



Preparation of Aminolignin from Paper Mill Sludge and Its Discolouring Flocculant Performance

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Lignin was extracted from paper mill sludge by the process of alkali dissolving and acid precipitating. Then a new kind of aminolignin discolouring flocculant was prepared with the lignin and dimethylamine epoxypropylamine (named as epoxy amimes monomer) as the raw materials and NaOH as the catalyst. The influencing factors such as the ratio of reactants, activation time, reaction temperature and reaction time on the preparation of aminolignin were investigated so as to optimize the reaction conditions. The products were characterized by using Fourier transform infrared spectroscopy. The possibility of aminolignin as a flocculant was examined by using simulated waste water of several dyes and the results show that it has a satisfactory decolourizing ability, which can afford a new method of effectively utilizing lignin and tackling paper mill sludge.

Key Words: Paper mill sludge, Aminolignin, Discolouring flocculant.

INTRODUCTION

The pulp and paper industry, an important component of economy in many countries, produces large quantities of wastewater treatment residuals-or paper mill sludge during pulping and paper making operations, which must be disposed in an environmentally safe manner. Typically disposal routes include land disposal and incineration. However, as increasing volumes of sludge have been produced, disposal routes are diminishing. Growing concerns about potential long-term effects of heavy metals associated with land disposal may place additional restrictions on this route. Due to space considerations, land disposal is severely limited in various regions and in some circumstances, may actually be cost prohibited. Incineration generally accounts for only a small percentage of total sludge disposals in most countries. This is mainly due to the availability and lower costs associated with alternative disposal routes.

Approximately 5.3×10^6 t of paper mill sludge was produced in 1995¹ and most of it was disposed in landfills. The US pulp and paper industry generates approximately 100 lb of paper sludge per ton of paper produced². The disposal cost of paper mill sludge is approximately half of the cost of wastewater treatment. Therefore, it is a pressing concern for the pulp and paper industry to develop alternative methods for disposing paper mill sludge to reduce costs without harming the environment. Hence, the paper manufacturing industry is interested in reducing the paper sludge disposal cost through

recycling and reuse. In the last few years some researchers³ have proposed paper sludge utilization in agriculture, but heavy metals contamination is also a concern in agricultural usage of biosolids. Now, safe and economical disposal of paper mill sludge is a key consideration for pulp and paper industry.

Paper sludge is mainly composed of organic substances such as lignin and some inorganic materials^{4,5}. Thus, the use of paper mill sludge to produce lignin-based materials may be an innovative way to recycle it.

Lignin is an important constituent of the biomass and among renewable polymers, it is exceeded in natural abundance only by cellulose. It is multifunctional phenolic polymer containing hydroxyl, carboxyl and carbonyl groups⁶. Therefore, the development of lignin and its derivatives have received growing attention in view of economic benefit and environmental protection. Many modification methods of lignin, such as sulfonation, polymerization, epoxy modification, oxidation and hydroxyl methylation have been reported to increase its sorption activity, therefore offering additional opportunities for its application as sorbents. Lignins have been proposed for the sorption of different synthetic dyes⁷, for treatment and decolouration of waste waters⁸. The introduction of basic amino groups into the lignin structure drastically alters its physical and chemical properties. It is converted from polyacid to polybase or polyampholite, which could provide new areas of lignin application.

In the present work, a new monomer with a high active epoxy group was prepared from dimethylamine at 40 °C. It

has an advantage of low cost in industrial practical application compared to the synthesis method proposed by the other researchers^{9,10}, which use trimethylamine as raw material under reaction temperature at 0~5 °C. Then, the epoxy group on the monomer was easily grafted into lignin. The grafted products were characterized by Fourier transform infrared spectroscopy. The aminolignin exhibits favourable flocculation performance and can effectively remove the coloured group of dyes in wastewater.

EXPERIMENTAL

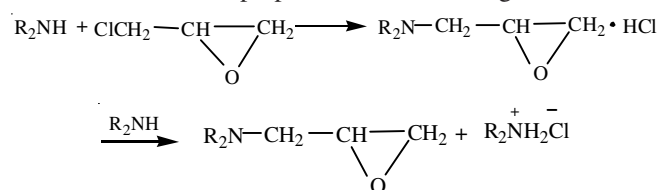
The paper mill sludge used in this paper originated from a paper mill located in Henan province of China, which uses a soda pulping process with rice and wheat straw as the raw materials of pulp. The commercial dyes, *e.g.*, acid black 210, leather red, leather yellow were used without further purification. The other reagents, such as dimethylamine and epoxy chloropropane were in analytical purity.

The analytical instruments used include a TENSOR27 FTIR spectrometer (Bruker Optics, Germany), a 5B-6 COD determinator (Lan Zhou Lian Hua Environmental Technical Co. Ltd., China), a PHS-2 pH-meter (Shanghai Leici Appliance Co. China) and a UV-2201 ultraviolet-visible spectrophotometer (Shimadzu, Japan).

Preparation of aminolignin

Extraction of crude lignin: The crude lignin was prepared as follow: firstly, hot water was added into a paper mill sludge sample, followed by the addition of 10 % NaOH (w/w) to dissolve the lignin; the pH of the filtrate was then adjusted with 10 % H₂SO₄ (w/w) for a complete precipitation and the temperature was kept in the region of 80-90 °C for 50 min; finally, it was filtered, rinsed and dried at 50 °C to obtain a crude lignin.

Preparation of epoxy amine monomer: The epoxy amine monomer was prepared as the following reactions:



Dimethylamine solution (136.5 g, 33 %, 1 mol) was added in a four-neck flask equipped with a condensator, mechanical stirrer, feed funnel and thermometer. Then, 96.4 g epoxy chloropropane was added dropwise into the flask under stirring and the reaction temperature was kept at 40 °C. After dropping, the reaction solution was stirred for 0.5 h and cooled to room temperature. The obtained monomer was a viscous and achromatous liquid. The reaction extent could be checked by adding a drop of AgNO₃ solution into a small amount of the reaction solution. A plenty of white precipitation appeared, showed that the monomer had already been produced.

Preparation of aminolignin: 10 g Crude lignin was immersed in 15 mL water and heated to 60 °C. Then 10 mL of 4 mol L⁻¹ NaOH solution was added as an initiator under stirring. After activation for 1 min, 10 g epoxy amine monomer was added into the solution. It was continuously stirred for

2 h and the reaction temperature was maintained at 60 °C. The obtained product was a sepia and viscous liquid. The pH of the product is about 13, solid content is about 19 % and density is about 1.015 kg L⁻¹.

Discolouring flocculation experiments: The predetermined concentrations of the reactive dyes ranged from 0 to 50 mg L⁻¹. A UV-2201 ultraviolet-visible spectrophotometer was used to determine their corresponding absorbance at the maximal absorbance wavelength (λ_{max}). The λ_{max} of acid black 210, leather red and leather yellow were 587 nm, 512 nm and 412 nm, respectively. Then the calibration curves of the reactive dyes were obtained.

A simulated dye effluent was prepared as follows: the initial concentration of the dye solution was 100 mg L⁻¹ and its pH was adjusted by adding a dilute HCl or NaOH solution into it. Then, a required dose of aminolignin was added into the simulated dye effluent and was mixed rapidly for 1 min, followed by slowly mixing for 5 min. The obtained floccules were allowed to settle down for 2 h. The corresponding absorbance of the upper solution was tested and the dye residual concentration was calculated from the calibration curve. Finally, the discolouring rate, denoted as R, could be obtained by the following formula:

$$R = (1-C/C_0) \times 100 \%$$

where, C₀ and C are the initial and residual concentrations of the simulated dye effluent (mg L⁻¹).

RESULTS AND DISCUSSION

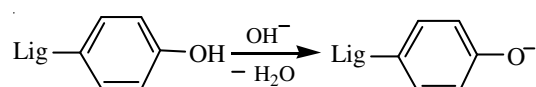
Influence of reaction conditions on synthesis of aminolignin

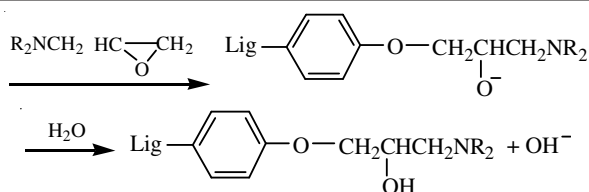
Selection and dosage of initiators: The key of a grafting reaction is to generate active center in the molecular chain, thus the catalyst is an important affecting factor. Generally, alkaline catalytic system and radical initiator are used for initiating phenolic hydroxyl group and alcohol group of lignin. The influence of different initiators on the flocculation efficiency was studied and the results are shown in Table-1. It shows that sodium hydroxide, which is cheaper, is determined as the optimal initiator. Furthermore, the results indicate that the discolouring rate reaches a maximum when the sodium hydroxide concentration is 4 mol L⁻¹.

TABLE-1
EFFECT OF DIFFERENT INITIATORS
ON DISCOLOURING EFFICIENCY

Initiator	Discolouring rate (%)		
	Acid black 210	Leather red	Leather yellow
2 % Na ₂ S ₂ O ₈	80.5	87.4	91.5
2 mol L ⁻¹ NaOH	90.5	88.5	84.7
4 mol L ⁻¹ NaOH	92.7	91.1	89.5
6 mol L ⁻¹ NaOH	88.6	87.4	81.7
2 % CeCl ₃	89.2	90.4	90.4
H ₂ O ₂ + Fe ²⁺	81.7	89.2	87.5

The aminolignin synthetic reaction activated by sodium hydroxide can be expressed as follow:





Obviously, the number of lignin phenoxyl anions increases as the catalyst concentration increases, thus the graft rate is enhanced and the obtained product has a better discolouring efficiency. But the reaction would be too drastic and even uncontrollable if the sodium hydroxide concentration is too high, then the other side effects would occur. It shows that when the sodium hydroxide concentration is 6 mol L^{-1} , the obtained black product becomes very viscous and has a poor dissemination in the dye solution; after being placed for a while, the product is easy to solidify and its discolouring performance declines. Therefore, in order to obtain a product with good discolouring performance, the appropriate sodium hydroxide concentration is 4 mol L^{-1} and the dosage is 15 % to dry lignin (mass per cent).

Influence of activation time on synthesis of aminolignin:

Activation time is essential for grafting. The influence of activation time on synthesis of aminolignin is shown in Table-2. It shows that as more lignin phenoxyl anions are produced with the increase of activation time, lignin is sufficiently activated. The best discolouring efficiency was achieved at 1 min activation. However, the molecule might lose activity if activation time is too long, thus reducing the graft efficiency and discolouring efficiency.

TABLE-2
EFFECT OF ACTIVATING TIME ON
DISCOLOURING EFFICIENCY

Activating time (min)	Discolouring rate (%)		
	Acid black 210	Leather red	Leather yellow
0.5	86.1	92.8	88.6
1.0	92.6	93.6	91.2
1.5	92.3	90.9	88.9

Influence of mass ratio on synthesis of aminolignin:

The discolouring efficiency of aminolignin increases with the increase in mass ratio of lignin to monomer and the results are shown in Fig. 3. This owes to the increase in collision chance between monomer and lignin phenoxyl anion. As the amount of monomer increases, a lignin phenoxyl anion could be surrounded by multiple monomers, so the reaction between lignin and monomers occurs completely. However, continuing increase in the monomer dosage would cause a decrease in discolouring performance and a higher cost. The appropriate mass ratio of lignin to monomer is 1:2.

Influence of temperature on synthesis of aminolignin:

Reaction temperature is another important factor that influences the discolouring performance of aminolignin. As the results shown in Table-4, higher temperature is conducive to the graft reaction and enhances the discolouring performance of the product, since the number of activated molecule increase with the higher reaction temperature. However, it begins to decrease once the temperature is over $60 \text{ }^\circ\text{C}$, as the spatial structure of aminolignin molecule might be damaged

at higher temperature. Therefore, the reaction temperature should not be too high and the optimal temperature for grafting is $60 \text{ }^\circ\text{C}$.

TABLE-3
EFFECT OF MASS RATIO ON DISCOLOURING EFFICIENCY

Mass ratio (lignin to monomer)	Discolouring rate (%)		
	Acid black 210	Leather red	Leather yellow
1:1	90.6	95.5	85.4
1:2	92.6	97.4	90.4
1:3	88.3	93.0	72.4

TABLE-4
EFFECT OF REACTION TEMPERATURE ON
DISCOLOURING EFFICIENCY

Temperature ($^\circ\text{C}$)	Discolouring rate (%)		
	Acid black 210	Leather red	Leather yellow
50	92.6	97.2	91.3
60	97.5	98.4	93.5
70	89.9	98.2	90.7

Influence of reaction time on synthesis of aminolignin:

Table-5 shows the effect of reaction time on discolouring performance of the product. The discolouring rate increases quickly in the beginning and reaches about 90 % in 1.5 h. It continues to increase slowly but turns to decrease after 3 h, since the grafted product maybe decomposes under too long time heating. The optimal reaction time for graft is 2 h.

TABLE-5
EFFECT OF REACTION TIME ON
DISCOLOURING EFFICIENCY

Time (h)	Discolouring rate (%)		
	Acid black 210	Leather red	Leather yellow
1.0	75.7	76.4	70.5
1.5	90.1	92.5	88.9
2.0	92.7	96.4	90.8
3.0	93.9	97.1	91.0
4.0	94.4	96.1	88.8

According to the above discussion, the optimal producing conditions for aminolignin are obtained: reaction temperature $60 \text{ }^\circ\text{C}$, reaction time 2 h, the mass ratio of lignin to the monomer 1:2 and the initiator dosage 15 % (mass percent) to dry lignin.

FTIR analysis of aminolignin: Previous studies show that the characteristic infrared frequencies of the functional groups in the lignin molecules are assigned to carbonyl groups, ethylenic double bonds, aromatic rings and hydroxyl groups¹¹⁻¹². In the IR spectrum of lignin (Fig. 1 curve a), the peak at 1511 cm^{-1} is attributed to the benzene rings. After amination, the IR spectrum (Fig. 1 curve b) shows a new strong peak at 1456 cm^{-1} , which is attributed to the characteristic peak of the N-H bend vibration of the ternary ammonium group; this peak covers the characteristic peak of the benzene rings of lignin at 1511 cm^{-1} . On the same time, the appearance of a new peak at 1026 cm^{-1} is ascribed to the characteristic peak of the ether bond (-C-O-C-). Therefore, it can be concluded that the ternary ammonium groups are grafted on lignin successfully.

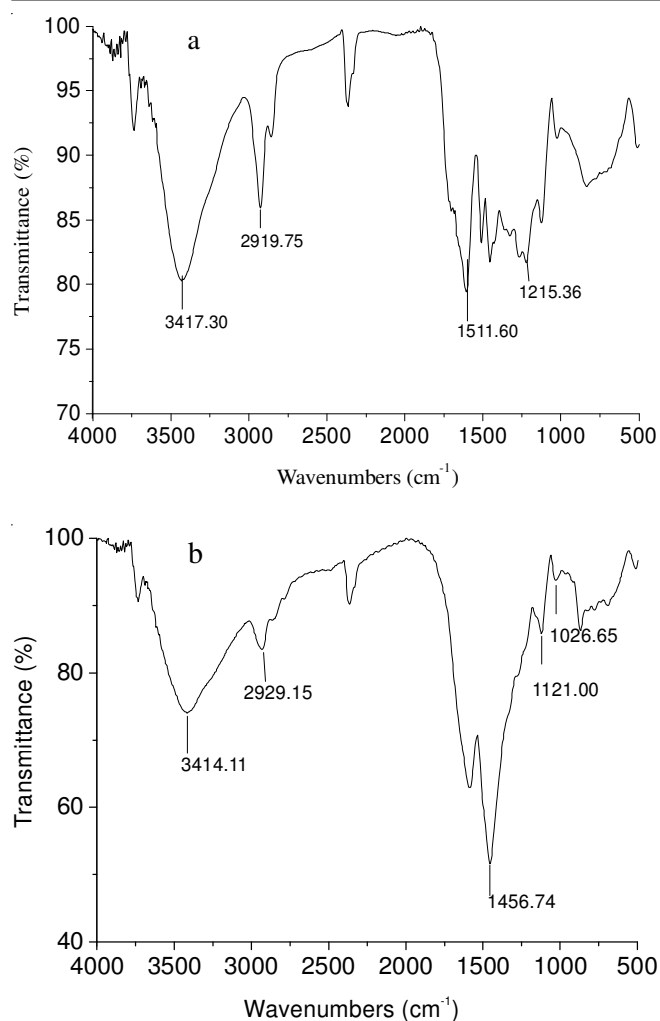


Fig. 1. FTIR spectra of lignin before (a) and after (b) amination

Discolouring performance of aminolignin

Influence of effluent pH on the discolouring efficiency:

The effect of effluent pH on the discolouring efficiency is shown in Fig. 2. The experimental results indicate that it varies with the dye variety. The effluent pH could affect the existing state and charge characteristics of aminolignin, thus change the combination forms and degrees of the aminolignin molecules with the dye molecules and finally affect the discolouring efficiency. Under an acidic condition, tertiary amine group of aminolignin can combine with H^+ and exists in the form of ammonium salt, thus its positive charge density increases and is favourable for flocculation and sedimentation. The excellent discolouring efficiency could be achieved among the pH range of 0.5 and 2.0.

Influence of aminolignin dose on the discolouring efficiency:

The aminolignin dose has an obvious effect on the discolouring efficiency and the results are shown in Fig. 3. If the flocculant dose is too small, it is difficult to form floc; on the contrary, too much dose will cause the floc to be surrounded by the remainder, thus the floc can be dispersed and the flocculating efficiency will decrease. Among the range of 0 and 4 $g L^{-1}$, the discolouring rate increases with an increase of the flocculant dose. The maximal discolouring rates reach 96.3, 97.2 and 86.1 % for the acid black 210, leather red and leather

yellow, respectively. When the dose exceeds 4 $g L^{-1}$, the discolouring rate remains almost constant for acid black 210 and leather yellow, but lowers for leather red. Moreover, the excessive dose would cause an increase in the chemical oxygen demand (COD) of the simulated dye effluents. Consequently, the flocculant dose should be adjusted in an ideal range.

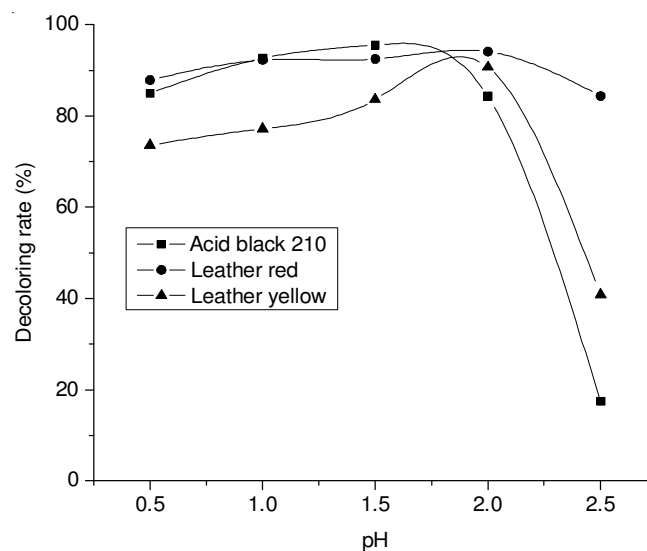


Fig. 2. Effect of pH on the discolouring efficiency for different dyes

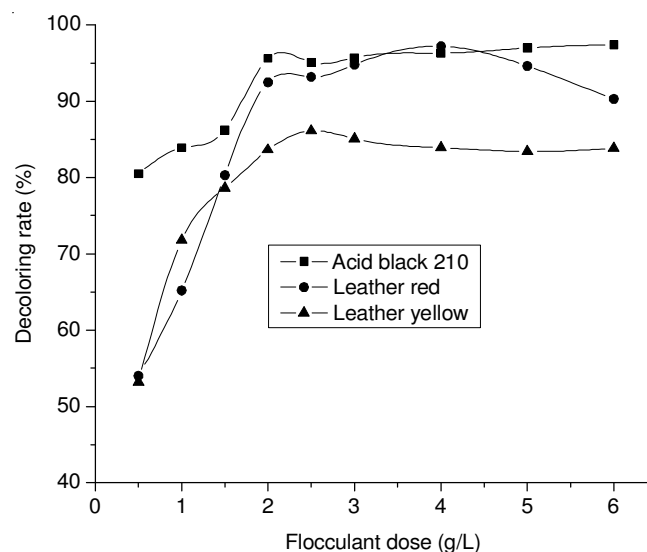


Fig. 3. Effect of flocculant dose on the discolouring efficiency for different dyes

Influence of aminolignin dose on the effluent COD_{cr} :

The lignin contains different aromatic compounds with various molecular weights and its composition is very complex. Therefore, excessive aminolignin dose will cause an increase in the COD_{cr} of the simulating effluent as well as the discolouring rate. It is necessary to study the relation between the aminolignin dose and the simulated effluent's COD_{cr} . The results are shown in Fig. 4 and Table-6. It indicates that the COD_{cr} increases with the increase in the flocculant dose. Furthermore, a lower COD_{cr} is obtained under a higher discolouring rate, which would not cause a secondary pollution. It is known

that the functional groups in the aminolignin molecules can react with the chromophore groups in the dye molecules to form the salt bonds and then the colourity of the simulated dye effluents decreases. Nevertheless, the unreacted aminolignin will cause the COD_{Cr} increase during the discolouring flocculation process, which results in a secondary pollution. Hence, it is very important to adjust the aminolignin dose to a suitable range.

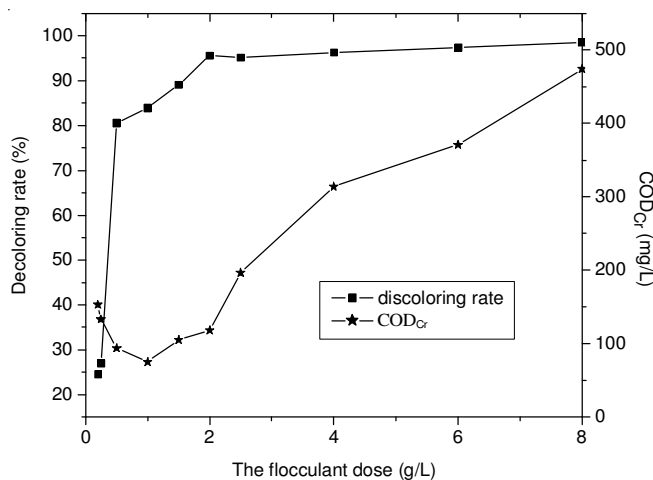


Fig. 4. Effect of flocculant dose on the discolouring efficiency for acid black 210

TABLE-6
 COD_{Cr} VARIATION OF DYE EFFLUENT
BEFORE AND AFTER TREATMENT

Simulating dye effluent	Flocculant dose ($g L^{-1}$)	Discolouring rate (%)	COD_{Cr} ($mg L^{-1}$)
Acid black 210	2.0	95.6	+13
Leather red	2.0	92.3	+132
Leather yellow	2.5	86.1	+233

Influence of initial concentration of dyes on the discolouring efficiency: The effects of the initial concentration of dyes on the discolouring efficiency are studied and the results are given in Fig. 5. It shows that under the same aminolignin dose, the discolouring rate increases with the increase in the initial concentration of acid black 210. Thus, the required aminolignin dose decreases with the increase in the initial concentration of the dye. The higher concentration of the dye may increase the collision probability between the dye molecules and the flocculant molecules and then accelerate the flocculation rate and improve the discolouring efficiency. This result also indicates that the flocculant is more effective for higher concentration dye effluent and lower the cost.

Influence of temperature on the discolouring efficiency: The experimental results show a small impact of temperature on the discolouring rate, but a higher temperature can speed up the flocculation settling rate and a good discolouring effect could be achieved in short time.

Influence of flocculation time on the discolouring efficiency: After flocculation reaction, the treated effluent was put into a 100 mL graduated cylinder for settlement. The height of the interface between the upper solution and the floc was recorded every 30 min and also the discolouring rate simul-

taneously. The effect of flocculation time on the discolouring efficiency for acid black 210 is given in Fig. 6. It shows that the floc settles rapidly in the first 30 min and after 1 h it tends to be stable. The discolouring rate reaches 95.0 % in 3 h.

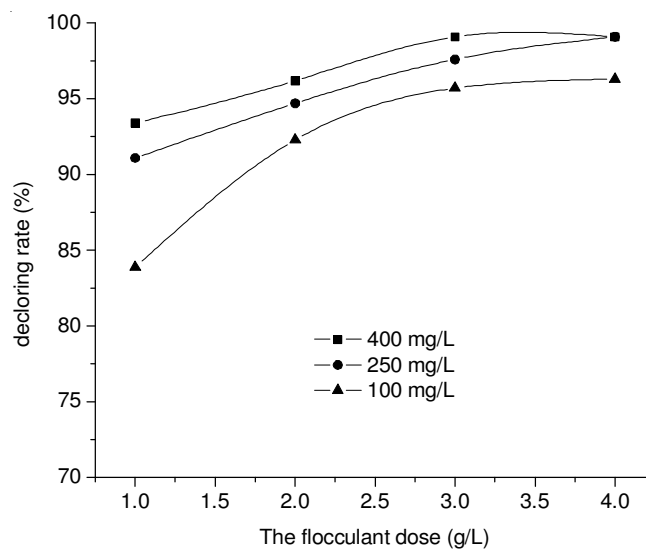


Fig. 5. Effect of initial concentration of dye on the discolouring efficiency for acid black 210

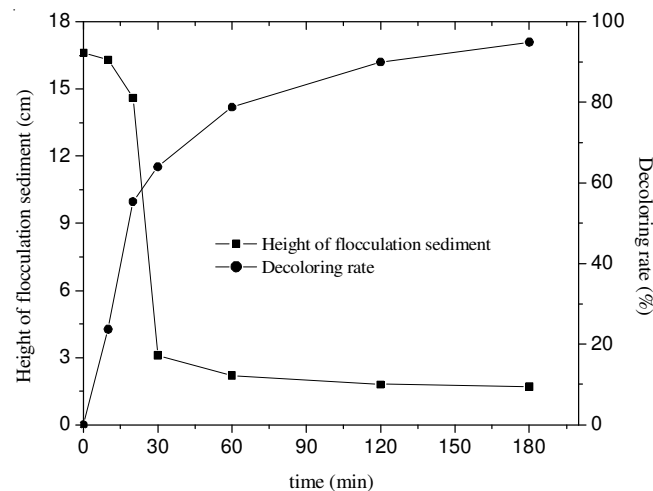


Fig. 6. Effect of flocculation time on the discolouring efficiency dye acid black 210

Mechanism of flocculation: The flocculation is due to the formation of electrical interaction or chemical bond between the dyes and aminolignin. A most possible flocculation mechanism may be the result of the bridging adsorption and charge patch between the negative charges on the particulate surfaces and the cationic groups of the interacting polymer. Under acidic condition, aminolignin exists in the form of ammonium salt, which is favourable for flocculation and sedimentation because of the increase in the positive charge density.

Conclusion

Aminolignin is prepared from paper mill sludge and can be used as a discolouring flocculant, which is an effective way to comprehensive utilization of paper mill sludge. Waste can be turned into useful materials by this method and the results show the good benefit of both economy and society. The

optimum conditions for the synthesis of aminolignin are as follows: reaction temperature at 60 °C, reaction time for 2 h and mass ratio of lignin to monomer at 1:2.

The aminolignin shows a satisfactory discolouring efficiency in the discolouring flocculation process. Under the optimum conditions, the discolouring rates for the acid black 210, leather red and leather yellow could reach 96.3, 97.2 and 86.1 %, respectively.

Excessive aminolignin dose could cause the increase of the effluent COD_{Cr} and result in the secondary pollution. Consequently, suitable aminolignin dose should be adjusted to avoid the secondary pollution and to achieve the excellent discolouring efficiency.

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