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Removal of Pb^{2+} from water environment using a novel magnetic chitosan/graphene oxide imprinted Pb^{2+}

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ABSTRACT

A novel, magnetic chitosan coating on the surface of graphene oxide was (Pb-MCGO) successfully synthesized using Pb^{2+} as imprinted ions for adsorption and removal of Pb^{2+} from aqueous solutions. The magnetic composite bioadsorbent was characterized by SEM, FTIR and XRD measurements. Batch adsorption experiments were performed to evaluate the adsorption conditions, selectivity and reusability. The results showed that the maximum adsorption capacity was 79 mg/g, observed at pH 5 and 303 K. Equilibrium adsorption was achieved within 40 min. The kinetic data could be fitted with a pseudo-second order equation. Adsorption process could be well described by Langmuir adsorption isotherms. The selectivity coefficient of Pb^{2+} and other metal cations onto Pb-MCGO indicated an overall preference for Pb^{2+}, which was much higher than non-imprinted MCGO beads. Moreover, the sorbent was stable and easily recovered, the adsorption capacity was about 90% of the initial saturation adsorption capacity after being used five times.

1. Introduction

Lead ions commonly exist in industrial and agricultural wastewater and acidic leachate [1] from landfill sites in relatively high concentration. They are quite harmful to human and living things, leading to a wide range of spectrum health problems, such as renal failure, nausea, coma,convulsions, cancer, and subtle effects on metabolism and intelligence [2]. Due to the importance of lead as a heavy metal ion contaminant in geochemical systems and its high toxicity, many techniques have been applied in the removal of Pb(II), such as flocculation [3], membrane filtration [4], solvent extraction [5], biosorption [6], chemical precipitation [7], reverse osmosis [8], adsorption [9], etc. Among these technologies, adsorption techniques have been shown to be a feasible option, both technically and economically.

Chitosan has been reported to have high potential for adsorption of metal ions [10–14]. Due to its accessibility, high effectivity and no harmful by-product, it is often chosen as an bioadsorbent for the removal or the recovery of hazardous dyes, proteins, heavy metals and so on [15–18]. Coating chitosan with magnetic fluids is a new method to expand function of the chitosan, and the method has been reported that it can improve the surface area for adsorption and reduce the required dosage for the adsorption of metal ions [19].

Recent researches have indicated that graphene oxide (GO) proved to be a promising material to adsorb metal ions and support for catalyst due to their extraordinary mechanical strength and relatively large specific area [19]. Based on favorable adsorption properties of chitosan and inherent properties of GO some researchers have explored the possibility of magnetic chitosan-GO composite as bioadsorbents [20]. Where the carboxyl group of GO chemically reacts with the amine group of chitosan with consequent formation of chemical bond between GO and biopolymer (magnetic chitosan). The preparation of MCGO is schematically illustrated in Scheme 1.

Surface imprinting technology is an emerging technology that has attracted much attention in generating recognition sites by reversible immobilization of template molecules on cross-linked macromolecular polymer matrixes. Molecularly imprinted polymers represent a new class of materials possessing high selectivity and good affinity for target molecules [21,22]. Ion imprinted polymers have shown great promise as a method for preparing materials, which are capable of ion recognition [23]. So far, a lot of metal ion imprinted polymers have been prepared, including, Cu(II) [24], Zn(II) [25], Ni(II) [26],and Mg(II) [27] imprinted ones, however, surface imprinting MCGO of Pb^{2+} has not been synthesized and applied in selective removing Pb^{2+} from aqueous solution. The preparation of Pb-MCGO is schematically illustrated in Scheme 2.

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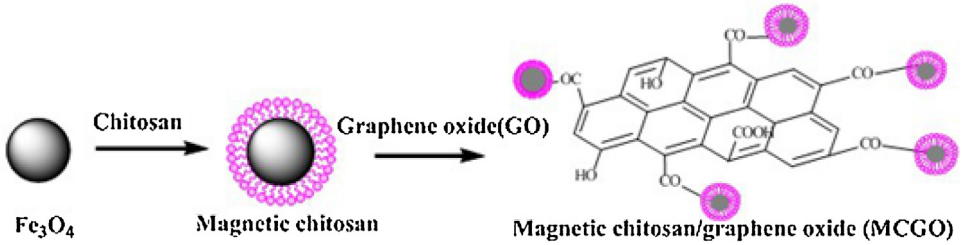


Scheme 1. Schematic depiction of the formation of magnetic chitosan (A) and MCGO (B).

In this work, Pb-MCGO was successfully synthesized, and applied to removing Pb^{2+} from wastewater. The kinetic of the Pb^{2+} adsorption on the Pb-MCGO composite have been investigated. The resulting Pb-MCGO composite could be utilized as a magnetically separable and efficient adsorbent for Pb^{2+} removal from water. Furthermore, high removal efficiency and selectivity in adsorbing Pb^{2+} can be achieved by applying the Pb-MCGO. This information will be useful for further applications in the treatment of practical waste effluents.

2. Materials and methods

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 (Tianjin, China). Commercially available magnetic Fe_3O_4 (20–30 nm outer diameters; 98% purity) was obtained from Tongrenweiye Technology Co., LTD. (Shijiazhuang, China). 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. Synthesis of graphene oxide(GO)

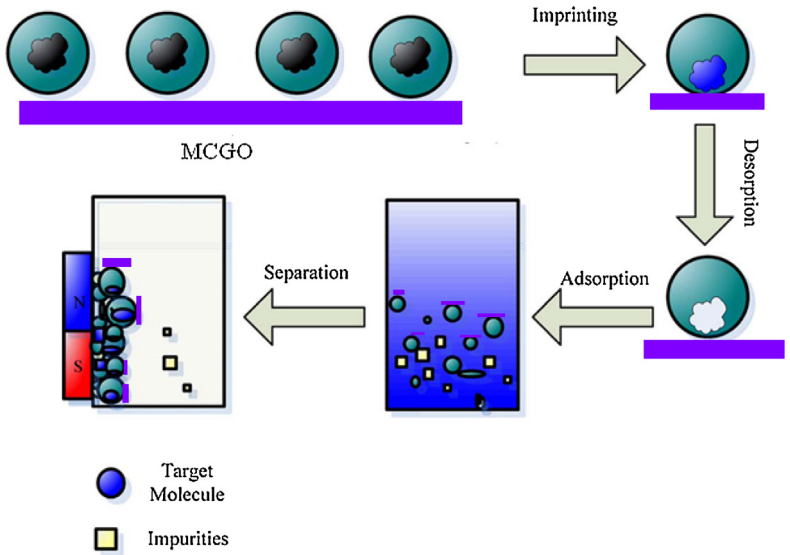
Graphene oxide was prepared from purified natural graphite by the modified Hummers method. Briefly, natural graphite and potassium permanganate were stirred with the mixed acid (H_2SO_4:HNO_3 = 9:1) for 12 h at 60 °C. Then, hydrogen peroxide was added in the mixed liquor and stirred for one hour resulting in bright yellow colored end product [28]. This material was washed with 2 M HCl till bisulfate ions were removed and then with copious amount of water till the solution became neutral. Subsequently, the GO was gotten by centrifuging, and was dried in vacuum desiccator.

2.3. Preparation of MCGO

The preparation process of MCGO was as follows: 2% (w/v) of chitosan solutions were prepared by dissolving 0.4 g of chitosan into 20 mL of 2.0 (v/v) acetic acid aqueous solutions under ultrasonic stirring for 2 h at room temperature. Subsequently, 0.1 g of magnetic nanosized Fe_3O_4 was added into the colloidal solution and the reaction system was continued to be stirred for 1.5 h. Some paraffin oil was slowly dispersed in the prepared mixture under stirring. After 0.5 h of emulsification, 3 mL of glutaraldehyde was added to crosslink chitosan [29]. Then, 0.3 g of GO was added and the mixed system was stirred continuously for 90 min in a water bath at 50 °C. pH of the reaction system was adjusted to 9–10 by using 1 mol L^{-1} NaOH and kept in a water bath for a further 60 min at 80 ± 0.2 °C. Black products (MCGO) were washed with petroleum ether, ethanol and distilled water in turn until pH was about 7. Then, the precipitate was dried in a vacuum oven at 50 °C. The obtained product was MCGO.

2.4. Preparation of Pb-MCGO

MCGO and Pb^{2+} were added in a flask and dispersed in distilled water by ultrasonic dispersion for 30 min. Some of epichlorohydrin was added. The mixture solution was stirred for 4 h, and then was at 40 °C for 24 h. And then, the beads were extensively washed with petroleum ether, ethanol,0.5 mL/L HCl and distilled water in



Scheme 2. Synthesis route of Pb-MCGO and their application for removal of Pb^{2+} with the help of an external magnetic field.