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An Effective Method For Removal of Dichromate Ion and Furfural From Aqueous Solutions Using A Nanoporous Adsorbent

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The effect of cationic template on the adsorption of dichromate ion and furfural in MCM-41 was investigated in this work. Cetyltrimethylammonium bromide (CTAB) was used as the cationic template for synthesis of MCM-41 (mobil composition of matter 41, a mesoporous material with a hexagonal array of uniform pores). The properties of synthesized sample were characterized with X-ray diffraction (XRD), FTIR and thermogravimetric analysis. The as-synthesized-MCM-41 samples were used for the separation of dichromate anion and furfural from aqueous solution and showed high adsorption capacity for both of them. The parameters investigated in this study include agitation speed, contact time, composition of adsorbent (in the presence and absence of surfactants) and initial dichromate and furfural concentrations. Adsorption uptakes were rapid on the adsorbent reaching equilibrium in less than 1 h. As-prepared material showed excellent adsorption capacity toward Cr (VI) and furfural (*i.e.* 2.43 mmol/g and 1.87 mmol/g, respectively). The materials without surfactant does not show affinity for ionic and organic analyte. Dominant sorption mechanisms were predicted to be electrostatic, hydrophobicity, hydrogen bonding and π-π interactions.

Key Words: Mesoporous, Furfural, Chromium, Sorption, Cationic template.

INTRODUCTION

Mesoporous materials are a class of nanoporous materials that were discovered at 1992 by the mobil oil researchers[1]. The discovery of mesoporous materials, in particular, hexagonal MCM-41, has attracted much research attention owing to their potential applications as catalysts, catalyst supports and absorbents[2-6].

Hexavalent chromium [dichromate ion ($Cr_2O_7^{2-}$) and chromate ion(CrO_4^{2-})] and its compounds are widely used in electroplating, leather tanning, cement, dyeing, metal processing, wood preservatives, paint and pigments, textile, steel fabrication and canning industries. These industries produce large quantities of toxic wastewater[7]. Its accidental ingestion causes stomach upsets ulcers, kidney and liver damages and even death. Chromium is also a known carcinogen[8]. The maximum concentration limit for Cr (VI) for discharge[9] into inland surface waters is 0.1 mg/L and in potable water is 0.05 mg/L.

Furfural is an organic compound that is stable in the room temperature and decomposes to CO and CO_2 at high temperature. Its solubility in water is about 83 g/L. Furfural accidental ingestion can cause death and its absorption from skin will damage the neurotic system and lungs of the human beings[10]. Furfural is used as a solvent for extractive refining of lubricating oils, as it is very effective in removing compounds containing oxygen or sulfur. Furfural is also a feedstock for producing furfuryl alcohol, which is used for making resins and tetrahydrofuran, an excellent solvent.This volatile organic compound is one of the major components of concern present in wastewater of petrochemical industry and petroleum refineries[11]. The separation of furfural from aqueous streams is an important field of study for the sake of industrial safety and environmental protection.

The common methods of organic compounds removal from aqueous solutions include biological removal, liquid-liquid extraction, hydrolysis, osmotic methods and adsorption[10]. Established methods for the removal of chromium oxyanions from wastewater include precipitation, electrochemical reduction, electrodeposition and adsorption[12]. Adsorption remained the most economical and widely used process for removal of hexavalent chromium. Activated carbons[13], clays[14], ion exchange resins[15] and bio-derived adsorbents from bagasse and rice husk[16] proved to be effective in removing hexavalent chromium from wastewaters. More recent works have shown that mesoporous materials[17-21] and magnetic particles[22] can have large adsorption capacity, excellent selectivity and improved powder recoverability for removal of toxic compounds from aqueous solutions. Most of the mesoporous adsorbents are synthesized with chemical grafting or direct insertion of organic functional groups into the silica frameworks of mesoporous materials such as MCM-41 and MCM-48 (mobil composition of matter 48, a mesoporous material of qubic array of uniform pores). Yoshitake *et al.*[23] prepared a series of adsorbents from MCM-41by grafting various polyamines. These adsorbents are capable to adsorb both cations and anions *i.e.*, iron(III) and arsenate.

This work describes preparation and characterization of a cationic adsorbent based on MCM-41 mesoporous material for the adsorption of $Cr_2O_7^{2-}$ anion and furfural molecule from aqueous solutions.

EXPERIMENTAL

Sodium metasilicate, cetyltrimethylammonium bromide (CTAB), sodium hydroxide, potassium dichromate and furfural were of analytical grade and purchased from Merck.

Synthesis of mesoporous adsorbent: MCM-41 was hydrothermally synthesized through the method reported by Vetrivel and Pandurangan[24] using a gel composition of SiO_2: 0.2 CTAB: 0.89 H_2SO_4: 120 H_2O. In a typical synthesis, 10.5 g of sodium metasilicate dissolved in 40 mL deionized water. This mixture was stirred for 0.5 h using a mechanical stirrer (350 rpm) and the pH of the solution was adjusted at 10.5 with continous stirring for another 0.5 h to form a gel. After that, 3.6 g of cetyltrimethylammonium bromide was dissolved in deionized water and added dropwise (25 mL/h) by means of a burette so that the gel was hanged into suspension. The suspension was transferred into a Teflon-lined steel autoclave and heated up to 120 ºC for 48 h. After cooling to room temperature, the product formed was filtered and washed with deionized water for several times. The white precipitate was then draied at room temperature and calcined in an air furnace at 550 ºC for 6 h (cal. MCM-41).

Characterization: The as-synthesized MCM-41 (as-MCM-41) mesoporous silica was characterized by X-ray diffraction spectroscopy (XRD, Philips 1830) and Fourier transform infrared spectroscopy (FTIR-8400S). The surfactant content of as-MCM-41 adsorbent was determined by thermogravimetric analysis. The TG-DTA analysis was conducted by means of a Stantone-Redcroft STA 1000 thermogravimetric analyzer with lidless platinum pans.

Adsorption of dichromate ion and furfural: Batch equilibrium experiments were carried out using as-synthesized MCM-41 as adsorbent. Potassium dichromate was used as the source of Cr(VI) in the aqueous solution. The dichromate ion (2000 mg/L) and furfural (2000 mg/L) stock solutions were prepared by dissolving 0.680 g of and 0.431 mL of furfural in 250 mL of deionized water. Two series of erlens containing potassium dichromate and furfural solutions of varying concentrations from 400 to 2000 mg/L of dichromate ion and 300 to 1200 mg/L of furfural, were prepared from the stock solutions. The system under investigation was agitated using a shaker (Stuart Scientific, UK).

Batch experiments were conducted at ambient temperature and constant pH ($pH = 5$), adsorbent dose and the volume of the solutions using the optimum conditions of pertinent factors, such as agitation rate, analyte concentration and contact time. Adsorption isotherm experiments were also carried out in mixtures consisting of 0.1 g of adsorbent and 25 mL of analyte solution with varying amounts of analyte concentration (dichromate solution with varying dichromate concentration from 400 to 2000 mg/L and furfural solution with varying furfural concentration from 300 to 1200 mg/L). The change in the analyte concentration due to adsorption was determined by UV-Vis spectrophotometer (UV mini 1240 Shimadzu).

Absorbance was measured at wavelengths (λ) 257 nm for dichromate ion and 228 nm for furfural. The removal efficiency (E) of adsorbent on analytes was defined as $E (\%) = [(C_0 - C_1)/C_0] \times 100$ where C_0 and C_1 are the initial and equilibrium concentrations of the analyte solution (mg/L), respectively[9].

RESULTS AND DISCUSSION

XRD pattern of cationic MCM-41: The XRD pattern for cationic MCM-41 sample is shown in Fig. 1. Three peaks at 2θ of 1.55, 3.41 and 4 can be seen in the XRD pattern of as-MCM-41. Apparently, the hexagonal arranged channels, which are represented by (100), (110) and (200) reflections, exist in the as-synthesized MCM-41 sample.

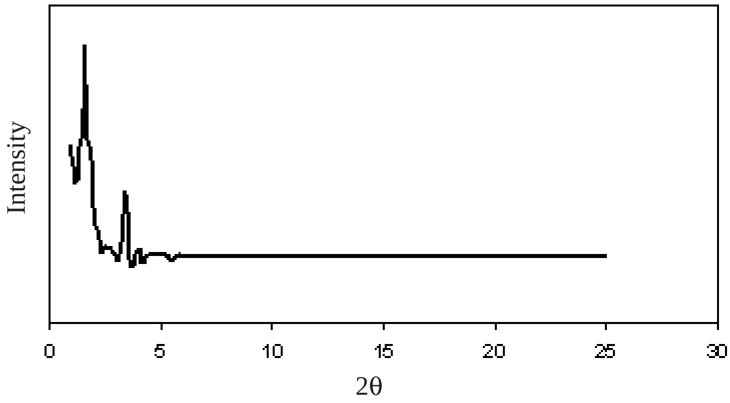

Fig. 1. XRD pattern of cationic MCM-41

Internal surface characteristics of the pores: FT-IR spectrum of calcined MCM-41 shows characteristic bonds of Si-O-Si at 1090 cm^{-1} for asymmetrical stretching and 800 cm^{-1} for symmetrical stretching. The bonds at 960 and 460 cm^{-1} can be assigned to the Si-O stretching and twisting, respectively. The sample indicates the presence of hydroxyl groups at 3730 cm^{-1}, adsorbed water molecules at wavelengths around 3440 cm^{-1} and carbon dioxide at 2340 cm^{-1}.

Thermogravimetric analysis: A very small step of weight loss was observed from 30 to 100 ºC that was associated with desorption of adsorbed water from the material. TGA analysis for as-MCM-41 material (Fig. 2) also shows a peak corresponding to surfactant (or template) removal at around 220 ºC. This is closely followed by another sharp peak at about 260 ºC, corresponding to the combustion of remaining carbon species. However, it appears that the second and third peaks have overlapped and are no longer distinguishable from each other.

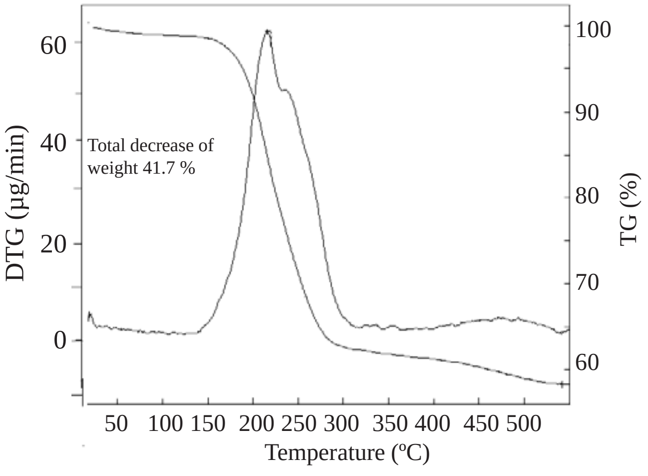

Fig. 2. Thermogram of as-MCM-41

Adsorption studies of as-MCM-41: The influence of some operational parameters such as agitation speed, contact time and analyte concentration on the adsorption of Cr(VI) and furfural was investigated. The Cr(VI) and furfural concentrations were determined colourimetrically with UV-Vis spectrophotometer. All of the adsorption measurements were conducted at the pH of about 5.

Effect of agitation speed: The effect of agitation speed on the removal efficiency of Cr(VI) and furfural was studied by varying the speed of agitation from 0 (without shaking) to 300 rpm, while keeping the analyte concentration, contact time and dose of the adsorbent constant. Chromium(VI) and furfural removal generally increased with increasing agitation speed from 0 rpm to 150 rpm (Fig. 3) while the adsorption capacity remained constant for agitation rates greater than 150 rpm. These results can be associated with the fact that the increase in the agitation speed, improves the diffusion of analytes in to the pores of the adsorbent. This also indicates that a shaking rate in the range of 100-150 rpm is sufficient to assure that the maximum cationic sites of surfactants existing in the pores of as-MCM-41 adsorbent are readily made available for Cr(VI) and furfural uptakes. For convenience, agitation speed of 150 rpm was selected as the optimum speed for all of the adsorption experiments.

Effect of contact time: Results (Fig. 4) indicate that the removal efficiency increased with an increase in contact time before equilibrium is reached. Other parameters such as dose of adsorbent, analyte concentration, agitation speed, pH, volume of the solution and temperature were kept constant (0.1 g as-MCM-41, dichromate ion = 2000 mg/L, furfural = 1200 mg/L and agitation speed = 150 rpm, pH = 5, V = 25 mL and T = 298 K).

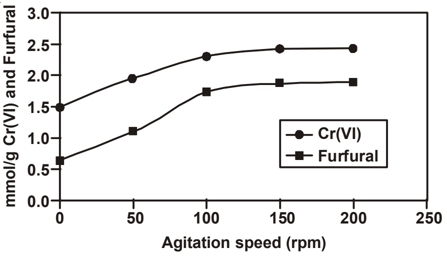

Fig. 3. Effect of agitation on the equilibrium removal efficiencies of Cr(VI) and furfural (Dichromate ion = 2000 mg/L, furfural = 1200 mg/L, contact time = 1 h, as-MCM-41 = 0.1 g, pH = 5)

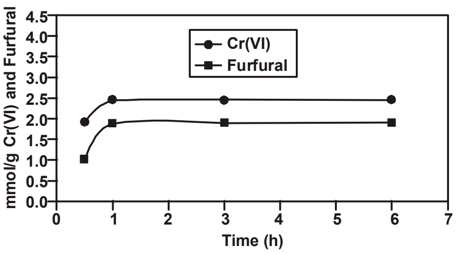

Fig. 4. Effect of contact time on removal of Cr(VI) and furfural (dichromate = 2000 mg/L, furfural = 1200 mg/L, agitation speed: 150 rpm, as-MCM-41= 0.1 g, pH = 5)

It can be seen that Cr(VI) and furfural removal efficiency increased when contact time was increased from 0.5 to 1.0 h. Optimum contact time for adsorbent was found to be 1 h. Hence the as-MCM-41 adsorbent requires a very short contact time to become saturated with analytes. High cationic surfactant concentrations and great availability of them in the pores of the adsorbent, which are required for electrostatic interaction with dichromate anions and aromatic furfural molecules, significantly improved the adsorption capacity and the process proceeded rapidly.

This result is important, as equilibrium time is one of the important parameters for an economic wastewater treatment system.

Effect of initial concentration: To get the equilibrium data, initial dichromate ion and furfural concentrations were varied while the other operational parameters were kept constant. Solutions of various concentrations of $Cr_2O_7^{2-}$ and furfural, between 400 to 2000 mg/L for $Cr_2O_7^{2-}$ and 300 to 1200 mg/L for furfural were prepared and 0.1 g of adsorbent powder were added to the 25 mL of solution and allowed to reach equilibrium at 25 ºC and pH of 5. About 1 h of equilibrium periods for sorption experiments were used to ensure equilibrium conditions. The solution was filtered to remove and recover the adsorbent. The remaining analytes in the solution after adsorption were measured by UV-Vis spectrometer. The results showed that cationic templated mesoporous adsorbent (as-MCM-41) has a very high adsorption capacity for both Cr(VI) and furfural. The as-MCM-41 adsorbent showed adsorption capacities of 2.43 mmol/g (126.39 mg/g) for Cr(VI) species (1.21 mmol/g for $Cr_2O_7^{2-}$ species) and 1.87 mmol/g for furfural.

Same adsorption procedures were applied for calcined-MCM-4 (cal. MCM-41) and the results did not show any significant adsorption for the analytes. It can be concluded that the existence of cationic template in the pores of as-synthesized MCM-41 material plays the main role in the adsorption of anionic and aromatic organic analyte. The results for Cr(VI) and furfural adsorption on the as-MCM-41 are shown in Fig. 5 (mmol analyte/g adsorbent) and Fig. 6 (mg analyte/g adsorbent).

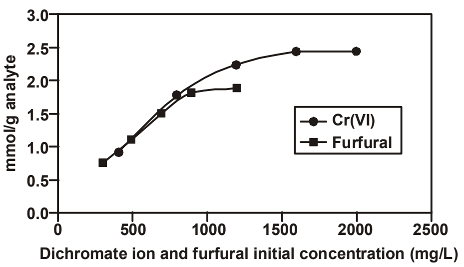

Fig. 5. Adsorption isotherms of Cr(VI) and furfural on as-MCM-41(mmol/g) (agitation speed = 150 rpm, contact time = 1 h, as-MCM-41 = 0.1 g, pH = 5)

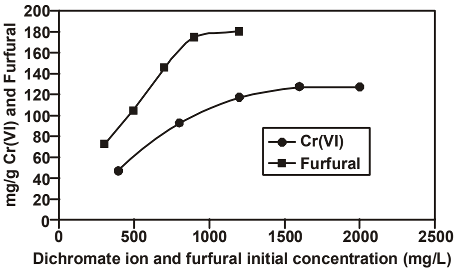

Fig. 6. Adsorption isotherms of Cr(VI) and furfural on as-MCM-41(mg/g) (Agitation speed = 150 rpm, contact time = 1h, as-MCM-41 = 0.1 g, pH = 5)

The removal efficiencies of cal. MCM-41 and as-MCM-41 for Cr (VI) and furfural are demonstrated in Table-1. As it is shown, mesoporous silica without surfactant does not show affinity for Cr(VI) and furfural.

TABLE-1
REMOVAL OF Cr(VI) AND FURFURAL ON THE
Cal. MCM-41 AND as-MCM-41 ABSORBENTS

Mesoporous materials	Cr(VI) absorption capacity (mg/g)	Furfural adsorption capacity (mg/g)
as-Synthesized	126.39	180
Calcined	≅ 0.5	≅ 10

In the present study, as-MCM-41 is used for dichromate ion and furfural removal from aqueous solutions. Table-2 shows the adsorption capacity of various adsorbents reported in the literature. When compared with other adsorbents, the results of this work indicate that as-MCM-41 mesoporous material has an improved capacity for all cases.

TABLE-2
Cr(VI) ABSORPTION CAPACITY OF VARIOUS ABSORBENT AS
REPORTED IN THE LITERATURE [Ref. 8,14-16,18,24,25-32]

Absorbent	Absorption capacity (mmol/g)
NH_2-MCM-41	0.91
Ozoned activated carbon	0.33
Modified clay	0.0068
Ethylenediamine grafted poly(glycidylmethacrylate-co-methylmethacrylate)	0.441
Chitosan	0.65
Cu^{2+}-EDA modified mesoporous silica	1.03
Organo-zeolite	0.0041
Cation-modfied zeolite	0.04-0.56
Milled peat	0.58
Actvated carbon alone	0.074
Modified activated carbon	0.125
Resin from soybean hulls	0.68
Lewatit-anion exchange resins	0.40-0.41
Functionalized SBA-15	1.72
N(3-Chloro-2-hydroxypropyl)trimethylammonium chloride modified corn stover	1.58

Conclusion

The present study introduces an appropriate alternative method for Cr(VI) and furfural removal from aqueous solutions, allowing the development of a new and more effective adsorbent in comparison with other adsorbents already in use. Surfactant-containing materials show excellent adsorption capacity towards Cr(VI) and furfural, respectively. Such difference in the adsorption capacity of the adsorbent towards ionic and non-ionic species has been interpreted on the basis of the coulombic interactions which occur between cationic part of the surfactants and the anionic part of the analytes (negative charge in Cr(VI) and aromatic ring in furfural). Multiplicate interactions including electrostatic, hydrophobicity, hydrogen bonding and π-π interactions may be involved in explaining different adsorption capacities for anionic Cr(VI) species and neutral furfural molecules. This work provides a basis for further applications of mesoporous materials prepared using a surfactant-based supramolecular approach as adsorptive substrates for adsorptive purposes and preconcentrators.

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