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Research paper

Adsorption of ammonium by different natural clay minerals: Characterization, kinetics and adsorption isotherms

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ABSTRACT

This research presented six natural clay minerals (NCM) evaluated for the effectiveness of NH_4^+ adsorption from aqueous solution. For the first time, the NH_4^+ adsorption capacities of kaolinite, halloysite, montmorillonite, vermiculite, palygorskite, and sepiolite were examined and compared in the same study. All the NCM were fully characterized by XRD, SEM/EDS, XRF, FTIR, CEC, zeta potential and nitrogen adsorption-desorption isotherms to better understand the adsorption mechanism-property relationship. Adsorption kinetics showed that the adsorption behavior followed the pseudo-second-order kinetic model. The adsorption isotherms fitted by the Langmuir model illustrated that among all the NCM studied, vermiculite (50.06 mg/g) and montmorillonite (40.84 mg/g) showed the highest ammonium adsorption capacities. Our results revealed that the cation exchange is the main mechanism for the NH_4^+ adsorption. Additionally, negatively charged surface, water absorption process and surface morphology of NCM might also contribute to the high adsorption capacity for the NH_4^+ . The maximum adsorption capacities for all NCM were rapidly obtained within 30 min with a dosage of 0.3 g/25 mL at pH of 7. The results illustrated that the NCM have significant potential as economic, safe and effective adsorbent materials for the NH_4^+ adsorption from the aqueous solution.

1. Introduction

With the rapid development of industry, improper disposal of industrial wastewater containing huge quantities of ammonium has led to eutrophication in rivers, estuaries, lakes and other water reservoirs (Wang et al., 2007; Mittal et al., 2009; Sun et al., 2015). This issue poses a significant risk to the availability of safe drinking water as well as human health (Rožić et al., 2000; Gupta et al., 2011a; Moradi et al., 2012). Therefore, effective removal of ammonium from industrial wastewater prior to discharge into natural water bodies is critical for water resources protection (Rožić et al., 2000; Gupta and Nayak, 2012).

Various methods, such as air stripping, biological degradation, adsorption techniques have been used for ammonium removal (Mittal et al., 2010; Gupta et al., 2011b; Moradi et al., 2012). For practical applications, adsorption method seems to be one of the most favored wastewater treatment techniques because of its environmental and economic sustainability (Gupta et al., 1998; Europea, 2003; Gefeniené et al., 2006; Marañón et al., 2006; Mittal et al., 2010; Moussavi et al., 2011). Abundant natural clay minerals (NCM) are inexpensive and can

be used as low-cost adsorbents due to their unique properties as well as no toxic effects to the ecosystems (Borisover and Davis, 2015; Ismajji et al., 2015; Sun et al., 2015; Zhu et al., 2016).

China has abundant NCM resources with high purity, available in many provinces (Yu et al., 2010; Liu et al., 2017; Xing et al., 2017). In addition, NCM are low cost (Kurniawan et al., 2006; Alshameri et al., 2014a; Franco et al., 2016) which are approximately 20 times cheaper than activated carbon.

However, investigations on the adsorption behaviors of NH_4^+ onto NCM are relatively scarce (Wang et al., 2014; Ismajji et al., 2015; Sun et al., 2015), but possess high importance for industrial wastewater treatment and grasping the fate of NH_4^+ in different types of environments. A systematic comparison study under identical experimental conditions will be helpful to understand the influence of structure and properties of NCM on their adsorptive behaviors towards NH_4^+ .

To the best of our knowledge, no comprehensive research has been conducted to investigate and compare NCM for NH_4^+ adsorption in the same study. Moreover, modification of natural minerals at a larger scale

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may increase the processing cost; therefore reliable water treatment by using non-modified clay minerals is highly desirable. In this study, six types of NCM-based adsorbents namely kaolinite, halloysite, montmorillonite, vermiculite, palygorskite, and sepiolite were investigated and compared their adsorption abilities for NH_4^+ .

The objective of this research is to evaluate the adsorption behaviors of NH_4^+ onto six NCM under identical experimental conditions. The adsorption kinetics, adsorption isotherms, effects of pH, adsorbents dosage and comparison of adsorption behavior of ammonium ion onto NCM were investigated. Moreover, In order to build the relationship between adsorption mechanism and minerals' property, the NCM samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray fluorescence (XRF), Fourier transform infrared (FTIR) spectroscopy, cation exchange capacity (CEC), N_2 adsorption-desorption isotherms and zeta potential analysis to obtain the mineralogical and physicochemical parameters. The insights obtained in this study are useful for applications of NCM in the environmental engineering and value-added utilization of natural mineral resources.

2. Materials and experimental methods

2.1. Materials and chemicals

All NCM were collected from China, namely kaolinite (Kaol) sample from Maoming, Guangdong province, vermiculite (Ver) sample from Lingshou, Hebei province, Calcium montmorillonite (Mt) sample from Chifeng, Inner Mongolia, palygorskite (Pla) sample from Mingguang, Anhui Province, sepiolite (Sep) sample from Baoding, Hebei province, and halloysite (Hal) sample from Linfen, Shanxi province. All the chemicals used, such as ammonium chloride (NH_4Cl), sodium chloride (NaCl), sodium hydroxide (NaOH) and hydrochloric acid (HCl), are of analytical grade.

2.2. Preparation for NCM samples

NCM were pulverized and passed through a 74 μm sieve. The NCM were washed with distilled water to remove soluble matter and then dried in an oven at 100 $^\circ\text{C}$ for 24 h.

2.3. Analysis and characterization methods

Powder X-ray diffraction (XRD) experiments were performed between 2 $^\circ$ and 70 $^\circ$ (2 θ) with a step size of 0.02 $^\circ$ and a measuring time of 0.8 s per step using a Bruker D8 Advance diffractometer with Cu-K α ($\lambda = 0.154$ nm) radiation operating at 40 kV and 40MA and identified using JCPDS files. The mass percentages of mineralogical composition of NCM were calculated by using a matrix-flushing method for quantitative multicomponent analysis (Chung, 1974) (Table S1).

The morphologies of NCM were investigated using SEM, operating at an accelerating voltage of 15 kV for photomicrographs (FESEM, SU8010, Hitachi, Japan). The samples were initially placed in a vacuum chamber for coating with a thin layer (few nanometers) of gold (Au).

The chemical compositions of the samples were tested by Netherlands PANalytical PW2424 X-ray fluorescence (XRF) spectroscopy. The prepared sample was fused with lithium metaborate–lithium tetraborate flux which also includes an oxidizing agent (Lithium Nitrate), and then poured into a platinum mould. The resultant disk was in turn analysed by XRF spectrometry. The XRF analysis was determined in conjunction with a loss-on-ignition at 1000 $^\circ\text{C}$. The resulting data from both determinations were combined to produce the total.

FTIR spectra were carried out using a Bruker Vertex-70 IR spectrophotometer (Manheim, Germany) at room temperature. The specimens were prepared by mixing 0.9 mg of sample and 80 mg of KBr followed by pressing the mixture into pellets. A pure KBr wafer was measured as the background. All spectra were collected over 64 scans at

a resolution of 4 cm^{-1} in the wavenumbers range from 400 to 4000 cm^{-1} .

N_2 adsorption-desorption isotherms were determined at 77 K on a Micromeritics ASAP 2020 system (Norcross, USA) at liquid nitrogen temperature (-196 $^\circ\text{C}$). Before the measurement, the samples were outgassed at 250 $^\circ\text{C}$ for 12 h. The specific surface area (S_{BET}) was calculated using the multiple-point Brunauer-Emmett-Teller (BET) method (Rouquerol et al., 2007).

The cation exchange capacity (CEC) was measured by adsorption of $[\text{Co}(\text{NH}_3)_6]^{3+}$ method (Zhu et al., 2007). 1.0 g of NCM sample was added into a 20 mL of 25 mmol/L $[\text{Co}(\text{NH}_3)_6]\text{Cl}$ solution, and shaken at 20 $^\circ\text{C}$ for 24 h. The Concentration of the $[\text{Co}(\text{NH}_3)_6]\text{Cl}$ solution after cation exchange was determined at 472 nm on a spectrometer (UV-759S, Jinghua, China). Subsequently, the CEC values of the samples were calculated from the difference between the initial and equilibrium concentration. Quality control was performed by repeating the experiments two times and average data was reported.

Zeta potential was conducted by a Malvern Instruments Ltd., UK, Zetasizer Nano ZS 90. For the zeta potential measurements, 10 mg (0.01 g) sample was added into a 50 mL of 20 mg/L ammonium solution and a magnetic bar was subsequently used for stirring it for 30 min at room temperature. The zeta potential was tested in a range of 6.3–2 pH. The initial pH was adjusted by different concentrations of 0.1 M, 0.01 M and 0.05 M of HCl solution. Quality control was performed by repeating the experiments two times and average data was reported.

2.4. Batch adsorption experiments

The stock solution was obtained by dissolving 3.8190 g of analytically pure NH_4Cl (dehydrated at 104 $^\circ\text{C}$ for 2 h) in distilled water to get an initial ammonium concentration of 1000 mg/L. The stock solution was further diluted with distilled water to get the desired concentrations of experimental working solutions. All batch adsorption experiments were carried out using stopper test tube (50 mL) in a thermostatic shaker with clay mineral/liquid ratio of 0.3 g/25 mL. The NH_4^+ concentration in solution was determined by the Nessler's method carried out with a UV-vis spectrophotometer at 420 nm (UV-759S, Jinghua, China). Quality control testing included experiments with blanks and duplicates.

2.4.1. Adsorption kinetics experiments

The optimum time required for the NH_4^+ adsorption to attain equilibrium was determined as a function of contact time in the range of 5–120 min of 10 mg/L NH_4^+ solution at a fixed pH 7 and 25 $^\circ\text{C}$.

2.4.2. Adsorption isotherm experiments

The effect of initial NH_4^+ concentration on the removal capacity of NH_4^+ in the batch adsorption experiment was evaluated by varying the concentrations in the range of 10–1500 mg/L for 2 h.

2.4.3. Effect of solution pH on NH_4^+ adsorption

The pH effect was tested in a range of 2–10 pH of 30 mg NH_4^+ /L for 2 h. The initial pH was adjusted by 1 M HCl or NaOH solution.

2.4.4. Effect of NCM dosage on NH_4^+ adsorption

NCM dosages were varied from 0.1 to 0.5 g at an initial ammonium concentration of 30 mg/L for 2 h.

The removal efficiency (%) for the six NCM and the equilibrium adsorption capacity (q_e) were calculated, respectively by using the following equations:

$$\text{Removal efficiency (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

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