Preparation and Characterization of New CrFeO$_3$-Carbon Composite Using Environmentally Friendly Methods to Remove Organic Dye Pollutants from Aqueous Solutions

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Abstract: Globally, environmental pollution is an important issue. Various pollutants present in water resources, such as bacteria, heavy-metal ions, and organic pollutants, cause serious problems to the environment, animals, plants, and human health. Among the water resources, pollutants, dyestuff, which is discharged from dyeing, textile, and other industrial processes, is an important class of pollutants. Removing these dye pollutants from water resources and wastewater is vital and important due to their toxicity. In this work, a CrFeO$_3$-carbon nanotube (CNT) adsorbent was synthesized using environmentally friendly methods. The synthesized CrFeO$_3$-CNT adsorbent was characterized stoichiometrically, spectroscopically, and morphologically. The synthesized CrFeO$_3$-CNT adsorbent was tested for the removal of two dyes: Methyl violet 2B (MV) and Azocarmine G2 (AC) from an aqueous solution. Crushing CrFeO$_3$ composite with multi-walled fullerene CNT to prepare CrFeO$_3$-CNT adsorbent improved the adsorption performance of free multi-walled fullerene CNT towards MV dye by 30% and towards AC dye by 33.3%.

Keywords: carbon nanotubes; metal oxide composite; dye adsorption; nanomaterials and applications

1. Introduction

Water, which covers about 71% of the earth’s total surface, is a valuable resource for sustaining life. Among this percentage, only 1% of total water is found as freshwater, which is used for various purposes (i.e., domestic use, agriculture, and drinking) [1]. The global population is increasing; human society is fast growing, and industrial technology is rapidly progressing and developing. This has led to a significant amount of environmental water pollution, and reusing sustainable resources such as water has become a serious issue of concern worldwide. Year after year, the demand for freshwater is exceeding supply in parts of the world, though freshwater resources remain limited. Obtaining freshwater in the future is of utmost importance and will depend on preserving the quality of water through treatment and recycling techniques.

Dyestuff is widely used in many industries, such as food processing, plastic, rubber, drug, printing, cosmetic, leather tanning, paper and paperboard, and textile [2]. Among the main industries that consume and produce a significant amount of wastewater that pollutes water resources are the dye and textile industries. The tremendous discharge of
dye and textile wastewater is viewed as one of the major contributors to water pollution. These industries apply synthetic dyes for the coloration of their products, and these processes, along with the large quantity of water usage, discharge the wastewater to natural water resources and environments. The largest amounts of dyes are being used in the textile industry, which is responsible for discharging undesirable dye effluents into natural water resources. Dyed wastewater contains dyestuff and synthetic textiles with a complex toxic aromatic ring and aromatic amine molecular structure, toxic not only for humans but also for aquatic life. It has many harmful effects on the environment and humankind, ranging from allergies and irritation to cancer and mutations [3–5].

The removal of highly harmful industrial dyes, heavy metals, and other contaminants from water/wastewater and industrial effluents is of the highest importance and a major environmental concern. There are numerous common treatment approaches for dye removal from water/wastewater, which can be divided into three categories [6]: biological methods, such as anaerobic textile–dye bioremediation systems, adsorption by dead/living microbial biomass, decolorization by white-rot fungi, and enzyme-incorporated processes; chemical methods, such as electrochemical destruction, photochemistry, ozonation and chemical reduction, chemical degradation, chemical precipitation, and electrochemical oxidation; and physical methods, such as coagulation and electrocoagulation, flotation, irradiation, ion exchange, adsorption, and membrane separation and filtration.

Among these processes, adsorption over porous materials has been considered a better approach and an attractive method, the most adaptable and feasible process, and is widely employed for water treatment and purification due to its environmentally friendly properties and efficiency, simplicity in design, ease of operation, low cost, smaller amounts of harmful byproducts, high removal efficacy, and insensitivity to toxic substances and pollutants [7,8]. Various materials have been reported in the literature [9–20] as adsorbents for the removal of organic dyes from polluted water and wastewater, such as activated carbon, zeolitic imidazolate frameworks (ZIFs), metal–organic frameworks (MOFs), various nanoparticles, zeolites, polymer resins, clays, and carbon-based nanomaterials such as fullerenes. Fullerences have a high surface-to-volume ratio, high electron affinity, and surface defects. They have many uses as solar cells, artificial photosynthesis, biomedical sciences, sensors, semiconductors, and surface coatings [21]. They are considered useful adsorbents for the removal of pollution from wastewater because they have a large surface area, defects, and lower aggregation tendency. We aim in this work to upgrade the adsorption performance of a multi-walled fullerene carbon nanotube towards two organic dyes (Methyl violet 2B (MV) and Azocarmine G2 (AC)) by combining a multi-walled fullerene carbon nanotube with a CrFeO$_3$ composite. For this purpose, a CrFeO$_3$ composite was prepared through the co-precipitation method of iron and chromium salts in the presence of urea. This composite was ground with carbon nanotube material in the presence of a few drops of methanol solvent to generate the CrFeO$_3$-carbon nanotube (CrFeO$_3$-CNT) product. The CrFeO$_3$-CNT product was used as an adsorbent for the removal of the dye through the process of adsorption. The properties of the synthesized adsorbent were characterized by using a Fourier-transform infrared spectrophotometer (FT-IR) and scanning electron microscope (SEM), as well as elemental analysis. The adsorption performance of the synthesized adsorbent was studied with two dyes, Methyl violet 2B (MV) and Azocarmine G2 (AC), and compared with the free carbon nanotubes.

2. Materials and Methods

2.1. Materials and Instruments

Analytical-grade iron(III) chloride (FeCl$_3$, 162.20 g/mol, purity $\geq$ 99.99%), chromium (III) chloride (CrCl$_3$, 158.36 g/mol; purity 99.99%), and chromium (III) nitrate nonahydrate ([$\text{Cr(NO}_3\text{)}_3$·9H$_2$O]; 400.15 g/mol; purity 99%) were from Merck (KGaA, Gernsheim, Germany). Methyl violet 2B (labeled as MV) (C$_{23}$H$_{26}$N$_3$Cl; 379.9 g/mol; dye content $\geq$ 75.0%), Azocarmine G2 (labeled as AC) (C$_{28}$H$_{21}$N$_3$; 399.48 g/mol; dye content $\geq$ 75.0%), and urea (NH$_2$CONH$_2$; 60 g/mol; purity $\geq$ 99.5%) were purchased from Sigma-Aldrich (Saint Louis,
MO, USA). The multi-walled fullerene carbon nanotube (CNT) was purchased from Alfa Aesar, Thermo Fisher Scientific (76870 Kandel, GmbH, Germany). Specifications of the CNT are: multi-walled, 3–20 nm OD, 1–3 nm ID, 0.1–10 microns long, 95% nanotubes. The dyes’ aqueous solutions throughout the experiments were prepared using deionized (DI) water. All materials were used as received without further purification. The instruments used to characterize the synthesized composite and adsorbent materials include a scanning electron microscope (SEM model JSM-6390LA JEOL) coupled with an energy-dispersive X-ray spectrometer (EDXRF model JED-2300) (Tokyo, Japan) for SEM-EDX data, a Bruker compact Fourier-transform infrared (FT-IR) spectrophotometer (model Alpha) (Bruker Optik GmbH, Ettlingen, Germany) for the IR spectra, and a Perkin-Elmer CHN Microanalyzer (model PE 2400 series II) (Perkin-Elmer Inc, Waltham, MA, USA) for the C, H, and N (in %) elemental analyses. A Perkin-Elmer UV/vis spectrophotometer (model Lambda 25) (Perkin-Elmer Inc, Waltham, MA, USA) was used for the ultraviolet–visible measurements. An X’Pert Philips X-ray Powder Diffractometer was used for the XRD measurements from a diffraction angle (2θ) of 5° to 70°.

2.2. Methods

2.2.1. CrFeO$_3$ Composite

FeCl$_3$ (1 mmol), CrCl$_3$ (1 mmol), and urea (6 mmol) were dissolved in a 100 mL binary solvent mixture (H$_2$O: MeOH) (1:1). The mixture was stirred for 24 h at 80 °C. The resultant precipitate was separated by filtration and washed several times with hot water to remove all unreacted compounds, and then thermally decomposed at 800 °C for 3 h in an air atmosphere to generate the nanostructured dark-red CrFeO$_3$ composite. This composite was also obtained by using another chromium salt [Cr(NO$_3$)$_3$·9H$_2$O] instead of CrCl$_3$. The composite generated from CrCl$_3$ was labeled as Composite A, and that generated from Cr(NO$_3$)$_3$·9H$_2$O was labeled as Composite B. The composites were ground into powder with a particle size of 2–4 mm and characterized by IR spectroscopy and an SEM-EDX instrument.

2.2.2. Adsorbent

A 100 mg amount of the CrFeO$_3$ composite was added to 1.0 g of the multi-walled fullerene CNT on a dry, clean, porcelain mortar. A porcelain pestle was used to mix the two materials thoroughly; after that, a few drops of methanol was added to the mixture, then all components were thoroughly mixed and ground together for 20 min. The black CrFeO$_3$-CNT adsorbent was collected from the mortar and vacuum dried in a desiccator with anhydrous CaCl$_2$.

2.2.3. Adsorption Experiments

In a typical run, 100 mL of aqueous dye solution (1 g/L; MV or 10 g/L; AC) was added into a 250 mL conical flask. The conical flask was put on a mechanical shaker. A 40 mg amount of the synthesized adsorbent amount was added to the dye solution. The mixture was shaken at room temperature. Aliquots (5 mL) were taken after pre-defined time intervals (2, 4, 6, 8, 10, 12 min) and centrifuged for 10 min to remove the adsorbent, then the absorbance was measured in a Perkin-Elmer UV/vis spectrophotometer at the wavelength of 588 nm in the case of MV and at 516 nm in the case of AC. All the dye adsorption experiments were repeated three times. The degree of decolorization of the dye was determined using the following equation [22,23]:

$$% \text{Decolorization degree} = \left(\frac{A_0 - A_t}{A_0}\right) \times 100$$

where $A_0$ is the initial absorbance of the dye solution, and $A_t$ is the absorbance of the dye solution at time $t$. 
3. Results and Discussion

3.1. Preparation and Characterization of Composites A and B

Composite A was generated by two stages:

Stage one:
Reacting 1 mmol of FeCl$_3$ and 1 mmol of CrCl$_3$ with 6 mmol of urea in a binary solvent mixture (H$_2$O: MeOH) (1:1) at 80 °C. This produced a solid precipitate with a brown color (Figure 1) containing [Fe(NH$_2$CONH$_2$)$_6$]Cl$_3$ and [Cr(NH$_2$CONH$_2$)$_6$]Cl$_3$ solid mixtures [24].

Stage two:
Thermal decomposition of the resultant solid mixture was performed at 800 °C for 3 h in an air oxygen atmosphere. This combustion generated the nanostructured dark-red CrFeO$_3$ composite (Composite A) (Figure 1) [24].

Composite B (Figure 1) was obtained by using another chromium salt; Cr(NO$_3$)$_3$·9H$_2$O was generated by the same two stages.

Figure 1. Photographs of (a) the solid [Fe(NH$_2$CONH$_2$)$_6$]Cl$_3$ and [Cr(NH$_2$CONH$_2$)$_6$]Cl$_3$ mixture, (b) CrFeO$_3$ composite generated using CrCl$_3$ slat after thermal decomposition at 800 °C (Composite A), (c) the solid [Fe(NH$_2$CONH$_2$)$_6$]Cl$_3$ and [Cr(NH$_2$CONH$_2$)$_6$](NO$_3$)$_3$ mixture, and (d) CrFeO$_3$ composite generated using Cr(NO$_3$)$_3$·9H$_2$O slat after thermal decomposition at 800 °C (Composite B).
Stage two:

Thermal decomposition of the resultant solid mixture was performed at 800 °C for 3 h in an air oxygen atmosphere. This combustion generated the nanostructured dark-red CrFeO₃ composite (Composite A) (Figure 1) [24]. Composite B (Figure 1) was obtained by using another chromium salt; Cr(NO₃)₃·9H₂O was generated by the same two stages.

Figure 2 depicts the IR spectra of the solid mixtures generated from stage one. These solids are Solid Mixture A, which contains [Fe(NH₂CONH₂)₆]Cl₃ and [Cr(NH₂CONH₂)₆]Cl₃, and Solid Mixture B, which contains [Fe(NH₂CONH₂)₆]Cl₃ and [Cr(NH₂CONH₂)₆](NO₃)₃. Generally, both mixtures displayed similar IR features, including the following absorption bands: (i) a broad medium-strong intensity band accumulated at 3340 cm⁻¹, which was assigned to the ν(NH₂) vibrations; (ii) a band with a medium intensity observed at 1632 cm⁻¹ in Solid Mixture A and at 1641 cm⁻¹ observed in Solid Mixture B. These are due to the ν(C=O) vibrations; (iii) a band appeared at 1440 cm⁻¹ in Solid Mixture A and at 1380 cm⁻¹ in Solid Mixture B. These could have resulted from the δ(NH₂) vibrations; (iv) a band resonated, respectively, at 830 and 811 cm⁻¹ Solid Mixture A and Solid Mixture B, attributed to the δ(NH₂) modes; and (v) a band resonating at 640 cm⁻¹ for both mixtures, attributed to the δ(NH₂) modes.

Figure 3 depicts IR spectra of Composites A and B. These composites are generated from stage two through the combustion of Solid Mixtures A and B at 800 °C. Both Composites A and B displayed similar IR features. The bands that resulted from the vibrations of –NH₂ bonds in Solid Mixtures A and B (i.e., ν(NH₂), δ(NH₂), δ(NH₂)) were no longer observed in their corresponding composites. Instead of these bands, only two bands were observed in the IR spectra of Composites A and B. These bands resonated at 547 and 450 cm⁻¹ for both composites and resulted from the ν(Fe–O) and ν(Cr–O) vibrations [25,26]. Figure 4a,b shows SEM micrographs of Solid Mixtures A and B, re-
spectively. EDX analysis indicated the presence of Fe, Cr, C, O, N, and Cl elements in Solid Mixture A and elements of Fe, Cr, C, O, and N in Solid Mixture B. Morphologically, there are no differences in the surface topology and shape of the microstructure between the two solid mixtures, as evidenced by their SEM pictures. Both mixtures consisted of small particles, and most of these particles had similar sizes. Solid Mixtures A and B had stone-like-shaped particles. This indicated that using chromium chloride salt, CrCl$_3$, or chromium nitrate salt, Cr(NO$_3$)$_3$·9H$_2$O, shows no differences in the morphology of the solid mixture. Burning Solid Mixtures A and B at 800 °C resulted in the formation of highly homogenized and uniform materials (Composites A and B), as evidenced by their SEM micrographs shown in Figure 5a,b. EDX analysis evidenced the presence of Fe, Cr, and O elements in both composites. The elemental percentages of these elements are listed in Table 1. These elemental percentages agree well with the proposed chemical structure for Composites A and B (CrFeO$_3$). EDX analysis showed the presence of 4% C elements in Composite A and 7% C elements in Composite B, which indicated that some carbons remain as residual from the combustion of Solid Mixtures A and B at 800 °C. Figure 6 depicts XRD spectra of Composites A and B. Both composites exhibited characteristic peaks related to chromium ferrite. The peaks appeared at 33.04°, 35.42°, 43.23°, 49.44°, 54.02°, 57.15°, and 62.74° in the XRD diffractogram of Composite A, associated with the Bragg’s reflection (220), (311), (400), (331), (422), (511), and (440), respectively, for typical chromium ferrite [27,28]. The corresponding values for Composite B were 32.18°, 35.14°, 42.85°, 46.51°, 52.13°, 55.89°, and 64.37°. The IR and XRD features of Composites A and B support the chemical structures of these composites derived through the above equations (CrFeO$_3$).
Figure 4. (a) SEM micrographs of Solid Mixture A: $[\text{Fe(NH}_2\text{CONH}_2)_6]\text{Cl}_3$ and $[\text{Cr(NH}_2\text{CONH}_2)_6]\text{Cl}_3$. (b) SEM micrographs of Solid Mixture B: $[\text{Fe(NH}_2\text{CONH}_2)_6]\text{Cl}_3$ and $[\text{Cr(NH}_2\text{CONH}_2)_6]\text{(NO}_3)_3$. 
Figure 4. (a) SEM micrographs of Solid Mixture A: [Fe(NH₂CONH₂)₆]Cl₃ and [Cr(NH₂CONH₂)₆]Cl₃. (b) SEM micrographs of Solid Mixture B: [Fe(NH₂CONH₂)₆]Cl₃ and [Cr(NH₂CONH₂)₆](NO₃)₃.

Figure 5. (a) SEM micrographs of Composite A. (b) SEM micrographs of Composite B.

Table 1. Percentage of elements of Composites A and B observed by EDX analysis.

| Composite | Fe  | Cr   | O    | C   |
|-----------|-----|------|------|-----|
| Composite A | 35.66 | 33.25 | 30.72 | 4   |
| Composite B | 35.71 | 33.30 | 30.78 | 7   |
3.2. Preparation and Characterization of the CrFeO$_3$-CNT Adsorbent

A multi-walled fullerene carbon nanotube (CNT) was used for the preparation of the adsorbent. Its SEM micrographs are presented in Figure 7. The SEM micrographs visualize the nanotubes, and EDX analysis showed that this material is 100% pure carbon. Figure 8 presents the IR spectra of this CNT material along with the synthesized CrFeO$_3$-CNT adsorbent material. No clear bands were observed in any area of the IR spectrum of the fullerene CNT. The IR spectrum of the synthesized CrFeO$_3$-CNT adsorbent material showed only one clear, broad absorption band with medium intensity resonating at 505 cm$^{-1}$, which can be attributed to the $\nu$(M–O) vibrations (M: Fe or Cr). The CrFeO$_3$-CNT adsorbent was generated by grinding the CrFeO$_3$ composite with the fullerene CNT material at a 1:10 molar ratio in the presence of a few drops of methanol solvent as described in Figure 9. This process produced a homogenate, black, solid adsorbent material that has a magnetic property (Figure 10). Information on the size, shape, surface morphology, topology, and elemental composition of the synthesized CrFeO$_3$-CNT adsorbent was collected from its SEM micrographs shown in Figure 11. The SEM micrographs captured between 1000× and...
2500× magnification revealed that the adsorbent material consisted of stone-like-shaped particles. These stones have different irregular shapes, sizes, and features. The surface of the particles is rough, and some of the particles are clumped into large agglomerates. EDX analysis evidenced the presence of iron, chromium, oxygen, and carbon elements in the adsorbent material.

Figure 7. SEM micrographs of the multi-walled fullerene CNT.

Figure 8. IR spectra of (a) the multi-walled fullerene carbon nanotube (CNT) and (b) the synthesized CrFeO$_3$-CNT adsorbent material.
Figure 9. Preparation of the adsorbent material by grinding Composite A with the CNT, (a) before grinding, and (b) after grinding in the presence of a few drops of methanol solvent.

Figure 10. Black, solid adsorbent material generated by grinding the CrFeO$_3$ composite.
3.3. Adsorption Performance

3.3.1. Investigated Dyes

The adsorption performance of the synthesized CrFeO$_3$-CNT adsorbent was investigated with two model dyes, Methyl violet 2B (MV) and Azocarmine G2 (AC). An aqueous solution of MV at pH = 7 has a violet color, whereas an aqueous solution of AC at pH = 7 has a pink color. Figure 12 shows the UV–visible spectra of MV (1 mg in 100 mL of deionized water) and AC (10 mg in 100 mL of deionized water). Both dyes absorb across a wide range from 200 nm to 650 nm. The MV dye displayed two absorption bands: (i) a narrow, weak band at 302 nm and (ii) a strong and broadband from 460 nm to 635 nm (~175 nm of width). This wideband has a $\lambda_{\text{max}}$ at 588 nm. The UV–visible spectrum of AC dye was characterized by two absorption bands: (i) a medium-intensity band that had two heads at 293 and 334 nm, where the two heads had approximately the same intensity, and (ii) a strong, broad absorption band that appeared at a much wider wavelength region. This wideband ranged from 460 nm to 588 nm and had two heads at 516 and 550 nm. The intensity of the head that appeared at 516 nm was a little higher than that at 550 nm.

![Figure 12](image_url)  
**Figure 12.** Electronic spectra of MV and AC in aqueous solution (pH = 7) (0.005 g of the dye content dissolved in 100 mL of deionized water).
3.3.2. Adsorption of MV

An aqueous solution of MV dye was prepared (1 mg in 100 mL of deionized water), then 40 mg of the fullerene CNT was added. The mixture was mechanically shaken at room temperature. Aliquots (5 mL) were taken every 2 min (2, 4, 6, 8, 10 min) and centrifuged for 10 min to remove the CNT material. The absorbance of the pure aliquot was measured spectrophotometrically, and the decrease of the intensity of the band at 588 nm was used as a measure of decolorization degree. Figure 13 illustrates the removal efficiency (%) of MV using 40 mg of the fullerene CNT at different contact times. This figure indicates that the fullerene CNT adsorbed around 96% of the dye content in 10 min. The test was run using 40 mg of the synthesized CrFeO$_3$-CNT adsorbent, which reached a decolorization degree of 98% after just 7 min, as indicated in Figure 14. This outcome suggests that crushing CrFeO$_3$ composite with fullerene CNT improves the adsorption performance of the free fullerene CNT towards MV dye by 30%.

Figure 13. Removal efficiency (%) of MV (1 mg in 100 mL of deionized water) using 40 mg of the fullerene CNT at different contact times.

Figure 14. Removal efficiency (%) of MV (1 mg in 100 mL of deionized water) using 40 mg of the synthesized CrFeO$_3$-CNT adsorbent at different contact times.
3.3.3. Adsorption of AC

An aqueous solution of AC dye was prepared (10 mg in 100 mL of deionized water), then 40 mg of the fullerene CNT was added. The mixture was mechanically shaken at room temperature. Aliquots (5 mL) were taken every 2 min and centrifuged for 10 min to remove the CNT material. The absorbance of the pure aliquot was measured spectrophotometrically, and the decrease in the intensity of the band at 516 nm was used as a measure of decolorization degree. The removal efficiency (%) of AC using 40 mg of the fullerene CNT at different contact times is shown in Figure 15 and using 40 mg of the synthesized CrFeO$_3$-CNT adsorbent is shown in Figure 16. These figures indicate that the fullerene CNT alone adsorbed around 96% of the AC dye content in 12 min, whereas the CrFeO$_3$-CNT adsorbent adsorbed around 95.5% of the AC content in just 8 min. This suggested that grinding CrFeO$_3$ composite with the fullerene CNT increases the adsorption performance of the free fullerene CNT towards AC dye by 33.3%.

![Figure 15](image1.png)

**Figure 15.** Removal efficiency (%) of AC (10 mg in 100 mL of deionized water) using 40 mg of the fullerene CNT at different contact times.

![Figure 16](image2.png)

**Figure 16.** Removal efficiency (%) of AC (10 mg in 100 mL of deionized water) using 40 mg of the synthesized CrFeO$_3$-CNT adsorbent at different contact times.
3.4. Adsorption Mechanisms, Reusability, and Regeneration

Fullerenes have surface defects, a high surface-to-volume ratio, and high electron affinity. Fullerene CNT can adsorb organic dyes into the spaces/defects between the carbon nanoclusters via surface complexation formation, film diffusion, intra-particle diffusion, and pore diffusion [29–31]. During the adsorption process, organic dyes can enter the mesoporous spaces of carbon nanoclusters (physisorption). The adsorption performance of the free fullerene CNT towards MV and AC dyes improved by 30% and 33.3%, respectively, after grinding the fullerene CNT with the CrFeO$_3$ composite, probably due to the physicochemical bond between dyes and the CrFeO$_3$ composite. The reusability of the synthesized CrFeO$_3$-CNT adsorbent was investigated by determining its desorption efficiency. After the adsorption experiment, the CrFeO$_3$-CNT adsorbent was filtrated off and washed with deionized water. Deionized water, 0.1 N H$_2$SO$_4$, 0.1 N HCl, 0.1 N HNO$_3$, 0.1 N KOH, and 0.1 N EDTA were used as eluting agents to elute adsorbed dyes from the CrFeO$_3$-CNT adsorbent. The most efficient desorbing solution to recover MV and AC dyes from the CrFeO$_3$-CNT adsorbent was HNO$_3$ (~93%). Reusability of the CrFeO$_3$-CNT adsorbent was determined by running and adsorption–desorption experiment for several cycles. We found that the CrFeO$_3$-CNT adsorbent can be reused at least 12 times in adsorption–desorption cycles.

4. Conclusions

With the fast development of our society, a large amount of wastewater polluted by heavy-metal ions and organic pollutants, such as dyes and others, are released from papermaking, textiles, leather, and paints, and other industries, causing serious environmental problems to animals, plants, and human health. Dealing with these environmental problems, not by methods that release more pollutants but by the use of environmentally friendly methods, is urgent and has attracted increasing attention worldwide. In this work, we aimed to improve the adsorption performance of a fullerene carbon nanotube (CNT) towards organic dyes by combining it with a CrFeO$_3$ composite by the grinding process. The synthesized CrFeO$_3$-CNT adsorbent was physicochemically (elemental analysis, SEM/EDX analysis, and FT-IR spectroscopy) characterized to describe its composition, texture, and surface morphology. Next, the batch technique was conducted to assess the adsorption performance of the synthesized CrFeO$_3$-CNT adsorbent in comparison with the multi-walled fullerene CNT material alone. Outcomes indicated that grinding a CrFeO$_3$ composite with a multi-walled fullerene CNT to prepare a CrFeO$_3$-CNT adsorbent increases the adsorption properties of the free fullerene CNT towards MV dye by 30% and towards AC dye by 33.3%. Combining a CrFeO$_3$ composite with a fullerene CNT not only improves the adsorption properties of the free fullerene CNT but also gives the fullerene CNT material magnetic properties, making it easily separable from the solution via an external magnetic field.

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References

1. Tariq, M.; Muhammad, M.; Khan, J.; Raziq, A.; Uddin, M.K.; Niaz, A.; Ahmed, S.S.; Rahim, A. Removal of Rhodamine B dye from aqueous solutions using photo-Fenton processes and novel Ni-Cu@MWCNTs photocatalyst. J. Mol. Liq. 2020, 312, 113399. [CrossRef]

2. Lei, X.; Li, X.; Ruan, Z.; Zhang, Y.; Pan, F.; Li, Q.; Xia, D.; Fu, J. Adsorption-photocatalytic degradation of dye pollutant in water by graphite oxide grafted titmate nanotubes. J. Mol. Liq. 2018, 266, 122–131. [CrossRef]

3. Zeng, Q.-F.; Fu, J.; Zhou, Y.; Shi, Y.-T.; Zhu, H.-L. Photooxidation Degradation of Reactive Brilliant Red K-2BP in Aqueous Solution by Ultraviolet Radiation/Sodium Hypochlorite. CLEAN Soil Air Water 2009, 37, 574–580. [CrossRef]

4. Ahmadipoury, S.; Haris, M.H.; Ahmadijokani, F.; Jarahiyian, A.; Molavi, H.; Moghadam, F.M.; Rezakazemi, M.; Arjmand, M. Magnetic Fe9O4@UiO-66 nanocomposite for rapid adsorption of organic dyes from aqueous solution. J. Mol. Liq. 2021, 322, 114910. [CrossRef]

5. Kumar, S.; Kaushik, R.; Purohit, L. Novel ZnO tetrapod-reduced graphene oxide nanocomposites for enhanced photocatalytic degradation of phenolic compounds and MB dye. J. Mol. Liq. 2021, 327, 114814. [CrossRef]

6. Hasanpour, M.; Hatami, M. Photocatalytic performance of aerogels for organic dyes removal from wastewaters: Review study. J. Mol. Liq. 2020, 309, 113094. [CrossRef]

7. Chi, Y.; Chen, Y.; Hu, C.; Wang, Y.; Liu, C. Preparation of Mg-Al- Ce triple-metal composites for fluoride removal from aqueous solutions. J. Mol. Liq. 2017, 242, 416–422. [CrossRef]

8. Peng, W.; Li, H.; Liu, Y.; Song, S. A review on heavy metal ions adsorption from water by graphene oxide and its composites. J. Mol. Liq. 2017, 230, 496–504. [CrossRef]

9. Seliaoui, L.; Silva, L.F.; Badawi, M.; Ali, J.; Favarin, N.; Dotto, G.L.; Ert, O.; Chen, Z. Adsorption of ketoprofen and 2-nitrophenol on activated carbon prepared from winery wastes: A combined experimental and theoretical study. J. Mol. Liq. 2021, 333, 115906. [CrossRef]

10. Hanafy, H. Adsorption of methylene blue and bright blue dyes on bayleaf capertree pods powder: Understanding the adsorption mechanism by a theoretical study. 2021, 332, 115680. [CrossRef]

11. Buema, G.; Lupu, N.; Chiriac, H.; Ciobanu, G.; Bucur, R.-D.; Bucur, D.; Favier, L.; Harja, M. Performance assessment of five adsorbents based on fly ash for removal of cadmium ions. J. Mol. Liq. 2021, 333, 115932. [CrossRef]

12. Baziar, M.; Zakeri, H.R.; Askari, S.G.; Nejad, Z.D.; Shams, M.; Anastopoulos, I.; Giannakoudakis, D.A.; Lima, E.C. Metal-organic and Zeolitic imidazole frameworks as cationic dye adsorbents: Physicochemical optimizations by parametric modeling and kinetic studies. J. Mol. Liq. 2021, 332, 115832. [CrossRef]

13. Bazzarella, A.Z.; Paquin, I.D.; Favoro, U.G.; Alves, R.D.O.; Altoé, M.A.S.; Profeti, L.R.; Profeti, D.; Profeti, L.P.R. Cu-bentonite as a low-cost adsorbent for removal of ethylenethiourea from aqueous solutions. J. Mol. Liq. 2021, 333, 115912. [CrossRef]

14. Hu, Q.; Bin, L.; Li, P.; Fu, F.; Guan, G.; Hao, X.; Tang, B. Highly efficient removal of dyes from wastewater over a wide range of pH value by a self-adaption adsorbent. J. Mol. Liq. 2021, 331, 115719. [CrossRef]

15. Suresh, M.; Sivasamy, A. Fabrication of graphene nanosheets decorated by nitrogen-doped ZnO nanoparticles with enhanced visible photocatalytic activity for the degradation of Methylene Blue dye. J. Mol. Liq. 2020, 317, 114112. [CrossRef]

16. Chowdhury, M.F.; Khondaker, S.; Sarker, F.; Islam, A.; Rahman, M.T.; Awual, R. Current treatment technologies and mechanisms for removal of indigo carmine dyes from wastewater: A review. J. Mol. Liq. 2020, 318, 114061. [CrossRef]

17. Soni, S.; Bajpai, P.; Mittal, J.; Arora, C. Utilisation of cobalt doped Iron based MOF for enhanced removal and recovery of methylene blue dye from wastewater. J. Mol. Liq. 2020, 314, 113642. [CrossRef]

18. Munjur, H.M.; Hasan, N.; Awual, R.; Islam, M.; Shenasheh, M.; Iqbal, J. Biodegradable natural carbohydrate polymeric sustainable adsorbents for efficient toxic dye removal from wastewater. J. Mol. Liq. 2020, 319, 114356. [CrossRef]

19. Abdi, G.; Alizadeh, A.; Amirian, J.; Rezaei, S.; Sharma, G. Polyamine-modified magnetic graphene oxide surface: Feasible adsorbent for removal of dyes. J. Mol. Liq. 2019, 289, 111118. [CrossRef]

20. Gomi, L.S.; Afsharpour, M.; Ghaseemzadeh, M.; Lianos, P. Bio-inspired N,S-doped siligraphenes as novel metal-free catalysts for removal of dyes in the dark. J. Mol. Liq. 2019, 295, 111657. [CrossRef]

21. Krotö, H.W.; Heath, J.R.; O’Brien, S.C.; Curl, R.F.; Smalley, R.E. C60: Buckminsterfullerene. Nature 1985, 318, 162–163. [CrossRef]

22. Dikkannan, M.; Gündüz, G.; Yilmaz, S.; Prihod’ko, R. Heterogeneous Fenton-like degradation of Rhodamine 6G in water using CuFeZSM-5 zeolite catalyst prepared by hydrothermal synthesis. J. Hazard. Mater. 2010, 181, 343–350. [CrossRef]

23. Centi, G.; Perathoner, S.; Torre, T.; Verduna, M.G. Catalytic wet oxidation with H2O2 of carboxylic acids on homogeneous and heterogeneous Fenton-type catalysts. Catal. Today 2000, 55, 61–69. [CrossRef]

24. Adam, A.; Saad, H.; Atta, A.; Alsawat, M.; Hegab, M.; Altalhi, T.; Refat, M. An Environmentally Friendly Method for Removing Hg(II), Pb(II), Cd(II) and Sn(II) Heavy Metals from Wastewater Using Novel Metal–Carbon-Based Composites. Crystals 2021, 11, 882. [CrossRef]
25. Adam, A.M.A.; Altalhi, T.A.; El-Megharbel, S.M.; Saad, H.A.; Refat, M.S. Using a Modified Polyamidoamine Fluorescent Dendrimer for Capturing Environment Polluting Metal Ions Zn$^{2+}$, Cd$^{2+}$, and Hg$^{2+}$: Synthesis and Characterizations. *Crystals* 2021, 11, 92. [CrossRef]

26. Refat, M.; Hamza, R.; Adam, A.; Saad, H.; Gobouri, A.; Al-Salmi, F.; Altalhi, T.; El-Megharbel, S. Potential Therapeutic Effects of New Ruthenium (III) Complex with Quercetin: Characterization, Structure, Gene Regulation, and Antitumor and Anti-Inflammatory Studies (Ru$^{III}$/Q Novel Complex Is a Potent Immunoprotective Agent). *Crystals* 2021, 11, 367. [CrossRef]

27. Köseoğlu, Y.; Oleiwi, M.I.O.; Yilgin, R.; Koçbay, A.N. Effect of chromium addition on the structural, morphological and magnetic properties of nano-crystalline cobalt ferrite system. *Ceram. Int.* 2012, 38, 6671–6676. [CrossRef]

28. Pandey, B. Mössbauer and magnetization studies of nanosize chromium ferrite. *Int. J. Eng. Sci. Technol.* 2010, 2, 80–88. [CrossRef]

29. Baby, R.; Saifullah, B.; Hussein, M.Z. Carbon Nanomaterials for the Treatment of Heavy Metal-Contaminated Water and Environmental Remediation. *Nanoscale Res. Lett.* 2019, 14, 341. [CrossRef] [PubMed]

30. Alekseeva, O.V.; Bagrovskaya, N.A.; Noskov, A.V. Sorption of heavy metal ions by fullerene and polystyrene/fullerene film compositions. *Prot. Met. Phys. Chem. Surf.* 2016, 52, 443–447. [CrossRef]

31. Kabir, M.M.; Mouna, S.S.P.; Akter, S.; Khandaker, S.; Didar-ul-Alam, M.; Bahadur, N.M.; Mohinuzzaman, M.; Islam, A.; Shenashen, M. Tea waste based natural adsorbent for toxic pollutant removal from waste samples. *J. Mol. Liq.* 2021, 322, 115012. [CrossRef]