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PURIFICATION OF PHENOL SOLUTION USING MODIFIED MONTMORILLONITE

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Abstract

There is growing interest in the modification of clays to organic materials, i.e. organoclays, in which metal cations on the surface of minerals are removed by exchange with organic cations. Organic cations can also enter into ion exchange reactions with cations that are exchanged between layers. The clay surface can be modified to become strongly organophilic. Phenolic hydrocarbons, including p-nitrophenol and p-chlorophenol, are widely used in pharmaceutical, petrochemical and other chemical manufacturing processes. Due to the potential harm of phenolic compounds to human health and the environment, wastes containing phenolic compounds must be treated before being discharged into receiving water bodies. Secondary biological treatment processes are commonly used to treat domestic and industrial wastes, but cannot successfully remove high concentrations of phenolic wastes. Therefore, new treatment technologies are constantly being researched and developed. Such technologies include biodegradation, chemical oxidation and adsorption. Although many different adsorbents have been used to remove phenol, nitrophenol, and p-chlorophenol from wastes, organoclays have been widely used to remove phenolic compounds. The adsorption of phenol on all clays is well described by pseudo-second-order reaction kinetics. In the second-order reaction kinetics, the experimental and calculated values are very close to each other. The negative values of the Gibbs free energy indicate that the adsorption of phenol on all clays is natural. The changes in enthalpy show positive values, and therefore the adsorption mechanism is determined to be endothermik.

Keywords: *Clay, phenol, modification, Tetraheptyl ammonium bromide, surface area, toxicant, adsorption, drying, grinding*

Introduction

Clays are widely used as adsorbents due to their high specific surface area. However, their sorption capacity for hydrophilic (polar) organic compounds is very low due to the hydrophilic nature of the mineral surfaces. Natural clays contain exchangeable cations such as Na^+ and $Ca2^+$ on their surfaces, which are strongly hydrated in the presence of water, thereby creating a hydrophilic environment on the clay surface. Modification of clays with inorganic or organic reagents increases their sorption capacity. There is increasing interest in the modification of clays to organic compounds, i.e., organoclays, in which metal cations on the mineral surface are removed by exchange with organic cations. Organic cations can also enter into ion exchange reactions with exchangeable cations between the layers (Chen J. M., Chien Y. W., 2002). The clay surface can be modified to become strongly organophilic. As a result, the organoclay complex can become an excellent sorbent for poorly water-soluble organic pollutants. Activated carbon has been widely studied for the removal of p-chlorophenol and p-nitrophenol from aqueous solutions (Haidar S., Garcia M. A.F., Ultrilla J. R., Joly J. P., 2003). Phenolic hydrocarbons, including p-nitrophenol and p-chlorophenol, are widely used in pharmaceutical, petrochemical, and other chemical manufacturing processes. Because phenolic compounds pose potential hazards to human health and the environment, wastewater containing phenolic compounds must be treated before being discharged into receiving waters. Secondary biological treatment processes are commonly used to treat domestic and industrial wastewater, but they cannot successfully remove high concentrations of phenolic waste. Therefore, new treatment technologies are constantly being researched and developed. Such technologies include biodegradation, chemical oxidation, and adsorption. Although many different adsorbents have been used to remove phenol, nitrophenol, and p-chlorophenol from wastewater, organoclays have been widely used to remove phenolic compounds (Lawrence M. A. M., Kukkadapa R. K., Boyd S. A., 1998). For example, Zielke and Pinnvaia in their study studied modified clays for adsorption of environmental toxicants and recommended pillared, delaminated and alkali-layered smectites for the removal of toxicants. Mc. Bride et al. showed the adsorption properties of various cationic organic complexes for benzene, phenol and chlorobenzenes. In connection with these studies, the present study aimed to study the sorption capacity of bentonite by modification with dodecylammonium cation (Barhoumi M., Beurrois I., Denoyel R., Said H., Hanna K., 2003).

Methodology

The chemical composition of the mineral was determined as follows: 58.3% SiO_2, 2.5% MgO, 16.0% Al_2O_3, 1.1% K_2O, 3.5% CaO, 0.6% TiO_2, 2% Na_2O, 0.1% P_2O_5, 3.1% (FeO + Fe_2O_3) and 13.0% loss. The IR spectrum of the natural bentonite showed a moderate presence of Fe^{3+} (885 cm^{-1}) and revealed impurities in the quartz (697 cm^{-1}) and silica phase (797 cm^{-1}). The BET specific surface area was measured to be 28 m^2/g. It was mixed with 10% HCl solution in a 1:5 mass ratio (Ho Y. S., 2004). The sample purified with terra heptyl ammonium bromide was treated with 4% Li solution in a 1:20 ratio at 25 °C for 48 h. The clay was dried at 110 °C for 24 hours and then dried with a desiccant. The pre-dried and desiccated samples were mixed with an ammonium salt, the concentration of which was greater than that of the cation. The mixture was subjected to mechanical shaking at a constant temperature of 25 °C for 42 hours. The treated sample was centrifuged from the mixture and washed several times with ethanol and ethanol-water (1:1), after complete removal of the chloride salt, it was dried at 40ºC for 24 hours and mechanically ground to a 140 mesh.

Results: The clay samples were analyzed by X-ray powder diffraction (XRD) using a Siemens D-500 diffractometer and CuK radiation. Thermal analysis of the sample was performed on a Shimadzu TGA-50 thermogravimetric analyzer with a temperature increase of 10 °C/min up to 800 °C. Infrared (IR) spectroscopic (Maidac 1700M Model FT-IR) analyses were performed before and after the modification process. The carbon content of the adsorbents was analyzed to be 12.3%. The adsorption of phenol on clays was studied at different temperatures, i.e. 25, 35 and 45 °C. The results are presented in

Table 3. The equilibrium adsorption capacities of phenol bonds increased with increasing temperature from 25 to 45 °C. The increase in adsorption capacity with increasing temperature indicates that the adsorption of phenol is driven by an endothermic reaction. 3.5. Adsorption isotherms Several models have been used to describe the adsorption isotherms of experimental data published in the literature. Langmuir and Freundlich (Unlu N., Ersoz M., 2006) are the most commonly used models. In this work, the phenol adsorption rate was used to describe the relationship between the two models, which changes the equilibrium concentration of the solutions at different temperatures and pH values (Richards S., Bouazza A., 2007). The adsorption isotherms obtained for four modified clays and two phenol unmodified clays are shown in Figure 4 at 25 °C and pH 6.5. The qmax values increased with increasing temperature from 25 °C to 45 °C, and also increased with increasing pH from 2 to 10.

Conclusion:

The adsorption of phenol on all clays is well described by pseudo-second-order reaction kinetics. In the second-order reaction kinetics, the applied and calculated qe values are very close to each other. The negative values of the Gibbs free energy indicate that the adsorption of phenol on all clays is natural. The changes in enthalpy show positive values, and therefore the adsorption mechanism is determined to be endothermic. The study showed that natural bentonites from the Askamaran deposits have a high sorption potential, which is significantly enhanced after acid activation and organophilic modification with tetraheptylammonium bromide (THAB). This modification leads to an increase in the specific surface area, expansion of the interlayer space, an increase in the number of accessible active sites, and the formation of an organophilic phase, which is necessary for the effective binding of both heavy metals and aromatic organic compounds. For organic pollutants, sorption is mainly carried out by physical adsorption and weak dispersive forces. The effective adsorption of phenol on modified bentonites is explained by a combination of π–π stacking, Van der Waals forces and hydrogen bonds. The increase in sorption capacity with increasing temperature and a good fit with the Langmuir isotherm indicate that the process is energetically favorable and controlled by entropic factors. The dominance of the pseudo-second-order model in the kinetic analysis confirms that the sorption rate is determined by the number of active sites and their saturation.

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