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Application of lead flocs fractal dimension by new poly-ferric-silicon coagulant

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ABSTRACT

Poly-ferric-silicon, made by the fly ash extract, is well in dealing with the lead industrial wastewater. Meanwhile combed with the application of fractal theory in coagulation, the test is conducted the jar test in different dosages and pH value, and found that the fractal dimension of flocs and the lead removal after precipitation can be showed a good correlation, so this is achieved the online monitoring the coagulation effect by flocs fractal dimension. Additionally, in order to assure the optimal hydraulic condition of the new type poly-ferric-silicon coagulant, the test is utilized orthogonal experiment to seek the best hydraulic energy consumption allocation scheme which is $G_1 = 67.7$ s^{-1}, $t = 3$ min, $G_2 = 57.8$ s^{-1}, $t = 5$ min, $G_3 = 23.9$ s^{-1}, $t = 7$ min by dividing the stirring intensity (G value) and stirring time (t value) into different three gears in flocculation stage. and got the appropriate flocs fractal dimension being 1.48, 1.66 and 1.80 in each stage of the distribution of energy consumption. So combing the energy consumption allocation scheme with fractal dimension, it not only be effectively illustrated the rational of the energy consumption allocation decision, but also offered the comparatively scientific design data for designing of the flocculation tank, being made the water treatment economical and efficient.

Keywords: Poly-ferric-silicon coagulant; Industrial wastewater with lead; Lead flocs fractal dimension; Energy distribution

1. Introduction

Coagulation is the important part in water treatment, and the feature of flocs [1], being produced in this process, can be an important indictor to evaluate the coagulation effect. However, because the flocs, being frangible and irregular [2,3], were not in-depth researched, and the coagulation effect was judged by the coagulant dosage and the quality of outflow.

Additionally the flocs growth needs appropriate hydraulic conditions. Because the growth speed is influenced by the lower mixing intensity, and the flocs structure can be broken in the higher mixing intensity, the favorable hydraulic condition is one of the important factors to obtain a better coagulant. Usually the stir condition was designed according to a fixed mixing intensity (G) and fixed time (t) [4,5], and the flocculation process was divided into three stages, on the basis of decreasing progressively of the G value and equivalent to the mixing reaction time in the flocculation tank. The G value and t value were experience data, and the discrepancies of the raw water quality, coagulant types and others coagulation condition were not considered, so the energy consumption distribution was hard to meet the actual requirements, not to mention the optimization of distribution [6,7].

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Because of limited flocs structure characteristics, people did not further study the flocs growth in coagulation, and could not verify the rationality of the hydraulic condition [8]. However, the fractal theory [9] appeared as a tool giving rise to the flocculation morphology research more in-depth [10,11]. The flocs' structures and properties can be described quantitatively by fractal dimension. From the current research trend, it can be found that researchers mainly studied the high turbidity water flocs [13], diatomite flocs [14], sludge flocs [15] and organic flocs [16]. For example, Jin [17] studied the flocs size distribution, and obtained the normal distribution function by calculating the standard deviation of any one time. However, because of the limiting of coagulant and other factors, the studies on metal ion floc characteristics are fewer.

In this test, a new type synthesize macromolecule coagulant — poly-ferric-silicon coagulant, good in dealing with lead wastewater, was prepared by the fly ash extract and ferric based [18]. In order to insure the correlation between the fractal dimension and lead removal, the test calculated the lead flocs fractal dimension in different dosages and pH values. Additionally in order to assure the optimum hydraulic condition of this novel coagulant, this test divided the flocculation stage into three different cases of mixing conditions, the flocs were picked up and fractal dimensioncalculated the after each stage and the flocs growth state was analyzed by the fractal dimension. So from the analyzing of flocs fractal dimension, a theoretical basis can be provided to control the operation conditions of coagulation process rationally.

2. Experimental

2.1. Materials and instruments

This experiment utilized the simulation lead wastewater by adding lead nitrate, sodium chloride and sodium thio-sulfate to running water. The simulation lead wastewater has turbidity 300 NTU, color 900, COD 80 and Pb^{2+} 20 mg/L.

The laboratory instruments mainly included:

1. JJ-4A synchronous mixed instruments with six stirrers;
2. COD tester;
3. atomic absorption spectrophotometer;
4. JEM-2010 transmission electron microscope;
5. computer, beaker, cylinder and plastic head dropper with large diameter.

2.2. Novel type coagulation made by self

In this work, first an appropriate amount of coal fly ashes was mixed with a certain molar concentration of sodium hydroxide solution, and the mixture was heated at constant temperature in bath oscillator for several hours, the supernatant could be extracted after cooling. Using the de-ionized water doubleing dilution the supernatant, the pH value was adjusted by sulfuric acid solution, at last it reacted with ferric potassium at a certain temperature. After seven days of polymerization, the poly-ferric-silicon coagulation was formed. At room temperature the density of coagulant was 1.55 g/cm^3, pH 2.3–2.5.

2.3. Method of calculation of fractal dimension of flocs

When the stirring was over, a little amount of flocs was picked up to cover-slip and photographs taken by JEM-2010 transmission electron microscopy. According to the image analysis method, using the function of floc projection area and perimeter [19] $A = \alpha P^{Df}$ and taking double logarithm to the abovementioned equation, the floc fractal dimension can be sought. In the test the floc fractal projection area and perimeter were calculated by ImageJ software. The method is shown in Fig. 1.

2.4. Hydraulic parameters of jar test [20]

The calculation formula of mixing power is followed in a jar test:

$$P = \frac{1}{32} C_D \rho \left(\frac{2\pi n}{60} \right)^3 bd^4 \quad (1)$$

velocity gradient

$$G = \sqrt{\frac{P}{\mu V}} \quad (2)$$

In this formula P means mixing power (W); C_D — resistance coefficient = 0.4; ρ — the density of water sample (kg/m^3) = 1.005×10^3 kg/m^3; b — the height of the slurry mixing blades (m) = 3.5 cm; d — the width of slurry mixing blades (m) = 5.5 cm; n is the speed (rpm); μ is the dynamic viscosity of water, being 1.006 ×10^{-3} Pa s at 20°C; V is volume of water sample (m^3) and G is velocity gradient (s^{-1}). Taking the relevant data to Eqs. (1) and (2), G value can be obtained — $0.0677 \times n^{1.5}$. The corresponding relation between G value and rotation speed is shown in Table 1.

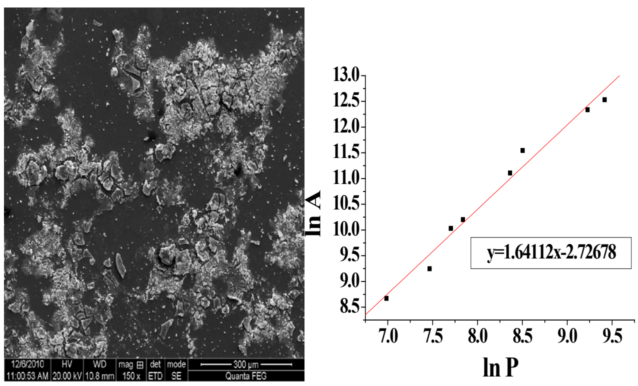

Fig. 1. The flocs photo and fractal dimension.

Table 1
The corresponding relation between *G* value and rotation speed

n (rpm)	*G* (s^{-1})
40	17.1
50	23.9
60	31.5
70	39.6
80	48.4
90	57.8
100	67.7
110	78.1
120	88.9
300	351.8

3. Results and discussion

3.1. Determination of fractal dimension in different dosages

The jar test was conducted after taking different dosages of the prepared poly-ferric-silicon coagulant into the lead industrial wastewater, and the optimum dosage could be obtained by analyzing the results. Firstly, it was switched on the six joint mixing apparatus at high-speed, mixed for 1 min at 351.8 s^{-1}, then slow-speed mixed for 15 min at 48.4 s^{-1}, at last the relevant indicators of water quality were determined after putting it aside for 15 min, thereby the optimum dosage could be assured. At the same time a little amount of flocs were picked up to the cover-slip, photographs taken and the flocs fractal dimension calculated. The results are shown in Table 2.

3.2. Determination of fractal dimension at optimum pH value

The pH value can be influenced the hydrolysis process of coagulation, especially the metal salt coagulation. Because the coagulation can be hydrolyzed into different products at different pH values, pH value is one of significant factors for the coagulation result. The coagulation jar test was carried out with the optimum dosage 5.42 g/L after transferring the raw water to different pH values. The results are shown in Table 3.

Table 2
The fractal dimension and removal in different dosage

Dosage (g/L)	Removal (%)	Fractal dimension
3.10	96.36	1.64472
5.42	96.48	1.67674
7.75	92.21	1.63219
10.07	95.86	1.60132
12.40	94.32	1.51277
15.50	94.28	1.50650

Table 3
The fractal dimension and removal at different pH values

pH value	Removal (%)	Fractal dimension
7.5	96.67	1.68822
8	97.02	1.7442
8.5	97.11	1.75055
9	97.38	1.81069
9.5	97.52	1.88924
10	96.51	1.66031

From the data of Tables 2 and 3, a conclusion can be drawn that a good correlation between flocs fractal dimension and lead removal is shown, so it can be used for online monitoring of the flocs fractal dimension in coagulation, and reflect the coagulation levels and treatment effect. When the dosage is 5.42 g/L, pH value 9.5, the flocs fractal dimension appears as the maximum value 1.88924, and the lead removal is the highest — 97.52%. At this time the energy consumption *Gt* value of the flocculation stage is 48.4 × 15 × 60 = 43500.

3.3. The energy distribution experiment of the jar test

In this part the experiment on the poly-ferric-silicon coagulant is still applied and the optimum dosage is 5.42 g/L. The jar test is mainly conducted for the distribution of energy consumption to the flocculation stage and the conclusion of the best hydraulic condition is obtained. The experimental program is unchanged: n_0 = 300 rpm, G_0 = 351.8 s^{-1}, t_0 = 1 min, and the slow mixing is divided into three different sections of time portfolio, namely first portfolio: *t*1 = 4 min, *t*2 = 5 min, *t*3 = 6 min; second portfolio: t_1 = 5 min, t_2 = 5 min, t_3 = 5 min; third portfolio: t_1 = 3 min, t_2 = 5 min, t_3 = 7 min. The velocity gradient of each mixing time portfolio is chosen from the range of values in 65–90 s^{-1}, 35–65 s^{-1}, 10–35 s^{-1}. At last the factors and levels of the energy consumption distribution is shown in Table 4.

The above level and factor portfolio is designed according to the orthogonal experiments. Because Table 4 has four factors and three levels, the L_9 (3^4) orthogonal experimental Table 5 is applied.

Table 4
The factors and levels of the energy consumption distribution

Level	Factor			
	G_1 (s^{-1})	G_2 (s^{-1})	G_3 (s^{-1})	Time portfolio of flocculation
1	67.7	48.4	31.5	Portfolio one
2	88.9	57.8	17.1	Portfolio two
3	78.1	39.6	23.9	Portfolio three

Table 5
The table of orthogonal experiment

Experimental sequence	Factors			
	G_1 (s^{-1})	G_1 (s^{-1})	G_1 (s^{-1})	Time portfolio of flocculation
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

After designing the orthogonal experimental table, the mixing experiment was conducted according to the above scheme, and the lead removal was detected after static sediment 15 min when the stir test was over. At the same time picking up a little amount of flocs to cover-lip to take photographs by JEM-2010 transmission electron microscopy when each stir stage is over, then the flocs fractal dimension is calculated.

From Table 6, by the lead removal and the flocs fractal dimension, it can be found that:

(1) According to the result of the poor, seeing that the stirring speed G is the major factor of influencing the treatment effect, and the order is $G_1 > G_2 > G_3$;
(2) At the first stage the appropriate flocs fractal dimension is 1.48 in the condition of (G_1 = 67.7 s^{-1}, t = 3 min), rather than the larger fractal dimension 1.55718 in the condition of (G_1 = 67.7 s^{-1}, t = 5 min). Analyzing that in the first stage the stir time couldn't be too long. The long stir time can get the larger fractal dimension flocs, but the flocs are not suitable for growth in the second stage. Because at this stage the flocs are formed by the compressed two-electron shell, and the attractive force between particles is not enough to resist the stir shear force, leading to the bigger flocs easily to be broken when the stirring speed is changeable, so the flocs are not suitable for growth in the next stage;
(3) At the second stage, the optimum portfolio is (G_2 = 57.8 s^{-1}, t = 5 min), and the appropriate flocs fractal dimension is 1.66. Thinking that the flocs are formed by the electrostatic adsorption and charge neutralization which is produced by the hydrolysis products of poly-ferric, and repulsion between particles is poor, the flocs structure is dense and not easily broken.
(4) At the third stage, the optimum portfolio is (G_3 = 23.9 s^{-1}, t = 7 min), and the appropriate flocs fractal dimension is 1.80. From the data knowing that the time of the third stage is enough long, so that it can be increased the collision probability, and the flocs

Table 6
The results of orthogonal experiment

Experimental sequence	Factors				
	G_1 (s^{-1}) D_f	G_1 (s^{-1}) D_f	G_1 (s^{-1}) D_f	Time portfolio of flocculation	Removal
1	1.47633	1.64945	1.80236	1	0.9752
2	1.55718	1.62064	1.73343	2	0.9707
3	1.51225	1.65325	1.72709	3	0.9691
4	1.49282	1.61586	1.72252	3	0.9682
5	1.45296	1.60243	1.71834	1	0.968
6	1.53758	1.57446	1.66775	2	0.9653
7	1.53865	1.64998	1.69541	2	0.9674
8	1.48179	1.66331	1.84641	3	0.9755
9	1.43625	1.59715	1.69864	1	0.9679
K_1	2.915	2.9108	2.916	2.9111	
K_2	2.9015	2.9142	2.9068	2.9034	
K_3	2.9108	2.9023	2.9045	2.9128	
k_1	0.972	0.9702	0.9723	0.9707	
k_2	0.9671	0.9714	0.9689	0.9678	
k_3	0.9702	0.9674	0.9681	0.9709	
R	0.0045	0.0040	0.0038	0.0031	

Notes: K_i is the index sum of each factor i level; $k_i = K_i/3$; R is poor, the size of poor reflects the impact degree to indicators of factor.

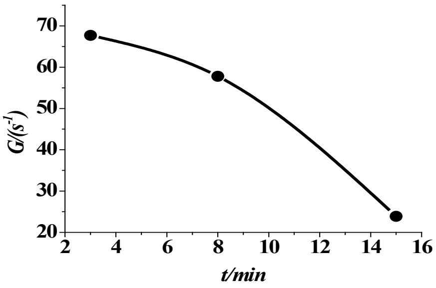

Fig. 2. The curve of energy consumption distribution.

are most dense and settlement. The lead removal is 97.55%.

(5) The energy consumption distribution chart is drawn through the optimum portfolio of each stage, as in Fig. 2.

Fig. 2 illustrates that the diversification of *G* value should be smooth, thereby the flocs can grow better. At this time the energy consumption *Gt* ($G_1t_1 + G_2t_2 + G_3t_3 = 67.3 \times 3 \times 60 + 57.8 \times 5 \times 60 + 23.9 \times 7 \times 60$) value of the flocculation stage is 39564.

4. Conclusions

(1) In the coagulation process, the coagulant of the optimum dosage range is 5.42–7.75 g/L and the optimum pH value is 9–9.5, the lead removal is up to 95%.

(2) By observing the floc structures, it could be found that the flocs were not spherical in theory. Combined with the diversification of floc structure, not only the coagulation effect in different coagulation conditions, was determined, but it was also calculated that two-fractal-dimension of lead flocs is between 1.5 and 1.9. When the coagulation is in the optimum condition, the flocs frame is dense and the size is large enough, which may be related with the strong static adsorption of a series of multi-core polymer the iron salt hydrolyzed into. In addition the result indicated that the fractal dimension showed a good correlation with the lead removal, which could help us achieving the online monitoring, and reflecting the coagulation levels and treatment effect.

(3 From the fractal dimension determinant, the appropriate fractal dimension for flocs growth in each stage is that in the first phase the fractal dimension being 1.48; in the second phase the fractal dimension being 1.65, and in the third phase the fractal dimension being 1.84. In this condition the flocs are most dense and easily settled. Additionally from the increasing speed of the fractal dimension, known that the increase of flocs is mainly in pre-middle phase, and the flocs are formed by the electrostatic adsorption and charge neutralization which is produced by the hydrolysis products of poly-ferric.

(4) By dividing the flocculation process into three different stages, favorable treatment results can be gained: view from the treatment effect, the removal is obvious improved; view from the energy consumption distribution, the optimum energy consumption distribution (*GT* value 39564) is less than (no allocation *GT* value 43500) 3996; view from the online monitoring the flocs fractal dimension, the flocs growth condition can be made clear, the process parameters controlled, suitable coagulant chosen and the equipment optimized.

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