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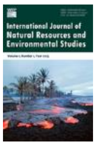

Graphene Composite Materials for Removal of Heavy Metals from Water: Progress and Prospects

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ABSTRACT

With the acceleration of the global industrialization process, heavy metal pollution has become increasingly serious. Heavy metal elements pose a grave threat to the ecological environment and human health owing to their high virulence, strong persistence, and bioaccumulation. Therefore, developing efficient and environmentally friendly water treatment technologies to remove heavy metal (HM) in water has emerged as current focus of environmental science research. Graphene has shown significant application potential in water treatment owing to its unique physical and chemical properties. In particular, graphene composites can be further improved in water treatment by combining graphene with other materials. This paper systematically combs and analyzes relevant literature in recent years and summarizes the research progress of graphene composites (GCs) in removing HMs such as lead, mercury, cadmium, chromium and arsenic from water. The application status, mechanism of action, and performance evaluation of GCs in removing HMs in water treatment are discussed in detail. Finally, the challenges and future development directions are analyzed. Valuable reference and guidance for the further development of GCs in the field of water treatment are provided.

KEYWORDS

Graphene, Composite materials, Water treatment, Heavy metals.

1. INTRODUCTION

Recently, as industrial activities have expanded unprecedentedly and urbanization has rapidly accelerated, heavy metal (HM) pollution has emerged as a pressing issue, gravely endangering both the ecological environment and human health. HMs, exemplified by lead, mercury, and cadmium, are renowned for their high toxicity, bioaccumulative nature, and resistance to degradation.

To tackle the challenge of heavy metal removal, environmental-friendly techniques have been proposed, with graphene and its composites standing out because of their unique properties. These include high specific surface area, strong adsorption capacity, and chemical stability. Graphene composites offer the added benefits of improved adsorption selectivity, stability, and regeneration, enhancing the efficiency and practicality of heavy metal removal.

2. ADSORPTION MECHANISM

Graphene and its composite materials possess the capability to effectively remove HMs from water through adsorption. The underlying adsorption mechanisms are diverse and encompass electrostatic adsorption, coordination adsorption, π-π interaction, cation-π interaction, as well as hydrophobic interaction. Notably, among these mechanisms, coordination adsorption and π-π interaction are predominant.

Graphene and its composites' adsorption of HM ions are affected by some crucial factors. These include pH level, adsorbent dosage, dwell time, initial content of HM, and coexisting ions. Understanding these factors is crucial for maximizing the efficiency of graphene-based water purification.

3. GRAPHENE COMPOSITES FOR HEAVY METAL IONS ADSORPTION IN WATER

3.1. Adsorption of Pb2+ in water

As one crutial HM, Pb2+ is sreiously toxic. Since Pb2+ is not easily degraded in the natural environment, a large amount of Pb2+-containing wastewater and exhaust gas is discharged into the atmosphere, rivers, lakes, and then introduced into the human body via the food.

Pan et al.[1] used porous mp-CA/GO (an aerogel made of calcium alginate/GO) for Pb2+ adsorption. This composite material achieved equilibrium within 40 mins during adsorption. The obtained adsorption capacity is up to 368.2 mg/g for Pb2+, as shown in Figure 1a.

In order to investigate the adsorption performance of Pb2+ on oxidized graphene and thiol-functionalized oxidized graphene, Yari et al.[2] prepared functionalized GO-G-SH on GO. They clarified and optimized the effects of time, pH, temperature, and cysteamine concentration on Pb2+ adsorption, as shown in Figure 1b.

Magnetic cobalt ferrite can also be combined with reduced graphene oxide to prepare excellent adsorbents. Zhang et al.[3] prepared CoFe2O4 rGO using a simple method. CoFe2O4 rGO could effectively adsorb Pb2+. CoFe2O4 rGO adsorbing HM ions could be easily regenerated from water under very low magnetic field gradients, which is expected to reduce water treatment costs, as shown in Figure 1c.

Graphene hydrogel can also be composited with some materials to prepare efficient adsorbents. Li et al.[4] synthesized lignosulfonic acid modified graphene hydrogel (LS-GH). It has a super large adsorption amount (1210 mg/g) for the adsorption of Pb2+. The material has large capacitance, low cost, environmental friendliness, and recyclability, making it an attractive adsorbent for large-scale wastewater purification, as shown in Figure 1d.

Hao et al.[5] proposed SiO2/GC materials. The SiO2/graphene composite material has a large adsorption amount for Pb2+ ions of 113.6 mg/g. This is much larger than that of pure SiO2 nanoparticles. This indicates that the composite is highly efficient and quickly reaches adsorption equilibrium, making it a practical and effective adsorbent for removing Pb2+ ions from various systems, as shown in Figure 1e.

Magnetic graphene oxide can also be combined with other materials to prepare adsorbents with excellent performance. Ma et al.[6]proposed magnetic GO grafted with poly (maleimide) dendrimers (GO/Fe3O4-3-PMAAM) nanocomposites. At 298 K, the obtained largest adsorption amount of GO/Fe3O4 g-G3.0 for Pb2+ is 181.4 mg/g (Figure 1f).

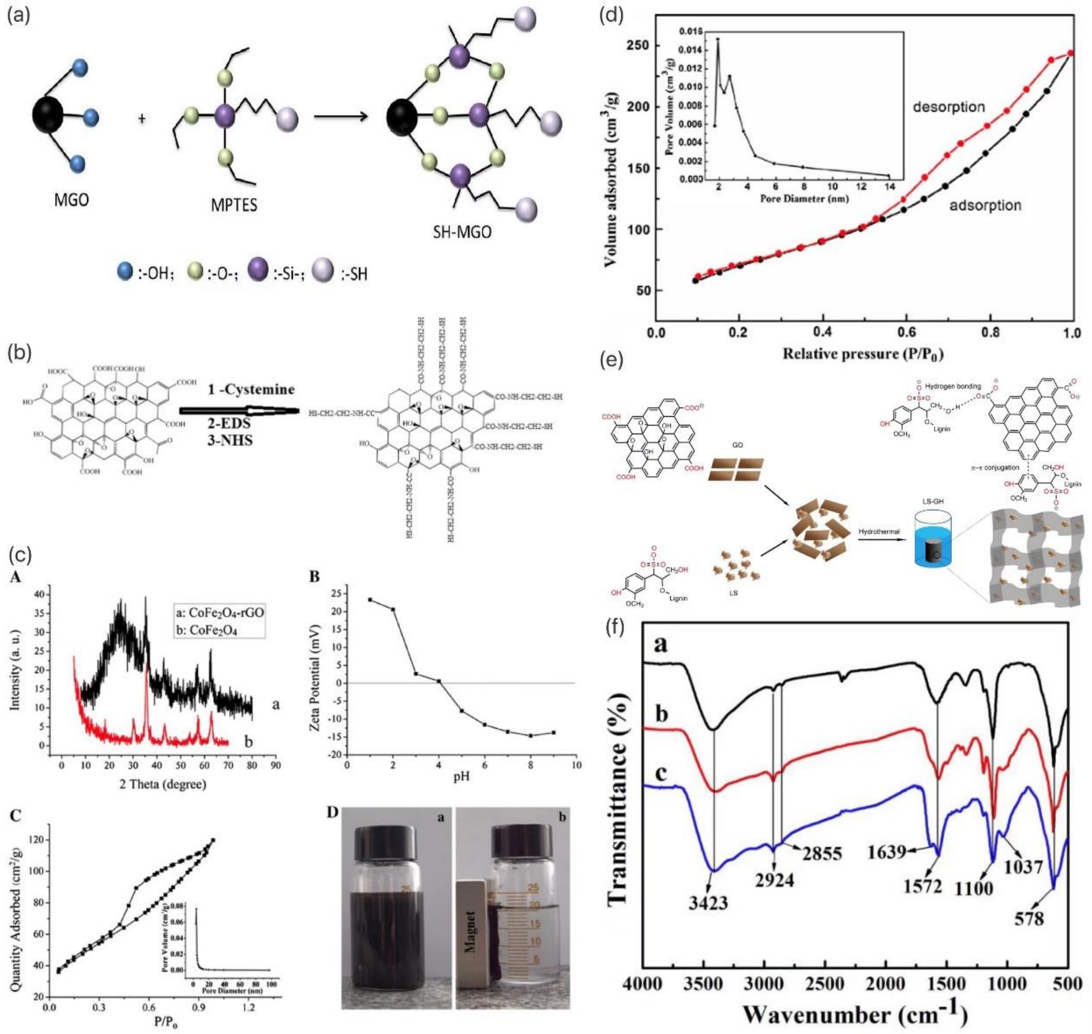

Figure 1. a: Schematic diagram of SH-MGO synthesis; b: Schematic diagram of CoFe2O4 rGO synthesis; c: Characterization of CoFe2O4-rGO (D); d: Adsorption-desorption isotherms and pores size distributions for SiO2/graphene composite; f: FT-IR spectra of GO/Fe3O4 based materials.

3.2. Adsorption of Cd2+ in water

Due to the good practical performance, Cd2+ is increasingly used in industry. However, with the expansion of its application, the pollution problem of Cd2+ wastewater is becoming increasingly serious.

The adsorption behavior of reduced GO composites modified by biosurfactants for Cd2+ in water was studied[7]. It was found that Cd2+ in water could be rapidly dislodged by TS-RGO. The π-π bond interaction led to spontaneous TS-RGO physicochemical adsorption, as shown in Figure 2a.

Dyeing wastewater has emerged as a significant source of environmental pollution owing to its complex composition and difficulty in being removed naturally. A new type of bio-nanomaterial MNMs was prepared[8]. The combined removal rate of Cd2+ and malachite green, typical pollutants in printing and dyeing wastewater, reached 80%, (Figure 2b).

To study the removal behavior of GO-based composites for Cd2+ in water, a new thiol-functionalized GO-based adsorbent SH-MGO (SH-CoFe2O4/GO) was prepared1. SH-MGO removes Cd2+ from water mainly through electrostatic interaction and chelation (complexation) reaction, as shown in Figure 2c.

Magnetic GO (MGO) was fabricated and used as an adsorbent to adsorb Cd2+ and ionic dyes such as methylene blue (MB) and orange G (OG)[9]. The obtained adsorption amount was up to 91.29 mg/g for Cd2+ (Figure 2d).

Magnetic GO was fabricated to remove HM ions[10]. The obtained MGO can be quickly separated from its aqueous solution. It shows outstanding adsorption performance for Cd2+. It has the large adsorption amount for Cd2+ being 128.2 mg/g, as shown in Figure 2e.

In order to remove Cd2+ from acidic aqueous media, Xue et al.[11] successfully prepared graphene oxide nanosheet. It has excellent Cd2+ removal ability under acidic conditions. The calculated maximum adsorption amount is about 44.64 mg/g, as shown in Figure 2f.

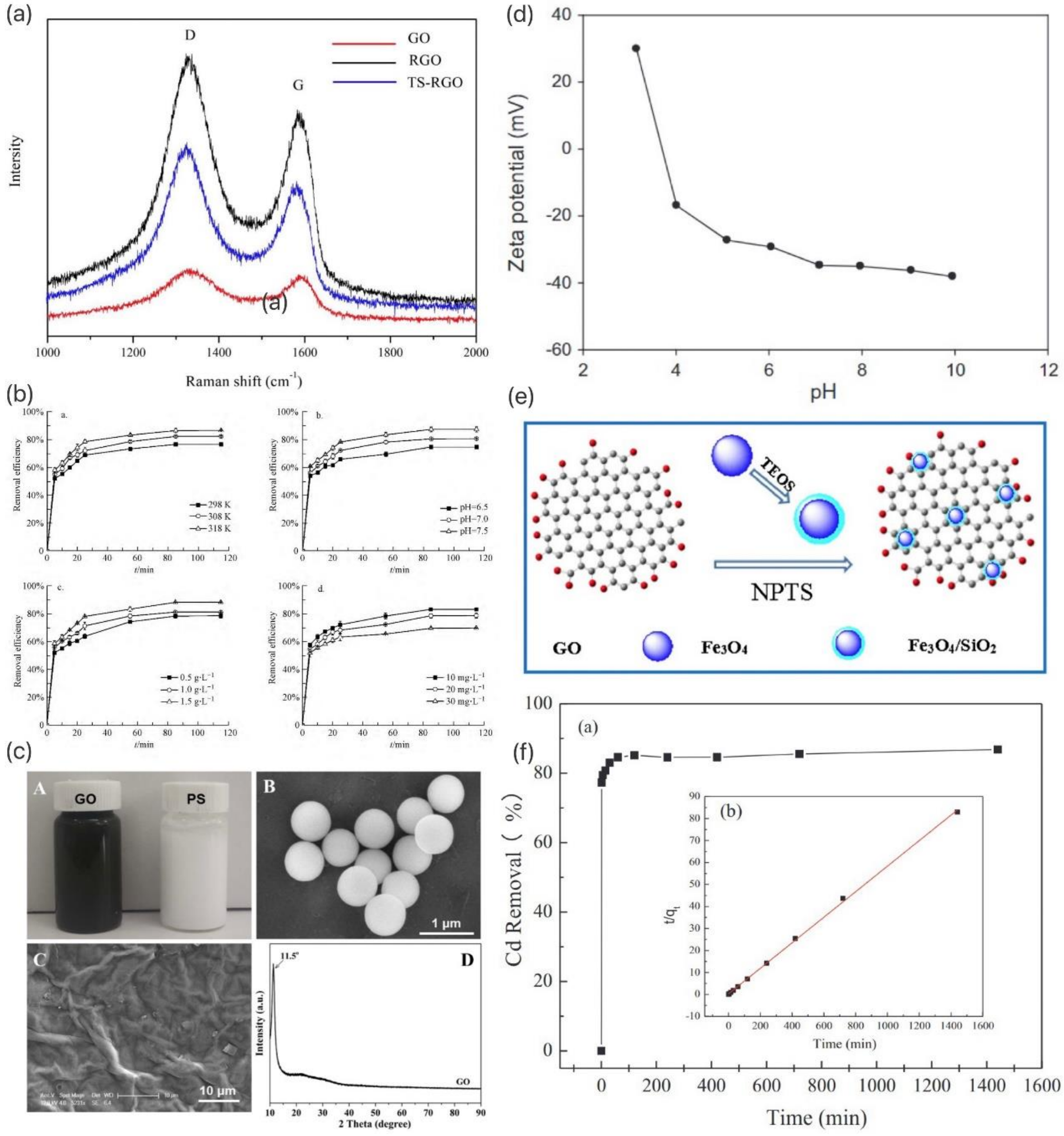

Figure 2. a: Raman spectra of GO, RGO, and TS-RGO; b: The effect of different conditions on the removal efficiency of Cd2+; c: Characterization of GO d: Zeta potential of MGO; e: Schematic diagram of Fe3O4/SiO2 GO synthesis; f: Effect of contact time on Cd2+ adsorption.

3.3. Adsorption of Hg2+ in water

Hg2+ and its compounds can bioaccumulate in the blood through the energy chain. Long-term exposure may cause damage to the nervous system and digestive system, which is extremely harmful to humans.

How to remediate HMs without causing damage to the environment has always been a challenge. A new graphene oxide/iron-manganese (GO/Fe-Mn) composite has been synthesized[12]. The data demonstrated that GO/Fe-Mn can be an eco-friendly and effective adsorbent for HM remediation, as shown in Figure 3a.

A graphene oxide/carrageenan composite hydrogel (SeCA-GH) adsorbent was prepared for the adsorption of Hg2+ in water[13]. The data showed, at 25°C, the adsorption efficiency of Hg2+ (50 g/L) on the hydrogel surface could reach 98.2%, as shown in Figure 3b.

How to achieve high selectivity in removing HM ions from wastewater has always been a difficult problem. To remove Hg2+ from wastewater, a unique silver/graphene sorbent has been synchronously synthesized[14]. The outcomes indicate that the huge surface of graphene supplies a favorable support for the silver particles. The Hg2+ removal efficiency achieves above 98%., as shown in Figure 3c.

Polyaniline/reduced graphene oxide composites were prepared by aniline polymerization[15]. The largest theoretical adsorption of Hg2+ by polyaniline/reduced graphene oxide was enhanced by 94% versus that of pure polyaniline., as shown in Figure 3d.

Poly (allyl acetoacetate)-grafted graphene oxide (GO-GAA) had been synthesized[16]. Elimination of Hg2+ from water suspension using GO-GAA as an adsorbent. It shows a higher adsorption capacity over pristine graphene oxide. The data indicated that the adsorption rate of GO-GAA could reach 95% of the maximum adsorption rate in less than 2 min, as shown in Figure 3e.

For better removal of Hg2+ from wastewater, polyacrylonitrile nanoparticles with PAN-PRGO were prepared [17]. Experiments demonstrated that the maximum adsorption of Hg2+ by HPAN-PRGO was 324.0 mg/g. At a concentration of 50 ppm, the HPAN-PRGO removed 100% of the Hg2+ with a very accelerated adsorption rate, as shown in Figure 3f.

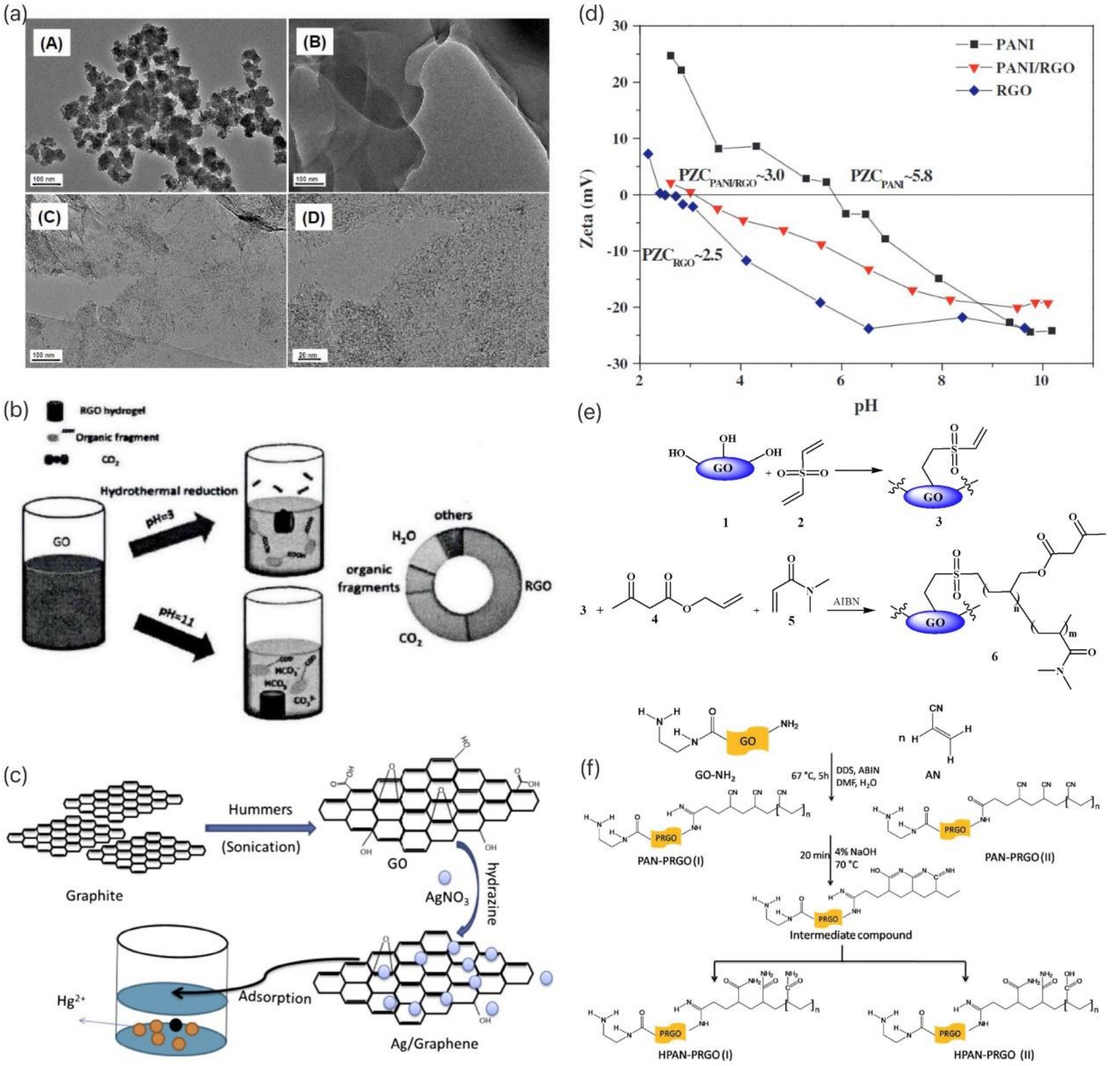

Figure 3. a: TEM images of Fe-Mn, GO and GO/Fe-Mn. b: Schematic diagram of converting GO into greenhouse gases; c: The synthesis process of silver/graphene adsorbent; d: Zeta levels of PANI, RGO and combined PANI/RGO complexes. e: The synthesis diagram of GO-GAA; f: Reaction mechanics of graphene oxide aminated with acetonitrile.

3.4. Adsorption of Cr in water

Cr exists mainly in the form of ionic compounds of Cr6+ and Cr3+ in the aquatic environment. However, the toxicity of Cr6+ is 100 times that of Cr3+. Long-term exposure to chromium-containing water and food will cause certain damage to human organs and may even induce cancer and lead to death.

Converting Cr6+ to Cr3+ can effectively reduce its toxicity to the environment. The conversion pathway of Cr6+ to Cr3+ in the application of graphene-based polymeric beads was investigated[18]. The outcome revealed that CS-PEI-GO polymer microspheres had a greater potential to absorb Cr6+ compared with CS and CS-pei microspheres, as shown in Figure 4a.

Mn doped TiO2 generated on reductive graphene oxide (rGO) was used to study photocatalytic extraction of Cr in sunlight[19]. At an original Cr6+ concentration of 20 mg/L, 97.32% of Cr was removed in 30 min and 99.02% in 60 min with sunlight irradiation., as shown in Figure 4b.

To enhance the removal rate of Cr6+ in aqueous solution, A new approach to Cr6+ removal from water using TiO2-rGO hydrogels with a three-dimensional (3D) network structure has been investigated[20]. TiO2-rGO materials demonstrate excellent sorption-photocatalytic properties. In continuous flow conditions, the sorption-photocatalytic activation of TiO2-rGO was sustained, and the Cr6+ removal rate was preserved at 100% continuously until the breaking point was attained, as shown in Figure 4c.

It is particularly difficult to eliminate HM ions from most industrial wastewater because it has been blended with stream water, making it acidic.[21] Functionalized graphene oxide was synthesized. The composites studied demonstrated an extremely high Cr6+ removal efficiency through a new mechanical pathway even at very elevated intensities, in comparison to previously reported results, as a consequence of the surface modification and the elevated protonation effect of nitrogen (present in DAP), as shown in Figure 4d.

In order to remove Cr6+ from acidic aqueous solution, a new graphene-based adsorbent (ED-RGO) was prepared[22]. ED-RGO has a higher elimination rate than other traditional adsorbents and can be extracted from suspension easily afterwards. At low pH, Cr6+ can be converted to low-toxicity Cr3+, as shown in Figure 4e.

A new sorbent for the elimination of Cr6+ was fabricated[23]. The data showed that the sorption of Cr6+ by GEC was highly correlated with pH, with the greatest magnitude of 86.17 mg/g at pH=2, as shown in Figure 4f.

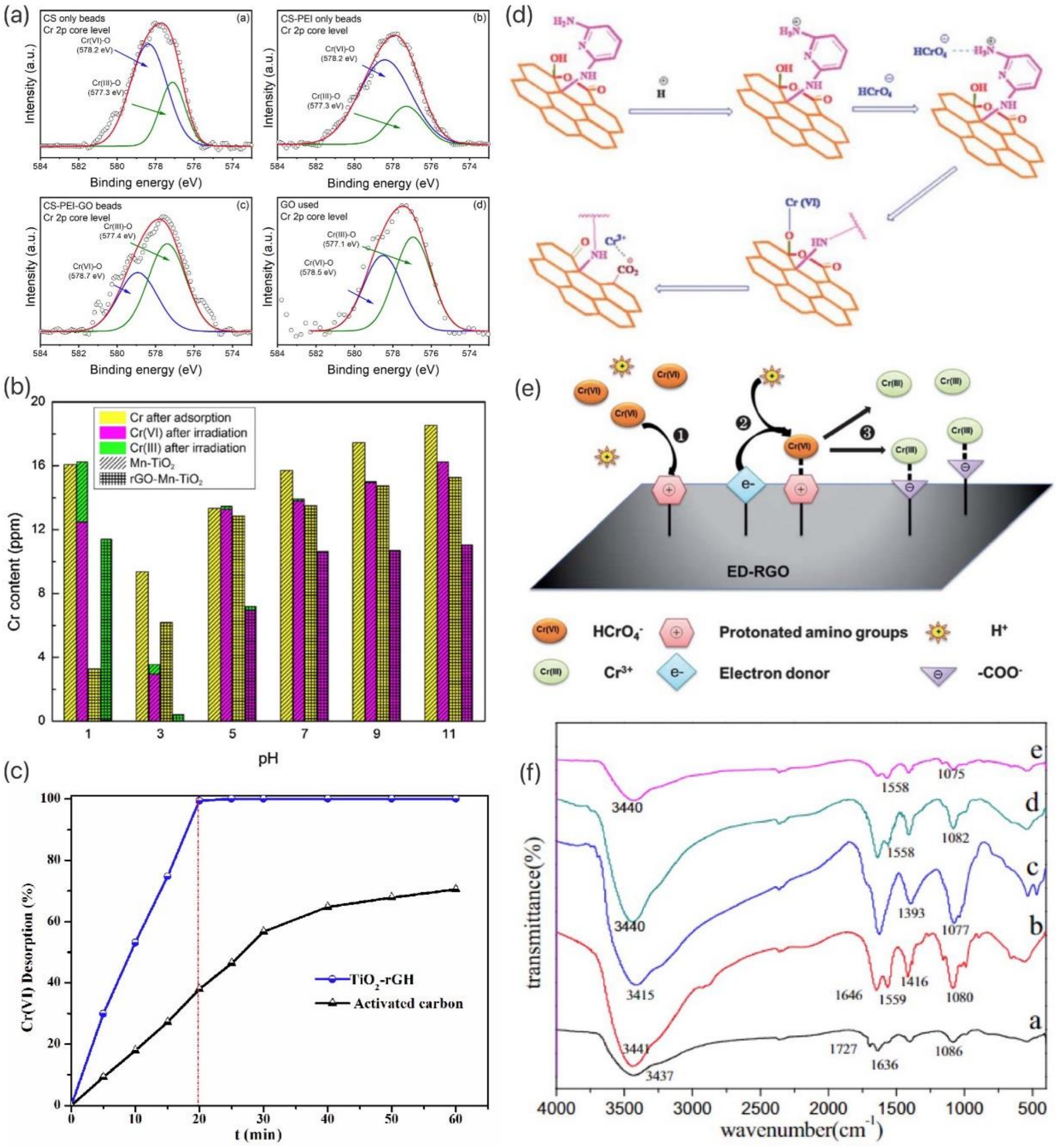

Figure 4. a: XPs spectra of CS based materials after exposition to Cr6+ solvent; b: The eliminate efficiency of Cr by different materials at different pH; c: Description of extraction effect of TiO2-rGH versus activated carbon; d: The removal mechanism of Cr6+; e: ED-RGO Proposal for a mechanism of Cr6+ removal; f: FT-IR spectra of GO, CS and GC based materials.

4. CONCLUSION AND OUTLOOK

HM elements are highly toxic, persistent and bioaccumulative, posing a critical hazard to the ecosystem and public health. Therefore, the exploitation of high-efficient and environmentally friendly water treatment technologies to remove HM pollution from water is currently a focus of scientific research on the environment. As an emerging nanomaterial, graphene shows tremendous potential for application in the field of water treatment based on its distinctive physical and chemical properties, such as high-ratio surface area, superior electrical conductivity and chemical resistance. In particular, graphene composites can be further improved by combining graphene with other materials. This paper systematically combed and analyzed the relevant literature in recent years, and summarized the progress of research on HMs removal by graphene composites. The utilization status of graphene composites in removing HMs in water treatment are discussed in detail.

Although graphene composites have made significant progress in removing heavy metals in water treatment, there are still some challenges, such as material recycling, potential environmental risks, and the economic feasibility of large-scale applications. Therefore, future research should focus on developing new efficient, environmentally friendly and economically viable graphene composites, optimizing their preparation processes, and deeply exploring their application effects and sustainability in actual water treatment scenarios. The outlook for graphene composites to remove heavy metals from water is as follows.

(1) Optimizing material design and preparation process. Future research will focus on optimizing the design and preparation process of graphene composites to further improve their efficiency and selectivity in adsorbing heavy metals. By introducing different functionalization strategies, such as the introduction of particular function blocks on the graphene surface by chemical modification, selective adaptation of specific heavy metal ions can be enhanced.

(2) Enhance the regeneration and reuse performance of materials. The regeneration and reuse performance of graphene composites after heavy metal adsorption is an important direction for future research. Developing an efficient regeneration process allows graphene composites to be reused after adsorption saturation through simple treatment, which not only reduces the treatment cost but also reduces the risk of secondary pollution.

(3) Promote practical application and industrialization. Although graphene composites have performed well in laboratory research, their application in large-scale water treatment systems remains challenging. Future work will focus on how to transform the excellent properties of these materials into practical applications and promote their industrialization. This includes the development of low-cost and efficient preparation processes, as well as integration and optimization in actual water treatment processes.

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