NEODYMIUM(III) SORPTION ONTO SODIUM BENTONITE AND MAGNETIC ACTIVATED CARBON: A COMPARATIVE STUDY

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In this paper, the liquid-solid extraction of neodymium(III) by sodium bentonite and magnetic activated carbon was reported. Neodymium (Nd) is a key element that widely applied in high-tech industries; various parameters, such as: the time, metal concentration, ionic strength, effect of initial pH etc., have been studied to assess the efficiency of sodium bentonite and magnetic activated carbon for the removal of Nd(III). Optimal extraction yield was achieved at pH equal to 9.1 for sodium bentonite and in the range of pH_i from 3.1 to 9.2 for the magnetic activated carbon. The time needed for magnetic activated carbon to absorb the maximum of Nd(III) is 100 min and 60 min for sodium bentonite. The experimental capacity obtained was 528 mg g^{-1} for magnetic activated carbon and 503 mg g^{-1} for sodium bentonite. In order to validate the performance of this extractants, kinetics and diffusional studies were also developed throughout this study. Adsorption equilibrium data were calculated for Langmuir and Freundlich isotherms. It was found that the sorption of Nd(III) on sodium and magnetic activated carbon was better suited to the Freundlich adsorption model.

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INTRODUCTION

The rare earth elements (REEs), including lanthanide elements as well as yttrium and scandium, are 17 in number. They are divided conventionally into two groups: the light group (Sc, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd) and the heavy group (Y, Tb, Dy, Ho, Er, Tm, Yb, Lu). The REEs are widely used in various field, such as chemical engineering, metallurgy, nuclear energy, optical, magnetic, luminescence, laser materials, high-temperature superconductors and secondary batteries, catalysis, red phosphors etc.[1-4] Rare earth elements (REEs) are of great importance owing to their unique physical and chemical properties best suited for the creation of advanced materials for high-technology devices.[5,6] A significant increase of rare earth metals production is expected in the coming years due to increasing demand for them.[7] Rare earth ores tend to be localized, and often include radioactive elements[8], they occur together in nature in some minerals, e.g. bastnasite, monazite and xenotime.[9]

Neodymium is one of the most abundant rare earth elements. Neodymium (Nd) is an important member of the first triad of the lanthanide series and its atomic number being 60.[2,5,6,9] Neodymium compounds were first commercially used as a glass dye and they are still used as a popular additive in glass. Its color, due to the Nd(III) ion, is often reddish-purple but changes with the type of lighting due to fluorescent effects. Neodymium oxides are also used as a laser material to replace ruby in order to produce a coherent light, as components of advanced materials such as high temperature ceramics and superconductors, and in catalytic systems.[10] Neodymium gains great attention due to

high demand in the Nd-Fe-B magnet industry, especially in high performance electric motors in hybrid electric vehicles and direct-drive wind turbine generators.[1, 3,11] Neodymium–iron–boron permanent magnets is costs less than samarium–cobalt permanent magnets.[2,5] Currently, (Nd–Fe–B) permanent magnets are used in hard disk drives, motors in hybrid cars and MRI machines, among others.[8] Since the development of the iron–neodymium–boron (Nd–Fe–B) permanent magnet in 1980, the production volume of neodymium metal has increased dramatically. Currently, about 10,000 tons of Nd-FeB alloy magnets are produced annually.[3,8,12] The separation from other rare earth elements requires energy consuming procedures; therefore, there is an industrial demand for the recycling of neodymium from scrap to save time and energy.[8,12]

Various methods can be used to recover this metal from aqueous solutions. Traditional methods, for example such as ion exchange, precipitation and solvent extraction have been found to be ineffective at a very low concentration of contaminated metal ions.[2] Adsorption is the most popular method in which activated carbon or ion exchange resins are usually applied. Adsorption phenomenon in solution systems plays a vital role in many areas of practical environmental technology, which are mainly in water and wastewater treatment due to several advantages such as high efficiency, simple operation and easy recovery/reuse of adsorbent.[13]

In recent years, the preparation of organic–inorganic superabsorbent composites has attracted great attention because of their relatively low production cost, high water absorbency and their considerable range of applications in agriculture and horticulture.[14] Recently, clays and clay minerals were found to be very important for preparation of this super absorbent nanocomposite.[15] The bentonite materials exhibit highly interesting properties, e.g. high specific surface area, cation exchange capacity (CEC), porosity, and tendency to retain water or other polar and non-polar compounds.[16]

An innovative technology that gains attention is the use of magnetic materials for magnetic separation of pollutants from effluents. In environmental applications, magnetic separation can be a promising method for a novel purification technique because it produces no contaminants such as flocculants and has the capability to treat a large amount of wastewater within a short time, and magnetic adsorbent can be quickly separated from a medium by a simple magnetic process.[17,18]

In this paper, the liquid-solid extraction of neodymium is performed by sodic bentonite and magnetic activated carbon. Various parameters have been studied to assess the performance of sodic bentonite and magnetic activated carbon for the removal of Nd(III). The nature and the properties of the sorbent materials play an important role in the effective retention of analytes from the sample solution.[19]

EXPERIMENTAL

Reagents

Neodymium solution at 10^{-2} M was prepared by dissolving of neodymium nitrate (3.3025 g) in 1 L of distilled water (purchased from Sigma-Aldrich). The initial pH of the sample solutions were adjusted by using dilutes HNO_3 or NaOH (from Sigma-Aldrich). $NaNO_3$ (from Merck) NaS_2O_3 (from Merck) were used in the salt effect. Arsenazo III solution (10^{-3} M) from Fluka was prepared by dissolving 0.0820 g sample in absolute ethanol. Hydrochloric acid (from Organics), sulfuric acid (from Fluka), nitric acid (from Cheminova) and acetic acid (from Riedel de Haen) were used from elution study.

The natural bentonite used in this study was obtained from deposits in the area of Maghnia, Algeria. For synthesis of magnetic activated carbon, $FeCl_2.4H_2O$ (from Sigma Aldrich), $FeCl_3.6H_2O$ (from Panreac), activated carbon (Aldrich Chemical Company Inc.), NH_4OH (from Sigma-Aldrich), HNO_3 and $Fe(NO_3)_2$ (from Sigma Aldrich) were used.

Apparatus

The extraction of Nd(III) was studied by the batch process using a stirring vibrator (Haier model). pH measurements were performed with a pH meter using a combined electrode mark (Adwa). Thermogravimetric analyses of samples (TGA) were performed using a SDT Q600 thermogravimetric analyzer at a heating rate of 20°C min^{-1}, under nitrogen atmosphere, at Tlemcen-Algeria. FTIR was performed using a Cary 630 FTIR from Agilent Technologies, at Tlemcen-Algeria. The BET-N$_2$ method was used to determine the specific surface area of the bleaching earths, using a Volumetric Analyzer (Nova-1000). A magnet and centrifugation for the recovery of the magnetic activated carbon and sodium bentonite, respectively, in the aqueous phase were used. Samples containing Nd(III) were analyzed by spectrophotometer (Analytik Jena Specord 210 Plus) with Arsenazo III as ligand.

Preparation of sodium bentonite

For the purification of bentonite, 120 g of natural bentonite was dispersed in 1.5 L of distilled water, and after agitation during 15 min; a buffer solution of sodium citrate (pH 7.3) was added. The mixture was heated under agitation at 75° C for 20 min and then, 15 g of sodium thiosulfate ($Na_2S_2O_4$) was slowly added. After 15 min under agitation, the mixture was cooled and centrifuged at a rotational speed of 6000 rpm for 15 min. The solid recovered was washed two times with HCl 0.05 M (1.5 L) during 3 h.

To convert the purified bentonite into sodium form an amount of bentonite was dispersed in NaCl solution (1 M) with a 1/5 mass ratio and after agitation for 2 h, the solid was separated by centrifugation at a rotational speed of 6000 rpm for 15 min, this operation was repeated three times. The solid was washed three times with distilled water, and it was dried at 40 °C for 3 days.[13]

The chemical composition of purified bentonite was found to be 64.7 % SiO_2, 18.1 % Al_2O_3, 0.95 % Fe_2O_3, 2.66 % MgO, 0.8 % K_2O, 0.61 % CaO, 0.2 % TiO_2, 1.43 % Na_2O, 0.05% As, 10.0% loss on ignition. The cation-exchange capacity (CEC) of bentonite was determined according to the ammonium acetate saturation method and was found to be 0.070 equiv. per 100 g of dry natural-Bt and 0.098 equiv per 100 g of dry Na–Bt. The BET specific surface area increase from 50 $m^2 g^{-1}$ in natural-Bt to 95 $m^2 g^{-1}$ in Na–Bt.[13]

Preparation of magnetic activated carbon

Dissolved $FeCl_3$ (7.8 g, 28 mmol) and $FeSO_4$ (3.9 g, 14 mmol) in 400 mL of water at 70 °C. Added 3.3, 6.6 or 9.9 g of activated carbon in different solutions to obtain the following adsorbent:iron oxide w/w ratios 1.0:1.0, 1.5:1.0 and 2.0:1.0. To these suspensions added a solution of NaOH (100 mL, 5 mol L^{-1}) drop wise to precipitate the iron oxides. Washed the obtained solid materials with distilled water and dried in an oven at 100 °C for 2 h. After the preparation a simple test with a magnet (0.3 T) was carried out showing that the whole material is completely attracted to the magnet.[20]

Extraction and analysis procedure

The batch experiments were carried out to evaluate the adsorption processes and the equilibrium states of Neodymium mobilization. Nd(III) solution was prepared by dilution of the high purity stock standard solution (10^{-2} mol L^{-1}). 4 mL of Nd(III) solution of known concentration, and 0.01 g of solid adsorbent (sodium bentonite or magnetic activated carbon) were mixed in an Erlenmeyer flask with stopper, under vigorous stirring. Both liquid and solid phases were separated by centrifugation for sodium bentonite and by magnet for magnetic activated carbon. The solid phase was regenerated for other applications and the liquid phase was measured by the UV-visible spectrometer.[21] The sample of Nd(III) was analyzed by a mixture of 100 µL Arsenazo III and 100 µL of Nd(III) in a medium of pH=3.0. The product of interaction of Arsenazo III with Nd(III) was determined at $\lambda_{max}=653$ nm.[22]

The percentage of neodymium ions that was extracted by the magnetic particles was determined by Eqn. (1) and the rate of Nd uptake, q_t (mg g^{-1}), was determined by Eqn. (2), where C_i, C_t and C_e were the initial, time and equilibrium Nd(III) concentration (mol L^{-1}), respectively; V(4 mL) was the volume solution; M molecular weight (g mol^{-1}), and m was the mass of the particles magnetic used (0.01 g).[18,21]

$$\varphi = \frac{C_i - C_e}{C_i} 100 \qquad (1)$$

where φ is the extraction yield in %.

$$q(mg/g) = (C_0 - C_e)V\frac{M}{m} \qquad (2)$$

Desorption procedure

After saturation of the magnetic particle by the neodymium ions, the regeneration of adsorbents is an important aspect in adsorption, using the HCl, HNO$_3$, H$_2$SO$_4$, CH$_3$COOH. We can determine the best eluting agent with Eqn. (3).[18,21]

RESULTS AND DISCUSSION

TGA of magnetic activated carbon

TGA of magnetic activated carbon showed a weight loss due to water vapor of approximately 10 % at temperatures lower the 100 °C and a weight loss of 65 % between 350 and 500 °C relating to the oxidation of carbon. A residual weight of 25 % was found after the oxidation of the activated carbon, bonded to the Fe oxide in the composite.
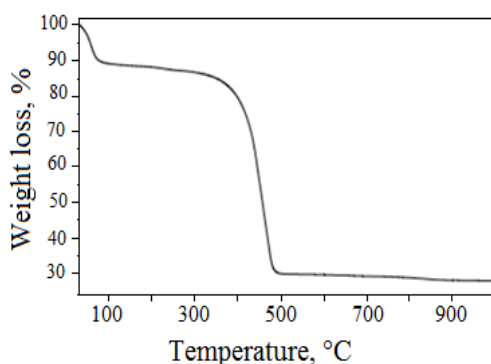

Figure 1. TGA patterns of magnetic activated carbon.

BET Analysis

BET surface area and microporous volumes obtained for both composites are shown in Table 1.

BET analysis showed that the specific surface area and micropore volume are affected by the presence of iron oxide in the magnetic activated carbon. It is found that the specific surface area decreases from 931 to 656 m^2 g^{-1} and we also noticed a decrease in the volume of micropores from 0.263 to 0.176 cm^3 g^{-1}. In both cases, a reduction of 30 % corresponds to the presence of iron oxide in the magnetic activated carbon.

Table 1. BET surface areas and microporous volumes for magnetic activated carbon.

Composite	BET surface area (m^2 g^{-1})	$V_{micropores}$ (cm^3 g^{-1})
Activated carbon	931	0.263
Magnetic activated carbon	656	0.176

XRD analyses of magnetic activated carbon

The XRD analyses of magnetic activated carbon suggest the presence of magnetite or a maghemite in the structure of composites (Figure 2). The peaks of magnetic activated carbon appear broader suggesting smaller crystallite size (ca. 25 nm for Fe oxide and 16 nm for the magnetic activated carbon, obtained by Scherrer's equation). Weak diffraction peaks at d=2.45 and 2.70 Å are also observe which might be related to the presence of small amounts of goethite and also some hematite.
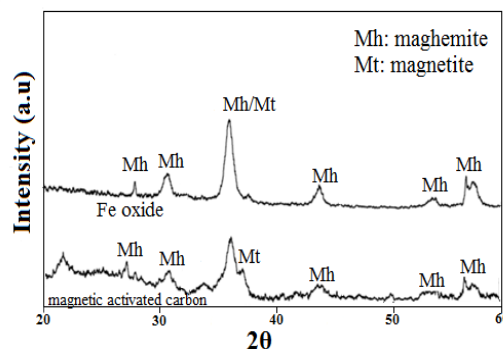

Figure 2. XRD for the magnetic activated carbon and Fe oxide.

SEM micrograph

The morphologies of the magnetic activated carbon were studied by scanning electron microscopy (SEM) (Figure 3).
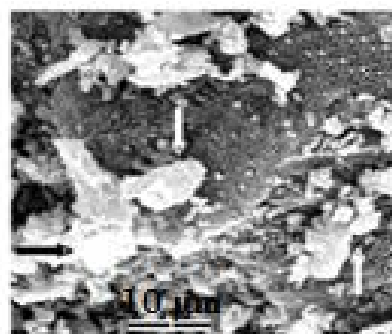

Figure 3. SEM micrograph of magnetic activated carbon.

Effect of initial pH

Both the pH and the ionic strength of solutions are regarded as the key factors during adsorption process, which is related to the formation of soluble metal complexes and subsequently their stabilities in aqueous solutions. It is well known that surface charge of adsorbent can be modified by charging the pH of the solution and the chemical species in the solution depends on this parameter.[1,23] Sorption of thorium by magnetic activated carbon and sodium bentonite were studied at different pH ranging from 2.0 to 9.2 and the results are show in Figure 4. The amount of magnetic particles, the initial concentration, and the contact time were kept to be constants. It is evident that percentage of extraction increases with increasing pH value in the range of 2.0 to 9.2 for sodium bentonite. At low pH values, protons are strongly competing with adsorbates.[24-26] Hence, adsorbent is less able to retain neodymium and adsorption of Nd is very low. After pH 2.0, adsorption of Nd increases sharply up to pH 3.0, for magnetic activated carbon. This evolution can be explained by the La Chatelier principle, when hydronium ions concentration decreases more (pH increase), the metal ions were extracted more and converted to the product. At this pH, (pH=3.0), the maximum yield extraction of Nd(III) was achieved.[6,27]
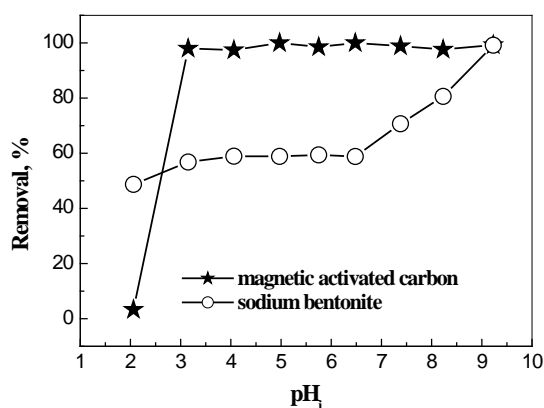

Figure 4. Removal of Nd(III) by magnetic activated carbon and sodium bentonite as a function of initial pH, $[Nd(III)]_0 = 10^{-3}$ mol L^{-1}, w=0.01 g, V=4 mL, $\emptyset$=250 rpm, room temperature.

Effect of contact time

The fast recovery of target element on adsorbent is very important in a large scale application. Thus, the influence of contact time on the recovery of Nd(III) was examined to determine the time required for the attainment of adsorption equilibrium. The effect of equilibration time on the extraction of 10^{-3} M. Nd(III) with 0.01 g of sodium bentonite and magnetic activated carbon has been studied in the range 1-180 min.[1,28]

Figure 5 illustrates the extraction yield as a function of time. It is seen that initially neodymium extraction yield increases as a function of time. For sodium bentonite, it reaches a maximum of 97 % in 10 min. For magnetic activated carbon, the time taken to reach a maximum of 97 % is 50 min. This difference can probably be attributed to a number of available active adsorption sites onto the two solid extractants.[1] After 10 min for sodium bentonite and 50 min for magnetic activated carbon, the Nd(III) adsorption did not change with time anymore. Hence, a contact time of

10 min and 50 min for sodium bentonite and magnetic activated carbon respectively, were sufficient to reach equilibrium. For sodium bentonite and magnetic activated carbon the t_{50} is 3 and 8 min, respectively. The equilibrium values of Nd uptake (q_e) on the magnetic activated carbon and sodium bentonite are 57.23 mg g^{-1} and 57.62 mg g^{-1}, respectively.
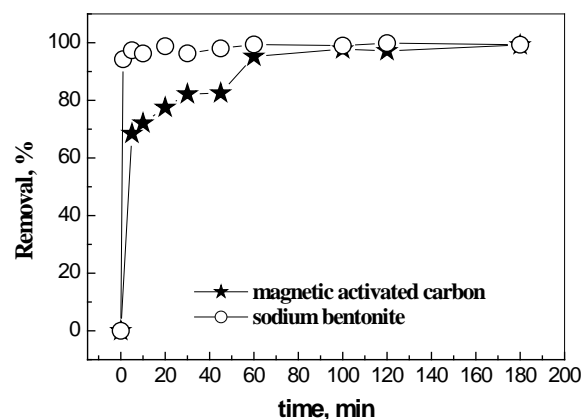

Figure 5. Removal of Nd(III) by magnetic activated carbon and sodium bentonite as a function of time, $[Nd(III)]_0=10^{-3}$ mol L^{-1}, w=0.01 g, V=4 mL, $\emptyset$ =2 50 rpm, room temperature
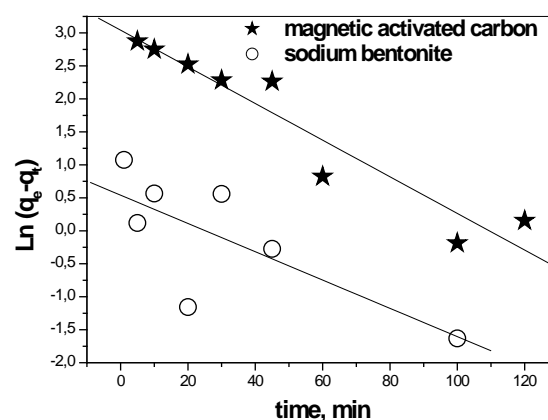
Adsorption kinetics

Figure 6. Pseudo-first order plot of Nd(III) adsorption kinetics onto the magnetic activated carbon and sodium bentonite as a function of time, w=0.01 g, V=4 mL, $\emptyset$=250 rpm, room temperature.

Kinetics of sorption describing the solute uptake rate, which, in turn, governs the residence time of the sorption reaction, is one of the important characteristics defining the efficiency of sorption.[29] Two popularly used kinetic models, pseudo-first-order (Eqn. 4) and pseudo-second-order (Eqn. 5),[27] were used to fit the data, as shown in Figures 6 and 7, indicating the linear forms of the pseudo-first order and the pseudo-second order kinetics respectively.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (5)$$

Here q_e and q_t are the amounts of sorbed Nd(III) on magnetic activated carbon and sodium bentonite at equilibrium and at time t, respectively (mg g^{-1}), k_1 is the first-order adsorption rate constant (min^{-1}), k_2 is the pseudo-second-order adsorption rate constant (g mg^{-1} min^{-1}).

The results presented in Figure 6, Figure 7 and Table 2 indicate that the pseudo-second-order kinetic model yields a better fit and suggest that the chemisorption processes could be a rate-limiting step. The correlation coefficients obtained are, 0.998 for magnetic activated carbon and 0.999 for sodium bentonite and the theoretical q_e values calculated from the pseudo-second-order equation are in agreement with the experimental data (Table 2), suggesting that adsorption system of neodymium by magnetic activated carbon and sodium bentonite are a pseudo-second-order reaction.
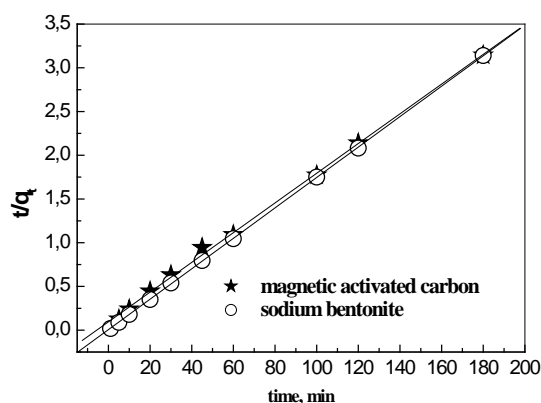

Figure 7. Pseudo-second order plot of Nd(III) adsorption kinetics onto the magnetic activated carbon and sodium bentonite as a function of time, w= 0.01 g, V= 4 mL, Ø=250 rpm, room temperature.

Table 2. Comparison of the Pseudo-First order and Pseudo-Second order models for sorption of neodymium on magnetic activated carbon and sodium bentonite at ambient temperature.

Composite	q_e (exp.) mg g^{-1}	Pseudo-first order	Pseudo-second order
Magnetic activated carbon	57.23	R=0.954 q_e(calc.)= 20.92 mg g^{-1} K_1=0.021	R=0.998 q_e(calc.) = 58.82 mg g^{-1} K_2=0.003
Sodium bentonite	57.62	R =0.749 q_e(calc.)= 1.716 mg.g^{-1} k_1=0.021	R =0.999 q_e(calc.)= 58.89 mg g^{-1} k_2=0.057

Boyd relationship represents an intra-particle diffusion model as follows.[30]

$$\frac{q_t}{q_e} = 1 - \frac{6}{\pi^2} \overset{e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \frac{x^3}{3!} + .., -\infty < x < \infty}{\sum_{n=1}} \frac{1}{n^2} \exp\left(-\frac{Dn^2\pi^2}{r^2}t\right)$$

(6)

Here D is the intra-particle diffusion coefficient and r is the particle radius. For short times (when q_t/q_e is less than 0.3), Eqn. (6) can be reduced to Eqn. (7).

$$q_t = k_{1D}\sqrt{t}$$ (7)

where k_{ID} is the intra-particle diffusion constant. The significant property of this equation is that, if the intra-particle diffusion is the only rate-limiting step, then the linear plot of q_t versus $\sqrt{t}$ should pass through the origin. On the other hand, if the intercept of plots do not equal zero, then it indicates that the intra-particle diffusion is not the sole rate determining step.[31] Then Eqn. (7) is modified to Eqn. (8).[32]

$$q_t = k_{1D}\sqrt{t}$$ (8)

where S is a constant and reflects the boundary layer effect. Investigation of various reports about the sorption rate shows that the intra-particle diffusion model is the most popular one for the diffusion rate-controlling step that has been used in conjunction with the surface reaction models to recognize the adsorption kinetics.
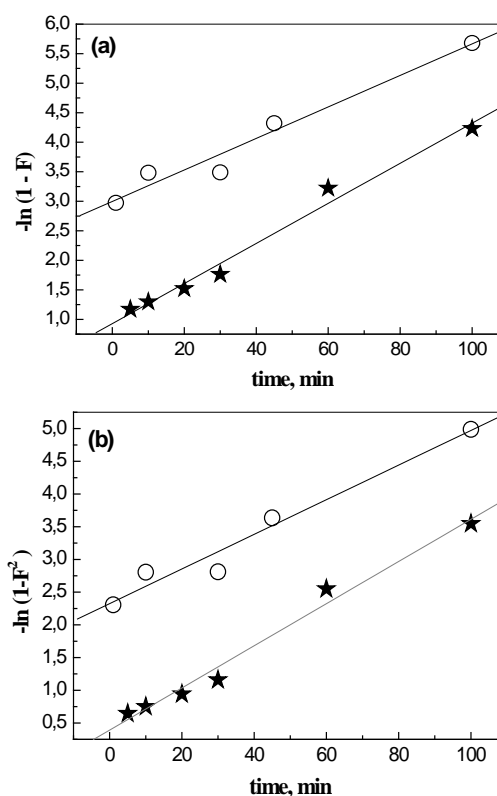

Figure 8. Intra-particle diffusion kinetic models for the adsorption of Nd(III), (a) magnetic activated carbon, (b) sodium bentonite, [Nd(III)]$_0$=10^{-3} mol L^{-1}, w=0.01 g, V=4 mL, Ø=250 rpm, room temperature.

The plot of the Boyd relationship for the sorption of neodymium, at initial concentration equal to 1 mmol L^{-1}, by sodium bentonite and magnetic activated carbon is shown in Figure 8. Based on this Figure, it may be seen that the intra-particle diffusion of Nd(III) onto the sodium bentonite and magnetic activated carbon occurred in 2 stages. The first linear represent the external mass transfer or film diffusion (boundary layer) and the rapid distribution of Nd(III) molecules onto the outer surface of sodium and magnetic activated carbon. The second linear portion corresponds to the intra-particle diffusion and binding of Nd(III) molecules

into the internal active sites of the extractants. Moreover, the second stage of the lines does not pass through the origin. This means that the intra-particle diffusion, although important over longer contact time periods, is not the rate-limiting step in the adsorption process of Nd(III).[13,18]

Diffusion study

The neodymium (III) transport from the solution phase to the surface of sodium bentonite and magnetic activated carbon occurs in several steps. The overall adsorption process may be controlled either by one or more of these steps. (i) The diffusion of ions from the solution to the surface of sodium bentonite and magnetic activated carbon, (ii) the diffusion of ions within the solid extractant, (iii) the chemical reaction between ions and functional groups of the extractants. If the liquid film diffusion controls the rate of exchange, the following relation can be used (Eqn. 9).

$$-\ln(1-F) = kt \qquad (9)$$

If the case of diffusion of ions in the sodium bentonite and magnetic activated carbon phase controlling process, then Eqn. (10) is used.

$$-\ln(1-F) = kt \qquad (10)$$

where F is the fractional attainment of equilibrium, which is expressed as $F=q_t/q_e$. In both eqns. (9) and (10), k is the kinetic coefficient or rate constant. k is defined by eqn (11).

$$k = \frac{D_r \pi^2}{r_0^2} \qquad (11)$$

where D_r is the diffusion coefficient in the sodium bentonite and magnetic activated carbon phase and r is the average radius of solids extractants.

When the adsorption of metal ion involves mass transfer accompanied by chemical reaction the process can be explained by the moving boundary model. This model assumes a sharp boundary that separates a completely reacted shell from an unreacted core and that advances from the surface toward the center of the solid with the progression of adsorption. In this case, the rate equation is given by Eqn. (12).[27, 29]

$$3 - 3(1-F)^{2/3} - 2F = kt \qquad (12)$$

The results of application of both the mathematical models are shown in Figure 9.

The comparison of the kinetic and diffusion parameters of Nd(III) sorption onto magnetic activated carbon and sodium bentonite (Table 3), shows that the adsorption of Nd(III) can be controlled by both diffusion model (film diffusion and particle diffusion) for both the extractants.

Effect of initial metal concentration

Solutions of Nd(III) of different concentrations were prepared and mixed each with the same mass of adsorbent (0.01 g). The results showed that the amount of Nd(III) sorbed per unit mass of the particles magnetic increased with the initial metal concentration (Fig. 10). At a concentration of 10^{-2} M of Nd(III), sorption capacities reach 528 mg g^{-1} for magnetic activated carbon and 503 mg g^{-1} for sodium bentonite. This sorption capacity is very interesting for liquid–solid extraction, because in the literature, most studies were done with liquid–liquid extraction.[33-37]
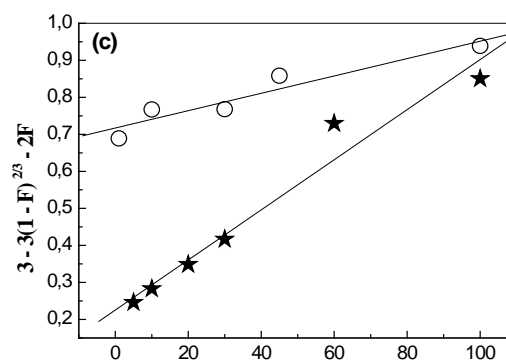

Figure 9. Plots of diffusion study for Nd(III) sorption on magnetic activated carbon (∗) and sodium bentonite (O) at different time. [Nd(III)]$_0$=10^{-3} mol L^{-1}, w=0.01 g, V=4 mL, Ø=250 rpm, room temperature: Film diffusion (a), interne diffusion (b), chemical reaction (c).

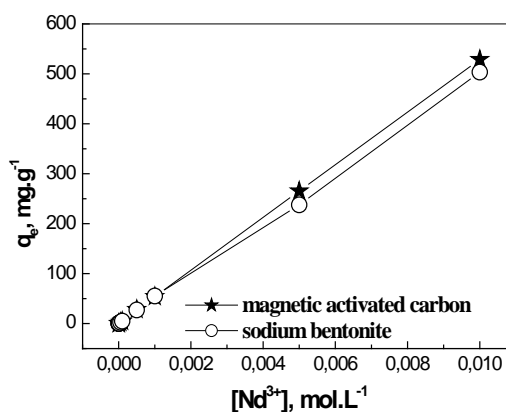**Figure 10.** Removal of Nd(III) magnetic activated carbon and sodium bentonite as a function of [Nd]. w=0.01 g, V=4 mL, Ø=250 rpm, room temperature.

Table 3. Kinetic and diffusion parameters of neodymium sorption onto magnetic activated carbon and sodium bentonite.

[Nd(III)]=10^{-3} M	Film diffusion Eqn. (9)	Particle diffusion Eqn. (10)	Chemical reaction Eqn. (12)
Magnetic activated carbon	K=0.033 min^{-1} R=0.991	K= 0.032 min^{-1} R=0.991	K=0.006 min^{-1} R=0.979
Sodium bentonite	K=0.026 min^{-1} R=0.981	K =0.026 min^{-1} R=0.981	K=0.002 min^{-1} R=0.951

Isotherm adsorption

The sorption data, commonly known as adsorption isotherms, are basic requirements for the design of adsorption systems.[18] The Freundlich and Langmuir isotherms are the most commonly used adsorption isotherms for describing a non-linear equilibrium of adsorbate between solution and adsorbent at a fixed temperature.[1] For the interpretation of both models, we have used the following equations.[38]

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \qquad (13)$$

$$\ln q_e = \ln K_F + n \ln C_e \qquad (14)$$

where C_e is the equilibrium concentration of Nd(III) (in mg L^{-1}), q_e is the amount of Nd(III) sorbed on the sodium and magnetic bentonite (mg g^{-1}), K_L is the Langmuir adsorption constant (L mg), q_m is the maximum amount of Nd that can be sorbed, K_F is the Freundlich adsorption constant and n is a constant that indicates the capacity and intensity of the adsorption, respectively.

The Freundlich isotherm correlated better than Langmuir isotherm with the experimental data from adsorption equilibrium of neodymium ions by magnetic activated carbon and sodium bentonite (Figures 11 and 12; Table 4). The correlation coefficients of Freundlich isotherm and Langmuir isotherm are very high.
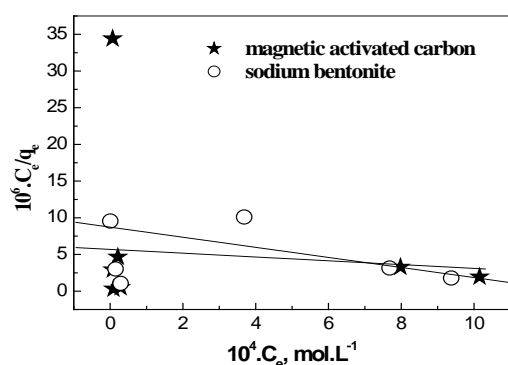
Effect of ionic strength

The effect of NaNO$_3$, NH$_4$NO$_3$ and Na$_2$S$_2$O$_3$ on the performance of extraction was studied. Figures 13 and 14 show the influence of ionic strength on sorption of neodymium by magnetic carbon activated and sodium bentonite.

Table 4. Isotherm models parameters for the adsorption of Nd(III) on magnetic activated carbon and sodium bentonite.

Composite	Langmuir isotherm	Freundlich isotherm
Magnetic activated carbon	R=0.254	R=0.961 K_F=2757954.94 n=1.269
Sodium bentonite	R=0.268	R=0.968 K_F=707858.858 n=1.092

Changing the ionic strength by the addition of an electrolyte influences adsorption in at least two ways,[39,40] one by affecting interfacial potential and therefore the activity of electrolyte ions and adsorption and secondly by affecting the competition of the electrolyte ions and adsorbing anions for sorption sites. Figures 13 and 14 show that the addition of all salts, increase the ionic strength and decrease extraction yield of Nd by magnetic activated carbon and sodium bentonite, this can be explained by a competitiveness in the extraction between Na$^+$/NH$_4^+$ and Nd(III).[41]

Figure 11. Langmuir isotherm plot for the sorption of Nd(III) onto and magnetic activated carbon and sodium bentonite.

Figure 13. Removal of neodymium by magnetic activated carbon as a function of electrolytes under standard conditions.

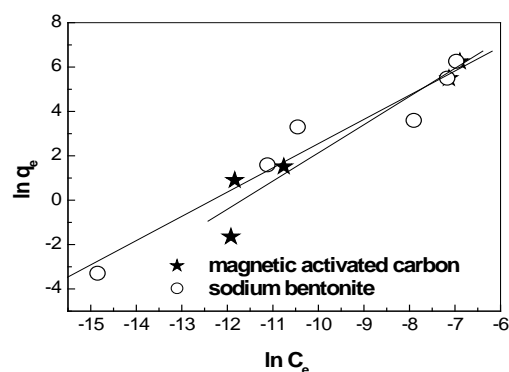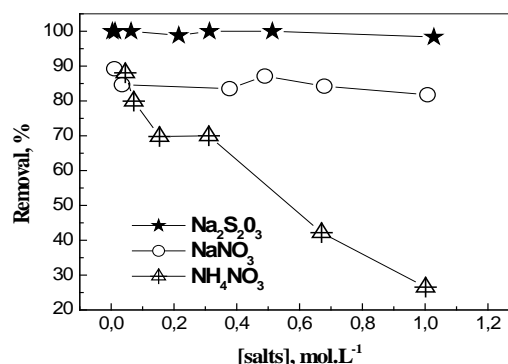**Figure 12.** Freundlich isotherm plot for the sorption of Nd(III) onto and magnetic activated carbon and sodium bentonite.
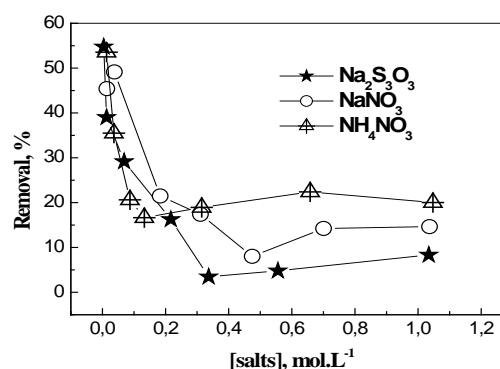

Figure 14. Removal of neodymium by magnetic activated carbon as a function of electrolytes under standard conditions.

Desorption study

Desorption is a key process in sorption studies because it determines the economic value of the sorption process. To investigate the feasibility of regenerating used adsorbent, desorption experiments were performed using various eluting agents, namely HCl, HNO$_3$, H$_2$SO$_4$ and CH$_3$COOH at a concentration of 0.5 mol L^{-1} after Nd(III) adsorption. To a saturated sample the appropriate sorbent (0.01 g), 4 mL of the selected acid was added and kept for 3 h. The elution yield is calculated by Eqn. (3). Though hydrochloric acid, nitric acid and acetic acid have given significant elution yield for magnetic activated carbon (close to 100 % in a single step), sulfuric acid showed a less efficiency. The elution kinetics was made to optimize this study. Figure 16 show the kinetics of elution efficiency. This study shows that initially desorption of neodymium is rapid, it reaches a value of around 80 % after 10 min of agitation for the three acids. Between 10 and 100 min, the elution yield is stable then it reaches its maximum value after 150 min of agitation (around 100 %). The behaviour of the three acids for the desorption is similar.
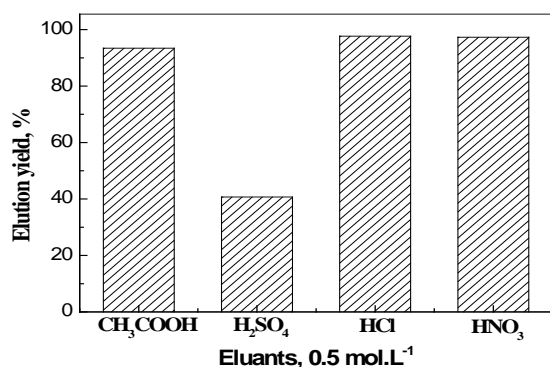

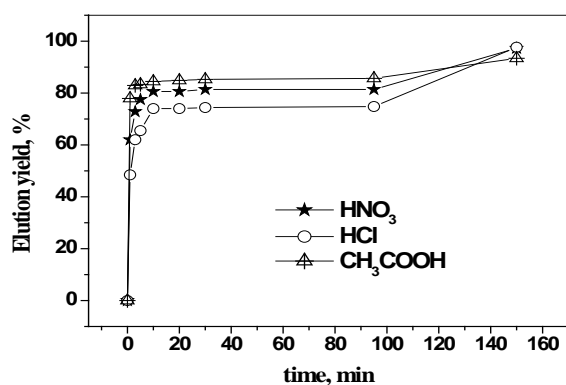**Figure 15**. Optimum eluants for quantitative recovery of neodymium.

Figure 16. Effect of contact time on the desorption of Nd(III).

CONCLUSION

The activated carbon magnetic and sodium bentonite were successfully applied for the removal of Nd(III) from seawater matrix. Equilibrium time, pH effect, kinetics, isotherms, ionic strength and effect of initial metal concentration were examined carefully. The characterization of magnetic activated carbon by BET, XDR and TEM indicate that the activated carbon was functionalized by iron oxide. The optimal adsorption efficiency could be observed over 99.9 % at pH 9.2 for sodium bentonite and in a range between 3.1 and 9.2 for magnetic activated carbon. The pseudo-second order model accurately fits the Nd adsorption kinetics for both adsorbent and the data agrees well with Freundlich adsorption isotherm model. The experimental capacity obtained was 528 mg g^{-1} for magnetic activated carbon and 508 mg g^{-1} for sodium bentonite. The sorption of Nd(III) achieves equilibration at 100 and 60 min for magnetic activated carbon and sodium bentonite, respectively.

The synthesized magnetic activated carbon has the great potential for fast and effective neodymium recovery from seawater media. The magnetic activated carbon have superiority in separation, it can be quickly separated from a medium by a simple magnetic process and the results obtained in this comparative study make this magnetic particle as promising material for sorption, immobilization and pre-concentration of rare earth elements, radioactive metal and heavy metal ions from large volume of solutions.

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