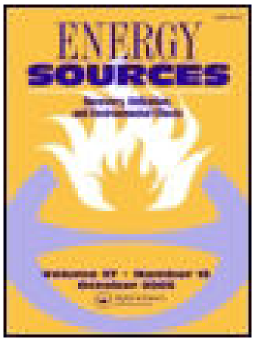

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Advance electrochemical oxidation of fipronil contaminated wastewater by graphite anodes and sorbent nano hydroxyapatite

Ramya Thangamani[a], Muthukumar Muthusamy[b], Premkumar Manickam Periyaraman[c], Amudha Thanarasu[c], Thiruselvi Devaraj[c], Anuradha Dhanasekaran[c], and Subramanian Sivanesan[c]

[a]Environmental Engineering Laboratory, Department of Environmental Sciences, Bharathiar University, Coimbatore, India; [b]Department Environmental Science, Central University of Kerala, Kasaragod, India; [c]Department of Applied Science & Technology, Alagappa College of Technology, Anna University, Chennai, India

ABSTRACT

Degradation of $C_{12}H_4Cl_2F_6N_4OS$ phenylpyrazole insecticide (Fipronil) by advance electrochemical oxidation in aqueous water solution was studied. The process efficiency was figured based on the COD, chloride, and fluoride reduction from fipronil. Further, we tried to highlight the importance of nano-hydroxyapatite (n-Hap) as a cost-effective nano sorbent for removal of fluoride from fipronil. From the advance electrochemical oxidation experiment, it was found that the COD removal was 79%, chloride 52%, and fluoride 80%. The intermediate of fipronil compounds was examined by GC-MS. The final results conclude that advance electrochemical oxidation process was effective for removal of fipronil synthetic wastewater.

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KEYWORDS
COD; degradation; fipronil; fluoride; nano hydroxyapatite

Introduction

Water treatment technology is increasingly focusing its attention on developing and improving methods of degrading pesticide-contaminated wastewater. As new pesticides arrive on the scene, their applications escalate at the field level every day. Consequently, the pollution levels sky-rocket in the wake of such large-scale pesticide usage, chiefly affecting the waterbodies in the environment. The most popular among the several pesticide compounds available today is fipronil (5-amino-1-(2, 6-dichloro-4-(trifluoromethyl) phenyl)), otherwise termed phenyl pyrazole. It finds use principally as a means of protection of the cash crops and most liberal-leafed plant species (Narahashi et al. 2007). Similar to most pesticides, fipronil is very harmful to the mammalian species and considered a powerful poison to humans (Barbier, Arreola-Mendiza, and Del Razo 2010). Fipronil contains fluoride as the initial constituent pollutant. While fluorosis has been regarded as a disease endemic to tropical climes, this is not fully true. Excessive exposure to fluoride induces susceptibility to fluorosis in all species, causing permanent bone decay and tooth tissue damage, and semi-permanent injury to the brain, liver, thyroid, and kidney (Gazzano et al. 2010). Table 1 shows comparison of electrooxidation process by graphite electrode and other electrode. In light of this knowledge, therefore, much care has been taken during the holocene years to develop practical and economical defluoridation techniques for wastewater treatment. Several oxidation methods have been used to treat pesticide-contaminated wastewater. During the recent years, the electrochemical technique has grabbed more attention than any other, for its higher efficiency when compared with the other methods (Asami et al. 1999; Hachami et al. 2010; Pozzo et al. 2005; Rabaaoui et al. 2013). In this work, hydroxyapatite was applied as a nano sorbent for removal of fluoride from man-made fipronil

CONTACT Subramanian Sivanesan sivanesh1963@gmail.com Department of Applied Science & Technology, Alagappa College of Technology, Anna University, Chennai, India.

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Table 1. Comparison of electrooxidation process by graphite electrode and other electrode.

Electrodes	Pollutants	Optimum pH	Optimum Current Density	% COD Removal	References
Graphite	Fipronil	9.0	7.5 $mAcm^{-2}$	78%	
Mixed oxide coated titanium mesh and stainless steel	methyl parathion, atrazine and triazophos	6.0	5A dm^{-2}	76%	Balakrishnan, Seeni Meera, and Venkatesan (2011)
Iron chips and granular activated carbon	Industrial pesticide waste Water	8.3	2 A	60.5%	Cheng et al. (2007)
Ti/Pt	Phosalone, azinphosmethyl and methidathion	5.0	5 kWh· kg^{-1}	65%	Vlyssides et al. (2004)
Dimensionally stable anode	Textile Dye	5.0	5A dm^{-1}	52.63%	AhmedBasha et al. (2012)
Graphite electrodes	Domestic wastewater	7.7	15 V	70%	Akarsu, Kıdeyş, and Kumbur (2017
Copper electrodes	Pharmaceutical waste water	7.0	12 V	68.29%	Patel, Vyas, and Patel (2016)
Three-dimensional electrodes	2-diethylamino-6-methyl-4-hydroxypyrimidine	3.0	15 V	35.17%	Ming et al. (2015)
BDD	5-butyl-2-(ethylamino)-6-methyl-4-pyrimidinyl dimethyl sulfamate	6.2	60 $mAcm^{-2}$	74.0%	ID El Mouden et al. (2012)

(pesticide)-rich wastewater. The hydroxyapatite medium is composed of a carbon structure which includes porous hydroxyapatite matrix (crystalline calcium phosphate hydroxide, which liberates ions that can be instantly replaced by fluoride ions). In this paper, we investigate and propose a highly progressive electrochemical oxidation process utilizing the hydroxyapatite as a supporting catalyst to enable the graphite electrode anodes in fipronil removal.

Experimental

Electrochemical reactor

An electrochemical oxidation reactor of 12.5 cm length, 10 cm diameter, and about 200 mL capacity, as well as a cylindrical glass trough, were utilized in the current study. In this study, 2 electrodes were placed under the vessel to enable stirring using a Teflon-coated magnetic paddle. The electrochemical oxidation cell was placed on a magnetic stirrer, and stirring was maintained uniformly for all the experiments. Figure 1 shows the conventional diagram of the electrochemical cell batch type and electrode assembly. Graphite in sheet form was utilized as the anode. A two graphite-sheet set (one each for the anode and cathode) acted as the electrodes. The magnetic stirrer maintained the solution in a state of agitation during the experiment. Spacers between the anode and cathode were used to prevent short-circuiting. Between the anode and cathode, the disruption was maintained at 1 cm to reduce the ohmic loss. The respective terminals of the DC rectifier were connected

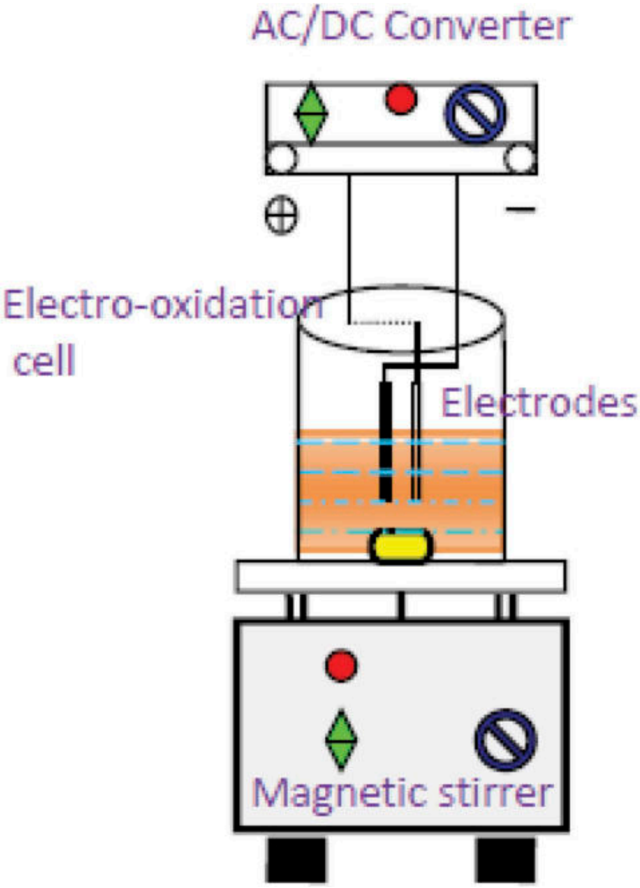

Figure 1. Schematic diagram of batch-type electrochemical cell.

to the anode and cathode conducts. The DC rectifier was fitted with a digital ammeter and voltmeter and connected to a stabilized power source electric power.

Reagents and materials

In this study, the chemicals utilized are listed: sodium chloride (NaCl), ferrous ammonium sulfate ($(NH_4)2SO_4FeSO_46H_2O$), potassium dichromate ($K_2Cr_2O_7$), mercuric sulfate ($HgSO_4$), silver nitrate ($AgNO_3$), potassium chromate, zirconyl chloride octahydrate ($ZrCl_2.8H_2O$), hydrochloric acid (HCl), anhydrous sodium fluoride and fipronil (5-amino-1-(2,6-dichloro-4-(trifluoromethyl) phenyl)), all being of analytical grade. Graphite anodes having 6 mm thickness were obtained from titanium and tantalum products, Chennai, India.

Parameters

The percentage of pesticide degradation factor was determined by assessing the COD. The COD was estimated by analyzing the open reflex method. The chemical oxygen demand test was done via the standard method of water and wastewater testing (APHA 1995). The titration method was used to determine the chloride, while the colorimetric method was used to assess the fluoride with the spectrophotometer at 570 nm.

Characterization of the nano hydroxyapatite

Characterization of nano-hydroxyapatite X-ray diffraction (XRD) analysis was done using a PAN analytical X-ray diffractometer X'PERT PRO (the Netherlands). Morphological characterization of the samples was performed with a scanning electron microscope (SEM, Hitachi-S4800). The presence of the functional groups concerned in their raw stages was studied using Fourier Transform Infrared Spectroscopy, FTIR (Perkin Elmer, USA) (Table 2). The FTIR spectra were recorded for the powdered form of the sample (Figures 2, 3, and 4).

Results and discussion

Various pH on COD removal

The pH of the sample was a significant factor in treating wastewater. For anodic oxidation, several studies are present that estimate the solution pH, but the findings showed wide variations and even conflicting ones according to the different organic structures and electrode materials involved (Bouya et al. 2013). The fact that sample pH exerts a definite influence on pesticide electrooxidation has been understood in several earlier works (Errami et al. 2011). A few authors mentioned that the oxidation process seems to be more effective when the medium is acidic. However, other studies mentioned that the process efficiency was better in an alkaline medium. According to this literature, this issue best understood by the fact that the influence exerted by the pH is strongly dependent upon the characteristics of the pesticide under investigation and those of the defending electrolyte.

Table 2. Some important functional groups assignments of hydroxyapatite nano particles.

S.No	Wave number	stretching mode	Functional group
(1)	3567.70	Ion stretching group	OH^-
(2)	1693.32	Carboxylates	CO_2
(3)	1035.76	Polysaccharides	CO
(4)	634.89	Alkyl halides	CBr
(5)	565.70	Alkyl halides	CBr

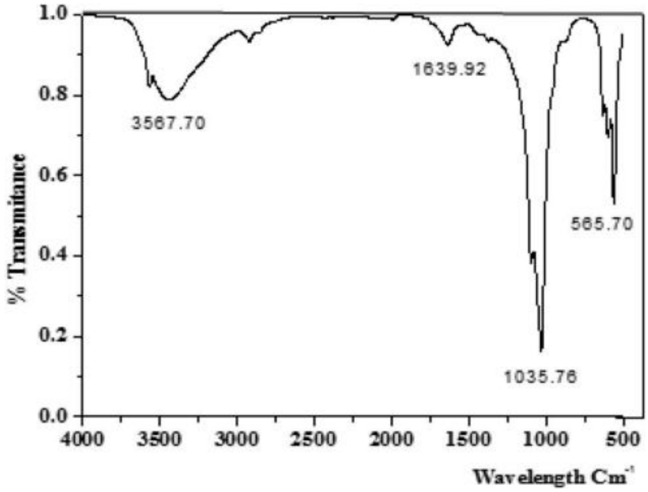

Figure 2. FTIR image on nHap.

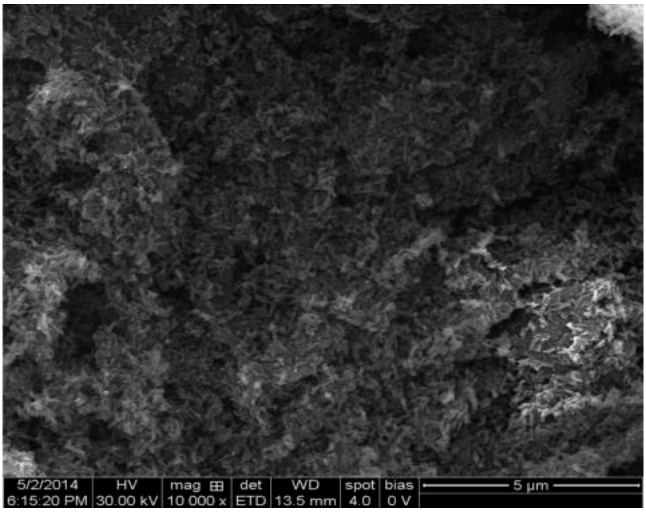

Figure 3. SEM image on nHap.

With the use of graphite electrodes, the effect of pH on the removal of COD via electrooxidation was analyzed. The experiments were done by altering the initial pH from 3 to 9 but maintaining the concentration of the supporting electrolyte at 2.5 g/L, and applying a current density of 2.5 mA/cm^2 and utilizing graphite electrodes, respectively. After 15 min, the samples were tested for COD removal efficiency and the results recorded are listed in Figure 5. It is evident that the maximum COD removal occurred at pH 9 (alkaline), and the COD removal was 48% using graphite electrodes. It was clear that the continuously rising high levels of the OCl^- radicals in the electrolytic cell triggered the pH increase. This pH gain resulting from pesticide removal was also reported by Errami et al. (2011) with BDD used as the anode to degrade the pesticide in sedimentary solutions (Errami et al. 2011; Salghi et al. 2011). According to Mohan, Balasubramanian, and Basha (2007), the response rate was lower in the acidic solutions because of the OH^- imbalance, and considerably greater in the basic solutions as the production of OCl^- ions supports the conducting reactions

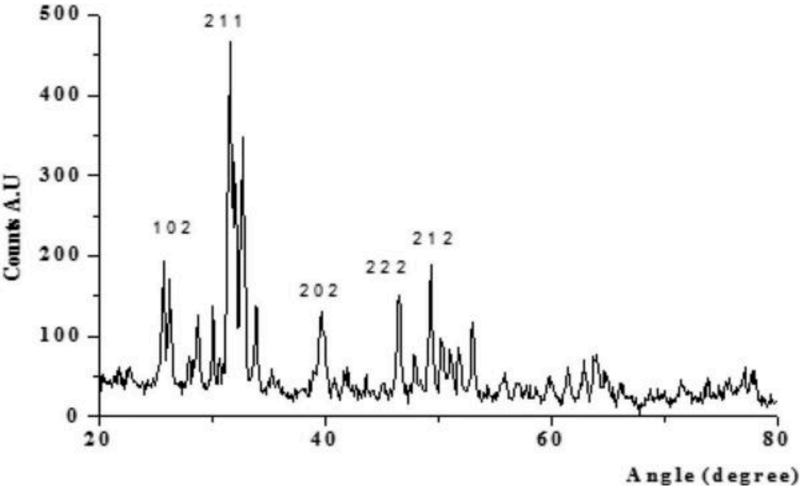

Figure 4. EDX image on nHap.

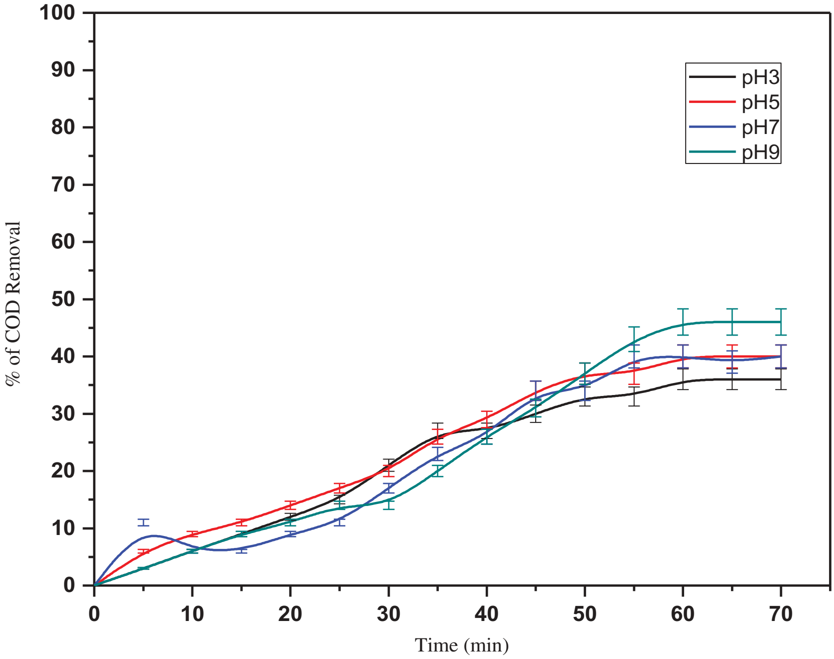

Figure 5. Various pH on COD removal.

involving Cl_2 (Mohan, Balasubramanian, and Basha 2007). Theoretically, basic condition (alkaline pH) of electrochemical oxidation could encourage the removal of the pollutants as they raise the Cl^- - Cl_2 - ClO^- - Cl^- redox circulation, and boost the indirect oxidation. The reason mentioned above is responsible for the maximum removal of COD at the basic pH level of 9.

Various pH on chloride removal

pH influences the chemical form of the oxidant present in the electrolyte. Electrolysis was performed at four different pH values between 3 and 9. Right through these processes, the electrochemical reactions occurring in the presence of the chloride ions can be represented as shown in the reactions mentioned below: (1–4)

$$2Cl^{-} + Cl(a) + 2e^{-}(\text{Standard potential of } Cl_2)\ (Eo = 1.40\,V) \tag{1}$$

$$Cl_{2(aq)} + H_2O\ +\ HOCl + H^{+} + Cl^{-}(\text{Eo of HOCl} = 1.49\,V) \tag{2}$$

$$HOCl\ +\ H^{+} + OCl^{-}(\text{Eo of } ClO^{-} = 0.89\,V) \tag{3}$$

$$\text{Coragen}\ +\ OCl^{-}\ \text{Intermediates}\ CO_2 + H_2O\ +\ Cl^{-} \tag{4}$$

Changes in the pH, control the equilibrium in the response (Eq…3); while the HOCl is predominant in the 3–5 pH range, the ClO^{-} was the major ions when the pH raised above 9.

The OCl^{-} and Cl_2 (aq) controlled oxidation process was to be more positive and stronger at basic pH., Figure 6. The balance of all of these developments produces an optimum NaCl concentration of around 59% of Cl_2 for the fipronil degradation at pH 9.

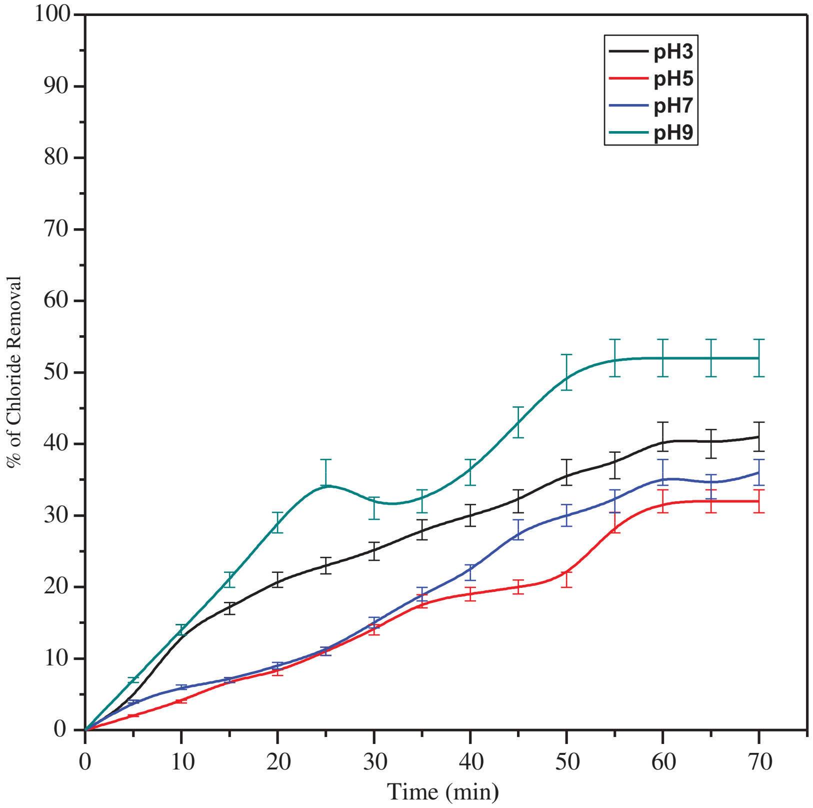

Figure 6. Various pH on chloride removal.

Various pH on fluoride removal

An investigation was done on the effect of pH in determining the fluoride adsorption onto nHap in the presence of graphite anodes at pH values of 3, 5, 7, and 9. The results were plotted, as indicated in Figure 7. At pH 3 it was clear that the maximum defluoridation capacity (69%) was attained, while the minimum was observed at pH9 (39%). A reduction in the degree of fluoride ion removal was noted besides the pH of the solution. One reason for the improved adsorption at low pH values may be the large number of H^+ ions released at this pH value. These neutralize the negatively charged OH^- ions at the adsorption surface, thus lowering the abundance of the fluoride ion diffusion. At the higher pH values, the adsorption decline may be potentially caused by the OH^- released in abundance, which increase the hindrance to the fluoride ion diffusion. When the pH of the solution is acidic, the fluoride anions are drawn to the positively charged nHap surface, because of the protonation of the nHap hydroxyl groups, thus encouraging the fluoride ions to collect at the surface. Therefore, a greater number of fluoride ions were drawn to the surface, raising the adsorption capacity of the nHap. As above the pH adsorption of fluoride anions was very slight because the nHap surface was negatively charged and it caused by the deprotonation of hydroxyl groups, inducing a natural repulsion between the fluoride anions and the nHap surface.

Various current density on COD removal

An influence the effect of current density on the electrochemical process has been discussed in several previous studies as a main affecting factor in the electrolysis process (Meaney et al. 2007). Degradation experiments were performed using 1000 ppm fipronil solution via electrooxidation utilizing 20 mg/L hydroxylapatite at various current densities (2.5, 5.0, and 7.5 mA/cm^2). The pollutants were oxidized selectively in the presences of the chemisorbed active oxygen, else they will become mineralized to CO_2 and H_2O. The efficiency of the current density achieved at higher amount of OCl^- production, it is more stable oxidant when compared with $HOCl^-$ (during alkaline pH). The high amount of OCl^- production caused degradation of pollutant into CO_2 and H_2O (Rodriguez et al. 2013). A high degree of

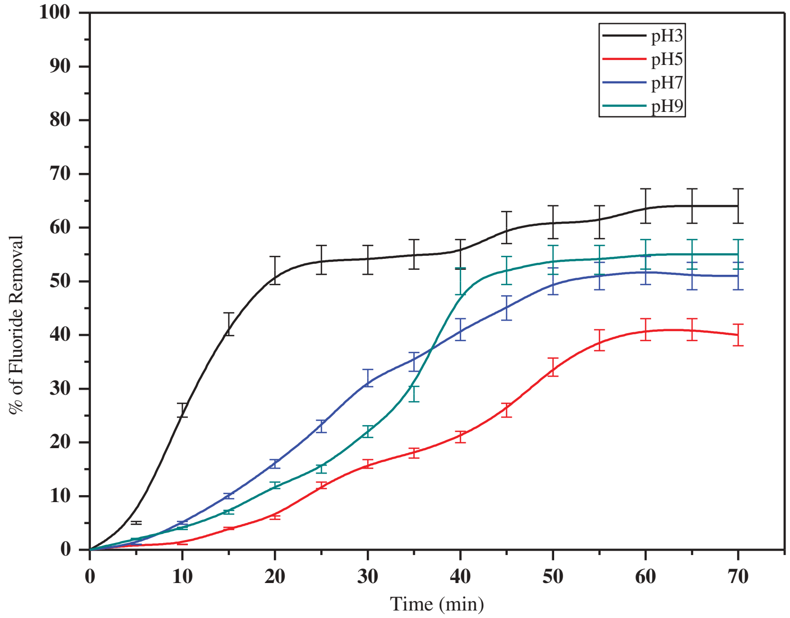

Figure 7. Various pH on fluoride removal.

removal was attained at the higher densities 7.5 mA/cm^2 within 60 min of electrolysis time. The COD removal attained a maximum of 74% with the higher density of applied current with 7.5 mA/cm^2 value within 60 min at pH9 as despite from Figure 8. This could be attributed to raise the rate of oxidant release at the current density where the rapid rate of organic removal occurred.

Various current density on chloride removal

Further increase of the current density was followed by a gradual increase in Cl$^-$ removal (Ghalwa, Gaber, and Munther 2012). A variety of current densities were applied to identify the optimum value for the chloride degradation. The optimum current density, at which the maximum chloride removal occurred was 7.5 mA/cm^2. This process was continued for 60 min at 25°C and pH 9 using graphite; the initial concentration of fipronil wastewater was 1000 mgL^{-1}, with NaCl at 2.5 g/L density. Electrooxidation was performed at 7.5 mA/cm^2 current density. At higher current densities the conduction between two electrodes was high within a short treatment time. Ghalwa et al. (2012) reported that the increase in current density during electrooxidation induces a rise in the chlorine produced. At this higher current density, an incredible theory of releasing OCl$^-$ ions to the pesticide solution is proposed. These reflections are conveyed in Figure 9. The maximum removal of chloride (56%) was achieved at the higher applied current density 7.5 mA/cm^2 within 60 min at pH 9 as depicted in Figure 9.

Various treatment time on COD removal

To reduce the power consumed and encourage the optimal electrochemical oxidation of fipronil, more experiments were performed by testing the various treatment times. The experiments were done on the percentage of COD removal as an operation of electrolysis time (30, 60, 90, 120, and 150 min) at a fixed current density of 7.5 mA/cm^2, electrolyte (NaCl) absorption of 2.5 mg/L and

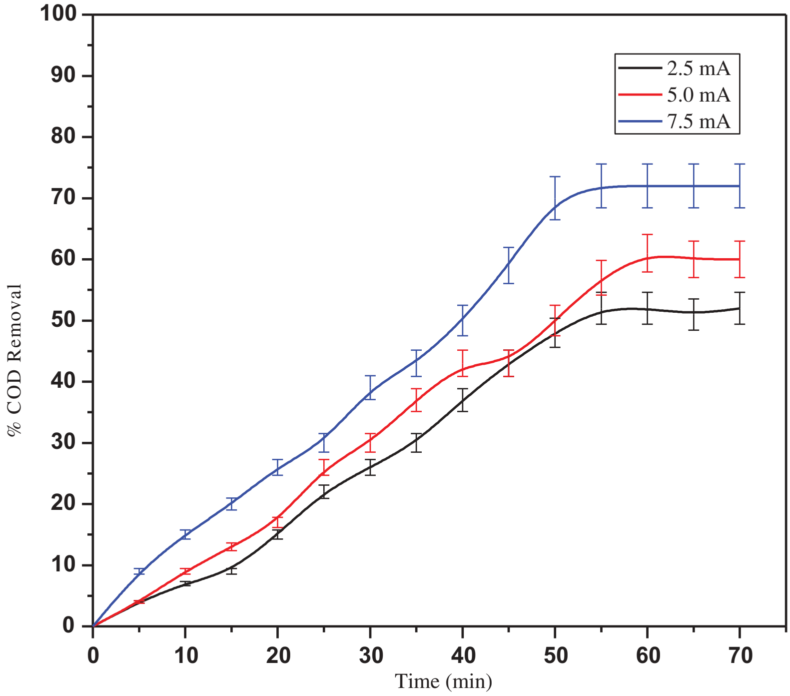

Figure 8. Various current density on COD removal.

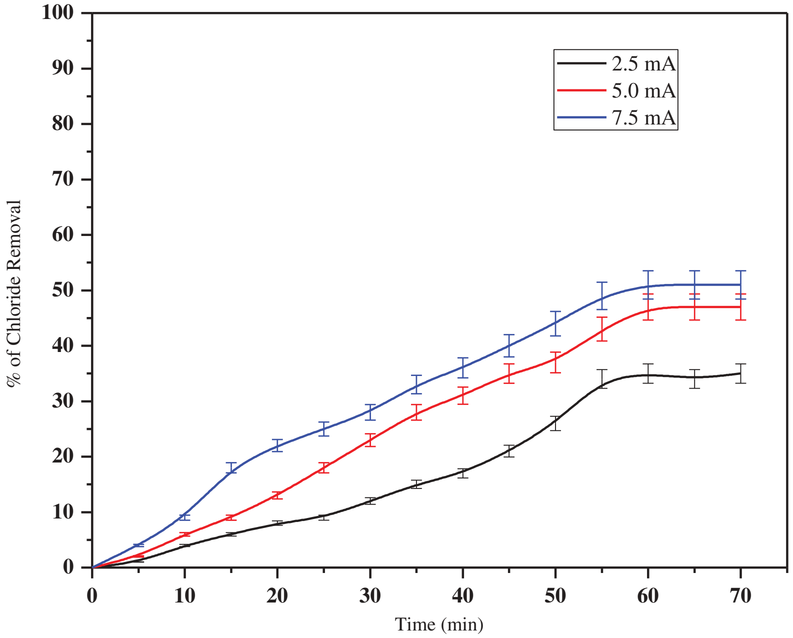

Figure 9. Various current density on chloride removal.

optimum pH 9. In presence of catalyst complete COD degradation occurred after 150 min of treatment time. The COD degradation was 57% at pH9 and current density of 7.5 mA/cm^2 in 60 min of treatment time. Within a treatment time of 150 min, the COD degradation was 69%. The whole, findings reveal that fipronil removal was directly proportional to treatment time. The rate of degradation was low at the beginning of the process and raised gradually to a monotonical value at the end of the process Figure 10.

Various treatment time on chloride removal

As the pH and current density were increased, the chloride removal also consequently increased. The treatment time for chloride removal by direct anodic oxidation may, to a certain degree, destroy the pollutants adsorbed on the anode surface. The series of reactions involving indirect oxidation during electrooxidation are shown in Eqs:

Anodic reactions

$$\rightarrow 2Cl^{-}Cl_2 + 2e- \tag{5}$$

$$\rightarrow 6HOCl + 3H_2O2ClO_3- + 4Cl^{-} + 12H^{+} + 1.5O_2 + 6e^{-} \tag{6}$$

$$\rightarrow 2H_2OO_2{+}4H + + 4e- \tag{7}$$

Bulk reactions:

$$\rightarrow Cl_2 + H_2OHOCl + H + Cl^{-} \tag{8}$$

$$\rightarrow HOClH^{+} + OCl^{-} \tag{9}$$

Cathodic reactions:

$$\rightarrow 2H_2O + 2e - 2OH^{-} + H_2 \tag{10}$$

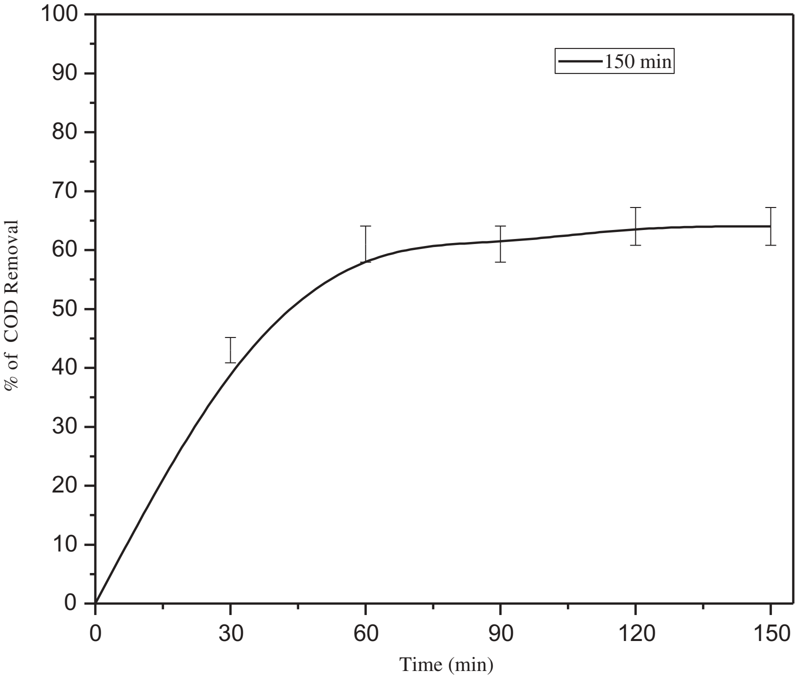

Figure 10. Various treatment time on COD removal.

$$\rightarrow OCl^- + H_2O + 2e^- Cl^- + 2OH^- \quad (11)$$

The hypochlorite (OCl^-) produced in Eqs. (5) and (6) is a strong oxidant which oxidizes sedimentary pesticide compounds. The anode material, current density, and chloride concentration were found to exert similar effects on the production efficiency of chloride/hypochlorite in the electrolysis process. The chloride removal efficiency is primarily dependent upon the density of the hypochlorite ions released by the electrodes, which in turn is a time-dependent process. When the length in time increases, the density of the chloride ions and their hydroxide flow also increase. The study was carried out by varying the electrolysis time up to 150 min at the supporting electrolyte concentration of 2.5 g/L with applied current density of 7.5 mA/cm^2 and at alkaline pH 9. The removal efficiency drastically increased in the first 60 min, reaching over 46% Figure 11. In latter, the degradation efficiency increased slightly decrease by 43% because of byproduct formation and again it reached 46% at 150 min.

Various treatment time on fluoride removal

Treatment time was observed to affect the fluoride removal by nano-hydroxyapatite. The treatment time curves seen in Figure 12 reveals the speedy adsorption of fluoride from 30 to 150 min, after which the adsorption rate gradually attained equilibrium at 150 min. Aggregation of fluoride molecules with the increase in treatment time and it almost impossible to diffuse deeper into the adsorbent structure at highest energy sates. This occurred because the mesopores get fully occupied and begin to resist the dispersal of the combined fluoride molecules in the adsorbents. To minimize the intake capacity and support optimizing the electrochemical fipronil oxidation, extra trials were conducted and different holding times were examined. Trials were conducted for the percentage of fluoride removal as a function of electrolysis time (30, 60, 90, 120 and 150 min) keeping the current density fixed at 7.5 mA/cm^2, and electrolyte (NaCl) concentration of 2.5 g/L with optimum pH 3. The maximum F^- adsorption occurred at 120 min (79%) of

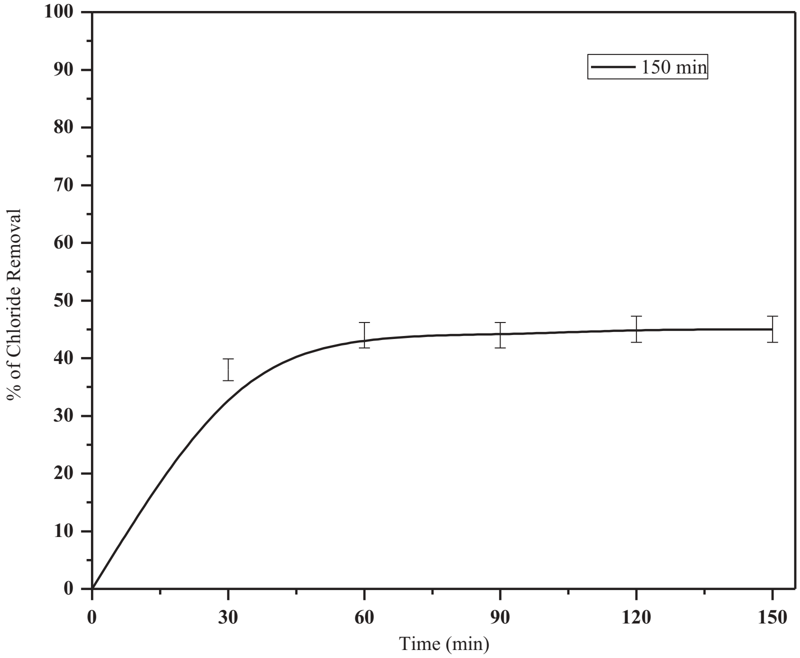

Figure 11. Various treatment time on chloride removal.

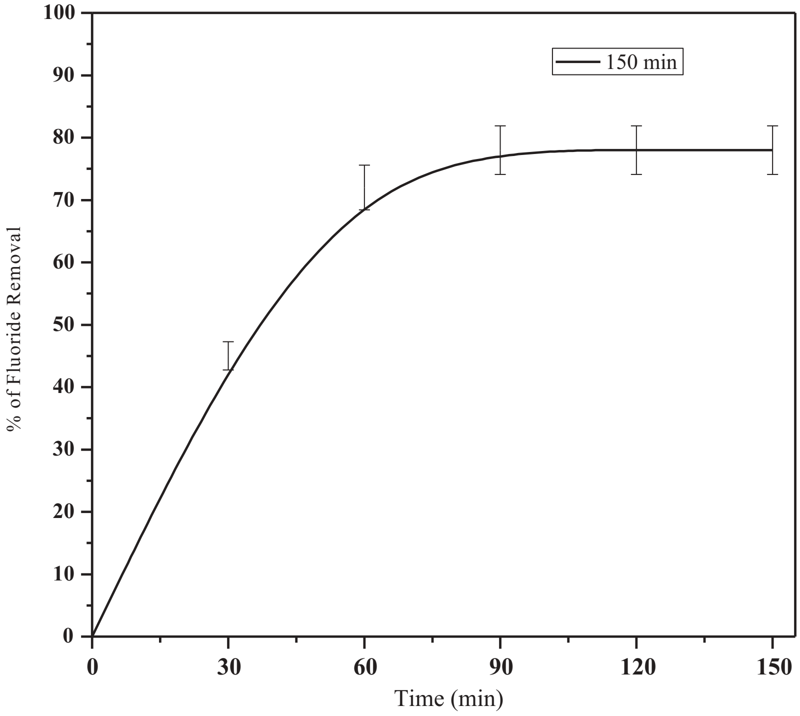

Figure 12. Various treatment time on fluoride removal.

the treatment time, current density was 7.5 mA/cm^2 within 60 min of treatment time. When the treatment time reached 120 min the fluoride degradation percentage was 80%, and it was maintained up to 150 min. The results definitely indicate that fluoride removal was primarily related to treatment time.

FTIR analysis

Figure 2 shows the comparison of the IR spectra of the untreated and treated pesticide effluents by the advanced electrooxidation process with nHap. The findings show that structural alterations have taken place in the electrolysis process. The characteristic pesticide effluent peak at 3356 cm^{-1} is caused by the N-H absorption of the atrazine molecule present in raw wastewater. Peaks noted at 1637 cm^{-1} were principally caused by the stretching absorption of the carbonyl (general) C = O groups. Besides, the peaks attained at 654.46 cm^{-1} are caused by the C–F stretch group's alkyl halide, respectively.

GC-MS analysis

The intermediate compound produced during the fipronil degradation process, utilizing a graphite-coated anode, was identified via GC-MS spectroscopy. The parts played by the electro catalyst and oxidation in COD removal are discussed. The chloride and fluoride; mainly attributed to the radicals, were primarily generated by the oxidant species (hydroxyl radical, hydrogen peroxide, hypochloric and hypochlorite ions depending on the pH) through electrooxidation. Table 3 lists the byproducts observed at 5 min with pH at 9 during the electrooxidation process. Figure 13 reveals that after 5 min of the oxidation process the important breaks up are released during the degradation process. The pesticide degradation and electrooxidation induce considerable mineralization which produces the substituted (N-N-disulfonyl-2,2-dichloro-1,1,1-trifluoro ethane,1,1-dichloro-1-fluoroethane, sulfonyl amide, sulfuryl fluoride, hydrogen sulfide) and other lower molecule compounds.

Conclusion

From the results, it is obvious that the fipronil removal was clearly more efficient when graphite anodes and nano hydroxyapatite were used. During electrooxidation, the maximum COD degradation and chloride and fluoride removal were achieved under acidic conditions. It is very clear that pH was a strong determinant in the electrooxidation processes. The removal rate was noted to rise by increasing the current density and treatment time. The GC–MS results prove that the maximum fipronil removal occurred at the higher molecular weight than at the lower molecular weight. Although the electrochemical methodologies effectively degraded the fipronil, the nanomaterial exerted a strong influence on the selection and the efficiency of the oxidation process.

Novelty of this study

A study on the efficiency of the electrode materials such as graphite, copper electrodes, mixed oxide coated titanium mesh and stainless steel, iron chips and granular activated carbon, Ti/Pt, dimensionally stable anode, copper electrodes, three-dimensional electrodes, and BDD was carried out through different electrochemical parameters in the degradation of the organic pollutants. Firstly, it has been

Table 3. List of intermediate compound present in fipronil degradation using electrooxidation process by graphite electrodes.

S.No	Compound	Molecular weight
(1)	N, N-disulfinyl ($C_4H_6O_6S2$)	214.216
(2)	2, 2-Dichloro-1,1, 1-Trifluoroethane ($CHCl_2CF_3$)	152.93
(3)	1, 1-Dichloro-1-fluoroethane ($C_2H_3Cl_2F$)	116.95
(4)	Sulfuryl fluoride (SO_2F_2)	102.06
(5)	Hydrogen sulfide (H_2S)	56.063

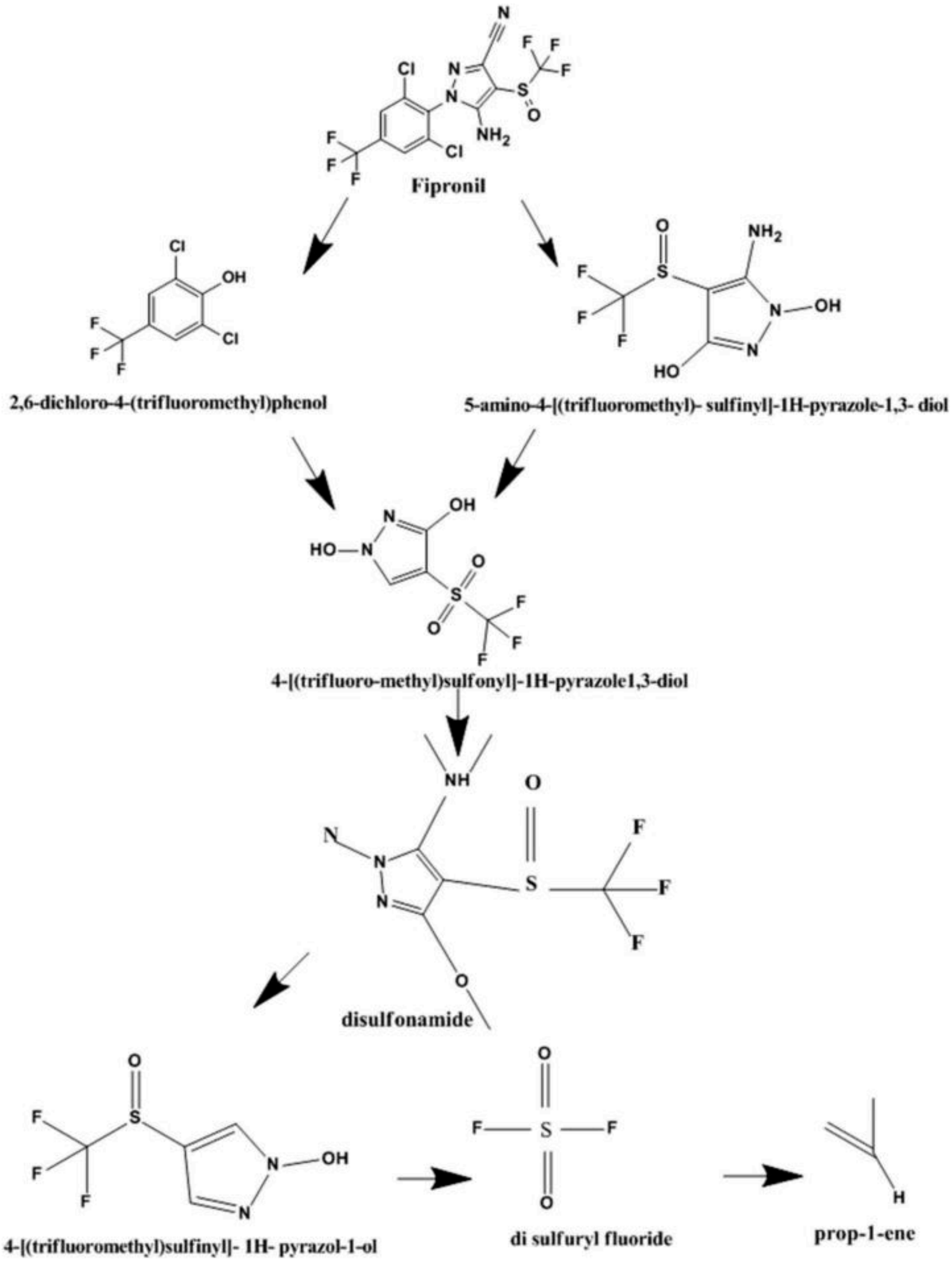

Figure 13. Fipronil degradation pathway on electrooxidation process by graphite electrodes.

proved that graphite electrode is more efficient than other electrodes because maximum removal of COD was achieved at 70 min while less than half of the initial organic pollutant was oxidized with other electrodes for the best conditions in the same electrolysis period. The efficiency of the electrolysis versus the current density was closer to 79% for graphite electrode using 7.5 $mAcm^{-2}$, as compared with other electrodes graphite consumes less current density when oxidized with organic pollutant. On the other hand, the obtained results point out that the graphite anode is the best anode material for the alkaline pH due to the generation of the high amount of different oxidants: hypochlorite's that permits not only the oxidation of organic pollutant but also its complete mineralization.

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