Original Article

Removal of Cr(VI) Species from Aqueous Solution by Different Nanoporous Materials

Mohammad Ghashghaee[*1], *Vahid Farzaneh* [2]

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ABSTRACT

Background: The removal of toxic metals from sewage and wastewaters is one of the most important concerns in the twenty first century. The removal of poisonous Cr(VI) from aqueous solution by different low-cost available nanoporous adsorbents was investigated in the present study.

Methods: Fumed silica, bentonite (BN), hydrotalcite (HT), MCM-41, Na-Y, mordenite (MOR) and SAPO-34 were used at different adsorbent-to-metal ion ratios. Two predominant species of Cr were considered including chromate and hydrogen chromate ions.

Results: Both HT and Na-Y adsorbed the toxic bichromate ions more favorably than other sorbents. Overall, the efficiency of the Cr removal followed the sequence of HT > SAPO-34 > MOR > MCM-41 > Na-Y > silica > BN. Because of its surface chemistry, HT with an uptake of 65.2 mg/g showed the highest toxic abatement among the seven adsorbents investigated under the acidic conditions, followed by the microporous materials SAPO-34 and MOR with uptakes of 41.2 and 41.0 mg/g, respectively.

Conclusion: Both HT and Na-Y adsorbed the toxic bichromate ions more favorably than other sorbents. The high pore volume and the apparent surface area of a non-functionalized MCM-41 were not effective in the adsorption of Cr compounds. Overall, HT was the best choice owing to its appropriate surface chemistry with respect to the Cr oxygenates.

Keywords: Adsorption, Clays, Chromium, Environment, Toxic Metals, Zeolites.

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INTRODUCTION

One of the most important problems in the twenty first century is the effluent pollutants and contaminants delivered to the environment, especially in water and wastewater streams. Removal of toxic metals from sewage and wastewaters [1-12] is a must from eco-friendly, health, and even economic points of view. Heavy metals are defined as elements with atomic weights of 63–200 and a specific gravity larger than 5 [11]. Metals such as Pb, Hg, Cd, As, Cr, Zn, Cu, and Mn are often classified as potentially hazardous elements when present in aquatic environment due to their toxicity to higher-life creatures and non-biodegradable nature [1, 3, 5]. Examples of their hazard to human health include diseases like itai-itai disease (mass Cd poisoning), As and Cd induced cancer, mutations and genetic damage due to Hg, brain and bone damage by Cu, Pb, and Hg, and lead poisoning [1, 3].

While Cr(III) is essential for the maintenance and control of glucose, lipid, and protein metabolism [13-14], hexavalent chromium is a powerful carcinogen and a serious health concern which is able to modify the DNA transcription process in humans and animals, leading to chromosomal aberrations [12, 15-17]. Acute exposure to Cr(VI) compounds causes nausea, diarrhea, kidney, liver, and gastric damage, internal hemorrhage, lung cancer, ulcer formation, and respiratory problems [11,16,18,19]. The main industries that contribute to water pollution by chromium are mining, leather tanning, textile dyeing, electroplating, metal finishing such as corrosion inhibiting and aluminum coating operations, magnetic tapes, pigments, wood protection, chemical manufacturing, nuclear power plants, electrical and electronic equipment, and catalysis [12,17,18, 20-22] which can encompass up to hundreds of mg/L of Cr(VI) while the regulated tolerance values are 0.1 and 0.05 mg/L for discharge into the inland surface and potable waters, respectively [15, 17, 19, 22-24].

1. Department of Process Design and Construction, Iran Polymer and Petrochemical Institute, Tehran, Iran.
2. Department of Applied Chemistry, Semnan University, Semnan, Iran.
* Corresponding Author: E-mail: m.ghashghaee@ippi.ac.ir

Among the several methods employed to remove chromium from industrial wastewater [5, 9-12, 16, 17, 20, 25, 24], the adsorption process can be considered as an effective and versatile technique for the abatement of such anionic compounds [9, 10, 12, 16-20, 22, 24, 26, 27]. Therefore, selective adsorption by biological materials, leaf powder, mineral oxides, activated carbons, polymer resins, and zeolites has been suggested for the removal of chromium [1, 28]. The redox potential or the Pourbaix E–pH diagrams present equilibrium data which indicate various oxidation states and chemical forms which exist within specified Eh and pH ranges. According to these diagrams [29], the abundant Cr(VI) oxyanions include chromate (CrO_4^{2-}) ion which forms predominantly at pH levels of 6.5–14, hydrogen chromate ($HCrO_4^-$), chromate (CrO_4^{2-}), and dichromate ($Cr_2O_7^{2-}$) ions at pH values of 0.7–6.5, and chromic acid (H_2CrO_4) at pH levels smaller than 0.7, with the dichromate ion being the most toxic form of this element [24,12,17].

The aim of the study was to removal of poisonous Cr(VI) from aqueous solution by different low-cost available nanoporous adsorbents.

MATERIALS AND METHODS

Adsorbents

Commercial samples of fumed silica, bentonite, MCM-41, Na-Y, Mordenite, and SAPO-34 were used as received. The hydrotalcite sample was prepared using the co-precipitation method as explained in the literature [30]. A solution of 1 mol of $Mg(NO_3)_2.6H_2O$ and 0.5 mol of $Al(NO_3)_3.9H_2O$ (with an Mg/Al molar ratio of 2) in 700 mL of deionized water was added to a vigorously stirred solution of 3.5 mol of NaOH and 0.943 mol of Na_2CO_3 (having a 1000 mL volume) so that the final pH was equal to 13. After heating at 65 °C for 18 h for the crystallization, the resulting precipitate was obtained by vacuum filtration, washed thoroughly with deionized water until neutral pH, and dried at 130 °C overnight. The resulting solids were calcined in air at 500 °C for 4 h.

Adsorption Experiments

The parent solution of Cr(VI) was prepared by dissolving 2.8286 g $K_2Cr_2O_7$ (Merck) in 1 L of double-distilled water. The adsorption of Cr(VI) was implemented using the HT, Na-Y, MCM-41, MOR, SAPO-34, silica and BN as absorbents in the $K_2Cr_2O_7$ solution at 55 °C for 110 min. The working solutions employed in the experimental tests were obtained with appropriate dilutions of the stock solution to the required concentration. The initial Cr(VI) concentration was 10–150 mg/L, and the adsorbent dosage was 0.1 g in 45 mL solution. The initial pH of the solution was adjusted accordingly with pH indicators. The working solution was pre-adjusted to the above-mentioned temperature at the pH of 5.5 by a 0.1 M HCl solution under constant stirring (250 rpm). After the adsorption test, the resulting solution was centrifuged at 3000 rpm for 5 min. The concentrations before and after adsorption of chromium ions were determined using UV-Vis analysis. Finally, the percentage removal of the hexavalent chromium was calculated as follows:

$$\% \text{ removal of Cr} = (C_0 - C_e) \times 100 / C_0$$

where C_0 and C_e are the initial and final equilibrium concentrations of Cr in the solution, respectively.

UV-Vis Analysis

The UV-Vis spectra were obtained using a UV-1650 spectrophotometer (Shimadzu, Japan), which involved a double-beam optics system with a spectral bandwidth of 2 nm, a wavelength accuracy of ±0.3 nm, and a wavelength repeatability of ±0.1 nm over a wavelength range of 190–1100 nm. The absorbance measurements were made using quartz sample cells with an optical path length of 10 ± 0.01 mm.

Nitrogen Adsorption Analysis

The BET data were obtained on a Quantachrome Chem-BET 3000 apparatus. The samples were degassed for 2 h at 120 °C before the adsorption.

RESULTS

Figure 1 depicts a sample of UV-Vis spectra for different Cr solutions. All of the samples have exhibited two peaks with respect to the absorbing wavelength. Figure 2 demonstrates the equilibrium concentration in the solution after the Cr removal by different adsorbents. This equilibrium concentration was determined after separation of the supernatant solution from the adsorbent. Figure 3 displays the results of Cr removal by different adsorbents for the solutions with 10 and 150 ppm of initial Cr concentrations, respectively. This figure demonstrates both of the

absorbance peaks for the selected low and high concentrations. Finally, Table 1 reports a summary of the adsorbent performances with respect to their textural properties. The performance data reported here include the uptake per volume of the nanopores, uptake per specific surface area, uptake per mass of the adsorbent and average removal percentage.

Table 1. A summary of the textural properties of the adsorbents and their sorption performances.

Adsorbent	BET Surface area, m^2/g	Monolayer uptake volume, cm^3/g	Average removal %	Uptake, mg/g	Uptake per area, mg/m^2	Uptake per volume, mg/m^3
HT	84.35	0.35	86.3	65.2	0.77	186.2
BN	105.15	0.34	14.2	10.8	0.10	31.9
Silica	175.14	0.5	23.1	11.9	0.07	23.7
MCM-41	937.21	2.05	52.4	37.8	0.04	18.5
Na-Y	18.4	0.35	50.1	32.8	1.78	93.6
SAPO-34	46.61	0.13	59.8	41.2	0.88	316.6
MOR	296.12	0.82	56.0	41.0	0.14	49.9

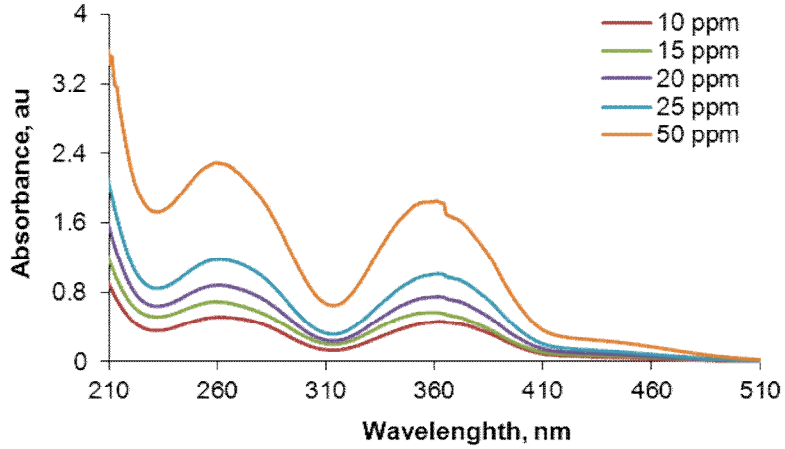

Figure 1. Absorption spectra for different Cr(VI) solutions.

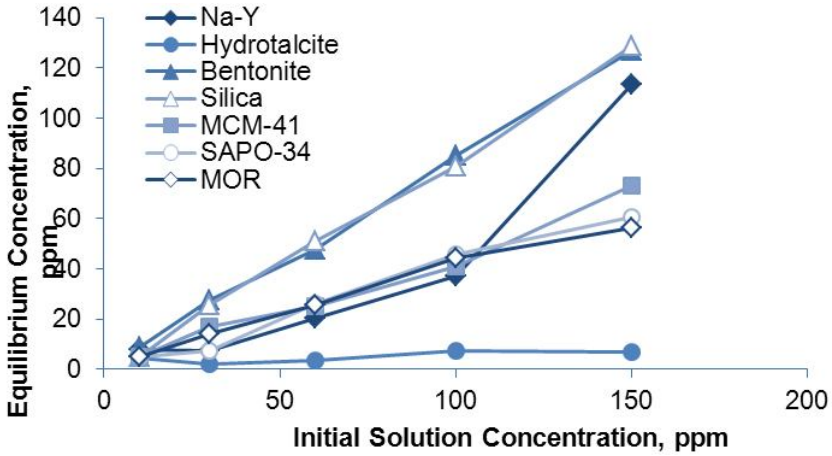

Figure 2. Equilibrium concentration after Cr(VI) removal by different adsorbents in terms of the initial concentration of the solution.

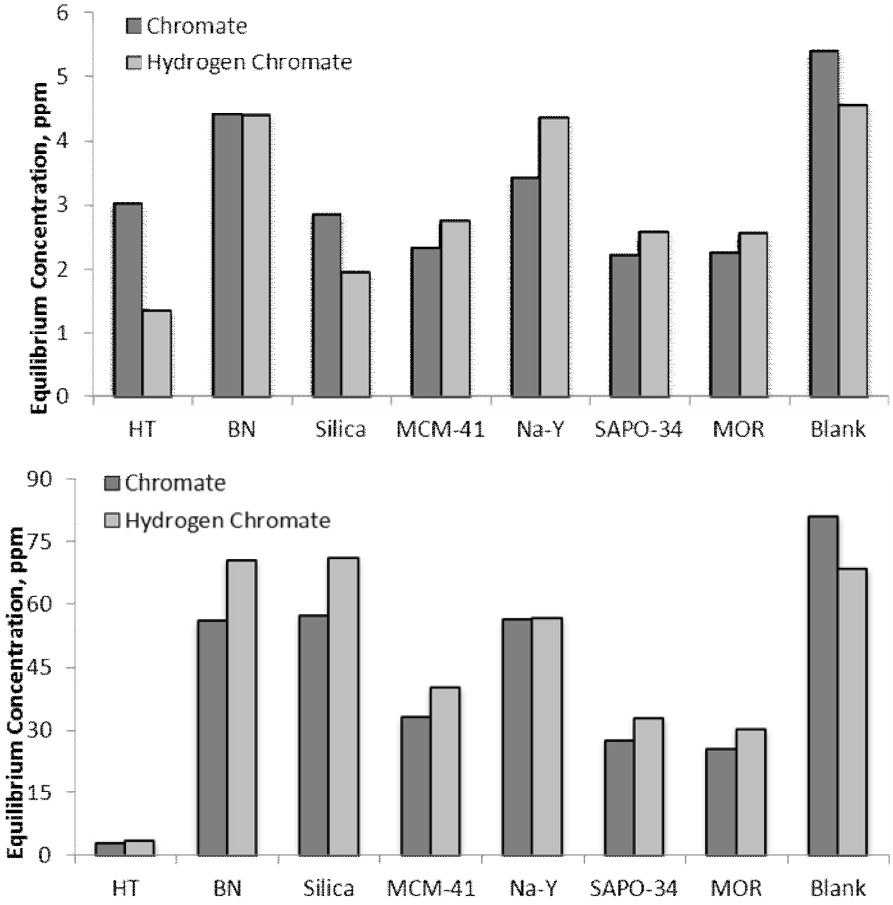

Figure 3. Detailed adsorption of chromate and bichromate ions by different adsorbents from a Cr solution of 10 ppm (top panel) and 150 ppm (bottom panel).

DISCUSSION

Hexavalent Cr is a potent oxidant, which can be easily reduced to the Cr(III) state. The following equations display the reduction of different Cr(VI) species in the presence of a reducing agent.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \leftrightarrow Cr^{3+} + 7H_2O \quad (1)$$

$$HCrO_4^- + 7H^+ + 3e^- \leftrightarrow Cr^{3+} + 4H_2O \quad (2)$$

Highly acidic conditions make hexavalent Cr change to the trivalent state [31-32]. In general, the hexavalent chromium species can exist in 7 forms depending on the pH and the total concentration of the Cr in the solution including chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$), hydrogen chromate ($HCrO_4^-$), dihydrogen chromate (H_2CrO_4), hydrogen dichromate ($HCr_2O_7^-$), tetrachromate ($Cr_4O_{13}^{2-}$), and trichromate ($Cr_3O_{10}^{2-}$) species, among which, hydrogen dichromate, tetrachromate and trichromate are not observed in solutions of a pH higher than 0 or at total Cr concentrations lower than 1 mol/L [33]. Then, according to the pH and the concentration range, three ions and one molecule had to be considered in the present research including CrO_4^{2-}, $Cr_2O_7^{2-}$, $HCrO_4^-$ and H_2CrO_4. In the absence of the interventions from other chemical species in the aqueous solution, the equilibrium reactions of the four considered forms of Cr are as follows [33]:

$$H_2CrO_4 \leftrightarrow H^+ + HCrO_4^- \quad (3)$$

$$HCrO_4^- \leftrightarrow H^+ + CrO_4^{2-} \quad (4)$$

$$Cr_2O_7^{2-} + H_2O \leftrightarrow 2HCrO_4^- \quad (5)$$

Hence, the total molar concentration of Cr^{6+} in the solution is:

$$C = [HCrO_4^-] + 2[Cr_2O_7^{2-}] + [CrO_4^{2-}] + [H_2CrO_4] \quad (6)$$

In more specific terms [33-35], only chromate ion exists at basic medium, the predominant species at neutral conditions are the CrO_4^{2-} and $HCrO_4^-$ ions, and the principal forms at acidic pH conditions include $HCrO_4^-$, CrO_4^{2-}, and a few moles of $Cr_2O_7^{2-}$ ions. Employing the UV-Vis technique, two peaks are observed for an aqueous solution of Cr(VI) compounds. As

presented in the spectra shown in Figure 1, the Cr(VI) solutions showed two peaks at ~260 and ~360 nm, which on the basis of the above discussion and the experimental conditions are assigned to CrO_4^{2-} and $HCrO_4^-$, respectively. As such, the total concentration of Cr in the solution is the sum of those of bichromate and chromate ions.

Overall, the calcined hydrotalcite (HT) has shown the best adsorption capacity and kept this performance up to high initial concentrations (the performance data shown in Figure 2). The other adsorbents illustrated an almost linear trend with respect to the initial concentration with their adsorptive power being lower than HT. Overall, the adsorption power of the adsorbents studied here follows the trend of HT > Na-Y ~ MCM-41 ~ MOR ~ SAPO-34 > Silica ~ BN when a solution of 100 ppm of Cr is to be treated. All of the adsorbents were almost equally effective for solutions of very low contaminations (with ~10 ppm of Cr), however.

Whereas most of heavy metals exist in a cationic form, the oxygenated compounds of Cr(VI) are anionic in natural aquatic systems [18]. The superior performance of the clay HT for the Cr removal is then attributable to the electronic structure of HT which entails encapsulation of compensating interlayer anions. This property is not observed for the rest of the adsorbents, including the clay bentonite (BN), though they are all porous materials. Therefore, the rest of adsorbents will be suited for the removal of anions such as Cr oxygenates only when proper functionalization is made on their surface. As an exception to the linear trends observed, Na-Y should be mentioned which is less capable of Cr removal at high concentrations. In terms of economics, therefore, the Na-Y sorbent is suggested to best operate for solutions of 100 ppm concentration or lower.

Figure 3 shows the results of Cr removal by different adsorbents for the solutions with 10 and 150 ppm of Cr concentration. As can be seen from the column graphs of a 10 ppm contaminated solution, HT and silica tend to adsorb hydrogen chromate than chromate in contrast to the rest of adsorbents which adsorb chromate more favorably. This is most probably because the acidic sorbents employed here are mostly microporous materials incapable of letting readily the bichromate ions in their pores. This observation is also in agreement with the fact that HT tends to absorb less cationic species more readily [36]. The zeolites, in contrast, have already protons on their surface, tending to absorb bichromate ions less favorably. Within a solution of 150 ppm, however, almost all of the adsorbents tend to remove chromate ions more favorably. Owing to its high tendency towards anions, HT has adsorbed the two Cr species almost equally. However, the alkali-containing Na-Y has also adsorbed chromate and hydrogen chromate equally, most probably due to its relatively high affinity to the more negative anion compared to the other sorbents. In terms of the abatement of the environmental danger, the HT and Na-Y sorbents would be considered more appropriate choices as they reduce the more toxic form of Cr species with a higher affinity.

As can be seen in Table 1, the average removal percentage or the uptake per mass of the sorbent averaged for the initial solutions of different concentrations follows the sequence HT > SAPO-34 > MOR > MCM-41 > Na-Y > silica > BN. If the available surface area has to be considered as a basis for comparison, however, the sequence is Na-Y > SAPO-34 > HT > MOR > BN > silica > MCM-41. In fact, the silica surface of the MCM-41 sample had a relatively low affinity to exchange or adsorb the Cr species in contrast to Na-Y, SAPO-34 and HT. Moreover, the uptake per volume changed in the order of SAPO-34 > HT > Na-Y > MOR > BN > silica > MCM-41, indicating that the pore volume of MCM-41 is not benefited as effectively as the pore volumes of HT and SAPO-34. In total, HT with an uptake of 65.2 mg/g should be considered a very suitable adsorbent for an aqueous solution of Cr(VI) species. After the best choice, the microporous substrates of SAPO-34 and MOR respectively with uptakes of 41.2 and 41.0 mg/g would be suggested as appropriate adsorbents for the Cr removal from aqueous solutions.

CONCLUSION

In terms of uptake per mass of the sorbent, the Cr removal followed the order of HT > SAPO-34 > MOR > MCM-41 > Na-Y > silica > BN where HT was the best choice owing to its appropriate surface chemistry with respect to the Cr oxygenate anions. Both HT and Na-Y adsorbed the toxic bichromate ions more favorably than the other sorbents. The high pore volume and the

apparent surface area of a non-functionalized MCM-41 were not effective in the adsorption of Cr compounds. Overall, HT with an uptake of 65.2 mg/g would be considered the best sorbent among the seven adsorbents investigated under the acidic conditions, followed by the microporous materials SAPO-34 and MOR with uptakes of 41.2 and 41.0 mg/g, respectively.

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