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Abstract: Rare earths are one of the most critical raw materials group. In an effort to develop an effective adsorbent for aqueous rare earths recovery, activated carbon (AC) was modified with pentaethylenehexamine. Both raw AC and modified activated carbon (MAC) were characterized by X-ray diffraction (XRD) and surface area analyses. The set of experiments was carried out with lanthanum, selected as representing of rare earths family, and the impacts of reactive time and concentrations of lanthanum were evaluated. The aqueous lanthanum adsorptive kinetics and capacity were also determined. The strong improvement in the efficiency values detected by using modified carbons (uptake 100% until initial concentrations of about 2600 ppm and release over 95%) demonstrated that the coordination mechanism due to modifying agent is effective. MAC presented lower kinetics and more than double adsorptive capacity as compared with AC. Furthermore, the adsorbent can be used successfully at least four times after regeneration for the removal of lanthanum.
The overall results demonstrated the potential utility of modification for enhancement of performances of AC-based materials for rare earths removal from aqueous solutions.

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Dear Editor,

Please find the electronic copy of our manuscript entitled: “Enhanced lanthanum adsorption by amine modified activated carbon” by E.M. Iannicelli Zubiani, P. Gallo Stampino, C. Cristiani, G. Dotelli, which we herewith submit for publication in *Chemical Engineering Journal.*

The manuscript is not under consideration for publication and has not been published elsewhere.

All authors agree with the contents of the manuscript.

Thank you in advance for your kind consideration.

Sincerely Yours,
Elena Maria Iannicelli Zubiani

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Highlights

Activated carbon was modified with pentaethylenehexamine to adsorb lanthanum.

The impacts of reactive time and concentrations of lanthanum were evaluated.

The aqueous lanthanum adsorptive kinetics and capacity were also determined.

The adsorbent can be used successfully at least four times after regeneration.

The modification enhanced AC-based materials for rare earths removal.

Enhanced lanthanum adsorption by amine modified activated carbon

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Abstract

Rare earths are one of the most critical raw materials group. In an effort to develop an effective adsorbent for aqueous rare earths recovery, activated carbon (AC) was modified with pentaethylenehexamine. Both raw AC and modified activated carbon (MAC) were characterized by X-ray diffraction (XRD) and surface area analyses. The set of experiments was carried out with lanthanum, selected as representing of rare earths family, and the impacts of reactive time and concentrations of lanthanum were evaluated. The aqueous lanthanum adsorptive kinetics and capacity were also determined. The strong improvement in the efficiency values detected by using modified carbons (uptake 100% until initial concentrations of about 2600 ppm and release over 95%) demonstrated that the coordination mechanism due to modifying agent is effective. MAC presented lower kinetics and more than double adsorptive capacity as compared with AC. Furthermore, the adsorbent can be used successfully at least four times after regeneration for the removal of lanthanum. The overall results demonstrated the potential utility of modification for enhancement of performances of AC-based materials for rare earths removal from aqueous solutions.

Keywords

Activated carbon; surface modification; adsorption; lanthanum

1. Introduction

Increased demand in clean energy applications and in other vital technologies, as well as simultaneous shortfall in supply, made rare earth (RE) metals and compounds to be considered the most critical raw materials group by the European Commission [1]. Nevertheless, a cost-effective and environmentally sound selective separation of REs remains a challenge to date [2].

From a technological point of view, primary and secondary REs sources are directly processed using hydrometallurgical routes [3]. Traditional methods that have been used to separate and/or recover aqueous REs include crystallization, chemical precipitation, ion exchange, solvent extraction, and adsorption [4, 5]. Among them, adsorption technique has been widely applied as an economical and efficient method [6-8]. Activated carbon (AC) is a common adsorbent that is often used for aqueous metal removal because of its excellent porous structures, specific surface properties, reusability, minimal costs, and environmentally benign nature [9, 10]. Apart from specific surface area, the surface chemistry of activated carbon has a significant influence on its capacity to adsorb inorganic pollutants, especially metallic cations [6]. Thus, many researches have modified the carbon by impregnation with foreign substances, a procedure that consists in the distribution of chemical species on the outer surface of the activated carbon [11, 12]. These substances may be metals or polymeric materials and, in general, the most successful solid phase extractors for metal ions are those immobilized basically by sulphur and nitrogen containing compounds [13]. Zhu et al. [9], for instance, modified the AC surface using an amine-terminated silylating agent (3-aminopropyltriethoxysilane, APTES) for substantially enhancing the AC adsorptive capacity for aqueous Hg ions, obtaining a faster rate of the Hg (II) adsorption and more than double adsorptive capacity. Mahaninia et al. [14] investigated the amination of activated carbon and its influence on copper adsorption, finding out an enhanced adsorption for copper on the modified activated carbons, mainly by the presence of amino groups. The selective removal of copper was studied also by Chouyyok et al. [15] comparing three new classes of nanoporous sorbents (a scaffold of mesoporous silica, mesoporous carbon, or activated carbon), designed around chelating diamine functionality. All three chelating diamine sorbents showed excellent Cu^{2+} removal (~95-99%) from river water and seawater over the pH range 6.0−8.0.

Also the authors investigated the modification of sorbents by amines but the modified matrix solid was of a different kind: clays were indeed modified with N-(methoxy-polyethylene glycol) ethylene diamine and pentaethylenehexamine ethylene diamine [16-18] pointing out the role of the amino groups to improve the uptake efficiency of the solid sorbent towards copper and lanthanum. At the right conditions, that were found pH 11 and an initial amino groups concentration around 2.5 mmol/g, the metals uptake was increased due to the presence of a coordination mechanism of the free amino groups towards the metal ions.

For this reason the objective of this study was to develop an innovative material based on AC modified with pentaethylenehexamine specific for removal and recovery of rare earths from aqueous solutions. Modified activated carbon (MAC) was expected to remove rare earths more efficiently than raw AC. The interaction mechanisms between adsorbate and adsorbent were investigated by analysing the effects of several variables such as pH, contact time and rare earth concentration. Desorption was also studied to evaluate the possibility of metal ions recovery and regeneration of the solid sorbent. The large set of experiments was carried out with lanthanum, selected as representing of rare earths family.

2. Materials and methods

2.1. Materials

Powdered activated carbon (AC supplied by Torchiani s.r.l.) was used as solid matrix. Main properties are reported in Table 1.

Table 1

Properties of the powder AC.

Sorbent	Humidity (%)	Ash (%)	Iodine	pH	Mesh	Density (kg/m^3)	BET surface area (m^2/g)
AC	10	10/15	225/600	8.7	99.8% of powder below 120 μm	600	575

The carbon powder was modified by impregnation of pentaethylenehexamine (PEHA hereafter, supplied by Sigma-Aldrich, technical grade). The polyamine, a viscous liquid material at room temperature, soluble in water, is characterized by a molecular weight of 232 g/mol, an initial pH of 11 and density at 25 °C equal to 0.96 g/mL.

Other reactants used in this study were lanthanum nitrate ($La(NO_3)\cdot 5H_2O$ 99.99%, Sigma Aldrich), HNO_3 (ACS, Sigma Aldrich), NaOH (ACS, Sigma Aldrich), and deionized water.

2.2. Preparation and characterization of modified activated carbon (MAC)

Modified AC (MAC, hereafter) was obtained according to previous studies [19]. In a typical experiment, 2.5 g of AC were mixed, in a jacketed reactor under vigorous stirring, with 50 mL of aqueous polyamine solution for a fixed time of 90 min. The initial polyamine concentration was set at 2.7 mmol/g. All the experiments were carried out at the controlled temperature of 30 °C. The pH of the solution was measured before and after the reaction using a Mettler Toledo FE20/EL20 digital pH-meter. The initial pH of the polyamine solution was about 11 and it remained constant throughout the reaction. At the end, the solid phase was separated by the liquid one using a centrifuge (HETTICH 32 RotoFix, 3500 rpm for 15 min). The solid, upon drying (one day at room temperature), was characterized by X-ray powder diffraction (XRD) patterns using a Bruker D8 Advance diffractometer. A graphite monochromator, a Cu K_α radiation, a scan step of 0.02° 2θ and a measurement of 1 s per step were applied. The pore structure of the samples, including the surface area (S_{BET}), the total pore volume (V_{tot}), the average pore diameter were determined from nitrogen adsorption/desorption isotherms at 77 K by using a surface area analyser (TriStar 3000).

The MAC sorbent thus obtained was used for the adsorption and desorption processes.

2.3. Adsorption experiments

A weighted amount of activated carbon or modified carbon was contacted with the lanthanum solution (solid/liquid ratio = 0.04 g/mL) at different initial La^{3+} concentrations, under vigorous stirring. Considering that the purpose of this study is the treatment of solutions directly coming from primary and secondary REs sources, the initial solution concentrations (10 - 200 mM) were selected to be as closer as the real case. Therefore, as already discussed for different solids [20], the use of concentrated solutions is of choice in order to demonstrate the feasibility of the method also in these cases. High concentrations are indeed preferred in industrial applications because they result in lower volumes to be treated.

To investigate the equilibrium adsorption time, the contact time was varied in the range 10 min - 24 h. At the end of the reaction, the solid was separated from the liquid using a centrifuge (HETTICH 32 RotoFix). Adsorption capacity values at equilibrium *qe* (mmol/g) were calculated from the mass balance equation as follows:

$$q_e\left(\frac{\text{mmol}}{\text{g}}\right) = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where C_0 and C_e are the initial and equilibrium concentrations of adsorbate (mmol/L), respectively; V is the volume of solution (L) and W is the mass of carbon or modified carbon (g). The adsorption efficiency (%) was calculated as:

$$AD\ (\%) = \frac{(C_0 - C_e)100}{C_0} \tag{2}$$

2.4. Desorption and regeneration tests

Desorption tests were performed by adding 1M HNO_3 solution under continuous stirring (magnetic stirrer, 500 rpm) to the metal-containing activated or modified carbon [19]. The experiments were performed at room temperature, for 90 min with a solid/liquid ratio of 0.026 g/mL. The amount of desorbed ions (*qe*de) was calculated from the following equation:

$$q_e\text{de} = \frac{(C_e de)V}{W} \tag{3}$$

where $C_e$de is the metal concentration in solution after the desorption step, V is the volume of the solution (L) and W is the mass of solid (g).

The percentage of desorbed lanthanum (DE) was calculated as:

$$DE\ (\%) = \frac{(q_e de)100}{q_e ad} \tag{4}$$

where *qe*ad and *qe*de are the amount adsorbed and desorbed on adsorbent, respectively.

The regeneration was studied only on MAC through sequential cycles of adsorption-desorption experiment. After MAC was exhausted for adsorption under high concentration of lanthanum, the solution was filtered carefully to retrieve the particles. Then, the particles were desorbed always by adding 1M HNO_3 solution. After the desorption experiment, MAC was dried one day at room temperature, regenerated to restore the amino groups by adding 1 M NaOH solution, separated, dried and finally allowed for the addition of fresh adsorbate solution for re-adsorption experiment. The adsorption and desorption procedures were repeated using the same adsorbent four times.

2.5. Analyses

The amount of the reacted polyamine was found as the difference of the polyamine concentration before and after the modification experiment, determined by Chemical Oxygen Demand (COD) analyses, using a Spectrodirect Lovibond instrument. In a standard instrumental procedure the unknown sample was oxidized by heating for 120 min at 150 °C [16, 21].

Concentrations of lanthanum were determined using Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP – OES, Perkin Elmer Optima 2000DV spectrometer). The measurement error is estimated to be within 1%.

3. Results and discussion

3.1. Characterization of the adsorbents

Preliminarily, the raw (AC) and the modified (MAC) carbon materials were characterized. **Fig. 1** shows the XRD spectra of AC and MAC: an almost amorphous structure can be detected with the main peak at around 25° that can indicate the presence of some graphite [22]. On the contrary, no information on the presence of the amine could be evinced.

The measured BET surface area of AC was 575 m^2/g. The impregnation of amino group on the AC significantly reduced the surface area to 69 m^2/g. Decrease in pore volume from 0.389 to 0.091 cm^3/g was also observed. Changes in the surface area and pore volumes were therefore attributed to the successful impregnation of the amine onto the AC surfaces, which blocked most micropores. The average pore diameter increased from 27.1 to 52.1 Å after coating, suggesting the preferential blocking of micropores [6].

After the confirmation of occurred impregnation, COD analyses were performed to quantify the polyamine effectively adsorbed by the solid matrix. The results showed that starting from an initial concentration of amine equal to 2.7 mmol/g the adsorbed polyamine is 0.8 mmol/g, about the 30% of the initial concentration.

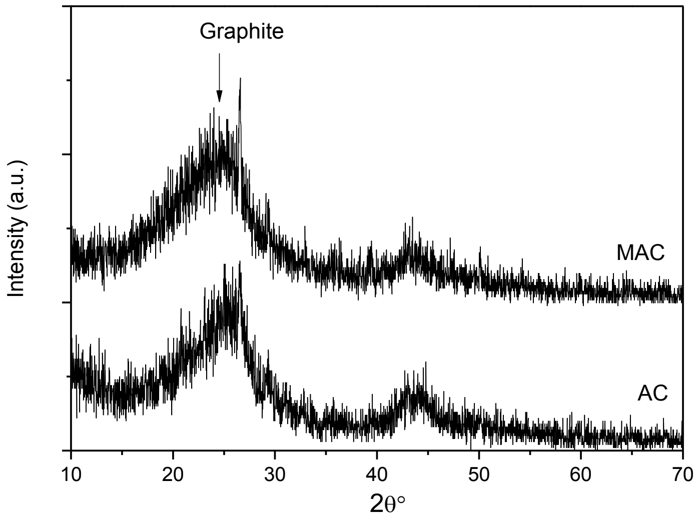

Fig. 1. XRD analysis of AC and MAC.

3.2 pH evolution during adsorption

The pH evolution was monitored throughout the experiments. In Fig. 2 the trends obtained starting from a lanthanum initial concentration of 19 mM are reported: the same trends are obtained for all the other initial lanthanum concentrations studied.

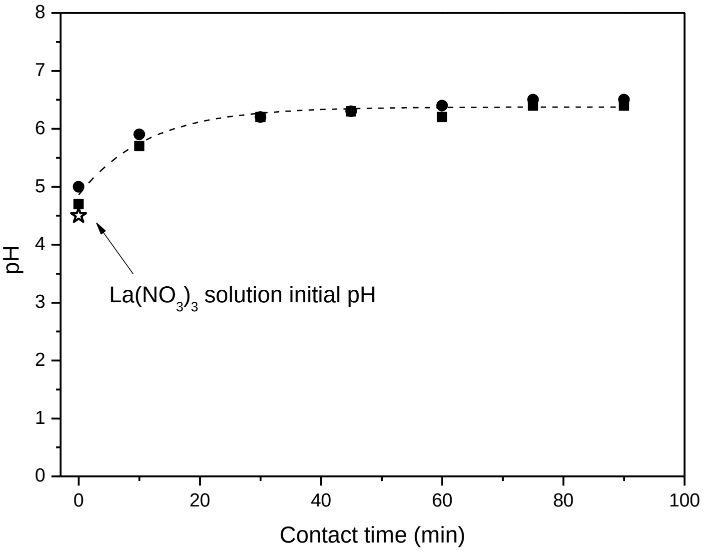

Fig. 2. pH evolution during La uptake experiments (initial concentration of lanthanum: 19 mM).

For both solids, upon contacting with the lanthanum solution, the pH quickly increased from 4.5 to about 6 in 15 min; then it remained constant till the end of the experiment (90 min). In this range of pH, no insoluble lanthanum species can be formed; therefore all the La^{3+} ions in solution were available for adsorption.

3.2. Adsorption kinetics

To evaluate the kinetic behaviours of the solids, they were contacted with a 19 mM lanthanum nitrate solution, corresponding to 0.48 mmol/g of available lanthanum ions in solution. The adsorption equilibrium time is defined as the time required for adsorbate concentration to reach a constant value. The equilibrium times for lanthanum adsorption were approximately 30 and 90 min for AC and MAC, respectively (Fig. 3). Compared to AC, surface modification of AC substantially improved adsorption ability (reaching the maximum uptake capacity of 0.48 mmol/g) but increased equilibrium time. This difference of equilibrium time between AC and MAC can be explained by the steric hindrance of the polyamine that affects (by preferential blocking of micropores) the intraparticle diffusion in the AC pores, still active in MAC even if the main mechanism is supposed coordination by amino groups, confirmed by the large difference in adsorption values also at short contact times.

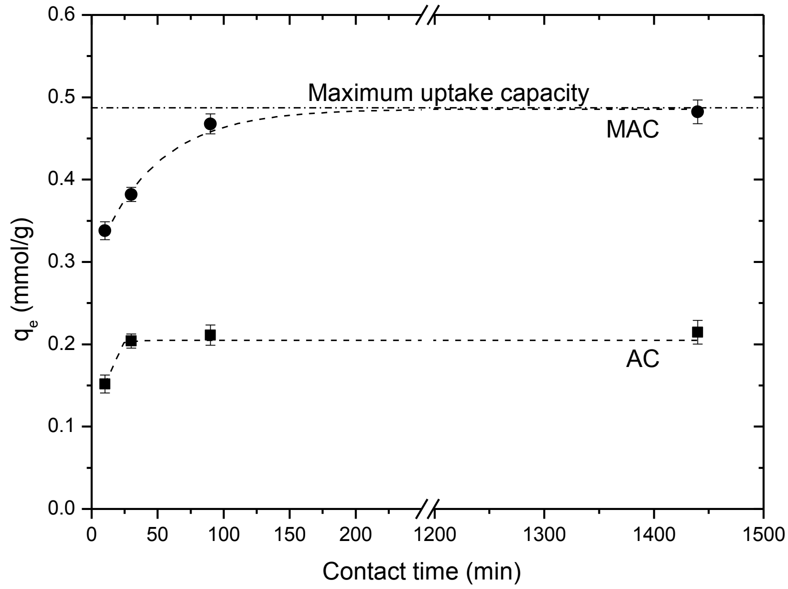

Fig. 3. Adsorption kinetics of lanthanum by AC and MAC (initial concentration of lanthanum: 19 mM).

Pseudo-first-order and pseudo-second-order kinetic models were used to evaluate the experimental data, in order to examine the controlling mechanisms of the adsorption process. A linear form of pseudo-first-order kinetics can be expressed as:

$$log_{10}(q_e - q_t) = log_{10}q_e - \frac{K_1}{2.303}\mathrm{t} \qquad (5)$$

where q_t and q_e are the adsorption capacities at time t and at equilibrium (mmol/g), respectively; K_1 is the rate constant of pseudo-first-order adsorption (min^{-1}).

The pseudo-second-order model based on the adsorption equilibrium capacity can be expressed as:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2} \quad (6)$$

where K_2 (g/(mmol·min)) is the rate constant of pseudo-second-order.

The kinetics parameters for lanthanum adsorption are listed in Table 2. The correlation coefficients (R^2) of the pseudo-second-order equation are higher than those of the pseudo-first-order equation. Also, the calculated q_e values are in better agreement with the experimental results for pseudo-second-order kinetic model, indicating better suitability of pseudo-second-order model to describe adsorption kinetics of lanthanum onto both the adsorbents. Pseudo-second-order kinetic model implies that the predominant process here is chemisorption, confirming also other literature studies where similar solid adsorbents were used [13].

Table 2

Pseudo-first-order and pseudo-second-order calculated q_e (cal) and experimental q_e (exp) values for AC and MAC. The kinetics parameters of the models are also reported.

	q_e (exp) (mmol/g)	**First-order kinetics model**			**Second-order kinetics model**		
		K_1 (min^{-1})	**q_e (cal) (mmol/g)**	**R^2**	**K_2 (g/(mmol·min))**	**q_e cal (mmol/g)**	**R^2**
AC	0.21	5.30×10^{-4}	0.02	0.09	2.68×10^{-5}	0.22	0.99
MAC	0.48	2.53×10^{-3}	0.05	0.71	2.66×10^{-5}	0.48	0.99

3.3. Adsorption isotherms

To evaluate the effect of initial concentration on the uptake, AC and MAC were contacted with a lanthanum nitrate solution at different concentrations (in the range 10 - 200 mM). As shown in Fig. 4 the lanthanum uptake increases with the lanthanum equilibrium concentration up to reach an asymptotic value that is considerably higher in case of the MAC modified carbon (0.8 mmol/g compared to 0.55 mmol/g for AC). The amount of the lanthanum adsorbed by MAC at equilibrium was found in some cases more than double than that of AC, even if the surface area resulted more than 8 times lower. This indicates that the surface modification treatment has significantly enhanced the capacity of activated carbon to bind aqueous lanthanum ions with the surface functional ligands. High adsorptive capacity is supposed accomplished by strong La-binding to -NH_2 and -NH groups formed on the AC surface.

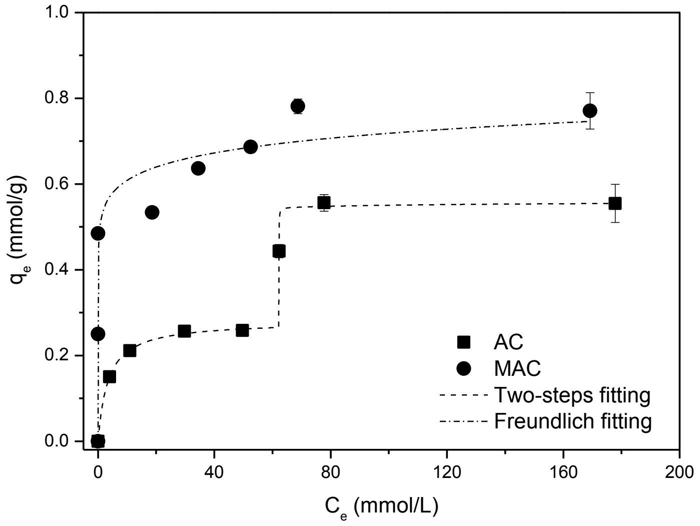

Fig. 4. Adsorption isotherm of lanthanum by AC and MAC (concentration range of lanthanum: 10 - 200 mM).

The experimental results concerning the equilibrium established between adsorbed lanthanum ions on the adsorbent and lanthanum ions remaining in solution were interpreted according to Langmuir and Freundlich adsorption isotherms [23].

The Langmuir model assumes a monolayer sorption onto a surface and no interaction between the adsorbed molecules, even on adjacent sites and it is represented by:

$$\frac{c_e}{q_e} = \frac{c_e}{q_{max}} + \frac{1}{q_{max}\,K_L} \qquad (7)$$

where q_{max} (mmol/g) is the maximum monolayer adsorption capacity of the adsorbent and K_L (L/mmol) is the Langmuir constant related to energy of adsorption.

Freundlich formulation was developed to present multilayer adsorption on a heterogeneous surface and the equation representing the Freundlich model can be written in the linearized form:

$$\log_{10} q_e = \log_{10} K_F + \frac{1}{n} \cdot \log_{10} C_e \qquad (8)$$

where K_F [mmol/(g·(mmol/L)$^{1/n}$)] and n are Freundlich constants related to the adsorption capacity and the adsorption intensity, respectively.

Values of Langmuir and Freundlich constants are reported in Table 3.

Very close regression coefficients were calculated in the case of adsorption on AC (R^2 = 0.83 for Langmuir and 0.86 for Freundlich), meaning that both the models are not enough accurate. Furthermore, a complex sorption mechanism appears to be active in this case: a two-steps process. For this reason the data were also fitted by a multi-step model, as suggested in literature [24], according to the equation:

$$q_e = \frac{q_1 K_1 C_e}{1+K_1 C_e} + \frac{q_2 K_2((C_e-b)+abs(C_e-b))}{2+K_2((C_e-b)+abs(C_e-b))} \qquad (9)$$

where q_1 and q_2 represent the adsorption capacities of the two steps (mmol/g), K_1 and K_2 are the adsorption equilibrium constants of the two steps (1/mmol) and b the limit concentration. The calculated parameters are: q_1 = 0.28, q_2 = 0.28, K_1 = 0.29, K_2 = 57.8, b = 62.2 and the obtained fitting has a coefficient correlation (R^2) equal to 0.99. For this reason it is the one reported in Fig. 4. According to literature [25], the interpretation of multi-steps models is related to the formation of uniform but different layers. In the present case bi-modal pore diameter distribution affecting the intraparticle diffusion in the AC pores could be supposed. This assumption finds a confirmation in the pore diameter distribution obtained by the desorption cumulative pore volume where it results a bi-modal distribution of diameters, one centred at 27.1 Å and the other one centred at much lower values since it is not detected by the measure.

Data of adsorption on MAC, indeed, were better fitted by Freundlich adsorption isotherm. The value of K_F, which related to the adsorption capacity, was 0.52 for MAC, whereas the unmodified AC was only 0.08 under the same conditions. This finding was due to that the chemical modification by the amine onto the AC surface increased the coordinating mechanism involved in lanthanum adsorption.

The Freundlich model suggests also that the adsorption process is taking place on heterogeneous surface with different mechanisms occurring. These mechanisms are: coordination of lanthanum ions by amino groups of the amine and intraparticle diffusion in the AC pores. In particular the intraparticle diffusion is supposed to be present even if slowed down by the steric hindrance of the polyamine, which blocks the micropores. Furthermore, the asymptotic value is reached both in AC and MAC at the same initial concentration representing a further confirmation that the amine addition does not hinder the mechanism of intraparticle diffusion but improves only the total captured ions amount, due to the presence of the amino groups. This difference in lanthanum ions adsorption between unmodified AC, where the mechanism is imputable only to intraparticle diffusion, and MAC, where the effect of the polyamine is present, is about 0.2 mmol/g at the plateau. In this perspective, it is reasonable to suppose that this difference is equal to the extent of coordination by the free amino groups. Starting from these hypotheses, it is possible to correlate the number of coordinating sites of the polyamine to the coordinated ions and to calculate a coordination number for lanthanum. The coordinating sites of the polyamine are the amino groups, equal to 4.8 mmol/g (0.8 mmol/g of loaded polyamine multiplied by 6 numbers of amino groups for each mmol of polyamine). Supposing that all the amino groups are involved in the coordination of the 0.2 mmol/g of lanthanum ions, the coordination number for lanthanum would be 24, i.e. 24 sites would be needed to trap each lanthanum ion. Nonetheless, this number disagrees with literature, because lanthanum ions were proved to have coordination numbers in the range of 6-13 [26-29]. Therefore, this data gives strong indications that the adsorption of the organic chains in solid matrix occurs not only covering the surface area but involving also the amino groups.

It is anyway worth to observe that also the Freundlich model does not fully fit the data, suggesting the overlapping of different mechanisms and the complexity of finding a model representing them.

Table 3

Langmuir and Freundlich constants for the adsorption of lanthanum on AC and MAC.

	Langmuir			Freundlich		
	q_{max} (mmol/g)	K_L (L/mmol)	R^2	K_F (mmol/(g·(mmol/L)$^{1/n}$)	n	R^2
AC	0.68	0.03	0.83	0.08	2.6	0.86
MAC	0.84	0.09	0.32	0.52	13.9	0.89

Table 4

Adsorption capacities of different adsorbents for lanthanum.

Sorbent	Max adsorption capacity (mg/g)	Equilibrium time (h)	pH	Ref.
AC	94.5	0.5	6	This study
MAC	116.7	1.5	6	This study
Carboxylic acid derivative of AC	89.5	1	6	[13]
AC modified with Schiff's base	144.8	1	6	[13]
Micro algal cells	100	6	6	[30]
2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester-grafted magnetic silica nanocomposites	55.9	1	5.5	[31]
Carboxylic acid functionalized diatomite	139.5	0.3	7	[32]
Polydopamine membrane	59.5	24	5	[33]
Iron oxide loaded calcium alginate beads	123.5	28	5	[34]
Biosorbents of animal (fish scales)	200.0	4	6	[35]
Biosorbents of plant origin (neem saw dust)	160.2	36		[35]
Bamboo charcoal	120	7	7.2	[36]
AC prepared from rice husk	175.4	1	3.5	[37]
Bentonite	37.3	-	6	[38]
Leaves powder of Platanus orientalis	28.7	1	4	[39]
Montmorillonite	56.9	-	6.7	[40]
Na-bentonite named GMZ bentonite	26.8	0.5	5	[41]
Sargassum biomass	73.6	0.7	5	[42]
Sargassum polycystum Ca-loaded biomass	125.0	24	5	[43]
Lewatit TP 214 Resin	38.5	60	5.2	[44]

Table 4 summarizes the values of the Langmuir maximum adsorption capacity (reported in mg/g) of other adsorbents. AC presents higher lanthanum adsorption performances when compared with other adsorbents reported in the literature; then, upon the amine addition, it approaches the capture capability of more valuable solids. So a comparison with these adsorbents indicates a high lanthanum adsorption capacity of the AC and MAC and further demonstrates the suitability for lanthanum adsorption.

3.4. Desorption and regeneration tests

Desorption studies are important to investigate the possibility for the recovery of metals adsorbed on the adsorbent surface, as well as for the regeneration of the adsorbent for subsequent reuse.

The desorption was performed following a methodology developed in a previous work [19]: by contacting the lanthanum containing AC and MAC with solutions at very acid conditions.

The studies on desorption process were performed at first on all the samples prepared at different initial metal concentration (from 10 to 200 mM of lanthanum concentration) to evaluate the effect of the different captured ions content. In Fig. 5 the desorbed lanthanum ions as a function of the adsorbed amounts are reported. Linear trends can be evidenced for both the materials, suggesting that desorption process is pH dependent in both the cases: as higher is the uptake, as higher is the release for every studied solid. But a difference can be detected between AC and MAC. The slopes of the fitting lines are slightly different, indicating a different and more efficient mechanism in the case of the modified carbon. This behaviour is supposed to be due to the coordination and further protonation of the amino groups.

Furthermore, it is important to note that the found linear trends do not correspond to the bisector: from Fig. 5 it is for instance evident that also in the case of MAC, characterized by a higher desorption efficiency, if 0.55 mmol/g of lanthanum ions are captured, only 0.40 mmol/g of lanthanum ions are then released, suggesting that only a multiple adsorption-desorption process could result in a total recovery.

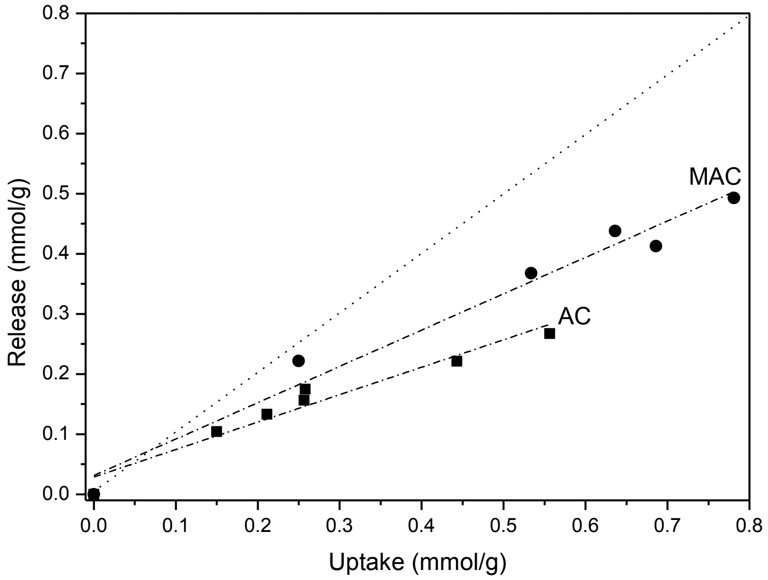

Fig. 5. Release as a function of captured lanthanum.

By desorption the metal recovery is obtained and, furthermore, the spent adsorbent can be reused. To test this reusability possibility, consecutive adsorption-desorption cycles were repeated four times using the same adsorbent in solutions. Only MAC sorbent is used in this set of experiments, due to the higher efficiencies showed both in adsorption and desorption, if compared to AC. Each cycle is characterized by 90 min of adsorption, separation, 90 min of desorption obtained with a 1M HNO_3 solution, separation, and a regeneration process to restore the amino groups protonated after release with 1 M NaOH. The results of desorption tests are shown in Fig. 6. The adsorption and desorption efficiencies of the MAC from the four cycles were 92.2, 99.9, 99.9, 99.9% for adsorption and 84.4, 76.9, 74.4, 70.0% for desorption, respectively: after four cycles, the lanthanum adsorption capacity of the MAC does not decrease while the desorption capacity decreases slightly from 84.4 to 70%.

The results in Fig. 6 clearly show that the modified activated carbon can be used repeatedly without a significant lost in its lanthanum adsorption capacity. This behaviour indicates that the adsorbent can be used successfully at least four times after regeneration for the removal of lanthanum.

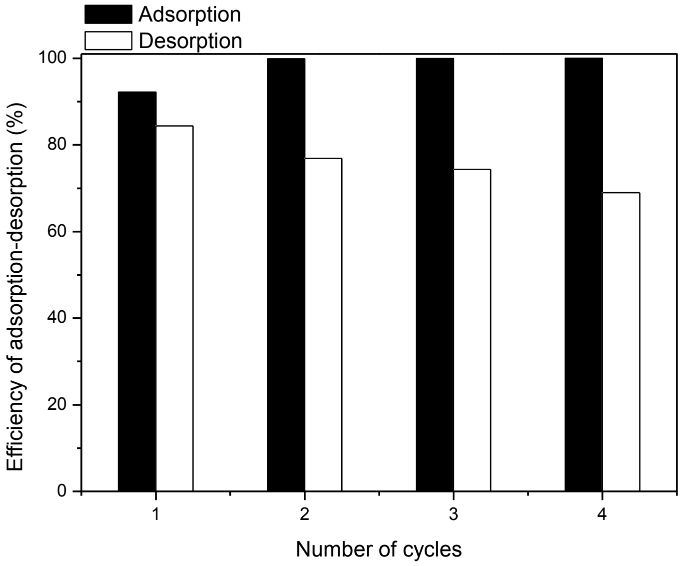

Fig. 6. Adsorption–desorption performance of MAC by multiple cycles of regeneration (lanthanum concentration 19 mM).

4. Conclusions

The adsorption of lanthanum onto activated carbon and modified activated carbon followed by desorption has a potential in terms of efficiency. The following main conclusions can be drawn:

(1) Both the studied systems are able to capture and desorb lanthanum ions even if a strong improvement in the efficiency values is detected by using modified carbons (uptake 100% until initial concentration of about 2600 ppm and release over 95%).

(2) Lanthanum adsorption seems to better follow a pseudo-second-order kinetic in both the systems.

(3) Intraparticle diffusion is the most reliable adsorption mechanism in the case of activated carbon, while coordination due to modifying agent overlapping to the still present but slowed down intraparticle diffusion has to be considered in the case of modified AC.

(4) There are strong indications that the adsorption of the organic chains onto the solid matrix occurs involving the amino groups, thus hindering the lanthanum accessibility to some of the NH/NH_2 groups in the further uptake step.

(5) The desorption step is efficiently carried out at pH =1 confirming that the release phase is greatly pH dependent.

(6) After four cycles, the lanthanum adsorption capacity of the modified activated carbon does not decrease while the desorption capacity decreases slightly from 84.4 to 70%. This behaviour indicates that the adsorbent can be used successfully at least four times after regeneration for the removal of lanthanum.

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