

Available online at www.sciencedirect.com

ScienceDirect

www.elsevier.com/locate/jes

JES
 JOURNAL OF
 ENVIRONMENTAL
 SCIENCES
www.jesc.ac.cn

3 Removal of ammonium ion from water by Na-rich birnessite: 2 Performance and mechanisms

4 Ya Cheng, Tinglin Huang*, Xinxin Shi, Gang Wen, Yuankui Sun

4 Key Laboratory of Northwest Resource, Environment and Ecology, MOE, Xi'an University of Architecture and Technology, Xi'an 710055, China
 5 Shaanxi Key Laboratory of Environmental Engineering, Xi'an University of Architecture and Technology, Xi'an 710055, China
 6

8 A R T I C L E I N F O

10 Article history:

11 Received 8 July 2016

12 Revised 25 November 2016

13 Accepted 8 December 2016

14 Available online xxxx

32 Keywords:

33 Ammonium ion adsorption

34 Na-rich birnessite

35 Hydroxyl ions

36 Negatively charged surface

37 Electrostatic interaction
 38

A B S T R A C T

Na-rich birnessite (NRB) was synthesized by a simple synthesis method and used as a high-efficiency adsorbent for the removal of ammonium ion (NH_4^+) from aqueous solution. In order to demonstrate the adsorption performance of the synthesized material, the effects of contact time, pH, initial ammonium ion concentration, and temperature were investigated. Adsorption kinetics showed that the adsorption behavior followed the pseudo second-order kinetic model. The equilibrium adsorption data were fitted to Langmuir and Freundlich adsorption models and the model parameters were evaluated. The monolayer adsorption capacity of the adsorbent, as obtained from the Langmuir isotherm, was 22.61 mg $\text{NH}_4^+\text{-N/g}$ at 283 K. Thermodynamic analyses showed that the adsorption was spontaneous and that it was also a physisorption process. Our data revealed that the higher NH_4^+ adsorption capacity could be primarily attributed to the water absorption process and electrostatic interaction. Particularly, the high surface hydroxyl-content of NRB enables strong interactions with ammonium ion. The results obtained in this study illustrate that the NRB is expected to be an effective and economically viable adsorbent for ammonium ion removal from aqueous system.

© 2016 The Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences.

Published by Elsevier B.V.

43 Introduction

45 Ammonium ion (NH_4^+) is the primary nitrogen polluting species
 46 in the hydrosphere. Ammonium ion discharged together with
 47 municipal, agricultural or industrial effluents is responsible for
 48 harmful effects such as eutrophication of lakes and rivers,
 49 decreased dissolved oxygen, toxicity to aquatic life, and
 50 increased corrosion rate of soil materials (Karadag et al., 2006;
 51 Yusof et al., 2010). Eutrophication of water bodies, a problem of
 52 global concern, has been identified as a major environmental
 53 problem for water resource management (Du et al., 2005; Zheng
 54 et al., 2008). In water supply plants, the ammonium ion present
 55 in raw water will react with chlorine to form disinfection
 56 byproducts, which could damage the human nervous system

and cause deterioration of the taste and odor of water. Hence, it is necessary either to control the ammonium ion contamination in raw water or to remove it before the water is disinfected with chlorine (Cai et al., 2015; Han et al., 2013). Controlling the ammonium ion in the raw water is the preferred solution.

A number of methods (e.g., ion-exchange, adsorption) have been developed to remove ammonium ion (Leaković et al., 2000; Liu et al., 2015; Mandowara and Bhattacharya, 2011; McVeigh and Weatherley, 1999; Wang et al., 2014). Among these strategies, adsorption is considered to be promising due to its high-efficiency, cost effectiveness and easy implementation (Zhu et al., 2012). As a result, many natural and synthetic materials have been developed and used as adsorbents for ammonium ion removal. However, these adsorbents were 70

* Corresponding author. E-mail: huangtinglin@xauat.edu.cn (Tinglin Huang).

always found to have slow adsorption kinetics, and their adsorption capacities may be limited (Alshameri et al., 2014; Kučić et al., 2012; Moradi, 2011; Nielsen, 1996; Rožić et al., 2000). In addition, increased awareness and understanding of the deleterious effects of ammonium ion released from wastewater treatment facilities into natural water systems has resulted in stringent laws restricting ammonium ion discharge. Therefore, the development of new adsorbents designed specifically for the rapid removal of ammonium ion from water is necessary.

Manganese oxides (MnO_x) with layered topologies are ubiquitous in the natural environment. Birnessite belongs to the family of layered hydrous manganese oxides. It possesses unique surface charge, cation exchange, and redox properties, which make it highly reactive with respect to sorption phenomena. Furthermore, birnessite can be synthesized easily under laboratory conditions and, consequently, has often been applied to remove heavy metals (e.g., copper, cadmium, lead and zinc) from water (Eren, 2009; Gadde and Laitinen, 1974; Han et al., 2006a, 2006b; Lefkowitz and Elzinga, 2015; Wang et al., 2007; Kanungo et al., 2004; McKenzie, 1980; Villalobos et al., 2005).

To the best of our knowledge, studies on the adsorption of ammonium ion by manganese oxide in water solution have been limited. Birnessite is the predominant naturally occurring manganese oxide in most environmental settings (Zhu et al., 2010). Thus, in this study, we examined the adsorption of ammonium ion from water by a birnessite-type manganese oxide. The adsorption kinetics and equilibrium isotherms of the uptake of ammonium ion on manganese oxide were studied. Additionally, the effects of initial ammonium ion concentration, contact time, pH, and the major ions present in groundwater on the adsorption process were investigated. The structural characterization of the adsorbents was used to preliminarily reveal the underlying sorption mechanism.

1. Materials and methods

1.1. Materials

Manganese chloride ($\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$), potassium permanganate (KMnO_4), sodium hydroxide (NaOH), ammonium chloride (NH_4Cl), calcium chloride (CaCl_2), and magnesium chloride (MgCl_2) were of analytical reagent grade. All solutions were prepared with deionized distilled water. $\text{NH}_4^+\text{-N}$ solutions of different concentrations were prepared by dissolving the required amounts of NH_4Cl in deionized distilled water.

1.2. Preparation of adsorbent

Birnessite-type manganese oxides with interlayer K^+ and Na^+ ions have been synthesized by redox reactions between KMnO_4 and MnCl_2 under alkaline conditions. In this study, the adsorbent sample was prepared based on the method reported by Luo and Suib (1997). Specifically, 160 mL of 0.5 mol/L $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ was added into 180 mL of 5.55 mol/L NaOH under constant stirring. After 2 hr of cooling, 160 mL of 0.2 mol/L KMnO_4 was added dropwise under constant stirring. The manganese oxide formed was allowed to settle and the supernatant was replaced with water several times until no more manganese ion was detected in the washing water. The

resultant sample was freeze-dried, ground, and sieved through a 100 mesh sieve before being used.

Birnessite is a layered Mn oxide consisting of stacked sheets of edge-sharing MnO_6 octahedra with water molecules in the interlayer space (Elzinga, 2011; Drits et al., 1998; Nakayama et al., 2008). Furthermore, due to the Mn site vacancies and substitution of Mn(III) for Mn(IV), the manganese oxide layer is always negatively charged (Elzinga, 2011), and thus in order to counterbalance the charge defects in MnO_6 sheets, cations (e.g., Na^+) will also be intercalated in the interlayer region.

1.3. Characterization of adsorbent

The manganese oxide sample solids were characterized by attenuated total reflectance Fourier transform infrared (ATR-FT-IR) spectroscopy, powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and nitrogen porosimetry to determine MnO_x mineralogy. Samples were randomly selected for characterization. To resolve the bands of functional groups and determine their frequency, spectral analysis was done for MnO_x sample solids before and after NH_4^+ adsorption using an FT-IR spectrometer (Thermo-Nicolet IS50) in the range of 500–4000 cm^{-1} . The structures of the samples were examined by XRD at room temperature using a Rigaku Ultima IV diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5606 \text{ \AA}$) operated at 40 kV and 40 mA, with data collected in the range of 5 to 80° at a scan rate of 5°/min and a step size of 0.02°. Phases were identified using JCPDS files. The surface and pore properties of the adsorbent were studied using nitrogen adsorption experiments using an Autosorb-1 (Quantachrome Instruments) at 77 K. The specific surface area of the adsorbent was calculated using the Brunauer-Emmett-Teller (BET) method. SEM images were taken on a Hitachi S-3400 N scanning electron microscope. The voltage used was 5 kV for the SEM studies. Zeta potential was conducted by a Malvern Instruments Zetasizer Nano ZS 90.

1.4. Batch adsorption experiments

Two different types of sorption experiments were performed: kinetics experiments, with reaction times ranging from 0 to 300 min, and isotherm experiments at 283, 293, 303 and 313 K to establish the maximum ammonium ion sorption after 30 min of equilibration, where the concentrations of $\text{NH}_4^+\text{-N}$ ranged from 2 to 50 mg/L. For both types of experiments, portions of the adsorbent samples were accurately weighed into 250-mL glass conical flasks to yield a final solid concentration of 0.5 g/L. The final volumes were adjusted to 100 mL with deionized distilled water after appropriate volumes of ammonium ion stock solution were added to yield the pre-selected $\text{NH}_4^+\text{-N}$ concentrations. The initial concentrations of $\text{NH}_4^+\text{-N}$ in the kinetics experiments were 2–25 mg/L. The suspensions were shaken at 150 r/min on a water bath shaker at 298 K.

To explain the adsorption behavior of manganese oxide, the effect of pH on the NH_4^+ adsorption capacity of manganese oxide was evaluated. The pH values were adjusted using dilute NaOH or HCl . The initial concentrations of $\text{NH}_4^+\text{-N}$ and manganese oxide used in these experiments were 10 mg/L and 0.5 g/L, respectively. To study the effect of cations (Na^+ , 181

Download English Version:

<https://daneshyari.com/en/article/5754228>

Download Persian Version:

<https://daneshyari.com/article/5754228>

[Daneshyari.com](https://daneshyari.com)