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Removal of thorium from water using modified magnetite nanoparticles capped with rosin amidoxime

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HIGHLIGHTS

- New low cost magnetic nanoparticles composite (DPAO-MNPs) prepared with high yield.
- DPAO-MNPs showed fast, effective adsorption for removal of thorium (IV) from water.
- DPAO-MNPs showed high removal efficiency of water pollutants.

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ABSTRACT

The present study describes synthesis and characterization of diacrylamidoxime triaethylenetetralevopimaramide (DPAO) and its use in surface modification of Fe_3O_4 magnetic nanoparticles to obtain DPAO-based magnetic nanoparticles (DPAO-MNPs). The prepared composite was characterized by FTIR, ^{1}HNMR, XRD, DLS, TEM, SEM and EDX. Vibrating sample magnetometer is used to determine the magnetic properties of DPAO-MNPs. Results of analyses indicate that the surface of Fe_3O_4 was successfully capped with DPAO. The adsorption features of the prepared composite towards thorium ions were investigated in a batch system. Kinetic study of Th(IV) adsorption on DPAO-MNPs indicate the adsorption equilibrium achieved within 150 min and is pH dependent. The adsorption results were described mathematically using Langmuir and Freundlich sorption models. The composite showed a maximum Th(IV) loading capacity of 666 mg/g at 25 °C and pH 4. The thermodynamic results indicated that the adsorption process was thermodynamically favorable, spontaneous and endothermic nature. The obtained results suggest that DPAO-MNPs composite may be considered as a potential fast, effective and simple adsorbent for sorption thorium(IV) from water.

1. Introduction

Thorium is a radioactive element occurs naturally and distributed widely over the earth's crust at rocks, soil, plants and water [1]. Thorium is attractive element in various fields like geology and medicine [2]. It is distributed in low concentration in the aqueous waste stream from mining nuclear materials. Thorium has been deemed as a conceivable nuclear fuel that can be used as a substitutional nuclear fuel in nuclear power plants by converting into ^{233}U [3]. It has a toxic nature, even at trace levels, causing public health and environmental problems as liver, lung and pancreatic cancer referred to the effluents containing Th(IV) [4]. Moreover, it is essential to accurate determination of Th(IV) to control its pollution. Therefore, the separation of Th(IV) from aqueous solutions is very important not only for environment protection but also for thorium resources reutilization [5]. Techniques used for both the removal and retrieval of radioactive ions include flotation, precipitation, coagulation, co-precipitation, extraction, membrane dialysis, ion exchange, reverse osmosis, electrolytic processes and chromatographic extraction [6–10]. Several techniques such as biosorption [11], ion-exchange [12], adsorption [13,14] and liquid–liquid extraction [15] have been also employed for the separation and preconcentration of Th(IV) from aqueous solutions. These techniques suffer from production of hazards materials that produce technical, economic and health problems. Adsorption

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represents the most widely applied efficient and versatile technique. It retains metal ions with a high selectivity and uses environmentally friendly processes for removal of hazard ions from aqueous solutions [16]. Th(IV) ions separation is applying adsorption technique which is favored waste treatment technique [17]. Sorption method provides a very competitive alternative to both precipitation and solvent extraction because of its simplicity, flexibility, ease of operation, cost effectiveness and low consumption of reagents [18]. Therefore, there is a great quest for studying new sorbents and many innovative adsorbents for thorium removal from aqueous solutions [19–25].

In the last decade, comprehensive investigations and developments were reported in the field of superparamagnetic iron oxide nanoparticles. Several types of iron oxide have been executed in the field of nano-sized magnetic particles (generally magnetite, (Fe_3O_4) or, maghemite, (γ-Fe_2O_3)) [26]. These materials often have distinct structural, chemical, electrical and magnetic properties enabling their use in novel applications e.g. biosensors, drug delivery, chemical and biochemical separation, environmental remediation and information storage [27,28]. Magnetic nanoparticles (MNPs) represent an important category of nanoparticles that can be manipulated applying a magnetic field. The application of magnetic materials for separation of pollutants from effluents received great attention in recent years [29,30]. MNPs possess high magnetic properties, large surface area and high contents of surface active sites produced adsorbents have high removal rate and adsorption efficiency as well as easy and fast separation of adsorbent from aqueous solution using external magnetic field. The superparamagnetic nanomaterials can be easily separated and reused due to their ability to loss the magnetic properties after removal the external magnetic field [31]. Accordingly, the main objective of the present work is to study the feasibility of thorium adsorption onto new modified MNPs adsorbent. Rosin as bioactive material is modified to prepare diacrylamidoxime triaethylenetetralevopimaramide that used to coat Fe_3O_4 nanoparticles. The application of the MNPs to remove thorium(IV) from aqueous solution is investigated and optimized to determine the adsorption kinetics and isotherms of Th(IV) on DPAO-MNPs.

2. Experimental section

2.1. Materials

Abietic acid (acid number 165 mg KOH g^{-1}) is separated from commercial rosin by recrystallization rosin from cooled concentrated acetone solution. Abietic acid was isomerized to levopimaric acid by heating to 180 °C for 1 h followed by increasing the reaction temperature to 220 °C for 1 h under the nitrogen atmosphere. Oxalyl chloride ($C_2Cl_2O_2$), triethylenetetramine (TETA), triethylamie (TEA), N,N-dimethyl formamide (DMF), acrylonitrile (AN), anhydrous ferric chloride and potassium iodide were purchased from Aldrich chemical Co.

Hydroxyl amine hydrochloride (40.1 g) was neutralized with alcoholic solution of sodium hydroxide (1 M) in the presence of 290 ml of (methanol:water 5:1) solution followed by filtration NaCl precipitate. The organic solvents were analytical-grade. $Th(NO_3)_4.5H_2O$ dissolved in deionized water was used to prepare thorium (1000 mg/L) stock solution.

2.2. Preparation of the adsorbent

2.2.1. Synthesis of diacrylamidoxime triaethylenetetralevopimaramide (DPAO)

Levopimaric acid (0.025 mol) was dissolved in 50 mL toluene and mixed with oxalyl chloride (0.03 mol) at 50 °C for 4 h. The gas generated in the reaction was absorbed by base solution. The unreacted oxalyl chloride was removed by vacuum distillation to obtain levopimaroyl chloride (PAC) solution. The PAC (0.025 ml) solution and TETA (0.0125 mol) were mixed and TEA (0.025 mol) was added dropwise at 10 °C until white precipitate is obtained the reaction stirred at room temperature for 24 h. The solution was filtered to remove triethylamine hydrochloride salt and toluene removed by vacuum distillation. Tetraethylenetriamino dilevopimaroylamide (TPA) was separated as light yellow powder. TPA (0.025 mol) was mixed with AN (0.025 mol) and DMF (10 mL) under N_2 atmosphere. Then, the reaction mixture was slowly heated over a period of 1.5 h up to 165 °C. The reaction was continued for 10 h at 185 °C. At the end of the process, the DMF solvent was removed by N_2 entrainment. Finally, tetraethylenetriamino dilevopimaroylamide acylonitrile (DPAN) adduct was separated by filtration of the precipitate from DMF solution into methanol.

The DPAN (0.0125 mol) was reacted with the prepared hydroxyl amine solution (40 mL at 70 °C for 2 h. The prepared diacrylamidoxime triaethylenetetralevopimaramide (DPAO) was isolated after filtrating and washing several time by water. The precipitate was treated with 0.1 M HCl solution for at least 5 min. Finally, DPAO was filtered and washed several times with water sand dried at 45 °C to constant weight.

2.2.2. Preparation of modified magnetite nanoparticles

A solution of anhydrous $FeCl_3$ (0.24 mol) in distilled water (300 mL) was prepared and mixed with potassium iodide solution (0.08 mol, dissolved in distilled water 50 mL) at room temperature under stirring to reach equilibrium for 1 h under N_2 atmosphere. DPAO (5 g) solution in ethanol (100 mL) added dropwise at the same time with 200 mL of NH_4OH (28%) under vigorous stirring at 40 °C. The temperature of the reaction mixture increases up to 50 °C for 30 min. The Fe_3O_4/DPAO nanoparticles separated from the reaction mixture by ultracentrifugation at 12,000 rpm, washed with ethanol three times and air dried at 25 °C.

2.3. Adsorbent characterization studies

The chemical structure of the nanoparticles was confirmed by Fourier Transform infrared (FTIR SPECTRUM 1000; Perkin-Bhaskar-Elmer Co., Boston, MA, USA).

^{1}HNMR (400 MHz Bruker Avance DRX-400 spectrometer; Bruker Analytische Messtechnik, Karlsruhe, Germany) used to elucidate the chemical structure of the prepared rosin derivatives using $CDCl_3$ as solvent.

High-resolution transmission electron microscopy (HR-TEM; JEM-2100 F, JEOL, Tokyo, Japan) used to investigate the morphology of magnetite nanoparticles at an acceleration voltage of 150 kV.

X-ray powder diffraction (XRD; MiniFlex X-ray diffractometer/PW 3710, Rigaku, Japan) equipped with Cu–Ka ($\lambda = 0.154$ nm) radiation used to investigate the crystal structure of nanoparticles.

Dynamic light scattering (DLS; Zetasizer Nano ZS (Malvern Instruments, Malvern, U.K.) measurements used to determine the particle size distribution and polydispersity index (PDI) of nanoparticles. The measurements were carried out with a 633 nm He–Ne laser using ethanol/water/(4/1) as solvent.

Zeta potential of the nanoparticles was measured by a Zetasizer 3000HS PCS (Malvern Instruments) using ethanol/water/(4/1) as solvent.

The magnetic characteristics of magnetite nanoparticles were evaluated using vibrating sample magnetometer (VSM; USALDJ9600-1).

A Scanning Electron Microscope (SEM) with Energy-Dispersive X-ray Spectrometer (EDX), (JEOL 6510 LA SEM, JEOL, Japan) was