Highly Efficient Fluoride Adsorption in Domestic Water with RGO/Ag Nanomaterials

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Reduced graphene oxide loaded silver (RGO/Ag) nanomaterials as a new nanocomposite film were prepared by in-situ redox method. The RGO/Ag nanomaterials were characterized by SEM, Raman spectra, XRD, UV-vis and TGA. The silver nanoparticles were well decorated and dispersed on the RGO nanosheets. Moreover, RGO/Ag nanomaterials were used to remove fluoride ion in domestic water. The influence factors including concentration of RGO/Ag, pH of water, the adsorption time and temperature on the removal rate of fluoride ion in domestic water were discussed. The results show that the removal ratio of fluoride in domestic water reaches up to 90% at the condition of 0.1g/L RGO/Ag, 60 °C and 20 h of adsorption temperature and time. Our RGO/Ag nanomaterials have great potentials for water treatment toward environmental remediation, especially for water treatment.

Keywords: Reduced graphene oxide; Silver nanoparticles; Fluoride; Water treatment

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1. Introduction

Fluorine is trace elements necessary for human body and adults under normal circumstances which people every day can obtain from ordinary water and food. However, fluorine contamination is increasingly serious in surface water and groundwater with the increase of discharging from various industrial processes. We once collected 10 samples of rural drinking water resources in Northern Shaanxi and found that the fluoride content in five samples are impermissibly high. Due to the high solubility of fluorine in water, high fluoride content in drinking water threatens the human environment. Drinking high fluoride water lead to fluorosis and dental fluorosis, even cause bone sclerosis or osteoporosis, bone deformation, even paralysis and make people lose labor ability. With increasing attention about clean environment and human health, technologies with high efficiency and low cost to remove the fluoride content in drinking water and wastewater are in urgent demand.

In recent years, as for the removal of fluoride the methods have involved in the use of cationic and anionic ion-exchange resins, chemical precipitation, flocculation, electrodialysis, membrane separation, adsorption, etc. However, for defluoridation of drinking water and wastewater, none of them can perfectly and completely overcome the problems from the pollution treatment cost, process complexity, and damage to the environment and removal efficiency. For example, flocculation of the sludge sedimentation is slow and difficult in the chemical precipitation. Dehydration fluoride wastewater sedimentation flocculants method commonly used aluminum salt. But the small amount of fluorine need use large amount of coagulant dosage which will produce large amount of sludge, so the treatment cost also is high. For the ion-exchange resins, efficiency is decreased in presence of other anion such as sulfate, phosphate and carbonate. In addition, the maintaining pH and regeneration of resin also are problems which maybe increase cost. The membrane separation method may remove all the ions present in water including some minerals which are essential for proper growth and enhance acid of water. The process is expensive compared to other options.

The adsorption with the simple operation, low processing cost, and good effect has been widely used in environmental management. Adsorption method is an especially effective way to deal with the low concentration of fluoride in wastewater. So it is the effective approach to solve the global water resources shortage and deterioration of water environment from a long-term perspective. In adsorption techniques, the most usually used adsorbent are the activated alumina, zeolite, activated carbon. But the adsorption capacity of these adsorption materials is not enough high and it is difficult to adsorb the low concentration fluoride. Therefore, it is extremely urgent to develop some new adsorbents or modify existing adsorbents to satisfy the application requirement.

Graphene as a newly emerging member of carbon materials has drawn much scientific attention since its discovery due to the sp2-hybridized single-atom-layer structure endowed with large surface area, unique mechanical and electronic properties, excellent mobility of charge carriers and high thermal conductivity. So graphene exhibits great promise for potential applications as adsorbent for water treatment. Graphene with an adsorption fluoride capacity of up to
17.65 mg/g at initial concentration of 25 mg/L at 298 K is an excellent fluoride adsorbent. In addition, considering the outstanding antibacterial properties of Ag, in this experiment, we reduced graphene oxide (RGO) loaded Ag nanoparticles (NPs) by in-situ redox method and then studied the influence of experimental parameters such as pH and temperature on the fluoride adsorption properties. It has been found that the removal fluoride ratio in water reaches up to 90% for 200 mg/L RGO/Ag adsorbent.

2. Materials and Experiment

2.1 Materials

GO was prepared by Hummers method according previous reports. Sodium fluoride (NaF) used in this study was obtained from Tianjin Kemiu Chemical Reagent Co., Ltd. Silver nitrate (AgNO₃) was purchased from Sinopharm Chemical Reagent Co., Ltd. Sulfuric acid (H₂SO₄), hydrogen peroxide (H₂O₂), anhydrous ethanol, and ammonia water were produced by Xi'an Chemistry Reagent Company. Potassium Permanganate (KMnO₄) was provided by Tianjin hedong district red cраг reagent factory. Unless otherwise stated, all solvents were of analytical grade.

2.2 Experimental method

2.2.1 Preparation of RGO/Ag

The stock solution of GO was prepared by transferring 10 mg GO into 100 mL deionized (DI) water and then dispersing the mixture using a Sonic Dismembrator (Fisher Scientific, Model F550) at 25% power for 30 min. The mixture was poured into a 250 mL round-bottom flask. And then, 7 mL NaOH (1 M) and 4 mL AgNO₃ (0.05 M) were added to the above GO solution. 1 mL CH₃O (37%) solution as a reduction agent for GO and AgNO₃ was slowly dropped in 15 min until the yellow solution is appeared to obtain Ag NPs. At last, the crude products were washed by alcohol for 3 times and kept drying at 80°C for 3 hours in the oven to obtain the RGO/Ag nanomaterials. Fig. 1 displays the preparation process of RGO/Ag nanomaterials.

2.2.2 Fluorine ion Removal of water by RGO/Ag nanomaterials

Adding the above RGO/Ag into DI water and dispersing for 10 min by ultrasonication obtain 100 mg/L RGO/Ag solution. Adsorption of F by RGO/Ag nanoparticles was tested by 100 mL mixing solutions containing 100 mg/L RGO/Ag and 100 ~ 10⁻⁶ M of F in centrifuge tubes on an oscillator. After overnight mixing, the samples were centrifuged at a speed of 10,000 rpm for 30 min. The supernatant samples were filtered through a 0.22 μm filter membrane and collected filtrate for analysis of soluble F concentrations using a fluorine ion selective electrode.

The removal ratio of fluorine ions adsorbed on RGO/Ag was calculated according the following formula.

\[ R = \frac{C_0 - C_1}{C_0} \times 100\% \]

where R is the removal ratio of fluorine ions. C₀ is the initial concentration of fluorine ions in the solution (M). C₁ presents the equilibrium concentration of fluorine ions after adsorption and filtration in the solution (M).

2.2.3 Characterization

The surface morphology and micro-structures of the RGO/Ag were investigated by Scanning Electron Microscope (SEM, Apollo 300). The surface morphology was obtained by scanning electron microscopy (SEM, JEOL JSM7500F) equipped with a cold cathode UHV field emission conica. X-ray diffraction (XRD) patterns were recorded on Rigaku XRD-600 (Japan) with Cu Kα irradiation at 40 kV and 40 mA. The scanning range is 0°~ 100° with 2°/ min. UV–vis spectra were acquired on a PerkinElmer Lambda-850 spectrophotometer (PerkinElmer Life and Analytical Sciences, Waltham, Mass, USA) using a couple of 1cm optical micro-cuvettes (Fischer Scientific, USA) with a sample volume of 0.1 mL. A 100-μL Hamilton syringe (Bonaduz, Switzerland) was used to transfer samples solutions into the micro-cuvettes. The Raman spectra were collected in high resolution.

Fig. 1 the synthesis schematic of RGO/Ag nanomaterials.
mode with a dispersive Raman spectrometer (Thermo Nicolet Almega XR) equipped with a CCD detector, optical microscope, digital camera, and 780 nm laser line with a laser source power of 30 mW (50% power was applied in the analysis). Raman signal was excited using the 514.5 nm wavelength of an Ar ion laser operating at 20 mW. The sample’s heat stability were tested with a dynamic thermogravimetric method in a range of 25 to 900 °C at a heating rate of 10 °C/min. A nitrogen gas flow at 60 mL min⁻¹ was used at below atmospheric pressure. The RGO/Ag nanomaterials before and after absorption of fluorine ions were characterized by fourier transform-infrared (FTIR) spectrometer (FTS2000) with KBr pellets. The scanning range was 400-4000 cm⁻¹, the resolution was 1.5 cm⁻¹, and the number of scans was 8 times. A high sensitive monocristalline fluoide electrode-based potentiometer.

The adsorption experiment was carried out to evaluate the adsorption mechanism and model by physisorption instrument (ASAP 2020) with 0.15 g GO/Ag sample. The degassing temperature was set at 350 °C and the heating rate was 10 °C/min for 4 h. After degassing, the sample tube is decreased to room temperature. Then the sample tube was installed at the analysis station, and then the Dewar bottle containing liquid nitrogen was placed and adsorbed for 6 h. A high sensitive monocristalline fluoide electrode-based potentiometer (PB-10, SaiDuoLiSi Corp., German, June 2013) was used to determine fluoride concentrations in water samples. Three replicates of each water sample were tested. In order to depict the standard curve of fluorine ion, 2.210 g NaF was dissolved in deionized water and transferred into 1000 mL volumetric flask, then diluted to scale with deionized water, shaking well. 10⁻⁴⁻⁵ M fluorine standard solution was obtained by successive dilution method. Take 10⁻⁴⁻¹⁰ M fluorine standard solution into 50 ml volumetric flask and add 10 ml total ionic strength adjustment buffer (TISAB) diluted with deionized water in the flask until the scale, shaking well. Then get 40 ml this solution into 50 ml beaker. The fluoride electrode and the reference electrode are inserted, and reading every half minute until the basic reading within the 1 min (< 1 MV). From low concentration to high concentration one by one The fluorine content is calculated according to the formula (1-2).

\[
C(F^-) = \frac{V_o \cdot C \cdot V (10^{-1})}{\Delta E} \tag{1-2}
\]

where \(V_a\) is the standard volume added (ml), \(C\) the concentration (M), \(V_o\) the volume of analyzed sample (ml), \(\Delta E\) the increase of potential (mV), and \(S\) the slope of the standard curve.

The TISAB was prepared as following: Adding 500 mL deionized water to the 1000mL beaker, then adding 50mL glacial acetic acid, 12 g sodium citrate, 58 g NaCl , putting the beaker in cold water bath, adjusting the solution to PH 5.0 - 5.5 with ammonia water (14M), comparing the pH test paper, Finally, it was diluted to 1 L with deionized water.

3. Results and discussion
3.1 RGO/Ag Nanostructures
Fig. 2 presents the morphology and structure of GO and RGO/Ag nanomaterials. Fig. 2a. shows the 3 D porous network with a crumpled sheet structure composed of randomly oriented graphene sheets. The unique structure largely preventing the aggregation of graphene oxide sheets endows a large surface area and great potential for further functionalization and absorbent materials. Fig. 2b reveals Ag NPs are uniformly encapsulated within the graphene oxide layers with high density, implying an efficient load of Ag NPs onto graphene oxide which avoids direct contact between Ag NPs. The EDS spectra also
exhibits the presence of the elements C, O for graphene oxide (Fig. 2c.) and the elements C, O and Ag for RGO/Ag nanomaterials (Fig. 2d.). The O content of RGO/Ag nanomaterials evidently decreases compared with graphene oxide revealing the graphene oxide also partly reduced in the preparation process of Ag Nps.

Fig. 3 shows the XRD curves of GO and RGO/Ag. GO has a sharp peak near 26°, which is the diffraction peak of graphite surface (002). Because the structure of GO contains a lot of defects and oxygen groups, the characteristic peak (001) appears at 2θ about 12°. The results show that the space arrangement of GO is not only regular on graphene plane but also contains oxygen groups. The oxygen groups are beneficial to be loaded Ag. After loaded Ag, a strong diffraction peak appears near 2θ about 38°, corresponding to the (111) crystal plane of cubic phase Ag, which is the characteristic peak of Ag, while the peak of oxygen group and graphite surface disappears obviously due to the strong intensity of Ag.

Fig. 4 shows the UV absorption spectra of GO and RGO/Ag nanomaterials. GO occurs a absorption band at 225 nm due to π-π* electron transition of aromatic C=C. In addition, there appears a shoulder at 300 nm which is attributed to the n-π* transitions of C=O. The two absorption peaks are the characteristic signals of GO. For the RGO/Ag nanomaterials, the peak of π-π* electron transition of aromatic C=C shifts from 225 nm to 250 nm because the reduced GO tends to be flat (closer to the smooth level of graphene) needing lower energy to transition. The signal at 375 nm is correspond to the Ag band. The results imply the AgNO3 was reduced to Ag, and the reduced GO was obtained at the same time.

Fig. 5 exhibits the Raman spectra of GO and RGO/Ag nanomaterials. GO occurs the D band peak at 1355 cm⁻¹ and G band peak at 1590 cm⁻¹. D peak is caused by C-C disordered vibration and characterizes the carbon atom of the sp² hybrid structure. The G band peak is due to the stretching vibration of C-C and characterizes the carbon atom of structure sp² hybrid structure. So, the peak intensity ratio (I_d/I_g) of D and G peak present structural regularity of carbon nanomaterials. Fig. 5 shows the RGO/Ag nanomaterials have the similar band, but a little red shift for D and G band peak. In addition, the I_d/I_g (0.95) of RGO/Ag nanomaterials is higher than the GO (0.92) which means that the Ag nanoparticles decrease the regularity degree of RGO. However, the C/O ratio of GRO/Ag increase compared with GO (see Fig. 5).

The oxygenic groups directly influence the stability of nanomaterials at high temperature. Thermogravimetric analysis (TGA) is a simple way to quantify the oxygenic groups of GO and RGO/Ag nanomaterials. The GO has a 12 wt% weight loss near 115 °C, evidently due to evaporation of water molecules held in the material (see Fig 6.). The second significant weight loss (26 wt% loss at 235 °C) is occurred from 180 to 235 °C of the GO. This is contributed to the loss of CO, CO2, and steam from the sample aroused by water evaporation and decomposition of labile oxygenic groups. The third weight loss (53 wt% loss at 1000 °C) is due to the decomposition of carbon skeleton of graphene oxide. Interestingly, the RGO/Ag nanomaterials lost a much smaller mass (5 wt % loss at 235 °C) over the temperature span, even only 10 wt% weight losses over the total testing temperature span. It is very likely due to a decreased amount of oxygen functional groups in the RGO/Ag nanomaterials as would be expected from the reduction process.
3.2 The fluoride ion adsorption property

With the development of modern industrialization, water source is getting worse and worse. But human requirement becomes higher and higher for the healthy environment. The increasing attention has been paid to the water treatment especially for the heavy metal and fluoride ions which is highly toxic for people health in recent years. The adsorption technique among all of the removal methods is the most perhaps adopted method due to the low cost and convenience. Nanomaterials show higher adsorption efficient than the corresponding bulk materials owing to the nano-sized effects. So, the RGO/Ag as the sorbents was used to treat the fluoride ion water. The influence of the concentration of RGO/Ag, temperature, pH and time of adsorption on the removal ratio were discussed. The concentration of RGO/Ag is considered as variate from 0.04 to 0.2 g/L with the constant of 60 °C, 20 h, and pH=7 and 10^{-5} M of the fluoride ion for the adsorption process (see Fig. 7a). With the concentration increasing of RGO/Ag, the removal ratios also are evidently improved because the more RGO/Ag bring the larger adsorption surface area to promote the faster electron transfer and obtain better adsorption capacity. But removal ratio holds around the 93.4% when the concentrations continually increase after 0.10 g/L which imply the adsorption and desorption performance of fluoride ion in water reach to the activated balance for the RGO/Ag adsorbent. So, the 0.10 g/L RGO/Ag is taken as the best content for the 10^{-5} M of the fluoride ion in water considering the cost and removal efficiency. Then, the solution pH is considered as variate from 4 to 10 with the constant of 60 °C, 20 h, 0.10 g/L of RGO/Ag and 10^{-5} M of the fluoride ion for the adsorption process to determine the removal ratio for fluoride ion in water (see Fig. 7b). As shown from the Fig. 7b, with the pH increasing (up to pH=7), the removal ratios also are gradually increase then keep the little amplitude around 98.7% from 7 to 10 for pH. The reason is that the negative RGO/Ag maybe be neutralized in acid media which decrease the removal fluoride ion efficiency. However, the increasing negative in the water improve the dispersibility of negative RGO/Ag due to charge rejection, and further promote the removal ratio. Usually, the pH is about 7 for drink water, so 7 of pH is adopted the best pH value. For the treating temperature, it can be found that the RGO/Ag obtain the best removal ratio at 60 °C from the Fig. 7c. About the treating time, removal ratio of the fluoride ion gradually increases with the prolonging treating time. However, when the adsorption time reaches 18 hours, the fluoride removal ratio reaches up to 90% and become stable after 20 h adsorption time. So we conclude that the best absorption is that the 0.10 g/L RGO/Ag, pH>7, 60 °C and 20h adsorption time, the fluoride removal ratio reaches up to 91%.

Fig. 8 (a) is distribution of pore size of GO/Ag. The pore size is about 2-11 nm indicating that GO/Ag nanomaterials is a micromesoporous material. Fig. 8 (b) is adsorption desorption curves of GO/Ag. The first steep stage of the isotherm curve is under the N\textsubscript{2} relative partial pressure region (P/P\textsubscript{0}=0.1~0.2) represents the saturated adsorption capacity of the monolayer. After a period of saturated adsorption, with the increasing of pressure, both adsorption and desorption are gradually decreased.
desorption have steep rise and fall under partial pressure region (P/P₀ ≈ 0.4–0.8), which means the multilayer adsorption. The adsorption capacity increases sharply with the P/P₀ increasing, which indicates that the pore distribution of the sample is more uniform. Fig. 8(c) and (d) were Langmuir and BET models by the physical adsorption instrument simulations, the adsorption behavior of the GO/Ag is the R² = 0.9998 by fitting the BET equation, and the fitting Langmuir equation is obtained with R² only 0.97187. The correlation of the fitted BET equation is higher than that of the Langmuir equation, which is shown that the adsorption behavior of the GO/Ag is in accordance with the BET adsorption model. The BET model indicates that the GO/Ag is mainly based on the multi-molecular layer adsorption.

Fig. 9(a) is the FTIR spectrum of RGO/Ag before and after absorption of fluoride ion. Absorption peak at 3423 cm⁻¹ shows -OH

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**Fig. 8**

(a) distribution of pore size, (b) adsorption desorption, (c) and (d) are Langmuir and BET models by the physical adsorption instrument simulations. For the adsorption behavior of the GO/Ag nanomaterials, the correlation coefficient (R²) is 0.9998 by fitting the BET equation, and the fitting Langmuir equation is obtained with R² only 0.97187.

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**Fig. 9**

(a) FTIR of RGO/Ag before (a) and after adsorption of F ions (b), (b) RGO/Ag adsorption mechanism for F ions.
stretching vibration, but the peak intensity become weaker after adsorption of fluoride ion. There are obvious peak at 1596 cm⁻¹ in the two curves, which show that they all contain the aromatic skeleton of C=C stretching vibration. The peak both with at 1346 cm⁻¹ should be assigned to the stretching vibrations of C-O indicating, oxidation of RGO/Ag after fluoride ion adsorption has been enhanced. However, the band positions are similar for RGO/Ag before and after absorption of fluoride ion. Infrared spectroscopy before and after adsorption is that RGO/Ag adsorbed F ions structure has not changed, that RGO/Ag treatment of high the mechanism of fluoride content by ion exchange, static electricity and so on. Such as Fig. 9(b) as shown fluorine ions are strongly adsorbed between GO and silver by means of static molecules.

5. Conclusion
RGO/Ag was prepared by oxidation-reduction reaction. The fluoride removal for RGO/Ag nanomaterials in water displays the best adsorption at 0.1 g/L of concentration, 60 °C of temperature and 20 h of adsorption time. The F ions in solution are quickly adsorbed on RGO/Ag nanomaterials, and multi-molecular layer adsorption of RGO/Ag is proceeded based on static electricity between RGO/Ag nanomaterials and Fions.

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Reference