A Novel Integration of CWPO Process with Fe$_3$O$_4$@C and Sonication for Oxidative Degradation of 4-Chlorophenol

M. Astaraki,[a,b] F. Aminsharei,[b,c*] S. Jorfi,[a,d*]
R. Darvishi Cheshmeh Soltani,[a,e] and M. Nasr-Esfahani[f]

[a]Department of Chemical Engineering, Najafabad Branch, Islamic Azad University, Najafabad, Iran

[b]Human Environment and Sustainable Development Research Center, Najafabad Branch, Islamic Azad University, Najafabad

[c]Department of Safety, Health and Environment, Najafabad Branch, Islamic Azad University, Najafabad, Iran

[d]Environmental Technologies Research Center, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran

[e]Department of Environmental Health Engineering, School of Health, Arak University of Medical Sciences, Arak, Iran

[f]Department of Chemistry, Najafabad Branch, Islamic Azad University, Najafabad, Iran

This current work deals with oxidative destruction of 4-chlorophenol (4-CP) with catalytic wet peroxide oxidation (CWPO) using Fe$_3$O$_4$@C and sonication (US) in aqueous solution. The Fe$_3$O$_4$@C catalyst was synthetized and characterized with Field Emission Electron Microscopy and X-Ray Diffraction. Effect of operational variables, including initial pH, catalyst dosage, H$_2$O$_2$ concentration, 4-CP concentration, and sonication were investigated. A removal efficiency of 99 % was obtained by the CWPO/US-Fe$_3$O$_4$@C process in selected conditions including pH 5, Fe$_3$O$_4$@C dosage of 0.8 g L^{-1}, H$_2$O$_2$ concentration of 20 mM, sonication power of 300 W, and reaction time of 60 min. Results indicated significant 4-CP removal with CWPO/US-Fe$_3$O$_4$@C (99 %) compared to CWPO (67 %) and US (10 %). According to the results, Fe$_3$O$_4$@C nanocomposite can be considered a cost-effective catalyst since it demonstrated acceptable reusability performance in degradation of 4-CP by CWPO/US-Fe$_3$O$_4$@C process.

Keywords:
4-chlorophenol, catalytic wet peroxide oxidation, Fe$_3$O$_4$@C catalyst, sonication, advanced oxidation
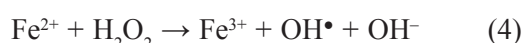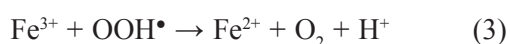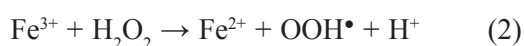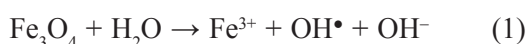
Introduction

4-Chlorophenol (4-CP) is an organo-chlorine compound extensively used in pharmaceutical, petrochemical, organic chemical manufacturing, and dye industries.[1] United States Environmental Protection Agency (USEPA) has introduced 4-CP as a priority pollutant due to carcinogenicity, persistence, and toxicity.[2] Therefore, investigation of treatment methods for degradation of 4-CP from waste streams is considered by researchers. Physicochemical treatment methods such as adsorption, precipitation, conventional oxidation, coagulation, and membrane filtration have demonstrated several drawbacks such as low efficiency, high cost, and limited capacity for high concentrations of pollutant.[3] Also, biological methods are not suitable due to low efficiency, long time required, and production of high amounts of sludge.[4] Catalytic wet peroxide oxidation (CWPO) as an advanced oxidation process, provides advantages such as simple equipment and operation under mild conditions, including low temperatures, and atmospheric pressure.[5] Application of H$_2$O$_2$ and a suitable catalyst in the CWPO promotes H$_2$O$_2$ decomposition to HO$^\bullet$, leading to production of powerful oxidizing agents. Since the products derived from the decomposition of H$_2$O$_2$ are oxygen and water, it is known to be an environmentally friendly agent, making CWPO-based treatment technologies safe.[6] Metal leaching adversely affects the efficiency of the process when plain metals are used as catalyst due to loss of the activity of the heterogeneous catalyst. In such conditions, a heavy washing of the metal phase (Fe leaching) occurs. On the other hand, the final effluent does not meet discharge limits in terms of Fe concentration, and a supplementary treatment is required for the recovery of Fe^{2+}/Fe^{3+} ions. Therefore, metal-free based catalysts in CWPO is of importance. Carbon can act
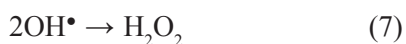
*Corresponding author: aminsharei.fa@gmail.com
*Corresponding author: sahand369@yahoo.com

as catalyst for the CWPO, which can have promising results based on activity as well as sustainability.[7,8] Fenton and Fenton-like processes generate •OH radicals, which are widely investigated for treatment of aqueous solutions due to simple operation and high efficiency. However, the Fenton reaction also has its drawbacks, such as low pH and production of iron sludge, which limit their applications.[9] The use of iron-containing solid heterogeneous catalysts to avoid these drawbacks can improve its performance for treatment of a variety of organic pollutants. Fe_3O_4 magnetic nanoparticles (MNPs) demonstrate high •OH production rate in Fenton-like reactions (Eqs.1–4). Coating Fe_3O_4 due to large specific surface area, small pore size, and an electron transfer of Fe^{2+} and Fe^{3+} ions in the octahedral sites provide unique electric and magnetic properties. In addition, Fe_3O_4 MNPs have advantages like high catalytic activity, and the potential for catalyst recovery for further reusage.[10,11]

$$Fe_3O_4 + H_2O \rightarrow Fe^{3+} + OH^\bullet + OH^- \qquad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OOH^\bullet + H^+ \qquad (2)$$

$$Fe^{3+} + OOH^\bullet \rightarrow Fe^{2+} + O_2 + H^+ \qquad (3)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^\bullet + OH^- \qquad (4)$$

Sonication (US) is a sound wave with frequency higher than approximately 20 kHz, which can act as an enhancer. The mechanisms of degradation in US irradiation is categorized into i) oxidation of non-volatile substances by free oxidizing spices in the solution, and ii) pyrolysis of volatile contaminants in bubbles.[12] Sonolysis of water leads to generation of HO• and H_2O_2 in solution, which is known as the cavitation phenomenon, and is summarized in Eqs. (5–7).[13]

$$H_2O + \text{Ultrasound wave} \rightarrow OH^\bullet + H^\bullet \qquad (5)$$

$$OH^\bullet + H^\bullet \rightarrow H_2O \qquad (6)$$

$$2OH^\bullet \rightarrow H_2O_2 \qquad (7)$$

Studies have shown that the integration of US and Fe_3O_4 with simultaneous presence of H_2O_2 at low pH increases the rate of HO• production.[11] Hence, the present study aimed to investigate a novel integration of CWPO process with Fe_3O_4@C and sonication for oxidative degradation of 4-chlorophenol.

Materials and methods

Material

4-CP (C_6H_4ClOH), NaOH (99.8 %), H_2O_2 (35 %), C_2H_5OH (98 %), H_2SO_4 (98 %), tert-butyl alcohol (TBA), $NaHCO_3$, HCl (99.8 %) KOH, NaCl, and $NaNO_3$ were all of analytical grade, and purchased from Merck Co., Germany.

Activated carbon synthesis

In order to prepare activated carbon, firstly, 5 g of waste polymer disk (3–5 mm) with 10 % HCl were placed in an ultrasound bath for 45 min, and then washed three times with distilled water. Following the above steps, carbonization was carried at 600 °C for 1 h in an electric furnace, and finally, the activation process was carried out with KOH solution.[14] The prepared carbon was milled and passed through sieves with 60 and 120 mesh sizes. The remainder on sieve size of 120, was collected and washed with deionized water in order to remove undesirable particles. Thereafter, the sample was placed in the oven at 120 °C for 1 h, and stored in a glass bottle to prevent moisture absorption before conducting experiments.[15]

Fe_3O_4 nanoparticles synthesis

Chemical co-precipitation method was used for synthesis of Fe_3O_4 nanoparticles through the co-precipitation of Fe^{2+} and Fe^{3+} in ammonia solution. Briefly, under constant stirring $FeCl_3 \cdot 6H_2O$ (0.02 M) and $FeCl_2 \cdot 4H_2O$ (0.01 M) were added into 100 mL of distilled water. The solution was then added dropwise into 10 mL of ammonia solution (25 wt %). Thereafter, deoxygenating of the solution was performed for 60 min at 90 °C by passing nitrogen gas. Finally, the synthesized magnetic Fe_3O_4 nanoparticles were washed with deionized water repeatedly in the vicinity of an external magnet, and dried in a vacuum freeze dryer.

Characterization of Fe_3O_4@C composite

In order to determine the crystalline phase of Fe_3O_4@C, the XRD analysis was applied (Model: GNR-MPD3000) using Cu anode at λ of 0.15 nm, voltage of 40 kV, and current intensity of 30 mA. Field Emission Scanning Electron Microscopy (Fe-SEM) (MODEL: Nanosord, Iran) analysis was carried out for characterization of the surface morphology. Moreover, the pHpzc of composite (point of zero charge) was determined according to pH drift method.[16]

Experimental procedures

CWPO/US-Fe_3O_4@C reactions were performed in a 250-mL cylindrical reactor in batch mode operation, while the contents were mixed with a magnetic stirrer (250 rpm). The reactor was placed in a water bath to control the temperature. For investigation of study goals in CWPO/US-Fe_3O_4@C process, a determined concentration of 4-CP was added into distilled water to provide synthetic wastewater. Sodium hydroxide (0.5 N) and sulfuric acid (0.5) were used to adjust the solution pH. Certain amounts of H_2O_2 and catalyst were also injected into the solu-
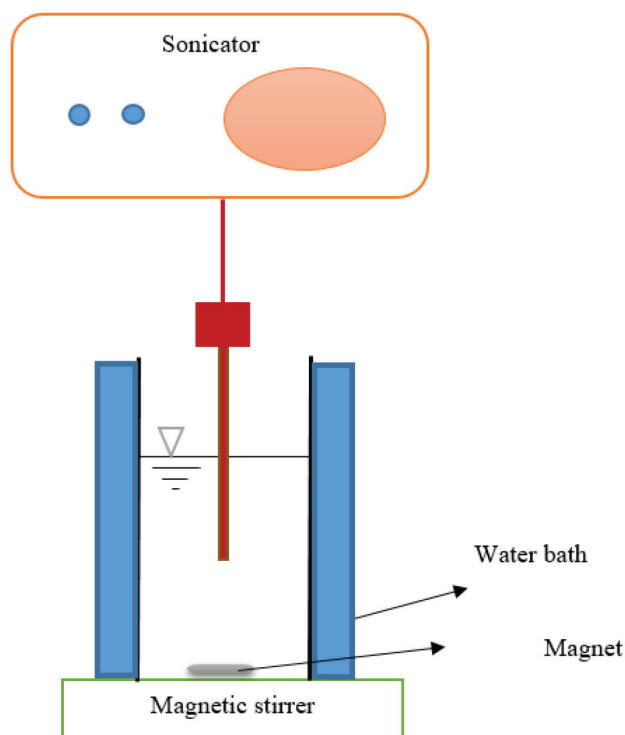
F i g . 1 – *Reactor of CWPO/US-Fe₃O₄@C*

tion. The US irradiation was provided using an US device (UP200S/UP400S) with a frequency of 24 kHz. The simple view of the reactor is shown in Fig 1. A magnet was then used to separate the catalyst from the sample solution, and analyzed immediately after certain time intervals. Each experiment was conducted in triplicate.

Analytical methods

4-CP concentration was measured by High-Performance Liquid Chromatograph (HPLC) (Model KNAUER, Germany) equipped with a 2500 UV detector. The detection wavelength of 4-CP was 280 nm. C18 column (Aquasil) (250 mm × 4.6 mm) was employed for the separation as the stationary phase. To measure the pH of the solution, a Metrohm pH meter was used (Model: E532, Germany).[17] Total organic carbon (TOC) was measured by the TOC analyzer (ShimadzuVCHS/CSN, Japan). The degradation efficiency of 4-CP (%) was computed with Eq (8):

$$DE\% = [4\text{-}CP]_0 - [4\text{-}CP]_t / [4\text{-}CP]_0 \cdot 100 \quad (8)$$

where $[4\text{-}CP]_0$ is the initial 4C-P concentration, $[4\text{-}CP]_t$ is the 4C-P concentration at times.

Results and discussion

Characterization of Fe₃O₄@C composite

The Fe-SEM images of Fe_3O_4 nanoparticles, carbon support, and Fe@C can be found in Fig. 2 (a, b, c, d). Results confirm the uniform distribution of Fe_3O_4 nanoparticles with spherical shape, and particle size ranging between 25–50 nm. As may be seen, the outer surface of carbon is covered with Fe_3O_4 nanoparticles, and successful deposition on the surface of carbon was proved. The XRD patterns of Fe_3O_4 nanoparticles, carbon support, and Fe@C composite are presented in Fig. 3. According to the results, sharp peaks of Fe_3O_4 were placed at 2θ of 22.5° and 29.6°. In addition, the small peaks were located at 2θ of 43.7° and 57.3° that corresponded to standard card (JCPDS, No. 00-054-0489). The sharp peaks of carbon were placed at 2θ of 21.18° and 32.64° that related to the standard JCPDS card no. (00-008-0415).

CWPO process

Effect of pH

For chemical and catalytic reactions like CWPO reaction, pH is a key parameter that affects the degradation of target contaminant in aqueous solution. According to Fig. 4a, the degradation efficiency of 4-CP decreased with increasing solution pH. The maximum 4-CP removal of 55 % was obtained at initial solution pH of 3, and the lowest rate was achieved at solution pH of 11. Favorable 4-CP removal at acidic pH might be attributed to the dissolution of iron from the catalyst that leads to the generation of a sufficient amount of •OH in acidic solution.[18] The decrease in 4-CP removal at higher pH values was due to the reduction in dissolved iron concentration and H_2O_2 concentration in the solution.[19,20] Moreover, self-decomposition of H_2O_2 played a negative role in removal of 4-CP at higher pH values.[21] Our findings also indicated that the pH_{zpc} of the catalyst was 7 (Fig. 4b); thus, at acidic conditions when the solution pH is lower than pHzpc value, the catalyst surface was positively charged and could adsorb anionic form of 4-CP. Therefore, the Fe_3O_4@C catalyst performance decreased with increasing solution pH. Our results were verified by the findings of Xu[18] and Jiang.[22] In addition, studies indicate that possible secondary pollution of Fe-containing sludge in Fenton-like processes at pH 5, is minimum.[10]

Effect of catalyst dosage

According to Fig. 5, increasing the dosage of the catalyst from 0.2 to 0.8 g L^{-1} positively affected the removal, and no significant effect occurred at catalyst dosage of 1.0 g L^{-1}. Higher catalyst amount provided more available active sites for activation of H_2O_2 which improved •OH production.[23] However, catalyst dosage higher than 0.8 g L^{-1} and accumulation of catalyst particles, decreased density of H_2O_2 adsorbing surface, and the reduction in active sites on the catalyst surface as well as scavenging of •OH by Fe species decreased the process efficiency.

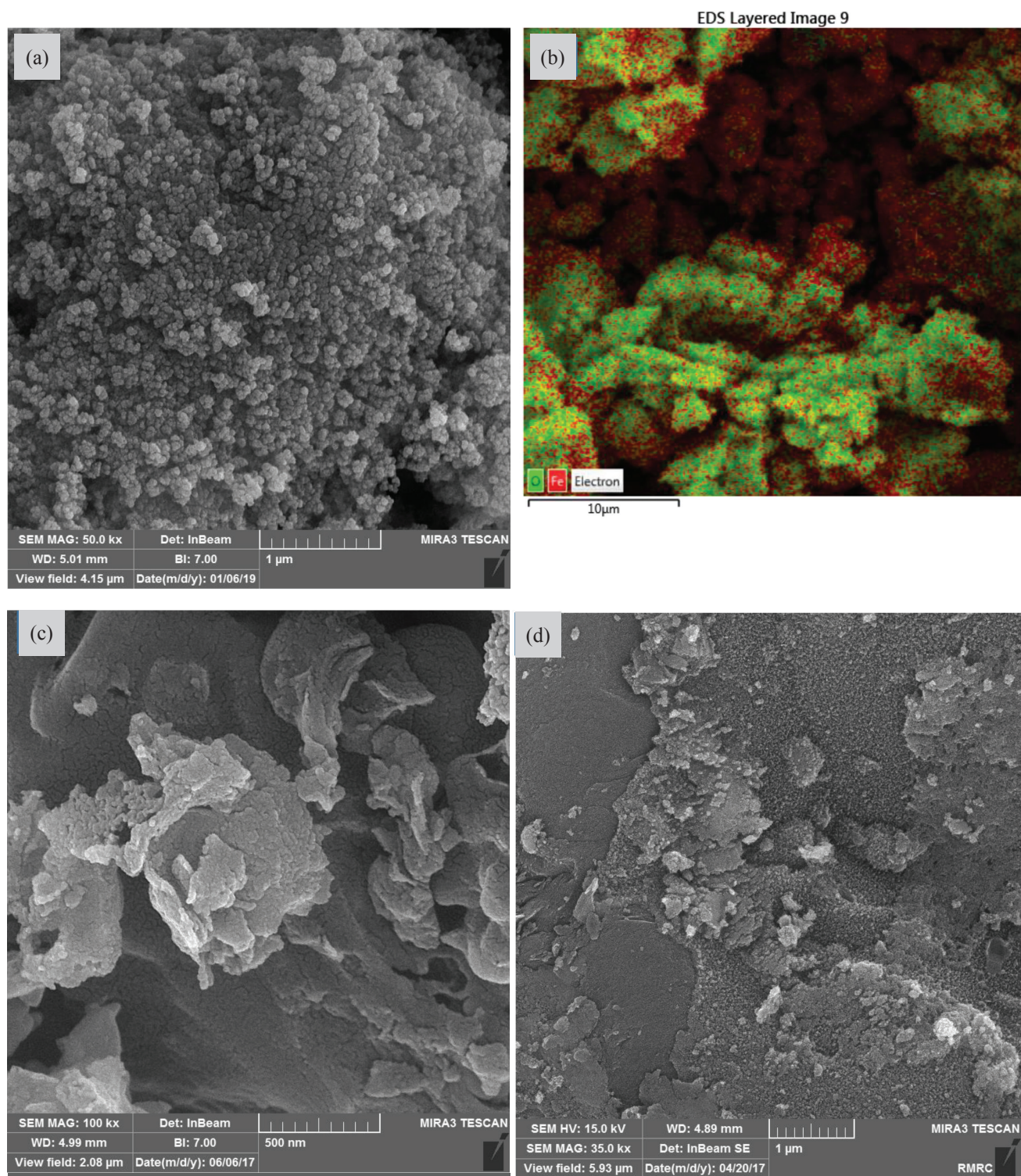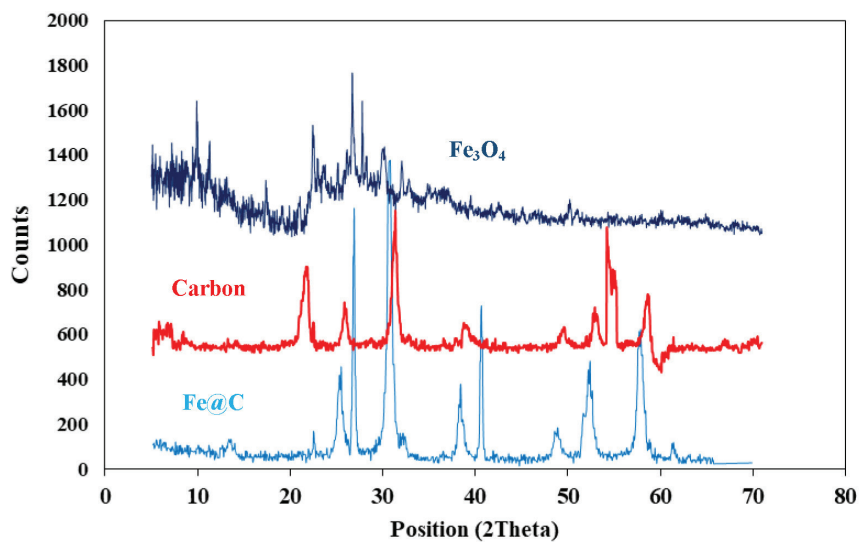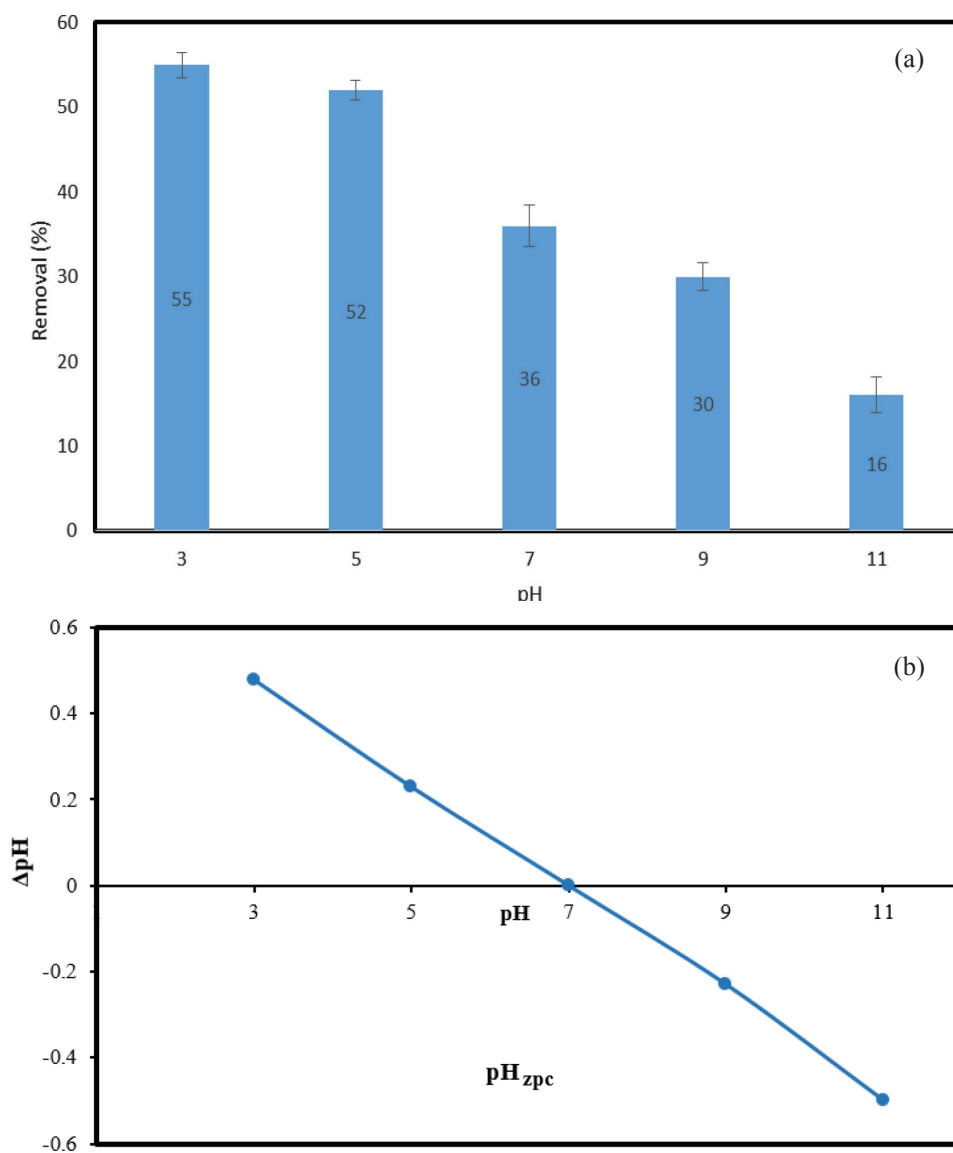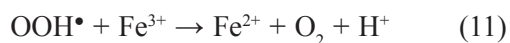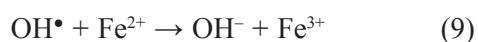Fig. 2 – *Fe-SEM images of synthetized composite (a) Fe_3O_4 nanoparticles, (b) EDS mapping of Fe_3O_4 nanoparticles, (c) Carbon support, and (d) Fe@C composite*

F i g . 3 – *XRD patterns of Fe$_3$O$_4$ nanoparticles, carbon support, and Fe@C*

F i g . 4 – *a) Effect of solution pH on 4-CP removal (initial 4P-C concentration of 100 mg L^{-1}, catalyst dosage of 0.4 g L^{-1}, H$_2$O$_2$ concentration of 5 mM, and ultrasonic power of 200 W), and b) pH$_{ZPC}$ of Fe$_3$O$_4$@C*

These undesirable reactions are indicated in Eqs. 9–11:[18,24,25]

$$OH^\bullet + Fe^{2+} \rightarrow OH^- + Fe^{3+} \quad (9)$$

$$OOH^\bullet + Fe^{2+} \rightarrow OOH^- + Fe^{3+} \quad (10)$$

$$OOH^\bullet + Fe^{3+} \rightarrow Fe^{2+} + O_2 + H^+ \quad (11)$$

Effect of H$_2$O$_2$ dosage

It can be observed that the 4-CP removal reached 91% at H$_2$O$_2$ concentration of 20 mM (Fig. 6). However, for H$_2$O$_2$ concentrations higher than 20 mM, no enhancement was obtained, and even a negative effect occurred. The reduced 4-CP removal at higher H$_2$O$_2$ concentration may be due to reaction of excess Fe^{3+} with excess H$_2$O$_2$, as well as the formation of hydroperoxyl radicals (HO$_2$$^\bullet$) according to Eq. 12, which in turn reduced the possibility of $^\bullet$OH to attach target pollutant.[26] Next was the scavenging of $^\bullet$OH by H$_2$O$_2$ according to Eq. 13 and 14, and the formation of radicals like HOO and O$_2^{-\bullet}$ with lower oxidation potential and less contribution in 4-CP degradation. Consequently, the H$_2$O$_2$ concentration of 20 mM was selected appropriate in subsequent experiments.[25,27]
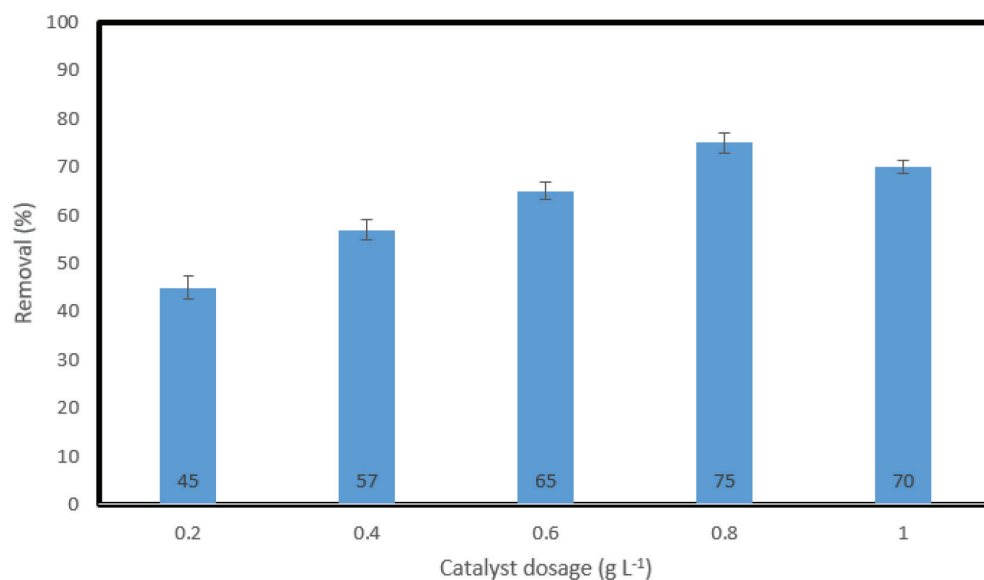

Fig. 5 – *Effect of catalyst dosage on 4-CP removal (initial 4-CP concentration of 100 mg L^{-1}, solution pH 5, H$_2$O$_2$ concentration of 5 mM, and US power of 200 W)*
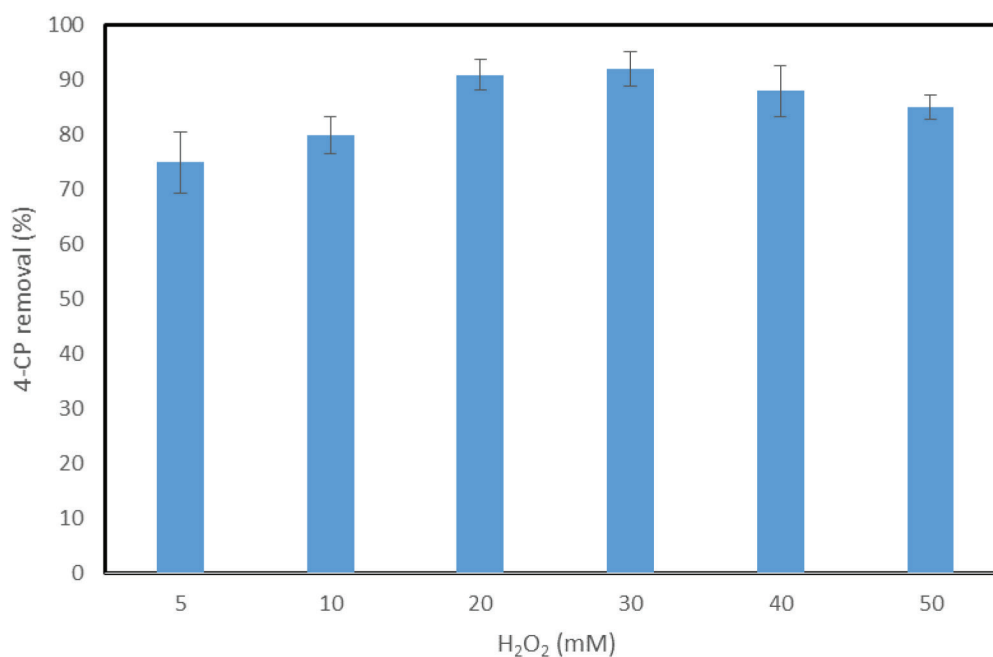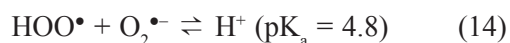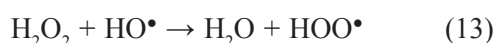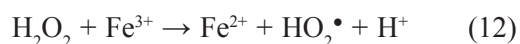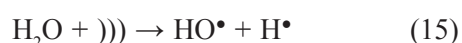

Fig. 6 – *Effect of H$_2$O$_2$ dosage on 4-CP removal (initial 4-CP concentration of 100 mg L^{-1}, solution pH 5, catalyst dosage 0.8 g L^{-1}, and US power of 200 W)*

$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \quad (12)$$

$$H_2O_2 + HO^{\bullet} \rightarrow H_2O + HOO^{\bullet} \quad (13)$$

$$HOO^{\bullet} + O_2^{\bullet-} \rightleftharpoons H^+ \ (pK_a = 4.8) \quad (14)$$

Effect of US power

Sonication is an oxidation process, which can easily be integrated in advanced oxidations to enhance the degradation mechanism and oxidation rate.[28,29] Fig. 7 indicates that by increasing the sonication power from 100 to 400 W, the removal had improved from 79 % to 100 %. Of course, there was no significant difference (p-value > 0.05) between the removal results of 300 W and 400 W. The increase in US power causes more cavitation bubbles and reactive radicals in solution through the bubble collapse as well as micro jetting, and chains of reactions originated by cavitation phenomenon or water sonolysis media based on Eqs. (15–18).[30]

$$H_2O +))) \rightarrow HO^{\bullet} + H^{\bullet} \quad (15)$$

$$HO^{\bullet} + O^{\bullet} \rightarrow H_2O \quad (16)$$

$$HO^{\bullet} + HO^{\bullet} \rightarrow H_2O_2 \quad (17)$$

$$H^{\bullet} + H^{\bullet} \rightarrow H_2^{\bullet} \quad (18)$$

Kinetics study

Kinetics study helps to understand the dynamics of chemical reactions. Furthermore, the study of kinetic models is needed to find the optimum conditions for the process in full-scale applications, and prediction of the rate constant for designing the reactor.[31] The kinetics of 4-CP removal was investigated to evaluate the function of CWPO/US-Fe$_3$O$_4$@C in selected conditions. High constant rate (K), demonstrates the remarkable process ability in destruction of pollutants. By plotting ln (γ_0/γ_t) against time and $1/\gamma_t$ against time, the kinetic constants of first and second order equations for CWPO/US- CWPO/US-Fe$_3$O$_4$@C process were explored, respectively, using Eqs. (19 and 20):

$$\mathrm{Ln}\ \gamma_0 / \gamma_t = k_1 t \quad (19)$$

$$(1/\gamma_t) - (1/\gamma_0) = k_2 t \quad (20)$$

where γ_0 and γ_t demonstrate initial and final concentration of 4-CP (mg L^{-1}) in saline oily wastewater, t is the reaction time (h), and k_1 and k_2 are corresponding rate constants (h^{-1}).[32] According to Table 1, the kinetic coefficients of first-order model were best fitted with findings of 4-CP degradation through CWPO/US-Fe$_3$O$_4$@C process in synthetic wastewater, with R^2 values of 0.99 and corresponding reaction rate constant of 0.76 h^{-1} (Fig. 8). Results were verified by Kantar *et al.* (2019) for degradation of phenolic compounds.[33]

T a b l e   1 – *Results of kinetics study of the CWPO/US-Fe$_3$O$_4$@C process*

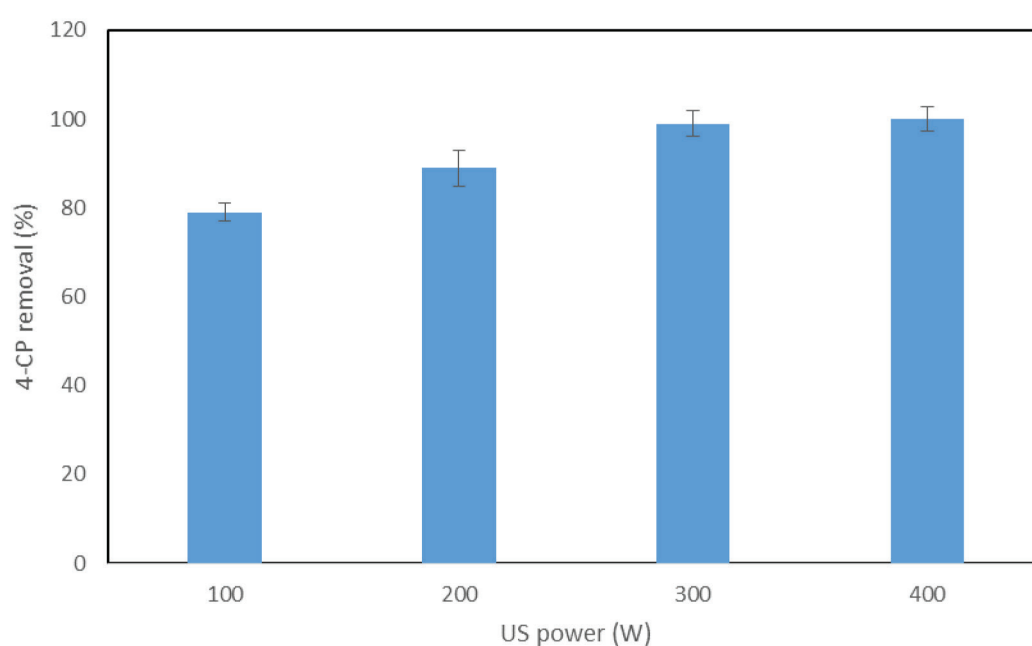| Parameter	First-order	Second-order
K	0.076 (h^{-1})	0.0067 (mol L^{-1} h^{-1})
R^2	0.99	0.65

F i g .   7 – *Effect of US power on 4-CP removal (initial 4-PC concentration of 100 mg L^{-1}, solution pH 5, catalyst dosage 0.8 g L^{-1}, and H$_2$O$_2$ concentration of 20 mM)*
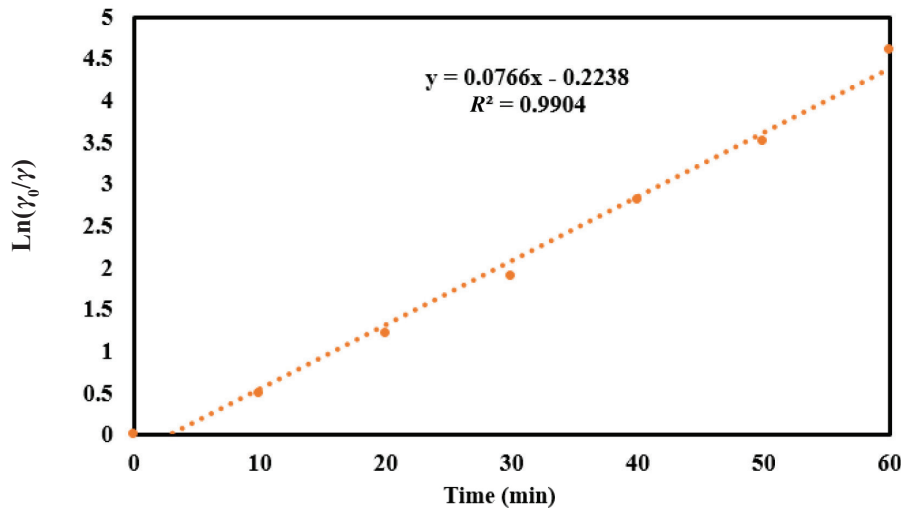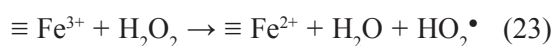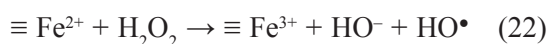
F i g . 8 – *First order kinetic model of CWPO/US-Fe$_3$O$_4$@C process of 4-CP*

Comparison of CWPO/US- Fe$_3$O$_4$@C process with other alternatives

The performance of 4-CP degradation by different processes including adsorption, US irradiation, H$_2$O$_2$, US/H$_2$O$_2$, US/Fe$_3$O$_4$, H$_2$O$_2$/Fe$_3$O$_4$, and CWPO/US-Fe$_3$O$_4$@C were evaluated under identical experimental conditions (Fig. 9). As may be seen, the sole application of US irradiation had a low effect on the 4-CP degradation process, which may due to insufficient •OH radical generation.[34] In addition, adsorption through Fe$_3$O$_4$/C composite demonstrated about 15 % removal mainly due to surface adsorption. In addition, the application of H$_2$O$_2$ alone led to a removal rate of about 21.3 %, which is a clear sign of low oxidation potential of H$_2$O$_2$.[13] Integration of H$_2$O$_2$ and US enhanced the 4-CP removal to 40 % after 60 min. This result was attributed to the dissociation of H$_2$O$_2$ by US, which produced •OH as described in Eqs. (21):[35]

$$H_2O_2 +))) \rightarrow 2\ HO^\bullet \qquad (21)$$

In the present study, the proposed US/Fe$_3$O$_4$@C system provided a removal efficiency of 55 %, indicating that the 4-CP molecules were attached to the surface of Fe$_3$O$_4$@C nanoparticles, and subsequently attacked by reactive spices. Therefore, the production of oxidizing agent on the surface of Fe$_3$O$_4$@C is an important issue in 4-CP degradation. In the binary system of Fe$_3$O$_4$@C/H$_2$O$_2$, the 4-CP degradation rate increased to 67 % in 1 h, which can be attributed to Fenton-like reactions (Eq. 22 and 23), heading to production of highly active •OH radicals.[36,37]

$$\equiv Fe^{2+} + H_2O_2 \rightarrow\ \equiv Fe^{3+} + HO^- + HO^\bullet \quad (22)$$

$$\equiv Fe^{3+} + H_2O_2 \rightarrow\ \equiv Fe^{2+} + H_2O + HO_2^\bullet \quad (23)$$

According to the results, the US/Fe$_3$O$_4$@C/ H$_2$O$_2$ process yielded a 4-CP removal of 99 % as the highest removal efficiency, which may be due to synergetic effect of Fenton oxidation and sonication that improve the production rate of reactive agents.[36] In this process, Fe^{2+} regeneration and Fe^{3+} reduction/regeneration cycle improve as a result of the sonication by dissociation of Fe−O$_2$, which subsequently increases the production of reactive radicals. The generated Fe^{2+} produces OH radical and regenerate Fe^{3+} through contribution in Fenton and sono-Fenton processes.[13] In this process, the nanoparticles provide high nucleation sites for the formation of cavities, and therefore the heterogeneous nature of nanoparticles acts as the main mechanism and enhances the process performance.[38] The high efficiency of proposed process may be related to dispersion of aggregated catalysts by US irradiation in solution, thus increasing the available sites of Fe$_3$O$_4$@C catalyst for the 4-CP molecules.

Reusability of catalyst

Catalyst reusability is a critical criterion for evaluation of catalyst application and its costs of synthesis, which should always be considered for the selection of a catalyst.[18] Stability of synthetized catalyst in CWPO/US-Fe$_3$O$_4$@C process was confirmed in five successive 4-CP degradation experiments. At the end of each cycle, the used catalyst was separated with an external magnet, washed three times with distilled water, and dried at 80 °C, then used for the next run. Results presented in Fig. 10 confirm that the catalytic activity of Fe$_3$O$_4$@C remained almost high during five consecutive experiments. According to the findings of the current work, a removal efficiency of 80 % was observed
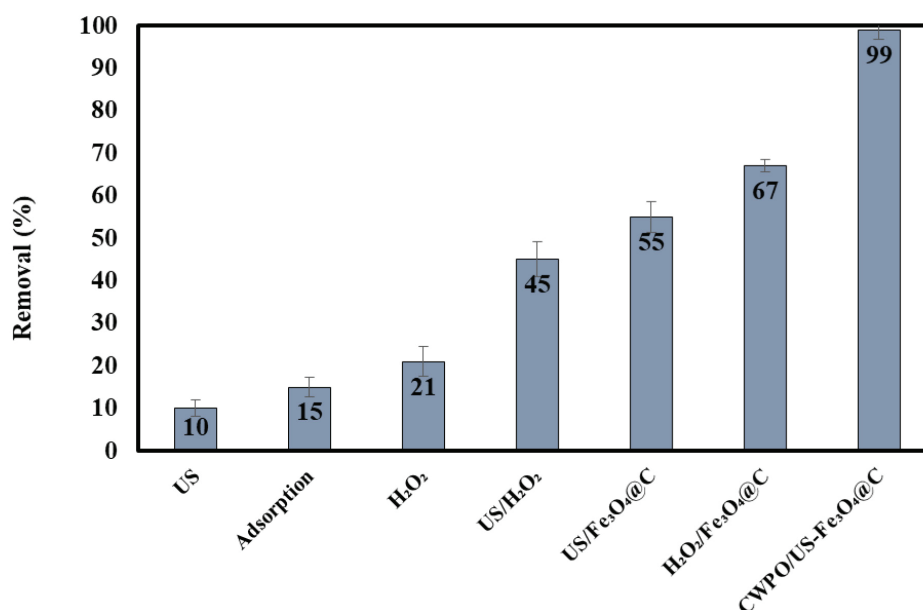
F i g . 9 – *Role of other alternatives in 4-CP removal (solution pH 5, initial 4-CP concentration 100 mg L⁻¹, catalyst dosage 0.8 g L⁻¹,*
H_2O_2 concentration of 20 mM, US power of 300 W, and reaction time of 60 min)

F i g . 1 0 – *Reusability of Fe_3O_4@C after five consecutive cycles at solution pH 5, initial 4-CP concentration 100 mg L⁻¹, catalyst*
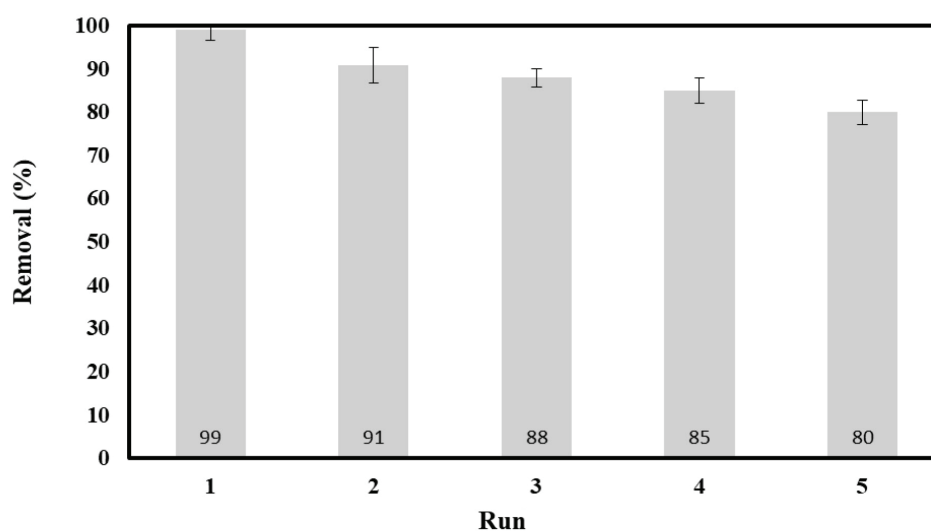*dosage 0.8 g L⁻¹, H_2O_2 concentration of 20 mM, US power of 300 W, and reaction time of 60 min*

after five runs. However, a slight decline in the process efficiency in 4th and 5th uses, could be ascribed to leaching of iron from the catalyst surface, and to the variations of the catalyst surface, as well as formation of intermediates on the catalyst surface, which in turn led to deactivation of catalyst.[39,40] Relatively low iron loss in consecutive runs indicated the stability of catalyst under experimental conditions studied. Increasing the Fe concentration in the solution after 5 cycles to 0.021 mg L⁻¹ was a sign of iron leaching from the catalyst.

Mineralization

In advanced oxidation technology, the final aim is to oxidize the organic pollutant to CO_2 and H_2O

completely.[41] Since the total organic carbon (TOC) reflects the changes in organic matter content, TOC removal efficiency is a significant criteria to evaluate the mineralization rate obtained by an advanced oxidation technology. Fig. 11 shows the results of TOC removal by the CWPO/US-Fe_3O_4@C process in selected conditions. The full destruction and removal of 4-CP was obtained after 60 min, while the TOC removal efficiency achieved 35 % after 60 min reaction. In any oxidation system, degradation of target pollutant is a gradual process in which destruction of pollutant proceeds step by step by sequential reactions. The possible oxidation pathway of 4-CP is presented in Fig. 12. Failure to detect 4-CP by analyzer does not mean that the organic
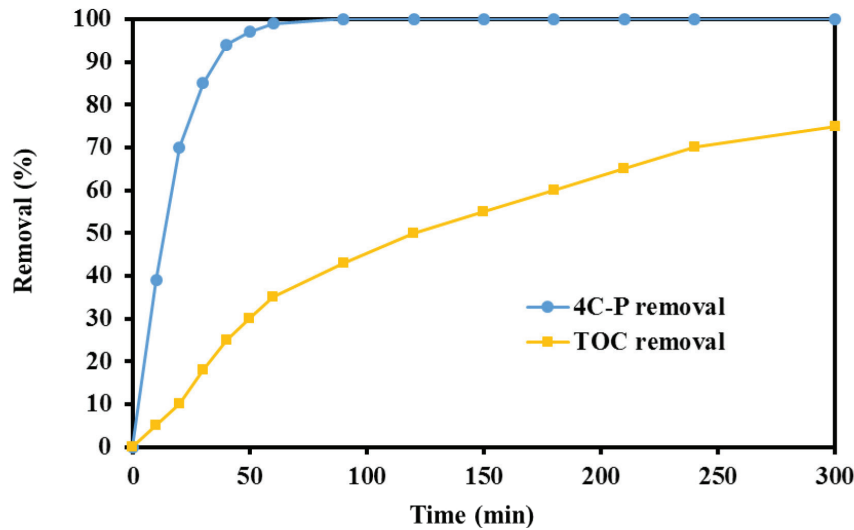
Fig. 11 – *Mineralization rate of 4-CP using CWPO/US-Fe₃O₄@C process in selected conditions*
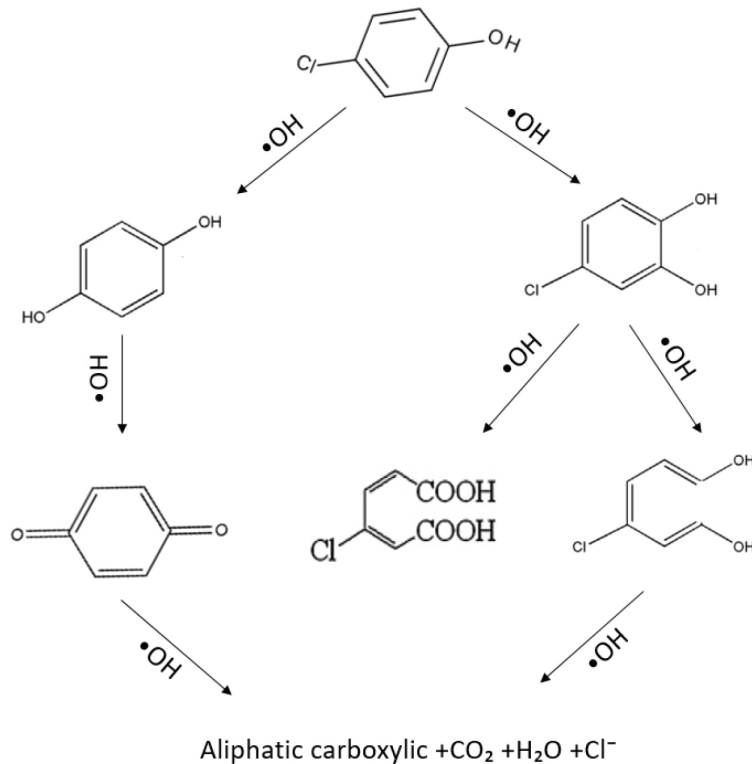

Fig. 12 – *Oxidation pathway of 4-CP*

matter is fully removed, since the mother molecule is converted to intermediate molecules, which are detected by TOC analysis. The difference between 4-CP and TOC is explained by the mentioned procedure. To obtain a safe effluent as well as discharge standards, providing a longer contact time is necessary to destroy the majority of organic matter resulted from initial destruction of 4-CP, and to observe the maximum available TOC removal.

Conclusions

In the current work, the efficiency of CWPO process was enhanced with sonication and $Fe_3O_4@C$ as a heterogenic catalyst for removal of 4-CP in aqueous solution. The best removal of 99 % was obtained at initial pH value of 5, sonication power of 300 W, catalyst dosage 0.8 g L^{-1}, H_2O_2 concentration of 20 mM, and reaction time of 60 min. 4-CP

degradation followed first-order model with reaction rate constant of 0.76 h^{-1}. Fe$_3$O$_4$@C demonstrated high stability during five successive runs with 80 % removal after five runs. Enhancement of CWPO process with sonication and Fe$_3$O$_4$@C catalytic oxidation led to significant 4-CP removal compared to individual processes. According to observed experimental data, it may be concluded that the CWPO/US-Fe$_3$O$_4$@C process qualified lab-scale phase, and as a reliable and efficient treatment process, it may be considered for a pilot scale study for the management of a real refinery or any other industrial wastewater.

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