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Research Article

A DECOLORIZATION STUDY OF CONGO RED DYE FROM AQUEOUS SOLUTION USING FUNGUS IMMOBILIZED BIOMASS

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ABSTRACT

For bioethanol production, enzymes are required which can be obtained after solid state fermentation and submerged fermentation of cellulosic biomass. After enzyme production, huge biomass is generated as a waste which can be used as an adsorbent. In the study, water hyacinth biomass left after enzyme production using solid state fermentation with the help of fungus *Emericella nidulans* was used as biosorbent. Firstly different dyes i.e. methylene blue, congo red, malachite green, reactive orange, reactive blue, reactive red and orange G were screened out. After screening, it was found that congo red was maximum decolorized, followed by malachite green and methylene blue. Percent decolorization was 83.7, 82.1 and 80.2 for congo red, malachite green and methylene blue respectively. Different process parameters were optimized using one factor one time and box behnken design of response surface methodology approach. Temperature 30°C and pH 5 was found to be optimum for congo red decolorization. Optimized parameters were adsorbent dose 0.1g, initial dye concentration 177 ppm and contact time 17h outcomes of the box behnken design.

INTRODUCTION

Dyes used in textile dyeing, paper printing and other industries. Presently, total production of dye is estimated as 7×10^5 to 1×10^6 tons per year. More than 1×10^5 commercial dyes are produced, out of which nearly 70 % are azo dyes. Nearly 66 % of the total dye production is used in the textile industries; where kilogram of dye processing required nearly 100 L of water and 10 to15 % of this dye enter the environment through effluents. Owing to their toxic, mutagenic or carcinogenic properties, the presence of these pollutants in water can cause serious public concerns with regards to human health and highly objectionable on aesthetic grounds, and it disturbs the aquatic ecosystem by interfering with light transmission (Grag *et al*. 2003; Fan *et al*., 2014; Rangabhashiyam *et al*.2014). Congo Red (CR) is the earliest synthetic benzedene based anionic azo dye formed for dying cotton directly. It is used in a number of industrial activities so found commonly in effluents (Sivakumar *et al*., 2014; Vimonses *et al*. 2009). Treatment of this type of effluents is difficult because congo red is resistant to bio and photo-degradation due to its complex aromatic structure, physicochemical, thermal, and optical stability properties (Pielesz 1999; Smaranda *et al*. 2011).

Various physical, chemical, biological, acoustic, radiation, and electrical methods are adopted for dye removal. Of these, the biological method is commonly used because it is cost-competitive and suitable for a variety of dyes. However, it has the disadvantages of large space and longer process times requirements and less flexibility in design and operation (Zvezdelina and Nedyalka 2012; Robinson *et al*. 2011). Thus, more researchers are investing their efforts towards the development methods for the treatment of dye-contaminated waste water. An adsorption-based approach, on account of its simple design and inexpensive nature, can be very effective in treating dye-contaminated waste-water (Peng *et al*., 2012). Adsorption studies have been made using different agro based adsorbents on the removal of textile dyes such as Formosa papaya seed powder (Pavan *et al*., 2014), cow bone (Salh, 2014), mangrove bark (Tan *et al*., 2010), ginger waste (Ahmed and Kumar, 2010), and peanut shells (Abbas *et al*., 2012). In present study, cellulosic waste of water hyacinth immobilized with *Emericella nidulans* left after enzyme production in biofuel generation was used as biosorbent for congo red decolorization.

MATERIALS AND METHODS

Biosorbent preparation

Fungus immobilized microwave alkali treated water hyacinth biomass was used for decolorization. *Emericella nidulans* grown on microwave alkali treated water hyacinth biomass for

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solid state fermentation for cellulolytic enzyme production (Singh *et al*., 2011) was used as adsorbent. The spent immobilized biomass left after enzyme production dried at 50°C and then dried biomass was utilized for dye decolorization.

Dyes screening study

Using the above biosorbent screening of dyes i.e. methylene blue, congo red, malachite green, reactive orange, reactive blue, reactive red and orange G was performed to find out maximum decolorized dye. For this experiments were performed at 150 ml flask using dye's simulated waste water of 100 mg/l concentration and 1g of biosorbent at 30°C. Then samples were taken after specific time and centrifuged at 10,000 rpm in triplicates, then analysed spectrophotometrically at λmax 673, 498, 617, 500, 610, 532 and 420 nm respectively (Ghosh and Reddy, 2013, Jia *et al*., 2014, Singh *et al*., 2012, Sun *et al*., 2013, Majumdar *et al*., 2015).

Optimization of congo red deolorization by OFAT and statistical methodology

Optimization of pH and temperature using OFAT (one factor at one time)

Biosorption experiments were carried out in 150 ml flasks by varying pH (2-8) and temperature (25-50° C) for contact period of 24 h with initial dye concentration of 100 ppm. The percentage of removal and adsorption capacity on spent immobilized biomass of water hyacinth was calculated by these equations (Singh *et al*., 2011):

$$\text{Percent removal (\%)} = (C_0\text{-}C_e) \div C_0 \times 100$$

$$\text{Adsorption capacity } \left(\frac{\text{mg}}{\text{g}}\right) q_e = (C_0 - C_e) \times V \div M$$

Where, the initial dye concentration (mg/L) is denoted by C_0 and the residual concentration of the dye (mg/L) is denoted by C_e, the quantity of dye adsorbed on adsorbent (mg/g) denoted by qe, volume (L) of solution by V and the mass of biosorbent (g) by M in the equation.

RSM approach

RSM was used to find out the key effects of different parameters on the biosorption of congo red by use of spent immobilized fungal biomass. Biosorbent biomass doses (A), initial dye Concentration (B) and time (C) was taken as independent parameters. BBD was employed for the experiments design which found fitted according to 2nd order polynomial model and regression coefficients obtained (Nachiyar *et al*., 2012, Prakash *et al*., 2014, Thyagarajan *et al*., 2014 and Arunkumar *et al*., 2014). All independent variables with selected range for congo red dye and Cd removal were given in table 1.

A polynomial quadratic equation fitted for evaluation of each independent variable effects to the response:

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC$$

Table 1 Independent variables with selected experimental range in the box behnken design experiment for congo red removal

Code	Parameters	Low level (-1)	Middle level (0)	High level (+1)
A	Adsorbent dose (g/L)	0.1	0.3	0.5
B	Dye concentration (ppm)	100	150	200
C	Time (h)	1	12.5	24

RESULT AND DISCUSSION

Using fungus immobilized cellulosic waste as a biosorbent screening study was performed to find out the dye which would be maximal decolorized. Results of screening study were presented below in table 2. Seven dyes were screen out and it was found that congo red was maximum decolorized, followed by malachite green and methylene blue. Percent decolorization was 83.7, 82.1 and 80.2 for Congo red, malachite green (Singh *et al*., 2012) and methylene blue respectively. Other then these three were decolorized to a small percentage as shown in table 2. Thus Congo red dye was selected for further optimization study.

Table 2 Screening of various dyes for decolorization using immobilized fungal biomass

Dye	λ max (nm)	% Decolorization
MB (Methylene Blue)	673	80.2
CR (Congo Red)	498	83.7
MG (Malachite Green)	617	82.1
RO (Reactive Orange)	500	1.7
RB (Reactive Blue)	610	5.3
RR (Reactive Red)	532	4.2
OG (Orange G)	420	2.6

Optimization of parameters for removal of congo red dye
Optimization of pH

The biosorption is decidedly reliant on the pH of a solution as it is one of the most important factors influencing the capacity of adsorbent. Since different pH provides variation in the degree of ionization of the adsorbate and surface properties/chemistry of adsorbent (Nandi *et al*., 2009). The medium's pH affects the chemistry of the chemicals present in dye waste, activity of different functional groups i.e. carboxylate, phosphate and amino groups on the surface, as well as the competition of dye molecules for the binding sites (George *et al*., 2012). From the present study, it can be seen that decolorization increased with a rise in pH as shown in Fig. 1. Percent decolorization of congo red was maximum at pH 5. Increasing pH up to 5 increases the percent decolorization after that decrease in the congo red decolorization.

Congo red is an anionic dye with two sulphonate groups which ionize in water and extent of ionization increases with raise solution pH may be a cause of decrease percent decolorization. Literatures have various studies with wide range of optimum pH from acidic to alkaline conditions but highly alkaline conditions are generally not suitable for biosorption (Liao *et al*., 2008). Li *et al*., 2014, worked on cassava residue for removal of congo red from aqueous solution. They found 81.6± 2.4% decolorization at ph 5.5, temperature 30°C and moisture content 60% after 60 days of cultivation. Singhal *et al*., 2016, found that pulp and paper mill effluent biosorption increased with a rise in pH. Adsorption capacity (qe) as well as percent

removal of colour was highest at pH 5. Dawood and Sen (2012) also studied the effect of pH on the adsorption of congo red by pine cone and they found that the maximum adsorption was at pH 3.5.

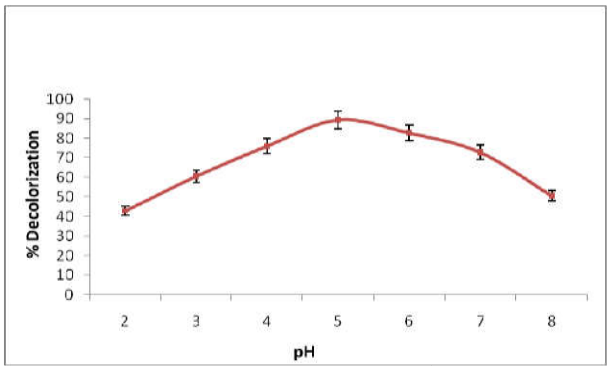


Fig. 1 Effect of pH on percentage removal of CR by *Emericella nidulans* immobilised on water hyacinth

Optimization of Temperature

Effect of biosorption medium temperature is another important physico-chemical process parameter because temperature will change the biosorption capacity of the biosorbent by changing energy-dependent mechanism of microbial biomass (Argun *et al*., 2008). When the amount of biosorption rises with increase in temperature then process is an endothermic. This increase may be because of increasing mobility of the dye molecules and/or an increase in the number of active sites for the biosorption. While the decrease of adsorption capacity with increasing temperature indicates that biosorption is an exothermic process. This decrease may be due to decreasing the adsorptive forces between the dye and the surface active sites of biosorbent thus amount of biosorption decreases (Salleh *et al*., 2011).

The temperature effect on congo red dye decolorization was studied in the range 25–50˚C (Fig. 2). The decolorization increased with increasing temperature from 25 to 30˚C and no significant drop down at 35˚C after that significant decrease in percent decolorization. Which indicates 30-35˚C range was suitable for *Emericella nidulans* immobilized on water hyacinth biomass. The increase in temperature favours dye molecules transport within the pores of the fungal immobilized biomass. In most of the studies suitable temperature was in the range 30–35˚C (Bayramoğlu *et al*., 2006, Arıca and Bayramoğlu 2007), Maheswari and Murugesan (2009), Ponnusamy and Subramaniam (2013), Li *et al*., 2014, Singhal *et al*., 2016).

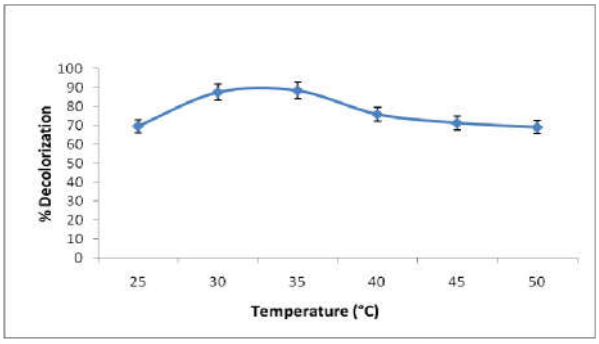


Fig. 2 Effect of temperature on percentage removal of CR by *Emericella nidulans* immobilised on water hyacinth

Optimization of parameters by Box-Behnken design (BBD)

Major factors were standardized by performing Design of Experiment (DOE) provided by Design Expert software version 9. On the basis of various combinations of DOE experiments was performed and reaction was formulated and analysis. The results were tabulated in table 3. Several works were formulated with respect to RSM and different parameters were analyzed (Nachiyar *et al*., 2012, Prakash *et al*., 2014, Thyagarajan *et al*., 2014 and Arunkumar *et al*., 2014). Decolorization varied noticeably with the conditions tested, in the range of 6.39 – 97.03 %. Minimum decolorization was found when adsorbent dose was medium at high level of dye concentration in minimum contact time (run 16). Decolorization value of 97.03 % was observed when adsorbent dose was high and medium level of dye concentration in 24 h contact time (run 1). The experimental results as shown in table 3 suggest that these variables strongly affect the decolorization.

Table 3 Experimental design and results of Box Behnken Design of Response Surface Methodology

Run	A:Adsorbent dose	B:Dye concentration	C:Time	Decolorization	Adsorption capacity	Desorption
	g	ppm	H	%	mg/g	%
1	0.5	150	24	97.03	88	3.01
2	0.3	150	12.5	91.89	153.15	4.97
3	0.3	150	12.5	90.05	145.81	6.27
4	0.5	100	12.5	44	40.32	20.67
5	0.3	150	12.5	82.5	150.31	3.01
6	0.3	100	24	93.05	129.89	3.01
7	0.5	200	12.5	20	20.31	23.46
8	0.3	200	24	92.7	129.78	6.97
9	0.3	150	12.5	94.78	157.72	7.58
10	0.1	200	12.5	22.09	171.89	29.05
11	0.1	100	12.5	20.8	199.91	38.5
12	0.5	150	1	14.87	25.04	8.74
13	0.1	150	24	79.01	215.05	5.83
14	0.3	100	1	19.76	75.2	10.53
15	0.3	150	12.5	89	140.75	8.58
16	0.3	200	1	6.39	82.91	9.8
17	0.1	150	1	18.67	153.35	16.83

The results obtained were subjected to analysis of variance with the regression model given as:

$$Y = 89.64 + 4.42\ A - 4.55\ B + 37.76\ C - 6.32\ AB + 5.45\ AC + 3.26\ BC - 31.75\ A^2 - 31.17\ B^2 - 5.50\ C^2$$

Where, Y is the response value (% decolorization) and A, B and C are the coded for adsorbent dose, initial dye concentration and contact time respectively. The adequacy of the model was analyzed using analysis of variance (ANOVA) presented in table 4.

The value of multiple correlation coefficients (R^2) was 0.993 indicating a better correlation between the observed and predicted values. A lower value for the coefficient of variation suggests higher reliability of experiment and in this case the obtained CV value of 7.66% demonstrated in table 5, a greater reliability of the trials. The p values, greater than 0.05, for all the responses indicate that lack of fit for the model was non-significant. No abnormality was observed from the diagnosis of residuals. Thus, it can be concluded that the model was statistically sound.

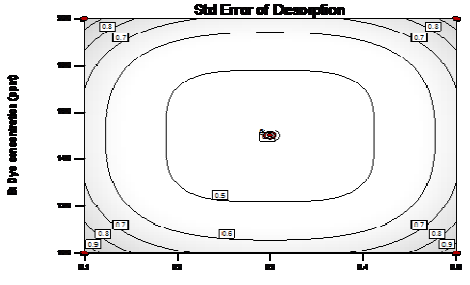
Table 4 Analysis of variation for the experimental results of decolorization, adsorption capacity and desorption by using box behnken design (quadratic model)

	% decolorization					Adsorption capacity					Desorption					
Source	Sum of Squares	df	Mean Square	F value	p-value Prob > F	Sum of Squares	df	Mean Square	F value	p-value Prob > F	Sum of Squares	df	Mean Square	F value	p-value Prob > F	
Model	21192.57	9	2354.73		< 0.0001	57414.48	9	6379.39	57.85	< 0.0001	1150.61	9	127.85	102.17	< 0.0001	Significant
A-Adsorbent dose	156.03	1	156.03	8.05	0.0251	45229.79	1	45229.79	410.17	< 0.0001	54.65	1	54.65	43.68	0.0003	
B-Dye concentration	165.89	1	165.89	8.56	0.0221	188.47	1	188.47	1.71	0.2324	20.07	1	20.07	16.04	0.0052	
C-Time	11408.05	1	11408.05	588.79	< 0.0001	5213.23	1	5213.23	47.28	0.0002	110.71	1	110.71	88.47	< 0.0001	
AB	159.90	1	159.90	8.25	0.0239	25.05	1	25.05	0.23	0.6482	0.14	1	0.14	0.12	0.7440	
AC	119.03	1	119.03	6.14	0.0423	251.86	1	251.86	2.28	0.1745	8.09	1	8.09	6.47	0.0385	
BC	42.38	1	42.38	2.19	0.1827	32.60	1	32.60	0.30	0.6035	0.63	1	0.63	0.51	0.5003	
A^2	4244.67	1	4244.67	219.08	< 0.0001	980.85	1	980.85	8.89	0.0204	409.39	1	409.39	327.16	< 0.0001	
B^2	4091.01	1	4091.01	211.15	< 0.0001	2776.20	1	2776.20	25.18	0.0015	380.44	1	380.44	304.03	< 0.0001	
C^2	127.29	1	127.29	6.57	0.0374	2070.49	1	2070.49	18.78	0.0034	175.55	1	175.55	140.29	< 0.0001	
Residual	135.63	7	19.38		771.90	7	110.27		8.76	7	1.25					
Lack of Fit	52.59	3	17.53	0.84	0.5368	600.18	3	200.06	4.66	0.0856	1.02	3	0.34	0.18	0.9072	Non Significant
Pure Error	83.04	4	20.76		171.71	4	42.93		7.74	4	1.93					
Cor Total	21328.20	16		58186.37	16		1159.37	16								

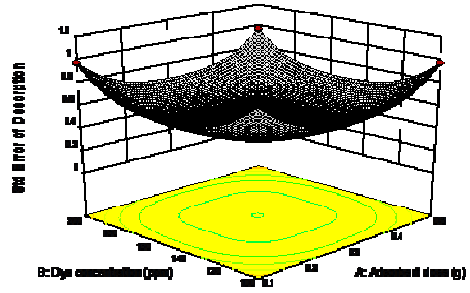
Table 5 ANOVA of response surface for Box Behnken Design

Statistical values	% decolorization	Adsorption capacity	Desorption
R-Squared	0.9936	0.9867	0.9924
Adj R-Squared	0.9855	0.9697	0.9827
Pred R-Squared	0.9545	0.8304	0.9755
Adeq Precision	27.436	25.011	30.778
C.V. %	7.66	8.76	9.83

After reviewing the entire the statistical outputs for design assessment and three dimentional plots. The minimum value of standard error relatively lie in low and flat error around the centroid which indicated the design points and polynomial fitness of the model (Fig. 3a,b). The residuals are used to check the homogenous variance assumption by plotting the (studentized) residuals against the predicted probability values. Homogeneously spread data about either side of zero line indicated the suitability of model for the present study (Fig. 4).

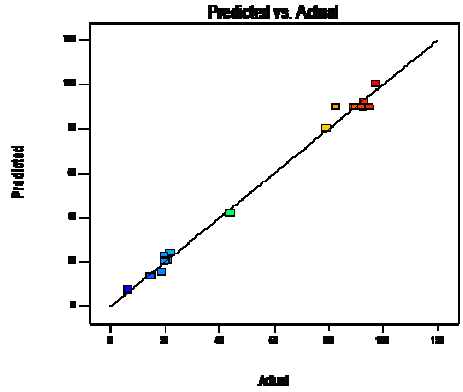


A

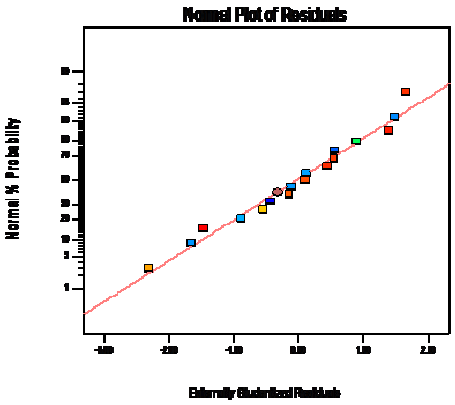


B

Fig. 3 Standard error of desorption (a) graph plot (b) 3D graph



A



B

Fig. 4 Diagnostic plot: (a) predicted versus actual; (b) normal probability plot of the studentized residuals

To study the interactive effect of three variables the perturbation graphs were used (Fig. 5). The perturbation plot of dye decolorization capacity against investigated variables implies the contribution of each factor to the bioremediation process.The perturbation plot illustrates decolorization percentage as each variables moves from the preferred reference with all other factors held constant at the middle of the design space (the coded zero level). The flat curves for (C) contact time indicates that the biosorption changes less due to the variables than (A) adsorbent dose and (B) dye concentration.

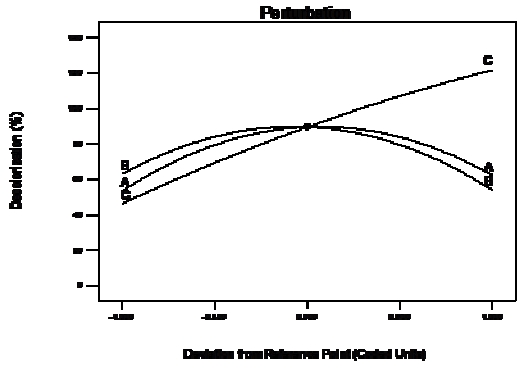


Fig. 5 represents perturbation plot showing the effects of all factors on removal of CR dye.

The adsorbent dose has been described as a factor that strongly influences the percent decolorization. The combined effect of adsorbent dose and dye concentration on dye decolorization is visible in Fig. 6. It may be seen that increasing adsobent dose level and dye concentration results in an increasing percent removal of the dye. Increasing the adsorbent dose provide larger surface area and availability of more dye binding sites; hence the rate of dye sorption increased even when the initial dye concentration remained constant.

The results are in agreement with those reported in the literature Khataee *et al*., 2009, Tsai and Chen, (2010). An important parameter which is generally used for the sorption studies is biomass dose, which determines the potential of biosorbent to remove dye at a given initial concentration (Vijayaraghavan *et al*., 2007). The maximum congo red removal 89.99%), was obtained with the biomass dosage of .314 g/L and initial dye concentration of 146.2 ppm as shown in Fig. 6.

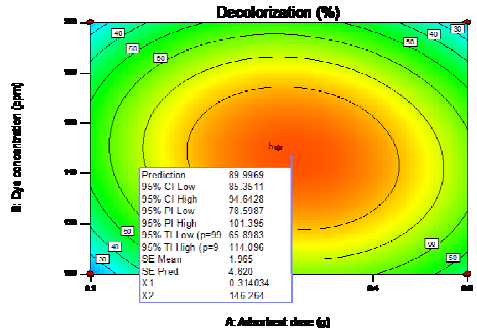


Fig. 6 Graph of desirability for maximum decolorization based on interaction between dye concentration and adsorbent dose

Initial dye concentration is also an important parameter in the adsorption process. It is found that at lower dye concentrations, there is no significant change in dye removal through increasing sorbent dose. On the other side, at higher dye concentrations, the dye uptake increases with increasing dose. This trend can be explained in this way that at lower dye concentrations there are not enough dye molecules in the solution to occupy all the available binding sites; thus an increase in the sorbent dose would not affect the amount of adsorption. On the contrary, at higher concentrations, the adsorption will be relatively higher due to presence of enough dye molecules in the solution to be adsorbed by relatively more active binding sites provided by increasing sorbent dose.

Khataee *et al*., 2010 found that dye removal efficiency was increased by increasing the initial malachite green concentration. It was attributed to an important driving force to overcome mass transfer resistances between the aqueous and solid phases. Reddy *et al*., 2010 studied biosorption of lead by Moringa oleifera and observed a decrease in the biosorption efficiency as metal ion concentrations increased. It was concluded that the active sites on the biomass surface were sufficient to adsorb lower concentration of metal ions.

The response surface model was used to predict the result by response contour plots and three dimensional surface plots. Surface plots demonstrating the effects of different process parameters, two parameters varied at a time while keeping the third at middle level, on the percent decolorization were shown in figs. 7 (a-c). The stationary points were examined by analyzing these plots. Interaction effects and optimal levels of the variables were determined by plotting these response surface contour plots which showed the behavior of response (% decolorization) with respect to simultaneous change in two variables.

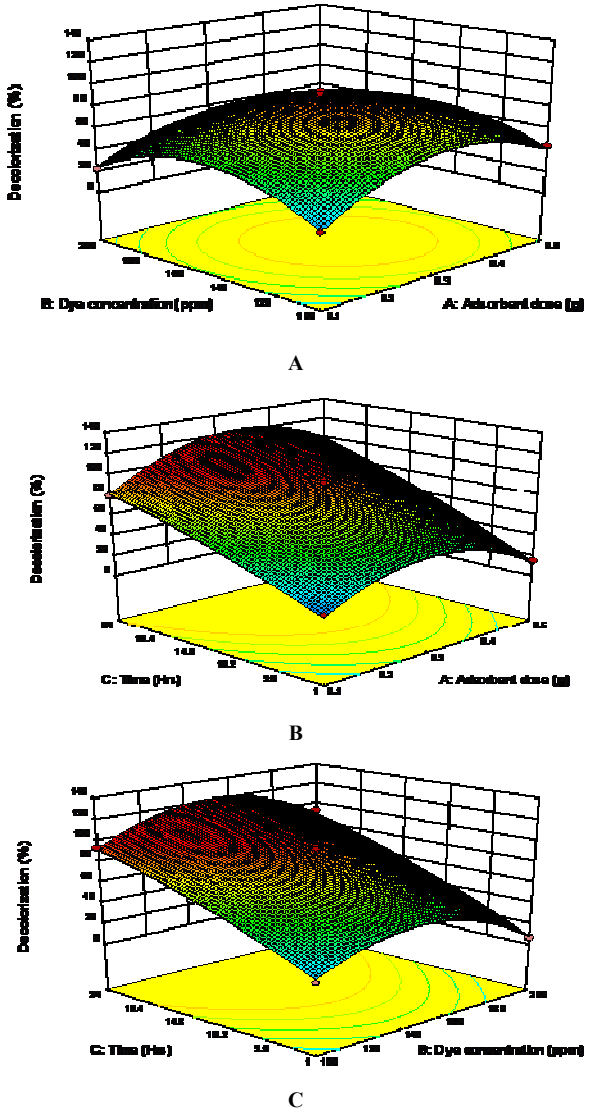


Fig. 7 Response surface plots showing the effects of (a) dye concentration and adsorbent dose, (b) time and adsorbent dose, (c) time and dye concentration on decolorization.

Fig. 7b showed the response surface plots to estimate decolorization over variabless adsorbent dose and time. Surface plot peak value shows optimum value of percent dye decolorization for the relative effects of these two variables by keeping the third one at middle level. Adsorbent dose shows convex curve towards z axis and contact time showed inclined percent decolorization towards z axis. A similar type of trend was obderved by Jaikumar and Ramamurthi, (2009) for his study of acid dye biosorption by brewery waste biomass The maximum predicted yield is indicated by the surface confined in the smallest curve of the surface diagram (Subramaniam and Ponnusamy, 2015). The optimum values drawn from these fig are close agreement with those get from optimizing the regression model Eq.

Fig. 7c showed positive interaction between contact time and dye concentration. The percentage of dye decolorization was increased raplidly with contact time and initial dye concentration. This indicates that higher the contact time between dye and adsorbent, higher is the removal efficiency till equillibrium is obtained. It may be due to the fact that dye molecules are preferentially adsorbed to the most active site of adsobent. The short contact time between dye and adsorbent gives less removal percentage of dye and equillibrium adsorption capacity and vice vesa.

From the interaction plots it can be concluded that adsorption was more favourable towards lower levelof adsorbent dose, middle level of dye concentration and higher level of contact time. Optimized parameters suggested by the model were adsorbent dose 0.1g, initial dye concentration 177 ppm and contact time 17h.

CONCLUSION

In the study, screening and optimization was performed for dyes decolorization. From the screening it was found that congo red was maximum removed using the biosorbent. Percent decolorization was 83.7, 82.1 and 80.2 for congo red, malachite green and methylene blue respectively. The interaction between different variables for congo red decolorization was studied using box behnken design. Optimized parameters were adsorbent dose 0.1g, initial dye concentration 177 ppm and contact time 17h outcomes of the box behnken design. Thus spent immobilized biomass of water hyacinth left after enzyme production proved an effective biosorbent.

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