International Journal of Engineering & Technology, *7 (4.18) (2018) 386-389*

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET

Research paper

Removal of Chemical Oxygen Demand (COD) from Synthetic Rubber Wastewater Via Foam Fractionation (FF) Method

N.A.Zainuddin[1]*, W.M.Hafiz[1], Noor Harliza Abd Razak[1], Siti Rohana Mohd Yatim[2]

[1]*Faculty of Chemical Engineering, Universiti Teknologi MARA (UiTM), Shah Alam, Selangor*
[2]*Department of Environmental Health, Faculty of Health Science, Universiti Teknologi MARA (UiTM), Shah Alam, Selangor*
**Corresponding author E-mail:nurain1465@uitm.edu.my*

Abstract

Foam fractionation (FF) with Physical Chemical Process (PCP) is one of the methods introduced to treat wastewater from synthetic rubber which contains high Chemical Oxygen Demand (COD) concentration. Wastewater sample from two different synthetic rubber industry which are Company A (A) and Company B (B) were used in this research. Batch reactor column FF of 40 cm height with an internal diameter of 8 cm was designed. The compressor air introduced into the reactor thru diffuser to produce bubbles at a constant pressure of 0.2 bar. The effect of aeration time (10,20,30,40 and 50 minutes) were investigated on the COD removal. Comparison on percentage (%) of COD removal by FF followed by PCP and PCP only were investigated. For PCP, chemical used was Polyaluminium Chloride (PAC) 18%, Sodium Hydroxide (NaOH) 48% and anionic polymer. COD value for raw sample and treated sample was tested using COD reagent in vial, reactor and spectrometer. The best aeration time for A is 10 minutes and B is 40 minutes. COD removal for A is 46%, from 32250 mg/l to 17550 mg/l and B is 23% from 1260 mg/l to 979 mg/l. FF is more efficient for removal of COD in high concentration of the wastewater. However, difference between FF combine with PCP versus PCP only for A is 1% and for B was unsuccessful. Therefore, FF technique is not effective method for COD removal.

Keywords: *Chemical Oxygen Demand (COD); foam fractionation; Physical Chemical Process (PCP); synthetic rubber; wastewater*

1. Introduction

Presently, Malaysia is the third largest rubber producer in the world, whereby the rubber industry is an economically and socially significant industry. In this industry there will be uses of surfactants and chemicals for the process. This consume large volumes of water for cleaning and washing that will lead to enormous amounts of effluent and inorganic wastes [1]. Moreover, the presence of compounds such as surfactants in effluent had imposed the growth of efficient water treatment process as they are difficult to degrade by chemical or biological methods [2]. Thus, the Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) will be increase and harmful to living things.

According to Environmental Quality (Industrial Effluent) Regulations 2009 based on the seventh schedule for rubber industrial (other industries) the acceptable COD contain discharge are 80 mg/L for standard A and 200mg/L for Standard B [3]. For rubber industrial the higher concentration of COD in the water means that it contains a lot of total dissolved solids (TDS), total suspended solids (TSS), total solids (TS), ammonia and phosphate [4]. Thus if the effluents are not well treated before discharge to the environment it can lead to serious depletion of dissolved oxygen which disturbs the normal aquatic system. In rubber industrial the main problem is high COD concentration, thus it is important to reduce the COD amount.

There are many methods that has been used widely in order to reduce the COD in industrial effluents such as Aerobic and Anaerobic Treatments [5], Physical Chemical Process (PCP) [6], Ozonation [1], Adsorbent method [7] and Advanced Oxidation Methods [2][6].

In this research the methods that are going to do is by using foam fractionation methods as a pretreatment process before the wastewater go to the next process which is PCP. The efficient of PCP compare to BP can be seen by percentage of COD removal efficiency. For example by using PCP the COD removal efficiency was 91% to 99% whereas for BP removal efficiency was 80% to 92% [1]. The concentration of COD can be assumed as three to one concentration of BOD [8]. Thus, as COD decreases the BOD level also decreases. FF process can be declared as adsorptive bubbles separation technique. This method comprises various mechanisms of separating dissolved or suspended materials by means of adsorption or attachment at the surfaces of bubbles rising through a feed solution [9]. The principles of foam fractionation are the production of foams consists of huge amount of bubbles that are generated by dispersing gas in liquid and for this research compress air was used as gas. There are many industries that already use FF method such as soy whey wastewater [10].

In the synthetic rubber industry, chemicals and large volumes of water were used for washing and cleaning that will lead to enormous amounts of effluent that contain high COD level. Thus it is important to focus on how to reduce the effluent in the best way. Previous studies on effluent treatment used BP such as pond technology which are high cost for operating and use large land area. In addition, long time is needed to reduce the nitrogen in the effluent. Another example is the use of aerobic and anaerobic treatment. This method is inexpensive and do not need a large land area but not effective in removing nitrogen because of an insufficient of dissolved oxygen for nitrification [1]. Moreover, the work also reported that the best solution to remove the COD level and surfactants in synthetic rubber wastewater is by using advanced oxidation process (AOP). However, this process has been proven to be an expensive technique [2]. Furthermore, typically in FF method the carbon dioxide gas is used in the treatment process which leads to high cost.

Therefore, in this study the concept of FF was used as pretreatment process in order to decrease COD. Carbon dioxide was replaced by compressed air which can reduce the cost. In addition PCP method will be used rather than BP which is easier to handle and do not need large land area. In this research, the effect of aeration time on COD removal was investigated. Comparison on percentage of COD removal between FF combine with PCP and PCP was studied.

2. Methodology

2.1. Materials

The wastewater sample was collected from two different synthetic rubber industry which are A with high COD concentration which is 32250 mg/l whereas B is low COD concentration which is 1260 mg/l. 10 litres of sample was taken and stored in container. The temperature and pH of the sample were taken on site to avoid any changes by using pH and temperature sensor. The samples were then transported immediately to the laboratory and stored properly. The sample collected need to be avoided from sunlight as the COD can react with light. The sample can only be used for 1 week to avoid degradation of samples, which will affect the results.

2.2. Experimental Setup

A schematic diagram of the experimental setup for batch FF method is shown in Fig. 1. A reactor bubble column of 8 cm inside diameter and 40 cm height was design in order to run this experiment.

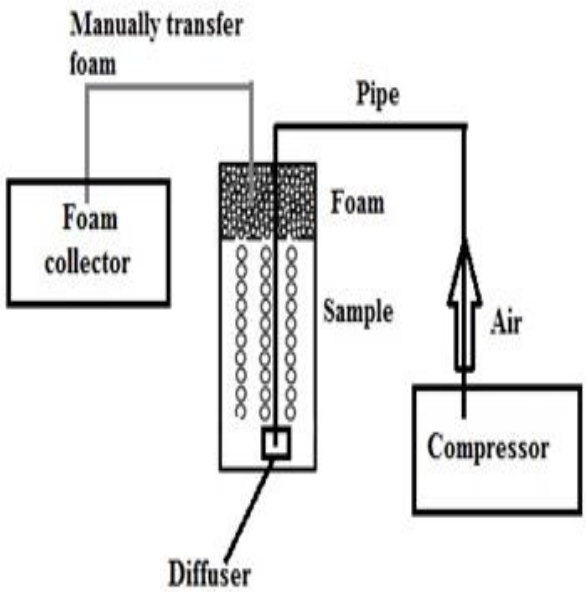

Fig. 1: Schematic diagram of experimental setup

2.3. Aeration operation

All experiments were conducted in a batch wise mode with respect to liquid [11]. 600 ml of wastewater sample was poured into the reactor column from the top of the reactor column with a dimension of 40 cm height and with an internal diameter of 8 cm.

Air from compressor was introduced from the bottom of the column and the pressure rate was kept constant at 0.2 bar and was monitored by using a pressure gauge. Different aeration time of 10, 20, 30, 40, and 50 minutes was applied to study the effect of aeration time on COD removal. The foam was flowed out at the top of the reactor and was collected at every different time of aeration. The COD concentration was then been measured.

2.4. Physical Chemical Process (PCP) and Jar Test

Basically in PCP methods, jar test was conducted by using flocculator stirrer. The objectives were to determine the optimal pH, coagulant and flocculant dosing [12]. PAC, NaOH and flocculants were used in order to achieve optimum pH for flocs produce which is 6 to 7 [13]. Other than pH adjustment, NaOH was used to increase the efficiency of the treatment to form hydroxide precipitate. Next anionic polymer was added in a small amount to enhance the accumulation of flocs for smooth settlement.

The objectives of conducting jar test were to determine the optimal pH, dose for PAC 18% (4.5 ppm), dose for NaOH 48% (12 ppm), and dose anionic polymer for water treatment process and to improve the coagulation and flocculation process as well as to evade high cost related with the usage of chemicals beyond the optimum dose. The preparations of chemicals was based on formula $M_1V_1=M_2V_2$. For preparations of PAC 18% (4.5 ppm), 20 ml of PAC was mixed with 80 ml of distilled water. Whereas for 12 ppm of NaOH 48%, 20 ml of NaOH was mixed with 80 ml of distilled water. In order to run JAR test the equipment need to be used are flocculator stirrer for mix process of coagulation and flocculation of chemicals. pH sensor was used to check the pH readings for every chemical solutions as pH plays an important part to optimize JAR test results.

6 beakers were prepared and 600 ml of wastewater sample was tested. JAR test is the process in which optimum dosing for chemical use is determine in order to reduce COD concentration, turbidity and other parameters that need to follow IER 2009. First of all, the samples need to be regulated at optimum pH based on characteristics of the wastewater sample by adding acidic or alkaline chemical. For this research PAC 18 % (4.5 ppm) was added to sample at various pH of 2 to pH 6. In this coagulation process stirrer was turned on at 180 rpm for 7 minutes. Then NaOH was added until pH 7 to 8 as optimum anionic polymer accumulate flocs was in that pH range. For flocculation process anionic polymer was added at 80 rpm about 5 minutes. Then, turn off the stirrer and allow for settling for 30 minutes.

After that the pH of each beaker was recorded and observed. The step will be repeat for other samples. There was different optimum dosing coagulant and polymer for both company. The results for optimal pH can be found from the graph of turbidity (NTU) versus amount of chemical used which smile line [14].

Then by using optimal pH, jar test for optimal coagulant dosing can be found by using the same jar test testing method where each of the beaker need to be adjust to constant optimal pH. Optimal coagulant can be found from the graph of turbidity versus volume of coagulant dosing. The lowest turbidity value remarks as optimal coagulant dosing. Lastly, for optimal flocculants dosing, optimal pH and coagulant volume was set constant for each beaker but different volume of flocculants was tested.

As turbidity can be related to COD concentration which is when turbidity high the COD concentration also high [15]. Turbidity will be increased back as increase the dose to coagulate fine particles can lead to inter-particle repulsion [16].

2.5. COD determination

The COD concentration of the sample will be check using COD reactor by digest high range vials on it and read the results using HACH DR900 spectrometer. This equipment was used to indirectly measure the amount of organic compounds in the sample. Basically, the sample collected contains high concentration of COD. Thus, it need to be dissolved in distilled water to make a dilution as the high range COD vials can only read up to 1500 mg/l.

Each type of sample will be take about 2 ml and add to high range vials and for blank sample fill with 2mL of distilled water to high range vials. The vials were mixed well. Next, all the vials were put into the COD reactor for digestion at 150 °C for 120 minutes. After that the vials will be left about 30 minutes to cool down and immediately reading of COD concentration will be read using spectrometer HACH DR900 in mode high range COD.

3. Results and Discussion

In this part the results for aeration time on percentage of COD reduction for A and B by using FF with PCP and PCP only will be discussed. In addition, the effect of turbidity also was discussed.

3.1. Effect of foam fractionation

For A, the higher reduction of COD concentration removal was at 40 minutes aeration which is from 32250 mg/l to 17100 mg/l as seen in Fig. 2 about 47% reduction removal. Whereas for lower reduction of COD concentration removal was at 30 minutes of aeration which is from 32250 mg/l to 18950 mg/l about 41% of reduction removal. The proven of the concentration reduction can be clarified as the bubble foam collection contain also have high COD concentration which generated by dispersing gas consist of thousands of bubbles which overflow from reactor [9]. Thus, from the results pretreatment by using FF can reduce a lot of COD concentration about 41-47 % reduction removal. But in this study, 10 minutes was selected as the best aeration time as the difference of percentage with 40 minutes of aeration only 1%. For 10 minutes aeration, 46% of COD was reduced whereas for 40 minutes aeration, 47% of COD was reduced. According to studied done[10], the flow rate of gas and aeration time used are play an important role in order to reduce contaminant [10].

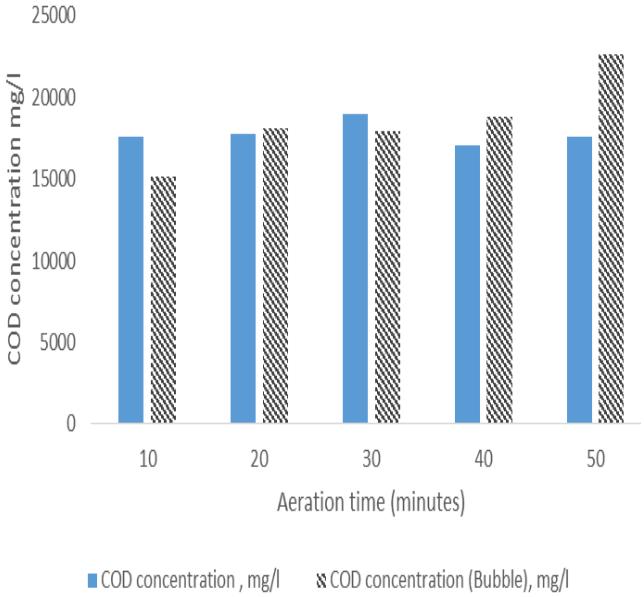

Fig. 2: Effect of aeration time on COD removal for Company A

There was varieties of removal percentage of COD which is must be monitored carefully to get optimum removal COD concentration as in olive oil industry the optimum process time was at 45 minutes which can give back effects if lower process time or longer time than 45 minutes [17]. For lower process time it have negative effects as time required for adsorption was not enough whereas for longer time the aeration give influences on the wetness of foam than the gas flowrate [17].

On the other hand, for B the higher reduction COD concentration was at 10 minutes about 23% which is from 1260 mg/l to 979 mg/l by referring Fig. 3. For comparisons with A, it can be seen that the different percent removal is significant which is for A, 47% can be reduced compare to B only 23%. This can be related with the high concentration of COD in A compare to B. According to [8], COD to BOD ratio was 3:1 [8]. Thus, as COD increased the BOD level also increased which a lots of bacteria in the wastewater for react with oxygen and reduce the COD in wastewater. As aeration process can help for aerobic process in which aerobic bacteria breakdown the waste within the wastewater sample to form a sludge [18]. Therefore, automatically COD concentration was decreased.

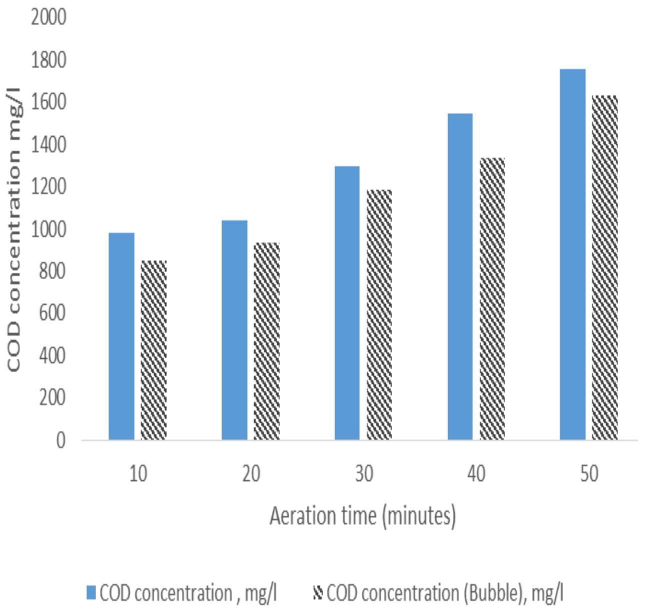

Fig. 3: Effect of aeration time on COD removal for B.

3.2. Effect of PCP methods for foam fractionation (FF) performance.

For different company there was different effect to the results of COD concentration and turbidity readings whether undergo FF with PCP or PCP methods only. The results for COD reduction was tabulated in Table 1.

Table 1: Comparisons COD reduction percentage for different methods to company A and B

Parameters	Turbidity, NTU		COD, mg/l		Percentage of COD removal (%)	
Company	A	B	A	B	A	B
Foam fractionation with PCP	34	57	3420	187	90	85
PCP only	55	41	3520	129	89	90

From the results for A, the reduction of COD concentration for FF with PCP methods is higher compared to PCP method only. For FF with PCP the reduction was from 32250 mg/l to 3420 mg/l which was about 90% compared to PCP method only which has a decrease of about 89% from 32250 mg/l to 3520 mg/l. The different between the two methods was only 1% which was too small. Although, there was a slightly different of COD concentration between both method, PCP chemical dosing for FF method such as NaOH and polymer was less compare to PCP method only about 2-3 ml. In addition, the sludge that form from the aeration with PCP is more thick as in process aeration itself have produce sludge compare with PCP methods only which straightly from chemical dosing only. The thick sludge for aeration come from process which increased the Dissolved Oxygen (DO) content in water in order to help microorganism them respire better and enhanced the decomposition of organic matter [19]. Compare to PCP only which the sludge are form from process coagulation and flocculation from chemicals only.

On the other hand, for B the PCP methods only are the best process compare to FF with PCP methods. For PCP method only, 90% of COD reduction which is from 1260 mg/l reduce to 129 mg/l. Compare for method of FF combine with PCP, only 85% of COD reduction was occurred, which is from 1260 mg/l to 187 mg/l . Thus, from the results it can be concluded that the FF method provide better effect in reducing COD concentration and chemicals used for sample with higher COD value.

From the results on turbidity for sample A and B it can be observed that it proportional to COD concentration as COD concentration is higher the turbidity also higher. Thus, turbidity readings for FF with PCP method are lower than PCP method only which is

34 NTU and 55 NTU respectively. Whereas for B, the lower turbidity readings was recorded with PCP method only which is 41 NTU and for FF with PCP method is 57 NTU. Besides, COD concentration amount of chemical dosing also can effects the readings of turbidity, where when it is overdose can lead to interparticle repulsion [16]. Thus, COD concentration and turbidity readings will increases.

4. Conclusion

In conclusion, FF method was effective to be used for wastewater with higher COD concentration. This was proven as COD concentration for A can be reduced up to 46% from 32250 mg/l to 17550 mg/l compare to B which only reduced about 23% from 1260 mg/l to 979 mg/l. On the other hands, for FF with PCP methods and PCP only methods there was too small different percentage effect for A which is 1% (90% - 89%) reduction removal of COD concentration whereas for B, PCP method only had higher reduction removal compare to foam fractionation with PCP which is 90%. Thus, from the results it can conclude that the foam fractionation with PCP was not successful methods as it only can cause a high cost in order to set up the foam fractionation reactor while only give too small effect reduction in COD concentration.

Acknowledgement

The authors are grateful for financial support provided by Institute of Quality and Knowledge Advacement (InQka), Universiti Teknologi MARA (UiTM) and UiTM.

References

[1] M. Mohammadi, H. Man, M. Hassan, and P. Yee, "Treatment of wastewater from rubber industry in Malaysia," *African J. Biotechnol.*, vol. 9, no. 38, pp. 6233–6243, 2013.

[2] S. Krishnan, K. Chandran, and C. M. Sinnathambi, "Wastewater treatment technologies used for the removal of different surfactants: A comparative review," *Int. J. Appl. Chem.*, vol. 12, no. 4, pp. 727–739, 2016.

[3] Department of Environment, "Environmental Quality (Industrial Effluent) Regulations 2009," *Environmental Quality Act 1974*. pp. 4010–4059, 2009.

[4] H. P. J. S. Pillai and K. Girish, "Rubber processing industry effluent treatment using a bacterial consortium," *Int. J. Curr. Microbiol. Appl. Sci.*, vol. 3, no. 10, pp. 775–782, 2014.

[5] A. R. Pendashteh, F. Asghari Haji, N. Chaibakhsh, M. Yazdi, and M. Pendashteh, "Optimized treatment of wastewater containing natural rubber latex by coagulation-flocculation process combined with Fenton oxidation," *J. Mater. Environ. Sci.*, vol. 8, no. 11, pp. 4015–4023, 2017.

[6] M. Massoudinejad, M. Mehdipour-Rabori, and M. H. Dehghani, "Treatment of natural rubber industry wastewater through a combination of physicochemical and ozonation processes" *J Adv Env. Heal. Res*, vol. 3, no. 34, pp. 242–9, 2015.

[7] U. Pathak, P. Das, P. Banerjee, and S. Datta, "Treatment of wastewater from a dairy industry using rice husk as adsorbent: Treatment efficiency, isotherm, thermodynamics, and kinetics modelling," *J. Thermodyn.*, vol. 2016, 2016.

[8] M. Henze and Y. Comeau, "Wastewater Characterization," *Biol. Wastewater Treat. Princ. Model. Des.*, pp. 33–52, 2008.

[9] Z. Erlangung, "A contribution to design foam fractionation processes der Technischen Universität Dortmund vorgelegt von Linz am Rhein," 2012.

[10] W. Liu, Z. L. Wu, Y. J. Wang, R. Li, N. N. Yin, and J. X. Jiang, "Recovery of Isoflavone Aglycones from Soy Whey Wastewater using Foam Fractination and Acidic Hydrolysis," *J. Ind. Eng. Chem.*, vol. 25, pp. 138–144, 2015.

[11] M. Poornaseri and M. Motavassel, "Removal of Trace Cadmium from Wastewater Using Batch Foam Fractionation," vol. 25, no. 4, pp. 901–904, 2013.

[12] B. Hua, J. Yang, J. Lester, and B. Deng, "Physico-Chemical Processes," *Water Environ. Res.*, vol. 85, no. 10, pp. 963–991, 2013.

[13] Z. L. Yang, B. Y. Gao, Q. Y. Yue, and Y. Wang, "Effect of pH on the coagulation performance of Al-based coagulants and residual aluminum speciation during the treatment of humic acid-kaolin synthetic water," *J. Hazard. Mater.*, vol. 178, no. 1–3, pp. 596–603, 2010.

[14] T. Jowa and L. L. Mguni, "Treatment of Low Turbidity Water Using Poly-Aluminium Chloride (PAC) and Recycled Sludge : Case study Chinhoyi," vol. 10, pp. 101–108, 2015.

[15] Z. Mucha and P. Kułakowski, "Turbidity measurements as a tool of monitoring and control of the SBR effluent at the small wastewater treatment plant-preliminary study," *Arch. Environ. Prot.*, vol. 42, no. 3, pp. 33–36, 2016.

[16] J. Pillai and D. Ph, "Flocculants and Coagulants: The Keys to Water and Waste Management in Aggregate Production," *Nalco*, no. December, p. 3, 2013.

[17] M. Nemati and S. Neysari, "In uence of the process parameters on the foam fractionation treatment of olive mill wastewater," vol. 23, pp. 17–20, 2016.

[18] J. Nadayil, D. Mohan, K. Dileep, M. Rose, and R. R. P. Parambi, "A Study on Effect of Aeration on Domestic Wastewater.," *Int. J. Interdiscip. Res. Innov. ISSN 2348-1226*, vol. 3, no. 2, pp. 10–15, 2015.

[19] J. Navisa, T. Sravya, M. Swetha, and M. Venkatesan, "Effect of bubble size on aeration process," *Asian J. Sci. Res.*, vol. 7, no. 4, pp. 482–487, 2014.