Removal of aniline and phenol from water using raw and aluminum hydroxide-modified diatomite
C. D. Wu, J. Y. Zhang, L. Wang and M. H. He

ABSTRACT
The feasibility of using raw diatomite and aluminum hydroxide-modified diatomite (Al-diatomite) for removal of aniline and phenol from water was investigated. Their physicochemical characteristics such as pHsolution, point of zero charge (pH_{PZC}), surface area, Fourier transform infrared (FT-IR) and scanning electron microscopy was determined. After the raw diatomite was modified, the surface area of Al-diatomite increased from 26.67 to 82.65 m² g⁻¹. The pH_{PZC} and pH_{solution} (10%) occurred around pH 5.2 and pH 8.6, respectively. The removal rates of aniline and phenol on diatomite and Al-diatomite decreased with increasing solution pH, while surface charge density decreased. The adsorption of aniline and phenol on diatomite presented a good fit to the Langmuir and Freundlich models, but the models are not fit to forecast the adsorption of aniline and phenol on Al-diatomite. The study indicated that electrostatic interaction was a dominating mechanism of aniline and phenol sorption onto Al-diatomite.

Key words | adsorption, aniline, diatomite, isotherm, phenol

INTRODUCTION
Aniline and phenol are important organic intermediates and also environmentally relevant pollutants, which widely present in the effluents from dyestuffs, pesticides, pharmaceuticals, petrochemicals, and other industries (Moreno-Castilla 2004; Laszlo et al. 2007). In consideration of the hazardous effects of aniline and phenol on human health at low concentrations, they have been included in the list of priority pollutants by most national environmental protection agencies (Yang et al. 2008; Wu et al. 2012). Consequently, efficient removal of aniline and phenol in aqueous as well as in non-aqueous solution has drawn significant interest.

In recent years, several treatment methods have been recommended for the treatment of wastewater containing aniline and phenol, such as adsorption (Laszlo et al. 2007), catalytic oxidation (Dobrynkin et al. 2005), and membrane filtration (Jadhav et al. 2001). Among those methods, adsorption is considered as a particularly competitive and effective method. Activated carbon is the most common adsorbent used in the removal of aniline and phenol from wastewater (Laszlo et al. 2007; Suresh et al. 2011). However, activated carbon with high adsorption capability is not economical due to the high costs associated with production and regeneration (Warhurst et al. 1996). Thus, the use of alternative cheap materials for removal of dissolved organic matter (DOM) is required.

Diatomite (SiO₂·nH₂O), which has a large internal surface area and porosity containing up to 80–90% voids, is a light and soft sedimentary rock with pale color and is available in large deposits around the world (Khraisheh et al. 2004; Wu et al. 2011). It has a unique combination of physical and chemical properties, which make it applicable as substrate for adsorption of organic pollutants (Al-Ghouti et al. 2005). Studies have shown that the surface area of modified diatomite was increased compared to natural diatomite so that the capability of adsorption was improved (Khraisheh et al. 2004; Aivalioti et al. 2012). Recently, some studies have reported that diatomite as a substrate is introduced into water along with aluminum salt to remove DOM (Al-Degs et al. 2000; Al-Ghouti et al. 2005; Erdem et al. 2005). Studies have shown that the surface area of modified diatomite was increased compared to natural diatomite so that the capability of adsorption was improved (Khraisheh et al. 2004; Aivalioti et al. 2012). Recently, some studies have reported that diatomite as a substrate is introduced into water along with aluminum salt to remove DOM (Park & Yoon 2003). It is known that the aluminum salt added will be hydrolyzed to produce aluminum hydroxide and then the aluminum hydroxide and Al³⁺ will be adsorbed and/or settled on the surface of the porous diatomite. So the surface
area and structure of the modified diatomite can influence the attractive forces between the adsorbent and adsorbate. So far, few studies on the change of the physical and chemical properties and the sorption characteristics of Al-diatomite have been reported.

The aim of this work is to examine the effectiveness of diatomite and Al-diatomite for removal of aniline and phenol. The physicochemical characteristics of these adsorbents such as the pH of the solution (\(\text{pH}_{\text{solution}}\)), the point of zero charge (\(\text{pH}_{\text{pzc}}\)), surface charge density and surface area will be studied. Furthermore, the effect of key parameters and the involved mechanisms of the adsorption processes, and the adsorption isotherms will be investigated.

**MATERIALS AND METHODS**

**Adsorbents**

Diatomite was obtained from the Clay Mining Factory, Zhejiang Province. The samples were washed with distilled water to remove fines and other adhered impurities, dried at 110 °C, and stored in tightly stoppered glass bottles. Surface modification was accomplished by treating the diatomite with aluminum chloride and sodium hydroxide (Khraisheh et al. 2004). Samples of diatomite (15 g) were immersed in 6 mol L\(^{-1}\) sodium hydroxide at 90 °C for 2 h. The mixture was then placed in 100 mL of 2.5 mol L\(^{-1}\) aluminum chloride (adjusted to pH 1–2 with hydrochloric acid) at room temperature for 10 h. The diatomite soaked by the solution with aluminum chloride was filtered and separated from the supernatant. The solid was then immersed in 6 mol L\(^{-1}\) sodium hydroxide, at room temperature, for 10 h to precipitate the aluminum hydroxide. The excess solution was decanted off and the diatomite left exposed to the air. The sample was then washed with water, dried at 110 °C, and stored in tightly stoppered glass bottles. In this work, the modified diatomite is referred to as Al-diatomite.

**Surface area**

The specific surface area of diatomite was estimated according to the Sears method (Sears 1956). The surface area \((S)\) was estimated from Equation (1) (Lowell & Shields 1984). The procedure was carried out in duplicate and the result was reported as an average.

\[
S(\text{m}^2 \cdot \text{g}^{-1}) = 32V - 25 \tag{1}
\]

where \(V\) is the volume of NaOH solution required to raise the pH value of the sample from 4 to 9.

The surface area for Al-diatomite was estimated according to the Zn\(^{2+}\) adsorption method (Kozawa 1959).

**Scanning electron microscope (SEM) analysis**

Samples of diatomite, Al-diatomite and Al-diatomite adsorbed with phenol were scanned using a PHILIPS XL-30 SEM.

**Adsorption studies**

Aqueous solutions of aniline and phenol, respectively, were prepared in a final concentration of 20–170 mg L\(^{-1}\) with 30 mg L\(^{-1}\) intervals. The adsorption isotherm experiments were carried out in 100 mL glass bottles, where 0.05 g of diatomite or Al-diatomite and 0.05 L of the appropriate concentration of the test aniline or phenol solution were added. The bottle samples were subsequently capped and shaken in a shaker for 24 h at 25 °C at 150 rpm. 0.1 mol L\(^{-1}\) HCl and 0.1 mol L\(^{-1}\) NaOH were used to adjust the solution pH (pH ranged from 2 to 12). After 24 h, the equilibrium was reached and the equilibrium concentration was estimated. The equilibrium concentration of aniline and phenol in the aqueous phase was analyzed using a UV-visible spectrophotometer (TU-1800SPC, China). Blanks were also used.

The adsorbed amount of the solute was calculated according to Equation (2):

\[
q_e = \frac{V \cdot (C_0 - C_e)}{m} \tag{2}
\]

where \(q_e\) (mg g\(^{-1}\)) is the amount of adsorbate adsorbed on adsorbent, \(V\) (L) is the volume of the equilibrium solution, \(C_0\) (mg L\(^{-1}\)) and \(C_e\) (mg L\(^{-1}\)) are the initial and the equilibrium concentrations of the solute, respectively, and \(m\) (g) is the weighed amount of the adsorbent.

**\(\text{pH}_{\text{solution}}\) and surface charge density**

The \(\text{pH}_{\text{solution}}\) of diatomite was carried out in 100 mL glass bottles, where 3 g of diatomite were added to 30 mL of deionized water. The mixture was then shaken in a shaker for 24 h. The pH of the mixture was recorded using a pH meter. The surface charge of diatomite was estimated by following an alkalimetric titration method (Noh & Schwarz 1989; Chen & Lin 2001).
RESULTS AND DISCUSSION

Characterization of diatomite

The scanning electron micrographs of diatomite, Al-diatomite and Al-diatomite adsorbed with phenol are shown in Figure 1(a)–(c), respectively. Diatomite frustules were examined in a SEM study. These frustules are divided into two main categories (Al-Degs et al. 2001): centric (discoid) and pennate (elongated), which are shown in Figure 1(a). However, Figure 1(b) shows that diatomite frustules have been completely modified with aluminum hydrate. It suggests that the diatomite structure is changed upon adsorbing aluminum hydrate. Figure 1(c) shows that the Al-diatomite with phenol has a tendency to form spherical agglomerates with a large void volume in addition to its highly porous structure. The high porosity of this material is one of the main reasons for it being considered as a potential sorbent for dissolved matter. The analytical results indicate that the surface area of natural diatomite used in this study is 26.67 m² g⁻¹.

The surface charge density as a function of solution pH is showed in Figure 2. As the solution pH increases, the surface charge density decreases. The intersection of the curve with the x-axis occurs at 5.2. So the PZC of the diatomite occurs at the pH value of 5.2 and the pH_{solution} (10%) is 8.6 under the same conditions. The hydroxyl groups present on the surface of the diatomite can gain or lose a proton, resulting in a surface charge that varies with changing pH (Park & Yoon 2003). At low pH, surface sites are protonated and the surface becomes positively charged:

\[ \text{H}^+ + \text{MOH} \rightarrow \text{MOH}^+ \quad (3) \]

At high pH, the surface hydroxides lose their protons and the surface becomes anionic.

\[ \text{MOH} \rightarrow \text{H}^+ + \text{MO}^- \quad (4) \]

Figure 1 | Scanning electron microscope (magnification 2,000×) of (a) diatomite, (b) Al-diatomite and (c) Al-diatomite adsorbed with phenol.
When the concentration of cationic MOH$_2^+$ sites equals the concentration of anionic MO$^-$ sites, the average surface charge is neutral at the PZC.

Characterization of Al-diatomite

In this study, the amount of Al$^{3+}$ and/or aluminum hydrate loaded on the surface of the diatomite was estimated to be approximately 0.23 g g$^{-1}$. The surface area of Al-diatomite was estimated to be approximately 82.65 m$^2$ g$^{-1}$ as mentioned above.

The diatomite surface contains silanol groups. A Fourier transform infrared (FT-IR) spectra can offer some indication of the ability of the organic matter to react with the silanol groups, which can indicate the adsorption mechanism involved. Figure 3 shows the FT-IR spectra of diatomite, Al-diatomite and Al-diatomite with phenol.

The vibration of the Si–OH bond results in a band at 3,700 cm$^{-1}$, together with a doublet, due to O–H deformation, at approximately 800 cm$^{-1}$. The main adsorption bands of diatomite occur at 3,690, 1,113, 1,047, 789 and 714 cm$^{-1}$. Diatomite and Al-diatomite exhibit two clear peaks at 789 and 714 cm$^{-1}$ of O–H vibration. Similar effects can be observed for the main Si–OH vibration at 3,700 cm$^{-1}$. It can be concluded from Figure 3 that the peak shifts from 3,690 to 3,652 cm$^{-1}$, when the phenol is adsorbed on Al-diatomite.

Effect of pH on the adsorption

The effect of pH on the percentage removal of aniline adsorbed on the diatomite and the Al-diatomite from aqueous solution is illustrated in Figure 4(a). From Figure 4(a), it can be noted that the maximum percentages of aniline removal from aqueous solution with diatomite and Al-diatomite occur at pH 4.45 and pH 2.2, respectively, and the extent of removal decreases as the solution pH increases. At lower pH, the percentage of aniline removal is relatively high, which may be attributed to the presence of the positive charge of the diatomite surface. Furthermore, as the surface charge density decreases with an increase in the solution pH (pH, pHPZC), the electrostatic repulsion between positively charged DOM (aniline) and the surface of the diatomite is lowered, which may result in an increase in the rate of adsorption (Chen & Lin 2001). Figure 4(b) illustrates the effect of pH on the percentage of phenol adsorbed on diatomite and Al-diatomite from aqueous solution. It shows that the two curves of the percentage for phenol removal decrease with increasing solution pH. The removal of phenol from aqueous solution on the diatomite is lower than that on the Al-diatomite. It can be explained by the
surface area of Al-diatomite being greater than that of diatomite. The maximum efficiencies of phenol removal with diatomite and Al-diatomite are achieved at acidic condition pH 4.45 and pH 2.1, respectively.

**Adsorption isotherms**

The studies on the adsorption isotherm of aniline and phenol onto diatomite and Al-diatomite were conducted under slightly acidic conditions at pH = 6 for two main reasons. Firstly, the removal rate of aniline and phenol with diatomite and Al-diatomite is better in acidic conditions. Secondly, the conditions are close to the actual wastewater. Their adsorption isotherms are shown in Figure 5. It shows that the equilibrium adsorption amount of aniline and phenol onto diatomite and Al-diatomite increases as their equilibrium concentration increases. At the same equilibrium concentration, the amount of aniline/phenol adsorbed at equilibrium onto Al-diatomite is much more than that on diatomite. The isotherms illustrate that the adsorption capacity of diatomite is greatly improved by modification with Al\(^{3+}\) and/or aluminum hydrate.

**Table 1** | Langmuir and Freundlich isotherm constants for aniline and phenol sorption onto diatomite and Al-diatomite

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorbate</th>
<th>(a)</th>
<th>(K_L)</th>
<th>(R^2)</th>
<th>(K_F)</th>
<th>(n)</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diatomite</td>
<td>Aniline</td>
<td>1.000</td>
<td>3.023</td>
<td>0.940</td>
<td>1.353</td>
<td>0.894</td>
<td>0.978</td>
</tr>
<tr>
<td>Diatomite</td>
<td>Aniline</td>
<td>0.00629</td>
<td>0.898</td>
<td>0.924</td>
<td>0.721</td>
<td>0.824</td>
<td>0.986</td>
</tr>
<tr>
<td>Al-diatomite</td>
<td>Aniline</td>
<td>0.00248</td>
<td>0.576</td>
<td>0.274</td>
<td>0.0878</td>
<td>0.642</td>
<td>0.845</td>
</tr>
<tr>
<td>Al-diatomite</td>
<td>Aniline</td>
<td>0.0221</td>
<td>3.617</td>
<td>0.822</td>
<td>0.117</td>
<td>0.747</td>
<td>0.894</td>
</tr>
</tbody>
</table>

\(a\) and \(K_L\) are Langmuir constants; \(a\) is related to the energy of adsorbent, \(K_L\) is related to the affinity between adsorbent and adsorbate.

\(K_F\) and \(n\) are Freundlich constants; \(K_F\) is an indicator of adsorption capacity, \(n\) refers to adsorption tendency.
It could be ascribed to the increase of its surface area, and the presence of the Al(OH)$_3$ (s) on the surface of Al-diatomite, which can adsorb acidic substances.

The models of Langmuir and Freundlich are adopted to describe the adsorption of aniline and phenol. The correlative parameters are listed in Table 1. It is shown that the adsorption of aniline and phenol on diatomite strongly agrees with Langmuir and Freundlich models with correlation coefficients more than 0.92 for all systems. But the adsorption of aniline and phenol on Al-diatomite does not fit the two models. The correlation coefficients of adsorption of aniline and phenol on Al-diatomite are lower than 0.9 for all the systems studied. It may suggest that the number of sites on the diatomite surface is limited and the aniline and phenol can form a monomolecular layer on the surface at maximum capacity. This also accords with the observation that the adsorption in an aqueous solution usually forms one layer on the diatomite surface, but multilayer adsorption occurs on Al-diatomite.

CONCLUSION

Modified Al-diatomite showed a higher tendency for removal of aniline and phenol from aqueous solution. The pH of aniline and phenol solution is a very important parameter. The removal percentages of aniline and phenol decrease as pH increases. The maximum percentage of aniline removal from aqueous solution with diatomite and Al-diatomite took place at pH 4.45 and pH 2.2, respectively, while the maximum removal percentage of phenol with them was achieved at pH 4.45 and pH 2.1, respectively.

The adsorption of aniline and phenol on diatomite can fit the Langmuir and Freundlich models well, but those models do not fit the adsorption of aniline and phenol on Al-diatomite. It is shown that adsorption of aniline and phenol from aqueous solution usually forms one layer on the diatomite surface while multilayer adsorption occurs on the Al-diatomite surface.

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REFERENCES


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