Removal of Phenol from Wastewater Using tea waste and optimization of conditions using response surface methodology.

C R Girish[a]*, Purushottam Singh[a] and Ashish Kumar Goyal[a]

*[a]Chemical Engineering Department, Manipal Institute of Technology,
Manipal – 576104, Karnataka, India.*

*ORCID: 0000-0002-1231-0810

Abstract

In the current work the capability of adsorbent prepared from tea waste to remove phenol from the wastewater was investigated. The adsorbent was prepared by treating with sulphuric acid to enhance the properties. The characterization of the adsorbent was done by measuring the surface area, pore volume and particle size. The influence of three operating parameters like pH, concentration and dosage on the percent removal was investigated using response surface methodology (RSM). From the central composite design, a quadratic model was developed with a correlation coefficient of 0.9509. The model was helpful in correlating the three experimental variables to the percent removal as the response. Equilibrium isotherms for phenol adsorption were investigated using Freundlich, Langmuir and Temkin isotherm models. The kinetic studies were carried out at the optimum conditions and it was observed that the data were fitting pseudo-second order model. The equilibrium data obeyed Langmuir model showing the monolayer adsorption capacity of 5.80 mg/g in the concentration range of 40- 180 mg/L.

Keywords- Phenol, tea waste, equilibrium, adsorption capacity, isotherm

INTRODUCTION

Phenol is one of the important pollutant coming out of the wastewater from the industries such as rubber, textile, pharmaceutical, pulp and paper, tanning, plastics, ferrous industries and petroleum refineries [1]. It causes harmful effects on the human beings and the aquatic environment. As per the Environmental protection agency its allowable concentration in the drinking water should be maintained less than 1 mg/L [2]. Phenol is designated as the 11th of the 126 priority pollutants by the Environmental Protection Agency [3]. Thus there is a need to treat phenol from the wastewater before it is released into the environment. Various methods such as biodegradation, membrane separation, solvent extraction, pervaporation, distillation, and adsorption are employed for treating phenol from wastewater [4]. Adsorption using commercial activated carbon is considered as the effective method to treat wastewater containing phenol. But the problem faced with activated carbon is that its production is from expensive raw material. Therefore, it has led to growing interest for producing adsorbent from the agricultural waste material [5].

Various agricultural materials were taken as raw materials for the preparation of the adsorbent as reviewed by the authros [6]. It was discussed that the adsorbent produced from these materials are cheaper, renewable, and abundantly available [7]. A number of agricultural derived wastes are used for preparing adsorbent in treating phenol from wastewater. The prominent among them are coconut coir pith [8], Sterculia alata [9], palm seed coat [10], cork [11], pinewood [12], oil palm empty fruit bunch [13]. The above materials are considered promising for producing the adsorbent at low cost. It also solves the menace of handling these waste [7].

Therefore to search new agricultural material for the adsorbent preparation, efforts are made to produce adsorbent from the Tea Fibre or Tea Fluff (waste of Camellia assamica and Camellia sinensis) obtained from a Tea Plantation in Sivasagar, Assam. The waste was taken for the study since it has no use in firewood or as manure. It is rarely used as a fodder for some mountain animals in and around Assam. The current study investigates the ability of the chemical treated carbon from tea waste to remove phenol. The batch experiments were done to determine the influence of operating parameters on the percent removal. The experimental parameters were optimized by response surface methodology. At the optimum conditions, kinetic studies were carried out. The isotherm studies were performed to determine the maximum adsorption capacity.

MATERIALS AND METHODS

A. Chemicals used

Phenol obtained from Merck India Ltd (AR grade) was used for the preparing stock solution of concentration 1000mg/L. The solutions of various concentration required for studies were prepared by the dilution of stock solution to proper proportions. The other chemical sulphuric acid from SD Fine Chemicals, AR grade was used for chemical treatment of adsorbent.

B. Adsorbent preparation

The Tea Fibre or Tea Fluff (waste of Camellia assamica and Camellia sinensis) obtained from a Tea Plantation in Sivasagar, Assam was selected for the preparation of the adsorbent. The material was cleaned with distilled water to remove the earthy matter and dried inside oven at 110°C for 1 h to remove the moisture content. 50 g of the dried powder was treated with 95 mL of 0.1 M sulphuric acid in 1000 mL beaker. The acid was allowed to react with the material for 15-20 min and then heated in a muffle furnace at 450°C for 1.5 hr in order to improve the properties of the adsorbent. Then the sample was continuously washed with water for removing excess chemicals [14]. The washing with water was continued till the pH value reaches 7 [15]. Then the sample was filtered, dried and stored for the experiments.

C. Characterisation of chemically treated carbon

The proximate analysis of the chemically treated carbon was conducted as per the standard procedure [16] to find out moisture content, volatile matter, fixed carbon and ash content. The moisture content present was found by heating a known amount of the sample inside an oven kept at a temperature of 110°C for 1 h. Then the residue was heated inside muffle furnace at 750°C for 8h to determine the ash content. It was heated to 900°C for 10min to find the volatile matter. The determination of particle size was done using particle size analyser (CILAS 1064, France). The pore volume and surface area were measured by BET apparatus (Smart Instruments, India). The surface morphology was studied using Zeiss company.

D. Adsorption studies

The adsorption experiments were carried out in 250 mL conical flask consisting of 200mL of phenol concentration100 mg/L. The flasks were shaken in an agitator at a speed of 125 rpm and at a temperature of 305 K upto the equilibrium conditions. The concentration of phenol was measured by U-V spectrophotometer (Shimadzu, Japan) at a wavelength of 270 nm. The studies were performed in duplicates and average value was taken.

E. Design of experiments

RSM is a statistical tool that uses experimental quantitative data to find model equations and optimum conditions [17]. A general RSM method namely central composite design was used in the present study to determine the influence of experimental conditions on adsorption of phenol. Therefore the current work investigates the effect of three independent variables pH, phenol concentration and adsorbent dosage at five coded levels (Table 1). At the optimum conditions

obtained, kinetic studies were conducted. The isotherm studies were performed for different values of concentration varying from 40 to 180 mg/L.

Table 1. Independent factors and its level.

Independent factors	Symbol	Range and level				
		$-\alpha$	-1	0	+1	$+\alpha$
pH	X_1	2.63	4	6	8	9.36
Concentration (mg/L)	X_2	32.95	50	75	100	117.04
Dosage (g)	X_3	0.48	1	1.75	2.5	3.01

The total number of experiments were calculated by considering factorial points, star points and center points. The complete design matrix for the experiments conducted and the results obtained (% removal) are represented in Table 2.

Table 2. Design matrix for the experimental variables and results obtained.

Expt No:	Coded variables			Actual variables			
	x_1	x_2	x_3	pH	Concentration (mg/L)	Dosage (g)	% removal
1	-1	-1	-1	4	50	1	50.72
2	1	-1	-1	8	50	1	41.4
3	-1	1	-1	4	100	1	52.17
4	1	1	-1	8	100	1	44.7
5	-1	-1	1	4	50	2.5	54.88
6	1	-1	1	8	50	2.5	52.66
7	-1	1	1	4	100	2.5	64.08
8	1	1	1	8	100	2.5	58.79
9	-1.68	0	0	2.63	75	1.75	60.46
10	1.68	0	0	9.36	75	1.75	55.62
11	0	-1.68	0	6	32.95	1.75	64.01
12	0	1.68	0	6	117.04	1.75	59.98
13	0	0	-1.68	6	75	0.48	45.58

14	0	0	1.68	6	75	3.01	66.62
15	0	0	0	6	75	1.75	61.78
16	0	0	0	6	75	1.75	62.74
17	0	0	0	6	75	1.75	60.6
18	0	0	0	6	75	1.75	62.8
19	0	0	0	6	75	1.75	65.12
20	0	0	0	6	75	1.75	63.34

RESULTS AND DISCUSSION

A. Characterisation of the adsorbent

The proximate analysis showed that moisture content, volatile matter, ash content and fixed carbon content was 8.44%, 43.46%, 6.7% and 41.4% respectively. The results shows that the adsorbent has high fixed carbon content signifying that the material possesses good adsorbent properties [18]. The surface area of the adsorbent was determined as 135.56 m^2/g and was comparable with different agricultural materials such as coir pith carbon 167 m^2/g [19], Ponkan mandarin peel 119.3 m^2/g [20], cork oak 195 m^2/g [11], pea nut hull 208 m^2/g [21]. The pore volume and average particle size of the adsorbent was obtained as 0.0432 cm^3/g and 40.84 μm respectively. Thus these results signifies that the chemically treated carbon is more suitable for the adsorption of phenol.

The Figure 1 shows the adsorbent sample before adsorption has a rough surface with heterogeneous pores of various sizes. The pores have the good potential for the adsorption of phenol molecules. The sample after the adsorption process (Figure 2) shows that a notable change in the adsorbent structure is observed. The pores are fully covered with adsorbate molecules [22, 23, 24].
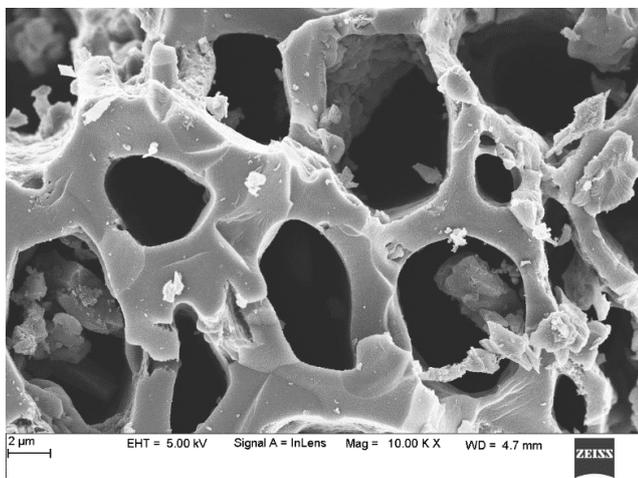

Figure 1: SEM of the sample before adsorption of phenol
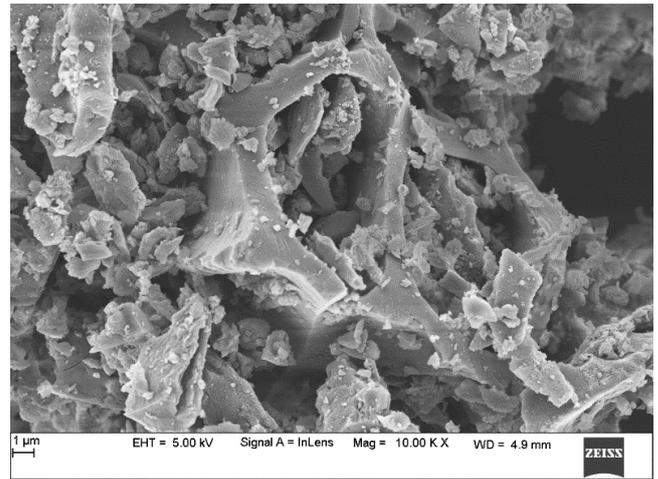

Figure 2: SEM of the sample after adsorption of phenol

B. Development of model equation

From the design matrix, a quadratic polynomial equation was obtained. The model equation is helpful in optimizing the experimental conditions [25]. The values of percentage removal were obtained in the range of 41.4 to 66.62%. The model equation in terms of coded factors by removing the insignificant terms for percentage removal is given as

$$\% \, des \, (Y) = 62.93 + 5.59 \times x_3 - 2.94 \times x_1^2 - 3.63 \times x_3^2 \tag{1}$$

The fitness of the model was verified by the values of correlation coefficient (R^2) and standard deviation [26]. The R^2 value for the equation was 0.9509 showing that 95.09% of the total variation in the response was because of experimental parameters. It also signifies that only 4.91% of the variations are not explained by the model and it may be because of residual error as shown in the ANOVA table [27]. The standard deviation value came to be 3.15. The closer the R^2 value to unity and lower the standard deviation, the more accurately the value of response can be obtained. Thus the above values also shows that experimental values were agreeing with the predicted values from the model [25]. The Coefficient of variation (CV) was found to be 4.87 showing a good precision and reliability with the experiments.

C. Analysis of Variance and optimization of parameters

The large value of F shows that maximum variation in the percentage removal is explained by the model. The P value also represents whether F value is sufficient enough to show significance of the parameter. Thus a factor with P value less than 0.05 and large F value is considered to be significant [28]. From the ANOVA analysis given in Table 3, the factor adsorbent dosage with F value of 22.16 and P value of 0.0008 signifies that the model was significant [25]. In this example, X_3, X_1^2 and X_3^2 were found to be significant terms. It

was also found that the optimum values for percent removal were lying within the experimental range of values. Therefore, it can be summarized that the experimental parameters have a significant influence on the percentage desorption. The optimum experimental conditions were found pH value of 5.48, phenol concentration of 92.9 mg/L and dosage of 2.4 g. The predicted percentage phenol removal was obtained as 66.02%. The verification kinetics experiments were carried out at the optimum conditions to check the validity of the proposed model [29] and the experimental value obtained was 60.38% showing that the predicted and the experimental values were matching with each other.

Table 3. ANOVA results for the removal of phenol by tea waste.

Parameter	Sum of squares	Degree of freedom	Mean square	F value	P value
Model	845.58	9	93.35	4.87	0.0105*
pH	78.97	1	78.97	4.09	0.0706
Concentration	13.77	1	13.77	0.71	0.4178
Dosage	427.46	1	427.46	22.16	0.0008*
pH*Concentration	0.084	1	0.084	0.004358	0.9487
pH*Dosage	9.86	1	9.86	0.51	0.491
Concentration*Dosage	15.07	1	15.07	0.78	0.3975
pH^2	124.91	1	124.91	6.48	0.0291*
Concentration^2	34.45	1	34.45	1.79	0.211
Dosage^2	189.9	1	189.9	9.85	0.0105*
Residual	192.86	10	19.29		

* The factors are significant

D. Adsorption isotherms

The knowledge of the adsorption isotherm is required for designing the adsorption equipment. The three isotherm models namely Langmuir, Freundlich, and Temkin model were studied to investigate the adsorbate– adsorbent interaction. It gives the equilibrium relationship between the adsorbate adsorbed on the adsorbent and adsorbate remaining in the original solution [30, 31].

Langmuir isotherm is derived on the following assumptions. Adsorption is of monolayer type and all the active sites are alike (find the meaning). Once an active site accommodates an adsorbate, it cannot adsorb any more pollutant. There is no interaction between the adsorbate molecules. All the molecules will have constant enthalpy and activation energy [30, 31]. It is represented as

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{k_l Q_m} \tag{2}$$

where Q_e the equilibrium adsorption capacity (mg/g), C_e the adsorbate concentration at equilibrium, Q_m the monolayer adsorption capacity (mg/g), k_l is the Langmuir constant relating the adsorption energy (L/mg). The model constants k_l and Q_m are obtained from the linear plot of $\frac{C_e}{Q_e}$ versus $\frac{1}{Q_m}$.

Freundlich isotherm is assumed that adsorption occurs on heterogeneous surfaces and results in multilayer adsorption. During the process, non-uniform distribution of energy takes place between the adsorbate and the adsorbent [32, 31].

The simplified form of Freundlich isotherm can be written as

$$log Q_e = log k_f + \frac{1}{n} log C_e \tag{3}$$

where Q_e the equilibrium adsorption capacity (mg/g), C_e the adsorbate concentration at equilibrium, k_f the model constant $(mg/g)(L/mg)^{1/n}$ and n the intensity of adsorption. The value of n above 1 shows that the adsorption is favorable. The constants k_f and n are evaluated from the linear plot of $log Q_e$ versus $log C_e$.

The Temkin isotherm shows the indirectly the adsorbate-adsorbent interactions on the isotherm. It also signifies that heat of adsorption decreases linearly with the adsorption on the layer [33, 34]. The equation is written in the simplified form as

$$Q_e = B ln A + B ln C_e \tag{4}$$

A and B are the Temkin model constants. From the straight line plot of Q_e versus $ln C_e$, the model constants are calculated.

The isotherm constants calculated from the model are shown in Table 4. It can be found from the values of regression coefficient that the experimental data is fitting with Langmuir isotherm. This signifies that adsorption is occurring in a monolayer on a homogeneous surface. It also shows that the uniform distribution of energy takes place during the adsorption process. The monolayer adsorption capacity was obtained as 5.80 mg/g.

Table 4. The values of calculated isotherm constants

Isotherm model	Parameter	R^2
Langmuir model	k_l =0.05519 L/mg, Q_m =5.80 mg/g	0.9353
Freundlich model	k_f =1.3483 $\left(\frac{mg}{g}\right)\left(\frac{L}{mg}\right)^{1/n}$, n =3.5574	0.8489
Temkin model	A =0.9607 L/mg , B =1.0718	0.8685

E. Kinetic studies

It is the study of the rates of chemical processes to investigate the factors that influences the rate [35]. The sorption kinetic studies are important in wastewater treatment because it gives important information on the reaction pathways and mechanism of sorption processes [36].

Pseudo-first-order model

The Lagergren first-order rate expression is written in simplified form as [31, 37]

$$log(Q_e - Q_t) = logQ_e - \frac{k_1}{2.303}t \qquad (5)$$

where Q_e is the adsorption capacity at equilibrium and Q_t is the adsorption capacity at any time t (mg/g), k_1 the first-order rate constant (min^{-1}). The values of rate constant (k_1) and equilibrium adsorption capacity (Q_e) are determined from the linear plot of $log(Q_e - Q_t)$ v/s t. The first order kinetics signifies the possibility of reversible physical adsorption.

Pseudo-second-order kinetic model

Pseudo-second-order model is expressed as [35]

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \qquad (6)$$

where k_2 the first-order rate constant (g/mg min). The model parameters are found from the plot of t/Q_t versus t. Later the calculated Q_e value was compared with the experimental data

in order to satisfy the kinetic model. This can be applied for systems where chemisorption becomes the slowest step.

Intra-particle diffusion model

For porous adsorbents, particle diffusion can be considered as the rate limiting step. The rate expression for the intra-particle diffusion is given in the simplified form as [38]

$$Q_t = k_i t^{0.5} + C \qquad (7)$$

where k_i is the intra-particle rate constant $(\frac{mg}{gmin^{0.5}})$, C the intercept that shows boundary layer thickness. If the plot of q_t vs $t^{0.5}$ passes through the origin, then it represents intra-particle diffusion is the rate limiting step. The above plot generally represents two linear steps that occurs simultaneously. The first step is the one where surface adsorption happens. In the second step intraparticle diffusion becomes the slowest step. The constants for both the linear sections are determined separately.

The kinetic constants calculated from the three kinetic models are shown in Table 5 and 6. From the results, it was found that the high regression coefficient value was obtained for pseudo-second-order kinetic model compared to other kinetic models. It was also observed that the theoretical value was matching with experimental value for second order model. This signifies that the chemical adsorption occurs on the adsorbent. Similar results were obtained in the reported work [22, 39].

Table 5. The constants of pseudo-first order model and pseudo-second order kinetic model

Conc, mg/L	Pseudo-first order model				Pseudo-second order model		
	k_1, min^{-1}	$(Q_e)_{cal}$, mg/g	$(Q_e)_{exp}$, mg/g	R^2	$k_2, g/mg\ min$	$(Q_e)_{cal}$, mg/g	R^2
92.92	8.98×10^{-3}	6.29	4.56	0.8592	1.50×10^{-3}	5.497	0.9333

Table 6. The constants of intra-particle diffusion model

Conc, mg/L	Intra-particle diffusion model					
	$k_{i,1}, (\frac{mg}{g}min^{0.5})$	C_1	R^2	$k_{i,2}, (\frac{mg}{g}min^{0.5})$	C_2	R^2
92.92	5.6411	-1.7675	0.9062	4.4822	0.4744	0.9208

CONCLUSIONS

The present study proved that adsorbent prepared from tea waste was effective in treating wastewater containing phenol. The characterization of the adsorbent and the proximate analysis showed the ability of the adsorbent to adsorb the pollutant. The experimental parameters such as pH, phenol concentration and adsorbent dosage were optimized using response surface methodology. The optimum conditions were

determined as pH of 5.48, concentration of 92.9 mg/L and adsorbent dosage of 2.4 g. A quadratic model was developed for showing the effect of variables on the response with the correlation coefficient of 0.9509. The ANOVA results showed that adsorbent dosage was having more influence on the percent removal. The adsorption process reached equilibrium conditions after 8 h. The equilibrium data followed Langmuir isotherm signifying that adsorption takes place in a monolayer.

The kinetic studies were carried out at the optimum conditions and three kinetic models were verified to check the suitability of kinetic data. The experimental data followed pseudo-second order model which signifies that chemical adsorption occurs on the surface of the adsorbent. The monolayer adsorption capacity was obtained as 5.80 mg/g showing that adsorbent prepared from tea waste is a promising adsorbent.

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