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Synthesis of powdered and granular *N*-(3-trimethoxysilylpropyl)diethylenetriamine-grafted mesoporous silica SBA-15 for Cr(VI) removal from industrial wastewater

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ABSTRACT

In this study, both powdered and granular *N*-(3-trimethoxysilylpropyl)diethylenetriamine (DAEAPTS)-grafted mesoporous silica SBA-15 were synthesized for hexavalent chromium (Cr(VI)) removal from industrial wastewater. The powdered adsorbents were synthesized via grafting DAEAPTS onto SBA-15. The Cr(VI) sorption characteristics of the adsorbents were examined under batch conditions in synthetic Cr(VI) solutions. Batch experiments revealed that the Cr(VI) sorption was favorable at acidic pH conditions with the greatest sorption at pH 3. The Cr(VI) sorption was a fast process, reaching equilibrium within 10 min. The maximum Cr(VI) sorption capacity was 330.88 mg/g. To overcome limitations of the powdered adsorbents for large-scale application (hydraulic and separation problems), the spherical granular adsorbents (average size = 1.13 ± 0.09 mm) were prepared through immobilizing the powdered DAEAPTS-grafted SBA-15 into a polymer blend (poly(vinyl alcohol) and sodium alginate). The granular adsorbents were applied for Cr(VI) removal from two industrial plating wastewaters in flow-through column experiments. In the experiment with wastewater 1 (Cr(VI) concentration = 328.7 mg/L), the Cr(VI) sorption capacity of the granular adsorbents was 158.8 mg/g. In the experiment with wastewater 2 (Cr(VI) concentration = 2671.6 mg/L), the pristine and regenerated adsorbents were tested to demonstrate that the granular adsorbents could be successfully regenerated and reused for Cr(VI) removal.

1. Introduction

Chromium (Cr) wastewater discharged from leather tanning, textile, dyeing, paint, and electroplating industries can cause serious environmental and health problems [1]. In aquatic environments, trivalent Cr(III) and hexavalent Cr(VI) are major forms of chromium; Cr(VI) is extremely water soluble and highly toxic, whereas Cr(III) is water insoluble and less dangerous [2]. Various technologies, such as chemical precipitation, sorption, membrane filtration, and solvent extraction, have been used to remove chromium from wastewater; among them, sorption is a simple and cost-effective treatment method [3]. Various materials, including activated carbon, zeolites, biosorbents, chitosan, and industrial waste sorbents, have been used as adsorbents for chromium removal from water and industrial wastewater [4]. However, cheap and efficient chromium adsorbents still need to be developed for adsorption process.

As adsorbents, silica-based functional materials have been prepared by several researchers for Cr(VI) removal from aqueous solutions [5,6]. Silica materials, such as silicates, mesoporous silicas, and silica gels, have been used as supports because of their physico-chemical stability, thermal resistance, and easy modification with organic groups [7]. Some researchers have prepared silica-based composites for Cr(VI) removal via modification with various polymers [8–10]. Linsha et al. [9] synthesized hybrid beads using amine-grafted bohemite/silica and poly(vinyl alcohol) for Cr(VI) removal. Nithya et al. [10] examined Cr(VI) sorption to nano-sized composites fabricated from silica gels and chitosan-g-poly(butyl acrylate). Others have synthesized surface-functionalized silica particles for Cr(VI) removal through modification with various organic functional groups [11–20]. Lam et al.

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[12] grafted 3-aminopropyltrimethoxysilane on mesoporous silica MCM-41 to prepare amine-functionalized adsorbents for Cr(VI) removal. Liu et al. [14] observed the Cr(VI) sorption to silica materials functionalized with quaternary ammonium and quaternary phosphonium. Wang et al. [16] examined the sorption characteristics of Cr(VI) ions to imidazole-modified silica gels. Wu et al. [18] modified mesoporous silica SBA-15 with ethylenediamine for Cr(VI) sorption. Dindar et al. [19] prepared amine-functionalized SBA-15 through surface-modification with aminopropyltriethoxysilane. However, most of these studies have been limited to the application of the silica-based adsorbents to the removal of Cr(VI) from synthetic solution but not from industrial wastewater.

N-(3-Trimethoxysilylpropyl)diethylenetriamine (DAEAPTS) is an example of an organosilane, which is a type of chemical compound derived from silanes. DAEAPTS has the molecular formula $C_{10}H_{27}N_3O_3Si$ and contains three amine functional groups [21]. DAEAPTS has been used by several research teams to synthesize surface-functionalized silica particles for gaseous contaminant removal, including formaldehyde [22], carbon dioxide [23,24], and nitrogen gas [25]. However, limited studies have prepared DAEAPTS-functionalized silica particles for the removal of aqueous heavy metal such as Cr(VI) [11], Cu(II) [26], Ni(II) [27], and Pb(II) [27]. To the best of our knowledge, however, no studies have synthesized both powdered and granular DAEAPTS-grafted SBA-15 for Cr(VI) removal from industrial wastewater.

The aim of this study was to synthesize granular adsorbents through immobilization of the DAEAPTS-grafted SBA-15 particles into polymer matrices for Cr(VI) removal from industrial plating wastewater. First, powdered adsorbents were synthesized via grafting DAEAPTS on the surfaces of SBA-15. The Cr(VI) sorption characteristics of the DAEAPTS-grafted SBA-15 were examined under batch conditions in synthetic Cr(VI) solutions. Batch sorption experiments were conducted under various experimental conditions, including varying pH, temperature, reaction time, and initial Cr(VI) concentration. Fourier-transform infrared (FTIR) spectrometry and X-ray photoelectron spectroscopy (XPS) were used to analyze the Cr(VI) sorption characteristics of the adsorbents. The powdered DAEAPTS-grafted SBA-15 has limitations as an adsorbent for large-scale application (hydraulic and separation problems) to Cr(VI) removal from industrial wastewater. To overcome these limitations, the granular media was prepared through immobilizing the powdered DAEAPTS-grafted SBA-15 into polymer matrices. The granular DAEAPTS-grafted SBA-15 adsorbents were applied for Cr(VI) removal from industrial plating wastewater under flow-through column conditions. The pristine and regenerated adsorbents were tested for Cr(VI) removal in column experiments.

2. Experimental

2.1. Synthesis of powdered DAEAPTS-grafted SBA-15

Chemicals provided from Sigma Aldrich (Saint Louis, MO, USA) were used in this study. SBA-15 was synthesized following the procedures described in Zhao et al. [28]: 6 g of pluronic P123 and 1 g of cetyltrimethylammonium bromide (CTAB, ≥99%) were dissolved in a mixture solution of 80 mL deionized water, 50 mL of ethanol (≥94%), and 100 mL of 2 M HCl (37%). The mixture solution was stirred at 30 °C for 1 h. 20 mL of tetraethylorthosilicate (TEOS, ≥99%) was then added into the solution. After stirring for 45 min at 40 °C and aging at 80 °C for 24 h under reflux conditions, a precipitate was obtained. The precipitate was filtered with a 0.45-μm membrane filter, washed with deionized water, and then dried under ambient conditions. The dried powder was calcined at 550 °C for 6 h using an electric muffle furnace (C-FMA, Vision Lab, Seoul, Republic of Korea) to remove the surfactant. Finally, SBA-15 was obtained via cooling followed by fragmentation with a mortar and pestle.

A powder form of DAEAPTS-grafted SBA-15 was prepared using a method modified from Mittal et al. [21]. Fig. 1 presents a schematic diagram of the synthesis of powdered DAEAPTS-grafted SBA-15: 0.5 g of SBA-15 was dispersed in 150 mL of anhydrous toluene. The solution was stirred at room temperature for 1 h. Then, 0.5 mL of deionized water and 4 g of DAEAPTS were added into the solution before the temperature was increased to 100 °C. Next, 0.5 mL of deionized water was added into the mixture solution. This mixture was vigorously stirred and refluxed for 24 h; the resultant slurry was washed with 400 mL of toluene. Then, the slurry was washed 3 times with 1 L of deionized water and dried at 70 °C overnight to obtain DAEAPTS-grafted SBA-15. Prior to its use in Cr(VI) removal experiments, the DAEAPTS-grafted SBA-15 was acid-treated in 0.1 M HCl solution for 6 h and dried at 70 °C overnight.

2.2. Synthesis of granular DAEAPTS-grated SBA-15

Based on the powdered DAEAPTS-grafted SBA-15, a granular form of DAEAPTS-grafted SBA-15 was prepared following the method described in Han et al. [29]. It is known that PVA is a water-soluble synthetic polymer with high tensile strength and flexibility. The blending of alginate with PVA could improve the strength and durability of hydrogel beads [29]. Fig. 1 presents a schematic diagram for the synthesis of granular DAEAPTS-grafted SBA-15: 20 g of poly(vinyl alcohol) and 2 g of sodium alginate were dissolved in 200 mL of deionized water and agitated on a magnetic stirring plate at 70 °C for 5 h. Then, 16 g of powdered DAEAPTS-grafted SBA-15 was added into the mixture solution with vigorous stirring to obtain the homogeneous suspension. The suspension was taken up by a plastic syringe and then dropped into a mixture solution of 5% boric acid and 1% $CaCl_2$ using a syringe pump (78-1100I, Fisher Scientific, Hampton, NH, USA) at a flow rate of 4 mL/min in order to form spherical adsorbents. The adsorbents remained in the aqueous solution for 24 h and were then oven-dried at 70 °C for 18 h in an electric muffle furnace to obtain granular DAEAPTS-grafted SBA-15.

2.3. Characterization of adsorbents

The characteristics of powdered and granular DAEAPTS-grafted SBA-15 adsorbents were analyzed using various instruments. Field emission scanning electron microscopy (FESEM, Supra 55VP, Carl Zeiss, Oberkochen, Germany) analysis was performed to visualize the adsorbents. Energy dispersive X-ray spectrometry (EDS, Carl Zeiss) analysis was conducted to analyze the elemental composition of the adsorbents. FTIR (Nicolet 6700, Thermo Fisher Scientific, Waltham, MA, USA) analysis was conducted to obtain infrared spectra of the adsorbents before and after Cr(VI) removal. XPS (XPS Sigma Probe, Thermo VG, London, UK) measurement with monochromatic Al $K\alpha$ radiation was performed to analyze the chemical characteristics of the adsorbents before and after Cr(VI) removal. N_2 adsorption-desorption isotherm analysis was performed using a surface area analyzer (BELSORP-max, BEL Japan Inc., Osaka, Japan). The size of granular DAEAPTS-grafted SBA-15 was determined by digital image analysis (number of adsorbent particles = 100) using ImageJ 1.43u software (National Institutes of Health, Bethesda, MD, USA). The mechanical strength of granular DAEAPTS-grafted SBA-15 was measured using a universal testing machine (Instron-5543, Instron Corp., Norwood, MA, USA) with a maximum load capacity of 50 N. Single wet composite was placed on the plate surface of the fixed grip, and then a moving grip compressed the specimen until it failed by cracking or breaking. The compression test was performed at a rate of 1 mm/min at an

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