SORPTION DYNAMIC FOR REMOVAL OF PHENOL FROM WATER AND WASTE-WATER ONTO BITUMINOUS COAL

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ABSTRACT

In present investigation, Bituminous coal in removing phenol has been studied. The effects of various factors such as particle size, pH, phenol concentration and temperature on sorption are investigated. The removal of phenol increased with decreasing adsorbent particle size, pH and increasing concentration and temperature. The study is followed the pseudo-first-order rate kinetics and is found that the sorption data fit well the Lagergren equation.

Key Words : Sorption, Bituminous coal, Phenol, Kinetic parameter, Langergren equation.

INTRODUCTION

The chemical environment contains four million know chemical and a very large number of unknown chemical. More than two thousand chemical contaminants have been found in waste water, about 750 of which have been identified in drinking water. Of these, more than 600 are of organic origin. Phenols are among the most common water pollutants. These phenols are introduced into surface water from industrial effluents such as those from oil refineries and coal tar, plastics, leather, dyeing. Pharmaceuticals and steel industries as well as from agriculture run off, domestics waste-waters and chemical spills. Phenols impart taste and odor problems to drinking water supplies even at parts per billion levels. Phenols are protoplasmic poison and so these damage all kind of cells.

Among the available methods for removing these pollutants adsorption is still one of the most preferred methods especially for effluents with moderate to low concentration. However, the use of carbon as an adsorbent is limited because of its high cost Utilization of low cast bituminous coal deserves greater attention in the field of waste-water management. Bituminous Coal is non-conventional adsorbent with good adsorbent qualities. A variety of adsorbent have been used for the adsorption of phenols. They include activated carbon [1,2], hydro-calcite[3] perlite and bentonite[4,5] etc. Bituminous coal has been the most widely used adsorbent for organics removal from aqueous phase. The applicability of this adsorbent for some organic

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compounds[6,7] and metal ions[8] removal from aqueous phase was investigated by other authors however very little data are available on the sorption dynamic of phenols on bituminous coal.

The main goal of this work is to investigate the effect of system. The effect of system variables namely particle size, pH, concentration of phenol and temperature on kinetics of phenol sorption on bituminous coal.. The applicability of kinetic model of Lagergren is analyzed by estimation of the rate parameter. This study shows the potentiality of bituminous coal as sorbet for phenolic effluents wherein continuous removal or collection can be achieved on a large scale.

AIMS AND OBJECTIVES

The present study is undertaken with the following objectives

1. To compare the performance and effectiveness of the adsorbents in removing phenols by sorption from municipal wastewater.
2. To determine the effect of size, pH, conc. and temperature on sorption process.
3. To examine the sorption rate constant to study the application of pseudo first order (Lagergren) rate equation.

MATERIAL AND METHODS

Standard phenol (supplied by Loba company, Bombay) solutions are prepared (500 mg/L) by weighing the purified grade chemical and dissolving them in minimum volume of acetone. Portion of this solution is diluted with distilled water similar to those of real waste-water sample. All reagents are of A.R.grade. Experimental solutions of desired concentration are prepared by successive dilution.

The bituminous coal is obtained from the coal mines of Brisingpur Pali Shahdol, M.P. (India). After being crushed with a hammer and grinded in a ceramic mill, the sample are sieved to produce the desired particle size fractions ranging from 600 µm to 300 µm and then these are placed in an electric oven for two hours at 110°Cand stored in a desiccators until use. Some of its typical (proximate analysis) results as well as physico-chemical characteristics are presented in **Table 1** and **Table 2**. These fractions are used in batch kinetic experiment without any pretreatment.

Batch kinetics sorption experiment of phenol is conducted by shaking 25ml of phenol solution with 1g of bituminous coal fraction in 100cm^3 Conical glass Stoppard flask (to avoid vaporization losses of phenol) at various particle sizes (300, 425 and 600µm), pH (2.0, 4.0, 6.5, 8.0 and 10.0), concentration of phenol (250, 350 and 500mg/L) and temperature(30, 40 and 50^{o}C) using thermostatic shaker at 200 rpm (similar to environmental condition) The sample are covered during the entire experiment to avoid phenol degradation by photolysis. The pH

Table 1 : Proximate Analysis of bituminous coal

Parameters	% by weight
Moisture	4.72
Volatile matter	27.30
Ash	21.64
Carbon	46.34

Table 2 : Physicochemical characteristics of bituminous coal

Constituents	% by weight
SiO_2	59.65
Al_2O_3	28.70
Fe_2O_3	7.81
CaO	1.46
MgO	1.23
MnO	0.31
TiO_2	1.68
Porosity	0.36 cm cm^{-1}
Surface Area	5.31 m^2g^{-1}
Density	1.50g cm^{-3}

of solution is adjusted with HCl or NaOH by using pH meter. The progress of sorption is determined by centrifuging the sorbate-sorbent solution at predecided intervals of time and analyse the supernatant liquid spectro-photometrically by 4-amino-antipyrine method at λ_{max} = 500nm. Each experiment is performed at least under identical conditions. Reproductively of the measurements are mostly within 2.5%.

RESULTS AND DISCUSSION

Kinetic Model

The sorption kinetics may be described by a pseudo-first order equation[9] the differential form of this equation may be written as

$$\frac{dq}{dt} = (q_e - q_t) \quad .....(1)$$

After integration applying the initial condition q = 0 at t = 0 and $q_t = q_t$ at t = t equation (1) becomes

$$\log \{q_e / (q_e - q_t)\} = k.\ t/2.303 \quad .....(2)$$

Equation (2) can be rearrange to linear form as

$$\log (q_e - q_t) = \log q_e - k.\ t/(2.303) \quad .....(3)$$

Where q_t (mg/g) is the amount of phenol sorbed at time t, q_e(mg g–1) is the amount sorbed at equilibrium and k is equilibrium sorption rate constant. The corresponding linear plots of log (q_e-q_t) versus t depicted in **Fig. 2, 4, 6** and **8** for sorption of phenol on bituminous coal under different conditions indicate the validity of applying equation (3) to the system known as Lagergren equation and relates to a pseudo-first -order sorption process. The value of rate constant, k, for sorption of phenol on bituminous coal under different condition are calculated from the slopes of these plots and are given in **Table 3**.

Effect of particle size

The effect of particle size of kinetics of phenol on bituminous coal is studied. The experimental kinetic curves are presented in **Fig 1**.The experimental data are described by pseudo-first-order model and are given in **Table 3**. The correlations between the particle size and the values of sorption rate are inversely proportional i.e. the decrease in particle size from 600 µm to 300 µm caused increase k (rate constant) values from 3.5×10^{-2} to 4.35×10^{-2} min^{-1} (calculated from linear plots of **Fig. 2**).Obviously the smaller particle offer

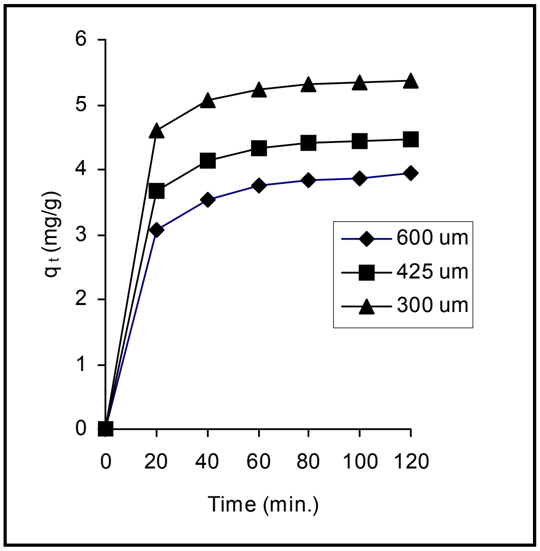

Fig. 1 : Sorption kinetics of phenol on bituminous coal.Conc. 500 mg/L; pH 6.5; Temp .303 K.

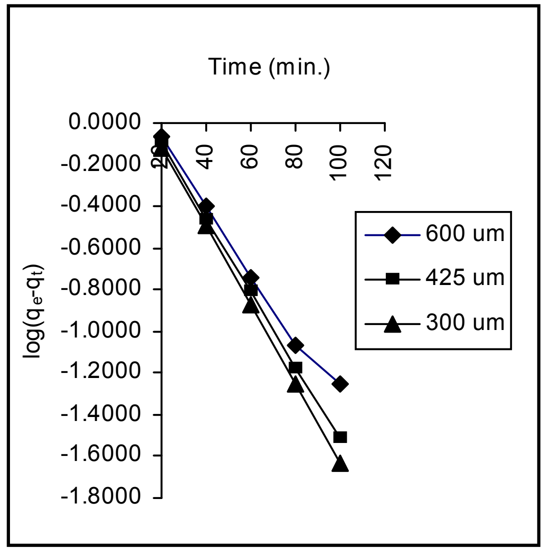

Fig. 2 : Lagergren plot for the sorption of phenol on bituminous coal. Conc.500 mg/L; pH 6.5; Temp. 303 K

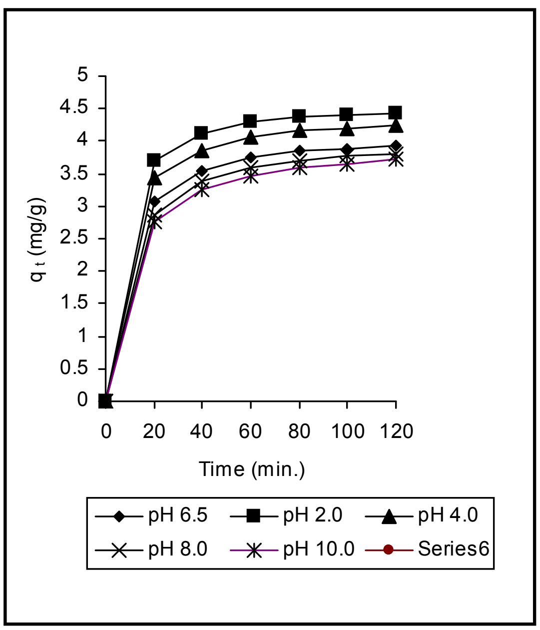

Fig. 3 : Sorption kinetics of phenol on bituminous coal. cccConc. 500 mg/L; Particle size 600 um; Temp. 303 K

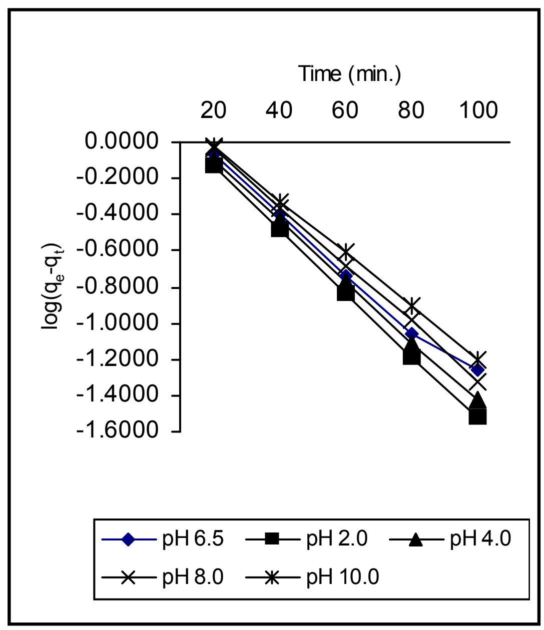

Fig. 4 : Lagergren plot of phenol on bituminous coal. Conc. 500 mg/L; Particle size 600 um; Temp. 303 K.

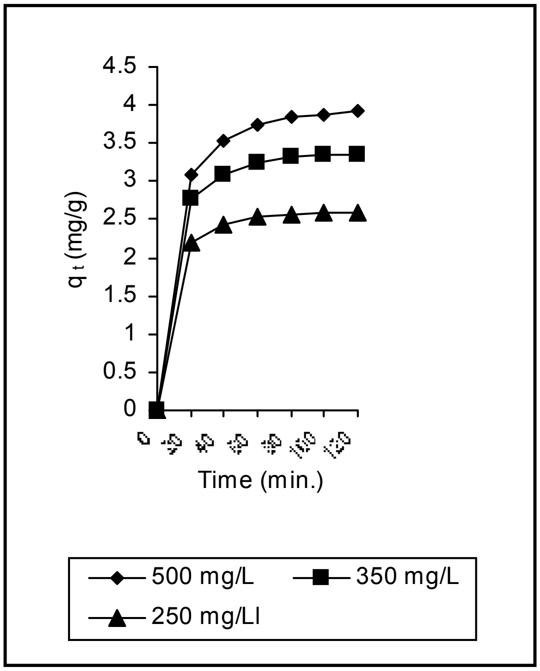

Fig. 5 : Sorption kinetics of phenol on bituminous coal. particle size 600um; pH 6.5; Temp. 303 K.

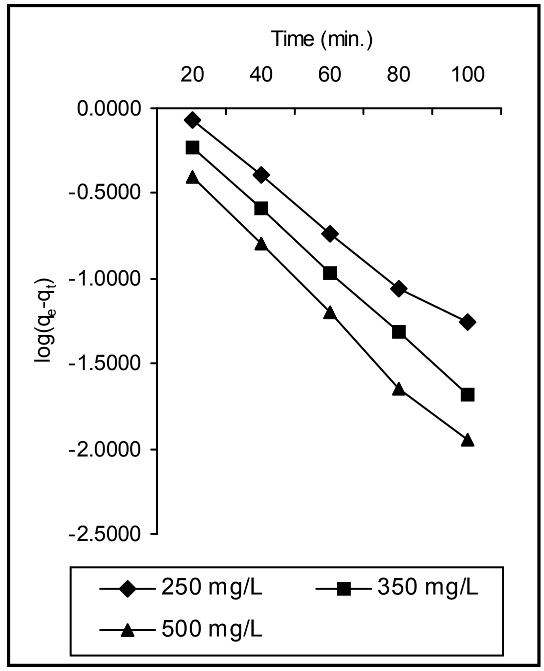

Fig. 6 : Lagergren plots of phenol on bituminous coal.Particle size 600um; pH 6.5; Temp. 303 K

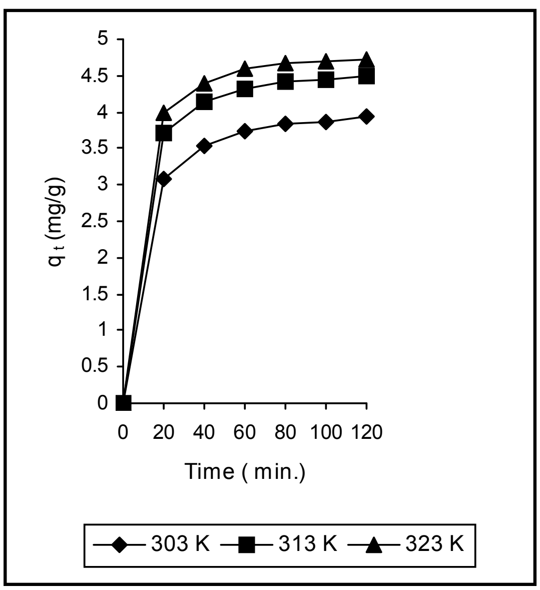

Fig. 7 : Sorption kinetics of phenol on bituminous coal. Conc. 500 mg/L; Particle size 600um;pH 6.5

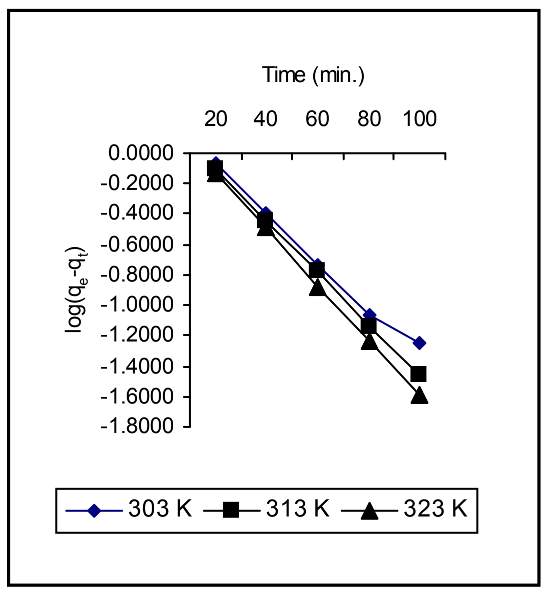

Fig. 8 : Lagergren plots of phenol on bituminous coal.Conc. 500 mg/L; particle size 600um; pH 6.5.

Table 3 : pseudo- first- order (Lagergren) rate constant of phenol on bituminous coal

Sorbate	Condition		Rate constant(min^{-1})
Phenol	partical size µm	600	3.50 x 10^{-2}
		425	4.03 x 10-2
		300	4.35 x 10-2
phenol	PH	2.0	4.01 x 10-2
		4.0	3.85 x 10-2
		6.5	3.50 x 10^{-2}
		8.0	3.43 x 10^{-2}
		10.0	3.41 x 10^{-2}
phenol	Cconct (mg/L)	50	4.53 x 10-2
		350	4.19 x 10-2
		500	3.50 x 10-2
phenol	Temp (k)	303	3.50 x 10-2
		313	3.89 x 10-2
		323	4.24 x 10-2

greater specific surface area, consequently there are more active sites available for the sorption of phenol molecules. A similar observations are also reported in the study on the adsorption of 4-chlorophenol on activated carbon[10].

Effect of pH

It is expected that the rate of phenol sorption onto bituminous coal will be varied with the available pH values of the solution when ion exchange development and application is one of the sorption process. The experimental kinetic curves are presented in **Fig 3**. The pH values used in this study are 2.0, 4.0, 6.5, 8.0, and 10.0 for the sorption of phenol on bituminous coal. The experimental results are described by the pseudo-first order rate constant, k, of sorption at various pH values (determined from the linear plots of **Fig. 4**) and are listed in table 3. This Table shows that there is a decrease in the sorption rate with increase in pH of the solution. The removal of phenol from aqueous solution by sorption is highly dependant on pH of the solution which affects the surface properties of the sorbet and phenol structure.

Decrease in pH probably results in a reduction of the negative charge at the surface of bituminous coal, thus enhancing, the sorption of the negatively charged phenolic ions. This may be explained on the basis of formation of a positively charged surface in an acid medium and negatively charged oxide surface in basic medium from hydroxylated oxide surface to bituminous coal which can be represented as :

$$H_2O + M^+ \leftarrow MOH \rightarrow MO^- + H_2O$$

acidic medium alkaline medium

At lower pH ,the lone pair of electrons on oxygen atom of un-dissociated-OH group present in benzene ring co-ordinates with highly positively charged surface .But at higher pH , the dissociated phenoxide ion ($C_6H_5O^-$) is expelled by highly negatively charged oxide surface. Thus the rate constant, k at different pH values are as follows :

k (pH 2.0)>k (pH 4.0)>k(pH 6.5)> k(pH 8.0)>k(pH 10.0)

The trend is similar to the sorption of nitro -substituted phenols on flyash[11].

Effect of concentration

The effect of concentration on kinetics of phenol on bituminous coal is investigated. **Fig.5** presents the experimental kinetics curve with phenol concentration in the range 250-500 mg/L. Obviously the increase in concentration of the solution leads to a decrease in the sorption rate constant. From the plot **(Fig. 5)** it could be seen that equilibrium is established after 120 minutes from the beginning of the process. The experimental results are described by the pseudo-first-order model of Lagergren **(Fig. 6)** and from this the rate constants are calculated. As shown in **Table 3** the values of rate constant decreased with an increase in initial phenol concentration. This is due to the fact that at higher concentration the fractional adsorption is low. Similar observations are reported in the study of adsorption of dye stuff on activated carbon from aqueous solution[12].

Effect of Temperature

The sorption experiments are conducted at various temperatures in the range 30°C to 50°C with bituminous coal **(Fig.7)** which shows that sorption rate constant increases with increasing temperature indicating the process to be the endothermic. The results suggest that the active surface centres available for the sorption are increased with temperature. Similar observation was also reported in the study for sorption of phenol and p-nitro phenol on clay[13].

CONCLUSION

The present study shows the potential of bituminous coal as sorbent for phenolic wastewater treatment .This treatment is simple and economic. Such a batch system will be applicable to small industries generating phenol-containing waste-waters. The sorption kinetics data thus generated may be used for designing a treatment plant for phenolic effluents wherein continuous removal or collection can be achieved on a large scale.

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