Original Research

Valorisation and Modification of Saharan Clay for Removal of Cu(II), Ni(II), Co(II) and Cd(II) from Aqueous Solutions

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Abstract

The organosilane-modified Saharan kaolin (KS) was prepared and tested as an adsorbent for Cu(II), Ni(II), Co(II) and Cd(II) removal from aqueous solution in comparison with original Saharan kaolin (K). Characterization of modified clay material and original clay was carried out by different methods (XRD, FTIR, TGA and SEM) in order to establish the link between synthesis, structures and properties. The hydrophilic properties of the clay surface have been modified, but not turned into hydrophobic ones. The graft has indeed a polar amine group and the chain length is too short to present an important hydrophobic character. The adsorption of heavy metal ions onto APTES-modified kaolin showed greater efficiency than original kaolin. The adsorption of metal ions by the original kaolin is dominated by the cation exchange phenomenon with a preferential order of selectivity: Cu(II)>Ni(II)>Co(II)>Cd(II), while adsorption on KS is mainly dominated by attraction of the chelating group of the amine in the same order of selectivity. This new hybrid organic-inorganic material may be a good alternative for separation and preconcentration of heavy metal ions.

Keywords: kaolin, organosilane, modified kaolin, heavy metal, adsorption

Introduction

A wide variety of toxic inorganic and organic chemicals are discharged into the environment as industrial wastes, causing serious water, air, and soil pollution. Water pollution caused by toxic heavy metal ions has become a serious environmental problem [1]. These toxic metal ions, even at low concentrations, have deteriorated water resources and drinking water and easily accumulated in the human body throughout the food chain, causing a variety of diseases and disorders [2]. So, it is necessary to remove these metal ions from industrial effluents for their subsequent safe disposal.

Many methods such as ion exchange, precipitation, membrane processes and reverse osmosis have been used for the removal of toxic metal ions [3-8]. However, these methods have several disadvantages such as incomplete metal ion removal, high reagent and energy requirements, the generation of toxic sludge or other waste products, and long desorption time. Adsorption is recognized as an effective and economic method for removal of pollutants from wastewaters [9].

In the last decades, kaolin clay plays a significant role in a wide range of environmental and medical

problems and its applications are continually increasing [10-11], especially as an adsorbent in the removal of organic contaminants and heavy metal ions from aqueous medium [12-16]. Covalent immobilization onto layer silicate supports of a desired chelate moiety, with the specific purpose of obtaining selective adsorbent materials, is one of the most important procedures to develop highly selective matrices. Designed applications to improve environmental quality through heavy metal ions removal have recently emerged. Moreover, the versatility of the kaolin clay support to be chemically modified induces its application to produce new materials available for removing contaminates from water and soils [17-22].

This clay is a significant component of many soils in Algeria, and there are large reserves in the southwest region. The specific physical and chemical properties and the large distribution of kaolin lead us to study and evaluate this clay. This investigation reports the modification of the Saharan Algerian kaolin surface with an amine-terminated organosilicon (3-aminopropyltriethoxysilane, APTES) to create new N-immobilized Lewis basic centers [23] and the use of natural and modified kaolin samples as alternative absorbents for extraction of toxic metals. The natural and modified kaolin surfaces were characterized by Fourier transform infrared spectroscopy (FTIR), x-ray diffraction (XRD), scanning electron microscopic (SEM) and thermogravimetric analysis (TGA). The adsorption performance of modified kaolin was tested for removal of heavy metal ions.

Materials and Methods

Materials

Clay

The kaolin used was collected from a natural deposit located in Tabelbala in BecharProvince, Algeria. The average surface area and CEC (cation-exchange capacity) of kaolin, which were measured using methylene blue technique, were 10.60 m^2/g and 8.01 meq/100 g, respectively [24].

Reagents

The reagents used in this study were all extra pure analytical grades. 3-aminopropyltriethoxysilane (APTES) used for APTES-kaolin (KS) was purchased from Sigma-Aldrich. Its chemical formula is ($C_9H_{23}NO_3Si$); it is a liquid product at 98% of purity with molecular weight of 221.37 g/mole. $Ni(NO_3)_2.6H_2O$, $CuSO_4.5H_2O$, $CoCl_2.6H_2O$ and $CdCl_2.2H_2O$ were purchased from Fisher Scientific (Pittsburgh, PA). Toluene and ethanol were of analytical grade. Distilled water was used in all experiments. The pH of solution was adjusted by using 0.1M NaOH or 0.1M HCl.

Methods

Functionalization of the Kaolin with APTES

20 g of natural Kaolin (K) dried at 105ºC was dispersed into 300 mL toluene by ultrasound for 15 min. Then, 20 mL of APTES was added dropwise during vigorous stirring. The dispersion was refluxed at 100ºC for 24 h [25]. The modified kaolin was centrifuged and washed with toluene, followed by volume mixture between ethanol and distilled water (75/25 v%), respectively. The product was dried at 105ºC and sieved. This composite material Kaolin/APTES is named (KS). The sketch in Fig. 1 shows the structure of products and the grafting process with different types of interaction between the surface of the clay and APTES a) hydrogen bonding, b) proton transfer and c) an amine in the high position.

Characterization Techniques

The x-ray diffraction pattern of powder was recorded on a Phillips-1730 (PAN analytical) x-ray diffractometer using Cu K α radiation (λ = 1.54Å) to characterize unmodified and modified clay minerals.
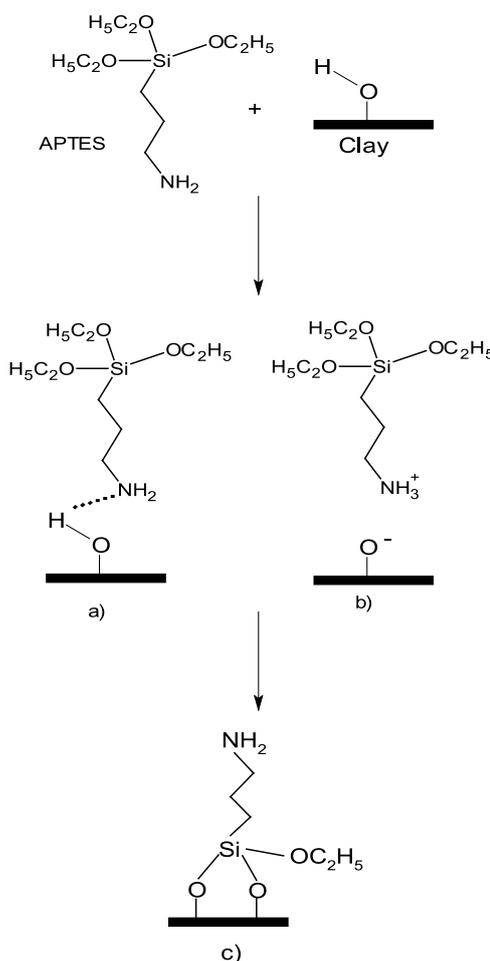

Fig. 1. Modification of natural clay surface with APTES.

The Fourier transform infrared (FT-IR) spectra using KBr pressed disk technique were conducted by Perkin Elmer Spectrum 2000 Infrared spectrometer. TG-DTA thermograms were plotted using the multimodule 92-10 Setaramanalyser operating from room temperature at up to 1000ºC in Al_2O_3 crucible at 10ºC/mn heating rate. The SEM study was carried out using a Hitachi S-4800.

Adsorption Experiments

The adsorption of Cu(II), Ni(II), Co(II) and Cd(II) metal ions on natural kaolin (K) and modified kaolin (KS) was undertaken in a batch equilibrium technique which was performed using different times of contact, initial concentrations of metal ion and pH values. Adsorption isotherms were studied at various initial concentrations of metal ion. The samples were equilibrated in a thermostated shaker bath GFL-1083 model. An Eppendorf 5702 Model digital centrifuge was used to centrifuge the samples. Cu(II), Ni(II), Co(II) and Cd(II) concentrations of solutions before and after adsorption were measured using a flame atomic absorption spectrophometer (Varian, SpectrAA-100, AAS). The amount of metal ion adsorbed per unit mass of natural or modified-kaolin was calculated by using the mass balance equation given in equation (1) [26].

$$q_e = (Co - Ce)V/m \qquad (1)$$

…where q_e is the amount of the adsorbed metal ion in mg/g, Co is the initial concentration and Ce is the concentration at equilibrium of metal ion solution in mg/L, V is the volume of the metal ion solution in mL and *m* is the mass of the materials in grams.

The maximum adsorption capacity q_m (mg/g) was calculated from Langmuir isotherm plot as described in equation (2) [27]. K_L is the Langmuir adsorption constant (L/mg),

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{k_L q_m} \qquad (2)$$

Results and Discussion

Coating of APTES on Kaolin Surface

Coating of APTES on kaolin surface was investigated by FT-IR, XRD, TG analysis and SEM microphotographs.

X-ray Diffraction (XRD) Analysis

The XRD analysis can provide brief information about the extent of kaolin crystallization and the organic incorporation by the (001) basal spacing. As seen in Fig. 2, the XRD pattern of kaolin (K) shows three intense diffraction peaks at 2θ value of 12.4°, 24.8° and
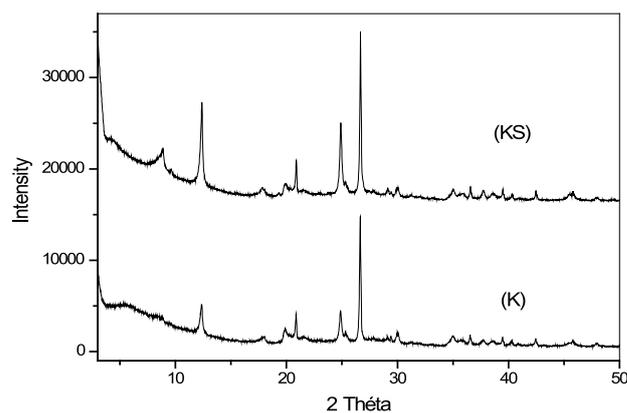

Fig. 2. X-ray diffraction patterns of original kaolin (K) and modified kaolin (KS).

26.6°, less intense peaks at 2θ of 36.7°, 39.6°, 48.0°, 50.1° and 60.1°, and humps at 2θ = 19.8-21.9°, 37.8-39.2° and 44.8-46.9°, which are all associated with kaolinite (K). Diffraction peaks of quartz (Q) could be found at 2θ values of 20.9°, 26.4°, 50.9°, 62.3° and 68.1°. Illite (I) was also detected at 2θ = 17.9°, 30.2°, 35.1°, 42.4° and 55°. Kaolin is clearly affected by coating with APTES, as observed by the change in the peak corresponding to (001) reflection to low angles (5.96° in (K) to 4.63° in (KS)). This result shows an increase in the interlayer distance of the kaolin from 1.48 nm to 1.91 nm. It has been reported that the coupling agents can be attached to clays by chemical bonding, adsorption and coating to form a monomolecular layer or oligomer film on the clay mineral surface [28].

FTIR Analysis

The FT-IR spectra of original (K) and modified kaolin (KS) are shown in Fig. 3. The new band at 1400 cm^{-1} of the modified kaolin indicates the deformation of –NH, and the band between 3317 and
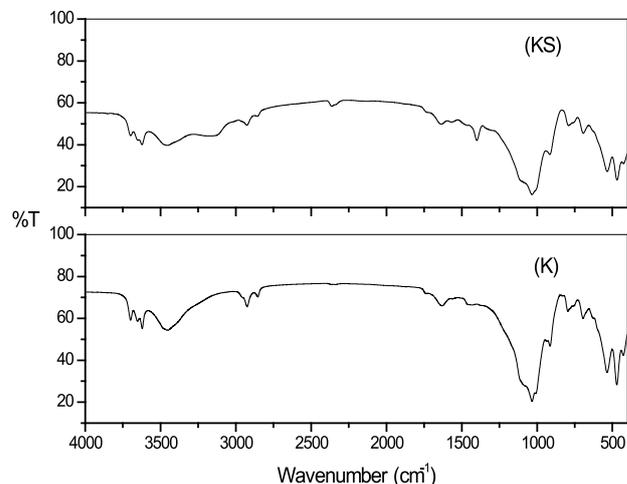

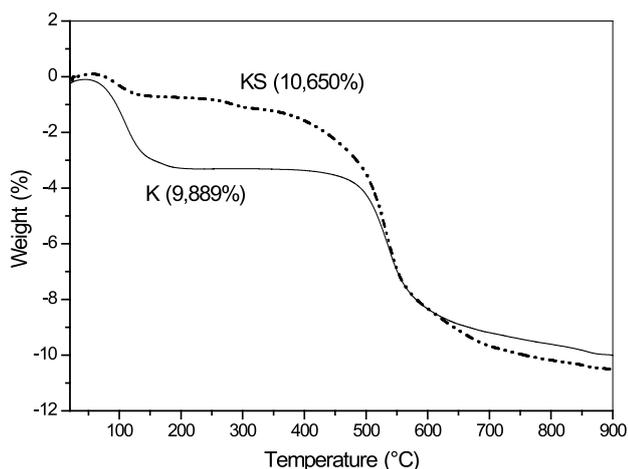Fig. 3. IR spectra of modified kaolin (KS) and natural kaolin (K).

Fig. 4.TG analysis of modified kaolin (KS) and natural kaolin (K).

Fig. 5. SEM of original kaolin (K) and modified kaolin (KS).

3067 cm^{-1} indicates the elongation of –NH and the absorption band at 2930 cm^{-1} corresponds to the C-H stretching vibration of CH$_2$ groups of APTES. These new bands confirm the presence of APTES on the clay [29]. These observations clearly indicate that the clay surface modification was carried out by APTES.

Thermogravimetric Analysis (TGA)

The TG curve of natural kaolin K (Fig. 4) suggested a loss of mass over a temperature of 63-205ºC, which was attributed to the loss of adsorbed water, and an additional loss over the temperature range of 450-900ºC due to both the elimination of coordinated water that become more strongly bonded to octahedral cations and the dehydroxylation of silanol [30].

Three mass losses were solved in the TGA curves of the APTES-modified clays. The first in the range of 60-250ºC was attributed to the removal of absorbed water and APTES molecules. The second at 250-430ºC was attributed to the removal of nitrogen fragments upon combustion. The loss of mass between 430 and 900ºC can be attributed to the decomposition of oxyethyl groups. Moreover, the loss of mass recorded on the natural kaolin (K) is about 9.89% and 10.65% on the modified kaolin (KS).

Scanning Electron Microscope (SEM) Analysis

SEM images of original and modified kaolin are shown in Fig. 5. The unmodified sample shows that there is a large mass form of the clay in thin layers. However, after modification with 3-aminopropyltriethoxysilane (APTES), the clay layers are arranged randomly, which leads to an increase in surface area. In addition, we observed the presence of a larger proportion of small-diameter grains in the modified sample, possibly due to the breaks generated during the modification. They also reveal an important presence of macros pores.
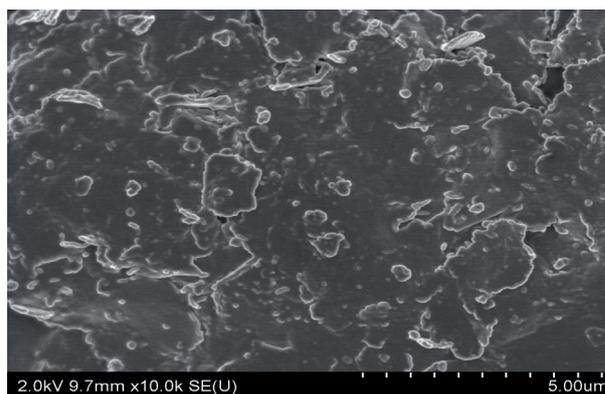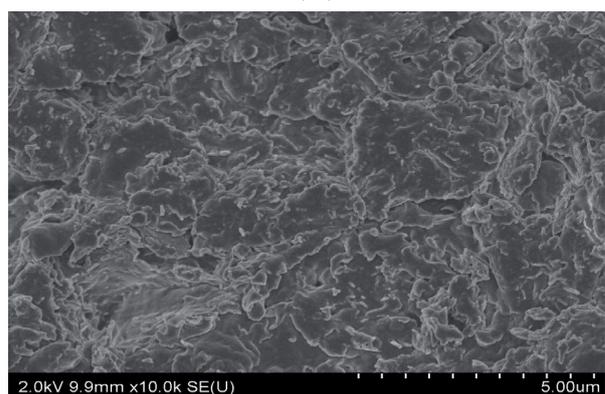
As indicated by the FTIR, XRD, ATG and SEM analysis of original and modified kaolin, APTES coating on the kaolin surface was successfully achieved.

Heavy Metals Adsorption on Original and Modified Kaolin

The retention of metal ions present in aqueous solutions can take place by various mechanisms such as precipitation, ion exchange, and adsorption, which is considered in the present work for the depollution of water contaminated with heavy metals such as cadmium, cobalt, copper and nickel. This technique can be controlled by physical or chemical attraction with surface functional groups [31-32].

The sorption isotherms of metal ions were fitted by Langmuir model and parameters predicted by this model using the linear adjustment are summarized in Table 1. The highvalue of R^2 indicated minimal deviation from the fitted equation, showing that adsorption data would follow the Langmuir equation.

A comparative study of Cu(II), Ni(II), Co(II) and Cd(II) heavy metals retention by natural clay and organosilane-modified clay is shown in Fig. 6, under the same conditions of pH = 5.9±0.2, T = 293 K, clay 10 g/L, C[M(II)] initial = 100 mg/L.We can see that modified kaolin showed greater efficiency in the adsorption of heavy metal ions of the aqueous solution. The highest

Table 1. Langmuir parameters for adsorption of Cu(II), Ni(II), Co(II) and Cd(II) onto natural kaolin (K) and modified kaolin (KS).

	Langmuir isotherm constants					
	Natural kaolin (K)			Modified kaolin (KS)		
	q_m(mg/g)	K_L (L/g)	R^2	q_m(mg/g)	K_L (L/g)	R^2
Cu	9.17	0.06	0.993	23.56	0.11	0.995
Ni	7.69	0.04	0.991	19.24	0.07	0.992
Co	7.29	0.02	0.993	18.79	0.26	0.999
Cd	7.16	0.06	0.980	18.13	0.10	0.997

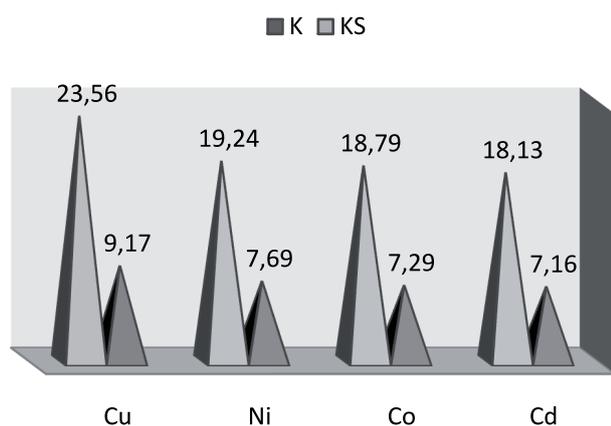

Fig. 6. Monolayer capacities (q_m in mg/g) of natural (K) and modified kaolin (KS)
pH = 5.9±0.2, T = 293 K, clay 10 g/L,
C[M(II)]initial = 100 mg/L.

adsorption capacity is observed for copper due to its small size compared to other metals. The adsorption of metal ions by the original kaolin is dominated by the cation exchange phenomenon [33]. This phenomenon of cation retention appears with a preferential order of selectivity: $Cu^{2+}>Ni^{2+}>Co^{2+}>Cd^{2+}$, while adsorption on KS is mainly dominated by the attraction of the chelating group of the amine in the same order of selectivity [34].

Conclusions

The immobilization of the 3-aminopropyltriethoxysilane (APTES) molecules onto Algerian Saharan kaolin surface was obtained with success,as indicated by the FTIR, XRD, ATG and SEM analysis and utility of the APTES-modified kaolin as an adsorbent has been investigated for the removal of cobalt (II), cadmium (II), copper (II) and nickel (II) ions from aqueous solutions. It was suggested that the functional amino groups on the surface of KS are the main available interaction sites for heavy metal ions. So, low adsorption capacity of natural clays would be enhanced by surface modification using organo-functional coupling agents. Therefore, chemical modification of clay surfaces would be useful for preparing new adsorbents for economic treatment of wastewater containing toxic heavy metals.This approach could be extended to the activation of other material surfaces with other functional groups to changing the surface properties of materials and extend the possible applications of this field.

Conflict of Interest

The authors declare that they have no conflict of interest.

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