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The use of graphene oxide membranes for the softening of hard water

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Strong chemical interactions between the oxygen-containing functional groups on graphene oxide (GO) sheets and the ions of divalent metals were exploited for the softening of hard water. GO membranes were prepared and evaluated for their ability to absorb Ca^{2+} and Mg^{2+} ions. These GO membranes can effectively absorb Ca^{2+} ions from hard water; a 1 mg GO membrane can remove as much as 0.05 mg Ca^{2+} ions. These GO membranes can be regenerated and used repeatedly.

graphene oxide membranes, soften hard water

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1 Introduction

The “hardness” of water refers to its concentration of metal ions. Because the amounts of calcium (Ca^{2+}) and magnesium ions (Mg^{2+}) in natural waters are usually far higher than other metal ions, the hardness of water refers to the total concentration of calcium and magnesium, expressed in terms of the calcium carbonate equivalent [1]. Excessive amounts of Ca^{2+} and Mg^{2+} in water result in serious consequences for household and industry uses, such as increasing morbidity rates from gallstones, clogged boilers and pipes, shortened operational life of equipment and, so on. Therefore, effective softening treatments for hard water are of fundamental importance for a sustainable society.

There are several conventional methods for preparing soft water, including an ion-exchange process using cation-exchange resin [2], addition of chemicals or chelating reagents [1], and cross-flow filtration using nanofiltration membranes [2,3]. Although these traditional methods are widely used and effective, they may still be unsatisfactory in some aspects. For instance, after treated with cation-exchange resin, water still contains salts of sodium that may corrode the surrounding area. Approaches that exploiting chemical or chelating reagents can not only influence water quality but also produce abundant waste that may pollute the environment. It means that employing nanofiltration membranes require advanced techniques and equipment, all of which increases the cost. Thus it is clear that novel and cost-effective methods for the softening of hard water are still greatly desirable.

Graphene, one atom thick and two-dimensional (2D) single-layer, has attracted enormous attention in the field of material science due to its excellent properties and unusual structural features [4,5], which make it extraordinarily promising for many potential applications [6,7]. Perfect graphene does not occur naturally, but large-scale preparation of graphene oxide (GO) is now possible through chemical exfoliation [8]. Even though this extensive chemical-attacking approach introduces various oxygen-containing functional groups (e.g., hydroxyl, epoxide, diol, ketone, and carboxylic) into the surfaces of the GO sheets and highly damages the intrinsic excellent properties of graphene, these oxygen-containing de-

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fects also impart very interesting and novel performance to the GO [6,8–10]. Accordingly, Park and co-workers reported that significant enhancement in the mechanical stiffness of GO paper can be achieved upon modification with a small amount of Mg^{2+} and Ca^{2+} ions [10]. They confirmed that the oxygen-functional groups on the basal planes of GO sheets and the carboxylate groups on the edges of the sheets can both bond to Mg^{2+} and Ca^{2+} ions. Motivated by these intriguing results, we wondered if GO can also be used as a softening agent for hard water to absorb the Mg^{2+} and Ca^{2+} ions from hard water. Herein, utilizing GO papers as filtration membranes, we report a simple yet versatile method for effective water softening through a vacuum filtration system. GO membranes are used to remove Ca^{2+} and Mg^{2+} ions from a hard-water sample with excellent efficiency. It is found that a 1 mg GO membrane can absorb as much as 0.05 mg Ca^{2+} ions (or a 1 g GO membrane can remove 50 mg Ca^{2+} ions). Moreover, the used GO paper can be regenerated by HCl or NaCl solution and recycled.

2 Experiment platform and procedure

GO is prepared from graphite by a modified Hummer's method [8]. The hard-water sample prepared through dissolving $CaCl_2$ in distilled water is employed as the feed-sample solution with a Ca^{2+} ion concentration of approximately 150 mg/L. The ability of GO membranes to adsorb Ca^{2+} ions is evaluated through the dead-end vacuum-filtration approach presented in Figure 1. First, the as-prepared GO powder is dispersed in distilled water in an ultrasonic bath (Gongyi Yuhua Instrument Co., Ltd., China; Model KQ400B, 400 W) for 30 min at room temperature to yield a clear solution at a concentration of 1 mg/mL (Step 1), In this process, GO is able to be completely exfoliated, down to individual sheets, and form a stable dispersed GO/H_2O solution [6,8,10]. Next, GO membranes are obtained by filtration of a specified amount of the above GO aqueous solution through vacuum filtration with water-membrane filters (47 mm diameter, 0.22 μm pore size; Tianjin Automatic Science Instrument Co., Ltd., China) (Step 2). The GO and filter membrane shosuld be preserved in wet conditions to avoid the drying of the GO membrane before being used for water softening. The effectiveness area for the GO membrane is around 12 cm^2. Then, the GO and water membrane filters are reattached to the vacuum filtration system; next, the hard-water sample solution is added and vacuum-filtrated by the GO membrane (Step 3). The concentration of ions in the resulting filtrate is analyzed by atomic absorption spectroscopy.

3 Results and discussion

First, the ability of GO membranes for Ca^{2+} absorption from hard-water sample solution is investigated. In Figure 1, 10 mL hard-water sample with Ca^{2+} concentration of about 150 mg/L is added to the funnel of the vacuum-filtration system and passed through the GO membranes. The concentration of the filtrate is then measured by atomic absorption spectroscopy; results are given in Figure 2. As can be clearly seen, the GO membranes exhibit outstanding efficiency in removing Ca^{2+} ions. For instance, a piece of 5 mg GO membrane is able to absorb about 0.25 mg Ca^{2+} ions. Furthermore, the concentration of residual Ca^{2+} in the filtrate is obviously decreased with the increasing of mass of the GO membranes. In the least-squares analysis shown in Figure 2, the straight line with an extremely high correlation factor (R = 0.997) gives a good fit to the data. Importantly, it can be calculated from the slope of the straight line that the adsorption ability of 1 mg GO membrane can reach as high as

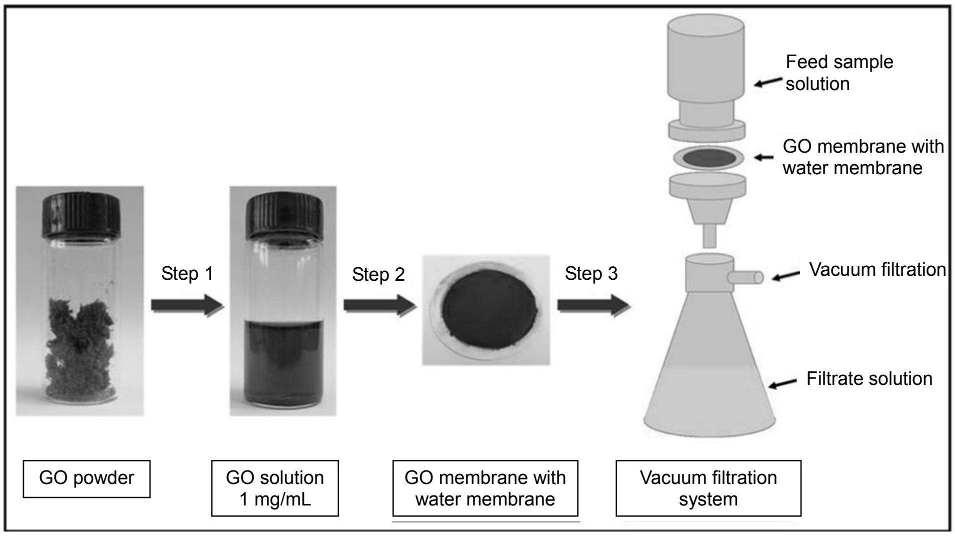

Figure 1 Schematic of the steps involved in the process of using GO membranes for hard-water softening.

Table 1 The concentration of Ca^{2+} ions for the feed sample solution and their filtrate, and the amount of Ca^{2+} ions adsorbed in GO membranes after filtration. The volume of all feed samples is 20 mL, and the mass for GO membranes is 5 mg

Samples	Concentration of Ca^{2+} ions in feed solution (mg/L)	Concentration of Ca^{2+} ions in filtrate (mg/L)	Amount of Ca^{2+} ions adsorbed in GO membranes (mg)
Sample-1	150	137	0.26
Sample-2	137	126	0.22
Sample-3	126	113	0.26
Sample-4	113	100	0.26
Sample-5	100	89	0.22
Sample-6	89	80	0.18

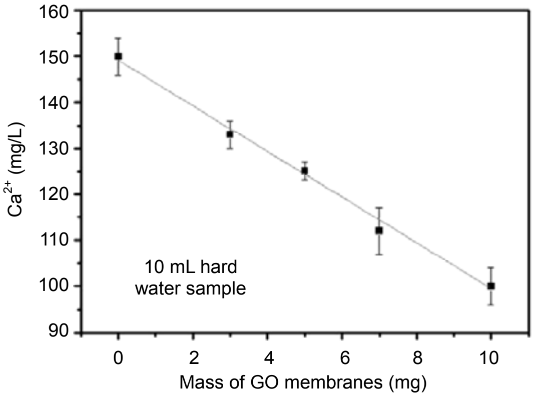

Figure 2 The concentration variation of Ca^{2+} for the hard-water sample (10 mL) vacuum-filtrated by GO membranes of different mass.

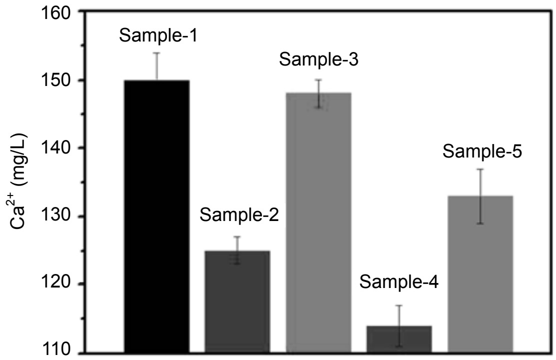

Figure 3 Sample-1: the original hard water sample. Sample 2: filtrated by 5 mg GO membrane. Sample-3: filtrated by the 5 mg GO membrane that was used in Sample-2. Sample-4: filtrated by the 5 mg GO membrane that was used in Sample-2 and then refreshed and filtrated by5 mL 1 M HCl. Sample-5: filtrated by the 5 mg GO membrane that was used in Sample-2 and then refreshed and filtrated by 5 mL 1 M NaCl.

0.05 mg (or a 1 g GO membrane can remove 50 mg Ca^{2+} ions). This performance of these GO membranes for removing Ca^{2+} ions from hard water is much higher than that of some conventional method or materials used to prepare soft water [1]. We also investigated the GO membranes' ability to absorb Mg^{2+} ions, and found that it is similar to their ability to absorb Ca^{2+} ions.

Moreover, it can be seen from Table 1 that the concentration change of Ca^{2+} ions in the feed-sample solution does not have obvious effects on the adsorption ability of the GO membranes. This indicates that GO membranes can thoroughly remove Ca^{2+} ions from the water sample by controlling the filtration times or the mass of the GO membranes.

The regeneration function of the filtration membranes is also an important property by which to evaluate their water-softening performance. It is worth noting that, similar to the conventional filtration membranes for softening hard water, our GO membranes can be regenerated by HCl or NaCl solution that contains monovalent cation ions. As can be seen in Figure 3, the Ca^{2+} ions absorption ability of the GO membrane that has been refreshed by 1 M HC1 is even better than that of pristine GO membranes. Whereas 5 mg pristine GO membranes can remove about 0.25 mg Ca^{2+} ions, the regenerated GO membrane can remove around 0.35 mg Ca^{2+} ions. These results indicate that our GO membranes can be refreshed and used repeatedly.

4 Conclusion

In this study, GO membranes were fabricated and used to absorb Ca^{2+} and Mg^{2+} ions from water for the purpose of hard-water softening. Due to the strong chemical interaction between the oxygen-containing functional groups on the GO sheets and the ions of divalent metals, GO membranes have effectively removed the divalent metals ions from the hard-water sample: a 1 g GO membrane can absorb as much as 50 mg Ca^{2+} ions. Importantly, the used GO membranes can easily be refreshed and recycled. Given the advantages of the inexpensive and abundant supply of graphite, as well as the solution processability of GO sheets at high purity and the simplicity of the dead-end vacuum-filtration system, GO membranes can be used commercially as effective materials for water softening.

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