Preparation of magnetic ionic liquid/chitosan/graphene oxide composite and application for water treatment

Leilei Li, Chuannan Luo *, Xiangjun Li, Huimin Duan, Xiaojiao Wang

Key Laboratory of Chemical Sensing & Analysis in Universities of Shando ng (University of Jinan), School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, China

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ABSTRACT

Magnetic chitosan and graphene oxide-ionic liquid (MCGO-IL) composites as biodegradable biosorbents were synthesized by impregnating MCGO with ionic liquid. The characteristic results of FTIR, SEM, and XRD showed that MCGO-IL were successfully prepared with large surface area and good magnetic responsiveness. They were used for the removal of Cr(VI) from simulated wastewater with a fast solid–liquid separation in the presence of external magnetic field. The influence of various analytical parameters on the adsorption of Cr(VI) such as pH, contact time, and initial ion concentration were studied in detail. The adsorption followed a pseudo-second-order kinetics. The equilibrium adsorption was well-described by the Langmuir isotherm mode and the maximum adsorption capacity was 145.35 mg/g. The stronger intermolecular hydrogen bond between MCGO-IL and Cr(VI) and the hydroxyl and amine groups were believed to be the metal ion binding sites. Moreover, the MCGO-IL could be repeatedly used by simple treatment without obvious structure and performance degradation. The obtained results indicated that the impregnation of the room temperature IL significantly enhances the removal efficiency of Cr(VI). The MCGO-IL may be suitable materials in heavy metal ion pollution cleanup if they are synthesized in large scale and at low price in near future.

1. Introduction

Toxic heavy metal ions in water bring many detrimental effects on environment and human health [1–3]. Among those heavy metal species, Cr(VI) is a commonly identified contaminant because of its high toxicity and mobility [4]. Chromium compounds are mainly used in electroplating, tannery and dyeing industries [5], their waste discharge is of prime concern. With better awareness of these problems, a number of technologies to remove Cr(VI) have been developed, including cyanide treatment [6], electro-chemical precipitation [7], reverse osmosis (RO) [8,9], ion exchange (IE) [10,11] and adsorption [12]. From the literature query, various adsorbents have been reported to remove Cr(VI) from wastewater, such as clay minerals, oxides, and zeolites [13–15]. However, separating and recycling these materials turn out to be a challenge especially when the particle size goes down to nanoscale and thus reducing the operation time in each cycle is urgently required in modern industry.

Nanostructured adsorbents exhibited remarkable advantages due to their higher surface areas and much more surface active sites than bulk materials [16,17]. However, there are two major challenges when using these nanomaterials. One comes from the easy oxidation/dissolution of the pure nanoparticles such as Fe nanoparticles (NPs), especially in acidic solution. The other is the difficulty to recycle these nanomaterials with such a small size. Hence, it is very urgent to develop new materials with large surface area, high adsorption capacity and stability to apply in water treatment.

More recently, Wang et al. [18] have reported the high capacity adsorption of hexavalent chromium using magnetic microspheres with dendrimer modification. Crini [19] has reviewed the importance of biopolymers in wastewater treatment. The biodegradability and excellent stability coupled with the active binding sites makes them well suited for adsorption of heavy metals. Prominent among the biopolymers is chitosan, because chitosan contains many oxygen-containing functional groups.

Graphene oxide (GO) contains a wide range of oxygen functional groups both on the basal planes and at the edges of GO sheets, such as –COOH, and –OH. These functional groups are essential for the high sorption of heavy metal ions, and allows GO to participate in a wide range of bonding interactions. GO shows high adsorption performance of metal ions, but cannot be easily separated from

treated water. In addition, the chitosan and graphene oxide are easy to aggregate, resulting in great reduction in the surface area, and is not beneficial for the adsorption of contaminants. Therefore, it is of great importance to develop nanostructured adsorbents with easy solid–liquid separation property.

As a potential environment-friendly solvent, room temperature ionic liquid (IL) has received intense scrutiny [20]. They have also been successfully applied in the area of separation science [21]. Recently, IL is receiving much attention owing to their unique properties, such as good ionic conductivity, wide potential window, high viscosity, high thermal stability, tunable solvent properties and low toxicity [22].

Based on the strong electrostatic/chemical interaction between IL and GO as well as improved dispersion of GO by IL [23], furthermore, the introduction of IL into functional composites could improve the performance of the corresponding composites and give rise to a wider range of applications [24]. Therefore, great efforts have been made towards the preparation of the IL functionalized GO composites. In addition, chitosan can also be dissolved, regenerated, and functionalized through the IL processing [25]. Accordingly, the synthesis of environment-friendly IL-functionalized composites and use them to solve environmental problems is of great significance.

In this paper, we introduced Fe_3O_4 particles to synthesize magnetic chitosan and graphene oxide (MCGO), and then we report the utility of MCGO as an excellent platform for impregnating the ionic liquid to formed MCGO-IL. The introduction of the magnetic could well solve the problem of difficult to separation, and the IL not only increase the water-solubility of the composite material but also could adsorb metal ions collaborate with MCGO by electrostatic attraction. The effects of the treatment time, initial ion concentration and pH values on the Cr(VI) removal are investigated for the prepared MCGO-IL. The adsorption kinetics is also investigated by fitting the experimental data with different models and the removal mechanism is proposed. The MCGO-IL are found to possess unique capability to remove Cr(VI) very quickly and efficiently from wastewater.

2. Experimental

2.1. Materials

Chitosan with 80 mesh, 96% degree of deacetylation and average-molecular weight of 6.36×10^5 was purchased from Qingdao Baicheng Biochemical Corp. (China). $FeCl_2 \cdot 4H_2O$ and $FeCl_3 \cdot 6H_2O$ were purchased from Damao Chemical Agent Company (Tijin, China). The reagents 1-ethyl-3-(3-dimethylaminoprophy) carbondiimide hydrochloride (EDC), N-hydroxyl succinimide (NHS), sodium hydroxide, glutaradehyde and acetic acid were Aldrich products, tetraoctylammonium bromide were purchased from Sigma Aldrich. Sulfuric acid was procured from Merck, India. All other reagents used in this study were analytical grade, and distilled or double distilled water was used in the preparation of all solutions.

2.2. Preparation of MCGO

GO was prepared from purified natural graphite by the modified Hummers method [26]. Magnetic chitosan and graphene oxide was prepared following the method of Fan L. et al. [27]. A solution of 0.05 M EDC and 0.05 M NHS was added to the GO dispersion with continuous stirring for 2 h in order to activate the carboxyl groups of GO [28]. To adjust the pH of the resulting solution was maintained at 7.0. 0.1 g of magnetic chitosan and the activated GO solution were added in a flask and dispersed in distilled water by
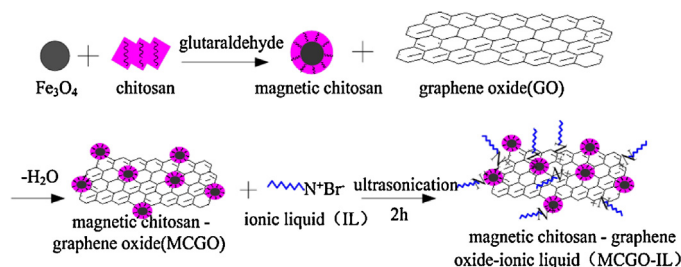
Scheme 1. Synthesis of MCGO-IL.

ultrasonic dispersion for 10 min. After ultrasonic dispersion, the mixed solutions were stirred at 60 °C for 2 h. The precipitate was washed with 2% (w/v) NaOH and distilled water in turn until pH was about 7. Then, the obtained product was collected by the aid of an adscititious magnet and dried in a vacuum oven at 50 °C. The obtained product was MCGO.

2.3. Preparation of MCGO-IL

MCGO-IL was prepared following the method of Santhana Krishna Kumara et al. [29]. 1.0 g of tetraoctylammonium bromide was dissolved in 15 mL methanol. 1.0 g of MCGO was taken in a round bottom flask and the dissolved ionic liquid was added dropwise and sonicated (Ultrasonic bath, Biotechnics, India) for 2 h with a 15 min intermittent time interval. The resulting solution was filtered, washed with methanol and the resulting IL impregnated MCGO was dried at room temperature and used for further adsorption studies. The preparation of MCGO-IL is shown in Scheme 1.

2.4. Characterization methods

A HH-15 vibrating sample magnetometer (Nanjing, China) was used to measure magnetization curve of samples. Wide angle X-ray diffraction (WAXRD) patterns were recorded by a D8 ADVANCE X-ray diffraction spectrometer (Bruker, German) with a Cu Kα target at a scan rate of $0.02°\ 2\theta\,s^{-1}$ from $10°$ to $80°$. Morphological structures of samples were examined by scanning electron microscopy (SEM) with a Hitachi SX-650 machine (Tokyo, Japan). FT-IR spectra were measured on a Perkin-Elmer 580B IR spectrophotometer using the KBr pellet technique.

2.5. Adsorption experiments

All batch adsorption experiments were performed on a model KYC-1102 C thermostat shaker (Ningbo, China) with a shaking speed of 180 rpm. Simulated wastewater with different Cr(VI) concentrations (60, 80, 100, 120, 140, 160, 180, 200 mg L^{-1}) were prepared by dilution of the stock $K_2Cr_2O_7$ standard solution with DI water. MCGO-IL (0.10 g) were added to 100 mL of the above Cr(VI) solution under mechanical agitation. For all adsorption tests, the initial pH values of the Cr(VI) solution were adjusted with 0.1 mol L^{-1} HCl solution or 0.1 mol L^{-1} NaOH solution. After the adsorption processes, MCGO-IL was conveniently separated by magnetic separation and the supernatant was immediately analyzed by atomic absorption spectrometry (WFX-1F2, China). To study the influence of initial pH on the removal of Cr(VI), the initial pH values of the solution were adjusted to 3.0, 4.0, 5.0, 6.0, 7.0 and 10.0. The concentration of MCGO-IL was 1.0 g L^{-1}, and the initial Cr(VI) concentration was 100 mg L^{-1}. The adsorption capacity and adsorption rate are calculated based on the difference in the Cr(VI)