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Preparation of GO-Based Iron-Containing and Adsorption of Cr in Water

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Abstract. The presence of Cr (VI) in the aqueous media is known to cause severe health issues in both humans and animals. Many technologies and especially adsorbents have been applied for its removal. In this work, Graphene oxide (GO) was prepared using the Hummers' method. A facile method was adopted to synthesize GO-Based Iron-Containing (GO-Fe) through the iron salt impregnation method. The GO-Fe was firstly applied as adsorbents for efficient elimination of Cr (VI) ions. Batch adsorption experiments showed that the adsorption of Cr (VI) on GO-Fe followed the pseudo-second-order kinetic model and Langmuir isotherm well, respectively. The absorption experiments showed that the GO-Fe have the largest adsorption capacity for Cr (VI) with the concentrations of $FeCl_2$ is 0.5mol/L. The GO-Fe exhibited excellent adsorption capacity of 31.24mg/g at pH 5.0, the contact time was 180 min, the dosage of GO was 0.5g/L and the initial concentrations of Cr (VI) was 40mg/L. This work highlighted the application of GO-Fe as novel and promising materials in the efficient elimination of Cr (VI) from contaminated water and industrial effluents in the environmental pollution management.

1. Introduction

Cr (VI) has been commonly used in a number of industrial processes, such as leather tanning, electroplating, mining and printing and dyeing [1]. It is quite dangerous to human and living things, leading to a variety of issues in the spectrum of health, include allergies, ulcers, and dermatitis. Cancer may be caused under certain conditions and may even lead to death in severe cases [2]. In order to reduce the risks associated with metal pollutants, it is essential that wastewaters be treated before being released to the environment [3]. Compared with other treatment technologies such as chemical precipitation [4], photocatalytic method [5] and ion exchange resin method [6], the adsorption procedure has attracted extensive attention due to its simplicity and low cost [7]. Numerous kinds of adsorbents such as activated carbon, fly ash and agricultural byproducts have been applied for the elimination of heavy metal ions from wastewater.

On the other hand, these materials have the disadvantage that the lack of model predictability and their incapability to elimination the contaminants in trace concentrations. Lack of specific surface area and the specific heavy metal adsorption capacity has also become the weakness of these materials. Therefore, the study on to find a new type of materials is of great concern.

Graphene oxide (GO) has excellent properties, the surface is rich in functional groups such as carboxyl, hydroxyl, ketone, and epoxy groups, which are favorable for the adsorption of heavy metal ions and provide a large number of active sites for functional modification [8]. As an ideal planar two-dimensional structure, a great specific surface area ($2630m^2 \cdot g^{-1}$), determined from the monolayer carbon structure [9]. In this sense, GO has great adsorption capacity for positively charged heavy metal ions in water, become the best nonporous absorbent. However, since the GO is negatively

charged in aqueous solution, the adsorption of heavy metal such as cationic heavy metal is better, and the adsorption of Cr (VI) and other anionic pollutants in water is poor. Therefore, it is necessary to improve the adsorption performance through modified methods.

At present, it is a hot research direction to modify the iron content of the material by the iron salt impregnation method. A lot of work has been done about the synthesis of nanocomposites by iron salt impregnation. For example, Xiao *et al*.[10] use iron-containing salt impregnation method for preparing iron-loaded activated carbon for the elimination of As (III) from the aquatic environment. Li *et al*. [11] prepared an iron-containing activated carbon IOCACAC for Cr (VI) Adsorption in water. In continuation of the previous study, GO-Fe is prepared by iron-salt impregnation method with a simple method, low cost, and no secondary pollution. The adsorption and mechanism of Cr (VI) in aqueous solution with GO-Fe is discussed. On the one hand, the application of graphene oxide is enlarged. The scope, on the other hand, provides basic data and theoretical research on the treatment of chromium pollution.

2. Materials and Methods

2.1. Synthesis of Graphene Oxide

All chemicals were of analytical grade and were used without any further purification. Graphene Oxide (GO) was synthesized according to the Hummers'method [12]. Flake graphite (3.0g) and $NaNO_3$ (0.75g) was dissolved in 98% concentrated H_2SO_4 (70ml) and then cooled in an ice bath (4 ℃ for 30min), stirred for 30 minutes to disperse it. 9g of $KMnO_4$ was added to a three-necked flask and stirred for 2h, after the solution is purple-green, keep the bath temperature controlled at about 35 ℃ and stirred the reaction for 1 hour, ultra-pure water (140ml) was added to solution then heated to a bath temperature (98 ℃ for 40min), when the solution is golden yellow after hydrolysis, added appropriate amount of H_2O_2 until no bubbles produced, filtered, and washed with 5% HCl, ultrapure water and ethanol for several times until the solution neutral and then dried at 60 ℃ for 24 h. The sample was eventually well maintained in a desiccator for future use.

2.2. Synthesis of GO-Based Iron-Containing

0.1g of GO was added to a certain concentration (0.005ml/L, 0.01mol/L,0.025mol/L,0.05mol/L, 0.1mol/L) of $FeCl_2$ aqueous solution (100ml) and dipped for 24h at room temperature. A certain amount of NaClO solution was added to a mixture every 8h then put it in a 70 ℃ electric heating oven to dry it for 24h, cooled to room temperature. Therefore, washed until there is no visible color and it is not red with potassium thiocyanate solution then continue to dry then get GO-Fe after grinding. The samples were characterized by SEM-EDS, FTIR and Zeta potentials.

2.3. Absorption Experiment

In this experiment, the method of static adsorption was adopted. At room temperature, a certain concentration of heavy metal Cr (VI) solution was placed in a conical flask. The pH value of the solution was adjusted with sodium hydroxide and hydrochloric acid. Put a certain mass of adsorbent material in the solution, placed on a shaker for a certain period of time, and after the reaction was completed, the remaining heavy metal chromium ions in the solution were measured by flame atomic absorption spectrometry (FAAS). The adsorption capacity of the heavy metal ions Cr (VI) in the aqueous solution are calculated by the following formula (1).

$$Q_e = \frac{(C_0 - C_e) \times V}{W} \tag{1}$$

Where C_0 and C_e are the initial and equilibrium Cr (VI) concentrations (mg/g). Q_e is the quantity of Cr (mg/g) absorbed on unit mass of adsorbent at equilibrium. V is the volume of the solution(ml), and W is the mass of the adsorbent(g).

## 3. Results and Discussion

3.1. Material Characterization

Fig.1shows the infrared spectrum of flake graphite powder, GO and GO-Fe. It can be seen from Fig.1, the absorption peak at $3444cm^{-1}$ in the infrared spectrum of GO is the stretching vibration absorption peak of O-H. $1740cm^{-1}$ is the stretching vibration absorption peak of COOH and C=O, $1645cm^{-1}$ is the bending vibration absorption peak of C=C, and the obtained GO infrared spectrum results are similar to those reported in previous literature [13], it shows that the synthesized GO molecules contain oxygen groups such as carboxyl groups and hydroxyl groups. The newly emerged absorption peak at $590cm^{-1}$ of the infrared spectral data of GO-Fe is the absorption peak of Fe-O of trivalent iron, this shows that Fe was successfully inserted into the graphene oxide and forming a new group.
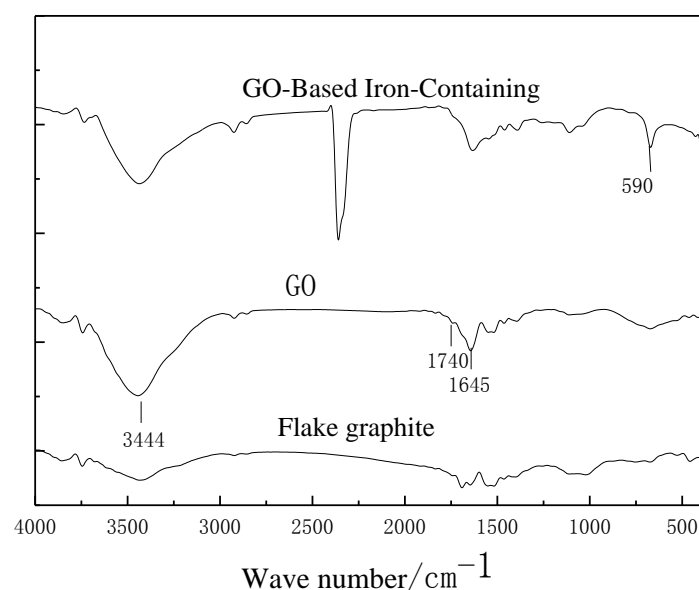

Figure 1. Infrared spectra of GO, GO-Fe and flake graphite

Fig.2 shows the SEM-EDS of GO and GO-Fe, spectral analysis of a little spectrum1 on the surface of the GO body indicated in Fig.2 (a). The result is as shown, it was found that GO is mainly composed of two elements: C and O, spectral analysis of the Spectrum3 of the surface of the GO-Fe body indicated in Fig.2 (b), the result is as shown; it was found that the content of GO-Fe is mainly composed of C, O, and Fe. The result of the insertion of iron into graphene oxide is consistent in the infrared spectra above.

Fig.3 shows Zeta potentials for GO and GO-Fe. It can be seen from Fig.3 that the Zeta potential is around -20mv at pH<7, when pH>7, the potential decreases slowly, when pH=10, its potential value is -47mv. When the pH is less than 7, the Zeta potential of GO-Fe is about 35mv, when the pH increases to 7, the potential value is 13mv, later when pH>7, the potential value of GO-Fe becomes negative, at pH=10, the potential value is -18mv. From this, it can be seen that GO is negatively charged in aqueous solution, and GO is positively charged under acidic conditions and negatively charged under alkaline conditions.
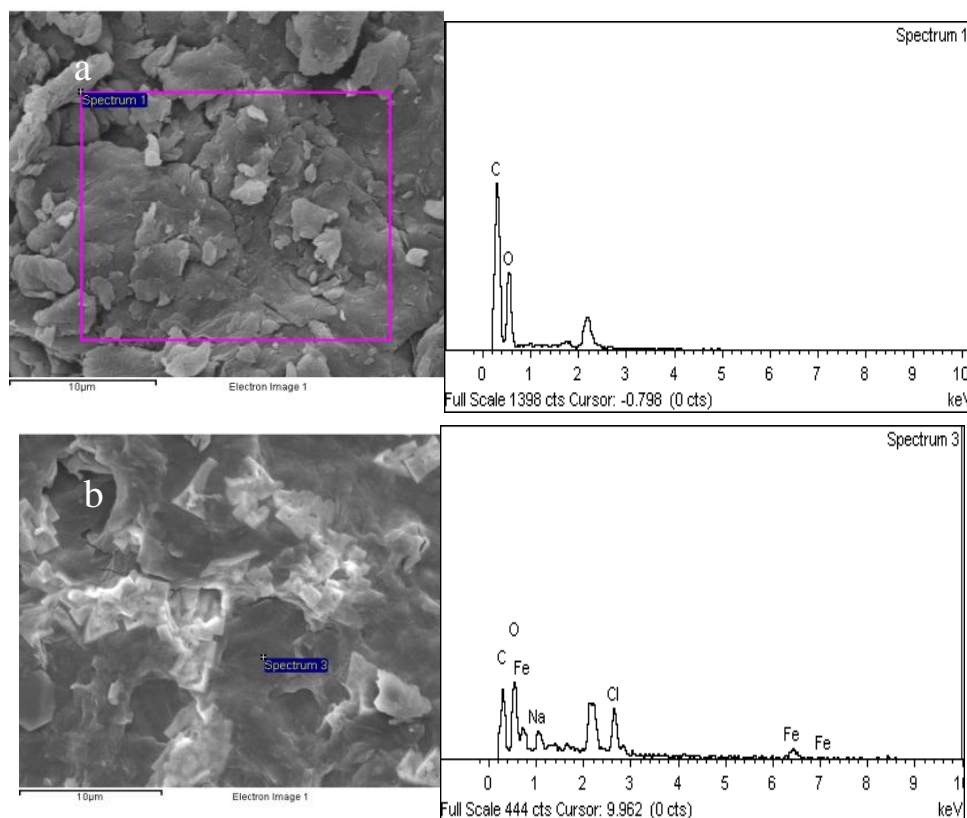
Figure 2. SEM-EDS of GO (a) and GO-Fe (b)
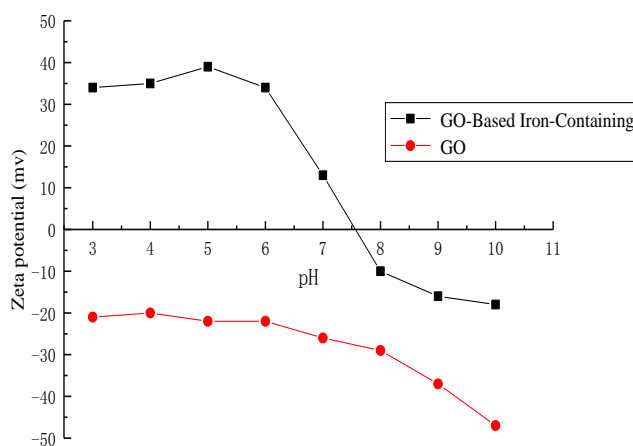
Figure 3. Zeta potentials of GO(a) and GO-Based Iron-Containing (b)

### 3.2. Effect of Iron Content on Adsorption of Cr(VI)

GO(0.1g) was added to 100ml of a certain concentration of the $FeCl_2$ aqueous solution, prepared GO-Fe with different iron content, Cr(VI)adsorption capacity as an indicator, the effect of ferrous chloride concentration on the adsorption performance of GO-Fe was investigated. The initial concentration of Cr(VI)in aqueous solution is 10mg/L and adjust solution pH to 5.0 then shock absorption after 180min, using FAAS to test the concentration of Cr(VI)in solution, the adsorption capacity of GO-Fe with different iron contents was calculated. The results are shown in Fig.4.

At acidic conditions, the main species of Cr (VI) was $HCrO_4^-$ and its concentration kept almost unchanged. With the solution pH increased, $HCrO_4^-$ was then transformed into CrO_4^{2-}. It can be seen from Fig.4, as the concentration of $FeCl_2$ aqueous solution continues to increase, the adsorption
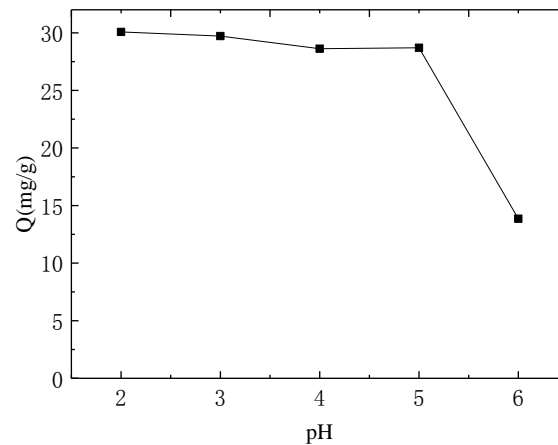
capacity of GO-Fe gradually increases, when the concentration of $FeCl_2$ is increased to 0.05mol/L, the adsorption capacity of GO-Fe is maximized, when the concentration of $FeCl_2$ gradually increases, the adsorption capacity tends to be stable. This may be due to the limited active sites on graphene oxide, with the increasing concentration of the aqueous $FeCl_2$ solution, the active sites on graphene oxide are continuously occupied and reduced, after reaching the saturation state, and the adsorption effect tends to be stable. With the addition of $FeCl_2$, the adsorption capacity of GO-Fe is significantly increased, when the concentration of $FeCl_2$ was increased to 0.05mol/L, the adsorption capacity was 15.71mg/g. The reason for the analysis from Fig.1and Fig.3 is that GO contains a large number of oxygen-containing functional groups, its Zeta potential is negative, negatively charged in aqueous solution, Cr(VI) electrostatic repulsion, the Zeta potential of the GO-Fe is positive, positive charge in aqueous solution, and electrostatic attraction of Cr(VI). At the same time, GO-Fe contains Fe-O functional group, complexation with Cr (VI), therefore, the adsorption capacity of GO-Fe is significantly improved compared to GO. This experiment selected the best $FeCl_2$ concentration of 0.05mol/L.

3.3. Effect of pH on Cr(VI)Adsorption

The mechanism of the synthesis and adsorption of GO-Fe is as follows: Added $FeCl_2$ to the graphene oxide solution then added NaClO to oxidize Fe^{3+}, it reacts with functional groups such as carboxyl and hydroxyl groups in graphene oxide. From the infrared data in Fig.5, a new group Fe-OH is formed in the GO-Fe. The Fe-OH group and the $HCrO_4^-$ in the aqueous solution adsorb Cr (VI) on the GO-Fe surface through complexation. At present, there is no unified conclusion about the model of Fe-OH group and Cr (VI)complexation. However, due to the easy desorption of adsorbed Cr (VI), it shows that the binding force between them is relatively weak and belongs to the characteristics of complexation in the outer region. Therefore, many researchers [14] believe that the surface complexation of Cr (VI) and Fe-OH groups belongs to the outer region complexation. The effect of pH on the adsorption of Cr (VI) on GO-Fe was investigated in the pH range of 2.0-6.0. The initial concentration of Cr (VI) in aqueous solution is 40mg/L, added adsorbent mass 50mg, the volume of the solution is 50ml, use hydrochloric acid to adjust pH, shock absorption after 180min at room temperature and determination of Cr (VI) concentration in solution by FAAS. The adsorption capacity of GO-Fe at different pH was calculated and the result is shown in Fig.5.
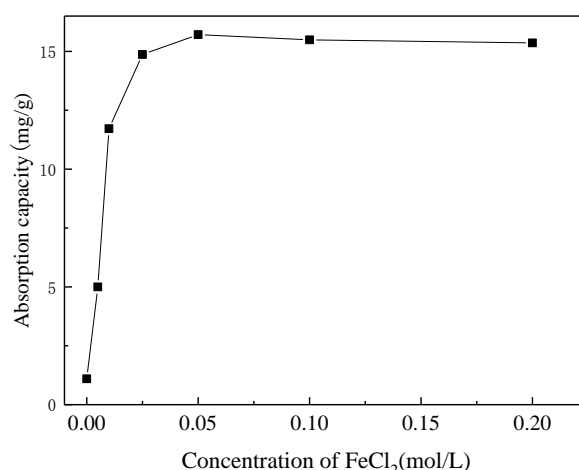
Figure 4. Effect of $FeCl_2$ concentration on Cr (VI) adsorption

Figure 5. Effect of pH on the Adsorption of Cr (VI)

It can be seen from Fig.5, as the pH increases, the adsorption capacity of GO-Fe decreases, when the pH is 2-5, the adsorption capacity of GO-Fe basically stabilizes, when the pH increased to 6, the adsorption capacity of GO-Fe decreased. The possible reason is, at pH between 2-5, the Cr (VI) in the aqueous solution exists mainly in the form of $Cr_2O_7^{2-}$ and $HCrO_4^-$, with little change in concentration; When the pH is 5-7, the concentration of $Cr_2O_7^{2-}$ and $HCrO_4^-$ decreases and the concentration of CrO_4^{2-} increases gradually; When the pH>7, the Cr (VI) in the aqueous solution exists mainly in the form of CrO_4^{2-}. When the pH is between 2 and 5, the concentration of $Cr_2O_7^{2-}$ and $HCrO_4^-$ remain almost the same. At the same time, we can see from Fig.3 that the Zeta potential of GO-Fe is basically unchanged, so the adsorption capacity of GO-Fe tends to be stable. When pH is 6, the concentration of $Cr_2O_7^{2-}$ and $HCrO_4^-$ decreases, the concentration of CrO_4^{2-} increases, and the adsorption capacity of iron-bearing GO on CrO_4^{2-} is relatively weak, so the adsorption capacity of iron-loaded GO decreases. At the same time, since the initial pH of the simulated Cr (VI) solution is close to 5.0, the optimum pH for the experiment is 5.0.

3.4. Adsorption Isotherm Analysis
In order to study the adsorption isotherms of Cr (VI) on GO-Fe, different adsorption isotherm models were used for fitting. Langmuir and Freundlich isotherm adsorption models are two commonly used methods for the analysis of adsorption data. Langmuir isotherm adsorption line assumes adsorption is monolayer adsorption, Freundlich assumes that the adsorption is a multi-layer adsorption because the adsorbent adsorption site and the adsorbed metal ions in the solution exist in various forms. The isotherm constants for each model were calculated from the linearized Eqs. (2)- (4)
The Langmuir adsorption model is shown below:

$$C_e/Q_e = C_e/Q_0 + 1/(Q_0 b) \tag{2}$$

The Freundlich adsorption model equation is as follows:

$$lnQ_e = (1/n)lnC_e + lnk_f \tag{3}$$

Langmuir adsorption constant R_L is an important parameter used to measure whether the adsorption system is effective if R_L is between 0 and 1, it means that the reaction system is effective and the reaction is easy to proceed. The formula is as follows:

$$R_L=1/(1+bC_0) \tag{4}$$

Here, C_e (mg/L) is the concentration of the adsorbate in solution after equilibrium is reached; Q_e (mg/g) represents the equilibrium adsorption capacity of the adsorbent; Q_0 (mg/g) represents the maximum adsorption capacity of the adsorbent; b (g/mg) indicates the adsorption strength (g/mg); K (mg/g) represents the adsorption performance constant of the adsorbent; $1/n$ denotes the Freundlich constant related to the adsorption strength; C_0 (mg/L) represents the initial concentration of the solution.

Table 1. GO-Fe Adsorption Isothermal Fitting Parameters

Adsorption materials	Freundlich adsorption model			Langmuir adsorption model			
	N	K	R^2	q_0	B	R^2	R_L
GO-Fe	3.305	12.16	0.96	33.00	0.543	0.9974	0.035~0.27

From Table 1, the correlation of the Langmuir adsorption model for chromium (VI) adsorption on GO-Fe is 0.9974. The Freundlich adsorption model has a correlation of 0.96. The maximum adsorption capacity of Cr (VI) in wastewater is 33mg/g. Therefore, the adsorption of hexavalent chromium on the GO-Fe is a mono-layer adsorption on the homogeneous surface and the Langmuir adsorption constant R_L obtained is between 0 and 1, which indicates that the adsorption of Cr (VI) by GO-Fe is easy to perform.

3.5. Mechanism Analysis

Since Cr (VI) has a high positive charge and a small radius, there is no simple presence of Cr^{6+} ions in solution. Cr (VI) exists mainly in the form of $Cr_2O_7^{2-}$, $HCrO_4^-$ and CrO_4^{2-} in water. Their conversions are shown in Equations (5) and (6) below.

$$HCrO_4^- \rightarrow H^+ + CrO_4^{2-} \tag{5}$$

$$2HCrO_4^- \rightarrow H_2O + CrO_7^{2-} \tag{6}$$

It can be seen from the Zeta potential data in Fig.4. When the pH is between 2 and 5, the Zeta potential of GO is about -20mv. With the increase in pH, the Zeta potential decreases. When the pH is 10, the Zeta potential is -47mv. Because $Cr_2O_7^{2-}$ and $HCrO_4^-$ are both negatively charged and GO electrostatically repulsive, GO has poor adsorption of Cr (VI). When GO is modified by iron, when the pH is between 2 and 5, the Zeta potential of GO-Fe is about 35mv, and it is electrostatically attracted by $Cr_2O_7^{2-}$ and $HCrO_4^-$ and adsorbs Cr(VI)on the GO-Fe surface.

4. Conclusion

Under acidic conditions, the GO-Fe contains Fe-O groups and the surface is positively charged .The zeta potential of the iron-loaded GO is positive and $Cr_2O_7^{2-}$ and $HCrO_4^-$ in the aqueous solution are adsorbed on the surface of the material by electrostatic action.The GO-Fe exhibited excellent adsorption capacity of 31.24mg/g at pH 5.0, the concentrations of $FeCl_2$ is 0.5mol/L, the contact time was 180 min, the dosage of GO was 0.5g/L and the initial concentrations of Cr(VI) was 40mg/L.

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