Vol. 43 2017 No. 3

DOI: 10.37190/epe170317

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# TREATMENT OF EFFLUENT (SKIM LATEX SERUM) FROM A RUBBER PROCESSING PLANT WITH FENTON'S REAGENT

The treatment effectiveness of Fenton's reagent using  $Fe^{2^+}$  catalyst to reduce chemical oxygen demand (COD) of skim latex serum and the effect of varying concentrations of  $H_2O_2$ ,  $Fe^{2^+}$  and initial solution pH on its treatment efficiency were investigated. The highest COD removal efficiency obtained was approximately 80% at optimum conditions. The treatment required either nominal or no acidification as initial pH of serum is very close to the optimum pH = 4. COD removal increased upon increasing  $H_2O_2$  and  $Fe^{2^+}$  concentrations. This study shows the suitability of using Fenton's process with  $H_2O_2$  and  $FeCl_2$  as a pre-treatment for skim latex serum. The findings reported here represent a potentially simpler and more cost-effective alternative treatment to other treatment methods since only reagents and not capital-intensive materials (such as membrane) are required.

# 1. INTRODUCTION

Skim latex serum is a by-product of treatment of latex effluent from rubber processing plants loaded with ammonia, sulfate, organic and inorganic substrates. It is an effluent generated during sulfuric acid coagulation of skim latex for recovering residue rubber [1]. Such effluent is prevalent in rubber-producing tropical countries such as Thailand [2] and Malaysia [3, 4]. Figure 1 shows schematically processes leading to generation of skim latex serum. Latex effluent is formed in the process of producing latex concentrate that involves washing, centrifugation and de-ammonization. The wastewater stream generally consists of excess field latex effluent, stabilizers such as ammonia, sodium sulfite or formaldehyde which are added to prevent premature coag-

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ulation of the field latex [5]. The field latex is then subjected to centrifugation to separate concentrated and skim latex. Skim latex is subsequently treated using coagulation with spent sulfuric acid to obtain scrap rubber and skim latex serum of which the latter is discharged as final effluent [6]. Major constituents of the serum include ammonia, sulfate, organic and inorganic substrates which can induce high chemical oxygen demand (COD) in receiving water bodies. Therefore, it is imperative to treat the serum prior to discharge to prevent high reduction of dissolved oxygen level in water bodies (detrimental to aquatic lifeforms) due to high COD concentrations in the serum.

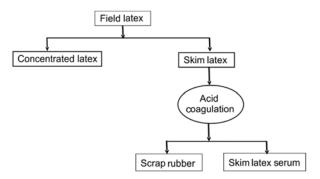


Fig. 1. Generation of skim latex serum (adapted from [6])

Previous studies on treatment of latex serum were mainly conducted using membrane-based technologies [7–9] and biological degradation processes [10, 11]. Applications of these technologies are generally established and effective, nonetheless, relatively high costs associated with membrane technologies as well as the intrinsically complex nature and relatively slower degradation rate of biological processes are some of the disadvantages associated with these technologies. In this context, the usage of Fenton's reagent as a relatively uncomplicated and previously untried process in treatment of the high-COD skim latex serum can be developed as an alternative process to the afore stated established technologies. Fenton's reagent is a highly effectual and suitable oxidative substance as it includes usage of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) which is advantageous due to its reasonable cost, high oxidizing power, easy handling and good solubility in water [12]. The reagent entails usage of either Fe<sup>2+</sup> or Fe<sup>3+</sup> catalysts to induce radical hydroxyl from H<sub>2</sub>O<sub>2</sub> to be utilized for rapid oxidation of organic-based substances in the serum. During Fenton's processes, H<sub>2</sub>O<sub>2</sub> is catalyzed by ferrous ions to produce hydroxyl radicals which subsequently oxidize organics in solution [13].

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH$$
 (1)

Fenton's reagent has been successfully applied in the treatment of dyes [14, 15], phenol-laden wastewater [16], landfill leachate [17] and polynuclear aromatic hydrocarbons [18]. Given the high COD of latex serum, it is surprising to note that the highly

effectual Fenton process has not been previously applied for its treatment (to the best of our knowledge). Judging by the high oxidative tendency of the produced hydroxyl ions, the authors hypothesize that the process can be effectively applied in treatment of skim latex serum as well. The objective of the study was to evaluate the treatment efficiency of Fenton's reagent using  $Fe^{2+}$  catalyst to reduce COD of skim latex serum by varying concentrations of  $H_2O_2$ ,  $Fe^{2+}$  and initial pH of the solution.

### 2. EXPERIMENTAL

The skim latex serum was collected from a latex concentrate plant in Tampin, Negeri Sembilan, Malaysia. It was collected in high-density polyethylene containers. The skim latex serum was light milky brown. Residual solids in the serum were removed manually using a sieve before the oxidation study. Analytical grade H<sub>2</sub>O<sub>2</sub> (35%) and FeCl<sub>2</sub> were used as a Fenton's reagent. Oxidation experiments using the reagent were conducted in Erlenmeyer flasks containing 50 cm<sup>3</sup> of the serum. Fenton's reagent was prepared at various concentrations of FeCl<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> within the ranges of 500-8000 and 1000–5000 mg/dm<sup>3</sup>, respectively. pHs were adjusted into a range of 2–5 via addition of dilute hydrochloric acid or sodium hydroxide. During the oxidation process, FeCl<sub>2</sub> was slowly added at the desired concentration followed by addition of H<sub>2</sub>O<sub>2</sub>. The flasks were then agitated using an orbital shaker at 200 rpm and 25 °C. Subsequent to 4 h of agitation, the solution was filtered prior to COD test (HACH COD reactor digestion method 8000). COD tests were performed only after pH of the filtered solution was increased to 7.5 to prevent interference caused by reaction of dichromate ions with H<sub>2</sub>O<sub>2</sub> which could occur in an acidic environment. Measurement of pH was carried out using Mettler-Toledo Delta 320 pH meter. Total suspended solids concentrations were determined by the USEPA gravimetric method adapted from Standard Methods for the Examination of Water and Wastewater, Section 2540B.

## 3. RESULTS AND DISCUSSION

### 3.1. CHARACTERISTICS OF SKIM LATEX SERUM

Initial characterization tests showed that the studied wastewater's pH, chemical oxygen demand (COD) and suspended solids were 4.48, 20,716 mg/dm³ and 218 mg/dm³, respectively (Table 1). These characteristic values are evidently higher than the permissible Malaysian regulatory effluent standard discharge limits. Standards A and B are enforced on processing plants located upstream and downstream of a water supply intake point along a river, respectively (as stipulated by Malaysia's 3rd Schedule Environmental Quality Act, 1974) [19]. It is apparent that treatment of the serum is necessary

before it can be discharged into the environment since the COD concentration alone is more than 200 times higher than the standard B discharge limit.

Table 1

Initial characteristics of the skim latex serum and its respective standard discharge limit by the Malaysian Department of the Environment [19]

Parameter	Raw effluent	Regulatory standard discharge limit	
		A	В
pН	4.5	6.0-9.0	5.5-9.0
COD, mg/dm <sup>3</sup>	20,716	50	100
Suspended solids, mg/dm <sup>3</sup>	218	50	100

### 3.2. TREATMENT

Figure 2 shows the effect of pH on COD removal with both  $Fe^{2+}$  and  $H_2O_2$  concentrations fixed at 2000 mg/dm<sup>3</sup>. The COD removal increases from about 42% to 82% when pH was increased from 2 to 4 prior to reduction to approximately 40% at pH 5. As such, the COD removal was shown to be maximum around pH 4. The sudden reduction of COD removal at pH from 4 to 5 was perhaps due to the rapid decomposition of  $H_2O_2$  and deactivation of ferrous catalyst with the formation of ferric hydroxo complexes [20, 21].

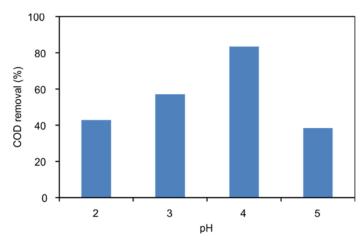


Fig. 2. Effect of pH on COD removal;  $[Fe^{2+}] = 2,000 \text{ mg/dm}^3$ ,  $[H_2O_2] = 2000 \text{ mg/dm}^3$ 

This result deviates slightly with the widely accepted concept that the optimum pH for Fenton processes occur around pH 3 [22] though Fenton reagent has not been previously used to treat skim latex serum. This may prove to be an advantage in treatment of

the serum as normal practice in Fenton processes entails acidification to pH 3 which may slightly limit the applicability of the process. Since pH of natural skim latex serum is around 4.5, it can be surmised that treatment of the serum requires minimal acidification or possibly none at all to achieve an optimum level.

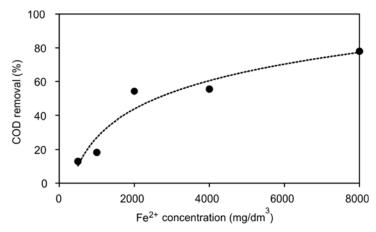


Fig. 3. Effect of Fe<sup>2+</sup> concentration on COD removal percentage; pH = 3; H<sub>2</sub>O<sub>2</sub> = 2000 mg/dm<sup>3</sup>

Figure 3 shows the effect of  $Fe^{2+}$  concentration on COD removal at pH 3 with  $H_2O_2$  concentration fixed at 2000 mg/dm<sup>3</sup>. The COD removal increases with the increase of  $Fe^{2+}$  concentration. This trend is in good agreement with a study by Alaton and Teksoy [15] who reported that COD removal from acid dyes increased upon increasing initial  $Fe^{2+}$  concentration. At  $Fe^{2+}$  concentration of 8000 mg/dm<sup>3</sup>, COD removal of approximately 78% was achieved.

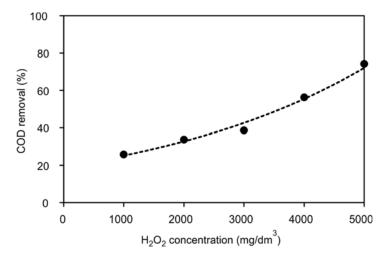


Fig. 4. Effect of  $H_2O_2$  on COD removal; pH = 3;  $[Fe^{2+}] = 1500 \text{ mg/dm}^3$ 

Figure 4 shows the effect of  $H_2O_2$  concentration on COD removal at pH 3 with  $Fe^{2+}$  concentration fixed at 1500 mg/dm<sup>3</sup>. It is obvious that there is gradual increment of COD removal upon increasing  $H_2O_2$  concentration. The average increment in COD removal is about 30% with the increase of 1 g/dm<sup>3</sup> of  $H_2O_2$ . This result is in good agreement with a study by Kang and Hwang [21] who also reported a gradual increment in COD removal efficiencies upon increasing  $H_2O_2$  concentration. This effect has been attributed to incremental hydroxyl radical generation (Eq. (1)).

Table 2

Highest COD removal efficiencies from latex serum using other treatment processes

Type of the treatment process	Initial pH	Highest COD removal [%]	Reference
Biological degradation	7.2-7.2	57	[11]
Membrane	3.75	67	[9]
Biological degradation	2.5-4.5	44	[10]
Fenton process	4.48	84	this study

Table 2 provides the highest COD removal efficiencies from latex serum using other treatment referred elsewhere. It is obvious that the Fenton process is very efficient for COD degradation from latex serum in view its very high COD removal efficiency at approximately 80%. As such, this indicates that the process can be effectively applied as a pre-treatment process for skim latex serum.

## 4. CONCLUSIONS

The high COD removal efficiency (ca. 80%) indicates the suitability of using Fenton's process as a pre-treatment process for skim latex serum. Generally, since the efficiency of Fenton's processes seldom is lower than 80%, it seems that the optimum concentrations of  $Fe^{2+}$  and  $H_2O_2$  for treatment of skim latex serum are around 8000 and 5000 mg/dm<sup>3</sup>, respectively. Treatment requires minimal acidification or possibly not required at all as initial pH of serum is very near to the optimum pH = 4. In the study, a simple serum treatment alternative has been proposed, which can be integrated with the more traditional treatment methods such as membrane and/or biological processes to enhance the overall cost-effectiveness.

### ACKNOWLEDGEMENTS

Assistance provided by S.L. Low in obtaining the skim latex serum is gratefully acknowledged. Technical assistance provided by Nurul Azliana Abu-Bakar, Zakiuddin Januari and Sarah Nor Afiza Mohd-Razali is appreciated. The authors also extend their appreciation to the Deanship of Scientific Research at

King Saud University for supporting this work through research group No. RGP-303. Y.P. Lim is supported by the Ministry of Higher Education through FRGS grant No. FRGS/1/2017/STG07/UITM/03/4.

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