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Original Research Paper

Preparation and characterization of organo-montmorillonites. Application in adsorption of the 2,4,5-trichlorophenol from aqueous solution

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ABSTRACT

X-ray diffraction has been used to study the changes in the surface properties of montmorillonitic clay through the changes in the basal spacings of sodium-montmorillonite (NaMt), acid-activated montmorillonite (AMt), pillared-montmorillonite (AlMt) and surfactant-intercalated organoclays. The basal spacing value of the NaMt increased from 12.01 to 18.1 Å by pillaring with Keggin ions ((hydroxyaluminum polycation) and until 21 Å by intercalation of the cationic surfactant in the interlayer space of the clay. Confirmations of the intercalated cationic surfactant have been characterized using Fourier transform infrared spectroscopy (FTIR). Thermogravimetric analysis shows that the thermal decomposition of montmorillonites modified with the cationic surfactant hexadecyltrimethylammonium (HDTMA) takes place in four steps. The surface areas of organo-montmorillonites were found to be much lower than that of raw montmorillonite. Surface areas of pillared and acid-activated montmorillonite are very high. This was explained by the emergence of the micropores and mesopores in the structure of the sample resulting from treatment. Adsorption of the 2,4,5-trichlorophenol (2,4,5-TCP) onto samples was studied. The greatest value of adsorption capacity of samples is attributed to the organo-montmorillonite (MtC16).

1. Introduction

Montmorillonite is widely used in a range of applications because of its high cation exchange capacity (CEC), swelling capacity, high surface area, and consequential strong adsorption and absorption capacities [1–3]. The montmorillonite is a 2:1 layered silicate. The inner layer is composed of an octahedral sheet of general form $M_{2-3}(OH)_6$ (M is typically Al), which is located between two SiO_4 tetrahedral sheets [4,5]. Replacement 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 charge on the clay surfaces. The charge imbalance is offset by the exchangeable cation Na^+ or Ca^{2+} in the interlayer. In aqueous phase, water molecules are intercalated into the interlamellar space of montmorillonite, leading to an expansion of the clays. The hydration of inorganic cations on the exchange sites causes the clay mineral surface to be hydrophilic. The clay properties can be enhanced by converting the montmorillonite to an organo-montmorillonite by ion exchange of the cation with a surfactant molecule. Modification of the montmorillonite with surfactant molecules changes the properties of the montmorillonite from hydrophilic to hydrophobic and organophilic. It also increases the basal spacing of the layers; such surface property changes will affect the applications of the organo-montmorillonite [6,7]. These solids show interesting properties toward adsorption for organic micropollutants such as phenol, phenolic compounds and other benzene compounds [8–10], pesticides [11–13], and dyes [14,3]. They have also confirmed their high affinity towards organic compounds.

The synthesis of a second class of organo-clays has focused on intercalation of long-chain quaternary ammonium cations in the interlayer space of pillared and acid-activated clay [15–17].

Water purification is of extreme importance in many parts of the world. Many of the world's water ways and water sources are polluted or contaminated with a phenols, chlorophenols. pesticides and herbicides. The objective of this study is to determine the feasibility of removal organic pollutants from water by the modified Algerian bentonite. Because the adsorption of the 2,4,5-TCP has not been reported, in this research it is used as a test molecule in the adsorption study. It well-known that bentonite is a low cost adsorbent compared to activated carbon. X-ray powder diffraction, thermogravimetric analysis, Fourier transform infrared (FTIR) spectroscopy, and surface area measurement (BET) techniques were used to study the changes in the structure and surface properties of prepared clay.

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2. Experimental

2.1. Materials

The bentonite used in this study was obtained from Hammam Boughrara (West Algeria). Its chemical composition was found to be: 69.4% SiO_2, 1.1% MgO, 14.7% Al_2O_3, 0.8% K_2O, 0,3% CaO, 1.2% F_2O_3, 0.5% Na_2O, 0.2% TiO_2, 0.05% As and 11% loss of ignition [18]. This bentonite is not a single phase but contains 97.1% of montmorillonite with presence of cristobalite and quartz [19]. Its cation exchange capacity (CEC) is 97 meq/g [20]. Sodium chloride (analytical grade); sulfuric acid (H_2SO_4, 98 wt.%), aluminium-chloride ($AlCl_3$, $6H_2O$), sodium hydroxide (NaOH), HDTMA ($C_{19}H_{42}NCl$, 99%) and 2,4,5-trichlorophenol (2,4,5-TCP) (purity of >99%) were purchased from Sigma–Aldrich Chemicals.

2.2. Sample preparation

The bentonite was converted to a sodium montmorillonite (NaMt) using the following procedure: 30 g of crude bentonite were mixed with 1 M NaCl solution and stirred for 24 h. After three successive treatments, the homoionic bentonite was dialyzed in deionized water until it was free of chloride. Then it was separated by centrifugation to eliminate all other solid phases (quartz, cristoballite). The Na^+-montmorillonite noted NaMt (fraction <2 μm) was recovered by decantation and dried at 80 °C.

The pillared clays were prepared with a procedure similar to that of reported by Khalaf et al. [18]. The pillaring oligocation was prepared from 0.2 M of $AlCl_36H_2O$ solution and 0.5 M of NaOH solution, with a basicity relationship OH/Al = 2,5. The sodium hydroxide solution was incorporated drop by drop into the aluminium chloride solution, which was maintained under vigorous stirring. The resultant solution was aged during 24 h. The polymeric solution was incorporated drop by drop into a suspension made with 10 g of NaMt. The amount of the incorporated oligocation has a ratio of 25 meq of Al per gram of clay to ensure complete saturation of exchange sites. The sample was washed in a dialysis membrane, dried at 80 °C and heated at 450 °C for 4 h 30 min. The resulting material was called pillared-montmorillonite noted AlMt.

The NaMt was treated under mechanical stirring with 1 M H_2SO_4 solution at 90 °C for 4 h. The mass ratio of the bentonite to the acid solution was 1:1. After activation, the solid was washed by distilled water until SO_4^{2-} free and dried at 80 °C. The derivate is an acid-activated montmorillonite noted AMt.

The NaMt, AlMt and AMt were treated with the cationic surfactant $HDTMA^+$ with the molecular formula $C_{19}H_{42}N^+$ for the purpose of sorption enhancement. Surfactant-modified montmorillonite was prepared by adding amounts of the cationic surfactant equivalent to 100% of the value CEC of montmorillonite. The surfactant was dissolved in 1 L of distilled water at 80 °C and stirred for 3 h. A total of 10 g of sample (NaMt, AlMt, AMt) was added separately to the 1 L surfactant solution. The dispersions were stirred for 3 h at 80 °C. The separated organo-montmorillonites were washed with distilled water. Washing was repeated until the supernatant solution was free of chloride ions, as indicated by the $AgNO_3$ test. The organo-montmorillonites were oven-dried at 80 °C until the water was completely evaporated. The derivates are MtC16 (organo-montmorillonite), AlMtC16 (organo-pillared-montmorillonite) and AMtC16 (organo-acid-activated montmorillonite), respectively.

2.3. Characterization of prepared samples

The distance between the layers of the modified clays, the basal spacing d_{001}, was determined by X-ray diffraction analysis using a Bruker D8 advance diffractometer operating at 40 kV and 30 mA with CuKα radiation ($\lambda = 0.15406$ nm). Radial scans were recorded in the reflection scanning mode from $2\theta = 1–80°$. Bragg's law, defined as $n\lambda = 2d \sin\theta$, was used to compute the crystallographic (d) for the examined clay samples. Thermal characterization of the materials was carried out by thermogravimetric analysis (TGA) on 30 mg sample by heating from 50 to 1000 °C at 5 °C/min, under nitrogen using a TA Instruments thermobalance TGA Q500. Nitrogen gas adsorption–desorption isotherms were measured using a Quanta Chrome Autosorb-1 instrument at 77 K. The measurements were made after degassing under vacuum at 180 °C for 6 h. The specific surface area (S.B.E.T) was calculated by the B.E.T method [21] and the pore size was calculated by the B.J.H method [22] using the adsorption and desorption isotherms, respectively. The total pore volume was calculated from the maximum amount of nitrogen gas adsorption at partial pressure (P/P_0) = 0.999. FT-IR study was carried out using FTIR 8400S Shimadzu having a standard mid-IR DTGS detector. FT-IR spectra were recorded, in the range of 400–4000 cm^{-1} with KBr pellets technique.

2.4. Adsorption isotherms

A constant volume of 2,4,5-TCP solution (50 mL) with varying initial concentrations (10–200 mg/L) was mixed with a constant amount of prepared samples (20 mg). The dispersions were shaken at a temperature of 20 ± 1 °C, under an agitation speed of 100 rpm. The dispersions were maintained at a constant pH of 4.0 over 120 min. The 2,4,5-TCP q_e loading (in mg per unit weight of sample) was obtained using the following equation:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \tag{1}$$

where C_0 and C_e in (mg/L) are initial and equilibrium TCP concentration, respectively. V (L) is the volume of the 2,4,5-TCP solution and m (g) is the adsorbent weight. The initial concentration C_0 and the equilibrium concentration C_e of TCP in solution were determined using ShimadzuUV-1700 UV–visible spectrophotomer at the wavelength of 290 nm.

3. Results and discussion

3.1. XRD study

The XRD pattern of NaMt (Fig. 1A) showed the reflection 2θ equals to 7.24° which corresponds to d_{001} spacing of NaMt and its value is 12.2 Å. This value indicates that some molecules of water were adsorbed in the layer space. The d_{001} for anhydrous montmorillonite heated over 400 °C is 9.60 Å [6,7]. After modification of montmorillonite with an amount of cationic surfactant (about CEC value), the d_{001} value shifts to 21 Å in MtC16 (see Fig. 1B). This indicated that the surfactant ions were entered in the interlayer space of the montmorillonite. Fig. 1B showed also two new d_{001} spacing. These new peaks are attributed to the sample AlMt and AlMtC16 with d_{001} of 18.1 Å. The increase in d_{001} spacing from 12.2 to 18.1 Å indicated the presence of Al_{13} like polymers in the interlamelar region. This polymer has structural formula, $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$. After intercalation of surfactant ions in AlMt sample no change in d_{001} spacing was observed. It can be concluded that insertion of the surfactant ions after the formation of stable pillars caused by heating of AlMt sample does not destabilise the porous network.

Fig. 1C showed that activation has affected mainly the d_{001} reflection. Acid activation of montmorillonite yielded two new peaks at 25 Å ($2\theta = 3.46°$) and 14.71 Å ($2\theta = 6°$). These were absent in the untreated montmorillonite. Appearance of new peaks