β -ketoester-functionalized magnetoactive electrospun polymer fibers as Eu(III) adsorbents

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Abstract

Blended polymer fibers based on a hydrophobic random copolymer having β -ketoester metal ion binding functionalities namely poly(methyl methacrylate)-random-poly(2-(acetoacetoxy) ethyl methacrylate) (PMMA-co-PAEMA) and the hydrophilic polyethylene oxide (PEO) were fabricated by electrospinning and further evaluated for the first time as adsorbents for the removal of Eu(III) from aqueous media. Moreover, magnetoactive fibrous analogues were prepared by incorporating preformed, oleic-acid coated Fe_3O_4 NPs within the polymer fibers during electrospinning. The Eu(III) adsorption was investigated as a function of pH and initial metal ion concentration whereas the effect of the Fe_3O_4 NPs and of the β -ketoester groups on the membrane adsorption efficacy was also investigated. The experimental data, which were well fitted by the Langmuir isotherm model, indicated increased affinity with increasing pH and reached maximum values ($\sim 95\%$) at pH 6.5. The presence of the β -ketoester functionalities as well as the incorporation of the Fe_3O_4 nanoparticles within the fibrous adsorbents affect positively the adsorption process and indicate the significance of chemical modification with respect to water purification and precious metal recovery using adsorbent-based technologies.

Keywords Lanthanide adsorption · β -ketoester · Magnetoactive fibers · Electrospinning · Water remediation · Metal recovery

1 Introduction

Europium and europium oxide are substances of high industrial interest, since they are employed in the manufacturing of various products and devices including fluorescent powders used in fluorescent lamps [1, 2], optical sensors [3–6] etc. Moreover, high amounts of Eu(III) radio-nuclides are produced in nuclear power plants along with other long-lived lanthanide and actinide radioactive fission products that lead to severe environmental contamination [7–12]. Among the long-lived trivalent lanthanides and actinides, Eu(III) is usually employed in experimental studies, due to its similar chemical properties to other

trivalent lanthanides and actinides [13], which however, exhibit higher toxicity and radioactivity rendering them inappropriate for use in experimental investigations.

Removal of lanthanides is of particular interest with respect to chemical separations, environmental remediation, in situ monitoring of aqueous solutions and material recovery from processing solutions and industrial wastewaters. The latter is necessary to cover the demand of lanthanides needed for the fabrication of different industrial products (e.g. catalytic converters, permanent magnets, ceramics etc.), that play a key role in green and sustainable energy production and manufacturing [14].

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Although the removal of europium from different mixtures is usually carried out by solvent extraction [15–19] or ion exchange [20–25], both methodologies make use of large amounts of harmful chemical substances. Therefore, the use of adsorption processes in the recovery of Eu(III) from wastewater is considered to be advantageous and it has been explored by various research groups as an alternative towards this purpose [26–31]. In this context several materials such as MOFs [32], boron nitride-based materials [33] layered double hydroxides [34], Al_2O_3 -based materials [35, 36], carbonaceous Nanofibers [37] and polymer-based nanocomposites [38] have been extensively investigated as possible adsorbents for the effective removal of (radio)toxic elements from aqueous systems.

Electrospinning is considered to be one of the most versatile methods employed for generating fibers in the nano- and micrometer range [39–41]. The electrospinning technique is simple, cost-effective and industrially scalable [42, 43], providing a straightforward way to produce long and continuous polymer nano- and microfibers. Moreover, electrospinning enables the incorporation of a variety of inorganic nanoparticles within the fibers, resulting to the generation of functional fibrous nanocomposites [44]. In addition, the possibility provided by this method for co-processing of polymer mixtures (blended fibers), generates new pathways for altering the chemical composition of the fibers and therefore expanding and tuning their properties including mechanical strength, thermal properties, porosity and permeability. Polymer fibers produced by electrospinning exhibiting the aforementioned properties are considered to be excellent candidates as adsorbents for the removal of harmful substances from wastewater including metal ions, pathogenic microorganisms and small organic molecules such as organic dyes and pharmaceutical compounds [45–50].

The development of effective adsorbents exhibiting high adsorption capacity and fast adsorption rates requires large surface areas and the presence of specific functionalities capable of promoting strong interactions between the metal ions and the adsorbent's surface. However, in many studies either materials with high surface areas and no metal ion adsorbing functionalities or with a high amount of metal ion functionalities but small specific areas and low adsorption rates have been reported. Based on the above, in the present study new functional electrospun fibers containing β -ketoester metal binding functionalities have been fabricated by electrospinning and further evaluated as adsorbents for the removal of Eu(III) from aqueous media. The possibility to incorporate magnetic nanoparticles within these materials resulted to the enhancement of metal ion adsorption and provided the possibility for magnetic separation.

2 Experimental

2.1 Chemicals and reagents

Ethyl acetate (EtOAc) (Fluka, 99.8%), tetrahydrofuran (THF) (Sharlau, HPLC grade), chloroform (CHCl_3) (Sharlau), and n-hexane (Sharlau, 96%) were used as received by the manufacturer. The two monomers methyl methacrylate (MMA) (99%) and 2-(acetoacetoxy) ethyl methacrylate (AEMA) (95%) were purchased from Sigma-Aldrich. MMA was used without further purification while AEMA was passed through a basic alumina column prior to polymerizations. Polyethylene oxide (PEO), $\overline{M}_n = 600\,000\text{ g mol}^{-1}$, was purchased from Sigma-Aldrich. The radical initiator 2,2'-azobis(isobutyronitrile) (AIBN, 95%) was purchased from Sigma-Aldrich and it was re-crystallized twice from ethanol prior to use. Deuterated chloroform (CDCl_3) (Sharlau) was used in ^1H NMR studies. The oleic acid-coated magnetite nanoparticles ($\text{OA.Fe}_3\text{O}_4$) were prepared by following an experimental procedure developed by Bica et al. [51]. The synthesis, surface coating and advanced purification steps are presented in detail by Vekas et al. [52].

Eu(III) stock solutions were prepared by dissolution of $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (Sigma-Aldrich) in aqueous solutions. As background electrolyte sodium perchlorate (NaClO_4) solutions were used. The metal ion concentration in solution was determined spectrophotometrically by means of arsenazo-III (Sigma-Aldrich) according to previously described methods [53, 54]. All experiments were performed under ambient atmospheric conditions ($p(\text{CO}_2) = 10^{-3.5}\text{ atm}$ and $25\text{ }^\circ\text{C}$).

2.2 Synthesis of PMMA-co-PAEMA random copolymer

Conventional free radical polymerization was employed for the synthesis of the PMMA-co-PAEMA random copolymer. The polymerization was carried out in a round-bottom flask, fitted with a rubber septum. The monomers MMA (20 mL, 0.1884 mol) and AEMA (11.98 mL, 0.0628 mol) were transferred with the aid of a syringe into a reaction flask equipped with a stirring bar. Ethyl acetate (32 mL) was subsequently added followed by the addition of the initiator AIBN (0.206 g, 0.00126 mol) dissolved in the same solvent. After dissolution, the reaction mixture was placed in an oil bath at $63\text{ }^\circ\text{C}$ for 7 h under inert (nitrogen) atmosphere. Polymerization was terminated by cooling the reaction down to room temperature. The produced PMMA-co-PAEMA random copolymer was retrieved by precipitation in n-hexane

(polymer solution to n-hexane in volume ratio 1:10) and it was left to dry *in vacuo* at room temperature for a few hours. Polymerization Yield: 55%.

^1H NMR (500 MHz, CDCl_3) δ [ppm]: 11.94 (s, $-\text{OH}$ (enol, AEMA)), 5.11 (br, s, $=\text{CH}$ (enol, AEMA)), 4.37 (br, $-\text{CH}_2$ (AEMA)), 3.59 (br, $-\text{CH}_2$ (AEMA) + br, $-\text{CH}_3$ (MMA)), 2.31 (br, $-\text{CH}_3$ (AEMA)), 2.04 (s, br, $-\text{CH}_3$ (enol, AEMA)), 2–0.84 (m, br, $-\text{CH}_3$ and $-\text{CH}_2$, polymer backbone).

Degrees of polymerization (DP) calculated ratio: PMMA:PAEMA = 20:1. M_n (number average molar mass): 99,842 $\text{g}\cdot\text{mol}^{-1}$; molar mass distribution: 2.4 (as determined by SEC).

2.3 Adsorbent fabrication

Electrospinning was employed for the fabrication of electrospun nanocomposite fibers based on the in-house synthesized hydrophobic and metal ion binding, PMMA-co-PAEMA methacrylate-based random copolymer, the commercially available and hydrophilic PEO homopolymer, and pre-formed $\text{OA}\cdot\text{Fe}_3\text{O}_4$ magnetic nanoparticles that were prepared by chemical co-precipitation as described in previous reports [51, 52]. The PMMA-co-PAEMA and PEO were mixed in CHCl_3 solution in the absence and presence of $\text{OA}\cdot\text{Fe}_3\text{O}_4$ nanoparticles (NPs) at room temperature. More precisely solutions of PMMA-co-PAEMA/PEO (solution concentration: 4% w/v; weight percentage proportion of PMMA-co-PAEMA/PEO: 30/70 respectively) were prepared, in the absence and presence of 37% wt. magnetic $\text{OA}\cdot\text{Fe}_3\text{O}_4$ NPs in respect to the total polymer mass.

Systematic parametric studies were carried out by varying the applied voltage, the needle-to-collector distance, the needle diameter and the solution flow rate so as to determine the optimum experimental conditions for obtaining microfibrinous membranes. All electrospinning experiments were performed at room temperature. Table 1 summarizes the amounts of the reactants used for the preparation of the polymer-based solutions that were further electrospun. For comparison purposes, a membrane analogue based on poly(L-lactide) (PLLA) and PEO containing the same $\text{OA}\cdot\text{Fe}_3\text{O}_4$ content (37% wt.) was also fabricated.

2.4 Adsorbent characterization

Proton Nuclear Magnetic (^1H NMR) spectroscopy was used to confirm the expected chemical structure of the PMMA-co-PAEMA random copolymer. ^1H NMR analysis was performed in CDCl_3 using an Avance Bruker 500 MHz spectrometer equipped with an Ultrashield magnet. The CDCl_3 contained traces of tetramethylsilane (TMS), which was used as an internal reference. The average molar mass and molar mass distribution of the PMMA-co-PAEMA copolymer were determined by Size Exclusion Chromatography (SEC). All measurements were carried out at room temperature using Styragel HR 3 and Styragel HR 4 columns. The mobile phase was THF, delivered at a flow rate 1 mL min^{-1} using a Waters 515 isocratic pump. The refractive index was measured with a Waters 2414 refractive index detector. The instrumentation was calibrated using poly(methyl methacrylate) ($\text{C}_5\text{O}_2\text{H}_8$) $_n$ (PMMA) standards with narrow polydispersity indices (MWs of 102, 450, 670, 1580, 4200, 14,400, 31,000, 65,000, 126,000, 270,000, 446,000, 739,000 g mol^{-1}) supplied by Polymer Standards Service (PSS). Thermal Gravimetric Analysis (TGA) measurements were used in order to determine the thermal stability of the copolymers and they were based on continuous measurement of weight on a sensitive balance (thermobalance) upon temperature increase. TGA measurements were performed on a Q-500 TA Instrument under an argon flow at heating rate of $10^\circ\text{C min}^{-1}$.

The nanocomposite fibrous membranes were generated by using a custom-made electrospinning set-up. The equipment included a controlled-flow, four-channel volumetric microdialysis pump (KD Scientific, Model: 789252), syringes with specially connected spinneret needle electrodes, a high-voltage-power source (10–50 kV) and custom-designed, grounded target collectors, inside an interlocked Faraday enclosure safety cabinet. The morphological characteristics of the fibrous membranes were determined by Scanning Electron Microscopy (SEM) (Vega TS5136LS-Tescan) in the absence and presence of $\text{OA}\cdot\text{Fe}_3\text{O}_4$ nanoparticles. The samples were gold-sputtered ($\sim 100\text{ nm}$) (sputtering system K575X Turbo Sputter Coater–Emitech) prior to SEM inspection.

X-ray Powder Diffraction patterns were obtained using Rigaku (30 kV, 25 mA) with $\lambda = 1.5405\text{ \AA}$ (Cu) in the range of 10 – 90° and at a scanning rate of $1^\circ/\text{min}$. The magnetic

Table 1 Quantities of the reactants used for the preparation of the PMMA-co-PAEMA/PEO and PMMA-co-PAEMA/PEO/ $\text{OA}\cdot\text{Fe}_3\text{O}_4$ solutions prepared in chloroform

Sample	Reactants				
	PLLA (g)	Copolymer (g)	PEO (g)	$\text{OA}\cdot\text{Fe}_3\text{O}_4$ (g)	CHCl_3 (mL)
PMMA-co-PAEMA/PEO	–	0.24	0.56	–	20
PMMA-co-PAEMA/PEO/ $\text{OA}\cdot\text{Fe}_3\text{O}_4$	–	0.24	0.56	0.47	20
PLLA/PEO/ $\text{OA}\cdot\text{Fe}_3\text{O}_4$	0.24	–	0.56	0.47	20

properties of the nanocomposite PMMA-co-PAEMA/PEO/OA.Fe₃O₄ fibrous membranes were determined at 300 K with a Vibrating Sample Magnetometer (VSM)-Model 880 from ADE technologies USA. Adsorption studies of Eu(III) onto the magnetite-free and magnetite-loaded electrospun fibers were performed on a UV 2401 PC Shimadzu UV-vis spectrophotometer operating at room temperature as described in the following.

2.5 Adsorption studies

The adsorption studies of Eu(III) onto the pristine and magnetoactive electrospun polymer fibers was investigated as a function of pH, and initial metal ion concentration by means of batch experiments. In these experiments the parameter under investigation was varied while other experimental parameters were kept constant. To investigate the effect of pH, to a polyethylene (PE) screw-cap bottles a specific amount of the fibrous adsorbent (10 mg) was placed in contact with 3 ml of an aqueous Eu(III) solution of known total metal ion concentration ($C_0 = 1 \cdot 10^{-5}$ M, $I = 0.1$ M) in which pH was varied between 1 and 8. Under ambient conditions and the selected metal ion concentration no precipitation of the solubility limiting phase is expected [55]. The pH was adjusted by addition of NaOH or HClO₄ (0.1–1 M). After 24 h incubation time, the pH was measured using a glass electrode (Hanna Instruments pH 211) and the analytical metal ion concentration in solution was determined spectrophotometrically (UV 2401 PC Shimadzu) by means of arsenazo-III. The molar extinction coefficients ϵ of the Eu(III)-arsenazo complex at 650 nm was $\epsilon_{\text{Eu(III)}} = (87,541 \pm 5176) \text{ L mol}^{-1} \text{ cm}^{-1}$ [56].

For studying the effect of the initial metal ion concentration, a specific amount of the adsorbent (10 mg) was placed in aqueous Eu(III) solutions (3 mL) of known concentration (1×10^{-4} – 7×10^{-6} M), $I = 0.1$ M and optimum pH 6. pH was adjusted as described above. The UV-vis

spectrum of the supernatant was recorded after 24 h for determining the amount of the adsorbed Eu(III).

The amount of the adsorbed Eu(III) on the fibrous membranes ($q_e \text{ mg g}^{-1}$) and % removal efficiency (% q_e) were calculated using the following equations [57]:

$$q_e = \frac{(C_0 - C_e)}{W} \cdot V \quad (1)$$

$$\%q_e = \frac{(C_0 - C_e)}{C_0} \cdot 100 \quad (2)$$

where $q_e \text{ (mol g}^{-1}\text{)}$ is the amount of metal ions adsorbed per unit amount of the adsorbent, $C_0 \text{ (mol L}^{-1}\text{)}$ is the initial metal ion concentration, $C_e \text{ (mol L}^{-1}\text{)}$ is the equilibrium concentration of metal ions in solution, $V \text{ (L)}$ is the solution volume and $W \text{ (g)}$ is the adsorbent mass.

3 Results and discussion

3.1 Adsorbent fabrication

Microfibrous membranes consisting of PMMA-co-PAEMA/PEO and PMMA-co-PAEMA/PEO/OA.Fe₃O₄ were produced by electrospinning as schematically illustrated in Fig. 1. For comparison purposes, magnetoactive PEO/PLLA/OA.Fe₃O₄ electrospun fibers containing the same magnetic content (37% wt.) as in the case of the PMMA-co-PAEMA/PEO/OA.Fe₃O₄ system was also prepared and investigated in regards to its adsorption capability. Based to our previous studies, PLLA/PEO electrospun fibers can successfully be employed as adsorbents for tetravalent thorium (Th(IV)) and hexavalent uranium (U(VI)) from aqueous media [58]. The fabrication of the PLLA/PEO/OA.Fe₃O₄ analogue, where the PLLA/PEO weight ratio was kept the same as in the case of the PMMA-co-PAEMA/PEO/OA.Fe₃O₄ system

Fig. 1 Schematic presentation of the synthetic methodology followed the fabrication of electrospun fibrous membranes, and representative photographs (white colored membrane: PMMA-co-PAEMA/PEO; brown colored membrane: PMMA-co-PAEMA/PEO/OA.Fe₃O₄)

(30:70 wt.), aimed in investigating the effect of the hydrophobic component on the metal ion adsorption efficacy, and the potential ability of the metal chelating β -ketoester moieties introduced within this component on enhancing the Eu^{3+} binding. For the successful preparation of these materials, optimum processing parameters were employed in regards to the polymer solution concentration, the applied voltage, the solution delivery rate, the needle diameter and the distance between the tip of the needle and the collector. Table 2 summarizes the experimental parameters used for the fabrication of the PMMA-co-PAEMA/PEO, PMMA-co-PAEMA/PEO/OA. Fe_3O_4 and PLLA/PEO/OA. Fe_3O_4 adsorbents.

3.2 Adsorbent characterization

3.2.1 Morphological characterization

Information on the morphological characteristics of the electrospun fibrous membranes, before and after immersion in aqueous solutions, were obtained by SEM.

Figure 2 provides the SEM images of the as-prepared PMMA-co-PAEMA/PEO (Fig. 2a) and PMMA-co-PAEMA/PEO/OA. Fe_3O_4 (Fig. 2b) fibrous mats. As seen in Fig. 2, the fibers exhibit a cylindrical shape and very good homogeneity in respect to their diameters which were determined to be 2.46 ± 0.12 and 2.79 ± 0.47 respectively, by using the Digimizer software.

The blending of the PMMA-co-PAEMA metal chelating random copolymer with PEO aimed in increasing

Table 2 Optimum experimental conditions employed for the fabrication of the PMMA-co-PAEMA/PEO and PMMA-co-PAEMA/PEO/OA. Fe_3O_4 electrospun fibrous membrane adsorbents

Sample's code	Electrospinning conditions			
	Needle (G)	Voltage (kV)	Needle-to-collector distance (cm)	(mL/h)
MMA-co-AEMA/PEO	18	20	25	2
MMA-co-AEMA/PEO/OA. Fe_3O_4	18	20	25	2
PLLA/PEO/OA. Fe_3O_4	16	25	25	4

Fig. 2 SEM images of **a** PMMA-co-PAEMA/PEO fibrous membranes and **b** PMMA-co-PAEMA/PEO/OA. Fe_3O_4 nanocomposite fibrous membranes

Fig. 3 SEM images of **a** MMA-co-AEMA/PEO fibrous membranes and **b** MMA-co-AEMA/PEO/OA.Fe₃O₄ (37% wt.) nanocomposite fibrous membranes after being immersed in an aqueous solution (pH 7)

the membrane's hydrophilicity and hence wettability in aqueous media. Upon immersing these materials in water, morphological changes were observed in the case of the PMMA-co-PAEMA/PEO system (Fig. 3a and b), owned to the hydration of the hydrophilic PEO. These results are in line with similar observations by us [58, 59] and other groups [60] on PEO-containing electrospun fibers immersed in aqueous media. In contrary, the high content of the hydrophobic OA.Fe₃O₄ NPs within the PMMA-co-PAEMA/PEO/OA.Fe₃O₄ nanocomposite fibrous analogues, resulted to the retaining of the initial fiber morphology and the prevention of the fibers' extended hydration and erosion (Fig. 3c and d).

3.2.2 Thermal stability

The degradation temperature of the produced fibrous membranes was determined by TGA measurements. The TGA traces of the polymer fibrous membranes in the absence and presence of OA.Fe₃O₄ nanoparticles are provided in Fig. 4. As seen in the thermograms, the pristine polymer membrane began to decompose at a

Fig. 4 TGA thermogram of OA.Fe₃O₄, PMMA-co-PAEMA/PEO and PMMA-co-PAEMA/PEO/OA.Fe₃O₄

Fig. 5 Magnetization curves of the PLLA/PEO/OA.Fe₃O₄ and the PMMA-co-PAEMA/PEO/OA.Fe₃O₄ nanocomposite fibrous membranes, both containing 37% wt. OA.Fe₃O₄

slightly lower temperature (~ 350 °C) compared to the nanocomposite analogue (~ 380 °C), while at ~ 420 °C, it decomposed completely losing almost all of its weight. The remaining residue observed in the case of the magnetite-containing membrane at higher temperatures ($T > 450$ °C) corresponds to the inorganic (Fe₃O₄) content [59], which was found to be in a very good agreement with the expected content (37% wt.).

3.2.3 Magnetic properties

The magnetic properties of the nanocomposite fibrous adsorbents were investigated by VSM at 300 K. Figure 5 shows the magnetization versus applied magnetic field strength plot ($M = f(H)$) corresponding to the PMMA-co-PAEMA/PEO/OA.Fe₃O₄ nanocomposite membrane loaded with 37% wt. OA.Fe₃O₄ and the PLLA/PEO/OA.Fe₃O₄ analogue having the same magnetic content (37% wt.). In both cases, the sigmoidal shape of the plots and the lack of a hysteresis loop demonstrate the superparamagnetic behaviour of these systems at ambient temperature whereas these materials exhibit similar saturation magnetization values.

As previously mentioned, the PLLA/PEO/OA.Fe₃O₄ electrospun fibrous analogue was prepared for comparison purposes. More precisely, in a previous publication we have demonstrated the effectiveness of PLLA/PEO electrospun fibrous mats towards the removal of radioactive metal ions from aqueous media [58].

The new material presented herein differs from the previously reported one in respect to: (a) the incorporation of polymer chains containing β -ketoester side-chain moieties, known for their strong ability to act as bidentate

ligands for different metal ions of various geometries and oxidation states [61–66] and (b) the introduction of magnetite nanoparticles. Based on previous reports, magnetic nanomaterials such as MnFe₂O₄ nanocubes [67] have been successfully employed as adsorbents for U(VI)/Eu(III). Moreover, it has been demonstrated that the incorporation of magnetic Fe₃O₄ nanoparticles within polymer matrices results in the enhancement of the adsorption ability of the resulting nanocomposite adsorbents [68–71]. In addition, the presence of Fe₃O₄ nanoparticles within the fibers enables the easy recovery of the adsorbent from aqueous media upon completion of the adsorption process by means of an externally applied magnetic field.

3.2.4 Nanocrystalline phase characterization

The nanocrystalline phase adopted by the OA.Fe₃O₄ nanoparticles embedded within the nanocomposite membranes was investigated by X-ray diffraction (XRD) spectroscopy. Figure 6 provides the powder XRD diffraction patterns of the PMMA-co-PAEMA/PEO/OA.Fe₃O₄ and the PLLA/PEO/OA.Fe₃O₄ electrospun membranes as well as the pattern corresponding to pristine OA.Fe₃O₄ nanoparticles. The diffractogram of the membranes display six broad peaks appearing at $2\theta \sim 30^\circ, 36^\circ, 43^\circ, 54^\circ, 58^\circ$, and 63° thus verifying the presence of magnetite (OA.Fe₃O₄) within this system [72, 73].

3.3 Adsorption studies

The effectiveness of the produced electrospun nanocomposite membranes in removing Eu(III) from aqueous solutions was investigated by varying different experimental parameters such as the solution pH, the initial metal ion

Fig. 6 XRD patterns of the pristine OA.Fe₃O₄ nanoparticles, the PMMA-co-PAEMA/PEO/OA.Fe₃O₄ and the PLLA/PEO/OA.Fe₃O₄ nanocomposite membranes containing 37% wt. OA.Fe₃O₄

Fig. 7 Schematic of the Eu(III) adsorption process by using the PMMA-co-PAEMA/PEO and the PMMA-co-PAEMA/PEO/OA.Fe₃O₄ as adsorbents. Photographs show the above-mentioned adsorbents immersed in aqueous media (white colored membrane: magnetite-free fibers; brown colored membrane: magnetite-containing fibers)

Fig. 8 The effect of pH on the relative adsorption of Eu(III) by the PMMA-co-PAEMA/PEO/OA.Fe₃O₄ nanocomposite electrospun membrane adsorbent

concentration and the membrane magnetic content. Figure 7 demonstrates schematically the adsorption process that takes place through the β -ketoester groups that are present onto the polymeric fibers. Comparison of the

adsorption efficiency of the β -ketoester-containing fibers to the PLLA-based analogues was carried out by maintaining the same experimental conditions.

3.4 Effect of pH

pH is a very important parameter which affects both speciation and the chemical behavior of metal ions in aqueous media. The effect of pH on the Eu(III) sorption onto the PMMA-co-PAEMA/PEO/OA.Fe₃O₄ adsorbent, is shown in Fig. 8. Experiments were performed up to pH 8 since above this value the formation of Eu(III) carbonate complexes, such as EuCO_3^+ and $\text{Eu}(\text{CO}_3)_2^+$ affect competitively the adsorption process. According to Fig. 8 the relative adsorption of Eu(III) increases with increasing pH, reaching at a maximum value $\sim 95\%$ at pH 6–7.

The effect of pH is attributed to the fact that with increasing the solution pH the concentration of protons decreases gradually favoring the Eu^{3+} cation binding by the ketoester groups. The adsorption edge for the present adsorption system is positioned at pH 6.5. The competition between the Eu^{3+} cations and the protons regarding their interaction with the β -ketoester group is shown below (Fig. 9).

Fig. 9 Schematic presentation of the competitive interaction between the Eu^{3+} cations and protons with the oxygen moieties of the β -ketoester group

3.5 Effect of initial metal ion concentration

In order to evaluate the maximum membrane adsorption capacity ($q_{\max}$ (mg g⁻¹) through the effect of initial metal ion concentration, adsorption experiments with different metal ion concentrations (1×10^{-6} – 1×10^{-4} M) have been performed at the optimum pH (pH 6) at room temperature. The Langmuir isotherm model was employed to fit the equilibrium experimental data. This empirical model assumes that the adsorption takes place at a finite number of homogeneous sites on the surface of the adsorbent until monolayer formation [74]. Once a site is occupied by a molecule, no further adsorption can take place. The Langmuir isotherm model is described by the following equations:

$$q_e = \frac{q_{\max} \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (3)$$

$$\frac{1}{q_e} = \frac{1}{q_{\max} \cdot K_L \cdot C_e} + \frac{1}{q_{\max}} \quad (4)$$

where, C_e (g L⁻¹) is the equilibrium metal ion concentration, q_e (g Kg⁻¹) is the amount of metal ions adsorbed at equilibrium per unit mass of adsorbent, $q_{\max}$ (g Kg⁻¹) is the maximum metal ion amount per unit weight of the adsorbent and K_L (L g⁻¹) is the Langmuir adsorption equilibrium constant that reflects the adsorption energy. The Langmuir adsorption isotherms expressing the relationship between q_e corresponding to the metal ion adsorption by the non-magnetic PLLA/PEO and PMMA-co-PAEMA/PEO and the magnetic PMMA-co-PAEMA/PEO/OA.Fe₃O₄ membranes versus C_e , which is the remaining

metal ion concentration in solution at equilibrium (24 h), are provided in Fig. 10a and b, respectively. The maximum adsorption capacity of europium ions onto the electrospun membranes was found to be 0.8×10^{-2} mol Kg⁻¹ for the PLLA/PEO adsorbent, 1.5×10^{-2} mol Kg⁻¹ for the PMMA-co-PAEMA/PEO adsorbent and 1.6×10^{-2} mol Kg⁻¹ for the PMMA-co-PAEMA/PEO/OA.Fe₃O₄ adsorbent. From the obtained results it can be concluded that the presence of the β -ketoester functionalities as well as the incorporation of the Fe₃O₄ nanoparticles within the fibrous adsorbents affect positively the adsorption process.

The Langmuir isotherm model fits very well the experimental data ($R^2 > 0.977$) indicating specific interaction between the membrane active moieties and the metal ions and formation of inner-sphere complexes [75].

The presence of β -ketoester groups increases significantly the adsorption capacity of the membrane because such moieties which are hard *Lewis* bases present higher affinity for the Eu³⁺ cations, which act as hard *Lewis* acids. Similarly the hydroxyl groups on the surface of the iron oxide nanoparticles associated with the magnetic membranes favor the binding of hard metal ions via the formation of inner-sphere surface complexes [76, 77], increasing further the adsorption capacity of the corresponding membranes.

4 Conclusions

Polymer-based fibrous membranes containing β -ketoester metal ion binding functionalities have been fabricated by electrospinning and employed as adsorbents for the removal of Eu(III) from aqueous media. In an effort to increase the adsorption capacity imparting at the same time magnetic response, these materials were further functionalized with superparamagnetic oleic acid-coated Fe₃O₄ nanoparticles. The adsorption capacity of the membranes for the lanthanide ions increases with increasing pH (adsorption edge at pH 6.5) due to the decreasing concentration of the competing protons that favours metal ion binding. The experimental data are well fitted by the Langmuir adsorption model indicating specific interaction by formation of inner-sphere surface complexes and resulting in maximum adsorption capacities. Membrane modification by adding moieties, which act as hard *Lewis* bases (e.g. ketoesters, hydroxyl groups) and present increased affinity for lanthanide ions, affects significantly the adsorption capacity of the membrane. Ongoing studies focus on the development of new functional electrospun fibers possessing hydroxyl- and amino- functionalities, exhibiting enhanced adsorption capacity and selectivity with respect to actinide partitioning from other nuclides in the spent

Fig. 10 Langmuir adsorption isotherms corresponding to the Eu(III) adsorption by the non-magnetic PLLA/PEO and PMMA-co-PAEMA/PEO and the magnetic PMMA-co-PAEMA/PEO/OA.Fe₃O₄ electrospun membranes

fuel and precious metal recovery from industrial effluents and seawater.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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