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Synthesis of Green Magnetite/Carbonized Coffee Composite from Natural Pyrite for Effective Decontamination of Congo Red Dye: Steric, Synergetic, Oxidation, and Ecotoxicity Studies

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Abstract: Green magnetite/carbonized spent coffee (MG/CFC) composite was synthesized from natural pyrite and characterized as an adsorbent and catalyst in photo-Fenton's oxidation system of Congo red dye (C.R). The absorption behavior was illustrated based on the steric and energetic parameters of the advanced Monolayer equilibrium model of one energetic site ($R^2 > 0.99$). The structure exhibits 855 mg/g as effective site density which induces its C.R saturation adsorption capacity to 436.1 mg/g. The change in the number of absorbed C.R per site with temperature ($n = 1.53$ (293) to 0.51 (313 K)) suggests changes in the mechanism from multimolecular (up to 2 molecules per site) to multianchorage (one molecule per more than one site) processes. The energetic studies ($\Delta E = 6.2\text{--}8.2$ kJ/mol) validate the physical uptake of C.R by MG/CFC which might be included van der Waals forces, electrostatic attractions, and hydrogen bonding. As a catalyst, MG/CFC exhibits significant activity during the photo-Fenton's oxidation of C.R under visible light. The complete oxidation of C.R was detected after 105 min (5 mg/L), 120 min (10 mg/L), 135 min (15 mg/L), 180 min (20 mg/L), and 240 min (25 mg/L) using MG/CFC at 0.2 g/L dosage and 0.1 mL of H_2O_2 . Increasing the dosage up to 0.5 g/L reduce the complete oxidation interval of C.R (5 mg/L) down to 30 min while the complete mineralization was detected after 120 min. The acute and chronic toxicities of the treated samples demonstrate significant safe products of no toxic effects on aquatic organisms as compared to the parent C.R solution.

Keywords: pyrite; coffee; magnetite; composite; adsorption; photo-Fenton's oxidation



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1. Introduction

The high-income industries in developing countries and the related discharges are the essential reason for the water pollution threats and their toxic impacts on various forms of life. The textile, printing, plastic, and paper industries involve the consumption of huge quantities of pigments and dyes [1,2]. Dyes that are vital aromatic compounds have been widely used. Its annual production has been reported 7×10^5 tons [3,4]. 10% to 15% of the annually produced synthetic dyes are disposed of into water bodies as untreated, non-degradable industrial wastewater causing adverse effects on all life forms [5–7]. Among the synthetic dyes, Congo red (CR) is an anionic toxic dye that is of a sodium salt of amine-4-sulfonic acid benzidindiazo-bis-1-navatella and is widely used in the textile industry [8–10]. The leakage of Congo red into the water resources is of several environmental drawbacks. This includes the depletion of dissolved oxygen and the destruction of the photosynthesis

system. Additionally, such hazardous chemical compounds cause suffocation of the aquatic organisms such as fauna and flora [2,11–13]. From a health point of view, CR dye is of carcinogenic, allergenic, mutagenic, and cytotoxic effects [2,10,14].

Therefore, the interested researcher as well as the responsible authorities suggested several physical and chemical techniques to decline the concentrations of the synthetic dyes. This includes advanced oxidation, adsorption, membrane separation, biological degradation, and nano-filtration. The adsorption technique is a simple, cheap, available, and very effective method in the decontamination of both organic and inorganic contaminants [10,15,16]. The reported advanced oxidation techniques involved photocatalytic, Sonocatalytic, Fenton's, and photo Fenton's oxidation were addressed as very promising methods during the remediation of the dyes [17,18]. The photo Fenton oxidation reactions can be divided into homogenous reactions and heterogeneous reactions [6,19]. The homogenous reactions that involve the interaction between hydrogen peroxide and dissolved ferrous iron ions are simple and inexpensive processes [6,20]. However, there are practical difficulties to scale up the reactions for commercial remediation of dyes and other organic compounds [20,21]. This is related to the consumption of huge amounts of iron, the formation of ferric hydroxide sludge as a byproduct, and the tight range of pH [20]. Therefore, the heterogeneous reactions were recommended as they can be applied within a wide pH range, of low iron consumption, excellent efficiency, and significant recyclability [19].

The Zerovalent iron, as well as the other iron-based green synthesized nanomaterials, is an environmentally friendly structure that was applied widely as adsorbents and heterogeneous catalysts [22]. The previous studies demonstrate the effective applications of such materials to remove the organic contaminants either by adsorption or by photo-Fenton's oxidation processes. This was assigned essentially to their significant surface area, reactivity, adsorption capacity, and band gap energy in addition to the existence of bisphenol caps which enhance their affinities for the common organic pollutants [23–26]. Green synthesized magnetite nanoparticles (Fe_3O_4) were assessed as potential adsorbents and heterogeneous catalysts of promising Physio-chemical properties and can be separated effectively from the treated solutions using an external magnet [27,28]. The synthesis of magnetite/carbon composites was introduced as stable and effective hybrid structures of enhanced electrostatic attractive forces and significant quantities of active functional groups (carboxyl groups) [27,28].

One of the main technical problems that face the synthesis of green iron oxide nanoparticles is the starting precursors. Unfortunately, most of the introduced studies about the synthesis of green iron oxide involved iron-bearing chemical salts as raw materials which raise the cost of fabrication cost [22]. Utilizing natural raw materials in the synthesis of green iron oxide will reduce the production cost and can result in significant changes in the morphological and surficial properties. Pyrite is one of the most famous natural iron sulfide minerals (FeS_2) that is of low economic value either as mining raw products or as by-products during the separation and beneficiation of precious metals [29,30]. Moreover, it is classified as an acid-generating mineral and its weathering results in toxic and hazardous acids that affected negatively the ecosystems and biodiversity in the mining sites including the highly toxic acid drainage wastewater in the mining sites [31]. Framboidal pyrite is a known form of pyrite that was classified in several literatures as a sedimentary mineral of biogenic origin and of considerable geological reserve [30,32–34]. Considering the chemical composition, reactivity, and textural properties of framboidal pyrite, it can be applied effectively in the synthesis of novel and advanced forms of green iron oxide nanoparticles of enhanced physiochemical properties.

Therefore, the current study aims to synthesize and characterization of low-cost magnetite/carbon green nanocomposite (MG/CFC) utilizing framboidal pyrite mining solid wastes as the iron-bearing precursor and commercial coffee as a precursor of carbon and the greed oxidizing reagent. The obtained structure was assessed as a potential adsorbent and heterogeneous catalyst for effective photo Fenton's oxidation of Congo red dye. The adsorption behavior was illustrated based on the advanced equilibrium properties

including the steric and energetic properties. The oxidation studies were assessed based on the main experimental parameters, kinetic properties, oxidizing radicals, synergetic effect, and suggested mechanism. This represents advanced recycling processes of pyrite solid waste and spent coffee powder in an innovative eco-friendly, simple, and low-cost hybrid structure of enhanced adsorption and catalytic properties during the decontamination applications of Congo red dye from the aqueous environment by photo-Fenton's oxidation system in the presence of commercial visible light source.

2. Results and Discussion

2.1. Characterization of the MG/CFC Catalyst

The XRD pattern of the synthetic Mg/CFC structure was compared to the used raw pyrite to confirm the transformation processes (Figure 1). The studied raw precursor exhibits the typical pattern of pyrite mineral with its characteristic peaks (Ref. No. 01-076-0963) (Figure 1A). The transformation of pyrite into Mg/CFC was confirmed by the remarkable changes in the obtained patterns and the identified phases. The patterns show the characteristic peaks of iron oxide (magnetite) (Ref. No. 01-076-0956; JCPDS. card No. 089-096) in addition to the broad peak of the amorphous carbon that is related to the coffee-based carbon substrate (Figure 1B). Such results confirm the formation of the composite between the precipitated green magnetite and the carbon-based coffee. Moreover, the detection of the iron phase as iron oxide reflects the extensive oxidation of the early-formed zero-valent iron into iron oxide [22,35].

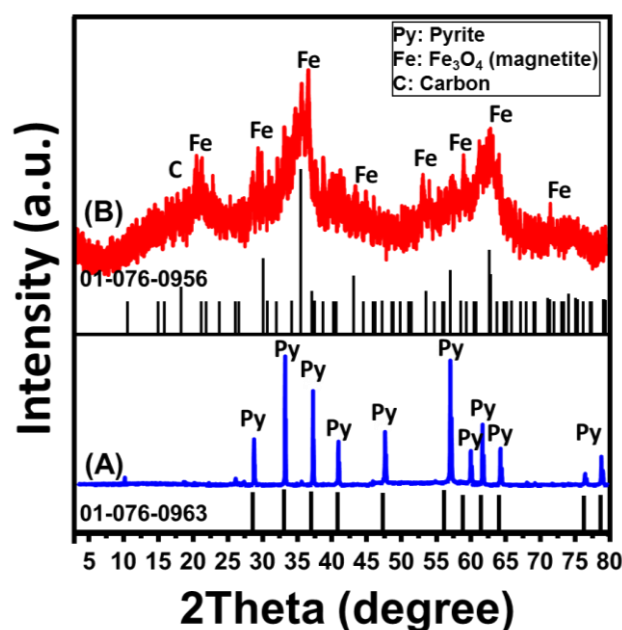


Figure 1. XRD pattern of the used raw pyrite (A) and the synthetic MG/CFC green nanocomposite (B).

This was supported significantly by the obtained SEM images of the synthetic structure (Figure 2). The surface of carbonized coffee particles exhibits irregular and wormy-like morphologies with numerous pores which give them significant surface area as carrier or substrate for the loaded green magnetite nanoparticles (Figure 2A). The synthesized green iron oxide appeared as bunches or clusters of numerous spherical nanoparticles related the precipitated Fe₃O₄ nanoparticles that exhibit random distribution over the surface of carbonized coffee grains (Figure 2B–E). This significant alteration and formation of green magnetite/carbon composite (MG/CFC) was confirmed also based on the EDX findings of both pyrite precursors and the synthetic product (Figure 2F). The elemental EDX composition of the raw pyrite reflected its common composition of two essential elements which are Fe (66.72%) and S (33.25%) (Figure 2F). After the synthesis of the green

magnetite/carbon composite (MG/CFC), the EDX spectrum demonstrates the complete removal of S from the composition and the existence of Fe and O as the components of magnetite and C as the representative element of the carbonized coffee particles (Figure 2F).

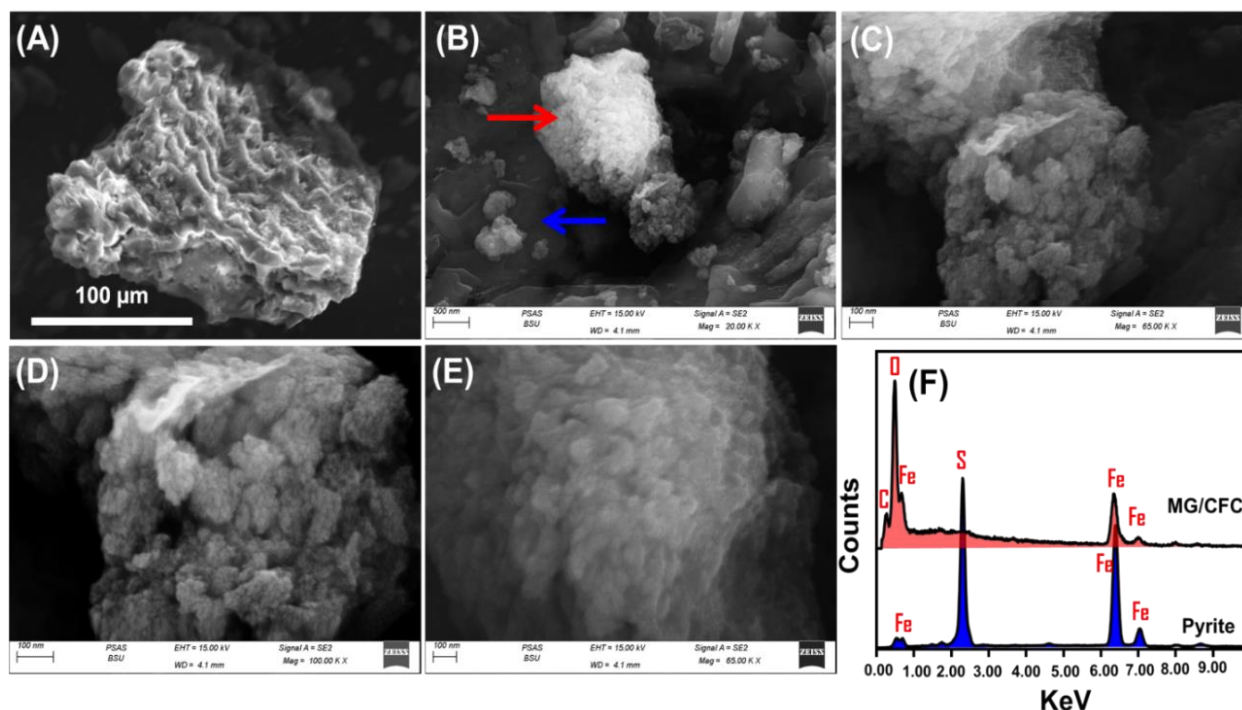


Figure 2. SEM images of the carbonized coffee grains (A), the synthetic green magnetite nano particles over the surface of carbonized coffee (B–E), and the EDX spectra of pyrite and the prepared MG/CFC composite (F).

Regarding the FT-IR spectra of pyrite, synthetic MG/CFC, and spent MG/CFC after the adsorption of C.R molecules, the observed spectra are in agreement with the chemical analysis (Figure 3). The spectrum of pyrite validates the existence of its main chemical groups such as Fe-O-OH (1087 cm^{-1}), Fe-S (666.63 cm^{-1}) and S-S (608.43 cm^{-1}) in addition to other bands related to the -OH stretching (3300 cm^{-1}) and vibration (556 cm^{-1}) of adsorbed water molecules or the weathering effects on the pyrite structure (Figure 3A) [36–38]. Regarding the spectrum of green magnetite/carbonized coffee structure, the identification bands of iron oxide were recognized at 456.4 cm^{-1} and 611 cm^{-1} which validates the Fe-O bonding (Figure 3B) [39,40]. The chemical groups of the carbonized coffee substrates were signified around 3184 cm^{-1} (O-H groups related to phenols, alcohols, or carboxylic acid), 2921.4 cm^{-1} (C-H of methylene ($-\text{CH}_2-$) and methyl groups ($-\text{CH}_3$)), 2859 cm^{-1} (C-H of cellulose backbone), 1638.9 cm^{-1} (carbonyl groups that are related to the polyphenolic compounds of coffee), 1409.5 cm^{-1} ($-\text{CH}_2$ and $-\text{CH}_3$ bending), 1112.9 cm^{-1} (C-O and C-C of cellulose), and $801\text{--}888.4\text{ cm}^{-1}$ (N- CH_3) (Figure 3B) [40–42]. The identified chemical groups demonstrate the expected valuable role for the carbonized coffee either as a substrate for magnetite as catalysts during the photo Fenton's oxidation of C.R dye or as an integrated component in the hybrid adsorbent. Regarding the spectrum of the spent MG/CFC after the adsorption of C.R dye, it shows an observable reduction in the intensities of the absorption bands of the essential chemical groups in addition to slight shifting (Figure 3C). This validates a significant effect for most of the chemical groups of both magnetite and carbonized coffee during the uptake of the C.R dye.

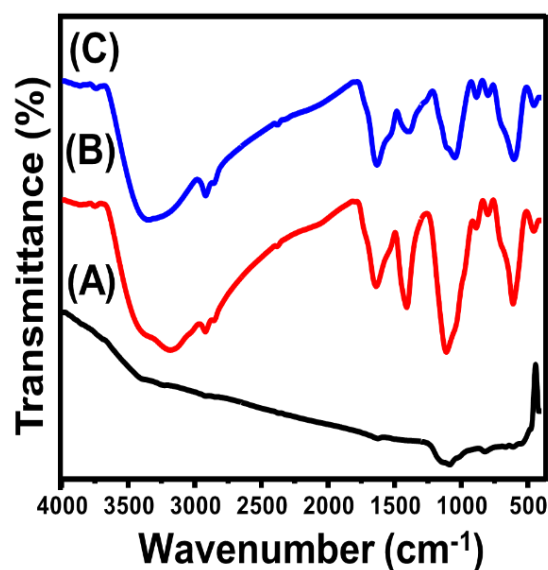


Figure 3. FT-IR spectra of the raw pyrite (A), the synthetic green magnetite nano particles over the surface of carbonized coffee (MG/CFC) (B), and spent MG/CFC after the adsorption of C.R molecules (C).

2.2. Adsorption Studies

2.2.1. Effect of pH

The pH value of the aqueous solutions during the uptakes processes of C.R. by MG/CFC is an essential factor that controls the dominance of the surficial charges as well as the dye molecules in the system. The pH (2–8) as an experimental variable was studied and the other effective variables were preserved at constant values [solid dosage: 0.2 g/L; volume: 100 mL; contact interval: 24 h; concentration: 50 mg/L; temperature: 293 K] during the performed experiments (Figure 4A). The experimentally detected C.R adsorption results signify the noticeable decline in the determined capacity of MG/CFC from pH 2 (143.3 mg/g) until pH 7 (94.6 mg/g) (Figure 4A). The high pH environments induce the generation of the negatively charged hydroxyl ions on the surface of MG/CFC as a result of the de-protonation of its chemical groups in the basic conditions [43]. The negatively charges C.R molecules are remarkably electrostatically repulsed by such deprotonated groups. The recognized behavior in terms of the studied pH validates is in agreement with the determined $pH_{(ZPC)}$. The determined $pH_{(ZPC)}$ of MG/CFC is 4.6 and reveals the high occupation of the MG/CFC surface with numerous negative charges during the uptake of C.R. at $pH > 4.6$ and positive charges at $pH < 4.6$.

2.2.2. Equilibrium Studies

Effect of C.R Concentrations

The investigation of the MG/CFC adsorption capacity in the existence of different C.R concentrations (50–350 mg/L) allows the experimental detection of the equilibrium behavior and actual saturation or maximum capacity of the MG/CFC structure. The other effective variables were preserved at constant values [solid dosage: 0.2 g/L; volume: 100 mL; contact interval: 24 h; pH: 2]. The temperature influence was followed from 293 K to 313 K (Figure 5B). The adsorption of C.R by MG/CFC structure is markedly enhanced when the tested C.R starting concentrations are high (Figure 4B). This enhancement effect is ascribed to an expected increase in the mobility or diffusion speed as well as the driving forces of the dissolved C.R molecules, which can prompt their interactions and collision rates with the essential and effective uptake sites on the MG/CFC surface [44]. The increment in the experimental C.R uptake efficiency is distinguished up to 250 mg/L during the three evaluated equilibriums tests which were performed at 293 K, 303 K, and 313 K (Figure 4B). Therefore, this concentration (250 mg/L) can be categorized as the experimental

C.R equilibrium concentration in the presence of MG/CFC as an adsorbent. The available active receptors that are present on the MG/CFC particles attain their saturation states and fully occupied with the C.R molecules. Therefore, the MG/CFC attains its maximum capacity as an adsorbent for C.R (331 mg/g (293 K), 351.3 mg/g (303 K), and 360.4 mg/g (313 K)) (Figure 4B).

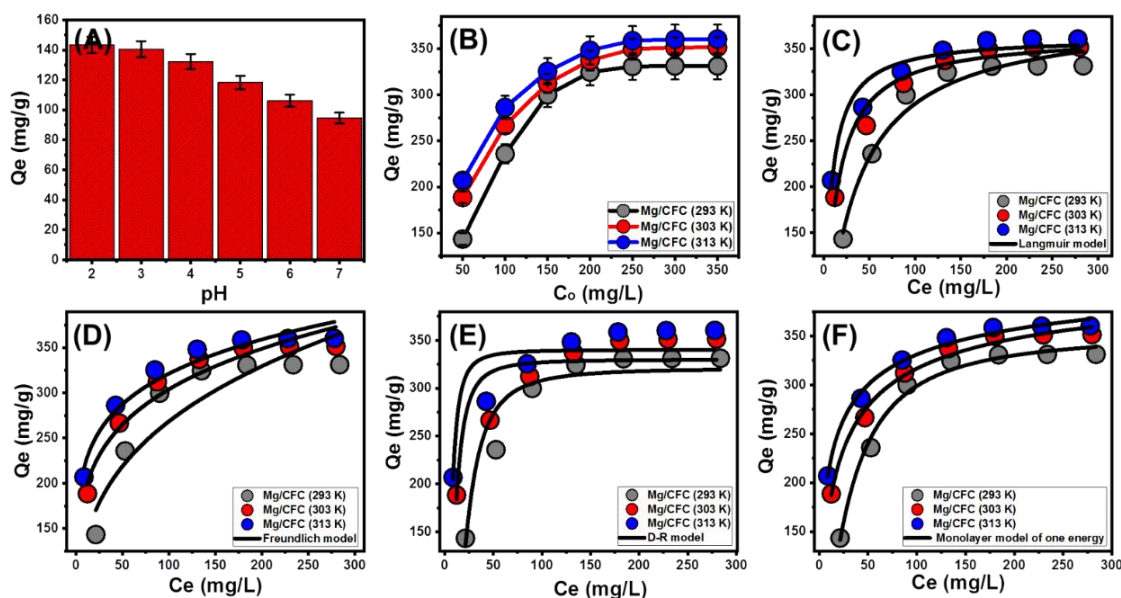


Figure 4. Effect of pH on the adsorption of C.R by Mg/CFC [dosage: 0.2 g/L; contact interval: 24 h; concentration: 50 mg/L; temperature: 293 K] (A), adsorption properties of Mg/CFC at different concentrations of C.R [dosage: 0.2 g/L; contact interval: 24 h; pH: 2] (B), fitting of the C.R adsorption data with Langmuir isotherm (C), fitting of the C.R adsorption data with Freundlich isotherm (D), fitting of the C.R adsorption data with D-R isotherm (E), and fitting of the C.R adsorption data with advanced monolayer model with one energy (F).

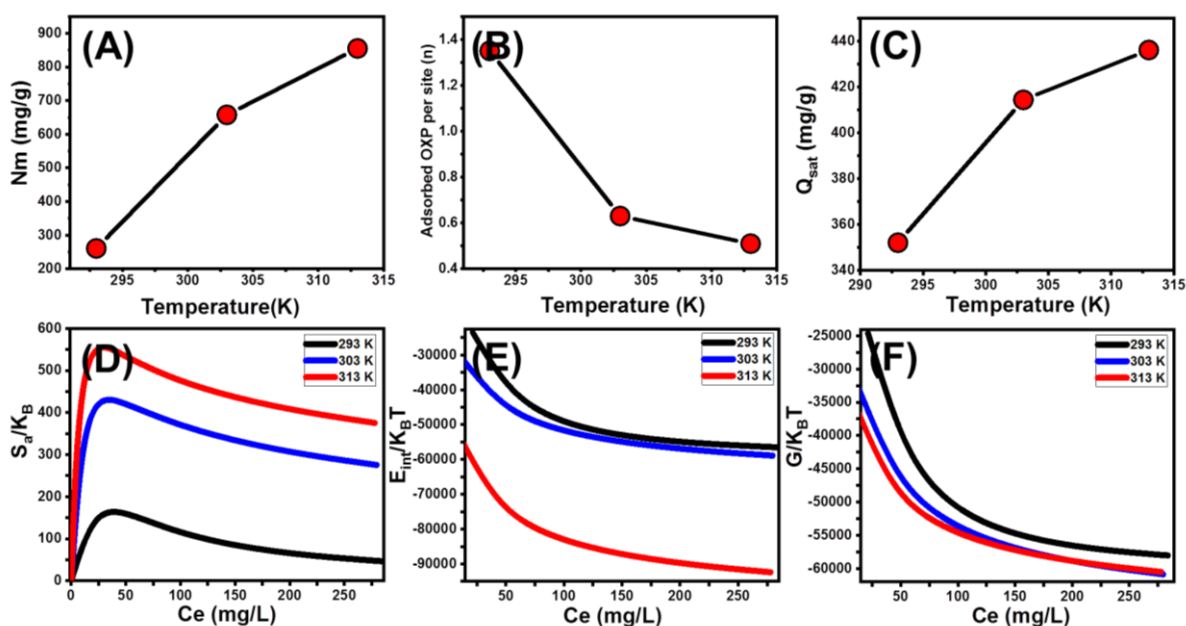


Figure 5. The change in (A) the number of adsorbed C.R molecules per each active site of MG/CFC, (B) the occupied active sites density by C.R molecules, (C) the entropy properties of the C.R adsorption reactions by MG/CFC, (D) internal energy of the C.R adsorption reactions by MG/CFC (E), and enthalpy of the C.R adsorption reactions by MG/CFC (F).

Classic Isotherm Models

The equilibrium properties of the occurred C.R adsorption reactions by MG/CFC carriers were illustrated considering the common assumptions of Langmuir (Figure 4C), Freundlich (Figure 4D), and Dubinin–Radushkevich (D-R) (Figure 4E) models. This was accomplished based on the non-linear fitting degrees with the illustrative equations of these models considering the values of correlation coefficient (R^2) as well as Chi-squared (χ^2) (Table 1; Figure 4C,E). Based on the recognized values of the fitting parameters, the C.R uptake process by MG/CFC exhibits the equilibrium properties of the Langmuir isotherm rather than the Freundlich model. This involved a homogenous C.R uptake process by the distributed active receptors throughout the surface of MG/CFC [45,46]. Furthermore, the obtaining of the RL parameter at values less than 1 demonstrates the favorable adsorption of C.R by MG/CFC as an adsorbent. Moreover, the Langmuir fitting parameters suggested theoretically the suitability of MG/CFC to adsorb up to 362.7 mg/g (293 K), 364.8 mg/g (303 K), and 388 mg/g (313 K) as maximum C.R adsorption capacities.

Regarding the investigated D-R model, its isotherm properties can signify strongly the energetic heterogeneity of MG/CFC as an adsorbent of C.R. regarding its homogenous or heterogeneous surface [47]. Moreover, the determination of the Gaussian energy (E) as obtained theoretical parameter of the D-R model illustrate significantly the nature of the dominant adsorption processes either of chemical or physical properties. The physically controlled uptake systems exhibit Gaussian energy < 8 KJ/mol while the chemically controlled system display values > 16 KJ/mol. The systems that show Gaussian energy values of 8 to 16 KJ/mol validate the dominant impact of weak chemical mechanisms or complex processes [46,47]. The Gaussian energies of C.R uptake by MG/CFC are 1.73 kJ/mol (293 K), 3.61 kJ/mol (303 K), and 5.43 kJ/mol (313 K) (Table 1). These values reflect the operation of physical mechanisms during the C.R uptake process by MG/CFC.

Table 1. The estimated mathematical parameters of the studied classic and advanced equilibrium models.

Parameters of the Classic Isotherm Models					
			293 K	303 K	313 K
MG/CFC	Langmuir model	Q _{max} (mg/g)	362.7	364.8	388.07
		b(L/mg)	0.14	0.079	0.029
		R ²	0.95	0.97	0.98
		χ ²	0.53	0.49	0.58
	Freundlich model	1/n	0.16	0.19	0.29
		k _F (mg/g)	153.5	122	68.9
		R ²	0.95	0.95	0.88
		χ ²	0.67	0.81	3.6
	D-R model	β (mol ² /KJ ²)	0.0166	0.0384	0.0169
		Q _m (mg/g)	321	330.1	340.2
		R ²	0.92	0.85	0.85
		χ ²	1.96	2.8	2.3
		E (KJ/mol)	1.73	3.61	5.43
Steric and energetic parameters of the advanced isotherm model					
MG/CFC		R ²	0.99	0.99	0.99
		χ ²	0.29	0.17	0.12
		n	1.53	0.63	0.51
		N _m (mg/g)	260.6	657.7	855.1
		Q _{Sat} (mg/g)	351.8	414.3	436.1
		C1/2 (mg/L)	28.8	17.3	10.79
		ΔE (kJ/mol)	8.2	7.3	6.2

Advanced Isotherm Models

The advanced isotherm studies [monolayer model of one energy site] were performed to present more mechanistic significances based on the equilibrium assumptions of the statistical physics theory. This model was assessed considering the best values of RMSE and R^2 which were obtained during the fitting processes (Figure 5F; Table 1). All the steric mathematical parameters of this model [n (number of adsorbed C.R molecules per site), N_m (density of the active sites), and Q_{sat} (the saturation capacity of MG/CFC as an adsorbent of C.R)], and energetic parameters [ΔE (uptake energy of C.R), S_a (entropy), G (enthalpy), and E_{int} (internal energy)] (Table 1).

Steric Parameters

The obtained number of the adsorbed C.R molecules per each active site (n parameter) of MG/CFC reveals the type of the operating adsorption mechanisms as well as the orientation (horizontal or vertical) of the uptake molecules (Figure 5A; Table 1). The adsorption systems that exhibit n value lower than 1 validate horizontal uptake of the dissolved ions via multi-docking and multianchorage mechanisms (one C.R. molecule might be adsorbed by more than one receptor or a fraction of molecule can be adsorbed per single site). Conversely, the systems which display n value of more than 1 ($n > 1$) validate vertical uptake of the C.R molecules by multiple molecular mechanisms (several C.R might be adsorbed by one receptor) [46,48]. The determined values of $n_{C,R}$ during the uptake of C.R by MG/CFC are 1.35 (293 K), 0.63 (303 K), and 0.51 (313 K) (Figure 5A; Table 1). Therefore, the C.R uptake process by MG/CFC at low-temperature conditions (293 K) involves the uptake up to two molecules by multimolecular mechanisms in a vertical orientation. At the high-temperature conditions (303 K and 313 K), each active site on the surface of MG/CFC can adsorb a fraction of the C.R molecule or each C.R molecule can be adsorbed by more than one site in horizontal orientation involving multianchorage mechanism [49]. The considerable declination in the $n_{C,R}$ in terms of the temperature value reflects a significant reduction in the aggregation behavior of the C.R molecules during their uptake in addition to the predicted increment in the active uptake sites (Figure 5A; Table 1). The increase in the uptake sites might be related to the impact of temperature in inducing the diffusion rates of the C.R molecules to be in contact with additional sites in the internal structure of MG/CFC.

The recognized $N_{m,C,R}$ values demonstrate strong enhancement in the quantities of the present active sites of MG/CFC or the occupied active sites density with temperature (260.6 mg/g (293 K), 657.7 mg/g (303 K), and 855.1 mg/g (313 K)) (Figure 5B; Table 1). These values are in agreement with the signified behavior of the $n_{C,R}$ parameter and the impact of the temperature on the dominance of the active sites. The high-temperature conditions are of positive activation influence on the active sites of MG/CFC either by the exposure of additional active sites or more energetic site groups [49,50]. The increase in the uptake temperature is associated with a decrease in the viscosity of the C.R. solution. Therefore, the dissolved C.R molecules exhibit a significant increase in their mobility and their diffusion rates to be in contact with additional active sites. Such increment in the $N_{m,C,R}$ values induce the adsorption capacity of MG/CFC especially at its saturation state (Q_{sat}) that increased by 351.8 mg/g (293 K), 414.3 mg/g (303 K), and 436.1 mg/g (313 K) (Figure 6C; Table 1).

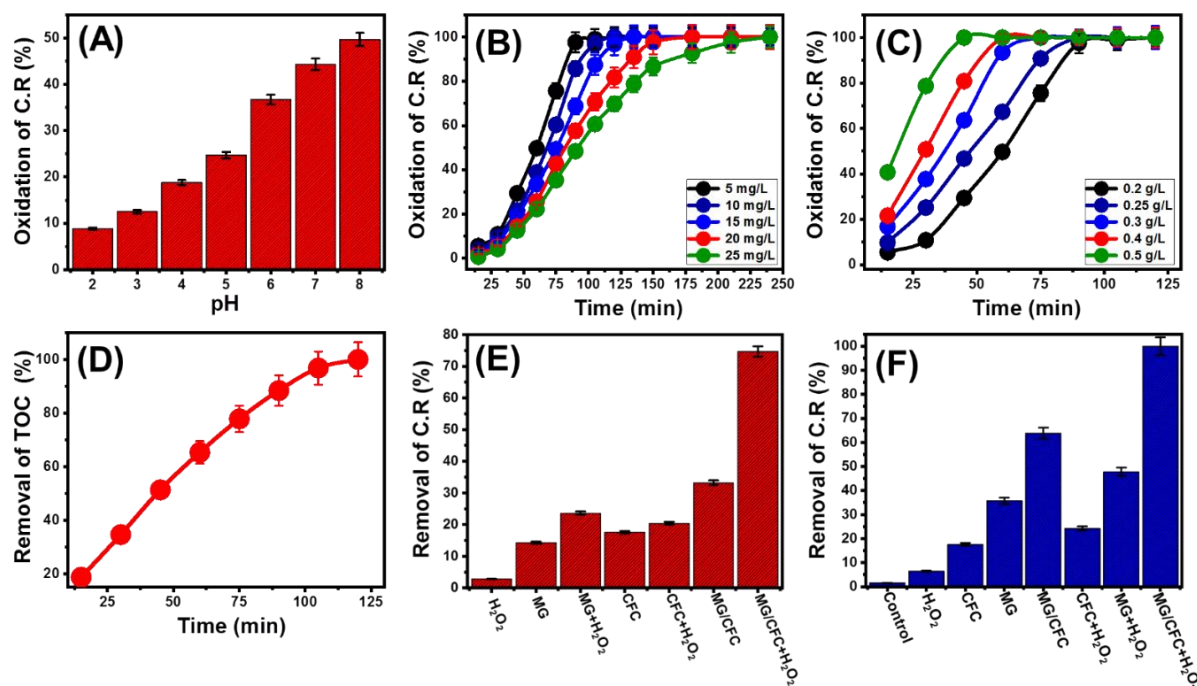


Figure 6. Shows (A) effect of pH on the oxidation of C.R. by MG/CFC [solid dosage: 0.2 g/L; interval: 60 min; concentration: 5 mg/L; temperature: 313 K; 0.1 mL H₂O₂], (B) oxidation behaviors of different concentrations of C.R. by MG/CFC [solid dosage: 0.2 g/L; temperature: 313 K; Fenton reagent: 0.1 mL H₂O₂], (C) effect of the MG/CFC dosages on the oxidation percentages of C.R. [C.R. concentration: 5 mg/L; temperature: 313 K; Fenton reagent: 0.1 mL H₂O₂], (D) the reduction in the TOC content during the oxidation of C.R. [C.R. concentration: 5 mg/L; dosage: 0.5 g/L; temperature: 313 K; Fenton reagent: 0.1 mL H₂O₂], (E) the synergetic effect of the integration processes between the components of the catalysts and hydrogen peroxide on the removal of C.R. in the dark by adsorption and Fenton reactions [dosage: 0.5 g/L; test interval: 60 min; temperature: 313 K; and C.R. concentration: 5 mg/L], and (F) the synergetic effect of the integration processes, visible light, and hydrogen peroxide on the removal of C.R. by photocatalytic and photo-Fenton's oxidation processes [dosage: 0.5 g/L; test interval: 60 min; temperature: 313 K; and C.R. concentration: 5 mg/L].

Energetic Properties

Adsorption energy

The adsorption energy of C.R. by MG/CFC (ΔE) can signify the nature of the operated uptake mechanism (physical ($\Delta E \leq 40$ kJ/mol) or chemical ($\Delta E > 80$ kJ/mol)). The physical processes might involve coordination exchange ($\Delta E = 40$ kJ/mol), hydrogen bonding ($\Delta E < 30$ kJ/mol), van der Waals forces ($\Delta E = 4$ to 10 kJ/mol), dipole forces ($\Delta E = 2$ to 29 kJ/mol), and hydrophobic bonds ($\Delta E = 5$ kJ/mol) [50,51]. The ΔE of the MG/CFC adsorption system was calculated according to Equation (1) considering the solubility of C.R dye and its concentration at the half saturation state of MG/CFC [49].

$$\Delta E = RT \ln \left(\frac{S}{C} \right) \quad (1)$$

The theoretically determined ΔE values of the C.R uptake process by MG/CFC are 8.2 kJ/mol (293 K), 7.3 kJ/mol (303 K), and 6.2 kJ/mol (313 K) (Table 1). These values validate the uptake of C.R. by MG/CFC according to physical mechanisms which might be involved dipole bond forces, van der Waals forces, and hydrogen bonding in addition to the electrostatic attraction. Furthermore, the positive signs of these values validate the endothermic properties of the C.R adsorption reactions by MG/CFC.

Thermodynamic functions

The illustration of the entropy (S_a) properties significantly validate the order and disorder properties of the surface of MG/CFC as an adsorbent of C.R dye at its different studied concentrations and uptake temperature values. The values were obtained theoretically from Equation (2) considering the steric parameters of the assessed advanced model [52].

$$\frac{S_a}{K_B} = N_m \left\{ \ln \left(1 + \left(\frac{C}{C_{1/2}} \right)^n \right) - n \left(\frac{C}{C_{1/2}} \right)^n \frac{\ln \left(\frac{C}{C_{1/2}} \right)}{1 + \left(\frac{C}{C_{1/2}} \right)^n} \right\} \quad (2)$$

The obtained S_a values show remarkable declination at significant rates in the existence of high C.R concentrations validating a decrease in the disorder properties of MG/CFC and considerable docking of the C.R molecules on the free effective sites in the existence of low dye concentrations (Figure 5D) [49,53]. The equilibrium C.R concentrations which are the corresponding values of the highest S_a values (21.3 mg/L (293 K), 12.3 mg/L (303 K), and 8.6 mg/L (313 K)) are close to the previously estimated concentrations at half saturation states of MG/CFC (Figure 5D). Consequently, no more C.R molecules can be docked again by the active sites of MG/CFC beyond these concentrations. Moreover, this reflects a significant declination in the diffusion behavior and freedom degrees of C.R molecules as well as the free active sites of MG/CFC [54].

The other thermodynamic functions including the internal energy (E_{int}) and free enthalpy (G) were obtained theoretically according to Equations (3) and (4), respectively, depending on the estimated steric parameters and the translation partition (Z_v) value [52].

$$\frac{E_{int}}{K_B T} = n N_m \left[\left(\frac{\left(\frac{C}{C_{1/2}} \right)^n \ln \left(\frac{C}{Z_v} \right)}{1 + \left(\frac{C}{C_{1/2}} \right)^n} \right) - \left(\frac{n \ln \left(\frac{C}{C_{1/2}} \right) \left(\frac{C}{C_{1/2}} \right)^n}{1 + \left(\frac{C}{C_{1/2}} \right)^n} \right) \right] \quad (3)$$

$$\frac{G}{K_B T} = n N_m \frac{\ln \left(\frac{C}{Z_v} \right)}{1 + \left(\frac{C_{1/2}}{C} \right)^n} \quad (4)$$

The adsorption of C.R by MG/CFC exhibits negatively signed E_{int} values with considerable increment with evaluated temperature from 293 to 313 K (Figure 6E). This suggests spontaneous and exothermic uptake of C.R by MG/CFC structure which is supported by the negatively signed values of enthalpy (G) which also increase in terms of the uptake temperature (Figure 5F).

2.3. Photo-Fenton Oxidation of C.R

2.3.1. Effect of Oxidation Parameters

Effect of pH

The oxidation efficiency of C.R dye by MG/CFC as an applied heterogeneous catalyst in terms of the adjusted pH was followed up to pH 8 after attending the adsorption/desorption equilibrium state. The essential effective variables were preserved at constant values [solid dosage: 0.2 g/L; volume: 100 mL; contact interval: 60 min; concentration: 5 mg/L; temperature: 313 K; Fenton reagent: 0.1 mL H_2O_2] during the performed experiments (Figure 6A). The recognized oxidation results demonstrate reversible behavior considering the obtained results during the C.R adsorption tests. The oxidation percentages of C.R by MG/CFC exhibit considerable enhancement at the high pH conditions as the percentages increased from 8.8% (pH 2) to 45% (pH 8) (Figure 6A). This difference in the behavior might be assigned to the significant inducing effect of the alkaline environments on the generated hydroxyl groups that are the essential initiators of the main oxidizing species during their oxidation into hydroxyl radicals [31]. The generation of such hydroxyl groups is assigned to the notable de-protonation of the functional groups of MG/CFC [6].

Additionally, the expected uptake of C.R at very high quantities on the surface of MG/CFC at the acidic condition reduces the interaction chances between the light photons and the catalytic sites of MG/CFC as well as the Fenton's reagent which reduces the catalytic performance of MG/CFC.

Effect of C.R Concentrations at Different Oxidation Intervals

The catalytic properties of MG/CFC in terms of the tested oxidation interval (15–240 min) and the C.R concentrations (5–25 mg/L) were followed considering the main variables at constant values [solid dosage: 0.2 g/L; volume: 100 mL; temperature: 313 K; Fenton reagent: 0.1 mL H₂O₂] during the performed experiments. The MG/CFC structure as heterogeneous catalysts in photo Fenton, oxidation systems of C.R displayed noteworthy oxidation properties within considerable treatment intervals (Figure 6B). The MG/CFC structure achieved complete oxidation for 5 mg/L, 10 mg/L, 15 mg/L, 20 mg/L, and 25 mg/L of C.R after 105 min, 120 min, 135 min, 180 min, and 240 min, respectively (Figure 6B). The marked declines in the oxidation activity of MG/CFC with the increase in the C.R concentration might be assigned to the high accumulation of the adsorbed C.R molecules as a layer on the surface of the catalyst. Such a thick adsorbed layer in addition to the weak penetration properties of light at the high C.R concentrations in the solutions weakens the interaction efficiency between the surface of MG/CFC and the incorporated Fenton reagent as well as the light photons [55]. This negatively affects the generation efficiency of the effective oxidizing species and in turn, the actual rate of the occurred Fenton oxidation reactions. Such weakening in the oxidation rates is notable in terms of the expansion in the oxidation interval until the establishment of the equilibration state at which the system shows a neglected or nearly fixed oxidation rate. This oxidation behavior is assigned to the continuous diminution of the generated oxidizing species during the performed C.R degradation processes over time until occurring the complete the consumption after a certain interval [56].

Effect of Catalyst Dosage at Different Oxidation Intervals

The oxidation rates in terms of the MG/CFC dosages were followed from 0.2 g/L until 0.5 g/L as an essential parameter to induce the photo Fenton's oxidation efficiencies of certain concentrations as well as the required oxidation interval which was followed from 5 min until 120 min (Figure 6C). The main variables were selected at constant values [C.R concentration: 5 mg/L; volume: 100 mL; temperature: 313 K; Fenton reagent: 0.1 mL H₂O₂] during the performed experiments. The high dosages of MG/CFC validate notable enhancement in the C.R oxidation rate causing remarkable declination in the required interval to achieve the complete oxidation of the test C.R concentrations. The incorporation of MG/CFC as catalysts at systematic dosages of 0.2 g/L, 0.3 g/L, 0.4 g/L, and 0.5 g/L resulted in complete oxidation of 5 mg/L of C.R after 105 min, 75 min, 60 min, and 45 min, respectively (Figure 6C). This behavior was reported widely in literature and signifies the extensive increase in the quantities of the active catalytic sites as well as the exposure surface. This provides a significant increase in the interaction interface between C.R molecules and the surface of MG/CFC as well as the quantities of generated oxidizing species in the system [57,58].

2.3.2. Mineralization Efficiency

The mineralization properties of the oxidized C.R molecules in the existence of MG/CFC as heterogeneous catalysts in photo Fenton's oxidation system were followed to confirm the complete conversion of the dye into safe end products. The mineralization degree was evaluated by detecting the concentrations of the TOC content in the treated C.R solutions at the best experimentally studied oxidation conditions [C.R concentration: 5 mg/L; volume: 100 mL; MG/CFC dosage: 0.5 g/L; temperature: 313 K; Fenton reagent: 0.1 mL H₂O₂] within oxidation interval from 5 min until 120 min. However, the complete oxidation or de-colorization of C.R was detected after 45 min, and the complete mineraliza-

tion was detected after 120 min achieving a 100% removal percentage of TOC (Figure 6D). Therefore, the papered MG/CFC structure is a highly effective environmental catalyst that can be applied for complete photo Fenton's oxidation of C.R molecules into safe and end products. The notable differences between the required intervals for the complete de-colorization of C.R molecules and their complete mineralization reflects the formation of intermediate compounds during the progressive oxidation of the dye.

2.3.3. Synergetic Properties of Oxidation System

The influence of the integrated components either the carbonized spent coffee (CFC) or the pyrite-based green magnetite (MG) on the performance of the studied MG/CFC composite either as an adsorbent or as a heterogeneous catalyst was inspected considering the following conditions:

- H_2O_2 (0.1 mL) without catalyst and a light source (Figure 6E)
- CFC, MG, and MG/CFC without H_2O_2 or a light source as a separated test (adsorption) (Figure 6E)
- H_2O_2 + catalyst (CFC, MG, and MG/CFC) without the light source (Fenton's oxidation) (Figure 6E)
- visible light source without catalyst or H_2O_2 (Figure 6F)
- visible light source+ H_2O_2 (0.1 mL) (Figure 6F)
- visible light source+ catalyst (CFC, MG, and MG/CFC) (photocatalytic oxidation) (Figure 6F)
- visible light source+ catalyst (CFC, MG, and MG/CFC) + H_2O_2 (photo-Fenton's oxidation) (Figure 6F)

The experiments were accomplished based on certain values for the following variables: MG/CFC dosage: 0.5 g/L; volume: 100 mL; test interval: 60 min; temperature: 313 K; and C.R concentration: 5 mg/L. The direct effect of the visible light source exhibited a neglected oxidation impact on the C.R molecules (1.6%) while the tests which were performed using only H_2O_2 (0.1 mL) had a slightly greater oxidation effect than the detected effect of the light source (2.8%) under the same experimental conditions. The combination between the light source and H_2O_2 (0.1 mL) enhances the oxidation efficiency of C.R to 6.4%. The incorporation of carbonized spent coffee (CFC), green magnetite (MG), and their composite (MG/CFC) without H_2O_2 and light source resulted in adsorption removal percentages of 17.6%, 14.3%, and 33.2%, respectively. This demonstrates the value impact of the integration processes between them on the C.R uptake properties either by introducing additional active chemical groups adsorption sites) or by enhancing the surface area.

The incorporation of CFC, MG, and MG/CFC in the presence of H_2O_2 (0.1 mL) without the light source (Fenton's oxidation system) demonstrates notable Fenton's oxidation activities of MG and MG/CFC and no oxidation activity for CFC considering the oxidation percentage of the incorporated H_2O_2 . The determined C.R removal percentages are 20.4%, 23.6%, and 74.4% in the existence of CFC, MG, and MG/CFC, respectively. Similar behavior was detected during the incorporation of them in the presence of the light source without H_2O_2 (photocatalytic oxidation system). The removal percentages of C.R increased to 35.7% and 63.8% using MG and MG/CFC, respectively, as compared to the achieved results by adsorption. The fixed removal percentage of C.R (17.6%) either by adsorption or photocatalytic processes using CFC demonstrates the photocatalytic activities of MG and MG/CFC as compared to CFC. The combination between developed catalysts (MG and MG/CFC), H_2O_2 (0.1 mL), and the light source (photo Fenton's oxidation system) appear to be of enhanced oxidation effects on the dissolved C.R molecules as the removal percentages upgraded to 50.8% (MG), and 100% (MG/CFC). Therefore, the incorporation of MG/CFC as a green and low-cost catalyst in a photo-Fenton oxidation system toward the dissolved C.R dye is recommended strongly instead of separated photocatalytic or Fenton-oxidation systems.

2.3.4. Kinetic and Quantum Yield Studies

The kinetic properties of the occurred photo-Fenton's oxidation of C.R dye by MG/CFC were illustrated considering the common assumptions of first-order (Equation (5)) (Figure 7A,B) and second-order (Equation (6)) (Figure 7C,D) kinetics. The values of R^2 , as well as χ^2 , were considered to estimate the linear regression fitting degrees between the results and the studied models [57].

$$C_t = C_0 e^{-k_1 t} \quad (5)$$

$$\frac{1}{C_t} = \frac{1}{C_0} + k_2 t \quad (6)$$

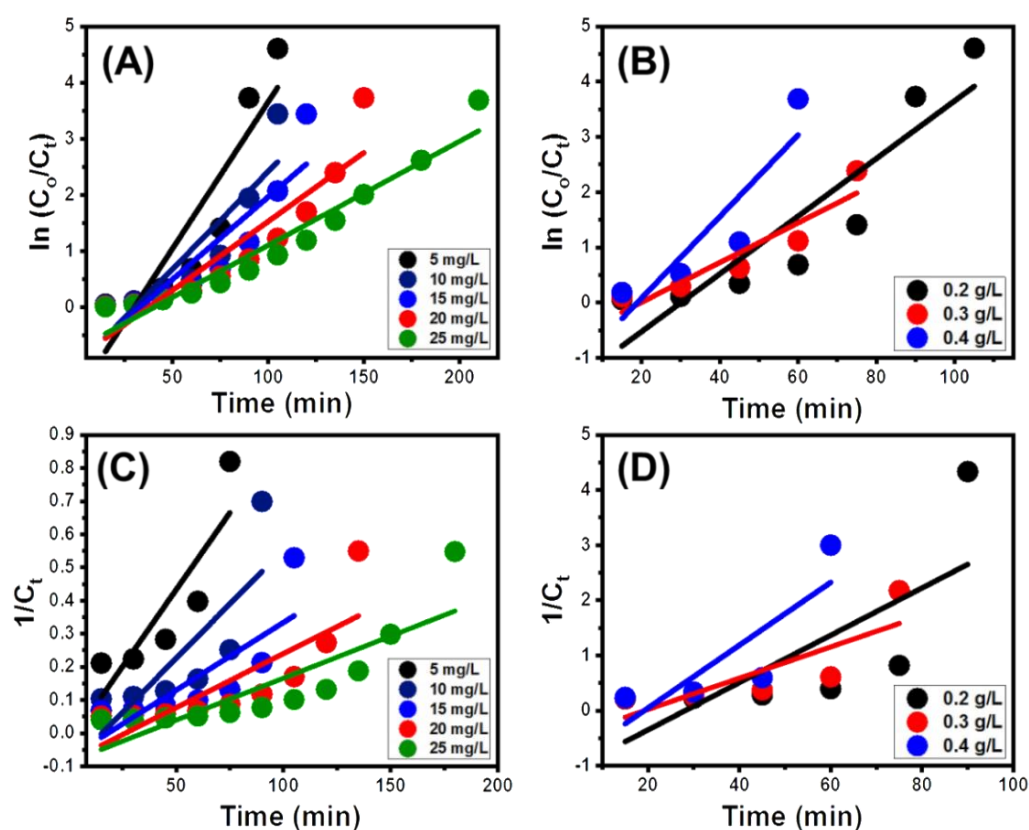


Figure 7. Fitting of the C.R photo-Fenton's oxidation results using MG/CFC with First order (A,B) and Second order (C,D) kinetic models.

The recognized fitting degrees validate the occurrence of the C.R oxidation processes by MG/CFC according to the kinetic behaviors of the First-order model either in terms of the C.R concentration or the applied dosages of MG/CFC. This kinetic behavior demonstrates the controlling effect of one of the assessed experimental variables (MG/CFC dosage, C.R concentration, and oxidation duration) on the efficiency of the MG/CFC-based photo-Fenton's oxidation system of C.R dye. The reported cases that show agreement with the two kinetic assumptions at the same time reveal the possible cooperation of more than one oxidation mechanism or more than one of the generated oxidizing radicals. The obtained kinetic rate constants of the evaluated models exhibit marked increment and declination in terms of the increase in the MG/CFC dosages and C.R concentrations, respectively, which are in significant agreement with the reported experimental behaviors (Table 2).

Table 2. The estimated correlation coefficient, kinetic rate constants, and quantum yield values.

		First Order		Second Order		Quantum Yield (ϕ)
		R^2	K_1	R^2	K_2	
Dosage	0.2 g/L	0.83	0.052	0.75	0.0092	5.34×10^{-8}
	0.3 g/L	0.87	0.0652	0.66	0.0428	6.73×10^{-8}
	0.4 g/L	0.81	0.0739	0.70	0.0569	7.63×10^{-8}
Concentration	5 mg/L	0.83	0.052	0.75	0.0092	5.34×10^{-8}
	10 mg/L	0.80	0.034	0.63	0.0065	3.51×10^{-8}
	15 mg/L	0.81	0.029	0.63	0.0040	2.99×10^{-8}
	20 mg/L	0.84	0.024	0.66	0.0032	2.47×10^{-8}
	25 mg/L	0.93	0.018	0.72	0.0025	1.859×10^{-8}

The apparent values of the quantum yield (ϕ) of the performed oxidation experiments were obtained based on the rate constant of the fitting processes with the first-order kinetic model (k_1), molar absorptivity (ϵ_λ ($\text{cm}^{-1} \text{M}^{-1}$)), the intensity of the light source ($I_{0,\lambda}$ ($\text{Einstein I}^{-1} \text{S}^{-1}$)), and the cell length (ℓ (cm)) (Equation (7)). The ϕ values validate the quantities of the charge carriers that can provide the best oxidation effects on the C.R molecule per the absorbed light photon [6,59]. Therefore, their estimated values can reflect the performances of the studied photo-Fenton's oxidation system in terms of the experimental variables. These values reflect notable agreement with the experimental studies and demonstrate the enhancement effect of the MG/CFC dosages on the photo-Fenton's oxidation of C.R dye (Table 2).

$$\phi = \frac{K_1}{2.303 \times I_{0,\lambda} \times \epsilon_\lambda \times \ell} \quad (7)$$

2.3.5. Suggested Oxidation Mechanism

Effective Oxidizing Species

The essential and effective oxidizing species were detected to follow the occurred oxidation mechanism as well as the pathway. This was accomplished based on the common trapping tests in the presence of isopropanol, 1-4 benzoquinone, and EDTA-2Na as effective scavenging or trapping chemical reagents of the hydroxyl ($\text{OH}^\bullet$), superoxide ($\text{O}_2^{\bullet-}$), and electron-hole pairs (h^+) oxidizing species, respectively. The test was completed at the best experimentally studied oxidation conditions [C.R concentration: 5 mg/L; volume: 100 mL; MG/CFC dosage: 0.5 g/L; oxidation interval: 60 min; temperature: 313 K; Fenton reagent: 0.1 mL H_2O_2] in the existence of 1 mmol of the scavenging reagents. The decolorization percentages of C.R declined notable from 100% to 10.2% (isopropanol), 81.7% (1-4 benzoquinone), and 92.3% (EDTA-2Na) (Figure 8A). Therefore, the dominant oxidizing species during the Photo-Fenton's oxidation of C.R by MG/CFC are the hydroxyl radicals followed by considerable impact for the generated superoxide radicals ($\text{O}_2^{\bullet-}$).

The probe molecule tests using terephthalic acid ($5 \times 10^{-4} \text{M}$) were applied to follow the produced hydroxyl radicals. The terephthalic acid ($5 \times 10^{-4} \text{M}$) probe and NaOH ($2 \times 10^{-3} \text{M}$) were mixed with the C.R solution in the MG/CFC-based photo-Fenton's oxidation system. The quantities of hydroxyterephthalic acid which were produced during the oxidation of terephthalic acid were used as indicators of the generated quantities of oxidizing $\text{OH}^\bullet$ species. This was followed based on the changes in the intensities of the measured photoluminescence spectroscopy (PL) spectra using a fluorescence spectrophotometer (Figure 8B). The notable intensification in the measured PL spectrum in terms of the gradual increase in the oxidation duration supports the previous experimental finding about the controlling impact of the $\text{OH}^\bullet$ species during the performed photo-Fenton's oxidation processes of C.R by MG/CFC (Figure 8B).

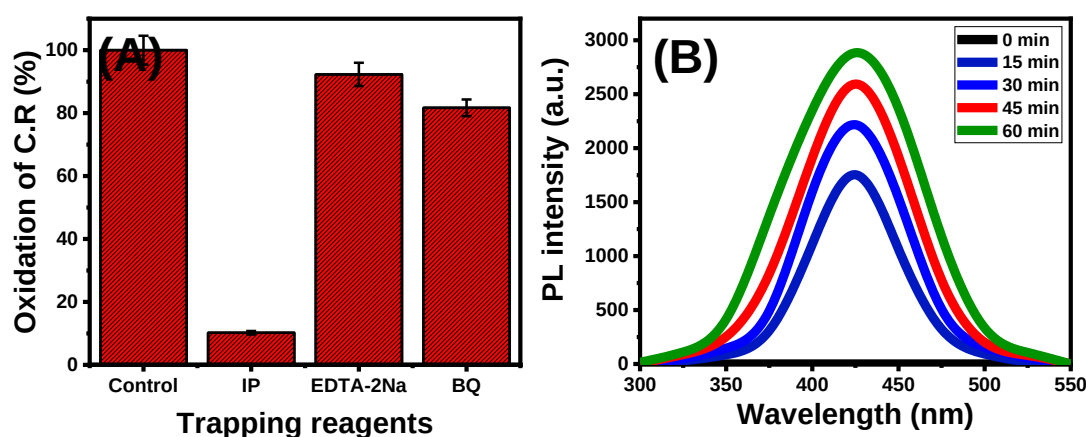
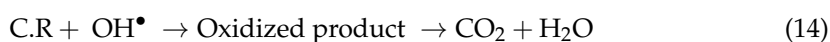
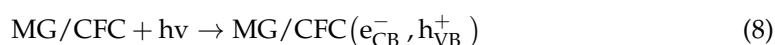


Figure 8. The results of the oxidizing species scavenging tests during the oxidation of C.R by MG/CFC (A) and the changes in the intensities of the PL spectra at different oxidation intervals (B).

General Oxidation Mechanism

The Photo-Fenton's oxidation of C.R molecules by MG/CFC involved complex effects of photocatalytic and Fenton's oxidation processes (Figure 9). Both of the operating processes started with effective adsorption of the C.R molecules on the surface of MG/CFC and parallel generation of the main oxidizing species. The photocatalytic process involved the excitation of the outer electrons of MG/CFC by the photons of the used visible light source, which typically causes the significant generation of electron–hole pairs (h^+) (Figure 9) [60,61]. The migrated electrons during this process interact with the present oxygen ions forming new oxidizing species (superoxide radicals ($O_2^{\bullet-}$)) [60]. The direct interaction between the formed electron–hole pairs (h^+) and the water molecules cause significant water splitting processes producing $OH^\bullet$ oxidizing species [62]. The formed oxidizing species are of oxidation and degradation effect on the organic structure of C.R molecules as presented in Equations (8)–(14) [63].



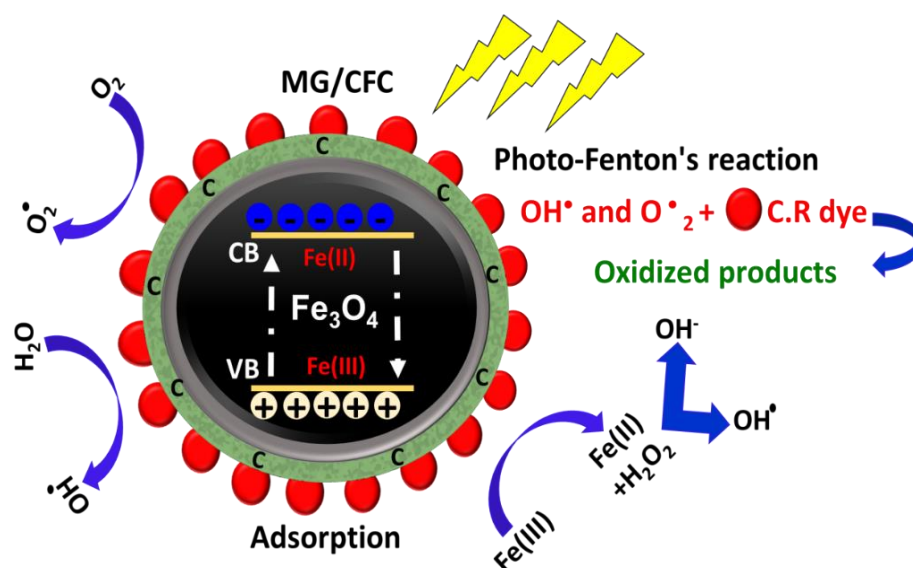
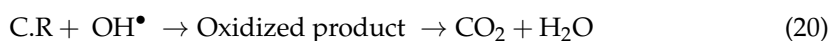
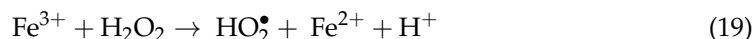
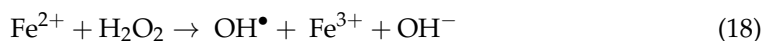
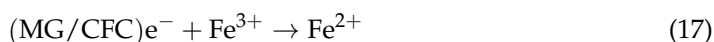
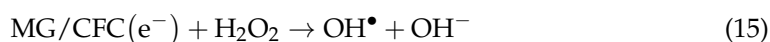


Figure 9. Schematic diagram for the suggested photocatalytic and photo-Fenton's oxidation of C.R by MG/CFC.

For the Fenton oxidation processes, the migrated electrons interact with the incorporated hydrogen peroxide molecules which are associated with the photolysis effect. The photolysis of the hydrogen peroxide results in the formation of free hydroxyl groups $\text{OH}^\bullet$ in the solutions which in turn oxidize immediately into $\text{OH}^\bullet$ species during their interaction with the electron-hole pairs (h^+) [6]. As a cooperative process, the interaction effect of the migrated electrons on the supported green magnetite causes a significant chemical reduction of its ferric ions (Fe(III)) into ferrous ions (Fe(II)) that oxidize again by the hydrogen peroxide (Figure 9) [6]. The oxidation reaction results in the formation of ferric ions Fe(III) and more $\text{OH}^\bullet$ species as oxidizing radicals (Figure 9). The $\text{OH}^\bullet$ species induce the re-formation of the ferrous ions (Fe(II)) by a series of Fenton-like reactions which occurred in a regenerative and continuous process. The formed $\text{OH}^\bullet$ species during all the mentioned processes exhibit direct oxidizing effects on the organic structure of C.R (Equations (15)–(20)) (Figure 9).



2.4. Recyclability

The stability and reusability of MG/CFC as the used catalyst or as an adsorbent were studied to assess the suitability of the product to be escalated for realistic and commercial applications. After the performed oxidation test of C.R., the incorporated MG/CFC fractions were re-extracted by filtration using Whitman filter paper. The extracted spent MG/CFC fractions were washed for 5 runs and each run consumed 10 min and then were rinsed by NaOH (0.01 M) for about 5 min. The rinsed MG/CFC fractions were washed again with distilled water and dried at 343 K for 12 h to be applied in an additional oxidation test. The reusability studies were performed for the MG/CFC fractions which were incorporated at the best experimentally conditions [oxidation interval: 60 min; C.R concentration: 5 mg/L;

volume: 100 mL; MG/CFC dosage: 0.5 g/L; temperature: 293 K; Fenton reagent: 0.1 mL H₂O₂]. The same regeneration steps were performed for the incorporated MG/CFC during the adsorption tests and the reusability experiments were conducted at the same conditions but without H₂O₂ or light source. The determined C.R oxidation percentages demonstrate the significant stability and reusability values of MG/CFC as a heterogeneous catalyst. The determined C.R oxidation percentages during the reusability runs are 100% (Run1), 98.7% (Run2), 96.4% (Run3), 93.2% (Run4), and 87.4% (Run5) (Figure S1). The measured C.R adsorption removal percentages during the reusability runs are 33.2% (Run1), 31.6% (Run2), 27.4% (Run3), 22.8% (Run4), and 16.3% (Run5) (Figure S1). The previously detected results either by adsorption or photo-Fenton's oxidation can be enhanced strongly either by using higher dosages of MG/CFC or by expanding the oxidation intervals.

2.5. Ecotoxicity Properties

The acute and chronic toxicities of the C.R polluted solution at different oxidation intervals towards both Fish and green algae were assessed according to the criteria of Chinese hazard evaluation (HJ/T1542004) and European Union classification. The increment in the values of acute and chronic toxicity (mg/L) demonstrated declination in the ecological risk and vice versa. This was assessed considering the treated C.R samples at the best experimentally conditions [oxidation interval: 60 min; C.R concentration: 5 mg/L; volume: 100 mL; MG/CFC dosage: 0.5 g/L; temperature: 293 K; Fenton reagent: 0.1 mL H₂O₂]. The recognized results validate notable increases in the measured acute and chronic toxicity values with increasing the photo-Fenton's oxidation intervals in the existence of MG/CFC catalysts as compared to the untreated C.R solution as control sample (Table 3). This displays the environmental value to apply the synthetic structure (MG/CFC) in low cost, effective, and ecological safe oxidation of synthetic dyes.

Table 3. Acute toxicity and chronic toxicity of C.R and the tread samples at different oxidation intervals using MG/CFC.

Compound	Fish (LC ₅₀)	Green Algae (EC ₅₀)	Fish (ChV)	Green Algae (ChV)
C.R control	0.534	0.311	0.077	0.812
30 min	87.8	71.4	3.86	6.4
60 min	486.9	213.6	211.3	153.7
90 min	4754.4	566.2	1341.6	387.4
120 min	10320.2	924.3	1672.8	934.5

For acute toxicity; LC₅₀ or EC₅₀ <1 (highly toxic), 10 < LC₅₀ or EC₅₀ <100 (harmful), and LC₅₀ or EC₅₀ >100 (Not harmful); For chronic toxicity; ChV < 0.1 (highly toxic), 1 < ChV <10 (harmful), and ChV >10 (Not harmful).

2.6. Comparison Study

The value of the synthetic MG/CFC as promising low-cost and effective adsorbents and heterogeneous catalysts during the removal of C.R dye was compared with synthetic structures in the literature (Table 4). The obtained results validate higher adsorption properties of MG/CFC than several studied adsorbents as well as the raw pyrite sample. Moreover, the recognized catalytic activity of MG/CFC towards the effective oxidation of C.R dye validates its higher efficiency than several studied materials as well as the raw pyrite considering the essential factors [oxidation percentage, tested volume, C.R concentration, light source, and oxidation duration]. Considering such enhanced technical advantages as well as the commercial value of MG/CFC, which is realized through the facile synthesis, low cost, and use of extensively available precursors, MG/CFC can be used more effectively in the practical and realistic applications, compared to several types of the reported expensive catalysts.

Table 4. Comparison between the adsorption and catalytic activities of MG/CFC and other studied materials in literature.

Catalysts	Dosage	Conc.,	Light Source	Oxidation (%)	References
Ni-TiO ₂	0.02 g/L	10 mg/L	450 W Xe lamp	180 min, ca. 92.3%	[17]
CuO NPs	0.01 g/L	5 × 10 ^{−5} M	100 W electric bulb	120 min, ca. 91%	[64]
BE/CH@Co ₃ O ₄	0.02 g/L	25 mg/L	visible light source	240 min, ca. 98.8%	[65]
ZBiSe-NPs	0.225 g/L	40 mg/L	UV-1602 double beam	120 min, ca. 99.6%	[66]
CoMoO ₄ /PDS	0.8 g/L	100 mg/L	500 W xenon lamp, PDS (0.5 mmol/L)	35 min, ca. 96.9%	[67]
SnO ₂ -Fe ₃ O ₄	0.03 g/L	18 mg/L	14 W UV lamp	90 min, ca. 50.76%	[68]
TiO ₂ -CoFe ₂ O ₄	0.08 g/L	100 mg/L	150 W metal Halide lamp	250 min, ca. 97%	[69]
MG/CFC	0.5 g/L	5 mg/L	metal Halide lamp, 0.1 mL H ₂ O ₂	45 min, ca. 100%	This study
MG/CFC	0.2 g/L	5 mg/L	metal Halide lamp, 0.1 mL H ₂ O ₂	105 min, ca. 100%	This study
MG/CFC	0.2 g/L	10 mg/L	metal Halide lamp, 0.1 mL H ₂ O ₂	120 min, ca. 100%	This study
MG/CFC	0.2 g/L	20 mg/L	metal Halide lamp, 0.1 mL H ₂ O ₂	180 min, ca. 100%	This study

Adsorption		
Adsorbents	Adsorption capacity (mg/g)	References
MNPs@NiFe LDH	79.6	[70]
Zn-MOF	355.16	[71]
Fe ₃ O ₄ -OPBC-2 NCs	299.82	[72]
Fe ₃ O ₄ - OPBC-1 NCs	317.33	[73]
polyacrolein (PA-1)	140.8	[72]
Pyrite	123.4	This study
MG/CFC	436.1	This study

3. Methodology

3.1. Materials

Natural framboidal pyrite was delivered from Central Metallurgical and Development Institute as raw material to be used as a precursor during the synthesis process. Nitric acid solution (69% AR/ACS) was obtained from Loba Chemie Pvt Ltd.; India was used to dissolve the pyrite samples. Synthetic Congo red dye (benzidinediazo-bis-1-naphthylamine-4-sulfonic acid (C₃₂H₂₂N₆Na₂O₆S₂)) was used as a source of the dye pollutants (Sigma Aldrich; Egypt). Hydrogen peroxide (30%; PIOCHEM, Egypt) was used during the Fenton's and photo-Fenton's oxidation. Nitric acid solution and sodium hydroxide pellets were used as pH modifiers.

3.2. Synthesis of MG/CFC Green Nanocomposite

The raw pyrite sample was ground extensively to be within the size range from 25 µm up to 100 µm. 50 g of the ground pyrite was dissolved within 100 mL of nitric acid at 313 K for 48 h. The spent coffee extract was prepared by boiling 10 g of the coffee powder within 100 mL of distilled water for 10 min. After that, 100 mL of the coffee extract containing the coffee residuals was mixed with 200 mL of the pyrite aqueous solution (pyrite/nitric acid). After a certain mixing period, the pH was adjusted to about pH 10 and left for 24 h at room conditions to confirm the successful precipitation of the iron nanoparticles. After that, the obtained products were washed with distilled water for several runs and dried at 333 K for 48 h. Finally, the product was carbonized at 573 K at digital electric muffle furnace for 24 h to produce a hybrid product of coffee-based MG/CFC green composite (Figure 10).

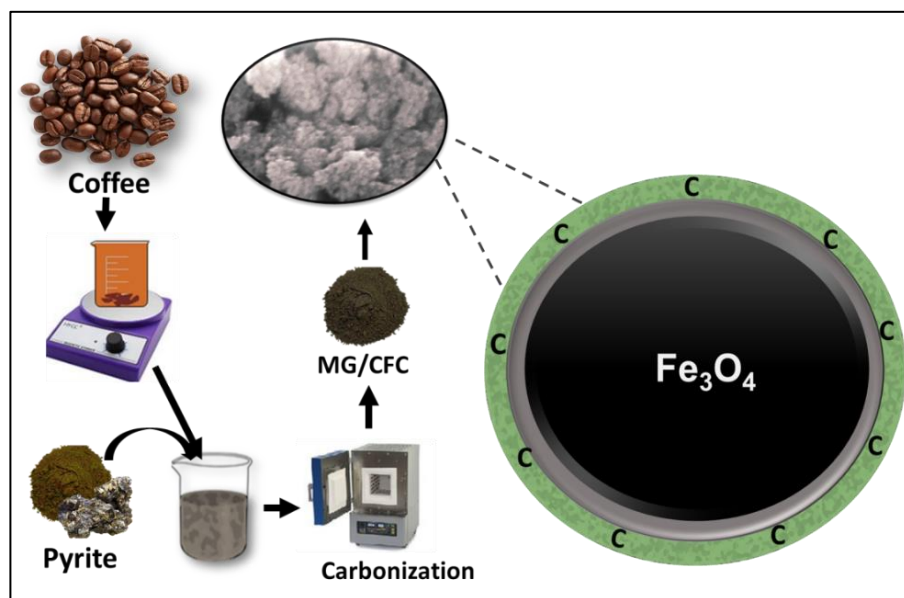


Figure 10. Schematic diagram for the synthesis of MG/CFC green composite from pyrite and coffee.

3.3. Characterization

The crystal structures of the prepared products were investigated using an X-ray diffractometer (PANalytical-Empyrean type). The used X-ray is Cu-K α X-ray and the producing source is Cu anode which is provided with 40 mA as operation current and 40 kV as determination voltage. The SEM morphological images of the prepared structures were performed utilizing the Scanning-Electron Microscope (Gemini, Zeiss-Ultra 55) after coating the particles with thin film of gold. Meanwhile, the TEM images of the internal structure were addressed using Transmission Electron Microscope (JEOL-JEM, 2100). The chemical composition of the structure and the essential chemical functional groups were inspected using a dispersive X-ray system (EDX) and FT-IR spectrometer ((FTIR–8400S) in the transmission mode, respectively. During the FT-IR investigation, the modified samples were milled with KBr powder and then the mixtures were compressed utilizing a hydraulic press into pellets which were fixed in the sample holder of the FT-IR spectrometer. The microstructural features as the surface area and porosity were determined considering BET and BJH methods, respectively, using a Beckman Coulter surface area analyzer (SA3100 type) after degassing step for 15 h at 105 °C and the measuring temperature were adjusted at 77 K.

3.4. Batch Adsorption Studies of C.R Dye

The adsorption of C.R dye by MG/CFC was completed in batch forms considering the common adsorption parameters of pH (2–8) and concentration (50 mg/L–350 mg/L) considering the temperature at different values (303–323 K). This was performed considering the other factors at certain values (100 mL for the dye volume, 24 h for the adsorption duration, and 0.2 g/L for the MG/CFC dosage). The tests were conducted in triplicate forms considering the average results during the determination of C.R uptake capacity with a standard deviation of less than 5.6%. The adsorption capacities were estimated based on Equation (21) by measuring the residual C.R concentrations in the treated samples using a UV-vis spectrophotometer at a wavelength number of 520 nm.

$$Q_e \text{ (mg/g)} = \frac{(C_o - C_e)V}{m} \quad (21)$$

The Q_e (mg/g), C_e (mg/L), C_o (mg/L), m (mg), and V (mL) symbols are the actual C.R adsorption capacity, rest concentration, started dye concentration, MG/CFC quantity, and dye volume, respectively. The equilibrium properties of the C.R uptake processes were

followed based on the common isotherm models considering the correlation coefficient (R^2) (Equation (22)) and chi-square (χ^2) (Equation (23)) for the classic isotherm models. For the classic models based on the statistical physics theory (Table 5), the fitting degrees were considered according to the values of R^2 and root mean square error (RMSE) (Equation (24)). This occurred based on the values utilizing the values of $Q_{e,exp}$ (experimental uptake capacity) and $Q_{e,cal}$ (theoretical uptake capacity), m' (the recognized results), and p (experimental variables).

$$R^2 = 1 - \frac{\sum (Q_{e,exp} - Q_{e,cal})^2}{\sum (Q_{e,exp} - Q_{e,mean})^2} \quad (22)$$

$$\chi^2 = \sum \frac{(Q_{e,exp} - Q_{e,cal})^2}{Q_{e,cal}} \quad (23)$$

$$RMSE = \sqrt{\frac{\sum_{i=1}^m (Q_{e,cal} - Q_{e,exp})^2}{m' - p}} \quad (24)$$

Table 5. Nonlinear equations of kinetic, classic isotherm, and advanced isotherm models.

Classic Isotherm Models		
Model	Equation	Parameters
Langmuir	$Q_e = \frac{Q_{max} b C_e}{1 + b C_e}$	C_e is the rest ions concentrations (mg/L), Q_{max} is the maximum adsorption capacity (mg/g), and b is Langmuir constant (L/mg)
Freundlich	$Q_e = K_f C_e^{1/n}$	K_f (mg/g) is the constant of Freundlich model related to the adsorption capacity and n is the constant of Freundlich model related to the adsorption intensities
Dubinin–Radushkevich	$Q_e = Q_m e^{-\beta \varepsilon^2}$	β (mol ² /KJ ²) is the D-R constant, ε (KJ ² /mol ²) is the polanyiil potential, and Q_m is the adsorption capacity (mg/g)
Advanced isotherm models		
Model	Equation	Parameters
Monolayer model with one energy site (Model 1)	$Q = n N_o = \frac{n N_M}{1 + (\frac{C_1}{C_2})^n}$	Q is the adsorbed quantities in mg/g n is the number of adsorbed ion per site
Monolayer model with two energy sites (Model 2)	$Q = \frac{n_1 N_{1M}}{1 + (\frac{C_1}{C_2})^{n_1}} + \frac{n_2 N_{2M}}{1 + (\frac{C_2}{C_1})^{n_2}}$	N_m is the density of the effective receptor sites (mg/g) Q_o is the adsorption capacity at the saturation state in mg/g
Double layer model with one energy site (Model 3)	$Q = Q_o \frac{(\frac{C}{C_1})^n + 2(\frac{C}{C_2})^{2n}}{1 + (\frac{C}{C_1})^n + (\frac{C}{C_2})^{2n}}$	$C_1/2$ is the concentration of the ions at half saturation stage in mg/L C_1 and C_2 are the concentrations of the ions at the half saturation stage for the first active sites and the second active sites, respectively
Double layer model with two energy sites (Model 3)	$Q = Q_o \frac{(\frac{C}{C_1})^n + 2(\frac{C}{C_2})^{2n}}{1 + (\frac{C}{C_1})^n + (\frac{C}{C_2})^{2n}}$	n_1 and n_2 are the adsorbed ions per site for the first active sites and the second active sites, respectively

3.5. Photo-Fenton's Oxidation of C.R Dye

The catalytic properties of MG/CFC as a heterogeneous catalyst during the photo-Fenton oxidation of the C.R molecules were evaluated in the existence of hydrogen peroxide (0.5 mL) as Fenton's reagent and visible light source. All these tests were considered after attending the adsorption/desorption equilibrium state and then the catalyst was mixed with the C.R solutions (50 mL) at pH 7 considering the C.R concentration (5–25 mg/L), MG/CFC dosages (0.2–0.5 g), and oxidation interval (30 min–360 min). This was conducted at a fixed volume of 50 mL, at pH 7, and a fixed volume of H₂O₂ (0.5 mL) as a Fenton reagent. The used light source is a Metal halide lamp of 400 W power, 490 nm average wavelength, and 18.7 mW/cm² incident light intensity. All the performed C.R oxidation tests were repeated for three runs and the average result of the tests were considered during all the explanation with a standard deviation of less than 4.3%. The oxidation percentages of C.R utilizing MG/CF were determined according to Equation (5) while the mineralization

degree was followed based on the reduction in the TOC content in the solutions using TOC-VCPH (Shimadzu, Japan).

$$R, \% = \frac{(C_o - C_e) \times 100}{C_o} \quad (25)$$

3.6. Ecotoxicity Studies

The ecotoxicity properties of C.R polluted water before and after the treatment steps toward the aquatic organisms (green algae and fish) was followed using with Ecological Structure Activity Relationship (ECOSAR) predictive program either the chronic toxicity or the acute toxicity. Both the chronic and acute toxicities were determined in terms of EC50, LC50, and ChV (mg/L). The LC50 value reflects the concentrations of the pollutant that can cause inhabitation for 50% of fish after 96 h as exposure time while EC50 reflects the required concentration to inhibit the growth of green algae by 50% and ChV reflects the chronic toxicities effects of the C.R pollutants.

4. Conclusions

Magnetite/carbonized coffee (MG/CFC) composite was synthesized successfully from pyrite and applied in effective decontamination of C.R dye by adsorption and photo-Fenton's oxidation process. MG/CFC achieved 436.1 mg/g adsorption capacity of C.R and the adsorption process was controlled by physical processes based on the energetic studies ($\Delta E = 6.2\text{--}8.2$ kJ/mol). The steric studies reflect the saturation of MG/CFC with 855 mg/g active site density and each C.R molecule can be adsorbed by more than one site by multianchorage process at the best temperature (313 K). As a catalyst, it shows notable activity during the visible light-based photo-Fenton's oxidation of C.R (5 mg/L) achieving complete degradation after 30 min and complete mineralization after 120 min using 0.5 g/L of MG/CFC and 0.1 mL of H_2O_2 . The acute and chronic toxicities of the treated samples reflect their safe effects on aquatic organisms (fish and green algae) as compared to the parent C.R solution.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal13020264/s1>, Figure S1: the recyclability properties of MG/CFC as an adsorbent and catalyst during the photo-Fenton's oxidation of C.R.

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