

$$q_e = K_F C_e^{1/n} \tag{5}$$

Table 3. Linear forms of the Langmuir isotherm.

Isotherm type	Linear form	Plot
Langmuir type 1	$C_e/q_e = C_e/q_m + 1/K_a q_m$	C_e/q_e vs C_e
Langmuir type 2	$1/q_e = (1/K_a q_m)(1/C_e) + 1/q_m$	$1/q_e$ vs $1/C_e$
Langmuir type 3	$q_e = q_m - q_e/K_a C_e$	q vs q_e/C_e
Langmuir type 4	$q_e/C_e = K_a q_m - K_a q_e$	q_e/C_e vs q_e

Table 4. Biosorption isotherm constants for the biosorption of Everdirect orange-3GL dye onto rice husk.

Isotherm model	Everdirect orange-3GL			
	Free	CMC immobilized	PVA-alginate immobilized	HCl treated
Langmuir type 1				
q_m(mg/g)	28.41	23.36	6.89	30.96
K_a(L/mg)	0.061	0.029	0.051	0.201
R_L	0.095	0.2655	0.408	0.031
R^2	0.986	0.905	0.953	0.999
Langmuir type 2				
q_m(mg/g)	27.17	21.74	8.77	30.12
K_a(L/mg)	0.074	0.0333	0.036	0.268
R_L	0.080	0.238	0.491	0.023
R^2	0.976	0.975	0.997	0.995
Langmuir type 3				
q_m(mg/g)	27.21	20.07	6.81	30.11
K_a(L/mg)	0.074	0.0396	0.052	0.267
R_L	0.081	0.208	0.403	0.023
R^2	0.914	0.738	0.867	0.983
Langmuir type 4				
q_m(mg/g)	27.88	23.46	7.49	30.19
K_a(L/mg)	0.067	0.029	0.045	0.263
R_L	0.087	0.262	0.438	0.024
R^2	0.914	0.738	0.867	0.983

Where, K_F is the Freundlich isotherm constant (mg/g) related to the bonding energy. K_F is defined as the distribution coefficient and suggests the amount of dye sorbed on the biosorbent for unit equilibrium concentration. The value of n indicates whether the biosorption process is favorable or not. The value of n for favorable adsorption should be greater than 1. Linear form of Freundlich isotherm equation is:

$$\ln q_e = \ln K_F + 1/n \ln C_e \tag{6}$$

The value of K_F, correlation coefficient and n of four dyes are presented in Tables 6 and 7, respectively. For Everdirect Orange-3GL, the R^2 value (0.95) for CMC immobilized biomass showed that the experimental data fitted well to Freundlich isotherm model and for Direct Blue-67, the experimental data of free, immobilized and HCl treated biomass described good fitness to Freundlich isotherm model. The values of n are greater than 1 representing that the biosorption of Everdirect Orange-3GL and Direct Blue-67 onto rice husk is a favorable physical process.

Temkin isotherm

The Temkin isotherm model (Temkin and Pyzhev, 1940) suggests an equal distribution of binding energies over the number of exchanging sites on the surface. The distribution of these energies depends on the number of functional groups on the dye molecule and the biosorbent surface. There is equal distribution of maximum binding energy during the biosorption process. The decline in the heat of adsorption is linear but not logarithmic in nature.

Table 5. Biosorption isotherm constants for the biosorption of Direct blue-67 dye onto rice husk.

Isotherm model	Direct blue-67			
	Free	CMC immobilized	PVA-alginate immobilized	HCl treated
Langmuir type 1				
q_m(mg/g)	50.00	28.17	3.83	50.0
K_a(L/mg)	0.018	0.021	0.028	0.071
R_L	0.223	0.317	0.545	0.066
R^2	0.937	0.903	0.944	0.974
Langmuir type 2				
q_m(mg/g)	52.63	23.42	3.022	71.43
K_a(L/mg)	0.016	0.029	0.039	0.075
R_L	0.233	0.253	0.462	0.062
R^2	0.989	0.990	0.992	0.989
Langmuir type 3				
q_m(mg/g)	44.57	25.75	3.413	37.001
K_a(L/mg)	0.022	0.025	0.033	0.0703
R_L	0.186	0.285	0.503	0.07
R^2	0.834	0.612	0.892	0.879
Langmuir type 4				
q_m(mg/g)	49.44	35.37	3.698	38.492
K_a(L/mg)	0.018	0.015	0.029	0.062
R_L	0.218	0.395	0.532	0.075
R^2	0.834	0.612	0.892	0.879

Table 6. Comparison of the isotherm parameters for the biosorption of Everdirect orange-3GL dye onto rice husk.

Isotherm model	Everdirect orange-3GL			
	Free	CMC immobilized	PVA-alginate immobilized	HCl treated
Freundlich				
K_F	6.41	1.51	1.28	13.42
n	3.37	1.77	3.26	5.53
R^2	0.942	0.946	0.823	0.942
Temkin				
A (l/g)	0.949	0.300	1.303	15.69
B	5.40	5.02	1.236	4.12
R^2	0.951	0.927	0.985	0.964

The linear form of Temkin isotherm can be written as

$$q_e = B\ln A + B\ln C_e \qquad (7)$$

Where, $B = RT/b$, T is the absolute temperature in Kelvin and R is the universal gas constant (8.314J mol^{-1} K^{-1}). A is the equilibrium binding constant and B is corresponding to the heat of sorption. The results of the isotherm parameters/constants are displayed in Tables 6 and 7, respectively. The correlation coefficients for both direct dyes with free, CMC immobilized, PVA-alginate immobilized and HCl treated biomass were high and showed good linearity. So, it can be said that the experimental data of all dyes was also better fit to Temkin isotherm model.

Biosorption kinetic models

The rate of biosorption process depends on the physical

Table 7. Comparison of the isotherm parameters for the biosorption of Direct blue-67 dye onto rice husk.

Isotherm model	Direct blue-67			
	Free	CMC immobilized	PVA-alginate immobilized	HCl treated
Freundlich				
K_F	2.09	1.035	0.148	5.213
n	1.69	1.465	1.359	2.42
R^2	0.952	0.959	0.998	0.966
Temkin				
A (l/g)	0.208	0.216	0.375	0.639
B	10.11	6.134	0.678	8.087
R^2	0.952	0.863	0.959	0.967

and chemical properties of the biosorbent material and the mass transfer mechanism. Various kinetic models have been suggested for explaining the order of reaction. The kinetics of direct dyes onto rice husk was analyzed using pseudo-first order (Lagergren, 1898), pseudo-second-order (Blanchard et al., 1984) and Elovich (Chien and Clayton, 1980) kinetic models. The applicability of these kinetic models was determined by measuring the correlation coefficients (R^2). The higher the value of R^2, the higher the applicability of the model to the data.

Pseudo-first-order kinetic model

Pseudo-first-order kinetic model is based on the fact that, the change in dye concentration with respect to time is proportional to power one. The differential equation is described as follows:

$$dq_t/dt = k_1(q_e - q_t) \qquad (8)$$

Where, q_e and q_t are the biosorption capacity (mg/g) at equilibrium and time t, respectively, k_1 is the rate constant (L min^{-1}) of pseudo-first order kinetic model.
After integrating the just stated equation and applying boundary conditions t = 0-t and q_t − 0-q_t, the equation becomes:

$$log (q_e/q_e - q_t) = k_1/2.303.t \qquad (9)$$

By rearranging the mentioned equation, the following linear form is obtained

$$log (q_e - q_t) = log (q_e) - k_1/2.303.t \qquad (10)$$

The values of rate constant k_1, q_e calculated, q_e experimental and R^2 of Everdirect Orange-3GL and Direct Blue-67 dyes are presented in Tables 8 and 9, respectively. These tables showed that, the q_e calculated is not equal to q_e experimental and the values of R^2 values of all dyes

with free, CMC immobilized, PVA-alginate and HCl treated biomass are not satisfactory. Mostly, the first order kinetic model is not fitted good for whole data range of contact time and can be apply for preliminary stage of biosorption mechanism (Aksu and Donmez, 2003). This suggested that, the biosorption of both direct dyes is not likely to follow the first order kinetic model. Demir et al. (2008) showed that, the biosorption of MB onto L. cylindrical fibers did not follow the first order kinetics.

Pseudo-second-order kinetic model

Pseudo-second order kinetic model is also based upon the biosorption capacity of the biosorbent material. The biosorption mechanism over a complete range of the contact time is explained by the pseudo-second order kinetic model. The different equation is shown further as:

$$dq_t/dt = k_2(q_e - q_t)^2 \qquad (11)$$

Where, k^2 (g/mg min) is the second order rate constant of biosorption process.
By integrating and applying boundary conditions t = 0-t and q_t − 0-q_t, the stated equation can be written in linear form as follows:

$$(t/q_t) = 1/k_2 q_e^2 + 1/q_e. (t) \qquad (12)$$

The second order parameters, k_2, q_e calculated, q_e experimental and R^2 of Everdirect Orange-3GL and Direct Blue-67 dyes are shown in Tables 8 and 9, respectively. The values of q_e calculated and q_e experimental for all dyes are quite the same. The correlation coefficients (for free, immobilized and HCl-treated biomass) for direct dyes are also very high which showed that the pseudo-second-order kinetic model fit well to kinetic data. The results predicted that the effectiveness, suitability and applicability of pseudo-second order-kinetic model was more than that of

Table 8. Comparative study of kinetic parameters for the biosorption of Everdirect orange-3GL dye onto rice husk.

Kinetic model	Everdirect orange-3GL			
	Free	CMC immobilized	PVA-alginate immobilized	HCl treated
Pseudo-first order				
$K1(L\ min^{-1})$	13.13×10^3	11.97×10^3	5.77×10^3	15.89×10^3
q_e experimental (mg/g)	19.92	9.29	1.805	25.697
q_e calculated(mg/g)	2.29	1.89	1.0567	2.716
R^2	0.925	0.854	0.5552	0.890
Pseudo-second order				
$K_2(g/mg\ min)10^4$	0.00628	0.00762	0.0129	0.00397
q_e calculated (mg/g)	20.408	9.615	1.852	26.67
R^2	0.999	0.999	0.989	0.999
Elovich				
$\alpha(mgg^{-1}min^{-1})$	15.64×10^2	50.12×10^2	28.25×10^2	30.08×10
$\beta(gmg^{-1})$	0.353	0.712	2.638	0.253
R^2	0.893	0.953	0.969	0.929

Table 9. Comparative study of kinetic parameters for the biosorption of Direct blue-67 dye onto rice husk.

Kinetic model	Direct Blue-67			
	Free	CMC immobilized	PVA-alginate immobilized	HCl treated
Pseudo-first order				
$K1(L\ min^{-1})$	9.21×10^3	10.61×10^3	11.976×10^3	18.424×10^3
q_e experimental (mg/g)	16.27	7.25	0.62	19.85
q_e calculated(mg/g)	1.94	1.72	1.48	2.447
R^2	0.924	0.734	0.598	0.898
Pseudo-second order				
$K_2(g/mg\ min)10^4$	0.0089	0.0083	0.078	0.0065
q_e calculated (mg/g)	16.37	7.496	0.634	20.449
R^2	0.999	0.998	0.998	0.999
Elovich				
$\alpha(mgg^{-1}min^{-1})$	33.92×10^9	29.05×10	60.76×10^3	79.56×10
$\beta(gmg^{-1})$	0.711	0.980	0.029	0.420
R^2	0.987	0.969	0.1003	0.985

pseudo-first order kinetic model. The results also suggested that, chemisorption type interaction was developed between direct dyes and rice milling waste biosorbent material. Ozacar and Sengil (2003) suggested that the removal of reactive dyes onto calcinated alunite obeyed the second order kinetic model. Ncibi et al. (2009) reported that, the removal of textile metal-complexed dye by *Posidonia oceanica* (L) leaf sheaths and uptake of Congo red from aqueous solution by calcium rich fly ash followed pseudo-second order kinetics.

Elovich kinetic model

Elovich kinetic model can also be used to explain the biosorption process. The equation is written as follows

$$dq_t/d_t = \alpha\ exp\ (-\beta q_t) \qquad (13)$$

Where, α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is the de-sorption constant (g mg^{-1}). For simplification, it is assumed that, $\alpha\ \beta \gg t$. After applying the boundary conditions q = 0 at t = 0 and $q_t = q_t$ at t =t. The stated

Table 10. Thermodynamic parameters for the biosorption of Everdirect orange-3GL dye onto rice husk.

Temperature (°C)	Everdirect orange-3GL											
	Free			CMC immobilized			PVA-alginate immobilized			HCl treated		
	ΔG°	ΔH°	ΔS°	ΔG°	ΔH°	ΔS°	ΔG°	ΔH°	ΔS°	ΔG°	ΔH°	ΔS°
30	1.23	13.31	39.28	1.67	9.95	27.13	5.80	19.76	54.81	-0.38	47.30	153.59
35	1.10											
40	1.05			1.58			2.42			-.0310		
45	0.94											
50	0.71			1.043			2.101			-0.811		
55	0.54											
60	0.37			0.8356			1.401			-3.802		
65	-0.25											
70	-0.26			-0.71			-1.005			-5.532		

*$\Delta G° = $ kJ mol^{-1}; $\Delta H° = $ kJ mol^{-1}; $\Delta S° = $ J mol^{-1} K^{-1}.

equation can be written in the following form:

$$q_t = 1/\beta \ln(\alpha \beta) + 1/\beta \ln(t) \tag{14}$$

The values of α, β and correlation coefficient R^2 for Everdirect Orange-3GL and Direct Blue-67 are given in Tables 8 and 9, respectively. The values of R^2 of both dyes with free, immobilized and HCl-treated biosorbent were found to be good. The experimental data showed the good fitness to Elovich kinetic model. The applicability of both pseudo-second order and Elovich kinetic model to experimental data showed the chemisorption attraction between direct dyes and rice husk biosorbent.

Thermodynamic model of biosorption

Various thermodynamic parameters including standard Gibbs free energy change ($\Delta G°$), standard enthalpy change ($\Delta H°$) and standard entropy change ($\Delta S°$) were calculated from the temperature data obtained from the biosorption of Everdirect Orange-3GL and Direct Blue-67 onto rice husk at different temperatures (303 to 343 K). The following equation is applied to calculate thermodynamic parameters.

$$\Delta G° = - RT \ln K_a \tag{15}$$

Where, $K_a = (q/C_e)$; R is the gas constant (8.314 J/molK) and T is the absolute temperature (K).
According to Van't Hoff equation:

$$\Delta G° = \Delta H° - T\Delta S° \tag{16}$$

$$\log(q/C_e) = -\Delta G°/2.303RT = -\Delta H°/2.303RT + \Delta S°/2.303RT \tag{17}$$

The values of $\Delta G°$ and $\Delta H°$ for both dyes were determined from the slope and intercept of Van't Hoff graph.

The values of different thermodynamic parameters of both dyes are described in Tables 10 and 11, respectively. The negative value of $\Delta G°$ reflects the spontaneity and feasibility of biosorption of dyes on the biosorbent, whereas the positive $\Delta G°$ values shows that the process is not spontaneous at lower temperature. Results showed that the biosorption of both direct dyes were spontaneous at high temperature. The positive value of $\Delta H°$ indicated that the biosorption of Everdirect Orange-3GL and Direct Blue-67 on the rice husk was endothermic in nature. The biosorption capacity increased with increase in temperature. This might be due to increase in diffusion of direct dyes into the pores of the biosorbent surface and formation of new binding sites at higher temperature (Yahya et al., 2008). The process was endothermic in nature. The positive value of entropy ($\Delta S°$) shows the increase in randomness at the solid/liquid interface and reflects a good affinity of biomass towards both direct dyes (Tewari et al., 2005). Namasivayam and Yamuna (1995) described the removal of Direct Red 12B by biogas residual slurry as endothermic process. Namasivayam et al. (1996) reported that, the biosorption of dyes on orange peel was spontaneous in nature at the studied temperature. Bayramoĝlu and Arica (2007) studied the temperature effect on the removal of direct dyes by *Trametes versicolor* biosorbent.

Conclusions

The following conclusions were drawn from the present investigations:

1. The results described that various physical and chemical modifications/treatments showed different effect on the biosorption capacity of rice husk.
2. Acidic pH, high dye concentration and high temperature favored the biosorption of direct dyes.
3. HCl treated biomass took less time to reach the

Table 11. Thermodynamic parameters for the biosorption of Direct blue-67 dye onto rice husk.

Temperature (℃)	Free			CMC immobilized			PVA-alginate immobilized			HCl treated		
	ΔG°	ΔH°	ΔS°	ΔG°	ΔH°	ΔS°	ΔG°	ΔH°	ΔS°	ΔG°	ΔH°	ΔS°
30	0.82	40.64	130.1	1.98	11.21	31.07	6.09	23.03	54.99	-0.64	22.91	78.05
35	0.36											
40	0.26			1.397			5.84			-1.933		
45	0.28											
50	-2.08			0.835			5.432			-2.037		
55	-2.64											
60	-2.85			0.772			4.98			-2.571		
65	-3.32											
70	-3.74			-0.803			-3.758			-3.622		

*ΔG°= kJ mol^{-1}; ΔH°= kJ mol^{-1}; ΔS°= J mol^{-1} K^{-1}.

equilibrium and immobilized biosorbent took more time when compared with free biomass in the biosorption of two direct dyes.

4. The HCl treatment of the rice husk biomass enhanced the biosorption capacity of Everdirect Orange-3GL and Direct Blue-67 dyes, whereas PVA-alginate immobilization reduced the amount of dyes sorbed to a great extent when compared with free biomass for Everdirect Orange-3GL and Direct Blue-67 dyes, respectively.

5. Experimental data obtained from the biosorption of Everdirect Orange-3GL dye onto free, immobilized and treated biomass was best fitted to Langmuir type 1, 2 and Temkin isotherms, while for Direct Blue-67 dye, Langmuir type 2, Freundlich and Temkin isotherms showed good fitness.

6. The biosorption of both direct dyes followed the pseudo-second-order and Elovich kinetic models.

7. Thermodynamic studies presented that the process was feasible and spontaneous at high temperatures and endothermic in nature. The study showed that, rice husk can be used successfully to clean the environment and can be applied practically in industries.

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