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Preparation of surface anion imprinted polymer by developing a La(III)-coordinated 3-methacryloxyethyl-propyl bi-functionalized graphene oxide for phosphate removal

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ABSTRACT

A novel phosphate surface-imprinted polymer (GO-IIP) with high performance has been prepared by developing a La(III)-coordinated 3-methacryloxyethyl-propyl (MPS) bi-functionalized graphene oxide (GO). La(III) modified graphene oxide (GO-La) was used as functional monomer and methyl methacrylate (MMA) was used as auxiliary functional monomer. The synthesized GO-IIP exhibited higher adsorption capacity and outstanding selectivity and recognition for the binding of phosphate than GO-NIP. The equilibrium adsorption isotherms can be well fitted by the Langmuir model and the maximum adsorption capacity was higher as 104.3 mg/g at 25 °C. The results showed that GO-IIP exhibited excellent selectivity, good reusability and could be an ideal adsorbent for removing phosphate from wastewater.

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1. Introduction

Excess discharge of phosphate from industrial and agricultural productions into runoff is one of the major factors for the deterioration of water quality such as eutrophication. Eutrophication could facilitate the fast growth of blue and green algae that leads to serious environmental and esthetic problems [1,2]. Therefore, it has become quite imperative for removing phosphorus from wastewater before their discharge into the environment [3,4]. However, selectivity of phosphate is particularly difficult in a conventional removal process due to the presence of other competing anions, namely, chloride, bicarbonate, sulfate and dissolved organic matters, the presence of these competing anions also greatly reduces the removal efficiency of phosphate. So it is of great significance to develop and identify a new method that processes high selectivity toward the phosphate ion from water. Several methods including ion exchange, chemical precipitation, biological treatment and adsorption have been investigated to selectively remove phosphorus from aqueous solution [5]. Among various available technologies for phosphate decontamination, the adsorption method is relatively highly efficient, economical and simple due to its simple operation and low sludge production [6].

The most important for advanced adsorption approach is how to find a suitable phosphate adsorbent with an efficient removal of phosphate. Various types of new adsorbents have been developed for phosphate removal, such as aluminum compounds [7,8], hydrous zirconium oxide based nanocomposites [9], silica and graphene [10]. However, these adsorbents cannot satisfy both the large adsorption capacity and anti-interference ability. In recent years, because of its high affinity with ligands exchange and electrostatic interactions for enhancing anions adsorption, lanthanum (La) has attracted a lot of attentions in wastewater treatment technology [11–13]. More importantly, compared with transitional metals, lanthanum exhibited more adsorptive capability for phosphate, and suitable lanthanum may be environment-friendly and nontoxic. Previous studies have shown that lanthanum containing materials were promising to sequestrate phosphate from water [14,15]. The results of many studies reveal that lanthanum-based substrates such as La-modified clays [16], lanthanum (III) doped mesoporous silicates [17,18] and La-modified zeolite [19] are promising sorbent materials for the enhancement of phosphate adsorption effectively.

Graphene oxide (GO), a functionalized graphene derivative, has recently attracted tremendous attention for its potential use in adsorption science due to its two-dimensional structure, ultrahigh surface area (theoretical special surface area of 2630 m^2/g),

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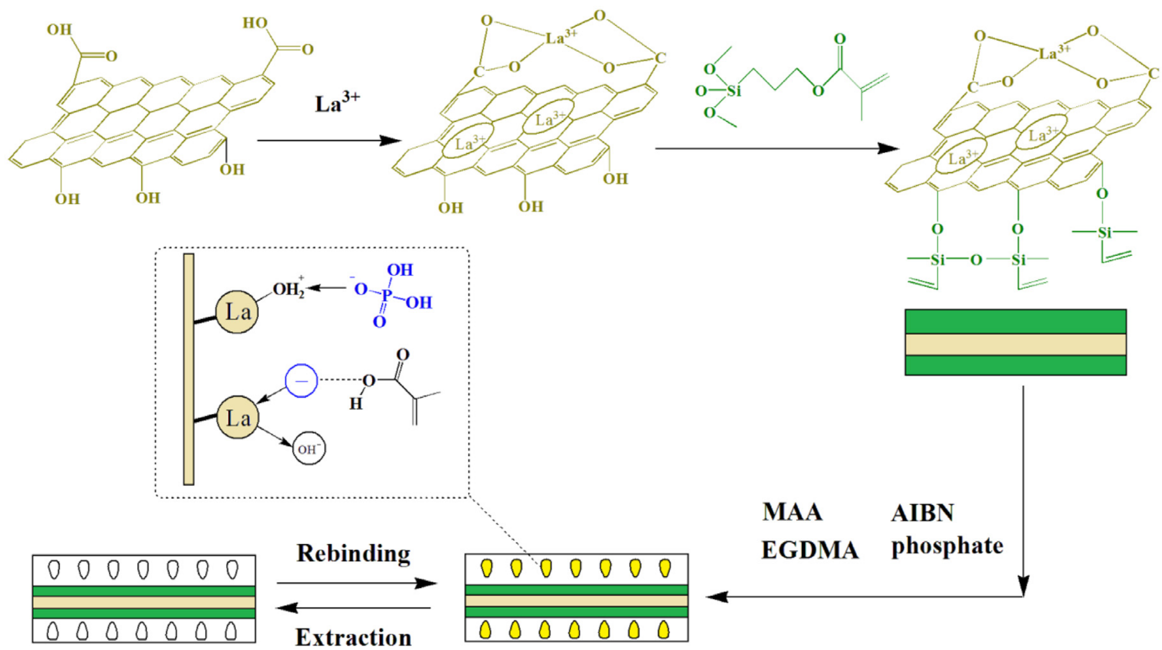

Scheme 1. Depicting the ion-imprinting process on GO surface.

and favorable surface chemical property (hydroxyl, carboxyl and epoxyl groups) [20,21]. In addition, graphene oxide can be easily suspended or dispersed uniformly in the water due to its low density. Therefore, the adsorbent has more contact area with the water soluble targets [22]. It has been reported that graphene nanosheets have been used for the removal of phosphate from water. For example, Vasudevan and Lakshmi synthesized graphene for the removal of phosphate [23], and Zong et al. reported that zirconia-functionalized graphite oxide could be an effective adsorbent for the removal of phosphate ions from aqueous solution [24]. However, traditional sorbents will be limited in the further applications in wastewater treatment technology because of their unsatisfactory selectivity for phosphate.

Molecularly imprinted polymers (MIPs) are synthetic materials having selective recognition sites capable of rebind the target molecule [25–27]. Ion-imprinted polymers (IIPs) recognize target ions after imprinting and retain all virtues of MIPs, which are similar to MIPs [28,29]. In recent studies, IIPs as selective sorbents for template ions have received much attention, and their applications in enrichment of ions, separation and selective preconcentration as well as in the removal of toxicant ions from aqueous medium for protecting the environment have been widely reported [30,31]. However, most of the reported IIPs are metal ion-imprinted polymers, and anion imprinted polymers are rarely recorded in the reported literature [32,33]. More importantly, traditional single functional monomers have low binding affinity for the target molecule. Therefore, there is an increasing demand to develop utilize dual functional monomers or new functional monomers for improving the imprinting efficiency. In addition, due to the large anion radius, the formation of hydrogen bonds in water, the greater impact of pH value and other reasons, the present study often focuses on cationic imprinted polymers instead of anionic imprinted polymers. As a result, it is of great significance for the application and exploration of new effective anionic imprinted polymer.

Based on the high phosphate affinity of La, ion recognition technology of surface anion imprinting and large surface area of GO, a novel phosphate surface anion imprinted polymer (GO-IIP) has been prepared by developing a La(III)-coordinated 3-methacryloxyethyl-propyl bi-functionalized graphene oxide surface imprinting technique. The morphologies and structures of GO-IIP were well characterized by SEM, TEM, FT-IR and N_2 adsorption–desorption techniques. Finally, GO-IIP was utilized as sorbent for adsorption of phosphate, its selectivity and regeneration were all conducted. The GO-IIP provided an effective and reliable solution for removing phosphate from polluted water samples.

2. Experimental

All the chemicals, apparatus, preparation and adsorption experiments can be seen in supporting information.

3. Results and discussion

3.1. Preparation

The preparing process of GO-IIP was shown in Scheme 1. In the first step, lanthanum modified GO complexes were prepared according to the coordination of carboxyl group and La^{3+} ions. The wrinkles and edges of graphene oxide were full of carboxyl group, which is favorable to form coordination reaction between La^{3+} ions and carboxyl group. Subsequently, by chemical modification using a silane coupling MPS, vinyl groups were introduced into the surface of lanthanum modified GO complexes, which provide a site for polymerization reaction. Then, the vinyl group-capped lanthanum modified GO complexes were placed into the polymerization solution composed of cross linker (EGDMA), monomer (MAA), template NaH_2PO_4 and initiator (AIBN), where MAA could coordinate with NaH_2PO_4 as the functional monomer and form the imprinted polymer layer. Specifically, the selectivity of a specific target ion is obtained by providing the polymers with cavities during the imprinted process, and complexing ligands are arranged so as to size, coordination geometry, coordination number and match the charge of phosphate. The ionic recognition site is also created, which is a specific location for the phosphate by spatial orientation and chemical functionality. The adsorbed phosphate is removed with 0.02 mol/L NaOH after polymerization. Finally, a thin phosphate ion-imprinted polymer layer can be formed