



Technical Note

Adsorption of some heavy metal ions on sulfate- and phosphate-modified kaolin

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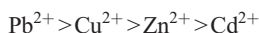
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Abstract

Kaolin (bright white lumps) from Ubulu-Ukwu in Delta State of Nigeria was modified with $200 \mu\text{g mL}^{-1}$ of phosphate and sulphate anions to give phosphate- and sulfate-modified adsorbents, respectively. The adsorption of four metal ions (Pb^{2+} , Cd^{2+} , Zn^{2+} , and Cu^{2+}) was studied as a function of metal ions concentration.

The metal ions showed stronger affinity for the phosphate-modified adsorbent with Pb^{2+} , Cu^{2+} , Zn^{2+} , and Cd^{2+} giving an average of 93.28%, 80.94%, 68.99%, and 61.44% uptake capacity. The order of preference for the various adsorbents shown by the metal ions was as follows:



Desorption studies showed that the phosphate-modified adsorbent had the highest affinity for the metal ions, followed by the sulfate-modified clay while the unmodified clay had the least affinity.

The experimental data were fitted by both the Langmuir and Freundlich models.

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1. Introduction

Extraction and processing of metal ions and wastewater effluents from chemical-based industries have led to the contamination of soil, surface

waters, and ground water resources with heavy metals throughout the world (Paulson, 1997). The heavy metals through natural weathering and transport processes are dispersed beyond their sources to surrounding soils, surface, and ground waters, endangering the quality of water and plant used for human consumption (Fuge et al., 1993). Some remediation technologies have been used to restore contaminated sites. The technologies include excavation and land filling of metal-contaminated soils

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and waste which is expensive and in situ chemical immobilization involving the addition of chemicals like phosphates (Vangronsveld and Cunningham, 1998). Adsorption technique is one of the most efficient methods of cleaning the environment of heavy metal pollutant. In this case, the adsorbent should possess high selectivity with respect to the heavy metal ions and should be relatively cheap and readily available (Dipa and Bhattachayya, 2002).

Due to dearth of information on the adsorption of heavy metal ions with phosphate and sulphate modified kaolinite, this article therefore reports the change in the CEC, retention ability, and selectivity for Pb, Cd, Zn, and Cu in aqueous solution.

2. Materials and methods

2.1. Materials

Kaolin, in bright white lumps, was collected from Ubulu-Ukwu, Delta State, Nigeria. After collection, stones and other heavy particles were removed from the sample. The clay was then crushed, ground, and sieved through a 230-mesh sieve. A part of the kaolin was kept dispersed in doubly deionised water in a 1-L beaker for several hours. It was further purified using the method of Moore and Reynolds (1989).

2.2. Measurement of physicochemical properties

The surface area was measured by methylene blue adsorption (Barton, 1987). The silica and alumina content of the samples were determined by Atomic absorption spectroscopy while Fe^{2+} and Fe^{3+} were determined as described by Vogel (1996). The effective cation exchange capacity was obtained by the method of Juo et al. (1976). It involves the summation of the exchangeable acidity and the cation exchange capacity of the adsorbent. The mineralogical composition of the clay sample was determined with a DIANO 2100*E X-ray diffractometer (CuK α radiation).

2.3. Modification of the kaolinite

Kaolin (0.5 g) was shaken with 30 mL of 200 $\mu\text{g}/\text{mL}$ of $\text{KH}_2\text{PO}_4/\text{Na}_2\text{SO}_4$ in a rotary shaker for 24 h. The samples were washed thrice with 30 mL portion of doubly deionised water to remove excess SO_4^{2-} and H_2PO_4^- ions. (Test for phosphate and sulphate was negative).

2.4. Metal ion adsorption

About 30 mL of the standardised metal ion solutions (Pb^{2+} , Cd^{2+} , Zn^{2+} , and Cu^{2+}) of concentrations 300–700 mg L^{-1} was added to 0.5 g each of the modified and unmodified clay. The pH of Pb^{2+} , Cd^{2+} , and Zn^{2+} solutions was adjusted to 7.0, while that of Cu was adjusted to 6.0. The dispersions were placed on a rotary shaker for 24 h. The supernatants obtained after centrifugation were analysed by Atomic Absorption Spectrophotometry (AAS 200A Buck Scientific Model). The amount adsorbed was calculated from the concentration difference.

2.5. Metal ion desorption

Desorption studies were carried out by shaking the washed dispersions used for the adsorption studies with three portions of 1 M NH_4Cl (at pH 5) for 45 min. The suspensions were centrifuged and the supernatant analysed by Flame Atomic Absorption Spectrophotometry (FAAS).

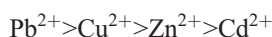
3. Results and discussions

3.1. Physicochemical properties

The mineralogical composition of the kaolin showed that it consisted mainly of kaolinite ($\approx 61\%$). Other components are shown in the Table 1. The surface area of the kaolin by methylene blue adsorption was $12.8 \text{ m}^2 \text{ g}^{-1}$.

3.2. Adsorption studies

The metal ions showed a higher affinity for the modified kaolin and H_2PO_4^- modified clay displayed a higher adsorption capacity than sulfate-modified clay at all the concentrations of the metal ion concentrations (Table 2). The adsorption of the metal ions by the modified and original kaolin followed the order:



This order follows the ease of hydrolysis of the cations (Forbes et al. 1976; Brummer, 1986). Alkalinity measure of pH ≈ 6 or 7 at which the adsorption was carried out enhanced the sorption of the monovalent cations (such as ZnOH^+), which also increases the adsorption (Ma and Uren, 1998).

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