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Adsorption Studies on Modified Magnesia Cement

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Abstract: Adsorption removal of actinide and lanthanide ions from aqueous solutions using modified synthetic humic acid magnesia cement was investigated. Experiments were carried out as a function of solute concentration and temperature (25–50°C). Several kinetic models were used to test the experimental rate data and to examine the controlling mechanism of the adsorption process. Various parameters such as effective diffusion coefficient, activation energy and entropy of activation were evaluated. The study showed that the pore diffusion is the rate limiting for the metal ions studied. The results indicated that modified synthetic humic acid magnesia cement (MF-2) can be used as an efficient adsorbent for removal of actinide and lanthanide ions from radioactive wastewaters.

Keywords: adsorption, actinide, lanthanide, magnesia cement

INTRODUCTION

Humic substances are brown and black biopolymers associated with soil, sediment, and particulates suspended in water and consist of material derived from the degradation of animals and plants (1, 2). These substances are a mixture of weak-acid polyelectrolytes, organic macromolecules exhibiting a large range of molar-mass distribution, substructures, and functionalities (3, 4). It is reported that metal ions complex formation by humic acid, HA, can reduce their bioavailability and toxicity (5, 6). The nature of the interaction between HA and cations in the environment is therefore of considerable importance. However, the physical chemistry of such interactions leads to

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a distribution of different types of metal binding (7, 8). Therefore, the mobility and transport of metal ions in the environment is affected by the presence of these humic substances (1).

Gadolenium (Gd) is present with uranium as fission products as well as in different uranium minerals. Gd is important in controlling the neutron fluxes in nuclear reactors (9). This species can act as diluent for nuclear fuels without impairing or reducing neutron capture by the target.

One of the most important practical method for treatment of radioactive waste is adsorption (10). Cost-effective alternative technologies or sorbents for treatment of metal contaminated waste streams are needed. At low concentrations, removal of such pollutants is more effectively implemented by ion exchange or adsorption on solid sorbent (11). However, improved sorption capacity of ion exchange resins may have advantages over non-specific adsorbents.

Adsorption on cement is a promising technique for this purpose (12). The use of magnesia cement is not so popular because it disintegrates and loses its strength on prolonged exposure to water due to the leaching out of magnesium chloride from the cement. Therefore, the resultant mass contains essentially magnesium hydroxide, which is porous in nature and thereby lowers the strength of the cement (13). The potential use of Sorrel's cement as adsorbent material for treating some ions contaminated water was examined (14–16). In these previous works, preparation of magnesium oxy-chloride, Sorrel's cement, was modified by the introduction of iron in its structure (MF-1) to increase its chemical stability and strength as well as its adsorption capacity. It is found that this material is suitable for use in immobilization of nuclear waste in cement matrix. Humic acid is present in aquatic nature and its presence with adsorbent materials can not be excluded. Therefore in the present work, the MF-1 adsorbent previously developed (14–16) was further modified by interaction with humic acid (MF-2). In a previous work (17), adsorption of chromium by MF-2 was studied. It was found that MF-2 can be used as an adsorbent for effective removal of Cr(VI) from aqueous solution. Quantitative removal of these metals from synthetic nuclear power plant coolant water confirmed the validity of the results obtained in these studies.

Adsorbents based on magnesium hydroxide are considered as layered double hydroxide. Their general composition may be represented $M^{II}n\ M^{III}(OH)_{2n+2}\ X$, where $2 = 2-5$ and X is a charge balancing anion. The layers have the $Mg(OH)_2$ structure in which the trivalent metal isomorphously substitutes the divalent one (18). This substitution creates positively layers balanced by the anions in the interlamellar space. Consequently, a variety of ions may be exchanged or adsorbed (19).

The objective of this study is to investigate the applicability of the modified synthetic humic acid magnesia cement, MF-2, as an adsorbent material for the removal of lanthanide, represented by gadolinium, and actinide ions, examplified by uranium, from aqueous solutions and to examine the kinetics of adsorption and other parameters involved.

EXPERIMENTAL

Chemical

All the chemicals used were of analytical grade products and obtained from BDH, England.

A Modified Magnesia Cement (MF-2) Adsorbent Preparation and Characterization

Sorrel's cement F5 was prepared as reported in literature (20, 21). In this respect, F5 was prepared by dissolving 1 M $MgCl_2 \cdot 6H_2O$ in deionized water followed by the addition of equivalent amount of 5 M MgO powder with through mixing. The mixture was left for 3 days at 75°C for dryness.

The modified magnesia cement (MF-1) was prepared by dissolving 1 M $MgCl_2 \cdot 6H_2O$ and 1 M $FeCl_3$ in 100 ml deionized water. To this solution, 5 M MgO was added, and the slurry was thoroughly mixed and poured in circular plastic dishes (10 mm in diameter × 3 mm high) and left for 3 days at 75°C to cure.

MF-1 was further modified to adsorbent MF-2 by thoroughly mixing 16 g of the prepared MF-1 with 50 ml aqueous solution containing 50 mg of humic acid. It is found that the humic acid is completely sorbed on MF-1. This was identified by the absence of the UV-Vis absorbency of humic acid solution measured at 365 nm. After filtration, the product was dried at 75°C to get adsorbent, MF-2.

The humic acid used in this work was separated from the bottom sediments of Ismailia Canal, near Cairo-Egypt and it was purified to remove any residual cations or anions and to reduce the ash content following the procedure described by Nash et al. (22). Energy dispersive spectroscopy (EDS) was used to analyze the chemical composition of the adsorbents surface using Jeol LV-5600 made in Japan. The elemental composition of the investigated MF-2 was carried out by the Central Analytical Laboratory, Atomic Energy Authority.

The morphology and the particle diameters of the product was determined using a Joel-JSM-1200EX II scanning electron microscopy (SEM), X-ray diffraction (XRD) using Unique II X-ray spectrometer, Mo-Sc anode target tube, 70 kV, 15 mA and LiF-220 analyzing crystal. The FTIR spectroscopy was carried out in the reflectance mode, using a Perkin Elmer Model 1725 X. Infrared spectra were scanned across the wave number from 4000 to 400 cm^{-1}. Thermal analysis was carried out using a Shimadzu thermogravimetric analyzer, TGA, at a heating rate of 20°C per min.

UV-visible spectrum measurements were performed using Shimadzu, UV-visible spectrophotometer model UV-160, Japan.

Acid-base Behavior of MF-2

The adsorbent (MF-2) was characterized by potentiometric titration to determine the acid-base behavior at ionic strength of 0.1 M. In this concern, 0.02 g of investigated sample was taken in 25 ml water and mixed for about 15 min. using magnetic stirrer. To this mixture, 12.5 ml of 0.1 M $NaClO_4$ were added and the sample titrated with 0.1 M HCl. The pH was measured with microprocessor bench pH-meter of Hanna instruments type. Measurements were taken when the drift of the signal was below 0.01 unit min^{-1}, unless 10 min have elapsed; in this case, the measurement was nevertheless taken and the titration continued. The end point was determined from the maxima of the first derivative of the titration curve.

Adsorption Experiments

Blank experiments were carried out to study the precipitation in the studied pH ranges. The experiment was performed with 10 ml of metal ions solution in polypropylene bottles at different pH values in the absence of adsorbent. The concentration of metal ions in the solution before and after pH adjustment was determined and the amount of metal ions precipitated was determined by difference.

Adsorption experiments were performed with 10 ml of solution in 25 ml polypropylene bottles. 0.03 g and 0.1 g MF-2 were added to each solution for Gd(III) and U(VI), respectively. The mixtures were placed on a shaker set at 100 rpm. After 90 min, the samples were filtered and the filtrate was analyzed spectrophotometrically (23) to determine Gd(III) and U(VI) content. For investigation of the effects of adsorbent weight and contact time, 25 mg/l of Gd(III) and 350 mg/l U(VI) with 0.03 g and 0.1 g of MF-2 were used for Gd(III) and U(VI), respectively. Gd(III) or U(VI) solution was adjusted to a desired pH using 0.1 N HCl or dilute NaOH solutions.

The loading capacity of the adsorbent for Gd(III) and U(VI) were studied by repeating the adsorption step with the same adsorbent weight and volume of the solution until the adsorbent is saturated with the metal ions. In this concern, 0.1 g of adsorbent was shaken with 50 ml of the solution containing 25 mg/l Gd(III) in 0.001 M carbonate medium. Also, 50 ml of the aqueous solution containing 350 mg/l U(VI) in carbonate solution was shaken with 0.5 g of MF-2. The two phases were separated by centrifugation and Gd(III) and U(VI) concentration were determined in solution. The amount of metal ions adsorbed was determined by differences. This batch equilibration step was repeated on the separated adsorbent using fresh solution containing the metal ions and under similar conditions till saturation of the metal ions on the adsorbent used is found.

Kinetic Experiments

In kinetic investigations, Gd(III) and U(VI) concentrations varied in the range 5–25 mg/l and 300–600 mg/l, respectively, when the effect of their concentrations was studied. A thermodynamic study was carried out at 0.01 M carbonate solution containing 25 mg/l Gd(III) or 350 mg/l U(VI) at different temperatures (10–50°C) in thermostat water bath. For this purpose, a known amount of adsorbent was added, 0.1 g and 0.5 g to 50 ml of Gd(III) and U(VI) solutions, respectively, in a double-jacket conical flask connected to a thermostated water bath. At different time mixing intervals, the solutions were separated and analyzed to determine the uptake of Gd(III) and U(VI).

RESULTS AND DISCUSSION

Adsorbent Characterization

Elemental analysis of the prepared adsorbent is given in Table 1. From thermal analysis the prepared material showed good thermal stability up to 250°C, with a little loss of water. At a higher temperature, the adsorbed humic acid starts to decompose.

The initial morphology of MF-2 shows fibrous or stone like pieces and by comparing its morphology with that obtained before and after adsorption of the two metal ions, a notable difference was found in the absence of many spots which is a development due to the uptake of two metal ions on the surface leading to a rough appearance as shown in Fig. 1. The average particle size and the radius of MF-2 were found 12 μm and 0.6×10^{-5} m, respectively, as determined by SEM.

Table 1. Percentage of elemental concentrations (%) in MF-2 adsorbent sample by EDS and elemental composition

Element	Element, %
O	49.60
Mg	24.72
Cl	1.22
Fe	4.96
Nitrogen	0.80
Carbon	13.81
Hydrogen	3.98
Sulphur	0.15
Total %	99.24

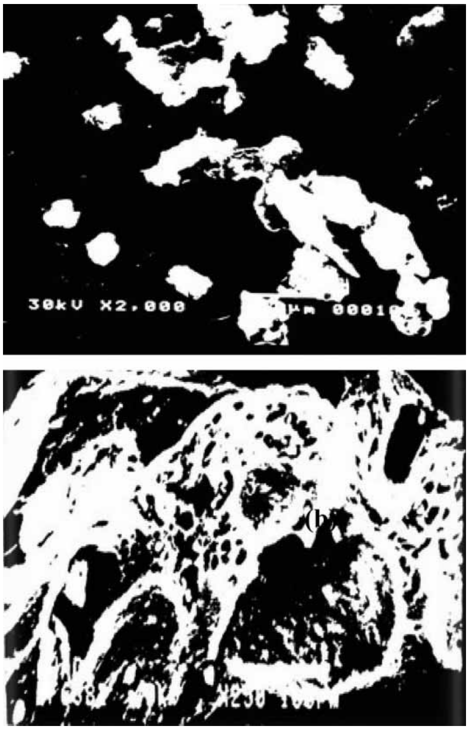

Figure 1. SEM of MF-2 before (a) and after (b) adsorption of metal ions.

The IR spectrum of MF-2 before loading uranium or gadolinium, Fig. 2, has a similar feature to that of humic materials specially in the wave number range 1100–4000 cm^{-1} (24). The main absorption bands of this sorbent are the OH absorption band at about 3400 cm^{-1} broadened by hydrogen bonding, the aliphatic CH stretching at 2918 cm^{-1} and 2846 cm^{-1}, the carboxylic C═O stretching (shoulder) at 1616 cm^{-1} and the carboxylate broad absorption band at 1460 cm^{-1} (24). Other small bands observed in the spectrum at 1084, 857, and 564 cm^{-1} are related to the M(Mg or Fe)-OCl vibrations (25). Comparing this IR spectrum with those loaded with metal ions, the main changes observed are the following;

i. the IR absorption bands at 3696, 3442, 2918, and 2856 cm^{-1} observed for the IR spectrum of MF-2 suffered very slight changes when MF-2 is loaded with uranium or gadolinium, (Fig. 2),
ii. the carboxylic band at 1460 cm^{-1} of MF-2 split into two bands at 1481 and 1424 cm^{-1} in the spectrum of MF-2 loaded uranium. In case of gadolinium, the 1460 cm^{-1} band disappeared and three absorption IR bands were developed at 1476, 1424, and 1383 cm^{-1}. These indicate

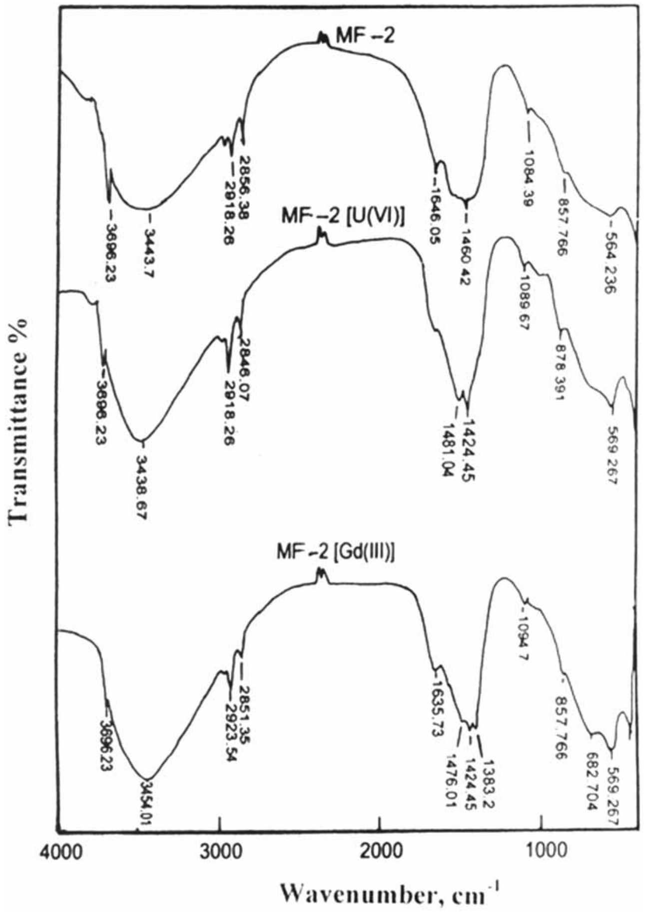

Figure 2. Infrared spectra of MF-2 before (curve 1) and after (curve 2) adsorption of U(VI).

that the metal ions are bonded to the caboxylate anions of humic acid adsorbed on the adsorbant.,

iii. in the low wave number region below 9000 cm^{-1} a slight shift in these bands was obtained for the IR spectrum of uranium loaded MF-2 whereby in the case pf Gd loaded MF-2, a small new band was observed at 682 cm^{-1}.

To assess the acid-base behavior of the MF-2 adsorbent, the hydroxyl groups in the adsorbent were determined by direct titration. The hydroxyl group capacities was determined from the maxima of the first derivatives of the titration curve (26). The number of hydroxyl groups is determined from the maximum of the first derivative, and found to contain 5.75

meq $\cdot$ OH^{-1}/g. This value is higher than that determined for MF-1, 0.25 meq $\cdot$ OH^{-1}, for magnesia cement without humic acid (27).

Adsorption Investigation

Unless otherwise stated, the concentrations of Gd(III) and U(VI) in solution were 25 mg/l and 350 mg/l, respectively. The equilibrium parameters of MF-2 for adsorption of Gd(III) and U(VI) from dilute carbonate solution (0.001 M) comparable with natural water were studied.

MF-2 is an effective adsorbent for the removal of Gd(III) and U(VI) over the pH range 3–11. In all cases, the equilibrium pH was found to be in the range 9.4–9.8. For comparison, a blank adsorption was studied for the two elements to exclude possible precipitation or adsorption of elements by the glass container in the pH range studied. Within the concentration range of the elements under study, it is found that there is no precipitation or adsorption on the glass vessels. In case of Gd(III), the amount of Gd(III) adsorbed increased up to 25 mg/l after which Gd(III) was precipitated.

The effect of contact time for adsorption equilibrium of the two metal ions from carbonate solution by MF-2 was studied, Fig. 3. The removal efficiency increases with time and attains equilibrium within 60 min for Gd(III) but after 150 min. for U(VI). The adsorbent weight was varied from 0.02 to 0.3 g/10 ml and equilibrated for 2 h. The experimental results revealed that Gd(III) and U(VI) removal efficiency increases to the maximum value using 0.03 g/10 ml and 0.1 g/10 ml weight of adsorbent for Gd(III) and U(VI),

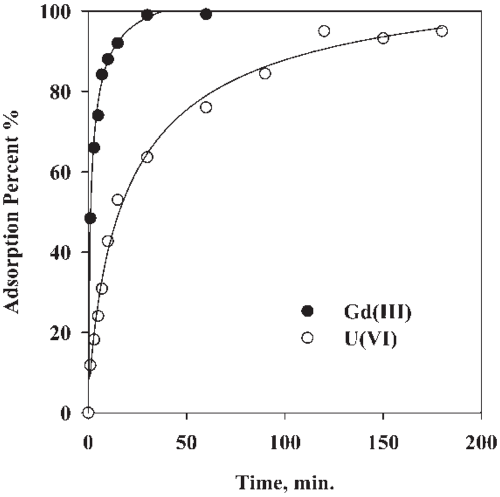

Figure 3. Effect of contact time on the adsorption of 25 mg/1 Gd(III) and 350 mg/1 U(VI) from 0.01 M carbonate soluation. pH = 9.5 MF-2 weight for Gd(III) = 0.03 g/10 ml MF-2 weight for U(VI) = 0.1 g/10 ml.

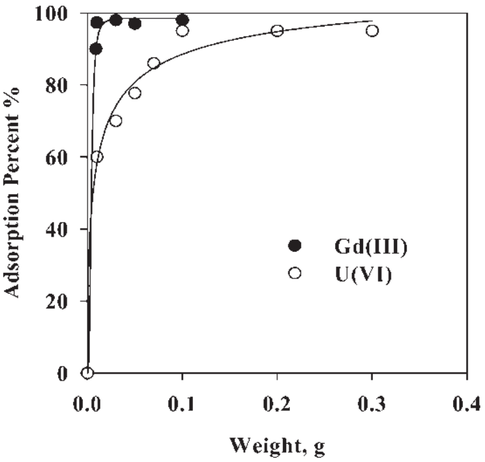

Figure 4. Effect of weight of adsorbent (MF-2) on the adsorption of 25 mg/l Gd(III) and 350 mg/l U(VI) from 0.001 M carbonate solution. pH = 9.5 Contact time = 2 hr.

respectively, as seen in Fig. 4. Further increase in the weight of the adsorbent has no effect on the removal precetage.

The role of Gd(III) and U(VI) concentration on the adsorption were studied using MF-2 within the range 10–25 mg/l for Gd(III) and 300–650 mg/l for U(VI). The results obtained are represented in Fig. 5. as a relation between the

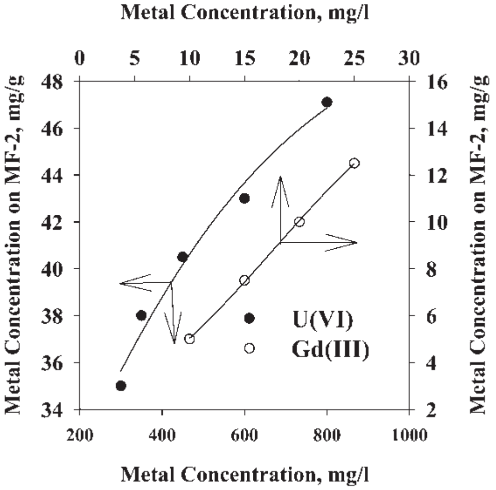

Figure 5. Effect of initial Gd(III) and U(VI) concentration on its concentration in the solid phase when adsorbed with MF-2. pH = 9.5 Contact time = 2 hr MF-2 weight for Gd(III) = 0.03 g/10 ml MF-2 weight for U(VI) = 0.1 g/10 ml.

concentrations of the metal ions in the solution and in MF-2 adsorbent. From this figure, it is clear that the concentration of U(VI) in the adsorbent increase with increasing their intial concentration in solution up to a concentration of 650 mg/l. In case of Gd(III), the amount of Gd(III) adsorbed increased up to 25 mg/l after which Gd(III) was precipitated.

The maximum loading capacity of the adsorbent for Gd(III) and U(VI) was found to be 35.94 mg/g after 16 adsorption stages and 43 mg/g after only one stage for Gd(III) and U(VI), respectively. It is worth comparing the adsorption of the modified adsorbent, MF-2, with MF-1 which do not contain humic acid under similar experimental conditions. The adsorption capacity of MF-2 for both metal ions are higher than that obtained using MF-1. In this concern, the capacity of Gd(III) and U(VI) of MF-1 is 17 mg/g after 8 adsorption stages and 13 mg/g after 4 stages, respectively.

The investigated equilibrium removal of U(VI) ions can be mathematically expressed in terms of the adsorption isotherms. The adsorption data are commonly fitted to the Langmuir or the Freundlich model.

The Langmuir equation was applied to the adsorption equilibrium for MF-2:

$$(C_e/q_e) = 1/(Q_o b) + C_e/Q_o \tag{1}$$

where C_e is the equilibrium concentration (mg dm^{-3}), q_e the amount adsorbed at equilibrium (mg/g), and Q_o is the Langmuir constant related to the monolayer adsorption capacity.

The linear plots of $C_\mathrm{e}/q_\mathrm{e}$ versus C_e show that the adsorption obeys the Langmuir model, (see Fig. 6.) Q_o determined from the Langmuir plot, was 47.55 mg/g, Fig. 6 which is comparable with the adsorption capacity.

The Freundlich adsorption isotherm was also applied for the adsorption of the same metal ion by the MF-2. The experimental results obtained for the adsorption of U(VI) on the MF-2 at room temperature ($25 \pm 1^\circ$C) under optimum conditions of contact time and the weight of the adsorbent was found to obey the Freundlich adsorption isotherm (28).

$$log\, q_e = log\, k + 1/n\, log\, C_e \tag{2}$$

where q_e is the amount of U(VI) removed per unit weight of adsorbent (mg g-1); C_e the concentration of U(VI) at equilibrium; n is a constant representing the intensity of adsorption.

The data obtained in this study fit the Freundlich adsorption isotherm as shown in Fig. 7. The plot of log q_e versus log C_e, Fig. 7, for various initial concentrations of U(VI), Fig. 7, found to be linear, indicating the applicability of the classical adsorption isotherm to this adsorbate–adsorbent system. The adsorption intensity (n) for U(VI) was found to be 10. This value indicates efficient and favorable adsorption for uranium (29).

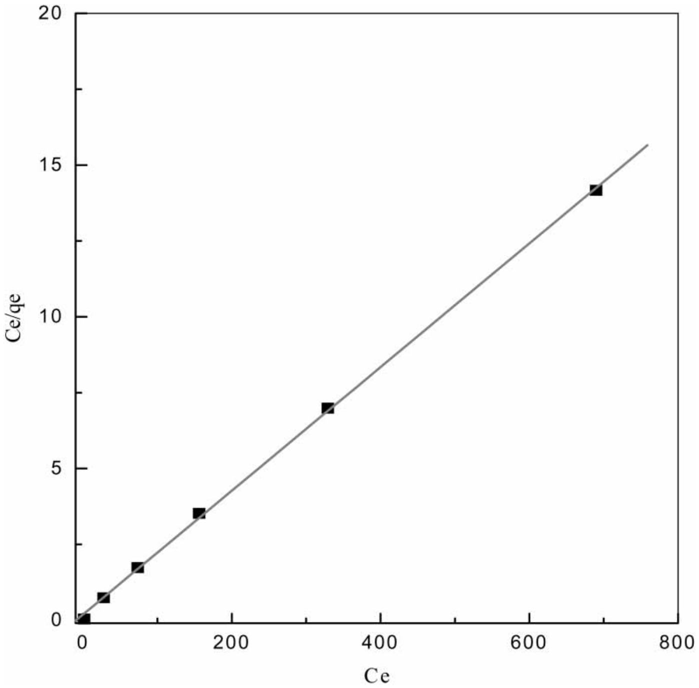

Figure 6. The Langmuir adsorption isotherm for U(VI) on the MF-2.

Kinetics Investigation

It is well-recognized that the characteristic of adsorbent surface is a critical factor that affects the adsorption rate parameters and diffusion resistance plays an important role in the over all transport of solute (film and particle diffusion). To describe the changes in the adsorption of studied ions with time, several kinetic models were tested. The rate constant of each metal ion removal from the solution by MF-2 was determined using pseudo-first-order rate models.

The Lagergren first-order rate expression (30) is written as:

$$log\ (q_e - q_t) = log\, q_e - (k_1/2.303)\ t \tag{3}$$

where q_e and q_t are the amounts of metal ion adsorbed onto adsorbent at equilibrium and at time t (mg/g), respectively, and k_1 is the rate constant of first-order adsorption (min^{-1}).

The slopes and intercept of the linear plots of log-log ($q_e - q_t$) versus t, as shown in Figs. 8–9 are given to determine the first order rate constant. It was observed that the adsorption of both ions followed the Lagergren equation over the entire range of shaking time explored. The values of the first order rate constants increase with the increase in temperature as reported in Table 2.

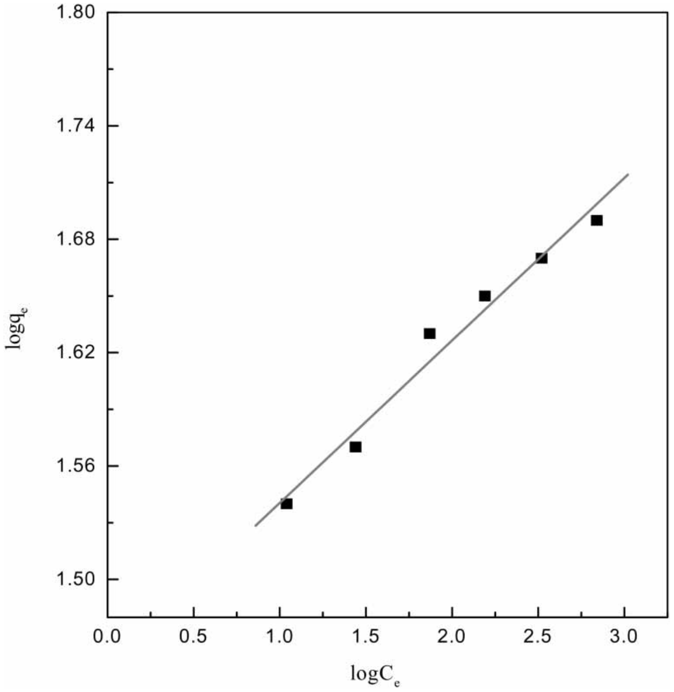

Figure 7. The Freundlish adsorption isotherm for U(VI) on the MF-2.

Other simplified models are also tested because the Lagergren equation cannot give a definite mechanism. It is also known that with intensive stirring of the adsorptive system, the interaparticle diffusion of the solute adsorbed from the solution into the adsorbent pores could be a limiting step. In this study, two models, namely the Weber and the Morris models and that suggested by Helfferich (31) were also used, Figs. 10, 11. The Weber and Morris (30) equation is written as:

$$q_t = k_d\ t^{1/2} \tag{4}$$

where k_d, is the rate constant of interaparticle transport.

According to this model, plotting a graphic relation of q_t versus $t^{1/2}$, if a straight line passing through the origin is obtained, it can be assumed that the involved mechanism is a particle diffusion of species.

Kinetic data were also analyzed by the procedure given by Helfferich (32). Various parameters were calculated by Boyd et al. (33).

$$F=1-\frac{6}{\pi^2}\sum_{n-1}^{\infty}\frac{1}{n^2}\ \exp\left[-n^2\,Bt\right] \tag{5}$$

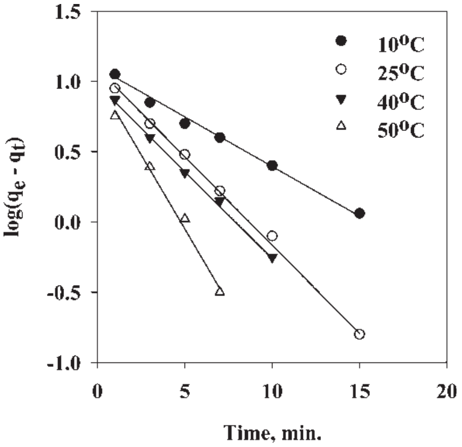

Figure 8. First order plots for the adsorption of GD(III) by MF-2 in 0.001 carbonate soluation at differernt temperatures.

and

$$B = \pi^2 D_i / r_o^2 \tag{6}$$

where F is the fractional attainment of adsorption at time t ($F = q_t/q_e$), B is a mathematical function (the slope of Bt vs t plots), D_i is a self-diffusion coefficient of the ions, n is an integer number, and r_o refers to the radius of the particles as determined by (SEM).

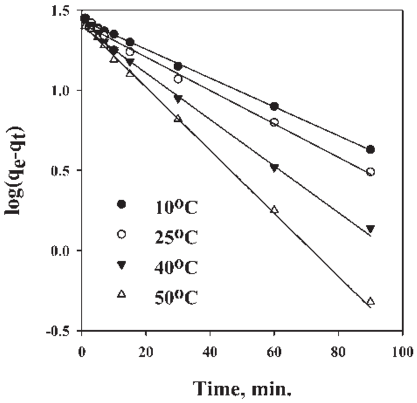

Figure 9. First order plots for the adsorption of U(VI) by MF-2 in 0.001 M carbonate soluation at different temperatures.

Table 2. Rate constants for the adsorption of 25 mg/l Gd(III) and 350 mg/l U(VI) with MF-2

	Overall rate constant K, × 10^2 min.$^{-1}$	
Temperatures, °C	Gd(III)	U(VI)
10	1.39	4.54
25	1.96	4.70
40	2.08	5.30
50	2.75	6.51

Bt values for the determined values of F were obtained from Reichenberg's table by using the equation (5) derived by Reichenberg (34):

$$Bt = 2\pi - \pi^2 F(t)/3 - 2\pi\,[1 - (\pi/3)F(t)]^{1/2} \tag{7}$$

Figures 12, 13, depict the Bt versus time plots for Gd(III) and U(VI) at different temperatures. The linearity test of Bt test versus time plots is employed to distinguish between the film and particle diffusion controlled rates of adsorption process. The plots are linear and pass through the origin, indicating that the adsorption process to be particle diffusion at all studied temperatures. The value of D_i calculated at 10, 25, 40, and 50°C are presented in Table 3.

If film diffusion is to be the rate determining step in the adsorption of ions on the adsorbent surface, the value of diffusion coefficient (D_i) should be in, the range 10^{-6}–10^{-8} cm^2/s. In case the pore diffusion is the rate limiting, the diffusion coefficient (D_i) should be in the range 10^{-11}–10^{-13} cm^2/s

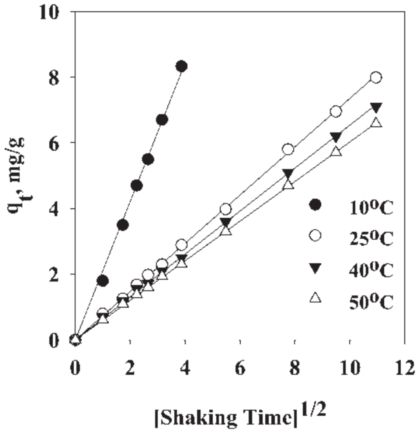

Figure 10. Morris-Weber plots for kinetic modelling of Gd(III) adsorbed onto MF-2.

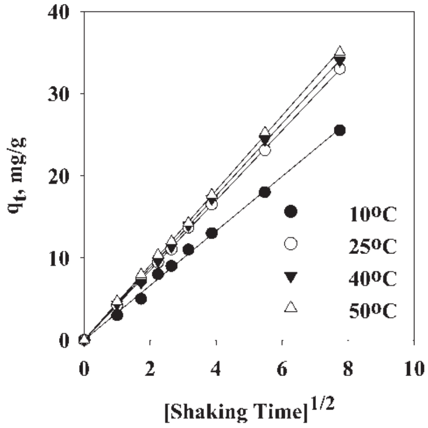

Figure 11. Morris-Weber plots for kinetic modelling of U(VI) adsorbed onto MF-2.

(35). Since D_i obtained in the present work is in the order of 10^{-12} cm^2/s, therefore the rate limiting step for MF-1 and MF-2 is governed by pore diffusion. It is worth mentioning that the diffusion coefficient of MF-2 is higher than that obtained previously for MF-1 without humic acid (27). This indicates that the sorbed humic material enhance the adsorption of the metal ions.

Plotting of $\ln D_i$ versus $1/T$ gave straight line as shown in Fig. 14 enables the calculation of the energy of activation (E_a) from the Arrhenius equation:

$$D_i = D_o\ e^{-Ea/RT} \tag{8}$$

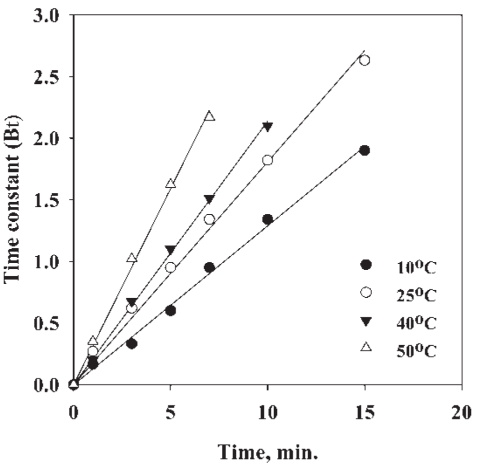

Figure 12. Time constant (Bt) versus time of Gd(III) at different temperatures.

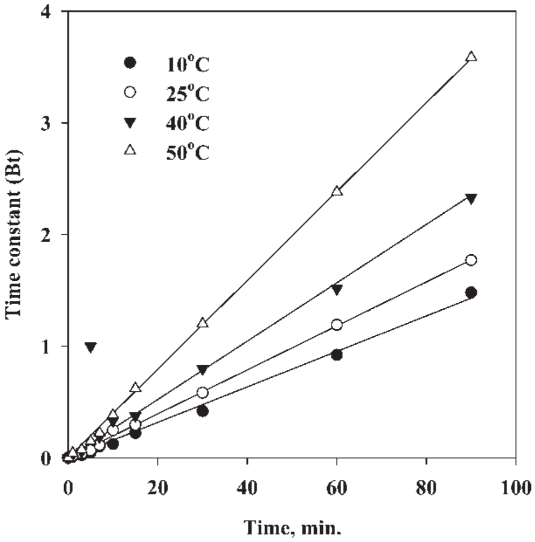

Figure 13. Time constant (Bt) versus time of U(VI) at different temperatures.

The entropy of activation ΔS^* can be calculated from D_o by substituting in the equation proposed by Barrer et al. (36)

$$D_o = 2.72(KTd^2/h)\ exp^{\Delta S^*/R} \tag{9}$$

where K is Boltzmann constant, T is 273°K, d is the average distance between two successive particles in the process of diffusion which was taken as 5×10^{-8} cm (37), and h is Plank's constant.

The heat of activation of the adsorption, ΔH^*, was calculated from the following equation (38):

$$\Delta H^* = E_a - RT \tag{10}$$

Table 3. Diffusivity of Gd(III) and U(VI) adsorbed onto MF-2

	Diffusion coefficient, $D_i, \times 10^{12}$ cm^2/s	Diffusion coefficient, $D_i, \times 10^{12}$ cm^2/s
Temperature, °C	Gd(III)	U(VI)
10	1.97	7.71
25	2.57	10.79
40	2.80	10.70
50	3.57	15.15

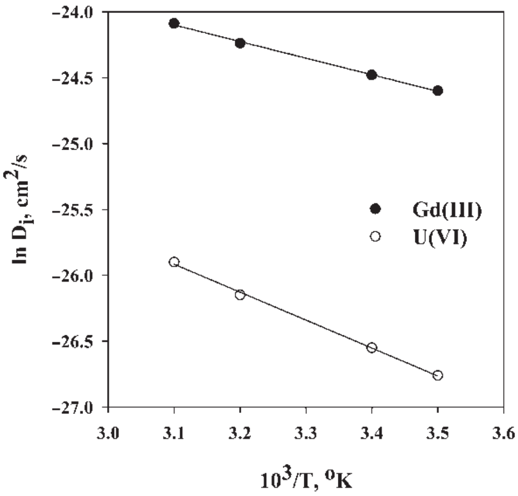

Figure 14. Arrhenius diagram of Gd(III) and U(VI) adsorbed on MF-2.

The energies of activation, E_a, for Gd(III) and U(VI) were calculated from the slope of straight lines in Fig. 14. E_a values are $-10.56\ kJ \cdot mol^{-1}$ and $17.21\ kJ \cdot mol^{-1}$ for Gd(III) and U(VI), respectively. Since the chemical controlled reaction has activation energy equals to or higher than $20.9\ kJ/mol^{-1}$, whereas in the diffusion controlled processes it has lower values (39), therefore, the adsorption of Gd(III) and U(VI) are diffusion controlled.

The values of ΔH^* were calculated from equation (10), and found to equal $8.08\ kJ\ mol^{-1}$ and $14.73\ kJ\ mol^{-1}$ for Gd(III) and U(VI), alternatively. The enthalpy of activation is a mean of the height of energy barrier which must be overcome to attain the transition state, i.e., the larger value of ΔH^*, the slower the adsorption (40). Since the value of ΔH^* for adsorption of U(VI) is positive and much higher than that of Gd(III), therefore, the height of the energy barrier which has to be overcome the activated state of U(VI) is very high. Further the calculated ΔS^* values for Gd(III) and U(VI) were found to equal $-65.27\ Jmol^{-1}K^{-1}$ and $-97.10\ Jmol^{-1}K^{-1}$, respectively. The negative values of entropy of activation obtained for the adsorption of both metal ions normally reflect that no significant change occurs in the internal structure of adsorbent during the adsorption of ions (41).

CONCLUSION

The maximum loading capacity of adsorbent for Gd(III) and U(VI) was found to be 35.94 mg/g after 16 adsorption stages and 43 mg/g after only one stage for Gd(III) and U(VI), respectively. The modified adsorbent MF-2, containing the adsorbed humic acid, has a higher adsorption capacity for uranium and gadolinium than the adsorbent MF-1 which do not contain humic acid under similar expzerimental conditions. The diffusion coefficients of the adsorbent MF-2 is higher than that obtained previously for the sorbent MF-1, without humic acid. This indicates that the sorbed humic material enhance the adsorption of the metal ions.

The kinetics of adsorption of Gd(III) and U(VI) by the MF-2 follow first-order reversible kinetics and pore diffusion is the rate limiting for Gd(III) and (VI) adsorption. The results also demonstrate that particle diffusion mechanism plays a significant role in the adsorption. The values of ΔH^* and ΔS^* were calculated for Gd(III) and U(VI) at 25°C. The values of ΔH^* were found to equal $8.08\ \mathrm{kJ \cdot mol^{-1}}$ and $14.73\ \mathrm{kJ \cdot mol^{-1}}$ for Gd(III) and U(VI), respectively, while ΔS^* were found to equal $-65.27\ \mathrm{Jmol^{-1}K^{-1}}$ and $-97.10\ \mathrm{Jmol^{-1}K^{-1}}$ for Gd(III) and U(VI), alternatively.

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