Ultimate Eradication of the Ciprofloxacin Antibiotic from the Ecosystem by Nanohybrid GO/O-CNTs

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ABSTRACT: Eradication of pharmaceutical drugs from the global ecosystem has received remarkable attention due to the extensive horrible consequences on the human immunological system and the high rate of human deaths. The urgent need for drug eradication became the dominant priority for many research institutions worldwide due to the sharp increase of antimicrobial resistance (AMR) in the human body, which inhibits drug effectiveness and leads ultimately to death. Nanohybrid GO/O-CNTs was fabricated from graphene oxide (GO) cross-linked via calcium ions (Ca^{2+}) with oxidized carbon nanotubes (O-CNTs) to eradicate the well-known ciprofloxacin antibiotic drug from aqueous solutions. The ciprofloxacin drug is medically prescribed in millions of medical prescriptions every year and typically exists in domestic and wastewaters. Characterization of the nanohybrid GO/O-CNTs was carried out through spectroscopic (Fourier Transform Infrared (FTIR) and X-ray diffraction (XRD)), thermal (Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG)), and microscopic (scanning electron microscopy (SEM)) techniques. Optimum parameters for the drug eradication process from aqueous solutions were verified and selected as follows: contact time = 4 h, pH = 6.0, temperature = 290 K, %CaCl_2 = 0.5%, GO/O-CNT ratio = 4:1, and adsorbent mass = 1.0 mg. The equilibrium data were fitted to different adsorption isotherms, and the Langmuir isotherm provided the best fit to our data. Dynamic studies demonstrated a pseudo-second-order removal process for the ciprofloxacin drug, and thermodynamic parameters confirmed exothermic drug adsorption (−27.07 kJ/mol) as well as a physisorption process. For the sake of fighting against the generated AMR, our working strategy demonstrated a removal efficiency of 99.2% of the ciprofloxacin drug and drug uptake as high as 512 mg/g.

INTRODUCTION

In recent years, the presence of pharmaceutical medicines and drugs in sewage, wastewaters, and domestic waters has been found to be responsible for huge ecotoxicological effects on human health in different countries. The toxic side effects of pharmaceuticals in water resources are extremely dangerous and have serious consequences on human health, animals, and plants. Several studies have described the harmful effects of pharmaceuticals on the aquatic environment and their adverse ability to influence sexual functions and endocrine activity of humans and animals. Nano- or microscale concentrations of drugs were not previously considered harmful, but it has become tremendously important to carefully monitor their concentrations in aquatic environments. Growing drug concentrations, especially antibiotic drugs, in sewage treatment effluents, wastewaters, and drinking waters are mainly due to poorly metabolized drugs in the human body secreted through human urine or dislodged feces routes. The increased annual consumption of pharmaceutical drugs has led to an increase in their concentration in wastewaters, which has reached 15 g per year per person, and it is expected to increase in the future to 50–150 g. If the concentration of such drugs exceeds the shelf concentration, they can become toxic to humans, animals, and plants. Therefore, drug concentration in wastewaters must be measured to assess the ecotoxicity on a daily basis. Latest statistics indicate that there are more than 3700 approved pharmaceutical drugs in the world. This huge number of drugs indicates how difficult it is to treat their toxicity efficiently and how complicated their removal techniques are in wastewaters.

Bacteria can frequently generate resistance against antibiotic drugs in the human body called antimicrobial resistance (AMR). The generated resistance occurs through mutations in their genes or by acquisition of foreign DNA coding through horizontal gene transfer, and the bacteria can survive, and even grow, in the presence of antibiotic drugs, leading to a condition under which the drugs become noneffective on the patient, which aggravates with time and, at the end, may lead to...
death. The most recent global statistics has declared 700,000 deaths in 2016 related to AMR and non-effective drugs, and the human mortality rate will reach 10 million per year by the year 2050. Antibiotics in the aquatic environment were considered responsible for human endemic disruption. Moreover, pharmaceutical drugs caused a decrease in the number of fish through increasing intersex and reducing fecundity and an increase in mortality rates of birds, especially vultures. Such horrifying information if not treated carefully can threaten the survival of humans, animals, and plants on the globe. Therefore, innovative eradication strategies must be established to remove drugs entirely from wastewaters, and new government regulations must be established and enforced to eradicate pharmaceutical drugs from wastewaters. The ciprofloxacin antibiotic is a widely used antibiotic that targets Gram-negative and Gram-positive bacteria. According to the U.S. government data, there were more than 7 million medical prescriptions for ciprofloxacin in 2019. Different countries have confirmed the presence of ciprofloxacin in their municipal wastewaters and drinking water. The risk quotient (RQ) scale for ciprofloxacin was identified as a high risk to the environment. Desbiolles found that ciprofloxacin is one of the most hazardous pharmaceuticals in 75% of Mediterranean wastewater samples. Due to the chemical structure of ciprofloxacin, it is considered a genotoxic compound, so it needs close monitoring and treatment. Zhang conducted a study on the relation between antibiotics and heavy metals, and the results showed that the interaction of the antibiotic, ciprofloxacin, with a group of heavy metals, copper, zinc, and cadmium, via coordination sites gave rise to complexes that are more toxic than the interacting compound (Figure 1).

Figure 1. Ciprofloxacin drug.

Versatile techniques have been employed to remove pharmaceutical drugs from wastewater, such as the conventional activated sludge process, anaerobic sludge digestion, biosorption, oxidation, reverse osmosis, removal using activated carbon, photobioreactors, and nanotechnology. Carbon nanotubes (CNTs) have two forms: single-walled and multiwalled carbon nanotubes arranged in a hexagonal shape with outer diameters of 4–30 nm, inner diameters of up to 0.4 μm, length of around 1 μm, and a high adsorption surface area of over 1000 m²/g. Carbon nanotubes (CNTs) have high adsorption capacity due to their porous nature and are used to remove pharmaceutical products from wastewater. Graphene consists of a two-dimensional carbon layer that makes graphene the thinnest material ever and has a specific surface area of about 2630 m²/g; many scientific disciplines are concerned with the research on graphene, such as physics, materials science, chemistry, and biology. Recently, oxidized graphene (GO) nanocomposites have been used to eliminate pharmaceutical and personal-care products. GO has a higher ability to adsorb polar materials than nonpolar ones; the reason behind this is the strong interactions between polar materials and polar functional groups on GO.

In this work, we synthesized new nanohybrid materials composed of graphene oxide (GO) and oxidized carbon nanotubes (O-CNTs) to fully eliminate the ciprofloxacin drug from aqueous solutions. The ultimate eradication strategy was established toward fighting against the induced antimicrobial resistance (AMR) formed thereafter. The innovative nanohybrid material was characterized by different techniques. Optimum conditions, dynamics, and thermodynamics for the eradication of drugs were also investigated.

## EXPERIMENTAL SECTION

**Materials.** Carbon nanotubes were purchased from Nanocyl NC7000, graphene was purchased from Sigma-Alrich, and the ciprofloxacin drug (>99%) was gifted by a local pharmaceutical company. Other reagents were of analytical grade and were used as received. Tween 80, purchased from BBC chemicals, was used as a dispersion surfactant, and its micellar average molar mass was 79,000. Concentrated acids used in the study were HCl (Scharlau), H₂SO₄ (Riedel-de Haën), HNO₃ (BBC Chemicals), and H₃PO₄ (Riedel-de Haën). H₂O₂ was obtained from Merck.

**Investigation Techniques.** Fourier Transform Infrared (FTIR) Spectroscopy. A Bruker FTIR spectrometer was used to investigate functional groups after the oxidation process of graphene and multiwalled carbon nanotubes (CNTs). Spectra were recorded in the range of 4000–400 cm⁻¹ using KBr pellets. Thermogravimetric analysis (TGA), with a Netzsch Proteus thermogravimetric analyzer, was performed to study the thermal stability of GO and multiwalled CNTs before and after the oxidation processes. The samples were heated from ambient temperature to 900 °C at a heating rate of 10 °C/min under a stream of inert N₂ gas. The derivative thermogravimetry (DTG) technique was used to determine the decomposition temperature of the samples. Scanning electron microscopy [SEM; Inspect F50 scanning electron microscope equipped with a high-resolution Schottky field emission gun (FEG), high-vacuum Bruker energy-dispersive spectrometry (EDS) microanalyzer, and XFlash silicon drift detector (SDD)] was used to study the topological changes of graphene and multiwalled CNTs before and after the oxidation processes. The samples were sputtered by gold ions before being imaged. All images were tuned and resolved by software programs of the instrument. UV−vis spectrophotometry (Hach Lange DR5000 UV−vis spectrophotometer) was used to detect ciprofloxacin concentrations at different time intervals. The samples were scanned in the range of 200–800 nm and the maximum wavelength (λmax) was selected as 275 nm. The calibration curve for the ciprofloxacin drug was established, and the drug concentration was monitored accordingly. For X-ray diffraction (XRD) studies, a Rigaku X-ray diffractometer (Ultima IV; 1 and 5 mm) with Cu Kα radiation was used. An accelerating tube voltage of 40 kV and a tube current of 40 mA were used to study the crystalline structure of graphene and multiwalled CNTs before and after the oxidation process. The scanning rate was 2°/min in the angle range from 5 to 60°.

**Preparation of GO.** Graphene (225 mg) was mixed with 30 mL of a mixture of sulfuric acid (H₂SO₄) and phosphoric acid (H₃PO₄) (9:1 ratio) under continuous stirring for 6 h according to Hummers’ method. Later on, 1.32 g of potassium permanganate (KMnO₄) was added, and 675 μL...
of hydrogen peroxide (H$_2$O$_2$) was slowly dropped to remove unreacted KMNO$_4$. Diluted hydrochloric acid (HCl) was added, and the solution was centrifuged and decanted. Eventually, the final product was washed with a concentrated HCl:H$_2$O solution (1:3 ratio) and dried.

**Preparation of O-CNTs.** Briefly, 2.0 g of multiwalled carbon nanotubes was placed in a dried 50 mL round-bottom flask equipped with a condenser and 30 mL of 9.0 M HNO$_3$ solution was slowly added. The mixture was refluxed at 75 °C for 24 h, and after completion, the oxidized CNTs were filtered and the suspended O-CNTs particles were collected by centrifugation. The oxidized CNTs (O-CNTs) were purified from nitric acid traces by continuous washing with distilled water several times until the pH of the filtrate solution became neutral. The O-CNT sample was dried at room temperature and stored until used.

**Synthesis of Nanohybrid GO/O-CNTs.** Graphene oxide (GO, 0.5 g) was dispersed in 150 mL of 2.5% Tween 80 surfactant solution (w/w) under continuous stirring at 70 °C for 2 h to make a water-dispersed graphene oxide (GO) solution. Similarly, in a separate tube, 0.5 g of oxidized carbon nanotubes (O-CNTs) was dispersed in 150 mL of 2.5% Tween 80 surfactant solution at 70 °C to make a water-dispersed CNT solution.

The dispersed solutions of GO and O-CNTs were slowly mixed and added dropwise into a CaCl$_2$ solution to make 2% CaCl$_2$ concentration under stirring (100 rpm). For complete nucleation of the nanohybrid sample, the mixture was left stirring overnight at ambient temperature. The final nanohybrid product was collected by centrifugation, and the nanohybrid GO/O-CNT materials were dried and stored until used elsewhere.

**Ultimate Drug Eradication.** The nanohybrid GO/O-CNT material was placed in ciprofloxacin drug solutions of various concentrations and shaken in a Memmert shaker for various periods of time. After completion, the sample was centrifuged at 4000 rpm for 15 min, and the supernatant was decanted. The ciprofloxacin drug uptake by the nanohybrid GO/O-CNTs was calculated from the following relation

$$q_e = \frac{C_0 - C_e}{W} V$$

where $q_e$ is the equilibrium drug uptake (in mg/g), $C_0$ is the initial concentration of the drug (in mg/L), $C_e$ is the equilibrium drug concentration (in mg/L), $V$ is the volume of the solution (in L), and $W$ is the mass of the nanohybrid material (in g).

Batch adsorption experiments were conducted to investigate and optimize the adsorption conditions. For optimization of contact time, 1 mg of nanohybrid was added into ciprofloxacin solutions having a concentration of 15 ppm for time intervals from 0.5 to 48 h. The following parameters were kept fixed during experiments: pH = 6.0, solution volume = 30 mL, temperature = 17 °C, GO/O-CNT ratio = 1/1, and %CaCl$_2$ = 2.0%. For optimization of the mass of nanohybrid, different masses in the range of 1–5 mg were used for the eradication process at fixed pH = 6.0, solution volume = 30 mL, contact time = 4 h, temperature = 17 °C, GO/O-CNT ratio = 1/1, and %CaCl$_2$ = 2.0%. For optimization of temperature, batch adsorption experiments were carried out in the 290–303 K range at fixed pH = 6.0, solution volume = 30 mL, contact time = 4 h, nanohybrid mass = 1 mg, GO/O-CNT ratio = 1/1, and %CaCl$_2$ = 2.0%. For optimization of solution pH, different pH values in the range 2–11 were used at fixed contact time = 4 h, solution volume = 30 mL, temperature = 17 °C, nanohybrid mass = 1 mg, GO/O-CNT ratio = 1/1, and %CaCl$_2$ = 2.0%. For optimization of the CaCl$_2$ cross-linker, different concentrations were used (0.5, 2, and 4%) at fixed pH = 6.0, solution volume = 30 mL, contact time = 4 h, nanohybrid mass = 1 mg, temperature = 17 °C, nanohybrid mass = 1 mg, GO/O-CNT ratio = 1/1, and %CaCl$_2$ = 2.0%.

**Desorption Process.** Desorption of adsorbed drugs on the surface of the adsorbent is a particularly important step toward the reuse of the adsorbent over and over in the drug eradication process. This permits the reuse of nanohybrid GO/

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O-CNTs several times to remove the ciprofloxacin drug from aqueous solutions. For this purpose, 500 mg of nanohybrid GO/O-CNTs was immersed in 500 mL of 0.4 M NaOH solution and allowed to mix overnight at ambient temperature; then, the nanohybrid was decanted and washed several times with distilled water to remove traces of the ciprofloxacin drug. Nanohybrid GO/O-CNTs was dried and stored until reused again.65

**RESULTS AND DISCUSSION**

**Structural Composition.** Carboxylic-functionalized graphene and carbon nanotubes were observed and identified through the Fourier transform infrared (FTIR) technique. Figure 2 shows the FTIR spectra of graphene oxide (GO), oxidized carbon nanotubes (O-CNTs), and nanohybrid GO/O-CNTs. In addition, Table 1 illustrates the characteristic vibrational assignments and their corresponding wavenumbers. In graphene oxide, a broad peak of the hydroxyl (OH) group at 3447 cm−1, peaks of asymmetric and symmetric carboxylate (COO−) groups at 1632 and 1385 cm−1, carbonyl (C=O) group at 1711 cm−1, and epoxy groups (COC) at 1031 cm−1 proved the successful oxidation process of graphene. Moreover, the peak of delocalized C=C stretching at 1645 cm−1 proved the accomplished oxidation process without complete destruction of the graphene carbon skeleton. This is a very critical step because in some oxidation processes, a collapse of the carbon skeleton of nanoparticles may occur. Likewise, in oxidized carbon nanotubes (O-CNTs), peaks of dense hydroxyl (OH) groups at 3451 cm−1, respective asymmetric and symmetric carboxylate (COO−) groups at 1625 and 1385 cm−1, carbonyl (C=O) group at 1709 cm−1, and epoxy groups (COC) at 1080 cm−1 demonstrated the complete oxidation process of CNTs. In addition, the appearance of a dense delocalized C=C peak at 1649 cm−1 endorsed the retained carbon skeleton of CNTs during the oxidation process. Nanohybrid GO/O-CNTs equally shows the functional groups of GO and O-CNTs. Cross-linking of carboxyl groups (COO−) of GO and O-CNTs via Ca2+ ions was established by a decrease in the intensity of asymmetric and symmetric COO− peaks and an instantaneous increase in the intensity of the carbonyl (C=O) peak (Figure 2).

**Thermal Stability.** The thermal stability of compounds was measured by thermogravimetric analysis (TGA) and its derivative thermogravimetry (DTG) technique evaluated the ability of the sample to withstand elevated temperatures until it decomposed. The midpoint peak of DTG thermograms shows the decomposition temperature and displays the thermal stability of samples. Figure 3A,B shows the TGA and DTG thermograms of graphene oxide (GO), oxidized carbon nanotubes (O-CNTs), and nanohybrid GO/O-CNTs, respectively. Two decomposition temperatures of GO are observed at 225 and 680 °C, respectively. The peak below 100 °C is attributed to adsorbed water on the surface of GO. The peak at 225 °C is assigned to pyrolysis of labile oxygen functional groups, such as CO2, CO, gases, and steam.32–34 The peak at 680 °C is due to the destruction of the carbon skeleton of graphene oxide.35 In contrast, oxidized carbon nanotubes display no degradation temperature up to 900 °C, as observed in the DTG thermogram (Figure 3B), which confirms the absence of disordered carbon responsible for degradation and the presence of a tough carbon skeleton during the oxidation process.36 It may also indicate that the oxidation process occurs on the external surface of carbon nanotubes, as evidenced by FTIR spectra. On the other hand, nanohybrid GO/O-CNTs displays the onset of decomposition at 250 °C and its end at 450 °C with the midpoint peak of decomposition at 350 °C for different GO:O-CNTs ratios (Figure 3B). During the cross-linking of carboxylate groups (COO−) of GO with the carboxylate groups (COO−) of O-CNTs, the decomposition temperature of the labile oxygen groups in GO increased from 225 to 350 °C, and moreover, the peak at 680 °C disappeared in the nanohybrid samples. This demonstrated that the thermal stability of GO sheets increased due to cross-linking with O-CNT cylinders at all GO:O-CNTs ratios of the nanohybrid.

**Crystal Structure and Interlayer Spacings.** The crystal structure of the new nanohybrid materials was identified from X-ray diffraction (XRD) patterns. The spacing between the

| nanomaterial               | wavenumber (cm−1) | vibrational assignments          |
|---------------------------|-------------------|----------------------------------|
| graphene oxide (GO)       | 3447              | O–H stretching                   |
|                           | 3042              | aromatic C−H stretching          |
|                           | 2979              | asymmetric C−H stretching        |
|                           | 2886              | symmetric C−H stretching         |
|                           | 1711              | C==O stretching                  |
|                           | 1645              | conjugated C=C stretching        |
|                           | 1632              | asymmetric C−H stretching        |
|                           | 1385              | symmetric COO− stretching        |
|                           | 1031              | COC stretching                   |
|                           | 3451              | O–H stretching                   |
|                           | 3031              | aromatic C−H stretching          |
|                           | 2975              | asymmetric C−H stretching        |
|                           | 2882              | symmetric C−H stretching         |
|                           | 1709              | C==O stretching                  |
|                           | 1649              | conjugated C=C stretching        |
|                           | 1625              | asymmetric COO− stretching       |
|                           | 1385              | symmetric COO− stretching        |
|                           | 1080              | COC stretching                   |
|                           | 3342              | O–H stretching                   |
|                           | 3005              | aromatic C−H stretching          |
|                           | 2918              | asymmetric C−H stretching        |
|                           | 2851              | symmetric C−H stretching         |
|                           | 1734              | C==O stretching                  |
|                           | 1644              | conjugated C=C stretching        |
|                           | 1632              | asymmetric COO− stretching       |
|                           | 1346              | symmetric COO− stretching        |
|                           | 1067              | COC stretching                   |

Table 1. Characteristic FTIR Vibrational Assignments with Their Wavenumbers for Graphene Oxide (GO), Oxidized Carbon Nanotubes (O-CNTs), and Nanohybrid GO/O-CNTs
crystal planes of graphene, graphene oxide, carbon nanotubes (CNTs), oxidized carbon nanotubes (O-CNTs), and nanohybrid GO/O-CNTs was calculated using Bragg’s equation as follows

\[ n \lambda = 2d \sin \theta \]  

(2)

where \( n \) is chosen as 1, \( \lambda \) is the X-ray wavelength taken as 1.5406 Å using Cu Kα radiation, \( \theta \) is Bragg’s angle, and \( d \) is the interlayer spacing between crystal planes. A distinctive diffraction peak (002) of graphene at 26.14° with an interlayer spacing of 3.4 Å corresponds to hexagonal crystalline graphite between graphene nanosheets, as illustrated in Figure 4. However, GO displays two lower intensity peaks at 11.55 and 23.00° with interlayer spacings of 7.7 and 3.9 Å, which match with hexagonal crystalline graphite. The interlayer spacing between crystalline planes alters with the degree of oxidation; the higher level of oxidation of GO yields several functional groups on the surface of GO and, subsequently, larger interlayer spacings between GO nanosheets. The appearance of broad peaks with wider interlayer spacing values indicates the formation of irregular disordered structures due to labile oxygen functional groups on the surface of GO nanosheets. Moreover, CNTs have two peaks at 25.66 and 43.38°, representing the (002) hexagonal graphite and the (100) diffraction of graphite. Likewise, O-CNTs have the same two peaks appearing in CNTs with higher intensity values. The increase in the intensity of peaks for O-CNTs provides evidence for the successful oxidation process, and the identical peak angles for O-CNTs and CNTs prove that the crystal structure is not affected by the oxidation process. Nanohybrid GO/O-CNTs shows two peaks at 24.7 and 42.9°, regardless of the ratio of GO to O-CNTs. These diffraction peaks correlate with the (002) and (100) crystal planes. Peak broadening of nanohybrid GO/O-CNTs is attributed to the crystalline defects and disordered structures and to the exfoliation process that occurs during the formation of nanohybrids.

**Topology.** The topological structure and morphological changes of nanoscale adsorbents were monitored using the scanning electron microscopy (SEM) technique. Graphene shows two-dimensional nanosheets stacked above each other with 1–2 μm flake size and versatile flake thickness (Figure 5A). However, graphene oxide shows 2D nanosheets but with exfoliated flakes. The exfoliation occurs due to crystalline defects that appear on the nanohybrid surface during the oxidation process (Figure 5B). The thin GO flakes hold hydroxyl, carboxyl, and epoxy functional groups on their inner and outer surfaces. On the other hand, oxidized multiwalled carbon nanotubes (O-CNTs) show cylindrical-shaped nanotubes that hold labile oxygen functional groups (i.e., hydroxyl, carbonyl, carboxyl, and epoxy) on their surfaces (Figure 5C). When cylindrical O-CNTs are cross-linked with sheets of GO via Ca²⁺ ions, the carboxyl groups of GO and O-CNTs bind through the cross-linking agent (Ca²⁺). The threads of O-CNTs settle down on the surface of the GO sheets, as demonstrated in Figures 5D,E. Likewise, at the 1:4 ratio, a higher content of threads of O-CNTs are cross-linked with GO nanosheets (Figure 5F).

**Optimum Parameters for Ultimate Eradication.** Versatile parameters and conditions were designed to inspect the optimum conditions for ultimate eradication of drugs from aqueous solutions. For this purpose, batch adsorption experiments were processed, and the parameters were investigated in the following order: contact time, nanohybrid mass, temperature, solution pH, percent of cross-linking agent.
nanohybrid mass, chains of GO and O-CNTs established intermolecular interactions and accumulated above each other, thus covering many of the active sites, which inhibited drug uptake. In addition, for temperature optimization, batch adsorption experiments were carried out in the 290–303 K range. Obviously, as the temperature increased, the drug uptake decreased. This was due to the increased kinetic energy of the surface of nanohybrid GO/O-CNTs and the ciprofloxacin molecules in solution, which depleted the drug uptake and minimized the adsorbent–adsorbate interactions.

**Solution pH, %Cross-linking Agent, and GO/O-CNT Ratio.** The influence of solution pH on the drug uptake was investigated in the range pH = 2−11 (Figure 6D). Drug uptake shows a distribution curve over the pH range with the maximum uptake at pH = 6.0. Adsorption of ciprofloxacin on the surface of nanohybrid GO/O-CNTs occurs via H-bonding and/or π−π stacking interactions. Furthermore, the ciprofloxacin drug has two pKₐ values of 5.9 and 8.9. At pH < 5.9, ciprofloxacin is protonated and holds positive charges, and at pH > 8.9, ciprofloxacin is deprotonated and holds negative charges. In both cases, the presence of charges weakens and diminishes H-bonding interactions between ciprofloxacin molecules and the surface of nanohybrid GO/O-CNTs, which lowers the drug uptake. In the pH 6−7 range, the ciprofloxacin drug becomes chargeless and the strongest H-bonding with the adsorbent surface occurs; hence, the maximum drug uptake takes place.

The effect of concentration of the cross-linking agent (% CaCl₂) in the nanohybrid and its relation to drug uptake is investigated in Figure 6E. Clearly, the increase in concentration of CaCl₂ in the nanohybrid backbone structure leads to a large decrease in the drug uptake due to the formation of small-sized nanochannels in the GO networks that eliminate sorbed water and, certainly, prevent larger molecules, such as the ciprofloxacin drug, from being adsorbed on the inner layers of the nanohybrid adsorbent. Furthermore, the variable ratios of GO to O-CNTs in the nanohybrid give rise to different microstructures that show versatile drug uptake, as described in Figure 6F. The maximum drug uptake of 512 mg/g was obtained using 1:4 ratio of GO to O-CNTs. Apparently, the 1:1 ratio shows the lowest drug uptake due to cooperativelydiminished H-bonding interactions and/or adsorbate interactions.66

**Ultimate Eradication of Ciprofloxacin from Aqueous Solutions.** The ultimate eradication of the drug is an extremely essential part in this study, not only due to the importance of drug eradication from aqueous solutions but also due to the significance of fighting against the generated antimicrobial resistance (AMR) in the human body. The generated AMR will ultimately lead to drug deactivation in the human body and to massive number of deaths associated with generated AMR.14 To investigate the entire eradication process of the drug, different initial concentrations of the drug (5−15 ppm) and different nanohybrid adsorbent masses (1−5 mg) were used (Figure 7A). The removal efficiency (in %) was calculated with respect to the initial concentration of the drug under optimum conditions. Obviously, a high removal efficiency was obtained using a high nanohybrid mass and low initial concentration of the drug. The maximum efficiency for the entire removal process was 99.2% at 5 ppm of the drug using 5 mg of the nanohybrid adsorbent.
Regeneration of Nanohybrid GO/O-CNTs. Batch adsorption experiments on the regenerated adsorbent have proved the possible regeneration of nanohybrid GO/O-CNTs for multiple adsorption–desorption processes. The average removal efficiency of three tested samples of the regenerated adsorbent was reduced only by 2.0% compared to the original fresh adsorbent. This also reflected the high structural stability of the nanohybrid adsorbent against continuous washing with basic aqueous solutions.

Ciprofloxacin Eradication Dynamics. Versatile models for drug eradication dynamics were investigated, and the drug uptake proved to be a pseudo-second-order model, with the correlation coefficient value ($R^2$) exceeding 0.99. The second-order model is as follows

$$\frac{t}{q_t} = \frac{1}{kq}\frac{1}{q_e^2} + \frac{t}{q_e}$$

\(3\)
where $q_e$ is the equilibrium drug uptake (in mg/g), $q_t$ is the drug uptake at time $t$ (in mg/g), $k_2$ is the rate constant of drug uptake (in g/mg min), and $t$ is the time (in min). By plotting $t/q_t$ against time $t$, the equilibrium drug uptake ($q_e$) and the rate constant of removal ($k_2$) were determined (Table 2). The calculated equilibrium drug uptake ($q_e$) was 250 mg/g, and the rate constant of removal ($k_2$) was $4.71 \times 10^{-4}$ g/mg min with a correlation coefficient ($R^2$) of 0.996 (Figure 7B).

Furthermore, the mechanism of drug adsorption was validated using the intraparticle diffusion model. $q_k t C_{t}^{1/2} = q_k t C_{t}^{1/2} = q_k t C_{t}^{1/2} = q_k t C_{t}^{1/2}$ where $k_p$ is the intraparticle diffusion constant (in mg/g min$^{0.5}$), and $C_t$ is the adsorption constant (in mg/g). Plots of $q_t$ versus $t^{1/2}$ in Figure 7C show two different straight lines, which suggest an intraparticle diffusion mechanism and prove that many steps control the overall drug uptake process. The steps include quick external pore diffusion (film diffusion) followed by slow sorption on the internal pore surface of the nanohybrid adsorbent (pore diffusion).

The Boyd model was used to determine the rate-controlling step of the adsorption process as follows

$$F = \frac{q_t}{q_e}$$

$$B_t = -0.4977 - \ln(1 - F)$$

where $F$ is the equilibrium fractional attainment calculated from eq 5, $B_t$ is the time constant (1/min), and $B_t$ is calculated from eq 6. According to the Boyd model, the plot of

Table 2. Kinetic Rate Constants for Ciprofloxacin Removal Using a Pseudo-Second-Order Kinetic Model

| $q_{exp}$ (mg/g) | $k_2$ (g/mg min) | $q_{calc}$ (mg/g) | $R^2$ |
|-----------------|-----------------|------------------|--------|
| 0.232           | $4.71 \times 10^{-4}$ | 250.0            | 0.996  |

Table 3. Adsorption Isotherm Parameters for Ciprofloxacin Drug Removal

| isotherm parameters | temperature (K) | 290 | 298 | 303 |
|---------------------|-----------------|-----|-----|-----|
| Langmuir $q_{max}$ (mg/g) |                   | 270.3 | 253.2 | 227.3 |
| $K_L$ (L/mg)       |               | 0.316  | 0.222  | 0.197  |
| $R^2$              |               | 0.968  | 0.984  | 0.982  |
| Freundlich $1/n$   |               | 0.322  | 0.391  | 0.403  |
| $K_F$ ((mg$^{1-1/n}$ L$^{1/n}$)/g) |           | 94.63 | 69.06 | 58.28 |
| $R^2$              |               | 0.942  | 0.990  | 0.986  |
| Temkin $K_T$ (L/mg) |                   | 4.25   | 2.14   | 1.83   |
| $B_T$ (mol/L)      |               | 45.07  | 44.08  | 48.92  |
| $R^2$              |               | 0.915  | 0.974  | 0.970  |
| D–R $q_{max}$ (mg/g) |                   | 379.7  | 387.2  | 349.0  |
| $B$ (mol$^2$/kJ)   |               | 0.01   | 0.0063 | 0.0061 |
| $E$ (kJ/mol)       |               | 7.07   | 12.60  | 12.80  |
| $R^2$              |               | 0.930  | 0.980  | 0.979  |
The plot of Bt versus t that forms a straight line and passes through the origin is direct proof that the adsorption process is controlled by the intraparticle diffusion mechanism. Otherwise, the film diffusion step is the rate-determining step. Our results show that the straight lines of all drug uptake processes do not pass through the origin, which suggests that the drug uptake process is controlled by rapid external pore diffusion (the film diffusion step).72,76

Ciprofloxacin Eradication Isotherms. Isothermal determination of the amount of drug adsorbed on the surface of an adsorbent can be best described by adsorption isotherms. In general, the number of vacant active sites and the size of pores on the surface of the adsorbent play major role in the determination of the amount of drug adsorbed. Four adsorption models were applied to the adsorption of the ciprofloxacin drug on the surface of the nanohybrid GO/CNT system: Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherms, respectively. The adsorption isotherms exhibited linear curves with the highest correlation coefficients ($R^2$) of 0.97–0.98. The linearized form of the Langmuir isotherm is as follows

$$q_e = \frac{q_{\text{max}} K_L C_e}{1 + K_L C_e}$$

(7)

where $q_{\text{max}}$ is the maximum amount of drug adsorbed by a complete monolayer, $q_e$ is the equilibrium drug uptake (in mg/g), $C_e$ is the equilibrium concentration of the drug (in mg/L), and $K_L$ is the equilibrium constant of adsorption (L/mg). The plot of $C_e/q_e$ versus $C_e$ forms a linear curve, for which the constants, $q_{\text{max}}$ and $K_L$, are calculated.71 Furthermore, the Langmuir adsorption isotherm for the ciprofloxacin drug at various temperatures is shown in Figure 7. The maximum drug uptake was found to decrease from 270.3 to 227.3 mg/g as the temperature increased from 290 to 303 K. Likewise, the equilibrium constant ($K_L$) values decreased as the temperature increased (Table 3). Obviously, as the temperature increased, the kinetic energy of the drug molecules increased and also the kinetic energy of the surface of the adsorbent, which weakened the drug adsorption and led to fewer drug molecules adsorbed on the hot surfaces of the adsorbent.

On the other hand, the Freundlich isotherm equation is as follows

$$q_e = K_F C_e^\alpha$$

(8)

where $q_e$ is the equilibrium uptake (mg/g), $K_F$ is the Freundlich constant related to the adsorption capacity ($\text{mg}^{(1-1/n)} \text{L}^{(1/n)}/\text{g}$), $C_e$ is the equilibrium concentration of the drug (mg/L), and $\alpha$ is the heterogeneity factor.72 The plot of $\ln q_e$ versus $\ln C_e$ forms a linear curve.71 Table 3 shows the Freundlich parameters along with the correlation coefficients ($R^2$).

For the Temkin isotherm, the linear form is as follows

$$q_e = B_T \ln K_T + B_T \ln C_e$$

(9)

where $q_e$ is the equilibrium uptake (mg/g), $B_T = RT/b_T$, where $b_T$ is the Temkin constant related to the heat of adsorption (J/mol), $R$ is the universal gas constant (8.314 J/molK), $T$ is the temperature (K), $C_e$ is the equilibrium concentration of the drug (in mg/L), and $K_T$ is the maximum binding energy constant (L/mg). The plot of $q_e$ versus $\ln C_e$ forms a linear curve.71 Table 3 illustrates the adsorption isotherm parameters along with the correlation coefficients ($R^2$). As can be noted, all three models could fit the experimental data.

The Dubinin–Radushkevich (D–R) linear form is as follows

$$\ln q_e = \ln q_{\text{max}} - \beta e^2$$

(10)

where $q_e$ is the equilibrium uptake (mg/g), $\beta$ is the mean free energy (mol $^2$/kJ $^2$), $e$ is the Polanyi potential $RT \ln \left(1 + \frac{1}{C_e} \right)$, where $R$ is the universal gas constant (8.314 J/molK), $T$ is the temperature (K), $C_e$ is the equilibrium concentration of the drug (in mg/L), and $E$ is the free energy (kJ/mol) equal to $1/\sqrt{2\beta}$. The plot of $q_e$ versus $\beta e^2$ forms a linear curve.78 Experimental determination of ciprofloxacin uptake by various adsorbents is discussed in Table 4.

Table 4. Ciprofloxacin Uptakes Using Different Adsorbents

| adsorbent                        | maximum uptake (mg/g) | reference literature |
|----------------------------------|-----------------------|---------------------|
| sodium alginate/graphene oxide   | 86.12                 | 79                  |
| activated carbon                 | 300                   | 80                  |
| carbon nanotubes                 | 140                   |                     |
| carbon xerogel                   | 280                   |                     |
| Fe-pillared clays                | 122.1                 | 81                  |
| graphene oxide                   | 379                   | 82                  |
| carbon nanotubes                 | 190                   | 83                  |
| carbon nanotubes                 | 120                   | 84                  |
| TiO$_2$ nanotube/graphene oxide   | 181.8                 | 85                  |
| magnetic chitosan-grafted GO      | 282.9                 | 86                  |
| graphene                         | 156.7                 | 87                  |
| granular activated carbon        | 68                    |                     |
| cupric oxide nanoparticles       | 73.86                 | 88                  |

Ciprofloxacin Eradication Thermodynamics. Many important outputs can be extracted from the thermodynamic parameters, such as how strongly the adsorbate attaches to the surface of the adsorbent (i.e., chemisorption or physisorption process), exothermic or endothermic processes, and entropic changes that occur throughout the adsorption process. The adsorption process is considered to be physisorption when the $\Delta^oG^o$ value is around 20 kJ/mol and chemisorption when the value is 80–400 kJ/mol.69 Results of ciprofloxacin removal illustrated in Table 5 suggest that the adsorption of the drug on the nanohybrid adsorbent is physisorption. The thermodynamic parameters could be determined using eq 10 as follows

$$\ln K_T = -\frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R}$$

(11)
where $K$ is the equilibrium constant determined from the Langmuir adsorption isotherms, $R$ is the universal gas constant, $T$ is the absolute temperature of adsorption (K). The plot of $\ln K$ versus reciprocal temperature ($1/T$) yields the enthalpy change ($\Delta H^\circ$) and entropy change ($\Delta S^\circ$) from the slope and intercept, respectively (Figure 7F), and the Gibbs free energy ($\Delta G^\circ$) values are calculated from $\Delta G^\circ = -RT \ln K$.$^{90}$

Furthermore, the exothermic enthalpy change ($\Delta H^\circ$) value pointed to the successful bond formation of the drug with the nanohybrid adsorbent at the interface, and the positive entropy change ($\Delta S^\circ$) value indicated an entropy increase as a result of the adsorption process.$^{91}$

## CONCLUSIONS

In this article, new nanohybrid adsorbents were synthesized and characterized for ultimate eradication of the ciprofloxacin antibiotic from aqueous solutions. Nanohybrid GO/O-CNTs was composed of graphene oxide (GO) cross-linked via calcium ions (Ca$^{2+}$) with oxidized carbon nanotubes (OCNTs) in a water-dispersed Tween 80 solution. The nanohybrid adsorbents were characterized using spectroscopic, thermal, and microscopic (FTIR, TGA, DTG, XRD, and SEM) techniques. The new nanohybrid was validated for ultimate eradication of the ciprofloxacin antibiotic from aqueous solutions. The ciprofloxacin antibiotic drug is medically prescribed in millions of medical prescriptions every year and hence exists in sewage treatment effluents, wastewaters, and domestic waters. Optimum parameters were validated for the eradication process, such as contact time, nanohybrid mass, solution temperature, solution pH, %cross-linking agent, and GO/O-CNT ratio. Ciprofloxacin removal dynamics displayed a pseudo-second-order fit with an intraparticle diffusion mechanism. Thermodynamic parameters of ciprofloxacin removal revealed a physisorption process and confirmed a simple desorption process. Our results provided outstanding drug eradication of up to 99.2% and ultimate drug uptake of 512 mg/g. In conclusion, the ultimate eradication of drugs from aqueous solutions is a proactive step in the right direction against the generated antimicrobial resistance (AMR) in the human body that may increase with time and, eventually, lead to disastrous deaths and epidemics.

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