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Pretreatment of piggery digestate wastewater by ferric-carbon micro-electrolysis under alkalescence condition

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Abstract−Due to the low COD/TN ratio, piggery digestate wastewater is non-biodegradable and pathogenic; its advanced treatment is becoming a wide-spread environmental concern. In this study, the process of Fe-C micro-electrolysis was applied to pretreat piggery digestate wastewater. Fe-C micro-electrolysis was confirmed effectively to enhance biodegradability of the piggery digestate wastewater. Response surface methodology (RSM) was employed to study the interactions between factors and optimize operating parameters. The optimum conditions for Fe-C micro-electrolysis were found to be 150 g/L of dosages of Fe-C particles, 6 L/h of aeration rate and 9 h of hydraulic retention time at pH 7.6, respectively. Under these conditions, the obtained chemical oxygen demand (COD) removal efficiency was 52.62%, and the ratio of BOD/COD increased from 0.13 to 0.285, which showed improvement of biochemical property. Furthermore, SEM analysis indicated the surface configuration of Fe-C particles. More important, this process could effectively pretreat the piggery digestate wastewater and avoid the generation of secondary pollution.

Keywords: Piggery Digestate Wastewater, Ferric-carbon Micro-electrolysis, Response Surface Methodology, Alkalescence Condition

INTRODUCTION

In the past two decades, there has been a considerable increase in pig farming in China and other developing countries. The National Bureau of Statistics of the People's Republic of China reported that 7.35 billion pigs had been slaughtered in 2014, indicating a 2.7% increase with respect to the previous year [1]. Statistically, recorded piggery wastewater discharged to the environment was above 11 million tons in 2014. Practicing of "open dumping" of piggery wastewater has a high possibility in leading to significant health and environmental consequences due to the uncontrolled decomposition of waste, which may eventually result in the outbreak of diseases, proliferation of foul odors, eutrophication of water body and climate change [2]. Given the holophytic nutrition, piggery wastewater has been used as fertilizer directly [3]. However, this management has a poor feasibility in many countries due to the limited field resources, especially in China with a large population. Piggery waste commonly consists of high-strength suspended solids (SS), organisms and nutrient [4], but the quality of piggery wastewater discharged from pig farms varies greatly, mainly due to the different collection modes of manure, which includes fermented bed, urine-free manure, combined manure with urine, and soaked manure with urine [5].

Anaerobic digestion (AD) is a useful technology to degrade livestock manure, producing biogas and digestate. The digestate still contains high concentrations of inorganic nutrients, low carbon/nitrogen (C/N) ratio and low BOD/COD (B/C) ratio, and thus requires post remediation strategies [6]. Piggery digestate wastewater has its characteristic that its discharge could lead to pollution of the environment and cause epidemic diseases besides the characteristics of the digestate wastewater. Anaerobic-aerobic combined process, as an engineering treatment technology with robust adaptability, is commonly used to treat piggery wastewater because of its simultaneous removal of carbon, nitrogen and phosphorous. However, it is more difficult to remove organics under low C/N ratio and B/C ratio for aerobic process [7]. Thus the digestate with low B/C ratio could not be treated with a biological process. Hence, physical/chemical processes may be required before the biological treatment process [8].

Fe-C micro-electrolysis process with better COD removal efficiency and simple operation is suitable for pilot scale study. Fe-C micro-electrolysis based on the electrochemical reaction between the iron surface and activated carbon can effectively improve wastewater biodegradability. In addition, Fe^{2+} and H^+ generated during micro-electrolysis have high chemical activity [9] and are believed to break down the carbon chains of organic contaminants. Moreover, oxygen may compete as an electron acceptor under aerated conditions, leading to the generation of H_2O_2 in situ [10,11]. The generated H_2O_2 subsequently combines with Fe^{2+}, forming Fenton's reagent that oxidizes contaminants in the wastewater. Organic contaminants can also be removed through adsorption and co-precipitation by ferrous and ferric hydroxides under alkaline conditions. At the same time, activated carbon can also act as an absorbent to remove a fraction of the organic contaminants [12]. Currently,

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this technology has been widely applied in industrial wastewater such as antibiotics [13], olive mills [14], and coking wastewater [15]. The advantages of the micro-electrolysis technology include (1) high process efficiency, (2) simple reactor construction, (3) moderate operating costs, and (4) the availability of moderate cost, plentiful raw materials [16]. However, micro-electrolysis technology with the traditional filler (zero-valent iron and granular active carbon) has several disadvantages, such as hardening, blocking and inactivation [17,18]. These problems could result in the decrease of the reaction points and then result in the deterioration of treatment performance. To solve these problems, the newly designed spherical Fe-C particles have been used in the experiment, and these new spherical Fe-C particles have following advantages: (1) Fe and activated carbon sintered together and they could hardly be separated; (2) the resistance of the original cell reaction would be reduced, which would enhance the electron transfer efficiency and improve treatment efficiency; and (3) activated carbon tiny particles could be detached from the filler after Fe dissolved to alleviate activated carbon clogging problem to some extent [18].

Compared with other above-mentioned industrial effluents, the piggery digestate wastewater has its characteristics as introduced above. So it is more difficult to remove organics under low C/N ratio and B/C ratio for biological treatment. Therefore, it is necessary to develop effective pretreatment technologies to remove the organics and improve the biodegradation. Fe-C micro-electrolysis process has been extensively used in many kinds of wastewater because of no consumption of electric power resources, low cost, convenient operation and maintenance. At the same time, this process has high removal efficiency of COD and could significantly increase the B/C ratio.

The average COD, NH_3-N and pH of the piggery digestate wastewater are 2,000-2,500 mg/L, 400-800 mg/L and around 7.6. To the best of our knowledge, no study has reported on the treatment of piggery digestate wastewater with Fe-C micro-electrolysis. In the present work, Fe-C micro-electrolysis method was used to process the wastewater. This study aims to (1) investigate the treatment efficiency at laboratory scale, and (2) get the optimal conditions of Fe-C micro-electrolysis method.

MATERIALS AND METHODS

1. Experimental Materials

In the experiment, the characteristics of the wastewater were studied before the experiment began, and the average influent COD, NH_3-N and pH was 2,000-2,500 mg/L, 400-800 mg/L and around 7.6, respectively. The piggery digestate wastewater was obtained from a pig farm in Shang Rao, Jiangxi Province.

Hydrochloric acids (HCl), sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) were supplied by LinFeng Chemical Reagent Company (Shanghai, China). Silver sulfate (Ag_2SO_4), ammonium iron (II) sulfate ($(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$) and hexaammonium heptamolybdate tetrahydrate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$) were supplied by XiLong Chemical Co. Ltd. (Guangzhou, China). Potassium dichromate ($K_2Cr_2O_7$) was obtained from Sinopharm Chemical Reagent Company (Shanghai, China). Mercury (II) sulfate ($HgSO_4$) was supplied by Shanghai Zhanyun Chemical Co. Ltd. (Shanghai, China). All reagents used in this work were of analytic grade and were used without any further purification.

Newly designed spherical Fe-C particles were different from the conventional micro-electrolysis process that combined separated Fe and activated carbon particles together. The Fe, activated carbon and other materials powders were well mixed, and then were sintered together under an oxygen-free circumstance. The spherical Fe-C particles mainly composed of 80% Fe (measured by dry weight), 10% activated carbon and 10% impurity. The diameter of filer particles ranged 1 to 2 cm, while its average specific gravity, spe-

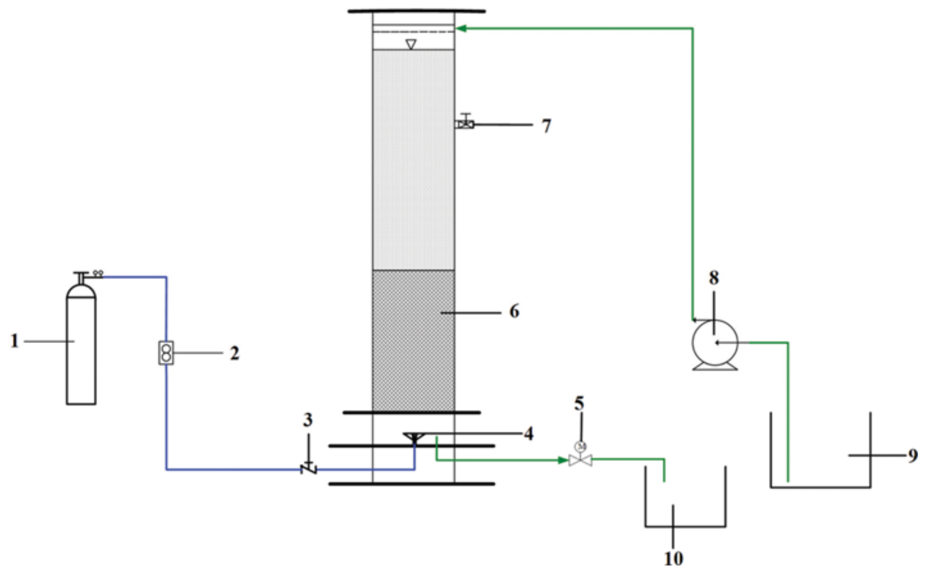

Fig. 1. Schematic diagram of Fe-C micro-electrolysis reactor.

1. Oxygen gas tank 3. One way stop return valve 5. Electromagnetic valve 7. Sampling taps 9. Raw wastewater tank
2. Gas flowmeter 4. Glass applicator 6. Fe/C filter 8. Infow pump 10. Outlet tank

cific surface area and physical strength were 1.78 ton/m^3, 1.5 m^2/g and 1,350 kg/m^2, respectively. The advantages of these new spherical Fe-C particles were introduced in Section 1.

2. Fe-C Micro-electrolysis Procedure

The general schematic presentation of the experimental system is shown in Fig. 1. The pH value of piggery digestate wastewater was adjusted with sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH), and measured with a pH meter (PHs-3C, Leici, Shanghai). The piggery digestate wastewater was pumped into the equalization tank to regulate the water quantity and quality. The Fe-C micro-electrolysis tank was packed with spherical Fe-C particles. The Fe-C micro-electrolysis tank was constructed of organic glass components.

3. Experimental Methods

Fe-C particles were placed on the diaphragm as a packing layer. A total of 150 mL of wastewater was placed in the cell being in a temperature controlled water bath. Then the experiment was carried out when the constant flow pump and gas tank were switched on. The resulting solution was centrifuged to remove any traces of active carbon or Fe powder, and then analyzed for the concentration of COD and BOD. The experimental results were mainly based on the residual concentrations of COD and BOD.

4. Analytical Methods

COD and BOD were determined by the methods of the Chinese National Environmental Protection Agency standard [19]. COD was determined by the potassium method, and BOD was determined by speedy testing method of microorganism sensor. The pH measurements were performed using a pH meter (Model-PHs-3C, Leici, Shanghai). DO is measured by a portable DO meter (Orion, 310D-1, USA). The surface structure and components of samples were analyzed by JSM-6701F scanning electronic microscope (SEM).

5. Fe-C Micro-electrolysis Optimization by Response Surface Methodology (RSM)

Response surface methodology (RSM) is an empirical statistical

Table 1. Experimental parameters of Box-benhnken design

Standard order	Independent variables				Response variables
	X_1 A^a (L/h)	X_2 pH (a.u.)	X_3 HRT^a (h)	X_4 D^a (g/L)	RCOD^b (%) Experimental (predicted)
1	2 (−1)	6 (−1)	6 (0)	150 (0)	28.63 (29.02)
2	6 (1)	6 (−1)	6 (0)	150 (0)	36.73 (39.36)
3	2 (−1)	10 (1)	6 (0)	150 (0)	13.59 (19.03)
4	6 (1)	10 (1)	6 (0)	150 (0)	16.73 (24.41)
5	4 (0)	8 (0)	3 (−1)	100 (−1)	8.91 (11.57)
6	4 (0)	8 (0)	9 (1)	100 (−1)	14.71 (19.64)
7	4 (0)	8 (0)	3 (−1)	200 (1)	27.30 (30.44)
8	4 (0)	8 (0)	9 (1)	200 (1)	31.47 (36.88)
9	2 (−1)	8 (0)	6 (0)	100 (−1)	16.00 (14.87)
10	6 (1)	8 (0)	6 (0)	100 (−1)	21.92 (23.89)
11	2 (−1)	8 (0)	6 (0)	200 (1)	42.49 (34.07)
12	6 (1)	8 (0)	6 (0)	200 (1)	46.11 (40.79)
13	4 (0)	6 (−1)	3 (−1)	150 (0)	28.00 (26.52)
14	4 (0)	10 (1)	3 (−1)	150 (0)	16.32 (14.60)
15	4 (0)	6 (−1)	9 (1)	150 (0)	39.05 (34.32)
16	4 (0)	10 (1)	9 (1)	150 (0)	26.28 (21.31)
17	2 (−1)	8 (0)	3 (−1)	150 (0)	24.97 (26.34)
18	6 (1)	8 (0)	3 (−1)	150 (0)	38.69 (34.72)
19	2 (−1)	8 (0)	9 (1)	150 (0)	31.76 (34.11)
20	6 (1)	8 (0)	9 (1)	150 (0)	44.45 (41.46)
21	4 (0)	6 (−1)	6 (0)	100 (−1)	16.68 (14.87)
22	4 (0)	10 (1)	6 (0)	100 (−1)	10.56 (3.94)
23	4 (0)	6 (−1)	6 (0)	200 (1)	29.45 (34.45)
24	4 (0)	10 (1)	6 (0)	200 (1)	20.26 (24.74)
25	4 (0)	8 (0)	6 (0)	150 (0)	25.69 (24.74)
26	4 (0)	8 (0)	6 (0)	150 (0)	27.18 (24.74)
27	4 (0)	8 (0)	6 (0)	150 (0)	23.52 (24.74)
28	4 (0)	8 (0)	6 (0)	150 (0)	24.81 (24.74)
29	4 (0)	8 (0)	6 (0)	150 (0)	22.48 (24.74)

^{a}DO-aeration rate, HRT-hydraulic retention time, D-dosages of Fe-C particles

^{b}RCOD, removal efficiency of chemical oxygen demand technique that can be employed to study the interactions between factors and optimize operating parameters [20]. RSM generates a mathematical model that accurately describes the process. In this work, a four-factor-three-level Box-Behnken design (BBD) [20-22] was applied, requiring 29 experiments (Table 1) for the optimization of extraction parameters. These independent variables were concentration of aeration rate (X_1, 2-6 L/h), pH (X_2, 6-10), hydraulic retention time (X_3, 3-9 h) and dosages of Fe-C particles (X_4, 100-200 g/L).

Removal efficiency of chemical oxygen demand, RCOD (%), was calculated in the following way:

$$\mathrm{RCOD}\ (\%) = \left(1 - \frac{COD_i}{COD_e}\right) \cdot 100 \qquad (1)$$

where RCOD (%) - is the removal efficiency of chemical oxygen demand, COD_i - chemical oxygen demand of influent wastewater (mg O_2/L), and COD_e - chemical oxygen demand of effluent wastewater (mg O_2/L).

Table 1 shows the coded (in parenthesis) and the uncoded values of the independent variable dissolved oxygen, pH, hydraulic retention time, dosages of Fe-C particles and the experimental values of the response variable RCOD. The responses ranged as 8.91%< RCOD<46.11%, clearly showed that the reaction conditions strongly affected the effect of piggery digestate wastewater treatment.

The quadratic regression model of the RCOD using Box-Behnken experimental design was based on the uncoded levels of the independent variables. In this work, the RCOD is given by:

$$\begin{aligned}\mathrm{RCOD}\ (\%) = {} & 24.74 + 3.93X_1 - 6.23X_2 + 3.63X_3 + 9.03X_4 - 1.24X_1X_2 \\ & - 0.26X_1X_3 - 0.58X_1X_4 - 0.27X_2X_3 - 0.77X_2X_4 \\ & - 0.41X_3X_4 + 6.6X_1^2 - 3.38X_2^2 + 2.83X_3^2 - 2.93X_4^2\end{aligned} \qquad (2)$$

In Eq. (2), RCOD represents the removal efficiency of chemical oxygen demand, X_1 represents the aeration rate, X_2 represents the pH, X_3 represents the Hydraulic Retention Time and X_4 represents the dosages of Fe-C particles.

To describe the relationship between dependent and independent variables, the fitting of model was evaluated by means of ANOVA tests, showing the terms which were statistically significant for a confidence level of 95% (*p*-value<0.05), and those which were not statistically significant (Table 2). The quadratic regression model has an *F*-value of 5.36 and a *p*-value less than 0.0017, which indicates that the model is significant at the 95% confidence level. The *F*-value and *p*-value are used to measure the significance of the coefficients of the model and the corresponding terms are more significant if the absolute *F*-value becomes greater and the *p*-value becomes smaller. The data in Table 2 show that RCOD is not significantly affected by the interaction terms X_1X_2, X_1X_3, X_1X_4, X_2X_3, X_2X_4, X_3X_4, X_2^2, X_3^2 and X_4^2 as in these cases p>

Table 2. Analysis of variance (ANOVA) concerning the variable responses degree of chemical oxygen reduction

Source[a]	Sum of squares	Degrees of freedom	Mean square	RCOD[b]	
				F value	P-value
Model	2360.76	14	168.63	5.36	0.0017[c]
X_1	185.57	1	185.57	5.90	0.029[c]
X_2	466.25	1	466.25	14.81	0.0018[c]
X_3	157.91	1	157.91	5.02	0.042[c]
X_4	977.41	1	977.41	31.05	<0.0001[c]
X_1X_2	6.15	1	6.15	0.20	0.665[d]
X_1X_3	0.27	1	0.27	0.0084	0.928[d]
X_1X_4	1.32	1	1.32	0.042	0.840[d]
X_2X_3	0.3	1	0.3	0.0094	0.924[d]
X_2X_4	2.36	1	2.36	0.075	0.788[d]
X_3X_4	0.66	1	0.66	0.021	0.886[d]
X_1^2	282.26	1	282.26	8.97	0.0097[c]
X_2^2	73.98	1	73.98	2.35	0.147[d]
X_3^2	51.82	1	51.82	1.65	0.220[d]
X_4^2	55.67	1	55.67	1.77	0.205[d]
Residual	440.64	14	31.47		
Pure error	13.46	4	3.36		
Cor total	2801.41	28			
R^2		0.8427		R^2adj.	0.6854
Mean		26.03		R^2pred	0.1141
C.V.%		21.56		Adeq precision	9.30

[a] X_1, aeration rate; X_2, pH; X_3, hydraulic retention time; X_4, dosages of Fe-C particles
[b] RCOD, removal efficiency of chemical oxygen demand
[c] Significant at 5% probability (p<0.05)
[d] Non-significant

0.05. And the interaction reactions X_1, X_2, X_3, X_4 and X_1^2 were significant (p<0.05). After neglecting the insignificant terms based on 5% level of significance, Eq. (2) could be expressed as the following:

$$\text{RCOD}(\%)=24.74+3.93X_1-6.23X_2+3.63X_3+9.03X_4+6.6X_1^2 \quad (3)$$

In addition, the factors R^2 and adjusted R^2 are calculated to check the model adequacy. Indeed, such an analysis shows the close agreement between the experimental results and the theoretical values predicted by these models as high values of R^2 (>0.84) and $R^2_{adj.}$ (>0.68) are observed for RCOD (Table 2), confirming that the fitted models can satisfactorily explain the total variability of the responses within the range of independent variable studied. The value 9.30 of "Adeq. precision" that measures the signal-to-noise ratio is greater than 4, indicating an adequate signal. Therefore, this model can be used to navigate the design space.

According to the results of statistically designed experiments, the optimum conditions of micro-electrolysis treatment piggery digestate wastewater were as follows: aeration rate=6 L/h, pH=6.0, hydraulic retention time=9 h and dosages of Fe-C particles=200 g/L. Under these conditions, COD removal efficiency predicted by the model was 51.76%.

To confirm these results obtained above, verification experiments were carried out under optimal conditions: aeration rate=6 L/h, pH=6.0, hydraulic retention time=9 h and dosages of Fe-C particles=200 g/L. Finally, a mean value of 50.23%±0.58% was quite close to the predicted value (51.76%), confirming the validity of response model.

RESULTS AND DISCUSSIONS

1. Effect of Initial pH

The pH has been deemed as one very important factor affecting the treatment efficiency in micro-electrolysis system. The treatment capability of micro-electrolysis generally originated from its half-cell reactions, and large amount of H^+ would be consumed at the very first step according to Eq. (4)-(9). Thus, it is reasonable to evidence that a lower pH is more effective for piggery biogas slurry treatment in micro-electrolysis system [10,23].

Iron anode (oxidation):

$$Fe\,(s)\rightarrow Fe^{2+}\,(aq)+2e \quad E_0(Fe^{2+}/Fe)=+0.44\,V \quad (4)$$

$$Fe^{2+}\,(aq)\rightarrow Fe^{3+}\,(aq)+e \quad E_0(Fe^{3+}/Fe^{2+})=+0.77\,V \quad (5)$$

Cathode (carbon):

$$2H^+\,(aq)+2e\rightarrow 2[H]\rightarrow H_2(g),\ E_0(H^+/H_2)=0\,V \quad (6)$$

Carbon cathode (reduction) in the presence of oxygen:

Acid: $O_2\,(g)+4H^+\,(aq)+4e\rightarrow 2H_2O$

$$E_0(O_2/2H_2O)=+1.23\,V \quad (7)$$

$$O_2\,(g)+2H^++2e\rightarrow H_2O_2\,(aq) \quad E_0(O_2/H_2O_2)=+0.68\,V \quad (8)$$

Neutral to alkaline

$$O_2\,(g)+2H_2O+4e\rightarrow 4OH^-\,(aq) \quad E_0(O_2/OH^-)=+0.40\,V \quad (9)$$

Fe^{2+} and the new eco-hydrogen [H] had a high chemical activity, which could make organic matter chain scission, and change the organic functional groups, so biodegradability of organic wastewater significantly improved, which could provide favorable conditions for the follow-up biological treatment.

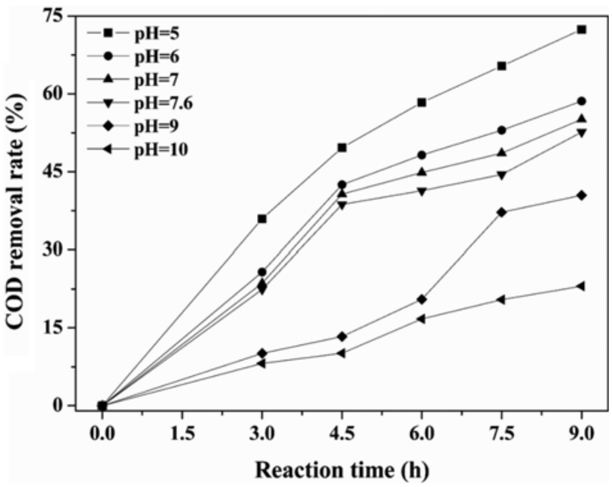

Fig. 2. Effect of pH value on COD removal (Experimental conditions: dosages of Fe-C particles=150 g/L, reaction time=9 h, oxygen existing).

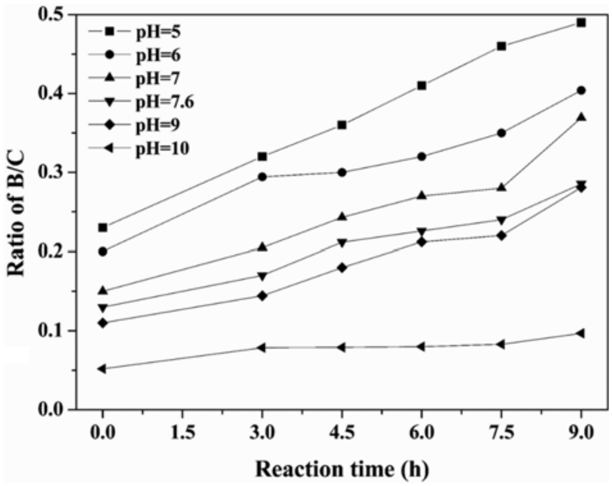

Fig. 3. Effect of pH value on ratio of B/C (Experimental conditions: dosages of Fe-C particles=150 g/L, reaction time=9 h, oxygen existing).

Different pH conditions had different influences on the removal rate of COD. To understand the effect of initial solution pH on COD removal rate by Fe-C micro-electrolysis at initial pH 5-10, experiments were carried out for 9 hours and the results are shown in Fig. 2 and Fig. 3. Analytical samples were drawn from the reaction suspension every 90 min. As shown in Fig. 2, when pH was 5.0, Fe-C micro-electrolysis showed the best performance to dispose piggery digestate wastewater after acidification, and removal rate of COD was 72.40%. And there was an abrupt decrease of COD removal rate from 72.40% to 23.04% when the pH value varied from 5 to 10. These results are in agreement with data reported by Chen [24], who observed that degradation rates of the organic wastewater decreased while the pH value increased. The reason was that Fe in low pH condition occurred the following reaction:

$Fe+2H^+ \rightarrow Fe^{2+}+H_2$. A lot of H^+ existed in low pH condition, which responded fast; but it was not that the lower the better, because the lower pH would change the existing form of the product, such as flocs that were generated after the reaction were destroyed, and the reaction of which produced colored deterioration of the treatment effect of Fe^{2+} was bad. Moreover, in the course of dynamic micro-electrolysis, the nascent states of species such as [H], Fe^{2+}, and Fe^{3+} would react with the contaminants in the wastewater by means of redox reaction, flocculation-absorption, complexing, and electro-deposition [15]. For instance, it has been reported [16,25] that the chelated metal irons by organic compounds could be removed from aqueous solution by iron hydroxides prepared from micro-electrolysis through the adsorption-coprecipitation process, so a similar case probably had happened in this process. All in all, the effects mentioned above could be responsible for the formation of hydroxyl-containing organic compounds and the removal of COD.

As shown in Fig. 3, when pH was 5, the ratio of B/C was 0.490. When pH was 7.6, the ratio of B/C was 0.285. Thus, the highest COD removal rate and the ratio of B/C was achieved at pH=5. However, the Fe-C particles were seriously corroded and decomposed in the wastewater at low pH, which would cause a problem that the reaction could be clogged by activated carbon. So pH=7.6 was selected for rest experiments, taking into account the cost of treatment.

After Fe-C micro-electrolysis, pH value of solution rose from 5.0 to 6.5. After reacting, the solution of pH value for 7.6 rose to 8.7. The pH value of solution increasing after reaction was mainly due to that cathode H^+ became [H], and generated H_2 at last. This was advantageous to Fe-C micro-electrolysis and the pH rise can provide conditions for subsequent biochemical treatment.

2. Effect of Dosages of Fe-C Particles

The dosage is an important operational parameter for an economical wastewater treatment process. Based on the principle of micro-electrolysis reactions, a bigger cathode area can increase the number of iron carbon micro cell under anode surface area fixed

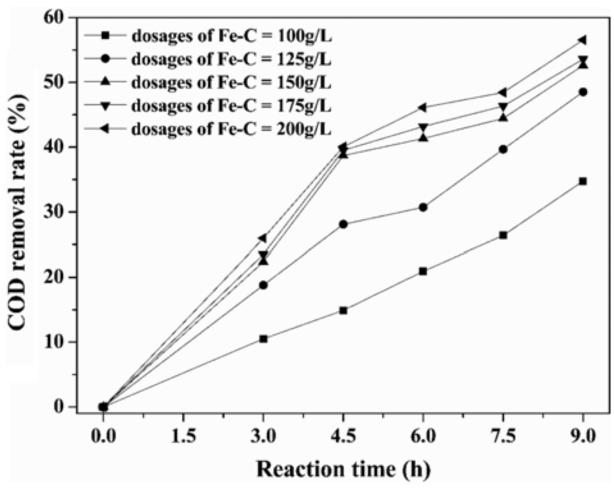

Fig. 4. Effect of dosages of Fe-C particles on the removal of COD (Experiment conditions: pH=7.6, reaction time=9 h, oxygen existing).

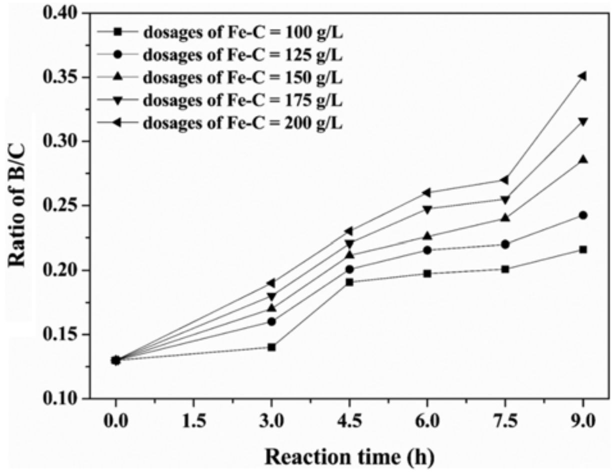

Fig. 5. Effect of dosages of Fe-C particles on the ratio of B/C (Experiment conditions: pH=7.6, reaction time=9 h, oxygen existing).

in certain extent. Therefore, optimal dosages of Fe-C particles should be selected to achieve the excellent degradation of piggery digestate wastewater. The effect of particles on COD and B/C was investigated (Fig. 4 and Fig. 5).

As Fig. 4 shows, when the dosages of Fe-C particles ranged from 100 to 200 g/L, the removal rate of COD ranged from 34.76 to 56.53%. At the same time, there was no significant difference on COD removal rate when the dosages of Fe-C particles ranged from 150 to 200 g/L. Fe-C micro-electrolysis treatment the piggery digestate wastewater mainly depended on the primary cell response, redox reactions, coagulation and sedimentation and so on to treat the organic matter. When the dosages of Fe-C particles were low, the number of micro-electrolysis would be significantly reduced, thus weakening the electrolysis reaction degrading the COD. And the balance between Fe and C electrode surface would be broken, which would consume the amount of iron. A large amount of Fe^{2+} was accumulated and might react with •OH, hence the removal efficiency of COD was weakened. Increasing the dosages of Fe-C particles can improve the removal effect to organic matter [26]. The results of this study were identical with Guan's [27], who observed that when the Fe and C electrode surface was not balance, a large amount of Fe^{2+} would be generated and could react with •OH, then the effect was weakened. As shown in Fig. 5, the effect of dosages of Fe-C particles on the ratio of B/C was remarkable. When the dosages of Fe-C particles were increased from 100 to 200 g/L, the ratios of B/C was increased from 0.216 to 0.351. Considering the treatment situation, the dosages of Fe-C particles of 150 g/L was appropriate for rest experiments.

3. Effect of Aeration Rate

Aerobic and anaerobic experiments were carried out, respectively, and the results are shown in Fig. 6 and Fig. 7. As shown in Fig. 6, the removal rate of COD is 28.67% for the anaerobic experiment with nitrogen pumping in, while it is 52.62% for the aerobic experiment with oxygen pumping in. It is shown clearly in Fig. 7 that the aeration also had a better impact on the ratio of B/C efficiency. The ratios of B/C were 0.242 and 0.285 for nitrogen and oxygen conditions, respectively. Our results confirmed the finding

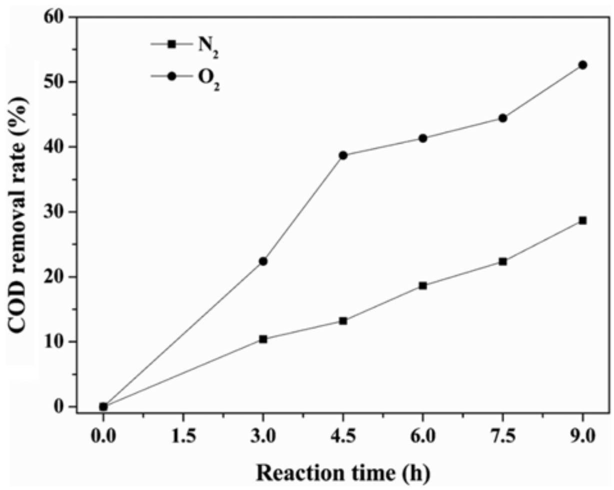

Fig. 6. Effect of ventilation condition on removal rate of COD (Experimental conditions: dosages of Fe-C particles=150 g/L, pH=7.6, reaction time=9 h).

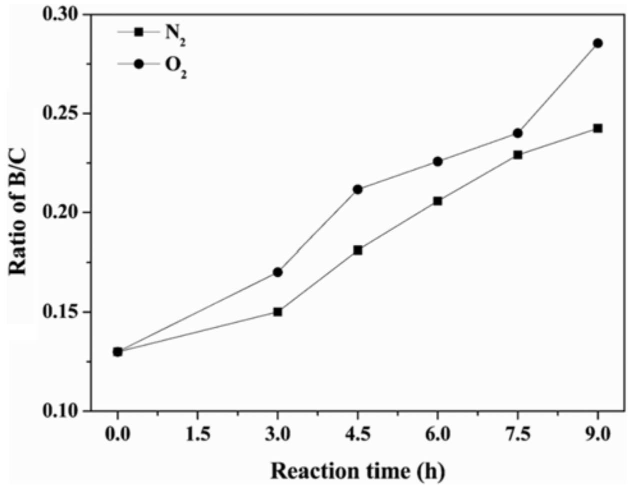

Fig. 7. Effect of ventilation condition on ratio of B/C (Experimental conditions: dosages of Fe-C particles=150 g/L, pH=7.6, reaction time=9 h).

of Han [28], who observed that the removal efficiency of COD increased sharply with aeration amount increasing from 0 to 12.5 L/min. The removal efficiency of COD showed an obvious change with aeration and without aeration. In the absence of aeration, the reaction at the cathode was to reduce H^+ to active H and H_2, such as Eq. (6). Anodic iron was only oxidized to Fe^{2+}, such as Eq. (4) and Eq. (5). Therefore, the COD removal rate and the ratio of B/C should be mainly attributed to the reduction of active H and fresh H_2. In the presence of aeration, the hydroxyl peroxide could form at the cathode with aeration [29], such as Eq. (8) which can induce the Fenton reaction with Fe^{2+} generated at anode. Therefore, the COD removal rate and the ratio of B/C should be mainly improved by the oxidation of hydroxyl radical generated during the Fenton reaction. Moreover, aeration provided not only oxygen for cathode reaction but also the driving force, which was conductive to activation of the surface of iron. So it could be concluded that the aeration had a beneficial effect on the Fe-C micro-electrolysis [30-32].

Since the piggery digestate wastewater could still contain high concentrations of organic carbon and inorganic nutrients, low C/N ratio and low B/C ratio, it must be correctly managed to avoid any impact on the environment [33]. Nevertheless, it is more difficult to remove organics under low C/N ratio and B/C ratio for aerobic process. Thus, pretreatment processes may be required before the biological treatment process. The traditional pretreat processes have their advantages. Hydrolysis acidification process is a common pretreat process, which could improve the biodegradability of wastewater and could depolymerize complicated molecules and insoluble contaminants into simpler monomers and dissolvable compounds [34-36]. However, it has its insufficient points, such as initial pH, limit of operating conditions, choice of microorganism [37]. Micro-electrolysis process used in this work would not have these shortages. As is well known, this process is a physical/chemical process. It could be mostly carried out unlimited except initial pH. Struvite precipitation is another common pretreat process, which not only can remove NH_4^+ and P from digestion centrate, but also can recover the NH_4^+ and P as a valuable fertilizer [38,39]. Then, the C/N ratio of digestion centrate could be increased. But this process is a physical process, that could not depolymerize complicated molecules and insoluble contaminants and improve the biodegradability of digestion centrate. Micro-electrolysis process used in this work not only could change the C/N ratio and B/C ratio of the digestate wastewater, but also could remove part of the organic matter. The B/C ratio was increased from 0.13 to 0.285, indicating that the bio-degradability of the wastewater was greatly improved [40], and COD removal efficiency was 52.62%. From the above results, compared with other pretreat processes, Fe-C micro-electrolysis process used in this work had high removal efficiency of COD and could significantly increase the B/C ratio. This would be in favor of aerobic process.

4. Fe-C Micro-electrolysis Mechanism of Piggery Digestate Wastewater

4-1. SEM Analysis

To confirm the morphological changes of Fe-C particles, the microscopic observation of Fe-C particles samples was visualized (Fig. 8). The differences in Fe-C particles appearance were obvious. As shown in Fig. 8(a), the raw surface of Fe-C particles was clean and uniform. The SEM image (Fig. 8(b)) of Fe-C particles after reaction showed that there were a few amorphous particles and agglomerates on the surface of Fe-C particles. Moreover, the surface of Fe-C particles was corroded but still uniform. This indicates that the zero-valent iron and activated carbon of the Fe-C particles is sintered and cannot be separated uneasily. At the same time, with the action of aeration, the agglomerates and precipitates on the surface of Fe-C particles could be taken away by wastewater. Nevertheless, the reaction points would gradually decrease and thereafter result in the deterioration of treatment performance by using the traditional zero-valent iron and activated carbon particles. The decreased treatment performance to a certain extent indicated the serious problem of inactivating and blocking of zero-valent iron and activated carbon [18]. Therefore, the Fe-C particles could efficiently resolve the problems of hardening, blocking and inactivation.

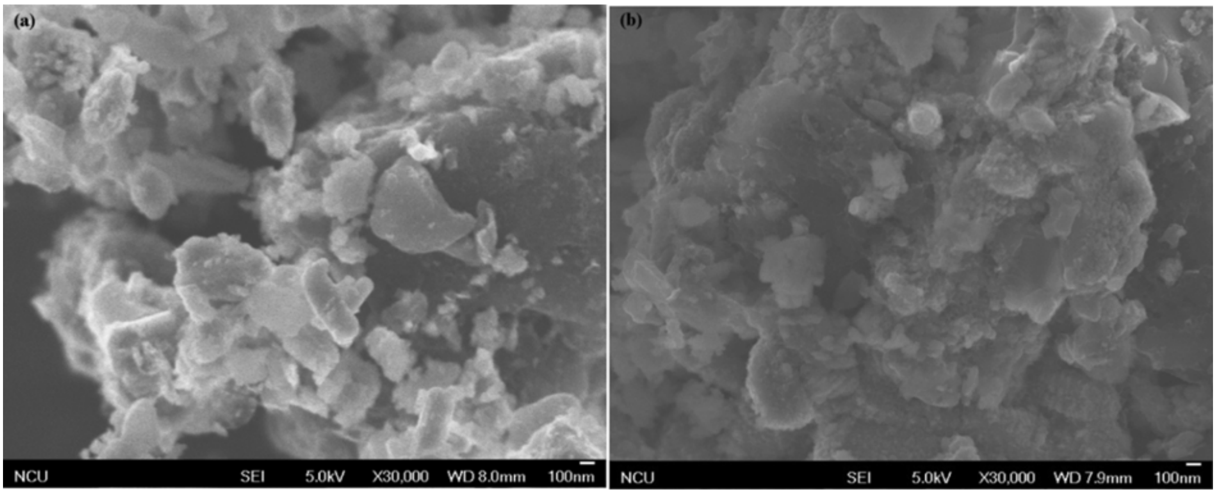

Fig. 8. Morphological structure images of Fe-C particles. (a) Before reaction, (b) after reaction.

4-2. Preliminary Degradation Mechanism of Fe-C Micro-electrolysis

To illustrate further the reason for the decay of COD and the change of the B/C ratio in effluent, the degradation mechanism by the Fe-C micro-electrolysis was proposed as follows:

The micro-cell reaction that occurs in the Fe-C-O_2 system fits the following reaction [24,41]:

$$O_2+2H^++Fe\rightarrow Fe^{2+}+H_2O_2 \quad (10)$$

Fe^{2+} is rapidly released into the solution because of the dissolution of iron. Then, H_2O_2 is generated and combined with Fe^{2+} to form Fenton's reagents, which could generate •OH according to Eq. (10) [42,43]:

$$H_2O_2+Fe^{2+}+H^++\rightarrow Fe^{3+}+H_2O+\bullet OH \quad (11)$$

The hydroxyl radical •OH has such an extremely great redox potential (E^0=2.80 V vs SHE) that it can react almost non-selectively with organic pollutants at near-ambient temperature and pressure [44-49]. The reaction equation was shown as follows:

$$RH+\bullet OH\rightarrow R\bullet+H_2O \quad (12)$$

At the same time, Fe^{3+} and OH^- could react to generate ferric flocculants, which could bring about electrocoagulation with pollutants of piggery digestate wastewater.

Based on the phenomena described in the previous paragraph, *t*-butanol was added into the reaction system to study the contribution of •OH. The removal rate of COD is shown in Fig. 9. As shown in Fig. 9, in ME system, the removal rate of COD was different before and after the addition of *t*-butanol. And the removal rate of COD decreased from 51.69±1.5% to 44.32±1.35%. The *t*-butanol reacted with the produced •OH, acted as an •OH radical scavenger, resulting in the reduced concentration of •OH radicals when it was added into the system. Thus, this finally terminated the propagation reaction by the reactive radicals and decreased the COD removal rate of the piggery digestate wastewater.

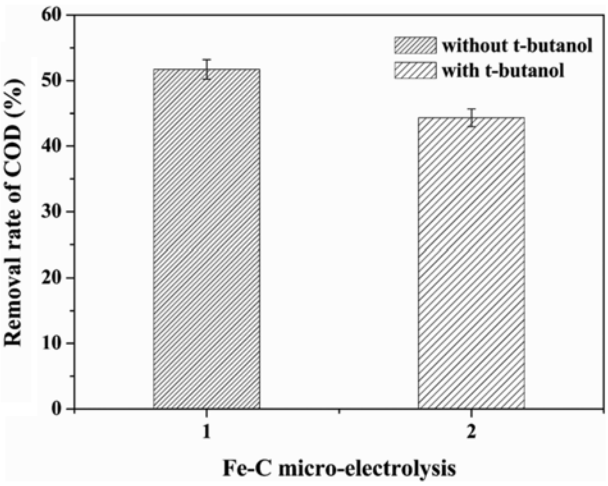

Fig. 9. Removal rate of COD with the addition of t-butanol (Experimental conditions: dosages of Fe-C particles=150 g/L, pH=7.6, reaction time=9 h, oxygen existing).

CONCLUSION

To avoid the disadvantages of the traditional iron-carbon micro-electrolysis, newly designed Fe-C particles were developed. With the use of Fe-C micro-electrolysis reaction as a primary treatment, the piggery digestate wastewater can be degraded and more biodegradable. Experimental results demonstrated that the treatment conditions, such as the pH, dosages of Fe-C particles and aeration rate, had significant influence on degradation efficiency and ratio of B/C, and that •OH played an important role in the degradation of the piggery digestate wastewater. The results demonstrated that the piggery digestate wastewater can be successfully pretreated by the process of Fe-C micro-electrolysis with the newly designed Fe-C particles.

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