

Investigation of Aniline Adsorption onto Spherical Carbon: Optimization Using Response Surface Methodology

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ABSTRACT

In the present study, spherical carbon was used to optimize the removal efficiency for aniline by using Response Surface Methodological approach. The carbon sample was obtained by the commercial activated spherical carbon and treated with phosphoric acid and sodium hydroxide. The surface structure of spherical carbon was analysed by Scanning Electron Microscopy coupled with Energy Dispersive X-ray Analysis. The effect of four parameters, that is, pH of the solution (2-11), initial aniline concentration (10-70 mg/L), temperature (25-55°C) and adsorbent dose (0.02-0.3 g/100 mL) was optimized for the removal of aniline. A Box-Behnken experimental design was employed for the optimization of adsorption of aniline on spherical carbon to ensure high adsorption efficiency in a low adsorbent dose and high initial aniline concentration. The analysis of variance showed a high coefficient of determination value ($R^2 = 0.9749$) and satisfactory prediction second-order model was derived. Maximum aniline removal efficiency was predicted and experimentally validated.

Key words - Aniline, Adsorption, Box-Behnken design, Response Surface methodology, Spherical carbon.

I. INTRODUCTION

A large number of the volatile organic compounds have serious health problems and some of them are cancer-causing. The removal of toxic contaminants from aqueous waste streams is currently one of the most important environmental issues being researched. To remove these compounds from chemical and industrial wastewater, activated carbons are widely used in industry [1, 2]. Aniline toxicity in wastewater is largely contributed by industries like dyes, varnishes, herbicides and explosives. Once it enters into the food chain through air or contaminated drinking water, it damages haemoglobin in the blood. Exposure to aniline causes nervous conditions such as euphoria and headache. Continuous exposure increases ataxia and weakness [3]. The permissible limit for aniline in water is 10 ppm [4]. Consequently, there has been a growing interest in developing processes of removing this compound from water. Adsorption is often the preferred separation process since it can be used for removing variety of organics from aqueous system [5].

Batch mode adsorption studies were done using conventional method of analysis, which is accurate but time consuming. So, in order to obtain optimized variable value in minimum number of experiments, Response Surface Methodological (RSM) approach was adopted for investigating the adsorption of aniline onto spherical carbon. Several researchers have used RSM for optimization of the adsorption process at batch mode for removal of pollutants [6-8]. This has facilitated the optimization of process variables in minimum number of experiments [9, 10].

RSM is a collection of statistical and mathematical techniques used for developing, improving and optimizing any process or product design or system or for that matter any experiment under study. Principal RSM used in experimental design are central composite, Box-Behnken and Doehlert design. Box-Behnken is a spherical revolving design requires an experiment number according to $N = k^2 + k + cp$ where k is the factor number and cp is the replicate number of central point. It has been applied for the optimization of several chemical and physical processes [11]. It was used in the empirical study of the relationship between measured responses and a number of input variables with the aim of optimizing responses [12]. The methodology has provided a new prospective approach for investigating the profundity of carbon science, in particular, adsorption science, in terms of better reproducibility of results and process optimization with minimum number of experiments. This methodology is widely used in chemical engineering, notably to optimize the adsorption process [13, 14].

The present work is concerned with the adsorption of aniline onto commercial spherical carbon and modified carbons. The investigation of combined effect of four process parameters like pH, initial aniline concentration, temperature and adsorbent dose from aqueous solution onto spherical carbon using Box-Behnken model experimental design by Design Expert Version 8.0.7.1.

II. MATERIALS

2.1 Adsorbent

Polystyrene sulphonate based activated spherical carbon procured from Vijay Sabre India Pvt.

Ltd., Mumbai, India, was used as a precursor adsorbent in this study. The samples were washed with double distilled water to remove fines and impurities, dried at 105°C and named as ASC.

2.2 Treatment with Phosphoric acid

About 15g of carbon was poured into a beaker containing 12 mL of phosphoric acid to obtain an impregnation mass ratio of 1:1. The volume was topped up to 35 mL by addition of distilled water. Then the mixture was stirred thoroughly before drying in the oven at 110°C for 24 hours. After drying, the samples were placed in crucibles and kept at a temperature of 700°C in an inert atmosphere (N₂). For the washing process, 1M potassium hydroxide (KOH) was used. About 50 mL of 1M KOH was poured into a beaker containing carbon and mixed well. Then the carbon was separated using filter paper. Washings were carried out till the sample fell in the pH range of 6-6.5. The resultant samples were dried at 105°C for 24 hours and named as PSC.

2.3 Treatment with sodium hydroxide

The adsorbent was treated with 2M sodium hydroxide and kept at a temperature of 120°C for 2 hours. After 2 hours, the samples were kept at an inert atmosphere (N₂) at 700°C for 1 hour. The samples were then washed with 1M HCl. It was then repeatedly washed with hot distilled water until the washed water became neutral. The carbon was oven dried at 80°C for 6 hours and stored in an airtight container and named as SSC.

III. METHODS

The adsorbents were analysed for various parameters like pH, ash content and moisture content by standard methods [15]. The surface area measurements of the adsorbents were obtained using BET method with nitrogen gas at 77K using Smartsorb surface area analyser [SMART SORB 92/93, Smart Instruments Ltd]. The surface functional groups in the adsorbent were measured using Boehm titration method [16]. Scanning Electron Microscopy (SEM) was employed to observe the surface morphology of the adsorbents using a model Quanta 200 FEG, Japan, in combination with Energy Dispersive X-ray analysis (EDX) for qualitative analysis of elemental constituents of the adsorbents.

A stock solution of aniline (1000 mg/L) was prepared by dissolving aniline solution (AR grade) in 1.0 L deionized water. All working solutions of desired concentrations were obtained by successive dilution of this stock solution. The pH of the solution was adjusted after adding the adsorbent to required value by adding either 0.01M HCl or 0.01M NaOH using pH meter after calibrating with pH 4.0, 7.0 and 10.0 buffers. The aniline concentration in the test solution was determined by Gas Chromatograph (Agilent 7890A, United States).

3.1 Adsorption Experiments

The experiments were performed to study the removal of aniline from aqueous solution. A predetermined amount of adsorbent was added to 100 mL solution of known concentration in 250 mL Erlenmeyer flasks at temperature 25 ± 2°C for 420 minutes. At predetermined time interval, the adsorbent was separated by centrifugation at 4000 rpm at 10 minutes. Samples were taken out at regular intervals and the residual aniline concentration in the solution was determined using Gas Chromatograph. The batch process was used in this study so that there is no need for volume correction. Batch adsorption experiments were performed by contacting the three samples of different weights (0.02 – 0.3 g) with 100 mL of the aqueous solution of different initial concentrations (10 – 70 mg/L) at solution pH (2-11) and at different temperatures (25 - 55°C). The remaining concentration of aniline in each sample after adsorption at different time intervals was determined by gas chromatograph. The percent aniline removal (R%) was calculated for each run by following expression (Eq. 1):

$$R(\%) = \frac{C_i - C_e}{C_i} * 100 \quad (1)$$

Where C_i and C_e were the initial and final concentration of aniline in the solution in mg/L. The adsorption capacity (mg/g) of SSC for each concentration of aniline at equilibrium was determined as follows (Eq. 2):

$$q_e(\text{mg/g}) = \frac{(C_i - C_e)V}{M} \quad (2)$$

Where C_i and C_e as stated above, V is the volume of the solution in mL and M is the mass of the adsorbent (g).

3.2 RSM and Variables Optimization

Box-Behnken model is preferred as design model since relatively few combinations of the variables are adequate to estimate potentially complex response function. This design is an independent, rotatable or nearly rotatable quadratic design in which the treatment combinations are at the midpoints of the edges of the process space and at the centre. It basically involves the process of planning and designing an experiment so that the appropriate data may be collected which is then analyzed and interpreted, resulting in valid and objective conclusions. In a statistically designed experiment, we simultaneously vary the factors involved in an experiment at their respective levels so that a large amount of information can be gained with minimum number of experimental trials. The optimization involves three major steps [10]: (a) Performing statistically designed experiments, (b) Estimating the coefficient in a mathematical model and predicting the response and (c) Checking the validity of the model.

In the present study, RSM was used in the empirical study of the relationship between the measured responses and a number of input variables with the aim of optimizing response. Percentage removal of aniline is the response of the system while the four process parameters, adsorbent concentration [0.02-0.3 g/100 mL], pH [2-11], temperature [25-55°C] and initial adsorbate concentration [10-70 mg/L] were independent variables.

The four process variables viz., initial adsorbate concentration, pH, adsorbent dosage and temperature are represented by X_1 , X_2 , X_3 and X_4 respectively. These original variables have been transformed as coded variables x_1 , x_2 , x_3 and x_4 , which are usually defined to be dimensionless with mean zero and the same standard deviation [17]. This transformation is done by the following Eq. (3):

$$X_{ij} = \frac{X_{ij} - \left[\frac{\max X_{ij} + \min X_{ij}}{2} \right]}{[(\max X_{ij} - \min X_{ij}) / 2]} \quad (3)$$

where $i = (1, 2, 3 \dots n)$ variables and $j = (1, 2, 3 \dots N)$

A second order polynomial model with interaction terms was fit to the experimental data obtained from the experimental runs conducted on the basis of Box-Behnken experimental design model [18]. The system is stated by the following Eq. (4):

$$Y = b_0 + \sum b_i X_i + \sum b_{ii} X_i^2 + \sum b_{ij} X_i X_j \quad (4)$$

It results in all the values of X_1 , X_2 , X_3 and X_4 falling between -1 and +1. As shown in the Table 3.1, low, middle and high levels of each variable are designated as -1, 0 and +1.

Table 3.1 Different variables and levels used in the experiment study

Variables	Low level	Middle level	High level
Initial concentration (mg/L), X_1	10 (-1)	40 (0)	70 (+1)
pH, X_2	2 (-1)	6.5 (0)	11 (+1)
Temperature (°C), X_3	25 (-1)	40 (0)	55 (+1)
Adsorbent dose (g/100 mL), X_4	0.02 (-1)	0.16 (0)	0.3 (+1)

where Y is the percentage of adsorption of adsorbate, b_0 the offset term, b_i the first orders main effect, b_{ii} the second order main effect and b_{ij} the interaction effect. In total, 29 experiments are needed to calculate 14 coefficients of the second-order polynomial equation which was fitted on the experimental data (Table 3.2).

Table 3.2 Box-Behnken design matrix for the variables with the observed response for aniline removal

Experimental run	Variables				Response % removal of aniline, Y
	Initial Conc. (mg/l), X_1	pH, X_2	Temperature (°C), X_3	Adsorbent dose (g/l), X_4	
1	40	6.5	40	0.16	79.8
2	40	11.0	25	0.16	77.3
3	70	6.5	55	0.16	62.9
4	10	6.5	25	0.16	99.8
5	40	2.0	40	0.30	55.3
6	40	2.0	25	0.16	70.3
7	10	6.5	40	0.02	78.2
8	40	6.5	40	0.16	79.8
9	40	6.5	55	0.02	48.6
10	10	2.0	40	0.16	51.5
11	40	2.0	40	0.02	40.7
12	40	2.0	55	0.16	43.1
13	40	6.5	25	0.30	98.1
14	40	6.5	25	0.02	92.5
15	40	11.0	40	0.02	42.4
16	40	11.0	55	0.16	42.9
17	70	11	40	0.16	55.6
18	40	11	40	0.3	49.8
19	40	6.5	55	0.30	71.1
20	40	6.5	40	0.16	79.8
21	10	11.0	40	0.16	34.4
22	70	2.2	40	0.16	37.8
23	70	6.5	25	0.16	95.7

24	70	6.5	40	0.30	77.8
25	10	6.5	40	0.3	71.9
26	40	6.5	40	0.16	79.8
27	10	6.5	55	0.16	72.6
28	40	6.5	40	0.16	79.8
29	70	6.5	40	0.02	51.9

IV. RESULTS & DISCUSSION

4.1 Characterization of adsorbents

Physico-chemical characterization of adsorbents were performed to obtain a better interpretation of the mechanism involved during the adsorption process and explore the changes in the physical (surface area), chemical properties (ash, pH) of the adsorbents after chemical treatment. The physico-chemical properties of the adsorbents are given in Table 3.

Surface area is the most important micro-structural parameter of the adsorbents for defining their properties [19]. In this study, the adsorbents were sieved to get the particle size of 300 μm in order to provide more adsorption sites for adsorption. The surface area of ASC was found to be higher i.e. 1156 m^2/g as compared to SSC and PSC which had surface area 1081 and 923 m^2/g respectively (Table). PSC showed lesser surface area owing to the phosphoric acid treatment causing specific surface area to decrease [20]. The observed difference in surface area among the investigated adsorbents may be attributed to the type of starting material and chemical treatment provided [21]. The pore diameter and pore volume of ASC is high compared to that of SSC and PSC (Table 3.1). This indicates that chemical treatment decreases the surface area as well as the pore structure of an adsorbent.

The pH_{pzc} values of the adsorbents indicate whether they are acidic or basic in nature. The pH_{pzc} of SSC was basic in nature i.e. 9.6 (Table 3.1). This is because of the NaOH followed by thermal treatment, whereas ASC is slightly acidic ($\text{pH} = 5.3$) and phosphoric acid treated PSC is acidic in nature, i.e. 4.1. The acidic nature of the carbon adsorbents may be attributed to the presence of carboxyl, phenolic and other acidic functional groups on their surface.

Acid treatment increases the surface groups mainly carboxylic acids, anhydrides, lactones, phenol and carbonyls. Most of these oxygen-containing groups have an acid character, leading to acidic surface for the adsorbent PSC. The basicity values decrease with the increase of the amount of oxygen-containing surface groups in PSC as compared with ASC (Table 4.1).

In SSC, the basicity values increase with the increase of the basic character groups. The thermal treatment enables the fixation of oxygen in the active sites generated by the decomposition of carboxylic

acid, lactone and phenol groups. The new oxygen-containing surface groups are basic pyrone-type groups, which results from the combination of the ether-type oxygen groups just formed and the remaining carbonyl groups [22-24]. Thus, PSC has the highest acid character and SSC, the most basic one. ASC has an acid character as well.

Table 4.1 Characteristics of the adsorbents

Parameter	ASC	PSC	SSC
Raw material	Sulphonated polystyrene	Sulphonated polystyrene	Sulphonated polystyrene
BET surface area, m^2/g	1156	923	1081
Pore diameter (\AA)	20.25	17.78	18.26
Total pore volume (V_{tot}) (cc/g)	0.6215	0.5748	0.6166
Ash content (%)	4.69	1.91	2.12
Moisture content (%)	4.15	4.67	4.39
pH_{pzc}	5.3	4.1	9.6
Particle size (μ)	300	300	300
Acidity (meq/g)	0.625	0.717	0.354
Basicity (meq/g)	0.284	0.211	0.549
Basicity – acidity (meq/g)	-0.341	-0.506	0.195

SEM technique was used to provide direct observation of changes in the surface morphology of three adsorbents. Fig. 3.1 shows SEM photographs of ASC, PSC and SSC at a magnification of 6000x and at a resolution of 5 μm . It was observed from the micrographs that the external surface of the adsorbents is made up of rough and multilayer surface, exhibiting a heterogeneous structure with irregular morphology in terms of shape and size. The SEM images show texture and porous structure of adsorbents having dense agglomerated cluster type morphology.

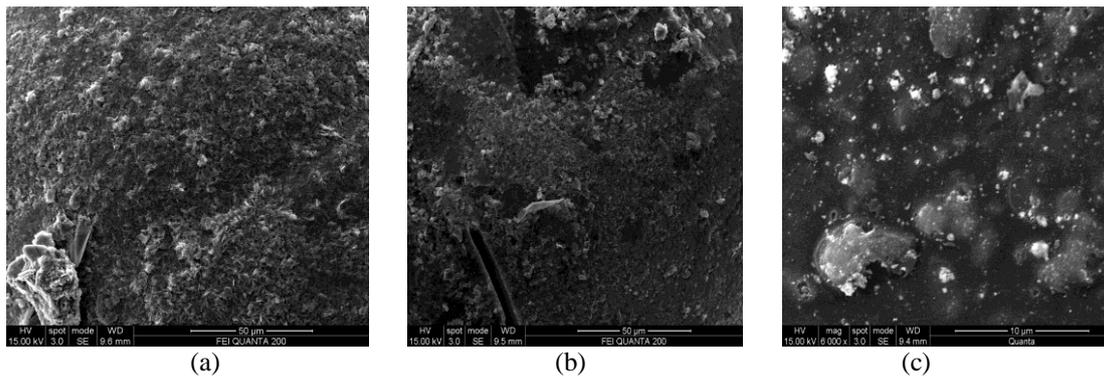


Figure 3.1 SEM micrographs of (a) ASC, (b) PSC and (c) SSC

Another major demarcation found in the three adsorbents was a difference in the elemental composition as shown by EDX. Table 4 shows the elemental composition for the three adsorbents. It is clearly seen that carbon percentage was more in ASC and SSC. The ash content proves the same results that the carbon content is high in ASC and SSC (Table 3.1). The percentage of oxygen was more in PSC and proves the presence of oxygen containing groups. It was found that the carbon percentage had decreased significantly from 94.38% in ASC, 71.1% in PSC and 89.33% in SSC (Table 4.2). Subsequently, the oxygen percentage increased from 4.2% to 22.97% in PSC and 7.19% in SSC. Furthermore, the presence of Aluminium was indicated in the spectra of three adsorbents. The presence of Phosphorous in PSC and Sodium in SSC is due to the fact that the adsorbent samples were treated with phosphoric acid and sodium hydroxide respectively.

Table 4.2 Elemental composition of adsorbents

Elements	ASC (%)	PSC (%)	SSC (%)
Carbon	94.38	71.10	89.33
Oxygen	4.20	22.97	7.19
Aluminium	1.42	0.41	0.72
Phosphorous	-	5.11	-
Sodium	-	-	1.84

4.2 Adsorption Isotherms

Langmuir and Freundlich isotherm models were used in the present study to provide an objective framework to the generated equilibrium adsorption data. Out of these two investigated models discussed above, the Langmuir model fitted well to the adsorption data inferred from the high R^2 value. The results of the models are given in the Table 4.3.

The results of adsorption kinetics showed that pseudo second order equation was able to better describe the adsorption of aniline molecules as evidenced from the correlation coefficient values as well as better predicted value for q_e than those of first order equation given in Table 4.4.

Aniline adsorption onto SSC shows higher adsorption than ASC and PSC, as seen by comparing

Q_0 values for both the adsorbents (Table 4.3). Hence, justify the validity of the thermal treatment modification process for spherical carbon and optimize the four parameters for SSC.

Table 4.3 Adsorption constants for Langmuir and Freundlich isotherm models

Adsorbent	Langmuir Parameters			Freundlich Parameters		
	q_0 (mg/g)	b (L/mg)	R^2	K (mg/g)	n (L/mg)	R^2
ASC	108.0	0.1283	0.994	12.02	1.125	0.973
PSC	93.59	0.1598	0.986	12.59	1.147	0.970
SSC	127.0	0.1006	0.992	11.39	1.107	0.974

Table 4.4 Adsorption constants of pseudo first and second order models

Adsorbent	q_e (exp) (mg/g)	Pseudo-first order model			Pseudo-second order model		
		q_e (cal) (mg/g)	k_1 (min ⁻¹)	R^2	q_e (cal) (mg/g)	k_2 (g/mg/min)	R^2
ASC	93.14	0.66 92	0.00 78	0.94 33	116.2 8	0.0001	0.978 2
PSC	58.32	0.55 78	0.00 78	0.96 39	71.94	0.0001	0.979 9
SSC	119.3 2	0.74 71	0.01 01	0.82 77	138.8 9	0.0001	0.981 8

4.3 RSM approach

Box-Behnken model was used as experimental design and a statistically practicable second order polynomial equation was fitted to model the exhibited response-variable relationship. Response surfaces were plotted based on the fitted second order polynomial equation.

An empirical relationship between the response and the input variables expressed by the following fitted second order polynomial equation (Eq. 5):

$$Y = 78.20 - 2.22X_1 + 0.31X_2 - 16.04 X_3 + 5.81X_4 + 8.72X_1X_2 - 1.4X_1X_3 + 8.05X_1X_4 - 1.8X_2X_3 - 1.8X_2X_4 + 4.22X_3X_4 - 3.76X_1^2 - 27.39 X_2^2 - 6.84 X_3^2 - 5.24X_4^2 \quad (5)$$

Above polynomial Eq. (5) for aniline was applied for response surface estimation for obtaining optimized condition for maximum adsorption percentage. The actual and predicted adsorption of aniline percent is shown in the Fig. 4.2. Actual values are the ones which are measured response data for the particular run and the predicted values are the evaluated from the model.

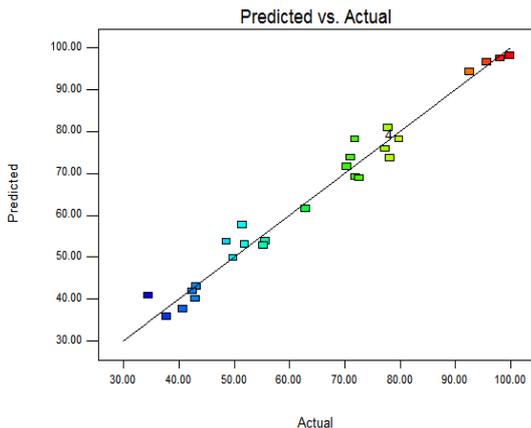


Figure 4.2 Actual and predicted plot for the adsorption of Aniline

The values of R^2 and R^2_{adj} for aniline were found to be 0.9749 and 0.9497 respectively, which indicates that there is correlation between the observed and the predicted values. Moreover, the standard deviation between the measured and the modeled results is 4.31%. This means that regression model provides an excellent explanation of the relationship between the independent variables and response.

4.4 Statistical analysis

The ANOVA (Table 4.5) shown that the equation adequately represented the actual relationship between the response and the significant variables. The model is considered to be statistically significant because the associated Prob.>F value for the model is lower than 0.05. The lack-of-fit term is non-significant as it should be. The non-significant value of lack of fit (more than 0.05) showed that the quadratic model was valid for the present study [8].

Table 4.5 Analysis of variance (ANOVA) for quadratic model for aniline adsorption

Source	Sum of square	DF	Mean square	F-value	Prob. >F
Mean	1.262E+005	1	1.262E+005		
Linear	3553.41	4	888.35	3.14	0.0329
2FI	668.87	6	111.48	0.33	0.9137

Quadratic	5864.22	4	1466.06	78.91	<0.0001	Suggested
Cubic	147.38	8	18.42	0.98	0.5246	
Residual	112.71	6	18.79			
Total	1.366E+005	29	4709.14			

4.5 Response Surface Estimation for the maximum removal of aniline

The interferences obtained from the response surfaces to estimate maximum removal of aniline, with respect to each variable and their effects on adsorption are given below:

4.5.1 Effect of initial concentration and pH

Adsorption experiments were carried out as per the selected model with selected range of aniline concentrations and pH to investigate the combined effect of aniline concentration and temperature on the system. RSM was used and results are shown in the form of 3-D plots. Fig. 4.3 shows the results. The initial concentration was increased from 10 to 70 mg/L and pH from 2 to 11 keeping temperature and adsorbent dose constant (40°C and 0.16 g/100 mL).

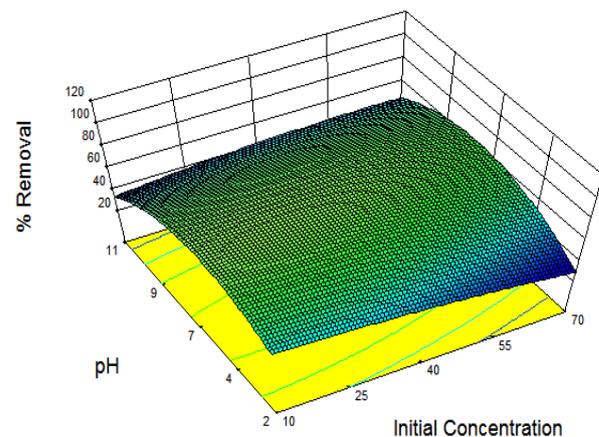


Figure 4.3 Effect of aniline concentration and pH on percentage removal of aniline

The removal of aniline decreases with increase in the concentration of aniline. pH also plays an important role for a combined effect. The maximum removal is 79.8% shows at pH 6.5. Both acidic and basic medium decreases the removal of aniline. In the acidic medium, electrostatic repulsion between positive protons of the surface of adsorbent and positive molecules of aniline (anilinium cation) leads to decrease in the removal of aniline [25]. In alkaline medium, the repulsion of negative charges on the adsorbent and aniline will reduce the adsorption of aniline. The decrease in aniline adsorption under alkaline pH condition may be due to the presence of excess OH ions and the aniline molecules for the adsorption sites [26]. The maximum removal of aniline

of 79.8% obtained at initial concentration of 40 mg/L, pH 6.5, constant temperature (40°C) and constant adsorbent dose (0.16 g/100 mL).

4.5.2 Effect of Initial concentration and Temperature

Fig. 4.4 represents the effect of temperature and initial concentration on the percentage removal of aniline under constant pH (6.5) and adsorbent dose (0.16 mg/L). The removal of aniline decreases with increase in the initial concentration. This might be due to the lack of available active sites at higher concentration resulting in increased competition for the adsorption sites and the adsorption process increasingly slows down [27].

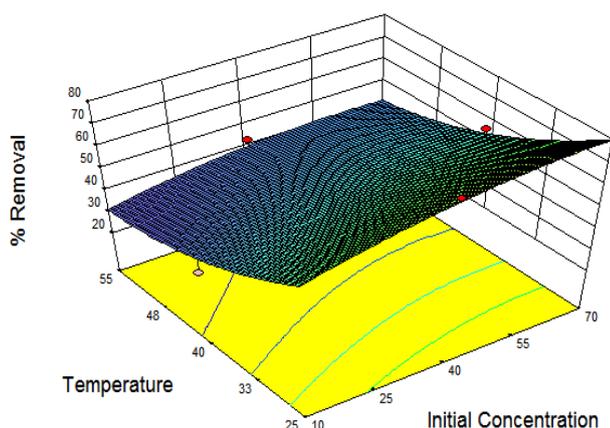


Figure 4.4 Effect of aniline concentration and temperature on percentage removal of aniline

The increase in temperature further decreases the removal of aniline. From the results, it is concluded that the process is exothermic. Since the adsorption is an exothermic process, the increase of adsorption temperature prevents the adsorption. Moreover, at high temperature, the adsorption capacity of the carbon is reduced due to possible loss of active sites. The maximum removal of aniline of 99.8% showed at temperature (25°C), initial concentration (10 mg/L), constant pH (6.5) and constant adsorbent dose (0.16 g/100 mL).

4.5.3 Effect of Initial concentration and Adsorbent dose

Combined effect of adsorbent dose and initial concentration has been analyzed (Fig. 4.5) and it has been estimated that as aniline concentration increases from 10 to 70 mg/L and adsorbent dose increases from 0.02 to 0.3 g/100mL, when pH is constant (6.5) and temperature at 40°C.

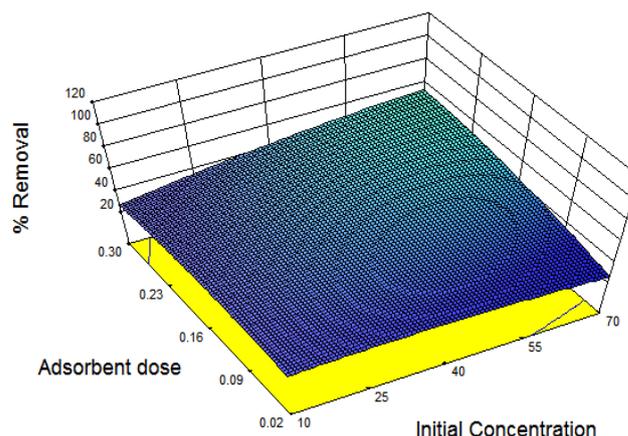


Figure 4.5 Effect of aniline concentration and adsorbent dose on percentage removal of aniline

The decreased removal of aniline with increase in its concentration may be due to the lack of adsorbent surface area to accommodate more aniline molecules. The increase in the adsorbent dose increases the removal of aniline molecules due to availability of more active sites. The maximum removal of aniline is 79.8% achieved at initial concentration (40 mg/L), adsorbent dose (0.16 g/100 mL), constant pH (6.5) and constant temperature (40°C).

4.5.4 Effect of Temperature and pH

Fig. 4.6 shows the three dimensional response surfaces of the interactive effect of temperature and pH at constant initial concentration (40 mg/L) and adsorbent dose (0.16 g/100 mL). From the figure, it is seen that increase in temperature decreases the removal of aniline. The removal of aniline decreases from 77.3 to 42.9% at pH 11 and from 70.3 to 43.1% at pH 2. The results show that the process is exothermic.

And at the same time, pH also plays a major role in the adsorption process. In both acidic as well as alkaline medium, the removal of aniline decreases. This is due to the competition with hydrogen ions in the acidic medium and hydroxide ions in the alkaline medium. The removal of aniline is high at the neutral pH medium. The maximum removal of aniline is 79.8% observed at pH 6.5, temperature 40°C, constant adsorbent dose 0.16 g/100 mL and constant initial aniline concentration of 40 mg/L.

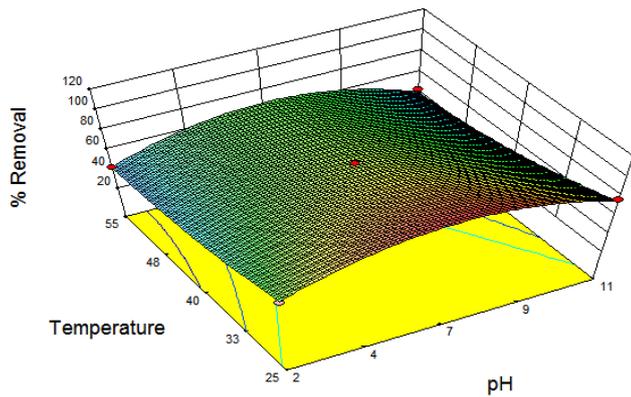


Figure 4.6 Effect of temperature and pH on percentage removal of aniline

4.5.5 Effect of pH and Adsorbent dose

Fig. 4.7 shows the combined effect of adsorbent dose and pH on the adsorption of aniline at constant temperature (40°C) and initial concentration (40 mg/L). Figure reveals that increase in adsorbent dose increases the removal of aniline. At pH 2, removal of aniline increases with increase in the adsorbent dose from 40.7 – 55.3% and at pH 11, increases from 42.4 – 49.8%. This is due to increased availability of active adsorption sites and surface area at higher adsorbent dose.

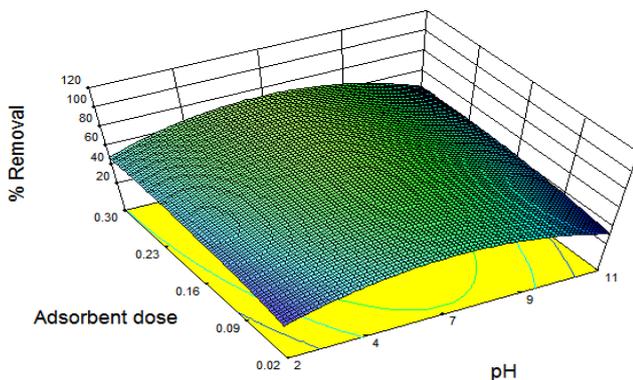


Figure 4.7 Effect of adsorbent dose and pH on percentage removal of aniline

Both acidic as well as alkaline medium shows minimum removal of aniline. And pH 6.5 shows the maximum removal of aniline at 79.8%. This is because, in acidic medium, there is competition with hydrogen ions in the acidic medium and with hydroxide ions in the alkaline medium. The maximum removal of aniline is 78% was observed at pH 6.5, adsorbent dose 0.016 g/100 mL, constant temperature 40°C and constant initial aniline concentration 40 mg/L.

4.5.6 Effect of Adsorbent dose and Temperature

The interactive effect of adsorbent dose and temperature on the adsorption of aniline at constant pH 6.5 and initial aniline concentration 40 mg/L is shown in Fig. 4.8. At 25°C, the removal of aniline increases with increase in the adsorbent dose from 92.5 – 98.1% and at 55°C, the removal increases from 48.6 – 71.1%.

It is due to the increase in surface area and adsorbent active sites.

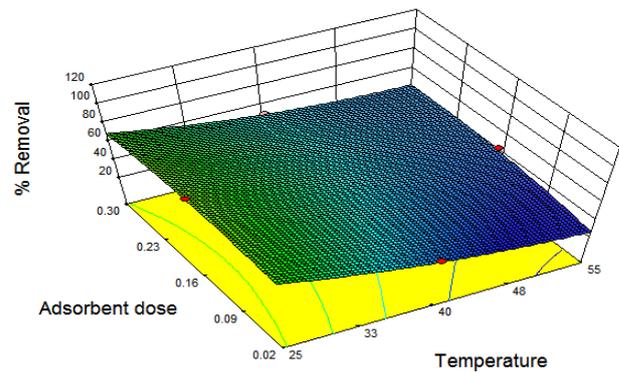


Figure 4.8 Effect of adsorbent dose and temperature on percentage removal of aniline

As temperature increases from 25 - 55°C, the removal of aniline decreases from 92.5 – 48.6% at 0.02 g/100 mL and from 98.1 – 71.1% at 0.3 g/100 mL. It reveals that increase in temperature decreases the removal efficiency of aniline. The maximum removal of aniline is 98.1% achieved at temperature 25°C, adsorbent dose 0.3 g/100 mL, constant pH 6.5 and initial aniline concentration 40 mg/L.

To support the data given by numerical modelling under optimized conditions, confirmatory experiments were conducted with the parameters suggested best for removal by the model for both aniline (Initial concentration 10 mg/L, pH 6.5, temperature 25°C and adsorbent dose 0.16 g/100 mL) and the percent removal was found to be 99.8% (Table 4.6). It was found that results are in accordance with the suggested model given by RSM software.

Table 4.6 Optimal aniline adsorption conditions for the model

Parameters	Initial concentration (mg/L)	pH	Temperature (°C)	Adsorbent dose (g/100 mL)	Response
Parameters (given by the model)	10	6.5	25	0.16	99.8
Suggested solutions	40	6.5	40	0.16	78.2
Actual results obtained after confirmation experiments	40	6.5	40	0.16	79.6

V. CONCLUSION

The study was taken with the purpose of finding the feasibility of spherical carbon for the removal of aniline from the aqueous solution by using Response Surface Methodological approach, which proves to be very effective and time saving technique for studying the influence of process parameter on response factor by significantly reducing the number of experiments and hence facilitating the optimum conditions. SSC shows high adsorption capacity than other two adsorbents. The adsorption of aniline follows

pseudo-second order kinetics. So, SSC was found suitable to optimize the adsorption of aniline from aqueous solution. The experimental results showed that under optimum conditions, adsorption of aniline onto spherical carbon is viable and technically feasible.

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