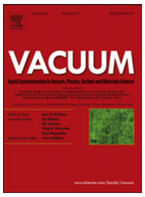
Vacuum 89 (2013) 1–6

Contents lists available at SciVerse ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum



Adsorption of Cr(VI) on 1,2-ethylenediamine-aminated macroporous polystyrene particles

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A R T I C L E I N F O

Article history:
Received 19 May 2012
Received in revised form
27 August 2012
Accepted 28 August 2012

Keywords:
Cr(VI)
Macroporous polystyrene particles
Animation
Adsorption

A B S T R A C T

An adsorbent, 1,2-ethylenediamine-aminated macroporous polystyrene (EDA-PSt) particles was used to adsorb Cr(VI) from aqueous solution. Effect of pH value, contact time, temperature, adsorbent dosage and initial Cr(VI) concentration on adsorption amount of Cr(VI) on EDA-PSt were investigated. The results showed that the adsorption isotherm can be well described by the Langmuir equation and the adsorption kinetics fitted to the pseudo-second-order model. According to Langmuir equation, Q_m was calculated to be 175.75 mg g^{-1}. The breakthrough curve experiment showed that the dynamic adsorption capacity for Cr(VI) on EDA-PSt was 100.06 mg g^{-1}. The adsorbed Cr(VI) could be desorbed by 0.1 mol L^{-1} NaOH and the desorption ratio was 67.28%.

1. Introduction

Hexavalent chromium, Cr(VI), has been regarded as a typical heavy metal pollutant generated from industries including electroplating, pigment manufacture, metal cleaning, leather tanning, mining, chromate preparation, as a biocide etc [1]. Soluble Cr(VI) is highly toxic, pollutes the soil and water, and causes cancer, skin allergies, genetic defects [2–4]. It is necessary to eliminate Cr(VI) from the environment, in order to prevent the deleterious impact of Cr(VI) on ecosystem and public health. The US Environmental Protection Agency (EPA) has set a maximum contaminant level of 0.05 mg L^{-1} for Cr(VI) in potable water [5,6].

A large number of techniques have been developed to remove Cr(VI) ions from wastewater, including chemical reduction/precipitation [7,8], ion exchange [9], adsorption [10], and membrane separation (dialysis/electrodialysis [11], electrolysis [12], reverse osmosis [13,14] etc.), among which, adsorption has become by far the most promising and widely used one to remove heavy metal ions because of its high efficiency, easy handling, economical effectiveness and availability of different adsorbents. Therefore, choosing an economical, effective and environmentally friendly Cr(VI) adsorbent is very important.

Most adsorbents used in Cr(VI) removal were prepared by introducing selective functional groups to porous materials such as activated carbon [15], straw [3], coir pith [16], and synthesized polymer beads [17,18] due to their large surface area, low cost, or reusability [19,20]. The introduced functional groups will modify the chemical composition of the matrix surface and hence improve their adsorption behaviors [21]. Among these functional groups, amino-contained groups have been found to belong to the most effective ones for removing Cr(VI) [22,23]. Shen et al. [24], Kyzas et al. [25], and Niu et al. [23] have applied amino-modified rice hull, chitosan derivatives, resin via SI-ATRP, nano-Fe_3O_4 magnetic polymers, respectively, for removing Cr(VI).

Polystyrene (PSt) particles have excellent chemical and physical properties that make them not easy to be degraded and damaged. Therefore, PSt-based adsorbents are usually used repeatedly. Unmodified PSt particles are not suitable to adsorb substances from aqueous solutions because the surface is hydrophobic and lack of selective groups. However, their hydrophilicity and selectivity are increased after modified. Previously we have prepared an adsorbent by aminating macroporous polystyrene (PSt) particles using 1,2-ethanediamine (EDA). The prepared EDA-PSt contented high density of imino group (2.75 mmol g^{-1}) which can act as functional group to adsorb anions. Since the prepared EDA-PSt has such high density of functional group, it is expected to have excellent performance to remove Cr(VI) from aqueous solution. However, related research has not been reported in literatures. In this article, EDA-PSt was used as an adsorbent to adsorb Cr(VI) from aqueous solution. Effects of pH value, contact time, initial Cr(VI) concentration and adsorbent dosage on adsorption amount were investigated. On-column adsorption and desorption of the adsorbent toward Cr(VI) were also studied.

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http://dx.doi.org/10.1016/j.vacuum.2012.08.012

2. Materials and methods

2.1. Materials

The EDA-aminated macroporous PSt particles (EDA-PSt) were prepared using the macroporous polystyrene (PSt) particles (EDA-PSt, diameter = 0.35–0.45 mm, specific surface area = 30 m^2 g^{-1}) obtained from Zhejiang Zhengguang Industrial Co., Ltd (Zhejiang Province, China) according to our previously published work [26]. Ten grams of PSt particles, 5 ml of chloroacetyl chloride, 5 g of $AlCl_3$ and 150 ml of dichloromethane were added into a 500-ml three-necked flask equipped with a mechanical stirrer and reacted at room temperature (25 °C) for 7 h. Then the particles were filtered using a sintered-glass funnel (G3), and washed successively with cold HCl solution (0.2 mol L^{-1}), water and THF, followed by suction-drying. The suction-dried particles, 60 ml of THF, 40 ml of ethanol, 20 ml of EDA, and 10 g of $NaHCO_3$ were added into a 250-ml three-necked flask equipped with a mechanical stirrer. After reaction at 80 °C for 18 h, the product was washed with ethanol and water successively in a sintered-glass funnel (G3), followed by suction-drying. The suction-dried adsorbent was further dried in vacuum at 105 °C for 2 h and then stored in an airtight vial. Ten grams of suction-dried EDA-PSt produced 5.089 g of dry EDA-PSt powder. The functional group was determined to be imino group according to the methods described in reference [26] and the density was 2.75 mmol g^{-1}. All chemicals were purchased from Beijing Chemical Plant (AR grade).

2.2. SEM and BET measurements

The morphologies of Pst particles before and after amination were observed using a HITACHI S-4800 scanning electron microscope (HITACHI, Japan). Pore diameter and specific surface area of the microspheres before and after reaction were determined by accelerated surface area porosimeter (ASAP) system 2010 (Micromeritics, USA). Samples were degassed under vacuum for 8 h at 40 °C prior to measurement.

2.3. Zeta potential measurement

Before the measurement, EDA-PSt was grinded to powder. The zeta potential of the EDA-PSt powders with or without 500 mg L^{-1} Cr(VI) at the pH values of 1.0–7.0 were measured using the Zeta Meter (Malvern Nano-ZS90, Britain). The pH value of the solution was adjusted with 0.1 mol L^{-1} NaOH and 0.1 mol L^{-1} HNO_3. All data were determined three times, and the average value was adopted.

2.4. Batch adsorption of Cr(VI) on EDA-PSt

Adsorption of Cr(VI) on EDA-PSt was conducted in batch experiments. The stock solution of Cr(VI) was prepared by dissolving $K_2Cr_2O_7$ in deionized water. The pH value was adjusted using 0.1 mol L^{-1} HNO_3 or NaOH solutions. In batch adsorption, EDA-PSt was added into Cr(VI) solution at a known concentration, temperature and pH value thermostat oscillator. After a desired period of adsorption, the solution was moved out and the concentrations of Cr(VI) in the liquid samples were determined by an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) (ICP-Optima 2100 DV, Perkin-Elmer, USA). The adsorption amount was calculated according to the following equation.

$$Q = V(C_0 - C_1)/m \tag{1}$$

where Q is the adsorption capacity (mg g^{-1}); C_0 is the initial concentration of Cr (VI) (mg L^{-1}), C_1 is concentration of Cr(VI) after adsorption (mg L^{-1}); V is the solution volume (L); m is the adsorbent dosage (g).

2.4.1. Effect of initial pH on adsorption amount

Six portions of EDA-PSt (0.2 g each) was added into six 100-ml conical flasks containing 30 ml of 500 mg L^{-1} Cr(VI) solution with the initial pH value of 1, 2, 3, 4, 5 and 6, respectively, then the flasks were put into a thermostat oscillator with a constant temperature of 25 °C and rotary rate of 200 rpm. After adsorption for 10 h, the solution was moved out and the concentration of Cr(VI) ions was measured by ICP-OES.

2.4.2. Effect of contact time on adsorption amount

Cr(VI) solution (pH 2.0, 500 ml) with an initial concentration of 500 mg L^{-1} was added to a 1000-ml conical flask equipped with a mechanical agitator which was set at the speed of 180 rpm. Then, 2 g of suction-dried EDA-PSt equilibrated to pH 2.0 was added to the flask at 25 °C. The concentration of Cr(VI) in the solution at different time was measured by ICP-OES and the adsorbed amount of Cr(VI) was calculated.

2.4.3. Adsorption isotherm

The adsorption isotherms were measured at pH 1.0 at 25, 35, and 45 °C, respectively. For each temperature, 0.2 g of EDA-PSt was weighed into ten 100-ml conical flasks, into which 3–30 ml, with 3 ml incremental, of Cr(VI) stock solutions were added. The solution was then diluted to 30 ml with diluted HNO_3 (pH 2.0). The flasks were placed in a shaker at preset temperature. After adsorption for 10 h, the concentration of Cr(VI) was measured by ICP-OES.

2.4.4. Effect of the adsorbent dosage on adsorption capacity

A series of varied amount of EDA-PSt equilibrated to pH 2.0 were added into conical flasks containing 30 ml of 500 mg L^{-1} Cr(VI) solution (pH 2.0). After adsorption for 10 h at 25 °C in a 200-rpm thermostat oscillator, the concentration of Cr(VI) ions was measured.

2.5. Dynamic adsorption and desorption of Cr(VI)

Six grams of EDA-PSt were packed in a glass column (200 × 10 mm I.D.) and equilibrated with HNO_3 solution (pH 2.0) until the pH of effluent reached to 2.0. Eighty hundred milliliters of Cr(VI) solution (pH 2.0, 523.43 mg L^{-1}) was then flown through the column. Elution of Cr(VI) was performed using 0.1 mol L^{-1} NaOH. Flow rate of both the loading and elution was controlled at 1 ml min^{-1} using a peristaltic pump. The effluent was collected every 10 ml and the concentration of Cr(VI) was determined by ICP-OES.

3. Results and discussion

3.1. Morphologies of the particles

Morphologies of the PSt particles before and after amination were observed through SEM and the images are shown in Fig. 1. After amination, the original morphology of PSt particles became smoother and the pore size distribution changed, meaning that the reactions changed the structure of the particles.

3.2. Pore size distribution and specific surface area of the particles

Pore size distribution and specific surface area of the particles were measured using BET method and the results are shown in Table 1. After amination, although the average pore size remained nearly unchanged, the specific surface area and pore volume