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Effect of Ultrasonic Irradiation on COD and TSS in Raw Rubber Mill Effluent

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Abstract

The problem of inadequate clean water is expected to grow worse in the next coming decades. Finding new ways are important to solve this problem. Sonochemical oxidation is one of the advanced oxidation methods in the area of wastewater. Its simple application combined with the production of degradable by-product make the system attractive as an alternative treatment process for difficult- to-treat waste such as rubber effluent. Organic compounds in liquid exposed to acoustic cavitation may act differently according to the physical and chemical properties of the effluent. Batch experiments of sonication were carried out to evaluate the effectiveness of the ultrasonic irradiation of organic compounds in raw rubber mill effluent at different power densities. The degradability of the effluent was assessed based on the changes in the value of COD and TSS values exposed to ultrasonic energy or power density ranging from 0.024W/cm to 0.188W/cm. The highest COD and TSS reduction values were 91% and 76%, respectively was obtained at power density of 0.024W/cm^3 after 90 min irradiation. The study shows the optimum conditions for maximum efficacy of the ultrasonic reactors.

Keywords: rubber wastewater; ultrasonic irradiation; organic pollutant; hydroxyl radical

1. Introduction

The rubber industry is one of the most important industries in Malaysia and contributes a large portion to the total national income. It usually generates large quantities of wastewater everyday containing high concentration of organic matter, suspended solids and nitrogen (Kumlanghan *et al.,* 2008). The generations of the effluent are mostly due to the processing process when converting the liquid sap to latex. Some of the chemicals that are present in the effluent are highly toxic. In addition, the vulcanisation of latex into rubber also releases effluents that are highly toxic to the environment. The releases of raw rubber effluent contains approximately 427 mg/L of COD, while for TSS was 1368 mg/L based on the study conducted by Oladoja *et al.,* 2006. The chemical properties may be different from other rubber industry depending on condition of their operation. Thus, selection of treatment of this wastewater under controlled conditions is very important in controlling the release of harmful wastes to the water body. The current methods that have been applied in rubber wastewater treatment are anaerobic-cum-facultative lagoon system, anaerobic-cum-aerated lagoon system, aerated lagoon and oxidation ditch system (Vijayaraghavan *et al.,* 2007). Some of these treatment processes are incomplete, impractical or unviable.

The use of ultrasonic in wastewater has been a subject of research and represents one of the few physical treatment methods available today. It is able to remove pollutants through production of radicals in the bubble of cavitation that can react with refractory compounds. In addition, chemical oxidation processes may be of a great interest with the toxic compound but are very expensive as they to totally mineralize a complex wastewater. The biological processes are cheap, but they are powerless to oxidize the toxic compounds (Gonze *et al.,* 2003). So, ultrasonic treatment can be an interesting option. In this study, ultrasonic process was selected as a treatment method owing to its several advantages. The advantages include the process can be carried out in ambient global condition, decomposition of volatile and semi-volatile organic compounds in aqueous phase, does not require the use of extra chemical, avoid the need to remove the excess of toxic compounds prior to discharge, and transform the refractory organic pollutants into highly degradable products (Ning *et al.,* 2005; Kim *et al.,* 2007; Findik *et al.,* 2006). Mainly, ultrasonic decomposition of organic compounds is brought by the formation and collapse of high-energy cavitation bubbles. Upon collapse, the solvent vapor is subjected to enormous increases in both temperature (up to 5000 K) and pressure (up to several thousand atm). Under such extreme conditions the solvent molecules undergo

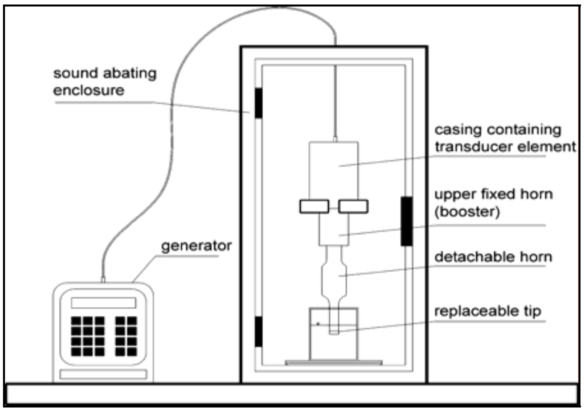

Figure 1. Experimental set-up (Naddeo *et al*., 2007)

homolytic bond breakage to generate radicals. When water is sonicated, H_2O_2, HO_2, H and OH radicals are produced, the latter being a strong oxidizing agent (E_h=2.33 V) which can react with organic compounds (Kim *et al.,* 2007). There are several factors that might affect the efficiency of ultrasonic degradation of pollutants such as the initial concentration of pollutions, frequency, temperature, and pH.

The aim of this study was to investigate the effects of ultrasonic irradiation on the raw rubber mill effluent based on reduction chemical oxygen demand (COD), and total suspended solids (TSS) of raw rubber mill effluent expose to varying ultrasonic power density and irradiation duration.

2. Research Methodology

The raw rubber mill effluent was collected from a rubber processing factory which was established since 1972. The sample was stored at 4°C to prevent the wastewater from undergoing biodegradation due to microbial action

Fig. 1 show the schematic diagram of the experimental set up used. The ultrasonic apparatus consisted of a generator, a converter and a sonotrode supplied by LE equipment under the brand Branson (S-450D). The reactor in the shape of rectangular prism 300 mm in width, 425 mm in height and 300 mm in length was used. The power input could be adjusted from 0-72W with the frequency 20 kHz. A transducer probe of the ultrasonic generator was inserted from the top into the wastewater about 2-3cm. The rubber sample was sonicated in a 500 ml beaker. The water level inside the surrounding bath was maintained by of cold water, and subsequently the temperature was maintained constantly at 30±2°C.

Ultrasound was transmitted into the 250 ml of rubber effluent sample through the tip of probe for 30, 60, 90 and 120 min of exposure duration. The power density used for irradiating the wastewater varied from 0.024 to 0.188W/cm^3. The experiments were run inside the waterproof sound abating closure to avoid airborne contamination. The effects of ultrasonic irradiation were evaluated based on the changes of the COD and TSS concentration of the raw and sonicated samples. The pH and temperature of wastewater before and after sonication were determined. The COD and TSS concentration was measured based on the Standard Methods described in “Methods for the examination of Water and Wastewater”. The pH was measured by a Model Orion 5 pH meter. All the experiments were repeated at least 3 times.

3. Results and Discussion

The characteristics of the raw rubber effluent are as follows: COD=6775 mg/L, BOD=341 mg/L, pH=6.66, temperature=28.9°C. The effect of ultrasonic irradiation has been conducted on rubber mill effluent and the results showed that there was reduction on COD and TSS of the initial concentration.

It was observed that the initial percentage reduction increased with the increase in ultrasonic power. A continual increase in power density does not necessarily imply continual increases in sonochemical destruction. It is very common that at certain powers, the percentage reduction may decrease.

3.1. The effect of ultrasonic irradiation on the COD percentage reduction

The results on the effect of ultrasonic on COD reduction at different ultrasonic exposure time are presented in Fig. 2. It indicated the trend of reduction varying with exposure times and power density. The trend shows that percentage reduction increases as time and power density increases. The percentage reduction started to decrease when it reached 120 min of irradiation except for 0.06 W/cm^3 of power density which achieved 91% of COD reduction. The highest COD percentage reduction can be achieved at 0.024 W/cm^3, 90 min and 0.06 W/cm^3, 120 min while the lowest COD percentage reduction was at 0.024 W/cm^3, 30 min that is 24% of COD reduction. The power input at 0.096 W/cm^3, 0.144 W/cm^3 and 0.188 W/cm^3 also affected the COD reduction but smaller compared to 0.024 W/cm^3 and 0.06 W/cm^3 that reached 91% of reduction. It is possible that the cavitating bubble size and the duration of the collapses that decrease with the increase of the power density. The growth cycle of a cavitating bubble is dependent on the power density of the applied ultrasound. When power density increased, the growth time cycle decreases. This

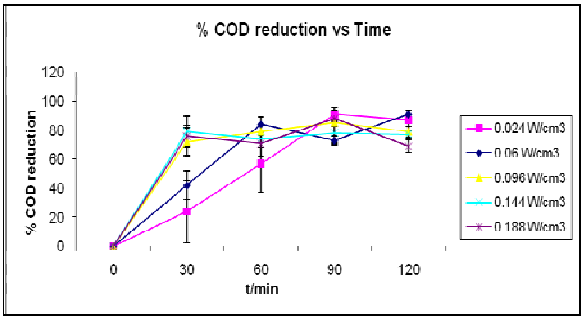

Figure 2. The changes of COD percentage reduction by ultrasonic irradiation in raw rubber mill effluent with time. (20kHz). Error bars represent the standard error of three replicate measurements of the sample.

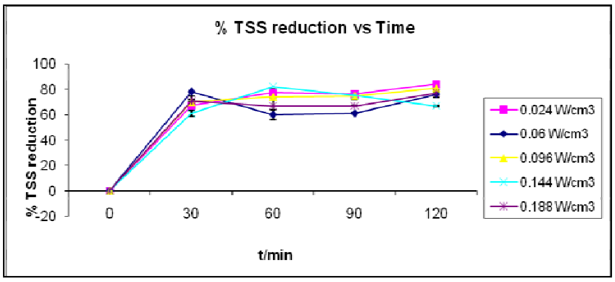

Figure 3. The changes of TSS percentage reduction by ultrasonic irradiation in raw rubber mill effluent with time. (20 kHz). Error bars represent the standard error of three replicate measurements of the sample.

decrease in growth times results in smaller maximum sizes at higher power density and thus less violent collapses. Cavitation collapses are fewer but more violent at lower frequencies. The true effects of ultrasonic are attributed to the radical formed during the implosive collapse of cavities (Sharma *et al.,* 2009). From the results, 90 min irradiation time, 0.024 W/cm^3 was the optimum power density compared to 120 min irradiation time, 0.06 W/cm^3 even though both of it has the highest COD percentage reduction. It is because lesser time and energy is needed to degrade the wastewater

3.2. The effect of ultrasonic irradiation on the TSS percentage reduction

The enhancement of TSS reduction efficiency by ultrasonic irradiation at various power densities and irradiation times is presented in Fig. 3. The TSS percentage reduction increased significantly at 30 min ultrasonic irradiation at all power density, but became unstable from 60 min to 120 min of irradiation at all power density. The percentage reduction was from 60% to 84%. When ultrasonic power was increased to 0.144 W/cm^3, the TSS percentage reduction declined at 120 min of irradiation. The highest percentage reduction was 84% which fall at 0.024 W/cm^3, 120 min while the lowest percentage reduction was 60% at 0.06 W/cm^3, 60 min. When a solid is present in an aqueous medium, the analyte present in the solid may be partially or totally extracted into the liquid medium and the sample size of the particles is diminished and subsequently increasing the total solid surface in contact with the liquid (Naddeo *et al*., 2007). When solid particles are in the vicinity of the cavitation bubble, the implosion may occur symmetrically or asymmetrically, depending on the proximity of the solids. Symmetric cavitations create shock waves which propagate to the surrounding solids causing microscopic turbulence and/or thinning of the solid-liquid film. This phenomenon is called *microstreaming* and is thought to be responsible for increasing the rate of mass transfer of reactants and/or products through the film. When solid particles are in close proximity to the bubble, it is unable to collapse symmetrically. This is known as *asymmetric cavitation* and is responsible for the formation of microjets of solvent which bombard the solid surface, leading to pitting and erosion (Hagenson and Doraiswamy, 1998; Grnman *et al.,* 2007).

The main physical effect of powerful implosion of cavitation bubbles in the water is the fragmentation of the suspended solids

3.3. Effect of power density

The most important parameters for application of ultrasonic are the power inputs. For every treatment process, there is an optimum power density depending on the nature of the wastewater. Figs. 2-3 show that the results of ultrasonic power effect on the reduction of COD and TSS concentration with the increasing power from 0.024 W/cm^3 to 0.188 W/cm^3 and sonication from 30 to 120 minutes times as well. The power inputs clearly affect the COD and TSS removal when different power density is applied to the wastewater.

As presented in Table 1, although the effluent could not meet the Malaysian standard after ultrasonic irradiation, but it have proven its capability to reduce the concentration of the raw effluent in shorter duration compare to biological treatment method that have been applied in the rubber factory.

4. Conclusion

From the results, it can be said that the COD and TSS in the rubber wastewater can be efficiently reduced

Table 1. The comparison between Malaysian wastewater standard, raw rubber effluent before and after ultrasonic irradiation.

	COD (mg/L)	TSS (mg/L)
Standard Malaysian Rubber (SMR)	250	150
Before Ultrasonic (Raw)	6775	1494
After Ultrasonic (0.024 W/cm^3, 90 min)	567	365

by the ultrasonic irradiation process. Low power density is capable of reducing the COD and TSS concentration compared to high power density. From the study, 0.024 W/cm^3 has shown to be the effective to reduce the COD and TSS concentration among all the other power density. So, it can be concluded that higher power density is not necessary since it consume more energy. Treatment performance can be maximized by choosing optimal operating conditions depending on the characteristics of the wastewater. Ultrasonic irradiation alone may not be suitable for completely to treat complex wastewaters of high organic load. In this respect, the efficiency may be improved by coupling ultrasonic with other advanced oxidation processes such as by adding catalysts, pH adjustment and etc. Alternatively, ultrasonic could be used as a pretreatment stage in a sequential chemical and biological treatment process.

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