



Response surface methodology approach for optimization of adsorption process for the removal of Indosol Yellow BG dye from aqueous solution by agricultural waste

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ABSTRACT

This study was designed to explore the adsorption capacity of agricultural waste biomass for the removal of Indosol Yellow BG dye from aqueous solutions. Screening test was performed to select one adsorbent with maximum adsorption potential. Peanut husk biomass was selected as potential adsorbent after screening test. Peanut husk biomass depicted maximum adsorption capacity (22.47 mg/g) as compared to other adsorbents (sugarcane bagasse, corncobs, cotton sticks, and sunflower). The effect of different physical and chemical treatments on the adsorption capacity of peanut husk biomass was investigated, and acetic acid-treated biomass depicted very good adsorption capacity (25.05 mg/g) for the removal of Indosol Yellow BG dye. Box–Behnken experimental design was used for batch study. Batch experiments were conducted to explore the effect of three important process parameters viz., initial dye concentration, adsorbent dose, and pH. Maximum dye removal (58.01 mg/g) was achieved at 200 mg/L initial dye concentration, 2 pH, and 0.17 g adsorbent dose. Higher initial dye concentration, lower pH, and lower biosorbent dose were found to be feasible conditions for maximum dye removal. Desorption study was also conducted by using different concentrations of NaOH, and maximum desorption (44.5%) was achieved with 1 M NaOH solution. The results indicated that acetic acid-treated peanut husk biomass could be used as potential adsorbent for the treatment of dye containing wastewater.

Keywords: Agricultural wastes; Peanut husk; Pretreatments; Indosol Yellow BG; Box–Behnken experimental design; Desorption study

1. Introduction

During the last few decades, the contamination of water resources has aroused the public concern because of the adverse effects of contaminated water

on health and environment [1]. The water pollution problem has been intensified due to rapid industrialization since last few decades. Among the different industries, the textile industry is playing a very prominent role in enhancing water pollution [2]. The indiscriminate disposal of textile effluents results in entrance of synthetic dyes into water

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bodies which has intensified numerous threatening deteriorations toward the public health and food chain interference [3].

Different treatment technologies have been adopted by different researchers for the treatment of textile wastewater [4]. These technologies include membrane filtration, ion exchange, electrokinetic coagulation, photocatalytic degradation, electrochemical oxidation, etc. All these technologies have different color removal capabilities. Overall, these processes have been found efficient in treating the textile wastewaters but these methods also pose certain limitations [5]. The high cost and membrane fouling problems limit the application of membrane filtration process. Coagulation process leads to the generation of sludge which results in high disposal costs. Ion exchange process is too expensive to accommodate wide range of dyes [6]. In underdeveloped countries, the high operating costs of these water treatment technologies result the financial constraints to treat the wastewater before discharge to the environment, and hence, these methods cannot be used by small industries to treat the wide range of dye wastewater so some cost effective and efficient treatment technologies should be adopted for wastewater treatment [7].

Adsorption has been found simple, inexpensive, efficient, sludge-free, and economically feasible process for the removal of pollutants from wastewater without leaving behind any toxic degraded products [8]. Activated carbon has been proved as an efficient adsorbent for the pollutant removal from aqueous solutions. But due to its high cost and difficulty in regeneration, alternative cheaper and efficient adsorbents have been explored by different researchers for the removal of dyes [9]. Researchers have done extensive work on the removal of dyes by using agricultural waste materials, and research results proved that the agro-wastes depict very good adsorption potential for the dyes [10,11]. So keeping in mind the adsorption potential of agricultural wastes, this study was designed to investigate the adsorption potential of agricultural waste biomasses for the removal of Indosol Yellow BG dye from aqueous solutions in batch mode using Box–Behnken experimental design. Effect of different chemical and physical treatments on the adsorption capacity of biomass was also explored.

2. Materials and methods

2.1. Preparation of biomass

Five different agricultural waste materials (sugarcane bagasse, peanut husk, corncobs, cotton sticks, and sun flower) have been collected from different

areas of Punjab and Pakistan. These waste materials were washed with tap water and then distilled water in order to remove dust. The washed and dried biomasses were ground with a food processor (Moulinex, France) and sieved using Octagon sieve (OCT-DIGITAL 4527-01) to a 300- μm mesh size.

2.2. Modification of biomass

After screening test, the selected biomass was modified physically and chemically. During physical treatments, autoclaving (biomass was autoclaved at 121°C for 15 min) and boiling (5 g of biomass/100 mL of H₂O and boiled for 30 min) were carried out. In chemical modifications, 1 g of the biosorbent was treated with 5% solution of different acids (HCl, H₂SO₄ and HNO₃ and CH₃COOH), alkali (NaOH), surfactants (CTAB, SDS, Triton X-100), chelating agents (PEI, EDTA and glutaraldehyde), and organic solvents (benzene and methanol). Then, all the modified biomasses were washed with double-distilled water and filtered. The modified adsorbents were dried in oven at 60°C for 24 h and ground it [12].

2.3. Preparation of aqueous dye solutions

Indosol Yellow BG dye was obtained from Clariant Pakistan Limited, Faisalabad, Pakistan, and was used without further purification. Stock solution of dye was prepared by dissolving 1 g of dye in 1,000 mL of double-distilled water. The experimental solutions of different concentrations ranging from 10 to 200 mg/L were made by further dilutions. Indosol Yellow BG dye was anionic in nature, and its λ_{max} was found to be 392 nm.

2.4. Experimental design

Box–Behnken experimental design was employed for this study which has been proved appropriate for fitting the quadratic surface [13]. Three important process variables (initial dye concentration (*A*), adsorbent dose (*B*), and pH (*C*)) were selected for this study. A total of 17 experimental runs were generated by Design Expert software (version 7.0.0) by using the following formula:

$$N = K^2 + K + CP \quad (1)$$

where *K* is the number of variables and *CP* is the number of replicate of center points.

The coded values of process variables are obtained by the following equation:

$$x_i = X_i - X_o / \Delta X \quad (2)$$

$$i = 1, 2, 3, \dots, K$$

where X_i = real value of independent variable, X_o = value of X_i at central point, ΔX = step change, and x_i = dimensionless value of process variable.

The second-order equation used to show the relationship between dependent and independent variables was given as

$$y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 + \varepsilon \quad (3)$$

where y —the response variable; β_0 —intercept; $\beta_1, \beta_2, \beta_3$ —the coefficients of A, B, C ; $\beta_{12}, \beta_{13}, \beta_{23}$ —coefficients of cross products; $\beta_{11}, \beta_{22}, \beta_{33}$ —coefficients of quadratic terms; $\varepsilon \sim N(0, \sigma^2)$.

A positive sign in the equation represents a synergistic effect of the variables, while a negative sign indicates an antagonistic effect of the variables. The optimum values were obtained by solving the regression equation, analyzing the contour plot, and also by setting the constraints for the levels of the variables.

The upper and lower limits of independent variables for the removal of Indosol Yellow BG dye are presented in Table 1.

2.5. Batch experimental program

The batch experiments were conducted as designed by the Box–Behnken experimental design at 120 rpm and 30°C for 1 h of agitation time to check out the effect of initial dye concentration (A), biosorbent dose (B), and pH (C) on the removal of Indosol Yellow BG dye. Solution pH was adjusted using 0.1 M NaOH and HCl. After 1 h of agitation, the samples were taken out and centrifugation was performed at 5,000 rpm for 20 min and concentration of remaining

dye solution was determined by using UV–vis spectrophotometer (Schimadzu, Japan). The responses were recorded in the form of adsorption capacity (mg/g).

The equilibrium adsorption uptake, q_e (mg/g), was calculated using the following relationship:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (4)$$

where C_o is the initial dye concentration (mg/L), C_e is the equilibrium dye concentration (mg/L), V is the volume of the solution (L), and W is the mass of the adsorbent (g).

Indosol Yellow BG dye can be desorbed from the dye-loaded biomass to regenerate the adsorbent and adsorbate. Desorption study was performed using NaOH (0.2–1.0 M). The % age desorption can be estimated by using following equation:

$$\text{Desorption (\%)} = \frac{\text{amount of dye desorbed (mg/g)}}{\text{amount of dye adsorbed (mg/g)}} \times 100 \quad (5)$$

2.6. Scanning electron microscope analysis

The surface structure of peanut husk biomass was analyzed by JEOL JMT 300 scanning electron microscope (SEM).

3 Results and discussion

3.1. Screening study

The screening test was conducted to select one agricultural waste material among the five different agro-industrial wastes with maximum biosorption capacity for the removal of Indosol Yellow BG dye

Table 1
Experimental ranges and levels of independent variables

Factors	Ranges and levels		
	−1	0	+1
A: initial dye concentration (mg/L)	10	105	200
B: adsorbent dose (g)	0.05	0.17	0.30
C: pH	2	5.5	9

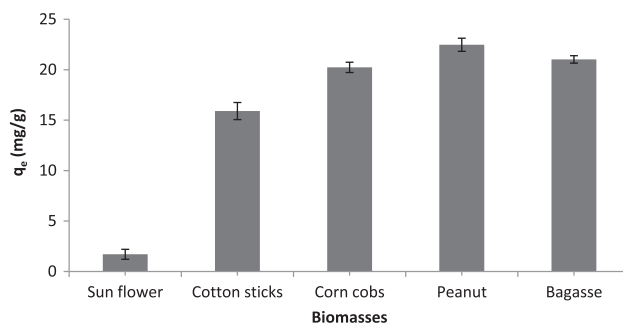


Fig. 1. Screening of different agro-industrial wastes for the removal of Indosol Yellow BG dye.

from aqueous solution. The result of screening test is shown in Fig. 1. The results showed that peanut husk biomass depicted maximum biosorption capacity (22.47 mg/g) for the removal of Indosol Yellow BG dye so peanut husk biomass was selected for further studies.

3.2. Modification of adsorbent

The adsorption capacity of the adsorbents can be enhanced by surface modification techniques. To enhance the adsorption capacity of peanut husk biomass, different physical and chemical treatments were carried out and results are presented in Fig. 2. The surface modification technique has helped in improving the adsorption capacity of peanut husk biomass as depicted by Fig. 2. Almost all the treatments enhanced the adsorption capacity of peanut husk biomass except the treatment with NaOH, PEI, CTAB, and SDS. The maximum biosorption capacity (25.05 mg/g) was achieved with CH₃COOH treated biomass. Acid treatments generally enhance the adsorption capacity of biomasses due to the cleanup of the surface impurities and increase in the surface area by opening the available sites for adsorption [14]. The treatment with NaOH resulted in significant decrease in adsorption capacity of peanut husk biomass because of the de-protonation of functional groups present on the surface of adsorbent responsible for the adsorption process [15]. The Indosol Yellow BG dye is anionic in nature, and anionic dye molecules face repulsion with deprotonated functional groups resulting in decrease in adsorption capacity of adsorbent. Treatment of peanut husk biomass with anionic and cationic surfactant (SDS and CTAB) also resulted in reduction of adsorption capacity as compared to the non-treated biomass.

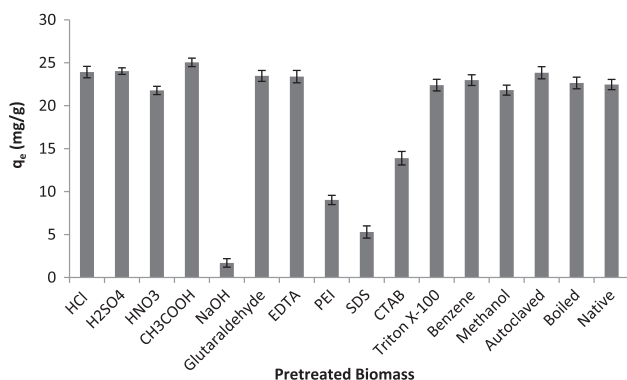


Fig. 2. Effect of pretreatments on the adsorption capacity of peanut husk biomass.

This might be due to the fact that these treatments produce hindrance in the attachment of dye anions to the surface of biosorbent resulting in its low biosorption capacity [2,16]. Treatment of biomass with PEI also resulted in decreased adsorption capacity of adsorbent which is due to the cross-linking of functional groups present on the surface of biomass which results in their unavailability for the binding of dye anions. Physical treatments (autoclaving and boiling) resulted in enhancement of adsorption capacity of peanut husk biomass which might be due to the exposure of more binding sites by the release of mineral and organic acids from the surface [12].

3.3. Response surface methodology

To check out the effect of three important process variables (initial dye concentration (*A*), adsorbent dose (*B*), and pH (*C*)), on the adsorption capacity of acetic acid-treated peanut husk biomass for the removal of Indosol Yellow BG dye, batch experiments were conducted as designed by Box–Behnken experimental design. The experiments were conducted with different combinations of three parameters, and the experimental results indicated that these three parameters significantly affect the adsorption capacity of adsorbent for the removal of Indosol Yellow BG dye. The experimental results are presented in Table 2 which depicts a close agreement between the experimental and predicted adsorption capacities of acetic acid-treated biomass for the dye removal. This close agreement between the experimental and predicted adsorption capacities is a confirmation for the good model prediction efficiency. The model prediction efficiency can also be described in terms of value of R^2 , and R^2 value should be closer to 1 for the model with good prediction efficiency. Table 3 shows that the value of R^2 is 0.992 which is closer to 1. According to some statisticians [17], the value of R^2 only is not so reliable for the assessment of model prediction efficiency because the value of R^2 increases with the increase in model terms irrespective of their statistical significance. This problem can be solved by comparing the value of R^2 with the value of R^2_{adj} . This is because of the fact that the value of R^2_{adj} decreases if insignificant terms are added in the model. Hence, if there is large difference between the values of R^2 and R^2_{adj} , it means that some nonsignificant terms have been included in the model [18]. Table 3 shows that there is reasonable agreement between the values of R^2 and R^2_{adj} . The maximum dye removal (58.01 mg/g) was achieved at lowest experimental pH (pH 2) and highest initial dye concentration (200 mg/L).

Table 2

Box–Behnken design matrix for the real and coded values along with experimental and predicted results for the removal of Indosol Yellow BG dye

Run order	Real (coded) values			Adsorption capacity (mg/g)	
	A	B	C	Experimental	Predicted
1	105(0)	0.05(-1)	9(+1)	7.79	7.05
2	10(-1)	0.17(0)	2(-1)	2.11	4.05
3	10(-1)	0.05(-1)	5.5(0)	6.25	6.49
4	105(0)	0.17(0)	5.5(0)	24.18	23.35
5	105 (0)	0.17(0)	5.5(0)	22.17	23.35
6	200(+1)	0.17(0)	9(+1)	17.93	15.99
7	105(0)	0.3(+1)	9(+1)	14.16	16.33
8	10(-1)	0.17(0)	9(+1)	0.17	0.67
9	105(0)	0.17(0)	5.5(0)	23.70	23.35
10	200(+1)	0.3(+1)	5.5(0)	29.06	28.82
11	105(0)	0.17(0)	5.5(0)	23.53	23.35
12	105(0)	0.3(+1)	2(-1)	16.70	17.44
13	200(+1)	0.05(-1)	5.5(0)	42.0	44.68
14	105(0)	0.05(-1)	2(-1)	53.0	50.83
15	105(0)	0.17(0)	5.5(0)	23.16	23.35
16	10(-1)	0.3(+1)	5.5(0)	0.91	-1.77
17	200(+1)	0.17(0)	2(-1)	58.01	57.51

Note: A: initial dye concentration (mg/L); B: adsorbent dose (g); C: pH.

Table 3

Analysis of variance (ANOVA) results for response parameters

Final equations with coded factors	R^2	R^2_{adj}	Predicted R^2	Adequate precision	Coefficient of variation
$Y_{TY\ BG} = 23.35 + 17.20A - 6.03B - 11.22C - 1.90AB - 9.54AC + 10.67BC - 3.58A^2 - 0.22B^2 - 0.22C^2$	0.992	0.982	0.884	34.43	10.46

Residual graphs were also used to check out the suitability of model. These residual graphs present a visual display of difference between actual and predicted adsorption capacities [19]. The residual plot is presented in Fig. 3. The normality assumption was satisfied as the residual plot approximated along a straight line.

For the visualization of responses at different levels of independent variables, two-dimensional contour plots were studied and are shown in Fig. 4. The effect of initial dye concentration and adsorbent dose on the removal of Indosol Yellow BG dye is presented in Fig. 4(a) which indicated that both the independent variables significantly affect the adsorption process. The increase in initial dye concentration resulted in increase in the adsorption capacity of acetic acid-treated peanut husk biomass increased. Maximum dye removal (42 mg/g) was achieved at 200 mg/L initial dye concentration. The initial dye concentration acts as an important driving force to overcome the mass

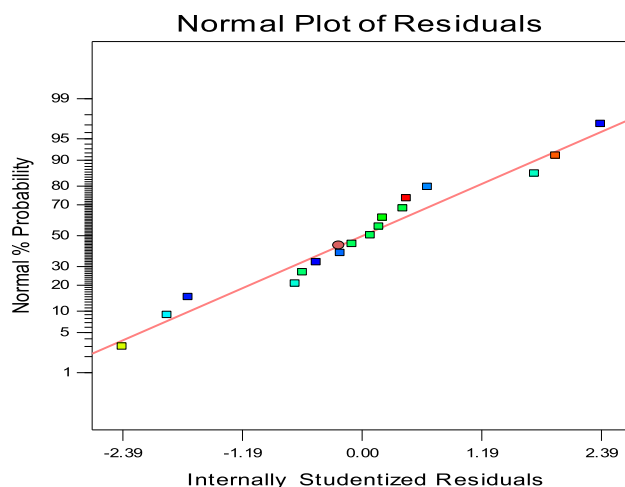


Fig. 3. Normal probability plot of residuals for Indosol Yellow BG dye.

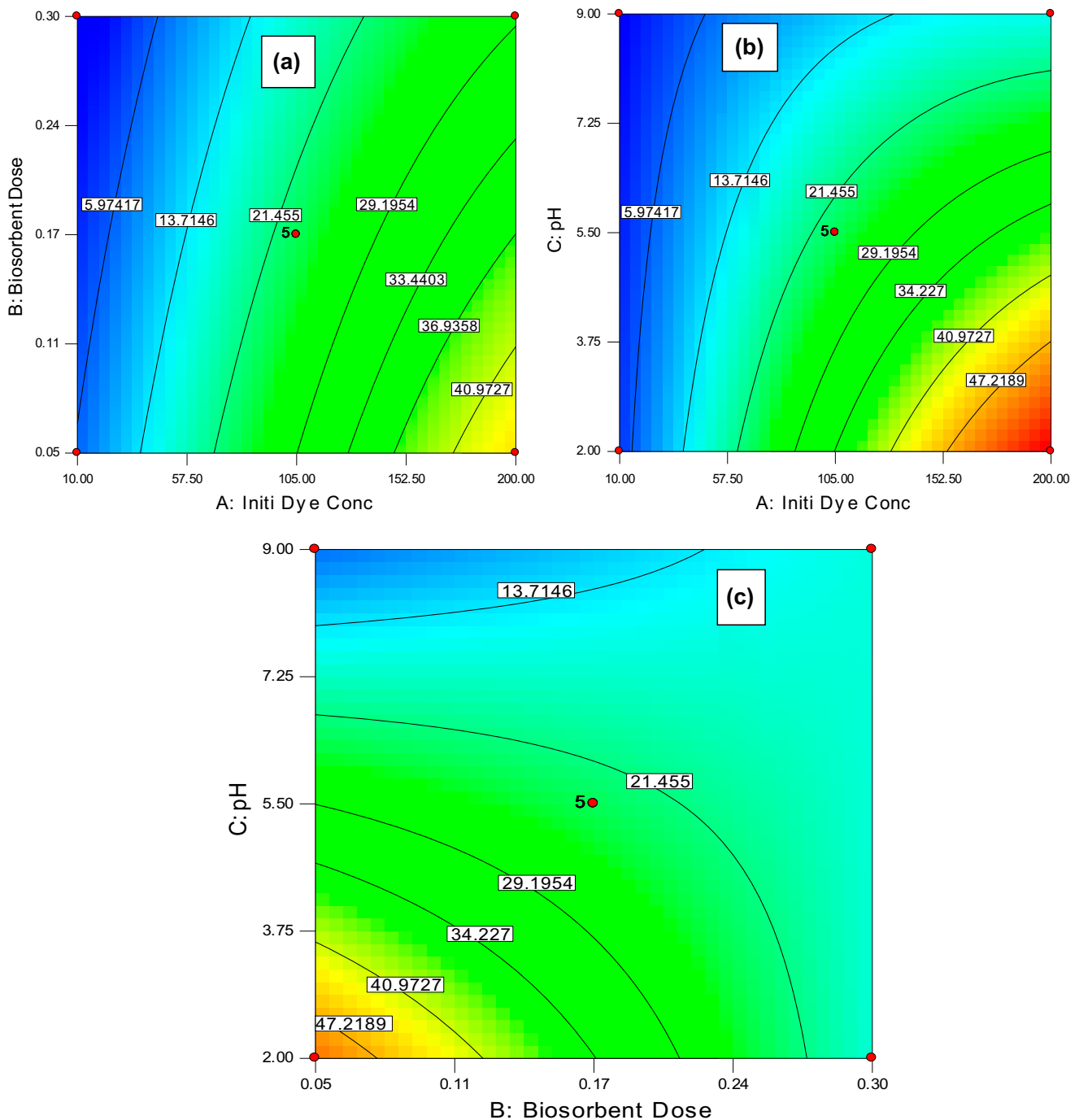


Fig. 4. Interaction effect of: (a) Initial dye concentration and biosorbent dose, (b) Initial dye concentration and pH, and (c) Biosorbent dose and pH (c).

transfer resistance [20]. The higher initial dye concentrations result in boosting up the adsorption process [21]. Khaled et al. also investigated the effect of initial dye concentration on the removal of Direct Navy Blue 106 dye using orange peel activated carbon by varying the initial dye concentration from 50 to 150 mg/L with

different adsorbent doses [22]. The results showed an increase in the amount of dye adsorbed per unit mass of adsorbent with the increase in initial dye concentration. Similar results have also been reported by different researchers [2,23,24]. Another important factor regarding the biosorption process is biosorbent dose

because this factor determines the capacity of biosorbent for a given initial concentration of the adsorbate [25]. The effect of biosorbent dose was also explored by conducting experiments at different biosorbent doses and results indicated that by increasing the adsorbent dose there is remarkable decrease in adsorption capacity (mg/g) of acetic acid-treated peanut husk biomass for the removal of Indosol Yellow BG dye. Maximum dye removal was observed at lowest level of adsorbent dose (0.05 g). At higher adsorbent doses, the overlapping or aggregation of biomass takes place which leads to the decrease in number of active sites available for the attachment of dye molecules resulting in decreased adsorption capacity [26]. Another important factor is that at high adsorbent dosage, the available dye molecules become insufficient to completely cover the available binding sites on the adsorbent, which usually results in low solute uptake [27]. Different researchers have worked to check the effect of biosorbent dose on the biosorption process and found similar results [28,29].

The combined effect of initial dye concentration (A) and pH (C) on the removal of Indosol Yellow BG dye was presented in the form of counter plot (Fig. 4(b)). Experiments were conducted at different levels of pH and initial dye concentration keeping the adsorbent dose constant at 0.17 g. The results indicated that solution pH plays an important role in the adsorption process [30]. It affects the solution chemistry of dyes and functional groups of adsorbent [31]. It monitors the magnitude of electrostatic charges on adsorbent and adsorbate. The contour plot showed that the increase in pH resulted in the decrease in adsorption of Indosol Yellow BG dye by acetic acid-treated peanut husk biomass. This can be due to the fact that at acidic range of pH, protonation of functional groups may take place which facilitates the attachment of dye anions on the surface of adsorbent [15]. At higher pH levels, the concentration of OH⁻ ions increase in the solution which compete to the negatively charged dye anions for attachment to the adsorbent surface. Hence, the adsorption of anionic dyes decrease at higher pH levels [32]. Gong et al. worked on the adsorptive removal of Sunset Yellow dye onto peanut waste biomass and found a decrease in adsorption capacity of dye with the increase in solution pH [33]. Some other researchers also reported similar results for the adsorption of dyes [34–36]. The adsorption of dye was also found to be favorable at higher initial dye concentration.

The combined effect of adsorbent dose (B) and pH (C) was studied by conducting experiments at different levels of these two variables keeping the initial dye concentration (A) constant at central level

(105 mg/L). The dye removal was found to be favored at lower adsorbent dose and lower pH. Maximum dye removal (47.2 mg/g) was achieved at 0.05 g adsorbent dose and at pH 2 (Fig. 4(c)).

The simultaneous effect of all the three independent variables on the adsorption capacity of acetic acid-treated biomass for the removal of Indosol Yellow BG dye was determined with the help of perturbation plot (Fig. 5). In perturbation plot, the response change is determined by moving one variable from the chosen reference point keeping the other variables at coded zero level. The perturbation plot showed that all the three independent variables viz., initial dye conc. (A), adsorbent dose (B), and pH (C) significantly affects the adsorption capacity of acetic acid-treated peanut husk biomass. The adsorption of Indosol Yellow BG dye was found to be more dependent on the variation in initial dye concentration as shown by the sharp curvature for this parameter as compared to the biosorbent dose and pH.

3.4. Desorption study

Desorption study was conducted to investigate the possibility of regeneration of adsorbent and adsorbate. As adsorption of dye was favored at low pH, NaOH was used as desorbing agent. At different concentrations of NaOH, desorption of dye was found to be different (Fig. 6). Desorption increased with increase in concentration of NaOH. Maximum desorption (44.5%) was achieved with 1 M NaOH solution. This is due to the fact that surface of adsorbent acquires negative

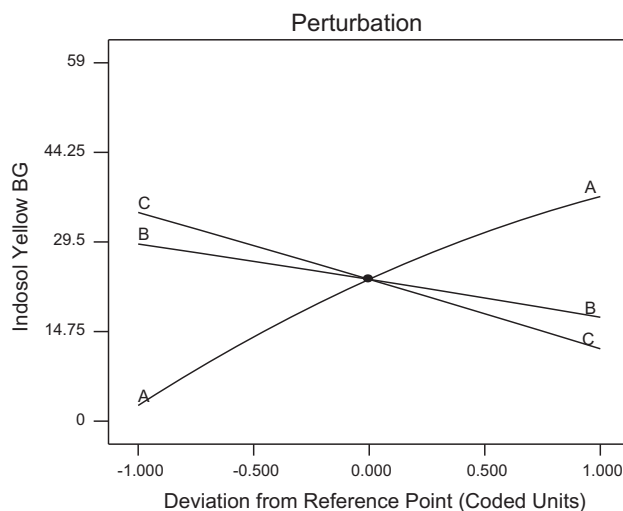


Fig. 5. Overlay perturbation plot of all the independent variables for adsorption of Indosol Yellow BG.

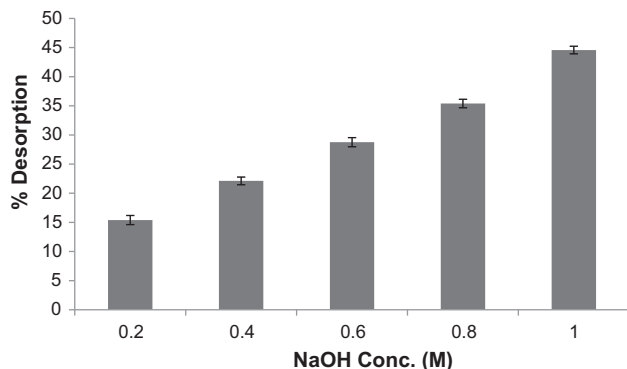


Fig. 6. Desorption study.

charge in the presence of NaOH which results in the repulsion with dye anions and leads to the detachment of dye molecules [37].

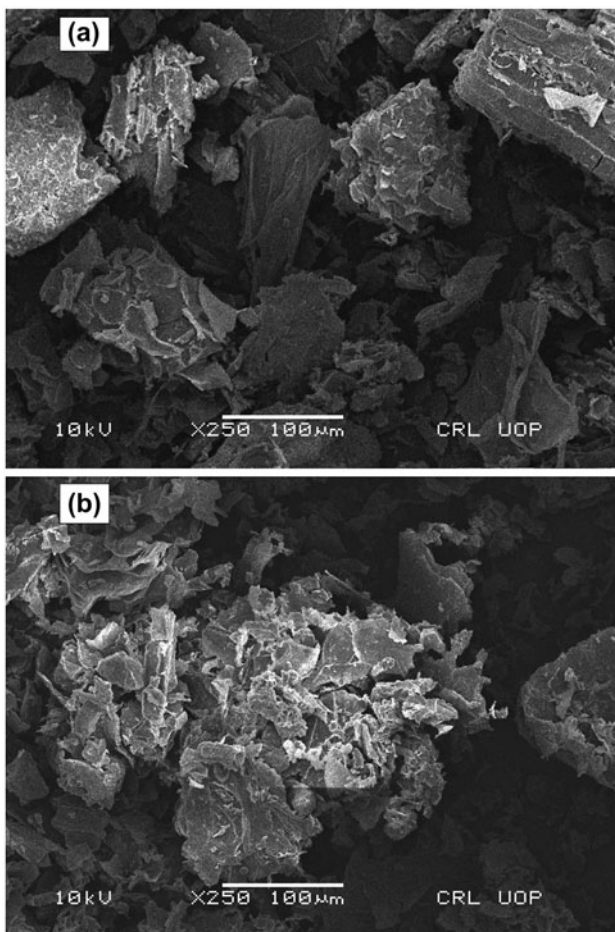


Fig. 7. SEM analysis of: (a) Unloaded and (b) Indosol Yellow BG dye-loaded peanut husk biomass.

3.5 SEM analysis

The surface morphology of unloaded and dye-loaded biomass was also shown in SEM images (Fig. 7(a) and (b), respectively). These photographs indicated the porous structure of peanut husk biomass which is helpful in adsorption process.

4. Conclusion

The utilization of agricultural waste for the removal of Indosol Yellow BG dye from aqueous solution was investigated during this study. Acetic acid-treated peanut husk biomass depicted maximum adsorption potential among the different other chemically and physically treated forms of peanut husk biomass. Batch experiments were conducted as designed by Box–Behnken experimental design. Maximum dye removal (58.01 mg/g) was achieved at 2 pH, 0.17 g adsorbent dose, and 200 mg/L initial dye concentration. 44.5% of the adsorbed dye was desorbed during desorption study using 1 M NaOH solution. The results proved that acetic acid peanut husk biomass has a very good adsorption potential for the removal of Indosol Yellow dye from textile wastewater.

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