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Inhibitory effect of hydrogen ion on the copper ions separation from acid solution across graphene oxide membranes

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ABSTRACT

Graphene-based materials have many unique features including atomic thickness and well-defined nanochannels, making their great properties for filtration and separation. The removal of low-level heavy-metal ions (e.g. Cu^{2+}) by graphene oxide sheets has been discussed to ascertain their adsorption capacity, but separation and recovery of massive copper ions with graphene oxide (GO) membranes remain to be further studied. Besides, the permeation across GO membranes involving different ions in the very same solution is rarely investigated. Hence, the permeation properties of GO membranes concerning single and mixed solutions of acid and salt were examined in this study, and inhibitory effect of hydrogen ion on the copper ions transport was observed. Expectedly, GO membranes perform obvious permeation rate differences to acid (*i.e.* H_2SO_4, HCl) and copper salts (*i.e.* $CuSO_4$, $CuCl_2$) when they are tested individually. The diffusion coefficient of H^+ is 16 times larger than that of Cu^{2+} when the anion is SO_4^{2-}, and twice in the case of Cl^-. The differences are mainly determined by physical screening of the capillary channels in the film for ions with different hydration radii and the rapid migration of hydrogen ions in solution. Furthermore, Experiments were carried out using mixed solution of acid and copper salt with the same anion and concentration. It was shown that the existence of H^+, whose own transmission decreased by only 1.6 times, reduced the penetration of Cu^{2+} by an order of magnitude in the same time interval. We supposed this remarkable inhibitory effect is associated with shrink of interlayer spacing and competitive adsorption of H^+ against Cu^{2+} on the surface of GO membranes in mixed solution. The properties of GO membranes show great application prospects in separation and wastewater reuse.

1. Introduction

The treatment and reuse of waste water produced from industrial activities is a worldwide environmental concern [1–5]. Copper is widely used in many applications such as electricity, electronics, electroplating, and other emerging fields [1,2,6]. The effluents from these industries are mostly acidic liquids containing a great deal of copper ions, the discharge of which is confronted with two major problems, namely environmental pollution and waste of resources. In the past few decades, various approaches including coprecipitation [7], replacement-deposition, ion exchange [8], adsorption [9], biosorption [10], and membrane filtration [11], *etc*. have been researched or adopted to separate and recover copper ions from industrial wastewater. Among these, the first two methods are simple to operate and achieve the purpose of copper recovery, but they will face other problems of impurity separation and sludge treatment. The next two ways of ion exchange and adsorption, especially the later, are usually suitable for solution containing copper with low concentration [8], but not satisfactory enough for initial handling of waste liquids. Compared to aforementioned several methods, membrane processing is one of the most promising treatments for separation and recovery of heavy metals ions like Cu^{2+} due to its simplicity, low cost, and excellent selectivity [12,13].

Recently, considerable interest has been aroused by carbon-based nanomaterials [3] (e.g., graphene [14,15,16,17], graphene oxide [18,19], carbon nanotubes [20,21,22], carbon nitride [23] and quantum dots [24]) and nanostructure [25] for their potential applications in areas such as separation, purification, energy, water-harvesting and water treatment due to their exceptional physicochemical properties [19,26–32]. Especially graphene oxide (GO) bear many

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hydroxyl and epoxide on their basal planes as well as carbonyl and carboxyl located at the sheet edges [33,34], which makes it promising for use in treatment of heavy metal ions [35–40]. Yang et al. [35] studied on the adsorption performance of GO for Cu^{2+} and demonstrated that GO nanosheets can be folded and aggregated by Cu^{2+} in aqueous solution with a huge adsorption capacity because of the interaction between oxygen-containing functional groups and Cu^{2+}. The maximum adsorption of GO is around 10 times of that of active carbon, ranking GO among the most effective adsorbents for Cu^{2+} removal. Chen et al. [36] synthesized a new type of triethylenetetramine-magnetite reduced graphene oxide (TET-MRGO) composite, showing a high adsorption capacity (about 209.1 $mg{\cdot}g^{-1}$) toward Cu^{2+} with excellent selectivity and effective adsorption-desorption performance. In addition, the adsorption ability of three-dimension graphene macroscopic objects (3D-GMOs) also has attracted much attention. Mi et al. [37] prepared graphene oxide aerogel by dry freezing method, removal performance of which for Cu^{2+} in aqueous solution was tested. The adsorption equilibrium was achieved in 15 min, and adsorption capacity for Cu^{2+} at room temperature was about 19 $mg{\cdot}g^{-1}$. Li et al. [38] reported that 3D-GMOs were fabricated by CVD method with $NiCl_2{\cdot}6H_2O$ as catalyst, which were used as electrolyte electrode to remove various heavy metal ions including Cd^{2+}, Pb^{2+}, Ni^{2+} and Cu^{2+} with resulting adsorption rate of 434, 882, 1.68 and 3.82 $mg{\cdot}g^{-1}$ respectively.

As can be seen from previous reports, graphene oxide really has high adsorption capacity, but as an adsorbent, it can only be used as a follow-up technological process to deal with solutions containing heavy metal ions of low concentration. Alternatively, a large number of GO sheets can be stacked layer-by-layer to form a laminate structure [27,41]. Within the laminate, also known as GO membranes, a network of nanocapillaries is formed by the connected interlayer space and edges of sheets, affording excellent selectivity toward various ions [31,32]. Sun et al. [31] demonstrated selective ion penetration properties of freestanding GO membranes, which mainly suggested that sodium salts permeated through the film quickly, whereas heavy-metal salts infiltrated much more slowly. Joshi et al. [32] obtained micrometer-thick GO films by means of vacuum filtration and experiments on ions with different radii showed that GO membrane can block all solutes with hydration radii larger than 0.45 nm, and the rates of ions with smaller hydration radii is several thousand times higher than what is expected for free diffusion. Subsequently, Sun et al. [42] discovered the efficient recovery of ionized hydrogen from iron-based electrolytes using GO membranes. Certainly, there are also plenty of additional reports that indicate potential applications of GO in fields including separation and water treatment [43–51].

However, selective separation in real sense usually involves separating several different solutes from the same solution. That is to say, in the actual selective separation process, the simultaneous transport of various acids, bases and salts will involve the interaction between solutes. Taking copper enrichment from acid pickling wastewater as an example, the effective separation of copper salts and acids is needed. Actually, previous work mainly focused on the permeation rate of ions in different solutions, most of which only contained unitary solute, but selective permeation of different ions in the very same solution with multicomponent is rarely reported [31]. In this work, permeation rates of individual and mixed solution, which contained acids and copper salts with the same anions, were tested to investigate the potential application of GO membranes for separation and recovery of Cu^{2+} from acid solution. The results suggested that H^+ can be transmitted across GO membrane at greater permeation rate than Cu^{2+} and inhibit the transport of Cu^{2+} in mixed solution, which is mainly determined by the shrink of interlayer spacing as well as competitive adsorption and rapid migration of hydrogen ions. These exceptional properties would make graphene-based films promising materials in applications of ion separation and industrial water treatment. Due to the limitations of our work, only acidic copper solutions were tested in this paper. In the future, the interaction between other common ions (including K^+, Na^+, Ca^{2+}, Mg^{2+}, *etc.*) and hydrated hydrogen ions need to be further studied in order to understand the transmission characteristics of the graphene oxide membranes more clearly.

2. Materials and methods

2.1. Preparation of GO membranes

Graphite oxide was synthesized using the Hummers' method [52] starting from natural flake graphite powder (325 mesh, 99.9%), which was exposed to a mixture of concentrated sulfuric acid, sodium nitrate and potassium permanganate for oxidation. Typically, a mixture of concentrated H_2SO_4 (115 mL, ≥98%) and $NaNO_3$ (2.5 g, AR) was added into 5 g graphite flakes under stirring in an ice bath to ensure the temperature less than 5 °C. $KMnO_4$ (9.0 g, AR) was added slowly to keep the temperature of suspension lower than 20 °C for 1 h. Then the temperature of the suspension was brought to 35 ± 3 °C and maintained for 1 h. Successively, 200 mL water was slowly stirred into the paste, turning to brown in color and causing an increase in temperature to 90 °C. The diluted suspension was maintained at this temperature for 30 min. At the end of 30 min, suspension was then further diluted to approximately 250 mL water and followed by a slow addition of ~5 mL H_2O_2 (30%, AR), turning the color of the solution from dark brown to bright yellow. After settled overnight and supernatant liquid removed, the remaining solid material was then washed and subsequently centrifuged (6000 rpm for 10 min) by turns until the supernatant was neutral (pH = 6.0–7.0). Finally, the thick colloid was diluted to a certain volume and graphite oxide flakes can be obtained by means of spray-drying.

The prepared graphite oxide flakes were exfoliated in water by sonication (150 W for 10 min) to obtain monolayer or multilayer graphene oxide nanosheets suspension with concentration of 0.5 $mg{\cdot}mL^{-1}$. GO membranes were formed by vacuum filtration of a certain volume of the obtained suspension on a Nylon filter (diameter: 50 mm, pore size: 0.2 μm, thickness: 100 μm). The films used in this paper were all prepared by filtration with 2 mL suspension.

2.2. Characterizations

The structure of laminated films was confirmed by X-ray Diffraction (XRD, X' Pert Pro, Panalytical and SmartLab 9 kW, Rigaku) in a range of $5^\circ \le 2\theta \le 30^\circ$. The surface chemical composition was determined by characterization of X-ray Photoelectron Spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher Scientific). Fourier Transform Infrared Spectra (FTIR 5700, Nicolet) over the range of 4000–500 cm^{-1} was utilized to identify the functional groups. Raman spectra are recorded using a spectrometer (B&W Tek) with 532 nm diode laser. The morphologies of GO sheets and membranes were examined by Atom Force Microscope (AFM, Nano Wizard 4, JPK) and Scanning Electron Microscope (SEM, MIRA3 LMH, TESCAN). In addition, the hydrophilicity of GO membrane is tested by contact angle measurement (OCA25, Dataphysics). The Energy Dispersive Spectra (EDS, Aztec Energy Standard X-MaxN 20, Oxford Instruments) of the film after experiments is also presented. The concentrations of trace copper and sulfur in drain solution were measured by ICP-AES (IRIS Intrepid II XSP, Thermo Elemental).

2.3. Permeation experiments

The experiments on ions transport were carried out using a handmade devise, as shown in Fig. 1(a), which consists of two compartments separated by the studied GO membranes with Nylon underneath in the middle. The membranes were sandwiched between two acrylic plates (40 mm in diameter) with an aperture of 30 mm in diameter in the center, as presented in Fig. 1(b). The plates were clamped between silicon rubber rings. In a typical experiment, 160 mL of a 0.1 $mol{\cdot}L^{-1}$