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Analysis of Dissolved and Colloidal Substance Degradation in Old Corrugated Container White Water by Fenton Method

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In order to degrade the dissolved and colloidal substance (DCS) in white water system of waste paper, Fenton method, as an advanced oxidation processes, was employed in treating old corrugated container (OCC) recycling white water to reduce negative effect on paper properties and running performance of the paper machine. In this study, the optimum conditions were determined as pH was 4, $[H_2O_2] = 1$ mol/L, $[H_2O_2]/[FeSO_4\cdot 7H_2O] = 1.75$ for the Fenton process. Under these conditions, the removal rate of COD_{Cr} and dissolved and colloidal substance is reaching to 75.41 and 46.72 %, respectively. The stability of dissolved and colloidal substance to metal ion by Fenton treated in wastepaper white water is significantly improved.

Keywords: Fenton method, White water, Dissolved and colloidal substance, Stability.

INTRODUCTION

In the pulp and paper industry, the water use minimization is a constant target. White water is the main wastewater in paper-making process. old corrugated container, as a raw material of renewable fiber, has extraordinary high recycle rate[1]. Thus old corrugated container white water has become a common target which the paper mills have to dealing with. Nowadays, most paper mills use enclosing white water circuit to reduce water consumption and environment pollution. However, with the increasing percentage of white water reuse, the harmful substances will accumulate in the white water system[2], including extractions, dissolved and colloidal substance and sulphate, which has adverse effects on the paper making machine and paper properties[3]. They may lead to various problems, such as unsteady quality of production, accumulation of anionic trash and greater possibility of paper break. According to the research, the main reason of the issues is the rapid increase of dissolved and colloidal substance in the enclosing white water circuit.

In corrugated paper making process, amount of adhesives, synthetic adhesives, resin component (aliphatic acid and ester), oil, wax, ink and hot-melting adhesives exist as dissolved and colloidal substance, especially colloidal substance in white water system. These substances accumulate in the system, losing balance, gathering together and causing stickies deposition problem when the system environment changed. This reaction directly influenced paper appearance quality, papermaking machine operating performance and frequency of cleaning and overhaul[4].

Fenton oxidation process is one of the advanced oxidation technologies, the reaction causes the dissociation of the oxidant and the formation of highly reactive hydroxyl radicals that attack and destroy the organic pollutants. It is widely utilized on wastewater industry for it's rapid decomposition and high oxidation rate. The classic Fenton reagents are a mixture of H_2O_2 and ferrous iron salt [Fe(II)], which generate hydroxyl radicals ($^{\bullet}OH$). Ferrous iron reacts with H_2O_2, generating hydroxyl radicals. The generation of the radicals can involve a complex reaction sequence in an aqueous solution[5].

Wastewater treatment processes by means of Fenton's method are known to be very effective in removal of many hazardous organic pollutants from water. However, there's still no report about employing Fenton reaction in recycling white water. In this research, Fenton reaction treating old corrugated container recycling white water was investigated. In order to offer a technology for the method, the white water quality variation from Fenton processing were analyzed. This study also researched the optimum process, expecting to achieve enclosing white water circuit.

EXPERIMENTAL

Preparation of old corrugated container white water: The laboratory simulation white water was prepared by old corrugated container which was provided by Guangxi Mingzu printing company. The preparation method is: old corrugated container was torn up into 5 cm × 5 cm pieces. Put the pieces into bucket which weighed by 3 % concentration. Keep the paper pieces in the water for 0.5 h, took them out after squeezing and rubbing. The water left in the bucket is called process-water of papermaking. Repeated this process and soaked paper pieces with 3 % concentration. After five times, the water left in the bucket is laboratory simulation white water.

Fenton reaction: Fenton's process was carried out in batch operation as described elsewhere, added quantitative ferrous sulfate solution (10 %) in the white water before the corresponding proportion hydrogen peroxide (30 %) was added. Adjusted reaction pH by experimental scheme, after 0.5 h reaction time, changed the pH to 7. Aerated for 20 min and then added 0.5 mL polyacrylamide for flocculation. Stopped agitating, let it stood for 0.5 h and then went through filter paper. Treatments of white water were carried out by Fenton treatment using single-factor tests. The parameters were investigated as Table-1 showed.

TABLE-1
INFLUENCING FACTOR OF FENTON TREATMENT

pH	H_2O_2/mol/L	$H_2O_2/FeSO_4{\cdot}7H_2O$
3	0.5	1.0
4	0.75	1.25
5	1.0	1.5
6	1.25	1.75
7	1.5	2.0

Test of COD_{cr}: COD_{cr} was measured by the method of potassium dichromate.

Separation of dissolved and colloidal substance: Put white water into centrifuge, 2000 rpm, 0.5 h. Acquired supernatant liquid was the dissolved and colloidal substance white water.

Metal ions to dissolved and colloidal substance stability: NaCl, $CaCl_2$ and $Al_2(SO_4)_3{\cdot}18H_2O$, represented Na^+, Ca^{2+} and Al^{3+}, added into 50 mL white water which pH was adjusted to 7 with 100 rpm agitation, respectively. After 5 min reacting, put the solution into centrifuge for 0.5 h under 3000 rpm. The supernatant liquid was measured for residual turbidity to characterize the dissolved and colloidal substance instability degree.

RESULTS AND DISCUSSION

Effect of pH: As can be seen in the Fig. 1, pH values ranged from 3 to 7. The COD_{cr} concentrations is much lower than untreated white water. It is speculated that large molecules which exist in white water system were degraded by oxidative degradation to smaller size entering the size ranging of dissolved and colloidal substance. Some macromolecule even decomposed to soluble substance, increased conductivity.

As is vividly illustrated, dissolved and colloidal substance content and COD_{cr} content are far from perfect when pH higher than 4. The oxidation efficiency of Fenton's reagent may decrease because ferric ions could form $Fe(OH)_3$[5]. $Fe(OH)_3$ has a low activity and will not react with hydrogen peroxide[6]. The ferric ions in the solution that can react with hydrogen peroxide are so reduced. In the mechanism in which ferric ions react with hydrogen peroxide is the rate-limiting step.

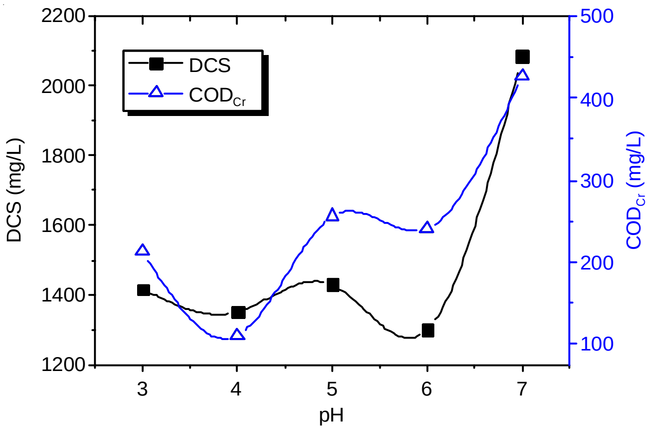

Fig. 1. Effect of initial pH on COD_{Cr}, dissolved and colloidal substance concentration

When the pH is 3, the dissolved and colloidal substance and COD concentration are higher, it may because of the mechanism of Fenton reaction. The concentration of hydrogen ions is too high when pH is 3, it will slow down the formation of $FeOOH^{2+}$, which consecutively causes the production rates of ferrous ions and hydroxyl radicals to decrease as well. Consequently, the Fenton process has the highest efficiency when the pH is around 4.

Hydrogen peroxide concentration: From Fig. 2, COD_{cr} and dissolved and colloidal substance concentration is decreased along with the increasing of H_2O_2 concentration when H_2O_2 dosage is low. This is because Fenton reagent has the oxidative power, resulting in the reaction of hydroxyl radicals to remove organics in the white water system. This mechanism reflect to the experiment result is that H_2O_2 dosage ascent directly influences the significance of oxidation,and the degradation level of organics in the white water was higher.

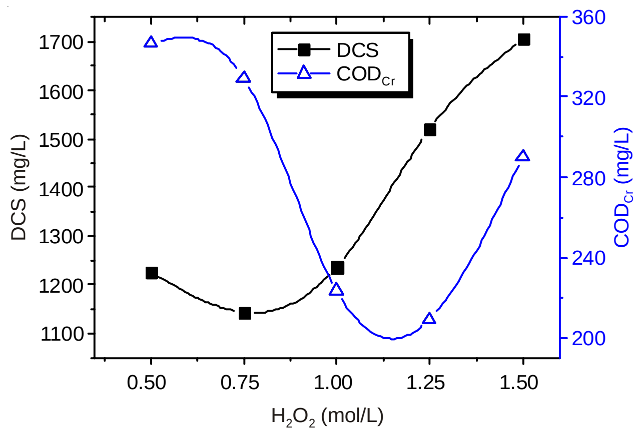

Fig. 2. Effect of H_2O_2 dosage on COD_{Cr} and dissolved and colloidal substance concentration

When excessive amounts of H_2O_2 added in the system, Fe^{2+} oxidized to Fe^{3+}, which means H_2O_2 was expended with non-productive as well as the production of $^{\bullet}OH$ was inhibited. On the other side, H_2O_2 can act as an $^{\bullet}OH$ scavenger as well as an initiator, the great amount of H_2O_2 can also depress the generation of hydroxyl radical $^{\bullet}OH$, lower the dynamics rate of oxidization[7]. This could be the explanation of why reaction is not as complete as in the H_2O_2 proper dosage solutions at

0.5 h, which has a higher removal rate of COD and dissolved and colloidal substance.

Fenton reaction degraded the large molecules which exist in white water system to smaller size entering the size ranging of dissolved and colloidal substance by doxidative degradation. When increasing the dosage of H_2O_2, abundant Fe^{2+} oxidized to Fe^{3+}, which means Fe^{2+} was sharply decreased in the white water system. By Wink *et al.*[8], Fe^{2+} has the capability to react with H_2O_2 to form complex, which has the ability of flocculation. Cheng *et al.*[9] research told us, the flocculation ability is a significant content of Fenton reaction. This ability has great influence to dissolved and colloidal substance and COD in the system. There for, the reduction of Fe^{2+} directly affected the concentration of complex and lower the capability of sedimentation. This is the reason why the dissolved and colloidal substance concentration in treated white water is higher than untreated. Moreover, the oxidized Fe^{3+} should be taken into account in dissolved and colloidal substance of white water system, which is another reason[10].

The H_2O_2 left in treated white water can also react with potassium dichromate solution, leading to the ascendant of COD_{cr} concentration[11]. In conclusion, the optimum dosage of H_2O_2 is 1 mol/L.

Ferrous sulfate concentration: As shown in Fig. 3, with the improving of Fe^{2+} concentration, dissolved and colloidal substance and COD_{cr} were declined. This could be explained by the fact that the concentration of catalyst Fe^{2+} is lower than needed and the $^{\bullet}OH$ generation is limited which is unfavorable to catalytic reaction. Therefore macromolecules and macro-stickies in the white water system are unable to degrade completely. Sedimentation efficiency would be undesirable for ferrous complex concentration is low.

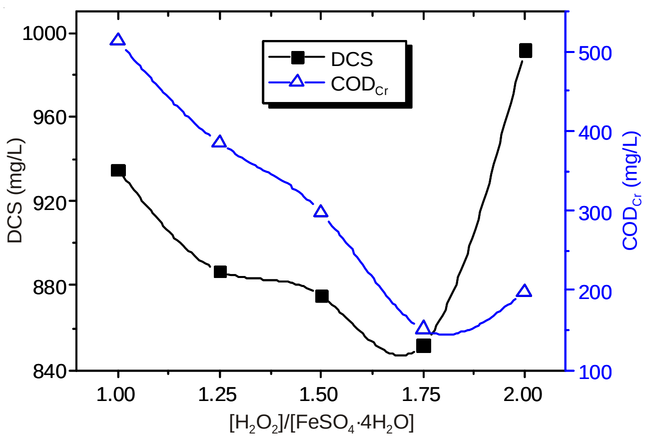

Fig. 3. Effect of $FeSO_4{\cdot}7H_2O$ dosage on COD_{Cr} and dissolved and colloidal substance concentration

Following the increasing of Fe^{2+} concentration, catalytic action was more efficient. However, when the concentration was high enough, adding more Fe^{2+}, the COD and dissolved and colloidal substance would ascend. This is because the $^{\bullet}OH$ mainly reacts with the ferrous ion and not hydrogen peroxide. In another words,too much Fe^{2+} will accelerate the H_2O_2 decomposition rate, even make the reaction time too short to react with organics, but with other $^{\bullet}OH$. This will make Fenton reaction in a low removal rate. Too much Fe^{2+} exist in the white water system will make COD_{cr} and dissolved and colloidal substance improved. Overall, the optimum $[H_2O_2]/[FeSO_4{\cdot}7H_2O]$ is 1.75.

Parameters analysis on the optimum condition: When the white water treated in the optimum condition according to the above results, parameters were tested as follows:

As shown on the Table-2, the removal rate of COD and dissolved and colloidal substance were reaching to 75.41 and 46.72 %, respectively on the optimum reaction condition. Surprisingly the removal rate of CS is up to 94.54 %. This is a direct demonstration that Fenton reaction has an efficiency effect on white water system which can remove large amounts of stickies exists in white water system. The absolute value of Zeta potential raised from 8.3 to 20.6 which means the repulsion between all kinds of particles are improved[12]. This is the reason why the capacity of flocculation decreased and the stability of dissolved and colloidal substance is raised. Conductivity and salinity are raised in the system, that could be a evidence of stickies degradation. The stickies and macromolecules were broke into pieces even into soluble substances, improved the stability of white water system.

TABLE-2
PARAMETERS OF WHITE WATER
BEFORE AND AFTER FENTON METHOD

Parameters		Original white water	Fenton treating white water
Dissolved and colloidal substance (mg/L)		1600.0	852.5
DS (mg/L)		955.0	812.5
CS (mg/L)		747.5	40.8
COD (mg/L)		615.6	151.4
Z-average (r. nm)		1309.0	164.7
Zeta potential		-8.3	-20.6
Turbidity (NTU)		41.6	11.9
Metal ions (mg/L)	Al	59.68	28.3
	Ca	175.2	131.3
	Fe	57.6	162.4
	Mn	7.4	3.8
	Pb	9.2	1.6
	Sr	3.1	0.2
	Zn	6.3	2.0

Inorganic metal ions can compressed colloid particles of electric double layer, reduce the distance between particles. Distance decrease will cause instability of dissolved and colloidal substance, when it decreases to zero. The higher valence metal ions, the greater the effect intensity. The metal ions change of Fenton treatment before and after shows that the concentration of heavy metal ions in the white water is much lower. Among them, Al^{3+}, as a kind of high valence iron, its concentration fell significantly. Al^{3+} also known as a natural flocculants, has the capability to cause dissolved and colloidal substance flocculation and instability. Other metal ions also leading to an increase demand of cationic in water. Thus, Fenton treated white water can decrease the concentration of metal ion and improve the performance of water reuse.

Dissolved and colloidal substance stability to various metal ions: Metal ions in dissolved and colloidal substance water can influence the stability of dissolved and colloidal substance[13]. While enhancing the metal ions, turbidity is reduced. Inorganic metal ions can depress the electric double layer of colloidal particles by shorten the distance between particles. When the distance reduced to zero, dissolved and colloidal substance in the system will converge and lose their balance. Metal ion with higher valence has stronger influence to dissolved and colloidal substance stability. In the paper-making process, Na^+, Ca^{2+}, Mg^{2+} and Al^{3+} are common metal ions. So in this study, Na^+, Ca^{2+} and Al^{3+} are chosen to investigate the influence of metal ions which existence in single form to dissolved and colloidal substance stability[14].

Figs. 4-6 illustrated the effect of NaCl, $CaCl_2$ and $Al_2(SO_4)_3$ to dissolved and colloidal substance stability. As shown in the fig, while the dissolved and colloidal substance loses its stability in untreated old corrugated container white water, the treated white water is still maintained stable. When the metal ions were added into the untreated white water, the trend of dissolved and colloidal substance stability dropped significantly. However, metal ions in Fenton treated white water, dissolved and colloidal substance instability showed a slow trend of descendant, which mean dissolved and colloidal substance in white water is more stable after Fenton treating.

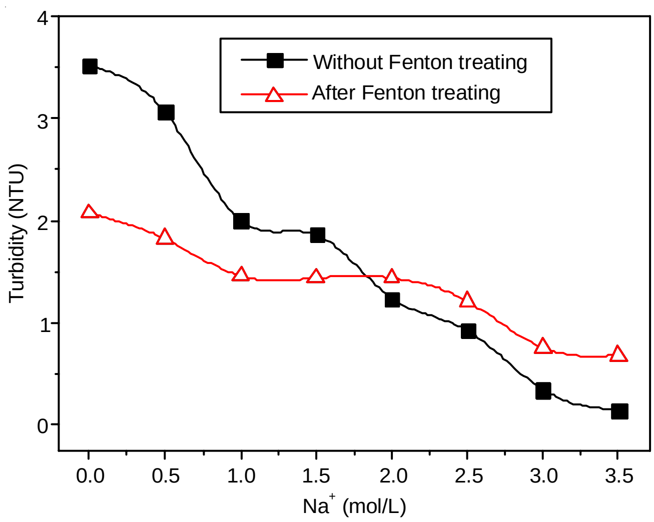

Fig. 4. Effect of NaCl concentration to dissolved and colloidal substance stability

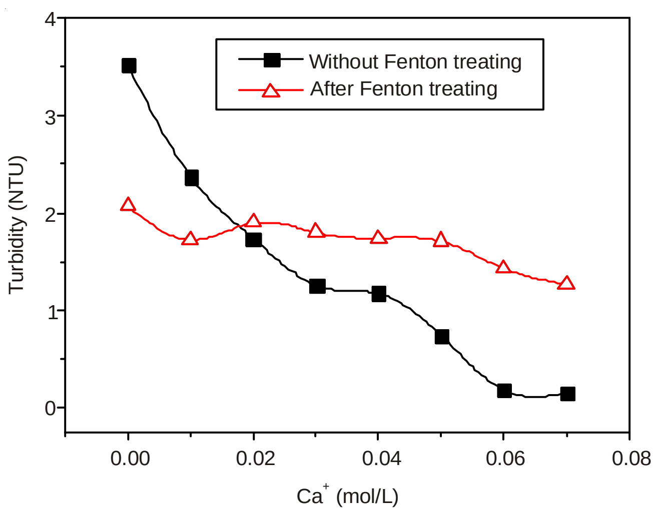

Fig. 5. Effect of $CaCl_2$ concentration to dissolved and colloidal substance stability

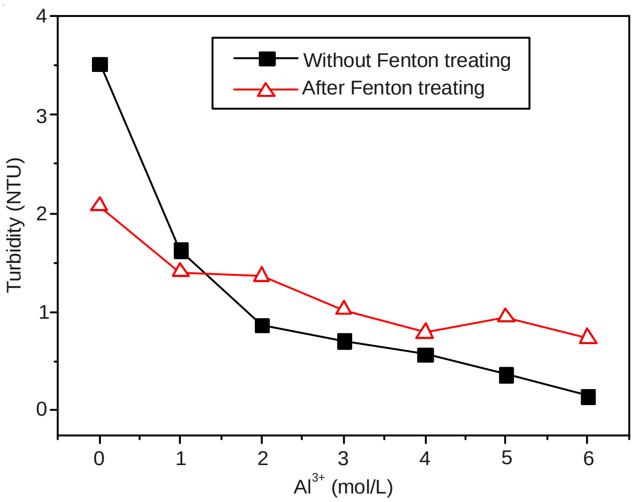

Fig. 6. Effect of $Al_2(SO_4)_3$ concentration to dissolved and colloidal substance stability

Conclusion

Shown by single factor experiment, the optimum conditions were determined as pH = 4, $[H_2O_2]$ = 1 mol/L and $[H_2O_2]/[FeSO_4{\cdot}7H_2O]$ = 1.75 for the Fenton process. Under these conditions, the removal rate of COD_{cr} and dissolved and colloidal substance is reaching to 75.41 and 46.72 %, respectively. Furthermore, the dissolved and colloidal substance stability to metal ions was raised, which is conducive to improve white water quality and industrial reuse. However, for the expensive price of Fenton reagent, further research is needed to investigate the proportion of Fenton treated circulating white water.

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