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Treatment of Pulp and Paper Mill Effluent Using Photo-fenton's Process

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Abstract: Wastewater from pulp and paper mill is one of the most important sources of pollutants mainly due to the pulping and bleaching processes. This study evaluates the effectiveness of photo-Fenton's process in reducing organic and suspended solid in pulp and paper mill wastewater. The photo-Fenton's process produces the strongest oxidation and consumes lower Fe^{2+} compared to the conventional Fenton's process. The conditions of the photo-Fenton's process were optimized such as the initial pH, the H_2O_2 concentration and the $FeSO_4.7H_2O$ concentration. It was found that the optimal pH for Fenton's process was pH 5. The optimal initial concentration of H_2O_2 and $FeSO_4.7H_2O$ were 500 and 400 mg L^{-1}, respectively. The overall efficiency of BOD_3 and TSS reduced by the Fenton's process under optimal conditions attained up to 87.5 and 87.0%, respectively. Thus, the photo-Fenton's process has the potential to be used in the treatment of pulp and paper effluent.

Key words: Pulp and paper mill, photo-fenton's process, wastewater

INTRODUCTION

Wastewater from pulp and paper mill is one of the most important sources of pollutants mainly due to the pulping and bleaching processes. Dissolved substances such as lignin and hemicelluloses from pulping process and particulate matter from the bleaching process that are present in wastewater cause a problem for conventional pulp and paper mill wastewater treatment plants due to its toxicity (Sell, 1992). Pollutants generated from pulp and paper mill wastewater have brought chronic effects to human being and other living organisms. Recently, studies have proven that plant sterols found in wood extractives possess the ability to disturb hormonal action in many aquatic organisms (Kostamo *et al*., 2004).

One of the most effective technologies to remove organic pollutants from wastewater is the Fenton's process. Fenton's reagent is a mixture of hydrogen peroxide (H_2O_2) and an iron (II) salt (Fe^{2+}) that is known to be effective in the removal of many hazardous organic pollutants from industrial wastewaters such as from an olive mill (Khoufi *et al*., 2004), tanning industry (Rakmi *et al*., 2004), textile (Kuo, 1992) and acid manufacturing (Wan Peng *et al*., 1996). However, one of the limitations using the conventional Fenton's process is high Fe^{2+} consumption (Kavitha and Palanivelu, 2004).

Recent reports indicate that a combination of H_2O_2 and UV irradiation with Fe(II), so-called the photo-Fenton process, can significantly enhance the decomposition of many refractory organic compounds such as pesticides, nitrobenzene, chlorophenols, nitrophenols, dibutyl-phthalate, PCBs and bisphenol A (Katsumata *et al*., 2005). Xu *et al*. (2004a) reported that a combination of H_2O_2 and UV irradiation with Fe(II) produces the strongest oxidation compared to the conventional Fenton process. The acceleration of the decomposition of organic compounds is believed to be in the order of the photolysis of iron aquacomplex, $Fe(H_2O)_5(OH)^{2+}$ (represented hereafter by $Fe(OH)^{2+}$), to provide a new importance source of hydroxl radicals (OH•) (Brand *et al*., 1998). Further, the photolysis of $Fe(OH)^{2+}$ regenerates.

Fe(II) (Eq. 1 and 2), represent that the photo-Fenton reaction would need low Fe(II) concentration compared with the conventional Fenton process.

$$Fe^{2+} + H_2O_2 \rightarrow Fe(OH)^{2+} + OH\bullet \quad (1)$$

$$Fe(OH)^{2+} + u\mu \rightarrow Fe^{2+} + OH\bullet \quad (2)$$

Furthermore, the $Fe(OH)^{2+}$ can absorb light at wavelengths up to ca. 410 nm, while TiO_2 photocatalysis can use photon with a wavelength close to 380 nm (Hoffmann *et al*., 1995). Therefore, the photo-Fenton process can be expected to be an efficient method of wastewater treatment and promotes the rate of degradation of various organic pollutants.

The objective of this study is to investigate the effect of several process parameters for photo-Fenton process

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such as pH, initial H_2O_2 and $FeSO_4$ concentration to reduce biochemical oxygen demand (BOD) and total suspended solids (TSS) in pulp and paper mill wastewater.

MATERIALS AND METHODS

Wastewater: The wastewater samples were obtained from Sabah. Forest Industries (SFI) Sdn. Bhd. The sampling location was at a point before a biological treatment plant. Collected samples was then stored in plastic containers and stored at 4°C till further used.

Photo-Fenton's process: All the treatments were carried out in a reactor (internal volume 400 mL) equipped with UV light under magnetic stirring. The volume of the reaction was 400 mL. The initial pH of reaction mixture was adjusted with NaOH or HCl. The reaction was initiated by adding $FeSO_4.7H_2O$. After 10 minutes of stirring, H_2O_2 was added. The reaction was stopped after another 50 minutes by raising the pH value to 11. The treated sample in the reactor vessel was transferred into BOD bottles for overnight storage in the refrigerator to allow the settling process to occur. Supernatant was taken out for analysis.

Analysis: BOD_3 and TSS were measured according to Standard Methods (APHA, 1985). pH was measured using pH meter (WTW, Germany).

RESULTS AND DISCUSSION

Effect of initial pH: The effect of initial pH on degradation of BOD_3 and TSS using the photo-Fenton process is shown in Fig. 1. The BOD_3 reduction increases rapidly while TSS reduction increasing gradually as the pH goes from 2 to 5. When the pH reaches a value of 5, both parameters begin rapidly decrease as it goes up to 6. Therefore, the photo-Fenton reaction is strongly affected by the pH of the solution. Generally, the optimal pH of the photo-Fenton reaction is around 3 because the main species at pH 2-3, $Fe(OH)^{2+}(H_2O)_5$, is the one with the largest light absorption coefficient and quantum yield for OH• radical production, along with Fe(II) regeneration, in the range 280-370 nm (Katsumata *et al.*, 2005). However, the optimal pH was obtained was 5 due to the reactions of organics or its intermediate products that might react with iron species followed by the formation of iron complexes and these could assist the catalytic cycles of iron in the photo-Fenton system. Fukushima and Tatsumi (2001) reported that the degradation of pentachlorophenol (PCP) was enhanced at pH 5 by the presence of humic acid (HA) in the photo-Fenton system because the complexation of Fe(III) with HA contributed to the stabilization of iron species.

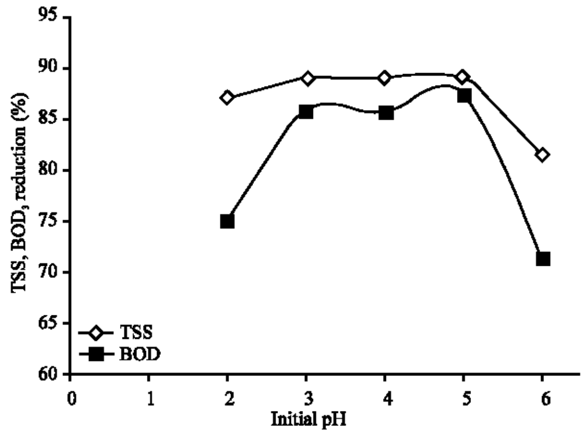

Fig. 1: BOD_3 and TSS reduction by the photo-Fenton's process for various initial pH values at 300 mg L^{-1} H_2O_2 and 300 mg L^{-1} $FeSO_4.7H_2O$

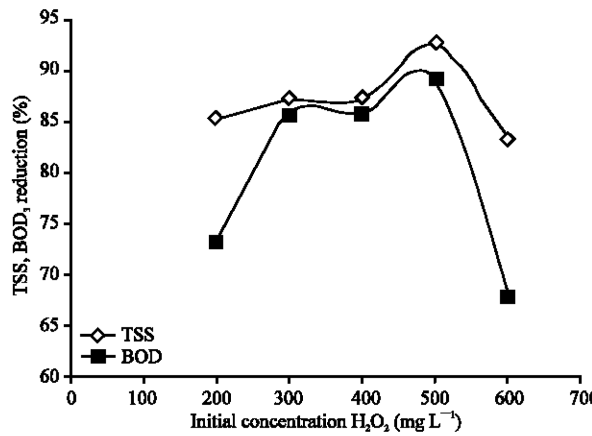

Fig. 2: BOD_3 and TSS reduction by the Fenton's process for various initial concentration of H_2O_2 at pH 5 and 300 mg L^{-1} $FeSO_4.7H_2O$

Effect of initial H_2O_2 concentration: Figure 3 shows the effect of initial H_2O_2 concentration on the degradation of BOD_3 and TSS with the use of photo-Fenton process. As expected, the degradation rate of BOD_3 and TSS increased with the increasing of concentration of H_2O_2 added until 500 mg L^{-1}. This can be explained by the effect of the additionally produced OH• radicals. However, as the initial concentration exceeds 500 mg L^{-1}, the reduction starts to decrease rapidly probably due to concentration of the ferric precipitant and self-decomposition of peroxide, catalysed by Fe^{3+} that produces water and oxygen (Casero *et al.*, 1997).

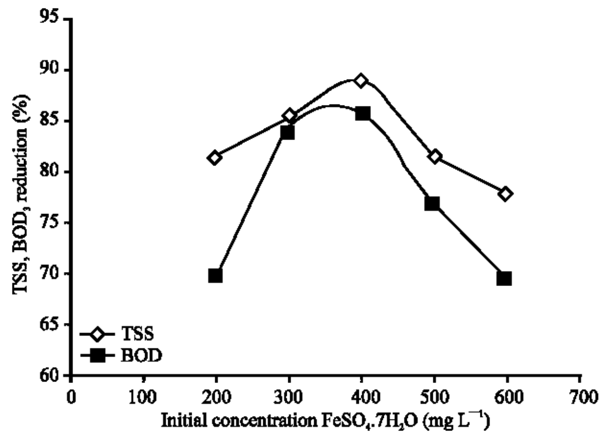

Fig. 3: BOD_3 and TSS reduction by the Fenton's process for various initial concentration of $FeSO_4.7H_2O$ at pH 5 and 300 mg L^{-1} H_2O_2

Effect of initial $FeSO_4.7H_2O$ concentration: The effect of $FeSO_4.7H_2O$ initial concentration on photo-Fenton's process was studied by varying the dosage of $FeSO_4.7H_2O$ from 200-600 mg L^{-1}. The effect of $FeSO_4.7H_2O$ dosage is shown in Fig. 3. As the initial concentration of $FeSO_4.7H_2O$ increases, the TSS and BOD_3 reduction also increase until the initial concentration of $FeSO_4.7H_2O$ exceeds 400 mg L^{-1}. A rapid decrease in the reduction of TSS and BOD_3 is observed as the initial concentration is more than 400 mg L^{-1}. Bali *et al.* (2004) also found decreases in decolorization and mineralization of dyes wastewater due to excess Fe(II). This phenomenon is due to the scavenging effect of OH• radical (Bali *et al.*, 2004) and slow regeneration of Fe^{2+} from Fe^{3+} (Xu *et al.*, 2004b).

Performance of the photo-Fenton's process under optimal conditions: When the wastewater treated in photo-Fenton's optimal conditions i.e pH 5, initial concentration of H_2O_2 and $FeSO_4.7H_2O$ is 500 and 400 mg L^{-1}, respectively; the value of BOD_3 and TSS found in pulp and paper mill effluent can be reduced up to 46.9 and 46.7 mg L^{-1}, respectively. The efficiency of BOD_3 and TSS reduction can be attained up to 87.5 and 87.0%, respectively. This result is complied with Standard B amended by the Department of Environment.

CONCLUSIONS

The optimum parameters for the treatment of pulp and paper mill wastewater using photo-Fenton process are pH 5 and initial concentration of H_2O_2 and $FeSO_4.7H_2O$ are 500 and 400 mg L^{-1}, respectively. The reduction level of BOD_3 and TSS were 87.5 and 87.0%, respectively.

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