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Column study of Cr (VI) adsorption onto modified silica–polyacrylamide microspheres composite

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HIGHLIGHTS

- We have introduced a procedure for synthesis of silica–polyacrylamide composite.
- The capability of produced composite was investigated in removal of Cr (VI).
- The results showed a good capability for removal of Cr (VI) using the composite.
- Regeneration of composite after adsorption was done with 0.02 M NaOH successfully.

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ABSTRACT

Adsorption of Cr (VI) from aqueous solution was studied using a continuous fixed bed column which is packed with a new micro-porous composite particle developed in this study. This composite particle is composed of silica porous particle in which acrylamide is polymerized within the pore regions of the silica particles. The composite particle was supposed to maintain the mechanical properties of polyacrylamide as efficient absorbent to serve appropriately in the continuous processes. In order to enhance the adsorption capacity of the composite particle, it was modified with ethylenediamine. Scanning electron microscopy (SEM), Fourier transforms infrared spectroscopy (FT-IR) and thermogravimetry analysis (TGA) was applied to characterize the adsorbent. It was shown that polyacrylamide itself within the pore region of silica particle is also porous possibly because of the evaporation of solvent during the drying process. The effect of various parameters such as feed concentration (50–200 mg/L), feed flow rate (3–10 mL/min) and sorbent amount (250–750 mg) on the breakthrough characteristics of the adsorption system was investigated appropriately. Two well-known column adsorption models, Thomas and Adams–Bohart models were applied to fitting the experimental data. The results showed that the Thomas model was suitable for the description of breakthrough curve at all experimental conditions, while Adams–Bohart model was suitable for an initial part of dynamic behavior of column.

1. Introduction

Releasing of pollutant materials such as heavy metal ions from industrial effluents threats the environment and public health. Among heavy metals, chromium is a toxic pollutant that is being introduced into natural water and human environment by a variety of industrial waste waters including paint and pigment manufacturing companies, corrosion control, stainless steel production, fertilizers, leather tanning, chrome plating, wood preservation, and textiles [1]. When chromium concentration in body reaches 0.1 mg/g body weight, it can cause damage and create various problem such as liver damage and pulmonary congestion [2,3]. Chromium predominantly exists in two oxidation states, hexavalent (Cr (VI)) and trivalent (Cr (III)). Cr (VI) has a high mobility in soil and aquatic system and is more toxic than the trivalent one [4]. In the recent decades, researchers have concentrated on developing various methods that can effectively remove heavy metal ions from water and environments. General methods for removing heavy metal ions include filtration, chemical precipitation, chemical oxidation and reduction, ion exchange, and electrochemical treatment [5]. In comparison with other conventional methods for removing heavy metals from the waste water, adsorption has various advantages like economic viability, availability, profitability, ease of operation, high efficiency and friendly to environment [6]. Adsorption process can perform in batch and continuous mode. Batch mode experiments are usually done to measure the capability and effectiveness of adsorption process using specific adsorbent

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and to determine the maximum adsorption capacity. For industrial purposes the continuous adsorption in fixed-bed column is often desired [7]. However determining the design parameters is important in the continuous removal of Cr (VI) contaminated waste water.

Polymeric adsorbent with various functional groups is expected to have a good capability for adsorption of heavy metals and other pollutant from the waste water. Chitosan [8], polyacrylamide hydrogels [9], poly (2-hydroxyethylmethacrylate) [10], polyacrylonitrilefibers [11] and polyaniline–polyethyleneglycol composite [4] were applied for removal of heavy metal ions from waste water. One of the major disadvantages of polymeric adsorbents is poor mechanical stability especially in continuous fixed bed studies. The mechanical properties of this material can be improved by combining with the materials that have good mechanical properties. In this study we have produced modified silica–polyacrylamide microspheres composite and investigated its capability as adsorbent for removal of Cr (VI) from synthetic solution in a continuous flow system. It must be noted that because of very high swelling ratio of amine modified polyacrylamide [9], it cannot be used as an adsorbent in column studies without enhancing the physical properties.

For producing amine modified silica–polyacrylamide microspheres we used a technique so-called polymerization in packed bed [12]. The technique involves the following steps. (1) Packing porous solid supports (silica microspheres) in a column, (2) filling the pores of the solid with polymerization solution followed by polymerization and (3) post-treatment of the silica–polyacrylamide composite. Since, the presence of amino groups on the surface of the adsorbents has been reported to be effective in adsorption of chromium ions [11,13–14], the amination reaction of the produced silica–polyacrylamide composite was also carried out with ethylenediamine.

2. Materials and methods

2.1. Materials

Acrylamide (AAm), *N,N′*-Methylene bisacrylamide (MBA), ammonium persulfate (APS), ethylenediamine, dimethylformamide (DMF), 2,2,4-trimethylpentane and potassium dichromate were purchased from Merck Chemical Company (Germany). Silica porous particle (Si1000, pore size1000 Å, diameter 45–75 μm, pore volume 0.77 mL/g) was purchased from Silicycle (Canada).

2.2. Synthesis and post treatment of adsorbent

The composite particles, i.e. silica porous particle filled with polymeric material, were prepared according to the following procedure. Firstly, the glass column (1 cm internal diameter and 15 cm height) was packed with 0.5 g of silica particles and subsequently the column was closed with silicon rubber. The schematic representation of the setup is shown in Fig. 1. In this setup, vacuum was applied from the bottom of the column for 5 min to remove air from the column and also from the silica pores. After closing the outlet valve of column the pre-prepared polymerization solution (AAm (700 mg), MBA (77 mg) and APS (5 mg) in DMF (1.2 mL)) was injected into the packed column and then the polymerization solution was pushed into the pores of silica via nitrogen gas for 2 min at the pressure of 2 bar. It should be noticed that the polymerization solution was degassed for 1.5 min under nitrogen flow and at ice bed prior to the injection. To remove any residual solution remaining between the silica particles, the column was washed with trimethylpentane (4 mL). Also to intercept the way out of penetrated solution from the silica pores the level of trimethylpentane was maintained as level as silica particles in the column. Afterward the column was transferred to an oven at 40 °C for at least 16 h. After completion of the radical polymerization process in silica pores, the composite particles were removed from the column. To remove and eliminate the solvent (DMF), the composite particles were washed with distilled water several times, washed further with methanol and finally dried under vacuum at 60 °C for 12 h. Fig. 2 illustrates the overall process used for producing silica–polyacrylamide composite microspheres synthesized in this study.

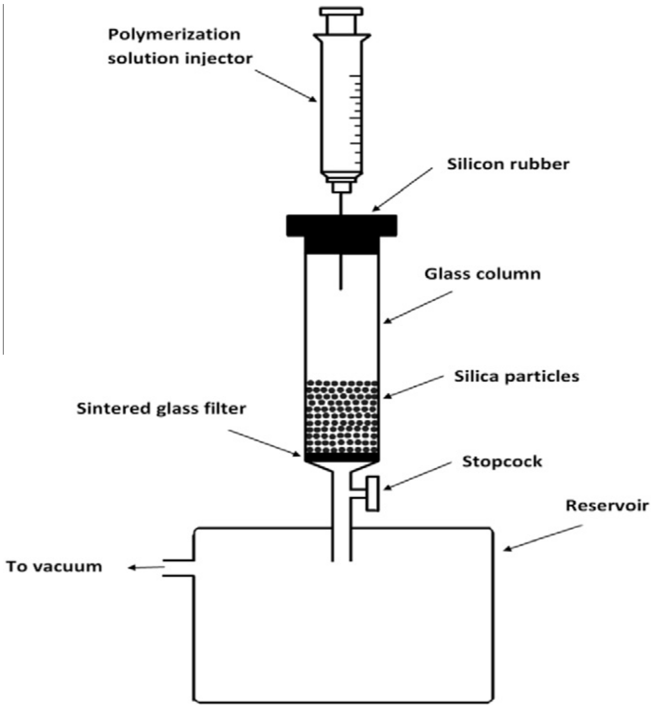

Fig. 1. Schematic representation of system used for production of silica–polyacrylamide composite.

To enhance the adsorption capability of composite, post modification of the silica–polyacrylamide microspheres was carried out with ethylenediamine. For this purpose 2 g of the composite particles was reacted with excess amount of ethylenediamine. The reaction was carried out in round bottom flask equipped with a reflux condenser at 100 °C for 9 h. Afterward the reaction mixture was poured into methanol and the modified particles were separated

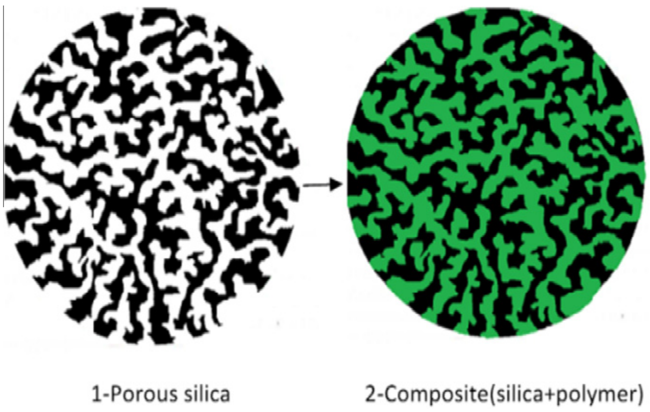

Fig. 2. Schematic view of porous silica particles and composite particles prepared in this study.