

Removal of diazinon from aqueous solutions using 3D electrochemical system including a nanocomposite of microbial cellulose/nanomagnetite

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ABSTRACT

In this study, with the aim of improving the diazinon removal efficiency, a 3D electrochemical system was provided including microbial cellulose/Fe₃O₄ (MC/Fe₃O₄) nanocomposite. The MC/Fe₃O₄ nanocomposite was utilized for the activation of persulfate (PS) in the diazinon decomposition process. The characterization of the MC/Fe₃O₄ nanocomposite was determined by FE-SEM, FT-IR, XRD and TGA analysis. The operating variables including initial pH, NaCl concentration, PS concentration, initial diazinon concentration, current density and time were investigated. The proposed 3D electrochemical system in the optimal conditions of 10 mg/L initial diazinon concentration, pH 3, 0.2 g/L NaCl, 0.07 mmol/L PS, 3.54 mA/cm² current density and energy consumption of 12.61 kWh/m³ during 60 min reached to the complete removal of diazinon and 84.4 % TOC removal. According to the obtained results, the MC/Fe₃O₄ nanocomposite has the high efficiency of diazinon and TOC removal, as well as the consumption of NaCl, PS and lower energy in a shorter period of time compared to general electrochemical processes. Therefore, the reactions provide not only on the surface of the main electrodes but also on the surface of the particle electrode. It can improve the performance of electroabsorption and electrocatalysis in the chemical electrooxidation system.

1. Introduction

Pesticides are a concern for environmental sustainability, and modern agricultural practices require a large number of pesticides worldwide to protect agricultural products [1]. Agriculture is the main source of water pollution by pesticides [2]. Based on their chemical composition, pesticides are divided into four main groups, including organochlorines, organophosphates, carbamates, and pyrethroids [3]. Organophosphorus poisons are one of the large groups of poisons used in agriculture, which include 40 % of the pesticides used in agriculture [4].

Diazinon is a broad-spectrum insecticide that is considered as one of the most widely used organophosphate poisons and is one of the most common organophosphates detected in groundwater, drinking water, and surface water [5]. According to the proposed standards, the maximum concentration allowed in drinking water is 20 µg/L [6].

According to these issues, it is necessary to treatment these types of

pollutants from water sources and use appropriate methods to purify water contaminated with diazinon. Until now, various methods such as advanced oxidation process (AOPs), surface adsorption, membrane separation, filtration, biological processes and electrocoagulation have been proposed to remove diazinon. Each of the above methods have some advantages and limitations [7]. Among the advanced oxidation methods for wastewater treatment, electrochemical technology is reliable and easy and is particularly popular as green chemistry [8]. Electro-fenton technology, which combines electrochemical methods with the Fenton process, is one of the advanced oxidation processes that can produce hydroxyl radicals and destroy pollutants in the presence of divalent iron ions and hydrogen peroxide. Generally, conventional electrochemical processes consist of a two-dimensional electrode, whose main disadvantages are long mass transfer distance, low current efficiency, limited size of electrodes, and generation of reduction reaction species only on the surface [9]. In order to solve these problems,

Abbreviations: DIZ, Diazinon; DC, Direct current; EO, Electrooxidation; HCl, Hydrogen chloride; NaOH, Sodium hydroxide; NaCl, Sodium chloride; MC, Microbial cellulose; HS, Hestrin-Schramm medium; PS, Persulfate; SSM, Stainless Steel Mesh; XRD, X-ray powder diffraction; FT-IR, Fourier-transform infrared spectroscopy; TGA, Thermo-gravimetric analysis; FES-EM, Field emission scanning electron microscopy.

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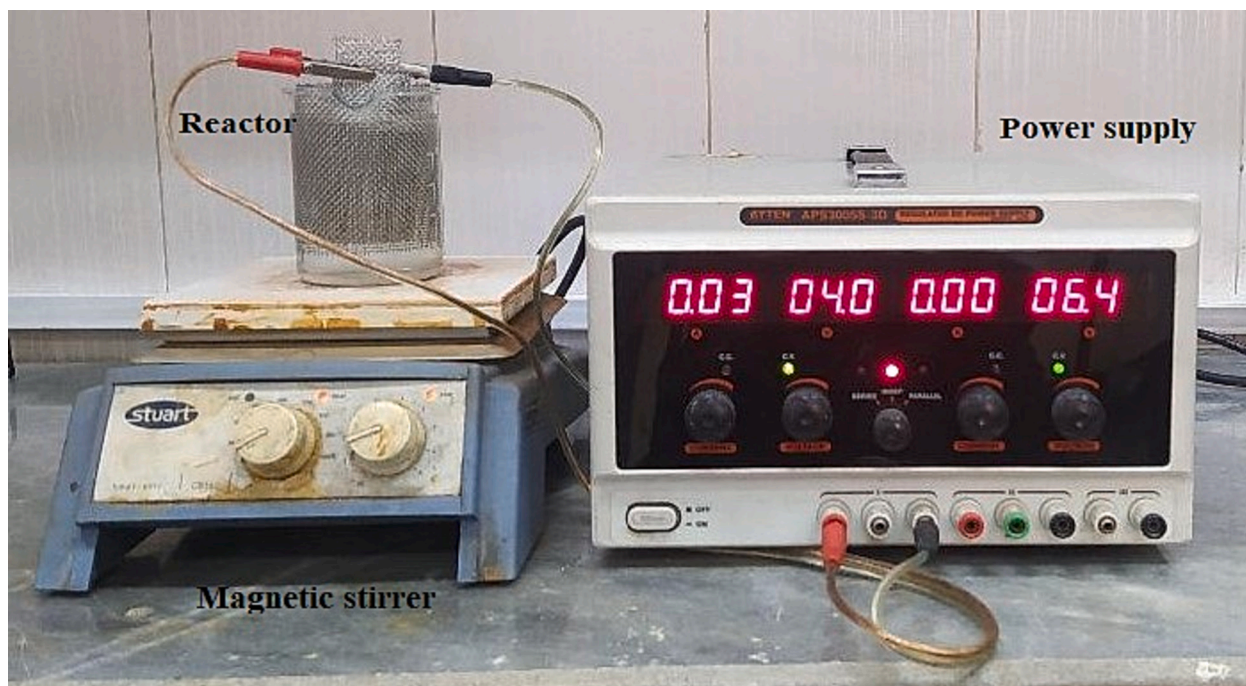


Fig. 1. The reactor set up.

particles are placed between the anode and cathode electrodes, so that they can form microelectrodes under the electric field and the conditions for performing the three-dimensional electro-fenton process are created [10]. During the process of electrochemical reactions, the electrodes of the particles can be converted into microelectrodes, one side of which can be considered the anode and the other side the cathode in the electric field. Therefore, electrochemical reactions can not only be carried out on the surface of the main electrode, but also extend to the surface of the particle electrodes, and as a catalyst, it can improve the performance of electroadsorption and electrocatalysis in the chemical electrooxidation system. As a result, the three-dimensional electro-fenton process increases the electrolytic efficiency, current, mass transfer, catalytic effect and reduces energy consumption [11]. Moreover, in the three-dimensional electrochemical system, the distance between the reactants is also shortened, thus increasing the current efficiency and purification capacity [12]. Removal of pollutants in three-dimensional systems is 10 to 50 % more than two-dimensional systems [13]. Considerable research has been done on the preparation of particle electrodes for three-dimensional electrochemical systems. Sulfate radicals $SO_4^{\cdot-}$ based on advanced oxidation processes can be produced using persulfate. Sulfate radicals have a stronger oxidation activity ($SO_4^{\cdot-}$: 2.5–3.1 V) than hydroxyl radicals ($\cdot OH$: 2.7–2.8 V) and have better stability, high oxidation ability, longer life, and a wider pH range [9]. In addition, persulfate can decompose a wide range of organic pollutants that cannot be decomposed by other purification methods [14]. Due to its high reduction potential, persulfate has high oxidation ability and selectivity to eliminate most of the resistant organic pollutants. Therefore, using PS to replace liquid H_2O_2 in AOPs is an efficient method. In order to produce sulfate radicals, persulfate must first be activated by one of the methods of heat, UV and transition metal ions [9]. Depending on the catalyst, the electro-fenton process is classified into homogeneous and heterogeneous types. During the homogeneous electro-fenton process, reactions occur in the liquid phase. The main disadvantages of this type of operation are separation problems, recovery of metal ion after purification, need for high iron content, production of metal ion and a metal hydroxide containing sludge. Through the heterogeneous type of electro-Fenton process, reactions occur on catalyst surfaces at active sites. Solid catalysts in heterogeneous electro-fenton process such as

divalent iron hydroxide ($Fe(OH)_2$), hexavalent divalent iron ($Fe(H_2O)_6^{2+}$), trivalent iron chloride ($FeCl_3$), hematite (Fe_2O_3), goethite ($\alpha-FeOOH$) and magnetite (Fe_3O_4) are quickly recovered from the aqueous sample and are used without losing the active sites. On the other hand, Fe_3O_4 magnetic nanoparticles are a rich source of iron and have advantages such as magnetic separation, simple synthesis, low cost, and compatibility with the environment [15]. The main problem in the application of magnetic nanoparticles is related to their possible aggregation. In magnetic solid catalysts with a substrate with Fe_2O_4 and Fe_3O_4 , usually from polymers, biopolymers, and mineral materials [16]. The biopolymers such as microbial cellulose, chitosan, biochar and alginate have other advantages such as biodegradation- adaptability, low cost, availability, and low degree of toxicity. In recent years, the use of microbial cellulose as a substrate in industrial wastewater treatment has been proposed. Some studies on microbial cellulose/magnetite nanoparticles with its applications have been made in sensors, electromagnetic shielding and removal of heavy metals [17]. In this study, microbial cellulose has shown good performance due to its ease of use, low cost, low toxicity and high stability. The Fe_3O_4 nanoparticles are immobilized on the microbial cellulose surface and it utilized as 3D electrochemistry agent for activation of PS. To the best of our knowledge, there is rare report about utilization of the 3D electrochemical system using the nanocomposite.

2. Materials and methods

2.1. Chemicals

Diazinon analytical grade (99 % pure), potassium persulfate ($K_2S_2O_8$), divalent iron chloride ($FeCl_2$), trivalent iron chloride (97 %) ($FeCl_3$), ammonia (NH_3), phenanthrene 97 % as internal standard, acetic acid, chlorobenzene and acetone were purchased from Merck, Germany. The initial pH value of the solution was adjusted by adding 0.1 M hydrogen chloride (HCl) or sodium hydroxide (NaOH). The experiments were performed at the ambient temperature of 25 °C.

2.2. Preparation of MC/Fe₃O₄

In this study, the production of microbial cellulose was done by general reported method. Briefly, a single colony of *Acetobacter xylinum* was inoculated in Hestrin-Schramm (HS) medium containing 2 % glucose, 0.5 % pepton, 0.5 % yeast extract, 0.27 % disodium phosphate, 0.115 % citric acid. The produced cellulose was washed twice for 30 min in 5 % sodium hydroxide under a temperature of 80 °C. Then, the microbial cellulose is washed with distilled water. After the preparation of microbial cellulose, the amount of 8.48 g of trivalent iron chloride (III), 2.25 g of divalent iron chloride (II) and microbial cellulose were inserted in 400 cc of distilled water under a temperature of 80 °C and nitrogen gas. After 1 h of colloid formation and turning the clear orange to opaque color, 25 cc of ammonia was added to turn the color of the solution to black. The MC/Fe₃O₄ was separated and washed by a magnet after 30 min. Finally, the produced nanocomposites were dried in an oven at a temperature of 100 °C for 60 min and powdered in a mill.

2.3. Analysis

The characterization of the MC/Fe₃O₄ nanocomposite has been presented in our last publication [18]. The residual concentration of diazinon was measured using a gas chromatography (perkinelmer, United States) with FID detector and HP-5 capillary column (30 m × 32 mm × 0.25 μm film thickness). Briefly, 2 mL of the sample was filtered with a 0.22 μm filter and it was added into a laboratory tube with a volume of 10 mL. 100 μL of acetone as dispersion solvent containing 2 mg/mL of phenanthrene as an internal standard and 100 μL of chlorobenzene as extraction solvent were added to the sample. After 3 min of stirring, the sample was centrifuged at 3000 rpm for 9 min. The GC temperature program was as follows: At first, the column temperature was set at 70 °C, then the temperature was increased by 12 °C per min until it reached 280 °C and remained at this temperature for 1 min. The injector and detector temperatures were 250 °C and 270 °C, respectively. Nitrogen was used as a carrier gas at a flow rate of 4 mL/min. The flow rate of air was 350 mL/min and hydrogen was 35 mL/min.

2.4. Experiment procedures

All experiments were conducted in a glass reactor with a volume of 150 cc at ambient temperature (25 ± 1 °C) with a stirrer (Fig. 1). The initial pH value of the diazinon sample was adjusted to 3.0 using 0.1 M hydrogen chloride (HCl) before the experiment. Various amount of sodium chloride as an electrolytic support, potassium persulfate oxidant and MC/Fe₃O₄ nanocomposite were added to the reactor. Anode and cathode were both made of steel mesh. The SSM electrodes were placed in a cylindrical form in the middle of the reactor, the outer cylinder with a larger area as the cathode and the inner cylinder with a smaller area as the anode were 1 cm away from the cathode.

3. Results and discussion

3.1. Characteristics of the MC/Fe₃O₄ nanocomposite

FE-SEM analysis shows surface morphology of the nanocomposite. The microbial cellulose is composed of fibers with regular random spaces. The micrographs of MC/Fe₃O₄ nanocomposite shows the Fe₃O₄ nanoparticles are non-uniform and small spherical particles are immobilized on the microbial cellulose fibers and filaments. The fracture peaks correspond to the standard Fe₃O₄ XRD pattern with number 003-0863 and show the presence of Fe₃O₄ cubic crystals in MC/Fe₃O₄ [19]. In the microbial cellulose curve, sharp peaks at 2θ 15, 17 and 22 degrees, which show the breakdown of the cellulose crystal structure [20]. The observed peaks in Fe₃O₄ and MC/Fe₃O₄ graphs are at 20/30, 35/52, 43/20, 53/82 and 57/36 degrees, which are (220), (311), (400) respectively. (422), (511), and (440) are assigned, they show the crystal

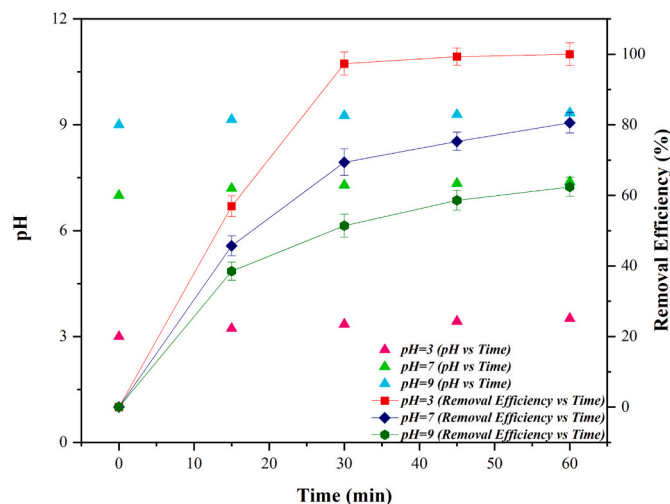
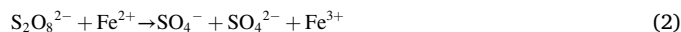


Fig. 2. Effect of pH on diazinon removal (initial diazinon concentration 10 mg/L, sodium chloride 0.2 g/L, persulfate dosage 0.07 Mmol/L, nanocomposite dosage 0.25 g/L and current density 3.54 mA/cm² during 60 min).

structure of Fe₃O₄. Subsequently, TGA analysis was performed for the thermal stability of MC/Fe₃O₄ nanocomposite at temperatures of 250–7000 for the pyrolytic destruction of MC. The TGA results shows the initial weight loss at 160 °C as 6.71 %, which could be due to the release of water from the surface of the microbial cellulose. 20 % weight loss at the temperature of 160–400 °C in the second stage and 13.34 % at the temperature of 400–700 °C in the third stage is related to pyrolytic destruction of cellulose [21]. The remaining weight of Fe₃O₄ was about 59.7 % by weight.

3.2. Catalytic performance

In order to confirm the ability of the proposed system in removal of diazinon, the control experiments were examined under optimal conditions. The addition of MC/Fe₃O₄ nanocomposite can form a 3D electrochemical system. This additive solid catalyst can play the role of mutual exchange of cathode and anode and expand the range of electro-oxidation reaction to catalyst surfaces [8]. The three-dimensional electrochemical process using MC/Fe₃O₄ nanocomposite has provided 99.99 % efficiency for diazinon removal in optimal conditions. On the other hand, the used nanocomposite has pores and a high surface area that can produce iron (II) under electrochemical reactions to produce strong sulfate radicals through PS activation (Eqs. (1)–(2)) and efficiency improve the reaction [22].



In order to determine the diazinon mineralization, the TOC was determined in optimal conditions at 0, 30 and 60 min. The initial TOC concentration was 45 mg/L. The obtained results showed that after 30 and 60 min, the TOC removal efficiency was reached to 77.8 % and 84.4 %, respectively.

3.3. Effect of initial pH

An important factor in the 3D electrochemical system is pH, because it directly effects on the oxidation [22]. As shown in Fig. 2, when the pH increased from 3 to 9, the diazinon removal efficiency reached from 99.99 % to 62.4 %. According to the obtained results at pH 3, 7 and 9, the removal efficiency was reached 99.99 %, 80.6 % and 62.4 %, respectively. Moreover, adding of the MC/Fe₃O₄ nanocomposite did not have a significant effect on changing the pH of the solution. In acidic pH,

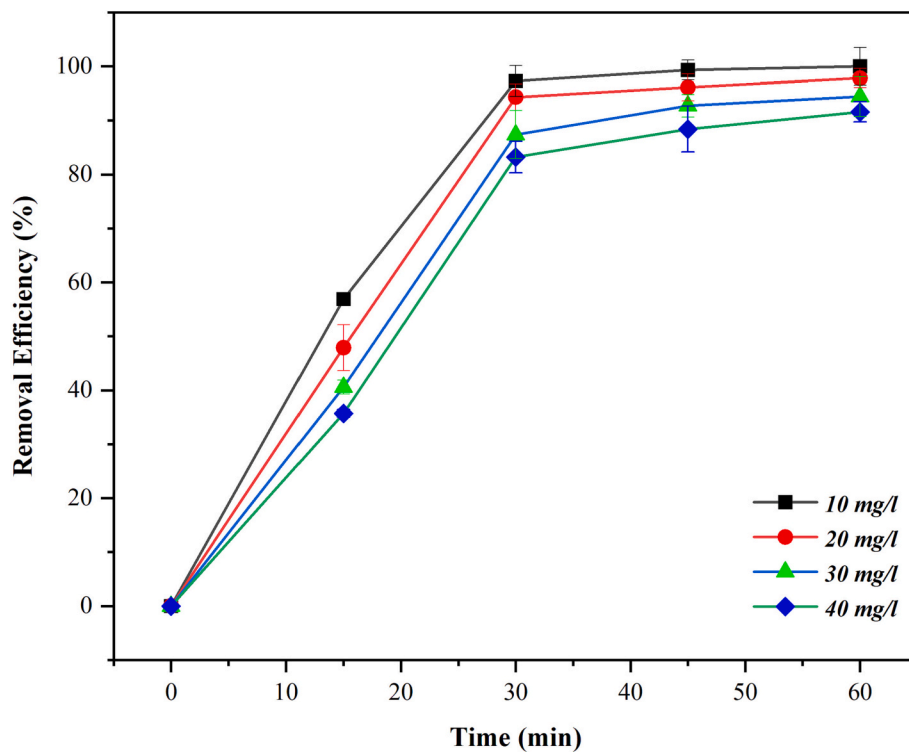


Fig. 3. Effect of initial diazinon concentration on diazinon removal efficiency (pH 3, sodium chloride 0.2 g/L, persulfate dosage 0.07 mmol/L, nanocomposite dosage 0.25 g/L and current density 3.54 mA/cm² during 60 min).

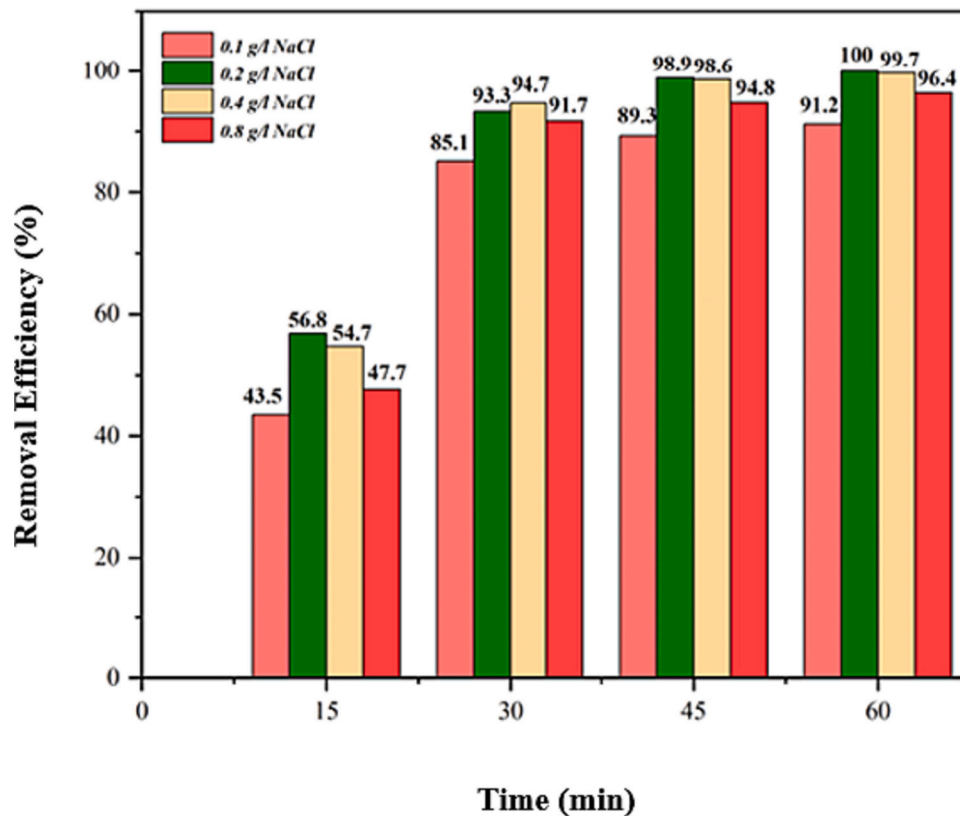


Fig. 4. Effect of sodium chloride concentration as the supporting electrolyte on diazinon removal efficiency (pH 3, initial diazinon concentration 10 mg/L, persulfate dosage 0.07 mmol/L, nanocomposite dosage 0.25 g/L and current density 0.54 mA/cm² during 60 min).

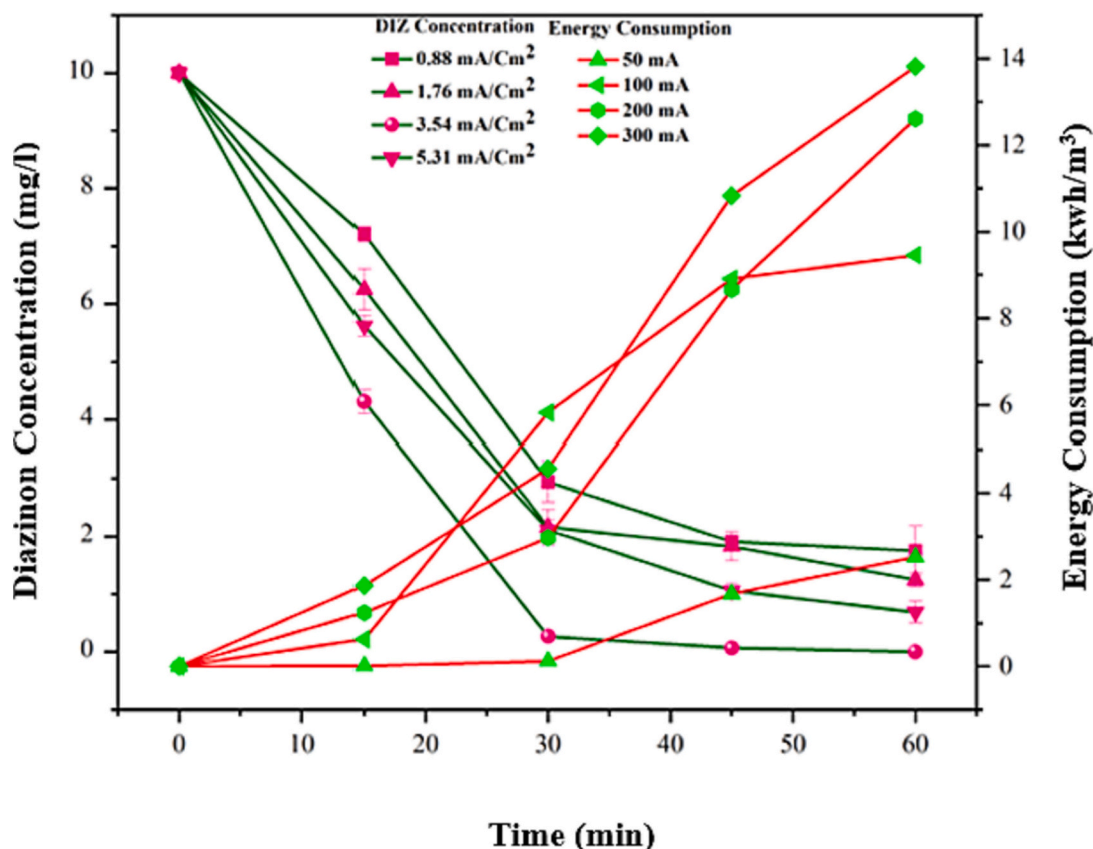
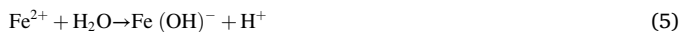


Fig. 5. Effect of current density on diazinon removal efficiency and energy consumption (pH 3, initial diazinon concentration 10 mg/L, sodium chloride concentration 0.2 g/L, persulfate dosage 0.07 mmol/L and nanocomposite dosage 0.25 g/L in 60 min).

the amount of H^+ ions is high. The H^+ ions can convert persulfate to active sulfate radicals (Eqs. (3)–(4)).



The reason for the decrease in efficiency at higher pH is related to the decrease in the concentration of ferrous ion (Fe^{2+}) in the solution, which happens after the formation of Fe^{2+} complexes and precipitation in the form of hydroxide. The decrease in Fe^{2+} concentration ultimately causes a decrease in the formation of sulfate radicals (Eq. (5)). A decrease in the efficiency of the electrooxidation process is occurred with decrease of the Fe^{2+} [23]. Moreover, at higher pH, the removal of diazinon decreased due to the precipitation of Fe^{3+} ionic hydroxyls and their absorption in the MC/ Fe_3O_4 powder nanocomposite structure.



Similarly, the electrochemical removal of diazinon using aluminum electrode was reported at pH 3 [24]. It was reported the 81.1 % efficiency for removal of diazinon by advanced oxidation process at pH 3 [25].

3.4. The effect of the of diazinon initial concentration

The pollutant concentration is an effective parameter in the oxidation processes [26]. As shown in Fig. 3, with increasing of the diazinon concentration from 10 to 40 mg/L, the removal efficiency from 99.99 % decreased to 79.1 % during 60 min. Generally, as the initial concentration of pollutants in wastewater increases, the removal efficiency decreases using the oxidation process. The decrease in the efficiency of diazinon removal was reported from wastewater, when the initial

concentration increased from 1 to 10 mg/L [27]. Moreover, the removal of diazinon by persulfate activation process using $SnS_2-Fe_3O_4-rGO$ was reported that by increasing of the initial concentration of diazinon from 5 to 15 mg/L, the removal efficiency decreases from 97 % to 49 % [28]. Therefore, with the increase of the initial concentration of diazinon, the efficiency of the removal process decreases.

3.5. The effect of supporting electrolyte

Supporting electrolyte is one of the effective factors in the electrochemical system [29]. The diazinon removal efficiency increases with increasing of the supporting electrolyte from 0.1 to 0.2 g/L (Fig. 4). The degradation efficiency of diazinon using various concentration of NaCl (0.1, 0.2, 0.4, and 0.8 g/L) as the supporting electrolyte were obtained 89.1 %, 93.3 %, 96.1 %, and 91.7 %, respectively. The obtained results showed that 0.2 g/L of sodium chloride as the supporting electrolyte was the optimum. The reason for using sodium chloride as a supporting electrolyte is that it can produce the chlorine ions. With the presence of chlorine ions in the solution, various types of active chlorine such as OCl and HOCl are produced, which have the ability to oxidize organic compounds (Eqs. (6)–(8)). The HOCl has the ability to produce hydroxyl radicals in the presence of Fe^{2+} (Eq. (9)). Moreover, in the high concentration of chloride ions, it can destroy sulfate and hydroxyl radicals, which can be caused by the absorption of chloride ions on the surface of the electrodes and its deactivation, which causes a drop in efficiency (Eq. (10)) [29].



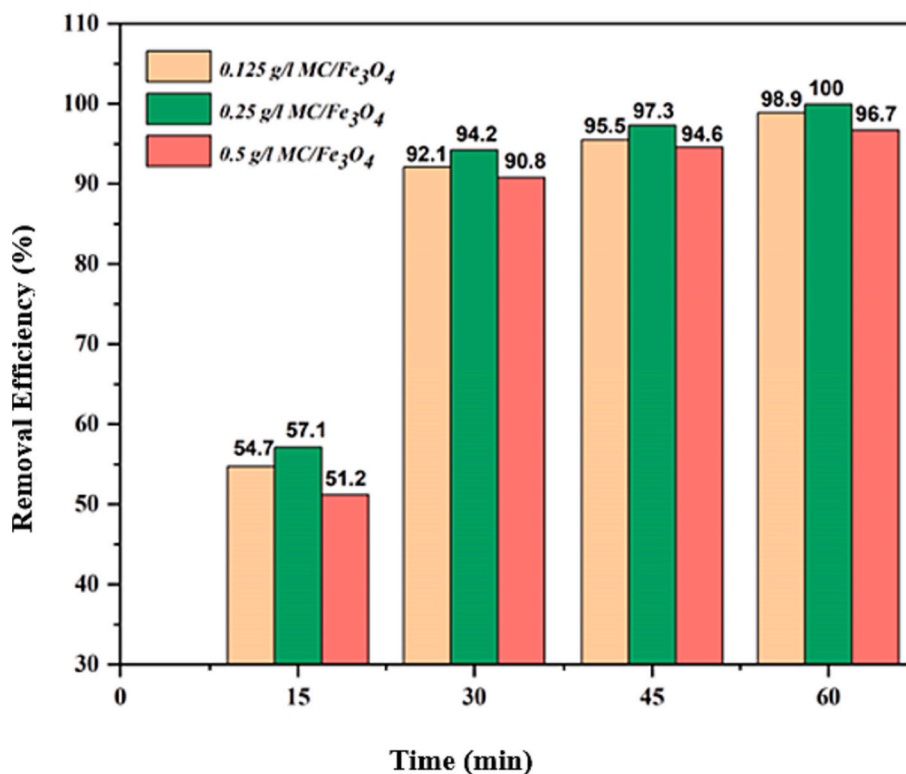


Fig. 6. Effect of MC/Fe₃O₄ nanocomposite on diazinon removal efficiency (pH 3, initial diazinon concentration 10 mg/L, sodium chloride 0.2 g/L, persulfate dosage 0.07 mmol/L, and current density 3.54 mA/cm² during 60 min).



It was reported that utilizing of the NaCl as supporting electrolyte to remove malathion in the electrocoagulation process [30]. With increasing of NaCl from 1 to 2.5 g/L, the removal rate of malathion increased. By increasing of the supporting electrolyte up to 3 g/L, the efficiency decreased. At high concentration of sodium chloride, all the excess ions reacted with hydroxyl radicals to produce Cl[·], which is less reactive than hydroxyl radicals [30]. It has been reported that the presence of chlorine ions has a positive effect on the COD removal in the electrochemical system. Increasing the sodium chloride from 5 to 10 g/L did not significantly increase the efficiency of pyrimidine removal [31].

3.6. Effect of current density and energy consumption

The current density is one of the most important effective parameters in the 3D electrochemical system, because it effects on the electrochemical oxidation and the polarization behavior of the electrodes. Moreover, it directly affects process performance and operating costs [6]. As shown in Fig. 5, the concentration of diazinon decreased from 10 to 1.75 mg/L at the current density of 0.88 mA/cm². The 99.99 % diazinon removal was obtained at the current density of 3.54 mA/cm² during 60 min. With the appropriate current density, the particles are polarized to form microelectrodes that can enhance oxidation. The production of sulfate radicals increased on the electrodes with the increase of the current density, which leads to the improvement of the elimination process [26]. At the higher current density, the removal rate decreased. For example, at a current density of 5.31 mA/cm², the efficiency of 93.1 % was achieved, because increasing the current density to more than 3.54 mA/cm² led to the production of large amounts of Fe²⁺ ions and their accumulation in the solution (Eq. (11)). The 97.88 % diazinon removal efficiency was reported using Pb/β-PbO₂ anode under

conditions of pH 4, current density of 9.6 mA/cm² during 120 min [8]. The current density has a direct effect on energy consumption. Fig. 6 shows the changes in energy consumption in terms of current density and time. By increasing the current density from 0.88 to 5.31 mA/cm², the energy consumption increased from 2.522 to 13.82 kwh/m³. Therefore, with the increase in current density, the amount of energy consumption increases [6]. The energy consumption of 2.52, 6.31, 12.61 and 13.82 kwh/m³ were obtained using the induced current density of 0.88, 1.77, 3.54 and 5.31 mA/cm², respectively. The 99.46 % removal of diazinon through a photocatalytic process was reported using immobilized MgO nanoparticles, the maximum efficiency of diazinon removal during 120 min with energy consumption of 15.58 kwh/m³ [32]. Sludge produced in the system has two origins; 1) sludge resulting from anode sacrifice and, 2) Precipitation of nanomagnetite/microbial cellulose nanocomposites.

We have obtained 0.88 mA/cm² as the optimum current density. In the current density the sludge production was very low. But by increasing the current density from 0.88 to 5.31 mA/cm², we have high amounts of the sludge in the system. Moreover, the percoitated nanocomposite could be collect by magnet.

3.7. Effect MC/Fe₃O₄ dosage

As shown in Fig. 6, the diazinon removal was 79.3 % without utilizing of the MC/Fe₃O₄. The 98.9 % of diazinon removal efficiency was obtained by increasing the amount of the nanocomposite to 0.125 g/L and the removal efficiency reached 98.9 %. When the initial dose of nanocomposite increased to 0.25, the 99.99 % removal efficiency was achieved. After adding MC/Fe₃O₄ nanocomposite, its catalytic effect showed better performance than 2D electro-oxidation process. In the 3D electro-oxidation system, the reaction path is shortened and the efficiency of electron transfer increases. Then it improves the activation of potassium persulfate and the production of active species [26]. Moreover, by increasing the amount of the nanocomposite to 0.5 g/L, the

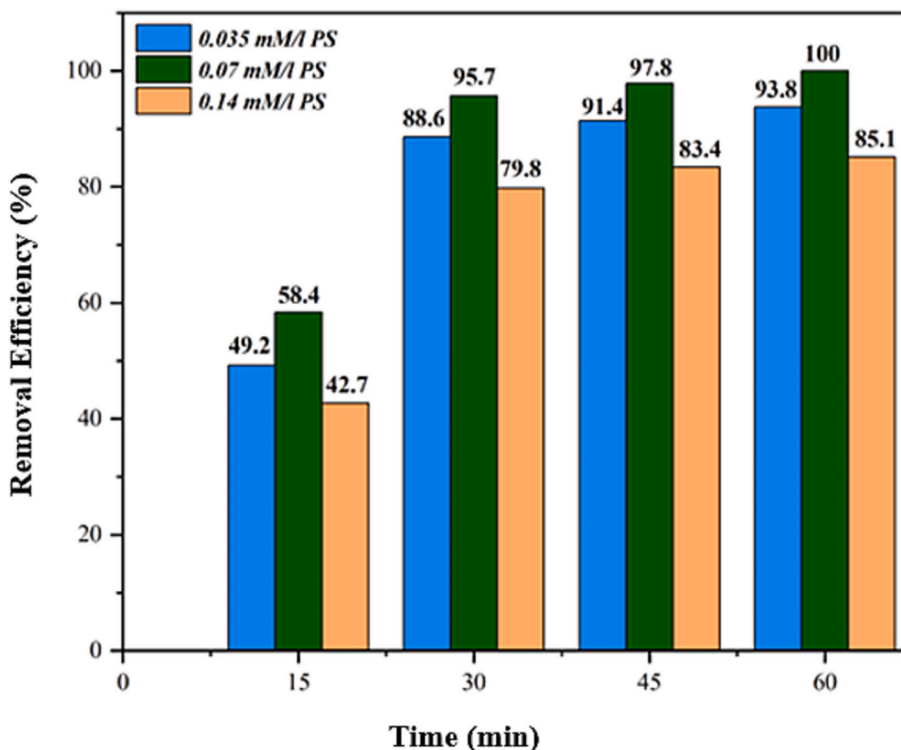


Fig. 7. Effect of persulfate concentration on diazinon removal efficiency (pH 3, initial diazinon concentration 10 mg/L, sodium chloride 0.2 g/L, nanocomposite dosage 0.25 g/L and current density 3.54 mA/cm² during 60 min).

Table 1
Comparison of persulfate dosage and operating parameters in different studies.

Pollutant	Activation system	Persulfate dosage (mM/L)	Diazinon concentration (mg/L-mg)	Time (min)	Efficiency (%)	Reference
Diazinon	WO ₃ -Fe ₃ O ₄ /g-C ₃ N ₄ -PS	1	5	60	95	[27]
Diazinon	SnS ₂ -Fe ₃ O ₄ /rGO	1	5	40	99.9	[28]
Diazinon	MC/Fe ₃ O ₄ -EO	0.07	10	60	99.99	This study

removal efficiency decreased and reached 96.7 %.



3.8. The effect of persulfate (PS)

Persulfate is one of the effective parameters on the production of sulfate radicals in processes [36]. As shown in Fig. 7, when the sample did not contain persulfate, the diazinon removal rate was 71.4 % in the EO/MC-Fe₃O₄ system. The diazinon removal efficiency increased from 0.035 to 0.07 mmol/L with the increase of persulfate dosage and reached the complete removal efficiency, which is due to the production of more sulfate radicals through the oxidation reaction [37]. The obtained results showed that increasing the concentration of persulfate from 0.07 to 0.14 mmol/L decreased the diazinon removal efficiency. Table 1 compares the amount of persulfate in this study with other studies. At the high persulfate concentration at side reaction creates between SO₄^{·-} radical and PS (Eqs. (12)–(13)):



3.9. Effect of reaction time

Another essential factor in oxidation processes is time [27]. The reason can be that the increase in time in many treatment systems leads

Table 2
Equations used in this study.

Characterization	Equation	References
Diazinon removal efficiency	$\frac{C_0 - C_t}{C_0} \times 100$	[40]
TOC removal efficiency	$\frac{TOC_0 - TOC_t}{TOC_0} \times 100$	[40]
First-order-kinetic model	$\ln\left(\frac{C_0}{C_t}\right) = K_t t$	[28]
Pseudo first-order-kinetic model	$\log(q_e - q_t) = \log q_e - k_{ad}\left(\frac{t}{2.303}\right)$	[28]
Second-order-kinetic model	$\frac{1}{C} = \frac{1}{C_0} + kt$	[24]
Pseudo second-order-kinetic model	$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e}$	[41]
Energy consumption	$E_{sp}\left(\frac{kwh}{m^3}\right) = \frac{1000PT}{60V \log\left(\frac{C_0}{C_f}\right)}$	[25]

to more contact between the pollutant and the sulfate radical [38]. The degradation rate of diazinon reached 99.99 % from 50.9 % by increasing the reaction time from 15 to 60 min. In addition, with the increasing of the time, available sulfate radicals decrease due to the consumption of sulfate radicals and iron (II) ions [39].



Table 3
Parameters of kinetic rate models for diazinon removal.

Kinetic model	Parameters	Concentration (mg/L)			
		10	20	30	40
First order	k_1 (min^{-1})	0.15	0.068	0.052	0.044
	R^2	0.94	0.92	0.93	0.94
Second order	k_1	13.426	0.037	0.01	0.005
	R^2	0.51	0.93	0.96	0.97
Pseudo first order	k_1 (min^{-1})	0.138	0.013	0.008	0.009
	R^2	0.72	0.03	0.02	0.03
Pseudo second order	k_2 (g/mg/min)	54.011	0.224	0.069	0.036
	R^2	0.51	0.85	0.91	0.91

3.10. Kinetic study

In order to study of the diazinon removal kinetic, first-order, second-order, pseudo-first-order and pseudo-second-order kinetic models were evaluated (Table 2).

The obtained results show the highest correlation coefficient is related to the first-order kinetic model, which indicates that the kinetic follows the first-order kinetic model compared to other models. With increasing of the diazinon concentration from 10 to 40 mg/L, the constant value of the kinetic reaction decreased from 0.15 to 0.044. The comparison of the reaction constant value (k) of this study with other scientific reports determines that the reaction efficiency of the 3D electrochemical process with MC/Fe₃O₄ particle electrode is higher than other processes. The obtained kinetic rates are shown in Table 3.

3.11. Mineralization study

In order to estimate the amount of diazinon mineralization in the electrooxidation system with persulfate activation through MC/Fe₃O₄ nanocomposite, the total organic carbon was determined. As shown in Fig. 8, the concentration of TOC was 45 mg/L at the beginning. After 30

min, its concentration reached 10 mg/L, which shows that most of the TOC removed was happened in the first 30 min. At the 60 min, the TOC concentration decreased from 10 to 7 mg/L and the removal efficiency increased from 77.8 % to 84.4 %. Table 4 shows the comparison between TOC removal efficiency in this study and other studies.

3.12. The radical scavenger studies

The most active radicals produced during the degradation of diazinon were investigated by scavenger experiments. As shown in Fig. 9, complete removal efficiency was achieved, when we did not add any scavenging agent in the sample. In the presence of methanol as a sulfate radical scavenger, tert-butanol as a hydroxyl radical scavenger, benzoquinone as a superoxide scavenger and sodium azide as a single oxygen scavenger with a concentration of 30 mmol/L, the efficiency of the process was evaluated. The obtained results showed that the main factor in diazinon removal was the sulfate radical (Eqs. (15)–(17)). By addition of the methanol to the system, the efficiency decreased by 32 %. Moreover, the diazinon removal mechanism was investigated by persulfate and MC/Fe₃O₄ nanocomposite. Initially due to the reaction of

Table 4

Comparison of TOC removal efficiency and operating parameters at various studies.

Removal system	pH	Time (min)	TOC efficiency (%)	DIZ efficiency (%)	Reference
PS/UV	5	60	69	95	[42]
PS/UV	5	40	78	99.9	[43]
Ultrasonic radiation	3	60	30	98	[44]
Electrochemical/ Pb/ β -PbO ₂	4	120	79.86	97.88	[8]
Ozonation/mg-Al	8.5	70	74	92	[45]
EO-MC/Fe ₃ O ₄	3	60	84.4	99.99	This study

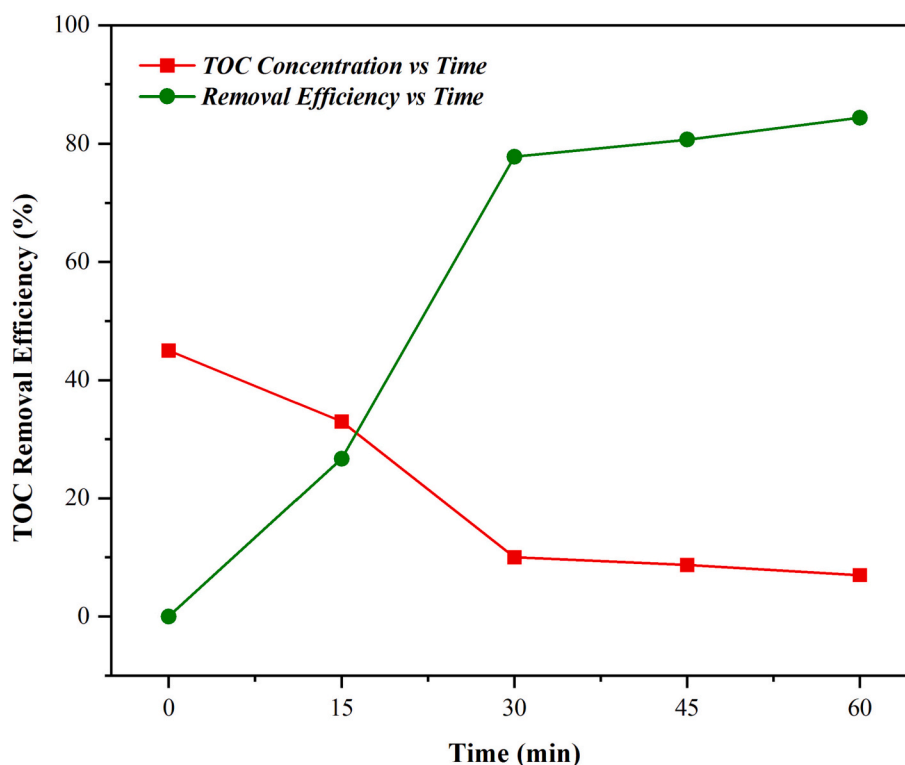


Fig. 8. The effect of diazinon mineralization on its removal efficiency (pH 3, initial diazinon concentration 10 mg/L, sodium chloride 0.2 g/L, persulfate dosage 0.07 mmol/L and nanocomposite dosage 0.25 g/L and current density 3.54 mA/cm² during 60 min).

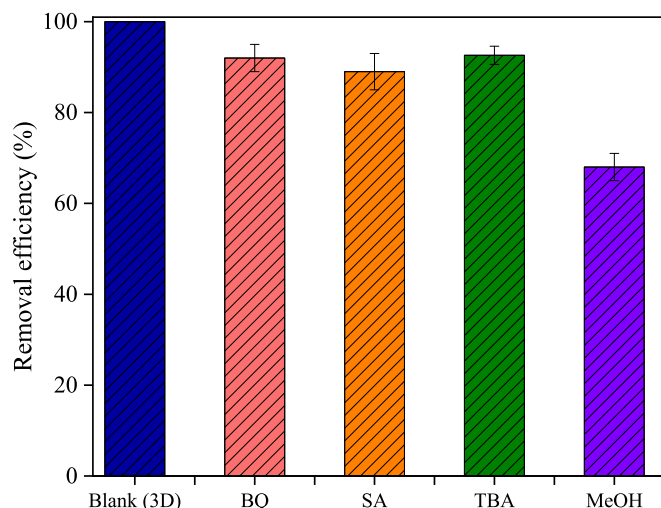
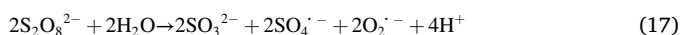
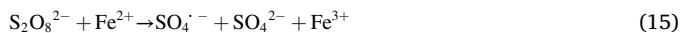


Fig. 9. Effect of scavengers on diazinon removal efficiency (pH 3, initial diazinon concentration 10 mg/L, sodium chloride 0.2 g/L, persulfate dosage 0.07 mmol/L and nanocomposite dosage 0.25 g/L and current density 3/54 mA/cm² during 60 min).

immobilized Fe₃O₄ nanoparticles on microbial cellulose with peroxydisulfate (S₂O₈²⁻), Fe²⁺ is oxidized to Fe³⁺ and electrons are released. The S₂O₈²⁻ reacts with the electron released from Fe²⁺ and produces sulfate radical [44].



The use of Fe₃O₄ nanoparticles as a catalyst has been reported for the

activation of PS in heterogeneous oxidation systems [38]. Activation of persulfate by MC/Fe₃O₄ catalyst and production of SO₄^{•-} radical can be done both on the surface of the catalyst due to the absorption property of Fe₃O₄ and in the electrolyte solution. As shown in Fig. 10, the lowest removal rate was related to PS alone. When the MC/Fe₃O₄ nanocomposite was examined alone without current, the adsorption rate of diazinon was 43.8 %. When the current was induced with MC/Fe₃O₄-EO, the removal efficiency increased to 71.4 %. In this case, in addition to adsorption diazinon by nanocomposite, the electrooxidation process also occurs on the surface of nanocomposite. However, high efficiency was not achieved. According to scavenging experiments, sulfate radical was the most effective radical in diazinon removal.

4. Conclusion

This study showed that MC/Fe₃O₄ nanocomposite and persulfate were the main factors during the electrooxidation process in diazinon removal. Optimum conditions for removal of diazinon include pH 3, persulfate 0.07 mmol/L, MC/Fe₃O₄ 0.25 g/L, initial concentration of diazinon 10 mg/L, 0.2 g/L. The efficiency of diazinon removal and its mineralization after 60 min was 99.99 % and 84.4 %, respectively. According to the experimental results related to scavenger materials, the sulfate radical (SO₄^{•-}) was the main factor in the removal of diazinon, which was produced during the electrooxidation reaction by persulfate and magnetite nanoparticles in the nanocomposite structure. In addition, factors such as hydroxyl radical (•OH), non-radicals of superoxide (O₂^{•-}) and single oxygen (¹O₂) were also effective in reducing of diazinon concentration. The like-electroenton process was highly efficient in acidic conditions and improved the efficiency. The advantage of using MC/Fe₃O₄ nanocomposite caused the synergistic effect of absorption and like-electroenton processes in the removal of diazinon.

CRedit authorship contribution statement

All authors read & approved the final manuscript.

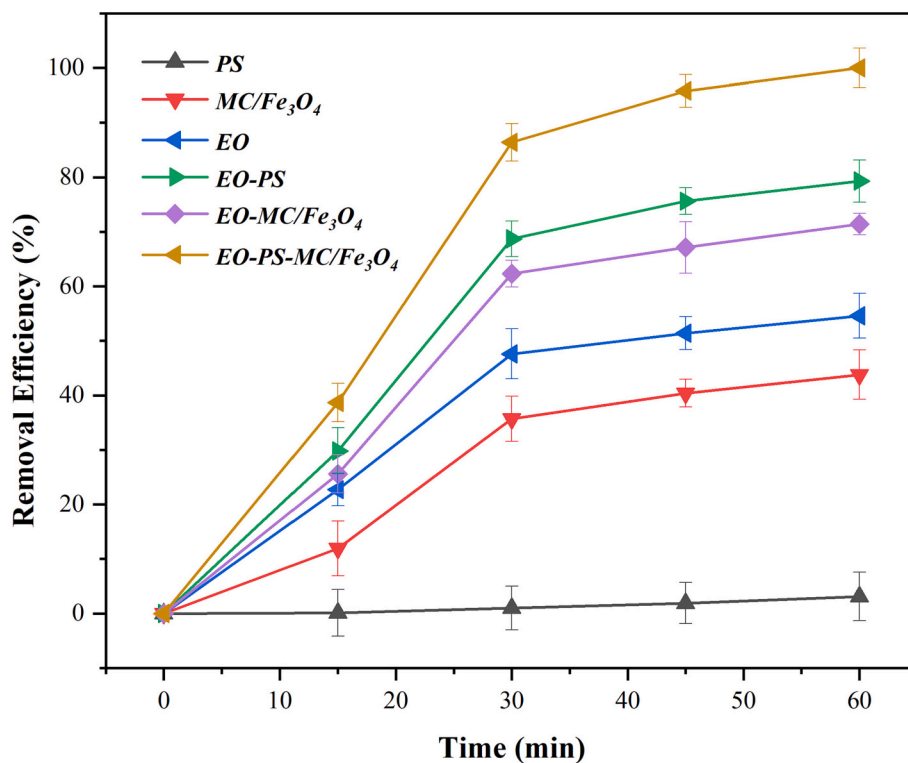


Fig. 10. Role of processes involved in diazinon removal (Initial diazinon concentration 10 mg/L, current density 3.54 mA/cm² and pH 3) Anode and cathode and absorption process by PS and MC/Fe₃O₄ (initial diazinon concentration 10 mg/L, pH = 0.5 ± 3 and no current).

Declaration of competing interest

The authors declare that they have no competing interests.

Data availability

The data have been presented in the manuscript

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