Study on Preparation and Application in Flocculants of Modified Lignin

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Abstract

The lignin sulfonate was modified with olefins monomer by the method of radiation graft polymerization, by which a new type of natural polymer flocculants can be made. And results of the flocculation and sedimentation are tested in the furfural wastewater treatment process. Furfural wastewater is a complex composition, whose COD is about 20000mg / L, is difficult to be treated by conventional methods. Our results showed that the kind of flocculants can remove 50 percent COD or more from furfural wastewater after aerating and adjusting pH value to 9.

Keywords: Lignin, Irradiation, Flocculants, Furfural wastewater

As a general plant of polymer, lignin is the main material to support plant growth, it constitute the cellulose with cellulose and hemicellulose together. Lignin in plants is the most abundant and most important organic polymer after cellulose. Lignin is non-toxic, source and rich in renewable resources, so it is widely used in industry. Generally, the commercial lignin is the derivative product from paper making by-products. Such as leather, dyestuff, food, architecture, and agricultural industries, it's mainly used as raw materials (such as mulan grain preparation) and additives (such as adhesives, dispersant, chelating agent and emulsifier) (Zhan HuaiYu. 2005).

Lignin, also can use as a flocculent flocculant modified lignin, due to several points such as the sources of the raw materials, inexpensive, non-toxic, easily biodegradable etc, and shows good application prospect. But there are some problems of low molecular weight and average less active absorption points, through the method of cross-linking reaction and condensation reaction, people want to change the spatial configuration and increase and molecular weight. Moreover, people try to introduce flocculation properties of functional and to improve the lignin flocculation properties further (Qiu XueQing, LouHongMing. 1999). Lignin can increase its quality of molecules after grafting in vinyl monomers; it's also a method to improve lignin's flocculation. Qianjun Liu etc(Liu Qianjun, ZhanHuaiYu, Liu mengru & WuHong. 2003). Use potassium sulfate as the initiator and acryl amide monomer to preparate the decoloring agents lignin flocculation. GuiZhen Fang etc(Fang GuiZhen, HeWeiHua & Song ZhanQian. 2003). Synthesize flocculant - lignin salt. B. Phillips (R. B. Phillips, W. Brown & V. Stannett. 1973; R. B. Phillips, W. Brown & V. Stannett. 1972) was studied the irradiation graft copolymerization reaction between styrene and lignin.. These researches contributed to the application of the lignin flocculant.

Base on the past research , this paper use lignosulphonate salt as photo base, join olefins grafted monomer, using irradiation graft polymerization method to preparate natural polymer flocculant lignin. This method is characteristic by the reaction process doesn't need solvent; the reaction process doesn't attract small molecules, so the process of using this kind of flocculant will not cause secondary pollution. We use the flocculant to deal with the furfural wastewater by flocculating sedimentation. Mainly because of COD is about 20000mg/L, pH < 2. According to the characteristics of furfural wastewater, we design the corresponding process. Practice has proved, in appropriate conditions, can achieve very good result flocculation.

1. Experimental

1.1 Raw material and equipment

(1)Llignosulphonate sodium/Beijing; technology Co., LTD. Beijing plant acid, Acetone Beijing chemical plants, Beijing olefin plant monomer.

(2)Furfural wastewater quality

Tan appearance, including a solid aerosol particle

COD 23025 mg/L

pH 4

(3)Rotating evaporator (RE-52AA) Shanghai vibration; the laboratory equipment Co., LTD. Circulating water pump (SHB - multi-purpose type III) trading Co., LTD. Of Zhengzhou wall, 60Co emitter, Chinese academy of sciences, Changchun institute of applied chemistry.

1.2 Flocculant preparation methods

300ml acetic acid was dropped into 500ml flask. drop 150g lignosulphonate sodium into the flask slowly and group by group, of partial, then mix the lignin to be soluble by glass rod. put the flask of lignosulphonate mixed with acetic down for 10 minutes, and then put the filtered solid material into the flask, add appropriate acetone, and the do twice suction filter. We can get purificated yellow lignosulphonate after dry. According to the proportion of purification weigh

of lignosulphonate salt and olefin monomer, grinding, mixing, controlling conditions for radiation graft polymerization reaction which use 60Co as radiant point.

1.3 Furfural wastewater flocculating sedimentation

Taking fresh water samples from furfural, aerating, adding flocculants and auxiliary sorbents according to the design scheme, mixing fastly for1min, stilling for 10min, getting the supernatant and calculating COD as well as COD removal.

1.4 Flocculant surface morphology analysis

We adopt the Nano - I atomic force microscope (type: S - favor - 0000-1) from American Schmidt Co to scan the water.

1.5 Flocculants structure characterization

We adopt the UV - 1240 type uv-vis spectrophotometer from Japanese to do the ultraviolet spectroscopic analysis.

1.6 Furfural COD value method

We adopt HACH COD tester (DR - 2010) from American, the temperature is 150°C, dispelling time is 2h..

2. Results and Discussion

2.1 Flocculant surface morphology analysis

We should make the sample to 0.02 g/L solution and spin coat on the slides about 1500 r/min in room temperature, In order to dry it, we observe the surface morphology in the atomic force microscope. Lignosulphonate salt is a three-dimensional granular structure of organic polymer, there's no organic polymer chain in its molecular structure. We can see from figure 2.1, sodium lignosulphonate is flat, 32.01 nm to devide; the surface properties of modified sodium lignosulphonate is changed. There are some obviously uniform and divide 46.32 nm to rise. This is because of in the modified lignin, the grafted surface by - C - C - composed of amorphous polymer composition of linear low molecular characteristics, main chain molecules, flexibility and good symmetry. When there-dimensional structure lignosulphonate salt on grafting, flexible chain on the surface properties of sodium lignosulphonate produces more changes, grafted long -chain formation obviously uplift and excluded in polarity membrane surface.

2.2 grafted lignin up spectral analysis

Lignin was typical of aromatic compounds. Aromatic compounds have characteristics of ultraviolet absorption, 280 nm will appear a stable absorption peak when there is aromatic substituent in lignin structure. Figure 2.2 shows ultraviolet absorption spectrum lines of lignosulphonate salt and modified lignin sulfonate olefin monomers.

The graph shows that lignin has obvious absorption peaks around 205nm and 280nm of ultraviolet spectrum. The monomer which is grafted to the lignin has been saturation, it lose phenacylmethylene groups to become substituent and there is greater space a resistance. A resistance can make the substituent which conjugate with benzene originally to be rejected out of benzene plane, and resistance also can not make substituent electrons overlap completely with benzene PI system , thus affecting the spectrum. Wave of benzene and the intensity of absorption with wave depend on the planar angle between substituent and benzene. After adjacent bits replace, because of the resistance increases, the factors make Angle reduced, cause absorption electronic overlap with strength successive reduced. Substituent produced blue affect in 280nm. The scope of absorb with strength reduction depends on how long and how much is grafting long chain. Modified sodium lignosulphonate.

2.3 Liquid pH value of furfural COD removal rate

In the Flocculating sedimentation furfural wastewater determination experiment which is in the condition of 8h aeration and different pH value, we can see modified lignin flocculent effect is different and the settlement of COD lower level is not the same. After the aeration the pH of furfural wastewater rise from 4 to approximately 7, and there is a settlement in the solution, then add flocculants and auxiliary sorbents, a large number of floce sedrmation will separate out from solution. From graph 2.3 we can see the biggest decline of COD occurs in the pH-9. Because the condensation reaction occurs under this condition and molecular weight increase ceaselessly

to format the aerosol particles, in addition flocculation agent can play a good role of bridge to prompt to macromolecular flocculating sedimentation.

2.4 Flocculant for COD removal rate of consumption

Taking 250ml fresh furfural liquid; 8h aeration, adjust it to pH - 9. the graph 2.4 shows the change of furfural wastewater COD after adding the Modified lignin natural organic polymer flocculant and auxiliary adsorbent. As we can see from the graph when the amount of flocculants is bigger than 2g, the COD removal rate of furfural wastewater will be more than 50%, if we increase the amount of flocculants; the COD removal rate will reach the highest rate of 60%, the COD removal rate increase. Therefore, in the processing of dealing with furfural wastewater, the advisable dosing quantity of modified lignin flocculants is 8g/L.

3. Conclusion

Irradiation graft copolymerization method is a kind of green chemical processing method. We can get the natural organic polymer flocculants when the modified lignin sulfonates has been processed, the flocculants is cheap price, non-toxic side effects, no secondary pollution and according with environmental protection requirement. the best condition of using This new type of flocculants is : pH-9 of solution, dosage for 8g/L, if it is combined with other technology, the COD removal rate can reach more than 50 percent in the furfural wastewater treatment engineering.

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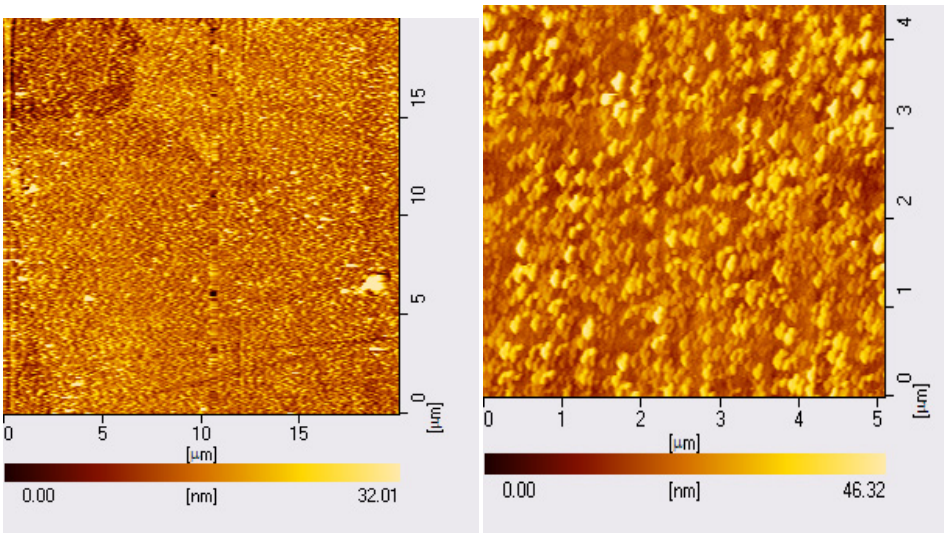

a. Before the modified lignin surface morphology b. Grafted modified lignin surface morphology

Figure 2.1 Modified lignin sulfonate membrane surface morphology

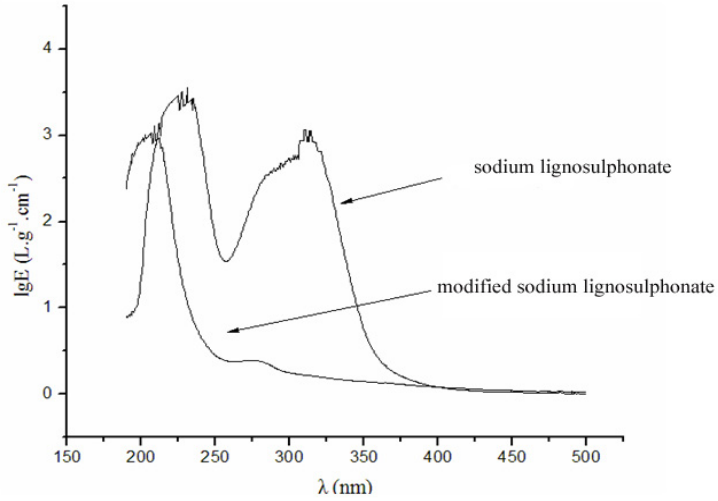

Figure 2.2 Modified lignin sulfonate up spectra

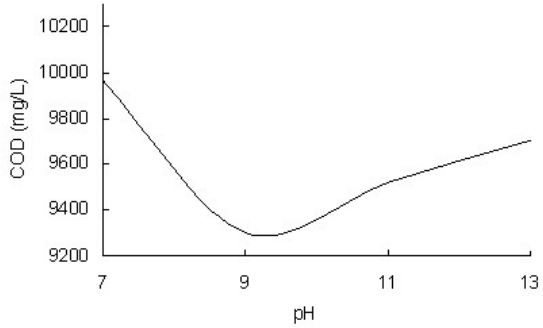

Figure 2.3 of furfural wastewater pH value of COD removal

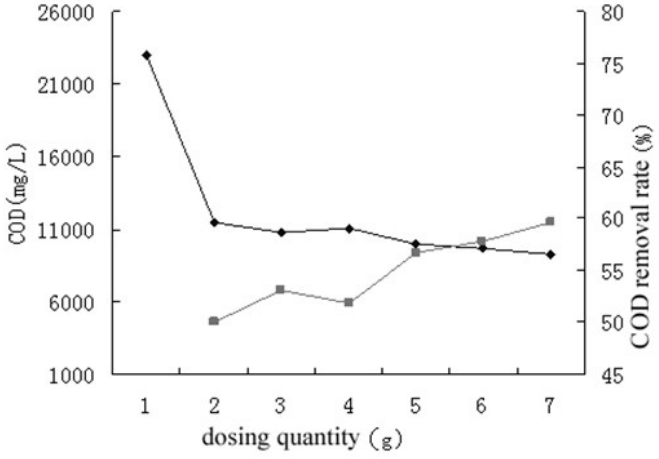

Figure 2.4 modified lignin flocculant dosing quantity of COD removal