Kinetic Modeling of Phenol adsorption on *Azadirachta indica* as a Potential Adsorbent

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Abstract

These days Biowaste as a raw material for producing porous adsorbent has been used widely for treating wastewater. Present work aims to prepare a chemically activated natural adsorbent obtained from Neem sawdust (*Azadirachta indica*). This Biosorbent is tested for removing toxic organic pollutants like phenol from wastewater containing different concentrations of phenol. A batch wise experiment was performed to eliminate phenol from lab made solution mixture. An equilibrium adsorption of phenol was studied as a function of contact time, the initial phenol concentration and the solution temperature. Loading capacity of phenol on activated adsorbent was obtained as 15.44 mg/g at solution temperature of 305 K, adsorbent concentration of 5 g/L and initial phenol concentration of 150 mg/L. To study the performance of adsorbent, experimental data was fitted with Langmuir and Freundlich isotherm models. Data fitting shows that the phenol adsorption was best described by Langmuir Isotherm ($R^2=0.951$ and $q_{max}=50$ mg/g).

Keywords: Phenol, neem sawdust, adsorption, adsorption isotherms, wastewater.

Introduction

Phenol is a white crystalline substance having a characteristic odor. It is a weak acid and considerably soluble in water. It was one of the first compounds inscribed into the list of priority pollutants by the USEPA (US Environment Protection Agency)\(^1\). Wastewater containing phenol creates a severe environmental trouble since microbial degradation of phenol takes place too gradually or does not persist at all\(^2\). The ever increasing environmental awareness in the recent times has led to closer monitoring of quality of water and wastewater\(^3\). Large group of pollutants are included in the list of organic compounds\(^4\), among which phenol is found in a variety of synthetic organic compounds. It is discharged from wastewater of various chemical industries like dye and pesticides manufacturing industries. Various types of phenols are found in the wastewater of industries like plastic, rubber, paper and pulp, tanning, resin manufacturing, pharmaceutical, petroleum etc.\(^1\)

Adsorption technique stays extensively favored compared with other methods because of its cost, ease of design and operation and compatibility with toxic pollutants. Along with adsorption, other available techniques used for phenol removal consists of distillation, extraction, bacterial techniques, chemical techniques, oxidation methods\(^5\), electrochemical precipitation methods\(^6\), ion-exchange methods\(^7\), photo catalytic degradation\(^8\), reverse osmosis\(^9\) etc. Various disadvantages associated with these techniques includes unsatisfactory treated effluent quality, high cost of operation, use of large amount of chemicals for oxidation processes, ion-exchange, potential source of secondary pollution, difficulty in regeneration causing disposal problems.

In addition to above written qualities, adsorption does not form the harmful substances after the treatment. Most commonly and commercially used adsorbent is activated carbon\(^10\), attributable to its highly porous nature and high adsorption capacity resulting from high surface area of the activated carbon surface. But its high cost and considerable losses during thermal regeneration open the door for searching alternative low cost adsorbent with improved qualities. The present study deals with development and utilization of low-cost adsorbent for phenol adsorption from aqueous streams.

Material and Methods

**Chemicals:** All the chemicals used for adsorbent treatment and colorimetric detection of Phenol were Lab reagent (LR) grade obtained from RANKEM Industries. Stock solution of phenol is prepared by dissolving 0.5 gm crystalline Phenol in De-ionized water which is then made up to 500 ml to make 1 ppm stock solution. Subsequent solutions of phenol are then prepared by diluting this stock solution.

**Adsorbent Preparation:** Cheap and non-conventional adsorbent was prepared from Neem sawdust acquired from local Neem trees. The collected Neem sawdust was washed thoroughly with De-ionized water to carry off impurities soluble in water and particles sticking on surfaces. After washing, Neem sawdust was put to convection oven for 24hrs to be dried at 80°C till the weight of sample becomes constant. Such dried mass is then treated chemically with 1N H\(_2\)SO\(_4\) used in the ratio of 1/10 (sawdust/H\(_2\)SO\(_4\)) at 150°C for 24 hrs\(^11\). Treated mass is then immersed in 1/10 NaHCO\(_3\) solution during the course of a
night to neutralize remaining acid afterward it is dried in convection oven at 150°C. Dried and treated adsorbent thus obtained was grounded and sieved to get definite particle sizes which are then stored in air tight plastic bottles for further use.

**Equilibrium study:** Batch adsorption experiment was performed by using Neem sawdust at two different initial concentration of phenol i.e. 75 mg/L and 150 mg/L. Aqueous solution was taken in a conical glass and stirrer at 150 rpm in shaking incubator at natural pH of the solution. A sample volume of 5 ml was collected at a definite time intervals, filtered and analyzed by UV-Visible Spectrophotometer to measure the reduced concentration of the phenol at 540nm.

Amount of Phenol adsorbed per mass of adsorbent (q) and Sorption efficiency (%) can be estimated by using the following equations:

\[
q = \frac{(C_o - C_e)}{M} \times V
\]

\[
SE = \frac{(C_o - C_e)}{C_e} \times 100
\]

Where, q is mg of phenol adsorbed per g of sorbent, mg/g. C_o is Initial phenol concentration, mg/L and C_e is phenol concentration at different intervals of time, mg/L. V is the of solution volume in liter. M is weight of Biosorbents, g and SE is Sorption Efficiency in percent.

**Results and Discussion**

**Effect of contact time:** It is important to study the result of equilibrium adsorption time on phenol adsorption capacity since contact time between the liquid phase and solid phase and transfer of solute from liquid to solid phase influences mass transfer rate. Contact time of adsorption is also helpful in providing Isotherms and its nature. To learn the effect of contact time on phenol retention, a batch study was performed at constant stirring speed of 150 rpm and varying initial phenol concentration C_o from 75mg/L to 150 mg/L.

Figure 1 shows that equilibrium retention time for phenol adsorption is different for different quantity of initial phenol dosing in the feed mixture and as we increase contact time, percent phenol removal increases accordingly. For phenol concentrations of 75 mg/L and 150 mg/L an equilibrium adsorption time of 120 min and 60 minutes was obtained respectively. From figure 1 it is inferred that stirring the sample more than equilibrium time brings no change in concentration.

**Effect of Initial Concentration of Phenol:** Result of Initial adsorbate concentration (C_o) on percent removal of phenol is illustrated in Figure 2 at constant bioadsorbent (Neem Sawdust) dose of 5g/L and 305 K temperature. In the present study percent removal of phenol was studied at two initial phenol concentrations of 75mg/L and 150 mg/L and percent removal obtained was 55% and 41.17% respectively.

Figure 4 show that phenol uptake increases with increase in phenol concentration i.e. 10.31 to 15.44 mg/g at initial phenol concentrations of 75 to 150 mg/L respectively. Increase in phenol loading capacity with Initial phenol concentration can be explained by considering increase in concentration gradient or decrease in mass transfer resistance at higher concentrations.
Effect of Temperature: Effect of temperature on phenol adsorption was studied at constant phenol concentration (C_{o}) of 75 mg/L. Phenol adsorption capacity was tested at two different temperatures i.e. 305K and 311K by keeping other parameters constant like adsorbent dosing (5g/L) and speed of rotation (150 rpm). Graph between contact time and adsorbent loading (q mg/mg) is shown in figure 3. This temperature study shows that as adsorption temperature was increased from 305K to 311K, phenol adsorption goes on decreasing from 10.31 mg/g to 7.95 mg/g. A decrease in phenol adsorption capacity with increase in temperature may be explained by rise in the available thermal energy causing desorption^{13}.

Adsorption Isotherms: The equilibrium of adsorption of toxic organic chemical like phenol is modeled using two isothermal classical models. These models are vital for designing the adsorption system.

Freundlich isotherm^{14,15} represents a nonlinear adsorption model. This model assumes that the adsorption of phenol molecules takes place by interaction between molecules onto a heterogeneous surface^{16}. The general equation of this model is written as

\[ q_e = K_f C_e^{1/n} \]

Where, coefficient K_{f} (mg/g) indicates adsorption capacity and n stands for adsorption intensity. This equation can be linearized as follows.

\[ \log q_e = \log K_f + \frac{1}{n} \log C_e \]
Effect of Initial concentration of phenol on Equilibrium retention

Table 1

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Freundlich</th>
<th>Langmuir</th>
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</thead>
<tbody>
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<td></td>
<td>$K_f$ (L/mg)</td>
<td>$1/n$</td>
</tr>
<tr>
<td>Values</td>
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<td>0.684</td>
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Langmuir model corresponds to one the first theoretical treatments of nonlinear adsorption. It assumes that adsorbate loading takes place by monolayer sorption on homogenous surface and no interaction between adsorbed molecules turn out. The Langmuir model is characterized by the following equation

$$q_e = \frac{q_{max} b C_e}{1 + b C_e}$$

Where $q_{max}$ and $b$ are Langmuir constants related to maximum adsorbent loading (mg/g) and adsorption energy (L/mg) respectively.

In present analysis, equilibrium data is modeled for phenol adsorption on the Neem sawdust to examine the applicability of both models. The values of constants for both of the models i.e. Langmuir and Freundlich are listed in Table 1. Analysis of data summarized in table 1 indicates that the value of regression coefficient is higher in Langmuir model ($R^2 = 0.951$) than Freundlich model ($R^2 = 0.93$). Value of constant $1/n$ less than one i.e. 0.684 indicates the productive adsorption.

Conclusion

Adsorption gives advantages of low cost, availability at ease, profitable, easily operable and high sorption efficiency when compared with the usual techniques like, ion exchange and membrane filtration principally from cost-effective and environmental points of view. In the present work, Neem sawdust was chemically activated and its phenol binding capability was investigated. This work concludes that activated Neem sawdust (Azadirachta indica) is a good quality absorbent and have high loading capability towards phenol retention from aqueous mixtures.

Parameters effecting phenol adsorption on Neem sawdust was investigated as time of contact, initial concentration of phenol and temperature of synthetic solution mixture. This work concludes that for adsorption of toxic organic chemical like phenol, easily available, very low cost adsorbents can be used. An increase in temperature decreases phenol retention on adsorbent whereas increase in initial phenol concentration decreases percent removal of phenol. Retention of phenol on bio-adsorbent increased when there was increase in concentration of phenol in the solution mixture from 75-150 mg/L. Models describing the phenol adsorption phenomena on Neem sawdust was found as Freundlich and Langmuir models. Regression of the equilibrium data illustrates that the Langmuir isotherm equation represents better adsorption of phenol ($R^2 = 0.951$) as compared to Freundlich ($R^2 = 0.930$).

References


