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Enhanced treatment of aqueous solutions from fenamiphos pesticide using electrocoagulation

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ABSTRACT

The purpose of the present work is to study the effectiveness of electrocoagulation method for the removal of organ phosphorus fenamiphos pesticide from aqueous solutions using iron and carbon (Fe-C) electrodes. The influence of several experimental parameters (e.g. initial pesticide concentration, pH, type of electrolyte, current density, temperature and reaction time) on the performance of electrocoagulation (EC) process for the removal of fenamiphos was investigated. The results showed that the removal efficiency reached to 90% at optimal conditions i.e. pH = 6.7, inter electrode spacing = 1 cm, operating time = 60 minutes and current density = 18.5 mA/cm^2, initial concentration of 50 mg/L, and temperature of 20 °C. These results imply that the maximum removal of fenamiphos from the aqueous solution can be achieved by EC process.

KEYWORDS: electrocoagulation, iron, carbon, fenamiphos, pesticide, water treatment.

INTRODUCTION

Owing to the intensive agriculture within the last three decades, the varieties of pesticides employed have increased considerably. The presence of these chemicals in groundwater, streams, rivers, lakes, and wastewater effluents may present serious problems to the environment, human health, and the equilibrium of ecosystems [1]. Fenamiphos (ethyl 4-methylthio-m-tolyl isopropylphosphoramidate) belongs to the family of organophosphorus pesticides (OPPs). This group is one of the chemical pesticides now widely used in agriculture, and account for more than 36% of the total world market of chemical pesticides [2]. Fenamiphos can be applied at different stages of plant growth such as pre-planting, pre- and post-harvest on a variety of plants including vegetables, citrus and others [3]. Fenamiphos and its major metabolites, fenamiphos sulfoxide and fenamiphos sulfone, are very highly toxic *via* the oral route, with reported LD50 values of 2 to 19 mg/kg in the rat. The inhalation toxicity of the compound is also high, with reported inhalation LC50 values in rats of 0.11 to 0.17 mg/L [4, 5]. Different technologies have been reported for the treatment of water and wastewater such as: nanotechnology biodegradation [6], photolysis and photodegradation [7] and photocatalytic degradation [8, 9]. An interesting alternative to these methods is the electrocoagulation (EC). EC is an electrochemical method for treating polluted water, which has been successfully applied for treatment of soluble or colloidal pollutants, such as wastewater containing heavy metals, emulsions and suspensions [10]. EC is considered one of the most effective methods for water treatment [11, 12]. The present work focuses on the removal of organophosphorus fenamiphos pesticide from aqueous solution by electrocoagulation process using Sacrificial Anodes.

MATERIALS AND METHODS

Chemicals

The pesticide used in the present work was fenamiphos pesticide solutions which were

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prepared by dissolving a commercially available pesticide in distilled water. Commercial fenamiphos of a concentration of 400 g L^{-1} was used to prepare a stock solution of pesticide (1000 mg/L) by dissolving a specific quantity of the pesticide in distilled water and suitably diluting to the required initial concentrations. Different standard solutions of the pesticide with concentration from 30-150 mg L^{-1} were prepared to measure its removal at different conditions. The properties of the fenamiphos are given in Table 1. All chemicals used, such as sodium chloride, sodium sulfate, sodium carbonate, potassium chloride, sodium fluoride, sodium hydroxide, sulfuric acid, potassium dichromate, were of analytical grade and purchased from Merck. Distilled water was used for the preparation of solutions. The pH of the working solution was adjusted to the desired values with 0.1N HCl or 0.1N NaOH.

Equipment and procedures

The electrocoagulation unit consists of a 100 ml electrochemical reactor with carbon-iron electrode (cathode and anode) with an effective surface area of 5.4 cm^2. The electrodes were 10 mm × 10 mm and inter electrode distance was 1 cm. The electrodes were positioned vertically and parallel to each other. The current density was maintained constant by means of a precision DC power supply, model (DZ040019) EZ Digital Co. Ltd. (Korea). The pesticide concentration was determined using a double-beam UV-Vis spectrophotometer, model UV 1601 from Shimadzu (Japan) at 249 nm. Hot Plate (model HB502, BIBBY STERILIN LTD. (U.K.)), a pH meter (model AC28, TOA electronics Ltd., (Japan)) and Water bath (model SB-650, Tokyo Kikakkai CO. Ltd., (Japan)) were used during the experimental process. The schematic diagram of the experimental set up is shown in Figure 1.

Analysis

The removal efficiency of fenamiphos was measured with the double-beam UV-visible spectrophotometer at λ_{max} = 249 nm using a calibration curve with standard error ± 0.5%. To calculate the removal efficiency of fenamiphos pesticide from water in this experiment the following equation was applied:

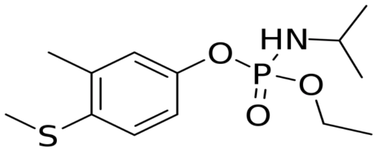
$$\%E = [(A_0 - A) / A_0] \times 100 \quad (1)$$

where A_o and A are absorbance values of pesticide solutions before and after treatment, respectively at λ_{max} [10].

Mechanism of electrocoagulation process

Figure 2 presents the mechanism of electrocoagulation process. In the EC process, the coagulants were generated *in situ* as a result of electrically dissolving the consumable carbon-iron

Table 1. Properties of fenamiphos.

Pesticide	**Fenamiphos**
IUPAC name	((*RS*)-*N*-[Ethoxy-(3-methyl 4-methylsulfanylphenoxy)phosphoryl]propan-2-amine
Chemical structure	
Solubility in water	400 mg/L
Chemical formula	$C_{13}H_{22}NO_3PS$
Molecular weight (g/mol)	303.40 g/mole
λ_{max}	249 nm

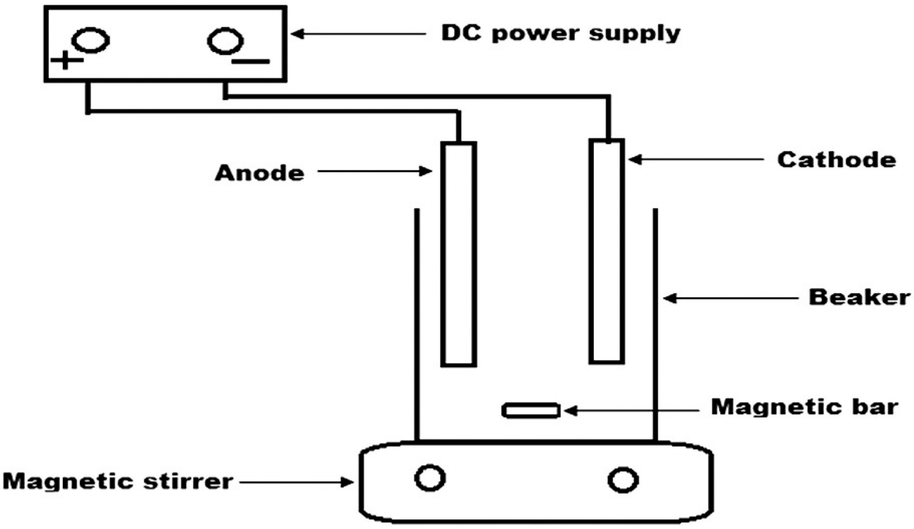


Figure 1. Experimental setup included magnetic stirrer, magnetic bar, beaker, cathode, anode and DC power supply.

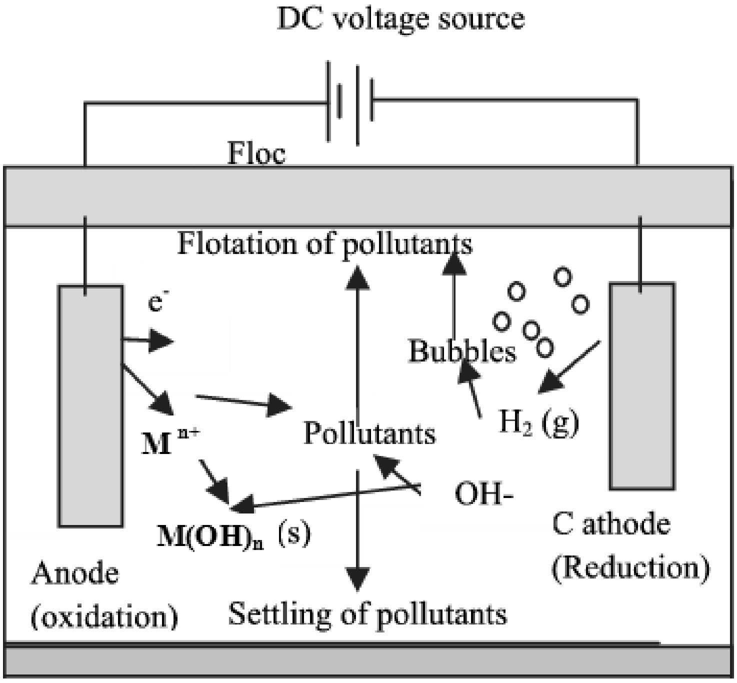


Figure 2. Mechanism of electrocoagulation process.

(C/Fe) electrodes. The ion generation takes place at the anode; hydrogen gas is released from the cathode [12].

The water contaminants are treated either using chemical reactions and precipitation or by physical and chemical attachment to colloidal materials being generated by the electrode erosion. They are then removed by electroflotation, sedimentation, or filtration. A current is passed through a metal electrode, oxidising the metal (M) to its cation (M^{n+}). Simultaneously, water is reduced to hydrogen gas and the hydroxyl ion (OH^-). Electrocoagulation thus introduces metal cations *in situ*, electrochemically, using sacrificial anodes [13, 14].

Reaction mechanism of EC

At the anode:

$$4Fe_{(s)} \rightarrow 4Fe^{+2}_{(aq)} + 8e^- \quad (2)$$

$$4Fe^{+2}_{(aq)} + 10\ H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe\ (OH)_{3(s)} + 8H^+_{(aq)} \quad (3)$$

At the cathode:

$$8H^+_{(aq)} + 8e^- \rightarrow 4H_{2(g)} \quad (4)$$

Overall

$$4Fe_{(s)} + 10\ H_2O_{(l)} + O_{2(g)} \rightarrow 4Fe(OH)_{3(s)} + 4H_{2(g)} \quad (5)$$

RESULTS AND DISCUSSION

Effect of electrolyte concentration

Increasing the electrolyte concentration leads to the increase in solution conductivity which has an influence on current generation and energy consumption. Many researchers have found NaCl as the best supporting electrolyte [15]. Figure 3 presents the effect of sodium chloride on the removal efficiency of fenamiphos at 60 min using (C/Fe) electrodes at initial concentration of 50 mg/L, current density of 18.5 mA/cm^2, pH of 6.7 and temperature of 20 ^{o}C. Figure 3 shows that the best result was obtained at 1 g/L NaCl concentrations. At this parameter the fenamiphos removal efficiency reached 90% using (C/Fe) electrodes.

Effect of current density

The applied current is a significant parameter that affects the treatment efficiency of the electrocoagulation degradation method [16, 17]. The influence of the variation of this parameter between 9-55 mA/cm^{-2} on the removal efficiency of fenamiphos at 60 min using C with Fe at initial concentration of 50 mg/L, NaCl concentration of 1 g/L, pH of 6.7 and temperature of 20 ^{o}C was examined. Figure 4 indicates that a current of 18.5 mA/cm² gives fenamiphos a removal efficiency of 90%. This result means that when the current density increases, the efficiency of ion production on the anode and cathode increases. Accordingly there is an increase in coagulant generation which leads to increase in pesticide removal [18, 19].

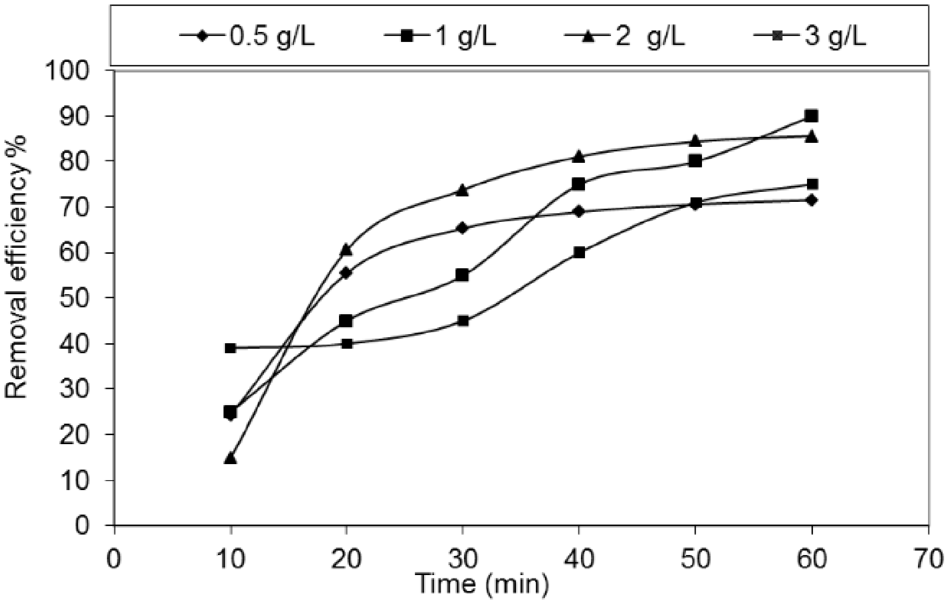


Figure 3. Effect of electrolyte concentration on the removal efficiency of fenamiphos using C/Fe electrodes.

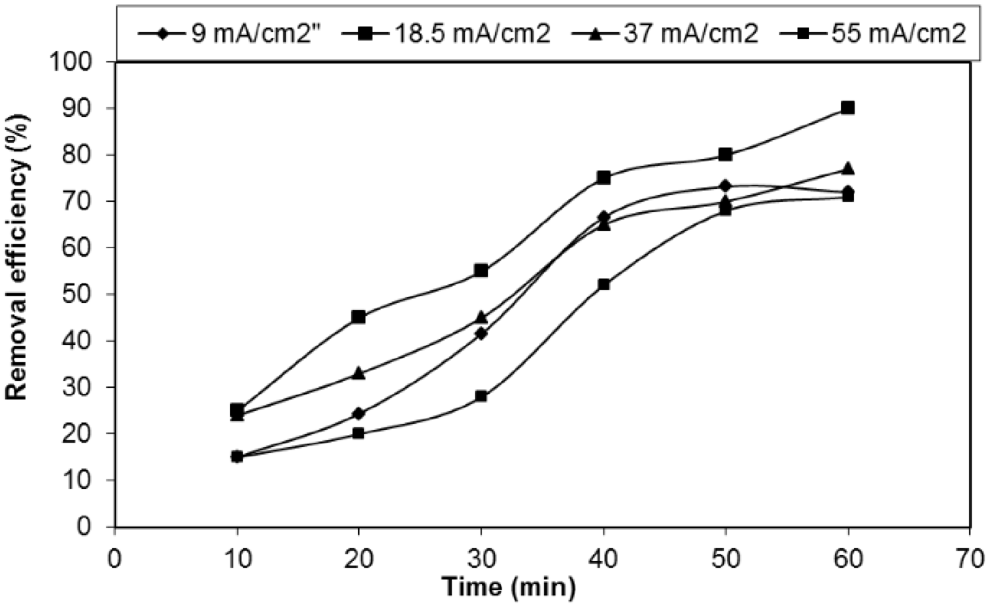


Figure 4. Effect of current density on the efficiency of fenamiphos using C/Fe electrodes.

Effect of pH

The pH is an important operating factor or essential parameter that affects the efficiency and performance of electrocoagulation [17, 20]. A series of experiments were carried out to evaluate the effect of initial pH using solutions containing a sample with an initial pH varying in the range 2.5-8 to show how pH will affect the electrocoagulation efficiency in removing the studied pesticide.

The removal efficiency of the pesticide was low in acidic medium, meanwhile, in neutral and alkaline medium the removal efficiencies were much higher due to the formation of hydroxide species which adsorb the pesticide molecules and cause the increase of the removal efficiency. The percentage removal was increased by increasing the pH. From Figure 5 it can be observed that below pH 2.5 there is a decreasing trend in adsorption whereas the maximum adsorption of fenamiphos pesticide is observed at pH 6.7.

Effect of temperature

Studying the effect of temperature on the removal of pollutants through EC is very important because of the relation between adsorption and temperature. Effect of temperature ranging from 10 to 40 °C on the removal efficiency of fenamiphos at initial concentration of 50 mg/L, current density of 18.5, pH of 6.7 and NaCl concentration of 1 g/L was studied. Figure 6 indicates that the removal efficiency was optimum at 20 ^{o}C. At temperature between 30-40 ^{o}C, the current efficiency begins to decrease. In this case, the volume of colloid M(OH) decreases and pore production on the metal anode will stop [14].

Effect of the electrolyte type

Figure 7 illustrates the effect of electrolyte type on the removal efficiency of fenamiphos at 60 min using C/Fe electrodes at a current density of 18.5 mA/cm^2, pH of 6.7, inter electrode distance of 1 cm and temperature of 20 ^{o}C in the presence of different supporting electrolytes including NaCl, Na_2SO_4, KCl, and Na_2CO_3. According to Figure 7 the pesticide removal at NaCl is better than KCl, Na_2CO_3 and Na_2SO_4. Na_2SO_4 and NaF electrolytes showed the least efficiency in the degradation of the pollutant. This may be attributed to the formation of an adherent film on the anode surface which poisons the electrode surface. Also, these electrolytes do not contain chloride ions (Cl^-) in their structures and may form stable intermediate species that could not be

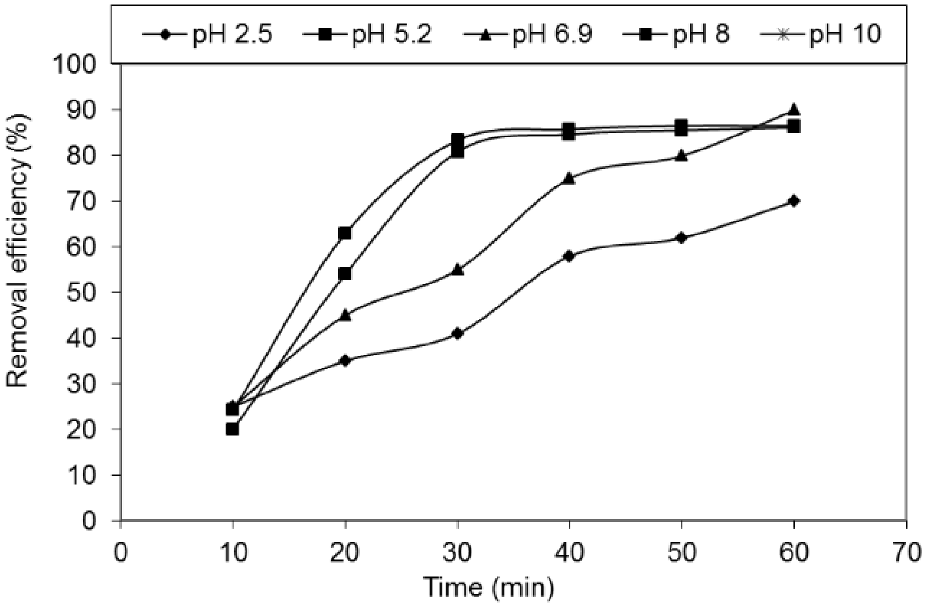


Figure 5. Effect of pH on the removal efficiency of fenamiphos using C/Fe electrodes.

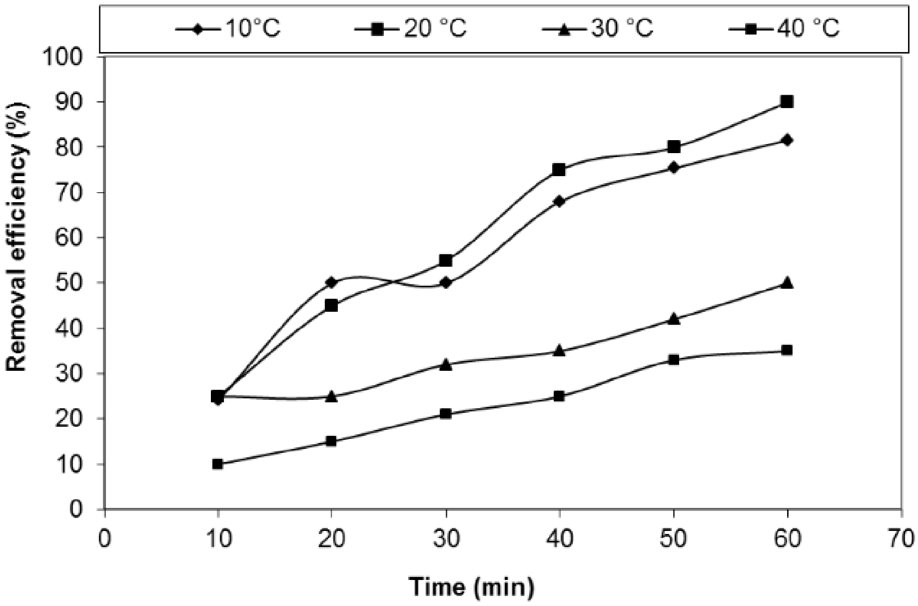


Figure 6. Effect of temperature on the removal efficiency of fenamiphos using C/Fe electrodes.

oxidized by direct electrolysis. These observations were also confirmed in another study [21].

Effect of initial pesticide concentration

To determine the influence of initial pesticide concentration on the removal efficiency of the tested pesticide using electrocoagulation, different initial concentrations in the range of 30-150 ppm were tested using C/Fe electrodes at a current density of 18.5 mA/cm^2, pH of 6.7, inter electrode distance of 1 cm, NaCl concentration of 1 g L^{-1} and temperature of 20 ^{o}C.

Figure 8 presents the effect of the initial pesticide concentration on the removal efficiency. It was found that when the initial pesticide concentration increases, the removal efficiency decreases due to the insufficient amount of the coagulant produced which adsorbs all pesticide molecules. Accordingly, pesticide removal decreases. The maximum removal was obtained at initial concentration of 50 mg/L.

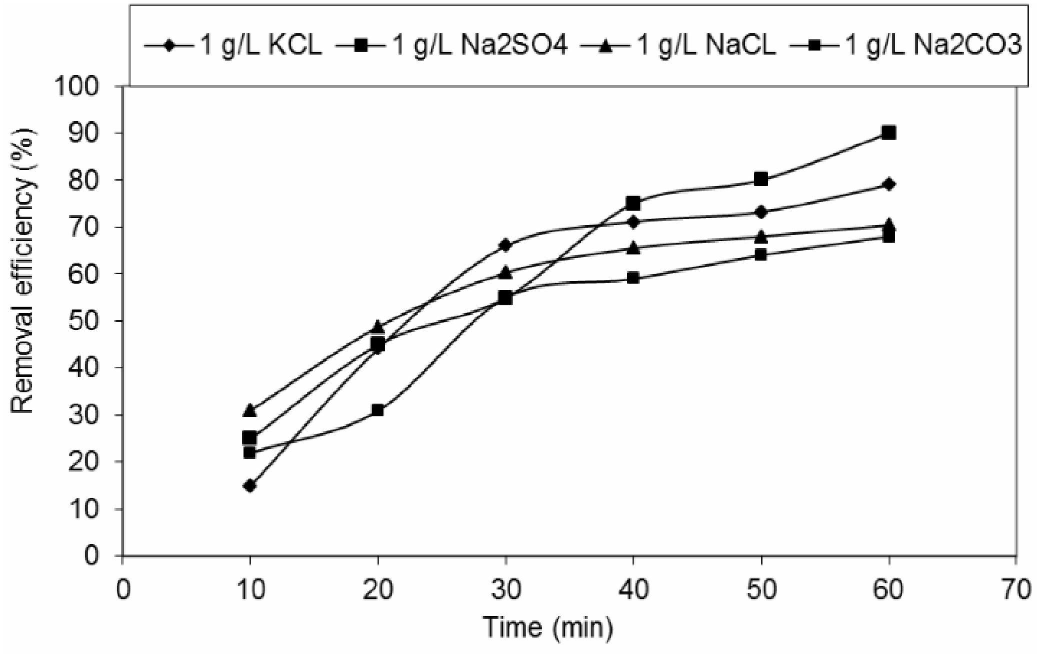


Figure 7. Effect of type of electrolyte on the efficiency of fenamiphos using C/Fe electrode.

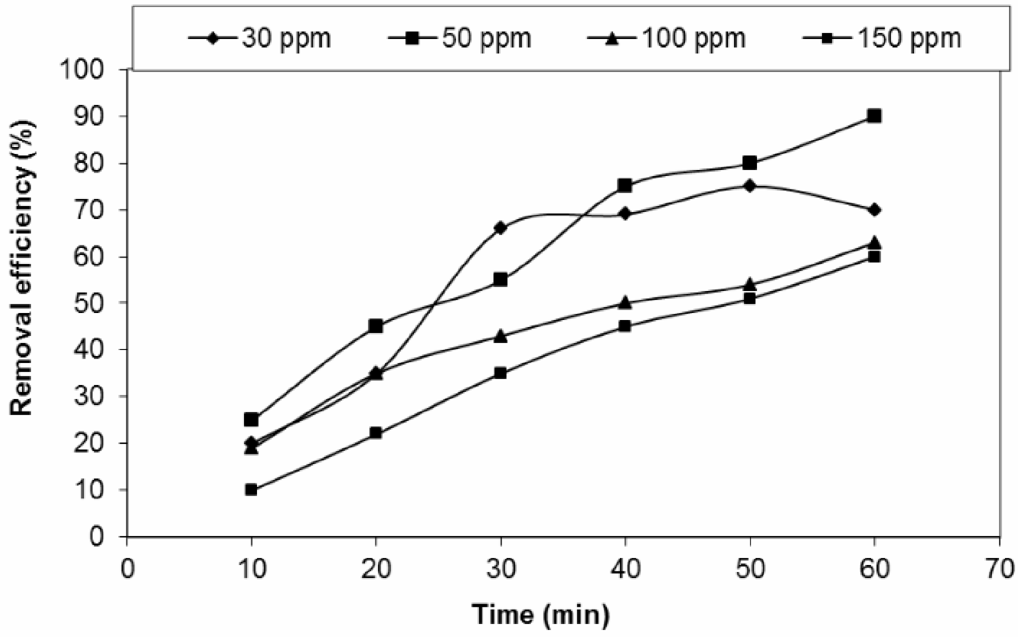


Figure 8. Effect of initial concentration on the removal efficiency of fenamiphos using C/Fe electrodes.

CONCLUSION

1. This study mainly focuses on the process of electrocoagulation (EC) for the removal of fenamiphos pesticide from aqueous solution using carbon-iron electrode (as cathode and anode).
2. The effects of some parameters, such as initial pH, initial pesticide concentration, current density, type of electrolyte, and temperature, on the removal efficiency of the pesticide were investigated.
3. The results showed that the best achieved removal efficiency for fenamiphos using the EC was 90% using C/Fe electrodes at 60 min at the following operating conditions: an initial pH of 6.7, initial pesticide concentration of 50 mg/L, current density 18.5 mA/cm^2, salt concentration of 1 g/L and temperature of 20 ^{o}C.
4. The results indicate that the EC process using carbon electrodes seems to ensure an efficient treatment method to remove pesticides from water.

CONFLICT OF INTEREST STATEMENT

No conflicts of interest.

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