Scientific paper

Chromate Removal Using Novel Modified MCM-41 Nanoporous Silica: Synthesis and Characterization of Novel Terpyridine-Modified MCM-41

Elahe Sattari,[1,2] Elahe Moazzen,[1] Mostafa M. Amini,[1,*]
Homira Ebrahimzadeh[1] and Mohammad Reza Poor Heravi[2]

[1] *Department of Chemistry, Shahid Beheshti University, G.C., Tehran 1983963113, Iran*

[2] *Department of Chemistry, Pyame Noor University (PNU), PO Box. 97, Abhar, Iran*

* *Corresponding author: E-mail: m-pouramini@sbu.ac.ir;*
Tel: +98-21-29903109; fax: +96-21-22431663

Received: 30-07-2012

Abstract

Novel terpyridine-functionalized MCM-41 nanoporous silica was synthesized and characterized by X-ray powder diffraction (XRD), infrared (IR) spectroscopy, transmission electron microscopy (TEM), and thermal (TGA-DSC) and elemental analyses. The application of functionalized nanoporous silica was investigated for the removal of chromate, which is one of the most harmful pollutants in the environment. The effects of several parameters including the sample pH, adsorption kinetic and maximum adsorption capacity of functionalized nanoporous silica in the removal of chromate were studied.

Keywords: Terpyridine; Functionalized nanoporous silica; MCM-41; Chromate

1. Introduction

Heavy metal ions such as chromium, copper, lead, nickel, and zinc ions in the environment, and specifically in the food chain, can cause serious health problems.[1–3] Among the above-mentioned metals ions, chromium is the most toxic; it is generated by many industrial processes, such as electroplating, leather tanning, metal finishing, and textile manfacturing.[4–6] Accidental chromium ingestion can cause indigestion, kidney, and liver damage, ulcers, and even death, as chromium is a carcinogen.[7–8] The frequently used methods for the removal of chromium (in the form of chromate anions) from wastewater include precipitation,[9] electrochemical reduction (with ferrous ion),[10] electroplating,[11] adsorption,[12] solvent-impregnated resins extraction[13] and micellar-enhanced ultra filtration.[14] These methods often require a large amount of high-purity organic solvents, in which most of them are harmful to health and can cause serious environmental problems.[15]

Adsorption has been the most economical and widely used technique for the removal of hexavalent chromium. This method has several advantages, such as low cost, ease of use, high preconcentration factor, and flexibility in choosing the solid phase.[16] A number of sorbents, such as zeolite,[17] carbon,[18] Ambersorb,[19] Moss (Hylocomium splendens),[20] TiO_2,[21] Chromosorb,[22] and nanoporous materials,[23] have been applied for the removal of chromium. Each sorbent has its own advantages and disadvantages. For example, carbons are stable in both acidic and alkaline pH environments, but they suffer from low surface areas. As another example, zeolite has high thermal and mechanical stability but is difficult to modify. Among these sorbents, nanoporous silicas with a large adsorption capacity have attracted a considerable amount of interest in recent years and have become good candidates for chromium removal.[24] Although these materials have several fascinating properties, such as large pore size, thick pore wall, and high thermal and mechanical stability, their applications are restricted without modifications.[25–26] In this work, novel terpyridine-modified MCM-41 nanoporous silica was prepared and after characterization, its applicability for the removal of chromium ions from aqueous media was investigated.

2. Experimental

2. 1. Materials and Instrumentation

All reagents used in this study (HCl, HNO_3, H_2SO_4, NaOH, KCl, Na_2CO_3, K_2CrO_4, toluene, ethanol, acetone, chloroform) were of analytical grade and were purchased from Merck Company (Darmstadt, Germany). Terephthaladehyde, 3-aminopropyltriethoxysilane, 2-methyl pyridine ketone and ammonium acetate used for functionalization were purchased from Merck Company. Double-distilled water from a Milli-Q purification system (Millipore, Bedford, MA, USA) was used for the preparation of solutions. A stock solution (1.0 mg mL^{-1}) of Cr(VI) was prepared by dissolving an appropriate amount of potassium chromate in double-distilled water.

A Rayleigh UV-2100 model double beam UV–Vis spectrophotometer with a tungsten lamp as the light source was used for the absorbance measurements. A 10 mm matched quartz cell was used to measure the absorbance of the analyte. The pH was measured at 25 ± 1 °C with a digital WTW Metrohm 827 Ion analyzer (Herisau, Switzerland) equipped with a combined glass-calomel electrode. The CHN analysis was performed on a Thermo Finnigan Flash EA112 elemental analyzer (Waltham, MA, USA). IR spectra were recorded on a Bruker IFS-66 FT-IR spectrophotometer. BET surface areas were measured by nitrogen adsorption technique using a Micromeritics ASPS 2010 analyzer. Low-angle X-ray diffraction patterns were obtained on a Philips-PW 17C diffractometer with Cu K_α radiation.

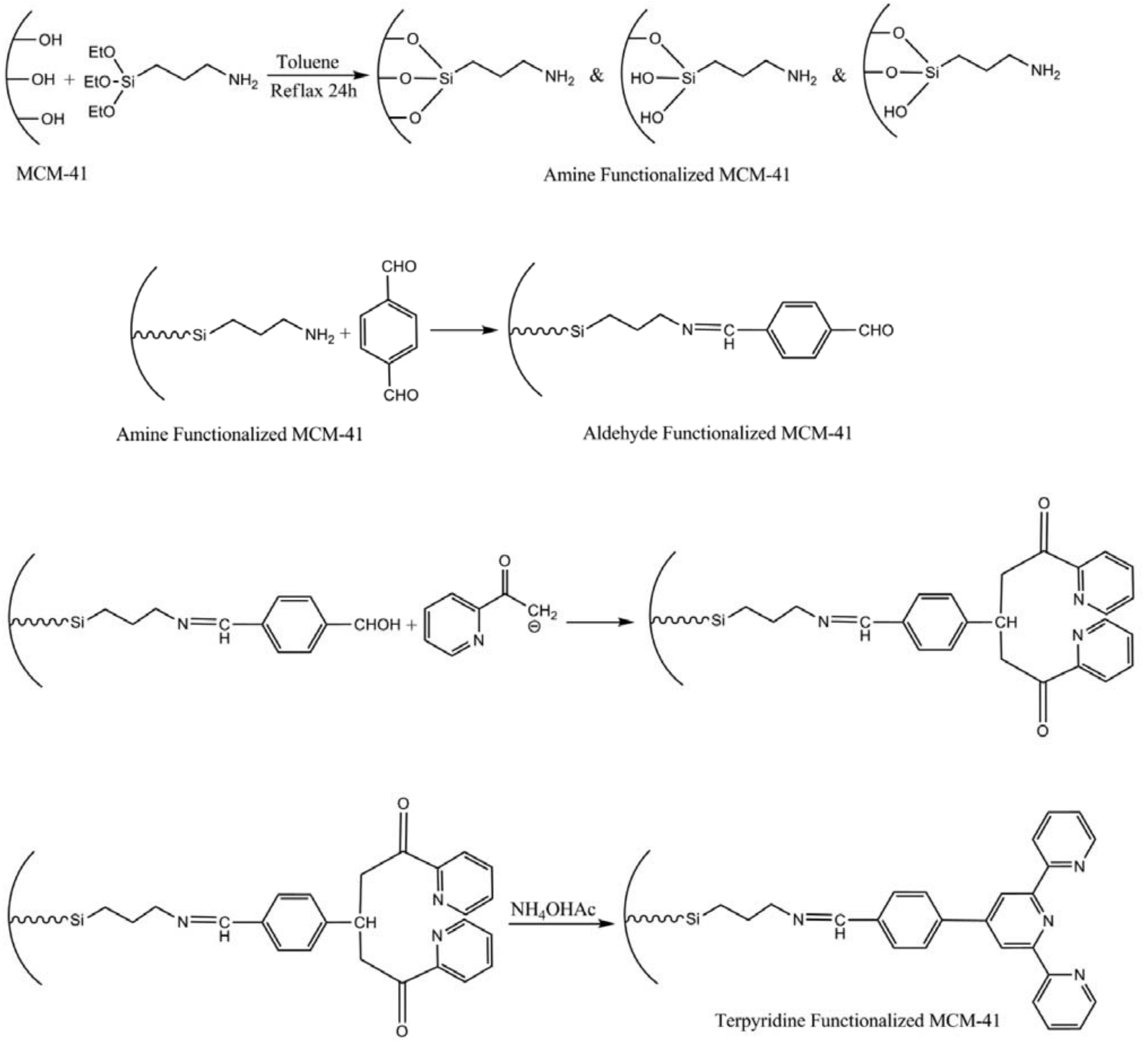

Fig. 1. A schematic diagram for terpyridine-modified MCM-41 synthesis

2. 2. Synthesis of MCM-41 Nanoporous Silica

MCM-41 nanoporous silica was prepared by sol-gel methods according to the published procedure.[27]

2. 3. Synthesis of Terpyridine-Modified MCM-41

Amine-functionalized MCM-41 was synthesized by reacting of 3-aminopropyltriethoxysilane with MCM-41 in toluene.[28] Then 1.0 g of amine-functionalized MCM-41 was suspended in 50 mL ethanol and 2.0 g of terephthalaldehyde was added. The mixture was refluxed for 24 h. Aldehyde-functionalized MCM-41 (MCM-41-CHO) was filtered and washed with ethanol. In the next step 1.0 g of MCM-41-CHO was again suspended in a methanoic solution of 2-methyl pyridine ketone, and the pH was adjusted at 9 using NaOH. The product was filtrated after 24 h, washed with ethanol, suspended in 50 mL ethanol containing ammonium acetate, and refluxed for further 24 h. The resulting material was washed copiously with ethanol and dried at room temperature. Terpyridine- functionalized nanoporous silica (MCM-41-terpy) was characterized by XRD, IR, TEM, and elemental analysis. A schematic diagram for the modification of MCM-41 by terpyridine is illustrated in Figure 1.

2. 4. Adsorption Procedure

A glass column was packed with 200 mg of MCM-41-terpy, and the end of column was blocked by two polypropylene filters to prevent loss of the nanoporous material during sample loading. Prior to extraction, the column was preconditioned successively with 5 mL absolute ethanol, 5 mL toluene, and 5 mL absolute ethanol and then washed with double- distilled water until it became free of organic solvent. A 50 mL standard solution containing 1 mg L^{-1} Cr(VI) (after adjusting the pH of sample to 3.0 by adding HNO_3 or NaOH solution) was passed through the column at a flow rate of 7 mL min^{-1} using a peristaltic pump. Afterwards, the analyt in the eluent was reacted with diphenylcarbazide solution, and it was measured by a UV spectrophotometer at λ = 548 nm.[29]

3. Discussion

3. 1. Terpyridine Functionalization

The IR spectrum of aldehyde-modified silica is represented in Figure 2b. The aldehyde functional group peak appeared at 1703 cm^{-1} and the C=C peak of its phenyl ring at 1644 cm^{-1}. These peaks clearly confirm the functionalization of MCM-41 by aldehyde. The IR spectrum of MCM-41-terpy (Fig. 2c) is compared to the IR spectra of MCM-41-CHO and bare MCM-41 in Figures 2b and 2a, respectively. As can be seen, the peaks at 1533 and 1629 cm^{-1} unambiguously confirm the formation of terpyridine-functionalized MCM-41.

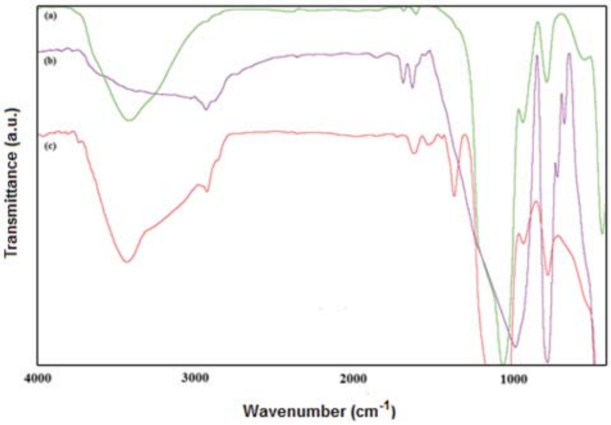

Fig. 2. The IR spectra a) MCM-41, b) Aldehyde-functionalized MCM-41, c) terpyridine functionalized MCM- 41.

A comparison of the low-angle XRD diffraction patterns of terpy-MCM-41 with the MCM-41 shows that the pore structures of nanoporous silica remain intact after functionalization (Fig. 3). For further elucidation, the TEM micrograph of MCM-41-terpy was recorded. The TEM micrograph is in good agreement with the XRD, suggesting that the pores remained unchanged after functionalization (Fig. 4).

The elemental analysis of MCM-41-terpy shows approximately 1.04 mmol/g terpyridine grafted on MCM-41 (C = 31.20%, H = 2.1%, and N = 5.86%). The decrease of surface area (S_{BET}) from 1098 to 537 m^2 g^{-1} confirmed

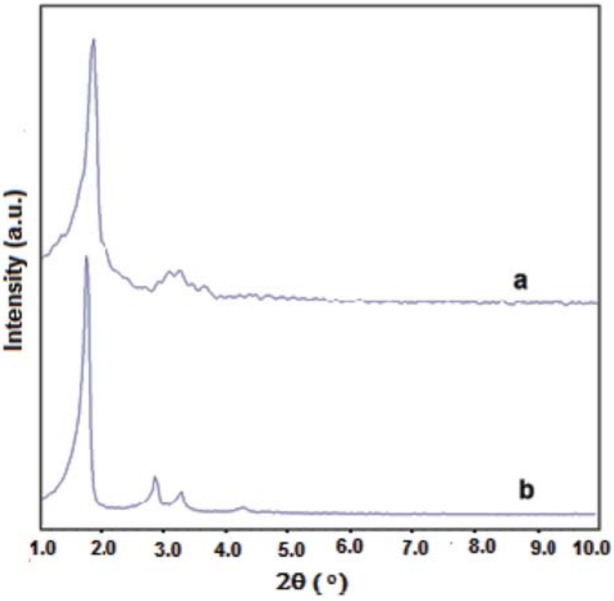

Fig. 3. XRD patterns of a) MCM-41 b) terpyridine-modified MCM-41.

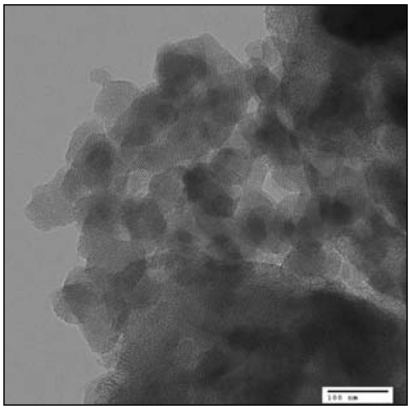

Fig. 4. TEM micrograph of terpyridine-modified MCM-41.

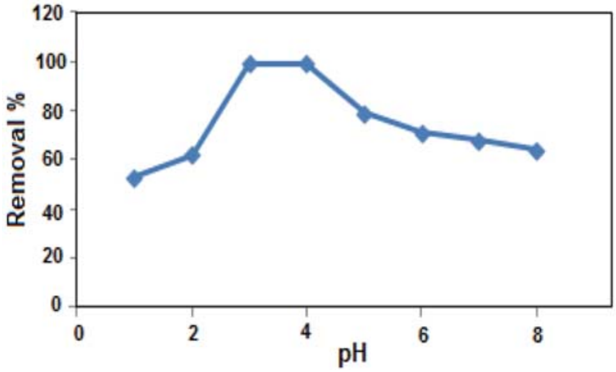

Fig. 6. Effect of pH on chromate removal by terpyridine- modified MCM-41.

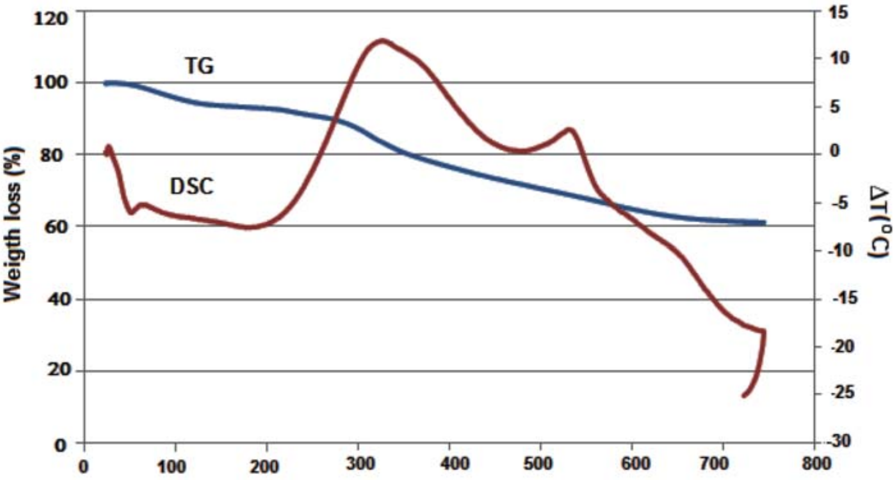

Fig. 5. Thermogram (TG/DSC) of terpyridine-modified MCM-41.

that the functionalization had occurred inside the nanoporous silica pores. For further analysis, the thermal analysis was performed on this sorbent (Fig. 5). The results show that the sorbent is stable up to 195 °C. Furthermore, an approximate 38% decrease in weight confirms the elemental analysis results.

3. 2. Adsorption Study

One of the many applications of this modified nanoporous silica, MCM-41-terpy, could be its potential use for the removal of harmful anions from aqueous solutions. In this context, we used this material as an adsorbent to remove chromate anions.

3. 3. Effect of the pH

The most effective parameter that affects the adsorption process is pH. Therefore, the pH of the solution was the first optimized parameter. To investigate the effect of pH on the extraction efficiency, the pH of the six individual 50 mL sample solutions containing 5 mg L^{-1} of chromate ions were adjusted to the pH range of 2–9 using an HNO_3 or NaOH solution. As can be seen in Figure 6, quantitative removal for terpy-MCM-41 was obtained at a pH of 3–4, while pH recovery was considerably decreased (Fig. 6) beyond this level. According to these data, it can be suggested that (as in pH level under 3) the $HCrO_4^-$ converts to H_2CrO_4, and there is no ion exchange possible with the pyridinium group and H_2CrO_4, therefore, the adsorption decreased. Interestingly, in pH levels above 4, the pyridinium groups convert to pyridine and also results in a decrease of adsorption.

3. 4. Maximum Adsorption Capacity

The capacity factor of MCM-41-terpy was determined by investigating the amount that is required to remove a specific amount of Cr(VI) ions from the solution. For this study, 0.005 g of MCM-41-terpy was added to an aqueous solution containing 1.0 mg of Cr(VI) ions, and the retained chromate ions content was determined by visible spectrophotometry. The results show the maximum capacity of 114 mg g^{-1} (0.97 mmol g^{-1}) for MCM-41-terpy.

3. 5. Effect of Flow Rate on Removal Efficiency

The kinetic of adsorption was investigated by passing the same analyte from the column with a different flow rate. To investigate the effect of flow rates of the sample solution on chromate removal efficiency, a 50 mL solution of 1 μg mL^{-1} Cr(VI) was passed through the column under optimum conditions with a peristaltic pump in the range of 1–20 mL min^{-1} and the remaining chromate was detected by UV spectrometer after reacting with diphenylcarbazide. The results show the removal is efficient (more than 95%) in the flow rates less than 16 mL min^{-1} (Fig. 7). The decrease in the removal efficiency by increasing the flow rate can be attributed to the lack of equilibrium between the chromate and MCM-41-terpy.

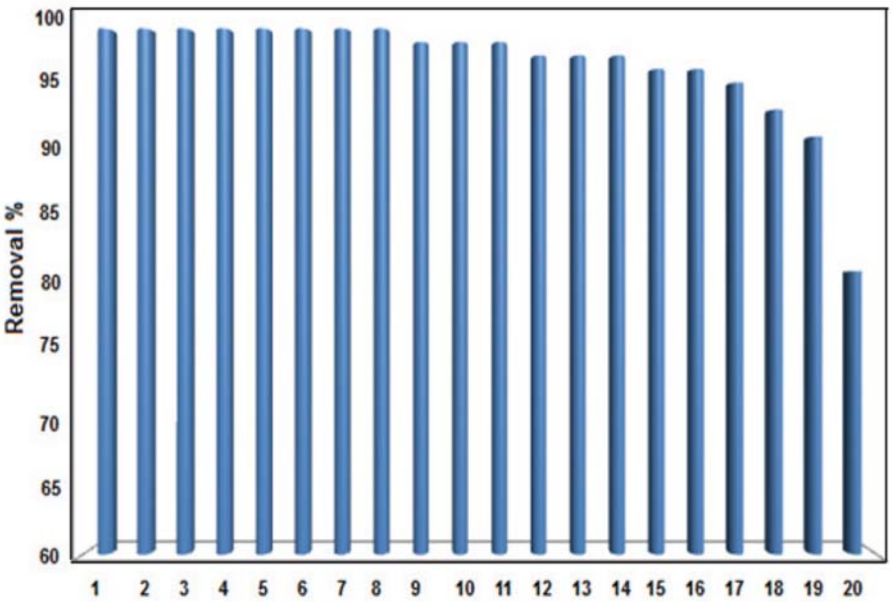

Fig. 7. Effect of sample flow rate on chromate removal by terpyridine-modified MCM-41.

3. 6. Selectivity Studies

The impact of various anions and cations on chromate ion removal was also studied. For this purpose, the removal procedure was applied in the presence of each interfering anion or cation with a defined concentration ratio. As indicated in Table 1, these studies indicated that the high concentration of cations causes no significant decrease in the chromate removal since the adsorption mechanism is ion exchange. However, anions such as arsenate could interfere in chromate removal using MCM-41-terpy as a sorbent.

Table 1. Selectivity studies for chromate removal in the presence of cationic and anionic interferences

Interference	Concentration Ratio X/ Chromate	Removal (%)
K^+/Cl^-	100	98.3
Ca^{2+}/ CO_3^{2-}	100	98.8
Cu^{2+}	100	97.4
Cd^{2+}	100	98.9
$HAsO_4^{2-}$	100	31.7

3. 7. Effect of Nanoporous Structure on Removal Efficiency

In order to investigate the impact of nanoporous structure on removal efficiency, the colloidal silica (nonporous) was functionalized with pyterpy similarly as described for the MCM-41. Then the removal parameters, such as pH, maximum adsorption capacity, and adsorption kinetic (flow rate), were compared to MCM-41-terpy. As the results in Table 2 show, there is no difference in the optimized removal pH, which can be attributed to the same functional group on both silicas. But in the case of other factors, the nanoporous structure of MCM-41 makes it a fascinating sorbent for chromate removal, as it has more adsorption capacity and efficiency in higher flow rates.

3. 8. Sorbent Reusability

In this regard, after removing the chromate, the sorbent was washed with a 1.0 mol L^{-1} KCl solution in a 0.1

Table 2. Comparison of removal performance of terpyridine-functionalized MCM-41 nanoporous silica to terpyridine-functionalized colloidal silica adsorbents

Adsorbent	Adsorption capacity (mg g^{-1})	Sample flow rate (mL min^{-1})	Best pH
Terpy-functionalized Nanoporous silica	114	16	3–4
Terpy-functionalized Colloidal silica	47	7	3–4

mol L^{-1} Na_2CO_3 solution, which eluted more chromate ions from the sorbent. Apparently, Na_2CO_3 causes the pyridine groups in terpyridine to lose their hydrogen and consequently there are no longer appropriate sites present for chromate ions to coordinate. Furthermore, KCl is necessary for replacing the bounded pyridine by chloride ions. The desorption-adsorption cycle was continued till a 5% drop-off in removal efficiency was measured. The results show that this material could be reused for chromate removal at least eleven times without any significant decrease in removal efficiency. This high reusability can be explained by the facts that the terpyridine-functionalized MCM-41 has high thermal and mechanical stability and the chemical bonds of terpyridine-functionalized MCM-41 are quite strong.

4. Conclusions

A new modified MCM-41 silica (terpyridine-modified MCM-41) was synthesized and characterized by X-ray powder diffraction (XRD), infrared (IR) spectroscopy, transmission electron microscopy (TEM), and thermal (TGA-DSC) and elemental analyses. The application of this material in the removal of chromate ions from aqueous solutions was investigated. The evaluated method was found to be simple and fast and could easily be applied for chromate ions removal. The terpyridine-modified MCM-41 had many advantages, including high adsorption capacity, thermal stability, and reusability. Moreover, the effect of the nanoporous structure of this sorbent has been investigated by comparing its efficiency with colloidal silica. The results show that the nanoporous structure has a significant influence on the terpyridine-modified MCM-41 efficiency, especially in terms of maximum adsorption capacity and the adsorption kinetic.

5. Acknowledgement

The authors thank the Vice-President's Office for Research Affairs of Shahid Beheshti University for supporting this work.

6. References

1. L. Cai, X. K. Li, Y. Song, M. G. Cherian, *Curr. Med. Chem.*, **2005**, *12*, 2753–2763.
2. T. Theophanides, J. Anastassopoulou, *Crit. Rev. Oncol. Hemato.*, **2002**, *42*, 57–64.
3. L. Noel, J. C. Leblanc, T. Guerin, *Food Addit. Contam.*, **2003**, *20*, 44–56.
4. H. Royle, *Environ. Res.*, **1975**, *10*, 39–53.
5. V. Suresh, M. Kanthimathi, P. Thanikaivelan, J. Raghava Rao, B. Unni Nair, *J. Cleaner Prod.,* **2001**, *9*, 483–491
6. O.Yamaguchi, M. Ida, Y. Uchiyama, S. Hanehara, *J. Eur. Ceram. Soc.*, **2006**, *26*, 785–791.
7. P. Outridge, A. Scheuhammer, *Rev. Environ. Contam. Toxicol.*, **1993**, *130*, 31–77.
8. C. R. Myers, J. M. Myers, B. P. Carstens, W. E. Antholine, *Toxic Subst. Mech.*, **2000**, *19*, 25–51.
9. X. Wang, S. O. Pehkonen, A. K. Ray, *Ind. Eng. Chem. Res.*, **2004**, *43*, 1665–1672.
10. L. E. Eary, D. Rai, *Environ. Sci. Technol.*, **1988**, *22*, 972–977.
11. G. E. Batley, J. P. Matousek, *Anal. Chem.*, **1980**, *52*, 1570–1574.
12. M. Karve, R.V. Rajgor, *J. Hazard. Mater.*, **2007**, *141*, 607–613.
13. N. Kabay, M. Arda, B. Saha, M. Streat, *React. Func. Poly.*, **2003**, *54*, 103–115.
14. L. Gzara, M. Dhahbi, *Desalination*, **2001**, *137*, 241–250.
15. J. Hu, G. Chen, I. M. C. Lo, *Water Res.*, **2005**, *39*, 4528–4536.
16. M. R. Ganjali, P. Norouzi, F. Faridbod, M. Ghorbani, M. Adib, *Anal. Chim. Acta*, **2006**, *569*, 35–41.
17. M. Chen, A. Zou, C. Zhong, J. Wang, *J. Anal. Sci.*, **2007**, *23*, 627–636.
18. I. Narin , M. Soylak , L. Elc´i, M. Dogan, *Talanta*, **2000**, *52*, 1041–1046.
19. A. Sari, D. Mendil, M. Tuzen, M. Soylak, *Chem. Eng. J.*, **2008**, *144*, 1–9.
20. Narin, Y. Surme, M. Soylak, M. Dogan, *J. Hazard. Mater.*, **2006**, *136*, 579–584.
21. E. Vassileva, K. Hadjiivanov, T. Stoychev, C. Daiev, *Analyst*, **2000**, *125*, 693–698.
22. I. Narin, M. Soylak, K. Kayakirilmaz, L. Elci, M. Dogan, *Anal. Lett.*, **2002**, *35*, 1437–1452.
23. D. Pérez-Quintanilla, I. del Hierro, M. Fajardo, I. Sierra, *Mater. Res. Bull.*, **2007**, *42*, 1518–1530.
24. H. Ebrahimzadeh, A. A. Asgharinezhad, N. Tavassoli, O. Sadeghi, M. M. Amini, *Int. J. Environ. Anal. Chem.*, **2012**, *92*, 509–521.
25. Kh. Mehrani, A. Mehrani, M. M. Amini, O. Sadeghi, N. Tavassoli, *Microchim. Acta,* **2011**, *173*, 521–527.
26. C. D. Nunes, A. Valente, M. Pillinger, A. Fernandes, C. Romao, J. Rochaa, I. Goncalves, *Mater. Chem.,* **2002**, *12*, 1735–1742.
27. K. Schumacher, M. Grun, K. K. Unger, *Micropor. Mesopor. Mater.*, **1999**, *27*, 201–206.

28. B. J. S. Jhonson, A. Stein, *Inorg. Chem.*, **2001**, *40*, 801–808.

29. M. Gardner, S. Comber, *Analyst*, **2002**, *127*, 153–156.

Povzetek

Sintetizirali smo nov MCM-41 nanoporozni silikat, funkcionaliziran s terpiridinom, in ga okarakterizirali z X-žarkovno praškovno difrakcijo (XRD), infrardečo spektroskopijo (IR), transmisijsko elektronsko mikroskopijo (TEM), termično (TGA-DSC) ter elementno analizo. Raziskovali smo uporabo funkcionaliziranega nanoporoznega silikata za odstranjevanje kromata, ki je eno od najbolj škodljivih onesnaževal v okolju. Proučevali smo vpliv številnih dejavnikov na odstranjevanje kromata, vključno s pH vzorca, adsorpcijsko kinetiko in maksimalno adsorpcijsko kapaciteto funkcionaliziranega nanoporoznega silikata.