Novel Silanized Graphene Oxide/TiO₂ Multifunctional Nanocomposite Photocatalysts: Simultaneous Removal of Cd²⁺ and Photodegradation of Phenols under Visible Light Irradiation

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ABSTRACT: Reduced graphene oxide (RGO)-TiO₂ nanocomposites have exhibited effective photocatalytic degradation of various organic pollutants. However, their poor solubility could limit their application in water and other organic solvents. In this study, new graphene-based cross-linked ethylenediaminetetraacetic acid (EDTA)-RGO-TiO₂ (ERGT) nanocomposites were synthesized for the removal of Cd(II) and photodegradation of phenol from wastewater by surface-functionalized cross-linking heavy metal chelating agent sodium edetate (EDTA) and photocatalyst titanium dioxide. The structural properties of fabricated nanocomposites were characterized using SEM, TEM, XPS, FTIR, XRD, UV−vis, gas sorption, and Raman spectroscopy analyses. Moreover, the adsorption of Cd(II) and the degradation of phenol under different conditions were studied. The experimental results revealed that the optimal catalytic degradation and adsorption performance could be achieved at pH 5.5, and the maximum absorption ratio of cadmium ions and the degradation efficiency of phenol can reach 178.2 mg/g and 90%, respectively. The results suggested that ERGT is a potential material for the removal of threatening pollutants from wastewater.

1. INTRODUCTION

In the past few decades, large amounts of industrial wastewater containing various kinds of pollutants have been discharged directly into natural water bodies, which aggravates the crisis of the water ecosystem and endangers aquatic life and human health.¹,² These pollutants can be broadly classified into three categories, including heavy metal ions (Cr³⁺, Ni²⁺, and Cu²⁺), toxic metal ions (Cd²⁺, As³⁺, and Hg²⁺), and dye waste.³,⁴ Many toxic heavy metals and aromatics dyes are released into the natural environment from various industrial activities, such as waste streams of electroplating, mining, battery manufacturing, alloy metallurgy, pigment and plastic industries, and petroleum refining processes.⁵⁻⁷ In particular, toxic metal ions cadmium (Cd²⁺) and phenol dyes are considered as the most common toxic wastes in industries, where these are difficult to degrade, readily accumulate in the water environment, and cause extensive damage to organisms.⁸,⁹ Therefore, it is imperative to seek more effective and low-cost methods to simultaneously remove these co-pollutants.¹⁰⁻¹²

In sewage treatment, conventional methods for removing heavy metal ions are chemical precipitation,¹³ chemical reduction,¹⁴ solvent extraction separation,¹⁵ physical adsorption,¹⁶ and ion exchange.⁵,¹⁴,¹⁷ Traditional removal methods of organic substances include adsorption,¹⁷ reverse osmosis¹⁸ and ultrafiltration,³ catalytic degradation methods,⁷ and so on. These methods are less efficient due to low degradation efficiency, high cost, secondary pollution, and toxic sludge production. Recent methods such as membrane selective adsorption and advanced photocatalysis are economical and highly efficient in removing metal ions and organic pollutants from wastewater.¹⁹ Recently, several studies have shown adsorption strategies for the removal of Cd(II) and photodegradation of phenol. Huang et al. reported a simple solvothermal synthesis of magnetic nanocomposite MGL for fast adsorption of Cd(II) from aqueous solution.²⁰,²¹ Shahbazi et al. reported a simple one-step hydrothermal synthesis of TiO₂@graphene nanocomposites for photocatalytic degradation of phenol in water.²¹⁻²³

In recent years, the synergy strategy of adsorption and photocatalysis is a newly emerging technology in the field of water pollution control.²⁴,²⁵ For degrading organic pollutants, the photocatalytic oxidation treatment of TiO₂ was considered as one of the most efficient and clean methods owing to its...
nontoxic nature, low cost, excellent environment-friendly nature, high chemical stability, and photocatalytic activity. However, the photocatalytic efficiency of TiO$_2$ is significantly limited due to its wide energy band gap ($\sim$3.2 eV), which constrains light absorption in the ultraviolet region of the solar spectrum (5%), and the rapid charge-carrier recombination rate of photoproduced electron–hole pairs. The former limitation has been overcome by doping TiO$_2$ with other metals or nonmetals to reduce the energy band gap of TiO$_2$, which extends the light absorption in the visible light region. The latter issue of the rapid recombination rate can be curbed by fabricating the heterojunction of TiO$_2$ with other semiconductors (WO$_3$, C$_3$N$_4$, etc.), carbon nanotubes, graphene oxide (GO), reduced graphene oxide (RGO), and metal nanoparticles, which have proven to be effective in inhibiting the recombination rate.

As a supporting material for TiO$_2$, RGO has gained increasing attention to increase the efficiency of TiO$_2$ in photocatalytic water treatment due to its large surface area, excellent charge carrier mobility, high transparency, tunable band gap, and easily changeable surface properties. It has been proven that combining TiO$_2$ with RGO is an effective way for reducing the band gap and the recombination of photoproduced electron–hole pairs to improve the photocatalytic activities under visible light. RGO-TiO$_2$ nanocomposites can increase charge transportation and extend the light absorption region but reduce the adsorption of pollutants and solubility in water or organic solvents compared to GO-TiO$_2$, which may limit its application in waste treatment. Several techniques have been developed to improve the adsorption ability and solubility of RGO-TiO$_2$. Chelating agents such as ethylenediaminetetraacetic acid (EDTA), diethylenetriamine pentaacetic (DTPA), and ethylene glycol tetraacetic acid (EGTA) have recently been reported as green and economic agents for EDTA-modified chitosan or GO via the chemical cross-linking technique. EDTA was not only low cost and environment-friendly compared to other cross-linkers but also functional groups of cross-linkers used in the chelating process of metal ions. EDTA is cross-linked to the GO surface through the electron transfer process and photocatalytic enhancement.

Herein, we report the design and fabrication of the novel cross-linked EDTA-RGO-TiO$_2$ (ERGT) nanocomposite with excellent adsorption capability for metal ions and photocatalytic ability in aqueous solution through a simple silanization modification strategy. Its characteristics (including structure, morphology, and chemical composition) were investigated in detail. Phenol was used as a probe molecule to determine the photocatalytic activity over ERGT photocatalysts. Interestingly, it was found that the photocatalytic activity of ERGT nanocomposites with optimized RGO content was high than that of pure RGO-TiO$_2$ and GO-TiO$_2$. Moreover, the synergic enhancement effect on photoactivity and photostability of ERGT was found when phenol and cadmium ions coexisted in water. It was also revealed that EDTA functional groups can not only improve the absorption ability of cadmium ions but also increase the photocatalytic activity of phenol molecules. Our result suggests that the ERGT nanocomposite has great potential for simultaneous removal of cadmium ion and phenol pollutants from wastewater.

2. RESULTS AND DISCUSSION

2.1. Characterization of Synthesized Materials.

2.1.1. TEM and SEM Analyses. The interior and superficial morphologies of the synthesized pure GO and ERGT were determined by SEM and TEM. The SEM image of GO nanosheets shown in Figure 1a exhibited irregular and wrinkled morphology. The prepared GO was found to be transparent, which established the two-dimensional nanosheets of GO. The SEM image of ERGT showed that the composite material adheres to the surface of GO, forming agglomerated smaller reunions (Figure 1b). To further understand the crystal morphology, we conducted TEM and EDX analyses on representative cross-sectional areas. From the TEM images of ERGT composites (Figure 1c,d), it can be observed that the RGO is partly covered by a large amount of well-crystallized TiO$_2$ nanoparticles with a size of 10–20 nm. From Figure 1d, the lattice fringe of RGO can be clearly identified. This result confirms that TiO$_2$ nanoparticles are successfully loaded onto the RGO sheets. It is also observed from Figure 1d that the lattice fringes with the interplanar spacing of 0.269 and 0.212 nm are perfectly equal to the lattice constants of the (111) and (200) crystal planes of anatase-phase TiO$_2$, respectively. Further observation of the TEM results clearly reveals that the interfaces between TiO$_2$ and RGO have been confirmed with the formation of a close interface connection, which is responsible for the rapid charge separation in the electron transfer process and photocatalytic enhancement.
The major element compositions of the photocatalysts were further revealed by EDX measurements. As shown in Figure 2, the main signals of C, N, O, Ti, and Si elements are simultaneously observed in the spectra of ERGT composites, offering strong evidence for the existence of all these elements. Figure 2 indicates that C, N, O, Ti, and Si elements are uniformly distributed throughout the sample, which signifies the existence of EDTA and TiO$_2$-RGO in the nanocomposites. SEM, TEM, elemental mapping, and EDX confirmed the successful fabrication of EDTA-RGO-TiO$_2$ nanocomposites.

2.1.2. FTIR Analysis. The infrared spectra obtained from the synthesized TiO$_2$, GO, RGO, and EDTA-RGO-TiO$_2$ composites with varying concentrations of TiO$_2$ are shown in Figure 3a. The two observed peaks situated at 1635 and 3432 cm$^{-1}$ correspond to the functional groups: $\text{−OH}$ bending and stretching vibrations of the adsorbed water molecules from the $\text{−OH}$ group, respectively. The spectrum of GO composites showed broad absorption peaks at 3425, 1630, and 1210 cm$^{-1}$, which were attributed to the O$\text{−H}$ stretching vibration, carboxyl C$\equiv$O stretching, and aromatic C$\equiv$C stretching, respectively.

For the EDTA-RGO-TiO$_2$ nanocomposites, the peaks assigned in the range of 750−1000, 1200−1500, and 1600−1750 cm$^{-1}$ were due to C$\equiv$O stretching vibration, carboxyl C$\equiv$O stretching, and aromatic C$\equiv$C bending vibrations, respectively.

The peaks at 500−1000 cm$^{-1}$ were a result of the combination of Ti$\equiv$O−C and Ti$\equiv$O−Ti vibrations. The Ti$\equiv$O−C vibration showed that there was strong bonding between GO and TiO$_2$. The peaks located between 1000 and 1100 cm$^{-1}$ could be ascribed to the modification of Si$\equiv$O bending vibrations. In addition, no peak of alkoxy residues confirmed the absence of impurities in the nanocomposite after calcination.

2.1.3. XRD Analysis. The crystal structure of the synthesized nanocomposites was evaluated by XRD. It has been reported that crystalline materials have more effective catalytic properties than amorphous materials. The XRD patterns of GO, TiO$_2$, and ERGT nanocomposites (with varying concentrations of TiO$_2$) are shown in Figure 3b. We can infer that they all are crystalline according to their detailed corresponding peaks shown in Figure 3b. The peaks observed at $2\theta = 25.4$, 38.1, 48.0, 54.5, and 62.8$^\circ$ are consistent with the anatase phase of TiO$_2$ and correspond to (101), (004), (002), (105), and (204) crystal faces, respectively. The XRD peak of the GO sheet shown at $2\theta = 10.58^\circ$ with the d-spacing is 0.85 nm, which is consistent with the (002) plane. Due to the reduction of GO during the reaction, no characteristic lamella peaks of GO are observed in ERGT nanocomposites. The possible reason is the relatively uniform dispersion of GO on the surface of titanium dioxide in the composite.

2.1.4. Raman Spectroscopy Analysis. The effect of variation in the RGO/TiO$_2$ weight ratio on the ordered and disordered crystal lattice structure of the synthesized nanocomposites was investigated via Raman spectroscopy. The Raman spectra of GO and ERGT nanomaterials with different weight ratios (TiO$_2$-1, 5, and 10 wt %) are shown in Figure 4 with the range of 0−4000 cm$^{-1}$ wavenumber.
The peaks of ERGT nanocomposites around 399.5, 526.1, and 652.7 cm$^{-1}$ were obtained from $E_{g1}$, $A_{1g}$ + $B_{1g}(2)$, and $E_{g1}$, which was found to match well with the anatase phase of TiO$_2$. The abovementioned observation confirmed that the anatase phase was dominant and correlated with XRD results. The Raman spectra of GO sheets showed two distinct characteristic bands in Figure 4a, D band (1350 cm$^{-1}$, which may arise due to the vibration of carbon atom sp$^2$) and G band (1598 cm$^{-1}$, which was produced by stretching between sp$^2$ hybrid carbon–carbon bonds). The ERGT nanocomposite spectra displayed peaks situated at 1380 and 1620 cm$^{-1}$ compared to D and G bands of GO sheets, respectively. The relative intensity of $I_D/I_G$ is a good indication to reflect the degree of reduction in GO. For the ERGT nanocomposites with different weight ratios ($I_D/I_G$ of Ti-1, 5, and 10% is 0.88, 0.67, and 0.74, respectively) and GO ($I_D/I_G$ is 0.98), the intensity ratio of $I_D/I_G$ decreases from 0.98 (GO) to 0.67 (ERGT-Ti-5%), indicating that the level of reduction is enhanced with the amount of TiO$_2$. This signifies a strong interaction between TiO$_2$ and GO sheets, and the ERGT nanocomposite can react better with the reactants.

2.1.5. Gas Sorption Surface Area Analysis. The gas sorption surface area provides an accurate measure of the surface area of the synthesized nanocomposites. In general, a large surface area could offer more active adsorption and catalytic sites for surface redox reaction, thus inducing higher photoactivity and absorbability. Therefore, nitrogen adsorption–desorption was employed to evaluate the effect of salinizing RGO-TiO$_2$ and GO sheets on the gas sorption surface area, pore size, and volume of synthesized samples (Table 1).

The gas sorption surface area of pure TiO$_2$ was determined as 82.3 m$^2$/g, the average pore volume was 5.5 nm, and the total pore volume was 0.113 cm$^3$/g$^{-1}$. The ERGT nanoparticles exhibited a larger pore volume (0.123–0.133 cm$^3$/g$^{-1}$). The gas sorption surface area of 143.2 m$^2$/g of ERGT (5% Ti) was 1.75 times higher than that of the pure TiO$_2$ (82.3 m$^2$/g) and was the largest among those of RGO-TiO$_2$ (5% Ti) (135.2 m$^2$/g), ERGT (10% Ti) (126.7 m$^2$/g), and RGO-TiO$_2$ (10% Ti) (112.3 m$^2$/g). Therefore, salinizing RGO-TiO$_2$ (5% Ti) has the largest gas sorption surface area, which was ascribed to its largest pore volume compared with the other samples. The gas sorption results revealed that EDTA salinizing RGO-TiO$_2$ and increasing the Ti content up to 5% in ERGT improved the surface area, which might enhance the photocatalysis of the ERGT due to the enhanced adsorption.

2.1.6. XPS Analysis. The surface chemical compositions and the interaction between the three components (Ti, O, and C)
of ERGT were studied using XPS analysis, and the results are shown in Figure 5. The full-scan XPS spectrum of ERGT revealed the presence of C, O, Ti, and Si (Figure 5a). The binding energies of O 1s, Ti 2p, C 1s, and Si 2p in the EDTA-RGO-TiO2 nanocomposites were located at 529.6, 461.1, 284.8, and 100.6 eV, respectively. The C 1s spectrum showed two main forms of C bonds located at 284.8 and 287.9 eV, which were related to C–C and C=O groups, respectively (Figure 5c).55 An intense O 1s peak at 529.6 eV was related to the Ti–O–Ti peak, and a broad and weak O 1s peak at 531.5 eV was related to the −OH group on the ERGT nanocomposite surface (Figure 5b).56 The binding energy peak of the Ti 2p spectrum was observed around 464.1 and 458.4 eV of pure TiO2 (Figure 5e) and 463.7 and 457.9 eV of ERGT (Figure 5f), which was due to the strong signal of C–C and C=O bonding, respectively. The results indicated that titanium dioxide and GO are connected in a stable Ti–O–C bonding form. The Si 2p spectrum showed a peak position located at 100.6 eV,57 which was related to Si–C or Si–O–C groups (Figure 5d). Therefore, it can be fully demonstrated that TiO2 and EDTA are successively attached to the GO surface, and the ERGT composite material is successfully synthesized.

2.1.7. UV−Vis Analysis. To study the reasons for the improvement of photocatalytic performance of ERGT materials, we need to know the difference between pure titanium dioxide and composite materials. The UV−vis spectrometer analysis revealed that the properties of the composite material changed greatly in two aspects. As shown in Figure 6a, the reduced band gap, moving toward visible light, increased the absorption of visible light, and Figure 6b showed reduced conformance of carriers. The UV−vis spectroscopy study confirmed that the band gap energy was 3.29 eV for TiO2 and 3.09, 3.04, and 2.98 eV for ERGT (1 wt % Ti), ERGT (10 wt % Ti), and ERGT (5 wt % Ti) nanocomposites, respectively. The band gap energies were found to decrease upon increasing the Ti concentration up to 10 wt %, which was mainly affected by visible light above 400 nm.57 Moreover, the ERGT nanocomposite material with a Ti content ratio of 5 wt % has a band gap energy of 2.98 eV, which can better utilize visible light. Also, the band gap energy reduction was due to the formation of the Ti–O–C bond, which further improves the utilization of visible light and reduces the rate of energy band recombination.48,58

2.2. Photocatalytic Activity. 2.2.1. Effect of Different Light Conditions on Degradation Efficiency. As a typical aromatic dye frequently detected in wastewater, phenol was selected as the model pollutant to first evaluate the photocatalytic degradation performance of ERGT under the UV−visible light condition. Before examination, it is necessary to determine whether ERGT samples can remove phenols by adsorption in dark conditions. As shown in Figure 7, when ERGT is added alone to phenol solution, only a small amount of phenols can be removed under dark conditions, suggesting that the ERGT only provides a weak affinity to phenols. Similar results were observed in previous research.59

To investigate the effect of the loading variation weight of TiO2 on ERGT toward its photocatalytic performance, Figure 7 shows the profile of photocatalytic degradation of phenols for pure TiO2, GO-TiO2, RGO-TiO2, and ERGT nanocomposites under UV and visible light conditions. It is evident that ERGT (5 wt %) shows better photocatalytic activity compared to pure TiO2, GO-TiO2, and RGO-TiO2 under UV or visible light conditions. We can observe that as the weight ratio of Ti is increased, the photocatalytic efficiency increases until the value of Ti reaches 5 wt %. With the increasing amount of Ti (ERGT 10 wt %), the photocatalytic activity starts to decline, owing to the decrease of the BET surface area and the weakness of the heterojunction between EDTA-RGO and TiO2. This implies that ERGT (5 wt %) with a Ti weight ratio of 5% shows the most suitable scale that assists in enhancing the photocatalytic performance by 3.2 times compared to pure TiO2.

Figure 7b,d shows the phenol photodegradation rate as a function of irradiation time for pure TiO2, TiO2-GO, TiO2-RGO, and various TiO2 loaded ERGT photocatalysts. Based on the previous studies,60 the photodegradation of dye molecules could correspond to a pseudo-first-order kinetic equation, which is well-known for the photocatalytic
Figure 5. (a) Full-scan XPS spectra of ERGT; (b-f) high-resolution XPS spectra of O 1s (b), C 1s (c), Si 2p (d), and Ti 2p (e,f) core levels for ERGT.

Figure 6. (a) UV–vis diffuse reflectance spectra and (b) band gap energy of TiO$_2$ and ERGT nanocomposites.
degradation of several dye molecules using a semiconductor photocatalyst. To quantitatively describe the difference between ERGT and the other composites, the most common rate law, pseudo-first-order kinetic equation, was adopted as follows

\[ \ln \left( \frac{c_t}{c_0} \right) = kt \]  

where \( c_0 \) and \( c_t \) represent the concentrations of phenols at the beginning and time \( t \), \( t \) is the irradiation time, and \( k \) is the photodegradation rate constant, which was evaluated from a linear fit to the experimental data as given in Figure 7b,d. All curves were nearly linear, revealing that phenol degradation conforms to the pseudo-first-order kinetics. The photodegradation rate listed in Table 2 revealed that ERGT 5% was 9 times, 2.8 times, 1.5 times, and 1.4 times higher compared to the pure TiO2, GO-TiO2, RGO-TiO2, and ERGT 10 wt % in light conditions, respectively, signifying that ERGT 5% showed higher photocatalytic efficiency.

The degradation rate of pure TiO2 reached 54.1% under ultraviolet light. Under visible light, it only reached 22.3%, but the catalytic performance of ERGT nanocomposites with different TiO2 contents was greatly improved. It can be inferred that the catalyst for the photocatalytic reaction of photoelectrons is TiO2, and GO and EDTA act as cocatalysts.61 The catalytic efficiency of GO-TiO2 and RGO-TiO2 is quite different. The reason is that after the reduction of

Table 2. Measured Band gap Energy and Degradation Percentage of Phenol under Light Irradiation

| sample     | band gap (eV) | visible light | ultraviolet light |
|------------|---------------|---------------|-------------------|
|            | degradation (%) | \( K \) (min\(^{-1}\)) | degradation (%) | \( K \) (min\(^{-1}\)) |
| TiO2       | 3.26          | 22.3          | 0.0012            | 54.1               | 0.0039 |
| GO-TiO2    | 3.22          | 54.4          | 0.0039            | 59.2               | 0.0041 |
| RGO-TiO2   | 3.01          | 80.3          | 0.0074            | 63.2               | 0.0061 |
| ERGT (1%)  | 3.09          | 80.2          | 0.0070            | 64.9               | 0.0065 |
| ERGT (5%)  | 2.98          | 90.1          | 0.0108            | 72.3               | 0.0073 |
| ERGT (10%) | 3.04          | 82.4          | 0.0078            | 69.1               | 0.0068 |

Figure 7. (a) Photodegradation and (b) kinetic photodegradation of 100 mg/L phenol under ultraviolet light; (c) photodegradation and (d) kinetic photodegradation of 100 mg/L phenol under visible light for the pure GO, TiO2, GO-TiO2, RGO-TiO2, ERGT-1, ERGT-5, and ERGT-10 nanoparticles.
GO, the interface charge separation is improved. GO has a negative charge due to the surface functional group, which affects TiO₂. Compared with other various materials, ERGT (5 wt %) exhibited excellent catalytic performance and its degradation rate reached 90.1%, which is caused by charge transfer between nanocomposite materials and synergistically enhanced the catalytic performance.

2.2.2. Effect of Different Concentrations of Phenols on Degradation Efficiency. The effect of different phenol concentrations on the photocatalytic performance of the ERGT-5 nanoparticle was investigated. Figure 8a shows the profile of photocatalytic degradation for three different concentrations of phenol (100, 200, and 300 mg/L) under visible light for ERGT-5 nanoparticles.

![Figure 8](image)

**Figure 8.** (a) Photodegradation and (b) kinetic photodegradation of different concentrations of phenol (100, 200, and 300 mg/L) under visible light for ERGT-5 nanoparticles.

In 300 mg/L phenol solution, the k value for phenol degradation by ERGT-5% was estimated to be 0.658 h⁻¹, which is 1.1 times and 1.03 times higher compared to that of 100 and 200 mg/L phenol, respectively. The higher degradation activity of ERGT-5 in high concentration might be ascribed to the adsorption amount of phenol on the surface of nanoparticles increasing to enhance the photocatalytic efficiency of ERGT nanoparticles in the high concentration phenol solution. Moreover, in comparison with other heterogeneous catalysts previously reported in the literature, ERGT-5 also exhibits a much faster rate constant. These comparisons validate that ERGT-5 is a highly promising catalyst to degrade phenols with high efficiency.

2.3. Optimization of Adsorption Conditions. The adsorption conditions, such as cadmium ion concentration, initial solution pH, and contact time, that resulted in the optimal Cd²⁺ adsorption were investigated. The effects of different adsorbents (RGO-TiO₂, ERGT-1 wt %, ERGT-5 wt %, and ERGT-10 wt %) at varying concentrations (10–100 mg/L) on the Cd²⁺ removal are illustrated in Figure 9. As shown in Figure 9a, the adsorption efficiency of the ERGT-5 nanocomposite was not only higher than those of the ERGT-10 and ERGT-1 nanocomposites but also significantly higher than that of the RGO-TiO₂ nanocomposite. With the increase of the ERGT-5 amount, the adsorption capacity was also increased rapidly, and then, it reached equilibrium with the dosage at 178.2 mg/g. In the following experiments, 50 mg/L was selected as the optimal dosage. In addition, the removal rate of the silanized RGO-TiO₂ was twice that of RGO-TiO₂. The results demonstrated that silanized RGO-TiO₂ dramatically enhanced the adsorption performance of heavy metals.

![Figure 9](image)

**Figure 9.** (a) Adsorption of 100 mg/L Cd²⁺ under visible light for RGO-TiO₂, ERGT-1, ERGT-5, and ERGT-10 under the same conditions; (b) equilibrium adsorption capacity of ERGT-5 under different pH effects.
Table 3. Calculated Parameters of the Kinetic and Isotherm Models for the Adsorption of Cd²⁺ on the ERGT-5 wt %

| model                        | parameter | 15   | 30   | 50   | 100  |
|------------------------------|-----------|------|------|------|------|
| Pseudo-first-order equation  | $q_{exp}$ (mg/g) | 79.87 | 110.7 | 116.8 |      |
|                              | $q_{calc}$ (mg/g) | 9.980 | 31.72 | 12.98 |      |
|                              | $K_t$ (1/min) | 0.024 | 0.072 | 0.122 |      |
|                              | $R^2$       | 0.398 | 0.892 | 0.995 |      |
| Pseudo-second-order equation | $q_{calc}$ (mg/g) | 100.02 | 110.1 | 115.3 |      |
|                              | $K_l$ (g/(mg-min)) | 0.010 | 0.048 | 0.049 |      |
|                              | $R^2$       | 0.999 | 0.999 | 0.998 |      |
| Langmuir model               | $q_m$ (mg/g) | 178.2 |      |      |      |
|                              | $K_l$ (mg)  | 1.568 |      |      |      |
|                              | $R^2$       | 0.994 |      |      |      |
| Freundlich model             | $K_f$       | 63.63 |      |      |      |
|                              | $N$         | 6.673 |      |      |      |
|                              | $R^2$       | 0.900 |      |      |      |

The effect of initial solution pH on the adsorption capacity of ERGT-5 for Cd²⁺ is shown in Figure 9b. As the pH increased, the adsorption efficiency of cadmium ions significantly enhanced and reached equilibrium when the pH was about 5. The initial solution pH values of cadmium ions (pH = 5–6) were equal to the balanced pH values approximately; therefore, there was no need to change the solution pH during the adsorption.

The effect of the contact time on the adsorption capacity of ERGT-5% is shown in Figure 9a. The adsorption equilibrium time and amount under different concentrations of cadmium ions were investigated. The adsorption capacity increased significantly at first and then tended toward equilibrium at 0 min for Cd²⁺. Moreover, when the contact times were 90 and 120 min, the removal ratio of ERGT-5% reached 90 and 98%, respectively. Then, the contact time of 120 min for the ERGT-5 was selected in the following adsorption experiment.

2.4. Adsorption Kinetics and Isotherms. Based on the optimization of adsorption conditions for Cd²⁺, it is necessary to investigate the adsorption kinetics and isotherms for an adsorption process. In this work, the adsorption data were analyzed by pseudo-first-order (2), pseudo-second-order kinetic eq 3, the Langmuir (4), and Freundlich isotherm models (5). The model equations are as follows

\[
\ln(q_e - q_t) = \ln q_e - k_1 t
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right) t
\]

\[
\frac{C_e}{q_e} = \frac{1}{k_1 q_m} + \frac{C_e}{q_m}
\]

\[
\ln q_e = \ln k_2 + \frac{1}{n} \ln C_e
\]

where $q_e$ and $q_t$ (mg/g) are adsorbed amounts of Cd²⁺ at time t (min) and equilibrium, respectively, $q_m$ (mg/g) is the maximum sorption capacity of ERGT-5, $k_1$ (L/min) and $k_2$ [g/(mg-min)] are the rate constants of the pseudo-first-order and pseudo-second-order kinetic models, respectively, $C_e$ (mg/L) is the equilibrium concentration of adsorbates in aqueous solution, and the parameters $k_l$ and $L/n$ are related to the equilibrium constant of the Freundlich isotherm model.

The results are shown in Table 3 and Figure 10a,b. The adsorption of Cd²⁺ onto the ERGT-5 fit the pseudo-second-order kinetic equation well compared with the pseudo-first-order equation because the correlation coefficients ($R^2$) were all above 0.99. Furthermore, the model fitting adsorption capacities ($q_{calc}$) obtained from the pseudo-second-order equation were in good agreement with the experimental value ($q_{exp}$). The result indicated that the adsorption process of Cd²⁺ was chemisorbed by the ERGT-5, and the valency forces might be primarily the force of the adsorption process between Cd²⁺ and the ERGT by sharing electrons.

The adsorption isotherms of the ERGT-5 for Cd²⁺ were performed with 100 mg/L ERGT-5 in 150 min of adsorption time and initial pH 6.0. As shown in Table 3 and Figure 10c, the $R^2$ value of the Langmuir model was higher than that of the Freundlich model. This indicated that the adsorption process fitted well to the Langmuir model. The maximum adsorption capacity ($q_m$) of the ERGT-5% calculated from the fitting model was 178.2 mg/g. As presented in Table 3, the adsorption capacities of ERGT-5% were higher than the other adsorbents in the literature.

2.5. Synergistic Removal of Cd²⁺ and Photodegradation of Phenol. The synergistic effect of adsorption of cadmium ions and subsequent photocatalytic degradation of phenol through ERGT-5 samples was investigated under visible light irradiation. Figure 11a shows the adsorption isotherm curve for simultaneous removal of phenol dyes and cadmium ions under visible light irradiation. Cd²⁺ ions are added into the phenol solution, and the concentration of Cd²⁺ by ICP spectrometry is examined during the photocatalytic reaction. During this reaction process, the concentration of Cd²⁺ ions is fixed at 100 mg/L and mixed with phenol (100 mg/L) solution. As shown in Figure 11b, the RGO-TiO₂ sample shows a very low adsorption capacity of Cd²⁺ ions of 78.2 mg/g. However, the silanization-treated ERGT-5 sample shows higher adsorption capacity compared to RGO-TiO₂. This high adsorption capacity indicated that the silanized surface of RGO-TiO₂ may have a great influence on the absorbability of photocatalyst nanocomposites. Figure 11a also shows that the equilibrium adsorption amount did not significantly change in Cd²⁺ and phenol mixing solution and single Cd²⁺ solution.
also shows that the phenol degradation degree increased with the Cd²⁺ concentration up to 50 mg/L in mixed solution and then decreased with further increase of the concentration of Cd²⁺ in solution, showing the maximum degradation degree of 92.5% in 50 mg/L Cd²⁺ ions under visible light irradiation. However, ERGT-5 does not show any photocatalytic activity under dark conditions. The result indicated that the photodegradation of phenol by ERGT-5 was boosted by visible light. To further accurately evaluate the photocatalytic activity at different concentrations of Cd²⁺ solutions, the slopes of each plot were calculated and the photodegradation rate constants (k) were obtained, as shown in Figure 11c. The reaction kinetics of photodegradation of phenol was fitted with the first-order reaction model. Figure 11c shows the synergistic effect of Cd²⁺ ion concentration on photocatalytic degradation of phenols by ERGT-5. The concentration of Cd²⁺ ions changes according to the fixed concentration of phenol (100 mg/L) solution during the photocatalytic reaction. The rate constant of ERGT-5 was improved after adding the Cd²⁺ ions into the phenol solution. In 50 mg/L Cd²⁺ ion solution, the k value for photodegradation of phenol by ERGT-5 reached 0.908 h⁻¹, which is 1.5 times and 1.2 times higher compared to that in 0 and 100 mg/L Cd²⁺ ion solution, respectively. This result indicated that the photocatalytic activity of ERGT-5 was remarkably enhanced by the adsorption of Cd²⁺ ions on the surface of nanocomposites.

The photodegradation efficiency of the photocatalyst highly depends on photoexcited charge carriers in the spatially separated localized catalytic sites. The efficiency of photo-generated charge separation over ERGT-5 was enhanced due to the surface of silanized ERGT adsorbed Cd²⁺ ions. The Cd²⁺ ions are absorbed and then deposited on the surface of ERGT-5 samples by photoreduction during the photocatalytic reaction. The photoreduction process of Cd²⁺ ions on the surface of silanized RGO-TiO₂ is similar to the previously reported work. The Cd²⁺ ions adsorbed on the surface of ERGT-5 could be photoreduced in a sequential two-electron transfer reaction from the carbonyl group bridges of Ti and Cd²⁺ ions (Ti−O−C−O−Cd) for rapid and efficient transfer of photoelectrons. Meanwhile, the metallic Cd increased the hydroxyl group during the photoreduction process.

The mechanism of action is that ERGT-5 nanoparticles accept electrons to promote charge separation. Under the excitation of light, the spectral band absorbs photoelectrons and forms electron holes (e⁻/h⁺). The possible reason is shown in Figure 12. The e⁻/h⁺ pair reacts with the adsorbed O₂ and OH⁻ to form hydroxyl radicals (•OH) and oxygen radicals (•O₂⁻), which in turn leads to the degradation of phenol because both •OH and •O₂⁻ have strong oxidizing properties. In the ERGT-5 nanoparticles, EDTA functional groups are connected to the RGO-TiO₂ interfaces to make ERGT-5 like a “hand” and “grab” the pollutants in the experimental sewage and then adsorb the pollutants (Cd²⁺ and phenol) on the surface of the material. As the reaction proceeds and the adsorption is also carried out simultaneously, part of the Cd²⁺ ions acts on the surface of titanium dioxide and GO to form the carbonyl group bridges of Ti and Cd²⁺ ions (Ti−O−C−O−Cd) as an activation region for rapid and efficient transfer of photoelectrons, and promotes subsequent rapid surface photocatalytic reactions. Finally, most of the phenol adsorbed on the surface of the material is degraded and converted into CO₂ and H₂O, and Cd²⁺ is reduced to elemental metallic Cd.

Figure 10. (a) Effect of the contact time on the adsorption of Cd²⁺ by ERGT-5. (b) Linear fit of pseudo-second-order kinetic equation for the adsorption of Cd²⁺ on ERGT-5; the initial concentrations of Cd were 15, 50, and 100 mg/L; pH = 5.5. (c) Adsorption isotherms of Cd²⁺ on the ERGT-5, fitted by Langmuir models; temperature: 25⁰C; adsorbent dosage: 1 g/L.
3. CONCLUSIONS

In this study, we studied the simultaneous removal of chromium ions and photodegradation of phenols by ERGT nanocomposites. The serial silanized RGO-TiO$_2$ nanocomposites were synthesized by EDTA-silanized and hydrothermal methods. The 5 wt % Ti in ERGT nanocomposites shows the best photocatalytic performance. Moreover, ERGT-5 wt % showed higher photocatalytic activity in simultaneous removal of chromium ions and photodegradation of phenols because of the synergistic effect of chromium ion adsorption on the surface of ERGT-5 wt %. The result suggests that the synthesized sample has great potential for environmental application.

4. MATERIALS AND METHODS

4.1. Chemicals. Graphite powder was purchased from Beijing Electric Carbon Co. (CP, 98%, 80 mesh). N-((trimethoxysilylpropyl)-ethylenediamine triacetic acid sodium (EDTA-silane, 40 wt % aqueous solution) was used as the silane functionalization agent and was purchased from J&K Chemical Technology (Shanghai, China). Tetraethyl titanate (TEOT) was purchased from Aladdin Chemical Company. Sulfuric acid (98 wt %), NaNO$_3$ (analytical grade), KMnO$_4$ (analytical grade), H$_2$O$_2$ (30%) solution, nitric acid (analytical grade), absolute ethanol (analytical grade), methanol (chromatographically pure), and acetone (analytical grade) were purchased from Sinopharm Group Chemical Reagent Co. Ultrapure water was used in all experiments.

4.2. Synthesis of GO. GO was synthesized by the modified Hummers method.$^{66}$ The synthesis procedure involves the oxidation of graphite using strong oxidizing agents like KMnO$_4$ and H$_2$SO$_4$, which act as supporting oxidizing agents. In detail,
1 g of graphite powder was exfoliated using 48 mL of H$_2$SO$_4$ (98%) in the presence of 0.5 g of NaNO$_3$ at 0 °C in an ice bath, followed by gradual addition of 9 g of KMnO$_4$ in small parts. After the addition of KMnO$_4$, the solution was stirred for 2 h in a water bath at room temperature. Subsequently, the reaction was terminated by the addition of 240 mL of ultrapure water, followed by 20 mL of H$_2$O$_2$ (30%) solution. Finally, the solid powders (GO) were collected by filtration, washed several times with HCl solution (10%) and ultrapure water, and dried in a vacuum oven at 60 °C overnight.

4.3. Synthesis of the GO-TiO$_2$ Nanocomposite. In a typical synthesis, 100 mg of GO was added to the 4:1 volume ratio of ethanol/water mixed solution and dispersed by ultrasonication for 3 h. After that, the mixed solution was transferred to a hydrothermal reactor containing 100 mL of polytetrafluoroethylene substrate, and then, 2.2 mL of TEOT was slowly added into the reactor as a titanium precursor and stirred for 2 h. Finally, a small amount of concentrated nitric acid was added (to inhibit the hydrolysis of tetrabutyl titanate), and the reaction condition was maintained at 80 °C for 12 h. After the reaction was completed, it was cooled to room temperature naturally, washed with deionized water and absolute ethanol several times, and finally dried at 60 °C for 2 h. The GO/TiO$_2$-5 wt % composite nanomaterial was obtained by filtration and washed with methanol and deionized water sequentially.

Finally, to reduce EDTA-GO-TiO$_2$ to ERGT, 500 mg of EDTA-GO-TiO$_2$ was dried in a vacuum oven at 150 °C for 12 h and then dispersed into 100 mL of DI water and reduced with hydrazine as the previously reported method. The final product ERGT was obtained by filtration, washed with methanol, water, and HCl sequentially, and oven-dried for further use (Scheme 1).

4.4. Silylation of the GO-TiO$_2$ Nanocomposite. The silanized nanocomposite product (EDTA-GO-TiO$_2$) was obtained by a simple salinization reaction. An appropriate amount of the GO-TiO$_2$ nanocomposite was added into 50 mL of ethanol and dispersed by ultrasonication for 2 h. Then, 5 mL of 10 wt % sodium N-(trimethoxysilylpropyl) ethylenediamine triacetate (EDTA-silane) was added into the ethanol solution and stirred at 65 °C for 12 h. After the reaction was completed, 100 mL of methanol was added to dilute the unreacted silane molecules. The product (EDTA-GO-TiO$_2$) was obtained by filtration and washed with methanol and deionized water sequentially.

Finally, to reduce EDTA-GO-TiO$_2$ to ERGT, 500 mg of EDTA-GO-TiO$_2$ was dried in a vacuum oven at 150 °C for 12 h and then dispersed into 100 mL of DI water and reduced with hydrazine as the previously reported method. The final product ERGT was obtained by filtration, washed with methanol, water, and HCl sequentially, and oven-dried for further use (Scheme 1).

4.5. Characterization Methods. 4.5.1. Instruments Used in the Experiment. The phase and lattice degrees of the sample were confirmed by an X-ray diffractometer (Ultima IV, Rigaku, Japan). The optical absorbance of the synthesized samples was determined using a UV−vis spectrophotometer (F-4500, Japan) in the diffused reflectance mode in a wavelength window of 200–800 nm. The functional groups contained on the surface of the nanometer sample were determined by FTIR spectroscopy (7300-200CM, Nichols, USA). The surface topography of the sample was determined by SEM (SUPRA 55, Hitachi, Japan) and TEM (FEI F200S). The specific surface area of the nanocomposite was accurately tested by BET surface area analysis (Tri Star II 3020M, USA). The XPS measurements were performed on ESCALAB 250Xi (TMAG, USA) using a Ka radiation. The lattice ordering and disordering of the synthesized composites were tested via Raman spectroscopy (Invia, Renishaw, UK).

4.5.2. Characterization of Samples. To study the functional groups of composite materials, through FTIR, the sample was mixed with KBr in a volume ratio of 1:55, compressed by an air compressor to obtain a thinner fast body, and then subjected to transmission light inspection. To observe the surface morphology of the materials, we used SEM and TEM. For SEM, because we used nanopowder materials, we prepared samples by the wet method, ultrasonically dispersed the samples in ethanol to form a dispersion, dropped them on the silicon wafer, and then tested them after drying the silicon wafer. For TEM, by a similar dispersion method, we added a very small amount of samples, ultrasonically dispersed the samples in acetone to form a
dispersion, immersed the copper mesh with a supporting film into the solution, and dried it for testing. The acceleration voltage of SEM is 3, 10, and 15 kV, and the acceleration voltage of TEM is 100 kV. Through XRD, the crystal structure of the composite material was studied. The test parameters are that the source material is copper-based emission, the scanning speed is $5^\circ$/min, and the scanning range is 5–90°. The energy band gap and surface structure of materials were studied by UV and Raman spectroscopy. The width parameter of the spectrum is that the wavelength range of the test material is 200–800 nm, the scanning speed is 300 nm/min, and the step length is 0.02 nm. Raman spectroscopy uses a solid-state diode-pumped laser with a laser source wavelength of 532 nm.

4.6. Photocatalytic Activity Measurement. The photocatalytic activity of the materials was studied under the irradiation of a 500 W high-voltage short-arc spherical xenon lamp (CEL-S500) and a 500 W mercury lamp (PLS-LAM500). The lamp has a fixed vertical distance of 15 cm from the top of the reaction system. To avoid errors caused by stray light, the experimental setup was kept in a dark environment with an ambient temperature of 25 °C. In all experiments, the reaction catalyst is 30 mg, and the reactant solution is 30 mL.

4.6.1. Effect of Different Light Conditions on Degradation Efficiency. To determine the accuracy of the experiment, the reaction solution was kept in the dark for about 30 min under constant stirring at 150 rpm before the start of light irradiation so that the surface of the catalyst could be sufficiently contacted with the reactants, and after reaching an equilibrium state, the dark environment was taken every 10 min. The lower 5 mL solution was recorded for absorbance on a UV–vis spectrometer. In addition, a control experiment was conducted by irradiating the contaminants under the same conditions in the absence of a catalyst. The photodegradation rate was determined by measuring the characteristic ultraviolet absorption peak of phenol at 278 nm as a function of the irradiation time. Each set of experiments was performed three times to determine the readiness of the test results.

4.6.2. Effect of Different Concentrations of Phenol on Degradation Efficiency. To investigate the effect of different concentrations of phenol on the degradation properties of the materials, we set up three groups of different concentrations of phenol contrast experiments; the concentrations were 100, 200, and 300 mg/L, respectively. The photocatalytic activity of ERGT composite was studied under the irradiation of a 500 W high-voltage short-arc spherical xenon lamp (CEL-S500). All experiments and test conditions were the same as those in the previous experiment.

4.7. Adsorption Experiments. 4.7.1. Effect of pH. The effect of pH on the adsorption performance of the adsorbent for cadmium ions was investigated by mixing 30 mg of the adsorbent with a 30 mL solution of Cd$^{2+}$ ions (100 mg/L) under different initial pH conditions. The initial pH is between 3 and 6. After centrifugation, the concentration of Cd$^{2+}$ was measured, and the dry weight was weighed.

4.7.2. Adsorption Kinetic Experiments. The kinetic experiments were performed by mixing 30 mg of ERGT with 30 mL of Cd solution in a beaker at pH = 5.5. The samples were taken by centrifugation at 10, 20, 30, 45, 60, 90, 120, 150, 180, and 240 min at predetermined times. Among them, the amount of adsorption is calculated according to the following formulas (6) and (7).

\[
q_t = \frac{(C_0 - C_t)V}{m}
\]

(6)

\[
q_e = \frac{(C_0 - C_e)V}{m}
\]

(7)

where $q_e$ (mg/g) and $q_t$ (mg/g) are the balanced adsorption and instant adsorption quantities, respectively, $C_0$ (mg/L) is the initial concentrations of Cd$^{2+}$, $C_t$ (mg/L) is the residual concentration, $C_e$ (mg/L) is the equilibrium concentrations, V (L) is the volume of the reaction solution, and m (mg/L) is the mass of the adsorbent.

4.7.3. Isothermal Sorption Experiments. The adsorption experiment was carried out for 12 h under the condition of pH = 5.5. 30 mg of ERGT was mixed with 30 mL of Cd$^{2+}$ solution. The initial concentration range of Cd$^{2+}$ was 10–160 mg/L. Finally, centrifugation was carried out to separate and measure the concentration of Cd$^{2+}$ and the dry weight of the adsorbent.

4.8. Synergistic Experiment. All experiments were carried out by mixing 30 mg of the adsorbent with a 30 mL solution of phenol and Cd$^{2+}$ ions with a known concentration on a shaker (150 rpm) for 12 h for synergistic analysis, in which a phenol solution having a concentration of 100 mg/L was used as a basic liquid, and cadmium sulfate was added thereto to make 15, 25, 50, 80, and 100 mg/L concentrations of cadmium ion solution. Thus, the reaction solution is a mixture of 100 mg/L phenol solution and different concentration gradients of cadmium ion solution. As a mixed reaction solution, three sets of parallel experiments are performed, and the test is the same as the foregoing experiment.

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P.X. wrote the main manuscript text. The design, growth, and characterization of graphene were conducted by P.X. S.X. and T.Y. provided support in the monitoring and verification of the results. K.J. reviewed the manuscript. All authors approved the manuscript.

## Notes

The authors declare no competing financial interest.
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