

## Effect of hydraulic retention time on nutrients and organics removal by FeGAC/H<sub>2</sub>O<sub>2</sub>-SBR treatment of pesticide wastewater

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Received 6 September 2019; Accepted 28 March 2020

### ABSTRACT

The study investigated the effects of 6, 12, and 24 h hydraulic retention time (HRT) in terms of nutrients and organics removal by combined iron granular activated carbon–hydrogen peroxide–sequencing batch reactor (FeGAC/H<sub>2</sub>O<sub>2</sub>-SBR) process from pesticide wastewater. The operating conditions of the pretreatment phase (FeGAC 15 g/L, H<sub>2</sub>O<sub>2</sub> concentration 300 mg/L, reaction time 120 min) achieved chemical oxygen demand (COD), total organic carbon (TOC) removal, and biodegradability (BOD<sub>5</sub>/COD ratio) index which made the wastewater amenable to biological treatment. The SBR was operated for a period of 88 d in three different reactors at HRTs 6, 12, and 24 h. The volumetric exchange ratio was kept at 50%. At HRT 12 h, COD removal efficiency (96.5% ± 2%) was maximum. An increase in HRT from 6 to 12 h, led to increased nutrients removal. Ammonia–nitrogen removal efficiency was 38.0% ± 4% and 61.0% ± 5% at 6 and 12 h respectively; while phosphorus removal efficiency was 84.4% ± 3%, 90.7% ± 4%, and 74.1% ± 5% at HRTs 6, 12, and 24 h, respectively. SBR was cycled for 12 h period, the first-order-kinetic constant ( $k_1$ ) was obtained and substrate removal was observed at 3.5 mg/L/h while the coefficient of determination ( $R^2$ ) was 0.94. These results indicate that HRT can affect biomass content, nutrients, and organics removal.

*Keywords:* Pesticide; Wastewater; Pretreatment; Degradation; Kinetics; FeGAC/H<sub>2</sub>O<sub>2</sub>-SBR

### 1. Introduction

Production of iron sludge in Fenton reaction has led to a number of research alternatives. Heterogeneous Fenton processes are sometimes proposed in order to overcome this particular problem. However, to circumvent iron sludge production in this study, iron impregnated activated carbon reaction with hydrogen peroxide was adopted according to Fan et al. [1] study. In this advanced oxidation process, iron enables granular activated carbon (GAC) to perform like a catalyst during pesticide wastewater degradation. The performance of this catalyst cum adsorbent is further strengthened by its strong graphitic internal structure and presence of functional groups on its surface [2,3].

The catalyst (FeGAC) also possess a good adsorbent characteristic. In addition during the pretreatment phase, oxidation strength of the hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) enhances the performance of the entire treatment with respect to degradation of pesticide wastewater and subsequent intermediates produced.

Sequencing batch reactor (SBR) process may be used as a post-treatment where AOP is used in the pretreatment of pesticide wastewater. SBR combines the advantage of operating in one single reactor at the same time, it removes the difficulty in the selection of needed appropriate volumes by each chamber, flow rates capacity of mixed liquor, as well as returned activated sludge requirements in a typical activated sludge wastewater treatment [4–6]. Although

SBR may be limited by poor settlement, which may lead to turbid effluent during its operation [7,8], other advantages makes it more preferable than activated sludge process.

SBR requires proper retention time because of its capability to influence the rate at which contaminants in wastewater can be degraded and removed. Several studies on combined Fenton and SBR have been reported [9–11]. However where combined studies were conducted, they had to contend with sludge removal from the pretreated wastewater before SBR treatment, and in other cases, the effects of the variations on the Fenton reagent on the SBR performance was studied [12]. A related study has considered using catalytic degradation of pollutants with Fe catalyst [13]. Other studies have considered the treatment of pesticide as a long-chain fatty acid inhibitor or as photo-system inhibitors [11], a combination of Fenton–SBR treatment of synthetic wastewater [14], mineralization of phenol by photocatalytic pretreatment, and SBR [12]. There is no literature available on heterogeneous Fenton treatment processes such as FeGAC/H<sub>2</sub>O<sub>2</sub> combined with SBR which considered the hydraulic retention time (HRT) effects on biomass, nutrients, and organics removal from real pesticide wastewater containing chlorpyrifos, cypermethrin, and chlorothalonil active ingredients.

This work aims to investigate the desirable HRT required in the SBR phase to reach satisfactory treatment of pesticide wastewater by monitoring various parameters in the reactor. The reaction order describing the biodegradation kinetics during the biological treatment (substrate removal rate) was evaluated during this study. A laboratory-scale experiment was conducted using industrial pesticide wastewater obtained from a production company. Comparison was made by monitoring the biomass, organic, and nutrient removal efficiencies at three different HRTs.

## 2. Materials and methods

### 2.1. Chemicals

GAC, Ferric nitrate (Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O), and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) (30%, w/w) were bought from Aldrich, Germany.

### 2.2. Analytical methods

The chemical oxygen demand (COD), biochemical oxygen demand (BOD<sub>5</sub>), mixed liquor suspended solid (MLSS), mixed liquor volatile suspended solid (MLVSS), total organic carbon (TOC), and NH<sub>3</sub>-N (ammonia –nitrogen) were measured following APHA standard methods as described in the manual [15], total phosphorus (TP) was measured by Hach method (USA) [16]. In order to stop the interference of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and to obtain accurate COD readings, the treated wastewater pH was increased more than 10 to enable H<sub>2</sub>O<sub>2</sub> to decompose into water and oxygen according to previous studies [17,18], pH meter produced by HACH was employed to measure pH during treatment. All sampling and testing were in duplicates. Pesticide concentration was determined using GC–MS following the method reported by Cortada et al. [19] described elsewhere.

### 2.3. Pesticide wastewater and municipal wastewater

The pesticide wastewater was supplied by a pesticide producing company. It was kept inside a 4°C room until needed. Table 1 shows the characteristics of the pesticide wastewater while Table 2 shows the characteristics of the municipal wastewater. This was obtained from a local sewage treatment plant (STP).

### 2.4. Experimental procedure

The schematic diagram of the experimental set-up is shown in Fig. 1.

#### 2.4.1. FeGAC preparation and Characterization

The FeGAC and GAC conductivity was determined according to the Standard Method 5210 [15] and was measured using MYRONL, USA EP meter ranging from 0.1 to 1,000 μS/cm. The surface area, micropore area, micropore volume, and average pore diameter were measured by Brunauer–Emmett–Teller (BET) surface area apparatus (ASAP 2000, Micrometrics) at 77°K by means of standard BET procedure using N<sub>2</sub> adsorption. Prior to the measurement, the FeGAC and GAC samples were degassed at 120°C for 3 h. The pH and point of zero charge (pHPZC) were determined by the solid addition method [20]. The bulk density of the GAC and FeGAC was determined using the method of Ahmenda et al. [21].

The GAC was purchased and reduced to a size of 425 μm. Ferric nitrate and GAC were mixed for 24 h (ferric nitrate 50 mg per g GAC). Thereafter, it was dried at 105°C. It was thereafter washed severally using deionized water, dried again at 105°C and stored until needed [1]. Table 3 shows the characteristics of the GAC and FeGAC, respectively.

Table 1  
Characteristics of pesticide wastewater

Parameter	Range
Chlorpyrifos, mg/L	805.56 ± 10.0
Cypermethrin, mg/L	105.75 ± 10.0
Chlorothalonil, mg/L	692.08 ± 10.0
Chemical oxygen demand (COD), mg/L	3,350.0 ± 100
Total organic carbon (TOC), mg/L	2,960.0 ± 100
Biochemical oxygen demand (BOD <sub>5</sub> ), mg/L	63.0 ± 5.0
BOD <sub>5</sub> /COD ratio, mg/L	0.02 ± 0.01
Ammonia–nitrogen (NH <sub>3</sub> -N), mg/L	57.4 ± 2.0
Nitrate (NO <sub>3</sub> -N), mg/L	13.1 ± 0.5
Total phosphate (TP), mg/L	79.0 ± 0.5
Chloride (Cl <sup>-</sup> ), mg/L	1,280 ± 0.5
Fluoride (F <sup>-</sup> ), mg/L	5.0 ± 0.5
Sulfate (SO <sub>4</sub> <sup>2-</sup> ), mg/L	500.0 ± 10
Conductivity, μS/cm	680.0 ± 10
Total suspended solids (TSS), mg/L	130.0 ± 5.0
Total volatile suspended solids (TVSS), mg/L	105.0 ± 5.0
Total nitrogen, mg/L	114.8 ± 2.0
pH	5.08 ± 0.5

#### 2.4.2. FeGAC/H<sub>2</sub>O<sub>2</sub> pretreatment

The pesticide wastewater was treated in a batch process using a stand-alone orbital shaker unit (twenty-five 200 mL in 250 mL pyrex flask). The FeGAC and H<sub>2</sub>O<sub>2</sub> were added before the experiment proceeded. The entire flasks were later withdrawn after 60 min reaction time and the pH increased above 10. Thereafter the sample was filtered using a 0.45 μm membrane diameter filter size.

Table 2  
Characteristics of municipal wastewater

Parameter	Range
Chlorpyrifos, mg/L	0.0
Cypermethrin, mg/L	0.0
Chlorothalonil, mg/L	0.0
Chemical oxygen demand (COD), mg/L	206.0 ± 100
Total organic carbon (TOC), mg/L	83.1 ± 10.0
Biochemical oxygen demand (BOD <sub>5</sub> ), mg/L	118.0 ± 10.0
BOD <sub>5</sub> /COD ratio, mg/L	0.02 ± 0.01
Ammonia-nitrogen (NH <sub>3</sub> -N), mg/L	10.5 ± 2.0
Nitrate (NO <sub>3</sub> -N), mg/L	4.7 ± 0.25
Total phosphate (TP), mg/L	6.8 ± 0.5
Chloride (Cl <sup>-</sup> ), mg/L	–
Fluoride (F <sup>-</sup> ), mg/L	–
Sulfate (SO <sub>4</sub> <sup>2-</sup> ), mg/L	28.4 ± 0.5
Conductivity, μS/cm	–
Total suspended solids (TSS), mg/L	–
Total volatile suspended solids (TVSS), mg/L	–
Total nitrogen, mg/L	–
pH	6.5 ± 0.5

#### 2.4.3. SBR treatment

The SBR cylindrical-shaped Plexiglas reactor had 15 cm internal diameter, 25 cm height, and was operated at a room temperature of 23°C ± 2°C. Oxygen was allowed more than 3 mg/L throughout the aeration phase. Calibrated variable flow peristaltic Cole Parmer pumps were used to automate the feeding and decanting actions. A timer was connected to the reactor for the timely operation of the fill, react, settle, and decanting stages in the SBR. Table 4 presents the operating conditions of the SBR. The supernatant collected after settling was filtered using a 0.45 μm membrane diameter size filter before measuring the required parameters.

### 3. Results and discussion

#### 3.1. Effect of FeGAC

To study the effect of FeGAC dosage, it was varied between 3 and 15 g/L at the rate of 250 rpm and a duration of 60 min. COD removal was between 32.1% and 64.2%; TOC removal was between 18.9% and 50.5%; BOD<sub>5</sub>/COD ratio remained between 0.21 and 0.36 for the range of 3.0 and 15.0 g/L FeGAC dosage, respectively (Fig. 2). The observed results show that increasing FeGAC dosage would lead to increased removal efficiency. This was due to the increased granular structure surface area and a number of adsorption sites that were available for pollutant adsorption [3,22].

#### 3.2. Effect of H<sub>2</sub>O<sub>2</sub> addition to FeGAC

In an effort to investigate the effect of H<sub>2</sub>O<sub>2</sub> addition at various concentrations, the concentration of H<sub>2</sub>O<sub>2</sub> was varied between 75 and 900 mg/L while 15 g/L FeGAC dosage was added to the beaker. After 60 min reaction time, COD removal ranged from 57.3% until 64.2%; TOC removal was

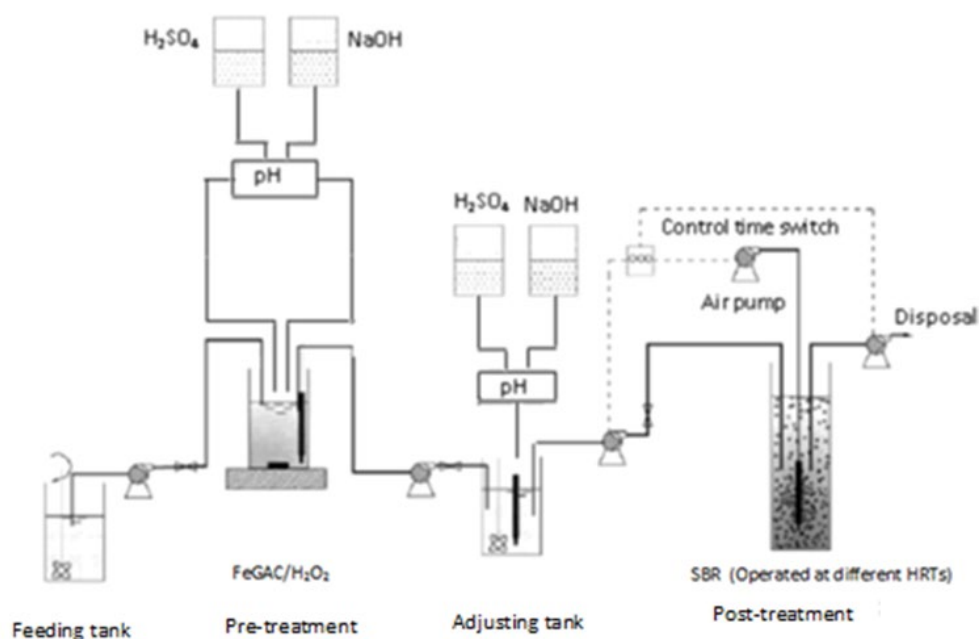


Fig. 1. Schematic diagram of set-up.

Table 3  
Characteristics of granular activated carbon (GAC) and Fe-granular activated carbon (FeGAC)

Parameter	GAC	FeGAC
Surface area (m <sup>2</sup> /g)	626	745
Micropore area (m <sup>2</sup> /g)	509	729
Micropore volume (mL/g)	0.23	0.20
Average pore diameter (Å)	15.35	23.79
Bulk density (g/mL)	0.52	0.81
Conductivity (μS/cm)	4.00	5.20
pH	5.65	4.80
pH <sub>ZPC</sub>	6.20	5.60

Table 4  
Operating conditions of the SBR at various HRTs

Operating parameter	Hydraulic retention time (HRT)		
	6	12	24
Operating parameter	6	12	24
Fill (min)	30	30	30
Aeration (h)	4	10	22
Settle (h)	1	1	1
Decant (min)	15	15	15
Idle (min)	15	15	15
Operating volume (L)	1.5	1.5	1.5
Decanted volume (mL)	750	750	750
Volume of reactor (L)	2	2	2

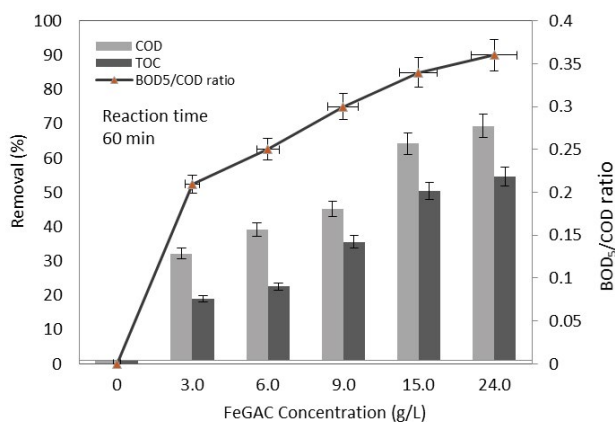


Fig. 2. Effect of FeGAC in terms of COD and TOC removal and BOD<sub>5</sub>/COD ratio.

from 43.1% until 50.5%, and BOD<sub>5</sub>/COD ratio was 0.28 until 0.32, between 75 and 300 mg/L H<sub>2</sub>O<sub>2</sub> concentration, respectively (Fig. 3).

In typical heterogeneous Fenton reactions between ferric or ferrous ions and hydrogen peroxide usually occur at the surface of the solids or catalyst and this would depend on the catalyst surface area [23,24]. Increasing the concentration of H<sub>2</sub>O<sub>2</sub> to fairly above 300 mg/L decreased the process degradation efficiency. This effect may be as a result of the scavenging of OH<sup>•</sup> by excess H<sub>2</sub>O<sub>2</sub> [25,26].

### 3.2.1. Commentary on combined FeGAC/H<sub>2</sub>O<sub>2</sub>-SBR process

During the preliminary studies, the performance of the FeGAC/H<sub>2</sub>O<sub>2</sub>-SBR processes deteriorated after the 8th cycle using the pesticide wastewater pretreated at 60 min. This was presumably due to nutrient deficiency and/or accumulation of non-biodegradable pesticide degradation products. Pretreatment time needed for pesticide degradation increased with organic load according to other studies [27]. Given a concentration of 200 and 500 mg/L, only 40% of the organics were removed. Thus, the best thing was to increase the reaction time of the pretreatment and to allow biological treatment to complete degradation of the wastewater was found to be 66% and 57%, respectively after an increase in the reaction time [27]. Nutrients, rather

than carbon or energy sources, may at times be the limiting material for microbial cell synthesis and growth. Required organic nutrients, known as growth factors, are sometimes needed by organisms as precursors for organic cell material, which cannot be synthesized from carbon sources. Sufficient nutrients are generally present in municipal or domestic wastewater, however for industrial wastewater, nutrients may need to be added to the biological treatment [28]. Therefore, to increase sustenance of the process, FeGAC/H<sub>2</sub>O<sub>2</sub>-SBR treatment of the pesticide wastewater was conducted with higher FeGAC/H<sub>2</sub>O<sub>2</sub> reaction time (120 min) before combining with the municipal wastewater during the SBR process.

For industrial pesticide wastewater treatment to be sustained, the presence of carbon alone may not be sufficient. Addition of domestic wastewater from a municipal plant to provide nutrients in the SBR treatment may be necessary. The pretreatment of the pesticide wastewater was therefore conducted (using the following operating conditions; 300 mg/L H<sub>2</sub>O<sub>2</sub> concentration, 15 g/L FeGAC dosage, and 120 min reaction time. Domestic wastewater was added to the pretreated wastewater at a ratio 1:3. Thereafter it was fed into the three SBRs (HRTs 6, 12, and 24 h).

### 3.3. Effect of HRT on MLSS and COD removal

This study investigated the effect of HRT on the MLSS and COD removal. After an initial 10 d start-up period, the adapted population indicated steady reactor MLSS content. The MLSS (biomass) content increased as the HRT increased from 6 to 12 h, but did not significantly improve with a further increase to 24 h. The biomass contents were an average of 3,580 ± 310; 4,130 ± 350; and 2,220 ± 460 mg/L at 6, 12, and 24 h, respectively (Fig. 4).

In the same vein, the COD removal followed similar behavior. The influent COD concentration was 436 ± 62 mg/L, while the effluent concentration was 34 ± 3.0, 15 ± 2.0, and 93 ± 5.0 mg/L at HRT 6, 12, and 24 h (Fig. 5). This indicated that the HRT had an effect on the biomass in the reactor [6,28]. There was no apparent improvement in MLSS content and COD removals when HRT was increased from 12 to 24 h HRT. COD removal efficiency was 92.2% ± 4%, 96.5% ± 2%, and 78.7% ± 3% at HRTs 6, 12, and 24 h, respectively. The reduction in the removal efficiency

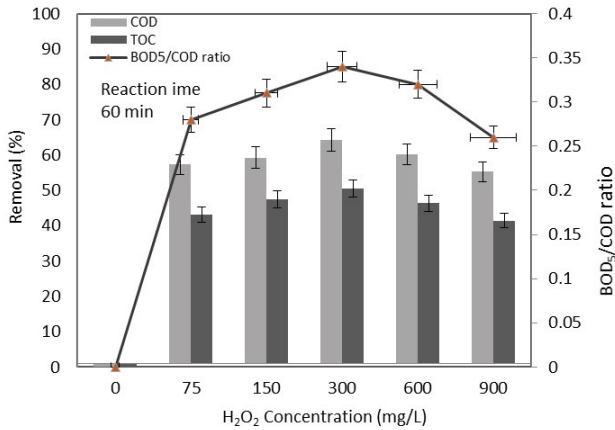


Fig. 3. Effect of FeGAC and H<sub>2</sub>O<sub>2</sub> addition in terms of COD and TOC removal and BOD<sub>5</sub>/COD ratio.

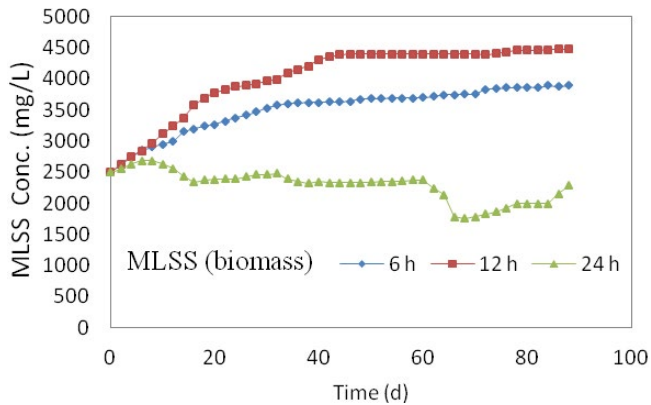


Fig. 4. Biomass contents at HRTs 6, 12, and 24 h in the operated SBR.

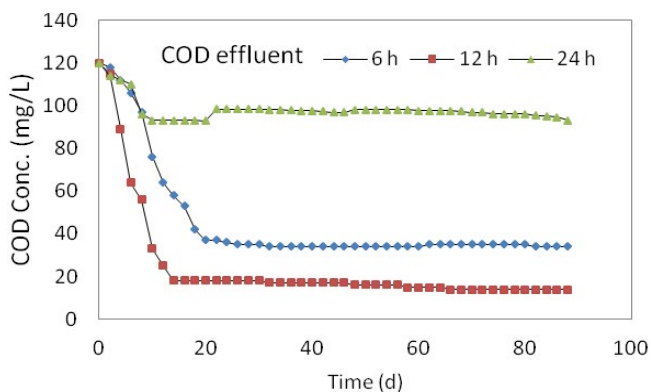


Fig. 5. Effluent COD concentrations at HRTs 6, 12, and 24 h in the operated SBR.

as time was increased may be a result of an accumulation of organic metabolites including polysaccharides and polymeric organic substances that were produced by bacteria in the SBR at longer HRT and may have become difficult to degrade [29,30].

### 3.4. Effect of HRT on ammonia–nitrogen removal

The effect of HRT on ammonia–nitrogen removal was studied. The influent NH<sub>3</sub>-N concentration was 10.0 ± 2.4 mg/L and the removal efficiency was 38.0 ± 4 and 61.0 ± 5 at HRTs 6 and 12, respectively. It was not stable at 24 h, leading to poor performance. The effluent concentration was 6.2 ± 1.4, 3.9 ± 1.3, and 16.7 ± 2.3 at HRTs 6, 12, and 24 h, respectively (Fig. 6). With a decrease in HRT from 24 to 12 h, ammonia–nitrogen removal improved significantly. On the other hand, when HRT was further decreased to 6 h, nitrogen removal was also seen to be better than at HRT 24 h. This may be as a result of a sufficient population of nitrifying bacteria between 6 and 12 h inside the reactor [31,32]. Higher concentration of biomass is reported to give a good retention capacity to the slow development of nitrifying bacteria [32,33]. This was further improved when they form clusters and remained in very close contact [6]. Growth of nitrifying bacteria was reported to have improved by mass transfer, for example, ammonium presence and oxygen diffusion at high biomass contents resulting in increased aggregation of suspended cells and leading to better sludge floc formation [34].

The decrease in HRT and corresponding increase in volumetric organic loading rate have been reported to provide more available organic carbon to assist in nitrification [6,35]. This may have resulted in higher nitrogen removal at HRTs 12 and 6 h. In summary, reduction of HRT was reported to be an effective method to improve anammox performance as a result of increasing nitrogen loading as it helps to stimulate the growth of anammox bacteria with sufficient biomass to assist the loading rate [35]. A study has reported that a lower HRT from 3 until 7.5 h was sufficient and above this range would be detrimental to the removal of nitrogen [36].

### 3.5. Effect of HRT on phosphorus removal

The effect of HRT on phosphorus removal was studied. The concentration of phosphorus at the influent was 15.0 ± 0.8 mg/L. The observed effluent concentrations were 3.2 ± 0.5, 1.9 ± 0.7, and 5.3 ± 1.5 mg/L at HRTs 6, 12, and 24 h, respectively (Fig. 7). The removal efficiencies were 84.4% ± 3%, 90.7% ± 4%, and 74.1% ± 5% at HRTs 6, 12, and 24 h, respectively. The SBR operated at HRT 12 h had a higher phosphorus removal than 6 and 24 h. Phosphorus removal improved with a decrease in HRT (from 24 to 12 h) was due to increased biomass content owing to improvement in the phosphate-accumulating organisms (PAO) growth [6]. Phosphorus removal may be due to higher biomass contents via sludge-assisted adsorption and precipitation [37,38]. Another related study confirmed that when excessive aeration during starvation conditions of SBR (activated sludge) occurs, there is a decrease in the phosphorus removal (phosphorus uptake stops) such as the case at HRT 24 h [39]. This may be attributed to the gradual depletion of pH and/or saturation of the biomass by poly-P. When COD addition to the reactor is made, phosphorus release would then occur. However, the released phosphate would not be taken up fully again [40,41]. A related study has opined that reduced HRT yields better removal



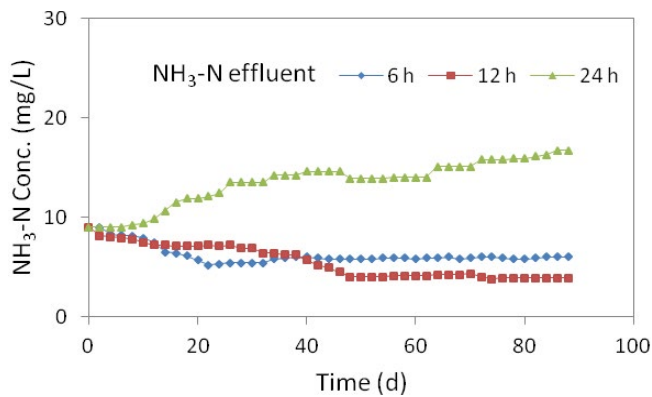


Fig. 6. Effluent  $\text{NH}_3\text{-N}$  concentrations at HRTs 6, 12, and 24 h in the operated SBR.

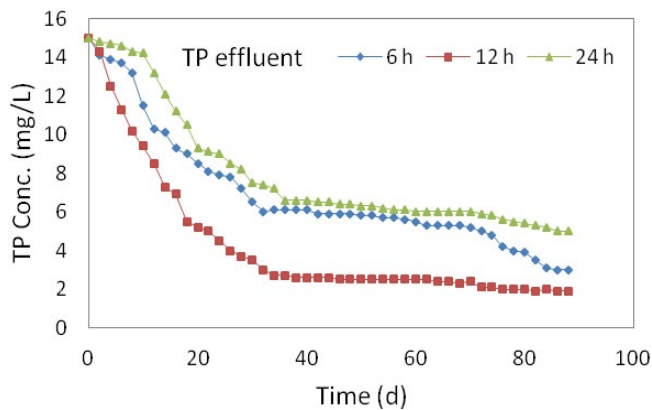


Fig. 7. Effluent TP concentrations at HRTs 6, 12, and 24 h in the operated SBR.

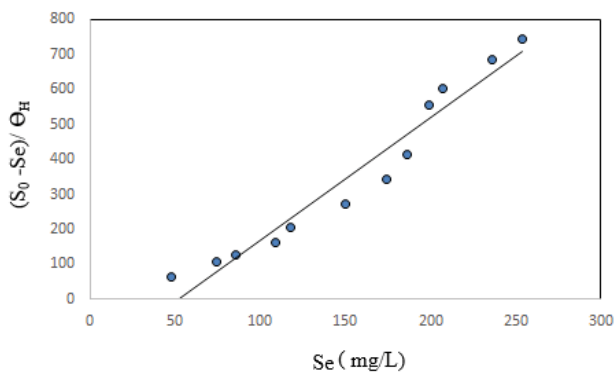


Fig. 8. Evaluation of biodegradation kinetics in FeGAC/ $\text{H}_2\text{O}_2$  – SBR process.

of phosphorus [42]. The dynamics and alternate aerobic and anaerobic environments were present. From Table 4, it can be seen there was fill, settle, decant, and idle time durations which were anaerobic in nature. This was sufficient to create the anaerobic environment in order to remove the phosphorus especially since it was already a low concentration after the 120 min pretreatment and dilution with domestic wastewater.

### 3.6. Biological degradation kinetics

The removal of the substrate was studied when the process was in a steady-state mode [43]. As can be seen in Eq. (1), the model expresses the rate of change in concentration of substrate with time according to Monod's model.

$$\frac{QS_0}{V} - \frac{QS_e}{V} - k_1 S_e \quad (1)$$

This was satisfactory since it has been shown that change in substrate ( $-dS/dt$ ) can be ignored at steady-state phase. Thus, a modified Eq. (1) is shown in Eq. (2).

$$\frac{S_0 - S_e}{\theta_H} = k_1 S_e \quad (2)$$

where  $\theta_H$  is the HRT,  $k_1$  represents the first-order-kinetic constant.

A plot of  $S_0 - S_e/\theta_H$  vs.  $S_e$  gave the slope of  $k_1$ . The remaining COD concentration of the pesticide wastewater effluent was calculated by employing the expression on Eq. (3). The measured substrate, in this case, was the COD of the pesticide wastewater.

$$S_e = \frac{S_0}{k_1 \cdot \theta_H + 1} \quad (3)$$

The usefulness of biological degradation kinetics cannot be over emphasized. It is important for monitoring reactor performance and optimization of the design process [44].

Since 12 h HRT was found most significant, the steady-state was examined for the biological degradation kinetics. Thus, SBR was cycled for 12 h period, the first order kinetic constant ( $k_1$ ) obtained was 3.5 mg/L/h. The coefficient of determination ( $R^2$ ) was 0.94 depicting a high performance. In another study where oxyfluorfen herbicide wastewater was treated under aerobic condition, the  $k_1$  obtained was 75 mg/L/h [45], when domestic wastewater was treated, it was also reported to be 0.125 mg/L/h [46]. These disparities may be obtained due to a number of reasons including, the type of wastewater, organisms present, reactor configuration including size, environmental factors such as pH and temperature [44,47]. However, the  $R^2$  (0.94) obtained shows that the data fit well to the model and confirmed by Monod's model (Fig. 8).

## 4. Conclusion

The effects of various HRT on nutrients and organics removal in FeGAC/ $\text{H}_2\text{O}_2$ -SBR process was studied. The pretreatment phase (FeGAC/ $\text{H}_2\text{O}_2$  process) degraded and improved the pesticide wastewater biodegradability. In the post-treatment phase using the SBR, decreasing HRT yielded an increase in the concentration of biomass (MLSS). A decrease in HRT achieved better phosphorus and ammonia-nitrogen removal. When HRT was decreased from 24 to 12 h, nitrogen-ammonia removal increased. When HRT increased from 6 to 12 h, COD removal increased up to 96.5%  $\pm$  2%. Ammonia-nitrogen removal efficiency was 38.0%  $\pm$  4%, 61.0%  $\pm$  5% at 6 and 12 HRT, respectively; while

phosphorus removal efficiency was  $84.4\% \pm 3\%$ ,  $90.7\% \pm 4\%$ , and  $74.1\% \pm 5\%$  at HRTs 6, 12, and 24 h, respectively. The HRT 12 h period was subsequently employed in the SBR to obtain the first-order-kinetic constant ( $k_1$ ) and substrate removal which was 3.5 mg/L/h while the coefficient of determination ( $R^2$ ) was 0.94. The combined FeGAC/H<sub>2</sub>O<sub>2</sub>-SBR under optimum operating conditions removed organic and nutrients from the pesticide wastewater containing chlorpyrifos, cypermethrin, and chlorothalonil at HRT 12 h.

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