

Research Article

Comparison of Five Advanced Oxidation Processes for Degradation of Pesticide in Aqueous Solution

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Abstract

The study compared the technical efficiency and economic cost of five advanced oxidation processes (Fenton, UV photo-Fenton, solar photo-Fenton, UV/TiO₂/H₂O₂ and FeGAC/H₂O₂) for degradation of the pesticides chlorpyrifos, cypermethrin, and chlorothalonil in aqueous solution. The highest degradation in terms of COD and TOC removals and improvement of the biodegradability (BOD₅/COD ratio) index (BI) were observed to be (i) Fenton - 69.03% (COD), 55.61% (TOC), and 0.35 (BI); (ii) UV photo-Fenton - 78.56% (COD), 63.76% (TOC) and 0.38 (BI); (iii) solar photo-Fenton - 74.19% (COD), 58.32% (TOC) and 0.36 (BI); (iv) UV/TiO₂/H₂O₂ - 53.62% (COD), 21.54% (TOC), and 0.26 (BI); and (v) the most technical efficient and cost effective process was FeGAC/H₂O₂. At an optimum condition (FeGAC 5 g/L, H₂O₂ 100 mg/L, and reaction time of 60 min at pH 3), the COD and TOC removal efficiency were 96.19 and 85.60%, respectively, and the biodegradation index was 0.40. The degradation rate constant and cost were 0.0246 min⁻¹ and \$0.74/kg TOC, respectively. The FeGAC/H₂O₂ process is the most technically efficient and cost effective for pretreatment of the pesticide wastewater before biological treatment. Copyright © 2018 BCREC Group. All rights reserved

Keywords: Fenton; UV photo-Fenton; Solar photo-Fenton; UV/TiO₂/H₂O₂; FeGAC/H₂O₂; Pesticide; biodegradability index (BI)

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1. Introduction

Advanced oxidation process (AOPs) are commonly used for pretreatment of recalcitrant (non-biodegradable) solution or wastewater to improve biodegradability [1]. The Fenton process is typically a reaction between iron salts

and hydrogen peroxide (H₂O₂) to produce hydroxyl (OH[·]) radicals. This occurs due to the catalytic decomposition of hydrogen peroxide in acidic pH [2]. In the UV photo-Fenton and solar photo Fenton processes, the formation of OH[·] radicals is doubled by photo reactions of H₂O₂ and/or Fe³⁺ producing OH[·] radical either directly or by regeneration Fe²⁺ [3]. The effective UV wavelength is from 100 to about 400 nm, whereas solar wavelength extends from about 280 to above 550 nm. The UV/TiO₂/H₂O₂ photo-

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catalytic process is another alternative usually recommended due to the super photocatalytic oxidation potential, optical and electronic attributes, no possession of mass transfer property, operation at ambient conditions, low cost, large band gap, commercial availability, non-hazardous nature and photochemical stability [4-5]. The reaction mechanism of UV/TiO₂/H₂O₂ process has been given elsewhere [6]. FeGAC/H₂O₂ process was implemented in the degradation of wastewater. It employs the adsorption capacity of GAC with iron oxide coated on its surface. The additional presence of H₂O₂ enables the production of hydroxyl radicals to further increase the degradation efficiency when applied in wastewater treatment. Reuse of the GAC was up to six times [7].

The novelty of this study was the modification of classical Fenton process in order to treat pesticide wastewater. Thus iron sludge was not produced during the process, and operation cost was minimized. This study compared the technical efficiency and cost of five advanced oxidation processes various (Fenton, UV photo-Fenton, solar photo Fenton, TiO₂ photocatalytic (UV/TiO₂/H₂O₂) and FeGAC/H₂O₂) for degradation of a recalcitrant aqueous solution of the pesticides chlorpyrifos, cypermethrin, and chlorothalonil.

2. Materials and Methods

2.1 Chemicals

Hydrogen peroxide (H₂O₂) (30% w/w), ferric nitrate (Fe₃(NO₃)₃·9H₂O) and ferrous sulphate heptahydrate (FeSO₄·7H₂O) were supplied by R&M Marketing, Essex, U.K. The TiO₂ powder (anatase, purity >99%) was obtained from Fluka. The pesticides used in the preparation of the aqueous solution were purchased from a local commercial shop. The Calgon Corporation, Pittsburgh, USA supplied the granular activated carbon (GAC) used.

2.2 Fe-Granular activated carbon (FeGAC)

The GAC was blended to reduce it to 425 μm size. The preparation of the FeGAC was according to a previous study [7].

2.3 Analytical methods

The BOD₅ and COD measurements were done in accordance to known Standard Methods [8]. In an effort to minimize an interference of COD values obtained, pH was raised above 10 immediately the pretreatment (during the FeGAC/H₂O₂ process) was completed. This was to enable H₂O₂ to decompose to O₂ and H₂O [9-

10]. The total organic carbon (TOC) analyzer (Shimadzu) was employed to measure TOC, while pH meter (HACH sension 4) was used in measuring pH during the entire process. Nessler Method (Method 8038) was used to measure ammonia-nitrogen (NH₃-N) [11]. Total phosphorus (TP) was measured by PhosVer 3 Method (Hach, 2002). The YSI 5000 dissolved oxygen meter was used to measure dissolved oxygen (DO). A UV lamp (230V 0.17A, 6 W, Spectronics Corp. NY, USA), with wavelength λ ~365 nm was used. A hand held solar radiometer (model 776E Dodge product, USA) was used for measuring outdoor solar intensity and was subsequently simulated in the reactor. Luzchem Solsim v1.2, (intensity approximately AM 1.5 solar spectrum, 300 W ceramic xenon lamp, λ 280-800 nm and maximum power 1.5 kW/m²) provided simulated solar irradiation.

2.4 Pesticide aqueous solution

Preparation of the pesticide aqueous solution was done using distilled water and was stored at 4 °C until required. Its constituents were CPF 100 mg/L, CPT 50 mg/L and CTN 250 mg/L. The COD was 1130.0 mg/L, TOC was 274.39 mg/L, and BOD₅/COD ratio was zero.

2.5 Cost estimation

Cost evaluation for UV incorporated treatment was based on electrical energy per order (EE/O) and calculated using Equation (1) similar to the study by Cañizares *et al.* [13]. This was chosen because the study considered operating cost in terms of electrical energy required by some of the processes examined.

$$EE/O(kWh/m^3) = \frac{pt \times 1000}{V \times 60 \log(C_{ini}/C_{fin})} \quad (1)$$

where, EE/O is the energy requirement (kWh/m³), *p* is the rated power of the lamp (kW), *V* is the pesticide aqueous solution volume (L), *t* is the half-life time in min for achieving 50% reduction of TOC, *C_{ini}* and *C_{fin}* are the initial and final concentration of the compound treated in terms of TOC, and the factor of 1000 was for conversion to cubic metre (m³) [12]. Cost of electricity depends on applicable country and this was found to be \$0.10 kWh [13].

2.6 Kinetic study

The pseudo kinetic rate equation for degradation in terms of TOC removal is given by the

following n th order reaction kinetics in Equation (2) [14].

$$\frac{-d[TOC]}{dt} = k * TOC^n \quad (2)$$

TOC removal may be described in accordance with the first or second order pseudo models [14]. Linearizing Equation (2) for pseudo first and second order kinetic models respectively gives Equations (3) and (4).

$$\frac{1}{[TOC]_t} - \frac{1}{[TOC]_0} = k * t \quad (3)$$

$$\frac{-d[TOC]}{dt} = k * TOC^n \quad (4)$$

where k is a pseudo-first-order rate constant, t is the irradiation time in min; C_0 the initial concentration of TOC in aqueous solution and C_t is the residual concentration of TOC at time t . The half-life ($t_{1/2}$) is known as the time needed to decrease the concentration of the TOC to half the initial value and it is calculated using Equations (4) and (5) for first and second order, respectively.

$$\frac{0.693}{k} \quad (4)$$

$$\frac{1}{[TOC]_0 * k} \quad (5)$$

The plots of $\ln([TOC]_0/[TOC]_t)$ and $1/[TOC]_t$ versus time were done in order to obtain the appropriate reaction order to describe all processes. The values of k from the slopes of the plots at different reaction time and the coefficient of determination values were obtained. The degradation of organic carbon in the pesticide aqueous solution as a function of reaction time was estimated.

2.7 Experimental procedure

In all five processes, except FeGAC/H₂O₂, laboratory study was conducted using 500 mL of the pesticide aqueous solution. The quantity of iron salt needed was added to this solution. Thereafter, an adjustment of the pH of the solution was done using either H₂SO₄ or NaOH. Stirring the solution to appropriate mix was done using a magnetic stirrer to ensure homogeneity. The required amount of H₂O₂ was thereafter added to the solution. In the UV photo-Fenton and TiO₂ photocatalytic processes, the aqueous solution was placed 5 cm un-

der the UV light at room temperature (23±2 °C). In the solar photo-Fenton process, a hand held portable solar radiation meter was used to measure the average daily irradiation and simulated inside the reactor preset to a light intensity of 0.85 kW/m² accordingly. In the UV/TiO₂/H₂O₂, the TiO₂ was placed in a beaker and H₂O₂ was added. The mixture was stirred under UV light at 23±2 °C. The FeGAC/H₂O₂ process was carried putting 200 mL pesticide aqueous solution inside a 250 mL conical flask. The FeGAC and H₂O₂ were mixed together a conical flask and they were put on an orbital shaker. At known time intervals, a conical flask was removed and a portion of the solution was filtered. In the different processes, samples were taken at known intervals of time, and were filtered by a 0.45 μm size filter before measurement of BOD₅, TOC, and COD concentrations. They were also filtered using a 0.20 μm size filter so as to determine pesticide concentration by high performance liquid chromatography.

3. Results and Discussion

3.1 Degradation and biodegradability improvement

The degradation and biodegradation (BOD₅/COD ratio) improvement of the pesticide aqueous solution for the five AOPs were studied. A comparison among them was conducted in terms of pesticide degradation and improvement of the biodegradability index under the obtained best operating conditions. The ranges of operating conditions are shown in Table 1. The different operating conditions and their corresponding results are presented in Tables 2 and 3. The reaction conditions which led to best operating conditions can be seen in Table 4.

The best operating conditions for degradation and improvement of biodegradability were: Fenton process - H₂O₂/COD molar ratio 3, H₂O₂/Fe²⁺ molar ratio 10 and ambient pH 3 [15]; UV photo-Fenton process - H₂O₂/COD molar ratio 2, H₂O₂/Fe²⁺ molar ratio 25 and ambient pH 3; solar photo-Fenton process - H₂O₂/COD molar ratio 2, H₂O₂/Fe²⁺ molar ratio 25 and, ambient pH 3; UV/TiO₂/H₂O₂ process - TiO₂ concentration 1.5 g/L, ambient pH 6, H₂O₂ concentration 100 mg/L and reaction time 300 min and FeGAC/H₂O₂ - FeGAC dose 5 g/L, H₂O₂ concentration 100 mg/L and ambient pH 3 (Figure 1). It should be noted that because of the heterogeneous nature of FeGAC/H₂O₂ and UV/TiO₂/H₂O₂ due to the introduction of GAC

and UV/TiO₂, respectively, there was no estimation using molar ratios as in the case of other AOP processes, and thus the experimental set up in both cases were uniquely different. The AOPs degraded and improved the biodegradability of the pesticide aqueous solution.

The FeGAC/H₂O₂ was observed to be most effective and UV/TiO₂/H₂O₂ was least with a corresponding BOD₅/COD ratio of 0.40 and 0.26, respectively. Biodegradability index between 0.3 and 0.4 is considered a cut-off limit between biodegradable and hard-to-biodegrade

Table 1. Range of values for the AOPs

AOP process	H ₂ O ₂ /COD Molar ratio	H ₂ O ₂ /Fe ₂₊ Molar ratio	TiO ₂ (g/L)	FeGAC (g/L)	H ₂ O ₂ (mg/L)
Fenton	1.0 - 4.0	2.0 - 150			
UV photo-Fenton	1.0 - 3.5	5.0 - 150			
Solar photo-Fenton	1.0 - 3.5	5.0 - 150			
UV/TiO ₂ /H ₂ O ₂			0.5 - 2.5		50-300
FeGAC/H ₂ O ₂				1.0 - 5.0	10-300

Table 2. Operating conditions and performances (Fenton Processes)

Process	H ₂ O ₂ /COD M.R	H ₂ O ₂ / Fe ²⁺ M.R	pH	Time (min)	COD rem. (%)	TOC rem. (%)	BOD ₅ /COD ratio
Fenton	1	50	3	60	28.91	17.85	0.17
	1.5	50	3	60	30.26	27.54	0.21
	2	50	3	60	37.31	29.73	0.24
	2.5	50	3	60	46.88	34.40	0.31
	3	50	3	60	50.23	40.26	0.33
	3.5	50	3	60	42.26	32.03	0.17
	4	50	3	60	37.88	30.09	0.14
	3	2	3	60	38.12	34.31	0.17
	3	5	3	60	45.06	47.12	0.18
	3	10	3	60	60.16	52.59	0.34
	3	25	3	60	53.32	43.66	0.32
	3	50	3	60	47.11	37.18	0.25
	3	100	3	60	30.44	31.35	0.17
3	150	3	60	25.31	23.03	0.14	
UV Photo-Fenton	1	50	3	60	58.98	50.03	0.26
	1.5	50	3	60	62.34	54.45	0.28
	2	50	3	60	77.82	61.15	0.37
	2.5	50	3	60	53.24	43.27	0.25
	3	50	3	60	47.37	40.23	0.23
	3.5	50	3	60	35.71	35.09	0.22
	2	5	3	60	55.26	46.15	0.26
	2	10	3	60	70.75	54.29	0.34
	2	25	3	60	78.56	63.76	0.37
	2	50	3	60	74.98	57.13	0.33
	2	100	3	60	62.25	54.34	0.32
	2	150	3	60	57.96	48.13	0.31
	1	50	3	60	39.03	25.15	0.25
Solar-photo Fenton	1.5	50	3	60	51.35	34.27	0.33
	2	50	3	60	72.08	57.56	0.33
	2.5	50	3	60	54.16	39.96	0.29
	3	50	3	60	40.17	33.27	0.23
	3.5	50	3	60	35.93	28.38	0.19
	2	25	3	60	32.41	27.33	0.19
	2	25	3	60	48.39	33.27	0.24
	2	25	3	60	61.47	47.87	0.31
	2	25	3	60	74.19	58.32	0.35
	2	25	3	60	41.86	38.85	0.24
	2	25	3	60	23.80	30.84	0.19

effluent [16]. Degradation of a mixture of dimethoate, oxydemeton-methyl, carbaryl and methidathion pesticides by AOP treatment obtained similar results [17].

3.2 Kinetics of pesticide degradation and half-life time

The pesticide degradation kinetics and half-life time for the substrates by the five AOPs was studied. The kinetics of pesticide degradation is a vital pre-requisite for predicting the rate of substrates degradation before the design of typical wastewater treatment plants so

as to optimize and lower the operating cost [18]. Several studies have reported pesticide degradation according to pseudo- first order [19-20]. To study the kinetics, the various AOPs were carried out using the operating conditions in Table 4.

The degradation of organic carbon in the pesticide aqueous solution as a function of reaction time is shown in Figure 2 for the five AOPs. The summary of rate constants (*k*), R2 and half life time are shown in Table 5. Estimation of the first and second order reactions were done to ascertain which one describes the

Table 3. Experimental operating conditions and results of UV/TiO₂/H₂O₂ and FeGAC/H₂O₂ processes

Process	H ₂ O ₂	TiO ₂ (g/L)	FeGAC (g/L)	pH	Time (min)	COD rem. (%)	TOC rem. (%)	BOD ₅ /COD ratio
UV/TiO ₂ /H ₂ O ₂	-	0.5		6	300	15.35	6.13	-
	-	1.0		6	300	20.76	7.38	-
	-	1.5		6	300	25.95	8.45	-
	-	2.0		6	300	22.51	7.48	-
	-	2.5		6	300	19.43	5.21	-
	50	1.5		6	300	32.69	17.79	0.22
	100	1.5		6	300	53.62	21.54	0.26
	150	1.5		6	300	42.18	18.56	0.24
	200	1.5		6	300	37.43	16.99	0.21
	300	1.5		6	300	33.39	13.52	0.17
FeGAC/H ₂ O ₂	-		1			56.90	41.38	-
	-		2			60.71	46.91	-
	-		3			67.96	50.15	-
	-		4			83.01	68.17	-
	-		5			85.75	72.15	-
	10		5			51.68	30.05	0.29
	25		5			59.12	36.87	0.34
	50		5			91.86	70.55	0.38
	100		5			96.19	79.15	0.40
	150		5			85.93	62.71	0.35
200		5			76.81	58.36	0.32	
300		5			74.16	54.09	0.29	

Table 4. COD and TOC removal (%) and optimum operating conditions of the different AOPs processes studied

Treatment process	COD Rem. (%)	TOC Rem. (%)	BOD ₅ /COD ratio	H ₂ O ₂ /COD molar ratio	H ₂ O ₂ /Fe ²⁺ molar ratio	TiO ₂ /H ₂ O ₂ mg/L	FeGAC/H ₂ O ₂ mg/L
Fenton	69.03	55.61	0.35	3.0	10		
UV photo-Fenton	78.56	63.76	0.38	2.0	25		
Solar photo-Fenton	74.19	58.32	0.36		25	1.5 g/L/100	
UV/TiO ₂ /H ₂ O ₂	53.62	21.54	0.26	2.0			
FeGAC/H ₂ O ₂	96.19	85.60	0.40				5 g/L/100

¹ Complete degradation of pesticides occurred in 1 min in all treatment processes

² UV lamp 6 W, (λ 365nm)

process appropriately. The reactions were found to follow pseudo-first order kinetics with rate constants and R^2 values shown in Table 5. The rate constant of UV/TiO₂/H₂O₂ and FeGAC/H₂O₂ was observed to be the lowest and highest, respectively. It is pertinent to mention that the highest rate constant may be due to increased OH⁻ production rate and adsorption/catalytic properties of the FeGAC. GAC is known to decompose H₂O₂. This occurs during the exchange of a surface hydroxyl group with hydrogen peroxide anion. The formed surface peroxide is known to have an increased oxidation potential and this provides the opportunity for another hydrogen peroxide molecule with release of oxygen and regeneration of the GAC surface [21]. This result confirms the significant effect of the five AOPs, but in particular FeGAC/H₂O₂ process capability in degrading of the pesticide in aqueous solution.

3.3 Cost requirement

The cost requirement for the five processes is one of the most important factors to consider in choosing an appropriate AOP treatment process. The overall costs are usually the sum of capital costs, operating cost and maintenance costs. For a full-scale system these costs strongly depend on the nature and the concentration of the pollutants, the flow rate of the effluent and the configuration of the reactor [13]. Efforts to develop standard procedures to estimate UV lamp electrical consumption has been reported [22]. The average prices of reagents were obtained from related study (Table 6) [12,

Table 5. AOPs kinetic constants and half-life

First order				
AOP process	k (min ⁻¹)	$t_{1/2}$ (min)	t , exp.(min)	R^2
Fenton	0.0115	60.3	60	0.9433
UV photo-Fenton	0.0156	44.4	60	0.9653
Solar photo-Fenton	0.0119	58.2	60	0.9627
UV/TiO ₂ /H ₂ O ₂	0.0008	866.3	300	0.9686
FeGAC/H ₂ O ₂	0.0246	26.0	60	0.8564

Second order				
AOP process	k (min ⁻¹)	$t_{1/2}$ (min)	t , exp.(min)	R^2
Fenton	0.0693	4.4	60	0.9410
UV photo-Fenton	0.0517	19.3	60	0.9523
Solar photo-Fenton	0.0511	19.6	60	0.9567
UV/TiO ₂ /H ₂ O ₂	0.0619	16.1	300	0.8473
FeGAC/H ₂ O ₂	0.0238	42.0	60	0.9372

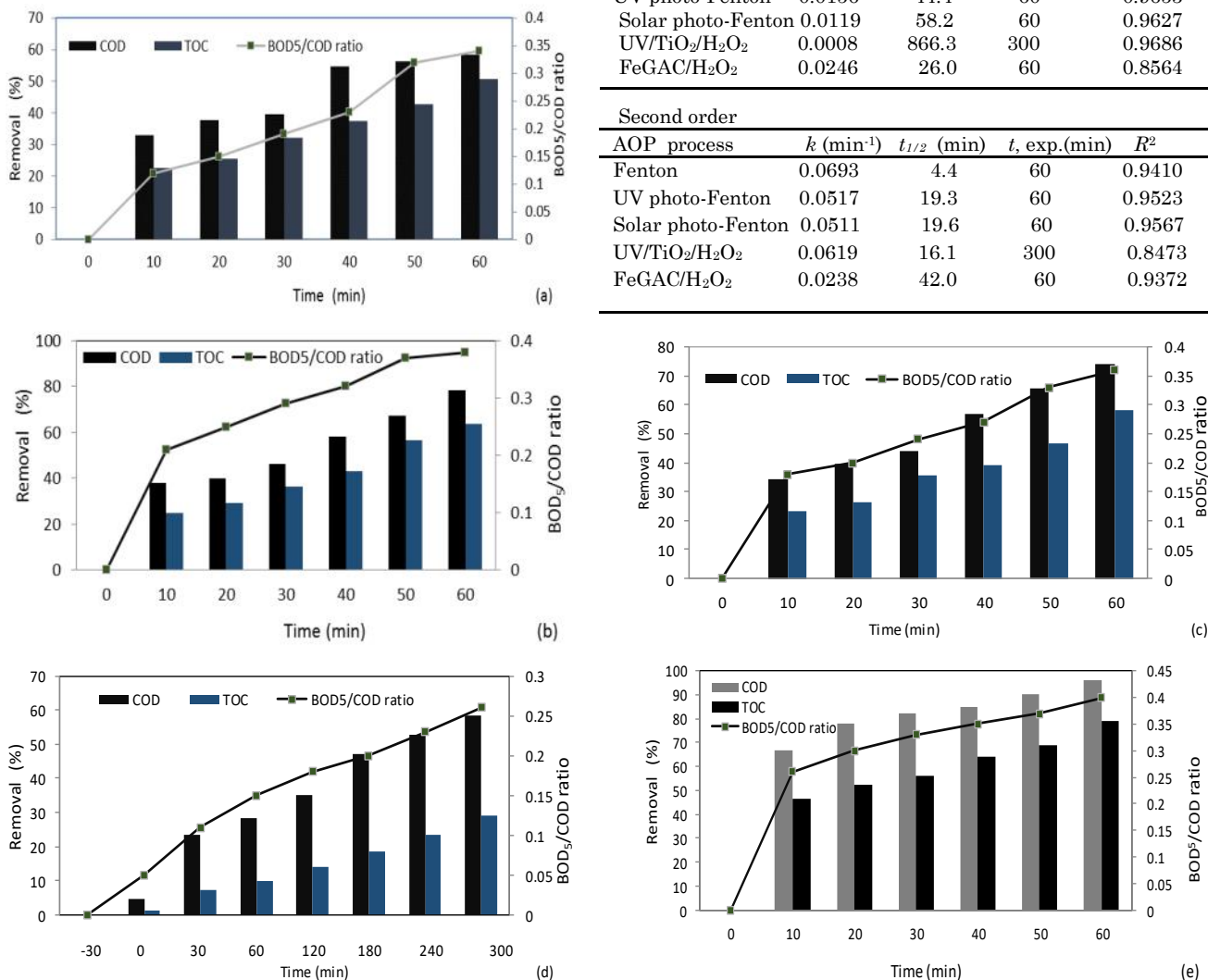


Figure 1. Degradation and biodegradability improvement by the various AOPs (a) Fenton, (b) UV photo Fenton, (c) Solar photo Fenton, (d) UV/TiO₂/H₂O₂, (e) FeGAC/H₂O₂ (degradation data presented here was obtained under best condition)

22-23]. Table 7 shows an estimation of the cost of operation per kg of TOC and this was calculated for the mineralization of 50% (half-life) of the initial TOC. As regards the operating costs, UV/TiO₂/H₂O₂ photocatalytic process was considerably the most expensive than the others owing to the nominal power of the UV lamp and the time required for pesticide degradation. However, costs could be considerably reduced when solar light is used [19]. The FeGAC/H₂O₂ process was observed to be the most attractive option for the pesticide degradation.

4. Conclusions

The five AOPs (Fenton, UV photo-Fenton, solar photo-Fenton, UV/TiO₂/H₂O₂, and FeGAC/H₂O₂) were all effective for degradation and improvement of the biodegradability of the pesticides aqueous solution. The technical efficiency and cost requirements of each process under the best operating conditions indicate

that UV/TiO₂/H₂O₂ was the least attractive option, whereas FeGAC/H₂O₂ was the preferred alternative. In addition, the highest rate constant obtained in FeGAC/H₂O₂ process could be due to the available adsorption sites on the FeGAC surface and catalytic property of the FeGAC and hence an increased OH[•] production. The study found FeGAC/H₂O₂ process to be cost effective in comparison to the other AOPs.

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Table 6. Price of reagent

Reagent	Unit	Price (\$)
H ₂ O ₂ [22]	kg	0.35
FeSO ₄ ·7H ₂ O [22]	kg	0.5
TiO ₂ [22]	kg	3.0
GAC [12]	g	0.001
Fe(NO ₃) ₃ ·9H ₂ O [23]	g	0.3

Table 7. Cost requirement for the studied AOPs

	Reagent	Fenton	UV-photo-Fenton	Solar photo-Fenton	UV/TiO ₂ /H ₂ O ₂	FeGAC/H ₂ O ₂
Chemical requirement (mg/L)	H ₂ O ₂	3602	2401	2401	100	100
	FeSO ₄ ·7H ₂ O	2945	785	785		
	TiO ₂				1500	
	Fe(NO ₃) ₃ ·9H ₂ O					200
	GAC					5000
Cost estimation (\$/kg TOC)	H ₂ O ₂	18.4	24.4	24.4		0.26
	FeSO ₄ ·7H ₂ O	21.5	5.7	5.7		
	TiO ₂				2.2	
	Fe(NO ₃) ₃ ·9H ₂ O				3.8	0.44
	GAC					0.036
Cost as per electricity EE/O (kWh/m ³)	UV	*4.0			*233	
Total cost \$/Kg TOC (half-life time)		39.9	34.1	30.1	239	0.74

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