Bulletin de la Société Royale des Sciences de Liège, Vol. 86*, special edition,* 2017*, p.*157 - 164

Preparation of a new modified clay with amino acid for anionic pollutant removal from water

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Abstract

Modified montmorilonite (Mt) as clay mineral with amino acid (M-AA) was synthesized by cation exchange method and used to remove anionic pollutants from water. The modified clay was characterized by X-ray diffraction (XRD) and zeta potential. XRD results showed that aminoacid can be intercalated into the Mt and increase the interlayer space of Mt. Positive zeta potential of modified Mt confirmed the modification of Mt with amino acid. The adsorption of pollutants onto modified Mt as a function of their initial concentration and solution pH was investigated. The removal efficiency was increased with increasing the pollutant initial concentration, however it decreased with increasing pH of solution. The maximum adsorption capacities of modified Mt with amino acid was 5 times larger than unmodified Mt. The regeneration studies were carried out up to 10 cycles for modified Mt and obtained results showed that modified adsorbent could also be effectively used for anionic pollutant removal from surface water for multiple adsorption-desorption cycles.

Keywords: Adsorption, Montmorillonite, Amino acid, Anionic pollutant, Water

1. Introduction

Anionic pollutants are one of the important classes of water pollutants that their high concentration in drinking water is a worldwide health concern. Arsenate, As(V), is one of the hazardous anionic pollutants and has been found responsible in numerous diseases of the skin, lung, liver and lymphatic cancer [1]. Arsenate is the dominant species in surface water due to the high redox potential [2]. Due to the health hazards associated with arsenic contaminated water, the World Health Organization (WHO) has set a maximum contaminant level (MCL) of 10 ppb for arsenic in drinking water [3].

Among the conventional methods, adsorption process receives more attention for removal of arsenate from water owing to its low cost, high efficiency, easy operation and flexibility [4, 5].

clay mineral as one of the wide spread materials can be used as adsorbent due to its low cost, large surface areas, cation exchange capacity and other advantages [4, 6]. Unmodified clay minerals display relatively low adsorption capacity for anionic pollutants due to the their negative surface charge [5]. Adsorption capacity of clay minerals can be improved by replacing the natural inorganic interlayer cations with suitable quaternary amine cations or other surfactants [7]. At present, the prevailing mechanism of adsorption of anions on organically modified Mt is believed to be the binding between anions and the positively charged surface of organoclays [8-10]. Amino functionalized clay minerals are considered as effective adsorbents for anionic pollutants due to their net positive surface charge. In this regard, Lee et al. [11] used amino-organoclay for anionic metals removal and showed that the electrostatic interaction between the anionic pollutants and the protonated amino groups causes to rapid adsorption. It is therefore concluded that the amino functionalization can convert the negative charge of clay to positive and make it promising adsorbent for the removal of anionic pollutants such as arsenic from contaminated water.

The main problem of amino functinalized clay minerals such as montmorillonite (Mt) is related to use of environmentally unfriendly solvents or surfactants in synthetic process as well as the complicated preparation methods. Therefore, it is vital to functionalize Mts with biodegradable and low toxic surfactants by using a simple method. Among the various surfactants with amine functional groups, arginine (Arg) amino acid has been used to modify Mt as a promising modifier.

Arg with two positive amine groups in pH lower its isoelectric pH value; $pH_{PI,}$ can modify Mt with a simple cation exchange method and adsorb anionic pollutants with other positive amine group.

High isoelectric points of Arg possess a potential to remove arsenate at natural pH through electrostatic force [12-15].

This study consists of the modification of Mt with amino acid and its application to anionic pollutant removal from water. Batch adsorption characteristics of amino acid modified Mt (M-AA) was investigated by fitting the experimental data to Langmuir and Freundlich isotherms. Finally, regeneration experiments were conducted to demonstrate the applicability of the M-AA for arsenic removal from surface water.

2. Materials and method

2.1. Materials

Natural montmorillonite (Cloisite Na^+) with cation exchange capacity (CEC) of 92.6 meq/100 g was obtained from Southern Clay Products Inc., USA. L-arginine was used as surfactants to modify the utilized montmorillonite. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Merck Chemical Co. Arsenate stock solutions were prepared by dissolving $Na_2HAsO_4.7H_2O$ (Sigma-Aldrich) in deionized water. All chemicals and reagents were analytical grade.

2.2. Synthesis of M-AA

Cation exchange method was used to modify the Mt by displacement of the sodium cations of Mt with the protonated amino acids. Typically, 0.2 g of Mt was dispersed in distillated water (25 mL) using a magnetic stirrer for 12 h at 30˚C to swell the montmorillonite. Measured amount of amino acid was separately dissolved in 25 mL distillated water; DI, while pH was adjusted to 3 by adding of 0.1 M HCl, dropwise. The amount of amino acid was equivalent to 3 times of CEC value of Mt. Then, it was added to the Mt solution and stirred for 4 h at 70 ˚C. After precipitation, the modified Mt was centrifuged and washed with DI water for several times. Rinsing with DI water was repeated thrice to ensure the complete removal of excess ammonium salt. Finally, the modified Mt was dried at 60 ˚C for 12 h.

2.3. Characterization methods

X-ray diffraction (XRD) patterns of samples were obtained by D500/Siemens diffractometer equipped with monochromatic Cu-Kα radiation (λ = 0.154 nm) under a voltage of 35kV and a current of 30 mA. All samples were analyzed in continuous scan mode with the 2θ ranging from 2° to 50°. The Bragg equation, $2d\sin\theta = n\lambda$, was used to calculate basal spacing (d-value) of mineral clays. The zeta potentials of adsorbents were measured by Nano ZS (red badge) ZEN 3600. The pH dependences of zeta potentials for Mts were measured in the aqueous solutions at different pH values, adjusted by NaOH and HCl aqueous solutions.

2.4. As(V) adsorption experiments

2.4.1. Adsorption isotherms

The adsorption isotherm experiments were conducted for different arsenate concentrations ranging from 5 to 20 ppm. For all tests, 100 ml of arsenate solution containing 0.1 g adsorbent was poured into volumetric flask and stirred for 24 h at 25 °C, while pH of the solution was adjusted to 7 ± 0.5. After reaching to equilibrium condition, solution was centrifuged at 10000 rpm for 20 min. The residual concentration of arsenate in the solution was determined by an atomic absorption spectrometer (Varian 220-Graphite Furnace, Shimadzu AA-670). The equilibrium adsorption capacity and removal efficiency of As(V) were calculated as follows:

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

$$\%\,\text{Removal} = \frac{(C_0 - C_t)}{C_0} \times 100 \tag{2}$$

where C_o (mg/L), C_e (mg/L) and C_t (mg/L) are concentrations at the initial, equilibrium and time t (min) in the solution, respectively, V is the total volume (L) of the arsenic solution and M is the mass (g) of dry adsorbent used in the adsorption study.

2.4.2. Effects of initial solution pH

In order to identify the effects of initial solution pH on arsenate adsorption, 0.1 g of adsorbent was added in the 100 ml solution containing 100 ppb arsenate at different pH ranging between 3 and 9. The pH of solution was adjusted by adding 0.1 M HCl or 0.1 M NaOH. Under continuous shaking for 24 h at 25 °C, the concentration of arsenate of each pH solution was determined.

2.5. Desorption and regeneration experiments

Adsorption-desorption cycles as one of the most interesting feathers of the current work, were conducted to investigate the reusability of modified adsorbents. Each cycle consisted of loading of the adsorbent (0.1 g) into the 100 ml of aqueous solution containing 100 ppb of arsenate at 25°C. After 24 h of adsorption test, the solution was centrifuged and adsorbents were separated. The used adsorbents were immersed in 100 ml water and pH of solution was adjusted according to the results of previous section and then the adsorption test was repeated.

3 Results and diqscussion

3.1. Characterizations of pristine and modified Mts

3.1.1. XRD analysis

XRD analysis is capable to measure the interlayer space of clay mineral. Fig. 1 exhibits the XRD results of Mt and M-AA. According to the XRD pattern of Mt, the typical reflection at 2θ = 8.84° related to the basal spacing of 0.98 nm. For M-AA the reflection at 8.84° shifts to 6.95° which is corresponded to 1.3 nm basal spacing. The increase in the interlayer space is attributed to the successful intercalation of amino acid molecule in the interlayer of Mt. In order to identify the arrangement of the amino acid molecule, dimensions of the amino acid molecules is necessary. According to the interlayer space increment (0.32 nm) of M-AA and width of Arg molecule (~ 0.3 nm), the interlayered amino acid molecule haS a monolayer arrangement [12].

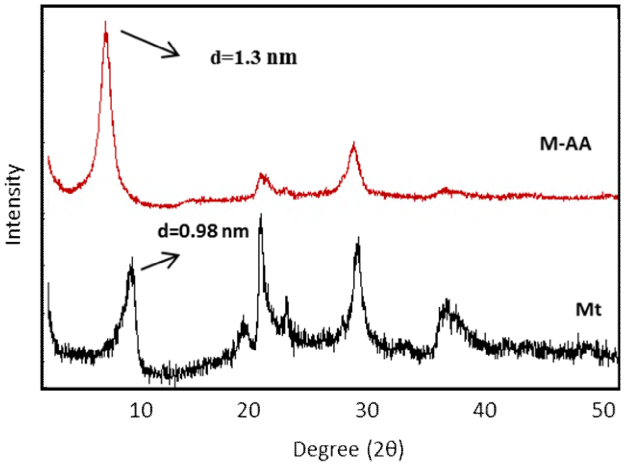

Fig.1: XRD patterns of Mt and M-AA

3.1.2. Zeta potential

Zeta potentials of Mt and M-AA adsorbents were measured in different pH and obtained results were shown in Fig.2. The zeta potential of Mt was negative, which was similar with other reports. Positive zeta potentials were observed for modified Mt in lower pH values. Zeta potential was transformed to negative values, with increasing the pH value. It is obvious that the isoelectric points of M-AA is about 8. Therefore, the positive zeta-potentials of modified Mt at neutral pH is due to the protonation of the NH_2 group of amino acid, while the negative values at higher pH values are attributed to the deprotonation of the carboxyl group of Arg. Positive zeta potential indicates that the modified Mt has positive surface charge, which would increase the electrostatic attraction between adsorbent surface and the anionic pollutant.

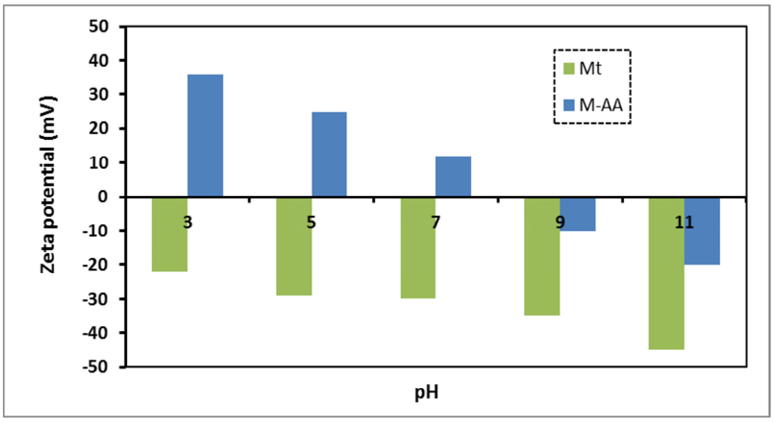

Fig.2: Zeta potential of unmodified Mt and M-AA

3.2. Adsorption experiments

3.2.1. Adsorption isotherms

The relationship between the equilibrium adsorption capacity of Mt and M-AA adsorbents versus the initial concentrations of the arsenic solutions were shown in Fig.3. In case of all samples, the adsorption capacity of As(V); denoted by q_e, increased as initial concentration of As(V) increases. The As(V) adsorption capacity of Mt was very low due to the negative charge of surface. However, the adsorption capacity for M-AA was about five times as large as Mt. These results implied that the modified Mts could attract As(V) anions due to their positive surface charge.

In order to correlate the equilibrium data, two main isothermal models including Langmuir and Freundlich were utilized as shown in Eqs. 3 and 4, respectively:

$$\frac{1}{q} = \frac{1}{K_L C_e q_{max}} + \frac{1}{q_{max}} \tag{3}$$

where K_L is the Langmuir adsorption constant (L/mg), C_e is the As(V) concentration in solution (mg/L) and q_{max} is maximal adsorption capacity (mg/g) and

$$\log q = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

where K_F is the Freundlich constant and n is the heterogeneity factor. The constants for the Langmuir and Freundlich isotherms were calculated by the linear regression of the isotherms and the obtained results were shown in Table 1. From R^2 values, it can be concluded that the Langmuir adsorption isotherm is more suitable to represent the adsorption isotherm of As(V) for modified adsorbents.

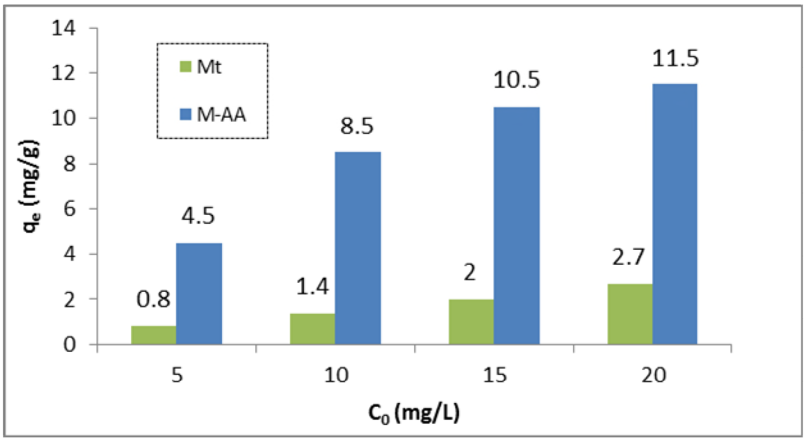

Fig.3: Adsorption isotherms for the adsorption of As(V) on unmodified and modified Mts. (Adsorbent dosage:1g/L, pH:7, T:25˚C)

Table1. Langmuir and Freundlich isotherm parameters for As(V) removal on M-AA

Adsorbent	Langmuir model			Freundlich model		
	K_L(L/mg)	q_{max}(mg/g)	R^2	K_F(mg/g)	1/n	R^2
M-AA	1.07	13.02	0.9944	6.291	0.311	0.895

3.2.3. Effects of initial solution pH on arsenic removal

Solution pH is the most prominent parameter in As(V) adsorption, because it seriously affects the surface charge of adsorbent and degree of ionization of the As(V) oxyanions. Fig. 4 illustrates the adsorption behaviors of As(V) on M-AA adsorent as a function of pH. At pH = 3.0, nearly 100 % of As(V) was adsorbed onto M-AA. It is due to the positive charge of modified Mt in acidic condition and thus it was capable to remove As(V) anions. A slight decrease in As(V) adsorption was observed with increasing the pH from 3 to 5 and 7.

By increasing pH over pH_{PI} of adsorbent, repulsion between the negative side chains of amino acid and As(V) anions causes to decrease the adsorption. Higher concentration of competitive anions (OH^-) in alkaline medium also has a negative impact on the removal of As(V) anions from water [16]. By increasing pH to 9, the absorption efficiency dramatically decreases to 45%. Despite of the lower As(V) adsorption at higher pH, this particular behavior can be potentially used in the regeneration process of modified Mt, since the adsorbed As(V) is easily dissociated from the adsorbent.

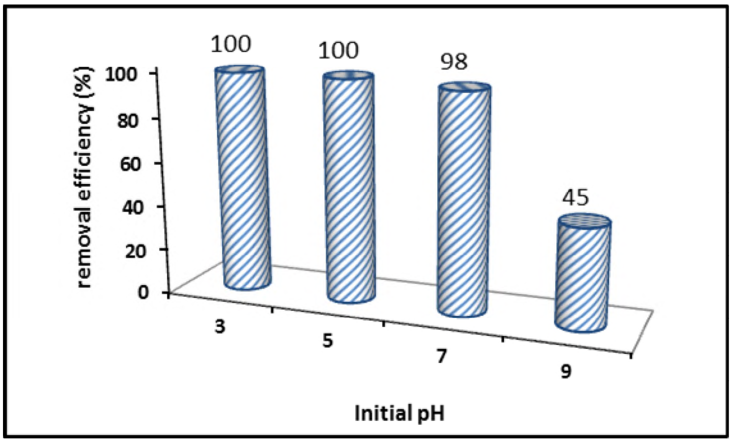

Fig.4:. Effect of pH variation on the As(V) removal efficiency of M-AA (As(V) concentration: 100 ppb, adsorbent dosage: 1g/L, T: 25˚C)

3.3. Regeneration studies

Adsorption-desorption trials of M-AA are shown in Fig. 5. The obtained results indicated that As(V) removal efficiency was more than 90% after 9 cycles. When adsorption-desorption cycle was increased to 10, the removal efficiencies of M-AA was decreased from 98% to 89.5.5%. Very high regeneration efficiency of modified Mts represents that As(V) anions are bound through reversible interaction.

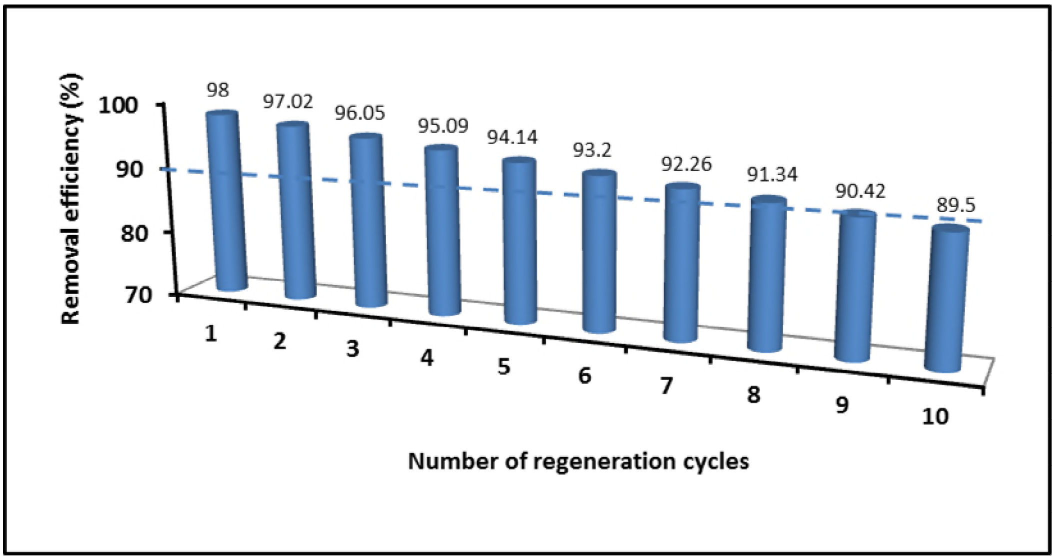

Fig.5. As(V) removal efficiency for M-AA from repeated adsorption/desorption cycles (As(V) concentration:100 ppb, adsorbent dosage:1g/L, pH : 7, T: 25˚C, contact time: 60 min)

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