

SYNTHESIS OF MAGNETIC GRAPHENE OXIDE/ β -CYCLODEXTRIN NANOHYBRIDS FOR THE REMOVAL OF CONGO RED FROM AQUEOUS SOLUTIONS

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ABSTRACT

In this work, a novel magnetic graphene oxide/ β -cyclodextrin (mGO/ β -CD) nanohybrid was synthesized via a three-steps process. Firstly, GO was treated with ionic surfactants cetyltrimethylammonium bromide (CTAB) and poly(sodium-4-styrenesulfonate) (PSS) and then was decorated with magnetic copper ferrite (CuFe_2O_4) nanoparticles via a solvothermal method. The obtained CuFe_2O_4 -GO nanohybrid was further modified with β -CD through a facile hydrothermal method. The final product (CuFe_2O_4 -GO/ β -CD) was characterized by Fourier transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), as well as, transmission electron microscopy (TEM). Furthermore, this study evaluated the performance of the CuFe_2O_4 -GO/ β -CD nanohybrid in the removal of Congo Red (CR) dye from aqueous solution, using ultraviolet-visible (UV-Vis) spectroscopy.

INTRODUCTION

Nowadays, the widespread industrial activity is responsible for the generation of serious environmental issues, such as water pollution. Organic dyes, such as Congo Red (CR), have been widely used in many industrial fields, such as textiles, paper, coatings and leather. Unfortunately, they are hardly destroyed by biodegradation due to their complex aromatic molecular structures and thus tend to persist in the environment. Furthermore, most dyes are highly toxic and can cause mutagenic or carcinogenic effects on aquatic life and human beings even at low concentrations. Therefore, the discharge of the organic pollutants has become a global environment concern over the last century. So far, numerous efforts have been developed for dyes removal, such as adsorption, photo-chemical degradation, coagulation-flocculation, oxidation, catalytic ozonation, etc. Among these techniques, adsorption is the most popular method due to its simplicity and low cost. Therefore, it is very important to develop novel adsorbents with high adsorption capacity and fast separation rates for treating large volumes of wastewater. ^[1,2]

In recent years, carbon-based materials have drawn considerable attention because of their high surface area and chemical stability. Graphene, which is a flat monolayer of carbon atoms tightly packed into a two-dimensional (2-D) honeycomb lattice, has been considered as an ideal adsorbent of organic dyes. However, its application in water treatment is limited due to its poor aqueous dispersibility. On the other hand, graphene oxide (GO) which is derived from graphene by introducing several oxygen-containing functional groups (-OH, -COOH, -C=O, -C-O-C) onto its basal planes and edges, is well dispersed in aqueous solutions. Nevertheless, the separation or recovery of GO adsorbents in heterogeneous systems still remains a steep challenge. Considering this point, the combination of GO adsorbent with magnetic nanoparticles (MNPs) is an ideal option for an easy separation process, as it could be easily retrieved by applying an external magnetic field. ^[3] In particular, transition metal oxides with spinel structures commonly referred to as ferrites are among one of the most important MNPs. Based on their crystal structures and magnetic properties, ferrites are classified as spinel (MFe_2O_4 , where M=Cu, Mn, Fe, Co, Ni, Zn, etc.), garnet ($\text{M}_3\text{Fe}_5\text{O}_{12}$, where M=rare earth cations), hexaferrite ($\text{SrFe}_{12}\text{O}_{19}$ and $\text{BaFe}_{12}\text{O}_{19}$) and orthoferrite (MFeO_3 , M=rare earth cations). Among these, especial attention has been given to spinel ferrite nanoparticles (SFNPs) due to their excellent magnetic properties and simple chemical composition. Spinel ferrites (Figure 1)

are homogeneous materials with a general chemical formula of AB_2O_4 , where A and B are metallic cations positioned at two different crystallographic sites, tetrahedral (A sites) and octahedral (B sites) and composed of Fe(III) as one of the main component in their structure. The cations of both positions are tetrahedrally and octahedrally coordinated to oxygen atoms, respectively. In the formula MFe_2O_4 , depending on the position of M(II) and Fe(III) site preference, three possible spinel ferrite structures are known, namely normal, inverse and mixed. [4] Even though magnetic GO-based adsorbents could be easily removed from aqueous solutions, they show relatively low adsorption capacity and efficiency. Therefore, research on the magnetic GO adsorbents with improved adsorption performance is still needed.

β -cyclodextrin (β -CD, Figure 2) is a cyclic oligosaccharide consisting of seven α -D-glucose units connected through α -(1,4) linkages and it has a hydrophobic inner cavity and a hydrophilic exterior. β -CD has a large number of hydroxyl groups which could possibly make hydrogen bonds either intramolecularly (between the secondary and tertiary-hydroxyl groups of adjacent glucose units) or inter-molecularly (between the β -CD and guest molecules). The forces that stabilize the inclusion complexes include van der Waals interactions between the hydrophilic moiety of a guest molecule and the cavity of β -CD, and also hydrogen bonding between polar functional groups of a guest molecule and the hydroxyl group of the β -CD. The β -CD molecules could selectively bind to various cationic and anionic species in their cavities to form stable host-guest inclusion complexes. [5] As it has been reported, the functionalization of magnetic GO with β -CD will offer the possibility to combine the high sorption capacity of β -CD and the separation convenience of magnetic GO. [6]

On the basis of the above considerations, we report the synthesis of $CuFe_2O_4$ -GO nanohybrid by a solvothermal route and its further modification with β -CD molecules through a simple hydrothermal method. The obtained $CuFe_2O_4$ -GO/ β -CD nanohybrid exhibits excellent adsorption capacity for CR dye.

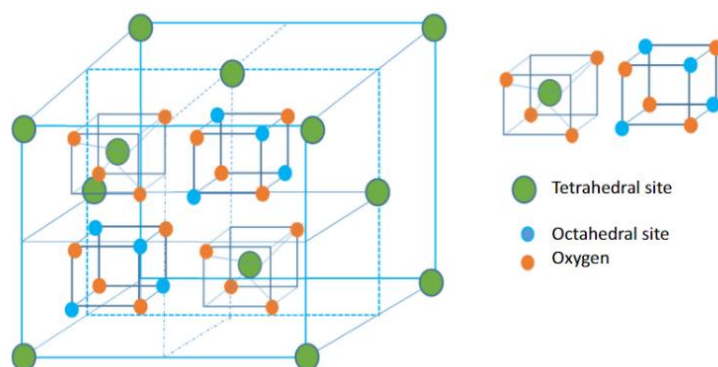


Figure 1. Schematic representation of spinel ferrite structure. [4]

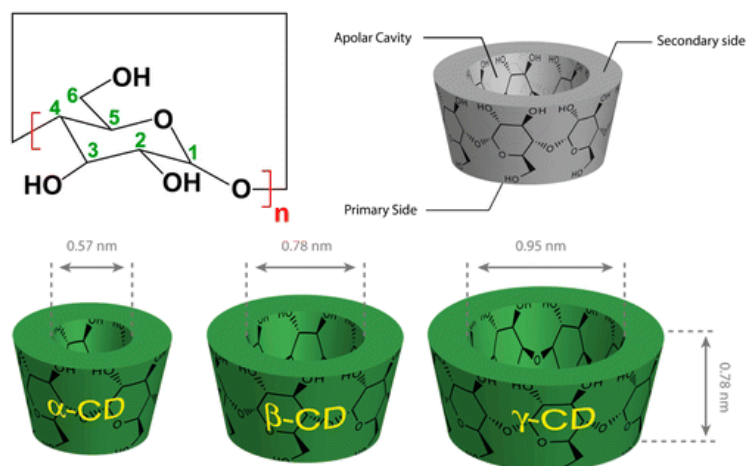


Figure 2. Top: Functional structural scheme of α -CD ($n = 6$), β -CD ($n = 7$), γ -CD ($n = 8$). Bottom: Geometric dimensions of cyclodextrins. [7]

EXPERIMENTAL

i. GO treatment with ionic surfactants CTAB & PSS

To begin with, GO was modified with ionic surfactants CTAB and PSS. Briefly, 200 mg of GO were dispersed in 266.6 mL of aqueous solution of CTAB 1% w/v with sonication for 30 min. After that, the mixture was centrifuged for 10 min at 4.000 rpm. The solid residue was washed with deionized (DI) water and then was dissolved in 266.6 mL of aqueous solution of PSS 1% w/v with sonication for 30 min. After 12 h, the above mixture was centrifuged for 10 min at 4.000 rpm. The black residue was dispersed in 50 mL of ethylene glycol (EG) by sonication for 30 min.

ii. Synthesis of CuFe₂O₄-GO nanohybrid

Following that, FeCl₃·6H₂O and CuCl₂·2H₂O were added to the above GO/EG solution so that the molar ratio of Cu:Fe was 1:2. Subsequently, 3.6 g of sodium acetate (NaAc) and 1.0 g of polyethylene glycol (PEG) were added, followed by stirring for 30 min. The mixture was then transferred to a Teflon-lined stainless steel autoclave and heated at 200 °C for 12 h. After the reaction was complete, the precipitate was filtered and washed several times with excess of DI water and acetone. Finally, the sample was dried overnight at a temperature of 60 °C in air to obtain the CuFe₂O₄-GO nanohybrid.

iii. Synthesis of CuFe₂O₄-GO/β-CD nanohybrid

The synthesis of CuFe₂O₄-GO/β-CD nanohybrid was carried out by a facile hydrothermal method. In a typical procedure, 25 mL of a homogeneous CuFe₂O₄-GO dispersion were added to 25 mL of a β-CD aqueous solution, followed by sonication for 30 min. Later, the mixture was transferred to a Teflon-lined stainless steel autoclave and heated at 90 °C for 12 h. The resulting material was centrifuged at 4.000 rpm and washed with excess of deionized water and acetone. The sample was dried at 60 °C in air overnight to obtain the final CuFe₂O₄-GO/β-CD nanohybrid.

iv. Adsorption experiments

Lastly, the adsorption capacity of the synthesized CuFe₂O₄-GO/β-CD toward CR dye was investigated. An initial stock solution of CR was prepared by dissolving CR dye in DI water. Typically, 10 mL of (50 mg/L) CR aqueous solution were added over 10 mg of the adsorbent material, sonicated and monitored over time. After phase separation between the solid and the liquid, the remaining CR in the solution was determined by UV-Vis measurements.

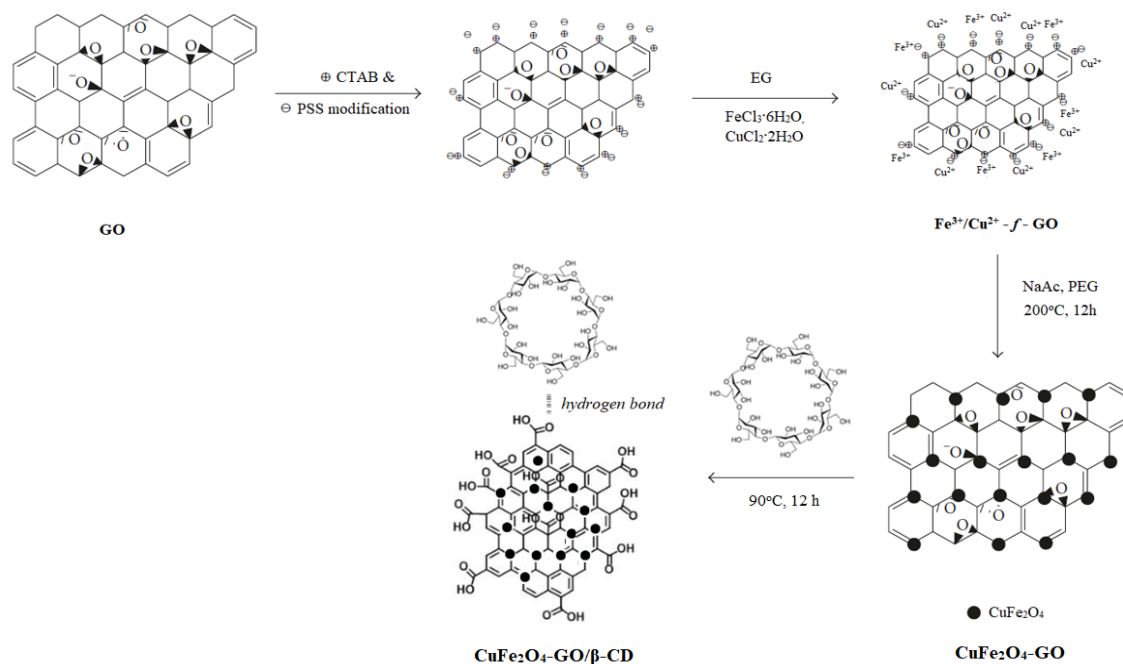
RESULTS AND DISCUSSION

i. Synthesis mechanism of the CuFe₂O₄-GO/β-CD nanohybrid

The CuFe₂O₄-GO/β-CD nanohybrid synthesis mechanism is schematically illustrated in Scheme 1. The overall synthetic procedure consists of three steps. Firstly, GO was modified with the cationic surfactant CTAB, which contains a positively charged polar head and a hydrophobic tail. It is well-known that GO consists of several oxygen-containing groups resulting in a negatively charged surface. This means that electrostatic interactions can occur between the ammonium cations of CTAB head and the negatively charged GO sheets. Afterwards, the anionic surfactant PSS is adsorbed onto the positively charged GO/CTA⁺ surface, forming a polymeric layer. The modification of GO nanosheets with the above surfactants lessens their aggregation.

The second step of the synthesis mechanism includes the formation of CuFe₂O₄ nanoparticles onto GO nanosheets, via a solvothermal method. During this process, the positively charged Cu²⁺ and Fe³⁺ ions can easily adsorb onto the negatively charged GO nanosheets via electrostatic forces. The formation of CuFe₂O₄ nanoparticles includes nucleation, growth of the primary crystal and self-assembly of the nanoparticle, while their morphology depends on several solvothermal factors, such as concentration of precursors, stabilization agent, precipitation agent or temperature.

Finally, CuFe₂O₄-GO was further decorated with β-CD molecules through a hydrothermal method; β-CD was assembled onto the surface of CuFe₂O₄-GO by hydrogen bonding. Hydrogen bonds are formed between the -OH and the -COOH groups of β-CD exterior and GO surface, respectively.



Scheme 1. Schematic illustration of the fabrication of CuFe₂O₄-GO/β-CD nanohybrid.

ii. Characterization of the CuFe₂O₄-GO/β-CD nanohybrid

It is known that FT-IR spectroscopy is one of the most common techniques to identify the presence of functional groups and chemical bonds in a synthesized material. In this study, the FT-IR spectra of CuFe₂O₄-GO/β-CD nanohybrid is presented in Figure 3. The broad band at 3.450 cm⁻¹ is attributed to the stretching and bending vibration of O-H groups of water molecules adsorbed on the sample, while the band at 1.725 cm⁻¹ corresponds to the stretching of the -C=O and -COOH groups on GO. In addition, the peak at 1.691 cm⁻¹ (aromatic C=C) can be ascribed to the skeletal vibrations of unoxidized graphene domains. The presence of two absorption bands at 560 cm⁻¹ and 418 cm⁻¹ can be also noticed. The former belongs to the stretching vibration of Cu²⁺ in octahedral site and the latter to the stretching vibration of Fe³⁺ in the tetrahedral site of CuFe₂O₄ nanoparticles. Furthermore, the FT-IR spectra exhibits characteristic absorbing peaks of β-CD. More specifically, the band at 1.155 cm⁻¹ is assigned to the coupled C-O-C stretching/O-H bending vibrations. The featured peaks at 1.030 cm⁻¹ and 1.080 cm⁻¹ are attributed to the coupled C-O/C-C stretching/O-H bending vibrations. The above results demonstrate that β-CD has been anchored on the surface of CuFe₂O₄-GO successfully.

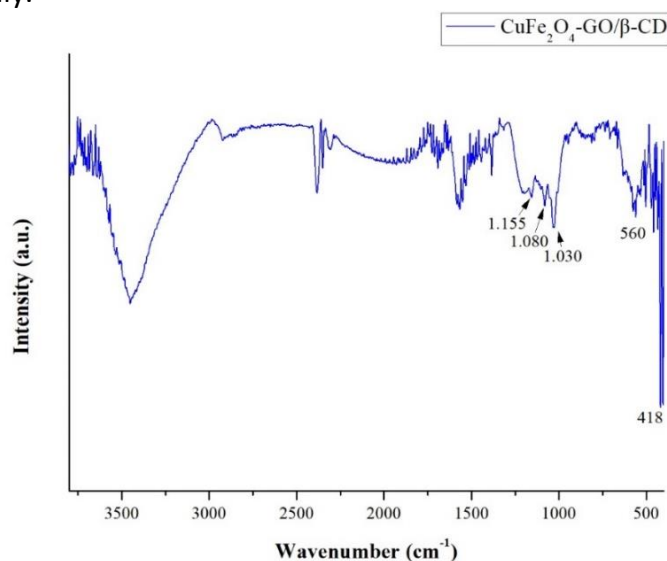


Figure 3. FT-IR spectra of CuFe₂O₄-GO/β-CD nanohybrid.

The crystalline structure of CuFe₂O₄-GO/β-CD nanohybrid was analyzed by XRD using Cu-K_α radiation ($\lambda = 0.15418$ nm). The XRD spectrum of CuFe₂O₄-GO/β-CD is presented in Figure 4. The diffraction peaks at $2\theta = 30.27^\circ$, 35.54° , 43.46° , 49.41° , 57.22° , 62.95° are assigned to the (220), (311), (400), (422), (511) and (440) crystal planes of CuFe₂O₄ with cubic spinel structure. The XRD pattern shows no other peaks, indicating dissimilar deposition of β-CD onto CuFe₂O₄-GO surface.

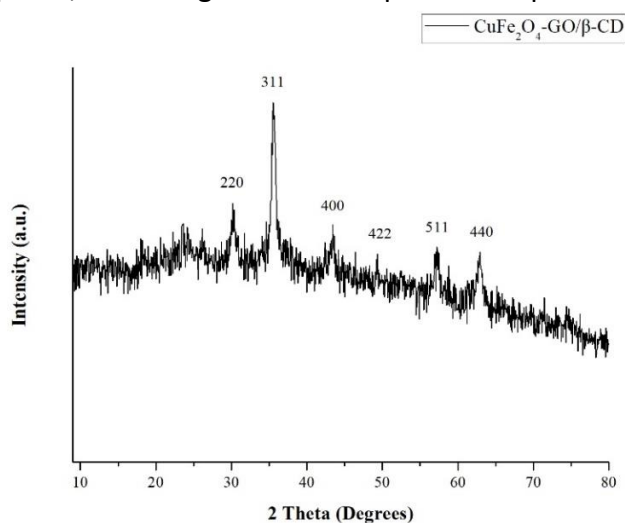


Figure 4. XRD pattern of CuFe₂O₄-GO/β- CD nanohybrid.

The morphology of CuFe₂O₄-GO/β-CD nanohybrid was characterized by SEM and TEM techniques. Figure 5 shows the representative SEM images of CuFe₂O₄-GO and CuFe₂O₄-GO/β-CD. It can be observed that CuFe₂O₄ nanoparticles have been successfully assembled on the surface of GO. These nanoparticles exhibit a number of different shapes including nanorods, spheres, as well as, cubes. As for the SEM image of CuFe₂O₄-GO/β-CD, it is difficult to notice β-CD due to its extremely small size. In Figure 6 TEM images of CuFe₂O₄-GO and CuFe₂O₄-GO/β-CD are presented. It is confirmed that spherical structures of CuFe₂O₄ were indeed anchored onto GO sheets. However, further characterization of CuFe₂O₄-GO/β-CD sample with high-resolution TEM (HR-TEM) is necessary in order to observe the modification of CuFe₂O₄-GO with β-CD molecules.

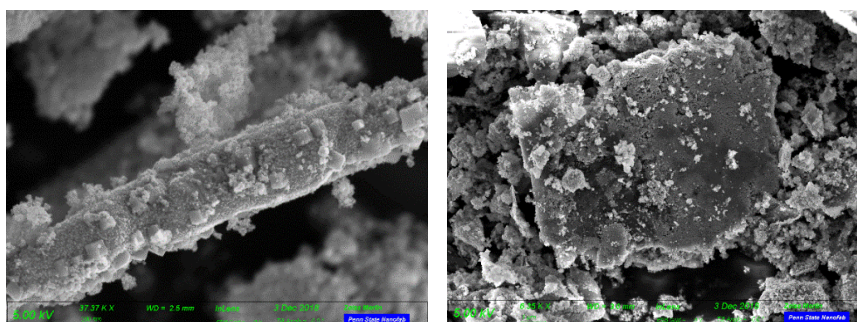


Figure 5. SEM images of CuFe₂O₄-GO (left) and CuFe₂O₄-GO/β-CD (right).

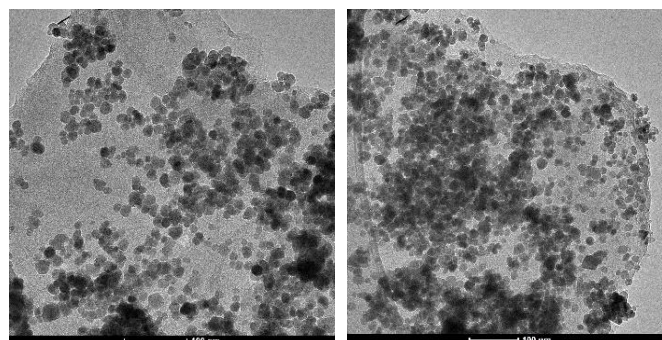


Figure 6. TEM images of CuFe₂O₄-GO (left) and CuFe₂O₄-GO/β-CD (right).

The adsorption behavior of $\text{CuFe}_2\text{O}_4\text{-GO}/\beta\text{-CD}$ nanohybrid in the removal of CR dye from aqueous solution was investigated at five different adsorption times (30 min, 45 min, 60 min, 120 min and 18 h), while the concentration of CR aqueous solution was maintained at 50 g/L. As it is presented in Figure 7, the characteristic UV-Vis absorption of CR at 497 nm was dramatically decreased in all cases. It can be clearly observed that the adsorption capacity of $\text{CuFe}_2\text{O}_4\text{-GO}/\beta\text{-CD}$ depends on its contact time with CR aqueous solution. This means that the nanohybrid showed better adsorption performance as the contact time with CR was increased.

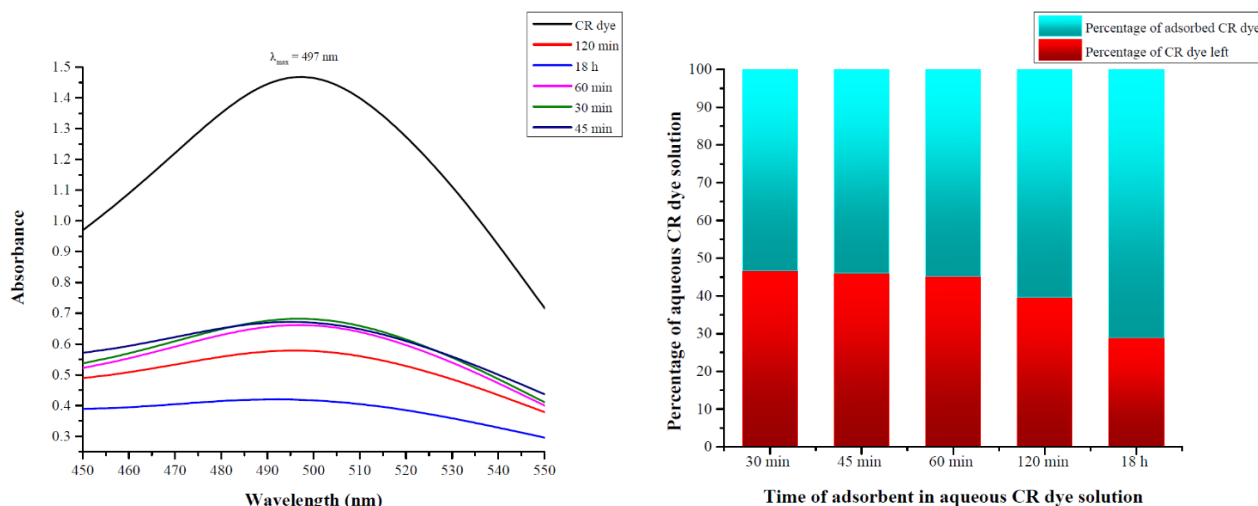


Figure 7. Variation of adsorption capacity of $\text{CuFe}_2\text{O}_4\text{-GO}/\beta\text{-CD}$ nanohybrid as a function of contact time with CR dye aqueous solution.

CONCLUSIONS

In summary, this work reports the synthesis and characterization of the magnetic $\text{CuFe}_2\text{O}_4\text{-GO}/\beta\text{-CD}$ nanohybrid. More specifically, $\text{CuFe}_2\text{O}_4\text{-GO}/\beta\text{-CD}$ was successfully synthesized by a three-steps process, including modification of GO with ionic surfactants, further decoration with CuFe_2O_4 nanoparticles and functionalization of $\text{CuFe}_2\text{O}_4\text{-GO}$ with $\beta\text{-CD}$ molecules. The final material was characterized by FT-IR, XRD, SEM, as well as, TEM analysis. The XRD pattern confirms the presence of the cubic spinel structure, CuFe_2O_4 , while FT-IR spectra showed that $\beta\text{-CD}$ has been anchored on $\text{CuFe}_2\text{O}_4\text{-GO}$ material. The performance of $\text{CuFe}_2\text{O}_4\text{-GO}/\beta\text{-CD}$ nanohybrid in the removal of CR dye from aqueous solution was also studied through UV-Vis measurements. This study demonstrated that the new synthesized magnetic material proved to be effective as a potential adsorbent for the removal of organic dyes from aqueous solution and a promising adsorbent for further utilization in water purification.

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