

Optimization of operating conditions in the purification of graphite oxide dispersions

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Abstract—In the graphite oxide (GO) suspension purification process, some metallic impurities in GO cannot be separated. The residual metallic impurities dominate graphite oxide properties and have a negative influence on applications. Therefore, the removal of metallic impurities from graphite oxide has been brought into focus now. Single factor experiments and orthogonal experiments are used to get the optimal purification condition. The results show that purification agent, temperature, stirring intensity and contact time affect the purification degree, and the purification agent is the most important element for the purification efficiency. The optimal purification condition is 10% hydrochloric acid (H10), 20 °C, 0 rpm and 60 min. Besides, the theoretical stage is calculated by the mass conservation equation and distribution balance equation and the minimum stage is 3 under the optimal purification condition.

Keywords: Graphite Oxide, Purification, Metal ions, Theoretical Stage, Orthogonal Experiment

INTRODUCTION

Graphite oxide (GO), one of the most important derivatives of graphene, has been extensively researched in the past few years. The main synthetic methods of graphene include Brodie [1], Staudenmaier [2], Hummer [3] and electrochemical methods [4]. In the preparation process of graphite oxide by Hummers method, strong oxidants, such as potassium permanganate and potassium chlorate, are used. Metallic impurities such as K^+ , Na^+ , Mn^{2+} remain in the graphite oxides, which dominate GO properties and have a negative influence on potential applications of GO [5]. Therefore, metallic impurities removal from graphite oxide has become an important subject.

Graphite oxide and its derivatives, such as graphene oxide, play a major role in a wide range of applications in physics, chemistry, biomedical, and materials science [6,7], including the fabrication of electronic [8], sensing, and energy storage devices [9]. These impurities can alter electrochemical properties [10], influence redox properties of biomarkers [11], have effects on adsorption properties [12] and also cause toxicological effects [13]. Moreover, considerable evidence shows that trace metallic impurities (down to 50 ppb levels) are responsible for some “noble metal catalyst” synthetic reactions [14]. It is well recognized that the electrochemical behavior of materials is very sensitive to the presence of heterogeneous impurities [15].

Graphite oxide has sufficient quantity of oxygen-containing functional groups (epoxide, hydroxyl, and carboxylic groups), large specific surface area and high water solubility. These properties make GO sheets promising as adsorbing metal ions [16,17]. Graphite oxide exhibits strong binding force with water, which enhances the

possibility of water molecules intercalating into graphite oxide layers. The layer space of graphite oxide further expands and graphite oxide collosol is formed. Then separation becomes difficult. The metal ions cannot be washed out completely and the subsequent large-scale application of graphite oxide is affected. These oxygenous groups react with metal ions to form metal ion complexes [18,19]. The commonly used purifying agents are deionized water, hydrochloric acid, alcohol [20], etc. Since metal ions have high solubility in deionized water, impurities are easily carried out every time in the process of washing. But during washing with deionized water, GO swells and the filtration is inefficient. The impurity ions cannot be taken out in later period. During the washing process with hydrochloric acid, the impurity ions are washed out efficiently, but the pH value of suspension is low. The suspension cannot achieve neutral and needs further treatment. The solubility of metal ions in alcohol [21] is low, so the removal quality of impurity ions is very small, although the GO does not swell.

The theoretical purification stages are calculated by mass balance equation and distribution balance equation. Through adjusting the purification process, the metal ions are washed out. To remove the residual metallic impurities from graphite oxide, isothermal adsorption theory is used as reference to discuss the balance mechanism of metal ions in the graphite oxide and provides theoretical guidance for the metal ions removal.

Since the relevant parameters are fewer and easily determined, the Langmuir and the Freundlich adsorption isotherm equation are widely quoted to reflect the surface properties of adsorbent and mass transfer between adsorbents. Then the mechanism analysis is carried out on the adsorption behavior. The experimental data for GO adsorbing metal ions is fit by Langmuir and Freundlich isothermal models [22,23].

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The Langmuir model is linear:

$$1/Q_e = 1/Q_m + 1/K_f Q_m C_e \quad (1)$$

Table 1. The experimental conditions for single factor

Influence factors	Contact time/h	Purifying agent	Stirring intensity/rpm	Temperature/°C
Purifying agent	4	W100 E80 H10	0	20
Contact time	4	W100	0	20
Stirring intensity	4	W100	0; 200; 400	20
Temperature	4	W100	0	20; 40; 60

Note: deionized water was abbreviated to W100, the purifying agent that the volume ratios of ethyl alcohol to deionized water was abbreviated to 80% was abbreviated to E80, the purifying agent that the volume ratios of hydrochloric acid to deionized water was abbreviated to H10

where Q_m (in milligrams per gram) represents the maximum amount of metal ions which form a complete monolayer on the surface of per unit weight of adsorbent, K_f is the equilibrium adsorption constant, Q_e is the amount of metal ions adsorbed at equilibrium (in milligrams per gram), and C_e is the equilibrium concentration of metal ions (in milligrams per liter).

The linearized Freundlich model is:

$$\log Q_e = 1/n \log C_e + \log K \quad (2)$$

where Q_e is the amount of metal ions adsorbed at equilibrium (in milligrams per gram), C_e is the equilibrium concentration of metal ions (in milligrams per liter), $1/n$ represents Freundlich intensity parameter and K indicates the adsorption capacity of GO.

Here, the optimal conditions of GO purification such as purification agent, contact time, stirring intensity and temperature were studied. To analyze the purification effects, the distribution ratios of K^+ , Na^+ , Mn^{2+} were measured and the optimal purification conditions were determined. Under the optimal operation conditions, the purification stages were theoretically calculated by mass conservation equation and distribution equilibrium equation using multilevel cross-flow purification. The concentrations of metal ions were theoretically calculated and compared with the experimental value, proving that this calculation method was accurate and provided theoretical guidance to industrial production.

MATERIAL AND METHODS

1. Preparation of Graphite Oxide

Graphite oxide was prepared from natural graphite using the modified Hummers method as described by Chen [24]. Aqueous dispersions with concentrations of 4 g/L were prepared by dilution from 25 g/L. The weight percentage concentrations of the dispersions were determined by weighing, drying and re-weighing the samples. The samples of 20 mL dispersions were dried at 50 °C by a dryer until the mass was constant in two hours. Then the quality of watch glass was w_0 , the quality after drying was w_1 , and the recycled mass was got by $w_1 - w_0$. The weight percentage concentrations were expressed by $(w_1 - w_0)/20$.

2. Single Factor Experiments

Measurements on the metal ion concentrations with GO were conducted to optimize purifying agent, contact time, stirring intensity and temperature.

When the GO was purified by purifying agent, part of the metal ions moved from solid phase to purifying agent. Then solid phase of graphite oxide and purifying agent was separated. The content of metal ions in the supernatant was used to characterize the purification effect. Kohlrausch pointed out that the molar conductivity of strong electrolyte had a linear relation with the square root of concentration in dilute solution. In this experiment, a variety of metal ions were removed by purifying agent at the same time. The metal ions in the supernatant had certain relations with conductivity, so the conductivity was used to characterize the change trend of metal ions.

A 200 mL graphite oxide suspension was centrifuged at 5,000 rpm (the separation coefficient is 1500) for 20 min. The solid at the bottom was taken out and drawn aside for later use. According to the experiment design, the solid at the bottom was diluted to 200 mL by different purification agent, stirring intensity and contact temperature, with the concentration of (4 g/L). Then 10 mL graphite oxide suspension was centrifuged at 5,000 rpm for 20 min after 10 min, 30 min, 60 min, 90 min, 120 min, 180 min and 240 min. The conductivity of the supernatant was measured after being diluted 20 times by the DDS-11A conductivity meter. The concrete experimental conditions are shown in Table 1.

3. Orthogonal Experiments

Orthogonal experimental method used a few rows of tables to test for the overall design, along with comprehensive comparison and statistical analysis. The good production conditions can be found through a few experiments. The production process was

Table 2. The conditions for orthogonal experiments

Factors	Purifying agent	Contact time/min	Stirring intensity/rpm	Temperature/°C
1	W100	60	0	20
2	W100	90	200	40
3	W100	120	400	60
4	E80	60	200	60
5	E80	90	400	20
6	E80	120	0	40
7	H10	60	400	40
8	H10	90	0	60
9	H10	120	200	20

achieved with high efficiency.

On the basis of single-factor experiments, an orthogonal experiment was carried out. The orthogonal experiment L9 (3×4) was made to study the effects of temperature, contact time, stirring intensity and purifying agent on the purification of graphite oxide. The orthogonal experiment conditions are shown in Table 2.

4. Distribution Equilibrium Curve

Graphite oxide suspensions with five different concentrations were prepared at the optimal condition according to orthogonal experiment. The suspensions were centrifuged at 5,000 rpm for 20 min when uniformly mixed. We assessed the amount of metallic impurities in supernatant and solid at the bottom by inductively-coupled plasma-mass spectroscopy (ICP-MS). ICP-MS was able to detect trace amount of metals to ppt levels.

RESULTS AND DISCUSSION

1. Single Factor Experiments

The metal ions in the supernatant had certain relations with conductivity, so the conductivity can be used to characterize the change trend of metal ions. In this experiment, a variety of metal ions were removed by purifying agent. The conductivity increased with the increase of time first and then reduced, an equilibrium state was reached at last.

1-1. The Effect of Contact Time on Distribution of Metal Ions

The graphite oxide suspension was purified by W100 under 0 rpm, 20 °C. The conductivity of supernatant was measured within four hours and recorded in Fig. 1. It can be seen that the conductivity of supernatant remained constant after 2 hours; thus the distribution of metal ions achieved a balance between the graphite oxide solid and supernatant.

The metal ions in graphite oxide moved into the purifying agent with the increase of contact time. When purifying agent was just getting connected with graphite oxide, the concentration grads of metal ions between graphite oxide and purifying agent were high, which improved the metal ions in solid phase moved into the purifying agent quickly. However, the initial state was unstable.

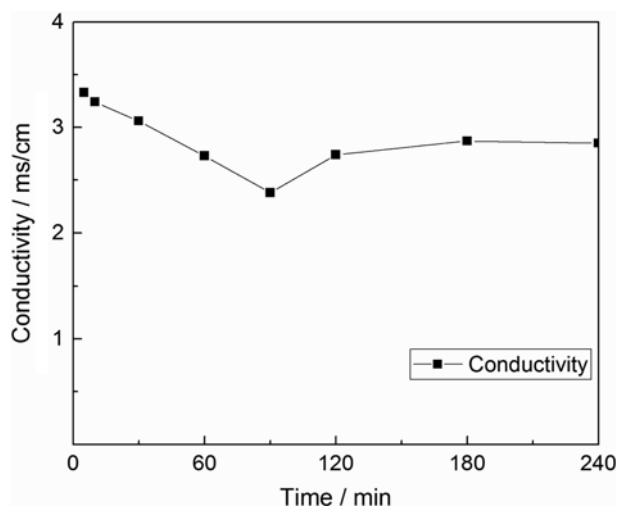


Fig. 1. The effect of contact time on distribution of metal ions.

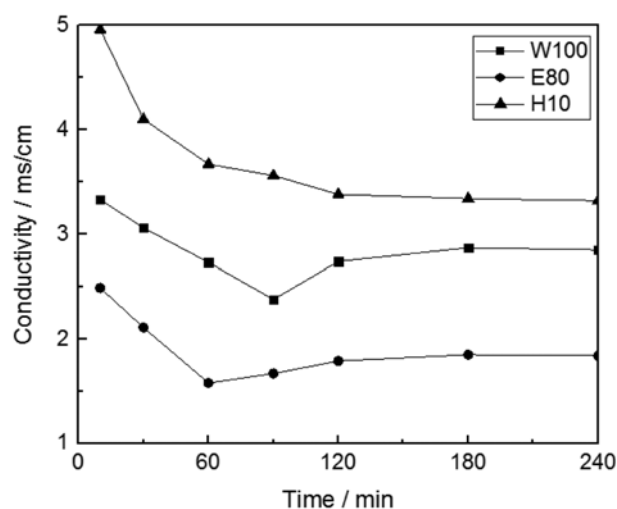


Fig. 2. The effect of purifying agent on distribution of metal ions.

Because the graphite oxide was negative, some metal ions were attracted to the graphite oxide with the increasing of contact time and the conductivity of supernatant decreased slightly. As the contact time increased, the concentration grads reduced and the migration power of metal ion decreased. Finally, distribution balance achieved.

1-2. The Effect of Purifying Agent on Distribution of Metal Ions

W100, E80 and H10 were used as the purifying agents to purify graphite oxide suspension, respectively. The conductivities of supernatants in experiments were measured, as well as the conductivities of purifying agents at the same experimental condition. The conductivity results in Fig. 2 were the values that subtracted the conductivities of purifying agents from the measured values of supernatants in experiments. As shown in Fig. 2, the conductivity of supernatant remained constant after two hours. Thus, the distribution of metal ions achieved a balance between the graphite oxide solid and supernatant. The conductivity of supernatant purified by H10, W100 and E80 was 3.4 ms/cm, 2.8 ms/cm and 1.6 ms/cm, respectively, when a balance was achieved. Purifying agent had a great influence on the distribution of metal ions. H10 had the best purification result.

H10 was used as an excellent purifying agent mainly because the pH had a great influence on the distribution equilibrium of metal ions. The hydrogen ions in solution competed with metal ions for the combination point on the surface of graphite oxide, which led to the decreasing of metal ions. The metal ions in graphite oxide were washed out by reducing the pH of solution. Because the solubility of metal ions in E80 was low, the impurity ions carried out by E80 every time were less than that by W100 and H10.

1-3. The Effect of Temperature on Distribution of Metal Ions

The graphite oxide suspension was purified under 20 °C, 40 °C, 60 °C and 80 °C, respectively. Fig. 3 shows that the distribution of metal ions achieved a balance between the graphite oxide solid and supernatant after two hours. The conductivity of supernatant purified at 20 °C, 40 °C, 60 °C and 80 °C achieved a balance of 2.8 ms/cm, 2.0 ms/cm, 3.4 ms/cm and 3.5 ms/cm. The temperature had a significant influence on the distribution of metal ions.

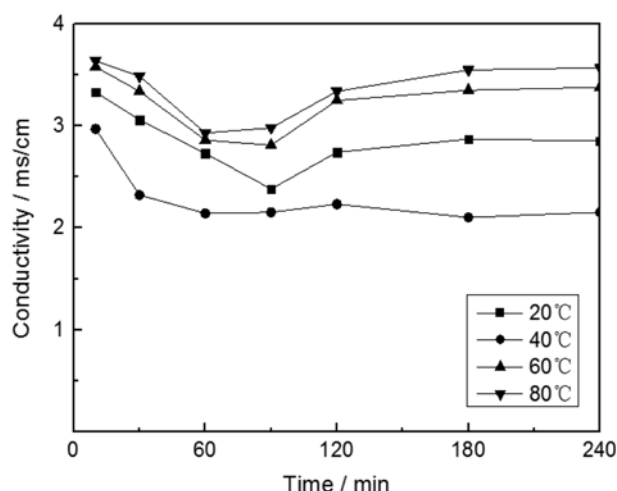


Fig. 3. The effect of temperature on distribution of metal ions.

The conductivity of supernatant under 80 °C was the highest because the kinetic energy of the system increased with the increasing of temperature and the ions were more active. The metal ions were easier to wash out from graphite oxide at higher temperature. Along with the removal of metal ions, the old chemical bond fractured and a new chemical bond was generated. The removal of metal ions was more sensitive to temperature, but the conductivity grew slowly when the temperature was higher than 60 °C. With the increase of temperature, more energy was used to heat the suspension. Considering purification effect and energy consumption, 60 °C was the best temperature in our experiment.

1-4. The Effect of Stirring Intensity on Distribution of Metal Ions

The graphite oxide suspension was purified under 0 rpm, 200 rpm, 400 rpm and 600 rpm, respectively. As shown in Fig. 4 the conductivity of supernatant remained constant after two hours; thus, the distribution of metal ions achieved a balance between the graphite oxide solid and supernatant. The conductivity of supernatant purified at 0 rpm, 200 rpm, 400 rpm and 600 rpm achieved a balance of 2.9 ms/cm, 3.4 ms/cm, 3.6 ms/cm and 3.6 ms/cm. The

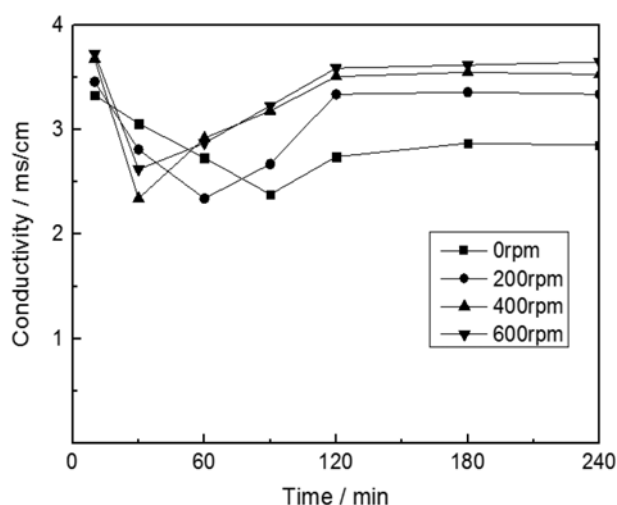


Fig. 4. The effect of stirring intensity on distribution of metal ions.

Table 3. The distribution ratio of metal ions under orthogonal experiment

Experiment	Distribution ratio of K ⁺	Distribution ratio of Na ⁺	Distribution ratio of Mn ²⁺
1	783.48	127.23	814.65
2	116.65	22.37	155.58
3	143.24	27.96	822.08
4	39.53	47.31	189.47
5	6.62	18.67	61.90
6	27.58	7.72	187.18
7	1702.36	81.92	599.71
8	400907.64	51.55	1734.23
9	401244.93	74.44	1201.22

conductivity increased little with the increase of stirring intensity when stirring intensity was higher than 400 rpm. The larger stirring intensity also led to an increase of fuel consumption. So 400 rpm had the best purification effect on the distribution of metal ions.

With the increase of stirring intensity, graphite oxide particles were distributed more evenly in the purifying agent. The contact area of graphite oxide and purifying agent increased and more metal ions in graphite oxide moved into the purifying agent.

2. Orthogonal Experiment

The distribution ratio was used to measure the distribution of metal ions in the liquid and solid phase, characterizing the purification effect of graphite oxide. The distribution ratio was expressed by Eq. (3), which was the ratio of the content of metal ion in supernatant to the content of metal ion in GO solid. The distribution ratio of metal ions, K⁺, Na⁺, Mn²⁺, respectively, is shown in Table 3. A higher distribution ratio was advantageous to the subsequent purification because more metal ions moved into purifying agent and the residual metal ions in the graphite oxide were less after primary purification.

Distribution ratio

$$= \frac{\text{the concentration of metal ions in supernatant}}{\text{the concentration of metal ions in GO solid}} \quad (3)$$

According to the distribution ratio of the three kinds of metal ions, orthogonal analysis was applied to find the best operating conditions. The experimental results are shown in Table 4. According to the significance principle, the optimal operating conditions of three kinds of metal ions were H10; therefore, H10 was chosen as the purification agent and H10 had the most significant impact. The optimal contact time and temperature for K⁺ and Na⁺ were 60 min and 20 °C, while the optimal contact time and temperature were 120 min and 60 °C for Mn²⁺. The optimal contact time of

Table 4. The optimal operating conditions of metal ions

Factors	K ⁺	Na ⁺	Mn ²⁺
Purifying agent	H10	H10	H10
Contact time/min	60	60	120
Stirring intensity/rpm	400	0	0
Temperature/°C	20	20	60

Table 5. Langmuir and Freundlich isotherm parameters for metal ions on GO

Metal ion	Langmuir model			Freundlich model		
	Q_e	b	R^2	$1/n$	K	R^2
Na^+	0.231	-0.016	0.238	0.497	0.226	0.914
Mn^{2+}	0.031	-0.003	0.281	0.501	0.035	0.967

Mn^{2+} was longer than that of K^+ and Na^+ . From an industrial viewpoint, 60 min was selected as the optimal contact time to save energy. The purification effects of Mn^{2+} at 60 °C and 20 °C were very close, so 20 °C was selected as the optimal temperature. For Na^+ and Mn^{2+} , the optimal stirring intensity was 0 rpm (in static state), while the optimal stirring intensity was 400 rpm for K^+ . In industrial production, high stirring intensity may lead to splash of suspension and waste energy. Thus, 0 rpm was selected as the optimal stirring intensity.

3. Isothermal Adsorption Equation

Graphite oxide suspensions of five different concentrations were prepared at the optimal operating condition. When they reached equilibrium state, the content of metal ions in supernatant and solid at the bottom was measured by ICP.

Langmuir and Freundlich equations were fitted to the isotherm data as shown in Table 5. The Freundlich isotherm better fitted with higher correlation coefficient ($R^2 > 0.9$) compared to the Langmuir isotherm. The high correlation coefficient of Freundlich isotherm indicated that metal ions strongly adsorbed to the surface of GO and the adsorption was monolayer.

In the Freundlich adsorption isotherm equation, it is generally believed that when $1/n$ is between 0.1-0.5, the adsorbate is not easily adsorbed; if $1/n$ is between 0.5-1, the adsorbate is easily adsorbed; and if $1/n$ is larger than 1, it is the preferential adsorption. In our study the values of $1/n$ of Na^+ and Mn^{2+} were 0.497 and 0.501. It was verified that GO had great potential to adsorb metal ions and the removal of metal ions from GO was difficult.

Under a certain temperature, metal ions moved on the phase interface. The concentration relation of metal ions between the purifying agent and graphite oxide solid was expressed by a distribution balance equation under a certain temperature [25]. The fitting equation was expressed by Eq. (4).

$$y = 1/(a + bx^c) \quad (4)$$

The fitting parameters are shown in Table 6.

The high correlation coefficient ($R^2 > 0.99$) indicated that the equation expressed the distribution equilibrium state fully accurately. When the concentration of metal ion in liquid phase is given, the concentration of metal ion in the solid phase can be calculated

Table 6. The fitting parameter of distribution balance equation

	Na	Mn
a	-1.49523	63.34352
b	5.92792	-31.40798
c	-0.24424	0.11338
R^2	0.99871	0.99966

according to the distribution balance equation.

4. The Determination of Theoretical Stage

Multilevel cross-flow purification technology is one of the most important methods of purification, which can purify the required material by mixing the solid and purifying agent together. Theoretical stage is an important part of this technology. It is calculated by the mass conservation equation and distribution balance equation, meanwhile providing theoretical guidance for industrial production.

The distribution balance equation is given as above mentioned. The mass conservation equation is shown by Eq. (5).

$$M \times y_i + \left(\frac{M \times w}{(1-w) \times \rho} \right) \times x_i + L \times x_p = L \times x_{i+1} + M \times y_{i+1} \quad (5)$$

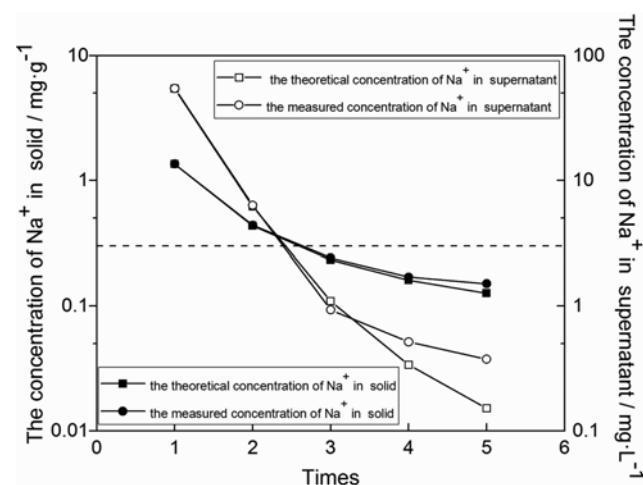
where, M is the mass of graphite oxide solid after centrifugation (g);
 w is the moisture content of solid phase at the bottom;
 ρ is the density of purifying agent (g/cm^3);
 L is the volume of purifying agent used every stage (mL);
 x_i is the concentration of metal ion in supernatant after the purification stage i (mg/L);
 x_p is the concentration of metal ion in purifying agent;
 y_i is the concentration of metal ion in graphite oxide solid after the purification stage i (mg/g);

In our experiments, we assumed that the GO was not lost during every purification stage. The value of M was constant and measured as 0.1 g. Graphite oxide was assumed to not swell after every purification stage and the value of w was 92%. We also assumed that there were no metal ions in purifying agent. The value of x_p was 0 and the value of L was 25 mL. When the value selected was taken into Eq. (6), the mass conservation equation was obtained as below:

$$0.00115x_i + 0.1y_i = 0.025x_{i+1} + 0.1y_{i+1} \quad (6)$$

The initial values of metal ions in graphite oxide were 14.95 mg/g for Na^+ and 105.43 mg/g for Mn^{2+} .

An iteration was operated through the above three conditions;

**Fig. 5. The comparison of concentration measured and theoretical calculation for Na^+ .**

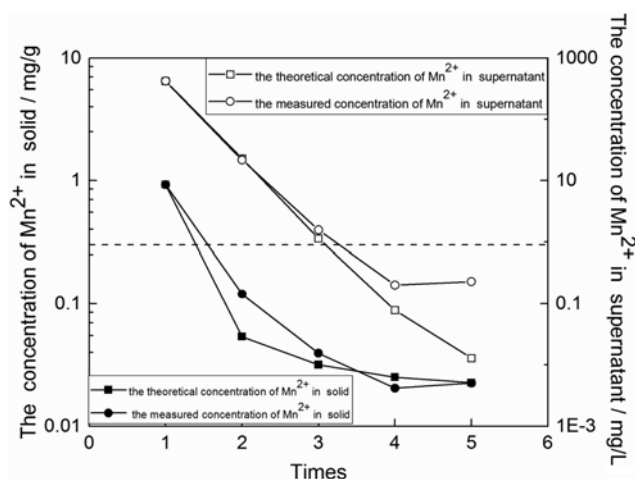


Fig. 6. The comparison of concentration measured and theoretical calculation for Mn^{2+} .

the minimum i value can be calculated by meeting $y_i < 0.3 \text{ mg/g}$. The minimum stage was 3 under the optimal purification condition by computing.

Under the optimal purification conditions, purification was carried out five times. The concentrations of metal ions in supernatant and graphite oxide solid were measured. The measured values and theoretical calculations were compared and shown in Fig. 5 and Fig. 6.

It can be seen from the figures that the values measured and theoretical calculation changed little in the previous two stages. With the increase of purification stages, the error between the measured value and the theoretical calculated value increased. The reason was that graphite oxide was assumed not to swell after every purification stage, and the value of moisture content of solid phase at the bottom after centrifugation was 92% in theoretical calculation. Whereas during the experiment, graphite oxide swelled slightly and the value of moisture content of solid phase at the bottom was higher than 92%. So the content of metal ions was higher than theoretical value. With the increase of purification stages, the error accumulated and the experimental value for concentration of metal ions in solid phase was lower than theoretical values. For Na^+ , the content in graphite oxide solid was down-to-standard after three stages; for Mn^{2+} , the content in graphite oxide solid can meet the requirements of purification after two times; thus three times was required. The theoretical calculation value generally represents the actual content of metal ions in graphite oxide and provides theoretical guidance for industrial production.

CONCLUSION

As a new type of extremely thin carbon nano-material, graphite oxide has excellent strength and thermal properties. But the residual metallic impurities in the graphite oxide dominate its properties and have a negative influence on the potential applications. Single factor experiment and orthogonal experiment were used to get the optimal purification condition. Purification agent, temperature, stirring intensity and contact time affected the purification

degree. It was found that metal ions achieved a balance distribution between the graphite oxide solid and supernatant after 2 hours, and the optimal purification condition was 10% hydrochloric acid (H10), 20°C , 0 rpm and 60 min. But during the washing with hydrochloric acid, the pH value of suspension was low; this will be studied in further research. Then theoretical calculation was studied. The theoretical stage is an important part of multilevel cross-flow purification technology. It can be calculated by the mass conservation equation and distribution balance equation. The sorption process of metal ions by GO conformed to the Freundlich isotherm better than Langmuir isotherm. The distribution balance equations were fitted with best. After theoretical calculation the minimum stage was 3 under the optimal purification condition.

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