



Research paper

Enhanced adsorption of potassium nitrate with potassium cation on H₃PO₄ modified kaolinite and nitrate anion into Mg-Al layered double hydroxideZhiwu Lei^a, Giovanni Cagnetta^b, Xuewei Li^c, Jun Qu^a, Zhao Li^a, Qiwu Zhang^{a,*}, Jun Huang^b^a School of Resources & Environmental Engineering, Wuhan University of Technology, Wuhan 430070, PR China^b State Key Joint Laboratory of Environment Simulation and Pollution Control (SKJLESPC), Beijing Key Laboratory of Emerging Organic Contaminants Control (BKLEOCC), School of Environment, POPs Research Center, Tsinghua University, Beijing 100084, PR China^c Zhengzhou University of Aeronautics, Zhengzhou 450015, PR China

ARTICLE INFO

Keywords:

Kaolinite
Mg-Al LDH
Potassium
Synergistic adsorption
Mechanochemical process

ABSTRACT

Kaolinite modification by grinding with H₃PO₄ was conducted to introduce more H⁺ for potassium exchange, therefore to enhance largely the capacity of potassium fixation. The precursor of Mg-Al LDH by milling both Mg and Al hydroxides was used to incorporate nitrate anions. The modified kaolinite and the synthesized LDH precursor were simultaneously used to achieve synergistic effect to raise the removal efficiency of potassium nitrate. The neutralization action between H⁺ ions exchanged with potassium cations from the kaolinite and OH⁻ ions exchanged with nitrate anions from the LDH allows the continuous exchanging to remove out potassium nitrate at high efficiency, achieving the desalination of the very difficult alkali metals salts. The process provides an effective way to desalinate the difficult alkali metal salts and recover potassium from some specific industrial wastewaters with the products serving as a slow-release fertilizer.

1. Introduction

Kaolinite is one of the well-known low-cost raw clays and numerous studies regarding the adsorptions of heavy metals (Arias and Sen, 2009; Chantawong et al., 2003; Cheng et al., 2012; Quintelas et al., 2009; Sari et al., 2007), inorganic anions (Denoyel and Rouquerol, 1991; Singh and Kanehiro, 1969) and organic ligands (Ghosh and Bhattacharyya, 2002; Nandi et al., 2009; Zhu et al., 2010) by kaolinite have been reported. Due to the limited adsorption capacity of raw kaolinite, modifications by humic acid (Balcke et al., 2002; Huang and Yang, 1995; Terashima et al., 2003; Ying et al., 2010), phosphate and sulfate (Adebowale et al., 2005; Unuabonah et al., 2007) have been also performed to increase the potentials for possible applications.

Recently, mechanochemical activation has drawn great attention and has been applied to many fields, such as surface modification (Ding et al., 2012), materials syntheses (Zhang and Saito, 2000), intercalation of urea (Makó et al., 2009) (NH₂CONH₂) into the kaolin structure, etc. Previously we used a mechanochemical route to prepare complex compounds of kaolinite with KH₂PO₄ (Solihin et al., 2011; Zhang and Solihin, 2009) to change the phosphate as insoluble in water to serve as a slow-release fertilizer. This time, we conducted ball-milling of kaolinite with H₃PO₄ instead of KH₂PO₄ to prepare a composite and introduce more exchangeable H⁺ to enhance the capacity for

incorporating K⁺ so that the modified kaolinite may adsorb potassium as high as several percent for practical application rather than just a removal phenomenon of alkali metals at low concentration of several ppm. The lower pH due to the exchanged H⁺ into water, however, may gradually impede the further exchanging progress. Layered double hydroxides (LDH), also known as anionic clays or hydroxalite-like compounds represented as [M_{1-x}²⁺M_x³⁺(OH)₂]^{x+}(Aⁿ⁻)_xn·mH₂O, have been widely used in environmental protection (Gong et al., 2016; Ju et al., 2017), pharmaceutical preparation (Rives et al., 2014), organic synthesis (Newman and Jones, 1998), elastomer doping (Basu et al., 2014), etc. We reported the enhanced adsorption capacity of LDH precursor by grinding the starting hydroxides and the exchanging property between anions is understood to be one main action (Qu et al., 2016; Zhong et al., 2016).

Technological progress has been steadily achieved on wastewater in order to recovery useful elements, like nutrients (N, P, K), and permit water re-use in agriculture or industrial processes. Thermal and membrane process are commonly utilized for salty (waste-) water (Alkudhiri et al., 2012; Bowen and Mukhtar, 1996; Drioli et al., 2015). Although renewable energy has been applied to reduce energetic cost (Ghaffour et al., 2015; Lourdes et al., 2002), such technologies are remarkably energy-consuming and have a notable environmental impact caused by brine discharge (Mezher et al., 2011). Moreover, removal of

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alkali metals is challenging because of the very high solubility of their salts in water. Among them, of which potassium is of primary interest because it is an essential element for plants growth and potash ores (the main source of K) have a limited distribution in the world. Recovery from waste streams or selectively from sea water might be a cheap K-source for developing countries (Batstone, 2015), thus supporting the continuous increase of world population (Adeoye et al., 2001). At present, the methods of removing potassium mainly include solvent extraction (Makrlík et al., 2008), ionic sieve membrane (Yuan et al., 2012), ion-exchange (Kim and Chang, 2009), electrodialysis (Acevedo-Morantes et al., 2011) and clay mineral adsorption (Cao et al., 2008). Thanks to the recent rapid developments on nano-materials, these technologies have been further improved, and new nano-engineered membranes, ion-exchanging materials, and adsorbents have been worked out (Baláz, 2008; Daer et al., 2015; Hosseini and Madaeni, 2017).

In the present work, kaolinite is first modified by phosphoric acid in a planetary mill and the product is characterized including the adsorption capacity of potassium. Then the modified kaolinite is used together with the precursor of Mg-Al LDH to expect a synergistic adsorption effect, so that the adsorption process may exhibit good performance high enough to compete with other methods for the desalination purpose of alkali metal salts. We propose a novel process to remove potassium nitrate from water to serve both desalination and potassium recovery from the significantly increased capacity of potassium incorporation.

2. Experiments

2.1. Materials

Phosphoric acid (H_3PO_4 , $\geq 85\%$), magnesium hydroxide ($\text{Mg}(\text{OH})_2$), aluminum hydroxide ($\text{Al}(\text{OH})_3$), potassium hydrophosphate (KH_2PO_4) and potassium nitrate (KNO_3) were bought from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China), and the purity grade of all reagents was analytical reagent. The raw kaolinite was obtained from a mine in Southern China.

2.2. Material preparation

Mixtures of kaolinite and H_3PO_4 were milled in a planetary ball mill (Pulverisette-7, Fritsch, Germany), with two stainless-steel milling pots (45 cm^3 inner volume each) and 7 steel balls ($\text{Ø}15 \text{ mm}$). Kaolinite weight was kept to 2.00 g, while H_3PO_4 was varied as 5, 10, 15, and 20%w/w of the kaolinite amount. The concentrated H_3PO_4 was added gradually by dropping onto kaolinite sample. Milling speed was changed between 200 and 600 rpm, whereas milling time was maintained constant at 60 min. The H_3PO_4 modified kaolinite (KP) was characterized by a set of analytical methods. 0.1 g of the samples was mixed with 10 mL distilled water and the corresponding pH was measured by a pH-meter (METTLER TOLEDO S210) to ascertain existence of free residual H_3PO_4 . Crystalline phases were identified by the X-ray diffraction analysis on a Rigaku Max-RB RU-200B diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5403 \text{ \AA}$) at 2θ between 5° and 70° , with a rated power at 12 kW. FT-IR spectra (Nicolet 6700, Thermo, Thermo Electron Scientific Instruments Corp., Madison, WI) were measured over $4000\text{--}500 \text{ cm}^{-1}$ range, using KBr as a diluent.

Precursor of Mg-Al LDH was prepared high energy ball milling of $\text{Mg}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$ (3:1 molar ratio), according to the procedure described in ref. (Wang et al., 2016). LDH precursor is constituted by an amorphous mixture of both hydroxides, and, when utilized in adsorption experiments, it reacts with water to give the corresponding LDH.

2.3. Adsorption experiments

Firstly, KP was investigated alone as K-adsorbent. 0.5 g KP,

prepared under different conditions, were agitated in 100 mL KNO_3 (100 mg/L of K^+) solution at ambient temperature for 3 h. Later, 10 mL sample was centrifuged ($8933g$) for 5 min; the supernatant underwent concentration measurement.

With regard to synergistic adsorption experiments, both KP (prepared at 450 rpm) and LDH precursor were employed at different weight ratios (viz. KP: LDH precursor = 0:5, 1:4, 2:3, 1:1, 3:2, 4:1, and 5:0). Adsorbent mixture (1.0 g) was agitated in 100 mL KNO_3 (70 mg/L of K^+) solution at room temperature for 3 h. Potassium concentration in solution was measured by atomic absorption spectrophotometer (Shimadzu AA-6880, Kyoto, Japan), while nitrate and phosphate concentrations were determined using a spectrophotometer (UVmini-1240; Shimadzu, Kyoto, Japan), the absorption wavelengths of which were 220 nm and 710 nm, respectively. Nitrate anions were directly measured, while phosphate-based developers were ammonium molybdate and ascorbate.

3. Results and discussion

3.1. Characterizations of the H_3PO_4 modified kaolinite

In order to enhance cation-exchange capability of kaolinite, KP was prepared by direct reaction between the clay material and H_3PO_4 through 60 min ball milling. Change in pH from the sample agitated in water was used to check the reaction degree of kaolinite with H_3PO_4 during the milling since the existence of free H_3PO_4 gave clearly a lower pH. The change in pH of the KP samples with the rotation speed of milling operation was shown in Fig. 1. For the sample prepared at 200 rpm, the value of pH was about 3.2, indicating the still existence of free H_3PO_4 . When milling speed was increased from 200 to 450 rpm, the pH value of samples was increased from 3.2 to 6.8, and remained constant around it with further increase in the milling speed up to 600 rpm. The pH value close to neutral range indicated that H_3PO_4 reacted with kaolinite into stable state without obvious dissociation when agitated in water.

XRD analysis of KP showed that kaolinite characteristic pattern was still identifiable in the product, when milling speed was lower than 300 rpm (Fig. 2). The raw kaolinite sample exhibited intense diffraction peaks located at $12.37, 20.33, 21.24, 24.89, 38.51, 62.28^\circ$, which corresponded to the (001), (-110) , $(-1-11)$, (002), $(-1-13)$ and $(-3-30)$ diffraction plane of kaolinite, respectively (JCPDS: 80-0886, space group: $\text{P}1(1)$, cell constants: $a = 5.158 \text{ \AA}$, $b = 8.942 \text{ \AA}$, $c = 7.397 \text{ \AA}$). With the increase of the milling speed, the peak intensity of kaolinite decreased gradually up to the amorphous pattern obtained

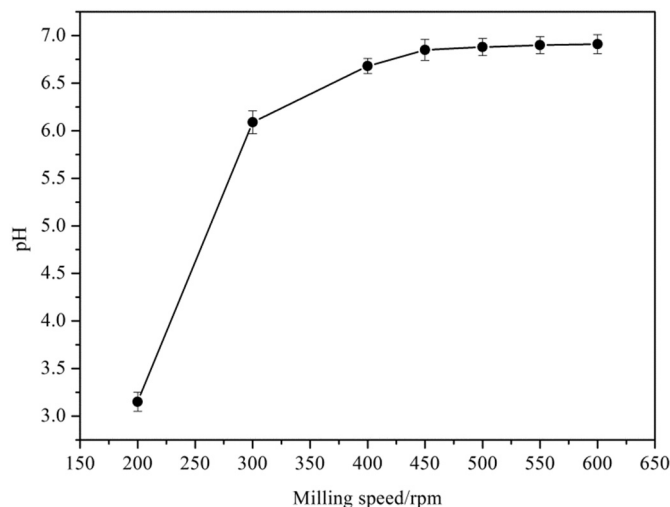


Fig. 1. MC reaction conversion of KP preparation with 10%w/w H_3PO_4 at different rotation speed.

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