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Cr(VI) uptake by a composite of processed diatomite with MCM-41: Isotherm, kinetic and thermodynamic studies

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ABSTRACT

Silica was dissolved from a processed diatomite (PD) at 110 °C/48 h to prepare and coat MCM-41 on the PD surface developing a composite of (PD/MCM-41). The new composite was characterized by different techniques (XRD, SEM, EDX and TEM) and used as an adsorbent for the first time in hexavalent chromium Cr(VI) uptake. The adsorption experiments were carried out as a function of solution pH, contact time, initial Cr(VI) concentration, temperature and PD/MCM-41dose. The highest removal efficiency (93.4%) of Cr(VI) occurred at pH 2.0 through electrostatic interaction. The majority of Cr(VI) was removed within 5 min of contact time and adsorption equilibrium was attained after 30 min. For determining the behavior of Cr(VI) uptake, Langmuir, Freundlich and Dubinin–Radushkevich (D–R) equations were applied to the experimental data. Freundlich isotherm with a correlation coefficient, $R^2 = 0.996$ described the adsorption data well. The chemical nature of Cr (VI) uptake was confirmed by the mean free energy (E=8.765 kJ/mol) calculated from the D–R model. The pseudo-second-order model fitted ($R^2 = 0.9999$) the sorption kinetics well. With large concentrations of chloride, phosphate, sulphate and fluoride in solutions, the synthetic composite exhibited high selectivity for Cr(VI) at pH 2.0. Thermodynamic parameters (ΔH, ΔG and ΔS) indicated that Cr(VI) sorption is spontaneous and endothermic.

1. Introduction

Due to the extensive use of chromium in different industries such as steel fabrication, electroplating, textile, leather tanning, paints and pigments, large amounts of chromium are discharged into the environment. In aqueous system, chromium occurs mainly in trivalent Cr (III) and hexavalent Cr(VI) forms with different toxic characteristics [1–3]. The toxicity of hexavalent form is 500 times higher than that of the trivalent form [4,5]. Human toxicity of hexavalent chromium has been recorded to cause irritation of skin, stomach ulcers, damage of nerve tissue and lung cancer [6,7]. The recommended maximum limits of Cr(VI) concentrations in drinking water and industrial wastewater are 0.05 mg/L and 0.1 mg/L, respectively [8,9] by the US Environmental Protection Agency (EPA).

Different techniques such as adsorption, ion-exchange, chemical reduction and biological processes were applied to remove hexavalent chromium from water [10,11]. Cr(VI) uptake from solutions by adsorption technique is desired due to its high efficiency, simple operation and low cost [8,12]. Previous studies used various materials such as montmorillonite nanocomposites [9], activated carbons [13], surfactant modified clinoptilolite and chabazite [14], carbons from agricultural wastes [15], diatomite-supported/unsupported magnetite nanoparticles [11], volcanic rocks [16], maize bran [17], natural Akadama clay [8], riverbed sand [18], modified rectorite [19], MnO_2 [20], montmorillonite clay [3], surfactant-modified zeolites and MCM-41 [21] and Fe_3O_4 coated polypyrrole magnetic nanocomposite [22]. Because there are very few anion exchangers such as layered double hydroxides in nature, all the above naturally occurring and slightly modified materials were tested but none of them were found to be effective for Cr anion adsorption. Hence there is a need to develop new synthetic anion exchangers. As-prepared MCM-41 loaded with surfactant was found to be selective for perchlorate because of the presence of excess entrapped cetyltrimethylammonium bromide by Komarneni et al. [23], and therefore, here a composite of diatomite and MCM-41 was tested for chromate uptake.

Among Egyptian diatomite deposits, El-Masakheet diatomite can be

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classified as low grade (diatomaceous earth) due to the presence of high concentration of calcite mineral and therefore, treatment of this diatomite was needed to enhance its physicochemical properties [24]. El-Masakheet diatomite with a composition of 61.65% SiO_2 and 21.27% CaO was subjected to thermo-chemical treatment [25]. The processed diatomite resulted in a high concentration of diatom frustules (92.58% SiO_2) without impurities blocking the pores [25] and this diatomite is a cost-effective silica source for MCM-41 synthesis on its surface.

The main objectives of this work were to (a) extract the silica from the processed diatomite (PD) by hydrothermal treatment to synthesize and coat MCM-41 on the surface of PD making a composite of diatomite with MCM-41(PD/MCM-41), (b) study the efficiency of MCM-41/PD composite for the uptake of Cr(VI) from aqueous solutions as a function of different factors such as pH, shaking time, Cr(VI) concentration, temperature, adsorbent mass and the presence of competitive ions, (c) investigate the adsorption kinetic and equilibrium models as well as thermodynamic parameters related to the Cr(VI) uptake process and (d) evaluate the interaction between the synthetic PD/MCM-41composite and Cr(VI) using various techniques.

2. Materials and methods

2.1. Materials

El-Masakheet raw diatomite has a chemical composition of 61.65% SiO_2, 1.27% CaO, 2.09% Al_2O_3, 1.65% Fe_2O_3 and 16.54% loss on ignition (LOI). This natural diatomite was processed by the method described previously [25]. The processed diatomite with high silica concentration (92.58%), cetyltrimethylammonium bromide (Aldrich, 99%) aqueous ammonia solution and distilled water were used as staring materials in the present study.

2.2. Synthesis of the PD/MCM-41composite

To synthesize MCM-41silica on the processed diatomite, the following procedure was used [26]: A 1.02 g of cetyltrimethylammonium bromide (CTAM) was first added to 50 ml H_2O in a Teflon vessel while stirring. After complete dissolution, 16.3 mL of aqueous ammonia solution was added while stirring for 20 min. To the above solution, 1.5 g of the processed diatomite was added with stirring for 30 min. After hydrothermal treatment of this mixture (110 °C for 48 h), solid-liquid phases were separated by centrifuging at 6000 rpm for 15 min. After washing the solid phase several times by distilled water, it was dried at 65 °C and kept for characterization and application.

MCM-41 silica was separately prepared using 1.02 g of CTAM, 57 ml H_2O, 8.17 g of aqueous ammonia solution (NH_4OH) and 5 ml of tetraethyl orthosilicate (Sigma-Aldrich, 98%) using the method described previously by Ref. [27].

2.3. Sample characterization

X-ray diffraction (XRD) patterns of the prepared PD/MCM-41composite were detected at a scanning speed of 2°/min using a Philips APD-3720 diffractometer with Cu Kα radiation under 40 kV and 20 mA. The morphological features of the developed composite were examined using SEM (JSM-6700F, JEOL, Japan), which was equipped with EDX for elemental analysis and by a transmission electron microscope (TEM; Model 2010, JEOL, Tokyo, Japan).

2.4. Effect of pH and determination of the point of zero charge (PZC)

The influence of pH on the uptake of Cr(VI) was investigated in the pH range from 2.0 to 10.0 using 0.05 g of the PD/MCM-41composite mixed with 100 mg/L of Cr(VI) concentration. The solution pH was adjusted by adding 0.01 M NaOH or 0.01 M HCl using pH meter (Hanna, HI 9025). The mixtures were shaken for 2 h at the stirring speed of 200 rpm using an orbital shaker (SHO-2D, Germany). After centrifuging, the Cr(VI) concentrations were determined by ion chromatography (DX-120 ion chromatography).

The pH at the point of zero charge (pH_{PZC}) of the PD/MCM-41composite is an important factor in describing the ionization behavior of its surface. The pH_{PZC} of the examined composite was determined using the previously described method [28]. The initial pH (pH_i) of 0.01 M NaCl was adjusted in the range from 2.0 to 10.0. At each starting pH, a fixed dose (0.1 g) of the composite was added to 50 mL of 0.01 M NaCl. After 48 h, the final pH (pH_f) of each solution was determined. By plotting (pH_f -pH_i) against (pH_i), the point at which pH_f -pH_i = 0 has been defined as the point of zero charge (pH_{PZC}) of the synthetic composite.

2.5. Adsorption experiments

A stock solution of Cr(VI) (1000 mg/L) was prepared by dissolving sodium chromate (Sigma-Aldrich) in deionized water. Cr(VI) concentrations for isotherm and kinetic experiments were obtained by diluting the stock solution with distilled water. Isotherm studies were conducted at room temperature (25 ± 2 °C) after equilibration of 25 mL of sodium chromate with different initial concentrations (60–140 mg/L) with 50 mg of the prepared PD/MCM-41composite. The solid-solution mixture was shaken at 200 rpm for 60 min using an orbital shaker. After centrifuging, the solutions were analyzed by ion chromatography to determine the final concentrations of Cr(VI).

For kinetic studies, a mixture of 0.05 g of the PD/MCM-41 composite and 25 mL of Cr(VI) with an initial concentration (100 mg/L) was prepared at room temperature. The mixture was shaken at 200 rpm for 5, 30, 60, 120, and 240 min of contact time. The Cr(VI) concentration in solution was determined after centrifuging the solid-solution mixture. The removed amount q_t (mg g^{-1}) and the uptake percentage (R %) of Cr(VI) at any time was calculated by the following equations [29,30]:

$$q_t = \frac{V(C_0 - C_t)}{m} \tag{1}$$

$$R\,\% = \frac{(C_0 - C_t)}{C_0} \times 100 \tag{2}$$

Where C_0 is the initial concentration (mg/L) of Cr(VI), C_t is the concentration of chromate at time (t), respectively, V is the solution volume (L) and m is the sorbent mass (g). All adsorption experiments were carried out using triplicates, and the results were averaged.

2.6. Nonlinear Chi-square test

Chi-square (χ^2) test which measures the difference between the calculated values of the applied model and the experimental data can be represented as follow [31]:

$$\chi^2 = \sum \frac{(q_{e,\mathrm{cal}} - q_{e,\mathrm{exp}})^2}{q_{e,\mathrm{exp}}} \tag{3}$$

where $q_{e,\mathrm{cal}}$ is the calculated data and $q_{e,\mathrm{exp}}$ is the experimental data. Small values of (χ^2) indicate the matching between the theoretical and the experimental data while the high Chi-square values represent the dissimilarity between the data [32].

2.7. Effect of temperature

The influence of temperature ranging from 30 to 55 °C on the removed amount of chromate was investigated using a mixture of 0.05 g of composite mass and 100 mg/L of Cr(VI) concentration. At all temperatures (30, 40, 50 and 55 °C), the solid-liquid phases were agitated at 200 rpm for 60 min.