

Article

Density Functional Theory Study on the Adsorption of Co(II) in Aqueous Solution by Graphene Oxide

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Abstract: Aiming at the removal of radioactive cobalt ions from water by graphene oxide (GO), the adsorption mechanism of Co^{2+} on graphene oxide was analyzed using the quantum chemical calculation software Gaussian 16 based on density functional theory. The influence of material structure factors such as carboxyl groups, hydroxyl groups, epoxy groups and graphene sheets as well as external environmental factors such as pH, temperature and interfering ions on the adsorption effect was determined, and the influence of external environment was verified through experiments. Through calculation and experiment, it was found that the existence of oxygen-containing functional groups on graphene oxide can improve the adsorption efficiency of the material appropriately, and increasing the pH under acidic conditions was also helpful to improve the adsorption effect. The material had certain selectivity for Co^{2+} , and the adsorption capacity and selectivity could be further improved when it was modified by increasing hydroxyl groups.

Keywords: GO; Gaussian; pH; temperature; interfering ions



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1. Introduction

When nuclear power plants use light water as a moderator and coolant, high-purity water will decompose H_2O_2 and O_2 under the action of radiation, resulting in corrosion of fuel surfaces and core structural materials. Corrosion materials become corrosion products after neutron activation and are important radioactive sources in nuclear facility wastewater. Compared with other nuclides in radioactive wastewater, ^{60}Co has a longer half-life (5.27a) and a higher content. Once it enters the environment and human body, it is bound to cause serious harm, and it is the object that needs to be focused on and removed in wastewater treatment.

As a new type of carbon material, graphene oxide (GO) has the characteristics of a large specific surface area and many oxygen-containing functional groups (including hydroxyl, carboxyl and epoxide groups) and can be further modified. It can be combined with radionuclides through coordination, electrostatic interaction and hydrogen bonding [1] and is expected to become an ideal adsorption material for removing radioactivity in water. In the process of the adsorption of metal ions by GO and GO-modified functional materials, experimental methods are usually adopted to explore the adsorption kinetics, thermodynamics and influencing factors of water environments; the study of the mechanism of interaction between GO and metal ions at the microscopic level is still in the initial stage. The research on the modification direction of increasing adsorption sites to improve adsorption performance lacks theoretical guidance. Especially in the process of treating radioactive wastewater, blind experiments also increase the radiation dose of experimental personnel. In this paper, GO is used to remove radioactive cobalt ions from water. Based on density functional theory (DFT), the quantum chemistry calculation software Gaussian 16 is used to calculate the adsorption mechanism of Co^{2+} by the material, analyze the factors affecting the adsorption effect of the material structure, and validate the calculation results

through experiments so as to provide more effective theoretical guidance for the functional modification of GO and more efficient adsorption experiments.

2. Theoretical Calculation Method

2.1. Density Functional Theory

Density functional theory (DFT) is a method of calculating energy as the density of particles in a system. Since the energy of a molecular system has a one-to-one correspondence with the electron density, and the electron density of a molecule is only a function of the position of each atom in space (x, y, z), the distribution of electron density in space can be obtained by solving the $3n$ degrees of freedom of n particles, and then the motion state of microscopic particles can be described qualitatively or quantitatively [2]. At present, density functional theory is one of the most widely used quantum mechanical methods, which is usually used to calculate the binding energy of molecules in chemistry and the band structure of solids in physics [3].

The theoretical basis of DFT is the theory of heterogeneous electron gas proposed by P. Hohenberg and W. Kohn, namely the Hohenberg–Kohn theorem [4], which mainly contains two parts. One is that the ground-state energy of identical Fermi subsystems regardless of spin is the only functional of the particle number density function. The second is that under the condition of a constant particle number, the energy functional reaches the minimum value in the correct particle number density function, which is equal to the ground-state energy of the system. The first part of quantification shows that the particle population density function is the basic variable to determine the ground-state physical properties of the multiparticle system. All the ground-state physical properties of the multiparticle system, such as energy, wave function and the expected values of all operators, are uniquely determined by the particle population density function. The second part shows that the minimum value of the energy functional can be determined by the ground-state particle population density function, and the minimum value is equal to the ground-state energy, so the variation in the energy functional to the particle population density is the way to determine the ground state of the system.

Kohn and Sham proposed that in order to find a concrete expression of the energy functional, the whole system of the interacting functional can be replaced by a separate, non-interacting functional, and all errors can be represented by a term called the exchange correlation functional $\text{Exc}[\rho]$ [5]. Therefore, the choice of the exchange correlation functional directly determines the accuracy of the calculated result. However, in the current DFT research, there is no specific function that can accurately express Exc . Exc is usually written as the sum of exchange energy E_x and correlation energy E_c . Different processing methods of the two constitute different methods in DFT calculation. Common functionals include Generalized Gradient Approximation (GGA) functionals, Local Density Approximation (LDA) functionals and mixed functionals. The solution of the energy of different systems is the process of obtaining the atomic coordinates through the established structural model and then solving the appropriate functional relations.

2.2. Gaussian Calculation Software

In order to solve the equation more accurately and quickly, various types of density functional computing programs have appeared. At present, the widely used chemical calculation software that can be used for DFT calculation include VASP [6], ORCA [7] and Gaussian [8]. These software can efficiently and quickly perform simulation calculations under microscopic conditions, so that density functional theory is increasingly applied to the research of material design and synthesis, macromolecules and biological systems, etc. Among them, Gaussian is the most widely used quantum chemistry software for the theoretical calculation and ab initio calculation of quantum chemistry, which has a powerful quantum chemistry calculation function. It can be used to calculate the structure and energy of the system, molecular orbital, polarization and hyperpolarization, vibration frequency, infrared and Raman spectra, magnetic properties, etc. At the same time, it

can also predict the chemical reaction path and calculate the transition-state energy and structure and other functions. Gaussian 16W has a strong ability to calculate aperiodic structures compared with other calculation software. Graphene oxide is composed of graphene with a periodic structure and rich oxygen-containing functional groups on the surface. In addition, considering the possible grafting structure of derivatives, the periodicity of material molecules will be destroyed. Therefore, the adsorption mechanism of graphene and its derivatives was investigated by using Gaussian software in this paper.

When using Gaussian software, you can use the GaussView GUI to draw the Gaussian molecular structure diagram and create the input file.gjf that contains the molecular coordinates, method and group information. Then, the input file can be imported to the Gaussian calculation and the system information can be analyzed based on the obtained output file. Gaussian software covers many types of calculation methods and basis sets to make it suitable for the calculation of different types of chemical systems. In the process of simulation calculation using Gaussian software, how to choose the appropriate method and basis group becomes the key to the accuracy of calculation results. In the process of Gaussian development, a variety of calculation methods have emerged, such as the semi-empirical method, self-consistent field theory, ordinary functional, double-hybrid functional and single-double iterative coupled cluster theory, etc. Compared with other types of methods, the ordinary functional has certain calculation accuracy, a moderate calculation amount, takes a short amount of time and is the most widely used [9]. The B3LPY method in the ordinary functional, which combines the Beeke-type three-parameter method [10] and the Lee–Yang–Part functional [11], is the most-used functional in quantum chemistry calculations and can be used on most systems. However, this method cannot describe dispersion attraction in van der Waals forces, so dispersion correction is required during parameter setting.

The base group is the wave function of the orbit of the system. The larger the base group, the smaller the approximation between the calculation result and the actual situation, and the higher the calculation accuracy, but the calculation amount and calculation time will also be greatly increased. In order to balance the workload and accuracy, Gaussian basis sets commonly used include the splitting valence group, polarization group, dispersion group, minimum group and high angular momentum group. Among them, the polarization group and dispersion group are usually used together with the splitting valence group. For example, 6-31g(d), 6-311+g(d,p), 6-311+g(2d,2p), etc. When transition-metal elements are involved in the system, specific base groups such as land12dz, lanl2tz, lanl2tz(f) or DEF2-TZVP can also be used for calculations.

3. GO Model Construction

In order to study the adsorption process theoretically, it is necessary to first construct the theoretical model of GO and then obtain the corresponding energy, electrostatic potential and charge distribution of the system by calculating and optimizing the structure through Gaussian software so as to complete the analysis of the adsorption mechanism and influencing factors.

Due to the diversity of graphite structures and the limitations of characterization and analysis techniques, the exact structure of GO has been controversial. At present, Hofmann [12], Ruess [13], Nakajima-Matsuo [14] and other structural models have been proposed successively, among which the “Lerf-Klinowski model” [15] proposed by Lerf and Klinowski has been widely recognized. The carbon skeleton of GO is divided into two parts: the unoxidized aromatic region and the oxidized, fat six-membered ring region. Epoxides, hydroxyl groups and carbon–carbon double bonds are randomly distributed on the base level formed by them, and a large number of hydroxyl and carboxyl groups are distributed on the edge of the base level. The Lerf–Klinowski model of GO is illustrated in Figure 1.

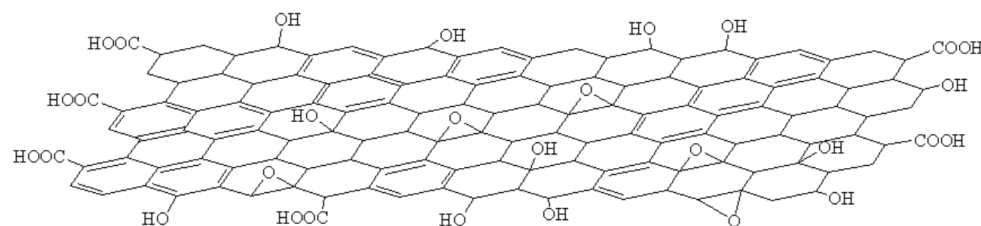


Figure 1. Lerf–Klinowski model of GO.

In this paper, the GO structure is constructed according to the Lerf–Klinowski model, the plane plan is drawn by ChemDrawPro8.0, the result file obtained by ChemDraw is converted by GaussianView6.0 and the input file containing the coordinates of each atom in GO in space is obtained. According to DFT, the spatial configuration of the material will have an impact on its energy size, so in the process of building the model, GO was optimized when the number of six-membered rings and the types and quantities of oxygen-containing functional groups were different; their optimal configurations and energies were calculated and the optimization results were tested by frequency calculation. In the optimization of the model, since the system containing only C, H and O involves only strong interactions and main-group elements, the traditional hybrid functional b3lyp and the polarization basis group 6-31G(d) were used for calculation. Considering the possible π - π stacking between GO molecules, the gd3 dispersion correction part was added to the keywords. The subsequent adsorption reaction occurs in the water phase, so the implicit solvent model SMD was also used to consider the effect of water.

3.1. GO with Different Number of Rings

GO can be seen as a derivative of graphene, that is, graphene is oxidized by a variety of oxygen-containing functional groups. Its adsorption on metal ions can be divided into two categories: physical adsorption and chemical adsorption. In terms of structure, the carbon atoms connected by an sp^2 hybrid are tightly packed into a single two-dimensional honeycomb graphene, which is mainly bound to metal ions through physical adsorption. In order to explore the influence of different numbers of six-membered rings in GO on structural stability and adsorption, graphene containing 4, 7, 10, 13, 16 and 22 six-membered rings (named GO4, GO7, GO10, GO13, GO16 and GO22, respectively) were constructed by GaussianView, their structure and energy in a stable configuration were calculated by Gaussian software, and their energy values are shown in Table 1.

Table 1. The energy of GO containing different numbers of six-membered rings.

The Type of GO	Energy/Hartree
GO4	−618.0725
GO7	−961.2273
GO10	−1228.0654
GO13	−1534.1856
GO16	−1840.2942
GO22	−2376.2528

By observing the change in its energy, it is found that the GO energy decreases proportionally with the increase in the number of its six rings, indicating that the molecular structure gradually tends to be stable with the increase in the number of rings and the probability of occurrence is greater in practice. However, considering that the increase in the number of rings will greatly increase the calculation amount of the Gaussian method, the calculation amount will be greatly increased. Therefore, in the process of exploring GO, GO containing 10 six-membered rings was selected for simulation calculation.

3.2. GO Containing Different Functional Groups

In order to analyze the influence of different types of functional groups on the adsorption process in the subsequent calculation, GO models containing different types of functional groups should be constructed. To simplify the calculation, it is assumed that each GO molecule contains only one functional group, that is, a hydroxyl group, carboxyl group or epoxy group, where the hydroxyl group exists on the base plane and on the edge of the base plane. The structure and energy of GO configurations containing different types of functional groups in the stable state are shown in Figure 2. The hydroxyl group is denoted as $\text{GO}(\text{OH})_s$ when it is present at the base level and $\text{GO}(\text{OH})_b$ when it is present at the edge of the base level; $\bullet$ represents a H atom, $\bullet$ represents a C atom and $\bullet$ represents an O atom.

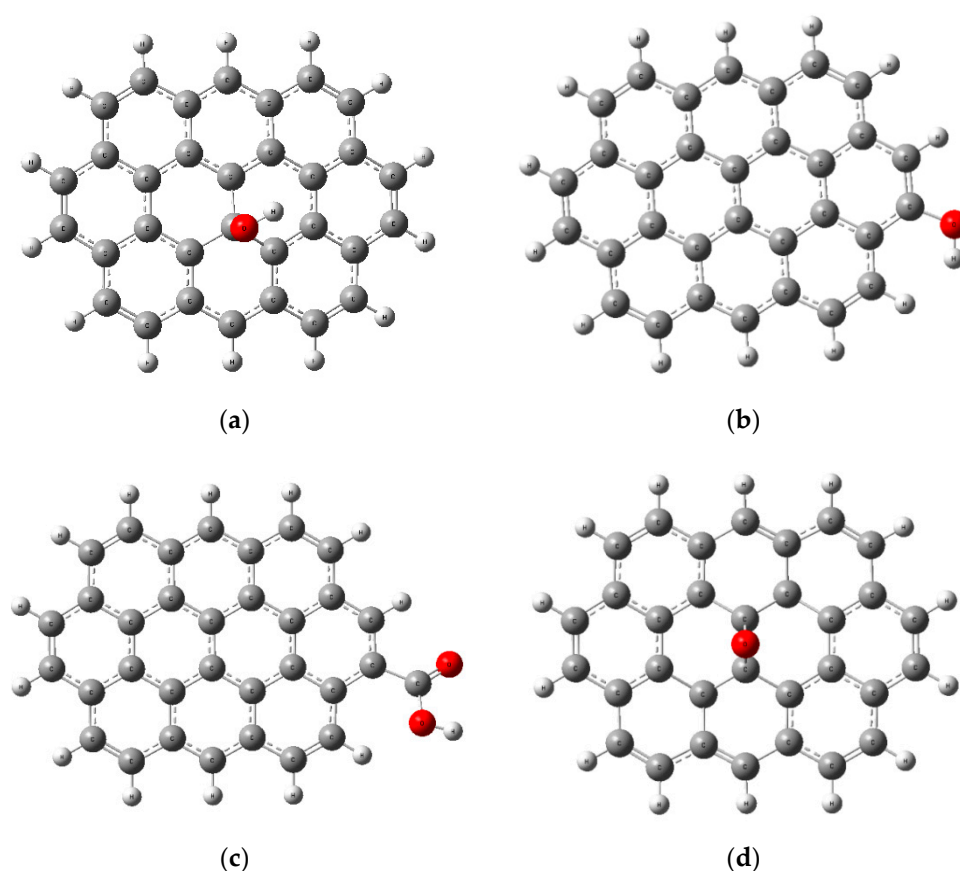


Figure 2. Structural model of GO with different functional groups in steady state: (a) $\text{GO}(\text{OH})_s$, $E = -1303.8118$ Hartree; (b) $\text{GO}(\text{OH})_b$, $E = -1303.2840$ Hartree; (c) $\text{GO}(\text{COOH})$, $E = -1416.6408$ Hartree; (d) $\text{GO}(\text{O})$, $E = -1304.3372$ Hartree.

Through energy calculations, it was found that $\text{GO}(\text{COOH})$ had the lowest energy in the stable state, indicating that compared with other types of functional groups, combining more carboxyl groups could improve the stability of the adsorbent.

4. Study on the Mechanism of GO Adsorption Process

Judging the adsorption mechanism of cobalt and manganese ions in radioactive wastewater by GO is an important way to improve the adsorption effect and further improve the performance of adsorbents. The outer electron arrangement of cobalt is $3d^7 4s^2$, respectively. In radioactive wastewater, cobalt loses two electrons, and the outer electron arrangement is $3d^7$, which exists in the form of positive bivalent ions. The adsorption effect of GO on CO^{2+} is more affected by GO structure and the external environment. To further explore, Gaussian software was used to calculate the relevant parameters of GO's

adsorption of CO_2^{2+} . The keywords in the input file are the same as those in Section 3. When metal ions are involved in the simulation process, the pseudopotential combined with the lanl2dz base set is used for calculation.

4.1. Influence of GO Structure on Adsorption

GO can be divided into graphene sheets and oxygen-containing functional groups on them. The loose, porous structure of GO enables it to have strong physical adsorption capacity. In addition, a cation– π bond interaction can occur between the π bond and Co^{2+} on the graphene sheet [16]. However, although the metal cation– π bond interaction can improve the adsorption capacity of a single GO to a certain extent, it also weakens the negative charge and hydrophilicity of GO, thus inducing the GO aromatic layer to form multiple structures and gather around the cation [17], resulting in a decrease in the overall adsorption efficiency of the adsorbent.

Oxygen-containing functional groups on GO also play an important role in the adsorption of metal ions. By calculating the electrostatic potential of GO containing different functional groups in a stable configuration, it was found that the graphene sheet is mainly positively charged, while the oxygen atoms in the oxygen-containing functional groups on it are surrounded by negative areas. Among all functional groups, the oxygen atoms on the epoxy group are the most electronegative, followed by hydroxyl, carboxyl and base-edge hydroxyl groups. The more electronegative the group is, the easier it is to bond with metal cations. The electrostatic potential diagram of GO containing different functional groups in a stable configuration is shown in Figure 3.

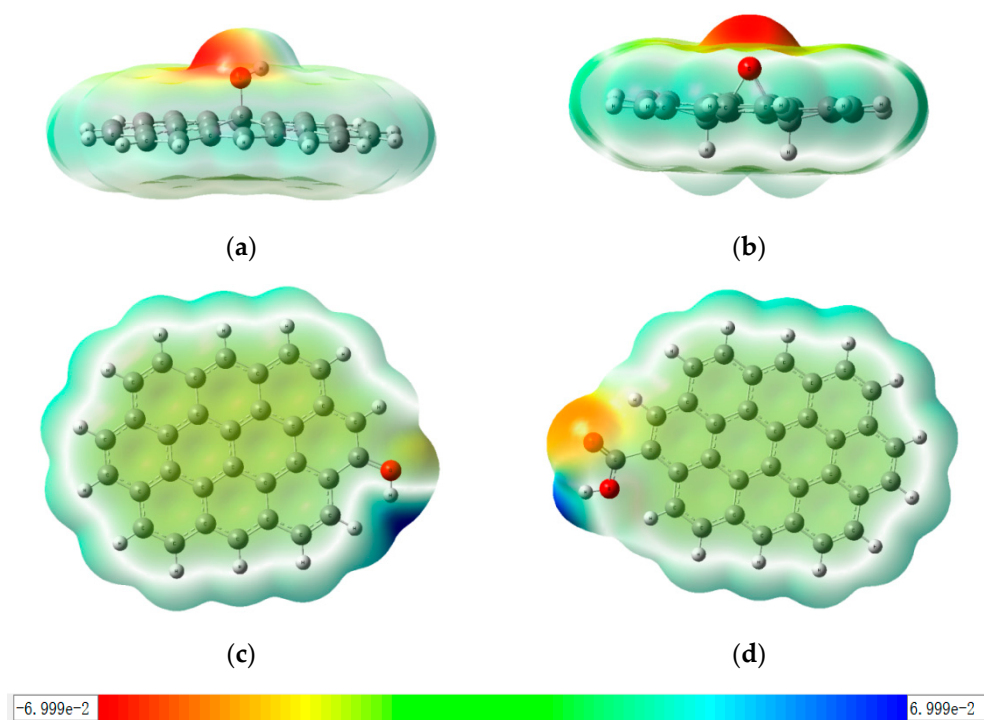


Figure 3. Electrostatic potential diagram of GO with different functional groups in stable configuration: (a) $\text{GO}(\text{OH})_s$, (b) $\text{GO}(\text{O})$, (c) $\text{GO}(\text{OH})_b$, (d) $\text{GO}(\text{COOH})$.

4.2. Influence of External Environment on Adsorption

The adsorption reaction of GO to metal ions is usually carried out in an aqueous solution, so the pH value, temperature and interfering ions of the aqueous solution will affect the adsorption effect. In this paper, the influence of various influencing factors on the adsorption process was analyzed through DFT calculation so as to lay a foundation for quickly finding the appropriate reaction conditions during the experiment.

4.2.1. pH

The pH value of the adsorption solution is closely related to the existence of hydrogen functional groups and metal ions on GO. When the acid is strong, a large amount of H^+ in the solution surrounds the material, increasing the protonation degree of GO, and the functional groups on the surface of GO exist in their original form. In this case, metal ions and adsorbents may be combined through coordination. When the pH of the solution gradually increases, H^+ on the GO surface gradually decreases, and some hydroxyl and carboxyl groups even remove H^+ in the form of $-O^-$ and $-COO^-$, which are directly combined with positively charged metal ions through electrostatic adsorption. If the pH continues to increase to more than 7, cobalt and manganese ions will be hydrolyzed and precipitated, which can also maintain a high removal rate, but it loses the significance of studying adsorption, so this paper only considers the case that the solution is acidic. In the acidic solution, $GO(COOH)$, $GO(OH)_s$, $GO(OH)_b$ and their structures after hydrogen ion removal, $GO(COO)^-$, $GO(O)_s^-$, $GO(O)_b^-$ and Co^{2+} , were placed in the same space, and Gaussian software was used to calculate the following results:

- (1) When $GO(COOH)$, $GO(OH)_s$ and $GO(OH)_b$ form complexes with Co^{2+} , the adsorption energy is negative, which means that the adsorption process requires external energy absorption, indicating that it is difficult for the complexes formed to exist stably.
- (2) When the pH gradually rises in the acidic range, $GO(COO)^-$ and $GO(O)_s^-$ can rapidly combine with Co^{2+} to form a stable structure. However, the existence form of $GO(O)$ is not affected by pH changes and can also combine with Co^{2+} to form a stable configuration. When $GO(COO)^-$ combines with Co^{2+} , the hydroxyl oxygen atom on the carboxyl group is connected with a metal ion, the structure is recorded as $[GO(COO) \dots Co]^+$, and the energy of the stable structure is -1561.056966 Hartree. The stable structure formed by $GO(O)_s^-$ and Co^{2+} is written as $[GO(O)_s \dots Co]^+$, its energy is -1448.23174 Hartree, and the stable structure formed by $GO(O)$ and Co^{2+} is written as $[GO(O) \dots Co]$ with energy of -1449.352687 Hartree.
- (3) When $GO(O)_b^-$ and Co^{2+} are placed in the same space, they also can form a stable configuration, but the Gaussian calculation shows that no chemical bond is formed between Co^{2+} and GO. Since the chemical bond type shown in the Gaussian calculation does not correspond to the actual situation one by one, in order to further determine whether there is a bond between them, this paper calculates the Mayer bond level of the complex through a powerful file-processing software Multifwn [18]. The Mayer bond level is calculated based on the wave function in quantum chemistry, which can be physically understood as the logarithm of electrons shared between atoms [18]. For single/double/triple bonds, the Mayer level is closer to 1.0/2.0/3.0, while for atoms with no or little bonding, the Mayer level is closer to 0. If the Mayer level is less than 0.5, it is considered weak bonding [19]. The Mayer bond level between the hydroxyl oxygen and Co^{2+} at the edge of the GO lamella is calculated to be close to 0, which proves that the chelation between the metal and the O atom is weak, which also corresponds to the weak electronegativity of the hydroxyl group at the edge of the graphene lamella.

After calculation, in a stable configuration, the energy of Co^{2+} is -144.742875 Hartree, and the energies of $GO(COO)^+$, $GO(O)_s^-$ and $GO(O)$ are -1415.785741 Hartree, -1302.989132 Hartree and -1304.337224 Hartree. The binding energy between GO and metal ions = metal energy + GO energy – energy after binding. The calculated adsorption energies of GO containing different functional groups on metal ions are shown in Table 2.

Table 2. Adsorption energy of Co^{2+} by GO containing different functional groups.

The Type of $[GO \dots Co]$	Binding Energy/Hartree
$[GO(COO) \dots Co]^+$	0.5283
$[GO(O)_s \dots Co]^+$	0.4997
$[GO(O) \dots Co]$	0.2725

The larger the binding energy value, the more energy released during the adsorption process, the easier the reaction will be, and the better the adsorption effect will be. It can be inferred from the simulation calculation results in Table 2 that under weakly acidic conditions, the carboxyl group on GO and the hydroxyl group on the base level have certain electronegativity, and electrostatic adsorption is the main force in the binding process with Co^{2+} . The epoxy group is more likely to bind to Co^{2+} through coordination.

4.2.2. Temperature

Temperature change will not only affect the energy of the adsorbent and the adsorbent in the stable existence, but also change the motion speed and contact probability of the particles in the solution, thus promoting or inhibiting the adsorption process of Co^{2+} by GO. In order to explore the effect of temperature on adsorption, the temperature was calculated by the keyword “temperature” setting in the Gaussian software, and the stable configurations and adsorption energy changes of $[\text{GO}(\text{COO})\dots\text{Co}]^+$, $[\text{GO}(\text{O})\text{s}\dots\text{Co}]^+$ and $[\text{GO}(\text{O})\dots\text{Co}]$ at 20 °C, 30 °C, 40 °C and 50 °C were solved.

The following results were found:

(1) With the gradual increase in temperature, $[\text{GO}(\text{COO})\dots\text{Co}]^+$ gradually changed from Co^{2+} connected with hydroxyl oxygen on a carboxyl group at 20 °C to a ring structure connected with Co^{2+} and two carboxyl oxygens at other temperatures, and its energy also increased correspondingly by 0.108951 Hartree; its stability decreased somewhat. The structure and energy changes of $[\text{GO}(\text{COO})\dots\text{Co}]^+$ are shown in Figure 4:

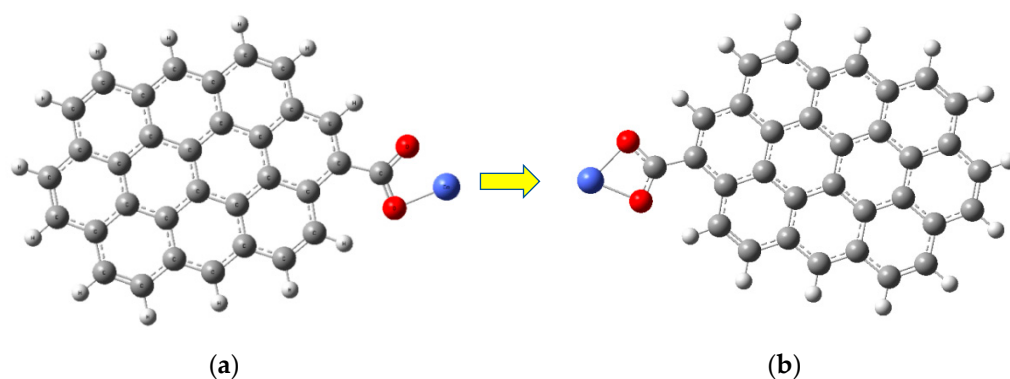


Figure 4. Influence of temperature change on $[\text{GO}(\text{COO})\dots\text{Co}]^+$ structure: (a) the structure of $[\text{GO}(\text{COO})\dots\text{Co}]^+$ at 20 °C; (b) the structure of $[\text{GO}(\text{COO})\dots\text{Co}]^+$ at 30 °C, 40 °C and 50 °C.

(2) With the increase in temperature, the structure of $[\text{GO}(\text{O})\text{s}\dots\text{Co}]^+$ and $[\text{GO}(\text{O})\dots\text{Co}]$ also underwent similar changes, from Co^{2+} connected to GO through hydroxyl oxygen atoms at 20 °C and 30 °C to the structure of Co^{2+} and the hydroxyl group separated from the graphene sheet, as shown in Figure 5.

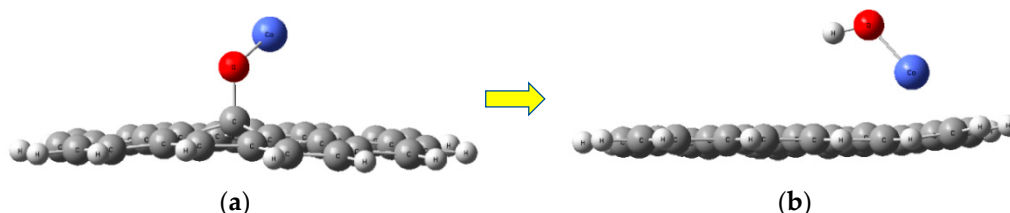


Figure 5. Influence of temperature change on $[\text{GO}(\text{O})\dots\text{Co}]^+$ structure: (a) the structure of $[\text{GO}(\text{O})\dots\text{Co}]^+$ at 20 °C; (b) the structure of $[\text{GO}(\text{O})\dots\text{Co}]^+$ at 30 °C, 40 °C and 50 °C.

It can be seen from the above calculation results that the influence of temperature on the adsorption capacity of different functional groups on GO is not the same. In order to accurately determine the influence of temperature on the adsorption, it is necessary to combine the analysis with experiments.

4.2.3. Interfering Ions

Radioactive wastewater produced by nuclear facilities is often mixed with a certain amount of equipment, valves, pipeline drainage and leakage; in addition, surface drainage and domestic water, which contain Na^+ , K^+ , Ca^{2+} and Mg^{2+} , may affect the adsorption capacity of GO on Co^{2+} . In order to analyze the influence of co-existing ions on adsorption, Gaussian software was used to calculate the adsorption process when GO and the above ions were placed in the same space under suitable pH and temperature conditions.

The following results were found via the Gaussian calculations:

(1) Co-existing ions can bind to the hydroxyl oxygen atom on $\text{GO}(\text{COO})^-$. The energy of Na^+ , K^+ , Ca^{2+} and Mg^{2+} in the stable state is -0.159212401 Hartree, -28.09549138 Hartree, -36.4406424 Hartree and -0.628838916 Hartree. The binding energy between $\text{GO}(\text{COO})^-$ and co-existing ions can be obtained as shown in Table 3:

Table 3. Adsorption energy of $\text{GO}(\text{COO})^-$ with different ions.

The Type of $[\text{GO}(\text{COO}) \dots \text{Different Ions}]$	Binding Energy/Hartree
$\text{GO}(\text{COO}) \dots \text{Na}$	0.3798
$\text{GO}(\text{COO}) \dots \text{K}$	0.3736
$[\text{GO}(\text{COO}) \dots \text{Ca}]^+$	0.3308
$[\text{GO}(\text{COO}) \dots \text{Mg}]^+$	0.3670

It can be seen from Table 3 that the adsorption capacity of GO containing only carboxyl groups is equivalent to that of all interfering ions. Compared with Co^{2+} , the relationship between binding energy is $E[\text{GO}(\text{COO})^- \dots \text{Co}^{2+}] > E[\text{GO}(\text{COO})^- \dots \text{Na}^+] > E[\text{GO}(\text{COO})^- \dots \text{K}^+] > E[\text{GO}(\text{COO})^- \dots \text{Mg}^{2+}] > E[\text{GO}(\text{COO})^- \dots \text{Ca}^{2+}]$; it can be seen that the carboxyl group on GO has a certain selectivity for Co^{2+} .

(2) As shown in Figure 6, $\text{GO}(\text{O})_s$ forms a stable configuration with each interfering ion. After Na^+ , K^+ , Ca^{2+} and Mg^{2+} combine with the O atom on the hydroxyl group, the C-O bond length gradually extends and finally breaks, forming graphene sheets and H-C-X (X represents interfering ion).

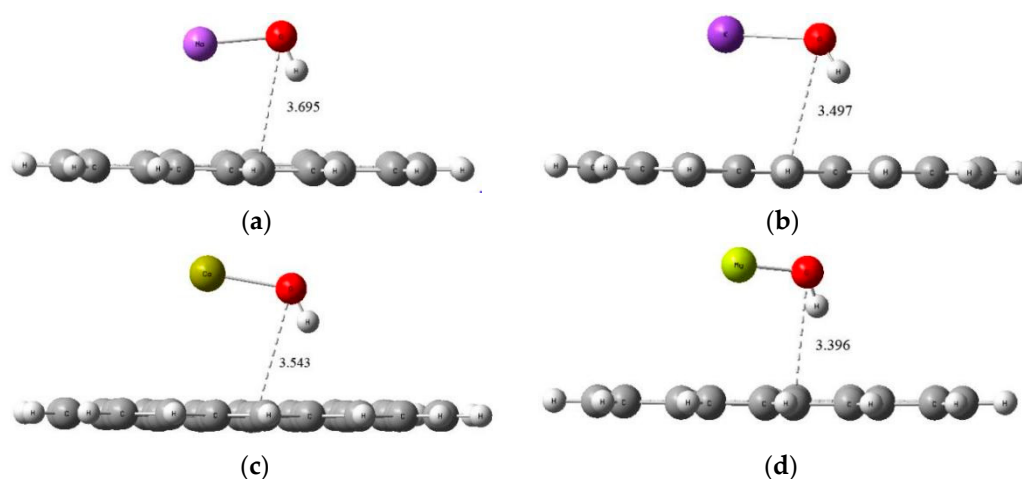


Figure 6. Stable configuration of $\text{GO}(\text{O})_s$ and each interfering ion: (a) the stable configuration of $\text{GO}(\text{O})_s$ and Na^+ ; (b) the stable configuration of $\text{GO}(\text{O})_s$ and K^+ ; (c) the stable configuration of $\text{GO}(\text{O})_s$ and Ca^{2+} ; (d) the stable configuration of $\text{GO}(\text{O})_s$ and Mg^{2+} .

(3) When $\text{GO}(\text{O})$ is placed in the same space with Na^+ , K^+ , Ca^{2+} and Mg^{2+} , the metal ion is bound to the O atom on the epoxy group and adsorbed on the GO surface. However, through calculation, it was found that the adsorption energy of $\text{GO}(\text{O})$ and interfering ions is negative, indicating that the adsorption process is energy release and adsorption does

not occur easily. The adsorption energy of GO(O) combined with different ions is shown in Table 4.

Table 4. Adsorption energy of GO(O) with different ions.

The Type of [GO(O)...Different Ions]	Binding Energy/Hartree
GO(CO)...Na	−0.0120
GO(CO)...K	−0.0121
[GO(CO)...Ca] ⁺	−0.0684
[GO(CO)...Mg] ⁺	−0.0479

It can be seen from the above calculation results that during the adsorption of Co²⁺ by GO, different functional groups and different adsorption conditions have different influences on the adsorption effect: appropriately increasing the pH of the solution within a certain range is conducive to the adsorption of metal ions by carboxyl groups and hydroxyl groups on the base plane. The effect of temperature change on adsorption efficiency should be considered comprehensively. The interaction between co-existing ions and the hydroxyl group on the GO surface is weak, but they can be strongly adsorbed by the carboxyl group on the GO surface and destroy the epoxy group on the surface of the material. In order to improve the selectivity of GO to Co²⁺, GO can be modified by increasing the number of hydroxyl groups.

5. Experimental Verification of Adsorption Properties of GO

To verify the Gaussian calculation results, experimental methods were used to determine the effects of pH value, temperature and interfering ions on the adsorption solution.

5.1. Experimental

5.1.1. Reagents and Instruments

The chemicals required for the experiment include the following: graphite (325mesh, QingdaoTengshengda, Qingdao, China), sodium nitrate (Aladdin, Los Angeles, CA, USA), 98% concentrated sulfuric acid (Tianjin Damao, Tianjin, Chian), potassium permanganate (Tianjin Damao), 30% hydrogen peroxide (Tianjin Damao), sodium hydroxide (Tianjin Damao) and hydrochloric acid (Tianjin Damao), all of which were commercially available analytically pure, and the experimental water was deionized water.

The analytical Instrument required for the experiment was an atomic absorption spectrometer (ContrAA700, Jena, Thuringia, Germany), which was used to determine the concentration of Co²⁺ in the solution before and after adsorption; the equipment required for material preparation included an ultrasonic constant-temperature oscillation box, a constant-temperature oscillation box, a blast-drying box, a freeze dryer and a precision pH meter.

5.1.2. Preparation of Graphene Oxide

Graphite oxide was prepared by the Hummer method [20]. Firstly, add 2 g graphite and 0.5 g NaNO₃ into concentrated H₂SO₄ and stir for 30 min and slowly add 3 g KmnO₄ in the ice bath and stir evenly; then, remove the ice bath and heat it up to 30 °C, add 100 mL water, keep the temperature above 98 °C and continue stirring for 30 min. Add a small amount of deionized water and 3 mL 30% H₂O₂; when the solution becomes bright yellow, stand and pour away the supernatant. Finally, use 200 mL 5% HCl solution and deionized water to wash the materials, and dry the graphite oxide at 60 °C to constant weight.

5.1.3. Characterization

The surface morphology of GO was observed by a scanning electron microscope (SEM), GeminiSEM 300, ZEISS, Germany; the functional-group structure of GO was observed by a Fourier infrared spectrometer (FTIR), TENSOR, Bruock, Germany; the thermal stability of GO was observed by a thermalgravimetric analyzer (TGA), STA449 F3, Netzsch, Germany.

5.1.4. Adsorption Experiments

The 0.02 g of GO powder was added to a 50 mL Co^{2+} solution and placed in a constant temperature shock chamber for shock, and the shock frequency was set to 140 min^{-1} . During the experiment, the atomic absorption spectrometer (flame method) was used to determine the concentration changes of Co^{2+} in the solution before and after adsorption under different conditions, and the adsorption capacity was calculated so as to determine the influence of pH, temperature, interfering ions and other factors on adsorption. Adsorption capacity q_t (mg/g) was calculated using Equation (1):

$$q_t = (c_0 - c_t) \times V / m \quad (1)$$

where c_0 is the initial concentration of Co^{2+} , mg/L; c_t is the concentration of Co^{2+} after adsorption, mg/L; V is the volume of solution, L; and m is the mass of the adsorbent, g.

5.2. Results and Discussions

5.2.1. Characterization

(1) SEM

As is shown in Figure 7, the SEM images of GO are presented at different measurement scales. It can be seen that GO exists in sheet form, the surface has certain folds, and the specific surface area is large.

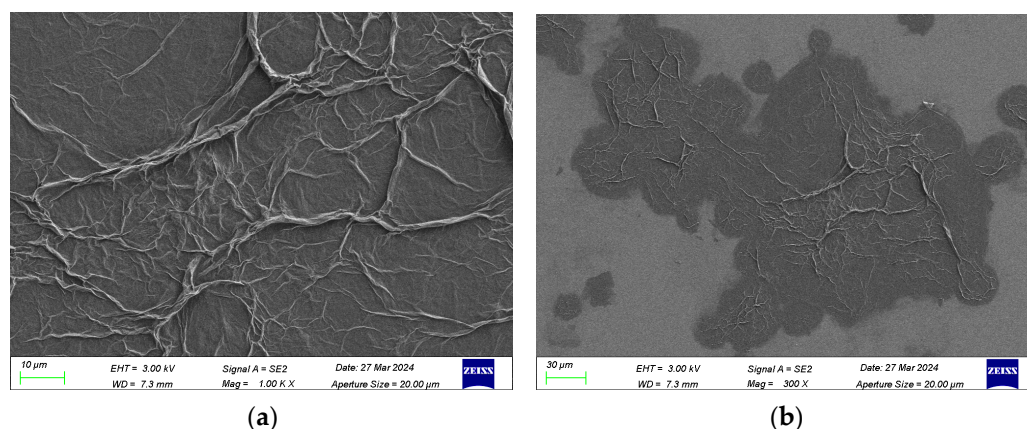


Figure 7. SEM images of GO at 10 μm scale (a) and 30 μm scale (b).

(2) FTIR analysis

As is shown in Figure 8, the GO only containing hydroxyl and carboxyl groups was constructed using Gaussian16 software, and the infrared spectra in its stable configuration were calculated. By examining the vibration modes of oxygen-containing functional groups on GO, it can be observed that the absorption peaks at 1295.59 cm^{-1} and 1689.70 cm^{-1} correspond to the deformation vibration of -OH. The absorption peak at 1750.79 cm^{-1} corresponds to both the deformation vibration of -OH and the stretching vibration of -C=O in the carboxyl groups. Additionally, at 3048.38 cm^{-1} , an absorption peak arises from superimposed stretching and deformation vibrations of -OH.

The infrared absorption spectra of GO measured by an infrared spectrometer are presented in Figure 9. However, because the Gaussian-constructed GO model is relatively simplified compared to the actual molecular structure, certain deviations in position and intensity of spectral peaks of the model GO and the actual model exist.

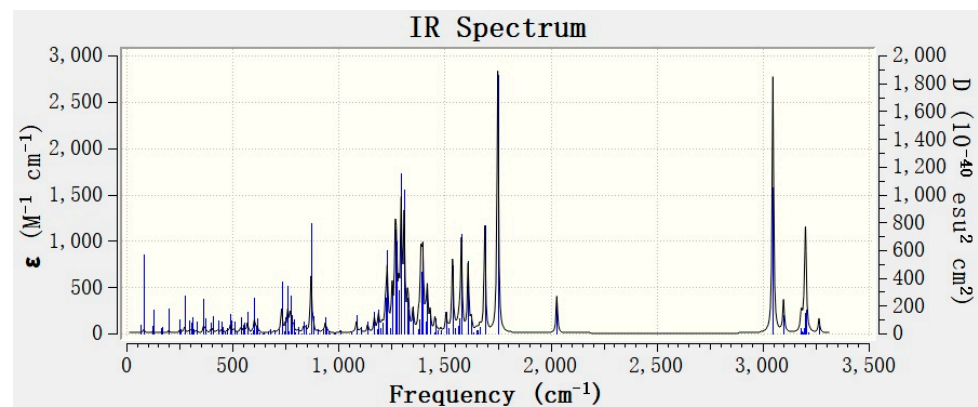


Figure 8. The infrared spectrum of GO model calculated by Gaussian software.

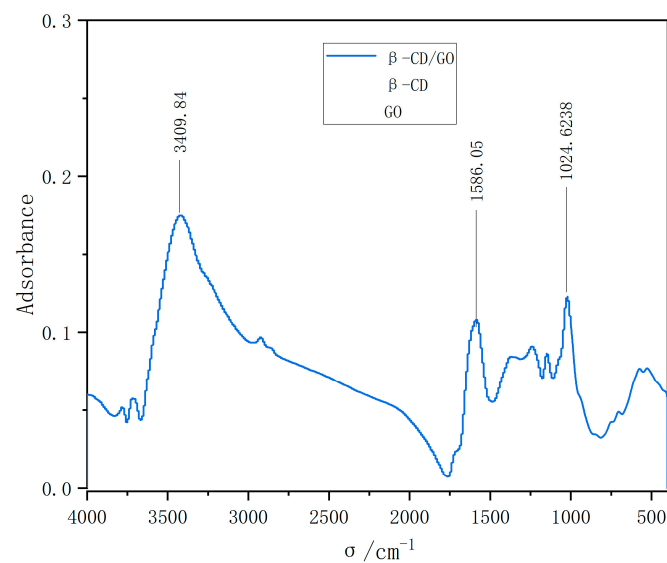


Figure 9. Infrared absorption spectra of GO.

5.2.2. Effect of Adsorption Conditions on Adsorption

(1) pH

Under the conditions of initial concentration $c_0 = 10$ mg/L, adsorption temperature $T = 30$ °C and adsorption time $t = 3$ h, the effect of pH on the adsorption of Co^{2+} by GO is shown in Figure 10. In the acidic range, the adsorption capacity also increases gradually with the increase in pH. When pH = 6, the adsorption capacity of Co^{2+} by GO is 8.04875 mg/g, which is consistent with the Gaussian simulation results.

(2) Temperature

Under the conditions of pH = 6, $c_0 = 10$ mg/L and $t = 3$ h, the influence of temperature on the adsorption of Co^{2+} by GO is shown in Figure 11. When the temperature ranges from 30 °C to 60 °C, the adsorption capacity of GO for Co^{2+} reaches the highest value at 50 °C, which is 11.23 mg/g, indicating the uncertainty of the effect of temperature on the adsorption effect.

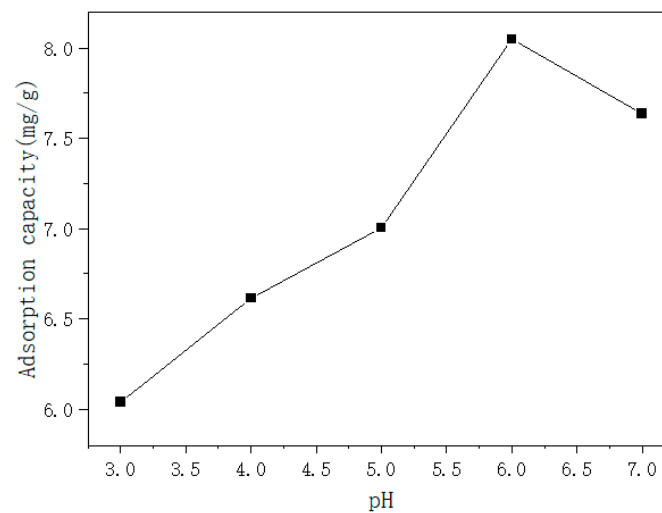


Figure 10. Effect of pH value on Co^{2+} adsorption by GO.

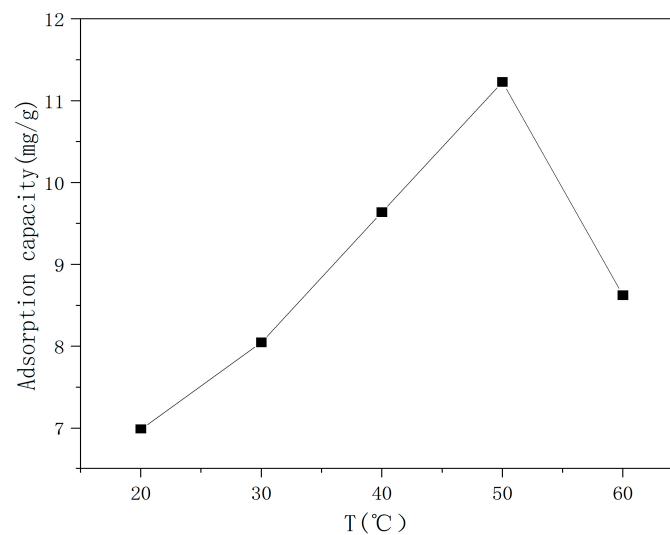


Figure 11. Effect of temperature value on Co^{2+} adsorption by GO.

(3) Interfering Ions

The effects of the co-existence of Na^+ , K^+ , Ca^{2+} and Mg^{2+} on the adsorption of Co^{2+} by GO were investigated at 50 °C. During the adsorption process, pH = 6, t = 3 h and the initial concentrations of Co^{2+} $c_0 = 10$ mg/L; the results are shown in Figure 12. It can be seen that Na^+ , K^+ , Ca^{2+} and Mg^{2+} contained in the solution have an inhibitory effect on the adsorption of Co^{2+} on GO. With the increase in the concentration of interfering ions in the solution, the equilibrium adsorption capacity of GO for Co^{2+} decreases rapidly at first and then gradually slows down until it approaches 0. The above experimental phenomenon further shows that some functional groups on GO can also bind to the above co-existing ions, which will have a certain effect on the adsorption of Co(II) .

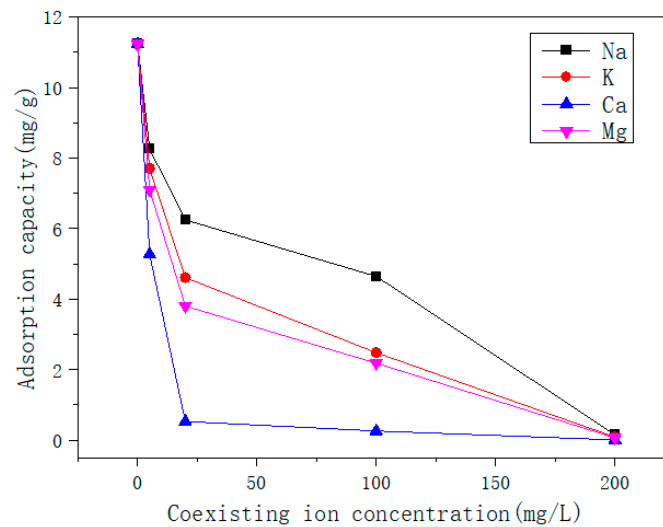


Figure 12. Effect of co-existing ions on the adsorption of Co^{2+} by GO.

6. Conclusions

By establishing the GO simulation configuration, the stability of the structure, the electrostatic potential, the orbital energy level and the binding energy between the structure and Co^{2+} under different environmental conditions were calculated, the adsorption mechanism and adsorption conditions of graphene oxide were analyzed, and the calculated results were verified by static adsorption experiments. Thus, the influences of the carboxyl group, the hydroxyl group, the epoxy group, the graphene sheet and the external environment such as pH, temperature and co-existing ions on the adsorption effect were determined, which provided theoretical guidance for the modification direction of graphene oxide and the selection of adsorption conditions. Through calculation and experiment, the following conclusions can be drawn:

- (1) With the increase in the number of six-membered rings on the graphene sheet, the material structure becomes more and more stable. The oxygen-containing functional groups on graphene oxide not only have certain electronegativity but can also combine with Co^{2+} to form stable complexes. However, the adsorption capacity of different functional groups is also different under different conditions.
- (2) pH has a great influence on the existence form of graphene oxide, and the adsorption effect is the best under weak acidic conditions. At this time, the carboxyl group and hydroxyl group on the base level are negatively charged due to proton loss and bind to Co^{2+} through electrostatic adsorption, while the epoxy group and Co^{2+} have strong stabilization energy and more easily bind to Co^{2+} through coordination.
- (3) The influence of temperature change on the adsorption capacity of different functional groups on GO is uncertain. Although it will increase the contact probability between adsorbent and adsorbent to a certain extent, it will also affect the stability of the adsorbed materials. Through static adsorption experiments, it was found that the adsorption capacity of Co^{2+} by GO reaches its maximum value at 50 °C.
- (4) For the wastewater containing Na^+ , K^+ , Ca^{2+} , Mg^{2+} and other interfering ions, although the carboxyl group on GO can effectively adsorb co-existing ions, it is difficult for the hydroxyl group and epoxy group on the base level to combine with it to form a stable structure, indicating that GO still has certain selective adsorption properties for Co^{2+} , and the static adsorption experiment also verified this calculation result. Since interfering ions can destroy the stability of the binding of epoxy groups to graphene sheets, increasing the number of hydroxyl groups on GO may be an effective way to improve the selective adsorption performance of materials.

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