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Biosorption of Direct Red-31 and Direct Orange-26 dyes by rice husk: Application of factorial design analysis

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ABSTRACT

The present work describes the biosorption potential of low cost and easily available rice husk for the adsorptive removal of Direct Red-31 and Direct Orange-26 textile dyes. In the present investigation a 5^3 full factorial design analysis experiment was employed to optimize the process parameters for enhanced adsorptive removal of Direct Red-31 and Direct Orange-26 textile dyes from aqueous solution. Factorial experiments with three factors initial dye concentration, biosorbent dose and pH at five levels were conducted in duplicate. The biosorbent efficiency for the dyes was determined after 3 h of treatment at 30 °C using suitable size of biosorbent (0.255 mm). Analysis of variance (ANOVA), *F*-test and *p*-values were used to study the main, two ways and three ways interaction effects. The values of regression coefficients ($R^2 = 0.999$) for both dyes confirmed the good fitness of model. A maximum biosorption capacity of 57.88 and 36.14 mg/g was observed at pH 2 and 3 for Direct Red-31 and Direct Orange-26, respectively, with 125 mg/L dyes concentration. The most significant variable was found to be dyes initial concentration. Moreover, the decolorization of both direct dyes was also affected by salts, heavy metal ions and surfactants.

Keywords: Factorial analysis; Direct dyes; Rice husk; Process optimization; Biosorption

1. Introduction

Textile industry is one of the important industries in Pakistan and uses different dyes to color the final products according to the demand of the consumers. Effluents from the textile industry are highly colored and their discharge into water channels makes water unfit for domestic, agricultural and industrial purposes (O'Mahony et al., 2002). Besides dyes, such effluents also contain a number of other contaminants such as alkalis, acids, electrolytes, heavy metal ions, dissolved and other suspended solids etc. These dyes containing effluents are toxic and even carcinogenic and thus posses a serous threat to aquatic life (Mohan et al., 2008; Ozer et al., 2005; Safa and Bhatti, 2010). The light penetration and photosynthetic activities of aqueous plants decrease due to color in water (Robinson et al., 2002; Kose, 2008). Direct dyes are water soluble molecules which contain ionic groups (mostly sulfonic acid or amino groups). These dyes are mostly resistant to biodegradation and therefore not removed by conventional techniques. Moreover, these dyes cause allergy, skin irritation, cancer and mutagenic diseases to living organisms (Anouzla et al., 2009).

The treatment of dyes containing effluents is one of the major environmental concerns due to the difficulties faced during conventional treatment methods. Various physical, chemical and biological methods, like adsorption, coagulation, precipitation, solvent extraction, membrane filtration techniques, chemical oxidation etc. have been used for the treatment of dye-containing effluents (Robinson et al., 2002; Gong et al., 2005), but these techniques are costly. Currently the focus of researchers is to exploit the use of waste biomasses and low cost materials as potential adsorbents for the removal of heavy metals and organic pollutants. Biosorption has been proved to be effective to treat dye effluents offering advantages over conventional techniques (Gong et al., 2005; Ponnusami et al., 2007).

Some low cost biosorbents like rice hulls, activated carbon from waste rubber tire activated rice husk, corn cobs, wheat husk are used to remove dyes from aqueous solutions (Gupta et al., 2006, 2007; Gupta and Suhas, 2009).

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Moreover, bottom ash and de-oiled soya have been also used to remove basic fuchsin (Gupta et al., 2008; Ali and Gupta, 2007). Rice is one of the important crops grown in Pakistan. Milling of rice crop produces rice husk as agriculture waste material (Kumar and Bandyopadhyay, 2006). It consists of silica, cellulose, hemicellulose, lignin etc. and is available in excess. The optimization of different factors is done by using 5^3 full factorial designs. Experimental design is an excellent tool for study the individual and interaction effects of all parameters simultaneously. Initial dye concentration, pH and biosorbent dose are important parameters in biosorption study. Thus in the present study the biosorption potential of low cost rice husk for direct dyes was investigated by varying these factors at five levels. Interactions between these factors were also studied and optimization was carried.

2. Materials and methods

2.1. *Preparation of biosorbent*

Fresh biomass of rice (*Oryza sativa*) husk was purchased 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 for 8 h, then for 24 h at 60 °C in an oven. The biomass 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, 0.500–0.710 and 0.710–1.000 mm. The sieved biomass was stored in plastic bottles for further use.

2.2. *Preparation of aqueous dye solutions*

Two direct textile dyes, Direct Red-31 and Direct Orange-26 (gifted by Sandal Dye Stuff Industry, Faisalabad, Pakistan) were used without further purification. Stock solutions of two dyes were made by dissolving 0.1 g of each dye in 1000 mL of double distilled water. By diluting the standard solutions of two dyes, various concentrations (25–300 mg/L) were made. Standard curves were developed through the measurement of the dye solution absorbance by UV/Visible Spectrophotometer (Hitachi U-2001).

2.3. *Batch biosorption*

The effect of important parameters such as pH, biosorbent dose and initial dye concentration on the biosorption of Direct Red-31 and Direct Orange-26 was studied at 30 °C for 3 h. Duplicate 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. To study the effect of pH, various pH's (1–8 for Direct Red-31 and 3–8 for Direct Orange-26) were adjusted using 0.1 M HCl and NaOH solutions. After certain time, the samples were taken out and centrifugation was performed at 2000 rpm for 20 min. The aliquots were used for the residual concentration of each dye.

The amount of dye adsorbed per unit mass was calculated using following equation:

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

Table 1 – Levels of factors for Direct Red-31.

	Levels				
Factors	1	2	3	4	5
Dye conc. (mg/L)	25	50	75	100	125
Biosorbent dose (g/L)	0.06	0.07	0.08	0.09	0.1
pH	2	3	4	5	6

Table 2 – Levels of factors for Direct Orange-26.

	Levels				
Factors	1	2	3	4	5
Dye conc. (mg/L)	25	50	75	100	125
Biosorbent dose (g/L)	0.06	0.07	0.08	0.09	0.1
pH	3	4	5	6	7

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

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

All the experiments were conducted in duplicate and results are reported as mean value.

2.4. *Statistical factorial analysis*

In this work, initial dye concentration, biosorbent dose and pH are taken as independent variables while the other variables like the particle size (0.255 mm mesh size), temperature (30 °C) and shaking speed (100 rpm) were kept constant. Two replicates of 5^3 full factorial design (Montgomery, 1997) having 125 experiments (with one replicate) were studied.

The three factors and the five levels are shown in Tables 1 and 2 for Direct Red-31 and Direct Orange-26, respectively. The coded values of variables with the responses (amount of dye sorbed mg/L) for two direct dyes are illustrated in Table 3.

2.5. *Effect of electrolytes, heavy metal ions and surfactants*

Five different electrolytes NaCl, $CaCl_2{\cdot}2H_2O$, $MgSO_4{\cdot}H_2O$, $NaNO_3$ and NH_4NO_3 were used. Various concentrations (0.01, 0.05, 0.1, 0.2, 0.3 M) of these electrolytes were prepared in dyes solution (50 mg/L). Control was also run having no electrolyte to compare the amount of dye sorbed onto the biosorbent. Various heavy metal ions such as Zn^{2+}, Ni^{2+}, Mn^{2+}, Hg^{2+} and Pb^{+2} in the form of salts were added in the flasks having 50 mg/L of dyes solution. Different concentrations of metal ions (25, 50, 75, 100, 125 mg/L) were used in this research. To study the effect of surfactants on the biosorption of direct dyes onto rice husk, four different surfactants, anionic: SDS (sodiumdodecylsulfate), cationic: CTAB (cetyltrimethyl ammonium bromide), non-ionic: Tween 80 and Triton X-100 were taken.

3. Results and discussion

3.1. *Analysis of variance (ANOVA)*

There are several important problems with the conventional approach of changing one or two variables in a run. It may

Table 3 – Design matrix for Direct Red-31 and Direct Orange-26.

Runs	Dye conc. (mg/L)	Dose (g/L)	pH	Amount of dye sorbed (mg/g)	
	A	B	C	Direct Red-31 Average	Direct Orange-26 Average
1	1	1	1	15.72	12.16
2	1	2	1	14.36	11.04
3	1	3	1	13.13	10.34
4	1	4	1	12.96	9.38
5	1	5	1	11.89	8.96
6	1	1	2	9.35	3.46
7	1	2	2	8.68	3.46
8	1	3	2	7.93	3.44
9	1	4	2	7.41	3.37
10	1	5	2	7.09	3.28
11	1	1	3	4.86	2.66
12	1	2	3	4.53	2.50
13	1	3	3	4.28	2.48
14	1	4	3	4.21	2.43
15	1	5	3	4.15	2.38
16	1	1	4	2.44	1.19
17	1	2	4	2.37	1.16
18	1	3	4	2.33	1.09
19	1	4	4	2.26	1.07
20	1	5	4	2.22	1.04
21	1	1	5	1.95	1.04
22	1	2	5	1.95	1.03
23	1	3	5	1.94	1.07
24	1	4	5	1.94	1.00
25	1	5	5	1.93	0.97
26	2	1	1	33.21	23.80
27	2	2	1	30.27	22.78
28	2	3	1	28.17	20.76
29	2	4	1	25.92	20.15
30	2	5	1	23.72	19.48
31	2	1	2	23.04	7.99
32	2	2	2	21.41	7.74
33	2	3	2	19.45	7.60
34	2	4	2	18.14	7.41
35	2	5	2	16.44	7.09
36	2	1	3	8.98	4.63
37	2	2	3	8.88	4.47
38	2	3	3	8.65	4.17
39	2	4	3	8.36	4.09
40	2	5	3	8.27	3.93
41	2	1	4	6.15	2.66
42	2	2	4	6.04	2.58
43	2	3	4	5.59	2.48
44	2	4	4	5.44	2.32
45	2	5	4	5.39	2.26
46	2	1	5	4.62	2.32
47	2	2	5	4.46	2.28
48	2	3	5	4.17	2.22
49	2	4	5	3.91	2.16
50	2	5	5	3.69	2.02
51	3	1	1	39.53	28.96
52	3	2	1	37.41	27.90
53	3	3	1	34.99	27.36
54	3	4	1	32.56	26.33
55	3	5	1	31.50	25.29
56	3	1	2	30.71	10.08
57	3	2	2	28.91	9.58
58	3	3	2	26.45	9.38
59	3	4	2	25.09	8.92
60	3	5	2	22.65	8.79
61	3	1	3	12.19	6.66
62	3	2	3	11.56	6.45
63	3	3	3	11.27	6.08
64	3	4	3	10.97	5.75
65	3	5	3	10.37	5.63
66	3	1	4	7.75	3.65

Table 3 (*Continued*)

Runs	Dye conc. (mg/L)	Dose (g/L)	pH	Amount of dye sorbed (mg/g)	
	A	B	C	Direct Red-31 Average	Direct Orange-26 Average
67	3	2	4	7.51	3.52
68	3	3	4	7.41	3.21
69	3	4	4	7.06	3.05
70	3	5	4	6.67	2.81
71	3	1	5	5.44	3.01
72	3	2	5	5.38	2.88
73	3	3	5	5.28	2.74
74	3	4	5	5.05	2.70
75	3	5	5	4.76	2.50
76	4	1	1	49.82	35.21
77	4	2	1	45.04	34.35
78	4	3	1	43.67	32.75
79	4	4	1	41.66	31.81
80	4	5	1	39.94	31.13
81	4	1	2	33.49	12.63
82	4	2	2	31.55	12.21
83	4	3	2	29.99	11.90
84	4	4	2	28.52	11.54
85	4	5	2	26.27	10.91
86	4	1	3	14.62	7.76
87	4	2	3	13.44	7.55
88	4	3	3	12.91	7.38
89	4	4	3	11.95	7.07
90	4	5	3	11.18	6.67
91	4	1	4	8.46	4.40
92	4	2	4	8.32	4.27
93	4	3	4	8.25	4.08
94	4	4	4	7.93	3.82
95	4	5	4	7.81	3.54
96	4	1	5	6.27	3.71
97	4	2	5	6.29	3.67
98	4	3	5	6.03	3.39
99	4	4	5	5.64	3.09
100	4	5	5	5.54	2.82
101	5	1	1	57.87	36.14
102	5	2	1	53.86	35.64
103	5	3	1	51.29	35.27
104	5	4	1	49.23	34.59
105	5	5	1	47.64	34.33
106	5	1	2	40.41	14.59
107	5	2	2	37.73	14.19
108	5	3	2	35.50	13.55
109	5	4	2	32.98	13.20
110	5	5	2	30.60	12.51
111	5	1	3	16.80	8.69
112	5	2	3	15.67	8.44
113	5	3	3	15.27	8.08
114	5	4	3	14.20	7.64
115	5	5	3	13.35	7.09
116	5	1	4	9.76	4.98
117	5	2	4	9.43	4.87
118	5	3	4	9.32	4.69
119	5	4	4	9.15	4.40
120	5	5	4	8.98	4.10
121	5	1	5	7.57	4.17
122	5	2	5	7.35	4.07
123	5	3	5	7.01	3.91
124	5	4	5	6.63	3.59
125	5	5	5	6.18	3.27

take several rounds of experiments to find the optimum point. In cases where variables must be changed in large steps the optimum may not be found at all. Factorial design consists of different treatments of all possible combinations of several levels of factors. It reveals the effect of interaction of process variables and improves process optimization. Moreover, the relative importance of all the factors can be evaluated simultaneously with less number of treatments (Carmona et al., 2005; Ravikumar et al., 2007) ANOVA partitions the total covariation of a bivariate sample, measured by the sum of the products of the deviations of variables from their means into component parts associated with specific source of variation (Kim et al., 2003).

The ANOVA results for Direct Red-31 and Direct Orange-26 are shown in Tables 4 and 5, respectively. In Tables 4 and 5 the sum of the squares used to estimate factors affect and Fisher's F-ratios and p-values are also shown. ANOVA of Direct Red-31 and Direct Orange-26 textile dyes showed that the main effects such as initial dye concentration, biosorbent dose, pH and two-ways and three ways interactions were highly significant ($p < 0.05$) and model was applicable very well. The p-value is very important to determine which interaction is significant or not. Smaller the p value, highly significant the factor (Ravikumar et al., 2007). The correlation coefficients (0.999) for Direct Red-31 and Direct Orange-26 were very high showing good fitness of statistical model.

Biosorption of Reactive Red RGB by acid treated rice husk from water solution was investigated by Ponnusami et al. (2007) using factorial design analysis. The effect of four factors pH, temperature, biosorbent dose and initial dye concentration at two levels were exploited. The results were analyzed statistically using the Student's test, analysis of variance, F-test and lack of fit to define most important process variables affecting the dye removal. pH was found to be the most significant variable.

Anouzla et al. (2009) used a 2^3 factorial experimental design to observe disperse dye removal. The results indicated that all the main factors such as pH, dose and dye concentration were significant and some two way interactions were non-significant. At pH 4.25, coagulant dose 1 mL and dye concentration 150 mg/L, the removal efficiency was found to be 99%.

Kose (2008) also used factorial design analysis for the biosorption of Remazol Black B using agricultural residue anion exchanger. The ANOVA showed that most significant factor was dye concentration and least significant interaction was pH: temperature. The removal of dye was enhanced with increase in dye concentration and temperature and decreased with increase in pH. Similarly the removal of distillery spent wash by fly ash was examined by Prasad and Srivastava (2009) using 2^3 factorial designs. The maximum removal (93%) was occurred at 5% dilution, 10 g biosorbent dose and 293 K temperature.

3.2. Normal probability

The normal probability plot is a graphical representation for determining either the data is distributed normally or not (Pokhrel and Viraraghvan, 2006). The residual values explain the difference between predicted values (model) and the observed values (experimental). The data is distributed normally if all the points fall close to the straight line. The normal probability plot of residual values for Direct Red-31 and Direct Orange-26 are shown in Figs. 1 and 2, respectively. It could be seen that the experimental points were reasonably aligned suggesting normal distribution. Plots of percentage normal probability versus residual indicated that all the points were found to fall in the range of +8.46 to −8.46 and +2.73 to −2.73 for Direct Red-31 and Direct Orange-26, respectively. Ponnusami et al. (2007) used acid-treated rice husk to remove reactive dye. He used four factors, pH, temperature, dye concentration and biosorbent dose with two levels. The biosorption percentage increased with increase in temperature, biosorbent dose and decreased with increase in pH and dye concentration. The normal probability plot showed that all the points were aligned showing normal distribution.

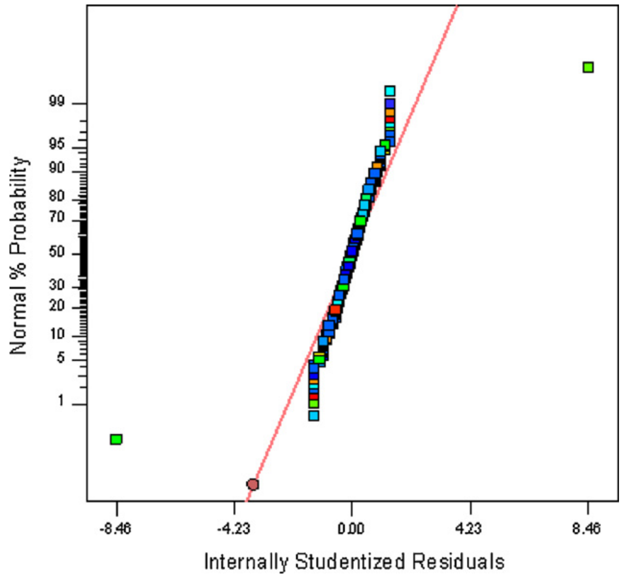

Fig. 1 – Normal probability plot of residuals for Direct Red-31 dye.

3.3. Effect of pH, biosorbent dose and dyes concentration

Dye biosorption is a pH dependent process. The pH of the solution influences the properties of biomass materials, affects the adsorption mechanisms and dissociation of the dye molecules. The results showed that the maximum biosorption of Direct Red-31 and Direct Orange-26 was observed at low pH 2.0 and 3.0, respectively (Figs. 3 and 4). At lower pH, the biosorbent surface turned out to be positively charged and electrostatic attraction develops between positively charged biomass and negatively charged anionic dyes (EI-Nemr et al., 2009). However, at basic pH, adsorption also decreases due

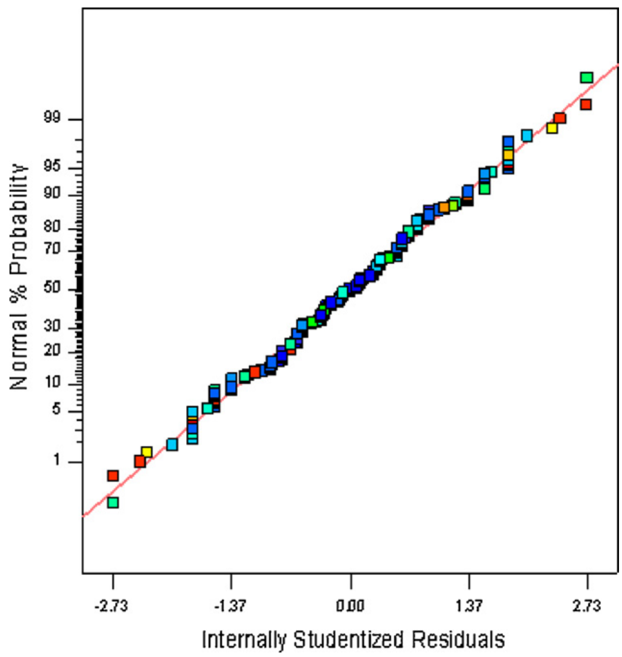

Fig. 2 – Normal probability plot of residuals for Direct Orange-26 dye.

Table 4 – ANOVA of biosorption of Direct Red-31: effect of dye concentration (A), biosorbent dose (B) and pH (C).

Source	Sum of squares	df	Mean square	*F* value	*p*-Value Prob > *F*
Model	47,950.45	124	386.70	6503.12	<0.0001 significant
A – Conc	9215.07	4	2303.77	38,742.66	<0.0001
B – Dose	425.93	4	106.48	1790.71	<0.0001
C – pH	32,858.31	4	8214.58	1381	<0.0001
AB	50.25	16	3.14	52.81	<0.0001
AC	5038.21	16	314.89	5295.51	<0.0001
BC	318.58	16	19.91	334.85	<0.0001
ABC	44.11	64	0.69	11.59	<0.0001
Pure error	7.43	125	0.059		
Cor total	47,957.88	249			

$R^2 = 0.999$, Adj $R^2 = 0.999$, Pred $R^2 = 0.999$.

Table 5 – ANOVA of biosorption of Direct Orange-26: effect of dye concentration (A), biosorbent dose (B) and pH (C).

Source	Sum of squares	df	Mean square	*F* value	*p*-Value Prob > *F*
Model	22,913.68	124	184.79	5689.28	<0.0001 significant
A – Conc	2775.78	4	693.95	21,365.32	<0.0001
B – Dose	58.46	4	14.62	450.00	<0.0001
C – pH	17,855.22	4	4463.81	1374	<0.0001
AB	3.64	16	0.23	7.01	<0.0001
AC	2174.32	16	135.90	4183.97	<0.0001
BC	37.15	16	2.32	71.48	<0.0001
ABC	9.10	64	0.14	4.38	<0.0001
Pure error	4.06	125	0.032		
Cor total	22,917.74	249			

$R^2 = 0.999$, Adj $R^2 = 0.999$, Pred $R^2 = 0.999$.

to presence of hydroxyl ions which shows competition with dye anions for binding sites (Arami et al., 2006; Khaled et al., 2009). Ardejani et al. (2008) examined 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. Maximum uptake of dye was observed at pH 2.0.

Adsorption efficiency decreases with increase in the biosorbent dose. The dye removal capacity decreased due to the unsaturation of the binding sites at large amount of biosorbent dose. Bulut et al. (2007) reported that the sorption of Direct Blue 71 by wheat shells from aqueous solution occurred at low biosorbent doses. Similar behavior regarding the biosorption of anionic dye on peanut hull was observed by Gong et al. (2005).

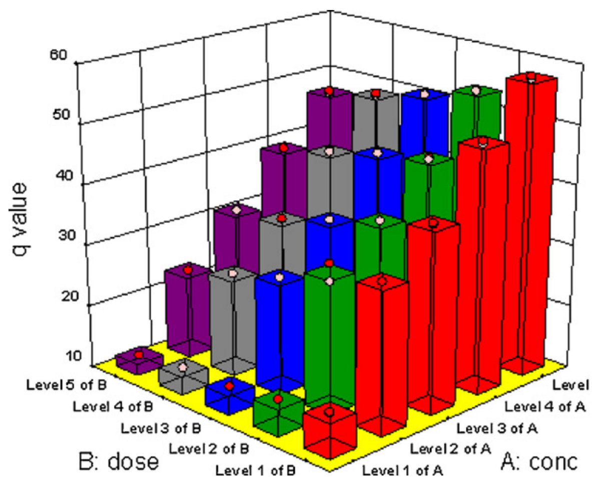

Fig. 3 – three way interactions between pH, biosorbent dose and initial dye concentration of Direct Red-31.

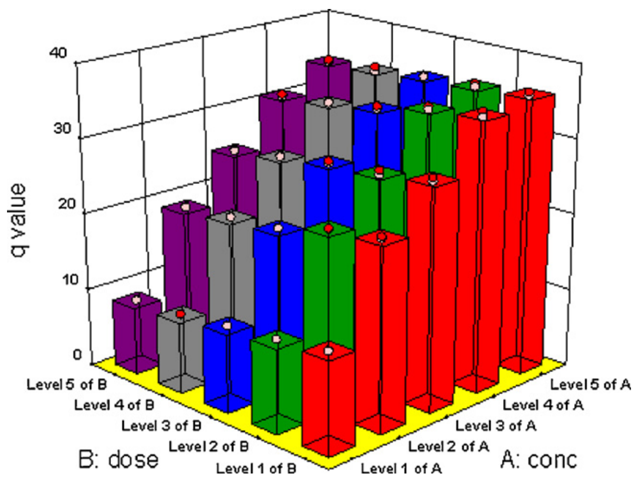

Fig. 4 – Three way interactions between pH, biosorbent dose and initial dye concentration of Direct Orange-26.

Increase in initial dyes concentration from 25 to 125 mg/g, the amount of dye sorbed on the biomass surface also increased. Bulut et al. (2007) also reported 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 stay unsaturated during the biosorption mechanism. Khaled et al. (2009) investigated the effect of initial concentration of Direct N Blue-106 on the biosorption of orange peel carbon. 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

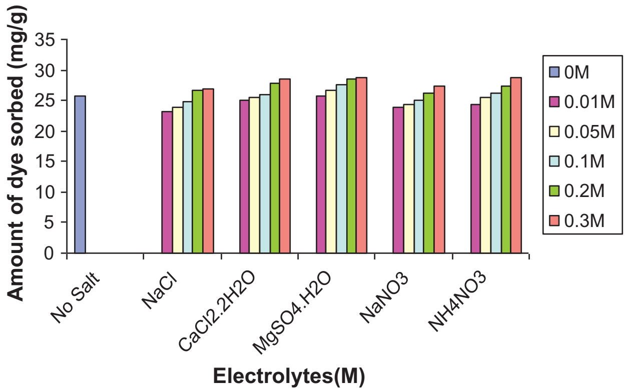

Fig. 5 – Effect of electrolytes concentrations on the biosorption of Direct Red-31 by rice husk.

150 mg/L at biosorbent doses 2, 4 and 6 g/L, respectively. Similarly the biosorption of Acid Blue 225 and Acid Blue 062 on *Paenibacillus macerans* increased with an increase dyes initial concentrations suggesting that available sites on the biosorbent are the limiting factor for dye removal (Colak et al., 2009). Figs. 3 and 4 showing interaction plots suggest strong interactions between initial dye concentration, biosorbent dose and pH (three way interaction) for Direct Red-31 and Direct Orange-26. Maximum removal (57.87 mg/g) was observed at initial dye concentration 125 mg/L, biosorbent dose 0.066 g/L and pH 2 for Direct Red-31 and 36.137 mg/g at initial dye concentration 125 mg/L, biosorbent dose 0.06 g/L and pH 3 for Direct Orange-26.

3.4. *Effect of electrolytes on the biosorption of direct dyes*

Industrial water contains various salts/electrolytes which considerably affect the dye biosorption. The effect of ionic strength (0.01–0.3 M) of NaCl, $CaCl_2{\cdot}2H_2O$, $MgSO_4{\cdot}H_2O$, $NaNO_3$ and NH_4NO_3 on the removal of direct dyes was investigated and the results are shown in Figs. 5 and 6. The results show that the amount of dye sorbed and percentage removal of Direct Red-31 and Direct Orange-26 increase with increase in the concentration of salts. This might be due to the fact that presence of these ions produced salting out phenomena and reduced the solubility of direct dyes into water and increased the biosorption onto the biosorbent. Moreover, increase in the ionic concentration increases the electrostatic interactions between the dyes molecules and biosorbent sites which result in an increase in dye removal.

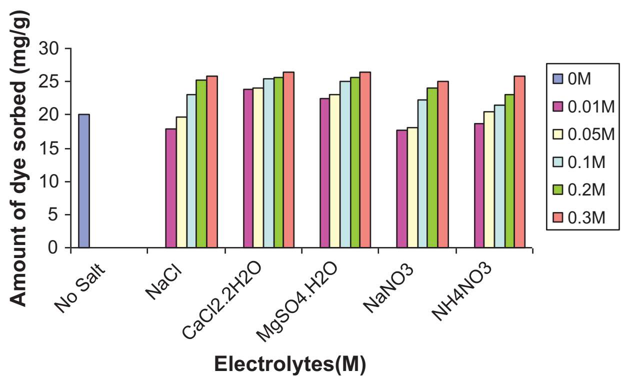

Fig. 6 – Effect of electrolytes concentrations on the biosorption of Direct Orange-26 by rice husk.

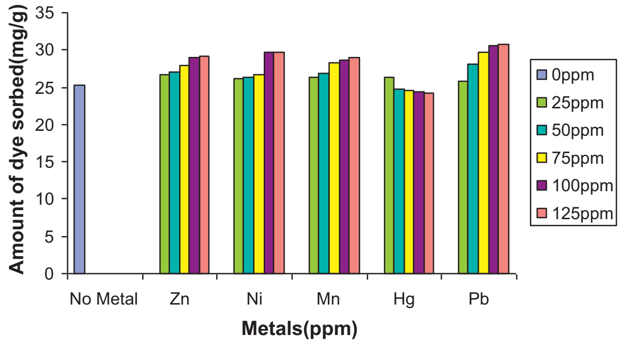

Fig. 7 – Effect of heavy metal ions concentrations on the biosorption of Direct Red-31 by rice husk.

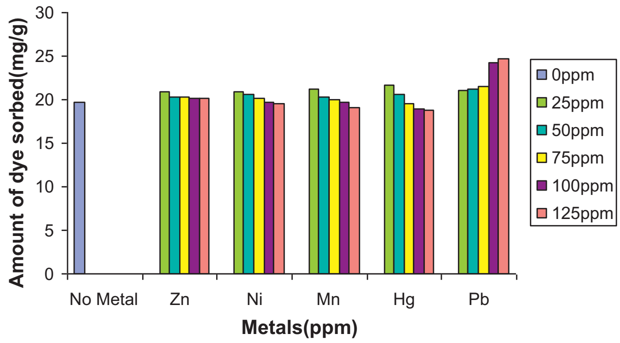

Fig. 8 – Effect of heavy metals concentrations on the biosorption of Direct Orange-26 by rice husk.

Janos et al. (2009) investigated that the biosorption of acidic dye increased with increase in the concentration of salts by using wood shaving biomass. At low concentration of salts, the amount of dye sorbed (mg/g) decreased. This was due to decrease in the electrostatic interactions between dye molecule and biosorbent surface, which ultimately decreases the dye adsorption (Gong et al., 2005; Grabowska and Gryglewicz, 2007).

3.5. *Effect of heavy metal ions on the biosorption of direct dyes*

In this research, the effect heavy metal ions such Zn^{2+}, Ni^{2+}, Mn^{2+}, Hg^{2+} and Pb^{2+} on the removal of Direct Red-31 and Direct Orange-26 was also investigated and the results are depicted in Figs. 7 and 8. The results show that the biosorption capacity decreased in the presence of Hg^{2+} ions and increased in the presence of Zn^{2+}, Ni^{2+}, Mn^{2+} and Pb^{2+} for Direct Red-31. For Direct Orange-26, the amount of dye sorbed increased by adding Pb^{2+} ions in the dye solution and decreased with the addition of Zn^{2+}, Ni^{2+}, Mn^{2+} and Hg^{2+} ions. Influence of Pb^{2+} on the biosorption of both direct dyes was more pronounced. Increase in the biosorption capacity of direct dyes with addition of certain metal ions might be due to complex formation between metal ions and dyes and binding to the surface of the biosorbent (Chen and Yang, 2005; Aksu et al., 2009). Other reason is the addition of metal ions produced the aggregation and flocculation of biomass and increased the biosorption capacity. Pb^{2+} ions caused great aggregation than any other metal (Li-Sheng et al., 2007). Reduction in the dyes removal with certain heavy metals might may be due to competition between H^+ ions and metal cations at low pH (O'Mahony et al., 2002). Another reason of decrease in the biosorption capacity of dyes is due to antagonistic effect of metal ions (Aksu and Isoglu,

Table 6 – Comparison of data reported in the literature and present study.

Biosorbent	Dye	pH	Biosorption capacity (mg/g)	Reference
Dead *Rhizopus arrhizus*	Reactive Orange 16	2	190	Liu et al. (2001)
Corynebacterium glutamicum	Reactive Orange 16	1	187	Liu et al. (2001)
Pristine *P. chrysogenum* biomass	Acid Blue 45	6.5	18	Liu et al. (2001)
Sawdust	Methylene Blue	8	9.78	Batzias and Sidiras (2007)
Rice husk	Direct Red-31	2	25.63	Present study
Rice husk	Direct Orange-26	3	19.96	Present study

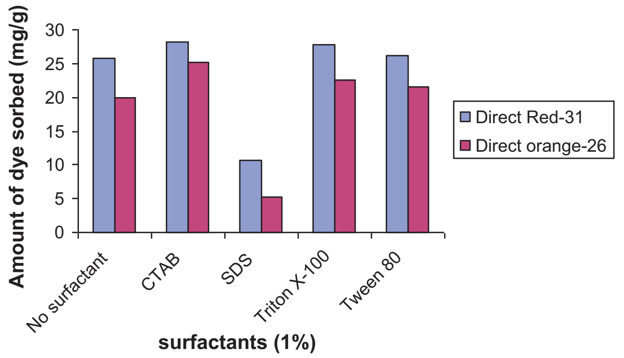

Fig. 9 – Effect of surfactants on the biosorption of Direct Red-31 and Direct Orange-26 dyes by rice husk.

2007). Murugesan et al. (2009) also showed the decrease in the sorption capacity of reactive dye in the presence of metal ions.

3.6. *Effect of surfactants on the biosorption of direct dyes*

Textile industries also discharge surfactants along with dyes into the water streams. The effect of surfactants on the direct dyes removal by rice husk was determined and results are reported in Fig. 9. Cationic surfactant, CTAB (cetyltrimethyl ammonium bromide), enhanced the biosorption of both direct dyes. This might be due to impregnation of cationic surface gives positive charge on the biomass surface and attracted strongly toward the negatively charged direct dyes (Oei et al., 2009). The biosorption capacity of rice husk reduced significantly by adding anionic surfactant, SDS (sodium dodecylsulfate). The reduction of biosorption capacity might be due to repulsive interactions between anionic surfactant and anionic dye molecules. The solubility of anionic dyes is less in SDS micelles than in the aqueous phase. Addition of non-ionic surfactants (Triton X-100, Tween-80) slightly increases the biosorption capacity of direct dyes. This might be due to interaction between the oxonium ions of non-ionic surfactants and sulfonic groups of ionic dyes (Kartal and Akbas, 2005). A comparison of different biosorbents for their dyes adsorption is also given in Table 6.

4. Conclusions

The results of present study clearly show that the rice husk is effective in the removal of Direct Red-31 and Direct Orange-26 textile dyes and can provide an economical and eco-friendly solution of such dyes from the aqueous solutions. The optimization process concluded that the uptake was improved by increase in initial dye concentration and decrease in biosorbent dose and pH. The ANOVA results reveal that the highly significant factor was initial dye concentration for Direct Red-31 and Direct Orange-26. Decolorization of direct dyes was affected by salts, heavy metals and surfactants. The dyes uptake efficiency could be enhanced by increasing the concentration of all salts. Cationic and non-ionic surfactants also increased the amount of dyes adsorbed. This describes that rice husk could be used as an efficient and promising biosorbent to remove the direct dyes from aqueous solution in the presence of salts, heavy metals and surfactants.

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