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Mechanism Study on Flocculating Organnic Pollutants By Chitosan with Different Molecular In Wastewater

Zeng De-fang, Liu Jun, Yan Huan
School of Resource and Environmental Engineering, Wuhan University of Technology; Hubei Key Laboratory of Mineral Resource Processing and Environment; Wuhan 430070, P.R.China

Abstract: This paper presents the effect of the molecular weight of chitosan on flocculation of simulation sewage. The flocculation process of different chitosan samples were analyzed in different deacetylation degree, dosage and pH. The different molecular weight of chitosan samples and simulation sewage were all laboratories homemade. The flocculating effects of chitosan increases with the increase of deacetylation degree; the flocculating effects of chitosan decreases with the increase of viscosity-average molecular weight, the viscosity-average molecular weight in 8.5~68×10^4 range. Some conclusions were different from classical theory, the higher molecular weight of chitosan, the better its precipitation effect is. This discovery of the phenomenon is important to perfect the existing polymer flocculation theory.

Keywords: *Chitosan, Molecular, Flocculation, Organic contaminant*

I. INTRODUCTION

Chitosan(CTS) as a kind of promising natural biomaterial[1-3,4], it research and application of chitosan in the field of water treatment, which mainly used for drinking-water and water supply in American [5,4] and applied to water treatment and sewage treatment in Japan[6]. Lots of carboxyl groups and amido groups were distributed in chitosan as cationic flocculant [7-9]. The organic pollutants such as carbohydrate, protein, nucleic acid and so on in the water were effective adsorbed and flocculating settling by adsorption, ion exchange, subsidence etc [2,3]. Up to now, which is widely studied is the removal efficiency of COD of chitosan flocculant on its dosage and its strong chelation to metal ions [10]. Due to the viscosity-average molecular weight and deacetylation degree of chitosan is the key factors [11-15] which related to the effect of flocculation. When chitosan is used in water treatment in the traditional, the viscosity-average molecular weight is greater than 1×10^6 and the removal of COD about 65% [1,3,16]. This paper, the effect of the 8.5-68×10^4 range of viscosity-average molecular weight of chitosan on the removal of COD was examined. Through experiment and mechanism analysis, to this kind of abnormal phenomenon demonstrated and explanation, so as to add and perfect the existing macromolecular flocculating theory provides a powerful experiment basis.

II. MATERIALS AND METHODS

2.1 Materials

2.1.1 Main experimental apparatus

BA120 type one ten thousandth digital display electronic microbalance (Shanghai Constant Balance instrument Ltd.); (0.5-0.6mm) Ubbelohde viscometer (Zhengzhou Zhongtian Experimental instrument Ltd.); Water bath (Fuhua Instrument Ltd.); Zeta potential measurement instrument (American Beckman Coulter company); Six joint electric blender (WuHan Meiyu Instrument Ltd.) etc

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2.1.2 Main experimental reagents

CTSm#: white powder, moisture 6%, ash content less than 2%, insolubles less than 2%, Mw=4.120x10^5, DD(%)=70, industrial class. CTSn#: white powder, Mw=6.108x10^5, DD(%)=85, industrial class. Anhydrous alcohol, NaOH, H_2O_2, potassium bichromate, ferrous reagent, ammonium ferrous sulfate, sulfuric acid silver, mercury sulfate, potassium hydrogen phthalate and soluble starch were of analytical grade. Edible soybean vegetable oil and bovine serum album with biological pure.

Water sample: Choosing soluble starch as carbohydrate of organic pollutants; "Bovine serum albumin" as protein of organic pollutants; Edible soybean vegetable oil as fat class of organic pollutants in simulation material. According to the requirements of the influent water in some sewage plants in Hubei province, COD=186 mg/L.

2.2 Experimental Methods

2.2.1 Deacelation degree determination

Double-saltation potentiometric titration method: weigh accurately 0.200g CTS in 20ml 0.1 mol/L HCl solution in a mechanical stir to completely dissolve, then titrated with 0.1 mol/L NaOH to neutralize, when the HCl in solution was completely neutralized, pH value would rise is the first saltation. The second stage for NaOH neutralized another part of HCl, which was the combination with CTS amino, when reaching the end of titration, pH value would rise named after the second mutation. The consumption of the NaOH mole number during the two saltation was equivalent to the content of amino in CTS molecules. The calculation formulas of deacetylation degree (DD) was as followed[16]:

$$DD(\%) = \frac{\Delta v \times C_{NaOH} \times 10^{-3} \times 16}{m \times 0.0994} \qquad (1)$$

Δv -the difference of the consumption volume of NaOH between two saltation (mL);
C_{NaOH}-the concentration of NaOH/mol^{-1}; m-weight of CTS/g; DD-deacetylation degree;
16-the molecular weights of amino; 0.0994-the theoretical content of amino.

2.2.2 Molecular weight determination

Viscosity measurement of the molecular weight of CTS: the viscosity of linear polymer generally was higher, which was relevant with its molecular weight. When the polymer external physical and chemical condition is determined, according to Mark–Houwinkequation ($[\eta]=KM^{\alpha}$[16]) can get the sample molecular weight M value, which K and α is constant about polymer, solvent, temperature[16]. Weigh accurately 0.500g CTS in 0.2mol/L of HCl and 0.1mol/L NaCl solution, mixed to dissolve, then filter and determined the viscosity with ubbelohde viscometer.

2.2.3 Flocculation experiment

At room temperature, taking 800mL water sample in 1000mL beaker adjusting pH, added different kinds of CTS, stirred in 350r/min 2min, then 75r/min 5 min in the six league mixer, then statically settled 20 min, at last determinated COD of treated water sample. And analysis flocculation characteristics of different CTS's molecular weigh.

III. RESULTS AND DISCUSSION

3.1 CTS deacelation degree and molecular weight

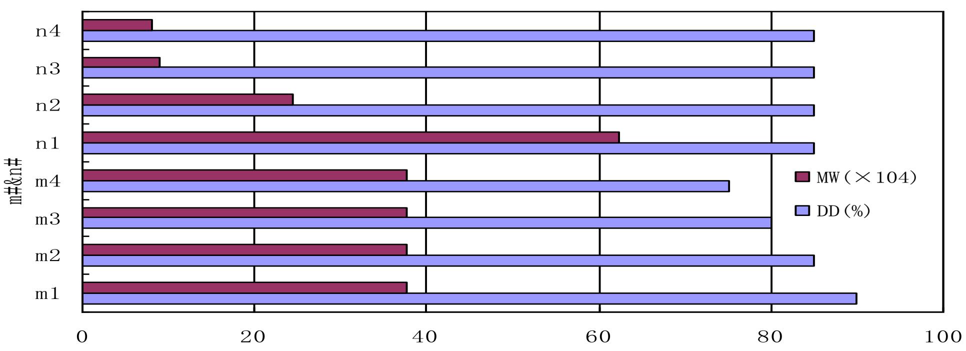

Figure 1 Deacetylation degree and molecular weight of CTS m# and n#

According to the formula (1) to deacetylation degree and molecular weight of CTS m# and n#, it can be showed in Fig.1. In Fig.1, the molecular weight of CTSm# were the same, but the deacetylation degree different; And deacetylation degree of CTSn# were the same, but the molecular weight different.

3.2 Effects of the CTS deacelation degree on flocculation

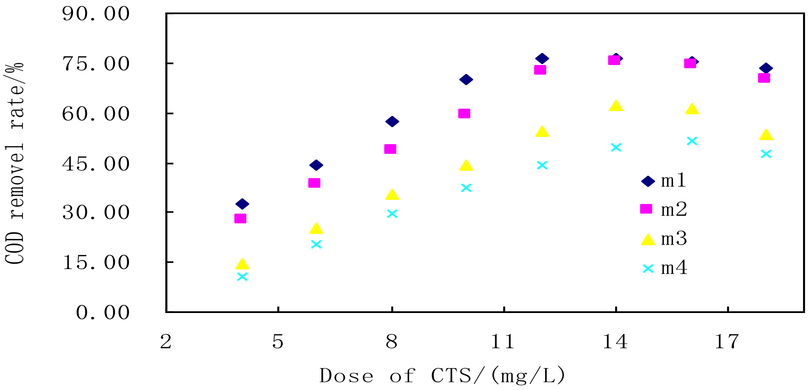

Figure 2 Effects of the CTS deacetylation degree on flocculation

Deacetylation degree is the influence factor of CTS on water purifying function, CTSm# were made into the same mass fraction of the solution, then flocculated the same amount of simulated sewage and determined the removal rate of COD. The results was showed in Fig.2, with the CTS deacetylation degree increased, the removal rate of COD in water also improved. When the deacetylation degree in 78~86.5%, the removal rate of COD reached a larger extent, and when the deacetylation degree was higher than 86%, the removal rate of COD ascending slowly and the effect is not distinct. With the increasing dosage of CTS, the removal rate of COD in water improved, but reaching a certain dosage, the removal rate of COD began to decline. Deacetylation degree was different; the best dosage was also different. The best dosage of m1, m2, m3 and m4 was 12.0-12.5mg/L, 12.3-13.0mg/L, 14.5-15.0mg/L and 16.6-17.0mg/L respectively.

3.3 Effects of the CTS molecular weight on flocculation

Molecular weight is the key index of CTS on water purifying function; CTSn# were made into the same mass fraction of the solution, then flocculated the same amount of simulated sewage and determined the removal rate of COD. The results was showed in Fig.3, with the CTS molecular weight increased, the removal rate of COD in water decreased. And with the increasing dosage of CTS, the removal rate of COD in water improved, but the removal rate of COD began to decline when reaching a certain dosage. Molecular weight was different; the best dosage was also different. The best dosage of n1, m2, n2 and n3 was 15.4mg/L, 13.5mg/L, 12mg/L and 9.5mg/L respectively. The result of the unit test indicated that the corresponding optimal dosage of low molecular weight was less than that of high one, the removal rate of COD would get the same effect.

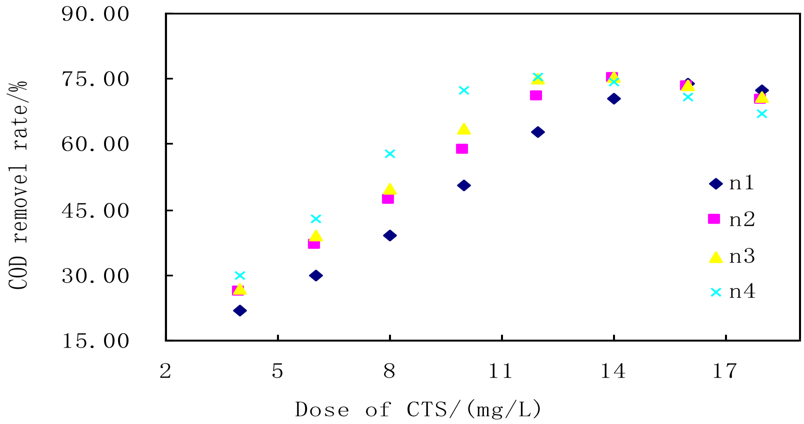

Figure 3 Effects of the CTS molecular weight on flocculation

It maybe for that low molecular weight of CTS combined blank position on the surface of particles quickly after dissolved, through an effect on electric neutralization to shorten the distance between the particles so as to flocculate. But with the increasing concentration of CTS, blank particle on the surface of particles were covered completely. At this time, CTS played a protective effect, so flocculation instead weakened. When the CTS concentration further increased, stretch structure of its molecular chain changed slowly into single chain structure, then mutually winded and form line-group structure. Mutual-winding degree of high molecular weight was high, and its molecular internal and intermolecular formed a large amount of hydrogen bond. The stable structure made a mount of CTS was difficult to dissolve in flocculation process, and repulsive force of CTS intermolecular was stronger, and caused molecules not easy to near each other and got together. Solubility of low molecular weight CTS was better, it was easy to close to each other between molecules. So low molecular weight CTS on the removal rate of COD in water was superior to high molecular weight CTS.

3.3 Effects of pH on flocculation

CTSn# was made into the same mass fraction of the solution, then flocculated the same amount of simulated sewage and determined the removal rate of COD in different pH. The results were showed in Fig.4. The COD removal trend of different molecular weight of the CTS was roughly the same in different pH. When the pH=5.5-7.0, the removal rate of COD rose gradually and then reduced with the increase of pH in water. And when pH was 6.0 to 6.5, the removal rate of COD reached the maximum. CTS was a weak cationic electrolyte, which played mainly electric neutralization in a low pH and CTS formed granular carbide and precipitated with pH increased so as to affect the removal efficiency of COD.

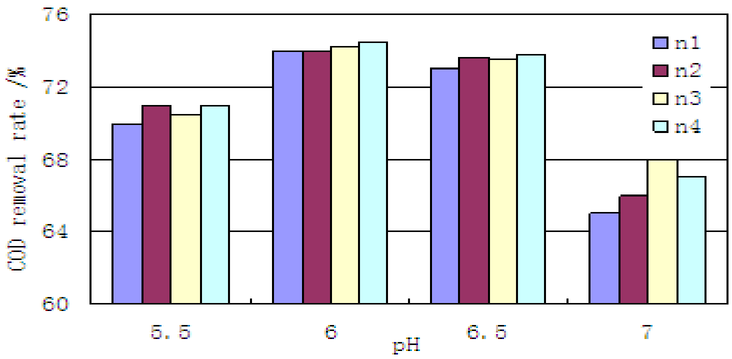

Figure 4 Effects of pH on flocculation

3.4 Effects of different viscosity-average molecular weight CTS on settling velocity in the flocculation process

The results of the settling velocity were shown in Fig.5. With the increasing dosage of CTS, settling velocity of flocs in water improved. Generally the flocs of high molecular weight CTS was bigger and faster formed, and could settle during the short time. In this test shown that n3 was the lowest, but the removal rate of COD of n3 was the best. This could be that the solubility and dissolution rate of high molecular weight CTS is relatively lower in the same concentration so that it was not easy to flocculate fully in the relatively short time and affected the removal efficiency of COD in water.

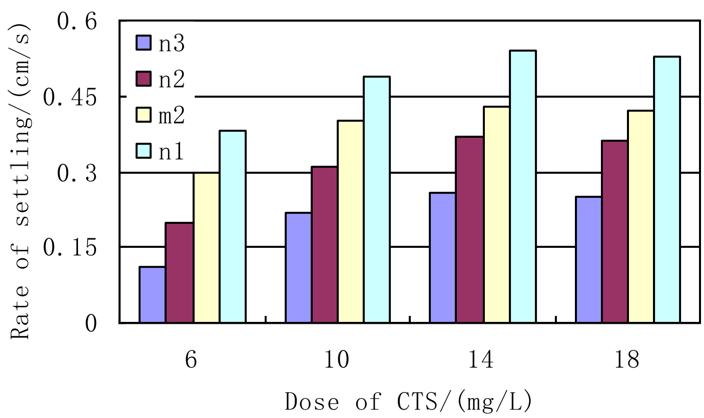

Figure 5 Effects of different viscosity-average molecular weight CTS on settling velocity in the flocculation process

3.6 Flocculation mechanism

From the above experimental results, ,molecular weight in $8.5\text{-}68\times10^4$ in a certain deacetylation degree range, low molecular weight CTS as a flocculant to treat sewage could have a better flocculation effect and a higher removal efficiency of COD, the corresponding amount will also decreased. The adsorption on the particles surface of polymer rooted in all kinds of physical and chemical action of intermolecular, such as electrostatic attraction, all kinds of coordination bond, hydrogen bond, etc. We found that a large amount of hydrogen bond between the intramolecular and intermolecular [17] of high molecular weight CTS. The stable structure made macromolecules CTS in weak-acid to dissolve difficultly and the repulsive force of CTS intermolecular was strong, so it was hard to near each other to concentrate. And low molecular CTS after dissolving in acidic condition are more likely to spread its molecular chain [18,19], which have a faster dispersed and strong electropositive, thus the neutralized on the surface of particle making colloid stability and settlement. The repulsion of low molecular weight between the molecules CTS was weak and easier to close to play a bridging role, quick adsorb. The principles of electric neutralization and bridging cause that low molecular weight CTS could effective settle particles in water. When the CTS molecular weight up to a certain value and CTS molecular chain length reached a certain length, the bridging flocculation played a leading role, the flocculation effect would be increased with the molecular weight increased obviously.

IV. CONCLUSIONS

The self-preparated CTS flocculated in the same sewage COD. The results showed that in the same molecular weight, with the CTS deacetylation degree increased, the removal rate of COD in water also improved, when deacetylation degree in 80~85%, the removal rate of COD reached a larger extent, and when the deacetylation degree is higher than 85%, the removal rate of COD ascended slowly and the effect was not distinct. Selecting chitosan as flocculating agent, should be comprehensive consideration of the cost and benefit. Secondly, when deacetylation degree was 85% and molecular weight in $8.5\text{-}68\times10^4$,the removal efficiency and dosing quantity of low molecular weight CTS was superior to high molecular weight in room temperature and pH=6.5. Thirdly, choosing n# samples and m2 sample to test the effects on the pH value in its best dosing quantity. When the pH value was in 6.0~7.0, with the increase of pH, the removal rate of COD after the first rise gradually reduce. When pH was neutral and a little acid, the removal rate of COD reached the highest. In molecular weight $8.5\text{-}68\times10^4$, with the high molecular weight, the flocculating constituent of CTS was larger and faster formed than that of low one, could settle in short time.

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