



Sorption of Phenol from Aqueous Solutions by the Use of Organoclays and Activated Carbon

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ABSTRACT

Sorption of aqueous phenol on organoclays mixtures was determined. Hexadecyltrimethyl ammonium bromide (HDTMA), dihexadecyldimethyl ammonium bromide (DHDDMA), trihexadecylmethyl ammonium bromide (THDMA) and tetrahexadecyl ammonium chloride (THDA) salts were added to cheto bentonite. Aqueous phenol sorption was monitored by UV-vis spectrometry and gas-liquid chromatography. It was observed that as the surfactant C_{16} alkyl side chains increased, the phenol sorption of organoclay decreased. The optimum cation exchange capacity (CEC) for the organoclays, specifically those containing HDTMA and THDMA was 2 to 2.5 meq/g surfactant per g clay.

INTRODUCTION

Due to ban on landfilling by the Hazardous and Solid Waste Amendments of 1984, there has been an increase in the remediation of hazardous wastes by cement-based solidification and stabilization (S/S) methods. These methods are now widely used for the disposal of hazardous wastes. Solidification is primarily used for containment of liquid wastes, while stabilization provides further interaction with the cement matrix. Because of the inorganic nature of cementitious materials, the methods have been primarily focused on the solidification/stabilization of inorganic wastes (Conner 1990). There have been some efforts to stabilize organic wastes using cementitious materials but these efforts have met only limited success. However, organoclays have been shown to be effective in adsorption of organic pollutants (Mortland 1970, Boyd et al. 1991, Jaynes & Boyd 1991). Quaternary ammonium surfactants ($R_1R_2R_3R_4N^+X$) are expected to enhance the organophilic nature of clay, and to enhance the clay's ability to stabilize organic compounds. The quaternary ammonium surfactants, such as cetyltrimethyl ammonium bromide, have cationic head groups and hydrocarbon chains. These organic cation salts replace the inorganic cations in the clay with the associated hydrocarbon chains, thereby imparting hydrophobic properties to clay. The clay material with enhanced hydrophobicity may be used for solidification and stabilization of organic compounds in a cementitious matrix.

MATERIALS AND METHODS

Clays and chemicals: Aldrich Chemical Company, Inc., Milwaukee, WI, supplied the following materials: 1. Hexadecyltrimethyl ammonium bromide (HDTMA), 98% pure, 2. Dihexadecyldimethyl ammonium bromide (DHDDMA), 97% pure, 3. Tetrahexadecyl ammonium chloride (THDA), 98% pure, 4. Crystallized phenol

Sherex Chemical Company Dublin supplied commercial grade trihexadecylmethyl ammonium bromide (THDMA), 90% pure. GSA Resources, Inc, Tucson, AZ supplied commercial grade cheto bentonite, known as calcium-montmorillonite. Calgon Carbon Corporation, Pittsburgh, PA, supplied activated carbon.

Equipment: In the adsorption and leaching studies, a water bath-shaker, made by American Optical Corporation, Buffalo, NY and a Centrifig model centrifuge made by Fisher Scientific, Pittsburgh, PA, were used. A Varian 3500 capillary gas-liquid chromatograph, made by the Varian Corporation, Walnut Creek, CA was used to determine equilibrium concentrations of phenol during clay studies. A 15-m \times 0.32-mm i.d. capillary column, coated with AT-1701, supplied by Altech, Deerfield, IL, was a vital part of the gas-liquid chromatograph assembly. An ultraviolet-visible 265 spectrometer, supplied by the Shimadzu Corporation, Kyoto, Japan, was used to determine aqueous phenol concentrations during activated carbon studies. Barnant Company, Barrington, IL, supplied a pH meter, model 500-2324.

Preparation of organoclays: Cheto bentonite clay was ground into a fine powder and dried at 100°C. Approximately 20 g of the dried powder was added to one litre water at 65°C. The appropriate quaternary ammonium surfactant salt was added in an amount matching the assumed cation exchange capacity (CEC) of the clay. For example, if an HDTMA organoclay were to be made from an assumed CEC of 1 meq surfactant per g clay, the amount of HDTMA surfactant to be added could be calculated from the following equation.

$$\text{HDTMA required} = (20 \text{ g clay})(1 \text{ meq/g clay})(1 \text{ eq}/10^3 \text{ meq}) \\ (364.46 \text{ g HDTMA-bromide}/1 \text{ eq}) = 7.289 \text{ g}$$

The solution was stirred on a hot plate overnight, allowed to cool and then filtered through Buchner funnel. After discarding the filtrate, the remaining organoclay was washed with at least two liters of water to remove any surfactant. The organoclay was dried in oven at 100°C for two hours, ground to fine powder and stored in a desiccator in a sealed bottle for future use.

Preparation of activated carbon and clay: Approximately 30 g of the chosen activated carbon or cheto bentonite clay was dried at least two hours at 100°C. The dried adsorbent was placed in a container, sealed, and stored in a desiccator.

Preparation of aqueous phenol solutions: Using a micropipette, five grams of liquid phenol was weighed into 500 mL volumetric flask. The flask was then filled with distilled water. The resulting 10,000 ppm phenol in water solution was used as an aqueous phenol standard. Aqueous phenol solutions of lower concentration were prepared from this solution by serial dilutions.

Adsorption procedure: One gram of dried activated carbon, clay or organoclay powder was placed into a 125 mL Erlenmeyer flask. Exactly 50 mL aqueous phenol solution of known concentration was pipetted into the flask and then sealed. Several flasks of various starting phenol concentrations were gently stirred for 20 hours at lab temperature to reach equilibrium and then pH of each solution was determined, as necessary.

Phenol concentration determinations by UV-visible spectrometry: In studying activated carbon, test tubes containing 10 mL of each equilibrium solution were centrifuged at a maximum speed of 3,300 rpm for five minutes. The centrifuged solutions were then analysed for their phenol concentrations by ultraviolet-visible spectrometry. The amount of phenol adsorbed was determined by the concentration difference between the starting solution and equilibrium solution.

Phenol concentration determinations by gas-liquid chromatography: Because ultraviolet-visible spectrometry was incapable of determining concentrations of aqueous phenol during clay studies, a gas-liquid chromatography method was developed. 10 mL of methylene chloride, 5 mL of 500 ppm aqueous hexanol internal standard solution, and 5 mL of the equilibrium phenol were placed in a separatory funnel; the mixture was shaken vigorously for 5 seconds. The bottom organic layer was drained off into a 2 mL sample vial for storage. The top layer was discarded. After all solutions were extracted, each solution was analyzed by gas-liquid chromatography. After sample injection, the gas-liquid chromatograph oven temperature was held at 70°C for one minute. Then the oven temperature programmed at a rate of 10°C/min to 130°C. This temperature was held at 130°C for one additional minute. The concentration of aqueous phenol in each solution was determined from a linear calibration curve based on the peak area ratios of phenol to hexanol peak areas.

RESULTS AND DISCUSSION

Sorption studies: Results of adsorption studies of activated carbon, cheto bentonite, and organoclays that were made using HDTMA, DHDDMA, THDMA and THDA are presented in Fig. 1 as adsorption isotherms. The results show essentially no phenol sorption on the cheto bentonite which contains no surfactant. There is no sorption on the cheto bentonite because no surfactants are present to open the clay's interlayer spaces to permit phenol to enter. Activated carbon is distinctly the superior adsorbent among those studied. This is in agreement with the results of Sell et al. (1992). However, Sell et al. (1992) used a slightly different organoclays than the one studied here. The organoclays, all show an enhanced adsorption capacity over the cheto bentonite clay but below that of activated carbon. The mechanism for adsorption by organoclays has been explained by Boyd et al. (1991), Jaynes & Boyd (1991a) and Lee et al. (1989) as the dissolution of an organic compound, such as phenol, into a bulk organic solvent phase, such as quaternary ammonium surfactant, where the bulk organic solvent phase is fixed upon the clay's surface. The mechanism for phenol adsorption by activated carbon has been explained by Deithorn & Mazzoni (1986) as the strong attraction by carbon atoms of activated carbon for phenol's carbon atoms by van der Waals forces.

The pH results, presented in Fig. 2, show that each adsorbent-adsorbate system is slightly basic to neutral. As more phenol remains in the equilibrium solution, the pH declines due to the acidic nature of phenol. The basicity of the organoclays increases in the order of HDTMA < DHDDMA < THDMA but that with THDA is acidic. However, the adsorptive capacity is in the order of HDTMA > DHDDMA > THDMA > THDA. This is consistent with the increasing number of C₁₆ alkyl side chains in the surfactant. Similar results were observed by Montgomery et al. (1988) who used organoclays with quaternary ammonium surfactants of one, two, and four C₁₈ alkyl side chains for the adsorption of phenol. There are two explanations for this behaviour. First, because the study was carried out on a common total mass basis, i.e., a combined one-gram amount of clay and surfactant, the overall amount of clay mass decreased as the increments of surfactant C₁₆ alkyl side chains increased from one to four. Therefore, less clay surface was available for the surfactant to attach to as the increments of surfactant C₁₆ alkyl side chains increased from one to four. The incremental increases of surfactant C₁₆ alkyl side chains are accompanied by increased interlayer space crowding, which results in less space for phenol. This second explanation is consistent with results from a study by Jaynes et al. (1991).

Rate of phenol adsorption: Fig. 3 shows the experimental results when HDTMA and THDMA surfactants, each with an assumed CEC of 1 meq per g, and activated carbon, were exposed to 8,000

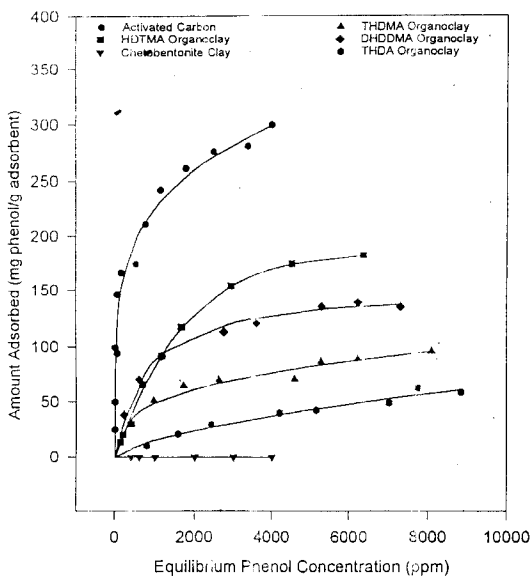


Fig. 1: Aqueous phenol adsorption isotherms obtained by plotting amount of phenol adsorbed per gram of adsorbent vs. equilibrium phenol concentration (ppm).

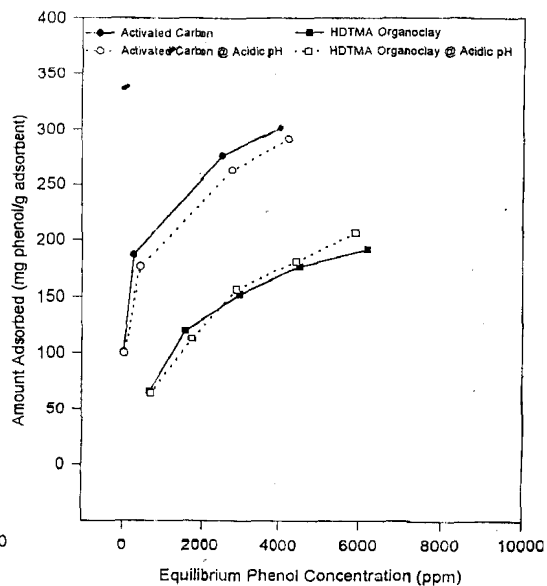


Fig. 2: Equilibrium pH curves obtained by plotting pH of phenol adsorbed on different adsorbents vs. equilibrium phenol concentration (ppm).

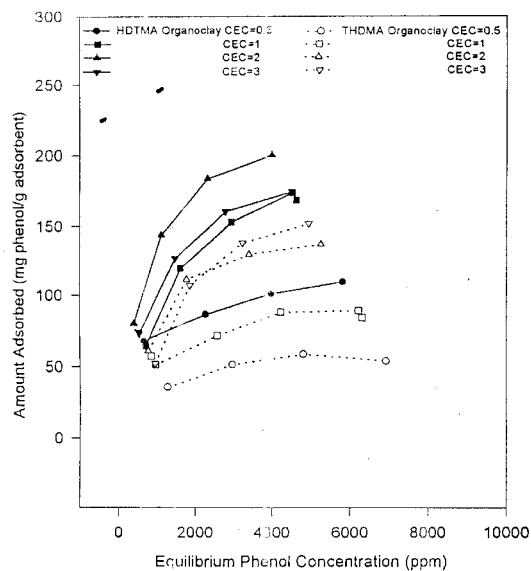


Fig. 3: Amount (mg) of phenol adsorbed per gram of adsorbent vs. time (hours).

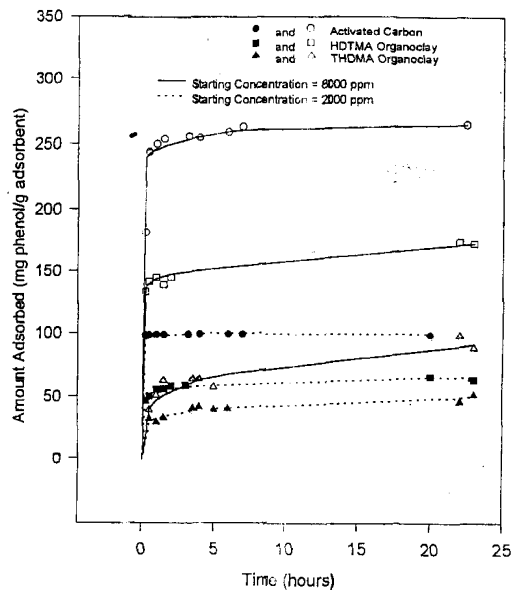


Fig. 4: Amount (mg) of phenol adsorbed per gram of adsorbent of assumed cation exchange capacity (CEC) vs. equilibrium phenol concentration (ppm).

and 2,000 ppm aqueous phenol solutions. Their adsorption capacities were followed with time as a variable.

Beginning with the results at the low aqueous phenol concentration of 2,000 ppm, activated carbon virtually reached its maximum adsorption value after only a few minutes. Both organoclays required a period of at least five hours to reach roughly 95% of its ultimate adsorption value at 22 hours. Further adsorption was still occurring beyond this time. At 8,000 ppm all three adsorbents required at least five hours to reach a 95% value of the ultimate adsorption value at 22 hours. Further adsorption was also continuing beyond this time. The rate results for the HDTMA organoclays are in agreement with results obtained by Sheriff et al. (1989) who investigated 2, 3-dichlorophenol adsorption from water on HDTMA organoclay and cheto bentonite clay. Generally, activated carbon adsorbed aqueous phenol much more quickly than the two organoclays.

Different cation exchange capacities: In an attempt to determine the optimum CEC for HDTMA and THDMA organoclays that will allow maximum adsorption of aqueous phenol, HDTMA and THDMA organoclays with assumed CEC values of 0.5, 1, 2 and 3 meq per g were prepared. Then the HDTMA and THDMA organoclays were allowed to adsorb aqueous phenol based on a common total mass basis of one gram. The experimental results are shown in Fig. 4. The data for CEC of 1 meq per g was taken from Fig. 1.

The HDTMA organoclays exhibit greater aqueous phenol adsorption when compared to that of THDMA organoclays. For example, the adsorption capacities are in order of: 0.5 meq HDTMA per g clay > 0.5 meq THDMA per g clay > 1 meq HDTMA per g clay > 1 meq THDMA per g clay.

pH effects on adsorption: No significant aqueous phenol adsorption difference was observed for the HDTMA organoclays at controlled pH 3 and at uncontrolled pH. The reason is that the phenol at pH 3 was below its pK_a of 9.9, which means the phenol was present as a neutral compound.

For activated carbon, a consistent, slight decrease in the adsorption for phenol was observed for the controlled pH 3 solutions relative to the uncontrolled pH solution. This may be due to destruction of the porosity structure of activated carbon by the acidic conditions, which results in a decreased surface area available for phenol adsorption.

CONCLUSION

The stabilization of aqueous phenol by organoclays is possible. The organoclays used in this study adsorbed more phenol than the cheto bentonite clay mineral by itself, but not as much as the activated carbon. The aqueous adsorptive capacity of aqueous phenol by the organoclays is in the order of the activated carbon > HDTMA > DHDDMA > THDMA > THDA for a given equilibrium phenol concentration. This is substantiated by pH studies and by studies of cation exchange capacities.

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