

## Study on the removal of the static Cr (VI) in water by graphene hydrogel (rGH)

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In this study, the reduced graphene hydrogel rGH with three-dimensional structure was prepared by chemical reduction method, that the adsorption and removal performance of heavy metal Cr (VI) in water was discussed. Graphene hydrogel is capable of high specific surface area, three-dimensional structure and narrow pore size distribution. Moreover, there are a large number of oxygen-containing functional groups such as hydroxyl groups on the surface of the material. Graphene hydrogel can remove Cr (VI) in water efficiently and continuously, and the removal of Cr (VI) in 1 ppm can keep over 99.5% in 6 hours, indicating the excellent application.

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### 1. Introduction

The adsorption method has the advantages of fast speed, strong adaptability, high efficiency and easy operation for the removal of heavy metal ions in water<sup>[1]</sup>. Relying on some materials with high surface energy and large specific surface area, it has strong adsorption for pollutants. The existing adsorption materials include activated carbon<sup>[2]</sup>, zeolite<sup>[3]</sup>, carbon fiber<sup>[4]</sup>, natural diatomite<sup>[5]</sup>, etc. The adsorption mainly depends on the adsorption active sites and interlayer adsorption sites in the pores. There are some problems, such as slow adsorption rate, small adsorption capacity, easy saturation, difficult desorption, high regeneration cost and difficult regeneration and recovery, which restrict the application of adsorption method in the removal of heavy metal ions in water.

A new graphene hydrogel (rGH), which has a three-dimensional macroporous structure, is further assembled into two dimensional graphene<sup>[6]</sup>. It not only maintains the lamellar structure of graphene, but also has the characteristics of rapid adsorption and enrichment of heavy metal ions, and is easy to separate from the three-dimensional network structure formed by two-dimension stacking. It solves the separation problem of graphene adsorbent material in water purification<sup>[7,8]</sup>.

Generally, the majority of teachers and students use the static adsorption method for research, that is, the photocatalytic reaction system (stirred tank reaction) as an important means to study adsorption and photocatalysis, which provides an effective numerical basis and simulation under ideal conditions for the reaction. However, these values are not enough to analyze the adsorption and photocatalytic reaction in the flow dynamic system. Therefore, the research on the removal of heavy metal ions in water by adsorption under flow dynamics and the promotion of its practical application are also of great guiding significance<sup>[9]</sup>. The adsorption and purification of heavy metal Cr (VI) in flowing state by rGH adsorption material was carried out. At the same time, considering that the concentration of pollutants in real life water is not fixed, the effect of continuous purification treatment under the conditions of flow rate and initial concentration of different Cr (VI) solutions was analyzed.

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## 2. Experimental

### 2.1. Preparation of graphene hydrogel (rGH) adsorbent materials

(1) Preparation of graphene oxide (Go) by Hummers method

Add 3.0 g of graphite (325 mesh) to 70 ml of concentrated sulfuric acid in ice bath and stir for 10 minutes, then add 1.5 g of sodium nitrate and 9 g of potassium permanganate (3 times as much as graphite), stir for 2.5 hours and avoid the temperature of the reaction system exceeding 20°C. Then the system was heated to 35 °C for 3.5 hours, then 150 ml of deionized water was added, the system temperature was increased to 95°C, stirring was continued for 1.5 hours, then 300 ml of deionized water and 20 ml (30%) of hydrogen peroxide were added successively, and then the reactants were washed with dilute hydrochloric acid, centrifuged and dialyzed to obtain graphene oxide (Go).

(2) preparation of graphene hydrogel (rGH) by chemical reduction method.

A certain amount of ascorbic acid (VC) was used to reduce the oxidation of graphene oxide, and then to react with 60 min at 95°C. The graphene hydrogel (rGH) was prepared by chemical reduction.

### 2.2. Characterization and adsorption of reduced graphene oxide hydrogel (rGH) adsorbent materials

The molecular structure and chemical bond of the samples were analyzed by thermo Nicolet avatar 370 spectrometer (FTIR); American micromeritics ASAP 3020 automatic physicochemical adsorbent (BET) was used for determination, The specific surface area and pore distribution of samples were determined by nitrogen adsorption method at liquid nitrogen temperature (77K); Xsam800 X-ray photoelectron spectroscopy (XPS) of Kratos company in Britain was used to determine the chemical composition of the sample and the chemical state of surface elements.

### 2.3. Characterization of adsorption properties of graphene hydrogel (rGH) materials.

Dynamic rGH hydrogel adsorption properties: in this experiment, the flow chart of dynamic rGH hydrogel adsorption purification device is shown in fig.1. The reactor is a glass filled column with an inner diameter of 0.8 cm and a length of 20.0 cm. Water inlets and outlets are set at the top and bottom, which are respectively filled with quartz glass to avoid the loss of adsorption materials. The solution flow rate is adjusted by YZ1515 peristaltic pump.

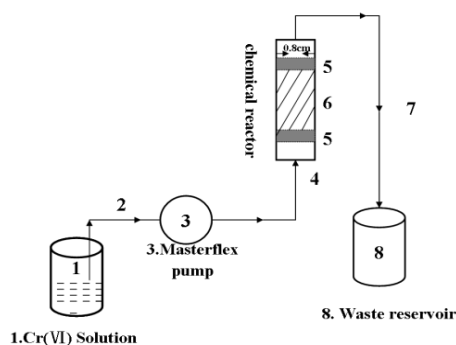


Fig. 1. Flow diagram of flow dynamic device.

The solution enters the reactor 6 from the 1 beaker through the 3 peristaltic pump through the rubber pipe 2, evenly distributes the water, flows out through the rubber pipe 7, and finally collects the waste liquid in the 8 beaker.

rGH hydrogel dynamic adsorption experiment process is as follows: 250 mg rGH hydrogel is placed in the reactor, set a certain speed of peristaltic pump, set a certain concentration of Cr (VI) solution, conduct adsorption experiments at a certain temperature, from start to run time, sampling, filtering and measuring concentration at regular intervals.

## 3. Discussion and Results

### 3.1. Characterization of graphene hydrogel (rGH)

In Fig.2, GO has a large wide peak at  $3413\text{ cm}^{-1}$ , corresponding to the stretching vibration peak of hydroxyl O-H, the stretching vibration peak of carbonyl C = O at  $1729\text{ cm}^{-1}$ , the C = C skeleton vibration peak of aromatic ring at  $1622\text{ cm}^{-1}$ , and the stretching vibration peak of alkoxy C-O near  $1063\text{ cm}^{-1}$ . Compared with GO, the intensity of the O-H stretching vibration peak corresponding to the reduced graphene oxide hydrogel at  $3435\text{ cm}^{-1}$  position decreased significantly, while the  $1729\text{ cm}^{-1}$  position corresponded to that the carbonyl C=O stretching vibration peak had disappeared, and the absorption peaks at  $1622$  and  $1063\text{ cm}^{-1}$  corresponded to the C=C skeleton vibration peak of graphite layer aromatic ring and the intensity of the stretching vibration peak of C-O obviously weakened. This shows that oxygen-containing groups still exist on the surface of rGH after reduction, which is conducive to the removal of heavy metal ions in water.

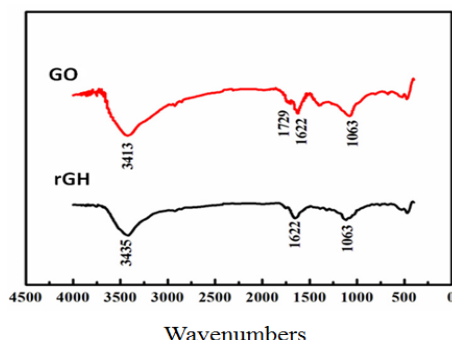


Fig. 2. GO and FTIR diagram of reduced graphene oxide hydrogels.

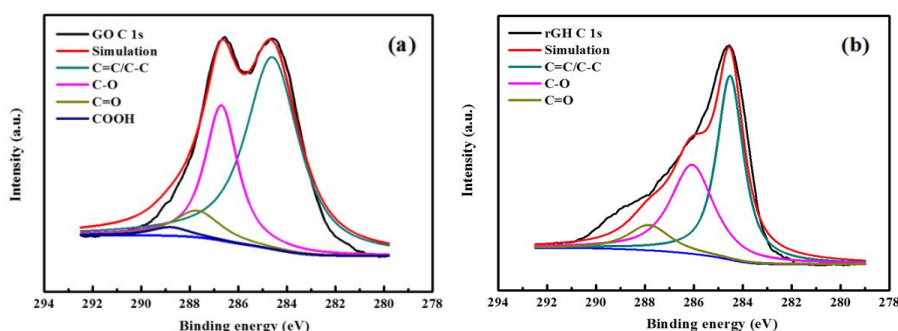


Fig. 3. (a) XPS diagram of C1s element of GO, (b) XPS diagram of C1s element of rGH.

As shown in Fig.3. XPS diagram of C1s elements of go and rGH, respectively. Compared with the C = C / C-C and C-O diffraction peaks of C1s of go at 284.8 EV and 286.6 EV, the intensity of the two diffraction peaks corresponding to rGH is weakened, especially the C-O diffraction peak. When go is reduced to rGH, the intensity of the diffraction peak is significantly reduced, which proves that part of the oxygen-containing functional groups of go are removed during the reduction process, and a large amount of SP3 hybrid carbon is transformed into SP2 hybrid carbon. It also shows that in rGH, the conjugated structure destroyed in the oxidation process has been reconstructed. At the same time, the reconstruction of the conjugated structure provides the possibility and guarantee for enhanced electron mobility. The removal efficiency of Cr (vi) in water will be further improved by a new adsorption material rGH. This will be further verified in the next adsorption performance evaluation.

### 3.2. Removal of Cr (VI) by rGH adsorption

Fig. 4 compares the adsorption ability of graphene hydrogel (rGH) and other common adsorbents to Cr (VI). The common adsorption materials  $\text{Al}_2\text{O}_3$  and  $\text{MnO}_2$  mainly rely on the surface hydroxyl to interact with Cr (VI) in aqueous solution. The hydroxyl site on the surface of the adsorption material provides the adsorption driving force, so as to achieve the removal effect of heavy metal ions in water and realize the purification of water; With the oxidation of graphite, oxygen-containing functional groups (such as hydroxyl, carbonyl, epoxy, etc.) are introduced

between graphite layers. Go ene has a large number of oxygen-containing functional groups, which improves its adsorption of Cr (VI); Go is reduced by hydrothermal method and freeze-dried to obtain graphene powder. Due to the action of certain van der Waals force, graphene flakes are prone to re accumulate to form graphite. Through

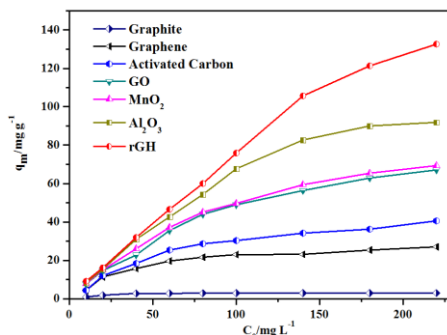


Fig. 4. Adsorption properties of different adsorption materials for Cr (VI).

The measurement of specific surface, the specific surface area of graphene powder is only  $51.21 \text{ m}^2 \cdot \text{g}^{-1}$  (Table 1). At the same time, there are only a small amount of oxygen-containing functional groups on the surface of graphene, The maximum adsorption capacity of Cr (VI) in treated water is only  $27.03 \text{ mg g}^{-1}$ , and the adsorption capacity of Cr (VI) is far weaker than that of other materials. However, after freeze-drying, the prepared rGH not only retains the excellent properties of graphene, but also its unique three-dimensional structure and uniform pore size distribution, large specific surface area of  $323.9 \text{ m}^2 \cdot \text{g}^{-1}$  (see Fig. 4 and table 1), provides more active adsorption sites, porous through network structure and surface adsorption characteristics provide better movement channels and places for adsorption reaction, It is beneficial to ion diffusion and reduce mass transfer resistance. It is applied to the adsorption, enrichment and removal of heavy metal ions in sewage, showing excellent potential such as fast adsorption rate and large adsorption capacity. At the same time, a large number of oxygen-containing functional groups such as hydroxyl and carboxyl groups are retained on the surface, providing more chemical adsorption sites through ion exchange, electrostatic interaction, complexation The role of van der Waals force in the treatment of heavy metal Cr (VI) in sewage will far exceed the application of pure graphene. The adsorption will reach equilibrium in a short time, and the maximum adsorption capacity is  $139.66 \text{ mg g}^{-1}$ .

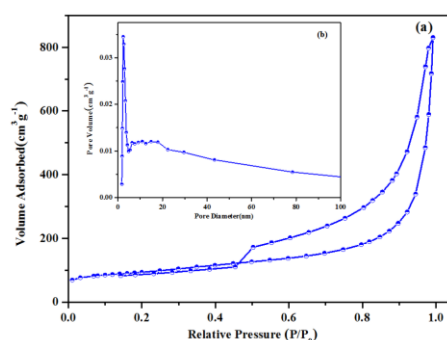


Fig. 5. (a)  $\text{N}_2$  adsorption-desorption curve of rGH, (b) pore distribution curve of rGH.

In order to further determine the specific surface and pore size of the adsorption materials, the specific surface area of each adsorption material was measured under the protection of liquid nitrogen. Fig.5 shows the  $\text{N}_2$  adsorption-desorption curve and pore distribution curve of rGH, belonging to the typical type IV isotherm specified by IUPAC<sup>[10]</sup>. RGH has obvious hysteresis loop in the range of relative pressure ( $P / P_0$ ) of 0.45-1.00, the adsorption capacity in medium and high pressure area changes greatly, and the BET specific surface area of rGH reaches  $323.9 \text{ m}^2 \cdot \text{g}^{-1}$ . The pore distribution curve of rGH is obvious, indicating that there are mesopores in rGH structure, and the average pore size is about 3.55 nm. It is proved again from Table 1 that compared with other adsorption materials, rGH material has larger specific surface area, more developed pore

structure and can provide more active adsorption sites, which is conducive to improving its contact probability with pollutant Cr (VI) and giving full play to its adsorption activity.

Table 1. Comparison of Cr (VI) adsorption capacity between rGH and other adsorbent.

Adsorbent	Specific surface area( $\text{m}^2 \cdot \text{g}^{-1}$ )	Maximum adsorption capacity ( $\text{mg g}^{-1}$ )
Graphite (purchased by Qingdao graphite)	2.75	2.92
GO	123.9	67.08
Graphene	51.21	27.03
Graphene hydrogel (rGH)	323.9	139.66
Activated carbon (Sigma-Alorich purchased)	122.46	40.56
Aluminium oxide, Y-type (Alfa Aesar purchased)	175	91.88
MnO <sub>2</sub> (Sigma-Alorich purchased)	108.34	69.36

The stability and repeatability of the new material rGH is an important factor to investigate whether it has practical application value. Therefore, we studied the stability of rGH material adsorption reaction to purify Cr (VI) in water, and compared it with the performance of traditional adsorption material activated carbon. The cyclic use results are shown in Figure 5. In the process of using the adsorption material, the heavy metal Cr (6) The concentration of the solution should be changed to the same 5 ppm concentration as the initial solution. After 5 cycles of experiments, the adsorption capacity of activated carbon decreased significantly, and rGH adsorption purified Cr (VI) The efficiency is still maintained at about 90%, showing high activity and good stability. It is proved again that the new material rGH adsorption purification effect, not only shows higher removal efficiency than activated carbon adsorption, but also has a significant advantage in recyclability. In general, composite rGH relies on its network gelation structure to avoid two-dimensional graphene and nano particles. The powder catalyst is difficult to separate by high-speed centrifuge, which is easy to recycle and reuse, and can maintain the stability of continuous adsorption and purification, so as to effectively purify the pollutant Cr (VI) in water.

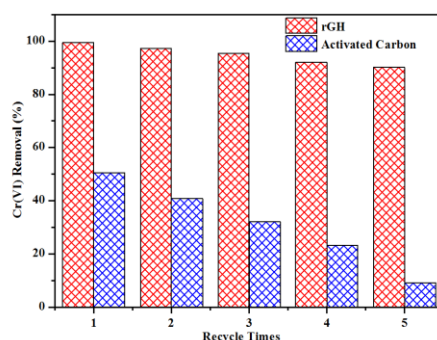


Fig. 6. Comparison of recycling of rGH and activated carbon adsorption purification Cr (VI).

rGH adsorption materials have good mechanical properties, three-dimensional cross-linked structure and efficient adsorption. They can quickly remove and purify heavy metal ions with different concentrations in sewage, and solve the problems of easy loss and difficult separation of most adsorption materials in practical dynamic application. We carried out rGH adsorption materials for heavy metal Cr (VI) in flowing state At the same time, considering that the concentration of pollutants in real life water is not fixed, the effect of continuous purification treatment under the conditions of initial concentration and flow rate of different Cr (VI) solutions is analyzed.

The filling amount of adsorbent directly affects the operation time of the whole reaction, and has an obvious impact on the adsorption process(Fig.6). Cr (VI) with a concentration of 2 ppm was sampled at an interval of 30 min through rGH with different filling amounts (0.1, 0.25 and 0.5

g) at a flow rate of 0.32 ml / min. the concentration was plotted with  $C_t/C_0$  as the ordinate and time  $t$  (min) as the abscissa.

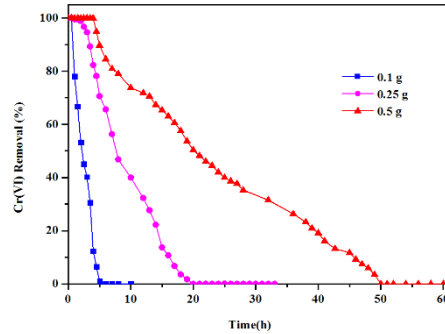


Fig. 7. Penetration curve under different filling amount.

With the increase of filling amount, the penetration point on the penetration curve moves to the right, and the slope of the whole curve gradually slows down (Fig. 7). The penetration time increases from 0.5 h to 4 h, and the saturation time increases from 5 h to 50 h. This is mainly due to the increase of filling amount, the increase of adsorption column height, the residence time of solution and the contact time between adsorbate and adsorbent, It is conducive to the adsorption reaction.

The change of flow velocity directly affects the penetration time and slope. The dosage is 0.25 g rGH. The flow adsorption performance of 2 ppm Cr (VI) at flow rates of 0.16, 0.32 and 0.48 ml / min respectively is tested. Samples are taken every 30 min to measure its concentration. The plot is made with  $C_t/C_0$  as the ordinate and time  $t$  (min) as the abscissa.

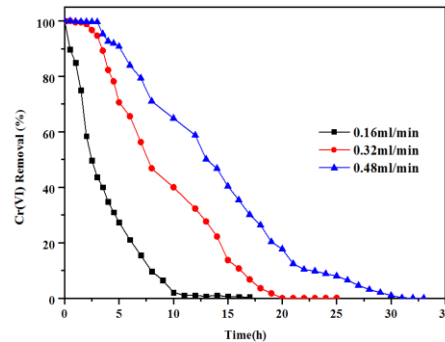


Fig. 8. Penetration curves at different flow rates.

As shown in Fig. 8, with the increase of flow rate, the residence time of Cr (VI) fluid in rGH decreases, and the two flow out without adsorption. At the same time, the slope of penetration curve will increase. This is because the mass transfer coefficient increases at a large solution flow rate, that is, the increase of flow rate leads to the rapid renewal of solutions around rGH activity and maintains a high concentration level. The adsorption saturation is shortened, so the slope becomes steeper. At the same time, from the perspective of mass transfer resistance, when the flow rate is high, the liquid film surrounding the rGH surface becomes thinner, so the liquid film resistance is reduced, so the adsorption rate is accelerated and the slope of adsorption breakthrough curve is increased.

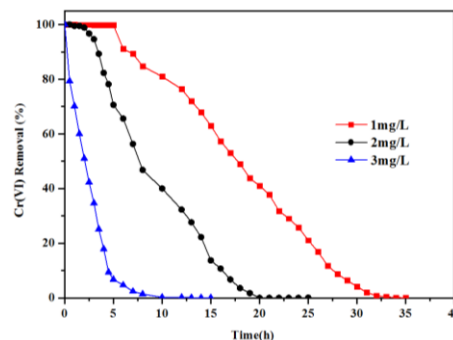




Fig. 9. Penetration curves under different initial concentrations.

Fig. 9 shows the adsorption and purification effect of rGH on different initial Cr (VI) concentrations (1, 2 and 3 ppm) in the flowing state. The effects of different initial concentrations on mobile phase adsorption are mainly reflected in two aspects: penetration time and slope. When the initial concentration of Cr (VI) is low, the penetration time of the adsorption penetration curve is longer. This is because compared with the high concentration solution, when the solution concentration is low, the movement speed of the mass transfer zone is slow, and the deep adsorption of heavy metal Cr (VI) in the water body is carried out. Within 6 hours of the reaction, the continuous and efficient removal and purification of 1 ppm Cr (VI) is carried out, and the adsorption rate is maintained at about 99.5-100%. As the adsorption site of rGH material reaches saturation, the removal rate decreases gradually, and finally reaches the state of adsorption saturation. When the initial concentration of Cr (VI) increases, the slope of the breakthrough curve will increase. This is because at higher solution concentration, the mass transfer driving force of the liquid phase increases, which accelerates the adsorption rate and quickly reaches rGH adsorption saturation. However, generally speaking, rGH removes heavy metal Cr (VI) with different initial concentrations in the flow state, It shows great potential in practical application.

With the increase of initial concentration and flow rate, the penetration time, saturation time and removal rate showed a downward trend, mainly because the increase of flow rate and initial concentration made the active sites of rGH composites surrounded by more Cr (VI), increased the mass transfer power, and shortened the penetration and saturation time of the reactor.

### 3.3. Mechanism analysis of Cr (VI) removal by rGH adsorbent

As mentioned above, the initial pH value in the solution greatly affects the adsorption performance of reduced graphene oxide hydrogel on Cr (VI)(Fig.10). The study shows that H<sup>+</sup> plays an important role in the adsorption process. Under the low pH value, the surface of the reduced graphene oxide hydrogel surface is protonated and positively charged, and the Cr (VI) anion is adsorbed quickly by electrostatic attraction. The adsorption process agrees with the Langmuir model, indicating that the reduced graphene oxide hydrogel has a limited adsorption site on Cr (VI). Physical monolayer adsorption occurs on the homogeneous surface. Then, Cr (VI) with strong oxidation can be easily reduced to chromium (III).

The reduction reaction is as follows:

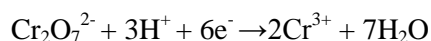
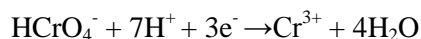


Fig. 10. Adsorption mechanism of graphene hydrogel on Cr (VI).

According to previous literature reports<sup>[11]</sup>, graphene is also a potential adsorption material for effective removal of heavy metal Cr (VI) in water. Most importantly, the three-dimensional graphene hydrogel rGH retained the excellent properties of graphene. At the same time, its unique three-dimensional structure and uniform pore size distribution provided more active adsorption sites for the adsorption reaction. The porous network structure and the surface adsorption characteristics provided better movement channels and enrichment sites for Cr (VI) in solution. It is beneficial to ion diffusion and reduce mass transfer resistance. At the same time, it can be seen from the infrared absorption spectrum that a large number of oxygen-containing functional groups such as hydroxyl groups are retained on the surface of rGH, providing more chemical adsorption

sites. Through the effects of electrostatic adsorption, ion exchange, surface chemical coordination, complex adsorption and van der Waals force, the heavy metal Cr (VI) in sewage The treatment of will far exceed the application of pure graphene.

#### 4. Conclusion

The graphene hydrogel rGH prepared by chemical reduction has unique three-dimensional network structure and pore size distribution, and a large amount of hydroxyl containing oxygen functional groups are retained on the surface of the material. The adsorption capacity is much higher than that of pure graphene for Cr (VI) adsorption. At the same time, the adsorption material rGH is easy to separate and desorb. It is recycled for 5 times, and the adsorption rate changes little, indicating that it has high stability. In terms of purification of heavy metal Cr (VI) by flow dynamic adsorption, it can effectively and continuously remove and purify heavy metal ions Cr (VI) in sewage at different initial concentrations and different flow rates, To solve the problems of easy loss and difficult separation of most adsorption materials in practical dynamic application, it has a great application prospect in practical water purification and treatment.

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