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Treatment of Livestock Wastewater by Bentonite Coated Chitosam

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Abstract: In this study a new type of flocculating agent-Bentonite Coated Chitosan was prepared to treat the livestock wastewater which came from the piggery. The bentonite coated chitosan was prepared of natural bentonite which was used as raw material and chitosan which was used as modifying agent. The raw concentration of the ammonia nitrogen and COD of the livestock wastewater were 1800~2200 mg/L and 2000~2100 mg/L. The study showed that the the best removal rate of them are 72.47% and 88.26% when the dosing quantities are 0.5g/L, stirring times are 20 min, stirring rates are 300 r/min, pH are 5, standing time are 60 min. The soil layer and shape of the chitosan did not changed after be modified.

Keywords: Ammonia nitrogen, bentonite, chitosan, CODcr, livestock wastewater from the piggery

INTRODUCTION

In recent years, livestock farm was developed to scale with the increasing demand of the livestock products. However the discharge of livestock wastewater is also increased (Jerz *et al*., 2011). Now the livestock wastewater is the primary pollution sources than industrial wastewater and domestic wastewater (Luting and Huafei, 2008). The livestock wastewater includes poultry excrement, piggery rinse water and so on Jinlian and Ning (2000).

This type of the wastewater has the advantages such as high concentration of the CODcr, the ammonia nitrogen and the SS (Jie, 2009; Zhiyong *et al*., 2007) .It will caused pollution surface water, underground water and farmland if random discharged (Xia *et al*., 2011). How to solve the livestock wastewater effectively is one of the most urgent problems to be settled especially during the twelfth five years plan that the ammonia nitrogen is added one of the water pollutant.

At present the livestock wastewater treatment are ABR (Shengqiong and Hongwang, 2011), SBR (Jian *et al*., 2009), USR (Sheng *et al*., 2011) and so on. However, these methods have the problems such as difficult to control, operation complicated, secondary pollution. This experiment prepared the bentonite coated chitosan which used natural bentonite as the raw material and chitosan as modifying agent to treat the livestock wastewater. In recent years the midified bentonite is used in the field of the heavy metals wastewater, organic wastewater and dyeing wastewater (Liping *et al*., 2010). It was a penetration that the Bentonite Coated Chitosan was used in the livestock wastewater firstly and the treatment efficiency was also proved in the study.

Table 1: The indexes of the raw livestock wastewater

pH	SS (mg/L)	Ammonia nitrogen (mg/L)	COD (mg/L)
9.0~9.5	1000~1100	1800~2200	2000~2100

Table 2: The chemical constitute of the bentonite

SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO
56.4	15.88	4.27	2.22	0.75
Na_2O	K_2O	TiO_2	MnO	Ignition loss
2.45	1.60	0.48	0.09	15.28

EXPERIMENTAL MATERIALS

The livestock wastewater used in the experiment was the effluent of a livestock farm in Shenyang Liaoning. The indexes of the livestock wastewater were showed in the Table 1.

The bentonite comes from the Heishan Liaoning. Its chemical constitute was showed in the Table 2.

The chitosan which decollation degree was 90% was dissolved with 5% (v/v) acetic acid solution in the 100 mL beaker. 50 g of the bentonite coated chitosan was stirred with 50~60 mL of the chitosan solution and putted in the microwave oven under 800 w for 5 min, heated, porphyrized, selected through 0.18 mm (Hong *et al*., 2009a).

METHODOLOGY

The bentonite coated chitosan was putted into livestock wastewater of 500mL, changed the pH and tiring for a time, stand and the residual concentration of the ammonia nitrogen and COD were measured and calculated as the flowing formula:

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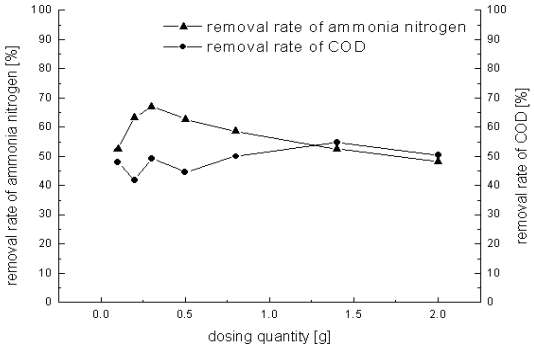

Fig. 1: The effect of the dosing quantity

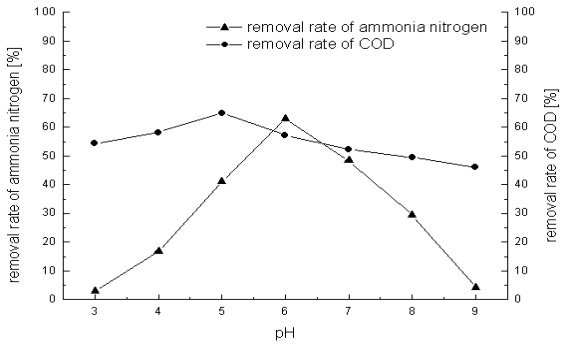

Fig. 2: The effect of the pH

$$\eta = \frac{A_0 - A}{A} \times 100\% \quad (1)$$

η = The removal rate (%)
A_0 = The concentration of the COD or ammonia nitrogen before treated
A = The concentration of the COD or ammonia nitrogen after treated.

RESULTS AND ANALYSIS

The effect of the dosing quantity: The livestock wastewater was treated at the conditions of the concentration of the pH was 5, the stirring rate was 300 r/min, the stirring time was 20 min and the standing time was 30 min. The effect of the dosing quantity was shown in the Fig. 1.

Figure 1 indicated that the removal rate of the ammonia nitrogen increased with the increase of the dosing quantity and meet the max when the dosing quantity was 0.2~0.5 g. The removal rate of the COD changed little at the removal rate of 45%. This was because the negative charge on the pollutant was neutralized by the bentonite coated chitosan and subsided at the function of adsorption bridge (Hong *et al*., 2009b). Considering the removal rate of ammonia nitrogen and COD, the proper dosing quantity was 0.5 g.

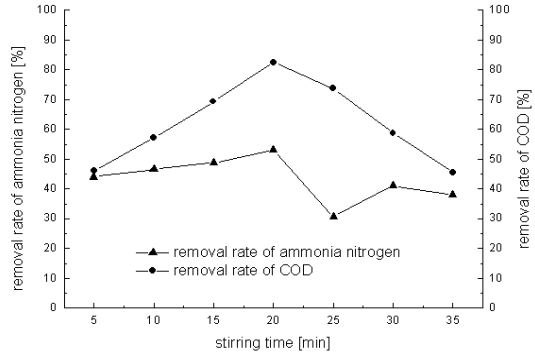

Fig. 3: The effect of the stirring time

The effect of the pH: The livestock wastewater was treated at the conditions of the concentration of the dosing quantity was 0.5 g, the stirring time was 20 min, the stirring rate was 300 r/min and the standing time was 30 min. The effect of the pH was shown in the Fig. 2.

Figure 2 indicated that the pH had a big impact on the removal rate of the ammonia nitrogen which the best treated effect was 6. This was because the pH had impact on the organic polymer adsorbent and the properties of the charge on the surface of the bentonite coated chitosan. At low pH value, there was more hydrogen ion which would compete with the ammonia ion in the bentonite coated chitosan. It was not good for the adsorption of the ammonia nitrogen. At high pH value, the surface of the adsorption was jammed easily (Hong *et al*., 2010). The impact on COD was not significant. The highest removal rate occurred when pH was 5.

The effect of the stirring time: The livestock wastewater was treated at the conditions of the concentration of the dosing quantity was 0.5 g, the pH was 5, the stirring rate was 300 r/min and the standing time was 30 min. The effect of the stirring time was shown in the Fig. 3.

Figure 3 indicated that the removal rate of the ammonia nitrogen and COD increased firstly and decreased with the increase of the stirring time. The biggest removal rates were occurred when the stirring time was 20 min. This was because the adsorbent was saturate and the adsorbent would be destroyed if last the stirring time. So the proper stirring time was 20 min in this experiment.

The effect of the stirring rate: The livestock wastewater was treated at the conditions of the concentration of the dosing quantity was 0.5 g, the stirring time was 20min, the pH was 5 and the standing time was 30 min. The effect of the stirring rate was shown in the Fig. 4.

Figure 4 indicated that the removal rate of the ammonia nitrogen and COD increased firstly and

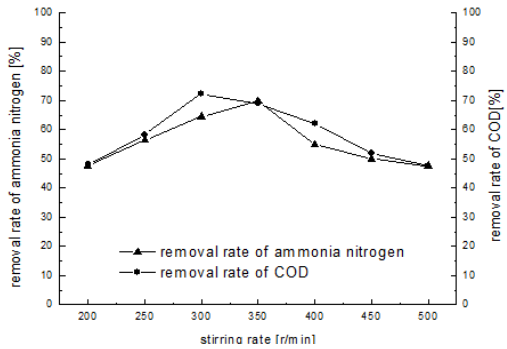

Fig. 4: The effect of the stirring rate

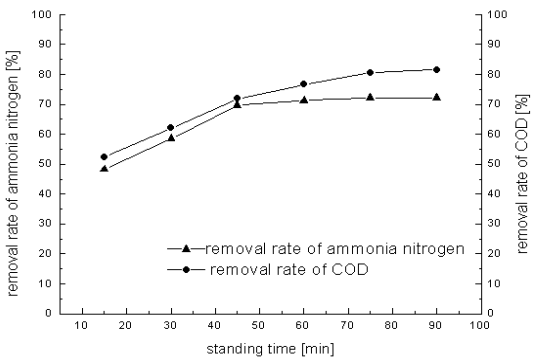

Fig. 5: The effect of standing time

decreased with the increase of the stirring rate. This was because low stirring rate made for bentonite coated chitosan spreading in the water sample. The adsorbent would also be destroyed if increased the stirring rate and the removal rate of the ammonia nitrogen and COD would decreased. Considering the removal rate of ammonia nitrogen and COD 350 r/min was the proper stirring rate.

The effect of the standing time: The livestock wastewater was treated at the conditions of the concentration of the dosing quantity was 0.5 g, the stirring time was 30min, the stirring rate was 300 r/min and the pH was 5. The effect of the standing time was shown in the Fig. 5.

Figure 5 indicated that the impact of standing time on ammonia nitrogen and COD were same approximately and the removal rate of them increased with the increase of the standing time. The removal rates did not changed if the standing time was more than 60 min. The ammonia nitrogen and COD were adsorbed and floated in the water sample after stirring. These adsorbent sinked under the gravity and the function completed when the standing time was 60min. So the proper standing time was 60 min in the experiment.

The single factor experiment indicated that the optimum process parameters of the livestock wastewater which treated by bentonite coated chitosan was the dosing quantity: 0.5 g, the pH: 5, the stirring time: 20 min, the stirring rate: 300 r/min and the standing time: 60 min

The orthogonal experiment: The table of the orthogonal experiment of L16 (4^5) was build base on the single factors of the concentration of the dosing

Table 3: The result of the orthogonal experiment

		Dosing quantity (g)	pH	Stirring time (min)	Stirring rate (r/min)	Standing time (min)	Removal rate of COD (%)	Removal rate of ammonia nitrogen (%)
1		0.3	4	15	300	45	76.47	51.27
2		0.3	5	20	350	60	78.42	67.08
3		0.3	6	25	400	75	62.78	49.13
4		0.3	7	30	450	90	61.28	50.84
5		0.5	4	20	400	90	68.57	61.10
6		0.5	5	15	450	75	81.05	61.15
7		0.5	6	30	300	60	82.71	62.64
8		0.5	7	25	350	45	64.29	44.00
9		0.8	4	25	450	60	65.19	56.82
10		0.8	5	30	400	45	66.39	42.72
11		0.8	6	15	350	90	58.65	48.27
12		0.8	7	20	300	75	72.56	62.38
13		1.4	4	30	350	75	59.92	61.79
14		1.4	5	25	300	90	78.20	70.08
15		1.4	6	20	450	45	72.56	45.28
16		1.4	7	15	400	60	56.77	48.70
COD	K_1	69.74	67.54	68.24	77.49	69.93		
	K_2	74.16	76.02	73.03	65.32	70.72		
	K_3	65.70	69.18	67.62	63.63	69.08		
	K_4	66.87	63.73	67.58	70.02	66.68		
	Range	8.46	12.29	5.45	13.86	4.100		
Ammonia nitrogen	K_1	54.58	57.75	52.34	61.59	45.82		
	K_2	57.21	60.25	58.96	55.29	58.81		
	K_3	52.55	51.33	55.01	50.41	58.60		
	K_4	56.46	51.48	54.50	53.51	57.57		
	Range	4.66	8.92	6.63	11.18	12.99		

Table 4: The result of the confirmatory experiment

	The removal rate of ammonia nitrogen (%)	The surplus of ammonia nitrogen (mg/L)	The removal rate of COD (%)	The surplus of COD (mg/L)
1	73.07	538.6	87.92	253.68
2	72.12	557.6	88.23	247.17
3	72.22	555.6	88.64	238.56
Average evalue	72.47	550.6	88.26	246.54

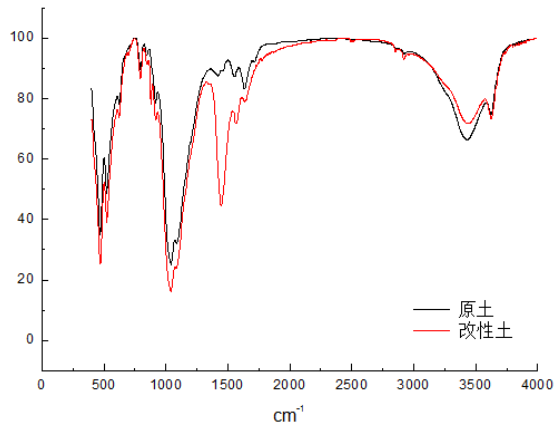

Fig. 6: The IR spectrum chart

quantity, the stirring time, the stirring rate, the pH and the standing time. The result was shown in Table 3.

The orthogonal experiment indicated that the optimum process parameters of the livestock wastewater which treated by bentonite coated chitosan was the dosing quantity: 0.5 g, the pH: 5, the stirring time: 20 min, the stirring rate: 300 r/min and the standing time: 60 min which is as the same as single factor experiment.

The impaction order of the COD was the stirring rate, the pH, the dosing quantity, the standing time and the stirring time. The impaction order of the ammonia nitrogen was the standing time, the stirring rate, the pH, the stirring time and the dosing quantity.

The confirmatory experiment: Under the orthogonal experiment optimum process parameters the livestock wastewater which raw pH was 9.0~9.5, the SS was 1000 mg/L, the NH3-N was 1800~2200 mg/L and the COD was 2000~2100 mg/L 3 times to check the result of the orthogonal experiment. The result was showed in Table 4.

The Table 4 indicated that the removal rate of ammonia nitrogen was 72.42% and the surplus of ammonia nitrogen was 550.6 mg/L. The removal rate of COD was 88.26% and the surplus of ammonia nitrogen was 246.54 mg/L when the livestock wastewater was treated by bentonite coated chitosan. The COD of treated livestock wastewater was meeting the《Discharge standard of pollutants for livestock and poultry breeding》 and the ammonia nitrogen needed secondary treatment.

The infrared spectroscopic analysis: Figure 6 indicated that the peak that around the 3434/cm was the absorption peak of O-H and N-H. The peaks appeared under the 1300/cm had concentrate with the bentonite coated chitosan. The basic structure was not changed after bentonite modified.

CONCLUSION

The livestock wastewater which raw pH was 9.0~9.5, the SS was 1000 mg/L, the NH_3-N was 1800~2200 mg/L and the COD was 2000~2100 mg/L was treated by the bentonite coated chitosan.

The optimum process parameters was that the dosing quantity: 0.5 g, the pH: 5, the stirring time: 20 min, the stirring rate: 300 r/min and the standing time: 60 min. The removal rate of COD and ammonia nitrogen were 88.26% and 72.47%.

The impaction order of the COD was the stirring rate, the pH, the dosing quantity, the standing time and the stirring time. The impaction order of the ammonia nitrogen was the standing time, the stirring rate, the pH, the stirring time and the dosing quantity.

The modifying agent didn't change the basic structure of the bentonite.

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