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Ionic liquid modified diatomite as a new effective adsorbent for uranium ions removal from aqueous solution

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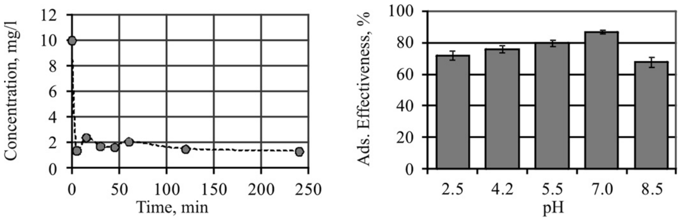
HIGHLIGHTS

- The diatomite modified by the ionic liquids was first synthesized and characterized.
- The kinetic and equilibrium of uranium adsorption onto the ionic liquid modified diatomite have been first investigated.
- The results of the high efficiency of uranium adsorption by the ionic liquid modified diatomite from aqueous solutions over a wide pH range.

GRAPHICAL ABSTRACT



The kinetics and the effect of the pH value on uranium(VI) adsorption by ionic liquid modified diatomite

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ABSTRACT

Modified diatomite was prepared by chemical treatment with 1-ethyl-3-methylimidazolium chloride solution. The properties of the modified diatomite have been studied using scanning electron microscopy, infrared absorption spectroscopy, thermogravimetric technique, zeta potential and carbon content analyzers. The adsorption of uranium(VI) from aqueous solutions onto the ionic liquid modified diatomite was studied using batch adsorption experiments. The parameters influencing the uranium adsorption, such as contact time, pH of solution, and initial uranium(VI) concentration were studied. Most of the uranium is adsorbed in the first 5 min. The maximum adsorption of the modified diatomite toward uranium under experimental conditions was 88 mg/g.

The experimental data for uranium adsorption were analyzed using the first-order kinetic model, the Freundlich, Langmuir, Sips and modified BET isotherm models. The study results showed the multilayer adsorption of uranium ions on modified diatomite.

1. Introduction

Environmental pollution due to uranium has largely been as a result of development of the nuclear industry, combustion of coal and other fossil fuels, as well as production and use of phosphate fertilizers. The world's volume of uranium mining wastes with uranium concentration in the range from several tens of milligrams to a few grams per kilogram accounts for about one billion cubic meters [1]. Nearly 40 million tons of phosphate fertilizers is used worldwide annually [2]. Uranium concentrations in such fertilizers may be from 5 to 150 mg/kg [3] compared to the content in natural soil that does not exceed a few milligrams per kilogram.

The release of uranium and the threat of environmental contamination due to its toxicity and radioactivity [4] promoted the development of various methods and technologies for the treatment of different uranium wastes. Chemical precipitation, lime

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softening, ion exchange, membrane separation and adsorption methods have been used for treating waste water contaminated with uranium but each of them has its intrinsic advantages and limitations [5,6]. Various inorganic and organic adsorbents have been investigated including activated carbon, natural and synthetic zeolites, clay minerals, diatomites, hematite, alumina and silica, ion exchange resins, humic acids, coir pith, chitosan, polymeric materials, and different biosorbents.

Modifications of adsorbents have allowed for significant improvement of functional properties. For instance, chemical modification using different organic compounds is extensively used for inorganic adsorbents. This method is widely covered in the literature and is of considerable use currently for modification of different siliceous adsorbents. From one of our previous studies, diatomite modified with a surfactant displayed a high adsorption capacity of 158.8 mg/g of uranium [7]. As a consequence, modification of diatomite using ionic liquids (ILs) looks promising owing to their chemical similarity to organic surfactants [8].

Ionic liquids have received considerable attention in recent years and their unique properties have been taken advantage of to synthesize polymer nanocomposites [9] and other new adsorbents [10,11]. ILs may be a promising alternative to classical organic solvents that are usually used for modification of different adsorbents. These compounds are being applied to modify silica [12], activated carbon [13], MCM41 and SBA15 mesoporous molecular sieves [14], aluminum oxide [15], titanium dioxide [11], montmorillonite [16,17], smectite [10], kaolinite and quartz [18], halloysite [19], magnetic nanoparticles [20], gallocyanine grafted hydrogel [21] and cellulose [22]. Among the possible mechanisms of ionic liquids immobilization on the active surface, depending on the nature of the adsorbent, the researchers suggested the interactions to be via cation exchange, electrostatic attraction, hydrogen bonds and covalent grafting.

The ionic liquid modified adsorbents may be used for adsorption of organic as well as inorganic compounds. For example, nanocrystalline smectite materials synthesized using different cationic ionic liquids were prepared as suitable matrixes for adsorption of biomolecules [10]. Negatively charged nanometer-sized TiO_2 modified with 1-hexadecyl-3-methylimidazolium bromide and 1-(2-thiazolylazo)-2-naphthol (TAN) was developed as a high capacity extraction adsorbent for nickel ions [11]. Recently, the ionic liquids modified chitin fibers were used for the extraction of uranium from seawater [23].

The objective of this work was to examine the ability of diatomite modified with ionic liquids to remove hexavalent uranium from aqueous solutions. Batch adsorption tests (kinetic and equilibrium) were conducted under static conditions. The influence of pH, contact time, different uranium concentrations on the adsorption behavior of uranium was investigated.

2. Materials and methods

2.1. Modification of diatomite

The raw diatomite used in these experiments was obtained from the Borownica deposit in the Eastern Carpathians area, Poland. Our preliminary investigation of the Borownica diatomite by XRD testifies that this mineral adsorbent mostly consists of diatom frustules as SiO_2 amorphous phases and traces of minerals such as montmorillonite, kaolinite, hematite and mica [7]. According to low temperature nitrogen adsorption data, the specific surface area (S_{BET}) of the raw diatomite was evaluated as 29 m^2/g with domination of cylindrical shaped meso- and macropores in pores structure [24].

The modification of raw diatomite was carried out by chemical treatment with a 2.5% aqueous solution of 1-ethyl-3-methylimidazolium chloride ($C_6H_{11}N_2Cl$) in the proportion 20 mg diatomite to 200 ml ionic liquid solution. The reaction mixture was stirred at room temperature for 24 h. After that, the solid phases were separated from the solution, washed using distilled water and dried at 60 °C for 16 h. Washing of the modified diatomite samples was repeated until no residual chloride ions were detected in the supernatant solutions by titration with $AgNO_3$ solution.

2.2. Characterization methods

The amount of ionic liquid cations loaded in the modified diatomite was calculated from the organic carbon content determined using a Total Organic Carbon Analyzer TOC-5000 combined with SSM-5000A (Shimadzu, Japan). Total carbon (TC) was detected in the samples applying catalytically aided combustion oxidation at 900 °C, while inorganic carbon (IC) was analyzed in the samples after pre-acidification at an oven temperature of 250 °C. Different amounts of dextrose ($C_6H_{12}O_6$) and sodium carbonate (Na_2CO_3)] were used to calibrate the instrument. TOC in the diatomite samples was calculated as a difference between TC and IC.

The specific surface area (S, m^2/g) of the diatomite covered by immobilized ionic liquid was evaluated via the following expression:

$$S = q * N * a \tag{1}$$

where q is the amount of the immobilized ionic liquid (mol/g), a is an area occupied by one cation of ionic liquid (m^2), and N is Avogadro's number (molecule/mol).

The surface morphology and the chemical composition of the raw and modified diatomite were characterized using scanning electron microscopy (SEM LEO 1430VP) equipped with an energy dispersive spectrometer (EDS, detector XFlash 4010 Bruker AXS). The thermal behavior of the diatomite samples was investigated in the temperature range 20–1000 °C using a TGA–DTA Thermal Analysis Instruments SDT 2960 derivatograph. The analysis was conducted with a linear heating rate of 10 °C/min in a nitrogen gas flow.

Fourier transform infrared spectroscopy (FTIR) spectra were obtained by means of Fourier Transform IR spectrophotometer Spectrum 2000 (Perkin Elmer) in order to determine functional groups on the diatomite surface after modification. The FTIR spectra in the wave number range from 400 to 4000 cm^{-1} were obtained by Br pellet technique. For each spectrum 65 scans were recorded at a resolution of 4 cm^{-1}.

Measurement of the size and surface charge of the diatomite was determined using Zestasizer Nano Series (Malvern Instruments Ltd., Great Britain) for diluted colloidal particles in 0.87% KCl buffer solution with pH values range from 2 to 12. Before measurement suspension was placed for 15 min in the ultrasonic bath and stirred with a magnetic stirrer for 5 min.

2.3. Batch adsorption experiments

Solutions of uranium(VI) were prepared by dissolving uranyl nitrate hexahydrate ($UO_2\,(NO_3)_2{\cdot}6H_2O$) in double-distilled water. The experiments were carried out in batch mode at 25 °C by shaking 100 ml uranium solution at different concentration with 0.1 g of modified diatomite. A 0.01 M NaCl solution was used as a background electrolyte to maintain an ionic strength. Kinetic studies were conducted with a 10 mg/l uranium solution at a pH of 4.3. In the equilibrium study, uranium concentrations between 5 and 500 mg/l were employed. The effect of pH on uranium adsorption was investigated in the pH range 2.5–8.5. The initial pH of the working solutions was adjusted to the desired pH value by addition of