Journal of Engineering and Applied Sciences 12 (Special Issue 8): 8454-8457, 2017
ISSN: 1816-949X

Study on the Intercalation of Butyl Pyridinium in Smectite Clay and Application for Chromate Adsorption

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Abstract: Smectite clay materials with interlayered structure have ability to be modified by intercalation of functional group. This study presents the study the thermodynamic and kinetics of the insertion butyl Pyridinium Ionic Liquid (IL) into the interlayer space of smectite clay. Chemical interaction of intercalated IL and its potency for adsorption application was intensively simulated for the adsorption of chromate ion. Preparation of IL-intercalated smectite was conducted using saponite and montmorillonite minerals. Physicochemical character of functionalized materials was studied by XRD, FTIR, gas sorption analyser and SEM-EDX. Materials adsorptivity towards chromate ion was performed in a batch adsorption system. IL-intercalated smectite was successfully prepared and it is found that the intercalation obey chemical adsorption with an endothermic condition. The increasing basal spacing of saponite by the intercalation is higher compared to that of montmorillonite. The IL-intercalated clays demonstrated the high adsorptivity for chromate ions.

Key words: Montmorillonite, demonstrated, chromate ions, smectite, thermodynamic, Indonesia

INTRODUCTION

Ionic Liquids (ILs) is one of green chemicals for replacing such toxic organic compounds. ILs are utilized in several application in organic synthesis, separation and environmental protection refer to their safety and less toxic compared to organic solvents usually used. In different schemes, clay is an inorganic material class with lamellar structure having high specific surface area and modifiable properties (Rios *et al*., 2013; Earle and Seddon, 2000). One of the possible mechanism for clay modification in order to prepare adsorbent material is organic compound-immobilized clay or called as organoclay (Taylor *et al*., 2000). Some previous researches present the feasibility of organoclay application for volatile organic compounds reduction as well as metal oxide anions (Leyva-Ramos *et al*., 2008; Pandey and Mishra, 2011). Refer to some replacements of organic compound immobilization in clay structure, ILs-immobilized clay is an interesting material as candidate for adsorption purposes (Thomas and Marvey, 2016; El-Zahhar, 2015).

In other side, chromium (VI) is known to be very toxic heavy metal and a common element of earth's cause it is carcinogen, mutagen and teratogen in biological systems. It can enter the environment through surface waters and even reach groundwater in a number of path ways. These include discharge of wastewater from industries such as those of electroplating and leather tanning. According to the guidelines recommended by the World Health Organization (WHO), the maximum level for Cr (VI) in drinking water is 0.05 mg/L. In very low level, chromium (VI) reduction over adsorption mechanism is popular method instead of some other costly procedure.

Based on those backgrounds, in this study, research on preparation, physico-chemical properties study and application of ILs-modified clay for Cr (VI) adsorption was conducted. Butyl pipyridinium was chosen as IL refer to its low cost and less toxicological effect to the environment. Aim of research was focused on physicochemical study of material as function of preparation variable, i.e., amount of IL in interlayer structure and its effects on adsorptivity.

MATERIALS AND METHODS

Montmorillonite clay (MMt) was collected from Pacitan, East Java. All other reagents such as Potassium dichromate ($K_2Cr_2O_7$) supplied from Merck, butyl Pyridinium bromide supplied from Sigma-Aldrich were specified to be ≥99% purity.

Preparation of Butyl Pyridinium immobilized Montmorillonite (BuPy-MMTs): BuPy-MMTs

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composites were prepared by ion exchange method. The solution of BuPy was dispersed into MMT suspension followed by stirring during 24 h at room temperature, then it was separated by filtration and washed several times until no bubble was detected. The composite of BuPy-MMTs were prepared in a varied IL content of: 1-3 mmol/100 g MMT. The obtained materials were dried in air at 60°C, ground and stored. The products from the preparation are designed as BuPy-MMT-1-3, respectively.

Materials characterization: Several spectroscopic techniques were used to characterize BuPy-MMTs:

- XRD patterns were obtained using a X-6000 Shimadzu angle X-ray powder diffractometer operating at 45 kV and 40 mA with CuKλ radiation
- FTIR spectra were recorded in absorption frequencies (400-4000 cm^{-1}) in an FTIR (Perkin Elmer)
- Scanning electron microscope (Seiko) was utilized for morphological analysis of the samples

Batch adsorption experiments: Adsorption of chromium (VI) experiments on BuPy-MMTs was performed in batch experiments. Initial concentrations of chromium ranged between 1-3 ppm were used. A mass of 0.2 g of adsorbents were mixed with V = 20 mL of chromium solutions in erlenmeyer flasks with glass caps. The samples were mixed by magnetic stirring at 150 rpm shaken for different times of adsorption (tads) at certain temperature (Tads). The pH solutions were adjusted by adding negligible volumes of 0.1 mol/L HCl or NaOH. After a given tads, the solid and liquid phases were separated by centrifugation at 15000 rpm. The residual concentration of chromium in supernatant were measured by UV/Visible spectrophotometer (UV/Vis HITACHI U-2010) at λ = 350 nm. The amount of chromium adsorbed at equilibrium on BuPy-MMTs was calculated using the following equation:

$$q_e = \frac{C_o - C_e}{C_o} \times V$$

Where:

C_o and C_e = The initial and the equilibrium concentrations of pollutants (mg/L), respectively
m = The mass of adsorbent (g)
V = The volume of the solution (L)

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of BuPy-MMTs samples and the change of d001 along the variation of BuPy content in the composites. For MMT, the basal spacing $d_{(001)}$ centered at $2\theta°$ = 7.7 was shifted to the lower $2\theta°$ in the BuPy-MMT indicating that the BuPy cations have been intercalated within the layered structure widened the basal spacing d(001) of MMT. The new peaks appearing at $2\theta°$ = 3.6 and 6.9 are attributed to organic cations associating predominantly flat with the silicate surface in an inclined paraffin-type structure via cation exchange of interlayer (Na+/$BuPy^+$) (Fig. 2).

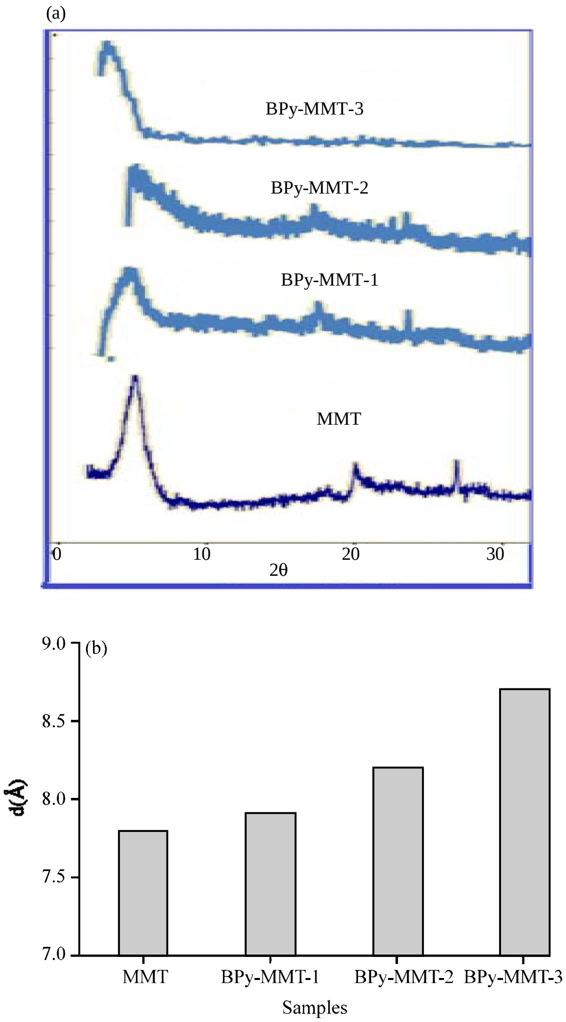

Fig. 1: a, b) The XRD patterns of BuPy-MMTs samples

The change in d_{001} affects the surface morphology of materials as represented by SEM profile in Fig. 3. A rougher and flaky surface is appeared after BuPy modification refer to the pore opening. Adsorptivity of the materials for Cr (VI) adsorption is presented by kinetics of Cr (VI) adsoption in Fig. 4.

From the kinetic curve it is confirmed that the adsorptivity of ByPy-MMTs samples are higher compared

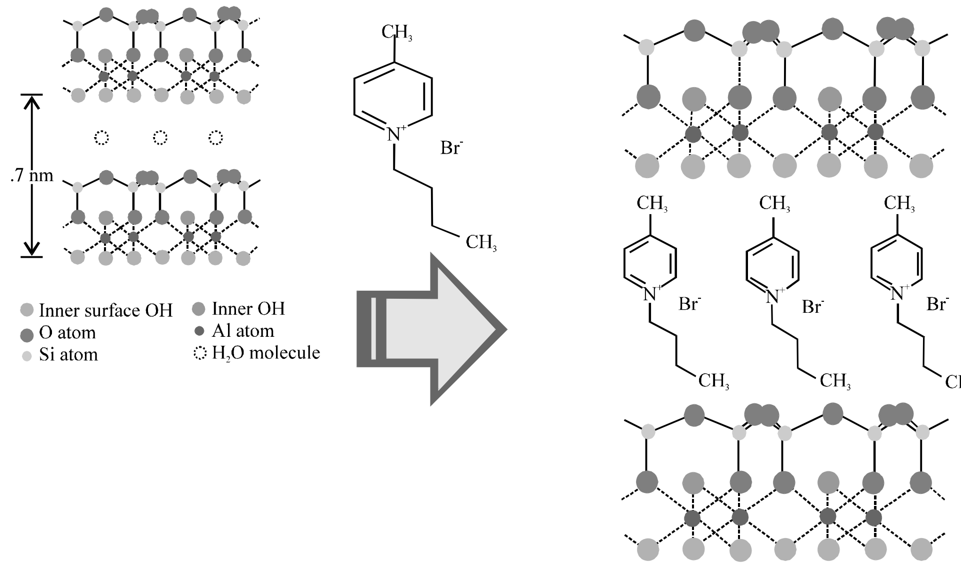

Fig. 2: Schematic representation of BuPy intercalation in MMT

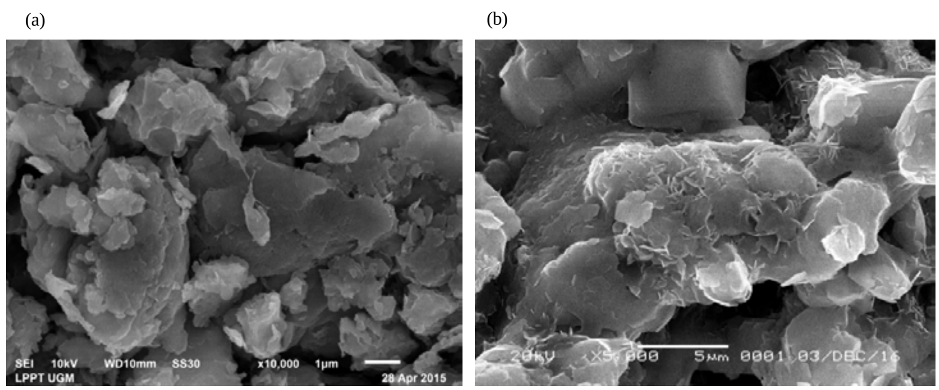

Fig. 3: SEM profile of: a) MMT and b) BuPy-MMT-1

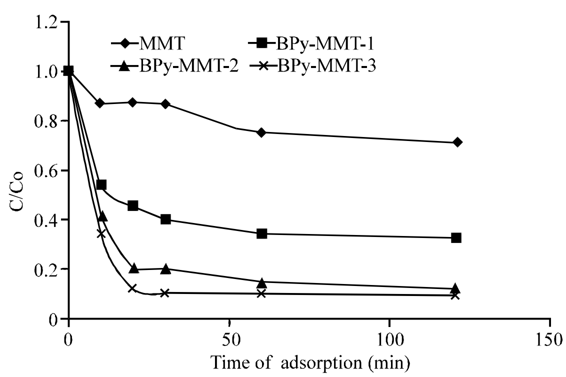

Fig. 4: Kinetics of Cr (VI) adsorption over MMT and ByPy-MMTs materials

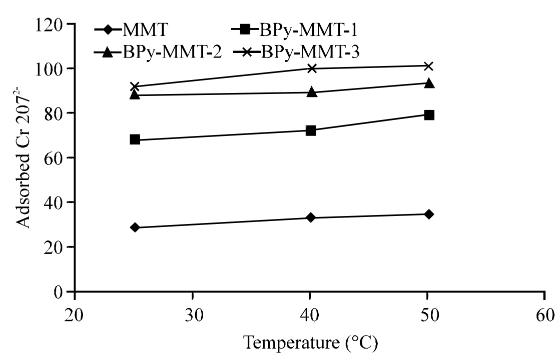

Fig. 5: Effect of temperature on Cr (VI) adsorptivity

to MMT as shown by the rapid Cr (VI) reduction along increasing time of adsorption. The higher content of BuPy the higher adsorptivity toward Cr (VI).

Furthermore, the adsorption of Cr (VI) is endotermic adsorption as reflected by the plot of effect of the temperature on adsorbed Cr (VI) in Fig. 5.

CONCLUSION

This study has shown that formation of Butyl Pyridinium-Montmorillonite composite was observed with increasing physical parameters for bichromate adsorption.

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