



Adsorption of Cr(VI) using silica-based adsorbent prepared by radiation-induced grafting

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ABSTRACT

Silica-based adsorbent was prepared by radiation-induced grafting of dimethylaminoethyl methacrylate (DMAEMA) onto the silanized silica followed by a protonation process. The FTIR spectra and XPS analysis proved that DMAEMA was grafted successfully onto the silica surface. The resultant adsorbent manifested a high ion exchange capacity (IEC) of ca. 1.30 mmol/g and the Cr(VI) adsorption behavior of the adsorbent was further investigated, revealing the recovery of Cr(VI) increased with the adsorbent feed and the equilibrium adsorption could be achieved within 40 min. The adsorption capacity, strongly depended on the pH of the solution, reached a maximum Cr(VI) uptake (ca. 68 mg/g) as the pH was in the range of 2.5–5.0. Furthermore, even in strong acidic (4.0 mol/L HNO₃) or alkaline media (pH 11.0), the adsorbent had a sound Cr(VI) uptake capacity (ca. 22 and 30 mg/g, respectively), and the adsorption followed Langmuir mode. The results indicated that this adsorbent, prepared via a convenient approach, is applicable for removing heavy-metal-ion pollutants (e.g. Cr(VI)) from waste waters.

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1. Introduction

The environmental pollution problem such as releasing industrial waste waters into rivers directly has been attracting more and more attention during the past few decades, and the most serious pollutants are heavy metal ions that mostly coming from industrial waters. These heavy metal ions could not only lead to direct and indirect health risk of human beings but also disserve the whole ecosystem, as a result the removal of those toxic substance from industrial effluents has been becoming an urgent issue. By far many kinds of treatment techniques have been employed to solve this problem, for instance ion-exchange, reverse osmosis, precipitation, filtration, coagulation, electrolytic recovery and so on [1–7]. Such techniques, however, have many disadvantages that include high chemical cost, low removal efficiency, high-energy requirement and the generation of secondary toxic slurries. Compounds con-

taining toxic elements like chromium (Cr) are widely used in a great number of modern industries such as leather tanning, electroplating, metal finishing and pigments production, which result in a large quantity of Cr(VI) ions discharged directly into industrial waste effluent. Researches [8–10] have indicated that the Cr(VI) ions can bring high toxic nature to the biological systems and human health: Inhalation of Cr(VI) may cause acute toxicity, irritation and ulceration of the nasal septum and respiratory sensitization (asthma); Ingestion of Cr(VI) may affect kidney and liver functions; Skin contact with Cr(VI) may result in systemic poisoning damage or even severe burns, and interference with the healing of cuts or scrapes, which may lead to ulceration and severe chronic allergic contact dermatitis; Eye exposure to Cr(VI) may cause permanent damage. Environmental Protection Agency (EPA) in US recommends that the amount of Cr(VI) in drinking water should be less than 100 µg/L. Due to its high toxic nature to biological systems, the removal of Cr(VI) from these liquid waste has attracted a mass of public's concern. In order to develop a proper method for the removal of Cr(VI) from industrial effluents, many adsorbents have been exploited, such as activated clay [11], ion exchange resin [12], activated carbon [13], natural rectorite [14], and zeolite [15].

Radiation grafting technique has been widely used to prepare adsorbents for removing the heavy metal ions from effluents in the past several decades [7,16–19] and the process can be carried out at room temperature. Plenty of functional materials

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were prepared by choosing different functional monomers and matrix materials freely. What's more, the adsorbents with different grafting yield (*GY*) can be easily prepared by controlling the irradiation conditions. Dimethylaminoethyl methacrylate (DMAEMA) has been grafted onto various matrix materials by radiation technique [20–24]. As tertiary and quaternary amino groups can be easily incorporated into matrix materials, the DMAEMA grafted materials have also been utilized for adsorption and separation of heavy metal ions [21,22,25]. Moreover, the hydrogels prepared by radiation crosslinking of DMAEMA has displayed a sound ability to adsorb metal ions like ReO_4^- [26].

Owing to its high surface area, fast adsorption kinetics and chemical stability under acidic conditions, silica has been extensively used as porous matrix to prepare adsorbents for heavy-metal-ions like Cr(VI) [27–32]. Being capable of immobilizing various organic molecules onto the surface, silica is usually organofunctionalized with chelation groups providing the scopes for trapping heavy metal ions. Several kinds of silica-based adsorbents for Cr(VI) have been prepared in the past few years [28,33–35]. However, the application of those resultant adsorbents was largely limited due to their poor stability under particular circumstance such as in strong acidic solutions. Whereas the organofunctionalized methods usually involved complicated procedures, inducing to high cost, low reaction efficiency etc, it was necessary to explore novel methods for preparing silica-based adsorbent. Recently, some vinyl monomers have been grafted onto silica with irradiation method, confirming the feasibility of preparing adsorbents via radiation-induced grafting of monomers onto silica matrix [36,37].

In this study, a tertiary-ammonium-type silica-based adsorbent for Cr(VI) adsorption was synthesized by radiation-induced grafting. The properties concerning the Cr(VI) adsorption such as adsorption kinetics and the befitting pH, especially their possibility to be utilized in extreme environments (e.g. strong acidic conditions and irradiation fields), were to be investigated.

2. Experimental

2.1. Materials

Silica was purchased from Qingdao Meigao Co. Ltd. DMAEMA (Acros) with purity of 99% was used as the monomer. Trimethylchlorosilane of chemical purity was supplied by Sinopharm Chemical Regent Co. Ltd. Other chemicals used were analytical reagent (AR).

2.2. Preparation of the adsorbent

The silica was first heated at 200 °C and then washed with 1.0 mol/L HNO_3 at about 100 °C. After dried in vacuum at 80 °C, the silica was silanized with trimethylchlorosilane at 110 °C in xylene for 8 h. The silanized silica was immersed in a 1.0 mol/L DMAEMA solution. After getting rid of oxygen by nitrogen flow, the samples were irradiated to desired absorbed dose by γ -ray at room temperature with a dose rate of 41.5 Gy/min. The DMAEMA grafted silica was washed with acetone in a Soxhlet's extraction device to remove residues and then dried in vacuum at 80 °C.

The DMAEMA grafted silica was immersed in 1.0 mol/L HCl to prepare the adsorbent via a protonation process (shown in Fig. 1), and then the adsorbent was washed with deionized water to remove the residue HCl. Finally, it was dried in vacuum and kept for further use.

The grafting yield (*GY*) of the samples was determined by thermogravimetric analysis in a Q600 SDT instrument (USA). The measurements were performed, with a nitrogen flow rate of

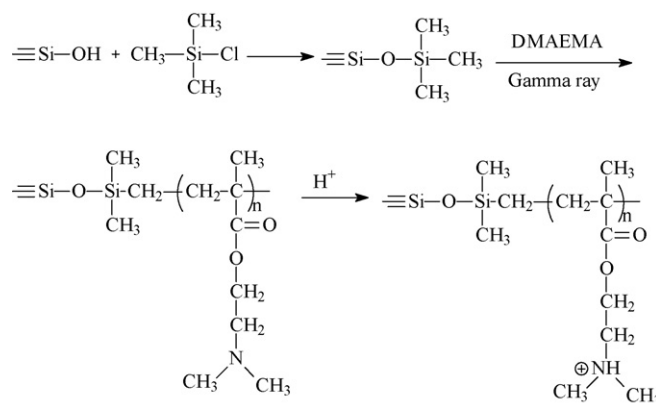


Fig. 1. Scheme of the synthesis route of the adsorbent.

100 mL/min, from room temperature to 1000 °C at a heating rate of 20 °C/min. According to the weight loss of the grafted silica due to the decomposition of the grafted DMAEMA, the *GY* was calculated as follows:

$$GY (\%) = \frac{W_g}{1 - W_g} \times 100 \quad (1)$$

where W_g is the weight loss percentage of the grafted silica due to the decomposition of the grafted DMAEMA.

2.3. Characterization of the adsorbent

Micro-FTIR analyses of the original silica, silanized silica and DMAEMA grafted silica was performed in a Nicolet (Magna-IR 750) spectrometer. The spectra were measured in the absorbance mode at a wave number range of 4000–600 cm^{-1} .

The ion exchange capacity (*IEC*) was determined by titration. The grafted silica with certain weight was immersed in a 0.05 mol/L HCl solution overnight at room temperature with periodic stirring. Then the solution was back titrated with 0.05 mol/L NaOH to neutral. The *IEC* (mmol/g) was calculated according to the following equation:

$$IEC = \frac{M_{\text{HCl}} - M_{\text{NaOH}}}{W} \quad (2)$$

where M_{HCl} is the initial mole of HCl, M_{NaOH} is that of the required NaOH, W is the weight of the grafted silica.

The X-ray photoelectron spectroscopy (XPS) analysis was performed with an AXIS-Ultra instrument from Kratos Analytical using monochromatic Al $K\alpha$ radiation (225 W, 15 mA, 15 kV) and low-energy electron flooding for charge compensation. To compensate for surface charges effects, binding energies were calibrated using C 1s hydrocarbon peak at a binding energy (BE) of 284.80 eV. The data were converted into VAMAS file format and imported into CASA XPS software package for manipulation and curve fitting.

2.4. Adsorption of Cr(VI) using the adsorbent

The stock Cr(VI) solution was prepared by dissolving $\text{K}_2\text{Cr}_2\text{O}_7$ in distilled water. Certain amount of HCl was added to stabilize Cr(VI) ions in the solution. After diluted to a total volume of 1.0 L, a stock solution with a Cr(VI) concentration of 1000 mg/L and HCl concentration of 0.02 mg/L was prepared. For the adsorption experiment, the Cr(VI) was determined using the Atom Emission Absorption Spectra (Hitachi, mode 180-60). The Cr(VI) uptake was calculated as

$$\text{Cr(VI) uptake} = \frac{(C_0 - C_e) \times V}{m} \quad (3)$$

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