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Statistical Optimization for the Adsorption of Acid Fuchsin onto the Surface of Carbon Alumina Composite Pellet: An Application of Response Surface Methodology

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ABSTRACT

Industrial effluents mainly enriched with different colored substances cause significant environmental problem. Various efforts have been made so far for the treatment of textile industry effluents but very little attention has been given for the removal of dyes from medicine industry waste water. Acid fuchsin is one of such dyes which are mainly present in the medicine industry waste water. In the present investigation, carbon-alumina composite pellet was developed for the removal of acid fuchsin dye from its aqueous solution. The removal of acid fuchsin was carried through batch adsorption and the effects of different parameters on the adsorption of acid fuchsin were studied through response surface methodology. The composite adsorbent was found to have an adsorption capacity of 181.82 mg g^{-1} for acid fuchsin. The adsorption process was optimized by using response surface methodology and the effects of various process parameters such as, temperature, solution pH, salt concentration and initial dye concentration on percent dye removal were determined by a four factor Box-Behnken design. The maximum dye removal percentage was obtained for an initial dye concentration of 10 mg L^{-1} and a solution pH of 7.5 whereas, the temperature is fixed at 35°C. Nevertheless, the maximum removal was found at zero salt concentration. Therefore, it can be concluded that the prepared adsorbent successfully remove acid fuchsin from its aqueous solution. Since the adsorbent is used in the pelletized form, it can be further used in a fixed bed column study.

Key words: Acid fuchsin, pellet, box-behnken design, composite adsorbent, alumina

INTRODUCTION

In the present decade, huge amount of colored effluent are directly discharge into water bodies due to rapid growth of industrialization cause significant environmental problems (Nwude *et al.*, 2011; Nasab *et al.*, 2010). A huge amount of colored effluents originated from different dye manufacturing units inevitably lost into water bodies each year while processing (Arunachalam and Annadurai, 2011; Morais *et al.*, 1999). These colored substances cause adverse effects on aquatic life by impeding the rate of photo synthesis (Osman *et al.*, 2009; Rajendran *et al.*, 2011). The hematological process of some biota also affects when these colored materials enter into their systems (Afaq and Rana, 2009; Wanchanthuek and Thapol, 2011). Various types of toxic dyes such as, acid dyes, basic dyes, reactive dyes and azo dyes are found in the inland surface water originating from their different manufacturing sources and users. Among all these dyes, acid dye is most widely used in pharmaceutical industry has a complex aromatic structure (Attia *et al.*, 2006). Acid fuchsin is one of such dyes used as an inhibitor of reverse transpose of immunodeficiency virus (Baba *et al.*, 1988), as a copper corrosion inhibitor (Bastidas *et al.*, 2003), in the preparation of organic inorganic hybrid nano-composite (Bin Hussein *et al.*, 2004) and as a laboratory reagent. Most of these dyes are reported to be carcinogenic in nature so often produce toxic amines over incomplete degradation which in turn necessities the pre-treatment of these colored effluents prior to disposal (Lata *et al.*, 2007; Vimonses *et al.*, 2009). The removal of color can be done by coagulation and flocculation (Amin, 2008; Santhy and Selvapathy, 2006), oxidation (Malik and Saha, 2003), membrane separation (Ciardelli *et al.*, 2001) and adsorption (Wu and Tseng, 2008) but adsorption is worth mentioning amongst all (Dekhil *et al.*, 2011). The activated carbon is one of the versatile adsorbents because of its large surface area and highly porous structure, but its high cost limits its widespread use.

Besides, the use of powdered form of adsorbent has the great disadvantage of separation after being used. To overcome this difficulty, the carbon may be used in its pelletized form. In addition to carbon, alumina could be used as a good adsorbent for acid dyes (Gupta and Suhas, 2009; Adak *et al.*, 2005). Therefore, the use of carbon-alumina composite pellet could be a better alternative for the removal of an acidic dye from its aqueous solutions (Balint and Miyazaki, 2009). The alumina has high mechanical properties and strong resistivity to thermal degradation (Mahmoud *et al.*, 2004, 2010a). It also exhibits a high affinity to anionic dyes under basic condition and vice-versa (Mahmoud *et al.*, 2010b). However, a few studies have focused on the removal of acidic dyes using polyurethane/chitosan composite (Zhu *et al.*, 2010), $MnFe_2O_4$/bentonite nano composite (Hashemian, 2010), $CuFe_2O_4$-AC composite (Zhang *et al.*, 2007), Fe_2O_4-AC composite (Yang *et al.*, 2008) but no approach has made for the removal of acid fuchsin using carbon alumina composite pellet. The adsorption process is influenced by various process parameters such as pH, initial concentration, temperature etc. and the effects of these parameters on the adsorption process can be studied through Response Surface Methodology (RSM) (Lee *et al.*, 2000). Therefore, in the present investigation a composite adsorbent was developed for the removal of acid fuchsin by using commercial carbon and alumina where polyvinyl alcohol was used as a binder. The effects of different process parameters namely, pH, initial concentration, temperature and salt concentration were studied through response surface methodology.

MATERIALS AND METHODS

Reagents: Commercial granular activated carbon was supplied by SD Fine Chem. Ltd. (Mumbai, India). The alumina powder for the present work was procured from Merck Specialities Pvt. Ltd. (Mumbai, India). Acid fuchsin and Polyvinyl Alcohol (PVA) was purchased from Loba Chemie Pvt. Ltd. (Mumbai, India). All the experiments were carried out at Indian Institute of Technology, Kharagpur, India in the month of June-July, 2011.

Preparation and characterization of the adsorbent: The Activated Carbon (AC), Alumina powder (Al) and PVA as a binder were mixed together in a weight proportion of 2:2:1. Then a small quantity of water was added to the mixture in order to prepare slurry which was then heated up to 80°C for 4 h in a constant temperature water bath. The heating process was carried out till a sticky mass was formed and then the mass was shaped into spherical pellets. The pellets were kept overnight in an air oven at 90°C and placed in tubular furnace where they were heated up to

300°C for 2 h in a flow of nitrogen gas (300 mL min^{-1}). Next the activation was accomplished by continuing the heating for 1 h. The resulting pellets were then cooled down to room temperature and stored in desiccator over silica gel. The prepared pellets were designated as Carbon-alumina Composite (CAC) pellets. The surface properties of the composite materials were analyzed by using BET apparatus (Autosorb-1, Quantachrome, USA).

Adsorption equilibrium: The surface morphology was investigated by using Scanning Electron Microscope (SEM) (Hitachi model SU-70) image and the surface functional groups were determined using Fourier Transform Infrared Spectroscopy (FTIR) (Spectrum-100, Perkinelmer, USA).

Preparation of dye solution: Acid fuchsine dye of commercial purity was used without further purification. The dye stock solution of concentration of 1000 mg L^{-1} was prepared by dissolving desired quantity of dye in distilled water. The experimental solutions of different initial concentrations were obtained by diluting the dye stock solution.

Equilibrium and kinetic study: Adsorption studies were performed by taking 100 mL of acid fuchsin solutions of varying initial concentration (25-175 mg L^{-1}) in a set of 250 mL conical flasks containing 0.1 g adsorbents. The flasks were agitated in an isothermal mechanical shaker at 35°C for 24 h to reach equilibrium. Whereas, the samples were withdrawn at various interval of time using micro-pipette for kinetic study and centrifuged for 10 min to separate the adsorbent particles. The corresponding concentrations of acid fuchsin were analyzed in a double beam UV-Vis spectrophotometer (Spectra scan UV 2600, Chemito, India). The effect of different parameters like pH, salt concentration, temperature and initial concentration on the percentage of the dye removal was determined by applying box behnken design.

Box behnken design: The response is taken as the percentage removal of dye and was calculated by using the formulae:

$$\text{Removal} = \frac{C_0 - C_t}{C_0} \times 100 \tag{1}$$

where, C_0 and C_t are the dye concentrations in mg L^{-1} at the beginning and at any time t (min), respectively.

Box Behnken Design (BBD): The Box Behnken method was used to determine the interaction between adsorption process parameters and response variable. Temperature (A), pH (B), salt (C) and initial concentration (D), were chosen as the independent input variables and the percent removal of fuchsine acid (Y) was taken as the response or dependent variable. The response variables were correlated to the independent variables by the following polynomial equation:

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta ij x_i x_j \tag{2}$$

where, Y is the response and β_0, β_i, β_{ii} and β_{ij} are coefficients of the intercept, linear, square and interaction effects, respectively. The regression model was statistically analyzed by using design expert software (Stat-Ease, Inc., version 8.0.4, Minneapolis, USA). The optimum values of the process parameters were obtained from numerical optimization. In the BBD the ranges of input variables are provided as per their higher and lower values and a design matrix is predicted by the software after performing possible permutations and combinations.

Kinetic study: Once, the experiments are carried out according to the design matrix, different experimental values of output variables are put in the design matrix to determine the optimum experimental conditions. Besides, The adequacy of the models was justified by the Analysis of Variance (ANOVA). It can be predicted from ANOVA that the parameters having probability of F-statistics value less than 0.05 are significant.

RESULTS AND DISCUSSION

Characterization of the prepared CAC pellets: The surface area, total pore volume and average pore size of CAC pellets were determined by BET surface area analyzer and the values were found to be 294.1 m^2 g^{-1}, 0.2643 cc g^{-1} and 35.95 Å, respectively (Table 1). The surface morphology of CAC pellets was determined by using SEM image. It can be seen from Fig. 1 that Al particles are uniformly dispersed on the surface of CAC. The FTIR spectrum of CAC pellets is shown in Fig. 2. The presence of various surface functional groups such as amine and alkenes were detected at 1019 and 1020 cm^{-1} of FTIR spectrum. Besides, the C-H and O-H bonds were detected at 1422 and 3350 cm^{-1}, respectively (Al-Jlil, 2010).

Kinetic study: In order to investigate the controlling mechanism for acid fuchsin adsorption, pseudo first and second order kinetic model were investigated. The equation corresponding to the pseudo-first-order kinetic model is expressed by Eq. 3-4 (Amin, 2009; Sharma and Goyal, 2010):

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (3)$$

Table 1: Results of Bet surface area analysis

Adsorbent	BET surface area (m^2 g^{-1})	Total pore volume (cc g^{-1})	Average pore size (Å)
CAC pellet	294.1	0.2643	35.95

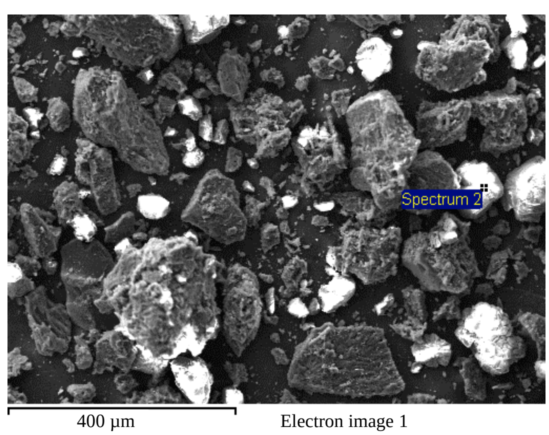

Fig. 1: The SEM image of CAC pellet

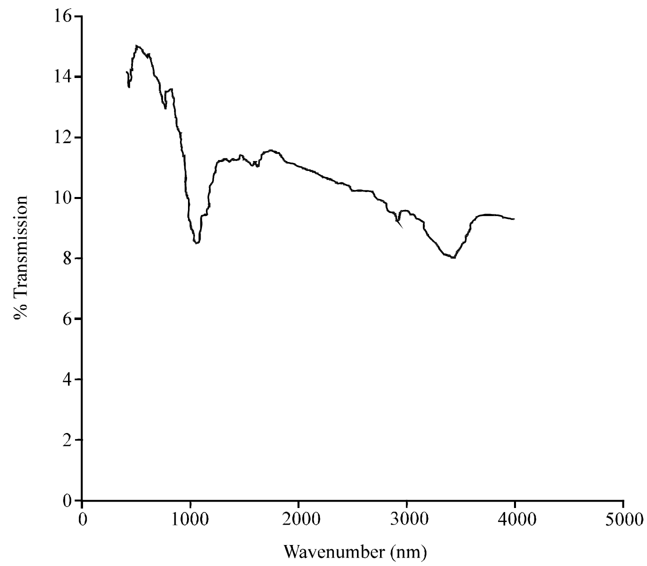

Fig. 2: The FTIR spectra of CAC pellet

Table 2: Adsorption kinetic constant, modeled by a pseudo first-order equation

	$q_{eq,exp}$	$q_{eq,\ calc}$	$q_{eq,exp}$	$q_{eq,\ calc}$	$q_{eq,exp}$	$q_{eq,\ calc}$		
Time	-------(50 mg L^{-1})-------		-------(100 mg L^{-1})-------		-------(150 mg L^{-1})--------		K_2 (mg L^{-1})	R^2 (mg L^{-1})
10	26.94	29.06	37.24	38.24	41.05	54.04	0.006 (50)	0.997 (50)
20	31.57	33.83	44.26	50.69	60.00	70.10	0.0013 (100)	0.987 (100)
35	33.68	36.39	53.42	58.91	77.89	80.45	0.0011 (150)	0.991 (150)
50	37.47	37.52	60.44	63.00	82.10	85.46		
70	39.15	38.32	63.49	66.06	84.73	89.16		
95	39.15	38.86	70.51	68.24	86.84	91.78		
120	39.15	39.18	71.12	69.57	91.05	93.38		

k_2 is the equilibrium rate constant for pseudo-first and second-order kinetics (g mg^{-1} min^{-1}); $q_{eq,exp}$ $q_{eq,\ calc}$ are the experimental and calculated equilibrium adsorption capacities in mg g^{-1} for second order kinetics

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (4)$$

where, q_e and q_t refer to the amount of dye adsorbed (mg g^{-1}) at equilibrium and at any time, t (min), respectively. The k_1 (min^{-1}) and k_2 (g mg^{-1}-min) are the equilibrium rate constant for pseudo-first and second-order kinetics. The experimental data were fitted well with the second order kinetics. The pseudo second order model fitted at different dye concentrations (50, 100 and 150 mg L^{-1}) is shown in Table 2. It is observed that the adsorption of acid fuchsin increased with increasing initial concentration and an adsorption capacity of 91 mg g^{-1} was reached after 120 min for the initial concentration of 150 mg L^{-1}, whereas, the adsorption capacity was found to be 39.15 mg g^{-1} for the initial concentration of 50 mg L^{-1} at the same time interval. So, the initial concentration has the significant effect on the adsorption. The values of the rate constant (k_2) at different acid fuchsin concentration are also shown in Table 2. It is observed that at the lower range of initial concentration the k_2-values increased, whereas, at higher concentration the k_2-values became almost constant. The values of good regression coefficient (R^2) were obtained for each concentration.

The adsorption isotherm: The equilibrium data were fitted to Freundlich, Langmuir and Tempkin isotherm. The Langmuir isotherm represents the unimolecular adsorption of the adsorbate molecule on the adsorbent surface (Ozturk and Kavak, 2005).

The model can be expressed as:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

where, K_L is the Langmuir constant related to the energy of adsorption (L mg^{-1}) and q_m is the maximum amount of adsorption corresponding to complete monolayer coverage on the surface (mg g^{-1}). Similarly the Freundlich isotherm can be used for non-ideal adsorption that involves heterogeneous surface energy systems (Ergene *et al*., 2009) and is expressed by the following equation:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (6)$$

where, K_F is a rough indicator of the adsorption capacity and 1/n is the adsorption intensity. Similarly, Tempkin isotherm describes the heat of adsorption and interaction between adsorbent-adsorbate molecules (Anbia *et al*., 2010). The Tempkin isotherm can be expressed as:

$$q_e = K_m \log (hC_e) \quad (7)$$

The experimental data fitted with different adsorption isotherm are shown in Fig. 3. It is observed that the equilibrium behavior was well described by the Langmuir isotherm model and

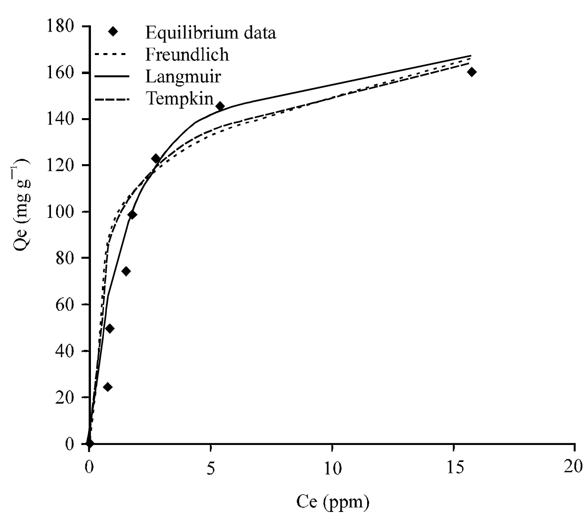

Fig. 3: Fitting of equilibrium models for fuchsin acid (volume-100 mL, rpm-2000, pH-6.01, temperature-303 K)

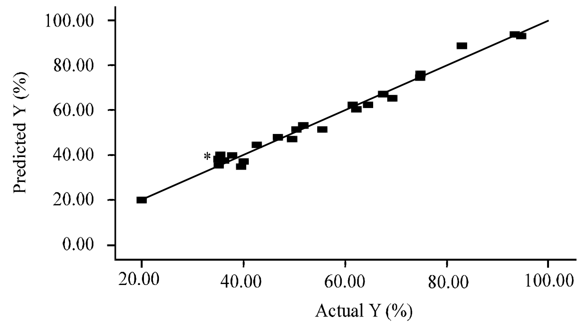

Fig. 4: The plot between predicted and actual value of percent dye removal. *Points plotted together factual and predicted values of percent dye removal

Table 3: Equilibrium model parameters

Isotherm model	Kinetic parameters
Freundlich $q_e = K_F C^{1/n}$	KF = 95.46885; n = 4.99
Langmuir $qe = \frac{K_1 q_m C_e}{1+K_1 C_e}$	KL = 0.696; qm = 181.82
Tempkin $q_e = K_m \log (hC_e)$	Km = 25.941; h = 34.87436

corresponding monolayer adsorption capacity was found to be 181.82 mg g^{-1}. The values of parameters obtained for various adsorption isotherms are given in Table 3. It is observed from the table that a value of R^2 (0.97) in case of Langmuir isotherm is better than other isotherms. Therefore, conformation of the experimental data into Langmuir isotherm model indicates the homogeneous nature of CAC surface.

Analysis of variance

Statistical modeling and analysis of variance (ANOVA): A four factor Box-Behnken design was used to optimize the adsorption process of acid fuchsin. The design matrix proposed by BBD contained twenty seven experimental runs with three replicates at the center points. The quadratic model was suggested by the software for percentage dye removal and the corresponding model equation is as follows:

$$Y = 35.22 + 4.03A + 14.13B - 15.08C - 11.60D + 3.03AB + 2.93AC - 9.64AD + 0.96BC - 6.14BD + 9.19CD + 3.27A^2 + 14.67B^2 + 15.19C^2 + 6.59D^2 \quad (8)$$

The ANOVA of percent removal of acid fuchsin is shown in Table 4. In the present study, A, B, C, D, AD, BD, CD, B^2, C^2, D^2 are significant model terms. The plot between predicted and actual values of percent dye removal is shown in Fig. 4. It showed a well agreement between actual and predicted values of response.

Effects of pH, salt, concentration and temperature on percent removal of acid fuchsin: The combined effect of temperature (A) and pH (B) on percent removal of acid fuchsin (Y) is shown in Fig. 5a. It is observed from Fig. 5a that percent removal of acid fuchsin increased with increase in solution pH and temperature upto 32°C and 64.71% removal was achieved with a solution pH and temperature of 32°C.

Table 4: The analysis of variance of percent dye removal

Source	Sum of squares	df	Mean square	F-value	p-value Prob>F
Model significant	9766.12	14	697.58	49.13	< 0.0001
Temperature (A)	194.89	1	194.89	13.72	0.0030
pH (B)	2394.85	1	2394.85	168.65	< 0.0001
Salt (C)	2729.49	1	2729.49	192.22	< 0.0001
Concentration (D)	1614.85	1	1614.85	113.72	< 0.0001
AB	36.75	1	36.75	2.59	0.1337
AC	34.31	1	34.31	2.42	0.1461
AD	371.44	1	371.44	26.16	0.0003
BC	3.70	1	3.70	0.26	0.6190
BD	150.72	1	150.72	10.61	0.0069
CD	337.85	1	337.85	23.79	0.0004
A^2	56.90	1	56.90	4.01	0.0684
B^2	1147.40	1	1147.40	80.80	< 0.0001
C^2	1231.12	1	1231.12	86.70	< 0.0001
D^2	231.44	1	231.44	16.30	0.0016

Source is the name of term analyzed; df is degree of freedom; Mean square is sum of square divided by degree of freedom; F-value is the ratio of mean square for the individual term to the mean square for the residual. The Prob>F value is the probability of F-statistics value and is used to test the null hypothesis

Effects of parameters: As the pH of the adsorbate solution increases the adsorbent surface become more and more basic which in turn enhance the electrostatic force of attraction between the cationic adsorbent surface and the anionic dye molecules leads to higher removal percentage (Chun *et al*., 2004). The effects of salt concentration (NaCl) (C) and temperature (A) on percent dye removal is shown in Fig. 5b. It can be depicted from Fig. 5b the percent removal increased with decrease in salt concentration and increase in temperature and 66.46% removal was achieved with a temperature of 32°C and at approximately zero salt concentration. The effect of ionic strength on percent removal of dye was studied at various pH ranging from 2-8. Theoretically, electrostatic forces between the adsorbent surface and adsorbate ions become attractive when the adsorbent surface will get positively charged. In such a situation, an increase in ionic strength will decrease the dye removal capacity. Conversely, when the electrostatic attraction is repulsive, an increase in ionic strength will increase adsorption (Alberghina *et al*., 2000). The experimental data from this study followed the first convention, as the adsorption of positively charged dye molecules on negatively charged activated carbon decreased with NaCl addition. Consecutively the effects of solution pH and salt concentration are shown in Fig. 5c. Here also the percent removal of acid fuchsin was varied in the same way with pH and salt concentration as discussed earlier. The effect of salt concentration and solution pH was reconfirmed by Fig. 5c. It is seen from Fig. 5c that 82.99% acid fuchsin removal can be achieved with a solution pH of 7.5 and in absence of salt. The combined effects of initial concentration (D) and temperature (A) are shown in Fig. 5d and it was noticed that the dye removal capacity increased with decrease in initial concentration and in increase in temperature. A removal capacity of 51.19% was observed with an initial concentration of 10 mg L^{-1}. As the concentration of the adsorbate solution increase, large number dye molecules get adsorbed on the adsorbent surface but, after a certain period of time saturation reached when no further adsorption takes place. With a high initial dye concentration the adsorbent surface gets saturated with a very shorter period of time results into lower dye removal capacity (El-Sayed *et al*., 2011). The concentration dependency of dye removal percentage was further

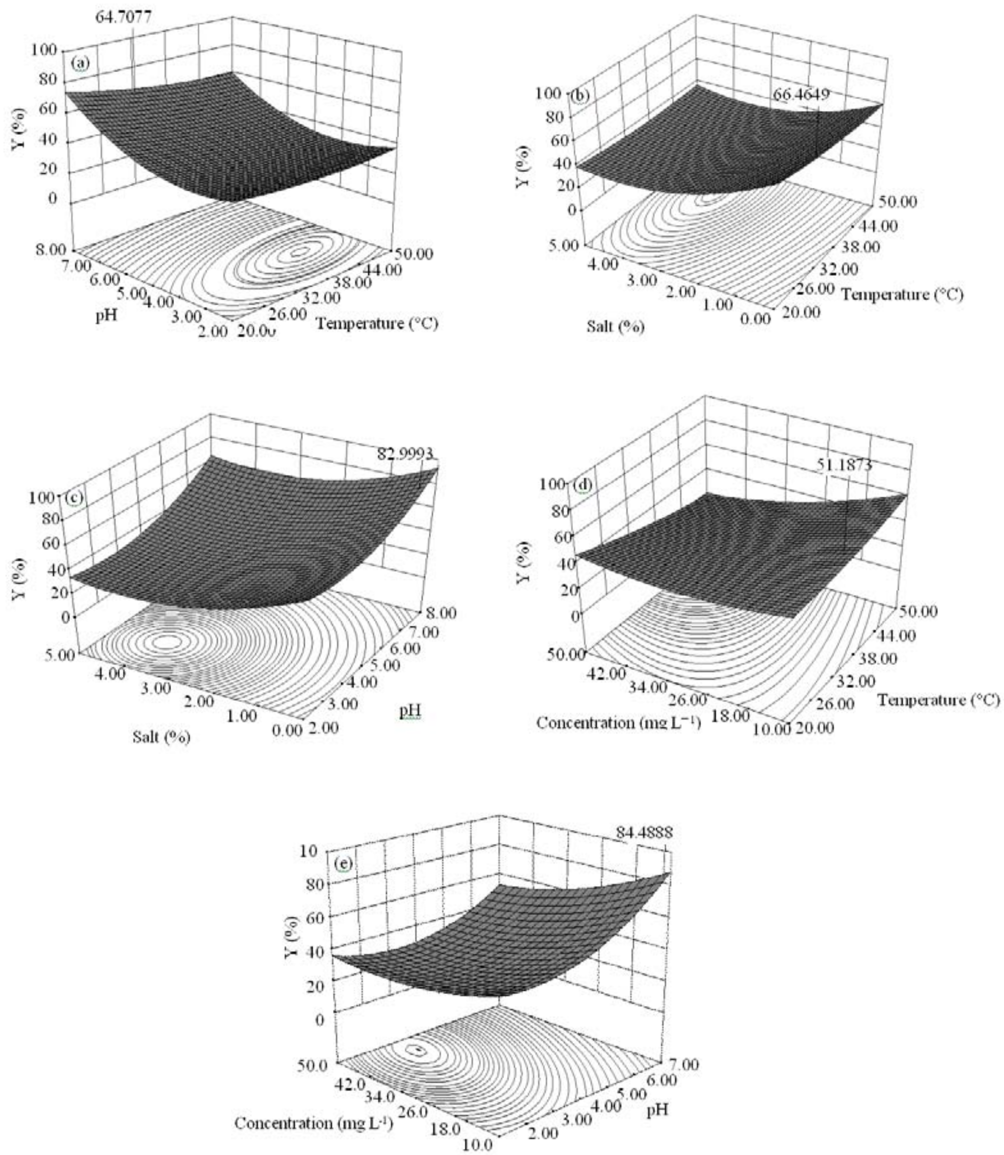

Fig. 5(a-e): The effects of different parameters on percent dye removal (a) effects of temperature and pH, (b) effects of salt and temperature, (c) effects of pH and salt, (d) effects of initial concentration and temperature and (e) effects of initial concentration and pH

verified by studying the combined effects of concentration and pH (Fig. 5e). In this case also the maximum removal (84.48%) was obtained at lower initial concentration (10 mg L^{-1}) and higher solution pH (7.5). Temperature had a significant effect on the removal of acid fuchsin. The adsorption capacity of acid fuchsin decreased at higher temperatures which indicates exothermic nature of the adsorption process. Moreover, the adsorption processes are exothermic in nature due to release of high amount of heat due to bond formation between solute and adsorbent (Faust and Aly, 1987).

CONCLUSION

The carbon alumina composite pellet had shown a good removal capacity for the dye acid fuchsin. With the implementation of this composite adsorbent some of the major drawback of the commercial adsorbents like high cost and low resistivity can be easily overcome. Besides, the presence of alumina in the pellet itself offers high mechanical properties. Many efforts has been made so far to remove various textile dyes form different industrial effluents but very little attention has been given on the removal of acid fuchsin which is largely present in the medicine industry waste.

The present investigation focuses our attention on this particular problem. The adsorption of acid fuchsin is influenced by various adsorption process parameters such as temperature, pH, salt concentration and initial dye concentration and effects of these parameters on the removal percent of acid fuchsin is studied through response surface methodology. The adsorption process is successfully optimized by using a four factor Box-Behnken methodology.

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