



Research on Flocculation Property of Bioflocculant PG-a21 Ca

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Abstract

This paper investigates the flocculation performance of polyglutamic acid-based bioflocculant PG-a21 Ca by processing kaolin suspension, studies the effects on the flocculation efficiency from the amount of flocculant, pH, temperature, hydraulic condition and etc. The results show that the flocculation rate of PG-a21 Ca to 1 g/L kaolin suspension is 95.8% under the condition that the amount of PG-a21 Ca is 300 mg/L, pH is 7, temperature is 25 °C, stirring speed of mixing is 350 r/min, stirring time of mixing is 50 s, stirring speed of reaction is 80 r/min, and stirring time of reaction is 4 min. Effects from wastewater processing show that bioflocculant PG-a21 Ca has better effects in treating domestic wastewater and higher removal rate of total phosphorus and ammonia nitrogen than the common chemical flocculants such as PAC and PFS. Meanwhile, PG-a21 Ca can effectively remove chlorophyll A in algae-contained lake water and make water clear, and partially remove COD and TP in wastewater from beer brewing.

Keywords: Bioflocculant PG-a21 Ca, Flocculation performance, Wastewater disposal, Polyglutamic acid

Flocculation technology has been widely applied in water processing field, especially in preprocess of various wastewater treatment. It has the benefits of low infrastructure investment and short processing time. There are two common flocculants at present: inorganic macromolecular compounds as represented by aluminum-iron series coagulant and synthesized organic macromolecular flocculants as represented by acrylamide polymer. However, it has been found that these flocculants have relatively serious safety issue and potential secondary pollution in practical applications. For example, aluminum ion may cause senile dementia; iron salt causes corrosion to equipment and may have relatively higher coloring; acrylamide polymer, an organic macromolecular flocculant, although non-toxic, is difficult to degrade and can cause secondary pollution; meanwhile, the original monomer acrylamide has strong neurotoxicity and can cause cancer. All above issues limit their applications. Therefore, it is necessary and important to develop a safe and non-toxic flocculant with high flocculating activity and without any secondary pollution.

Study on application of bioflocculant has reached wide areas including various wastewater disposal, such as suspension removal (Gong, Xiaoyan, 2003, p. 196-199; Li, Heping, 2000, p. 113-117; Huang, Xiaowu, 2004, p. 25-27), color removal (Zhuang, Yuanyi, 1997, p. 349-353; I. L. Shih, 2001, p. 267-272; Xin, Baoping, 2000, p. 97-102; J. Zhang, 2002, p. 517-522; Man, Yuezhi, 2003, p. 187-190). In recent years, the bioflocculant has attracted more and more attentions with its high efficiency, non-toxicity, easy decomposition, non secondary pollution, wide application areas, unique color removal effect and other benefits. Wang, Li (2008, p. 31-32) processed dyeing wastewater with Pullulans bioflocculant, its COD_{Cr} removal rate and turbidity removal rate are respectively 88.22% and 63.67%. Ma et al (2009, p. 196-200; 2008, p. 39-41) processed high algae-laden water by polymeric aluminum ferric chloride-compounded composite bioflocculant, wherein the composite bioflocculant was prepared with rice straw as substrate. The results indicated that the turbidity removal rates of chlorine dioxide-preoxidized high algae-laden water by the same amount of composite bioflocculant and polymeric aluminum ferric chloride are 89.1% and 60.5% respectively. Gong et al (2008, p. 4668-4674) separated a bacteria from soil. The bioflocculant produced from this bacterium has better flocculation effects at processing effluents from river, beer factory, meatpacking, soy sauce plant and pulp-paper mill. Fujita et al (2001, p. 237-243) purified wastewater from manufacturing plants of deinking chemicals, carbon ink, paint and bean products by a flocculant obtained from Q3-2 bacteria strain separated from recycled sludge of wastewater processing plant. Its flocculation effects are excellent, especially for processing effluents from deinking chemicals plant, wherein its flocculation efficiency is 91.4% and SS removal rate is 99.2%. However, it is less effective in processing wastewater from bean products. H. M. Oh et al (2001, p. 1229-1234) screened and secondarily screened a bacteria of high flocculation activity from sludge, and processed petrochemical wastewater by a flocculant produced from this bacteria. The flocculation effect was good, and its turbidity removal rate was up to 90.1%.

This paper studies the flocculation effects of commercialized polyglutamic acid-based bioflocculant PG-a21 Ca, applies it and other common flocculants in processing wastewater, compares and investigates the actual application value of bioflocculant PG-a21 Ca.

1. Materials, equipments and methods

1.1 Materials

(1) Reagent

Bioflocculant PG-a21 Ca, grey powder, formulated with polyglutamic acid, Ca and other minerals, manufactured by PLOY-GLU Company of Japan; Polymeric aluminum chloride (PAC), light yellow solid; Polymeric ferric sulfate (PFS), reddish-brown liquid; Kaolin, CR. All are purchased.

(2) Kaolin suspension

Add 1 g kaolin powder into 1,000 mL distilled water, stir uniformly to get kaolin suspension with concentration of 1 g/L.

1.2 Equipments

2R4-6 mixer for coagulation test, PHS-3C precise acidometer and STZ-A24 turbidimeter.

1.3 Methods

Add flocculant into 500 mL kaolin suspension, adjust pH; Stir at 350 r/min for 50 s, then stir at 60 r/min for 4 min by 2R4-6 mixer for coagulation test; Keep stationary for 15 min, then determine the turbidity of supernatant fluid by STZ-A24 turbidimeter. The flocculation activity is expressed by flocculation efficiency calculated with the following formula:

$$\text{Flocculation efficiency} = (\text{Initial turbidity} - \text{Turbidity after flocculation}) / \text{Initial turbidity}$$

The optimal application conditions are determined by comparing flocculation efficiency.

1.4 Analysis methods of water quality

Test COD, ammonia-nitrogen, TP and chlorophyll A respectively by potassium dichromate method, Nessler reagent photometric method, molybdenum-antimony anti-spectrophotometric method and acetone extraction-spectrophotometric method.

2. Results and Analysis

2.1 Process conditions affecting flocculation effects

2.1.1 Influence of the amount of PG-a21 Ca to flocculation

The amount of flocculant has a major effect on flocculation. In most of relevant literatures, the amounts of bioflocculants used for processing kaolin suspension are in the range of 1.0-20.0 mL/L, and most of cases need to add certain amount of calcium chloride or aluminum sulphate as coagulant aid. Their flocculation efficiencies can reach 90%. However, PG-a21 Ca is a bioflocculant from polyglutamic acid and Ca, its applied dosage is different from that of common bioflocculant. Figure 1 exhibits the influence of the amount of PG-a21 Ca to the turbidity removal effect of kaolin suspension. Figure 1 indicates that flocculation efficiency reaches 90% or more when the amount of PG-a21 Ca is above 250 mg/L; and small viscous flocs are formed in solution, many suspended substances on the solution surface, and the turbidity of solution is high when the amount is at 50 mg/L. With the increased amount, flocs in solution become bigger, suspended substances on the solution surface get less, and the solution is clearer. From the point of view benefit and cost, the optimal amount of PG-a21 Ca is about 300 mg/L.

2.1.2 Influence of pH to flocculation

Figure 2 exhibits the influence of pH to flocculation when initial turbidity is 123 NTU and the amount of PG-a21 Ca is 300 mg/L. From figure 2, we can see that flocculation efficiency is above 90% and keeps constant when pH is lower than 7, reaches the maximum when pH is exactly at 7, but decreases with the increase of pH when pH is higher than 7. It demonstrates that PG-a21 Ca is suitable to applying in acid circumstances and need to adjust pH if in alkaline environment. This is because biopolymer shows different electric states at different pH, in turn affects the surface electric property of kaolin powder. Flocculant is much easier to be absorbed onto the surface of kaolin particles when electrostatic repulsion is lower than electrostatic attraction between flocculant particles and kaolin particles.

2.1.3 Influence of stirring speed and stirring time to flocculation

It is required that flocculant is rapidly and uniformly mixed with wastewater during mixing stage, so rapid stirring in a short time is necessary. However, it is required not only to form flocs of flocculant and impurities, but also to prevent flocs from being deflocculated during the reaction stage, so slow stirring for a longer time is necessary.

With residual turbidity of supernatant after 15 min static settling as test index, a 4-factor-3-level orthogonal table is used to schedule 9 operation conditions of orthogonal experiment, with the four factors being stirring speed of mixing, stirring time of mixing, stirring speed of reaction and stirring time of reaction. The orthogonal experiment and the range analysis on it are shown in table 1.

From table 1, we can conclude that the influence from large to small is stirring speed of mixing, stirring time of reaction, stirring time of mixing and stirring speed of reaction. The optimal hydraulic conditions are respectively 350 r/min stirring speed of mixing, 3 min stirring time of reaction, 40 min stirring time of mixing and 80 r/min stirring speed of reaction.

2.1.4 Influence of temperature to flocculation

Figure 3 exhibits the influence of temperature to flocculation effect of PG-a21 Ca at the optimal hydraulic conditions when initial turbidity is 126 NTU and the amount of PG-a21 Ca is 300 mg/L. Figure 3 demonstrates that flocculation efficiency of PG-a21 Ca rises with the increase of temperature in the range of 5-60 °C, but decreases with the increase of temperature when the temperature is above 60 °C. It indicates that too high or too low a temperature of solution is unfavorable to the flocculation. This can be explained by chemical kinetics: suspended particle moves faster and collision frequency is greater at higher temperatures, this contributes to the increase in rate of reaction. However, when temperature is too high, although reaction speeds up, the formed flocs are too small and have stronger hydrating trend, as a result, it is difficult to be separated by precipitation. When temperature is too low, reaction slows down, the increase of shear intensity of water to flocculant makes flocs too small to be separated by precipitation.

2.2 Flocculation test of PG-a21 Ca on actual wastewater

Above test results indicate that bioflocculant PG-a21 Ca has good flocculation effects on kaolin suspension at proper conditions. For further study on the flocculation effects of PG-a21 Ca, flocculation tests of PG-a21 Ca on actual domestic wastewater, algae-contained lake water and wastewater from beer brewing were carried out, and its processing effects were compared with those of PAC and PFS.

2.2.1 Effects on actual domestic wastewater

Samples came from schoolyard domestic wastewater of Jinan University. Based on the preliminary tests, it is determined that the optimal amounts of PAC, PFS and PG-a21 Ca are 15 mg/L, 18 mg/L and 300 mg/L respectively. The processing results are shown in table 2. From table 2, we can see that the removal rate of COD, ammonia-nitrogen and total phosphorus by PG-a21 Ca is 50.6% (approximating that by PAC or PFS), 33.2% (much higher than that by PAC or PFS) and 85.1% (slightly higher than that by PAC or PFS). The concentration of COD, ammonia-nitrogen and total phosphorus in PG-a21 Ca-processed actual domestic wastewater meets the Grade 1 Level in the Integrated Wastewater Discharge Standard (8978-1996).

2.2.2 Effects on algae-contained lake water

Samples came from South Lake of Jinan University. Based on the preliminary tests, it is determined that the optimal amounts of PAC, PFS and PG-a21 Ca are 20 mg/L, 15 mg/L and 300 mg/L respectively. The results are shown in table 3. From table 3, we can see that the removal rate of total phosphorus by PG-a21 Ca is up to 97.8%, higher than that by PAC or PFS; removal rate of turbidity is above 90%, similar to PAC or PFS; removal rate of COD is slightly higher than that by PAC or PFS; removal rate of chlorophyll A and ammonia-nitrogen is much higher than that by PAC or PFS.

2.2.3 Effects on wastewater from beer brewing

Samples came from Zhujiang Beer. Based on the preliminary tests, it is determined that the optimal amounts of PAC, PFS and PG-a21 Ca are 400 mg/L, 350 mg/L and 400 mg/L respectively. The results are shown in table 4. From table 4, we can see that the removal rate of turbidity by PG-a21 Ca is up to 95.6%, higher than that by PAC or PFS; removal rate of total phosphorus and ammonia-nitrogen is much higher than that by PAC or PFS; removal rate of COD is slightly higher than that by PAC or PFS.

In short, the results of actual wastewater disposal demonstrate that flocs from PG-a21 Ca is much bigger than that from PAC or PFS, and much easier to be separated by precipitation.

3. Conclusion

(1) The results of flocculation test indicate that PG-a21 Ca is a bioflocculant with high flocculation efficiency and stable flocculation property. It has much better effects on removal of ammonia-nitrogen than PAC, PFS and similar products, excellent effects on removal of phosphorus, and similar effects on removal of COD as PAC and PFS.

(2) The concentration of COD, ammonia-nitrogen and total phosphorus in PG-a21 Ca-processed actual domestic wastewater meets the Grade 1 Level in the Integrated Wastewater Discharge Standard (8978-1996). PG-a21 Ca can efficiently remove chlorophyll A and turbidity in algae-contained lake water, and partially remove COD and TP in wastewater from beer brewing.

(3) The dosage needed and the cost of PG-a21 Ca are relatively high, which cause high operation cost and limit the wide range applications of PG-a21 Ca.

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Table 1. $L_9(3^4)$ orthogonal experiment and the range analysis

Serial number	Stirring speed of mixing (r/min)	Stirring time of mixing (min)	Stirring speed of reaction (r/min)	Stirring time of reaction (min)	Residual turbidity (NTU)
1	350	50	100	4	6.9
2	300	50	80	2	7.3
3	250	50	60	2	9.7
4	350	40	80	3	5.1
5	300	40	60	4	9.3
6	250	40	100	3	9.5
7	350	30	60	3	7.8
8	300	30	100	2	10
9	250	30	80	4	10.4
K_1	9.87	9.40	8.93	9.00	
K_2	8.87	7.97	7.60	7.47	
K_3	6.60	7.97	8.80	8.87	
Extreme difference	3.27	1.43	1.33	1.53	

Table 2. Effects of flocculant on actual domestic wastewater

Item		COD	Ammonia-nitrogen	Total phosphorus
Before process (mg/L)		143	21.7	1.75
PAC	After process (mg/L)	75.0	17.1	0.35
	Removal rate (%)	47.5	18.6	80.2
PFS	After process (mg/L)	69.8	17.6	0.27
	Removal rate (%)	51.1	18.9	84.7
PGa21 Ca	After process (mg/L)	73.3	14.5	0.09
	Removal rate (%)	50.6	33.2	85.1

Table 3. Effects of flocculant on high algae-laden lake water

Item		Turbidity (NTU)	Chlorophyll A ($\mu\text{g/L}$)	COD (mg/L)	Ammonia-nitrogen (mg/L)	Total phosphorus (mg/L)
Before process		18.2	48.3	132	2.2	0.48
PAC	After process	1.3	15.8	42	1.8	0.03
	Removal rate (%)	92.8	67.3	68.2	18.2	93.7
PFS	After process	1.1	12.6	39	1.7	0.02
	Removal rate (%)	93.9	73.9	70.4	22.7	95.8
PGa21 Ca	After process	1.2	8.7	37	1.3	0.01
	Removal rate (%)	93.4	82.0	72.0	40.9	97.9

Table 4. Effects of flocculant on wastewater from beer brewing

Item		Turbidity (NTU)	COD (mg/L)	Ammonia-nitrogen (mg/L)	Total phosphorus (mg/L)
Before process		133	1925	21.4	10.54
PAC	After process	12.5	1182	17.1	5.41
	Removal rate (%)	90.6	38.6	20.1	48.7
PFS	After process	11.0	1161	16.3	5.25
	Removal rate (%)	91.7	39.7	23.9	50.4
PGa21 Ca	After process	5.8	1122	14.1	4.39
	Removal rate (%)	95.6	41.7	34.1	58.3

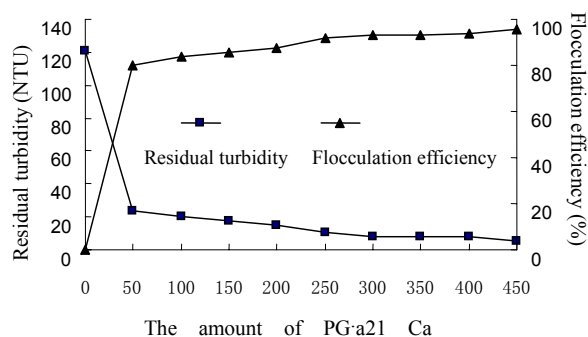


Figure 1. Influence of the amount of PG-a21 Ca to flocculation

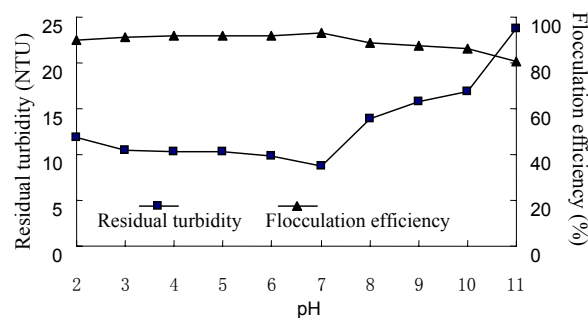


Figure 2. Influence of pH to flocculation

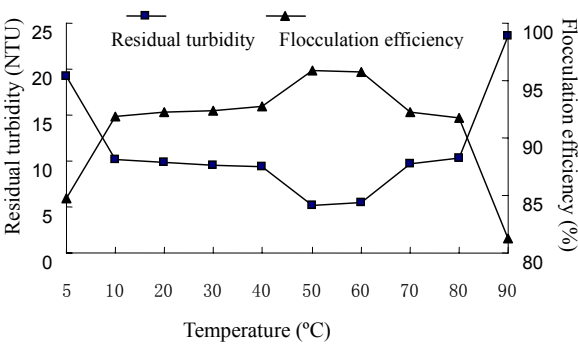


Figure 3. Influence of temperature to flocculation