Removal of Neodymium from Aqueous Solutions Using a New Fe-modified Nanoporous Adsorbent of Fe-MCM-41

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Abstract

In our study a new Fe-modified nano porous of MCM-41 was synthezied hydrothermally with cetyltrimethylammoniumbromide (C_{16}TAB) as surfactant and charactrizied using XRD, SEM, FT-IR and BET. This work reports the adsorption of Neodymium from aqueous solution onto Fe-MCM-41.100 ml of stock solution of Neodymium was prepared.Various factors such as pH,the amount of adsorbent were considered. The optimium conditions obtained were: pH value= 5-8,the amount of Fe-MCM-41=0.0025gr.The Langmuir, Freundlich, Temkin and Dubinin-Rudeshkuvich models have been applied and the equilibrium adsorption was found fit the Freundlich isotherm model(R^2= 0.98). The removal amount of adsorbed Neodymium was obtained 97% and charactrizied by Inductivity coupled optical emission spectroscopy (ICP-OES).

Keywords: Fe-MCM-41, Adsorption, Neodymium.

Introduction

Water pollution is the contamination of water bodies such as lakes, rivers, oceans, and groundwater caused by human activities, which can be harmful to organisms and plants which live in these water bodies. Water pollution by toxic heavy metals through the discharge of industrial waste is a worldwide environmental problem. The presence of heavy metals in streams, lakes and groundwater reservoirs has been responsible for several health problems with plants, animals and human beings [1]. Heavy metal contamination exists in aqueous waste stream from many industries such as metal plating, mining, tanneries, painting, car radiator manufacturing, as well as agricultural sources where fertilizers and fungicidal spray are intensively used [2,3].

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Concern about environmental protection has increased over the years from a global viewpoint. The removal of heavy metals such as Neodymium from aqueous solution, especially from wastewater is an important topic in environmental control. Neodymium compounds can be harmful for our eyes and skin; Also it is dangerous to inhale Neodymium gases and can cause lung cancer. The discovery of nanoporous materials with high surface areas provides many active sites for the removal of inorganic pollutants. Therefore, we decided to study more thoroughly the process of adsorption of Nd3+ using synthesis and characterization of Fe-MCM-41 as an adsorbent. These kinds of adsorbents(nanoporous material) are so much used in separation, catalysts, sensore, ecology and nanotechnology[4]; So synthesis of these materials have been drown with enough attention. To enhance the quality and efficiency of nanoporous compounds could we modify their structure by incorporation of the organic or inorganic reagents such as various ligands and some hetroatoms including Cu, Fe[5], Al[6], Zn, etc. These materials have been used as catalytic templates for the production of carbon nanotubes (CNTs) by acetylenepyrolysis at atmospheric pressure; therefore we used Fe as modifying agent to have an effective adsorbent for eliminating pollutants from aqueous solution.

Experimental
Material and apparatus

Cetyltrimethylammoniumbromide (C_{16}TAB), $Nd(NO_3)_3$ and Sodium silicate solution were purchased from Aldrich and Merck chemical companies. XRD: Phillips X'Pert mpd, X-ray diffractometer, BET: Quantochrome Nova 2200e, FT-IR: Bruker Vector 33, SEM: Phillips XL30, pH meter: Schott CG841, ICP-OES: Optima 7300V HF version.

prepration of nanoporous Fe- MCM-41

The synthesis of MCM-41 sample was started by dissolving cetyltrimethylammoniumbromide (C_{16}TAB)(surfactant) in distilled water, then sodium silicate (silicon source) and $Fe(NO_3)_3$ were added to it. Our work was done hydrothermally because the prepared above mixture was put in an electric furnace. The obtained precipitation was washed by HNO_3 to make many active sites for adsorbing solution and after drying, the adsorbent was prepared.

Adsorbate

A stock solution of Nd^{3+} was prepared (50 ppm) by dissolving required amount of Neodymium Nitrate [$Nd(NO_3)_3$] in distilled water. The stock solution was diluted with distilled water to obtain desired concentration (in 100 ml flask).

Batch adsorption studies
Effect of pH on Neodymium sorption

In order to study the dependence of the removal efficiency on pH, the experiments

were conducted in the pH range 3.45-8.3.We investigated optimum pH value by employing initial concentration of Nd^{3+}(10 mg L^{-1}) and 0.025 gr of Fe-MCM-41. The initial pH value were adjusted with 0.01M $CH_3COONa.3H_2O$, 0.01M CH_3COOH or 0.01M Na_2HPO_4, $NaH_2PO_4.H_2O$ to form a series of pH from 3.45-8.3. The suspension was shaken for 210 min and after that the solution was filtered and the amount of adsorbed Nd^{3+} charactrizied by ICP-OES.

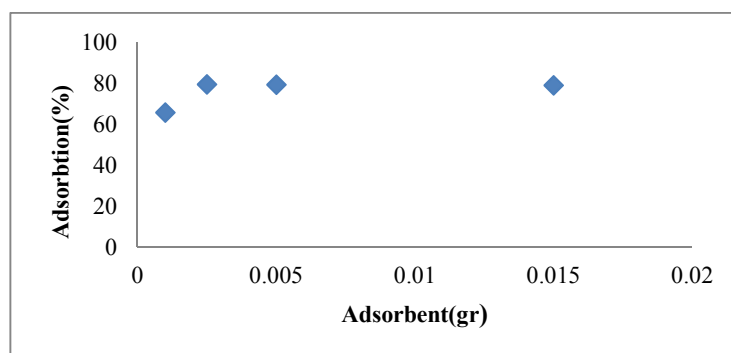*Effect of the amou nt of Fe-MCM-41*

The effect of sorbent amount on equilibrium uptake of Nd^{3+} with constant concentration and volume of Neodymium (10ppm and 25 ml) were studied and different amount of Fe-MCM-41(0.001gr, 0.005gr, 0.0025gr, 0.015gr) was added to each flask containing constant concentration of Nd^{3+}(10ppm) and kept on shaker for 210 min and after that, the amount of adsorbed Nd^{3+}analyzed by ICP-OES. The adsorption percentage was calculated using Eq.1:

$$\text{Adsorption (\%)} = 1 - \frac{Ceq}{Ci} \times 100 \quad \text{Eq.(1)}$$

Where C_i and C_{eq} are initial and the final concentration of studied Neodymium ion in its aqueous solution. The results are illustrated in Figure 1.

Figure 1. Effect of increasing the amount of Fe-MCM-41 on Nd^{3+} adsorption(T=25°C,the samples were shaken vigorously)

Equilibrium isotherms

Several equilibrium models have been developed to describe adsorption isotherm relationships. The Langmuir and Freundlich equations are the world-widely used models because of their simplicity. Langmuir adsorption isotherm is often used to describe the maximum adsorption capacity of an adsorbent and the Freundlich adsorption isotherm is an indicator of the extent of heterogeneity of the adsorbent surface. The Temkin suggests a linear decrease of sorption energy and The D-R model was also applied to estimate the porosity apparent free energy and characteristics of adsorption. These isotherm models can be expressed by the following equations:

• The Langmuir Eq.:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \left(\frac{1}{K_L\, q_{max}}\right)\left(\frac{1}{C_e}\right) \quad \text{Eq.(2)}$$

Where q_{max} is the maximum metal ions uptake per unit mass of adsorbent (mg/g), and b is

Langmuir constant (L/mol) which is related to the adsorption intensity. Therefore, a plot of C_e/q_e versus C_e, gives a straight line of slope 1/qmax and intercept $1/(q_{max}\ b)$ as shown in Figure 2.
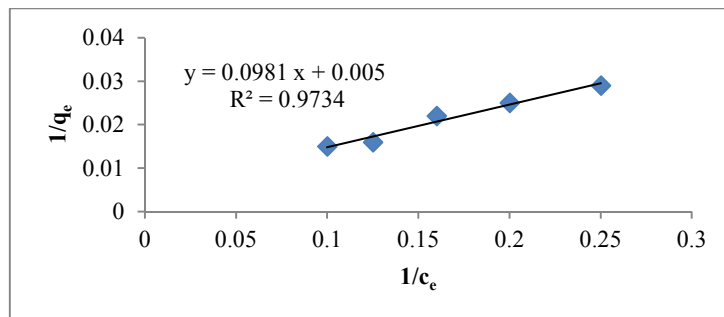

y = 0.0981 x + 0.005
R² = 0.9734

Figure 2.Langmuir isotherm plot for adsorption of Nd^{3+}.

• The Freundlich Eq.:

$$Log q_e = Log K_F + \left(\frac{1}{n}\right) Log C_e \quad \text{Eq.(3)}$$

Where the Freundlich constants KF and n,

which respectively indicating the adsorption capacity and the adsorption intensity, are calculated from the intercept and slope of plot lnqe versus lnCe as shown in Figure 3.
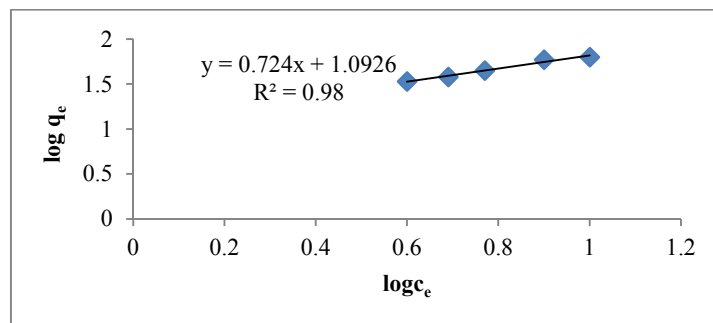

y = 0.724x + 1.0926
R² = 0.98

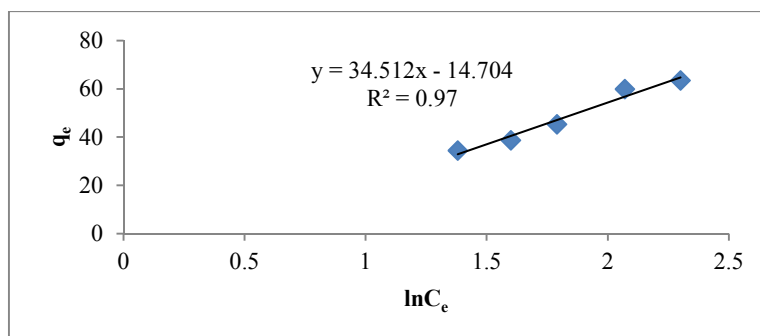**Figure 3.** Freundlich isotherm plot for adsorption of Nd^{3+}.

• The Temkin Eq.[7,8]:

$$q_e = \frac{RT}{b} Ln(A.C_e) \quad \text{Eq.(4)}$$

And also can be simplified to the following equation:

$q_e = \beta ln\alpha + \beta ln C_e$ Eq.(5)

Where $\beta=(RT)/b$, T is the absolute temperature in Kelvin and R is the universial gas constant, 8.314 (mol K)$^{-1}$. The constant b is related to the heat of adsorption[9,10]. The adsorption data was analyzed according to the simplified form and the result are shown in Figure 4.

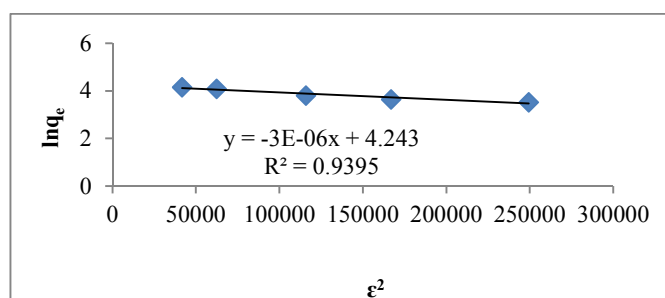**Figure 4.** Temkin isotherm plot for adsorption of Nd^{3+}.

- The Dubinin-Radushkevich (D-R) Eq.:

$$Lnq_e = LnQ_m - K\varepsilon^2 \quad \text{Eq.(6)}$$

Where K is a constant related to the adsorption energy, Q_m is the theoretical saturation capacity and ε isthe Polanyi potential calculated from following equation [11,12]:

$$\varepsilon = RT\,Ln\,(1+\frac{1}{C_e}) \quad \text{Eq.(7)}$$

The slope of the plot of lnqe versus ε^2 gives $K(mol^2(KJ^2)^{-1})$ and the intercept yields the adsorption capacity, $Q_m(mg\ g^{-1})$. The data obtained from this model are shown in Figure 5.

Figure 5. Dubinin- Radushkevich isotherm plot for adsorption of Nd^{3+}.

For these four discussed isotherm models, the amount of Nd^{3+} adsorbed at equilibrium onto Fe-MCM-41, qe (mgL^{-1}), was calculated by the following mass balance relationship:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad \text{Eq.(8)}$$

Where C_0 and C_e are the initial and equilibrium liquid-phase concentration of Nd^{3+}, respectively $(mg\ L^{-1})$; V is the volume of the solution(L), and W is the weight of Fe-MCM-41(gr).

Kinetic modeling and kinetic studies

Sorption studies were investigated using 0.0025gr of Fe-MCM-41 and constant concentration of Nd^{3+}(4ppm).The Fe-MCM-41 was thoroughly mixed with each flask containing solution of Neodymium and the suspension were shaken at room temperature for required time interval viz.5,15,60,240 min and after filtering the clear solution were analyzed for residual Nd^{3+} concentration in the solution by ICP-OES.

The pseudo-first order equation

The pseudo-first order equation [13-14], is generally expressed as:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad \text{Eq.(9)}$$

Where q_e and q_t are the sorption capacities at equilibrium and at time t, respectively (mg/g) and k_1 is the rate constant of pseudo-first order sorption (1/min). Integrating and applying

boundary conditions $0 \to t$ and $0 \to q_t$, gives:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \text{Eq.(10)}$$

When the values of $\ln(q_e - q_t)$ were linearly correlated with t, the plot of $\ln(q_e - q_t)$ versus t will give a linear relationship from which k_1 and q_e can be determined from the slope and intercept of the graph, respectively (Figure 6).
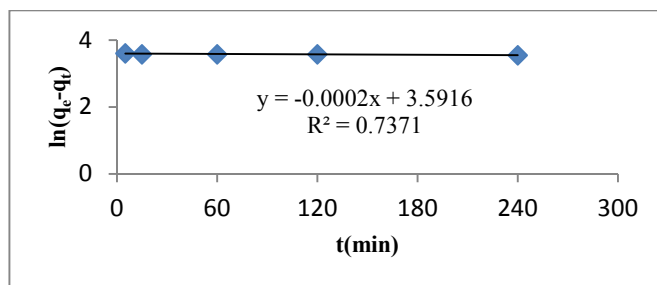

Figure 6. Pseudo first-order kinetic for Nd^{3+} adsorption onto Fe-MCM-41.

The pseudo-second order equation

The pseudo-second order chemisorptions kinetic equation [15–20] is expressed as equation:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \quad \text{Eq.(11)}$$

Where q_e and q_t are the sorption capacity at equilibrium and at time $t, (\text{mg g}^{-1})$ respectively and k_2 is the rate constant of the pseudo-second order sorption (g mg^{-1} min^{-1}). For the boundary conditions $0 \to t$ and $0 \to q_t$, the integrated form of above equation becomes:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad \text{Eq.(12)}$$

This equation can be rearranged and linearized to obtain:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \text{Eq.(13)}$$

The second- order rate constants were used to calculate the initial sorption rate, given by the following equation:

$$h = k_2 q_e^2 \quad \text{Eq.(14)}$$

if the second-order kinetic is applicable, then the plot of t/q_t versus t should show a linear relationship. Values k_2 and equilibrium capacity qe were calculated from the intercept and slope of plots of t/q_t versus t as shown as Figure 7.
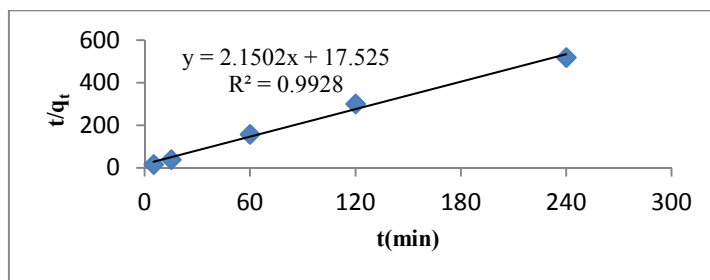
Figure 7. Plot of the pseudo second-order model.

Results and Dissection

Figure1 indicates that 0.0025gr of Fe-MCM-41 is an optimum amount and in 0.0025gr, we have maximum adsorption for Nd^{3+} and after that we have no significant rise in our data. Figures 2, 3, 4 and 5 show the data obtained from isotherm models which used in this research. The calculated value of the equilibrium isotherm models parameters are given in Table.1.

Table1. The isotherm models constant and R^2 for adsorption of Nd^{3+}.

Isotherms	Parameters	Value
Langmuir	q_{max}(mol/g)	200
	K_L(Lit/mol)	0.05
	$^*R_L$	0.6
	R^2	0.973
Freundlich	K_F	12.25
	1/n	0.724
	R^2	0.98
Temkin	α(Lit/mol)	0.65
	β	34.51
	R^2	0.97
D-R	$K(J^2)$	1.61
	Q_m(mol/g)	69.58
	R^2	0.939

* A dimensionless separation factor R_L was used to judge the favorable adsorption and has been applied in the following equation:

$$R_L = \frac{1}{(1 + K_L . C_0)} \quad \text{Eq.(15)}$$

Where K_L is the Langmuir constant and C_0 is the highest initial concentration(mg/L). If:

$R_L > 1$ Unfavorable

$R_L = 0$ Llinear

$0 < R_L < 1$ Favorable

$R_L = 0$ Irreversible

It is clear from the table that the correlation coefficient of Freundlich comparatively higher than the others. The order of R2 for isotherms was found as:

Freundlich(0.98) > Langmuir(0.973) > Temkin(0.97) > D-R(0.939).

The value of RL for adsorption of Nd3+ was 0.6. This value indicates that the adsorption behavior of Fe-MCM-41 is favorable for Neodymium (III) [R_L< 1].

Figures 8 and 9 ?????? indicate kinetic studies and it is clear that the second-order kinetic model is more applicable than first-order kinetic. The order of R2 for these models was found as following:

Second-order kinetic model (0.992) > First-order kinetic model (0.737)

And finally figures 10, 11, 12 and 13 show the pictures obtained from FT-IR,XRD ,SEM and BET respectively; The FT-IR spectrum shows a band at 660cm-1 which is related to formation of Si- O- Fe. The peak of Curve in XRD analysis represents the formation of nanoporous adsorbent because it appears at 2ө < 3(this is an area for all nanoporous compounds). The highlighted part in figure 11 is a good evidence for presence of Fe in our adsorbent (2ө ~ 4).The picture of SEM indicates our adsorbent has porous structure. BET is a method which is used widely for determination of pore sizes of nanoporous adsorbent. The important results for this method were highlighted in figure 13.
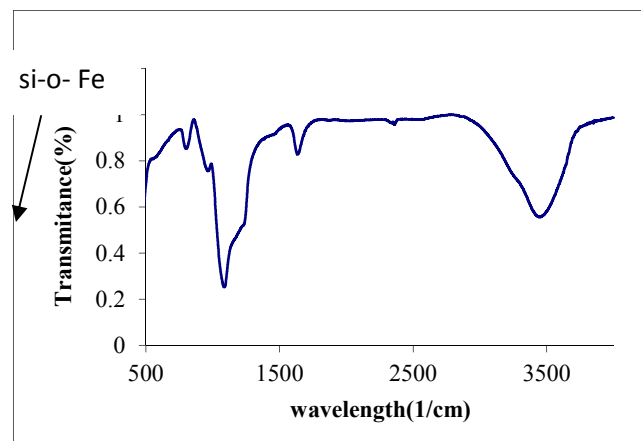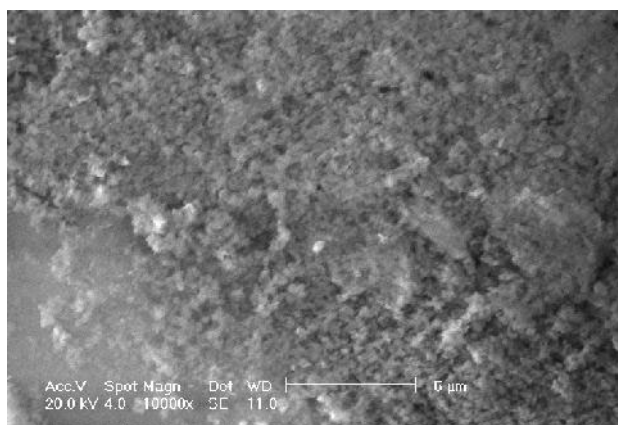

Figure 10. FT-IR spectra of Fe-MCM-41.
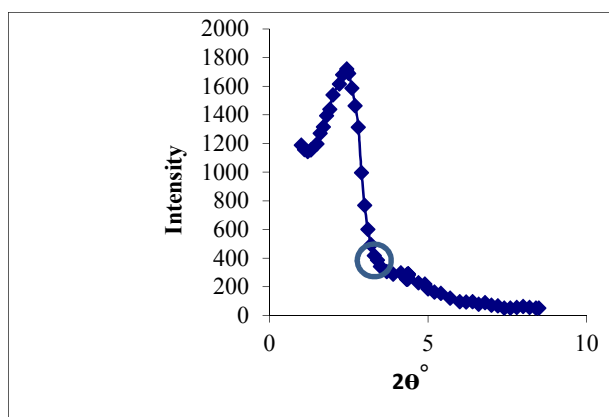
Figure 11. XRD pattern of Fe-MCM-41**.**

Figure 12. Scanning electronic micrographs of Fe-MCM-41.

Conclusion

Investigation of our adsorbent efficiency for removal of Nd^{3+}, is the real aim of our work and all results were satisfactory. The following major conclusions can be drawn based on the above study:

Optimization of pH and adsorbent mass was carried out. The experimental results have been analyzed by Langmuir, Freundlich, Temkin and D-R adsorption isotherms. Freundlich isotherm has a better fitting model than the others and has a higher correlation regression coefficient. The R_L value showed that Fe-MCM-41 was favorable for the adsorption of Nd^{3+}. The equilibrium adsorption is practically achieved in 210 min. The Fe-MCM-41 used exhibited a high selectivity towards Neodymium (III) removal from aqueous solution. The correlation coefficient for the second-order kinetic model is 0.992, which led to believe that the pseudo- second- order kinetic model provided good correlation for the sorption of Nd^{3+} onto adsorbent and it is much better than pseudo- first- order kinetic because R_2 for this model was obtained 0.737.

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