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Enrichment of lanthanides in aqueous system by cellulose based silica nanocomposite



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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- Cellulose based silica nanocomposites were synthesized.
 CLx/SiO₂ was used to investigate the
- CLX/SIO₂ was used to investigate the adsorption behavior of lanthanides.
 The surface modification highly effect
- the surface area of CLx/SiO_{2.}
- CLCA/SiO₂ exhibits compact particle packing and low surface area.
- CLN/SiO₂ seems to be a relatively effective adsorbent for lanthanides.



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ABSTRACT

Synthesis of cellulose based silica (CLx/SiO₂) nanocomposite was successfully carried out and employed for the removal of Eu(III), La(III) and Sc(III). Nanocomposite was characterized by TEM, AFM, SEM, XRD, FTIR and BET. TEM analysis indicated that the particle diameter of nanocomposite was in the range of 9-15 nm and silica particles was uniformly distributed throughout the nanocomposites. The presence of mixed phases of cellulose and SiO₂ was observed by FTIR and XRD. Experimental results showed that CLx/SiO₂ nanocomposite produced by sulfuric acid modification possess higher surface area than that of citric acid modified. Various parameters including contact time, pH, nanocomposite dosage, initial concentration, and temperature were optimized to achieve maximum adsorption capacity. The kinetics results revealed that the surface chemical sorption for Eu(III) and La(III) and physisorption for Sc(III). Also, the film diffusion was the rate-determining step of the adsorption process. Importantly, the isotherms fitted better to Langmuir for Eu(III) and La(III) than Freundlich. The positive values of ΔH^0 indicates that the adsorption process was endothermic and negative value of ΔG^0 indicates the feasibility of Eu(III), La(III) and Sc(III) removal by adsorption on CLN/SiO₂ nanocomposite and suggests the spontaneous nature of adsorption on nanocomposite. Desorption of adsorbate loaded on nanocomposite during adsorption process was easily carried out up to three cycles. The results indicate that the nanocomposite is an efficient adsorbent with good adsorption capacity for Eu(III), La(III) and Sc(III).

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1. Introduction

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http://dx.doi.org/10.1016/j.cej.2017.03.051 1385-8947/© 2017 Elsevier B.V. All rights reserved. In modern societies, the application of lanthanides is increasing due to the unique physical and chemical properties of rare earth



elements (REEs) [1]. REEs are employed extensively in chemical engineering, metallurgy, electronics, medicine, lasers, storage batteries etc. [1-4]. Numerous techniques have been used for the determination of REEs including atomic adsorption spectroscopy (AAS) [5], UV-vis spectroscopy [6,7], inductively coupled plasmamass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectroscopy (ICP-OES) [5,8]. Similarly, several techniques have been applied for the uptake of REEs from aqueous systems such as solvent extraction, ion exchange, solid-phase extraction, ion-selective electrodes [2–4] and adsorption [9–14]. But these methods are not preferred because of several disadvantages such as high consumption of reagent and energy, low selectivity, high operational cost and generation of secondary metabolites; in addition, these methods are also time consuming and labor-intensive [12]. However, adsorption method is the best technique because of cost, simplicity of design and operation [15]. Therefore, many researchers have started developing a cost effective and eco-friendly method to recover rare earth metals from aqueous environment [12]. The general class of nanocomposite inorganic/organic materials is a fast-growing area of research [16–18]. Hybrid organic–inorganic materials may be produced by nanoparticle deposition on the fiber surface [19]. Significant effort is focused on the ability to obtain control of the nanoscale structures via innovative synthetic approaches. The properties of nanocomposite materials depend not only on the properties of their individual components but also on their morphological and interfacial characteristics. This rapidly expanding field is generating many exciting new materials with novel properties [19].

The nanocomposite combine the most abundant natural polymer cellulose [14,16,20] with the inorganic nanoparticles of silica [21]. Cellulose being one of the world's most abundant natural polymer; the unique morphological properties of natural fibers given by the hierarchical self-assembly of the polymer chains have not seen in many synthetic fibers [14]. On the other hand, silica particles have wide application in industries related to the production of pigments, pharmaceuticals, ceramics and catalysts [21]. Furthermore, silica based adsorbent materials have industrial application for the removal of heavy metals and lanthanides [13,22,23]. Also, to improve the adsorptive properties a variety of functional groups grafted on the surface of mesoporous silica were also reported by several researchers [13,22–24].

In the present study, we synthesized two different acid modified cellulose based silica nanocomposite which were further characterized by using TEM, AFM, SEM, XRD, FTIR and BET. The nanocomposites were applied for the uptake of lanthanides from aqueous medium. The effects of important factors viz. contact time, pH, nanocomposite dosage, initial concentration and temperature on Eu(III), La(III) and Sc(III) adsorption onto cellulose based silica nanocomposites were studied. The aim of this work was to study the adsorption kinetics, equilibrium and thermodynamics employing different models along with the recovery of Eu(III), La(III) and Sc(III).

2. Materials and methods

2.1. Chemicals

Cotton linters cellulose (CL), tetraethyl orthosilicate (TEOS), ammonium hydroxide (NH₄OH), citric acid monohydrate (C₆H₈O₇. H₂O), sulfuric acid (H₂SO₄) and analytical grade acetone were purchased from Sigma Aldrich and used as received. Chlorides of europium(III), lanthanum(III) and scandium(III) (Sigma Aldrich) were used for the preparation of stock solutions (1000 mg/L). The working solutions containing different concentrations of Eu(III), La(III) and Sc(III) were prepared by stepwise dilution of the stock solution.

2.2. Preparation of CLx

Acid hydrolysis was done by using 15% H_2SO_4 and citric acid with a solid liquid ratio of 1:20. Briefly, 5 g of CL was added separately to 15% H_2SO_4 and citric acid under constant stirring (200 rpm) at 45 °C for 4 h. The suspension was diluted with cold water and cooled down to room temperature. The cellulose particles were separated by centrifugation (EPPENDORF 5810) at 4000 rpm for 10 min and dialyzed with water down to neutral pH; dried in oven (TERMAKS) at 60 °C for 12 h and ground to get fine powder by Tube mill (IKA Tube mill control). In text and figures, CLx was replaced by CLN or CLCA indicating H_2SO_4 and citric acid modified cellulose, respectively.

2.3. Synthesis of CLx/SiO₂ nanocomposites

1 g of CLx was added in 50 ml of deionized water and sonicated (BRANSON 2510) for 30 min. 2 ml of NH₄OH and 5 ml of TEOS was added in CLx suspension and stirred at 40 °C for 16 h. The suspensions were precipitated by adding 250 ml of acetone, filtered, washed with water several times, dried in oven at 60 °C for 12 h and ground to get fine powder.

2.4. Characterization

Particle size of nanocomposite was determined by using transmission electron microscopy (TEM, Model: Hitachi H-7600). For TEM analysis, synthesized nanocomposite was dispersed in ethanol and sonicated for 15 min and a drop of suspension was placed on carbon coated Cu grid. To study the surface morphology Park Systems NX10 was used for Atomic force microscopy (AFM) analysis with commercial NCHR tip. The scanner was calibrated in the XY directions using a 5 μ m grafting and in the Z direction using several conventional height standards. The measurement was performed in air at ambient pressure and humidity and the image was stored as 256×256 point arrays. Morphological characteristics of the nanocomposites were evaluated by SEM in a Hitachi S-4800 microscope operating at 10 kV. XRD patterns of nanocomposites were recorded on a PANalytical X-ray diffractometer using Co Ka radiation (λ = 1.790307 Å) in the 2 Θ range of 15–120⁰ operated at 40 kV and 40 mA. Fourier transform infrared spectroscopy of the CLN/SiO₂ and CLCA/SiO₂ was done by ATR-FTIR, Bruker Vertex 70 model, in a spectral range of 400–4000 cm⁻¹. The surface area and pore size of the synthesized CLN/SiO₂ and CLCA/SiO₂ nanocomposites were calculated using BET and BJH model at 77 K on Tristar[®] II Plus system. pH_{zpc} of CLN/SiO₂ and CLCA/SiO₂ was calculated by method reported earlier [11]. 0.2 g of CLN/SiO₂ and CLCA/SiO₂ was added in a solution of 0.01 M NaCl and pH was adjusted from 2 to 12 by addition of NaOH and HCl. After 48 h the final pH of solutions was measured and the point of intersection of pH_{final} vs pH_{initial} was noted as pH_{zpc} of nanocomposites.

2.5. Adsorption studies

The adsorption studies were conducted by mixing 30 mg adsorbent with 10 mL of Eu(III), La(III) and Sc(III) solution at desired concentration (25 mg/L). The mixtures were shaken in an orbital shaker (IKA KS 4000 ic control) with a constant speed of 200 rpm and temperature of 298 K for a given time, and then the adsorbents were separated by using 0.45 μ m PTFE membrane filter. After that, the concentration of Eu(III), La(III) or Sc(III) in the residual solution was measured by ICP-OES (Thermo iCAP 6300 series). The adsorp-

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