Removal of phenol from water by adsorption–flocculation using organobentonite

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Abstract

Bentonite modified with short chain cationic surfactant might be the basis of a new approach to removing organic pollutants from water. The treatment process involves dispersing bentonite to the contaminated water and then adding a small cationic surfactant so as to result in flocs which are agglomerates of organobentonite and bound organic pollutants. The flocs are then removed from the solution by sedimentation. Experimental results indicate that BTMA-bentonite displays a high affinity for phenol, possibly because phenol molecules interact favorably with the benzene ring in BTMA ion through increased π–π type interactions. Under appropriate operating conditions, 90% phenol removal and nearly 100% bentonite recovery could be achieved by the adsorption–flocculation process using BTMA-bentonite. Additionally, the insensitivity of the process to the changing ionic strength of the solution and rapid adsorption kinetics made adsorption–flocculation with BTMA-bentonite attractive for continuous treatment of large volumes of industrial wastewater. The bentonite may function as a recyclable surfactant support for the adsorption and subsequent combustion of organic pollutants. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Organobentonite; Adsorption; Flocculation; Phenol

1. Introduction

A montmorillonitic clay, bentonite, is characterized mainly by an Al octahedral sheet placed between two Si tetrahedral sheets. The isomorphous substitution of Al$^{3+}$ for Si$^{4+}$ in the tetrahedral layer and Mg$^{2+}$ for Al$^{3+}$ in the octahedral layer results in a net negative surface charge on the clay. This charge imbalance is offset by exchangeable cations (typically Na$^+$ and Ca$^{2+}$) at the clay surface. The layered structure of the clay facilitates expansion after wetting. Na$^+$ and Ca$^{2+}$ are strongly hydrated in the presence of water, resulting in a hydrophilic environment at the clay surface. Consequently, natural bentonite is an ineffective sorbent for nonionic organic compounds (NOC) in water, although it has a high surface area. As is well known, simple ion-exchange reactions can significantly modify the surface properties of natural bentonite. When organic cations (cationic surfactants) of the form (CH$_3$)$_3$NR$^+$, where R is an alkyl hydrocarbon, occupy the exchange sites of bentonite clay, the surface properties transform from hydrophilic to hydrophobic. Recent studies have shown that the molecular structure of cationic surfactants used to modify clay affects the mechanism of NOC sorption [1–4]. Smith et al. [1] demonstrated that small organic cations create a relatively rigid, nonpolar surface amenable to NOC uptake by adsorption, a surface characterized by a relatively high NOC uptake, isotherm nonlinearity, and competitive sorption. In contrast, large organic cations create an organic partition medium for NOC uptake through the conglomeration of their flexible alkyl chains, a medium characterized by a relatively low NOC uptake, isotherm linearity, and noncompetitive sorption. Lee et al. [5] confirmed the effectiveness of smectite intercalated with small tetramethylammonium (TMA) ion in removing...
benzene from water, and its potential for purifying benzene-contaminated water.

Activated carbon is widely applied for removing organic pollutants from water. The porous nature of this adsorbent material and its high internal surface area are favorable properties for adsorption. The adsorption of organic compounds by activated carbon is partly controlled by physical interactions, including size exclusion and microporosity effects [6,7]. As the molecular size of the organic compound increases, the rate of diffusion into the pores of the granular activated carbon (GAC) decreases. Further increases in the molecular size decrease sorption due to limited access to the interior pore structure of the carbon. Powdered activated carbon (PAC) with rapid adsorption kinetics caused by a small particle size may be used to increase carbon utilization and reduce the volume of the adsorber relative to a GAC adsorber. However, recovering small PAC particles from treated water may be awkward.

Dispersed in solution, bentonite exhibits a large surface area comparable to PAC because of swelling and layer delamination. Additionally, as noted previously, bentonite modified by the addition of the small cationic surfactant exhibits a high sorption capacity for NOC. Binding of cationic surfactant onto the negatively charged surface of bentonite also causes charge neutralization of the bentonite and subsequent coagulation. The floc is formed from all the bentonite in solution and can easily be removed from the solution by sedimentation. This quality combined with its ability to hold NOC makes bentonite flocculation with small cationic surfactant a possible basis for a new approach to wastewater and chemical separation techniques.

This study examines the feasibility of using bentonite modified by the addition of the small cationic surfactant to remove NOC from water. The treatment process involves dispersing bentonite to the contaminated water and subsequently adding a small cationic surfactant to create flocs, which are an agglomerate of organobentonite and bound NOC molecules. The flocs are then removed from the solution by sedimentation. Fig. 1 presents a flow diagram of the proposed process. This study evaluates the effectiveness of the proposed process in removing NOC from water and examining the major operating parameters that may control the process. Phenol is chosen to test the feasibility of the proposed process because it is classified by the US EPA as a priority pollutant and represents one of the more challenging classes of pollutants requiring removal from waste streams.

2. Materials and methods

2.1. Materials

Bentonite having cation-exchange capacity (CEC) of 97 meq 100 g\(^{-1}\) (determined by the BaCl\(_2\)-Triethanolamine method [8]) obtained from Aldrich Chemical Co. was used. It contained 3.6% sand, 7.3% silt, and 89.1% clay with an average particle size of 5 \(\mu\)m as reported by the supplier. Quaternary ammonium compounds were obtained from Aldrich Chemical Co. and used as received. Table 1 lists the molecular formulae, chemical purities, and abbreviations of these compounds. The NOC tested herein, phenol, was of analytical grade, purchased from Riedel-de Haen and used without further purification.

2.2. Phenol batch sorption experiments

Each batch test sample in the sorption experiments was prepared in a 22ml glass tube, with 0.2 g of bentonite together with a pre-calculated volume of
cationic surfactant solution and phenol stock (in methanol) and sufficient deionized water to bring the total fluid volume to 22 ml. The organobentonites were prepared at different saturated levels corresponding to the different amounts of CEC occupied by cationic surfactant. For example, the 50%, 75%, and 100% CEC saturated organobentonites were prepared by adding 0.097, 0.1455, and 0.194 mmol of cationic surfactant, respectively, into the above mentioned 22 ml glass tube. The pH of each sample was controlled at about 7.0 by HCl and NaOH solutions. The glass tubes were sealed with Teflon-lined septa and secured with open-port screw caps. Next, the samples were equilibrated for 8 h by rotating on a tube rotator at room temperature. Preliminary kinetic investigations revealed that sorption equilibrium was reached in less than 1 h. The aqueous phase was separated by centrifugation at 5000 rpm for 1 h. Aliquots of the supernatant were withdrawn from each sample for phenol analysis. The difference in the amount before and after sorption reveals the amount of phenol sorbed. All samples were run in duplicates, and the recovery of phenol ranged from 96% to 101%. Results of control experiment indicate the negligible sorption of phenol on clean bentonite surface. Phenol concentration was determined by using a high-pressure liquid chromatography instrument (HPLC, Jasco, Japan), equipped with a reverse-phase column (C-18, Phase Sep, UK) and an ultraviolet (UV) detector (270 nm, Model 975, Jasco, Japan) with isocratic operation (1 ml min\(^{-1}\)) of mobile phase (40/60 vol% acetonitrile/aqueous solution).

2.3. Flocculation experiments

For each test, a 1.2 g sample of bentonite was stirred in 190 ml of distilled water in a 250 ml beaker, fitted with four 0.25 in wide baffle plates and a 1 in diameter propeller, for 10 min. The suspension was then adjusted to pH 7.0 and further conditioned for 2 min. After conditioning, different amounts of organic cation (in 10 ml solution) corresponding to the different levels of saturation of the bentonite’s CEC were then added to the suspension while the propeller was rotated at 800 rev min\(^{-1}\). After 3 min of rapid mixing, the sample was stirred for a further 10 min at 200 rev min\(^{-1}\), then left to settle for 1 h. The concentration of bentonite in the suspension was estimated by absorbance measurements taken with a Shimadzu UV-160A spectrophotometer using 10-mm cuvettes at a wavelength of 650 nm. A calibration curve of the absorbance vs. bentonite concentration was obtained. Samples were taken before and after flocculation, and the absorbance was determined. The percentage of bentonite removal was calculated as usual.

2.4. Adsorption–flocculation experiments

For each test, a pre-weighed amount of bentonite was added to 190 ml of phenol containing solution in a 250 ml beaker fitted with four 0.25 in wide baffle plates and a 1 in diameter propeller to stir the sample. The suspension was then adjusted to pH 7.0 and conditioned for 3 min. Different amounts of organic cation (in 10 ml solution), corresponding to the different levels of bentonite’s CEC occupied were then added to the suspension, while the propeller was rotating at 800 rev min\(^{-1}\). After 3 min of rapid mixing, the sample was stirred for a further 10 min at 200 rev min\(^{-1}\), and then left to settle for 1 h. The concentration of phenol and bentonite in the supernatant were determined as described above.

3. Results and discussion

3.1. Phenol batch sorption experiments

Fig. 2 presents the sorption isotherms of phenol from water, onto the TMA-, BTMA-, TEA-, BTEA-, and TMH-bentonites, respectively, at 100% saturation of the bentonite’s CEC. The adsorption of phenol on the BTMA- and BTEA-bentonite corresponds to the L-type isotherm in Giles’ classification [9], reflecting a relatively high affinity between the adsorbate and adsorbent. The shape of the adsorption isotherms of TMA-, TEA-, and TMH-bentonites are S-type isotherms in Giles’ classification, suggesting that the adsorbate-adsorbate interaction is stronger than the adsorbate-adsorbent interaction. The relatively high affinity between phenol and BTMA- and BTEA-bentonite is probably the result of

<table>
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<th>Surfactant</th>
<th>Formula</th>
<th>Abbreviation</th>
<th>Purity (%)</th>
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<tbody>
<tr>
<td>Trimethylamine hydrochloride</td>
<td>(CH(_3))(_3)H(^+) Cl(^-)</td>
<td>TMH</td>
<td>98</td>
</tr>
<tr>
<td>Tetramethylammonium bromide</td>
<td>(CH(_3))(_4)Br(^-)</td>
<td>TMA</td>
<td>98</td>
</tr>
<tr>
<td>Benzyltrimethylammonium bromide</td>
<td>(CH(_3))(_3)(CH(_2)C(_6)H(_5))(^+) Br(^-)</td>
<td>BTMA</td>
<td>97</td>
</tr>
<tr>
<td>Tetraethylammonium bromide</td>
<td>(C(_2)H(_5))(_4)Br(^-)</td>
<td>TEA</td>
<td>99</td>
</tr>
<tr>
<td>Benzyltriethylammonium bromide</td>
<td>(C(_2)H(_3))(_3)(CH(_2)C(_6)H(_5))(^+) Br(^-)</td>
<td>BTEA</td>
<td>99</td>
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the phenol molecules interacting favorably with the benzene ring in BTMA and BTEA ions through increased π–π type interactions [10,11]. Meanwhile, the saturated uptake of phenol by BTMA-bentonite (34 mg g⁻¹) is considerably higher than that by BTEA-bentonite (21 mg g⁻¹), presumably due to the smaller size of the BTMA ion. Compared to the larger BTEA ions, the intercalated smaller BTMA ions can accumulate more tightly with only a slight steric interference on the interlamellar surfaces of the bentonite, to form a relatively rigid, nonpolar organic carbon surface for higher phenol uptake. Fig. 2 demonstrated that bentonite modified by the BTMA ion exhibits a high phenol uptake capacity under a low concentration of phenol in the solution, and may be an ideal organobentonite for adsorption–flocculation.

Fig. 3 shows the sorption isotherms of phenol on BTMA-bentonites saturated at different levels of bentonite’s CEC. The adsorption capacity of phenol on BTMA-bentonite saturated at 50–150% levels did not differ very significantly. Restated, the uptake of phenol on BTMA-bentonite does not increase with the number of intercalated BTMA ions from 50% to 100%, implying that not all the intercalated BTMA ions are available for phenol uptake. Presumably, only those BTMA ions intercalated at local high charge density regions of the interlamellar surfaces of bentonite can aggregate effectively to form a relatively rigid, nonpolar surface for phenol uptake. As expected, the sites within the local high charge density areas in bentonite are preferentially occupied when bentonite exchanges with BTMA ions. Fig. 3 shows that BTMA-bentonites saturated from 50% to 150% levels of bentonite’s CEC are equally effective in removing phenol from wastewater.

3.2. Flocculation experiments

Fig. 4 presents the flocculation of bentonite suspension at about pH 7.0, expressed in terms of percentage of solid removal, as a function of surfactant dosage (expressed in terms of % CEC of bentonite saturated). Evidently, BTMA, TEA, and BTEA ions cause effective solid removal (>99%) at surfactant dosages above 60% saturation of bentonite’s CEC. Clearly, the observed flocculation behavior can be attributed to the adsorption of cationic surfactant, resulting in the charge neutralization of bentonite. The restabilization of bentonite particles was not observed even at a surfactant dosage of 200% saturation of bentonite’s CEC, presumably due to the very large surface area of bentonite in suspension. Based on the results from phenol batch sorption tests and flocculation tests, BTMA-bentonite with 75% saturation of bentonite’s CEC was selected in the following adsorption–flocculation experiments based on the consideration of both treatment efficiency and cost.

![Fig. 2. Sorption isotherms of phenol on TMH-, TMA-, BTMA-, TEA-, and BTEA-bentonite.](image-url)
3.3. Adsorption–flocculation experiments

Fig. 5 presents the removal of phenol from water by adsorption–flocculation at two different initial aqueous phenol concentrations (10 and 20 mg L\(^{-1}\)) using various BTMA-bentonite (75% CEC of bentonite saturated) dosages. Phenol removal from water by adsorption–flocculation clearly increases with BTMA-bentonite...
dosage. When BTMA-bentonite dosage exceeded 2000 mg L$^{-1}$, the increase of phenol removal efficiency gradually begins to decline to a near constant level. Ninety percent phenol removal may be achieved at a BTMA-bentonite dosage of 8000 mg L$^{-1}$. The percentage of solid removal exceeded 99.9% for all tests (not shown in Fig. 5) indicating that the adsorption–floculation process was successful in removing phenol from water. The L-type isotherm of phenol on BTMA-bentonites, as shown in Fig. 2 indicates that for low aqueous phenol concentrations the isotherm is approximately linear. This linear part of the isotherm results in the percentage of phenol removal from water by adsorption–floculation at 10 and 20 mg L$^{-1}$ initial aqueous phenol concentrations being similar at various BTMA-bentonite dosages, as shown in Fig. 5.

Fig. 6 presents the percentage of phenol removal by BTMA-bentonite (dosage of 2000 mg L$^{-1}$) at different equilibrium values of pH. The greatest adsorption occurs at pH < 9, where most of the phenol is present as neutral phenol. Considerably low adsorption occurs at pH > 10, where the phenolate form is present in solution. This observation indicates that the uptake of phenol by BTMA-bentonite is in line with phenol uptake by activated carbon with hydrophobic interaction as the major mechanism. Fig. 7 shows the effect of ionic strength on the percentage of phenol removal by BTMA-bentonite (dosage of 2000 mg L$^{-1}$) at pH 7. Clearly, the percentage of phenol removal by BTMA-bentonite was not affected significantly by changing the ionic strength of the solution. This phenomenon is definitely an advantage of adsorption–floculation for the treatment of wastewater with a large ionic strength.

As stated before, bentonite dispersed in solution may exhibit a large surface area and rapid adsorption kinetics, comparable to PAC, because of swelling and layer delamination. The kinetic test result displayed in Fig. 8 illustrates that phenol uptake by BTMA-bentonite in adsorption–floculation process was completed within 5 min. The fast adsorption kinetics of BTMA-bentonite required a relatively brief contact time to bring about effective removal of phenol, which is definitely an advantage for the adsorption–floculation process in treating large volumes of water continuously.

4. Conclusions

The experimental results of this study demonstrate the feasibility of removing phenol from water using a novel adsorption–floculation process. The treatment involves dispersing bentonite to the phenol contaminated water and subsequently adding BTMA ion to create flocs, which are an agglomerate of BTMA-bentonite and bound phenol molecules. Under the appropriate operating conditions, 90% phenol removal and nearly 100% bentonite recovery could be achieved. The bentonite may function as a recyclable surfactant support for the
adsorption and subsequent combustion of organic pollutants. The fact that this technology is coupled with the general water treatment process is in itself advantageous. Flocculation is usually an integral part of water treatment, aimed at removing organic and inorganic colloids and dissolved organic matter.

Fig. 6. The percentage of phenol removal by BTMA-bentonite (dosage of 2000 mg L\(^{-1}\)) as a function of pH.

Fig. 7. The effect of ionic strength on the percentage of phenol removal by BTMA-bentonite (dosage of 2000 mg L\(^{-1}\)) at pH 7.
Acknowledgements

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References


Fig. 8. The kinetic test results of phenol uptake by BTMA-bentonite in adsorption–flocculation process.