Photo-Fenton like Catalyst System: Activated Carbon/CoFe$_2$O$_4$ Nanocomposite for Reactive Dye Removal from Textile Wastewater

Mohammad Reza. Heidari 1,2, Rajender S. Varma 3,* 4, Mohammad Ahmadian 1, Mohsen Pourkhosravani 4, Seyedeh N. Asadzadeh 5, Pouria Karimi 1 and Mehrdad Khatami 6,7,*

1 Department of Environmental Health Engineering, School of Public Health, Bam University of Medical Sciences, Bam, Iran; moheidari86@gmail.com (M.R.H.); moh.ahmadian@yahoo.com (M.A.); Karimi.pouria70@gmail.com (P.K.)
2 Student Research Committee, School of Public Health, Bam University of Medical Sciences, Bam, Iran
3 Regional Centre of Advanced Technologies and Materials, Department of Physical Chemistry, Faculty of Science, Palacky University, Šlechtitelů 27, 78371 Olomouc, Czech Republic
4 Department of Geography, Shahid Bahonar University of Kerman, Kerman, Iran; Pourkhosravani@uk.ac.ir
5 Student Research Committee, School of Public Health, Kerman University of Medical Sciences, Kerman, Iran; snasadzadeh3@gmail.com
6 NanoBioelectrochemistry Research Center, Bam University of Medical Sciences, Bam, Iran
7 Medical Ethics and Law Research Center, Shahid Beheshti University of Medical Sciences, Tehran, Iran
* Correspondence: varma.rajender@epa.gov (R.S.V.); Mehrdad7khatami@gmail.com (M.K.); Tel.: +1-(513)-487-2701 (R.S.V.); +98-936-266-2882 (M.K.)

Received: 14 December 2018; Accepted: 28 February 2019; Published: 7 March 2019

Abstract: The removal of dye from textile industry wastewater using a photo-Fenton like catalyst system was investigated wherein the removal efficiency of phenol and chemical oxygen demand (COD) was studied by varying various parameters of pH (3–11), reaction time (1–50 min), activated Carbon/CoFe$_2$O$_4$ (AC/CFO) nanocomposite dosage (0.1–0.9 g/L), and persulfate amount (1–9 mM/L). The highest removal rates of reactive red 198 and COD were found to be 100% and 98%, respectively, for real wastewater under the optimal conditions of pH = 6.5, AC/CFO nanocomposite dosage (0.3 g/L), reaction time, 25 min, and persulfate dose of 5 mM/L up on constant UV light irradiation (30 W) at ambient room temperature. The result showed that this system is a viable and highly efficient remediation protocol relative to other advanced oxidation processes; inexpensive nature, the ease of operation, use of earth-abundant materials, and reusability for removal of organic pollutants being the salient attributes.

Keywords: heterogeneous catalysts; photo-Fenton catalyst; CoFe$_2$O$_4$; dye removal

1. Introduction

Environmental pollution generated by industrial wastewater is one of the greatest problems the world is facing today and dyes are widely applied in many industries, such as leather, textile, plastics, paper, and other entities emanating from pharmaceutical and food industries [1–5]. Dyes effect the photosynthetic activities of aquatic lives and their ensuing byproducts are not biodegradable but are stable, carcinogenic, and hazardous to human health [6–8]. Dyes are usually classified on the basis of their chemical structure, such as anionic, cationic, and non-ionic [9,10]; reactive dyes are stable and anionic in character, and display resistance towards light [11,12]. Generally, the methods for the removal of dyes can be classified into the following categories, namely biological methods (anaerobic...
Advanced Oxidation Processes (AOPs) involve the generation of reactive oxygen species using a combination of strong oxidants such as H$_2$O$_2$, O$_3$, and catalysts by completely mineralizing the biodegradable compounds and the degradation of non-biodegradable organic pollutants [23,24]. The AOPs are an attractive option due to the usage of environmentally friendly chemicals and their high efficiency for the removal of persistent and synthetic organic compounds with short treatment times [25]. Some of the most popular AOPs are Fenton’s reaction, Photo-Fenton, Sono-Fenton, Electro-Fenton, electrochemical oxidation, TiO$_2$ photocatalysis, advanced ozonolysis, cavitation, and Fenton-like reaction [26], among others. In the Fenton reaction, the formation of hydroxyl radicals is the main event accomplished by different processes: (1) homogeneous Fenton process, involving iron salts and an oxidant under an acid medium; (2) heterogeneous Fenton process, involving a solid catalysis and oxidant (‘Fenton-like catalyst’); (3) photo reduction of Fe(III) to Fe(II) by ultrasound and UV (‘photo-Fenton and sono-Fenton processes’, respectively) [27]. Heterogeneous Fenton-like processes by solid catalysts (iron or other transition metals) have been applied over a wide pH range; reduce hydroxide precipitation and possibly facilitate solid/liquid phase separation [28]. Recently, an innovative treatment method based on heterogeneous Fenton-like catalysis oxidant activation has been researched as an alternative to conventional methods of the AOPs [29].

Persulfate (PS), as a strong oxidizing agent, for removal of a wide variety of inorganic and organic components, has received much attention owing to some of its great advantages [30,31]. The PS salts usually form S$_2$O$_8^{2-}$ anions, which efficiently remove most of the pollutants, being a powerful oxidant with high oxidation potential of SO$_4^{•−}$ at natural pH [32,33]. The PS can be activated using ultrasound, UV (Equation (1)) and heat that causes the hemolysis of the peroxide bond in the persulfate molecule. The persulfate is an oxidant ($E^0 = 2.01 \text{ V}$) and the powerful oxidizing species of sulfate free radicals ($E^0 = 2.6 \text{ V}$) can be formed through the cleavage of the O–O bond via activation or/catalysis process [34].

$$S_2O_8^{2−} + hv \rightarrow 2SO_4^{•−}. \quad (1)$$

Spinel ferrite (XFe$_2$O$_4$) is a stable, low-cost magnetic material, and widely used for the removal of various pollutants. Cobalt (Co) can be used to replace the cation X$^{2+}$ in XFe$_2$O$_4$ to enhance the catalytic activity of Fe spinel and in view of the separation of Fe$^{2+}$ from the catalyst structure the high activity for activation of the PS has been demonstrated (Equation (2)) [32].

$$S_2O_8^{2−} + M^{n+} \rightarrow SO_4^{−•} + M^{(n+1)+} + SO_4^{2−} \quad (2)$$

The nano ferrites are effective magnetic materials which have a band gap in the visible region; their integration with metal produces cobalt ferrite (CoFe$_2$O$_4$) nanoparticles. These low cost, non-toxic and abundant materials, have added magnetic separation possibility. In view of the magneto-optical coefficient at low temperature, that can exploit S$_2$O$_8$ under UV irradiation, these materials can be used as a powerful photocatalyst as they augment oxidizing power of Fenton reactions and oxidative dehydrogenation of hydrocarbons.

In this paper, we synthesized a Fenton-like catalyst for PS activation under UV irradiation to degrade reactive red 198 (RR198) dye. The degradation and mineralization of RR198 was investigated under varying conditions and assessed for the removal efficiency of RR198 and COD, including catalyst dosage, oxidant amount, RR198 concentration, and pH, including the kinetic models.

2. Materials and Methods

2.1. Materials

In this study, samples of effluent obtained from the textile Industry Factory located in Iran were used (Table 1). Reactive red 198 (RR 198) (molecular formula: C$_{27}$H$_{18}$ClN$_7$Na$_4$O$_{15}$S$_5$; weight:
968.21 g/mol), sodium persulfate (Na₂S₂O₈, ≥ 99%), sodium hydroxide (NaOH), and hydrochloric acid (HCl) were purchased from Merck, Germany. A stock solution of 1 g/L was prepared by dissolving 1 g of dye, and then made up to 1 L with dionized-H₂O [35]. This solution was filtered through 0.45 μm filter and stored in the dark. Na₂SO₄ with the concentration of 0.01 mol/L was added to provide the ionic strength. The pH variation was attained using HCl and NaOH solutions (0.1 N).

Table 1. Textile wastewater characteristics.

| Parameter mgL⁻¹ | BOD | COD  | TSS  | Ca²⁺ | Mg²⁺ | Cl⁻ | Na⁺ | K  | NO₃ |
|-----------------|-----|------|------|------|------|-----|-----|----|-----|
| Raw WW          | 185 | 880  | 479.2| 240  | 35   | 298 | 250 | 21 | 51  |

2.2. Preparation of Activated Carbon/CoFe₂O₄ (AC/CFO) Nanocomposite

2.2.1. Procedure for the Preparation of Nanocomposite

All chemicals were analytical grade and used as received without further purification. Deionized water was used throughout the experiments. FeCl₃.6H₂O and CoCl₂.6H₂O in a ratio of 2:1 were dissolved in 50 mL deionized water. Then, activated charcoal (AC) was added to the solution and the mixture was vigorously stirred at room temperature. Next, NaOH was added to the suspension within 1 h to adjust the pH to 13. The ensuing dark brown solution was subjected to microwave irradiation (450 W, temp. 53 °C and 45 min.); lightweight massive powder of AC/CFO particle formed quickly, and the black powder generated was isolated by using an external magnet. It was washed with deionized water three times and dried at 100 °C for 24 h.

2.2.2. Characterization of the Nanocomposite

The XRD of AC/CFO catalysts was recorded in the diffraction angle range of 2θ = 10–80° by an X’Pert PRO MPD P Analytical using Ni-FILTERED Cu Kα radiation (Figure 1). The characterization of the magnetic properties for the AC/CFO catalysts was carried out by Vibrating Sample Magnetometery (VSM) (LakeShore Cryotronics-7404) at room temperature (Figure 2). The microstructure, morphology, and chemical composition of AC/CFO catalysts were investigated by Field Emission Scanning Electron Microscopy (FE-SEM) (MIRA3TESCAN-XMU) (Figure 3).

Figure 1. Field Emission Scanning Electron Microscopy (FE-SEM) images of activated carbon/CoFe₂O₄ nanocomposite.
2.3. Photo-Fenton-Like System

The PF like system used consists of a Plexiglas cell (1000 mL) with one 30-W (UV-C) mercury lamp (Philips) in a quartz sheath that was fitted with an aluminum cover, typical of a batch reactor. In all the experiments, a magnetic stirrer (400 rpm) was used in the reactor to maintain monotonous concentration at ambient room temperature (21 ± 1 °C). The reaction was carried out under the pH range 2–11, using PS, (0.1–0.9 g/L) for 10–100 min duration, and at initial dye concentrations of 5–100 mg/L.

2.4. Analytical Methods

The amount of residual dye was determined by of spectrophotometer (Shimadzu UV/Vis, Japan) at $\lambda_{\text{max}}$ 518 nm and the mineralized carbon (CO$_2$) of dye was calculated by the difference between the initial and final Chemical Oxygen Demand (COD) concentrations (dichromatic closed reflux method) (5220-D; colorimetric) [36]; a pH meter and water bath for maintaining the reaction solution were used. The percentage of phenol removed was calculated according to (Equation (3)):
The equilibrium adsorption capacity was calculated based on (Equation (4)):

\[ q = \left( \frac{C_0 - C_t}{m} \right) V. \]  

where \( C_0 \) and \( C_t \) are the initial and residual concentrations of dye (ppm), \( q \) is the adsorption capacity (mg/g), \( V \) is the volume of dye solution (L), and \( m \) is the adsorbent mass (g). The fit of experimental data to the kinetic models was assessed by the correlation coefficient \( (R^2) \) (Equation (5)) and the residual root mean square error (RMSE) used for plotting the kinetic models, where \( n \) is the number of data points (Equation (6)).

\[ R^2 = \frac{\sum_{i=1}^{N} (q_e - q_{e,exp})^2}{\sum_{i=1}^{N} (q_e - q_{e,exp})^2 + (q_e - q_{e,exp})^2} \]  

\[ RSME = \sqrt{\frac{1}{n-2} \sum_{i=1}^{N} (q_e - q_{e,exp})^2}. \]

3. Results and Discussion

3.1. Characterization of Nanocomposite

3.1.1. FESEM and Morphology of AC/CFO

The FESEM images of AC/CFO shown in (Figure 1) depicts the formation of AC/CFO nanocomposite with an average particle size of about 30 nm. The surface morphology of nanocomposite shows the generation of cobalt ferrite particles on the surface of activated carbon; small aggregates were observed.

3.1.2. The XRD Analysis of AC/CFO

The XRD pattern of AC/CFO with the crystal phase structure of magnetic nanocomposite had diffraction peaks at \( 2\theta \) of about 18.42\(^\circ\), 30.25\(^\circ\), 35.58\(^\circ\), 53.59\(^\circ\), 57.15\(^\circ\), 62.71\(^\circ\) and 74.14\(^\circ\) (Figure 2).

These peaks, that are well indexed to the cubic spinel phase of \( \text{CoFe}_2\text{O}_4 \), are also in agreement with the literature data (JCPDS 96-591-0064) and reveal that, even in the reaction with AC, the crystal structure of the \( \text{CoFe}_2\text{O}_4 \) is well preserved. Similar results have been reported in the literature for the magnetic oxide-supported activated carbon [37].

3.1.3. Magnetic Properties of AC/CFO

The magnetic properties of the AC/CFO was evaluated by VSM at room temperature; the magnetization curve of AC/CFO displayed a ferromagnetic character (Figure 3).

In addition to ferromagnetic properties, the room temperature specific magnetization (M) versus applied magnetic field (H) curve measurement of the AC/CFO indicates that the values of coercive force [38], saturation magnetization and remnant magnetization are 433.02 Oe, 22.03 emu/g and 7.16 emu/g, respectively; a similar result was reported earlier by Xu et al. [39].

3.2. Catalytic Activity of Dye in the Presence of AC/CFO

The removal efficiency of dye under a variety of reaction conditions was investigated by varying the pH = 6.5, dye concentration of 50 mg/L, a catalyst dosage of 0.3 g/L, and \( \text{SO}_4 \) amount of 5 mM/L.
The experimental results show that the RR198 degradation attained for PS, UV irradiation, CFO alone, PS/UV, and Fenton (AC/CFO activated with H$_2$O$_2$) after 25 min contact, was 18%, 22%, 34%, and 38%, respectively (Figure 4); the COD removal efficiencies were 15%, 20%, 30%, 33%, and 59%, respectively, under the same conditions. These results showed, low oxidation potential of PS alone for generation sulfate radicals. The free radical production increases in the presence of PS under UV irradiation as PS gets activated by UV to produce a powerful oxidant, SO$_4$•, as the concentration of persulfate increased. However, PS would react with SO$_4$•, leading to the decrease of SO$_4$• concentrations and hence the removal efficiency of dye did not change significantly. According to Figure 4, the removal efficiency attained by CFO was the higher than that of UV irradiation and PS, which are mainly due to the high oxidation capacity. However, this finding indicates that the oxidation of dye by these processes is rather limited [30,40]. The highest removal efficiency of dye by AC, compared to that of oxidation processes, can be due to high specific surface area. When the AC/CFO nanocomposite was added, the removal of dye (79% in the reaction time of 50 min) changed significantly, indicating that the AC/CFO has much higher adsorption capacity for decolorization. The results show that increasing H$_2$O$_2$ concentration does not improve oxidation capacity compared to persulfate (removal efficiency = 59%). This may be due to the abundance of hydrogen peroxide that plays a radical scavenger role. Additionally, the excess H$_2$O$_2$ reacts with Fe$^{3+}$ to form hydroperoxyl radical which is weaker than hydroxyl radical. These results showed the synergistic effect between CFO and AC and the impregnation of CFO onto AC surface could cause an increase in dye removal by AC/CFO. In the reaction system of Fenton like catalyst (AC/CFO activated with PS), the removal efficiency of dye was 85.2% over 25 min. The high performance of this system is due to both, the adsorption and oxidation processes are involved in the removal efficiency of dye. Actually, results confirm that AC/CFO catalyst has a synergistic effect on PS for generation of sulfate radicals. When UV irradiation was (Equation (7)) added to the Fenton catalyst, the removal efficiency of dye was enhanced to much improved levels, 98.8% in the reaction time of 25 min.

$$\text{S}_2\text{O}_8^{2-} + \text{hv} \rightarrow 2\text{SO}_4^{\bullet}.$$ (7)

Based on these results, the catalytic ability of the PF like catalyst is higher than that of the typical Fenton like catalyst processes, which indicates that UV has high activating ability on PS which significantly enhanced the catalytic capacity of the AC/CFO nanocomposite. Therefore, this process overcomes problems typical of Fenton like catalysts. Excellent catalytic activity for the sulfate radical-based heterogeneous catalytic applications using cobalt ferrite (CoFe$_2$O$_4$), spinel ferrites, has been demonstrated due to its easy separation and high chemical stability. The additional AC/CFO nanocomposite led to the greater total surface area and number of active sites for PS activation to produce more SO$_4^{\bullet}$ radicals. The generation of SO$_4^{\bullet}$ radicals and the removal efficiencies of pollutants are increased under UV light irradiation in the photo-Fenton like process. Photo-Fenton technology combines photocatalytic methods with the Fenton process which could enable the continuous regeneration of Fe$^{2+}$ via different reduction processes, namely Fe$^{3+}$ with H$_2$O$_2$ or $\text{S}_2\text{O}_8$, intermediate organic radicals or directly at the cathode. Sulfate radicals based on AOPs can be generated from persulfate activated by heat, UV and transition metal ions. The Fe ion has been commonly deployed as the activator of persulfate to generate SO$_4^{\bullet}$ which is relatively more stable and selective than OH radicals for the oxidation of organic contaminants and it has been concluded that UV/PS is the more efficient and less energy consuming process than the UV/H$_2$O$_2$ process in the degradation of organic pollutants.

The photo-Fenton like process is based on the generation of SO$_4^{\bullet}$ radicals by catalytic decomposition of persulfate and AC/CFO nanocomposite in acidic media that prevents the precipitation of Fe ions; the ensuing Fe$^{3+}$ ions of nanocomposite may act as light-absorbing species to generate more SO$_4^{\bullet}$ radicals.
3.3. Effects of Operational Parameters Photo-Fenton like Catalyst

3.3.1. Effect of Solution pH

In AOPs processes, pH is one of the most important parameters for the removal efficiency; pH can strongly influence the dissolution of Fe$^{2+}$ from CFO and the stability and activity of the oxidant. As shown in Figure 5, the PF-AC/CFO process has demonstrated higher efficiency at pH 4.5 than at pH 6.5. It was probably due to the presence of iron and oxidant which shows maximum activity under acidic conditions.

As depicted, the highest RR198 degradation efficiencies of 100% and COD removal of 97% were attained at pH$_0$ = 4.5, and dye removal decreased with the increase of solution pH due to the surface charge of AC/CFO being more negative. Therefore, dye existed in its anionic form throughout the pH$_0$ investigated (pH$_0$ = 3–10). Under acidic conditions (pH = 4.5), the increase of the oxidation rate of dye due to Fe$^{2+}$ ions on the AC/CFO catalyst can well activate PS to form SO$_4$$^{•−}$, and also additional fraction of dissolved iron species released to the medium from the catalyst surface at pH = 4.5. As a result, the increasing pH (pH > 4.5) would lead to the precipitation of iron ion and the adsorption of Fe (OH) onto the AC/CFO surface that inhibits the transfer of dye from the solution to AC/CFO causing
reduction in the potential oxidation of dye and the decrease of dye removal [32]. At pH > 4.0, the soluble Fe$^{2+}$ ions decreased due to the formation of insoluble Fe (OH) complexes, therefore, decreasing the activation rate of PS and generation of SO$_4$$^{\bullet\bullet}$− (Equation (8)) [41]. On the other hand, at lower pH (pH < 4.5), high concentration of sulfate radicals is abundant which acts as sulfate radical scavengers. In addition, under this condition, a stable [H$_3$O$_2$]$^+$ ion is formed that reduces the reactivity with the Fe$^{2+}$ ion. Consequently, the efficiency of the photo-Fenton like process for dye removal is reduced both at high and low pH [42]. Moreover, the removal efficiency of dye at natural pH (pH = 6.5) is greater than 97% (Figure 6). Therefore, AC/CFO in the presence UV/PS shows an excellent catalytic activity for degradation of dye without using a neutralization process; so, it would be useful over a wide range of pH [43].

$$\text{SO}_4^{\bullet\bullet}^- + \text{OH}^- \rightarrow \text{SO}_4^{2-}.$$  \hfill (8)

Figure 6. Effect of catalyst dose on RR198 and COD removal efficiency, optimum conditions: [RR198 = 25 mg/L, PS = 5 mM/L, reaction time: 25 min, and pH = 6.5].

3.3.2. Effect of Catalyst Dosage

The effect of catalyst dosage on RR198 and COD removal was investigated at a constant PS = 5 mM/L, reaction time 25 min, and at pH 6.5 (Figure 6).

The increase in AC/CFO dosage from 0.1 to 0.3 g/L enhanced the adsorptive removal of dye. When the AC/CFO dosage was 0.3 g/L, the removal efficiency of dye increased to 99% and COD removal to 97.2%. In PF like catalyst the irradiation of ultraviolet promotes the generation and the release of Fe$^{2+}$ into the solution from the AC/CFO surface resulting in the reduction of the catalyst loading and enhancing the catalytic capacity of the catalyst in the presence of PS. Additionally, the increase of catalyst dosage results in an increased number of active sites of the catalyst for the activation of PS to generate sulfate radicals. Therefore, the increased addition of AC/CFO, achieves higher removal efficiency of dye.

The holes in the CoFe$_2$O$_4$ valence band can be used as oxidizing agents in the removal of dye. Therefore, the recombination of photo-generated electrons and holes (e/h) can enhance the photocatalytic activity of the nanocomposites and hybrids (Equations (9) and (10)). With enhancement of e/h, as increasing AC/CFO enables, the photocatalytic activity of the hybrids enhances further. The S$_2$O$_4$ is considered to have two functions in the photocatalytic process, it accepts a photogenerated electron to form sulfate radicals. The produced electron/hole enables oxidation and reduction processes to occur that electrons on the CFO surface of photocatalyst react with S$_2$O$_4$ to produce highly active SO$_4$$^\bullet$. Effective separation of the photogenerated electron/hole pairs at the composite photocatalyst interface lead to increased rates of photocatalytic activity. These holes (h$^+$) and sulfate radicals, being strong oxidizing agents, can mineralize organic contaminants completely. As a result, the combination
of AC/CFO–PS can effectively enhance the rate of photocatalytic depolarization and shorten the removal time for dyes in wastewater.

\[
\text{CoFe}_2\text{O}_4 + \text{hv} \rightarrow \text{CoFe}_2\text{O}_4 (\text{h}+\text{e}) 
\]
\[
\text{CoFe}_2\text{O}_4 (\text{e}) + \text{S}_2\text{O}_4 \rightarrow \text{CoFe}_2\text{O}_4 + \text{SO}_4^{*•} 
\]

The excessive dosages of catalyst could remove \(\text{SO}_4^{*•}\) radicals without reacting with contaminants, due to the reaction of PS for either producing \(\text{SO}_3^{•−}\) or recombining the formation of \(\text{S}_2\text{O}_8^{2−}\) [44]. Therefore, these results show that ferrous ion present in catalyst is an active agent in degradation of dye using PS activation [34,45]. However, the removal efficiency of RR198 was not changed significantly when the dosage of AC/CFO increased from 0.3 to 0.7 g/L; only slight increment in removal efficiency was discerned, although the sulfate radicals would be generated more quickly with further 0.3 g/L dosage of AC/CFO (Equation (11)).

\[
\text{SO}_4^{*•} + \text{SO}_4^{•−} \rightarrow \text{S}_2\text{O}_8^{2−} 
\]

Moreover, scavenging effects of \(\text{SO}_4^{•−}\) in the presence of excessive iron ions (Equations (12) and (13)) reduce the active sites of catalyst at higher dosages due to formation of self-binding and aggregates of iron ions in AC/CFO.

\[
\text{SO}_4^{*•} + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{SO}_4^{2−} 
\]
\[
\text{Fe (OH)}^2+ + \text{hv} \rightarrow \text{Fe}^{2+} + \text{SO}_4^{2−}. 
\]

3.3.3. Effect of Initial \(\text{S}_2\text{O}_8^{2−}\) Concentration

The effect of \(\text{S}_2\text{O}_8^{2−}\) concentration on RR198 and COD removal was investigated at a constant catalyst dosage of 0.3 g/L, reaction time 25 min, and at pH 6.5 (Figure 7).

![Figure 7](https://example.com/figure7.png)

**Figure 7.** Effect of PS dose on RR198 and COD removal efficiencies, optimum conditions: [RR198 = 25 mg/L, catalyst dosage = 0.3 g/L, reaction time: 25 min and pH = 6.5].

According to Figure 7, the highest RR198 and COD removal efficiencies were 99% and 95% respectively. With the increase of PS concentration to 5 mM/L, the removal efficiency increased significantly. However, PS would be generating more \(\text{SO}_4^{•−}\) at higher PS concentration. Hence, radical reactions may be occurring prior to the radical-organic reactions under these reaction conditions, when the dosage exceeded 5 mM/L, the removal efficiency decreased. In addition, excess sulfate radicals
are known to obstruct CFO e\textsuperscript{−} of the catalyst, which could induce consumption of SO\textsubscript{4}\textsuperscript{−•} at higher concentration of the oxidant (Equations (14) and (15)) [46]. Therefore, the overall removal efficiency is reduced when PS concentration is over 5 mM/L.

$$SO_4^{−•} + S_2O_8^{2−} → SO_4^{2−} + S_2O_8^{−•} \quad (14)$$

$$SO_4^{−•} + CFO e^{−} → SO_4^{2−} + CFO. \quad (15)$$

The high efficiency of dye removal in PF like catalyst may be ascribed to active radicals (SO\textsubscript{4}−•) oxidation.

### 3.3.4. Effect of Initial Dye Concentration and Kinetics of Degradation of RR198

The effect of different initial RR198 concentrations between 5 and 100 mg/L were investigated on RR198 and COD removal efficiency.

The highest RR198 removal efficiency and COD removal efficiencies were 98.9% and 97.28% respectively, as shown in Figure 8; increased concentration of RR198 would decrease the probability of reaction between free radicals and dye molecules.

![Figure 8](image-url)

**Figure 8.** Effect of initial dye on RR198 and COD removal efficiencies, optimum conditions: [PS = 5 mM, catalyst dosage = 0.3 g/L, reaction time: 25 min, and pH= 6.5].

Additionally, the intermediates which were produced during the reaction may cause the generation of the secondary radicals, thus consuming SO\textsubscript{4}−•. This may have an effect on the competition between dye molecules and its byproducts in reacting with reactive radicals [47]. Therefore, the removal of dye declined at high dye concentrations in the process of the PF like- AC/CFO; kinetics of degradation is necessary for the optimization of conditions. All the experiments were performed in different systems at temperatures of 10 to 35 °C (Table 2).

| Dye        | Kinetic Model               | Dye        | Kinetic Model               | Dye        | Kinetic Model               |
|------------|-----------------------------|------------|-----------------------------|------------|-----------------------------|
| Intra-particle diffusion | pseudo-second order | Intra-particle diffusion | pseudo-second order | Intra-particle diffusion | pseudo-first order |
| $q_t = k_i t^n + C_1$          | $\frac{1}{q_e} = \frac{1}{k_q q_e} + \frac{1}{q_e} t$ | $q_t = q_e \left(1 - e^{-k_it}\right)$ |
| 0.5        | $k_i$                      | 24.2       | $q_e, Cal (mg/g)$           | 22         | $q_e, Cal (mg/g)$           |
| 16.7       | $C_1$                      | 0.009      | $k_1 (\text{min}^{-1})$    | 0.07       | $k_1 (\text{min}^{-1})$    |
| 0.6        | $R^2$                      | 0.99       | $R^2$                      | 0.98       | $R^2$                      |
The results show a straight line $\ln \left( \frac{C_0}{C_t} \right)$ when plotted against time confirming the assumed pseudo-second-order kinetic; enhancement of the catalyst activity and oxidation reactions occur with the increase of temperature, and consequently, higher removal efficiency of RR198.

3.4. Determination of Radicals Present in the PF like Catalyst System

The dominant free radicals are involved in the PF like catalyst system. It was confirmed when two types of scavengers (ethanol and phenol) were used as radical quenchers (0.1–0.8 mM/L) (Figure 9).

![Figure 9](image-url)

Figure 9. Influence of two radical scavengers on removal efficiency of RR198 under optimum conditions.

Figure 9 illustrates that in the absence of a scavenger, the removal efficiency of 99%, decreased with the addition of ethanol and phenol into the solution; from 1 to 8 mM/L the removal efficiencies of RR198 decreased from 95.6% to 30% and 92% to 27%, respectively at reaction time 25 min. This showed that the main radical species formed during the PF like catalyst system were sulfate radicals. Ethanol is hydrophilic, which could only scavenge reactive radicals presented in the bulk solution; $\alpha$-hydrogen present in ethanol can rapidly quench $\text{SO}_4^{-}\bullet$ with the rate constant of $1.6–7.7 \times 10^7 \text{ M}^{-1}$. The phenol is hydrophobic, which penetrates into the pores of catalyst and is easier to adsorb on the surface of the catalyst [48,49].

3.5. Stability of the Catalyst

In a heterogeneous PF like catalyst, the stability of the catalysts is of great significant due to the economic and environmental effects. The stability was investigated through recycling of the catalyst and the results are shown in Figure 10. The reaction conditions deployed entailed the catalyst dosage, 0.3 g/L, the PS, 5 mM/L, pH value 6.5, with the initial RR198 dye concentration being 25 mg/L (Figure 10).

After each reuse cycle, the catalyst was washed with deionized water and added into the process. The removal efficiency of RR198 decreased slightly with the increase of the number of cycle runs. During eight consecutive runs (Figure 10), the removal efficiency of RR198 and COD decreased from 99.2% to 86%. This might be due to the adsorption of byproducts on the surface of AC/CFO. The limiting parameter for the Fenton-like catalyst process is the production cost of the solid catalyst [26]. Higher catalyst loading would increase the removal cost prohibitively; higher concentration would cause the generation of a large volume of sludge, which would necessitate the need for the sludge disposal process [24].
4. Conclusions

In this study, we have demonstrated that photo-Fenton like catalyst (UV-PS-AC/CFO) is a promising material for the removal of dyes; efficiency being better or comparable to other AOPs processes. The results of this study showed that the best efficiency for the removal of RR198 and COD reduction using PF like catalyst are 100% and 97%, respectively, under optimal conditions (PS, 5 mM/L, pH = 6.5, catalyst dosage = 0.3 g/L and time = 25 min). This protocol achieved highest dye removal efficiency for the elevated dye concentration at nearly neutral pH. Additionally, the AC/CFO nanocomposites displayed a high degree of stability and reusability. The scavenging capacity of PF like catalyst was calculated by using ethanol and phenol. Accordingly, the mechanistic study, indicates that degradation proceeds mainly through oxidation with SO$_4$$^-$ radical generated by AC/CFO activated PS and UV in the catalytic system. Additionally, the kinetic analysis, based on the experiment data, suggested that the adsorption can be better described by a pseudo-second-order kinetics model. We believe the demonstrated use of earth-abundant materials for addressing the environmental pollution will stimulate further studies in this remediation area.

Author Contributions: All authors have contributed the different sections and studies in this review article; M.K., M.R.H., S.N.A., P.K. and M.P. did the planning and conducted experiments, M.K., M.A. and R.S.V. wrote, corrected and edited the entire manuscript; Conceptualization, R.S.V. and M.A.; Investigation, S.A.; Methodology, M.R.H., M.P. and P.K.; Validation, M.K.; Writing—original draft, M.K.; Writing—review & editing, R.S.V.

Acknowledgments: This study was sponsored by Student Research Committee of Bam University of Medical Sciences (Grant. No. 97). The authors express their gratitude for the support and assistance extended by the facilitators during the research.

Conflicts of Interest: The author declares no competing financial interests.

References

1. Verma, S.; Nasir Baig, R.B.; Nadagouda, M.N.; Varma, R.S. Photocatalytic C-H activation and oxidative esterification using Pd@g-C$_3$N$_4$. *Catal. Today* **2018**, *309*, 248–252. [CrossRef]
2. Zhang, P.; Hou, D.; O’Connor, D.; Li, X.; Pehkonen, S.; Varma, R.S.; Wang, X. Green and size-specific synthesis of stable Fe–Cu oxides as earth-abundant adsorbents for malachite green removal. *Acs Sustain. Chem. Eng.* **2018**, *6*, 9229–9236. [CrossRef] [PubMed]
3. Khatami, M.; Alijani, H.; Sharifi, I.; Sharifi, F.; Pourseyedi, S.; Kharazi, S.; Lima Nobre, M.A.; Khatami, M. Leishmanicidal activity of biogenic Fe$_3$O$_4$ nanoparticles. *Sci. Pharm.* **2017**, *85*, 36. [CrossRef] [PubMed]
4. Khatami, M.; Alijani, H.Q.; Sharifi, I. Biosynthesis of bimetallic and core–shell nanoparticles: Their biomedical applications—A review. *IET Nanobiotech* **2018**, *12*, 879–887. [CrossRef] [PubMed]
5. Khatami, M.; Alijani, H.Q.; Fakheri, B.; Mobasser, M.M.; Heydarpour, M.; Farahani, Z.K.; Khan, A.U. Super-paramagnetic iron oxide nanoparticles (spions): Greener synthesis using stevia plant and evaluation of its antioxidant properties. J. Clean. Prod. 2019, 208, 1171–1177. [CrossRef]

6. Rahimi, S.; Poormohammadi, A.; Salmani, B.; Ahmadian, M.; Rezaei, M. Comparing the photocatalytic process efficiency using batch and tubular reactors in removal of methylene blue dye and cod from simulated textile wastewater. J. Water Reuse Desalin. 2016, 2, 574–582. [CrossRef]

7. Taghavizadeh Yazdi, M.E.; Modarres, M.; Amiri, M.S.; Darroudi, M. Phyto-synthesis of silver nanoparticles using aerial extract of salvia leriifolia benth and evaluation of their antibacterial and photo-catalytic properties. Res. Chem. Intermed. 2019, 45, 1105–1116. [CrossRef]

8. Karthik, K.; Dhanuskodi, S.; Gobinath, C.; Prabukumar, S.; Sivaramakrishnan, S. Fabrication of mgo nanostructures and its efficient photocatalytic, antibacterial and anticancer performance. J. Photochem. Photobiol. B Biol. 2019, 190, 8–20. [CrossRef] [PubMed]

9. Ahmadian, M.; Yosefi, N.; Toolabi, A.; Khanjani, N.; Rahimi, S.; Fatehizadeh, A. Adsorption of direct yellow 9 and acid orange 7 from aqueous solutions by modified pumice. Asian J. Chem. 2012, 24, 3094–3098.

10. Yagub, M.T.; Sen, T.K.; Afroze, S.; Ang, H.M. Dye and its removal from aqueous solution by adsorption: A review. Adv. Colloid Interface Sci. 2014, 209, 172–184. [CrossRef] [PubMed]

11. Marrakchi, F.; Ahmed, M.J.; Khanday, W.; Asif, M.; Hameed, B. Mesoporous carbonaceous material from fish scales as low-cost adsorbent for reactive orange 16 adsorption. J. Taiwan Inst. Chem. Eng. 2017, 71, 47–54. [CrossRef]

12. Samadi, M.T.; Zolghadrmnasab, H.; Godini, K.; Poormohammadi, A.; Ahmadian, M.; Shanesaz, S. Kinetic and adsorption studies of reactive black 5 removal using multi-walled carbon nanotubes from aqueous solution. Der Pharma Chem. 2015, 7, 267–274.

13. Gu, M.; Yin, Q.; Wang, Z.; He, K.; Wu, G. Color and nitrogen removal from synthetic dye wastewater in an integrated mesophilic hydrolysis/acidification and multiple anoxic/aerobic process. Chemosphere 2018, 212, 881–889. [CrossRef] [PubMed]

14. Singh, H.; Du, J.; Singh, P.; Yi, T.H. Ecofriendly synthesis of silver and gold nanoparticles by euphrasia officinalis leaf extract and its biomedical applications. Artif. Cellsnanomedicineand Biotechnol. 2018, 46, 1163–1170. [CrossRef]

15. Katheresan, V.; Kansedo, J.; Lau, S.Y. Efficiency of various recent wastewater dye removal methods: A review. J. Environ. Chem. Eng. 2018, 6, 4676–4697. [CrossRef]

16. Konicki, W.; Aleksandrzak, M.; Moszyński, D.; Mijowska, E. Adsorption of anionic azo-dyes from aqueous solutions onto graphene oxide: Equilibrium, kinetic and thermodynamic studies. J. Colloid Interface Sci. 2017, 496, 188–200. [CrossRef] [PubMed]

17. Babuponnusami, A.; Muthukumar, K. A review on fenton and improvements to the fenton process for wastewater treatment. J. Environ. Chem. Eng. 2014, 2, 557–572. [CrossRef]
24. Malakootian, M.; Yousefi, N.; Fatehizadeh, A.; Van Ginkel, S.W.; Ghorbani, M.; Rahimi, S.; Ahmadian, M. Nickel (ii) removal from industrial plating effluent by fenton process. Environ. Eng. Manag. J. 2015, 14, 837–842.

25. Moreira, F.C.; Boaventura, R.A.; Brillas, E.; Vilar, V.J. Electrochemical advanced oxidation processes: A review on their application to synthetic and real wastewaters. Appl. Catal. B Environ. 2017, 202, 217–261. [CrossRef]

26. Wang, N.; Zheng, T.; Zhang, G.; Wang, P. A review on fenton-like processes for organic wastewater treatment. J. Environ. Chem. Eng. 2016, 4, 762–787. [CrossRef]

27. Cheng, M.; Lai, C.; Liu, Y.; Zeng, G.; Huang, D.; Zhang, C.; Qin, L.; Hu, L.; Zhou, C.; Xiong, W. Metal-organic frameworks for highly efficient heterogeneous fenton-like catalysis. Coord. Chem. Rev. 2018, 368, 80–92. [CrossRef]

28. Munoz, M.; De Pedro, Z.M.; Casas, J.A.; Rodriguez, J.J. Preparation of magnetite-based catalysts and their application in heterogeneous fenton oxidation—A review. Appl. Catal. B Environ. 2015, 176, 249–265. [CrossRef]

29. Han, C.; Huang, G.; Zhu, D.; Hu, K. Facile synthesis of MoS2/Fe3O4 nanocomposite with excellent photo-fenton-like catalytic performance. Mater. Chem. Phys. 2017, 200, 16–22. [CrossRef]

30. Chen, L.; Cai, T.; Cheng, C.; Xiong, Z.; Ding, D. Degradation of acetamiprid in uv/h2o2 and uv/persulfate systems: A comparative study. Chem. Eng. J. 2018, 351, 1137–1146. [CrossRef]

31. Fakhri, A.; Naji, M.; Tahami, S. Ultraviolet/ultrasound-activated persulfate for degradation of drug by zinc selenide quantum dots: Catalysis and microbiology study. J. Photochem. Photobiol. B Biol. 2017, 170, 304–308. [CrossRef] [PubMed]

32. Jafari, A.J.; Kakavandi, B.; Jaafarzadeh, N.; Kalantary, R.R.; Ahmadi, M.; Babaei, A.A. Fenton-like catalytic oxidation of tetracycline by AC@Fe3O4 as a heterogeneous persulfate activator: Adsorption and degradation studies. J. Ind. Eng. Chem. 2017, 45, 323–333. [CrossRef]

33. Seid-Mohammadi, A.; Asgari, G.; Poormohammadi, A.; Ahmadian, M.; Rezaeivahidian, H. Removal of phenol at high concentrations using uv/persulfate from saline wastewater. Desalin. Water Treat. 2016, 57, 19988–19995. [CrossRef]

34. Shiraz, A.D.; Takdastan, A.; Borghei, S.M. Photo-fenton like degradation of catechol using persulfate activated by uv and ferrous ions: Influencing operational parameters and feasibility studies. J. Mol. Liq. 2018, 249, 463–469. [CrossRef]

35. Rahimi, S.; Ehrampoush, M.H.; Ghanieian, M.T.; Reshadat, S.; Fatehizadeh, A.; Ahmadian, M.; Ghanizadeh, G.; Rahimi, S. Application of TiO2/uv-c photocatalytic process in removal of reactive red 198 dye from synthetic textile wastewater. Asian J. Chem. 2013, 25, 7427–7432. [CrossRef]

36. American Public Health Association; American Water Works Association; Rice, E.W.; Baird, R.B.; Eaton, A.D.; Clesceri, L.S. Standard Methods in Examination of Water and Wastewater; American Public Health Association: Washington, DC, USA, 2012; Volume 32.

37. Ai, L.; Huang, H.; Chen, Z.; Wei, X.; Jiang, J. Activated carbon/CoFe2O4 composites: Facile synthesis, magnetic performance and their potential application for the removal of malachite green from water. Chem. Eng. J. 2010, 156, 243–249. [CrossRef]

38. Moussavi, S.; Ehrampoush, M.; Mahvi, A.; Ahmadian, M.; Rahimi, S. Adsorption of humic acid from aqueous solution on single-walled carbon nanotubes. Asian J. Chem. 2013, 25, 5319–5324. [CrossRef]

39. Xu, J.; Xin, P.; Gao, Y.; Hong, B.; Jin, H.; Jin, D.; Peng, X.; Li, J.; Gong, J.; Ge, H. Magnetic properties and methylene blue adsorptive performance of CoFe2O4/activated carbon nanocomposites. Mater. Chem. Phys. 2014, 147, 915–919. [CrossRef]

40. Babu, S.G.; Aparna, P.; Satishkumar, G.; Ashokkumar, M.; Neppolian, B. Ultrasound-assisted mineralization of organic contaminants using a recyclable laFeO3 and Fe3+/persulfate fenton-like system. Ultrasom. Sonochem. 2017, 34, 924–930. [CrossRef] [PubMed]

41. Su, E.-C.; Lee, J.-T.; Gong, Y.-J.; Huang, B.-S.; Wey, M.-Y. Photocatalytic conversion of ethylenediaminetetraacetic acid dissolved in real electroplating wastewater to hydrogen in a solar light-responsive system. Water Sci. Technol. 2018, 77, 2851–2857. [CrossRef] [PubMed]

42. Wang, K.; Niu, H.; Chen, J.; Song, J.; Mao, C.; Zhang, S.; Gao, Y. Immobilizing laFeO3 nanoparticles on carbon spheres for enhanced heterogeneous photo-fenton like performance. Appl. Surf. Sci. 2017, 404, 138–145. [CrossRef]

43. Palas, B.; Ersöz, G.; Atalay, S. Photo fenton-like oxidation of tartrazine under visible and uv light irradiation in the presence of laCuO3 perovskite catalyst. Process. Saf. Environ. Prot. 2017, 111, 270–282. [CrossRef]
44. Wang, X.; Min, J.; Li, S.; Zhu, X.; Cao, X.; Yuan, S.; Zuo, X.; Deng, X. Sono-assisted synthesis of cuo nanorods–graphene oxide as a synergistic activator of persulfate for bisphenol a removal. *J. Environ. Chem. Eng.* 2018. [CrossRef]

45. Tian, J.; Wu, C.; Yu, H.; Gao, S.; Li, G.; Cui, F.; Qu, F. Applying ultraviolet/persulfate (UV/PS) pre-oxidation for controlling ultrafiltration membrane fouling by natural organic matter (nom) in surface water. *Water Res.* 2018, 132, 190–199. [CrossRef] [PubMed]

46. Xu, H.-Y.; Wang, Y.; Shi, T.-N.; He, X.-L.; Qi, S.-Y. Process optimization on methyl orange discoloration in Fe₃O₄/rgo-H₂O₂ fenton-like system. *Water Sci. Technol.* 2018, 77, 2929–2939. [PubMed]

47. Fang, Z.-d.; Zhang, K.; Liu, J.; Fan, J.-y.; Zhao, Z.-w. Fenton-like oxidation of azo dye in aqueous solution using magnetic Fe₃O₄-MnO₂ nanocomposites as catalysts. *Water Sci. Eng.* 2017, 10, 326–333. [CrossRef]

48. Zhang, Y.; Tran, H.P.; Du, X.; Hussain, I.; Huang, S.; Zhou, S.; Wen, W. Efficient pyrite activating persulfate process for degradation of p-chloroaniline in aqueous systems: A mechanistic study. *Chem. Eng. J.* 2017, 308, 1112–1119. [CrossRef]

49. Liu, F.; Yi, P.; Wang, X.; Gao, H.; Zhang, H. Degradation of acid orange 7 by an ultrasound/zno-gac/persulfate process. *Sep. Purif. Technol.* 2018, 194, 181–187. [CrossRef]