REMOVAL OF PHENOL FROM AQUEOUS SOLUTIONS BY ADSORPTION

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ABSTRACT

Phenolic compounds are one of the most representative pollutants in industrial wastewater, and efficient removal and destruction of them have attracted significant concerns. The present study, a pongamia glabra flower (PGF) adsorbent was developed and its ability to remove phenol in aqueous solution was tested. Adsorption studies were performed in a batch system, and effects of various experimental parameters such as solution pH, contact time, initial phenol concentration, adsorbent concentration and temperature were evaluated upon the phenol adsorption onto PGF. Maximum phenol removal was observed at pH 6 equilibrium was attained after contact of 6 h only. The adsorption isotherms were in conformation to both Langmuir and Freundlich isotherm models. The kinetics studies indicated that the adsorption process was best described by the pseudo-second-order kinetics.

Keywords: Phenol, adsorption, spectrophotometric determination, isotherm, kinetics

1. INTRODUCTION

Phenol are widely used for the commercial production of a wide variety of resins including phenolic resins, which are used as construction materials for automobiles and appliances, epoxy resins and adhesives, and polyamide for various applications Phenolic compounds are common contaminants in wastewater, being generated from petroleum and petrochemical, coal conversion, pulp and paper and phenol producing industries[1]. The most important aspect is that, phenol is a colourless solid and easily miscible in water. So we cannot identify phenol in water through naked eye. Even small amount of phenol may cause severe diseases like cancer, nausea, vomiting, paralysis, smoky colored urine, etc. The toxicity of phenol, even at a trace level, attracts the environmental scientists to develop suitable technology for their removal from water. The various techniques proved effective for phenol removal from wastewater are reverse osmosis, biological degradation, chemical oxidation, precipitation, electro dialysis, adsorption,etc. Among these techniques, adsorption is a most versatile and
superior method for the removal of toxic pollutant. Adsorption process is known to be cost-efficient, easy and effective at moderate and low concentrations, rapid, and reproducible for the removal of pollutant, works without the addition of chemicals or UV radiation, etc. are the major advantages of adsorption technique.[2] The objective of this study was to investigate the adsorption potential of PGF for removal of phenol from aqueous solutions. The effects of experimental parameters such as initial pH of the solution, contact time, initial phenol concentration PGF concentration, and temperature were studied. The adsorption mechanisms of phenol onto to PGF were evaluated in terms of kinetics.

2. MATERIALS AND METHODS

2.1 Adsorbate

Phenol (C₆H₅OH) of analytical reagent (AR) grade (supplied by southern chemicals Ltd., India), was used for the preparation of synthetic adsorbate of various initial sorbate concentrations (Cₒ) in the range of 100-500 mg/l. The required quantity of phenol was accurately weighed and dissolved in distilled water and made up to 1 litre. Fresh stock solution was prepared everyday and stored in a brown colour glass bottle (to prevent photo-oxidation).

2.2 Preparation of adsorbent

Flowers of pongamia glabra, that are available plentifully in tropical climate like India, were collected and washed in running water a number of times to remove any adhering particles and dried at room temperature for 24 hr so that flowers were free of moisture. They were grounded, sieved and stored in an airtight inert enclosure to avoid moisture in the atmosphere.

2.3 Characterization of adsorbent

The physical and chemical characteristics of the adsorbents are important in order to estimate the adsorbate binding mechanism of the adsorbent surface. Fourier transfer infra-red (FTIR) analyzer was used to investigate the presence of functional groups. The FTIR spectra in the wave numbers ranging from 2060- 2011 as a broad band is assigned to C= C stretching vibrations, which may arise from the aldehyde group. On the other hand the band at 1009-1696 is assigned to the asymmetric stretching vibration of OH group of pongamia glabra flower.

2.4. Analysis of phenol

The concentration of initial and residual phenol in the adsorption media was determined spectrophotometrically. The absorbance of the colored complex of phenol was read at 510 nm.

2.5 Adsorption studies (batch studies)

To study the effect of various parameters (namely, pH, adsorbent dosage, initial concentration, contact time and temperature), batch experiments were conducted at room temperature (30±2 °C). For each experiment, 100 ml of phenol solution of known concentration, at varying amounts of adsorbents were taken in conical flasks (250 ml) and agitated continuously. The samples were equilibrated for 6 h, withdrawn at appropriate time and were filtered through Whatman filter paper (No. 42) and analyzed for phenol
concentration. The amount of phenol adsorbed by the adsorbent was calculated from the differences between the phenol concentration at initial time and after appropriate time using the following equation:

\[ q = \frac{V(C_0 - C_e)}{M} \quad \text{(1)} \]

Where \( C_0 \) is the initial sorbate concentration (mg/l), \( C_e \) is the final concentration in the solution (mg/l), \( V \) is the solution volume (l) and \( M \) is the mass of adsorbent (g).

3. RESULTS AND DISCUSSIONS

3.1 Effect of initial concentration

Fig.2 describes the effect of phenol initial concentrations on the removal percentage by pongamia glabra. The phenol removal percentage via pongamia glabra was found to decrease with increase in initial concentrations. Yet, the amount of phenol adsorbed per unit adsorbent increases with increase in initial phenol concentration due to the decrease of uptake resistance of solute from solution of phenol (refer Fig.3). At initial concentration of 100mg/l, the phenol uptake shown by pongamia glabra was recorded at 4.05 mg/g where as at the maximum initial concentrations of 500 mg/l, the amount increased up to 14.3 mg/g. The phenomenon is very consistent to the trend reported in literature [3]. An increment of the uptake was closely related to the greater mass driving force effect which permits more adsorbates to pass through from the bulk phase boundary to the surface. A suggestion has been made that when the surface was almost filled up with adsorbates, the second mechanism of intra-particle diffusion will be activated and this will enhance the adsorption further but in a very slow manner and very time consuming process as the reaction takes place inside the adsorbent.

![Fig.2. Effect of initial concentration of phenol](image-url)

(Initial concentration: 100 -500 mg/l, T : 30°C, t : 6 hr agitation rate = 150 rpm and w : 2g)
3.2 Effect of pH

The removal of phenol by pongamia glabra increases in pH range 2-6. The reverse trend was observed beyond pH 6. (Fig. 4) The uptake of phenol decreases at lower as well as higher pH values. At lower pH values the presence of H+ ions suppresses the ionization of phenol and hence its uptake on adsorbent is reduced. At higher pH range, phenol forms salts that readily ionize leaving the negative charge on the phenolic group. At the same time the of OH- ions on the adsorbent prevents the binding of phenoate ions that leads to low phenol adsorption. The pH of initial concentration was maintained for all the experiments at pH 6 because of the above factor.

3.3 Effect of adsorbent dosage

The effects of pongamia glabra flower concentration on the removal of phenol from aqueous solutions were investigated by using five different pongamia glabra flower concentrations in the range of 0.5 – 2.5 g and initial phenol concentration of 100mg/l at pH 6. As the pongamia glabra concentration was increased from 0.5 to 2.5g, the equilibrium adsorption capacity of pongamia glabra ($q_e$), decreased from 5.3 to 3mg/g, whereas, the phenol removal efficiency increased. The increase in adsorption percentage of phenol was probably due to the increased more availability of active adsorption sites with the increase in pongamia glabra concentration. The decrease in equilibrium adsorption capacity of pongamia
glabra for phenol uptake could be attributed to two reasons. First, the pongamia glabra particles aggregated with increasing the adsorbent concentration hence total surface area of the adsorbent decreased and diffusion path length of phenol increased. Secondly, the increase in pongamia glabra concentration at constant concentration and volume of phenol lead to unsaturation adsorption sites so the equilibrium adsorption capacity of pongamia glabra decreased.[5]

![Fig: 5 Effect of pongamia glabra flower concentration on phenol uptake](image)

3.4 Effect of temperature

The experimental results obtained from phenol adsorption when temperature was varied from 25 to 45°C the adsorption efficiency decreased with an increase in temperature. The decrease in adsorption efficiency indicates an exothermic process. This may be due to the increasing trend to desorb phenol from the interface to the solution or the distorted active sites on adsorbent.[6]

![Fig.6: Effect of temperature on the removal of phenol](image)

3.5 Sorption kinetics

The adsorption kinetics is one the most important data in order to understand the mechanism of the adsorption and to assess the performance of the adsorbents. Different kinetic models
including the pseudo-first-order, pseudo-second-order and intraparticle diffusion models were applied for the experimental data to predict the adsorption kinetics. The pseudo-first-order equation can be written as follows

\[ \ln(q_e - q_t) = \ln q_e - K_1 t \]  

where \( q_e \) (mg/ g) and \( q_t \) (mg/ g) are the amounts of phenol adsorbed at equilibrium and at time \( t \), respectively, \( K_1 \) (min\(^{-1}\)) is the pseudo-first-order rate constant. A straight line of \( \ln(q_e - q_t) \) versus \( t \) suggests the applicability of this kinetic model, and \( q_e \) and \( K_1 \) can be determined from the intercept and slope of the plot, respectively.

The pseudo-second-order model is in the following form

\[ \frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \]  

Where \( K_2 \) (g/mg min) is the rate constant of the second-order equation. The plot of \( t/q_t \) versus \( t \) should give a straight line if pseudo-second-order kinetic model is applicable and \( q_e \) and \( K_2 \) can be determined from slope and intercept of the plot, respectively.

The intraparticle diffusion equation is expressed as

\[ q_t = k_{id} t^{1/2} + C \]  

where \( k_{id} \) (mg/ g min\(^{1/2}\)) is the rate constant of intraparticle diffusion model. The values of \( k_{id} \) and \( C \) can be determined from the slope and intercept of the straight line of \( q_t \) versus \( t^{1/2} \), respectively.

For evaluating the kinetics of phenol – pongamia glabra interactions, the pseudo-first-order, pseudo-second-order and intraparticle diffusion models were used to fit the experimental data. The pseudo-first-order rate constant \( K_1 \) and the value of \( q_{e, \text{cal}} \) were calculated from the plot of \( \ln (q_e - q_t) \) versus \( t \), and the results are given in Table 1. The correlation coefficient \( (R^2) \) is relatively too low which may be indicative of a bad correlation. In addition, \( q_{e, \text{cal}} \) determined from the model is not in a good agreement with the experimental value of \( q_{e, \text{exp}} \). Therefore, the adsorption of phenol onto pongamia glabra is not suitable for the first-order reaction. From Table 1, the value of \( c \) obtained from intra particle diffusion model is not zero, and the correlation coefficient is not satisfactory thereby intraparticle diffusion may not be the controlling factor in determining the kinetics of the process. The linear plot of \( t/q_t \) versus \( t \) for the pseudo-second-order kinetic model is shown in Fig 7. The pseudo-second-order rate constant \( K_2 \) and the value of \( q_{e, \text{cal}} \) were determined from the model and the results are presented in Table 1. The value of correlation coefficient is very high \( (R^2 > 0.999) \) and the calculated \( q_{e, \text{cal}} \) value is closer to the experimental \( q_{e, \text{exp}} \) value. In the view of these results, the pseudo-second-order kinetic model provided a good correlation for the adsorption of phenol onto pongamia glabra in contrast to the pseudo-first-order and intraparticle diffusion model.[7]
Fig. 7. Pseudo-second-order kinetic model plots for phenol adsorption onto pongamia glabra flower.

Table: Parameters of pseudo-first order, pseudo-second order, intraparticle diffusion models

<table>
<thead>
<tr>
<th>$Q_{e,\text{exp}}$ (mg/g)</th>
<th>Pseudo first order</th>
<th>Pseudo second order</th>
<th>Intra particle diffusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_1$ (h$^{-1}$)</td>
<td>$q_e$ (mg/g)</td>
<td>$R^2$</td>
</tr>
<tr>
<td>14.3</td>
<td>0.398</td>
<td>1.10</td>
<td>0.556</td>
</tr>
</tbody>
</table>

3.6 Adsorption isotherms

Adsorption isotherm reflects the relationship between the amount of a solute adsorbed at constant temperature and its concentration in the equilibrium solution. It provides essential physiochemical data for assessing the applicability of the adsorption process as a complete unit operation. Langmuir and Freundlich isotherm models are widely used to investigate the adsorption process. The model parameters can be construed further, providing understandings on sorption mechanism, surface properties, and an affinity of the adsorbent. The Langmuir isotherm was developed on the assumption that the adsorption process will only take place at specific homogenous sites within the adsorbent surface with uniform distribution of energy level. Once the adsorbate is attached on the site, no further adsorption can take place at that site; which concluded that the adsorption process is monolayer in nature. Contrarily to Langmuir, Freundlich isotherm was based on the assumption that the adsorption occurs on heterogeneous sites with non-uniform distribution of energy level. The Freundlich describes reversible adsorption and is not restricted to the formation of monolayer. The linear form of Langmuir and Freundlich equations are represented by equation (5) and (6) respectively.

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \left(\frac{a_L}{K_L}\right)C_e$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e$$
Where \( q_e \) is amount of adsorbate adsorbed at equilibrium (mg/g), \( C_e \) is equilibrium concentration of adsorbate (mg/L), \( K_L \) and \( a_L \) are Langmuir isotherm constants (L/g) and (1/mg), respectively. \( K_L/a_L \) gives the Langmuir constant related to maximum adsorption capacity at monolayer, \( Q_0 \) (mg/g). \( K_F \) is Freundlich constant (mg/g)(l/mg)^{1/n} and 1/n is dimensionless heterogeneity factor.

Figs. 8 and 9 exhibit the linear plots of Langmuir and Freundlich for phenol adsorption onto pongamia glabra. The equilibrium data obtained from the adsorption of phenol onto pongamia glabra flower were fitted both the Langmuir and Freundlich isotherm models. The values of Langmuir constants, \( Q_0 \) and \( a_L \) obtained from the equation of linear plot of \( C_e/q_e \) versus \( C_e \) were found to be 17.8 mg/g\(^{-1}\) and 0.014 L/mg\(^{-1}\) respectively, with correlation coefficient \( (R^2) \) of 0.949. The values of Freundlich constants, \( K_F \) and 1/n were obtained from the linear plot of ln \( q_e \) versus ln \( C_e \) and found to be 1.10 and 0.480 respectively, with correlation coefficient \( (R^2) \) of 0.971. The Freundlich constant 1/n was smaller than unity indicated that the adsorption process was favourable under studied conditions. From the results [8], the adsorption pattern of phenol onto pongamia glabra was well fitted with both
Langmuir and Freundlich isotherm model. This may be due to both homogeneous and heterogeneous distribution of active sites on the surface of the PGF.

4. CONCLUSION

In this study, the ability of pongamia glabra flower to bind phenol was tested using equilibrium, kinetic. The results indicated that, adsorption capacity of the sorbent was affected by pH, temperature and initial phenol concentration. From the batch studies, 80% phenol removal yield was obtained at 100mg/l initial phenol concentration. The maximum phenol removal was achieved at pH 6. The Langmuir and Freundlich adsorption models were used to express the sorption phenomenon of the sorbate. The kinetics of phenol adsorption onto pongamia glabra flower was examined using the pseudo-first and pseudo-second-order kinetic models and intraparticle diffusion. The results indicated that the pseudo-second-order equation provided the best correlation of the sorption data. It can be concluded that the pongamia glabra flower is an efficient adsorbent for the removal of phenol from aqueous solution.

REFERENCE


