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Adsorption kinetic study: Effect of adsorbent pore size distribution on the rate of Cr (VI) uptake

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ABSTRACT

Adsorbents were synthesized to obtain novel silica nanoparticles with a broad pore-size distribution (herein referred to as USG-41). The material demonstrated fast adsorption rates with highest adsorption capacities following Langmuir adsorption. Kinetic data best fit the intraparticle diffusion model demonstrating a two-step, surface and pore, adsorption process with pore diffusion being the rate determining step. This data provides key evidence of internal pore chelation of dichromate ions by USG-41. In contrast silica adsorbents (SBA-15 and MCM-41) prepared with similar average pore sizes to USG-41, but with narrow pore-size distributions, had lower adsorption capacities and their kinetic date best fit pseudo-second order diffusion models indicating a one-step, surface only, adsorption process. This study clearly demonstrated that pores size distribution, not the surface area or the average pore size, was central to ensure optimum adsorbent performance for removal of Cr (VI) from contaminated water.

1. Introduction

Chromium is a potentially toxic element widely used in many engineering and chemical industries due to its durability and aesthetic quality [1]. Cr (VI) is an industrially important form of this element [2], however it is toxic and carcinogenic to humans and animals. Furthermore, Cr (VI) should not be digested due to its high mobility and bioavailability compared to the sparingly soluble trivalent Cr species [3]. Due to the different toxicities of Cr (VI) and Cr (III) analytical measurements should involve speciation rather than total Cr concentration to best evaluate the potential physiology and toxicological effects of exposure [4,5]. For this reason Cr (VI) concentrations have been determined in liquid and soil samples [6–8]. However, Cieślak-Golonka et al. [9] concluded that the speciation of Cr (VI) in the liquid phase is still a poorly understood field compared to its behavior in the gas and solid states where Cr generally exists with a co-ordination number of 4. In the liquid phase Cr (VI) co-ordination is more flexible; up to 7-coordinate in solution [9]. In the species distribution diagram of chromate (VI) in aqueous solution [10], at $2 \leqslant \mathrm{pH} \geqslant 6$, dichromate ($Cr_2O_7^{2-}$) is the most abundant species [11]. In some cases the dichromate dianion may form a trimer, as found, e.g. in rubidium trichromate or even a tetramer as in $K_2Cr_4O_{13}$ [12].

To develop a species dependent extraction method for removal of Cr (VI) from solution, in the presence of Cr (III), functionalized mesoporous silica nanoparticles have been explored due to their high metal uptake capacities, good physical and chemical stabilities, uniform structures made of mesopore channels regularly organized in space [13–15]. Silica based adsorbents are of particular interest as they exhibit enhanced accessibility to active centers [16,17], and fast mass transfer rates in the regular porous environment [18,19]. These combinations of factors have led to high capacity adsorbents [19]. To enhance performance and extraction capabilities, materials need to be designed carefully to provide ideal platforms for optimum adsorption. To this end a few papers report the results of kinetic studies on Cr (VI) adsorption onto sorbent materials, but with conflicting results. In some studies the kinetic data show compliance with the first order models [20–24], whereas others report pseudo-second order kinetic mechanisms [25–30].

In this paper, adsorbents containing silica nanoparticles with different porosity parameters were synthesized and amino-functionalized to be evaluated for Cr (VI) uptake. The linearized Langmuir and Freundlich equations were used to fit the equilibrium isotherms. Kinetic data were analyzed by pseudo-first, pseudo-second and intra-particle diffusion models to obtain the kinetic constants, establish the rate limiting step of Cr (VI) removal and postulate the mechanism of Cr (VI) removal by porous materials.

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2. Experimental

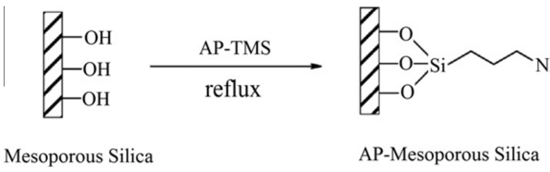
2.1. Materials and reagents

Potassium dichromate (+99%), 1,5-diphenylcarbazide, aqueous ammonia (30% NH_3), tetraethoxysilane (TEOS) 98%, hydrogen peroxide solution (30 wt.%), 3-aminopropyltrimethoxy-silane (AP-TMS), ethanol absolute, and toluene (+99%) were purchased from Sigma–Aldrich. Pluronic P123, $PEO_{20}PPO_{70}PEO_{20}$ was supplied from BASF Corporation. Nitric acid (HNO_3, 65 wt.%), hydrochloric acid (36%), and ammonium hydroxide (35%) were purchased from Fisher Scientific. Cetyltrimethylammonium bromide (CTAB), 98%, was supplied by BDH. Glassware was soaked in 5% HNO_3 overnight and cleaned with deionized water before use. All products were used as supplied and deionized water was used throughout this work.

2.2. Mesoporous silica preparations and functionalization

SBA-15 was prepared using the method reported in Ref. [31]. A surfactant tri-block copolymer solution of 4 g Pluronic P123, $PEO_{20}PPO_{70}PEO_{20}$ was dissolved in 120 cm^3 of 2 M hydrochloric acid and 60 cm^3 of distilled water in a sealed glass bottle at room temperature, and the mixture was magnetically stirred at 330 rpm. The surfactant solution was then heated to 40 °C and 11.3 g of TEOS was added and left for 24 h at 40 °C. The mixture was then placed in an oven for 5 days at 60 °C. The material was filtered and washed with water and dried overnight at 60 °C before calcination at 550 °C for 24 h. The resulting mixture had a ratio of SiO_2:0.0032 P123:4.4 HCl:144 H_2O.

MCM-41 was prepared according to the method reported in Ref. [32]. Briefly, 8.8 g of CTAB was dissolved in a mixture of 208 cm^3 of distilled H_2O and 96 cm^3 of aqueous NH_3 under slight warming (35 °C). Then, 40 cm^3 of TEOS was slowly added under stirring. After further stirring for 3 h, the gel was aged at room temperature for 24 h in a closed container. The product was obtained by filtration, washed with distilled H_2O, and dried in air at room temperature, the expected molar ratio was SiO_2:0.1 CTAB:14 NH_4OH:65 H_2O. To produce different pore size and pore size distribution of MCM-41, the organic template was removed using either microwave digestion (herein referred to as USG-41) or calcination [33]. In the microwave digestion method, approximately 0.3 g of as-synthesized MCM-41 was added to multiple Teflon vessels to which 5 cm^3 of HNO_3 and 2 cm^3 of H_2O_2 were added to each vessel. A MARS 5 microwave system, (CEM Corporation, Buckingham, UK) was used with a power output of approximately 1600 W, a pressure and temperature lower than 1.3 MPa and 200 °C, and a working frequency of 2450 MHz and 220 V for 15 min. The product (USG-41) was filtered, washed with copious amounts of distilled H_2O, and dried at 100 °C for 2 h. For calcination a second batch of MCM-41 was produced where template removal was performed using a conventional calcination rig by heating in air at 550 °C for 8 h. Surface modification of the materials was carried out by condensation using the AP-TMS with mesoporous material (Scheme 1). Briefly, approximately 5 g samples of USG-41, MCM-41, or SBA-15 were pre-treated at 140 °C for 2 h before being immersed in 50 cm^3 of toluene and 10 cm^3 of AP-TMS, in a 250 cm^3 flask. The mixture was refluxed for 4 h and the solid produced was filtered, washed with 100 cm^3 ethanol and oven-dried at 80 °C for 2 h to produce aminopropyl-functionalized mesoporous silica (AP-USG-41, AP-MCM-41, or AP-SBA-15).



Scheme 1. Modification of activated silica using 3-aminopropyltrimethoxy-silane.

2.3. Characterization of mesoporous silicas sorbents

The surface area of silica nanoparticulate materials used in this study was measured using nitrogen physisorption isotherms on a Micromeritics Gemini 2375 volumetric analyzer. Each sample was degassed prior to analysis for 6 h at 200 °C. The Brunauer–Emmett–Teller (BET) surface areas were calculated using experimental points at a relative pressure (P/P_o) of 0.05–0.25. The total pore volume was calculated from the N_2 amount adsorbed at the P/P_o of 0.99 for each sample and the average pore size distribution of the materials was calculated using the Barrett–Joyner–Halenda (BJH) model from a 30-point BET surface area plot. All samples exhibited a Type IV adsorption isotherm typical of mesoporous solids. Desorption isotherms were used to calculate the pore diameters. Infrared spectra of all samples were obtained in KBr pellets in the 4000–400 cm^{-1} region with a resolution of 4 cm^{-1}, by accumulating 64 scans using an ATI Mattson FTIR spectrophotometer. Elemental analysis (EA) was carried out using an Exeter Analytical CE440 elemental function.

2.4. Determination of Cr (VI) in aqueous samples

A Thermo Scientific iCAP 6200 ICP-OES was used for the determination of Cr (VI) in aqueous solutions. A 1000 ppm stock solution of Cr (VI) (0.2828 g of potassium dichromate was dissolved in 100 cm^3 distilled water) was used to prepare calibration standards (0.1–10 $\mu g\ cm^{-3}$) in 5% HNO_3. A quality control check solution was prepared at 1 $\mu g\ cm^{-3}$ to ensure the accuracy of the method used and was repeatedly analyzed after 20 samples. Method parameters used are shown in Table 1. The method detection limit (MDL) for Cr (VI) was 0.004 or 0.003 $\mu g\ cm^{-3}$ by using wavelengths of 267.7 or 283.6 nm, respectively.

Additionally, the possible presence of Cr (III) in sampled solutions was tested using a colorimetric method of determination. A 1 cm^3 aliquot of diphenylcarbazide solution (250 mg of 1,5-diphenylcarbazide was dissolved in 50 cm^3 acetone and stored in a brown bottle) was added to 1 cm^3 of each calibrant and the pH of the solution was adjusted to 1–2 by adding 0.2 cm^3 of 1 M hydrochloric acid. Prior to measurement the solution was allowed to stand for 15 min to ensure full color development. Derivatized solutions were measured using a SI Photonics (M-420) CCD array UV–vis spectrophotometer using a 1 cm absorption cell and an absorbance wavelength of 540 nm. Linear regression analysis of concentration vs. absorption gave typical regression lines of $y = 0.3555x + 0.0057$ with a correlation coefficient of 0.9986. Solutions of unknown Cr (III) concentration were determined after derivatization using the regression coefficients.

2.5. Adsorption isotherms

To study the maximum adsorption capacity of the Cr (VI) on USG-41, MCM-41, or SBA-15 the Langmuir [34] or Freundlich [35] models were applied to measured data. Solutions containing initial concentrations of Cr (VI) at 10, 50, 100, or 200 $\mu g\ cm^{-3}$ were prepared. To each solution 0.05 g of sorbent was added and the solution was stirred at 250 rpm for 120 min at room temperature, solutions were adjusted to provide a pH of 3. The amounts of Cr (VI) extracted at equilibrium, q_e (mg/g) were calculated according to the following equation: