Adsorption of rare earth metals from water using a kenaf cellulose-based poly(hydroxamic acid) ligand

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ABSTRACT

A kenaf cellulose-based poly(hydroxamic acid) ligand was synthesized from poly(methylacrylate) grafted cellulose and applied towards the adsorption of rare earth metals from aqueous media. The starting materials and final product were examined by FT-IR, FE-SEM, and ICP-MS. Remarkable maximum adsorption results were obtained for the earth metals La^{3+}, Ce^{3+}, Pr^{3+}, Gd^{3+}, Nd^{3+}, Eu^{3+}, and Sm^{3+}, with values of 260, 245, 235, 220, 210, 195, and 192 mg g^{-1}, respectively. The adsorption capacities of the ligand for adsorption of rare earth metals were well fitted with the pseudo-second-order rate equation. Further, the adsorption properties of the rare earth ions were nicely matched with the Langmuir isotherm model, ($R^2 > 0.99$), thus suggesting that the adsorbent surface of the ligand is monolayer and homogenous in nature. The reusability of the created ligand was evaluated by carrying out sequential sorption/desorption experiments, indicating that the developed adsorbent can be reused for at least 10 cycles without incurring any significant losses to its primary removal capabilities.

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1. Introduction

Lanthanide elements, commonly referred to as rare earth elements (REEs), comprise a group of metallic chemical elements consisted of a similar chemical and physical nature [1]. REEs are utilized in diverse industrial processes, such as in the production of superconductors, glass-pigments, additives, catalysts, medicines, and cosmetics [2]. Owing to their metallurgical, chemical, magnetic, electrical, catalytic, and optical properties, REEs are also extensively incorporated in the manufacturing of super-magnets, information storage systems, lighter flints, fluorescent lamps, batteries, lasers, and high technology electronics [3,4]. However, unlike other heavy and precious metals, with the exception of few locations in China, REEs are not easily found in ore deposits in concentrations that allow for easy extraction [5]. Owing to their increasing demand, the separation and recovery of worthwhile REEs metals from diluted aqueous streams is being undertaken alongside primary mining industry applications [6,7].

Various methods, such as solvent extraction [8], co-precipitation [9], and ion-exchange [10], have been utilized for pre-concentration and recovery of REEs; however, existing methods today are burdened by various limitations, such as secondary pollution and high operational costs [11]. Among different extraction methods, the adsorption of REEs on solid surfaces by coordination can be said to be one of the most acceptable methods available today, as the adsorption system is mostly non-toxic, and consists of a simple operation and the straightforward development of adsorbents [7,11]. Extensive studies regarding development and employment of such adsorbents have been reported for cellulose [11], chitosan [7], activated carbon [12], β-cyclodextrin [13], aminocarboxylic sorbents [14], β-cyclodextrin (β-CD) [15], silica [16], and titanium dioxide [17]. Of note, an EDTA-modified chitosan-based adsorbent was prepared and used for recovery of rare earth ions from water [7]. In other work, Michel et al. reported on the development of an EDTA-linked β-CD dimer showing good chemical sensing and strong complexes with Lanthanide ions [18].

Yong et al. [19] reported on the development of hydrogel adsorbents consisted of a monolithic open-cellular framework for enrichment of rare-earth metals. The obtained results showed rapid adsorption kinetics with equilibrium obtained at 30 min, with higher adsorption capacities of 384.62 and 333.33 mg g^{-1} for La and Ce, respectively. Sun et al. [20] described the synthesis of an adsorbent containing carbon nano-shells obtained from polydopamine, which has since been applied for adsorption of REEs in various high-tech industries [20]. To meet industry demands, various industrial processes being developed for pre-concentration and separation of REEs today include the use of techniques such as solvent extraction [21,22], ion exchange [23], adsorption [24], liquid membranes [25], and MIPs [26,27]. A practical adsorbent must be characterized by high selectivity for low concentration rare earth ions, absorbability at lower pH levels, rapid adsorption/desorption rates, high adsorption capacity, reusability, and a low cost of production. Among various methods

developed for such applications, Ogata et al. [28–30] prepared a diglycolamic acid where silica gel was used as a support due to its lower cost and higher chemical stability, presenting an adsorbent that could be particular useful for adsorption of rare earth ions. Kumar et al. [31] synthesized a polyhydroxamic acid from acryl amide that was subsequently employed for the simultaneous preconcentration of a whole series of rare earth metal ions from seawater.

A prospective method for preparation of absorbents involves the induction of particular monomers into polymers, which can then be grafted to the glucose units of the cellulose backbone by virtue of direct attachment, followed by further modifications to the grafted products into desired chelating ligands. Thus, the cellulose backbone is presented as a main-chain polymer, which could be grafted by the monomeric polymer via covalent bonding, using both the ionic and free-radical initiating methods [32,33]. In past research, the ceric ion (Ce^{4+}) was noted to display an intense effect for high yield grafting reactions through radical creation at specific sites on the glucose units of the cellulose backbone [33]. Indeed, cellulose has been shown to provide sound chemical and mechanical durability properties, which can be further enhanced through the grafting of copolymers and subsequent conversions of polymer ligands for coordination with metal ions [34].

The currently presented work utilized pure cellulose obtained from kenaf fibre. Pure cellulose was grafted with methyl acrylate through the chemical initiation method under optimum reaction parameters to obtain poly(methyl acrylate) (PMA) grafted kenaf cellulose [35]. Next, a desired poly(hydroxamic acid) ligand was prepared from the PMA, and subsequently employed towards the adsorption of rare earth metals from water.

2. Experimental

2.1. Materials

Kenaf cellulose was extracted according to our previously reported method [35]. Sulphuric acid (Lab Scan), methanol (Merck), lanthanum (III) chloride (Sigma-Aldrich), gadolinium (III) chloride (Sigma-Aldrich), neodymium (III) chloride (Sigma-Aldrich), praseodymium (III) chloride (Sigma-Aldrich), and cerium ammonium nitrate (CAN) (Sigma-Aldrich) were all used as received. A methyl acrylate monomer obtained from Aldrich was purified via vacuum distillation, then subsequently stored at −20 °C to prevent its polymerization.

2.2. Preparation of the poly(methyl acrylate) PMA-grafted copolymer

Our previously reported method was utilized to carry out the graft copolymerization reaction [35]. First, kenaf cellulose (3.0 g) and 500 mL distilled water were poured into a round-bottom flask. The reaction was carried out in a thermostat water bath under optimized reaction parameters for the creation of PMA-grafted cellulose; reaction temperature was 55 °C, while diluted sulfuric acid (50%), CAN, and methyl acrylate were added in quantities of 1.8 mL, 1.5 mL (in 10 mL deionized water), and 15 mL, respectively. The reaction was carried out under continuous stirring conditions for 2 h under an N_2 gas stream for removal of oxygen. The obtained product was brought to room temperature by running the flask under tap water, then poured into excess methanol (1 L) to precipitate out the copolymer product. The grafting copolymer was then removed and washed 3 times with methanol (80%), and subsequently dried at 60 °C [36].

2.3. Synthesis of the poly(hydroxamic acid) ligand

Hydroxylamine hydrochloride (10.0 g) was poured in 250 mL methanol (80%), with stirring continued until the $NH_2OH \cdot HCl$ was completely dissolved into the solvent. The mixture was cooled to 20 °C, and approximately 50% of NaOH was added to the solution until a pH level of 11 was reached, upon which NaCl was precipitated out as a white solid [36–38]. The white solid was removed using filtration, while the obtained clear

basic solution of hydroxylamine (NH_2OH) was transferred into a reaction flask set up on a thermostat water bath. Following, the PMA-grafted kenaf cellulose (4.5 g) was transferred into the hydroxylamine solution, and refluxed at 72 °C for 4 h. The obtained product of the polymer ligand, a solid polymer, was then removed from the mixture and washed at least 3 times with methanol (80%). Subsequently, the polymer ligand was reacted with 45 mL of HCl (0.12 M) in methanol (80%) to produce an H-form adsorbent. The product was again washed with methanol (80%) until free of excess HCl, and oven dried at 60 °C.

2.4. Optical sensing of cerium ions

Optical sensing of cerium ions was undertaken by first placing the adsorbent (150 mg) into 10 mL deionized water and a 10 mL acetate buffer with pH 6. Next, exactly 10 mL of Ce^{3+} ions in concentrations of 5 and 10 mg L^{-1} were added to the solution for a total volume of 20 mL; the solution was then shaken for 2 h until distinct colour separation was obtained. A blank solution was also used for comparison of colour development and identification of metal ions [39,40]. Once equilibration was reached at 2 h, the solid adsorbent was removed from the solution, then dried at 60 °C. For optical colour estimation, solid sample absorbances were determined by solid state UV–vis NIR spectrometry (UV-2600 Shimadzu).

2.5. Batch adsorption

Batch adsorption experiments were carried out for a series of rare earth metals (La^{3+}, Pr^{3+}, Gd^{3+}, Nd^{3+}, Eu^{3+} and Sm^{3+}). For each REE, 0.150 g adsorbent was added into a single metal ion (10 mL of 0.1 M) solution, with pH set in the range 3–6 by addition of an acetate buffer solution. All mixtures were shaken for 3 h at an agitation speed fixed at 200 vpm until equilibration was attained. Once equilibration was achieved, the adsorbent was removed from the metal ion solution. Next, the concentration of metal ions remaining in the solution was estimated by ICP-OES (Perkin Elmer, Optima 8300). Final (after adsorption) and initial readings were calculated with the use of Eq. (1).

$$q_e = \frac{(C_o - C_e)V}{L} \quad (1)$$

where C_o and Ce are the initial and equilibrium concentrations of metal (mg L^{-1}), respectively. Here, q_e is the equilibrium adsorption (mg g^{-1}), V represents the rare earth solution volume in liters, and L is the adsorbent mass in grams.

In order to assess the removal properties of the absorbent for trace level concentrations of rare earth metals, 5 mL of a metal ion solution
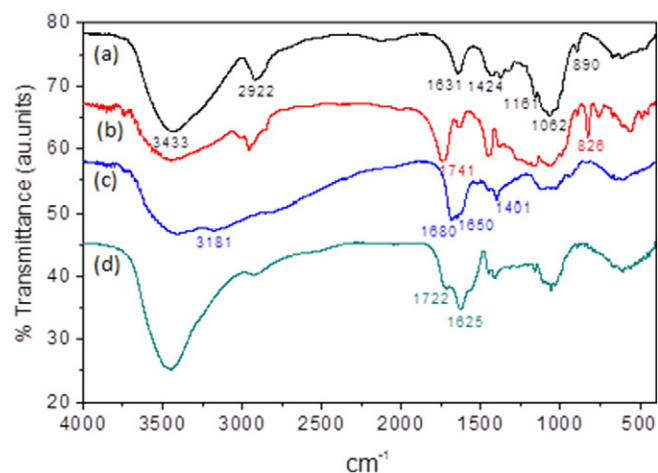

Fig. 1. FT-IR spectra of (a) kenaf cellulose; (b) poly(methyl acrylate) grafted kenaf cellulose; (c) poly(hydroxamic acid) ligand; and (d) poly(hydroxamic acid)-La metal complex.