EQUILIBRIUM AND KINETIC STUDIES OF PHENOL SORPTION BY CHITOSAN COATED MONTMORILLONITE

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ABSTRACT

In order to provide physical support for chitosan and increase the accessibility of the binding sites for sorption process applications, chitosan was coated on the surface of montmorillonite. For the optimization of the sorption of phenol on chitosan coated montmorillonite (CCM), effects of pH, initial concentration and temperature on the sorption of phenol by CCM were investigated. In order to find the sorption characteristics, the isothermal data were applied to Langmuir and Freundlich linear isotherm equation, and the thermodynamic parameters ($\Delta H$, $\Delta G$ and $\Delta S$) were also calculated according to the values of binding Langmuir constant $K_L$. The L type sorption isotherm between phenol and CCM suggests a relatively high affinity between the adsorbate and adsorbent, and the mechanism involved in the association of phenol with CCM were proton transfer, hydrogen bonding, London-Van der Waals forces because of lots of the OH and NH$_2$ groups in the chitosan chain. The negative $\Delta H$ constant confirmed that the more phenol was adsorbed by CCM at lower temperature and the driving force for sorption process is an enthalpy effect. The kinetics of the sorption process of phenol on CCM were also investigated using the pseudo-first order and pseudo-second order kinetics, results showed that the second order equation model provided the best correlation with the experimental results. It was reached that modification of chitosan with montmorillonite increased the possibility of utilization of chitosan for phenol remove from aqueous solution.

Keywords: Sorption; Chitosan; Phenol; Kinetics; Equilibrium

INTRODUCTION

Phenols are common soil and groundwater pollutants. These chemicals are classified as priority pollutants due to their toxic health effects at very low concentrations. Phenols in soil and groundwater are derivatives of natural biogeochemical processes or have their origins in anthropogenic materials such as pesticide mixtures. Soils contaminated with anthropogenic phenols are of specific environmental concern because of the ecological risk associated with their high toxicity and relatively high mobility in the soil and groundwater environment. The ingestion of such contaminated water in the human body causes protein degeneration, tissue erosion, and paralysis of the central nervous system and also damages of the kidney, liver and pancreas. The threshold value of phenol in water is 4000 $\mu$g/L. Therefore, it is considered necessary to remove the phenol form industrial effluents before discharging into the water stream. Sorption is superior in simplicity of design, initial cost, ease of operation and insensitivity to toxic substances in comparison with other physicochemical and biological techniques, such as the membrane filtrations coagulation/flocculation, ion exchange, advanced oxidation (chlorination, ozonation), flotation, chemical reduction and biological treatment (bacterial and fungal biosorption, biodegradation in aerobic or anaerobic conditions). Several investigations have studied the sorption of phenol on active carbon because of its large surface area, micro-porous nature, high adsorption capacity, high purity and easy availability.

Natural materials that are available in large quantities or certain waste form agricultural operations may have potential to be used as low cost adsorbents, as they represent unused resources, widely available and are environmentally friendly. Chitosan (2-amino-2-deoxy-β-D-glucan) is a partially deacetylated polymer of chitin by deacetylation with a strong alkaline solution. Many attention have been focused on the remove of trace metals from water by chitosan because of the coordination betweens the metal and the NH$_2$ groups in the chitosan chain, and the sorption of phenol from aqueous solution and its affecting parameters were also reported in our previous study, but it is slightly soluble at low pHs and poses problems for developing commercial applications. It is also soft and has a tendency to agglomerate or form a gel in aqueous solutions. In addition, the active binding sites of chitosan are not readily available for sorption. Transport of the contaminants to the binding sites plays a very important role in process design. Therefore, it is necessary to provide physical support and increase the accessibility of the binding sites for process applications. Clays are widely used as adsorbents due to their high specific surface area. On the one hand, their sorption capacity is very low for organic molecules that are highly water soluble, polar, or cationic. This is due to the hydrophilic nature of the mineral surfaces. Natural clay has a negative charge that is compensated by exchangeable cations, such as Na$^+$ and Ca$^{2+}$ on their surfaces. This study concerns the applicability of montmorillonite as a physical support for coating chitosan to remove phenol. Over the last 20 years, several studies have been carried out on the use of quaternary ammonium salt exchanged clays as adsorbents of many organic compounds from water.

In the present investigation an attempt was made to overcome these mass transfer limitations by synthesizing a biosorbent by coating chitosan on the surface of montmorillonite and evaluating its equilibrium sorption properties. The combination of the useful properties of montmorillonite and that of natural chitosan, could introduce a composite matrix with many application and superior sorption capabilities. Batch studies are carried out involving process parameters such as the effects of pH, the initial phenol concentration, temperature and contact time. Equilibrium analysis was conducted to understanding sorption process.

MATERIALS AND METHODS

Chemical reagents

Na-montomorillonite used was provided by 184 Bentonite Company of the 10$^{th}$ Agriculture Division of Xingjiang Construction Group in China, which is a fine powder with an average particle size of 75 $\mu$m in the dry state, a purity of 90%, an interlayer spacing of 1.44 nm, and a cation exchange capacity (CEC) of 92 mmol/100g. Stock solution of 1000 mg/L phenol (AR) was prepared with distilled water and stored in a refrigerator. Working solutions were prepared by diluting the stock solution with distilled water just prior to use. Chitosan with the deacetylation degree 88% was obtained from Kabo Co. (Shanghai, China), which was ground and sieved to 100-150 mesh. The viscosity ($[\eta]$) of sample used in this experiment is 280,000. The weight-average molecular weight was calculated by Mark-Houwink equation: $\eta_p$ = $kM_w^n$, where $\eta_p = 1.02\times10^{-3+DD+1.82}$, $k = 1.64\times10^{-6}$ and DD is the degree of deacetylation of chitosan. The weight-average molecular mass ($M_w$) of sample used in this experiment is 280,000.

Preparation of chitosan coated montmorillonite (CCM)

One gram montmorillonite was ground into paste in 100 mL deionized water, and then added in 100 mL 2 g/L chitosan solution with constant stirring for 1 h at 25°C. The pH of the solution was adjusted to 7.0-7.5 with 20 g/L sodium hydroxide solution and then was precipitated for 0.5 h at 25°C. The resulting CCM was filtered and washed with deionized water, and then dried at 40°C. XRD data was obtained using a DX-2000/DX-2500 X-ray diffractometers (Dandong, China) at room temperature without any further heat treatment. %OC (organic carbon)value of CCM was measured with HCl (10%, V/V) using a CNS Macro Elemental Analyzer (Elementar Analysensysteme GmbH, Germany). The specific surface areas of montmorillonite and CCM were determined by using BET method after N$_2$ adsorption/desorption at 77 K with Sorptomatic 1990, Germany.

Equilibrium studies

The sorption experiments were performed by batch method where samples of 0.1 g of CCM were equilibrated with 50 mL of solution containing various amount of phenol, under an intermittent stirring. Solutions pH was 1.
adjusted by using diluted solution of NaOH or HCl. The temperature (25, 35, and 45 °C) of the thermostatic bath was controlled within ±0.5 °C. In pH dependent experiments, the phenol concentration was constant at 40 mg/L for each sample. After a determined time (usually 24 h), the suspensions were centrifuged at 5000 rpm for 20 min, the concentration of phenol in the clear supernatant was determined using spectrophotometrically measurements. A SP-1105E 721-model spectrophotometer (Shanghai, China) was used throughout for the concentration determination of phenol at wavelength 510 nm using 4-aminoantipyrine as the chromogenic reagent. The pH measurements were carried out with a 25 pHS-2C model acidity meter (Leici Instrumental Factory, Shanghai, China), using a combination electrode.

The sorption capacity of CCM (qe) was evaluated by amount of phenol sorbed: $q_e = \frac{(C_0 - C_e) \times V}{W}$, (mg of phenol/g of sorbent) and by percent of phenol removal: $R\% = \left( \frac{C_0 - C_e}{C_0} \right) \times 100$, where: $C_0$ and $C_e$ are initial and the equilibrium concentration of phenol in solution (mg/L), $G$ is amount of sorbent (g) and $V$ is volume of solution (mL).

**Kinetic studies**
Effect of contact time was determined by the “limited bath” technique. A sample (1 g) of CCM was added to 500 mL volume of phenol solution, with initial phenol concentration 40 mg/L. Under stirring, the temperature of solution was held constant at 25 °C with a thermostatic bath and solutions pH was adjusted to 4.0 by using diluted solution of NaOH or HCl. After different time intervals (from 30 minutes to 24 hours), volumes of 1 mL supernatant were taken for spectrophotometrically measurements of phenol content.

**RESULTS AND DISCUSSIONS**

**Characterization of CCM**
XRD data was used to see the basal peak and investigated the $d_{100}$ value, there was no difference with the $d_{100}$ values of montmorillonite and CCM, which meant that chitosan could not enter the interior channels of montmorillonite. %OC value of CCM was found to be 5.22, the specific surface areas of montmorillonite and CCM were 256 m$^2$/g and 187 m$^2$/g, respectively. The amount of chitosan deposited on the surface of montmorillonite was calculated theoretically to be about 11.5% in CCM when chitosan was assumed to be with the formula (C$_3$H$_7$NO$_2$)$_n$.

**Optimization of the sorption of phenol on CCM**
$pH$ is an important parameter for adsorption of phenol from aqueous solution because it affects the solubility of phenol, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction. To examine the effect of $pH$ on the phenol removal efficiency, the $pH$ was varied from 2.0 to 10.0. The amount of phenol adsorbed show a declining trend with higher as well as with lower $pH$, and the maximum removal of phenol (more than 88% by the adsorbents) was observed at $pH$ 4.0 (Figure 1). Several researchers have studied the sorption-desorption of phenolic chemicals in soil-water and sediment-water systems. Phenols have been found to possess relatively high mobility in the aquifer environment because their sorption to mineral surfaces were usually minimal, soil organic matter (SOM) was found to be a dominant factor that influenced the fate of organic contaminants in soils and aquatic material, so the sorption of phenol by CCM was mainly contributed to chitosan. At low $pH$ (below 4.0), the amine group on chitosan is protonated to varying degree but phenol is not dissociated because phenol is a very weak acid and has resonance stability due to its anionic structure ($pK_a$ value of phenol is 9.98). Simultaneously physical and chemical adsorption were known as sorption, so the results indicated at $pH$ 4.0 the chemical affinity between the OH and NH$_2$ groups in the structure of chitosan and the OH group in the structure of phenol reached the top. Non-polar portions play an important role in hydrophobic interactions, the mechanism involved in the association of phenol with CCM were proton transfer, hydrogen bonding, London-Van der Waals forces because of lots of the OH and NH$_2$ groups in the chitosan chain.

The sorption capacity of the powdered adsorbent CCM for phenol was determined at different initial phenol concentrations. The results presented in Table 1 shown that the phenol amount adsorbed increased with increasing phenol concentration but the percent of phenol removal decreased. At low initial phenol concentration, the ratio of the number of phenol ions to the number of available adsorption sites was small and consequently the sorption was independent of the initial concentration, but as the concentration of phenol increased, the situation changes and the competition for adsorption sites became fierce. As a result, the extent of sorption came down considerably, but the amount adsorbed per unit mass of the adsorbent rose.

The sorption capacity of the powdered adsorbent CCM for phenol was determined at different temperature (Table 1). It indicated that less phenol was adsorbed at high temperature. The effect of ionic strength to sorption of phenol was also examined, sorption capacities of CCM for phenol increased with the increased in ionic strength.

**Figure 1.** The influence of $pH$ value on the sorption of the phenol on CCM.

**Table 1.** The influence of temperature on the sorption of phenol on CCM*  

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$C_i$(mg/L)</th>
<th>$C_f$(mg/L)</th>
<th>$q$(mg/g)</th>
<th>R(%)</th>
</tr>
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<tbody>
<tr>
<td>25</td>
<td>20</td>
<td>1.23</td>
<td>9.38</td>
<td>93.8</td>
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<td></td>
<td>40</td>
<td>4.78</td>
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<td>23.02</td>
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<td></td>
<td>100</td>
<td>54.13</td>
<td>22.94</td>
<td>45.8</td>
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</table>

* $C_i$: initial concentration of phenol; $C_f$: equilibrium concentration of phenol; $q$: sorption capacity of CCM; $R\%$: percent of phenol removal.
The values in Table 2 show that the experimental data were more suitable to the Langmuir model than the Freundlich model. This was in accordance with the shape of the sorption isotherms, which corresponded to type L (Langmuir type) in the Giles classification system for sorption of a solute from its solution.  

**Thermodynamic study**

As seen from Table 2 the values \( q_L \) of maximum sorption capacity, corresponding to monolayer coverage of the binding sites available in the sorbent, was obtained at different temperature. In the range 25-45°C an decrease of \( q_L \) was found with the increasing temperature.

Using the values of binding Langmuir constant \( K_L \), and the following equations, one can calculate the thermodynamic parameters \((\Delta H, \Delta G, \Delta S)\) (Table 3) of phenol sorption on CCM,

\[
\ln K_L = \frac{-\Delta H/(RT) + \text{constant}}{T} \tag{5}
\]

\[
\Delta G = -RT \ln K_L \tag{6}
\]

\[
\Delta S = (\Delta H - \Delta G)/T \tag{7}
\]

The negative values of apparent free energy change \((\Delta G, \text{kJ/mol})\) confirmed that the sorption process of phenol on CCM was a spontaneous process. The negative apparent enthalpy change \((\Delta H, \text{kJ/mol})\) computed from the slope of linear dependence of \(\ln q_L\) on \(1/T\) confirmed that more phenol was adsorbed by CCM at lower temperature. The negative apparent entropy change \((\Delta S, \text{J/mol K})\) characterized a decreased disorder of the system and the apparent entropy change values were almost. It can be suggested that the driving force for sorption process was an enthalpy effect.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Freundlich linear isotherm</th>
<th>Langmuir linear isotherm</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>( k )</td>
<td>( n )</td>
</tr>
<tr>
<td>25</td>
<td>9.68</td>
<td>3.096</td>
</tr>
<tr>
<td>35</td>
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<td>3.205</td>
</tr>
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<td>45</td>
<td>7.31</td>
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<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( \Delta G ) (kJ/mol)</th>
<th>( \Delta H ) (kJ/mol)</th>
<th>( \Delta S ) (J/mol K)</th>
</tr>
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<tbody>
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<td>-42.61</td>
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</tr>
<tr>
<td>318</td>
<td>-13.75</td>
<td>-27.40</td>
<td>-42.63</td>
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</tbody>
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<table>
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<tr>
<th>Table 4. The kinetic parameters of sorption process of phenol on CCM</th>
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<tr>
<td>( k_1 )</td>
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<tr>
<td>0.0065</td>
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</table>
instance, pseudo second-order kinetics was also observed in the biosorption of ph

effects. For the sorption of phenol by CCM on the basis of the experimental resu


daughter species at the initial stages of the contact period, a gradual slow down as it a


during the initial stage for adsorption leading to faster rate, in contrast to final stage where a


equilibrium period required for maximum removal was found to be 4-6 hours. However the soro


data. The kinetics of the sorption process of phenol on CCM was investigated using the pseu


temperature confirmed that more phenol is adsorbed by CCM at lower temperature, and the dri


CONCLUSIONS


For the sorption of phenol by CCM on the basis of the experimental results obtained, the sorp


given in Table 4. The results showed that the second order equation model provided the be


drilling force for sorption process is an enthalpy effect. The kinetics of the sorption process of phe


the experimental kinetic parameters of phenol on CCM were given in Table 4. The results showed th


REFERENCES