Science of the Total Environment 615 (2018) 549–557

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Magnetite nanoparticles supported on organically modified montmorillonite for adsorptive removal of iodide from aqueous solution: Optimization using response surface methodology

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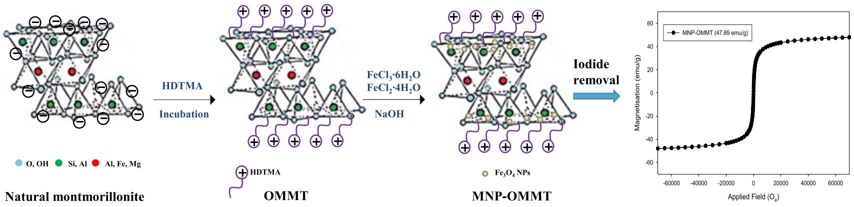
HIGHLIGHTS

- A novel MNP-OMMT was synthesized by a facile coprecipitation method.
- XRD, FT-IR, TGA, and MPMS analyses confirmed successful synthesis of MNP-OMMT.
- The MNP-OMMT was an excellent adsorbent for iodide adsorption.
- RSM was employed to determine the optimal conditions for enhanced iodide removal.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 August 2017
Received in revised form 28 September 2017
Accepted 30 September 2017
Available online 6 October 2017

Editor: D. Barcelo

Keywords:
Radioactive iodide
Montmorillonite
Response surface methodology
Optimization
Adsorption

ABSTRACT

Magnetite nanoparticles supported on organically modified montmorillonite (MNP-OMMTs) were successfully synthesized by a facile coprecipitation method. The surface of natural clay was modified using a cationic surfactant, hexadecyltrimethylammonium. The synthesized MNP-OMMTs were used as an adsorbent to remove iodide from aqueous solutions. The maximum adsorption capacity of the adsorbent was 322.42 mg/g, which is much higher than other previously reported adsorbents for removing iodide in aqueous solution. The experimental data were well fitted to a pseudo-second-order kinetic model, and the adsorption behavior followed the Langmuir isotherm. A thermodynamic study indicated that iodide adsorption was spontaneous and endothermic. The individual and combined effects of key process parameters (pH, temperature, and initial iodide concentration) were studied using a response surface methodology. The maximum iodide removal efficiency of 93.81% was obtained under the optimal conditions of pH 3.9, a temperature of 41.3 °C, and an initial iodide concentration of 113.8 mg/L.

1. Introduction

An increasingly large amount of radioactive liquid waste is generated by the operation of nuclear power plants and decommissioning of nuclear installations. In particular, radioactively contaminated seawater or groundwater caused by the most recent serious nuclear disasters is becoming an international concern. Among the various radionuclides in liquid radioactive waste, ^{129}I and ^{131}I, the radioactive isotopes of iodine generated during fission, are the most important fission products owing to their hazardous properties such as high fission yield, volatility, and solubility (Steinhauser et al., 2014). The half-lives of ^{129}I and ^{131}I are 15.7 million years and 8.04 days, respectively. Although ^{131}I has a relatively short half-life, it is problematic because it emits a large amount of radiation in a short time. Furthermore, 1,760,000 TBq of iodine was leaked in the Chernobyl disaster, and radioactive iodine above the criterion level was detected in several water treatment processes after the Fukushima nuclear accident (Pei et al., 2014).

Adsorption has been the most competitive method for removal of iodide in aqueous solution because of its simplicity, high efficiency, and

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https://doi.org/10.1016/j.scitotenv.2017.09.324
0048-9697/

availability (H. Zhang et al., 2013; Ikari et al., 2015). In recent years, various adsorbents capable of isolating radioactive iodide from aqueous solution, such as zeolite-based materials, minerals, Ag-based materials, and layered double hydroxide, have been investigated (Osmanlioglu, 2006; Kentjono et al., 2010; Yang et al., 2011; Bo et al., 2013; S. Zhang et al., 2013; Mao et al., 2016a, 2017). Further, the development of better and more easily available materials is ongoing.

Montmorillonite, which consists of an Al^{3+} octahedral layer sandwiched between two Si^{4+} tetrahedral layers, with cations balancing the negative layer charge in the interlayer spaces, has great potential as a versatile adsorbent because of its large specific surface area, low cost, environmentally friendly properties, and chemical stability (Marques Fernandes et al., 2016; Sarma et al., 2016). It has a high adsorption capacity for cations and exhibits a low adsorption capacity for anions owing to the strong electrostatic repulsion between its negatively charged surface and anions (Zhang et al., 2015). To address this problem, the surface of natural montmorillonite has been modified by replacing the exchangeable inorganic anions with cationic compounds (Wu et al., 2012; Jang and Lee, 2016). However, practical application of montmorillonites can easily contaminate water owing to their intrinsic property of forming a colloid in water. Moreover, these adsorbent materials can accumulate in the discharge, resulting in secondary pollutants. Therefore, it is very interesting to develop montmorillonites that support magnetic nanoparticles, which make these adsorbents magnetic and more easily separable from the solution (Yuan et al., 2009; Jo et al., 2008).

Response surface methodology (RSM) is a useful tool to study the interactions of two or more parameters. Compared with a conventional change-one-factor-at-a-time method, which is time-consuming and often leads to confusion in understanding the process parameters, this method is useful for evaluating the relationship between a set of parameters and the observed responses using experimental design and statistical techniques. In the last few years, RSM has been applied to optimize and evaluate many environmental processes (Jo et al., 2008; Jain et al., 2011; Absalan and Nikazar, 2016).

In this study, natural montmorillonites were organically modified, and magnetic nanoparticles were added for the removal of iodide in aqueous solution. The synthesized magnetite nanoparticle–organically modified montmorillonites (MNP-OMMTs) were characterized by scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy, a magnetic property measurement system (MPMS), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared (FT-IR) spectroscopy, thermogravimetric analysis (TGA), Brunauer–Emmett–Teller (BET) analysis, and zeta potential analysis. The performance of the MNP-OMMTs in adsorption experiments for iodide separation at various pH values, temperatures, contact times, and initial iodide concentrations was investigated. In addition, Box–Behnken design and RSM were employed to determine the optimal conditions for enhanced iodide removal efficiency.

2. Materials and methods

2.1. Chemical materials

Chemical reagents, montmorillonite, hexadecyltrimethylammonium (HDTMA, in the form of a 25 wt% solution in water), iron (II) chloride ($FeCl_2$, 98%), iron (III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, ≥99%), iodine (≥99.8%, ACS reagent), sodium hydroxide (NaOH, ≥97%, ACS reagent), nitric acid (HNO_3, 70%, ACS reagent) were purchased from Sigma Aldrich (South Korea) and used as received. To investigate the effects of competing anions on the iodide removal efficiency of the MNP-OMMT, simulated solution was prepared using sodium chloride (NaCl, ≥99.5%), calcium carbonate ($CaCO_3$, ≥99%, ACS reagent) and sodium sulfate (Na_2SO_4, ≥99%, ACS reagent) purchased from Sigma Aldrich (South Korea).

2.2. Synthesis of MNP-OMMTs

The natural montmorillonite was pretreated by repeated washing and a digestion procedure using distilled water and 35% hydrogen peroxide to remove impurities and organics from the clay particles (Jang and Yeo, 2015). Purified montmorillonite (3 g) was added to 100 mL of HDTMA (500 mg/L) solution. The precipitated montmorillonite was washed with distilled water several times, isolated by centrifugation, and then dried in an oven at 60 °C for 24 h. Then MNP-OMMTs were synthesized by a coprecipitation method, in which OMMT (0.5 g) was first added to an aqueous mixture of 1 M ferric chloride in 80 mL of distilled water and 2 M ferrous chloride in 20 mL of distilled water to form magnetite under stirring for 30 min at 20 °C. NaOH (2 M, 12.5 mL) was injected into the solution dropwise under sonication, and the color of the mixture changed rapidly from yellow to dark brown. The precipitated product was washed several times with distilled water by centrifugation until the supernatant solution became neutral. The obtained solids were dried in an oven at 60 °C for 24 h.

2.3. Characterization

XRD data were collected using an X'pert APD X-ray diffractometer (Philips, Netherlands) with Cu Kα radiation and a scanning range of 5–80°. An FT-IR spectrometer (PerkinElmer Spectrum, USA) was used to record FT-IR spectra in the range of 4000–400 cm^{-1}. TGA was performed using a thermal analyzer system (Q600, TA Instruments, Japan) by scanning from 0 to 800 °C at a heating rate of 10 °C/min under nitrogen atmosphere to prevent sample oxidation. XPS spectra were obtained using a Quantera SXM (ULVAC-PHI, Japan) to study the surface composition of MNP-OMMTs before and after iodide adsorption. The specific surface area of the synthesized nanocomposites was analyzed by Brunauer–Emmett–Teller (BET) method (Brunauer et al., 1938; Nawaz et al., 2017). The determination of the surface area was based on isotherms of adsorption and desorption of nitrogen at 77 ± 0.5 K using a surface area analyzer (Autosorb-iQ & Quadrasorb SI, USA). For MPMS analysis, an MPMS SQUID vibrating sample magnetometer (VSM) (Quantum Design Inc., USA) was used, and the zeta potential was measured using a Zetasizer Nano ZS (Malvern Instruments). Field-emission scanning electron microscopy (FE-SEM, HITACHI, Japan) was used to analyze the surface morphology and detect the surface elements of the nanoparticles.

2.4. Batch experiments

Batch experiments were performed using the prepared MNP-OMMTs to remove iodide in aqueous solution. The nanocomposites (20 mg) were added to 30 mL of iodide solution in 50 mL conical tubes. The tubes were constantly shaken for 2 h in a shaking incubator at 150 rpm. Samples were taken at predetermined time intervals and filtered through a 0.2 μm syringe filter. The residual iodide concentration in the solution was determined using a UV–Vis spectrophotometer (Cary 5000 UV–Vis-NIR, Agilent Technologies, USA). The effects of the adsorption parameters (initial iodide concentration, solution pH, contact time, and temperature) were investigated. The pH of the solution was adjusted to values between 1 and 11 using 0.1 M HNO_3 and 0.1 M NaOH. Kinetic studies were conducted using iodide solutions with different initial iodide concentrations (10–1100 mg/L) for different time intervals. The iodide sorption kinetics was analyzed using pseudo-first-order and pseudo-second-order kinetic models.

To investigate the co-existing ions effect, NaCl, $CaCO_3$, and Na_2SO_4 salts were added in parallel tests to 30 mL of aqueous solutions with an iodide concentration of 10 mg/L containing 20 mg of the synthesized MNP-OMMT. In all tests, the initial concentration of co-existing anions was 10 mg/L, and the pH of solution was kept at 3 using 0.1 M HNO_3. Then the test tubes were constantly shaken for 2 h in a shaking incubator at 150 rpm and 25 °C.