



Removal of nitrate by synthetic organosilicas and organoclay: Kinetic and isotherm studies

Moaz K. Seliem^{a,b}, S. Komarneni^{a,*}, T. Byrne^c, F.S. Cannon^c, M.G. Shahien^b, A.A. Khalil^d, I.M. Abd El-Gaid^b

^a Materials Research Institute, Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802, USA

^b Geology Department, Faculty of Science, Beni-Suef University, Egypt

^c Department of Civil and Environmental Engineering, The Pennsylvania State University, University Park, PA 16802, USA

^d Refractories, Ceramics and Building Materials Department, National Research Center, Dokki, Cairo, Egypt

ARTICLE INFO

Article history:

Received 29 August 2012

Received in revised form 5 March 2013

Accepted 10 March 2013

Available online 21 March 2013

Keywords:

Nitrate uptake

Organosilicas

Cloisite[®]10A

Adsorption kinetics

Adsorption isotherms

ABSTRACT

In this work, octadecyltrimethylammonium (ODTMA) chloride was used to prepare MCM-41 at room temperature while cetyltrimethylammonium (CTMA) bromide was used to synthesize MCM-48 and layered organosilica material under hydrothermal conditions. These synthetic organosilica materials, in addition to a commercially available organoclay, Cloisite[®]10A, were characterized by powder X-ray diffraction (XRD) and tested with the occluded surfactant as sorbents for nitrate. The Langmuir and Freundlich models were applied with determination of the equilibrium isotherms and the isotherm constants. Adsorption kinetics data were tested using pseudo-first-order, pseudo-second-order and intraparticle diffusion models. The results showed that the highest nitrate uptake capacities were achieved with Cloisite[®]10A (0.359 ± 0.003 meq/g) followed by a layered organosilica (0.287 ± 0.008 meq/g). MCM-48 and MCM-41 silica adsorbed 0.096 ± 0.002 and 0.157 ± 0.005 meq/g of nitrate, respectively. Kinetics studies showed that the adsorption followed pseudo-second-order kinetic model. Layered organosilica gave a good fit to the Langmuir model among all the studied samples with correlation coefficient (R^2) close to unity (0.99).

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

Several nitrogen-containing compounds such as nitrate, nitrite and ammonia have been frequently present as pollutants in drinking water and various wastewaters [1]. Fertilizers, industrial effluents and animal excretion are the most common sources of these nitrogenous compounds [2]. Nitrate (NO_3^-) has become one of the most common groundwater contaminants over the past few decades, and elevated concentrations in drinking water have created a serious problem throughout the world [3]. Increasing nitrate levels in surface and ground water sources can be related to anthropogenic use of high amounts of fertilizers for agriculture [4]. Elevated levels of nitrate in drinking water can cause gastric cancer, which results from the reduction of nitrate to nitrosamines in the stomach [5]. In addition, methemoglobinemia or blue baby syndrome, a serious health risk, occurs when nitrate is converted to nitrite, which then reacts with the hemoglobin to cause blueness of the skin of newborn infants [6]. Due to several hazards caused by nitrate, US EPA has set 10 ppm nitrate (as N) and 1 ppm nitrite (as

N) as the primary drinking water standards. Therefore, many materials and technologies for the removal of nitrate have been developed and tested, including: sepiolite, sepiolite activated by HCl, slag and powdered activated carbon [7], pulsing potential electrolysis [8], red mud [9], modified wheat residue [1], ammonium-functionalized MCM-48 [10], bio-electrochemical [11], Chitosan hydrogel beads [6], cross-linked Chitosan beads conditioned with sodium bisulfate [12], aquatic macrophytes [13], activated carbon prepared from sugar beet [14], nano-alumina [3], Zn/Al chloride layered double hydroxide [15], and organic surfactants modified clay minerals [16]. In our previous work, a variety of organosilicas such as MCM-41, MCM-48 and composites of MCM-48 with rice husk and organoclay minerals were studied and tested for the uptake of perchlorate [17]. The highest perchlorate uptake values were given by MCM-41 prepared using octadecyltrimethylammonium chloride, MCM-48 synthesized using cetyltrimethylammonium bromide and Cloisite[®]10A organoclay mineral. Therefore, organosilicas and organoclays appear to be promising materials for perchlorate uptake. Thus, the main objectives of this work were to (a) study the removal of nitrate by using the same previous synthetic organosilicas and organoclay materials, (b) to prepare layered organosilica using a high concentration of cetyltrimethylammonium bromide (CTMAB) under hydrothermal conditions, and (c) to study the adsorption mechanism of nitrate

* Corresponding author. Address: 205 Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802, USA. Tel.: +1 814 865 1542; fax: +1 814 865 2326.

E-mail address: komarneni@psu.edu (S. Komarneni).

by fitting the experimental data to different kinetic and adsorption models.

2. Materials and methods

2.1. Materials

The starting chemicals used in the synthesis of MCM-41 are octadecyltrimethylammonium (ODTMA) chloride (Fluka, 98% purity), tetraethylorthosilicate (TEOS) supplied by Johnson Matthey Co., (97% purity), ammonia solution and distilled water. Cetyltrimethylammonium (CTMA) bromide (Aldrich, 99% purity), TEOS, sodium hydroxide and distilled water were used to prepare MCM-48 silica. The organoclay mineral used in this study was Cloisite®10A supplied by Southern Clay Products, which was prepared by using a Na-montmorillonite with a CEC of 92 meq/100 g of clay and benzyltrimethyldecylammonium (BDDA) chloride as organic surfactant.

2.2. Methods

2.2.1. Synthesis of MCM-41 silica

The following procedure was used to synthesize MCM-41 at room temperature: 0.974 g of octadecyltrimethylammonium (ODTMA) chloride was added to 57 ml deionized H₂O in a beaker with stirring until complete dissolution. Then, 8.17 g of aqueous ammonia (NH₄OH) was added followed by 10 min of mixing. To the above solution, 5 ml of tetraethoxysilane (TEOS) was added and then mixed for 4 h. The molar ratio used for MCM-41 synthesis is as follows: 1.0 TEOS:0.13 surfactant:11 NH₃:144 H₂O. The measured pH of the mixture was 11.0. After synthesis, the products were centrifuged, and the solid products were washed with distilled water and ethanol several times to remove any remaining soluble salts. The solids were dried in an oven at 65 °C. The dried sample was gently ground and homogenized in an agate mortar with a pestle before characterization and nitrate adsorption studies.

2.2.2. Synthesis of MCM-48 silica

The following method was used to prepare MCM-48 silica: 1.01 g of CTMAB was first added to 30 ml deionized H₂O in a Teflon vessel with stirring. After completely dissolving the CTMAB, 0.58 g of NaOH was added to Teflon vessel and then the solution was stirred for 10 min. Then, 5.78 g of TEOS was added while mixing. The molar ratio used for MCM-48 synthesis is as follows: 1.0 TEOS:0.10 surfactant:0.52 NaOH:144 H₂O. The measured pH of the mixture was 12.2. After stirring for 20 min, the Teflon vessel was sealed in stainless steel Parr reactors and heated in an oven at 110 °C for 48 h to synthesize MCM-48 silica. After the hydrothermal treatment, the vessel was cooled down to room temperature. The contents from Teflon vessel were centrifuged to separate solids and solutions and the solid products were washed with distilled water and ethanol several times to remove any remaining soluble salts. The solids were dried in an oven at 65 °C. The dried sample was gently ground and homogenized in an agate mortar with a pestle prior to characterization and nitrate adsorption studies.

2.2.3. Synthesis of layered organosilica (MCM-50)

To synthesize layered (lamellar) organosilica, MCM-50 under hydrothermal conditions, the same method and starting materials as for preparation of MCM-48 silica were used, but the amount of surfactant (CTMAB) used was 3.03 g in the case of the layered organosilica sample.

2.2.4. Ion exchange with Cl⁻

A sodium chloride solution of 1 M concentration was prepared using NaCl (J.T. Baker) salt. Fifty milligrams of the MCM-48 or layered organosilica sample were put in centrifuge tubes. Then, 40 ml of the prepared solution was added to the samples and shaken in a shaker for 2 h. After centrifuging, a fresh 40 ml of solution was added to the samples and shaken for 2 h. After centrifuging, a final 40 ml from solution was added to the tubes and shaken for 24 h. The samples were centrifuged, washed with deionized H₂O and dried at room temperature. The dried samples were subjected to nitrate adsorption studies. These two materials were saturated with chloride to have the same anion as in the case of MCM-41 and Cloisite®10A because the surfactant used during the synthesis of the former two materials was CTMAB with bromide anions.

2.2.5. Sample characterization

X-ray powder diffraction patterns were obtained on a Scintag X-ray diffraction unit with Cu K α radiation in the 2 θ range of 1–10 at a scanning speed of 2° min⁻¹.

2.2.6. Nitrate uptake studies

The uptake of nitrate using the as-prepared MCM-41, MCM-48, layered organosilica and the organoclay mineral after saturation with Cl⁻ was carried out as follows: 25 ml of 1 mM sodium nitrate solution (i.e. 61.98 mg/L) was added to 0.05 g of the above as-synthesized materials in centrifuge tubes to conduct a batch equilibration study. The tubes were mixed by hand for one or two minutes before mixing on a shaker for 24 h. After 24 h equilibration, the solid and solution phases were separated by centrifugation. Then, 15 ml of each solution was collected in clean vials for nitrate analysis. All nitrate removal experiments were conducted using triplicates.

2.2.6.1. Kinetics studies. In order to determine kinetics of nitrate by MCM-41, MCM-48, layered organosilica and Cloisite®10A, 0.05 g of each sample was mixed with 25 ml of NO₃⁻ solution at a concentration of 1 mM in centrifuge tubes. The suspensions were mixed for 5 min, 30 min, 2 h, 8 h and 24 h on a shaker. The kinetics experiments were conducted in triplicate. The tubes were centrifuged, and 15 ml of each solution was collected in clean vials for nitrate analysis.

2.2.6.2. Isotherm studies. Nitrate ion exchange isotherms were determined after equilibration of 50 mg of MCM-41, MCM-48, layered organosilica and Cloisite®10A with 25 ml of 0.2, 0.4, 0.6, 0.8 and 1.0 mM nitrate solution by shaking for 24 h. Nitrate exchange isotherms experiments were also conducted in triplicate. The tubes were centrifuged to separate solid and solution phases. Then, 15 ml of each solution was collected in clean vials for nitrate analysis as above.

2.2.6.3. Effect of competitive anions and determination of K_d values. The effect of the competing anions such as Cl⁻, SO₄²⁻ or CO₃²⁻ (or HCO₃⁻) was investigated by equilibrating 0.05 g of each synthetic material with 25 ml of 1 mM of sodium nitrate mixed with 10 mM of NaCl or 5 mM of Na₂SO₄ or 5 mM of Na₂CO₃ in three unique solutions. The suspensions were mixed for 24 h on a shaker. The tubes were then centrifuged, and 15 ml of each solution was collected in clean vials for analysis. The distribution coefficient (K_d) is defined as the ratio of the amount of ion sorbed per gram of solid to the amount of ion remaining per milliliter of solution and is expressed as milliliters per gram [18]. K_d values and removal efficiency (NO₃⁻ removal, %) were calculated as follows:

$$K_d = \frac{C_o - C_e}{C_e} \times \frac{V}{m} \quad (1)$$

Download English Version:

<https://daneshyari.com/en/article/641709>

Download Persian Version:

<https://daneshyari.com/article/641709>

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