Removal of organic pollutants by surfactant modified zeolite: Comparison between ionizable phenolic compounds and non-ionizable organic compounds

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HIGHLIGHTS

► Surfactant modified zeolite could greatly retain organic pollutants.
► Uptake of organic compounds was due to the loaded surfactant.
► \( k_{uw} \) is crucial for the uptake of both ionizable and non-ionizable organic solutes.
► \( pK_a \) is another factor affecting adsorption process of ionizable organic pollutants.
► Adsorption mechanisms of the two kinds of organic pollutants were proposed.

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ABSTRACT

The aim of this study was to examine the adsorption capability and mechanism of hexadecyltrimethylammonium modified zeolite, which was synthesized from coal fly ash, for the removal of ionizable phenolic compounds (phenol, p-chlorophenol and bisphenol A, with different \( pK_a \)) and non-ionizable organic compounds (aniline, nitrobenzene, and naphthalene, with different hydrophobicity). The obtained zeolite was identified as type Na-P1 \( \left( \text{Na}_6\text{Al}_8\text{Si}_{12}\text{O}_{42} \cdot 12\text{H}_2\text{O}; \text{JCPDS code 39-0219} \right) \), which is classified into the gismondine group with a pore size of \( 3.1 \AA \times 4.5 \AA \) [100] and 2.8 \( \AA \times 4.8 \AA \) [101]. The adsorption of the two kinds of organic compounds was due to loaded surfactant bilayer because modified zeolite showed great ability for the removal of organic chemicals while little adsorption by zeolite was observed. The isotherm data of ionizable compounds fitted well to the Langmuir model but those of non-ionizable chemicals followed a linear equation. Uptake of ionizable compounds depended greatly on pH, increasing at alkaline pH conditions. In contrary, adsorption of non-ionizable chemicals was essentially the same at all pH levels studied. The adsorption of both kinds of organic compounds correlated well to \( k_{uw} \) value, suggesting that more hydrophobic organic contaminants are more easily retained by modified zeolite. Based on the different adsorption behavior, the uptake of non-ionizable pollutants was thought to be a single partitioning process into the surfactant bilayer. For ionizable compounds, however, interaction of the phenol group(s) with the positively charged “head” of surfactant additionally functions.

1. Introduction

Coal fly ash (FA) is a solid waste generated in large amounts worldwide; therefore, development of new techniques for its productive reuse is important. As a measure to recycle FA, zeolites synthesized from FA (ZFAs) have been extensively investigated in recent years. A number of zeolites have been produced from FA, including Na-P1, philipside, chabazite, F linde, harschelite, faujasite, analcime, zeolite A, zeolite X, zeolite Y, and hydroxyxosalite [1]. It is shown that ZFA is applicable for the removal of a number of pollutants from water, including ammonium [2–4], heavy metals [5–16], as well as phosphate [17,18]. Very encouraging results have also been obtained for ZFA to remove some waste gases from flue [19–21]. Regarding the decontamination of organic pollutants from water, satisfactory performance was only reported for methylene blue, a cationic dye [22]. Because the surface of zeolites is negatively charged and hydrophilic in nature, little affinity toward other organic pollutants such as anionic, ionizable and non-ionizable organic chemicals is thus expected. Nevertheless, researchers found that permanent negative charges in crystal structures enable natural zeolites to be modified by cationic surfactants so that they better retain organic pollutants [23–25]. Stimulated by this advance, we recently presented promising results for the removal of humic acid (in the form of sodium salt) from water by surfactant modified zeolite which was synthesized from FA (SMZFA) [26].
### Table 1
Chemical composition and some properties of FA and ZFA.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>FA</th>
<th>ZFA</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂ (%)</td>
<td>51.4</td>
<td>38.1</td>
</tr>
<tr>
<td>Al₂O₃ (%)</td>
<td>22.1</td>
<td>20.6</td>
</tr>
<tr>
<td>Fe₂O₃ (%)</td>
<td>9.7</td>
<td>8.5</td>
</tr>
<tr>
<td>CaO (%)</td>
<td>6.9</td>
<td>5.7</td>
</tr>
<tr>
<td>MgO (%)</td>
<td>1.6</td>
<td>1.3</td>
</tr>
<tr>
<td>Na₂O (%)</td>
<td>1.2</td>
<td>6.8</td>
</tr>
<tr>
<td>K₂O (%)</td>
<td>1.3</td>
<td>0.4</td>
</tr>
<tr>
<td>Moisture (%)</td>
<td>0.1</td>
<td>12.3</td>
</tr>
<tr>
<td>Others (%)</td>
<td>5.7</td>
<td>6.3</td>
</tr>
<tr>
<td>BET surface area (m² g⁻¹)</td>
<td>1.3</td>
<td>59.6</td>
</tr>
<tr>
<td>CEC (mmol g⁻¹)</td>
<td>&lt;0.03</td>
<td>1.872</td>
</tr>
<tr>
<td>ECCEC (mmol g⁻¹)</td>
<td>&lt;0.03</td>
<td>0.178</td>
</tr>
<tr>
<td>HDTMA loaded (mmol g⁻¹)</td>
<td>–</td>
<td>0.349</td>
</tr>
</tbody>
</table>

*TiO₂, carbon, SO₃, etc.*

*Internal cation exchange capacity.*

Most organic pollutants are either ionizable or non-ionizable compounds. Phenolic compounds are typical ionizable chemicals which are weakly acidic and thus could form organic anions at sufficiently high pH levels. Phenolic compounds are important in industry and draw much attention in the practice of water pollution control. While non-ionizable organic pollutants are permanently electrically neutral because they do not possess an ionizable group.

The current study focuses on the removal performance and mechanism of ionizable phenolic compounds and non-ionizable organic compounds by SMZFA.

### 2. Materials and methods

#### 2.1. Materials

ZFA was hydrothermally synthesized from FA that was obtained from the Shidongcheng electric power station in Shanghai, China. The sources of Si and Al in ZFA arose from the corresponding components in FA (Table 1). For zeolite synthesis, approximately 25 g of FA was placed in a flask and was mixed with 150 mL of 2.0 mol L⁻¹ NaOH solution. The slurry was boiled with reflux for 24 h with stirring. After centrifugation, the solid product (ZFA) was washed with doubly distilled water three times and twice with ethanol followed by drying in an oven at 60 °C. For surfactant modification, 500 mL of the solution of the surfactant, hexadecyltrimethylammonium (HDTMA) bromide, with a concentration of 55 mmol L⁻¹ was vigorously mixed with 10 g of ZFA at 50 °C for 4 h. These reaction conditions were adopted to assure high loading of surfactant. After being cooled to room temperature, the product was centrifuged, washed with doubly distilled water, dried in an oven at 60 °C and ground to pass through an 80-mesh sieve.

#### 2.2. Characterization of materials

For the chemical analysis, except for silicon, the samples were digested with hydrogen fluoride in conjunction with perchloric acid and dissolved later by hydrochloric acid. For silicon, the samples were melted with sodium hydroxide. The elemental concentrations were then measured in the digestions by Inductively Coupled Plasma Atomic Emission Spectrometry (IRIS advantage 1000). The crystalline phase(s) in the materials were identified by powder X-ray diffraction analysis on a D8 ADVANCE X-ray diffractometer using Ni filtered Cu-Kα radiation (40 kV, 40 mA). Particle morphology was observed by SEM using a JEOL JSM-7401F microscope. The FTIR spectra were recorded with a FT-IR spectrophotometer (SHIMADZU IRPrestige-21) using the KBr method. The specific surface area was determined on an ASAP 2010 from Micromeritics by fitting the amount of N₂ adsorbed at −196 °C for the BET equation after preliminary heating at 200 °C. Organic carbon content was measured by the difference in weight loss between 105 and 750 °C. The total cation exchange capacity (TCEC) was determined from the amount of retained ammonium by the ammonium acetate method [27]. The external cation exchange capacity was determined by adsorption of methylene blue from aqueous solution [28,29]. Zeta potential measurements as a function of medium pH were determined using a Malvern Instruments Zetasizer 2000 equipped with a microprocessor unit. Suspensions of 0.05 g/100 mL were prepared and the medium pH was adjusted by adding 0.1 mol L⁻¹ or 0.01 mol L⁻¹ HCl (or NaOH). The unit automatically calculated the electrophoretic mobility of the particles and converted it to the Zeta potential using the Smoluchowski equation.

#### 2.3. Adsorption experiments

Three phenolic compounds with different pKₐ and thus different ionizability (phenol, p-chlorophenol and biphenol A), and three non-ionizable compounds with different hydrophobicity (aniline, nitrobenzene, and naphthalene) were selected to assess the decontamination performance of ionizable and non-ionizable organic chemicals by SMZFA. Adsorption isotherms were prepared for FA, ZFA, and SMZFA, respectively. The materials were mixed with aqueous solutions containing the organic pollutants ranging in initial concentrations and then shaken continuously on an orbital shaker in a thermostatic chamber (model TS-2102C) at 25 ± 0.1 °C for 24 h. Our preliminary experiments confirmed that the reaction time of 24 h is sufficient for the solutes to reach equilibrium concentrations. The suspensions were then separated by centrifugation (for pollutants other than biphenol A) or filtration (for biphenol A) to yield a clear supernatant or filtrate for analysis of the equilibrium concentrations of the solutes. Blank test revealed little (<1.5%) adsorption of biphenol A by the filter. The concentrations were measured with UV/Visible Unico spectrophotometer (model UV-2102PCS) at the wavelength of 270 nm for phenol, 280 nm for p-chlorophenol, 276 nm for biphenol A, 230 nm for aniline, 268 nm for nitrobenzene, and 285 nm for naphthalene, respectively. The effect of pH on the removal of phenol, p-chlorophenol, biphenol A and naphthalene was determined at initial concentrations of 50, 50, 100 and 20 mg L⁻¹, respectively, over a pH range of 3–11. The pH was adjusted by adding 0.1 mol L⁻¹ or 0.01 mol L⁻¹ HCl (or NaOH) to the solutions. The amounts of solute adsorbed per unit mass of adsorbent were calculated from the differences between the initial and the final solute concentrations in solution before and after adsorption:

\[
q = \frac{(c_0 - c_e)W}{m}
\]

where \( V \) is the sample volume in L, \( c_0 \) is the initial solute concentration in mg L⁻¹, \( c_e \) is the equilibrium concentration in mg L⁻¹, and \( m \) is the dry weight of zeolite in g. Blank determinations including determinations for adsorbent in the absence of adsorbates and adsorbates in the absence of adsorbent were always carried out. All experiments were conducted in duplicate and the mean data are reported.

### 3. Results and discussion

#### 3.1. Characterization of the materials

Fig. 1a and b shows the scanning electron microscopy images of FA and ZFA. The original FA particles typically had spherical shapes at different sizes, with a smooth surface made of an aluminosilicate glass phase. Upon formation of zeolite, the surface became rough, indicating the deposition of clusters of zeolite crystals. Formation
of zeolite was confirmed by the shift of the band from 1074 cm\(^{-1}\) for FA to 995 cm\(^{-1}\) for ZFA on Fourier transformed infrared (FTIR) spectra (Fig. 1c), because tetrahedral Al is characteristic of the zeolite structure and an increase in tetrahedral Al (formation of zeolite) would induce a shift of the band within the range of 1180–950 cm\(^{-1}\) (which is assigned to the asymmetric internal T–O stretching vibration mode of the \(\text{TO}_4\) tetrahedra, where \(T = \text{Si} \text{ or Al}\) ) to a lower wavenumber [30,31]. The four bands at 438, 596, 675, 739 cm\(^{-1}\) are analogous to the Na-P1 zeolite obtained from thermally treated sediment [31]. Investigation by powder X-ray diffraction (Fig. 1d) identified the formed zeolite as type Na-P1 (\(\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32}.12\text{H}_2\text{O}\)), JCPDS code 39-0219). This zeolite is classified into the gismondine group with a pore size of 3.1 Å \(\times\) 4.5 Å \([100]\) and 2.8 Å \(\times\) 4.8 Å \([101]\) [32]. The presence of mullite and quartz in both FA and ZFA was also confirmed. The very wide reflection at low 2\(\theta\) values (3–18°) on XRD pattern of FA gives the evidence of the presence of amorphous material. Due to the production of zeolite, ZFA exhibited a greatly enhanced total cation exchange capacity (TCEC, 1.872 mmol g\(^{-1}\)) and Brunauer–Emmett–Teller (BET) area (59.6 m\(^2\) g\(^{-1}\)) when compared to FA (<0.03 mmol g\(^{-1}\) and 1.3 m\(^2\) g\(^{-1}\), respectively) (Table 1). It is worthy of note that ZFAs are usually not pure and contain a number of components other than zeolite. The comparison of the CEC value of a ZFA with that of a pure zeolite may provide a semi-quantitative estimate of the zeolite content in the ZFA given that the ZFA contained only one kind of zeolite. The zeolite content in ZFA of current study was estimated to be 44%, based on the CEC value of the pure NaP1 zeolite (4.30 mmol g\(^{-1}\)).

The external cation exchange capacity (ECEC) of ZFA, as measured by the adsorption of methylene blue from aqueous solution, was 0.178 mmol g\(^{-1}\), which accounts for 9.5% of TCEC. The external surface was used to load HDTMA because the pore size of zeolite is too small for the HDTMA cation to enter. The amount of HDTMA loaded was determined to be 0.349 mmol g\(^{-1}\) based on the difference in the carbon content between SMZFA and ZFA. This was nearly twice as the amount of ECEC, indicating that HDTMA formed a bilayer micelle on the external surface of ZFA. The FTIR absorption bands at 2850 and 2920 cm\(^{-1}\) (Fig. 1c), which are attributed to the symmetric and asymmetric stretching vibrations of \(\text{C–C}\) in the alkyl chain of HDTMA, indicate that HDTMA formed a bilayer micelle, rather than monolayer coverage [33,34].

3.2. Adsorption of ionizable phenolic compounds and non-ionizable organic compounds

Adsorption isotherms of the phenolic compounds from water on SMZFA are shown in Fig. 2. We conducted the adsorption experiments for FA and ZFA without surfactant modification at the same time, but as expected, little adsorption by these two materials was observed. This indicates that adsorption of phenolic compounds was due to the loaded surfactant bilayer.
Analysis of the results revealed that the Langmuir model showed good fits to the experimental data. The Langmuir model can be expressed as:

\[
\frac{C}{q} = \frac{C}{Q_m} + \frac{1}{bQ_m} \tag{1}
\]

where \(q\) is the amount of solute adsorbed per unit mass of adsorbent (mg g\(^{-1}\)), \(C\) is the concentration of solute in solution at equilibrium (mg L\(^{-1}\)), \(Q_m\) is the Langmuir adsorption maximum (mg g\(^{-1}\)), and \(b\) is a constant related to the binding strength of solute. The fitting results are shown in Table 2 and the adsorption maxima from the Langmuir isotherms are calculated and listed in Table 3. The adsorption ability of the phenolic compounds was in the order bisphenol A > p-chlorophenol > phenol. The maximum adsorption capacity of FA and ZFA was also listed but this was obtained from the adsorption capacity at the highest initial concentration investigated, not from the Langmuir model because the adsorption was too low to fit the model well.

Adsorption isotherms of the non-ionizable compounds from water on SMZFA are also shown in Fig. 2. In contrary to ionizable phenolic compounds, the adsorption isotherms of non-ionizable compounds followed a linear form, which is typical when the adsorption process is dominated by hydrophobic partitioning. The linear model can be expressed as:

\[
q = k_dC
\]

where \(q\) is the amount of solute adsorbed per unit mass of adsorbent (mg g\(^{-1}\)), \(C\) is the concentration of solute in solution at equilibrium (mg L\(^{-1}\)), and \(k_d\) is the adsorption distribution coefficient showing the adsorptive capability of adsorbents. The fitting results are given in Table 2, and the \(k_d\) values are listed in Table 3. The adsorption performance of SMZFA for non-ionizable compounds was in the order naphthalene > nitrobenzene > aniline. Similarly to ionizable phenolic compounds, adsorption of non-ionizable compounds was owing to the surfactant bilayer of SMZFA since both FA and ZFA exhibited very trivial adsorption and most are two low to build an isotherm model.

### 3.3. pH dependency of adsorption

Ionizable phenolic compounds differ from other organic chemicals in that they exist as different species, ionic or electrically neutral ones, depending on solution pH. The pH of the equilibrium suspensions which contained solid material was around 10.3, when no artificial adjustment of pH was done. The phenolic compounds are mostly ionized to form mono- or di-valent anions at this pH value. Specifically, the percentage of anion species calculated from the \(pK_a\) of the compounds is 72.0% for phenol, 89.5% for p-chlorophenol, and 89.1% for bisphenol A (in it, monovalent species 51.5%, divalent species 38.0%), respectively. On the other hand, the non-ionizable compounds occur completely as electrically neutral species regardless of pH value.

Dependency of adsorption on pH is illustrated in Fig. 3. It can be seen that the adsorption of ionizable phenolic compounds was
dependent on pH; the adsorption remained roughly unchanged at pH below about 7.5–8.0, while increase in pH above about this level resulted in a gradually enhanced adsorption. This behavior suggests that anionic species has higher affinity toward SMZFA than the neutral one. This behavior suggests the importance of the interaction of negative charge of organic anions with the positively charged heads of HDTMA. Measurement of Zeta potential showed that SMZFA was positively charged due to the formation of surfactant bilayer and modification of ZFA with surfactant caused a significant increase in Zeta potential (Fig. 4).

As anticipated, the adsorption of naphthalene, a non-ionizable organic chemical, did not show distinct pH dependency (Fig. 3).

3.4. Adsorption mechanism

Good fit of isotherm data of ionizable phenolic compounds to the Langmuir model suggests that they are likely adsorbed on specific sites of the surface of SMZFA. Possible mechanisms are proposed as follows: (1) the Coulombic interaction of anionic species of phenolic compounds with the positively charged “head” of HDTMA on both the inner layer and the outer layer (the interaction with HDTMA on inner layer was given in Fig. 5a). In this case, the hydrophobic benzene ring(s) was probably pointed to the inside of HDTMA bilayers, because this orientation could be stabilized by allowing the hydrophobic interaction between benzene ring(s) and the C16 tail of HDTMA to take place; (2) the coordination of the electron-donating oxygen atoms of phenol compounds with positively charged heads of HDTMA, but this interaction would be much weaker than 1) (Fig. 5b); and (3) the adsorption of uncharged phenolic compounds by hydrophobic partitioning into HDTMA bilayers (Fig. 5c). In each case, however, the hydrophobicity of the organic chemical would be important for adsorption process. This was supported by the positive relationship between $k_{ow}$ and adsorption maxima for the three phenolic compounds (Fig. 6).

Based on the substantial dependence of the adsorption on pH, it is deemed that the $pK_a$ value is another important parameter influencing the removal of phenolic compounds, besides $k_{ow}$. The $pK_a$ value of the ionizable phenolic compounds was as follows: phenol 9.89, p-chlorophenol 9.37, biphenol A 9.63 and 10.43. From the standpoint of ionizability, p-chlorophenol is more ionizable than phenol and thus should be more benign for being adsorbed. Hence, $pK_a$ value could interpret, in part, the higher adsorptive capability of p-chlorophenol than phenol. On the other hand, the greater adsorption of biphenol A might be due to the fact that it has two

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Table 3: Adsorption capacity of ionizable phenolic compounds and non-ionizable organic compounds by the investigated materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Phenol</th>
<th>p-Chlorophenol</th>
<th>Bisphenol A</th>
<th>Aniline</th>
<th>Nitrobenzene</th>
<th>Naphthalene</th>
</tr>
</thead>
<tbody>
<tr>
<td>FA</td>
<td>1.2</td>
<td>1.0</td>
<td>1.3</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>ZFA</td>
<td>1.3</td>
<td>1.5</td>
<td>2.7</td>
<td>N.D.</td>
<td>0.4</td>
<td>1.3</td>
</tr>
<tr>
<td>SMZFA</td>
<td>37.7</td>
<td>52.4</td>
<td>90.9</td>
<td>3.3</td>
<td>82.3</td>
<td>42-49.3</td>
</tr>
</tbody>
</table>

*For ionizable phenolic compounds, adsorption capacity was expressed by the maximum sorption capacity, which was calculated from the Langmuir model, while for non-ionizable organic compounds, it was expressed by the adsorption distribution coefficient $k_{ow}$, which was determined from the linear sorption isotherm. Units: $\times 10^{-3}$ L mg$^{-1}$ for non-ionizable organic compounds and mg g$^{-1}$ for ionizable phenolic compounds. N.D., not detectable.

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**Fig. 5.** Interaction mechanisms of phenol, as an example of organic pollutants, with SMZFA. In this figure, the meaning of the symbols are as follows: (a) the “head” of HDTMA; (—) the C-16 chain of HDTMA; ( ) zeolite in which “-” represents the negative charge. In (a) and (b) the interaction of the charged and uncharged phenol group with the “head” of HDTMA of the outer layer, as well as the interaction between the hydrophobic benzene ring of organic pollutants and the hydrophobic C-16 chain of HDTMA may function simultaneously to contribute to sorption.

**Fig. 4.** Zeta potential of ZFA before and after HDTMA modification as a function of pH.
phenol groups to interact with the “head” of HDTMA, in addition to its high hydrophobicity. However, in our current study, only the comparison of phenol and p-chlorophenol was made to elucidate the importance of $pK_a$ in the adsorption of ionizable phenolic compounds. Further investigation using more compounds with a series of $pK_a$ values but similar $K_{ow}$ values is thus needed in future to sufficiently support the conclusion.

For non-ionizable organic contaminants, the interaction mechanism was proposed as a single hydrophobic partitioning process into the surfactant bilayer. This was supported by the linear isotherm model (described previously) and the good positive relationship between $K_{ow}$ and $K_f$ (Fig. 6).

For either ionizable phenolic compounds or non-ionizable organic pollutants, hydrophobicity is a crucial factor for the adsorption process; compounds with low hydrophobicity have low adsorptive affinity toward SMZFA, while more hydrophobic contaminants can be more readily removed by SMZFA. This would be preferable because the former is less problematic and much biodegradable in environment or wastewater treatment systems.

4. Conclusions

After modification with the surfactant (HDTMA, hexadecyltrimethylammonium), zeolitic material that was hydrothermally synthesized from FA exhibited greatly enhanced adsorptive capability for both ionizable phenolic compounds and non-ionizable organic compounds. The adsorption of the two kinds of organic chemicals showed different isotherm type and the dependency on pH. The adsorption of non-ionizable compounds was a single partitioning process into the surfactant bilayer. In the case of ionizable phenolic compounds, nevertheless, interaction of the phenol group(s), either ionized or non-ionized, with the positively charged “head” of surfactant additionally functions.

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References


