

Treatment of pesticide wastewater by moving-bed biofilm reactor combined with Fenton-coagulation pretreatment

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Abstract

In order to treat pesticide wastewater having high chemical oxygen demand (COD) value and poor biodegradability, Fenton-coagulation process was first used to reduce COD and improve biodegradability and then was followed by biological treatment. Optimal experimental conditions for the Fenton process were determined to be Fe^{2+} concentration of 40 mmol/L and H_2O_2 dose of 97 mmol/L at initial pH 3. The interaction mechanism of organophosphorous pesticide and hydroxyl radicals was suggested to be the breakage of the P=S double bond and formation of sulfate ions and various organic intermediates, followed by formation of phosphate and consequent oxidation of intermediates. For the subsequent biological treatment, 3.2 g/L $\text{Ca}(\text{OH})_2$ was added to adjust the pH and further coagulate the pollutants. The COD value could be evidently decreased from 33,700 to 9300 mg/L and the ratio of biological oxygen demand (BOD_5) to COD of the wastewater was enhanced to over 0.47 by Fenton oxidation and coagulation. The pre-treated wastewater was then subjected to biological oxidation by using moving-bed biofilm reactor (MBBR) inside which tube chip type bio-carriers were fluidized upon air bubbling. Higher than 85% of COD removal efficiency could be achieved when the bio-carrier volume fraction was kept more than 20% by feeding the pretreated wastewater containing 3000 mg/L of inlet COD at one day of hydraulic retention time (HRT), but a noticeable decrease in the COD removal efficiency when the carrier volume was decreased down to 10%, only 72% was observed. With the improvement of biodegradability by using Fenton pretreatment, also due to the high concentration of biomass and high biofilm activity using the fluidizing bio-carriers, high removal efficiency and stable operation could be achieved in the biological process even at a high COD loading of 37.5 gCOD/(m² carrier day).

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Keywords: Fenton process; Moving-bed biofilm reactor; Pesticide wastewater; Bio-carriers volume; Tube chip type bio-carriers

1. Introduction

Wastewater emitted from the organophosphorous pesticide-manufacturing factory is hazardous and toxic and often has intensive color and disgusting odor. Its chemical oxygen demand (COD) is very high but biological oxygen demand (BOD) is relatively low. Therefore, it could inhibit the growth of microorganisms and is not easily biodegradable. Many researchers have been seeking suitable methods to treat pesticide wastewater. Physical-chemical and biological methods are the main treatment processes with their own traits [1]. Biological treatment is

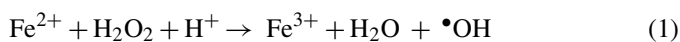
economical, but not so effective in refractory organic wastewater. Physical-chemical treatment can obtain high efficiency and is stable with a high quality effluent, but the treatment cost is very high. In the present case, the ratio of BOD_5 to COD of the pesticide wastewater was less than 0.2; especially its pH was about 2. Obviously, it could not be treated by biological process directly. So, it is not feasible to employ single physical-chemical or biological method in the treatment of this highly concentrated wastewater.

As for organophosphorous pesticide wastewater, some physical-chemical processes were employed, including wet oxidation [1], photo-Fenton [1,2], membrane anodic Fenton [3], electrochemical oxidation [4], heterogeneous photocatalytic oxidation [5,6], and the combinations of $\text{O}_3/\text{H}_2\text{O}_2$ and O_3/UV [7,8], supercritical carbon dioxide extraction [9], acidic hydrolysis and precipitation [10], etc. These investigations indicate that growing interest has been focused on advanced oxidation pro-

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cesses [11], AOP, which, by generating hydroxyl radicals that has a strong oxidation potential, can achieve two goals: (i) the reduction of COD; (ii) the detoxification and enhancement of the biodegradability in order to make next biological treatment possible. Though AOP takes many advantages of fast reaction rate and non-selective to pollutants and degrading refractory materials, one common and deadly disadvantage is high consumption of electrical energy for devices such as ozonizers, UV lamps, ultrasounds and heater, which results in rather high treatment cost. The only exception is the Fenton's process in which, under acidic condition, a $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ mixture produces HO^\bullet radicals, and the generally accepted reaction mechanism can be expressed as reaction (1).



The major advantages of the Fenton's reagent are: (1) both iron and hydrogen peroxide are cheap and non-toxic; (2) there is no mass transfer limitation due to its homogeneous catalytic nature; (3) there is no additional energy involved in using catalyst; (4) the process is technologically simple; (5) iron can also be used as a coagulant when adjusting the pH to remove part of the pollutants. Also, the disadvantage of Fenton's reagent was to need an acidic reaction condition (usually pH at 2–4) which could consume a lot of acid. In the present pesticide wastewater, its pH was about 2 which show potential advantage for Fenton reaction. Because of these features, Fenton's process has been applied in many areas [2,3,12–15]. However, Fenton's process was used in a simulated and low concentration pesticide wastewater rather than real wastewater from the pesticide factory [2,3,13–15].

Very few published papers to report the directly biological treatment of real pesticide wastewater because of its toxicity and poor degradability. Only Lin used anaerobic digestion [16] and aerobic treatment [17] of pesticide-plant wastewater, but long retention time over 20 days was needed. What is more, hardly any research was reported to use biofilm process to treatment pesticide wastewater. Moving-bed biofilm reactor (MBBR) is a highly effective biological treatment process that was developed on the base of conventional activated sludge process. It is a completely mixed and continuously operated biofilm reactor where the biomass is grown on small carrier elements that move along with water stream inside the reactor [18]. The fluidization inside reactor can be caused by aeration in an aerobic reactor and by a mechanical stirrer in an anaerobic or anoxic reactor. During the past decade it has been successfully used for the treatment of many industrial effluents including pulp and paper industry [19], poultry processing wastewater [20], cheese factory wastes [21], refinery and slaughter house [22], phenolic wastewater [23], newsprint mill wastewater [24], etc. It has also been applied for biological phosphorus removal [25]. Former

researchers have proved that MBBR possesses many excellent traits such as high biomass, high COD loading, strong resistance to impact, relatively smaller reactor volume and no sludge bulking problem and so on. It is well known that bio-carrier is the core of MBBR, the properties of bio-carrier can directly influence the ability for biofilm growth, the quantity of biomass and the effectiveness of treatment. The bio-carriers for MBBR should be provided with large surface area for microorganism growth, no congregation and blocking and good dispersion during the operation.

On the basis of the above understanding and considering the low pH of the pesticide wastewater, in this investigation, Fenton's process was specifically chosen to pre-treat the highly concentrated and non-biodegradable pesticide wastewater [8,14,15]. It was expected that not only the biodegradability was improved by oxidation but also the COD was reduced to some degree by oxidation plus coagulation at the same time. The pre-treated pesticide wastewater was further treated by MBBR. Owing to the importance of bio-carriers used in the MBBR just as mentioned above, tube chip type of polymer that was mixed with nano-size inorganic materials was used as bio-carrier. The treatment ability of the bio-carrier was evaluated by changing the loading volume of the bio-carrier. A minimum volume was obtained from the experiment in order to save the investment cost of the carrier in the practical wastewater treatment.

2. Materials and methods

2.1. Pesticide wastewater

The pesticide wastewater that was used in this experiment was obtained from a pesticide factory in Hebei Province, North of China. This factory produced many kinds of organophosphorous pesticide, such as Phorate ($\text{C}_7\text{H}_{17}\text{O}_2\text{PS}_3$), Terbufos ($\text{C}_9\text{H}_{21}\text{O}_2\text{PS}_3$), parathion-methyl and phoxim. So the wastewater from the workshop contained a lot of precursor chemicals and pesticides and was really complicated. The characteristics of the wastewater are shown in Table 1.

2.2. Process setup

Because of difficulties in treating the wastewater by using only biological process, we set up a hybrid process: pretreatment by using Fenton's oxidation which was followed by biological treatment of MBBR process. Fenton's oxidation process contains four stages of pH adjustment, oxidation reaction, neutralization, coagulation and precipitation [26]. The organic substances are removed during the two stages of the oxidation and coagulation. Fenton's treatment of pesticide wastewater

Table 1
The characteristics of the pesticide wastewater

COD (mg/L)	BOD ₅ (mg/L)	BOD ₅ /COD (mg/L)	pH	TP (mg/L)	OP (mg/L)	TKN (mg/L)	NH ₄ ⁺ -N (mg/L)	SO ₄ ²⁻ (mg/L)	Cl ⁻ (mg/L)
33700 ± 2100	6100 ± 700	0.18 ± 0.2	1.5–2.5	2120 ± 130	2040 ± 100	3300 ± 230	3080 ± 210	2530 ± 160	6370 ± 540

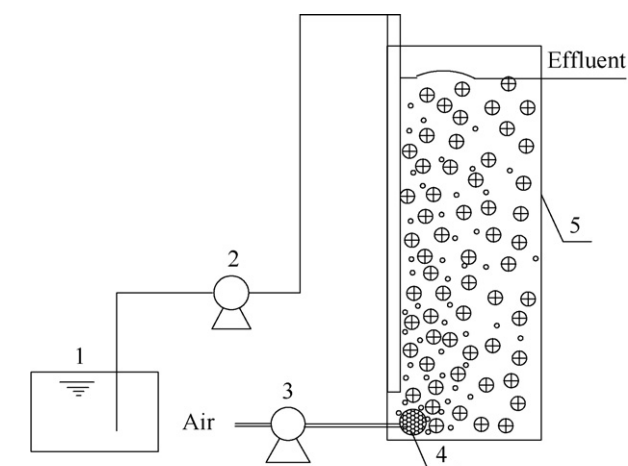


Fig. 1. Experimental setup for MBBR and photograph of bio-carrier: (1) reservoir, (2) pump, (3) air pump, (4) aerator, (5) MBBR.

was carried out at ambient temperature according to the following steps: (1) Pesticide wastewater was introduced into a 1-L beaker with a magnetic stirring bar, and the pH was adjusted to the designed experiment value; (2) the predetermined solutions of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and H_2O_2 were introduced into the pesticide wastewater in a single step; (3) after reaction for 2 h, some calcium hydroxide was added to adjust the pH to 7.5, to precipitate residual ferric ions and to coagulate the resulting sludge; (4) after Fenton-coagulation, stirring was turned off and the sludge was allowed to be settled. The analyses of treated wastewater were carried out using filtered samples.

Fig. 1 shows MBBR with a working volume of 5 L (length \times width \times height, $13 \times 13 \times 30 \text{ cm}^3$) and the tube chip shaped bio-carriers. The bio-carriers were made of organic polymer (high density polyethylene) that was mixed with nano-sized inorganic ingredients (coke powder, zeolite and so on); the nano-sized inorganic ingredients were purposely mixed to enlarge the surface area and roughness of the carrier for microorganism better accommodation. Its physical property

parameters were as follow: outside diameter of 10 mm, length of 17 mm, thickness of wall of about 0.3 mm, density of about $0.97\text{--}0.98 \text{ g/cm}^3$ and surface area of about $800 \text{ m}^2/\text{m}^3$. Upon aeration, the bio-carriers were fluidized perfectly with uniform distribution inside reactor, and the dissolved oxygen concentration in the reactor was maintained above 4 mg/L by adjusting the aeration amount.

2.3. Start-up of MBBR

In order to attach biofilm on the surface of the bio-carriers, the following fill-and-draw procedure was repeated for the initial start-up operation of the reactor. After introducing 50 vol% of bio-carriers inside the reactor, the pretreated wastewater (COD about 9300 mg/L after Fenton oxidation and coagulation) was diluted three times with tap water and the COD was around 3000 mg/L, then the diluted wastewater was charged full to the reactor. Some lacking micronutrients (MgSO_4 , 30 mg/L; MnSO_4 , 2 mg/L; CoCl_2 , 2 mg/L) were also added and its pH was adjusted to 7.5. Microbial inoculums were introduced with concentration of around 5000 mg/L. After oxidation by supplying air for 12 h, a half of mixed liquid was drained off and then the same volume diluted pretreated wastewater (COD about 3000 mg/L) was introduced for the next 12 h of the reaction. This procedure was repeated during the first week of the start-up. After one week a thin layer of biofilm could be observed on the inner wall of the carriers, and then the feed mode of wastewater was changed into continuous flow mode with initial HRT at one and a half day. Three weeks later, the COD removal efficiency reached nearly 80%, which can be considered as the accomplishment of biofilm cultivation and proliferation.

2.4. Analytical methods

BOD_5 , COD, organic phosphorus (OP), total phosphorus (TP), TKN and $\text{NH}_4^+\text{-N}$ were measured according to standard methods [27]. For the investigation of mechanism, phosphate concentration in the solution was analyzed by a Spectra-Physics P1000 HPLC equipped with a UV detector, and the reaction intermediates were determined using a gas chromatograph equipped with an electron ionization detector (EID). The SO_4^{2-} , PO_4^{3-} and Cl^- ions were measured using DX-120 ion chromatograph. The biomass attached on the bio-carriers was first desquamated by ultrasonic vibration for 15 min, then the mixed liquid was filtered and dried at 105°C to measure the dry weight. The biofilm activity was determined by specific oxygen uptake rate (SOUR) method [28].

3. Results and discussion

3.1. Optimization of Fenton process conditions

3.1.1. Effect of H_2O_2 dosage

The concentration of H_2O_2 was 30% in weight percent; 1 mL H_2O_2 solution contains 9.7 mmol pure H_2O_2 . After adjusting the wastewater pH to 2.0 and fixing Fe^{2+} dosage at 40 mmol/L, H_2O_2 dosage was varied.

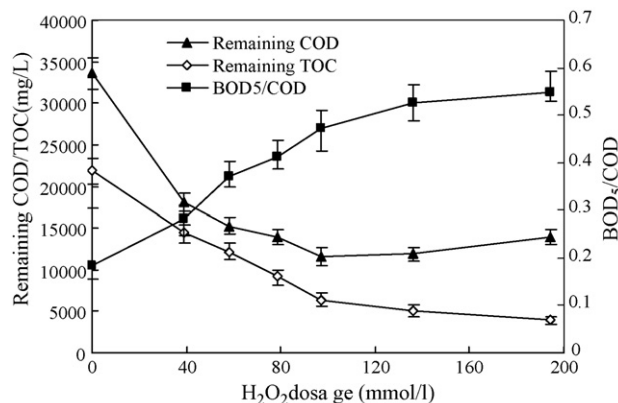
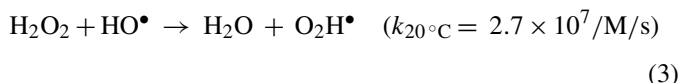


Fig. 2. Effect of H₂O₂ dosages on the COD removal and biodegradability.

The results in Fig. 2 indicate that H₂O₂ dosage has a great effect on the COD removal. Monotonic decrease in the COD and TOC and increase in the ratio of BOD₅/COD can be observed with increased dosage of H₂O₂ up to 97 mmol/L, beyond which the COD and BOD₅/COD ratio showed saturation, however, TOC still kept decreasing. The results establish that, judging from the BOD₅/COD tests, Fenton process can remarkably improve the biodegradability of the wastewater. The BOD₅/COD value can be increased over 0.3 as long as H₂O₂ dosage is kept over 58 mmol/L. It is well known that H₂O₂ dosage is the most important factor in Fenton reaction; generally, higher H₂O₂ dosage results in more extensive substrate degradation. However, Particular attention must be paid to H₂O₂ dosages in order to avoid the following undesired HO• radicals scavenging reactions occurring in the presence of an excess of H₂O₂ reagent [11].



Reaction (2) shows that the excess H₂O₂ will quickly oxidize the Fe²⁺ ions into Fe³⁺ ions, and make the oxidation reaction occur under the catalysis of Fe³⁺ ions not under that of Fe²⁺ ions. In addition, excess H₂O₂ will also decompose itself and the overdosed H₂O₂ interfered with the COD measurement due to its reduction [29], the change trend of COD and TOC was in accordance with this assumption. Thus, these undesired by-reactions will consume H₂O₂ and inhibit the production of OH•. Hereby, the optimum H₂O₂ dosage of 97 mmol/L was chosen from a comprehensive consideration of the experimental results and reagent costs.

3.1.2. Effect of Fe²⁺ dosage

In fact, Fe²⁺ ions only act as catalyst and are essential to promote producing hydroxyl radicals catalytically [11,26]. The dosage of Fe²⁺ ions has no effect on the reaction degree in principle, only influences the reaction rate. Higher concentrations of iron ions yield faster rates. The effect of Fe²⁺ dosages was investigated at the same H₂O₂ dosage of 97 mmol/L and at ini-

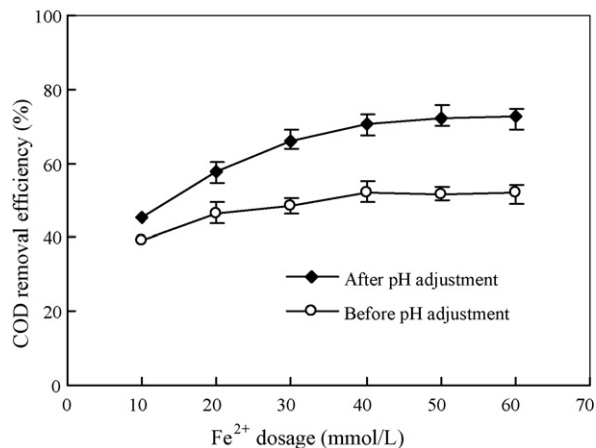


Fig. 3. Effect of Fe²⁺ dosages on the COD removal efficiency.

tial pH of 2.0, after 2 h reaction a half of the reacted solution was taken to adjust the pH to 7.0, and the results are shown in Fig. 3.

As seen from Fig. 3, the COD removal efficiency before or after pH adjustment both increased with the increase of Fe²⁺ dosage. The COD measurement before pH adjustment could be ascribed to Fenton oxidation and the removal efficiency had a slow increase from 39.37 to 52.25% when the Fe²⁺ dosage increased from 10 to 40 mmol/L; while the COD removal efficiency after pH adjustment had a larger increase from 45.45 to 70.71% in the same Fe²⁺ dosage range. The further COD removal after pH adjustment was due to the polishing step of the coagulation of residual Fe²⁺, which proved that the Fenton system not only can oxidize the organic pollutants but also possess coagulation function [13]. It was seemed that the appropriate Fe²⁺ dosage should be chosen at 40 mmol/L for practical pesticide wastewater. The COD removal efficiency was almost not modified when Fe²⁺ dosage was over 50 mmol/L, because the overdosed Fe²⁺ would scavenge HO radicals just as by-reaction (2). What is more, the effluent will become emulsified and difficult to precipitate with high sludge production, and the color of effluent also became deeper. Therefore, there existed an optimum ratio between H₂O₂ dosage and Fe²⁺ dosage in Fenton system; the molar ratio of about H₂O₂/Fe²⁺ = 2.425 was determined as an optimum value.

3.1.3. Effect of initial pH

The pesticide wastewater was adjusted to various pH values by adding sulfuric acid or sodium hydroxide while keeping the H₂O₂ and Fe²⁺ dosage constant at 97 mmol/L and 40 mmol/L, respectively. The effect of pH on the removal efficiency are shown in Fig. 4.

The COD removal efficiency reached up to 60% at the pH range of 2.5–4, and the highest removal efficiency of 63.05% was obtained at pH 3. It is well known according to the classical Fenton reaction theory [14,26] that, at high pH values, the production rate of OH• is inhibited, and what is more, the Fe²⁺ ions are precipitated as the form of hydroxide and lost their catalytic activity. At low pH values below 2.5, however, the important reaction (4) is difficult to occur; the Fe³⁺ ions cannot be straightly

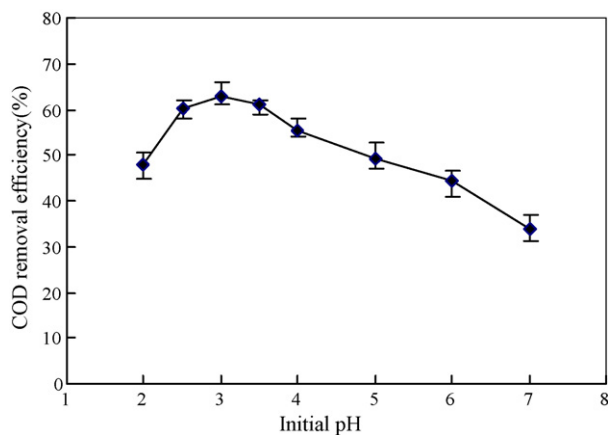
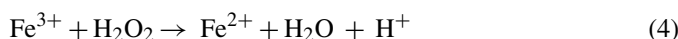


Fig. 4. Effect of initial pH on the COD removal efficiency.

reduced into Fe^{2+} ions and the catalytic reaction slowed down.



Therefore, the change of pH value directly influences the equilibrium of the forms of Fe^{2+} and Fe^{3+} , and affects the oxidative ability of Fenton reagent. Coincidentally, the pH value of the raw pesticide wastewater was about 2, which had potential advantage for Fenton reaction.

To sum up, the Fenton reagent was suitable to pre-treat the pesticide wastewater by considering to the treatment effect and cost and the characteristic of the wastewater. The optimum Fenton reaction conditions were the H_2O_2 dosage of 97 mmol/L and Fe^{2+} dosage of 40 mmol/L, respectively, at initial pH 3. Under this condition, the COD value could be evidently decreased from 33,700 to 12,100 mg/L and the BOD_5/COD ratio of the wastewater was enhanced from 0.18 to 0.47.

3.1.4. Speculation of interaction mechanism

In order to understand the mechanism for the interaction of the free hydroxyl radical with pesticides, pure phorate solution (100 mg/L) was used to investigate the oxidation mechanism because the real pesticide wastewater contained many complex substances. The temporal distribution of reacting species during the hydroxyl radical reaction in aqueous solution are shown in Fig. 5, and was conducted at the optimal conditions obtained above. Phorate in aqueous solutions was almost completely destroyed by Fenton oxidation within 20 min of reaction time. The sulfate ions appeared quickly and simultaneously with

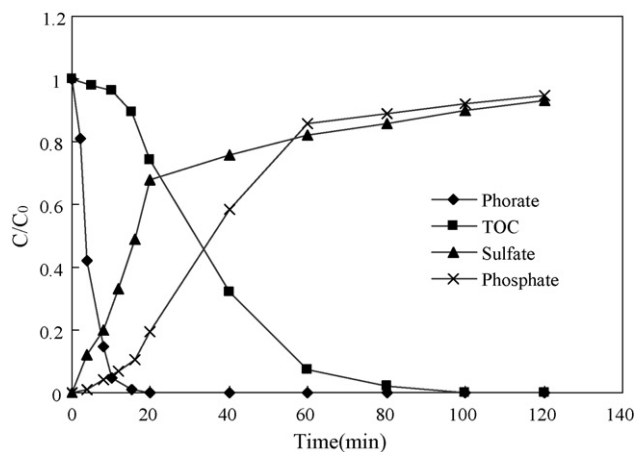
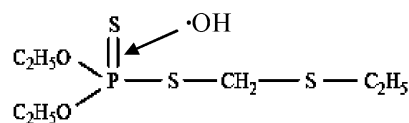


Fig. 5. The temporal species distribution during the decomposition of phorate in the solution.

the decomposition of phorate and about 70% of sulfate ions were transformed from the decomposition of phorate in the early 20 min, then the formation of phosphate and TOC reduction was to be proceeded sequentially and became accelerated from 20 to 60 min. The change of TOC reduction trend indicated that phorate was broken up and produced various organic intermediates (such as phorate sulfoxide, phoratoxon sulfone, diethyl phosphate, acetate and formic acid detected by GCD/EID), over 85% of TOC removal at 60 min of reaction time showed that the intermediates were further oxidized and mineralized into carbonates. Based on the experimental observations and the molecular structure of phorate shown below:



The simplified degradation pathway of phorate by Fenton oxidation was suggested to be in two steps: the initial step was considered to be the attack on the $\text{P}=\text{S}$ double bond by hydroxyl radicals and the formation of sulfate ions and various organic intermediates; the second step was the formation of phosphate and mineralization of intermediates.

3.1.5. Coagulation effect by $\text{Ca}(\text{OH})_2$ addition

For the subsequent biological treatment, the pH value of the reacted solution by Fenton oxidation must be adjusted to neutral condition and the Fe^{3+} should also be precipitated. So calcium

Table 2
The coagulation effect of $\text{Ca}(\text{OH})_2$ addition

$\text{m}_{\text{Ca}(\text{OH})_2}$ (g/L)	COD (mg/L)	Initial pH	Final pH	TP (mg/L)	OP (mg/L)	R_{COD} (%)	R_{TP} (%)	R_{OP} (%)
Raw	33700	2	—	2120	2040	—	—	—
0 ^a	12100	3.2	—	2120	113	64.39	0	94.46
2.0	10100	3.2	6.2	1230	70	70.03	41.98	96.57
2.5	9900	3.2	6.7	1090	52	70.62	48.58	97.45
3.2	9300	3.2	7.5	920	38	72.40	56.60	98.14
4.0	9200	3.2	8.4	770	37	72.70	63.68	98.19
6.0	8900	3.2	10.8	130	32	73.59	93.87	98.43

^a The Fenton-oxidized pesticide wastewater under the optimum conditions.

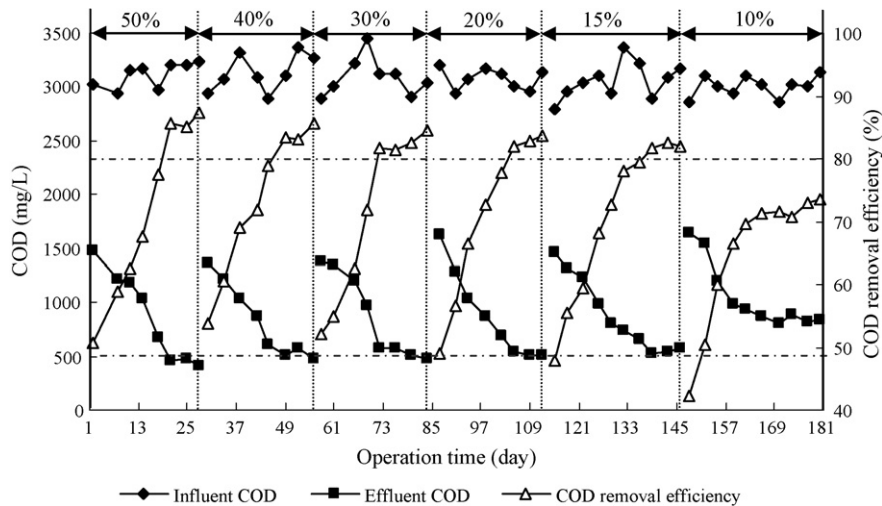


Fig. 6. COD removal efficiency at different bio-carrier volume.

hydroxide was chosen not only to adjust the pH, but also to coagulate the residual ferric ions for further removal of pollutants. Meanwhile, the Ca^{2+} ions can precipitate the resulted PO_4^{3-} ions. The coagulation effect of $\text{Ca}(\text{OH})_2$ addition are shown in Table 2.

Judging from the Table 2, after Fenton oxidation under optimum condition, the OP was greatly decreased from 2040 to 113 mg/L, which indicated the strong oxidation converted the OP into PO_4^{3-} ions. With the addition of $\text{Ca}(\text{OH})_2$ increasing from 2 to 6 g/L, the COD continuously decreased from 12,000 to 8900 mg/L, and the pH of the solution rose from 6.2 to 10.8, the TP removal efficiencies increased from 41.98 to 93.87%. Obviously, the TP was removed by the $\text{Ca}_3(\text{PO}_4)_2$ precipitates. The further removal of COD was ascribed to the co-coagulation function of the residual Fe^{2+} and $\text{Ca}_3(\text{PO}_4)_2$ precipitates. It was seemed that 3.2 g/L $\text{Ca}(\text{OH})_2$ addition was suitable for the subsequent biological treatment of the coagulated wastewater.

On the whole, the raw pesticide wastewater was pretreated by Fenton oxidation and coagulation under the optimal conditions, the COD was decreased from 33,700 to 9300 mg/L, the BOD_5/COD ratio was enhanced to over 0.47 and the pH was about 7.5. Till now, the pretreated wastewater could be tried to biological post-treatment.

3.2. Tests of MBBR

3.2.1. Effect of bio-carrier charge

After domestication of biofilm, the HRT of reactor was further reduced to one day, and then the performance of MBBR at different bio-carrier volume was studied at fixed HRT of one day and inlet COD of about 3000 mg/L, which gave the volumetric organic loading rate ($\text{OLR}_{\text{reactor}}$) of about 3 kgCOD/(m^3 day) for the reactor at different bio-carrier volume, it could be transformed to loading rate on the basis of bio-carrier area because this kind of bio-carrier has a surface area of 800 m^2/m^3 and the carrier filling volume was known, then the organic loading rate on the basis of bio-carrier area (OLR_{area}) could be expressed by

the following Eq. (5).

$$\begin{aligned} \text{OLR}_{\text{area}} &= \text{OLR}_{\text{volume}}/\text{carriersurfacearea} \\ &= (\text{OLR}_{\text{reactor}}/\text{carrierfillingvolume\%})/800 \end{aligned} \quad (5)$$

So when the bio-carrier volume was changed, the OLR_{area} would also change. In this test, the carrier volume was changed from 50 to 40, 30, 20, 15 and 10%, the corresponding OLR_{area} was about 7.5, 9.38, 12.5, 18.75, 25 and 37.5 gCOD/(m^2 carrier day), respectively.

The COD removal efficiency was sharply decreased from nearly 80 to 50% at the beginning stage of HRT reduction from one and a half day to one day (which corresponds to the inlet OLR_{area} of 7.5 gCOD/(m^2 carrier day)), just as seen from Fig. 6. However, as time passed on, the COD removal efficiency gradually increased to reach above 86% with less than 500 mg/L of the effluent COD. After obtaining a stable operation, the Bio-carrier apparent volume was successively reduced to 40, 30, 20, 15 and 10% by taking some bio-carriers out of the reactor. Similarly, the COD removal efficiency inevitably and acutely decreased from steady values of around 80 to around 50% at the beginning of reducing the bio-carriers volume. It was then gradually recovered steady values again in the passing second to third week. It was interesting to note that, when the bio-carrier volume decreased from 50 to 30%, there was little change in the time period to reach a steady state and its steady state removal efficiency. From the reduction of bio-carrier volume from 30 to 15%, it could be noticed that there was slight increase in the time period for recovering the steady state with accompanying decrease in its steady state removal efficiency, moreover, compared to COD removal efficiency, higher TOC removal efficiency of 92–85% (data not shown in the figure) could be achieved at the same bio-carrier volume. Up to this point, the system still kept a good and stable operation mode with the COD and TOC removal efficiency higher than 80 and 85%. With further reduction of the bio-carrier volume down to 10% (which corresponds to OLR_{area} of 37.5 gCOD/(m^2 carrier day)),

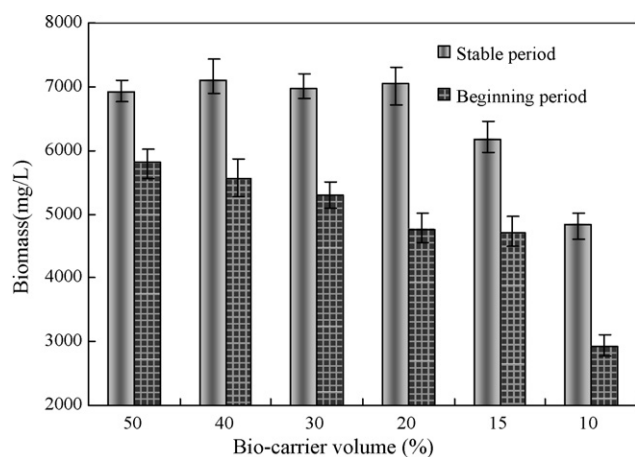


Fig. 7. Biomass variations at different bio-carrier volume.

the initial removal efficiency was declined sharply to 42.3% and stabilized at 72% in three weeks with the effluent COD value of over 800 mg/L. Therefore, it seems that the maximum allowable COD loading stays around 37.5 gCOD/(m² carrier day), beyond which the amount of biofilm on the 10% carrier is not enough to accommodate the incoming COD. The maximum allowable inlet COD loading, 37.5 gCOD/(m² carrier day), is very high considering the toxicity of the wastewater and good treatment results are achieved comparing with other investigation in the similar process [30].

3.2.2. Biomass variation during the operation

The total biomass in the MBBR was measured at the beginning period of the third day after changing bio-carrier volume and at the stable period of operation. Fig. 7 displays the total biomass at different bio-carrier volume. The total biomass at the beginning period decreased continuously with reduction in the bio-carrier volume. A sharp reduction in the biomass was observed when the bio-carrier volume was reduced to 10%, which coincide with the abrupt decrease in the removal efficiency with only 10% of bio-carrier volume as shown in Fig. 6. At stable operation conditions, the biomass amount was kept more or less the same around 6900–7200 mg/L with the bio-carrier volume between 20 and 50%. The total biomass was declined again remarkably to 4800 mg/L when the bio-carrier amount was reduced down to 10%, which coincides with abrupt decrease of the COD removal efficiency down to 72%.

3.2.3. Biofilm activity

Specific oxygen uptake rate is often one of the important factors that indicates microbial activity and the ongoing biochemical process [28,30]. The SOUR of biofilm in the MBBR with different carrier volume are shown in Fig. 8, the SOUR increased with the bio-carrier volume decreasing. Especially, the SOUR decreased quickly in the range of 10–20%, and then decreased slowly. The changes of biofilm activities at different bio-carrier volume could be explained by the difference of biofilm structure and composition which resulted from the great change of loading rate. The OLR_{area} was accordingly increased as the bio-carrier volume decreased, which could stimulate the

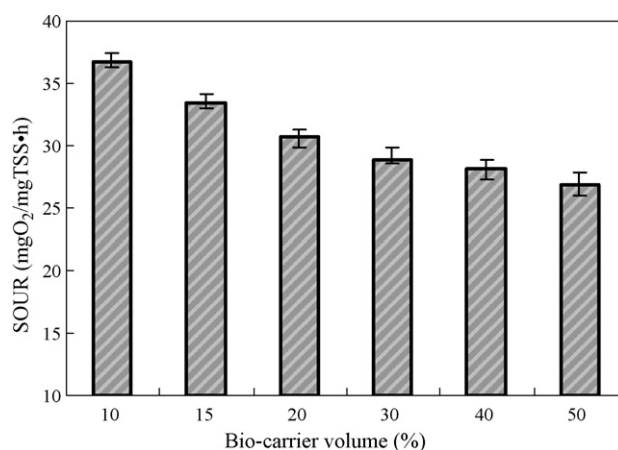


Fig. 8. SOUR changes at different bio-carrier volume.

microbial metabolism. When the bio-carrier volume was lower, such as 10, 15 and 20%, the biofilms formed were thicker and looser and fluffy with a lower density and a relatively higher surface area, which was helpful for oxygen diffusion in the biofilms, so the bacteria could reach a higher activity expressed by SOUR. However, when the carrier volume became higher, such as 40–50%, the collision and abrasion among the carrier particles became more intensive and the biofilms became thinner, denser and smoother, and this increased the oxygen and substrate diffusion limitation in the biofilms, so the activities of biofilms dropped accordingly. The SOUR tests also indicated that high loading could enhance the microbial activity and MBBR could successfully operate under high loading compared to activated sludge system.

4. Conclusion

Pesticide wastewater having high COD concentration and poor biodegradability (BOD₅/COD < 0.2) was difficult to degrade by single biological process. Therefore, Fenton process was used to pre-treat this wastewater. Fenton process can not only reduce COD to a desired degree but also improve the biodegradability for the subsequent biological treatment. The experimental results indicated that the optimum value of the H₂O₂ dosage was 97 mmol/L and that of Fe²⁺ dosage was 40 mmol/L at initial pH 3. The interaction mechanism of organophosphorous pesticide and hydroxyl radicals was suggested to be the breakage of the P=S double bond and formation of sulfate ions and various intermediates, followed by formation of phosphate and consequent mineralization of various intermediates. Under these optimum conditions, the COD could be sharply decreased from 33,700 to 12,000 mg/L, and the biodegradability (BOD₅/COD ratio) of the wastewater was enhanced from 0.18 to more than 0.47. In order to make the subsequent biological possible, 3.2 g/L Ca(OH)₂ was added to adjust the pH to 7.5 and to further coagulate the pollutants, the COD could be decreased from 12,000 to 9300 mg/L and the TP and OP removal efficiency was 56.60 and 98.14%, respectively.

In the subsequent biological treatment, a novel tube chip shaped bio-carrier was used in the MBBR. Large amount and

stable biofilms were attached on this novel bio-carrier and could tolerate inlet COD loading higher than 37.5 gCOD/(m² carrier day). As long as the bio-carrier volume was no less than 20%, more than 85% of COD removal efficiency with effluent COD no more than 500 mg/L could be obtained at inlet OLR_{reactor} of 3 kgCOD/(m³ day) with bio-carrier volume ranging 20–50%. The high biomass of about 6900–7200 mg/L that was attached on the surface of the bio-carriers and high biofilm activity insured the high COD removal efficiency and stable operation, supporting that the MBBR has excellent advantages such as flexibility, easy operation and strong resistance against loading impact. Therefore, Fenton process combined with the MBBR is a feasible and promising technology to treat highly concentrated refractory wastewater.

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