

# Batch kinetics and thermodynamics of chromium ions removal from waste solutions using synthetic adsorbents

M.S. Gasser\*, GH.A. Morad, H.F. Aly

*Hot Labs Centre, Atomic Energy Authority, 13759 Cairo, Egypt*

Received 26 February 2006; received in revised form 30 May 2006; accepted 28 July 2006

Available online 3 August 2006

## Abstract

Mg(OH)<sub>2</sub> was identified as a component in the magnesia cement being adsorbent for Cr(VI). Modified magnesia cement was prepared by the addition of ferric chloride and humic acid. The equilibrium adsorption of Cr(VI) on magnesia cement adsorbents (MF5-1) and (MF5-2) was investigated as a function of contact time, adsorbent weight, solute concentration and temperature. Tests of different isotherms have shown that the adsorption data fit the Langmuir and Freundlich isotherms at 25 ± 1 °C. The nature of the diffusion process responsible for adsorption of Cr(VI) on (MF5-1) and (MF5-2) adsorbents was discussed. The kinetics and mechanism of diffusion of Cr(VI) into (MF5-1) and (MF5-2) adsorbents from aqueous solution have been studied as a function of Cr(VI) concentrations and reaction temperatures. The adsorption of Cr(VI) on the MF5-1 and MF5-2 adsorbents follows first-order reversible kinetics. The forward and backward constants,  $k_1$  and  $k_2$  have been calculated at different temperatures between 10 and 50 °C. The heat of activation of the adsorption,  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  were calculated for Cr(VI) at 25 °C. The values of  $\Delta H^\ddagger$  were found 18.1 and 10.7 kJ mol<sup>-1</sup> for MF5-1 and MF5-2, respectively, while entropy change,  $\Delta S^\ddagger$ , were found -106.8 and -118.6 J mol<sup>-1</sup> K<sup>-1</sup> for MF5-1 and MF5-2, respectively. The study showed that pore diffusion is the rate-determining step in the adsorption of Cr(VI) ions for MF5-1 and MF5-2. MF5-2 was found more efficient for Cr(VI) adsorption than MF5-1. Also Cr(VI) can be adsorbed on MF5-2, whereas Cr(III) cannot. So, the competitive adsorption of multi-metals onto the MF5-2 adsorbent was studied. The studies showed that this adsorbent can be used as an efficient adsorbent material for the removal of Cr(VI) from water and nuclear power plant coolant water.

© 2006 Elsevier B.V. All rights reserved.

*Keywords:* Adsorption; Chromium; Isotherm; Kinetics; Thermodynamics; Mechanism; Wastewater

## 1. Introduction

Magnesium oxychloride cement (MOC) was discovered not long after Portland cement. MOC pastes are mixtures of MgO powder or calcined magnesite powder in which the major component is Mg(OH)<sub>2</sub> and MgCl<sub>2</sub> solutions of certain concentration (Mg(OH)<sub>2</sub>-MgCl<sub>2</sub>-H<sub>2</sub>O system). The major reaction reagents of MOC pastes (MgO-MgCl<sub>2</sub>-H<sub>2</sub>O system) have long been revealed to be four crystalline forms designated as F2, F3, F5 and F9. The numbers stand for the ratio of moles of Mg(OH)<sub>2</sub> to MgCl<sub>2</sub> in the formula for each form, as follows: 2Mg(OH)<sub>2</sub>·MgCl<sub>2</sub>·4H<sub>2</sub>O (F2); 3Mg(OH)<sub>2</sub>·MgCl<sub>2</sub>·8H<sub>2</sub>O (F3); 5Mg(OH)<sub>2</sub>·MgCl<sub>2</sub>·5H<sub>2</sub>O (F5); 9Mg(OH)<sub>2</sub>·MgCl<sub>2</sub>·H<sub>2</sub>O (F9) [1,2]. Selected results of magnesium chloride and oxygen-based metal-assembled compounds are summarized from the

perspective of these metals acting as catalysts for olefin polymerization [3]. This paper discusses our studies on the isolation of various metal-assembled compounds, the determination of their structures by X-ray crystallography and the relationship of their polynuclear structures to their activity as polymerization catalysts as well as to the field of molecule-functional-based materials. As Piotr demonstrate the attempts to prepare new metal-assembled pre-catalysts and to understand the chemistry of formation of these new complexes often led to unexpected reactions, which could be applied to syntheses of well-defined heterogeneous olefin polymerization catalysts.

The use of oxychloride cement is not so popular because it disintegrates and loses its strength on prolonged exposure to water, and by rising dampness of the ground due to leaching out of magnesium chloride from the cement. Therefore, the resultant mass contains essentially magnesium hydroxide, porous by nature, and thereby low in strength as cement [4,5].

The potential use of Sorrel's cement as adsorbent material for treating some ions in contaminated water was examined [6,7].

\* Corresponding author. Tel.: +20 101749083.

E-mail address: mona\_gasser@yahoo.com (M.S. Gasser).

In these previous works, preparation of magnesium oxychloride was modified by the introduction of iron in its structure to increase its chemical stability 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 is not excluded. Therefore, in the present work MF5-1 adsorbent developed was further modified by interaction with humic acid.

Chromium is a common pollutant introduced into natural waters from a variety of industrial wastewaters including those from the textile, tanning electroplating, dyeing, and metal finishing industries [8]. In solution, Cr exists in the oxidation states +3 and +6. In natural waters, the two main oxidation states are (III) and (VI), characterized by a markedly different chemical and hazardous behavior. The divalent state is unstable with respect to evolution of oxygen, trivalent state has broad stability, and hexavalent chromium occurs under strongly oxidizing conditions [9]. Cr(III) is considered as an essential element in mammals. It can maintain the metabolism of glucose, lipid and protein. Whereas, Cr(VI) is reported to be toxic to the biological system and can easily permeate biological membranes. Removal and recovery of chromium were carried out by using precipitation process [10]. Results show that the optimum pH is 8–9 and the good sludge with high settling rate and lower volume obtain by MgO precipitating agent. Hence the MgO is a good precipitating agent for removal and recovery of chromium from tanning wastewater. Rengaraj et al. [11] studied the removal of chromium from water and wastewater by ion-exchange resins.

As one of the most promising techniques for removal of chromium from industrial wastewaters, adsorption technology has been employed for many years and the effectiveness of various adsorbents has been demonstrated [12–14]. In principle, adsorption cannot only remove heavy metals but also recover and recycle them back into the industrial process [15]. The adsorbed material, toxic or valuable, is recovered in a concentrated form for disposal or reuse. The solid adsorbent can often be regenerated for reuse [16]. Activated carbon as the most common adsorbent used in the adsorption process shows higher efficiency for the adsorption of organic than inorganic matters. The spent activated carbon is either land filled or regenerated at rather high temperatures commonly used by commercial regenerators [17]. However, the regeneration loss may be as much as 10%, even with well-operated systems. Also, regeneration usually affects the properties of the carbon. Generally, the capacity of carbons is expected to be near 90% of the original value after regeneration [18]. As a result, the regeneration of this kind of adsorbent is limited because of its high cost, loss of capacity, and operating difficulties. Thus, there is a need to explore more suitable adsorbents for regeneration and recovery purpose.

All the above-mentioned materials present good adsorption capacity, but in general they are not able to reduce the heavy metal concentration below the discharge limits established in environmental legislation. Such discharge requirements can be matched using specific adsorbents characterized by a very high selectivity with respect to heavy metal.

Adsorption is the most widely used process for purifying the primary coolant in pressurized water reactor (PWR)-type

nuclear power plants, due to its high decontamination efficiency, simplicity and easy operation. Since the method is non-selective in removing radionuclides and non-radionuclides, there is a large volume of waste and volume reduction technology has not been developed for the management of this radioactive waste. The waste is usually stored for lengthy time periods in the nuclear power plant itself, or it has been solidified into a radioactive resin waste by cementation [19]. In order to minimize the generation of solid wastes, adsorption process must be optimized in purifying the primary coolant. The main objectives of this work were to prepare and investigate equilibrium and kinetic parameters of two modified adsorbents (MF5-1 and MF5-2) for the removal of chromium from water and nuclear power plant coolant water. The parameters which influence adsorption such as contact time, adsorbent weight, initial metal concentration and temperature were investigated. The results obtained are discussed in terms of different adsorption models. Also, competitive adsorption of coexisting multi-metals onto the adsorbent was studied.

## 2. Experimental

All reagents were of analytical grade and used without further purification.

### 2.1. Magnesia cement (MF5-1–MF5-2) preparation and characterization

MF5-1 was synthesized from 1 M  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  [11] and 1 M  $\text{FeCl}_3$  and 5 M  $\text{MgO}$  [6]. A new adsorbent (MF5-2) was prepared by adding 1 g/l humic acid to 16 g MF5-1 and shaking for 30 min. The amorphous product was collected on a Buchner funnel, washed with distilled water for removal of unreacted species. After that the product dried. The prepared material was ground to fine particles.

The morphology was determined using a Joel-JSM-1200EX II scanning electron microscopy (SEM), X-ray diffraction (XRD) using X Unique II X-ray spectrometer, Mo-Sc anode target tube, 70 kV, 15 mA and  $\text{LiF-220}$  analyzing crystal. The FTIR spectroscopy was carried out in the reflectance mode, using a Perkin-Elmer Model 1725 X instrument equipped with a horizontal attenuated total reflectance accessory ( $\text{ZnSe}$  reflecting crystal). Spectra were measured against a background of *n*-hexane and were scanned across the wavenumber from 4000 to  $400\text{ cm}^{-1}$ .

Energy dispersive spectroscopy (EDS) was used to analyze the chemical composition of the adsorbents surface by using Jeol LV-5600 made in Japan. The elemental composition of investigated MF5-1 and MF5-2 were determined by using Flash EA1112 made in Italy.

The adsorbents were characterized by potentiometric titration to determine the acid–base behavior at an ionic strength of  $0.1\text{ mol dm}^{-3}$ . In this concern, 0.02 g of investigated sample was dissolved in 25 ml water by stirring for about 15 min using a magnetic stirrer. Then, 12.5 ml of  $0.1\text{ mol dm}^{-3}$   $\text{NaClO}_4$  was added and the sample titrated with  $0.1\text{ mol dm}^{-3}$   $\text{HCl}$ . The pH of the solution reached equilibrium within 5–10 min after each addition of the acid. At this time the pH reading was taken. The

end point was determined from the maxima of the first derivative of the titration curve [20].

The adsorbents were characterized by potentiometric titration to determine the acid–base behavior of the MF5-1 and MF5-2 adsorbents, the hydroxyl groups in adsorbents were determined. In this concern, direct titration for the sample was performed and the hydroxyl groups capacities was determined from the maxima of the first derivatives of the titration curve.

## 2.2. Equilibrium studies

A stock solution of  $500 \text{ mg dm}^{-3}$  Cr(VI) was prepared from  $\text{K}_2\text{Cr}_2\text{O}_7$ . The solution was diluted as required to obtain standard solutions containing 10–200 and 70–400  $\text{mg dm}^{-3}$  Cr(VI) for MF5-1 and MF5-2, respectively. Adsorption experiments were performed with 10 ml of solution in 25 ml polypropylene bottles. About 0.1 g adsorbents were added to each solution. The mixtures were placed on a shaker set at 100 rpm at constant temperature. After 120 min, the samples were filtered. The adsorbents were separated, and the filtrate was analyzed spectrophotometrically [21] to determine Cr(VI) content. For investigation of the pH, adsorbent weight, contact time and temperature effects,  $70 \text{ mg dm}^{-3}$  ( $1.35 \times 10^{-3} \text{ mol dm}^{-3}$ ) and  $100 \text{ mg dm}^{-3}$  ( $1.9 \times 10^{-3} \text{ mol dm}^{-3}$ ) Cr(VI) with 0.1 g of MF5-1 and MF5-2 were used, respectively. The Cr(VI) solution was adjusted to the desired pH by using 0.1N HCl or dilute NaOH solutions.

## 2.3. Kinetic studies

Thermodynamic studies were carried out with a 0.001 M carbonate solution at different temperatures ( $10\text{--}50^\circ\text{C}$ ) in thermostat water bath. For this purpose, a known amount of adsorbent, 0.5 g was added to 50 ml of  $1.35 \times 10^{-3} \text{ mol dm}^{-3}$  (70 mg/l) and  $1.9 \times 10^{-3} \text{ mol dm}^{-3}$  (100 mg/l) Cr(VI) concentrations for MF5-1 and MF5-2, respectively, in a double-jacket connected to the circulator. A known amount of the solution was withdrawn at different time intervals and the metal ion determined. All the experiments were carried out at  $10, 25, 40$  and  $50^\circ\text{C} \pm 1$  and the results agreed to  $\pm 3\%$  for all reactions times.

In order to find an effective method of separation for Cr(VI) and Cr(III), the adsorption experiment was carried out using a solution containing 50 mg/l Cr(VI) and 50 mg/l Cr(III) ions. The effect of competitive adsorption of coexisting multi-metals onto MF5-2 was also investigated. The solution (50 ml) containing Cr(VI), Cr(III), Pb(II), Cd(II) and Zn(II) at initial concentrations of 50, 50, 50, 10, and 10 mg/l, respectively was agitated with 0.5 g of MF5-2 adsorbent. A known amount of solution was withdrawn at time interval and Cr(VI) concentration determined.

The chromium containing synthetic primary coolant water was prepared on basis of the analysis of chemical composition from the primary coolant in a nuclear power plant, and its concentrations are presented in Table 1. The different adsorbent weight (MF5-2) was used to study the removal of Cr(VI) from synthetic nuclear power plant. For investigation the effect of contact time on the removal of Cr(VI) by MF5-2 from synthetic nuclear power plant coolant water; 0.05 g/100 ml was used.

Table 1  
Composition of synthetic nuclear power plant coolant water

Compound	Concentration (mg/l)
$\text{Sb}_2\text{O}_5$	5
$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1
$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	30
$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	15
$\text{AgNO}_3$	5
$\text{H}_3\text{BO}_3$	20
$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	5
$\text{LiOH} \cdot \text{H}_2\text{O}$	1
$\text{CsNO}_3$	5

## 3. Results and discussion

### 3.1. Adsorbent characterization

The scanning electron microscopy SEM image of the surface of MF5-1 and MF5-2 used in adsorption experiments is shown in Fig. 1(a) and (b). The radii of MF5-1 and MF5-2 were found to be  $(1.1 \text{ and } 0.6) \times 10^{-5} \text{ m}$  for MF5-1 and MF5-2, respectively.

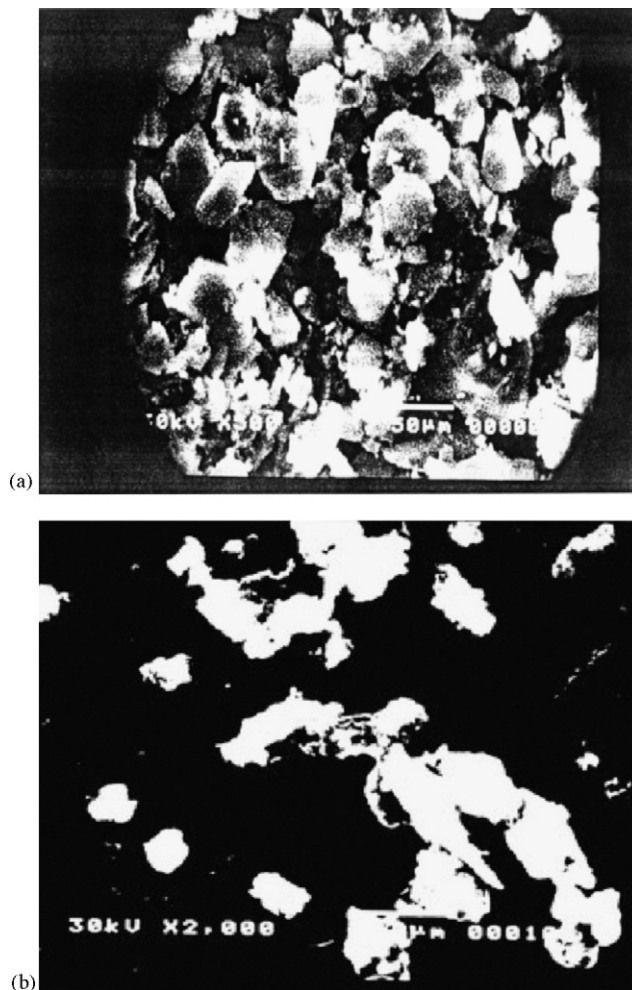


Fig. 1. Scanning electron microscope image of modified Sorel's cement of two adsorbents: (a) MF5-1 and (b) MF5-2.

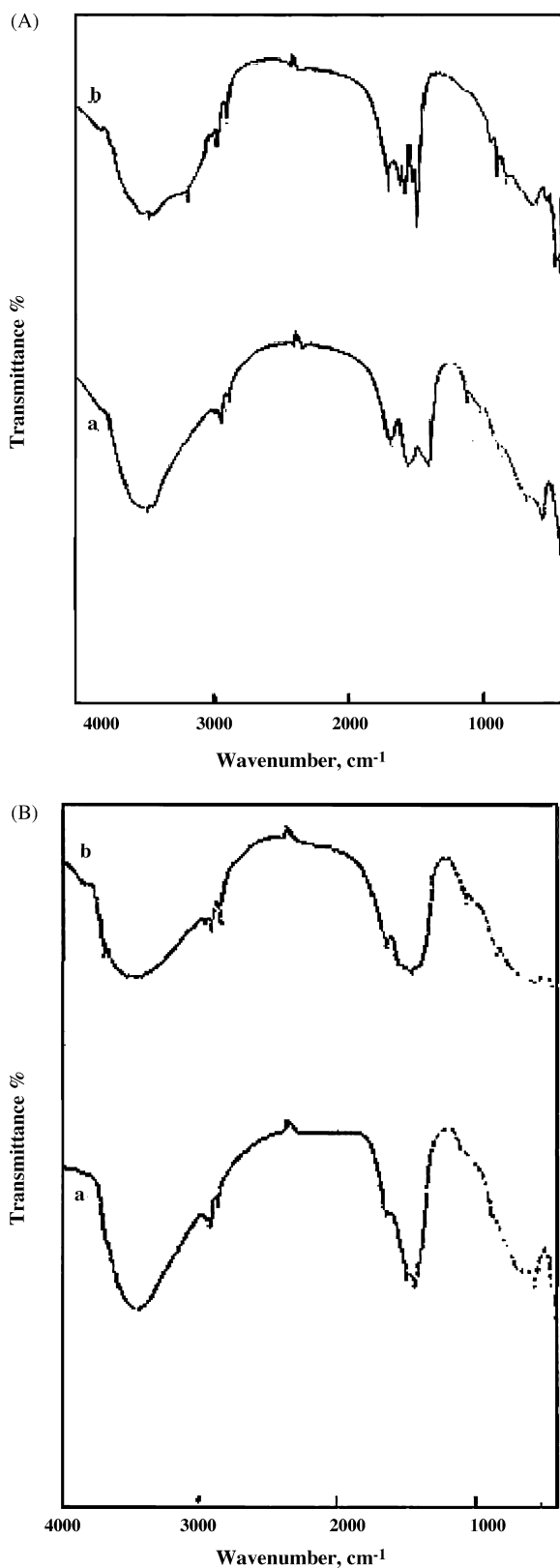


Fig. 2. Infrared spectra of MF5-1 and MF5-2: before (curve a) and after (curve b) adsorption.

The infrared (IR) spectrum of MF5-1 (Fig. 2A) is characterized by different absorption bands for water vibrations as well as hydrogen bonding bands in the region 3400–2800  $\text{cm}^{-1}$ . The free  $\text{H}_2\text{O}$  vibration is indicated by the presence of the band at 1640  $\text{cm}^{-1}$ . Other absorption bands observed in the region 1564–590  $\text{cm}^{-1}$  for the MF5-1 are related to the OCl vibration together with the coordinated M(Mg or Fe)–OCl vibrations. The spectra obtained for the adsorbed Cr(VI) on MF5-1 showed a slight shift for the band at 1929  $\text{cm}^{-1}$ , and noticeable shift to the band observed at 3423  $\text{cm}^{-1}$ . Further, the band of MF5-1 at 1440 and 1564  $\text{cm}^{-1}$  was decreased, and the band at 590  $\text{cm}^{-1}$  was observed. Three new bands were developed at 1084.39, 1002.14 and 672.4  $\text{cm}^{-1}$ . The aforementioned vibrations indicate that the adsorption of Cr(VI) affects the structure of MF5-1 in different ways. The bonding of the Cr(VI) is mainly related to interaction with oxygen and oxychloride of the adsorbent. The IR absorption spectrum of MF5-2 is given in Fig. 2B. The main difference between the IR spectrum of MF5-1 and MF5-2 is the shift in the positions of  $\text{H}_2\text{O}$  and OH bands in the region 1640–3423  $\text{cm}^{-1}$  and the presence of broad band at 1460  $\text{cm}^{-1}$  and a new small band at 1089.42  $\text{cm}^{-1}$ . These changes are mainly due to the presence of humic acid, which increases the number of active oxygen donors. Comparing the IR spectrum with those loaded with metal ion, the following main changes were observed: (i) the IR bands observed for MF5-2 which suffered slight changes are found at 3443.7, 2918.3, 2826.4, 1084.4 and 564.24  $\text{cm}^{-1}$ ; (ii) the bands observed at 3696.2 and 857.8  $\text{cm}^{-1}$  were absent in the presence of Cr(VI); (iii) the band at 1460.4 was not found when Cr(VI) was adsorption on MF5-2; (iv) new IR bands were observed at 682.5, 1429.5 and 1485.08  $\text{cm}^{-1}$  for MF5-2 adsorbed Cr(VI). The changes in the IR spectra of MF5-2 due to adsorption of Cr(VI) are relatively less than the changes observed in the case of MF5-1. This may indicate that the adsorption process by MF5-2 is less complicated than that of MF5-1.

X-ray diffraction (XRD) patterns of Sorel's cement before and after exposing to Cr(VI) (Fig. 3) reveal significant phase change from crystalline to amorphous form. Interaction of the cement with Cr(VI) leads to destruction of the crystal lattice of the untreated cement.

The percentage of elemental concentrations (%) in prepared adsorbents (MF5-1 and MF5-2) by EDS and elemental composition is given in Table 2. Elemental composition is one of the most important characteristics for MF5-2, which contains humic acid. Humic substances are composed predominately of carbon, oxygen, nitrogen, hydrogen and small amounts of sulphur as shown in Table 2.

The number of hydroxyl groups is determined for MF5-1 and MF5-2 from the maximum of the first derivative, and found to contain 0.25 and 5.75 mequiv.  $\text{OH}^{-1}/\text{g}$ , respectively.

### 3.2. Equilibrium studies

MF5-1 and MF5-2 are effective for removal of Cr(VI) over the pH range 4–11, Fig. 4. In all cases the equilibrium pH was found to equal 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

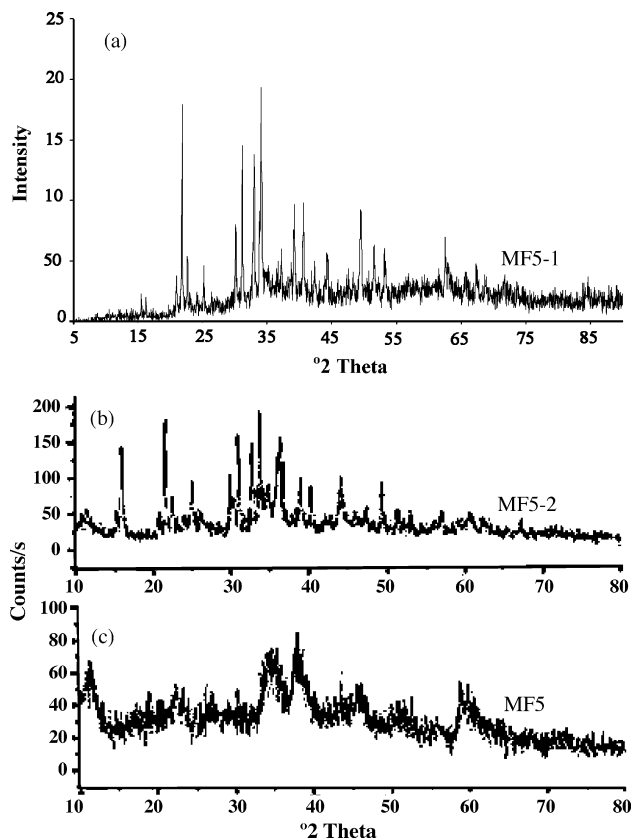


Fig. 3. X-ray diffraction (XRD) pattern for MF5-1 and MF5-2 adsorbents used in this work: before (curves a and b) and after (curve c) adsorption.

studied. There is no precipitation in the studied range. The dissolution of adsorbents increases at  $\text{pH} < 4$ .

The removal of Cr(VI) as a function of the adsorbents weight of MF5-1 and MF5-2 is shown in Fig. 5. The adsorbents weight were varied from 0.01 to 0.3 g and equilibrated for 120 min for the removal of 70 and 100 mg in  $10 \text{ ml}^{-1}$  of Cr(VI) for MF5-1 and MF5-2, respectively. The results show that both adsorbents have capacity in the removal of Cr(VI) but the capacity of MF5-2 for the removal of Cr(VI) is higher than MF5-1. As expected, the equilibrium concentration decreases with increasing adsorbents weight for a given initial solute concentration.

Table 2  
Percentage of elemental concentrations (%) in MF5-1 and MF5-2 adsorbent sample by EDS and elemental composition

Element	Element (%)	
	MF5-1	MF5-2
O	34.15	49.60
Mg	20.58	24.72
Cl	29.33	1.22
Fe	15.80	4.96
Nitrogen	–	0.60
Carbon	–	13.81
Hydrogen	–	3.98
Sulphur	–	0.15
Total %	99.86	99.24

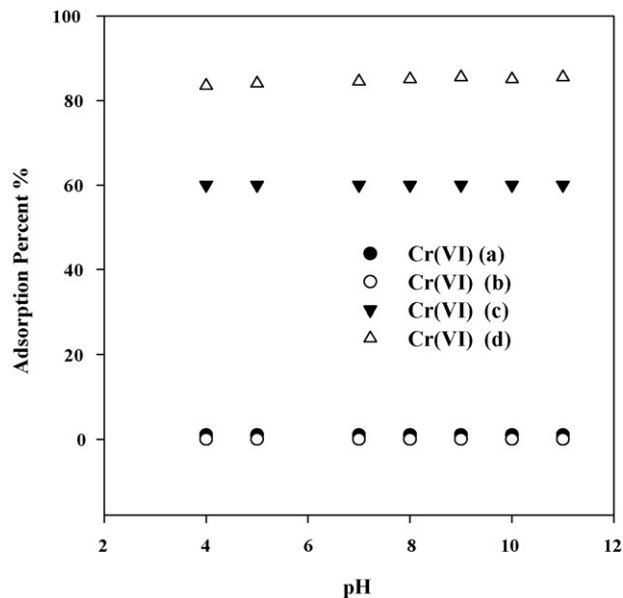


Fig. 4. Effect of pH on the adsorption of Cr(VI) from 0.001 M carbonate solution by two adsorbents. Adsorbents weight = 0.1 g/10 ml; (a) and (b) in the absence of adsorbents; (c) and (d) in the presence of adsorbents.

Fig. 6 shows the effect of contact time on the removal of Cr(VI) by MF5-1 and MF5-2. The removal efficiency increases with time. In the case of MF5-1, equilibrium attains within 30 min for 70 mg Cr(VI) in 10 ml 0.001 M carbonate solution. While in case MF5-2 the equilibrium attains within 90 min for 100 mg Cr(VI). The removal efficiency increases with time and attains equilibrium within 1 h for both adsorbents, suggesting the possible monolayer coverage of metal ions on the surface of the adsorbent [22].

Various concentrations of carbonate were utilized to remove 70 and 100 mg in  $10 \text{ ml}^{-1}$  of Cr(VI) for MF5-1 and

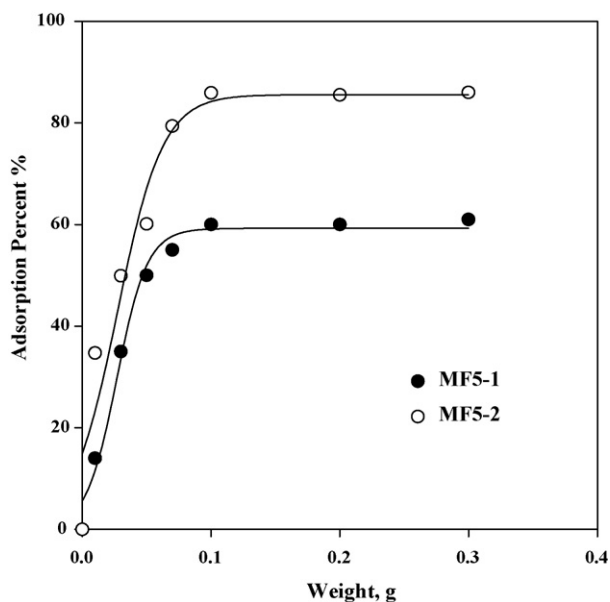


Fig. 5. Effect of weight of adsorbents on the adsorption from 0.001 M carbonate solution.  $\text{pH} 9.5$ ; contact time = 2 h.

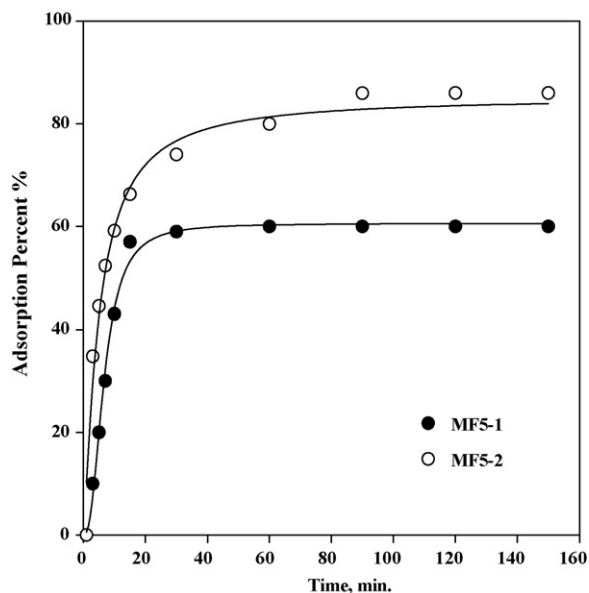


Fig. 6. Effect of contact time on the adsorption of Cr(VI) from 0.001 M carbonate solution by two inorganic adsorbents. Weight of adsorbents = 0.1 g/10 ml, pH 9.5.

MF5-2, respectively. The carbonate concentrations used covered the range from 0.005 to 0.1 mol dm<sup>-3</sup>. Fig. 7 shows the maximum removal of Cr(VI) at low carbonate concentration in the range (0.001 mol dm<sup>-3</sup>). Higher carbonate concentration decreased the percent removal of both metal ions.

The effect of initial Cr(VI) concentration on the adsorption were studied using MF5-1 and MF5-2 within the range 10–200 and 70–400 mg dm<sup>-3</sup> Cr(VI) for MF5-1 and MF5-2, respectively. The results obtained are represented in Fig. 8 as a relation between the concentrations of the initial metal ions in the solution and in MF5-1 and MF5-2 adsorbents. From this figure, it is clear that the concentration of Cr(VI) in the adsorbent increased with increasing initial concentration in solution.

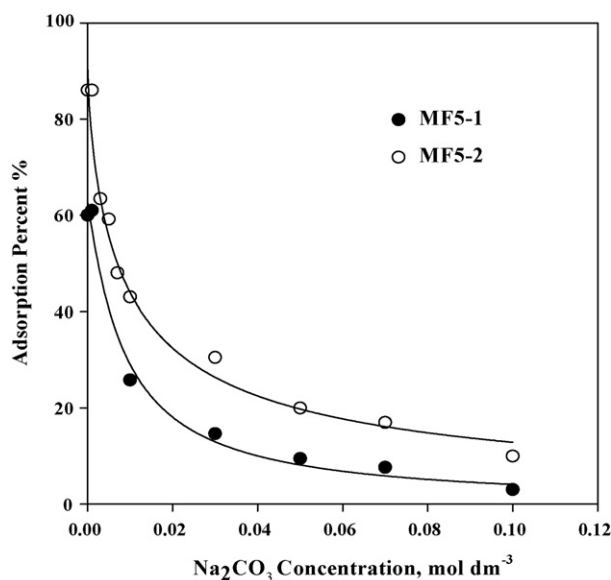


Fig. 7. Effect of carbonate on the adsorption of Cr(VI) by different inorganic adsorbents. pH 9.5; weight of adsorbents = 0.1 g/10 ml.

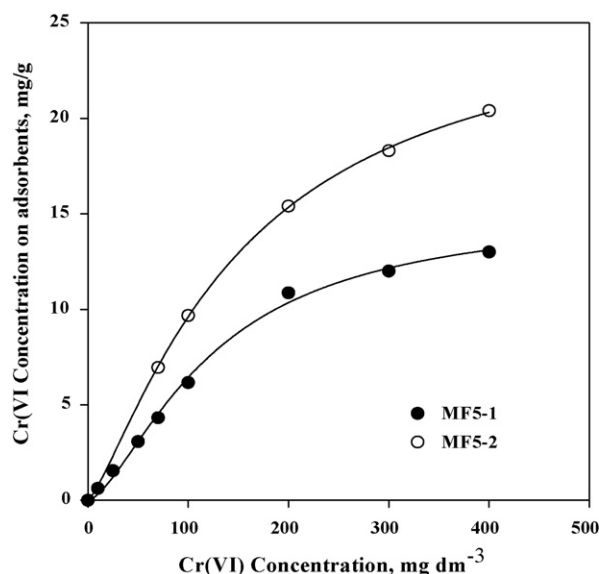


Fig. 8. Effect of initial Cr(VI) concentration in the solution on its concentration in the solid phase after adsorption. pH 9.5; adsorbents weight = 0.1 g/10 ml.

The effect of temperature on the adsorption of 70 and 100 mg in 10 ml of Cr(VI) for MF5-1 and MF5-2, respectively, from 0.001 M carbonate solution was studied at temperature values of 10, 25, 40, and 50 °C. The equilibrium constant values,  $K_c$ , were evaluated in the respective temperature degrees according to Eq. (1).

$$K_c = \frac{q_e}{C_e} \quad (1)$$

where  $q_e$  is the equilibrium concentration of Cr(VI) on the adsorbent,  $C_e$  is the equilibrium concentration of Cr(VI) in solution. The temperature effect on the metal adsorption could be evaluated in terms of their thermodynamic values calculated from the following relations:

$$\Delta G = -RT \ln K_c \quad (2)$$

where  $R$  is the gas constant (8.314 J k<sup>-1</sup> mol<sup>-1</sup>) and  $T$  is the absolute temperature.

$$\ln K_c = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (3)$$

where  $\Delta H$  is the enthalpy changes for the process equilibrium of the final products and  $\Delta S$  is entropy change.

$$\Delta S = \frac{\Delta H - \Delta G}{T} \quad (4)$$

The equilibrium constant  $K_c$ , for adsorption of Cr(VI) at different temperatures was calculated from Eq. (1). Plots of  $\ln K_c$  versus  $1/T$  gave straight lines with negative slope for MF5-1 and MF5-2, Fig. 9.  $\Delta G$  for both adsorbents were calculated from this figure at 298 K<sup>-1</sup> and found to be 3 and -68.6 kJ mol<sup>-1</sup> for MF5-1 and MF5-2, respectively. The values of  $\Delta H$  and  $\Delta S$  for MF5-1 and MF5-2 were calculated on the basis of the slope and intercept of the plot shown in Fig. 9. The values of  $\Delta H$  and  $\Delta S$  for MF5-1 were found to be -960 J mol<sup>-1</sup> and -13.3 J mol<sup>-1</sup> K<sup>-1</sup>, respectively. The negative  $\Delta H$  value indicates the exothermic

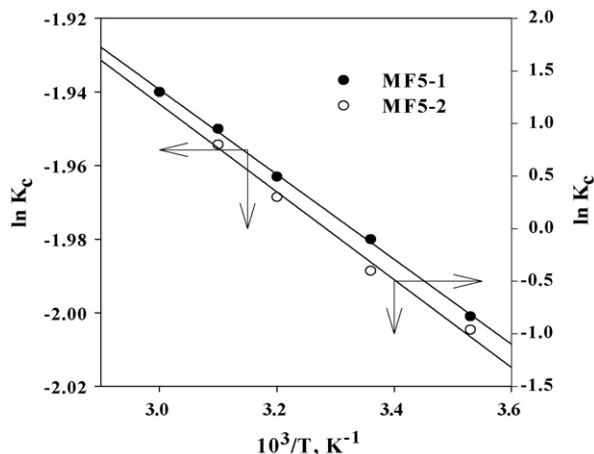


Fig. 9. Effect of temperature on the equilibrium constant of Cr(VI) adsorption from 0.001 M carbonate solution. pH 9.5; adsorbents weight = 0.1 g/10 ml.

character of MF5-1 adsorbent while the negative  $\Delta S$  value indicates the decrease in the randomness of the system. The values of  $\Delta H$  and  $\Delta S$  for MF5-2 were found to be  $-34.7 \text{ kJ mol}^{-1}$  and  $113.9 \text{ J mol}^{-1} \text{ K}^{-1}$ , respectively. The negative  $\Delta H$  value indicates the exothermic character of MF5-2 adsorbent while the positive  $\Delta S$  value indicates the increase of the randomness of the system.

The maximum loading capacity of adsorbent for MF5-1 and MF5-2 was found to be 7.2 and 10 mg/g Cr(VI), respectively.

The investigated equilibrium removal of Cr(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 MF5-1 and MF5-2:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad (5)$$

where  $C_e$  is the equilibrium concentration ( $\text{mg dm}^{-3}$ ),  $q_e$  the amount adsorbed at equilibrium ( $\text{mg g}^{-1}$ ), and  $Q_o$  is the Langmuir constant related to monolayer adsorption capacity. The linear plots of  $C_e/q_e$  versus  $C_e$  show that the adsorption obeys the Langmuir model, Fig. 10.  $Q_o$  determined from the Langmuir plot, were 18.8 and 22.4  $\text{mg g}^{-1}$ , for MF5-1 and MF5-2, respectively, Fig. 10.

The Freundlich adsorption isotherm was also applied for the adsorption of the same metal ion by the MF5. The experimental results obtained for the adsorption of Cr(VI) on the MF5-1 and MF5-2 at room temperature ( $25 \pm 1 \text{ }^\circ\text{C}$ ) under optimum conditions of contact time and weight adsorbent was found to obey the Freundlich adsorption isotherm [23].

$$\log q_e = \log k + \frac{1}{n} \log C_e \quad (\text{linear form}) \quad (6)$$

where  $q_e$  is the amount of Cr(VI) removed per unit weight of adsorbent ( $\text{mg g}^{-1}$ );  $C_e$  the concentration of Cr(VI) at equilibrium;  $n$  is constant representing the intensity of adsorption. The data obtained in this study fit to the Freundlich adsorption isotherm as shown in Fig. 11. The plot of  $\log q_e$  versus  $\log C_e$

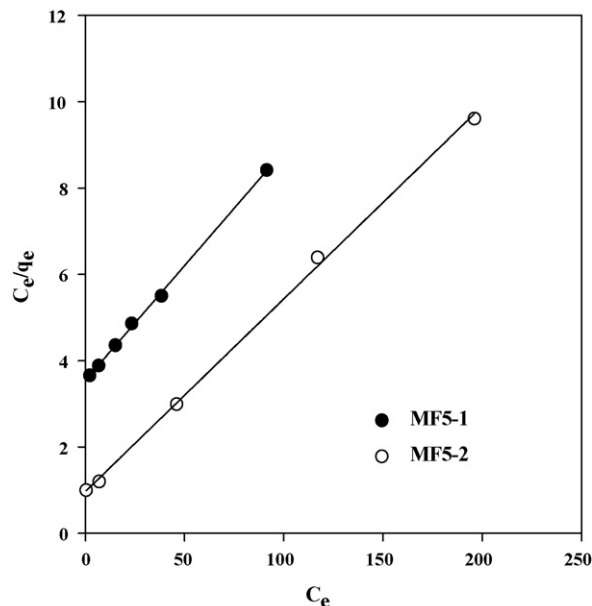


Fig. 10. The Langmuir adsorption isotherm for Cr(VI) on the MF5-1 and MF5-2.

for various initial concentrations of Cr(VI), Fig. 11, is found to be linear, indicating the applicability of the classical adsorption isotherm to this adsorbate–adsorbent system. Adsorption intensity ( $n$ ) for Cr(VI) was found to be 1.4, and 8.1 for MF5-1 and MF5-2, respectively. The value of  $n$  lies between 1 and 10, indicating favorable adsorption [24]. MF5-2 was found more efficient for Cr(VI) adsorption than MF5-1 due the presence of the humic acid, which makes the surface activated.

### 3.3. Kinetic studies

The order for the adsorption process of Cr(VI) on MF5-1 and MF5-2 surface has been examined by the Lagergren first-order

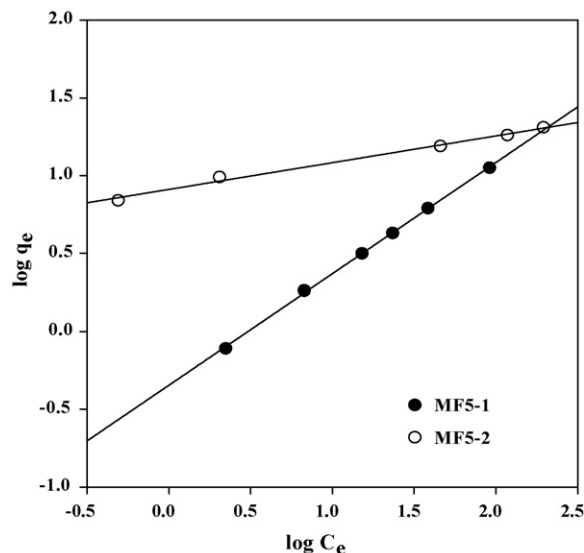


Fig. 11. The Freundlich adsorption isotherm for Cr(VI) on MF5-1 and MF5-2.

rate expression [25]

$$\log(q_e - q_t) = \log q_e - \left( \frac{K}{2.303} \right) t \quad (7)$$

by plotting  $\log(q_e - q_t)$  against time, where  $q_e$  and  $q_t$  are the amounts of Cr(VI) adsorbed at equilibrium and at time  $t$ , respectively, and  $K$  is the overall rate constant.

The heterogeneous equilibrium between the Cr(VI) solution and adsorbents may be expressed as



where  $k_1$  is the forward reaction rate constant and  $k_2$  is the backward reaction rate constant. These can be calculated by using the following equations:

$$K = k_1 \left( 1 + \frac{1}{K_c} \right) = k_1 + k_2 \quad (9)$$

and

$$K_c = \frac{k_1}{k_2} = \frac{q_e}{C_e} \quad (10)$$

where  $K$  is the overall reaction rate constant;  $q_e$  the equilibrium concentration of Cr(VI) on the adsorbents;  $C_e$  the equilibrium concentration of Cr(VI) in solution;  $K_c$  is the equilibrium constant. The values of  $K_c$ ,  $k_1$ ,  $k_2$  can be determined by using Eqs. (9) and (10).

The effect of Cr(VI) concentration was studied at concentrations within the range 10–70 and 70–400 mg dm<sup>-3</sup> for MF5-1 and MF5-2 at 25 °C and pH 9.8. The first-order plots of the results obtained are shown in Figs. 12 and 13. The different values of the rate constants,  $K$ , were calculated from the slope of these straight lines and are listed in Tables 3 and 4. The data in Table 3 show that the values of  $K$  slightly increases with increasing Cr(VI) concentration while there is almost no effect was noticed at the high concentration for MF5-1. While the data in Table 3 show that the values of  $K$  is almost no effect notice with Cr(VI) concentration for MF5-2. From Table 3, also it could be seen that the forward rate constants for adsorption of Cr(VI) were much higher than the backward rate constants [26] at low Cr(VI). The results imply that the reaction is reversible at Cr(VI) concentration higher than 70 mg dm<sup>-3</sup> for MF5-1. Also,

Table 3  
Effect of Cr(VI) concentration on the rate of its adsorption by MF5-1 and MF5-2

Cr(VI) concentration (mg dm <sup>-3</sup> )	Overall rate constant, $K$ ( $\times 10^2$ min <sup>-1</sup> )	Forward rate constant, $k_1$ ( $\times 10^2$ min <sup>-1</sup> )	Backward rate constant $k_2$ ( $\times 10^2$ min <sup>-1</sup> )
10	0.90	0.8	0.1
25	1.2	0.2	1
50	2.1	0.3	1.8
70	2	0.3	1.7
70 <sup>a</sup>	4.4	2.8	0.4
100 <sup>a</sup>	4.5	3.4	1.1
200 <sup>a</sup>	4.1	1.8	2.3
300 <sup>a</sup>	4	0.4	2.6

<sup>a</sup> MF5-2 adsorbent.

Table 4

Effect of temperature in the rate and diffusivity of Cr(VI) adsorption by MF5-1 and MF5-2

Temperature (°C)	$K$ ( $\times 10^2$ min <sup>-1</sup> )		$D_i$ ( $\times 10^{11}$ cm <sup>2</sup> /s)	
	MF5-1	MF5-2	MF5-1	MF5-2
10	1.95	3.74	2	2.6
25	2.03	4.54	2.1	3.6
40	2.11	4.40	2.9	3.7
50	4.9	4.10	4.9	3.9

$K$  is the overall rate constant;  $D_i$  is diffusion coefficient.

Table 3 shows that the forward rate constants for adsorption of Cr(VI) were much higher than the backward rate constants at low Cr(VI) concentration, the reaction is reversible at high Cr(VI) concentration in the range 200–300 mg dm<sup>-3</sup> for MF5-2.

The effect of temperature on the Cr(VI) adsorption were studied within the range 10–50 °C and pH 9.8. The first-order plots of the results obtained are shown in Figs. 14 and 15. The different values of the rate constants  $K$  were calculated from the slope of these straight lines and are listed in Table 4. The data in Table 4 show that the values of  $K$  slightly increases with increasing temperature in the range 10–50 °C for MF5-1. Also from this table the values of  $K$  slightly increases with increasing temperature in the range 10–25 °C, then slightly decreases at temperature range 40–50 °C for MF5-2.

The rate-controlling step in ion-exchange or adsorption is usually either liquid film diffusion or particle diffusion. The following equation [27] was derived when the kinetics of exchange is controlled by particle diffusion, which is generally used in this work.

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp - 1^2 Bt \quad (11)$$

and

$$B = \pi^2 \frac{D_i}{r_o^2} \quad (12)$$

where  $B$  is a mathematical function (the slope of  $Bt$  versus  $t$  plots),  $D_i$  is a self-diffusion coefficient of the ions,  $n$  is an integer number,  $r_o$  referring to the radius of the particles.  $Bt$  values for the observed values of  $F$  were obtained from Reichenberg's table by using the following equation derived by Reichenberg [28]:

$$Bt = 2\pi - \frac{\pi^2 F(t)}{3} - 2\pi \left[ 1 - \left( \frac{\pi}{3} \right) F(t) \right]^{1/2} \quad (13)$$

where  $F$  is the fractional attainment of adsorption. Figs. 16 and 17 depict the  $Bt$  versus time plots for 70 mg dm<sup>-3</sup> ( $1.35 \times 10^{-3}$  mol dm<sup>-3</sup>) and 100 mg dm<sup>-3</sup> ( $1.9 \times 10^{-3}$  mol dm<sup>-3</sup>) Cr(VI) for MF5-1 and MF5-2 were used, respectively. Cr(VI) at different temperatures for MF5-1 and MF5-2. 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 the adsorption process to be particle diffusion at all studied temperatures. The values of  $D_i$



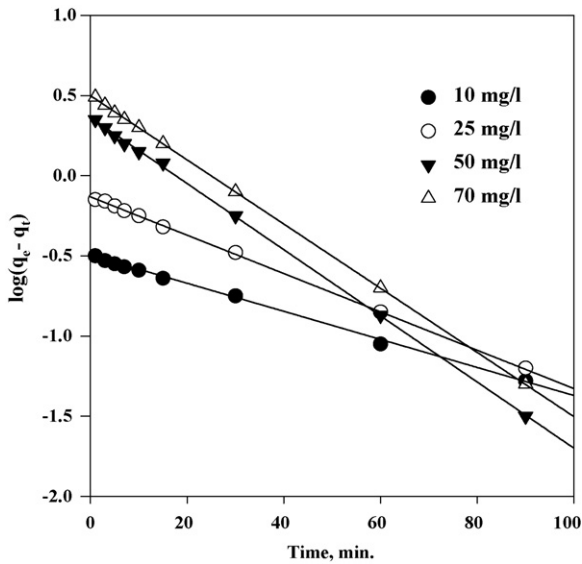


Fig. 12. First-order plots for the adsorption of Cr(VI) by MF5-1 from aqueous solution at different concentrations of Cr(VI).

calculated at 10, 25, 40, and 50 °C for MF5-1 and MF5-2 are presented in Table 4. The results show that the highest diffusion of Cr(VI) on MF5-1 is at 50 °C.

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  $10^{-6}$  to  $10^{-8}$  cm<sup>2</sup>/s. If pore diffusion is the rate limiting, the diffusion coefficient ( $D_i$ ) should be in the range  $10^{-11}$  to  $10^{-13}$  cm<sup>2</sup>/s [29].

Plotting of  $\ln D_i$  versus  $1/T$  gave straight line as shown in Fig. 18 enables the calculation of the energy of activation ( $E_a$ ) from Arrhenius equation:

$$D_i = D_o e^{-E_a/RT} \tag{14}$$

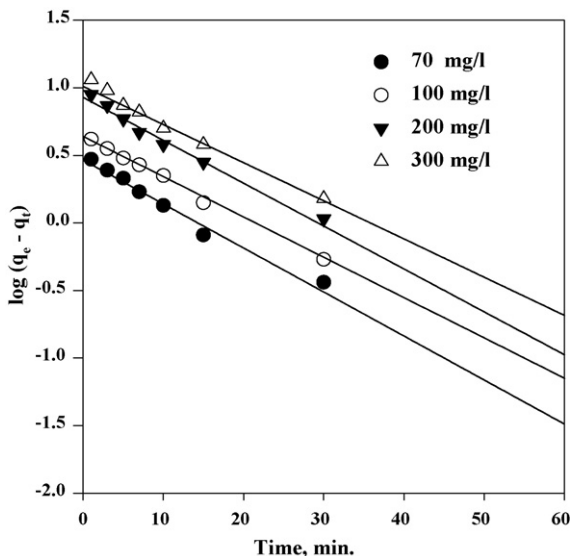


Fig. 13. First-order plots for the adsorption of Cr(VI) by MF5-2 from aqueous solution at different Cr(VI) concentrations.

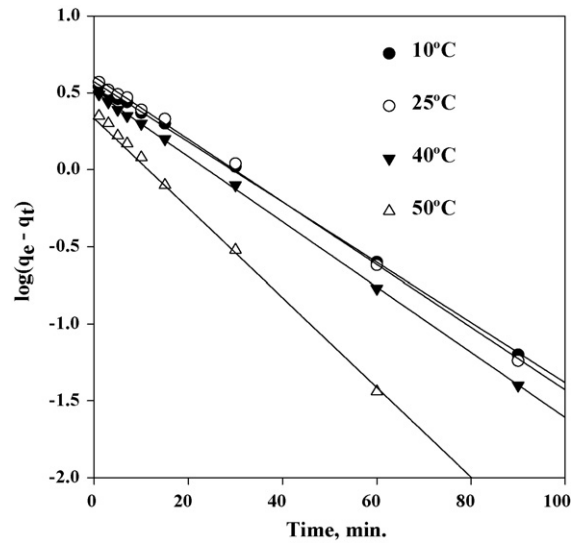


Fig. 14. First-order plots for the adsorption of Cr(VI) by MF5-1 in aqueous solution at different temperatures.

The entropy of activation  $\Delta S^*$  can be calculated for MF5-1 and MF5-2 from  $D_o$  by substituting in the equation proposed by Barrer et al. [30]:

$$D_o = 2.72 \left( \frac{KTd^2}{h} \right) \exp^{\Delta S^*/R} \tag{15}$$

where  $K$  is Boltzman constant;  $T$  273 °K;  $d$  the average distance between two successive particles in the process of diffusion which was taken as  $5 \times 10^{-8}$  cm [31];  $h$  is Plank's constant. The value of entropy of activation ( $\Delta S^*$ ) found to be  $-106.8$  and  $-118.6$  J mol<sup>-1</sup> K<sup>-1</sup> for MF5-1 and MF5-2, respectively.

The heat of activation of the adsorption,  $\Delta H^*$ , was calculated from the following equation [32]:

$$\Delta H^* = E_a - RT \tag{16}$$

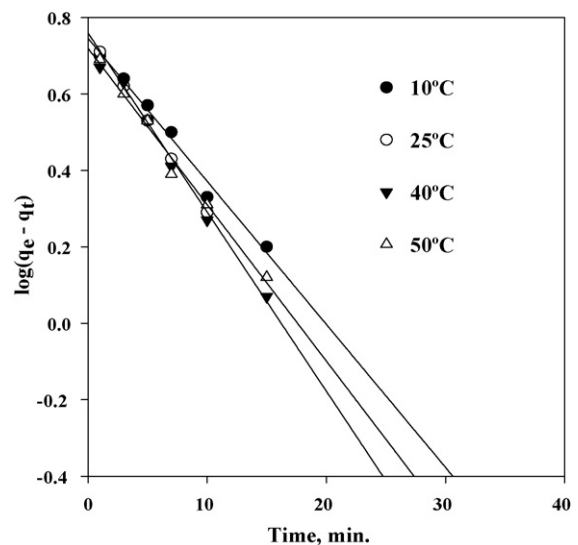


Fig. 15. First-order plots for the adsorption of Cr(VI) by MF5-2 in aqueous solution at different temperatures.

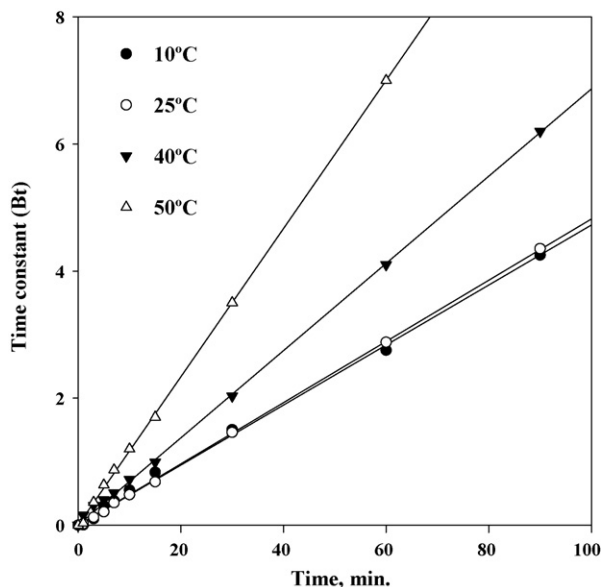


Fig. 16. Time constant ( $Bt$ ) vs. time of Cr(VI) on MF5-1 at different temperatures.

The energies of activation and the heat of activation of the adsorption for Cr(VI) for MF5-1 and MF5-2,  $E_a$  and  $\Delta H$ , were calculated from the slope of straight lines in Fig. 18. The activation energy ( $E_a$ ) was calculated for Cr(VI) on MF5-1 and MF5-2 from the slope of the straight lines and found to be 20.4 and 12.97 kJ mol<sup>-1</sup>, respectively. A chemical controlled reaction has an activation energy above 20.9 kJ/mol, whereas in the diffusion controlled processes, it has lower values [33]. Therefore, the adsorption of Cr(VI) on MF5-1 and MF5-2 is diffusion controlled. While  $\Delta H^*$  values are 18.1 and 10.7 kJ mol<sup>-1</sup> for MF5-1 and MF5-2, respectively. A low value of the activation energies suggests that the adsorption process is controlled by particle diffusion mechanism.

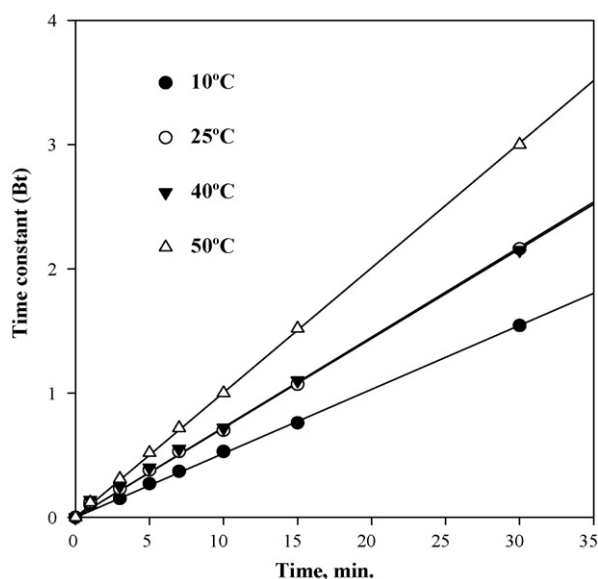


Fig. 17. Time constant ( $Bt$ ) vs. time of Cr(VI) on MF5-2 at different temperatures.

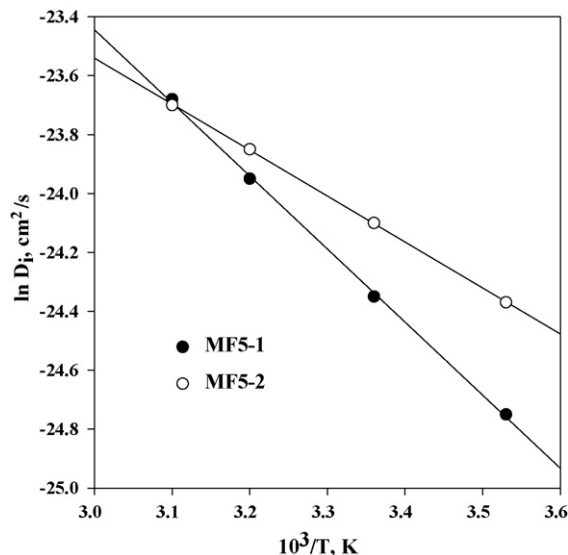


Fig. 18. Arrhenius diagram of Cr(VI) adsorbed on MF5-1 and MF5-2.

Fig. 19 shows the adsorption percent of Cr(VI) and Cr(III) as function of time. It can be seen that the adsorption of Cr(III) was constant during the run, while for Cr(VI), it is increased to 97% after about 90 min. Also, adsorption of coexisting multi-metal ions onto MF5-2 adsorbent was examined. The results showed that there is no effect in the presence of the other ions on the adsorption of Cr(VI).

Effect of adsorbent weight on Cr(VI) removal from the synthetic coolant water is shown in Fig. 20. Maximum adsorptive removal of Cr(VI) from wastewater agitated with 0.1 g of MF5-2 or greater weight.

The effect of contact time on the removal of Cr(VI) from this synthetic coolant water is shown in Fig. 21. The removal increases with time and attains equilibrium within 45 min.

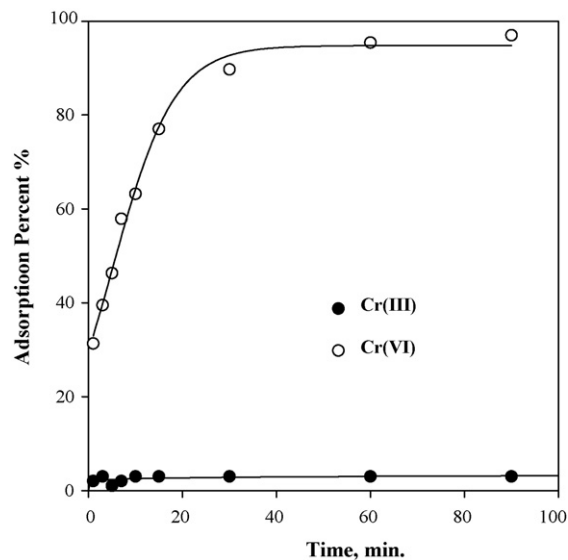


Fig. 19. Adsorption of Cr(III) and Cr(VI) on MF5-2: Cr(III) concentration = 50 mg dm<sup>-3</sup>; Cr(VI) concentration = 50 mg dm<sup>-3</sup>;  $T = 25^\circ\text{C}$ ; pH 9.5; adsorbent weight 0.5 g/50 ml.

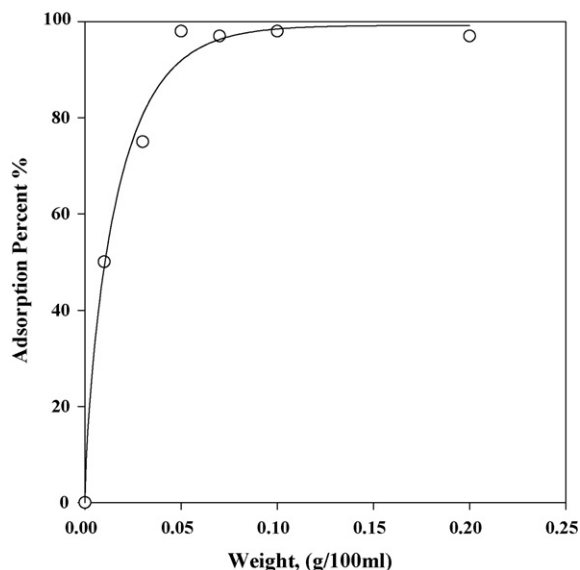


Fig. 20. Effect of weight of adsorbents on Cr(VI) removal from the synthetic nuclear power plant coolant water.

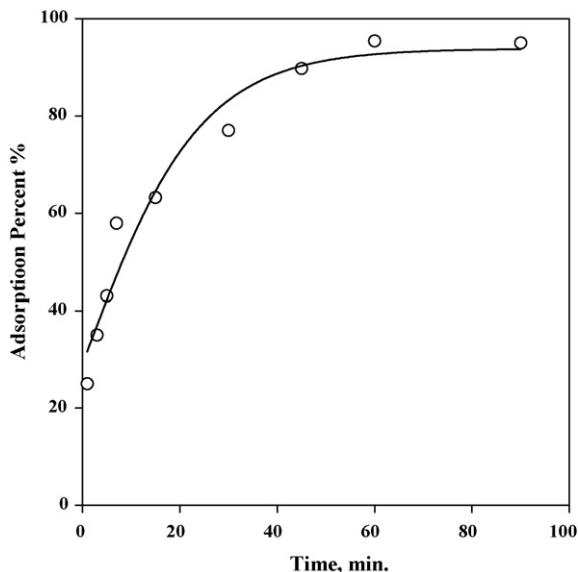


Fig. 21. Effect of contact time on the removal of Cr(VI) by MF5-2 from synthetic nuclear power plant coolant water. Adsorbent weight = 0.05 g/100 ml.

#### 4. Conclusion

MF5-1 and MF5-2 adsorbents 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 batch mode studies. The maximum loading capacity of adsorbent for MF5-1 and MF5-2 was found to be 7.2 and 10 mg/g Cr(VI), respectively. The kinetic data would be useful for the fabrication and design of wastewater treatment plants. The kinetics of adsorption of Cr(VI) by MF5-1 and MF5-2 follow first-order reversible kinetics. Increase of the temperature increased the adsorption, indicating the adsorption process is endothermic nature for MF5-1 and MF5-2. The pore diffusion is the rate-determining step in the adsorption of Cr(VI) ions for

MF5-1 and MF5-2. Particle diffusion mechanism plays a significant role in the adsorption. The values of  $\Delta H^*$  were found 18.1 and 10.7 kJ mol<sup>-1</sup> for MF5-1 and MF5-2, respectively. The  $\Delta S^*$  were found to be -106.8 and -118.6 J mol<sup>-1</sup> K<sup>-1</sup> for MF5-1 and MF5-2, respectively. The maximum conditions for Cr(VI) adsorption were applied for the separation of Cr(III) and Cr(VI). It was found that Cr(VI) can be adsorbed on MF5-2, whereas Cr(III) cannot. Also, adsorption of coexisting multi-metal ions onto MF5-2 adsorbent was examined. No effect in the presence of the other ions on the adsorption of Cr(VI) was observed.

#### References

- [1] P. Maravelaki-Kalaitzaki, G. Moraitou, Sorel's cement mortars decay susceptibility and effect on Pentelic marble, *Cem. Concr. Res.* 29 (1999) 1929.
- [2] S. Sorrel, On a new magnesium cement, *Compt. Rend.* 65 (1867) 102.
- [3] S. Piotr, Metal-assembled compounds: precursors of polymerization catalysts and new materials, *Coord. Chem. Rev.* 248 (2004) 1047–1060.
- [4] H. Bilinski, B. Matkovic, C. Mazuravic, T.A. Zunic, The formation of magnesium oxychloride phases in the systems MgO–MgCl<sub>2</sub>–H<sub>2</sub>O and NaOH–MgCl<sub>2</sub>–H<sub>2</sub>O, *J. Am. Ceram. Soc.* 67 (1984) 266.
- [5] L. Urwongse, C. Sorrel, The system MgO–MgCl<sub>2</sub>–H<sub>2</sub>O at 23 °C, *J. Am. Ceram. Soc.* 63 (1980) 501.
- [6] M.S. Gasser, Kinetics of Co(II) adsorption from aqueous solution on Fe(III) magnesium oxychloride sorbent, *Arab. J. Nucl. Sci. Appl.* 37 (2) (2004) 23.
- [7] A.M. Daifullah, N.S. Awwad, *Arab. J. Nucl. Sci. Appl.* 36 (3) (2003) 179.
- [8] L. Dupont, E. Guillon, Removal of hexavalent chromium with a lignocellulosic substrate extracted from wheat bran, *Environ. Sci. Technol.* 37 (2003) 4235.
- [9] C.F. Baes, R.E. Mesmer, *The Hydrolysis of Cations*, Wiley, NY, USA, 1976.
- [10] E. Abass, M. Alireza, V. Reza, *Am. J. Appl. Sci.* 2 (10) (2005) 1471–1473.
- [11] S. Rengaraj, K.H. Yeon, S.H. Moon, The removal of chromium from water and wastewater by ion exchange resins, *J. Hazard. Mater.* 87 (2001) 173.
- [12] K. Periasam, K. Srinivasan, P.R. Murugan, Studies on chromium(VI) removal by activated ground-nut husk carbon, *Ind. J. Environ. Health* 33 (4) (1991) 433.
- [13] S. Chand, V.K. Agarwai, C. Pavankumar, Removal of hexavalent chromium from wastewater by adsorption, *Ind. J. Environ. Health* 36 (3) (1994) 151.
- [14] N.K. Lazaridis, D.D. Asouhidou, Kinetics of sorptive removal of chromium(VI) from aqueous solutions by calcined Mg–Al–CO<sub>3</sub> hydroxalite, *Water Res.* 37 (2003) 2875.
- [15] V.K. Singh, P.N. Tiwari, Removal and recovery of chromium(VI) from industrial wastewater, *J. Chem. Technol. Biotechnol.* 69 (1997) 376.
- [16] Y.H. Wang, S.H. Lin, R.S. Juang, Removal of heavy metal ions from aqueous solutions using various low-cost adsorbents, *J. Hazard. Mater. B* 102 (2003) 291.
- [17] R.Q. Long, R.T. Yang, Carbon nanotubes as superior sorbent for dioxin removal, *J. Am. Chem. Soc.* 123 (2001) 2058.
- [18] D.O. Cooney, *Adsorption Design for Wastewater Treatment*, Lewis Publishers, Boca Raton, FL, 1999, p. 231.
- [19] D.W. Kang, K.B. Sung, S.H. Lee, H.Y. Kim, *J. Kor. Solid Waste Eng. Soc.* 15 (1998) 24.
- [20] F.J. Stevenson, *Humus Chemistry Genesis*, Wiley–Interscience, New York, 1982, p. 443.
- [21] Z. Marczenko, *Spectrophotometric Determination of Elements*, John Wiley & Sons, New York, 1976.
- [22] C. Namasivayam, K. Renganathan, Removal of Cd(II) from wastewater by adsorption on waste Fe(III)/Cr(III) hydroxide, *Water Res.* 29 (1995) 1737.
- [23] S. Glasstone, *A Textbook of Physical Chemistry*, Macmillan, Little Essex Street, London, 1946.
- [24] G. McKay, H.S. Blair, J.R. Garden, Adsorption of dyes on chitin 1. Equilibrium studies, *J. Appl. Polym. Sci.* 27 (1982) 3043.
- [25] S. Lagergren, K.S. Bil, *Vatenskapskad. Handl.* 24 (1898).

- [26] K. Srinivasan, N. Balasubramanian, T.V. Ramakrishna, Studies on chromium removal by rice husk carbon, *Indian J. Environ. Health* 30 (1988) 376.
- [27] G.E. Boyd, A.W. Anderson, L.S. Myres, The exchange adsorption of ions from aqueous solution by organic zeolites II. Kinetics, *J. Am. Chem. Soc.* 69 (1947) 2036.
- [28] D. Reichenburg, Properties of ion exchange resin in relation to their structure III. Kinetics of exchange, *J. Am. Chem. Soc.* 75 (1953) 589.
- [29] L.D. Michelson, P.G. Gideon, E.G. Pace, L.H. Kutal, Removal of soluble mercury from wastewater by complexing techniques, *Water Res. Technol.* 74 (1975).
- [30] R.M. Barrer, R.F. Bathalomew, L.V.C. Ress, *J. Phys. Chem. Solids* 12 (1961) 12.
- [31] J. Mathew, S.N. Tandon, *Can. J. Chem.* 55 (1977) 3857.
- [32] D.S. Flett, *Handbook of Solvent Extraction*, John Wiley & Sons, 1983.
- [33] K.J. Laidler, *Chemical Kinetics*, McGraw-Hill, 1975, p. 205.