International Journal of Emerging Technology and Advanced Engineering
Website: www.ijetae.com (ISSN 2250-2459, ISO 9001:2008 Certified Journal, Volume 7, Issue 5, May 2017)

Optimization of Phenol Adsorption Characteristics through Central Composite Design

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***Abstract*— The present study is confided to eradicate phenol through batch adsorption onto the surface of chemically modified clay from an aqueous solution. The phenol adsorption process was optimized by a half fraction central composite design. It was found that the initial adsorbate concentration, adsorbent dose and contact time had most significant effect on phenol adsorption. The adsorption efficacy was found to increase with increase in initial concentration and contact time whereas it deceased with subsequent increase in adsorbent concentration due to overcrowding of the adsorbent particles. A quadratic model had been proposed to optimize the given process and the optimum values of the experimental parameters were (solution pH of 4.0, initial concentration of 120 mg/L, adsorbent dose of 2 g/L, time of 73 min and temperature of 40 °C.).**

***Keywords*—Adsorption, Adsorbate, Adsorbent, Phenol, Central composite design, Optimization.**

I. INTRODUCTION

Phenol, a carcinogenic aromatic compound, is found to have indwelling toxicity when discharged into water bodies from effluents of paints, pesticides, polymeric resins, and petroleum and petrochemical industries [1]. The phenol is regarded as one of the conceivable pollutants which over degradation can produce various toxic intermediate compounds and defilement of these intermediates can lead to severe environmental pollution [2]. Phenol vapours may cause toxic effects on eye and skin including skin irritation and burning and over inhalation it may also cause edema and adverse effect on central nervous system. Other harmful effects of phenol include sour mouth and diarrhoea in case of human being. It is also proved to be fatal for aquatic life with a limiting value of 10-24 mg/L which in case of human being may vary from 9-25 mg/L for oral consumption and 150 mg/100 mL for blood contamination. The permissible limit of phenol for drinking water is 0.5 and 0.2 mg/L as per US Environmental Protection Agency (USEPA) Central Pollution Control Board (CPCB) respectively [3].

Various conventional treatment methods for the removal of phenol from wastewater have been studied so far which includes adsorption, ion exchange solvent-extraction, chemical coagulation, oxidation, membrane separation, photo catalytic degradation, biological treatment processes [4]. But the major shortcomings of theses processes are high cost, difficulty in operation and time consuming which in turn exalts the adoption of a new technique called adsorption which implies the use of a high surface area material (adsorbent) to annihilate a pollutant from its aqueous solution even if it is present at a very trace concentration. Different adsorbents were adopted to study the phenol removal from aqueous solution such as, sugarcane bagasse, nut shells, apricot stones, coconut shell, coconut husk, and tobacco stem etc [5] but no or very little effort had been made so far to investigate the phenol adsorption characteristics onto the surface of chemically modified soil. Therefore, in the present investigation the phenol removal efficacy of chemically modified soil had been studied and the adsorption process was optimized by using central composite design.

II. EXPERIMENTAL

A. *Preparation of adsorbent*

The surface modified adsorbent was prepared by treating the normal soil collected from the bank of Ganga River with zinc acetate dehydrate (98% pure). The impregnation ratio was maintained as 1:2. The soil was first collected from the river side and then sun dried in order to evaporate the excess water content in it. Once the soil completely dried it was then grounded and treated with zinc acetate dihydrate for 12 hrs. The impregnation ratio was selected based on the previous literature survey. The treated soil is then rinse with distilled water to remove excess zinc acetate dihydrate from the adsorbent surface and then it was again dried in an air oven at 105 °C for 30 min. All the reagents are used are of analytical grade and was supplied by Merck Specialist Pvt. Ltd., Mumbai, India.

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B. Batch adsorption

The batch adsorption was consummated by preparing different initial concentration solutions of phenol prepared by dissolving prefixed amount of phenol (99% pure) in distilled water. The solutions of different initial concentration ranging from 30 - 120 mg/L were prepared by subsequent dilution of a stock solution of 1000 mg/L. The solution pH was adjusted by using dilute HCl (35% pure) and NaOH (97% pure) solution. The effects of various experimental parameters were studied by taking 50 mL of phenol solution of a particular initial concentration (30 - 120 mg/L) and then adding the appropriate amount of adsorbent (1 - 3 g/L) in it. The solution was then agitated at a particular rpm for a predetermined time and then filtered to separate the adsorbent particle. The supernatant solutions were analysed in UV-Vis spectrophotometer (Chemito, Spectrascan 200) at 270 nm. The adsorption capacity was calculated from

$$q_t = \frac{(C_0 - C_t)}{w} V$$

Where, q_t (mg/g) is the adsorption capacity, C_t is the phenol concentration at any time t (mg/L), V is the volume of solution (L) and w is the weight of adsorbent (g).

C. Central composite design

The adsorption process was successfully optimized through a half fraction central composite design where the solution pH (A), initial adsorbate concentration (B), adsorbent dose (C), contact time (D) and temperature (E) were taken as the input variables and the phenol adsorption capacity Y is the response variable. The optimization was carried out by using Design expert software (Stat-Ease, Inc., version 10.0.6, Minneapolis, USA). The range and levels of the input variables are shown in Table I.

TABLE I
RANGE OF THE INPUT PARAMETERS

Factors	High	Low
pH(A)	3	7
Concentration(B)	30	150
Adsorbent dose(C)	1.5	3.5
Time(D)	15	155
Temperature(E)	25	45

III. RESULTS AND DISCUSSIONS

D. The analysis of variance (ANOVA)

In this study the phenol removal characteristics was predicted by a half fraction central composite design. The complete design matrix was comprised of thirty two experimental runs with six replicates at the centre points. The imperial correlation proposed by central composite design in terms of coded variables is given as follows:

Adsorption capacity (Y) = 32.66 - 0.29A + 9.59B - 8.07C - 1.70D + 0.24E + 1.17AB + 2.10AC+ 1.65AD - 2.52AE - 2.87BC - 1.56BD + 1.74BE + 0.63CD - 1.00CE - 0.42DE + $0.11A^2$ - $1.58B^2$ + $1.60C^2$ - $0.83D^2$ - $0.21E^2$

TABLE II
ANALYSIS OF VARIENCE OF THE OUTPUT VARIABLE

Source	SSE	DOF	MSE	F Value	p-value
Model	4507.81	20	225.39	64.11	0.0000
A	2.02	1	2.02	0.58	0.4640
B	2206.24	1	2206.24	627.54	< 0.0001
C	1562.06	1	1562.06	444.31	< 0.0001
D	69.63	1	69.63	19.80	0.0010
E	1.40	1	1.40	0.40	0.5411
AB	21.99	1	21.99	6.26	0.0294
AC	70.56	1	70.56	20.07	0.0009
AD	43.50	1	43.50	12.37	0.0048
AE	101.34	1	101.34	28.83	0.0002
BC	132.05	1	132.05	37.56	< 0.0001
BD	38.83	1	38.83	11.04	0.0068
BE	48.40	1	48.40	13.77	0.0034
CD	6.29	1	6.29	1.79	0.2080
CE	16.16	1	16.16	4.60	0.0553
DE	2.77	1	2.77	0.79	0.3938

The proficiency of the model was defended through analysis of variance (ANOVA). The ANOVA of phenol adsorption capacity q_t (mg/g) is given in Table II.

In the present study, the model F-value is predicted as 64.11 designating the significance of the proposed model and there lies only 0.01% chance of error.

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The parameters are found to have probability value less than 0.05 are said to be significant. The significant parameters are B, C, D, AB, AC, AD, AE, BC, BD, BE. The experiment s found to have a non significant lack of fit. The "Pred R-Squared" of 0.9407 is in reasonable agreement with the "Adj R-Squared" of 0.9760; i.e. the difference is less than 0.2.

E. Effects of experimental parameters

The effect of adsorbent dose and solution pH on phenol removal capacity is shown in Fig. 1. It is depicted from Fig. 1 that the adsorption capacity increased with decrease in adsorbent dose and solution pH. The possible reason may be due to overcrowding of the adsorbent particles [6]. The adsorption capacity of 46.15 mg/g was obtained with an solution pH and adsorbent dose of 3.2 and 2.2 mg/L respectively.

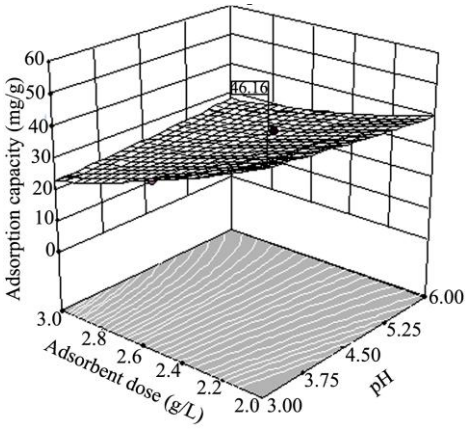

Fig. 1: The combined effects of adsorbent dose and solution pH on phenol adsorption

The effect of temperature and solution pH on phenol removal capacity is shown in Fig. 2. It is depicted from Fig. 2 that the adsorption capacity increased with increase in temperature and decrease in solution pH. The adsorption capacity of 37.12 mg/g was obtained with a solution pH and adsorbent dose of 3.2 and 40 °C respectively. The increase in phenol adsorption at lower solution pH may be described in the vicinity of the presence of various ionic state and functional groups on the adsorbent surface. Due to lower acidity, phenol is generally well adsorbed at lower solution pH. Besides, at higher pH values, different functional groups carrying negative charge accumulate on the adsorbent surface which in turn repulses the anionic molecules.

In addition to this at higher solution pH, phenol molecule can be degraded to form different salts which are then precipitated on the adsorbent surface leaving the surface futile [8].

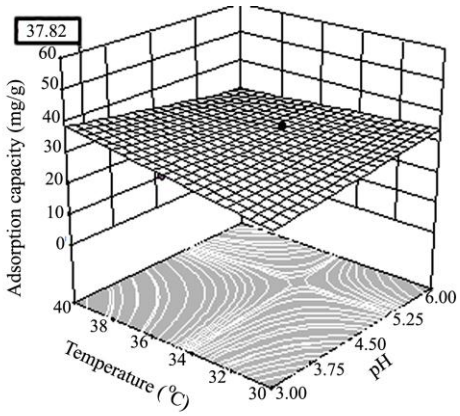

Fig 2. The combined effects of temperature and solution phenol adsorption

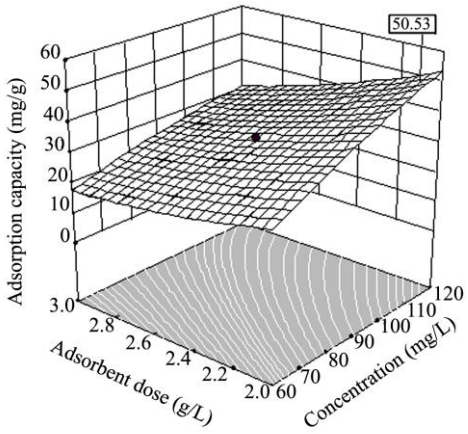

Fig.3: The combined effects of adsorbent dose and initial concentration on phenol adsorption

The effect of adsorbent dose and initial concentration on phenol removal capacity is shown in Fig. 2. It is illustrated from Fig. 3 that the adsorption capacity increased with increase in initial concentration and decrease in adsorbent dose. The adsorption capacity of 50.53 mg/g was obtained with a initial concentration and adsorbent dose of 115 mg/L and 2 g/L respectively. The increase in adsorption capacity with increased initial concentration may be attributed to the higher driving force of mass transfer at higher initial concentration and increase in number of vacant sites [7].

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F. Desirability and standard error of significant parameters

The desirability of the experiment was tested for the combined effect of two most significant parameters initial concentration and adsorbent dose. The desirability and the standard plot error are shown in Fig. 4. It can be seen from Fig. 4 that the desirability of the experiment at an initial concentration of 120 mg/L and adsorbent dose of 2 g/L. The value of the standard error is found to be decreased towards the centre of the contour.

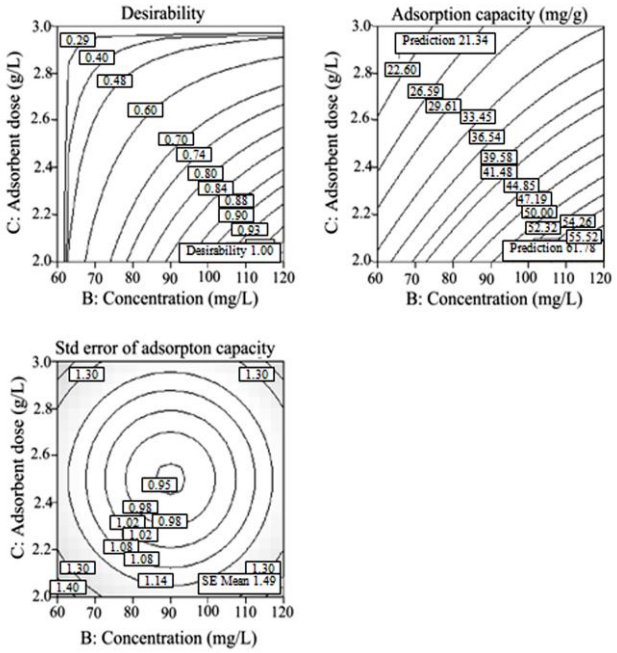

Fig.4: The desirability and standard error plot for phenol adsorption

G. Optimization of process variables

The numerical optimization was applied to optimize the phenol adsorption process and the optimum values of the experimental parameters are given in Table III. The adsorption capacity at this optimum condition was found to be 61.78 mg/g.

TABLE III
OPTIMUM VALUES OF PARAMETERS

Factors	Optimum value
pH(A)	4
Concentration (B) (mg/L)	120
Adsorbent dose (C) (g/L)	2
Time (D) (min)	73
Temperature (E) (°C)	40

IV. CONCLUSION

In the present investigation, the removal of phenol was studied onto the surface of chemically treated soil. The adsorption process was optimized by a half fraction central composite design. The optimum values of process parameters were obtained as solution pH of 4.0, initial concentration of 120 mg/L, adsorbent dose of 2 g/L, time of 73 min and temperature of 40 °C.

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