

Amino-functionalized mesoporous MCM-41: an efficient adsorbent for the removal of chromium (III) ions from aqueous solution

Inderpreet Kaur, Divya Mandiyal, Bhupinder Pal Singh, Rajeev Kumar and Jyoti Chawla

ABSTRACT

Amino-functionalized mesoporous MCM-41 (NH₂-MCM-41) has been synthesized and explored as sorbent for removal of trivalent chromium, from aqueous media. The chemical and morphological structures of NH₂-MCM-41 were investigated by scanning electron microscopy, energy-dispersive x-ray, and x-ray diffraction techniques. The best performance of NH₂-MCM-41 as sorbent for removal of trivalent chromium was observed at optimized conditions: pH 3, adsorbent dose (1 g/L), contact time (2 hrs) and temperature (40 °C). Langmuir isotherm model was best fitted to the experimental data with high value of regression coefficient compared to Freundlich and Temkin models indicating monolayer adsorption of the chromium ions on the surface of NH₂-MCM-41 with the maximum Langmuir adsorption capacity of 83.33 mg/g. The adsorption mechanism can be explained by the combined effects of strong chemical interaction of chromium (III) ions with the surface amino group and some un-reacted silicate groups of NH₂-MCM-41. Adsorption kinetics was best described by pseudo-second-order kinetics model as compared to pseudo-first-order and followed by both diffusion as well as intra-particle pore diffusion mechanism. Thermodynamic analysis revealed that the adsorption was highly favorable, spontaneous and endothermic in nature which allows application of amino-functionalized MCM-41 as a promising adsorbent for the treatment of industrial effluents and other environmental samples.

Key words | adsorption, amino-functionalized MCM-41, Freundlich, Langmuir, Temkin, trivalent chromium

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INTRODUCTION

The discharge of heavy metals such as lead, copper, zinc, manganese, cadmium, and chromium in water is of great concern as they may have adverse impacts on the environment and pose serious human health risks (Gupta *et al.* 2011; Saleh & Gupta 2012; Kumar & Chawla 2014; Chawla *et al.* 2015; Kumar *et al.* 2015). Chromium is one of the heavy metals which exists in different oxidation states with chromium (III) and (VI) as the most abundant species. Chromium (III) is likely to be oxidized to chromium (VI)

after water treatment. Chromium enters into the environment through natural processes as well as human activities. Chromium metal is often added to steel during the preparation of stainless steel due to high corrosion resistance and hardness of chromium (Erdam *et al.* 2004). Chromium containing leather waste mainly consists of collagen and chromium (III) complexes (Mahmood *et al.* 2012). Chromium compounds are also used in textile, plating and dyeing industries. Sanyala *et al.* (2015), in a recent study,

concluded that the aquatic ecosystems in the Ranaghat-Fulia region of West Bengal, India were greatly contaminated by chromium due to a number of handloom textile factories in the nearby area. The study also raised concerns regarding potential human health hazards through consumption of fish contaminated with chromium. The National Pollutant Release Inventory database (NPRI 2012) also listed 358 facilities that reported release of chromium compounds across Canada in 2012.

Chromium (III) is vital for normal operation of human vascular and metabolic systems as well as combating diabetes. The *in vitro* studies explained that chromium (III) has the possibility to cause DNA damage in cell culture systems (Eastmond *et al.* 2008; Khan *et al.* 2012). The WHO (2008) recommended the limit of chromium in drinking water be 0.05 mg/L. Chromium (VI) (CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$) is the most dangerous form of chromium as it enters the blood stream and may cause health problems including: allergic reactions, skin rashes, respiratory problems, nose irritations and nosebleed, ulcers, weakening of immune system, alteration of genetic material, lung cancer, kidney and liver damage, and may even cause death of the individual (Mohan *et al.* 2006; Wang *et al.* 2014; Ghosh *et al.* 2015).

Many techniques, such as ion exchange, reverse osmosis, nano-filtration, precipitation, and adsorption have been used for the removal of chromium from water but are expensive and involve heavy instrumentation (Shalan *et al.* 2001; Kozłowski & Walkowiak 2002; Ozaki *et al.* 2002; Rengaraj *et al.* 2002; Covarrubias *et al.* 2008; Golbaz *et al.* 2014; Kim *et al.* 2015). Adsorption is the most simple and economic method and involves simple laboratory equipment for the removal of chromium from water. Several studies have reported the application of various natural as well as synthetic adsorbents for the removal of various metal ions from water (Kumar & Chawla 2014; Chawla *et al.* 2015). For instance, a low-cost activated carbon (ATFAC) was synthesized from coconut shell fibers and utilized for chromium (III) removal from water/wastewater and evaluated for its adsorption capacity in comparison to commercially available activated carbon fabric cloth (ACF) (Mohan *et al.* 2006). The maximum adsorption capacities of ATFAC and ACF at 298 K were 12.2 and 39.6 mg/g, respectively. Chromium (III) adsorption increased with an increase in temperature and followed the pseudo-second-

order rate kinetics. The biosorption of chromium (III) ions from aqueous solution was investigated using lichen (*Parmelinatiaceae*) biomass (Uluozlu *et al.* 2008). The monolayer biosorption capacity of *Parmelinatiaceae* biomass for chromium (III) ions was found to be 52.1 mg/g with pseudo-second-order kinetics. In another report, amine-based polymer, aniline formaldehyde condensate (AFC) was applied as an adsorbent for removal of chromium (III) ions in an aqueous environment (Kumar *et al.* 2009). Adsorption increased with pH and a maximum removal of 80% was reported at pH 6. Formation of a multi-dentate coordinate bond between $[\text{CrOH}]^{2+}$ and $[\text{Cr}(\text{OH})_2]^{1+}$ and the deprotonated amino group ($-\text{NH}_2$) of AFC was suggested as a possible mechanism for removal of chromium (III) in an aqueous environment. Adsorption of chromium (III) on AFC followed the Langmuir isotherm model with maximum monolayer coverage of 30.77 mg/g (Kumar *et al.* 2009).

In recent years, much work has been done on the adsorption of heavy metals on mesoporous silica materials. These are mesoporous molecular sieves having a pore size between 2 and 50 nm. The widely used representatives of this family include MCM-41, MCM-48, and MCM-50. Of these, MCM-41 is the best known and most widely studied silica solid. It exhibits high specific surface areas, high crystallinity, high thermal stability, uniformity of hexagonal cylindrical pores, narrow pore distribution, and regulation of pore diameter from 1.5 to 10 nm (Aguado *et al.* 2009). The structures of mesoporous materials include amorphous silica containing an ample amount of silanol groups. The groups on the surface of these materials are weakly acidic which makes them an effective adsorbent and helps in the removal of dyes and heavy metal ions from their aqueous solution (Anbia *et al.* 2010; Wu *et al.* 2012; Gupta *et al.* 2013). The modified MCM-41 was used as adsorbent for the adsorption of organic dyes and metal ions from their aqueous solutions (Mittal *et al.* 2009, 2010; Qin *et al.* 2009; Northcott *et al.* 2010; Idris *et al.* 2011; Parida *et al.* 2012). There are two methods for surface modification of mesoporous silica materials, post-grafting and direct synthesis or one pot co-condensation. The one pot co-condensation method is dominant as it enables a higher and more homogenous coverage of moieties at the surface of mesoporous silica. Considering the important properties of functionalized silica-based materials, the present work aimed at the

preparation of low-cost and more efficient amino-functionalized mesoporous material (NH₂-MCM-41) based on surfactant cetyltrimethylammonium bromide (CTAB) by the co-condensation method and its application as an adsorbent for the removal of chromium (III) metal ions from aqueous solution.

MATERIALS AND METHODS

Experimental

Tetraethylorthosilicate (TEOS) 98% used for the preparation of mesoporous silica material was of reagent grade and purchased from Sigma-Aldrich, India. The surfactant, CTAB with 99% purity was obtained from Merck and employed as a structure directing agent. The organoalkoxysilane selected for the functionalization process was 3-aminopropyltriethoxysilane (APTES) of 99% purity, obtained from Sigma-Aldrich, India. The source of metal ions for conducting the adsorption experiments was chromium sulfate 99.99% (Sigma-Aldrich, India). Sulfuric acid 98% (LOBA Chemie, India) and sodium hydroxide 97% (Sigma-Aldrich, India) were used for adjusting pH while carrying out the pH experiment. The apparatus was washed thoroughly first with chromic acid of AR grade then with double distilled water.

Synthesis of NH₂-MCM-41 by co-condensation method

A mixture of 2 g of CTAB, 7 mL of 2 N NaOH and 80 mL of water was heated for 30 min at 80 °C. To the clear solution, 10 mL of TEOS and 1.34 mL of APTES were then added for the preparation of NH₂-MCM-41 (as-such). After the addition, white precipitates were formed after 3 minutes' stirring at 300 rpm. The reaction temperature was maintained at 80 °C for 2 hrs. The precipitates were filtered, washed and dried in a hot-air oven for 24 hrs. The as-such material (1 g) was acid extracted with a mixture of 100 mL of ethanol and 1 mL of concentrated HCl for removing entrapped surfactant. The material thus obtained was dried and stored in a clean vial for use as an adsorbent for the removal of chromium (III) ions from aqueous solution.

Adsorption experiment

A stock solution of Cr₂(SO₄)₃·12H₂O of 1,000 ppm was prepared by dissolving 11.69 g in 1 L of double distilled water. This solution was stored in a volumetric flask. The chromium solutions of different concentrations were prepared by diluting the stock solution. The adsorption experiments were carried out in batch mode by shaking the appropriate amount of NH₂-MCM-41 with chromium (III) solution (50 mL) and the process of adsorption was studied systematically in terms of pH (3–8), contact time (30 min to 12 hrs), adsorbent dose (0.5 g/L to 2 g/L), and initial concentrations (20 mg/L to 300 mg/L) at different temperatures (293 K, 298 K, 303 K, 313 K) in the reagent bottles at 150 rpm. After shaking the bottles, NH₂-MCM-41 was separated from the solution by filtration and the final concentration of chromium (III) was obtained by recording the absorbance of supernatant solution by using an absorption flame emission spectrophotometer (AA-6200, Shimadzu).

Statistical data analysis

All the experiments were carried out in triplicate and statistical analysis of data was performed using Microsoft Office Excel 2007 by applying regression analysis and one-way analysis of variance (ANOVA). Regression analysis gives R^2 value with value ranging from 0 to 1. An $R^2 = 1$ indicates that the regression line perfectly fits the data. One-way ANOVA was applied to check the significance of experimental data in terms of f-ratio.

RESULTS AND DISCUSSION

Characterization of amino-functionalized mesoporous MCM-41

The characterization of amino-functionalized mesoporous MCM-41 and adsorption of chromium (III) ions were investigated by various techniques. The results obtained are discussed in the following sections.

XRD analysis

X-ray diffraction (XRD) is a technique commonly used for identification of the structure of crystalline materials and analysis of unit cell dimensions. This technique allows detailed characterization of crystalline samples, determination of unit cell dimensions, and quantitative determination of modal amounts of minerals in a sample.

The adsorbent NH₂-MCM-41 was investigated by XRD and two sharp peaks were observed for NH₂-MCM-41 at 2θ of 0.5 and 2.0 as shown in Figure 1, which ensured the well-ordered hexagonal arrangement in the mesoporous structure. This result indicated that the mesoporous structure was not destroyed during the surface amino functionalization process.

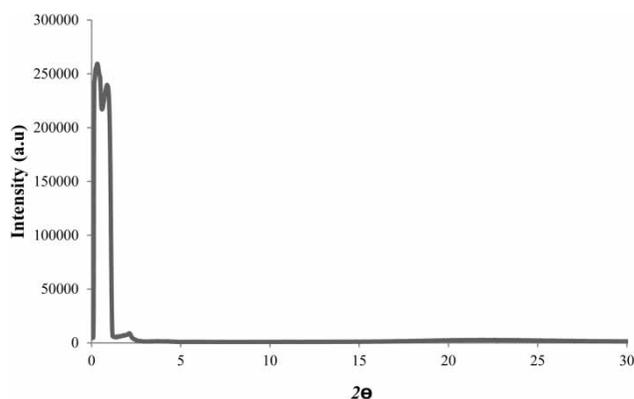


Figure 1 | XRD spectra of NH₂-MCM-41.

Characterization of the adsorbent by BET method

Analysis of the surface of adsorbent was carried out using Micromeritics ASAP-2020. The surface area of adsorbent was determined by Brunauer, Emmett, and Teller (BET) N₂ sorption procedure with liquid N₂ at -195.7°C . The BET surface area of NH₂-MCM-41 was found to be 155.1 m²/g.

Scanning electron microscope and energy-dispersive x-ray analysis

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons and giving information about the sample's surface topography. The SEM images of NH₂-MCM-41 were recorded before and after adsorption of chromium, as shown in Figure 2(a) and 2(b) using JEOL JSM-6100 SEM. The images were analyzed for their structural changes. It can be seen in Figure 2(a) that the surface of NH₂-MCM-41 consists of vacant sites. Further, Figure 2(b) shows filling of almost all the adsorption sites with chromium and the surface being covered non-uniformly. Hence, the adsorption of chromium changed the surface of NH₂-MCM-41 to a greater extent.

Energy-dispersive x-ray (EDX) spectroscopy allows the elemental analysis or chemical characterization of adsorbent NH₂-MCM-41 before and after adsorption and EDX spectra so obtained are shown in Figure 3(a) and 3(b). EDX spectrum of NH₂-MCM-41 did not show any characteristic peak for chromium (III), whereas an additional peak of

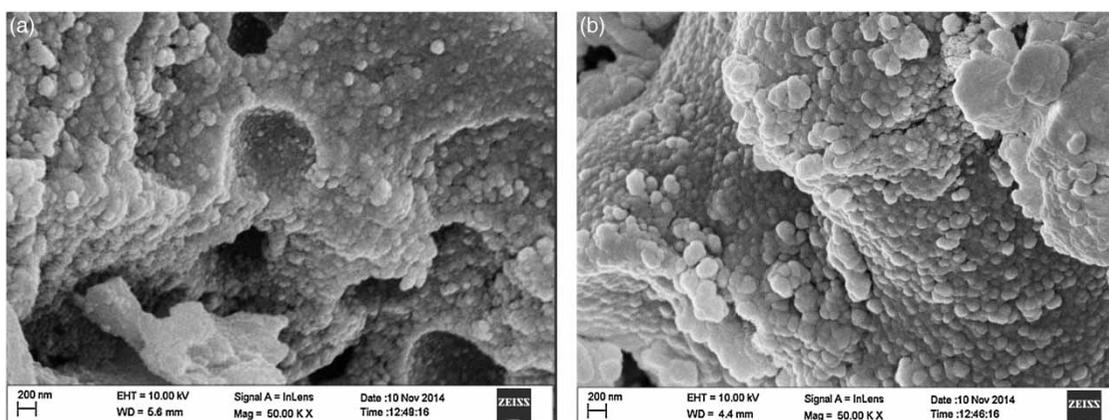


Figure 2 | SEM images of (a) NH₂-MCM-41 and (b) NH₂-MCM-41-chromium (III).

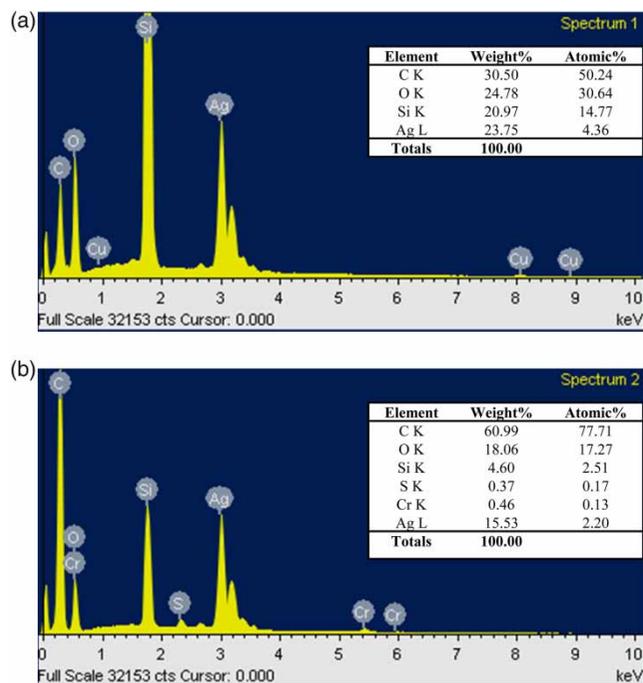


Figure 3 | EDX spectra of (a) NH₂-MCM-41 and (b) NH₂-MCM-41-chromium (III).

chromium (III) appeared at 5.5 KeV in the spectrum of chromium-loaded adsorbent which confirmed the adsorption of chromium (III) on the surface of adsorbent NH₂-MCM-41.

Adsorption of chromium (III) NH₂-MCM-41 from aqueous solution

The adsorption potential of NH₂-MCM-41 for chromium (III) removal from aqueous solution was investigated by varying experimental conditions such as pH, initial metal ion concentration, contact time, adsorbent dose, and temperature. The results of adsorption studies thus obtained are discussed in the following sections.

Effect of contact time

Contact time is a very important parameter which governs the process of adsorption and is one of the most effective factors in the batch adsorption process. In order to optimize the contact time for maximum adsorption capacity of the adsorbent, NH₂-MCM-41 for chromium (III), the effect of contact time on the adsorption of chromium (III) by NH₂-MCM-41 was investigated at adsorbent dose of 1 g/L for 50 ppm chromium

(III) solution from 0.5 hr to 12 hrs. Rapid adsorption of chromium (III) occurs in the first 30 minutes which led to the removal of 85% chromium (III). Further, it was observed that the percentage removal of chromium (III) increased from 85% to 92% in the next 2 hrs. Thereafter, the adsorption of chromium (III) increased marginally until it reached the equilibrium state. Hence, the optimum contact time of 2 hrs was maintained in further studies. Qin *et al.* (2006) explained in a study that the transfer rate of metal ions to the surface of sorbent was faster in the early stage, which led to high adsorption, and afterwards, adsorption becomes almost constant due to the lesser diffusion rate of metal ions into the intraparticles pores of the adsorbent.

Effect of adsorbent dose

Adsorbent dose plays a significant role in adsorption as it refers to the availability of adsorption sites. The effect of adsorbent dose was examined by varying the adsorbent dose from 0.25 g/L to 2 g/L for 50 ppm chromium (III) solution for contact time of 0.5 hr to 2 hrs. It was observed that the percentage removal of chromium (III) increased to 92% on increasing the dose of NH₂-MCM-41 from 0.25 g/L to 1 g/L for contact time of 2 hrs. The increase in chromium (III) adsorption with increasing adsorbent dose is due to increase in adsorbent surface area and availability of more adsorption sites. Study revealed that the adsorption sites remain unsaturated up to adsorbent dose 1 g/L and the number of available sorption sites increases. However, further increase in the adsorbent dose barely improved the percentage removal of metal ion. Therefore, the optimum dose of 1 g/L was fixed for further experiments. This may be attributed to overlapping of sorption sites as a consequence of overloading of adsorbent particles (Kumar & Gayothri 2009).

Effect of initial chromium (III) ion concentration

The effect of initial chromium (III) ion concentration was studied by taking various concentrations of chromium (III) solution ranging from 20 mg/L to 300 mg/L with optimum dose of 1 g/L and contact time of 2 hrs. It was observed that the adsorption of chromium (III) decreased with increasing concentration of chromium in the aqueous solution. At low concentration of metal ion, more of the

amine sites were available to bind with metal ions whereas at high metal ion concentration, the numbers of amine binding sites available are less with respect to the metal ions in the solution. This results in unfavorable conditions and hence, the adsorption of metal ions decreases. Shroff & Vaidya (2011) explained that increase in metal ions concentration caused more concentration gradient that led to a higher likelihood of collision among metal ions and the active adsorption sites, thereby increasing adsorption capacity. With further increases in metal ion concentration, the adsorption capacity remained constant because of saturation of the active adsorption sites.

Effect of pH

The initial pH of solution plays a vital role in the adsorption of metal ions as it affects the solubility of metal ions as well as the nature of functionality at sorbents' surface. In this study, the initial pH of solution was varied from 1 to 10. The effect of pH was studied at adsorbent dose of 1 g/L for 50 ppm chromium (III) solution and the pH was adjusted from 1 to 10 by the addition of 1N H₂SO₄ to get an acidic pH solution and 1N NaOH to get an alkaline pH solution. Figure 4 shows the variation of amount of chromium (III) adsorbed per unit mass of NH₂-MCM-41 (mg/g) (q_e) at various pH. The maximum adsorption capacity of chromium (III) was observed at pH value of 3. At pH lower than 3, the active sites became protonated and decreased the metal binding on the adsorbent surface, thus

decreasing the extent of adsorption. With increase in pH, the adsorption increased and reached the maximum at pH = 3. After that the adsorption fell with increase in pH maybe due to the formation of [Cr(OH)₆]³⁻ at higher pH values. The other reason for low adsorption at high pH may be due to the loss of mesoscopic hexagonal structure of NH₂-MCM-41 (Zhao *et al.* 1996). One-way ANOVA was applied and high variation between means of q_e values was observed at pH of solutions ranging from 1 to 10 (f-ratio = 2,556.25, $P \leq 0.001$), which confirmed the significantly better performance of adsorbent at pH 3. Therefore, pH 3 was selected as the optimum for the adsorption of chromium (III) metal ions on NH₂-MCM-41 for further studies.

Adsorption isotherms

Adsorption isotherms are quite helpful for determining the distribution of metal ions between solution and sorbents. Langmuir adsorption isotherm, Freundlich adsorption isotherm, and Temkin adsorption isotherm models were applied for adsorption of chromium (III) on NH₂-MCM-41 to evaluate the isotherm constants.

Langmuir adsorption isotherm

The Langmuir adsorption model is the most common model used to determine the adsorption capacity of an adsorbent. It is based on the assumption that maximum adsorption

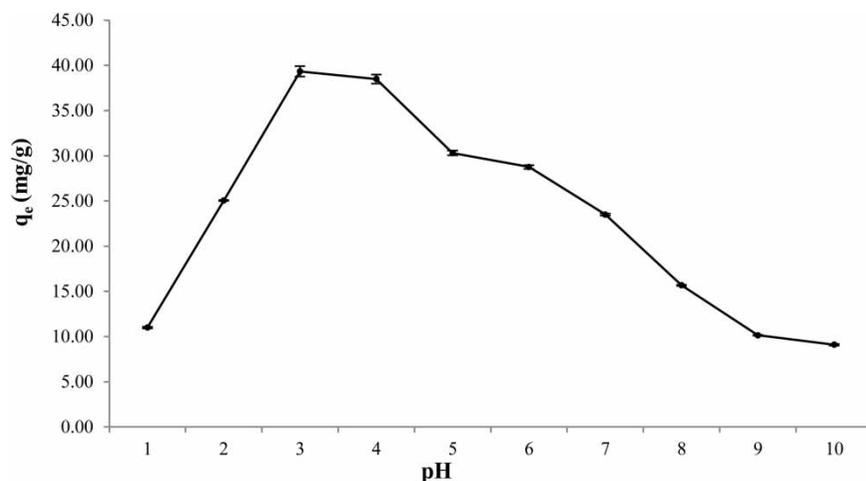


Figure 4 | Effect of pH on removal of chromium (III) ions using NH₂-MCM-41.

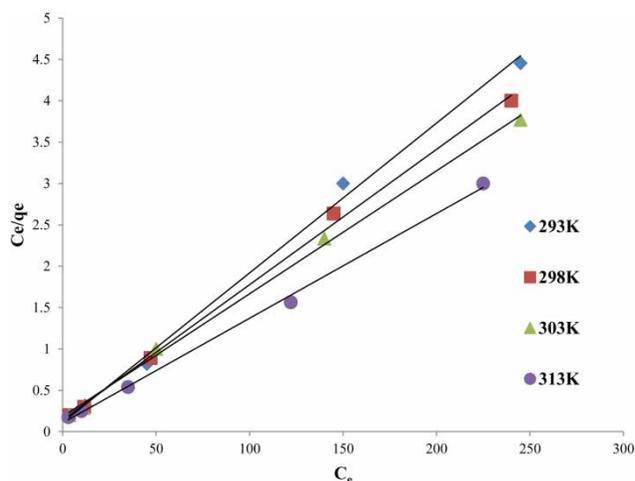


Figure 5 | Langmuir plots for adsorption of chromium (III) on $\text{NH}_2\text{-MCM-41}$.

occurs when a saturated monolayer of metal ions is formed on the adsorbent surface. A linear form of the Langmuir equation (Gupta & Ali 2004) can be expressed as follows:

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

where C_e is equilibrium concentration of metal ions (mg/L), q_e is the equilibrium amount adsorbed (mg/g), q_m is maximum adsorbed metal ion amount to complete monolayer coverage (mg/g), K_L is Langmuir constant related to energy of adsorption. Langmuir constant (K_L) is used to determine the dimensionless separation parameter R_L . Dimensionless separation parameter is the essential characteristic of Langmuir isotherms. The Langmuir isotherm plot for adsorption of chromium (III) ions on $\text{NH}_2\text{-MCM-41}$ was found to be linear with slope $1/q_m$ and intercept $1/(q_m K_L)$ (Figure 5). The parameters so obtained are summarized in Table 1.

It can be seen from the data that the value of q_m is increasing with increase in temperature which indicates that the amount of chromium (III) adsorbed per unit mass of $\text{NH}_2\text{-MCM-41}$ is increasing and the process of adsorption is favorable at high temperature. The feasibility of the process is expressed in terms of separation factor R_L which is given by the equation:

$$R_L = \frac{1}{(1 + K_L C_0)} \quad (2)$$

Table 1 | Langmuir adsorption parameters

| Langmuir constants | Temperatures | | | |
|--------------------|--------------|-------|-------|-------|
| | 293 K | 298 K | 303 K | 313 K |
| q_m (mg/g) | 55.55 | 62.50 | 71.42 | 83.33 |
| K_L (L/mg) | 0.166 | 0.112 | 0.077 | 0.113 |
| R^2 | 0.99 | 0.99 | 0.99 | 0.99 |
| R_L | 0.11 | 0.15 | 0.21 | 0.15 |

where K_L is Langmuir constant and C_0 is initial concentration of metal ions in (mg/L). The value of separation factor indicates the shape or type of isotherms. Isotherm will be linear if $R_L = 1$; irreversible if $R_L = 0$; favorable if $0 < R_L < 1$; and unfavorable if $R_L > 1$. The value of separation factor calculated by Langmuir isotherm model for the adsorption of chromium (III) on $\text{NH}_2\text{-MCM-41}$ is found to lie in the range of 0.10–0.21 (Table 1) which showed that the adsorption process is favorable. $R^2 = 0.99$ confirmed the best fit of regression line to data.

Freundlich adsorption isotherm

The Freundlich isotherm is basically an empirical relationship used to describe the adsorption on heterogeneous adsorbent surface (Gupta & Ali 2004). A linear form of the Freundlich equation can be expressed as:

$$\ln q_e = \ln K_F + \frac{1}{n} (\ln C_e) \quad (3)$$

where q_e is the equilibrium amount adsorbed (mg/g), K_F and n are Freundlich constants corresponding to adsorption capacity and adsorption intensity, respectively. The value of n varies in the range of 1–10 for classification of favorable adsorption (Chantawong et al. 2003). The high value of $1/n$ indicates preferential and high adsorption intensity towards adsorbent (Li et al. 2004). If the value of $1/n$ is below 1 it indicates a normal adsorption. On the other hand, $1/n$ being above 1 indicates cooperative adsorption. The Freundlich isotherm plot for adsorption of chromium (III) ions on $\text{NH}_2\text{-MCM-41}$ is found to be linear with slope $1/n$ and intercept $\ln K_F$ (Figure 6). The parameters so obtained are summarized in Table 2. It can be seen from the data that

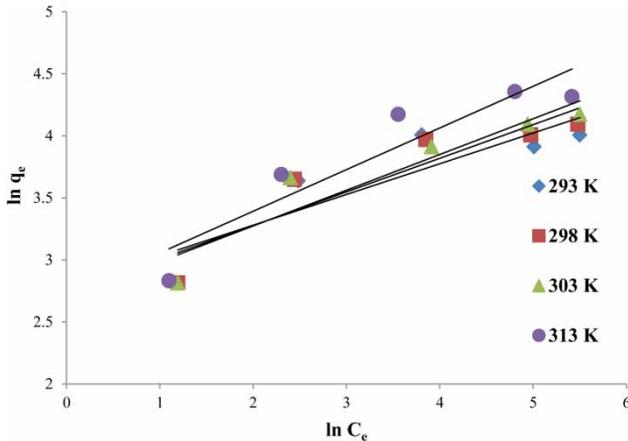


Figure 6 | Freundlich plots of $\ln C_e$ vs $\ln q_e$ for adsorption of chromium (III) on $\text{NH}_2\text{-MCM-41}$.

Table 2 | Freundlich adsorption parameters

| Freundlich constants | Temperatures | | | |
|----------------------|--------------|-------|-------|-------|
| | 293 K | 298 K | 303 K | 313 K |
| K_F (mg/g) | 16.17 | 15.41 | 14.85 | 15.18 |
| $1/n$ | 4.05 | 3.70 | 3.47 | 2.98 |
| R^2 | 0.77 | 0.84 | 0.88 | 0.86 |

the value of $1/n$ is more than unity for different temperatures which indicates that the adsorption of chromium (III) on $\text{NH}_2\text{-MCM-41}$ is a cooperative process (Granados-Correa et al. 2013; Shijie 2015). The values of $1/n$ greater than unity support multilayer or apparent multilayer behavior of adsorption which is an excellent model to describe cooperative adsorption. Apart from the homogeneous surface, the Freundlich equation is also suitable for a highly heterogeneous surface. It can be seen that the smaller values of $1/n$ (in the range of 2.98–4.03) indicate greater heterogeneity.

Temkin adsorption isotherm

The Temkin isotherm contains a factor that takes into account the adsorbent–adsorbate interactions. The model, by ignoring the very low and large values of concentrations, assumes that heat of adsorption (as function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with surface coverage. The Temkin

equation is represented as:

$$q_e = B \ln A + B \ln C_e \quad (4)$$

where $B = RT/b$, b is the Temkin constant which is related to heat of sorption (J/mol), R is the gas constant (8.314 J/mol K), and T is the absolute temperature (K). A is the Temkin isotherm constant (equilibrium binding constant), corresponding to the maximum binding energy (l/g); q_e is amount of chromium (III) absorbed per unit mass of $\text{NH}_2\text{-MCM-41}$ (mg/g) and C_e is concentration of chromium (III) in the solution at equilibrium (mg/L). The Temkin isotherm plot for adsorption of chromium (III) ions on $\text{NH}_2\text{-MCM-41}$ is shown in Figure 7 with slope represented by B and intercept represented by $B \ln C_e$. The Temkin parameters so obtained are summarized in Table 3. It can be seen from the data in Table 3 that the value of B lies in the range of 8.20 J/mol–14.18 J/mol for different temperatures indicating the process of physical adsorption.

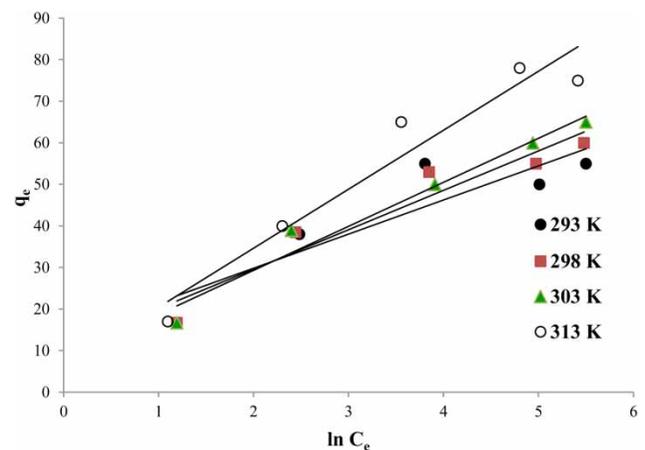


Figure 7 | Temkin plots of adsorption of chromium (III) on $\text{NH}_2\text{-MCM-41}$.

Table 3 | Temkin adsorption parameters

| Temkin constants | Temperatures | | | |
|------------------|--------------|--------|--------|--------|
| | 293 K | 298 K | 303 K | 313 K |
| B | 8.20 | 9.47 | 10.59 | 14.18 |
| A (L/g) | 5.10 | 3.06 | 2.14 | 1.55 |
| b (J/Mol) | 307.06 | 261.49 | 229.91 | 183.42 |
| R^2 | 0.81 | 0.92 | 0.97 | 0.94 |

Effect of temperature and thermodynamics of adsorption

The effect of temperature was studied by adding optimum adsorbent dose of 1 g/L to aqueous solutions of chromium (III) of appropriate concentrations at different temperatures, i.e., 293 K, 298 K, 303 K, and 313 K. The reagent bottles were stirred at 150 rpm in a temperature controlled orbital shaker at the appropriate temperature. From the study, it was observed that the adsorption capacity of sorbents increased with increasing the temperature, indicating the endothermic nature of adsorption.

The variation in the extent of adsorption with respect to temperature on the adsorbent surface has been explained on the basis of thermodynamic parameters, such as free energy change (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0). The thermodynamic study was carried out to gain information regarding the spontaneity and feasibility of the process of adsorption of chromium (III) on NH₂-MCM-41. Thermodynamic parameters for the adsorption of chromium (III) on NH₂-MCM-41 were calculated using the following equations:

$$\ln K_D = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (5)$$

$$K_D = \frac{q_e}{C_e} \quad (6)$$

where K_D is thermodynamic constant for the adsorption reaction at equilibrium, q_e is amount of chromium (III) absorbed per unit mass of NH₂-MCM-41 (mg/g), C_e is concentration of chromium (III) in the solution at equilibrium (mg/l), R is universal gas constant (8.314 KJ/mol), and T is absolute temperature (Kelvin).

The thermodynamic plot for the adsorption of chromium (III) ions on NH₂-MCM-41 is found to be linear, as shown in Figure 8, with the slope and intercept represented by $\Delta H^0/R$ and $\Delta S^0/R$, respectively. The values of ΔH^0 and ΔS^0 were determined from the slope and intercept. Gibbs free energy change (ΔG^0) of adsorption was calculated using the following equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (7)$$

The thermodynamic parameters recorded for the adsorption of chromium (III) on NH₂-MCM-41 are shown in Table 4. It can be seen from the data that the value of K_D (distribution ratio) is increasing with rising temperature, also indicating the endothermic nature of adsorption. The enthalpy (ΔH^0) and the entropy changes (ΔS^0) for the adsorption processes were calculated to be 8.9 KJ/mol and 0.039 KJ/mol/K, respectively. The positive value of ΔS^0 indicated that there is an increment in the randomness in the system solid-solution interface during the adsorption process. This increase of disorder in the

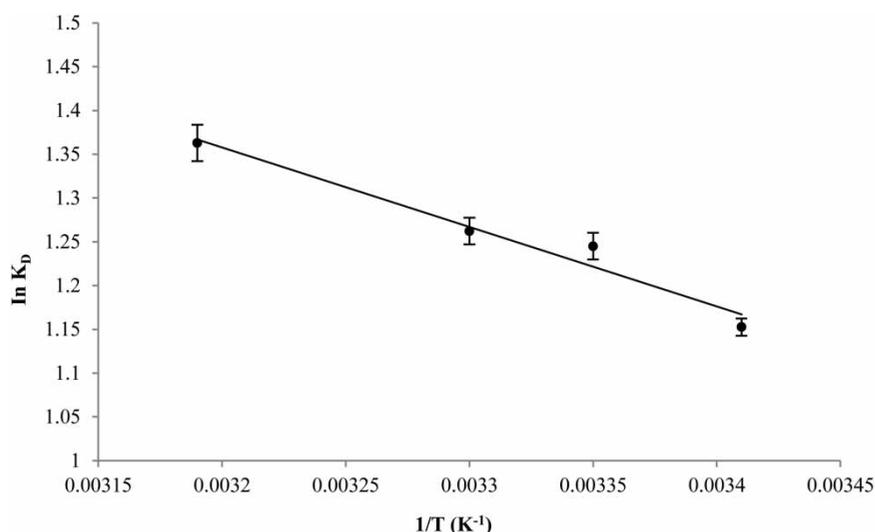


Figure 8 | Thermodynamic plot of adsorption of chromium (III) on NH₂-MCM-41.

Table 4 | Thermodynamic parameters for the adsorption of chromium (III) ions on NH₂-MCM-41

| Temperature (K) | K_D | ΔG^0 (KJ/mole) | ΔH^0 (KJ/mole) | ΔS^0 (KJ/mole/K) |
|-----------------|-------|------------------------|------------------------|--------------------------|
| 293 | 1.15 | -2.52 | 8.9 | 0.039 |
| 298 | 1.21 | -2.72 | | |
| 303 | 1.26 | -2.91 | | |
| 313 | 1.39 | -3.30 | | |

solid–solution could be the result of extra translational entropy gained by the water molecules previously adsorbed onto adsorbent but displaced by metal ions. The positive value of ΔS^0 reflected the affinity of the NH₂-MCM-41 for chromium (III) ions. In addition, the positive value of ΔH^0 indicated that the adsorption was endothermic. The negative values of ΔG^0 at various temperatures indicated the spontaneous nature of the adsorption process.

Kinetic study

Pseudo-first-order and pseudo-second-order were used to explain the mechanism of adsorption of chromium (III) ions on the surface of adsorbent (Demirbas et al. 2002; Zou et al. 2006). The pseudo-first-order kinetic model can be expressed by the equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (8)$$

A linear form of Equation (8) is:

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (9)$$

where k_1 (L/mg/min) is the adsorption rate constant of first-order kinetic models, q_e and q_t are amount of metal adsorbed per unit mass of adsorbent (mg/g) at equilibrium time t and at any time t . The values of k_1 were calculated from the slope of the linear plot of $\ln(q_e - q_t)$ versus time (Figure 9(a)).

The pseudo-second-order kinetic models can be expressed by the equation:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (10)$$

A linear form of Equation (10) is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (11)$$

where k_2 (L/mg/min) is the adsorption rate constant of second-order kinetic models. The values of q_e and k_2 can be calculated by the slope and intercept of plot of t/q_t versus t (Figure 9(b)).

The value of square of regression correlation coefficient (R^2) was determined for both the plots and calculated q_e values allowing one to check the agreement between the predicted and experimental capacity of adsorbent towards chromium (III) ions. R^2 of the developed pseudo-second-order reaction kinetics was found to be very close to unity compared to pseudo-first-order rate equation (Table 5) and calculated q_e value was found to be in good agreement with the experimental q_e value, which confirmed that the kinetics of adsorption of chromium (III) using NH₂-MCM-41 was best explained by the pseudo-second-order model rather than the pseudo-first-order model (Figure 9(a) and 9(b)). This could be explained by the adsorption of chromium on adsorbent occurring through the chemisorption mechanism which involves the valence forces through sharing or exchange of electrons.

Proposed mechanism of adsorption

The nature of surface of adsorbent in terms of type of functionalization plays a key role to describe the mechanism of adsorption. In the present study, ion exchange mechanism cannot be considered because of unavailability of exchangeable groups on the surface of sorbent. However, the adsorption of chromium (III) ions on the surface of NH₂-MCM-41 is as a result of strong chemical interaction between the surface amino groups of NH₂-MCM-41 and chromium (III) ion which is known as inner-sphere adsorption. The un-reacted silicate groups on the surface of adsorbent also contribute towards inner-sphere adsorption. This behavior can be explained on the basis of the HSAB principle which supports the faster and stronger bond formation between chromium (III) (hard acid) and amino and silicate groups (hard bases). Other weaker interactions between the other surface sites of NH₂-MCM-41 and chromium metal ions

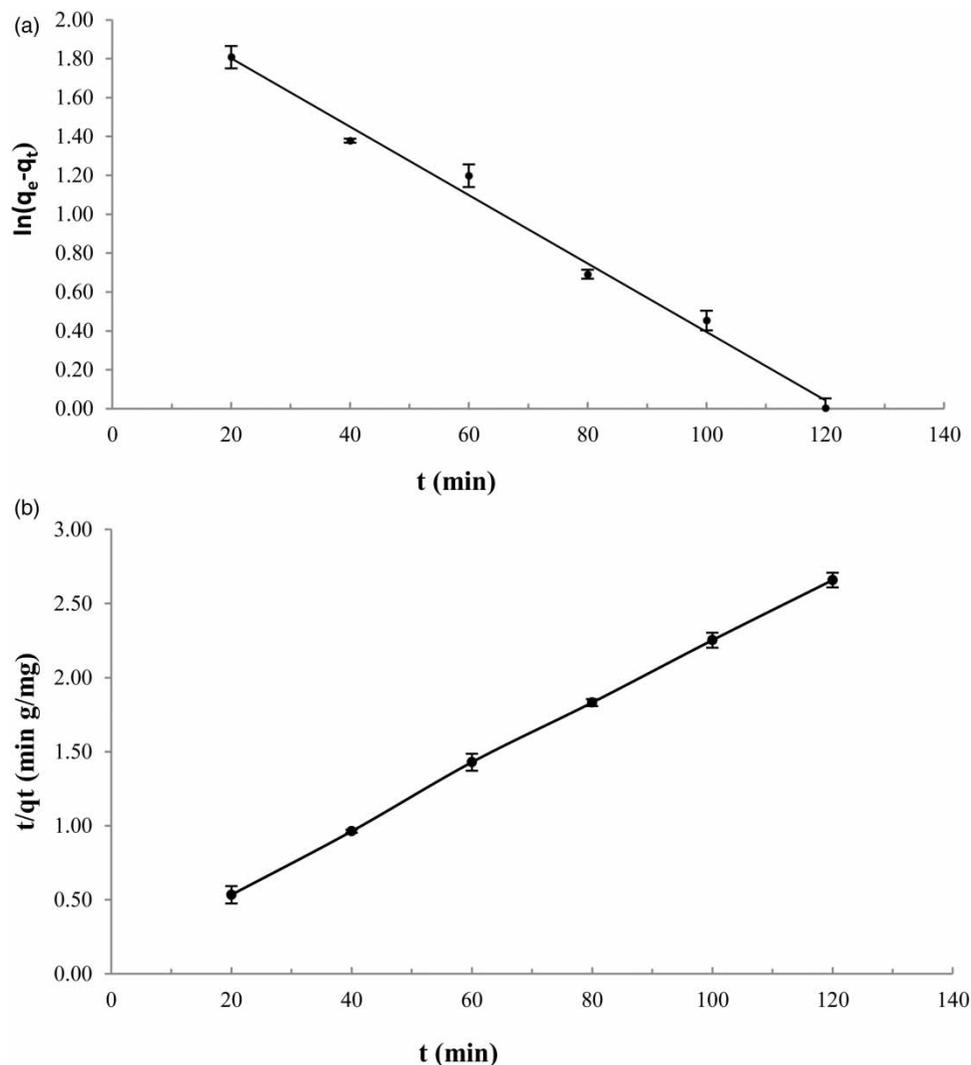


Figure 9 | (a) Pseudo-first-order adsorption plot of chromium (III) on NH₂-MCM-41 and (b) pseudo-second-order adsorption plot of chromium (III) on NH₂-MCM-41.

play important roles in adsorption and are called outer-sphere adsorption. The proposed mechanism for the synthesis of NH₂-MCM-41 and the adsorption of chromium (III) ion on the surface of NH₂-MCM-41 is as shown in Figure 10.

Table 5 | Kinetic parameters for the adsorption of chromium (III) ions on NH₂-MCM-41

| Model applied | q_e (mg/g) | k (min ⁻¹) | R^2 | q_e , exp. (mg/g) |
|-------------------------|--------------|--------------------------|-------|---------------------|
| (a) Pseudo-first-order | 8.31 | 0.017 | 0.99 | 46 |
| Model applied | q_e (mg/g) | k (g/mg/min) | R^2 | q_e , exp. (mg/g) |
| (b) Pseudo-second-order | 47.6 | 0.0041 | 0.99 | 46 |

Practical implications of current work

It is important to point out that contamination of water bodies by chromium due to industrial discharge is a serious issue as chromium has been detected in environmental water samples. It may enter the body through ingestion of contaminated water or fish from contaminated water and may pose unknown risks that are not well explored to date. There are many knowledge gaps regarding human health implications due to chromium toxicity because of insufficient *in vivo* studies. Sanyala et al. (2015), in a recent study, concluded that the aquatic ecosystems in the Rana-ghat–Fulia region of West Bengal, India were greatly

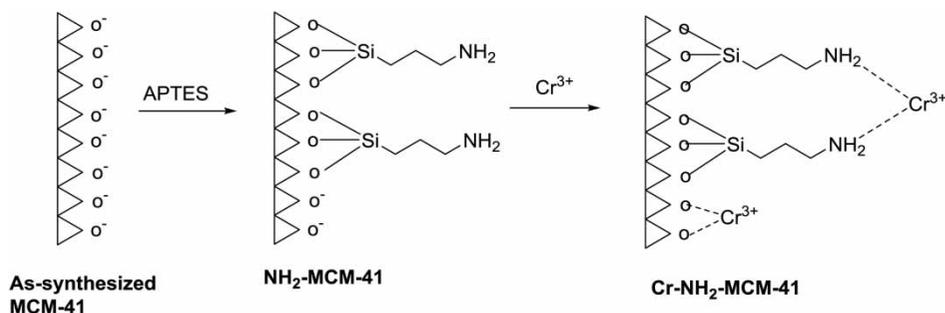


Figure 10 | Proposed mechanism for synthesis and adsorption of chromium (III) NH₂-MCM-41.

Table 6 | Comparison of NH₂-MCM-41 and other adsorbents for the adsorption of chromium (III) ions from water/wastewater samples

| S. no. | Adsorbents | Q_{max} (mg/g) | pH | Isotherm/Temp. | References |
|--------|---|------------------|-----|----------------|---------------------------------|
| 1. | Activated carbon produced from agricultural waste (cashew nut shells) | 12.91–14 | 3.5 | Langmuir/303 K | Tanguank <i>et al.</i> (2009) |
| 2. | Alder peat | 39.46 | 4 | Langmuir/RT | Komosińska <i>et al.</i> (2014) |
| 3. | Sedge peat | 49.06 | 4 | Langmuir/RT | Komosińska <i>et al.</i> (2014) |
| 4. | Smectite clay | 37.03 | 4 | Langmuir/RT | Komosińska <i>et al.</i> (2014) |
| 5. | Corn cob waste | 84.50 | 4.5 | Langmuir/298 K | Correa <i>et al.</i> (2013) |
| 6. | Polyacrylamide (PAA) | 84.03 | 4–6 | Langmuir/298 K | Mousavi <i>et al.</i> (2014) |
| 7. | Fungal biomass | 43.47 | 4 | Langmuir/298 K | Shoab <i>et al.</i> (2013) |
| 8. | Leaf biomass of <i>Calotropis procera</i> | 32.26 | 5 | Langmuir/303 K | Overah (2011) |
| 9. | Low cost activated carbon (ATFAC) | 12.20 | 6 | Langmuir/298 K | Mohan <i>et al.</i> (2006) |
| 10. | Activated carbon fabric cloth (ACF) | 39.56 | 6 | Langmuir/298 K | Mohan <i>et al.</i> (2006) |
| 11. | NH ₂ -MCM-41 | 83.33 | 3 | Langmuir/313 K | This study |

RT, room temperature.

contaminated by chromium due to the number of handloom textile factories in the nearby area. There is an urgent need for cheap and efficient remediation methods as well as more *in vivo* toxicity studies being required in order to ensure the presence of safer concentrations of chromium ions in aquatic bodies. The present study is very useful for practical application as it provides a very economic method for industrial effluent treatment.

Comparison with previous reports

Chromium contamination has been a serious environmental issue for many years and many research groups have attempted to find various adsorbents for the removal of chromium ions. The compiled information of different types of sorbents used for the removal of chromium (III) ions in

aqueous environments is presented in Table 6. It is clear from the table that all the sorbents already reported in the literature for the removal of chromium (III) ions from aqueous solution showed adsorption capacity less than 50 mg/g except for activated carbon synthesized from corn cob waste by Correa *et al.* (2013). In other words, it can be concluded that NH₂-MCM-41 possesses superior or comparable adsorption properties and can be applied as a promising adsorbent for removal of chromium ions from water.

CONCLUSION

In the present study, the amino-functionalized MCM-41 prepared by the co-condensation method was successfully prepared and applied as an effective adsorbent for the

removal of chromium (III) ions from aqueous solutions. The Langmuir isotherm model is best fitted with the experimental data with high values of regression coefficient ($R^2 = 0.996\text{--}0.998$) compared to the Freundlich and Temkin models, indicating monolayer adsorption of chromium ions on the surface of $\text{NH}_2\text{-MCM-41}$. The maximum Langmuir adsorption capacity was 83.33 mg/g. Kinetics of the adsorption process can be best explained by a pseudo-second-order model rather than pseudo-first-order model. The thermodynamic calculation showed that adsorption of the chromium ions on the surface of $\text{NH}_2\text{-MCM-41}$ is an endothermic process of a spontaneous nature. The results obtained in batch mode studies showed that $\text{NH}_2\text{-MCM-41}$ can be used as a viable and economic adsorbent for the removal of chromium (III) ions from aqueous solution.

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