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Valorization of El Haria clay in the removal of arsenic from aqueous solution

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ABSTRACT

The present work aims to focus on the contribution of El Haria clay aged the Maastrichtien-Paleocene, which level largely in Gafsa basin (Southern Tunisian). Clay of the El Haria Formation was considered a better and low-cost adsorbent for As(III) removal from aqueous solution. Mineralogical analysis showed that this material is composed of 80% smectite and 20% illite. The cation exchange capacity reaches 120 meq/100 g that especially confirms the presence of montmorillonite. Textural analyses reveal a porosity of 43% and a specific surface reaching 158 m^2/g. In this study, a Batch mode was used for As(III) adsorption on El Haria natural clay. We have varied several parameters such as pH and temperature. At 25°C, the As(III) adsorption showed that the ions of arsenic had more mobility in pH ranging from 3 to 9 and the maximum adsorption capacity reaches 75.4 mg/g. Mineralogical characteristics confer to the El Haria clays a better adsorption capacity of heavy metals.

Keywords: Valorization; El Haria smectite; Mineralogy; Arsenic removal

1. Introduction

Arsenic is a toxic metalloid of global concern. Generally, it is naturally originated but can be intensified by human activities such as applications of pesticides and wood preservatives, mining and smelting operations, and coal combustion [1,2]. Consequentially, elevated levels of arsenic have been worldwide reported in soils and groundwater. The maximum concentration limit recommended for drinking water by the World Health Organization is 10 mg/L. Remediation of arsenic contaminated soils and groundwater is necessary for providing safe drinking water. Several treatment methods such as coagulation, membrane separation, and adsorption/precipitation, anion exchange to remove arsenic from waters, and adsorption technologies to retain arsenic in contaminated water, have been developed [3–7]. Due to its environmental compatibility and possible cost-effectiveness, adsorption of arsenic from contaminated water shows a great potential for future developments. In southern of Tunisia,

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low-cost clay material is popular for arsenic removal from aqueous solution [8–13]. The main objectives of this research were: (1) Valorization of a cost-effective material with high arsenic removal efficiency and great settlement performance. (2) Evaluation of the adsorption capacity of smectite clay in aqueous arsenic removal, and the optimization of some parameters. (3) Proposition of the application of this material in real wastewater treatment.

2. Geological setting

The green raw clay (RC) material was collected from the Maastrichian-Paleocene deposits (i.e. Segui formation), outcropping in the south flank of Jebel Stah study site to the north of Gafsa district (Southern Tunisia) (Fig. 1). From geological viewpoint, the studied clay deposits were attributed to the Maastrichian-Paleocene continental formation. This deposit is more developed in the Jebel Stah location, where it consists of important thickness of green clay deposit [14–16].

3. Materials and methods

The clay sample collected from the Maastrichian-Paleocene Segui formation, Jebel Stah (Gafsa, South-western Tunisia) was washed with distilled water to remove soluble salts, sieved, and the desired fraction of less than $2\,\mu m$ was collected for subsequent analysis. Finally, the obtained clay was kept at 60°C. Mineralogical analysis of the randomly oriented powders as well as the separated clay fraction ($\leqslant 2\,\mu m$ sized subsample) has been carried out with an X-ray diffractometer (Philips PW 1710, Germany), using CuKα radiation (40 kV/40 mA). XRD patterns were recorded between $3^\circ \leqslant 2\theta \leqslant 45^\circ$ for the original clay powder and three oriented glass slides (i.e. untreated, glycolated, and heated to 520°C) to identify clay mineral associations. The clay fraction ($\leqslant 2\,\mu m$) was separated by sedimentation and centrifugation [8].

Chemical composition of the collected clay sample was performed by dissolving 1 g of dried clay in 50 mL of HNO_3. The mixture was evaporated to dryness; distilled water was then added to remove the remaining traces of acid, and the whole suspension was filtered with a filter paper (Whatman®, England). The insoluble residue mainly composed of insoluble silica (SiO_2) was estimated by gravimetric method [17] after calcination to 900°C for 1 h. The specific surface area was determined by the adsorption–desorption isotherms of nitrogen (BET-Surface Area Analyzer 2010, ASAP, USA). The total pore volume was determined by pycnometry. Infrared spectra were obtained using an FTIR-420 spectrophotometer (JASCO®, Shimadzu Corp., Japan).

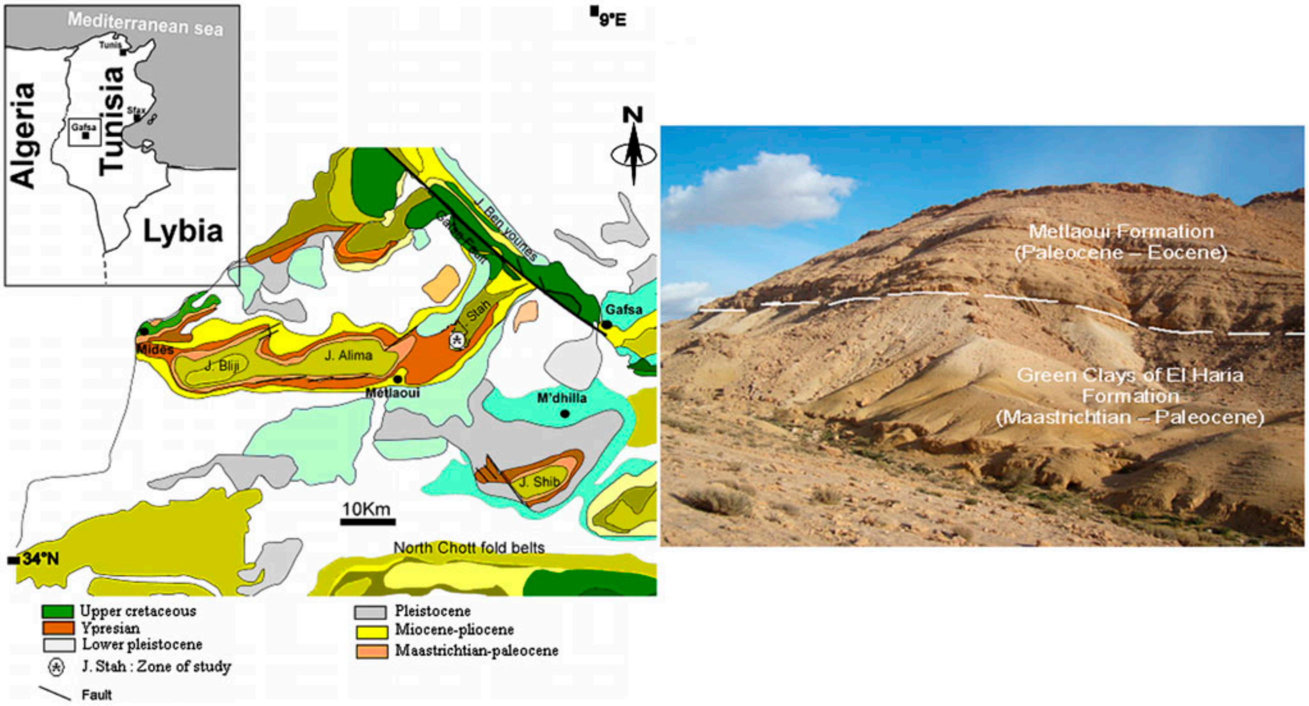

Fig. 1. Geological setting.

4. Experimental procedure

A stock solution of 100 mg L^{-1} As(III) was prepared by dissolving appropriate amount of $(CH_3)_3$ As (Aldrich Corp., Germany) in distilled water. This solution was diluted to 1–15 mg L^{-1} for adsorption experiments. About 0.5 g of clay was added to 50 mL of Hg (II) solution at initial pH 2. The suspension was mixed on a thermostated shaker bath operating at 25°C and 200 rpm during 420 min. It is noteworthy that the removal of arsenic by the green clay sample attained their equilibrium within 180 min. After the reaction, the suspension was centrifuged at 2,500 rpm for 20 min; the supernatant was withdrawn and stored at 4°C until analysis for As(III) by flame atomic absorption spectroscopy at a wavelength of 193.7 nm. The removed amount was determined from the difference between the initial and final concentrations. All the experiments were performed in triplicate.

The adsorbed amount is calculated by the difference between the final and the initial concentration (Eq. (1)) and measured by atomic absorption spectrometer. The same experimental data are adopted for other metals.

$$q_e = [(C_i - C_f) \cdot V]/M \quad (1)$$

where q_e is the amount of As^{3+} ions adsorbed on the clay (mg g^{-1}), C_i the initial As^{3+} ions concentration in solution (mg L^{-1}), C_f the final As^{3+} ions concentration in solution (mg L^{-1}), V the volume of the medium (L), and M the amount of the clay used in the reaction mixture (g).

5. Results and discussion

5.1. Characterization

Mineralogical analysis by X-ray diffraction indicated that the RC was mainly composed of smectite associated with illite, kaolinite, quartz, calcite, and feldspar. Regardless of the treatment, the peak of smectite prevailed at 17.50 Å for the oriented diffractograms. Kaolinite was identified by its peak at 7.15 in the untreated and glycolated diffractograms, but disappeared after heating to 520°C (Fig. 2). The loss on ignition, determined by calcination at 900°C for 2 h, was attributed to the evaporation of physically bound water near 100°C, the dehydroxylation of clay minerals near 500°C and the decomposition of calcite around 750°C [8]. The specific surface area of the sample, estimated to 158 m^2 g^{-1}.

Table 1 summarizes the main physicochemical and textural properties of the studied clay material. Results indicated that the studied sample was mainly composed of more than 40% of silica with subordinate aluminium and iron oxide; calcite was also observed (4.41%).

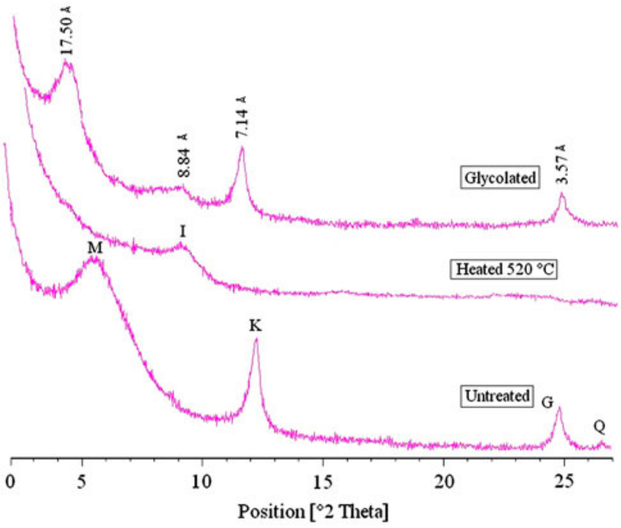

Fig. 2. XRD oriented diffractograms of green clay material.

Table 1
Chemical and physical characteristics of the RC (in mass %)

Oxides (%)	RC
SiO_2	43.67
Al_2O_3	20
Fe_2O_3	3
CaO	4.41
MgO	2.45
K_2O	1.5
Na_2O	1.45
LOI	18.5
V_p (cm^3 g^{-1})	0.18
pore size (nm)	2.23
χ (%)	43
S_{BET} (m^2 g^{-1})	158

LOI: Loss on ignition, V_p: Volume of pore, χ: Porosity (%), S_{BET}: Specific surface of BET.

These results were further confirmed by infrared analysis that indicated the characteristic peaks of silica near 1,000 cm^{-1} and those of calcite identified near 1,434 and 875 cm^{-1} (Fig. 3). In addition, the FTIR spectra of the studied clay sample indicated the characteristic bands of surface hydroxyl group (OH) vibrating near 3,690 and 3,600 cm^{-1}. The additional band was attributed to the presence of silica, while the stretching of C=O and Mg–OH groups occurred near 790 and 640 cm^{-1}, respectively [7].

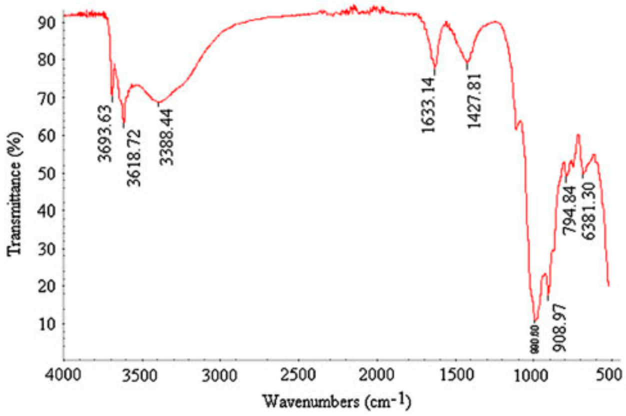

Fig. 3. FTIR spectra of clay material.

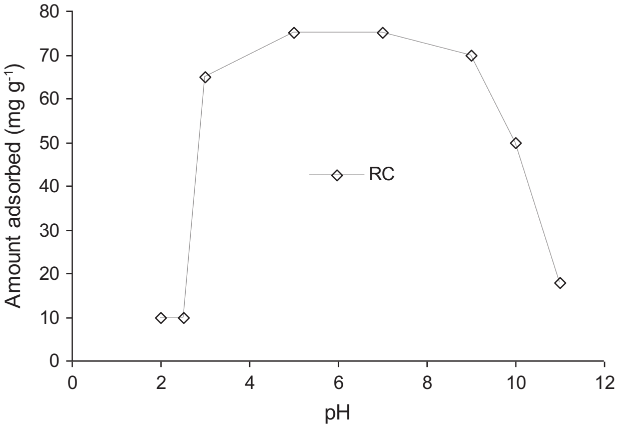

Fig. 4. Effect of pH on arsenic (III) adsorption onto (RC).

5.2. *Arsenic (III) adsorption*

In fact, several parameters were used in the adsorption technology. In this work, we were limited to the effects the essential parameters such as pH, concentration, and temperature.

The pH is one of the most important parameters controlling As(III) removal from water body. In order to investigate the optimum pH conditions for PFS usage, different pH conditions were adjusted with HCl or NaOH (Fig. 4). Arsenic removal efficiency of As(III) was decreased when $\mathrm{pH} < 3.0$ or $\mathrm{pH} > 9.0$. In the pH range of 3.0–9.0, arsenic removal efficiency of As(III) could reach above 75 mg/g. At pH lower than 3.0, therefore a competition between H^+ and As(III) ions about the free pores provided by clay material surface. Whereas, the increase of pH more than 9 contributed to the precipitation of species of As(III). Subsequently, the amount of As(III) adsorption obviously decreased.

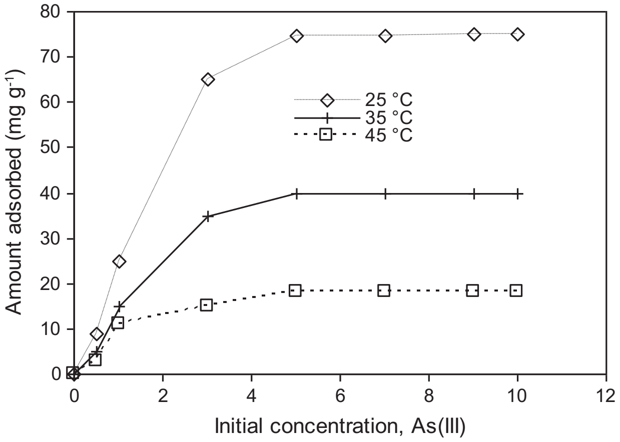

Fig. 5. Effect of temperature variation on arsenic(III) adsorption onto (RC).

The effect of temperature in the adsorption of As(III) ions on clay material (RC) was also investigated. The temperature was varied from 298 to 318 K at pH 6, contact time of 3 h, and As(III) ions concentration of 10 mg/L. According to Fig. 5, when the temperature increases, the As(III) ions capacities decrease and the metal retention reaches its maximum at 25°C. This confirms that adsorption is an exothermic phenomenon [17]. The same effect of the concentration increasing was observed and the best As(III) adsorption was detected in high concentration. A concentration >7 mg/L, a stage was observed which indicates material saturation.

6. Conclusions

Adsorption is a method that has been an important method used in arsenic removal. Most studies are focused on the type of adsorbent mediums and the economics of their regeneration. Arsenic(III) ions were removed in significant amounts by the smectite clay from Tunisia. The best amount adsorption of As(III) (75 mg/g) ions was detected at 25°C and in pH varied between 3 and 9. Finally, the characterization essentially by the mineralogical and FTIR analysis confirms that El Haria green clay is rich essentially in montmorillonite minerals, indicating hence its potential application in the wastewater treatment.

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