

SYNTHESIS OF A SILICATE MATERIAL FOR SEWAGE TREATMENT

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ABSTRACT

In this work, layered polysilicate Na-magadiite was synthesized by hydrothermal medium. The obtained magadiite is then intercalated by organic molecules. To reproduce the conditions for effluent treatment, the intercalation of these molecules is carried out in aqueous media without préintercalation by cationic surfactant. The synthesized materials are characterized by X-ray diffraction (XRD), infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM). The intercalated materials are then used in liquid-solid extraction of heavy metals such as lead and zinc. To maximize the performance of these solids, the extraction reaction is studied as a function of initial pH of the extraction solution, the concentration of this solution and contact time.

Keywords: layered polysilicate, magadiite, adsorption, heavy metal, pollution

1. INTRODUCTION

Natural layered polysilicates form a family which contained six (06) members: magadiite, makatite, kanemite, ilerite and silhydrite. Magadiite was first found in the deposits of lake magadi of kenya and described by Eugster 1967[1]. Magadiite is a layered silicate with the ideal formula $\text{Na}_2\text{Si}_{14}\text{O}_{29}\text{nH}_2\text{O}$ forms a series of sodium polysilicates[2,3].

The layer structure of this mineral is composed of one or multiple negatively charged sheets of SiOH tetrahedra where the negative charge is compensated by interlayer hydrated sodium ions [4]. The surface of magadiite contain silanol group (Si-OH) and siloxide group (Si-O). The interlayer between these layers contain Na^+ and H_2O . Na-magadiite can be prepared in a laboratory under hydrothermal conditions. It possesses some specific properties: It has a high capacity for ion exchange compared with smectites, interlamellar adsorption of water and polar organic molecules, grafting and transformation into crystalline layered silic acids by proton exchange [5, 6]. These properties could promote its application as cation exchanger or molecular sieves [7], adsorbents for environmental pollutants [8] and supports for catalyst [9].

The most important characteristic of lamellar solids is the possibility to expand their interlayer space which can introduce a large variety of organic molecules to form intercalation host-guest compounds, for various applications. For example, the intercalation of Na-magadiite with shorter organic cations such as tetrapropylammonium (TPA) is used as an intermediate to prepare zeolite materials [10], while, when it is intercalated with longer organic cations such as dodecyltrimethylammonium is used as an intermediate to facilitate the silylation of the interlayer space of magadiite [11], these compounds can be then used as precursors for pillaring reactions [12,13] and formation of polymer-inorganic nanocomposites [14,15]. In this study, Thiourea (MeO/Me) was applied as a grafting agent to make organically modified magadiite.

Thiourea modified magadiite was obtained in one step without preintercalation by ion exchange. It was characterized using X-ray diffraction (XRD), infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM).

These materials are used in liquid-solid extraction of heavy metals like lead. Properties of retention of material with regard to the metal elements in aqueous solution can be appreciated by the layout of different sorption isotherms. Lead removal capacity determined according to the model of Langmuir is higher with exchanged Magadiite thiourea than sodic magadiite.

2. EXPERIMENTAL

2.1 Preparation of Na-magadiite

Na-magadiite was hydrothermally synthesized according to the literature [1, 16, 17]. A mixture of colloidal silica, sodium hydroxide, water and ethyl alcohol, with a molar ratio of $\text{SiO}_2/\text{NaOH}/\text{H}_2\text{O}/\text{EthOH} = 1:0.13:14.17:1.78$ was sealed in a Teflon-lined autoclave at 150°C for 72h. The product was filtered, washed with distilled water and dried at 80°C for 24h. The resulting white powder was characterized by X-ray diffraction, infrared spectroscopy and scanning electron microscopy (SEM). Its cation exchange capacity (CEC), measured according to Kahr and Madsen [18], was 116.5 mol kg^{-1} .

2.2 Preparation of Thiourea intercalated Na-magadiite

Na-magadiite/thiourea (MeO/Me) was prepared according to the method developed by Cox and al [19, 20], 1mmole of thiourea was added to 20ml of ethyl alcohol and 20ml of distilled water. The mixture was stirred at the temperature of 25°C for 1h. 1g of Na-magadiite was added to the precedent mixture and the mixture obtained was stirred for 1h at the temperature of 25°C . The solid phase (Na-magadiite/thiourea) was separated by centrifugation and dried at 80°C for 24h.

2.3 Kinetic

2.3.1 Models

To identify the correct mechanism, several models must be checked for suitability and consistency over a broad range of system parameters. Different kinetic models used to fit the experimental data can be summarized as follows:

First-order kinetics model: the First-order kinetics adsorption model was suggested by Lagergren(1898) for the sorption of solid/liquid systems. It has been used by many authors (Namasivayam and Kadirvelu, 1999; Cheung et al, 2000; Chiron et al, 2003) and can be expressed in integrated form:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 \cdot t}{2.303}$$

Where k_1 is the rate constant of adsorption (min^{-1}) and q_e and q_t are the adsorption loading of lead (mg/g) at equilibrium and at time t (min) respectively. The equilibrium loading q_e (mg/g) is calculated from the langmuir adsorption isotherm. By plotting: $\log(q_e - q)$ against t , a straight line is obtained and the value of the rate constant k_1 can be calculated.

Pseudo-second-order kinetics model: Pseudo-second-order kinetics model (Ho and McKay, 1998; Namasivayam and Sumithra, 2004) is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

Where k_2 (g/mg min) is the rate constant of pseudo-second-order adsorption. Plotting t/q_t against t , a line is obtained and the rate constant k_2 as well as q_e can be calculated.

2.3.2 Lead removal kinetic study

The kinetic study was carried out on Na-magadiite (sample A) and Na-magadiite/thiourea(MeO/Me)(sample B) suspensions in 100mg/l of lead nitrate solution. Suspensions of 0.05 g sample A and sample B in 50ml of 100mg/l lead nitrate solution were stirred at the temperature of 25°C during different time intervals (10-180 min). The pH is fixed to 5 and 7. The obtained phases were separated and centrifuged. The lead concentration in the supernatants was measured by atomic absorption spectrophotometry by measuring the equilibrium pH (pHe).

2.5 Techniques of characterization

X-ray diffraction was carried out with Cu $K\alpha$ monochromatic radiation using a diffractometer Philips PW1830. The infrared spectra of our materials (KBr disc) were recorded on a spectrometer Perkin Elmer FT-IR in the region 500-4000 cm^{-1} . The scanning microscopy analyses were performed on a model LEO. Sterioscan 440 electron microscope in the backscattered mode. The technique used for the determination of lead is the atomic absorption spectrometer: AA-660, cat No. 206-10000-02, serial No. 28S00354, Shimadzu Corporation.

3. RESULTS AND DISCUSSION

3.1 Characterization of materials

3.1.1 X-ray diffraction

The XRD patterns of Na-mag and Na-mag/thiourea (MeO/Me) are shown in fig 1. The Na-mag showed a basal spacing of 1.54nm, which is very similar to that reported in the literature [21, 22, 23]. The reflexions of magadiite after intercalation reactions with thiourea were similar to the (001) reflexions of the original Na-mag, which indicates that the thiourea may be intercalated in the interlayer space of magadiite parallel to silicate layer to form a monolayer lateral arrangement. This results in agreement with the IR spectra, where the characteristic absorption bands of thiourea are existents in the fig 2b.

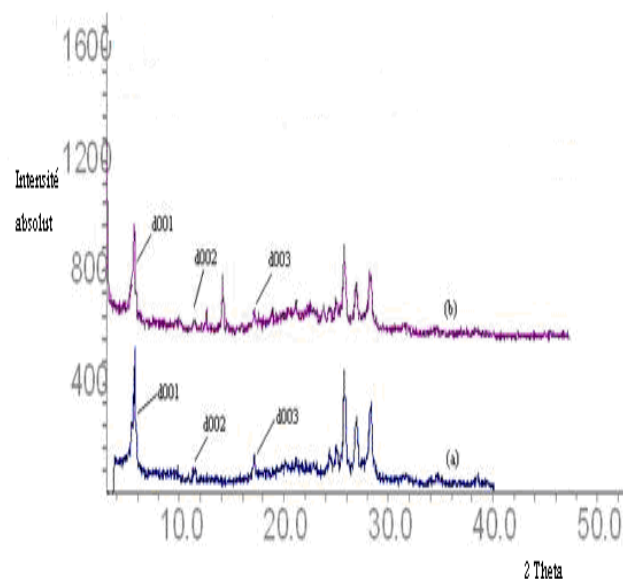


Fig. 4 X-ray diffractograms of (a) Na-mag and (b) Na-mag/thiourea(MeO/Me).

3.1.2 IR spectroscopy

Infrared spectra of Na-mag and Na-mag/thiourea (MeO /Me) are shown in fig 2(a) and 2(b) respectively. The IR spectrum exhibits a small sharp band appearing at 3666 cm^{-1} due to the weakly hydrogen bonded free SiOH stretching of isolated groups on the surface of magadiite. This weakly bonded free SiOH is responsible for silylation reaction. A broad band centered at 3470 cm^{-1} correspond to the OH stretching vibrations of interlamellar adsorbed water and also the strong hydrogen bonding SiOH stretching. A characteristic band is observed at 1630 cm^{-1} due to the presence of physisorption water. A band situated at 785 cm^{-1} due to the symmetric stretching of Si-O.

The IR spectrum of intercalated mag with mixed thiourea fig 2(b) was similar to those of the original magadiite in which the characteristic absorption bands of thiourea appeared completely in fig 2b. The bands at 3348 cm^{-1} represents N-H stretching vibration, the bands at 3142 cm^{-1} due to C-H stretching vibration of aromatic group, bands at 2961 cm^{-1} is assigned to C-H stretching vibration of methyl group and C=C stretching vibration at around 1525 cm^{-1} . All of these results confirm the presence of our thiourea in the interlayer space of magadiite.

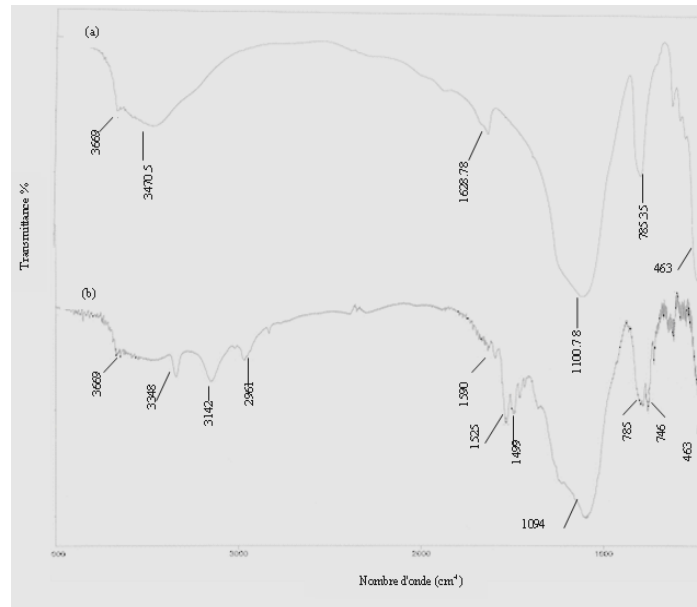


Fig. 4 Infrared spectra of (a) Na-mag, and (b) Na-mag/thiourea(MeO/Me).

3.1.3 Scanning electron microscopy (S.E.M)

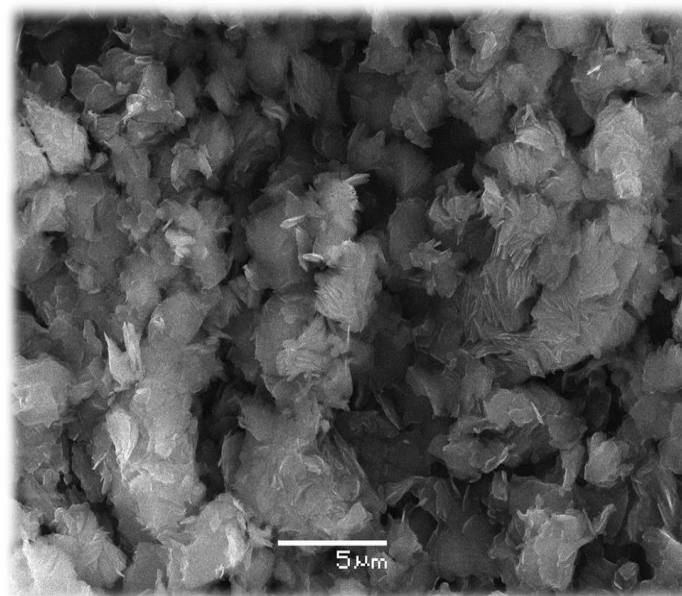
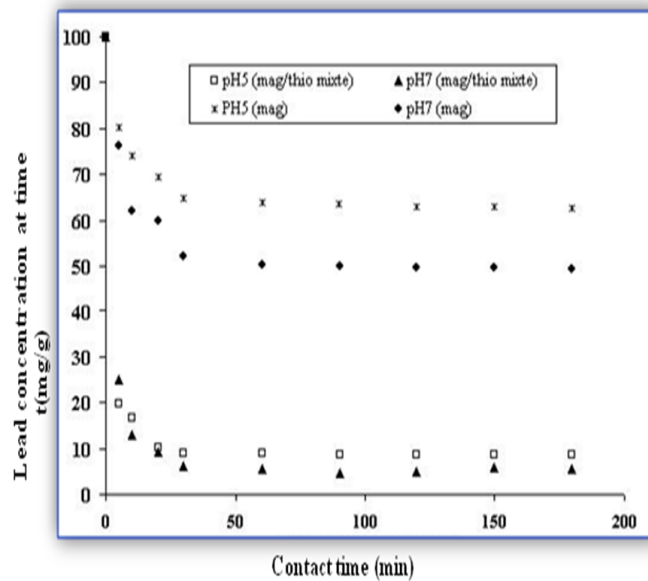


Fig. 4 Scanning electron microscopy of Na-mag**3.2. Study of lead removal by Na-mag, Na-mag/Thiourea(MeO/Me)****3.2.1. Kinetic Study**

Kinetics data of lead removal with Na-mag, and Na-mag/thiourea (MeO/Me) are shown in fig 4. We have drawn on this figure, the variations of lead concentration versus time.

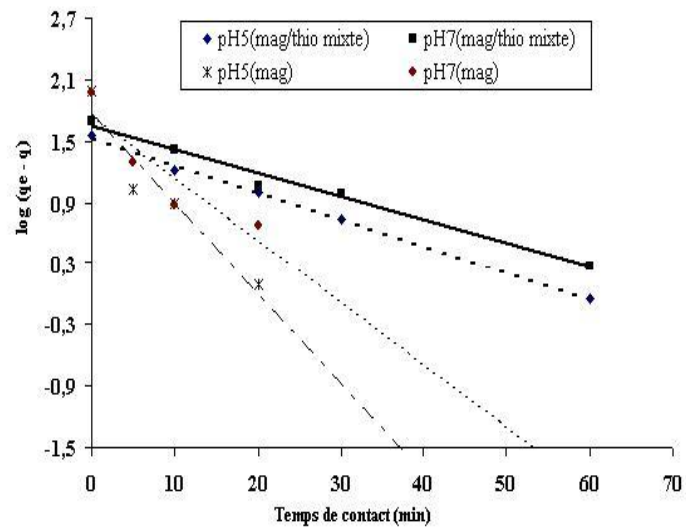
The curves in fig 4 show two branches: the first from $t=0-60\text{min}$, corresponding to a relatively rapid phase, the second from $t > 60\text{min}$ corresponds to the steady state, since the concentration at time t is practically constant (C_e).

The results for the pH 5 and 7 correspond to a removal rate of 40 and 50% for Na-mag, 90 and 95% for Na-mag/thiourea (MeO/Me), respectively. These results show that the adsorption is better at pH7.

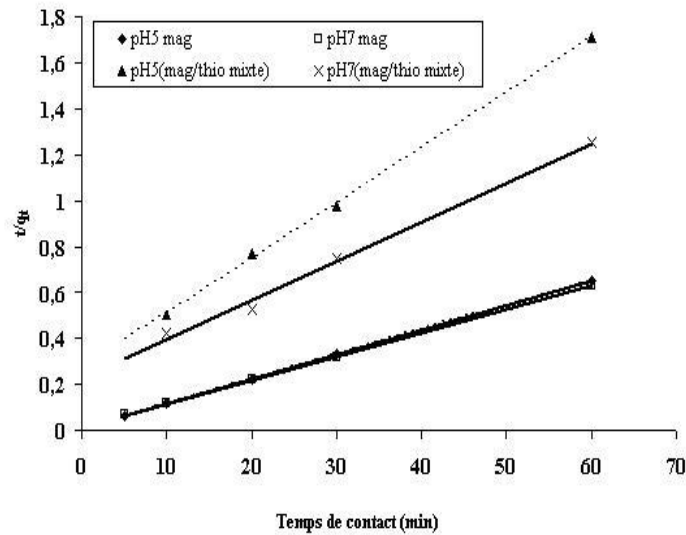
**Fig. 4 Lead removal kinetic on Na-mag and Na-mag/thio mixed for various pH (5 and 7).****3.2.2. Kinetic models**

The plot of $\log (q_e - q) = f(t)$, at different pH, we can determine the rate constant for reaction of order 1 (table 1).

The plot of the variation in the ratio t/qt versus time t (fig 5B) gives a straight $1/q_e$ slope and intercepts $(1/K_2q_e^2)$. The values obtained allow the determination of the rate constant for reaction of order 2 (table 1).



(A)



(B)

Fig. 4 (A) First –order kinetics model, (B) Pseudo-second-order kinetics model for various pH.

Table1 Experimental conditions, kinetic parameters and regression coefficients (R²) for the two kinetic models

| | | First order | | | Pseudo-second order | | |
|--------------------------|----|--|-----------------------------|------------------------------------|--------------------------------------|-----------------------------|--|
| | pH | 1 st order equation | R ₁ ² | K ₁ (mn ⁻¹) | 2 nd order equation | R ₂ ² | K ₂ (g.mg ⁻¹ .mn ⁻¹) |
| Na-mag/ thio mixte | 5 | Log (q _e -q) = -0,0263 t + 1,5232 | 0,99 75 | 0,060 | t/q _t = 0,0238 t + 0,2769 | 0,99 93 | 0,0020 |
| | 7 | log (q _e -q) = -0,0232 t + 1,6444 | 0,98 55 | 0,053 | t/q _t = 0,0171 t + 0,2254 | 0,99 41 | 0,013 |
| Na-mag | 5 | Log (q _e -q) = -0.0791t + 1.7696 | 0.90 76 | 0.0343 | t/q _t = 0.01 t + 0,0085 | 0,99 99 | 0,0117 |
| | 7 | Log (q _e -q) = -0.0482 t + 1.7423 | 0.86 91 | 0.0367 | t/q _t = 0,0099 t + 0,0164 | 0,99 93 | 0,006 |

Table 1 presents the results of fitting experimental data to first-order and pseudo-second-order models for different value of pH (5 and 7). It can be seen from table1 that the correlation coefficient (R²) varies in the order: pseudo-second-order > first order model under all experimental conditions, which indicates that the pseudo-second order model is the most suitable in describing the adsorption kinetics of thiourea on magadiite. Kinetic data fit this model with a correlation coefficient higher than 0.99.

4. CONCLUSION

Our work is part of a multidisciplinary field, it falls within the framework of safeguarding the environment while offering a new material "magadiite", a lamellar polysilicate synthesized and used in the treatment of pollutants such as heavy metals. We have a first approach the method of synthesis of magadiite soda called Mag-Na, and then intercalated with organic molecules such as "thiourea" to form the Mag-Na/Thiourea. The intercalation of thiourea is reached at one stage and the insertion is done in layers parallel to the lateral monolayer of siloxane. These materials are used in liquid-solid extraction of heavy metal like lead.

To study the performance of each material, we determined the kinetics of elimination of this pollutant by determining the optimum conditions (pH, contact time, kinetic).

The results of lead mining at room temperature for two materials (Na-magadiite, and Magadiite-Na/Thiourea) show their consistency with the pseudo second order kinetic model than the first order kinetic model.

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