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Research article

Optimizing the lanthanum adsorption process onto chemically modified biomaterials using factorial and response surface design

Andreea Gabor, Corneliu Mircea Davidescu, Adina Negrea, Mihaela Ciopec**, Ion Grozav, Petru Negrea, Narcis Duteanu*

Politehnica University of Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, 2 Piata Victoriei, RO 300006 Timisoara, Romania

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ABSTRACT

The rare metals' potential to pollute air, water, soil, and especially groundwater has received lot of attention recently. One of the most common rare earth group elements, lanthanum, is used in many industrial branches, and due to its toxicity, it needs to be eliminated from all residual aqueous solutions. The goal of this study was to evaluate the control of the adsorption process for lanthanum removal from aqueous solutions, using cellulose, a known biomaterial with high adsorbent properties, cheap, and environment friendly. The cellulose was chemically modified by functionalization with sodium β-glycerophosphate. The experimental results obtained after factorial design indicate optimum adsorption parameters as pH 6, contact time 60 min, and temperature 298 K, when the equilibrium concentration of lanthanum was 250 mg L^{-1}, and the experimental adsorption capacity obtained was 31.58 mg g^{-1}. Further refinement of the optimization of the adsorption process by response surface design indicates that at pH 6 and the initial concentration of 256 mg L^{-1}, the adsorption capacity has maximum values between 30.87 and 36.73 mg g^{-1}.

1. Introduction

Lanthanum is an important member of the rare earth elements (REEs), which appears in different aqueous radioactive waste streams and its effects have attracted much attention (Abdel Moamen et al., 2015; Hu et al., 2002). Pure metallic lanthanum has no commercial uses, but its alloys are used (Sui et al., 2014; Unal Yesiller et al., 2013) for superconductors, ceramics (Hirano and Suzuki, 1996) micro-fertilizer (Hu et al., 2002; Liang et al., 2005), metallurgical industry, medical application, in "flints" for cigarette lighters, studio lighting and cinema projection, or in optical glasses, while lanthanum salts are used in catalysts for petroleum refining.

Lanthanum is disposed or stored in the environment in different locations. During long-term exposure, lanthanum is very dangerous, especially in the working environment, due to the gasses that can be inhaled with air. Lanthanum can also cause cancer (Hirano and Suzuki, 1996).

In soil and ground water, lanthanum will be gradually bioaccumulated and this will eventually lead, in time, to a concentration increase in human and animal bodies (Barry and Meehan, 2000). Lanthanum causes damage to cell membranes, which has several negative influences on reproduction and on the functions of the nervous system. It also strongly accumulates in muscles (Hirano and Suzuki, 1996).

In the past, many techniques were proposed to remove lanthanum ions from wastewater with significant risks to human health and the environment, in general (Abdel Moamen et al., 2015). The most used techniques for lanthanum removal are precipitation, ion exchange and evaporation (Abdel Moamen et al., 2015; He and Loh, 2000; Hu et al., 2002). These methods differ in their efficiency and cost (Hokkanen et al., 2016).

Another method for lanthanum removal is adsorption, an advanced method for treatment of wastewater with REEs, because it presents several advantages such as: high efficiency, high adsorption capacity, the possibility of regeneration and utilization in multiple adsorptions-desorption cycles, and selectivity (Dobre et al., 2014; Gabor et al., 2016; Ion et al., 2015a).

There are many types of materials, natural or synthetic, all featuring economic or efficiency related advantages or disadvantages. Some of these materials, which show adsorption properties

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* Coresponding author.
** Corresponding author.
E-mail addresses: mihaela.ciopec@upt.ro (M. Ciopec), narcis.duteanu@upt.ro (N. Duteanu).

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are used for lanthanum removal from aqueous solutions, are graphite activated carbon, synthetic or natural inorganic and organic polymers, composite materials, ions exchangers, etc (Ciopec et al., 2012).

Cellulose is the most abundant biopolymer in nature and it has a low environmental impact. Among all the natural polymers, cellulose has good economic potential because of its abundance and its low cost. It can also be used as an adsorbent material, being an attractive alternative to synthetic adsorbents (Cortina and Warshawsky, 1997; Gabor et al., 2016; Ion et al., 2015a). Cellulose has adsorbent properties, but after surface treatment with chemical modifiers it is reported to be more effective in the removal and recovery of metals ions (Barud et al., 2008; Chen et al., 2011; Cheng et al., 2011; Dobre et al., 2014; Filho et al., 2000; Yang et al., 2014). The most used surface modifier are glycidyl methacrylate (GMA) (Hokkanen et al., 2016; Navarro et al., 1996; O'Connell et al., 2006a; O'Connell et al., 2006b, c), acrylonitrile (AN), hydroxylamine (Amidoxime) (Hokkanen et al., 2016; Kubota and Shigehisa, 1995; Kubota and Suzuki, 1995), glycidylmethacrylate (GMA)- grafted-titanium dioxide (Anirudhan et al., 2013; Hokkanen et al., 2016), *N*,*N*-methylenebis (acrylamide) (Hokkanen et al., 2016; Zheng et al., 2010), carboxyl anionic groups (Hokkanen et al., 2016; Liu et al., 2001) and acrylic acid with acrylamide (Bao-Xiu et al., 2006; Hokkanen et al., 2016).

The main goal of our study was to control the adsorption process for the lanthanum removal from aqueous solution, using the factorial design and response surface methodology (Can and Yildiz, 2006; Ion et al., 2015b; Zhao et al., 2009), known for its advantages: improved process, reduced development time and overall costs (Ciopec et al., 2012; Montgomery, 2013). The novelty of our approach is the method by which the material was obtained, and the fact that the precursor used for obtaining the adsorbent is “green”, cheap and environmental friendly.

The results of this study show the effect of modifying the cellulose surface with phosphate groups (sodium β-glycerophosphate) for lanthanum removal from aqueous solution, and the influence of initial pH, contact time, temperature, and initial concentrations of lanthanum on the materials adsorption capacity.

2. Materials and methods

2.1. Chemical products and instruments

Cellulose microcrystalline, Avicel PH-101, supplied by Sigma-Aldrich, Germany, with ~50 μm particle size was used as solid support. Sodium β-glycerophosphate, Na-β-Gly-P, 99% purity, supplied by Merck, Darmstadt, Germany, was used as modifying agent. To dissolve the Na-β-Gly-P, absolute ethanol, 99.2% purity supplied by SC PAM Corporation SRL, Romania was used. To prepare the lanthanum solutions, lanthanum salt, $LaCl_3$ $7H_2O$, Merck, Darmstadt, Germany, was used. Distilled water was used in all experiments. The pH of solutions was measured using CRISON MultiMeter MM41 with a glass electrode, which has been calibrated using various buffer solutions.

Lanthanum adsorption on the modified material was performed using a JULABO SW 23 shaker at 200 rpm. The concentration of lanthanum in aqueous phase was measured with an Inductive Coupled Plasma Atomic Mass Spectrometer (ICP-MS), using an ICP-MS BRUKER aurora M90 Model. The operating conditions of the ICP-MS are presented in Table 1 from supplementary materials. The drying of the modified material was carried out in an NITECH oven at 323 K. The drying of the modified material was carried out in an NITECH oven at 323 K.

2.2. Modified cellulose preparation

Modified cellulose was prepared using the dry method by placing one gram of cellulose for 24 h at ambient temperature (298 K) in ethanol containing 0,1 g of Na-β-Gly-P modifying agent. After 24 h modified cellulose was washed with deionised water and dried in a oven at 323 K for 24 h.

2.3. Lanthanum batch adsorption studies

The influence of several parameters (pH, time, initial concentration, and temperature) on the lanthanum adsorption was studied in batch experiments. In order to establish the effect of the pH, samples of 0.1 g modified cellulose were mixed with 25 mL of a 50 mg L^{-1} La (III) ion solution at several pH values (2, 4, 6 and 8). The pH value was adjusted using 0.05–2M HNO_3 or 0.05–2M NaOH solutions.

To study the influence of temperature and contact time on the adsorption process, the experiments were carried out using 0.1 g modified cellulose in 25 mL of a 50 mg L^{-1} La (III) ion solution for different contact times (15, 30, 45 and 60 min) and at three different temperatures (298 K, 308 K and 318 K).

Similar experiments were performed at 298 K temperature for 60 min, to study the influence of the initial concentration of La (III) ions, at different initial concentrations: 10, 50, 100, 150, 200, 250, 300, 350 and 400 mg L^{-1}. All the suspensions were stirred at 200 rpm.

After stirring, the samples were filtered and the residual concentration of lanthanum was determined by inductively coupled plasma-mass spectroscopy. The adsorption capacities are defined by equation (1).

$$q = \frac{(Ci - Cf)\cdot V}{m} \tag{1}$$

Where:

q – adsorption capacity of modified cellulose, mg g^{-1};
C_i – initial concentration of La (III) in solution, mg L^{-1};
C_f – residual concentration of La (III) after adsorption process, mg L^{-1};
V – volume of the aqueous solutions with La (III) content, L;
m – mass of the studied adsorbent, g.

2.4. Experimental design

The experiment was made in two stages:
Stage 1. Factorial design. The objectives of this stage are:

- Determining the variables which have significant influence on the adsorption process
- Determining where to set the controllable factors in the first stage, to obtain a maximum adsorption capacity.

Stage 2. Response Surface Design. The objective of this stage was to refine the optimization process, in order to increase the maximum value for the adsorption capacity. At this stage, the setting of the important controllable factors that lead to the maximum value for adsorption capacity was determined.

For both stages the software MINITAB 17.1.0 Statistical Software (2010) (Minitab, 2010) was used for planning the Factorial Design and Response Surface design.

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