EFFECT OF ULTRASONIC IRRADIATION ON LANDFILL LEACHATE

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1. Introduction

Due to increasing affluent lifestyle, commercial growth and continuing industrial in many countries around the world, particularly in developing countries, it has been accompanied by rapid increases in industrial and municipal solid waste production. Therefore, municipal solid waste (MSW) generation continues to grow in per capita which then releases many kinds of pollutants such as adsorptive organic halogen (AOX), heavy metals and xenobiotic (Renou *et al.*, 2008; Kurniawan *et al.*, 2006) to the environment which can remain as persistent organic chemicals. Thousands kind of chemical compounds are deposited in the landfill by human since the solid wastes collected are from different sources such as domestic wastes, municipal wastes and etc. Some of these chemicals will then find their own ways into the landfills, with the contact of water which finally form leachate. Much attention have been focused with this group of pollutants due to their potential health risk and the low concentration level accepted for drinking water quality standard enforced in most of the countries. Landfill leachate contains large quantities of specific micro-organic pollutants in micro-amount. These pollutants will leach out and subsequently contaminate the water body. Some of the organics which is initially not toxic may be transformed into toxic compounds. The effect of landfill leachate on water body such as creeks, streams and groundwater may last for centuries which are difficult to treat with conventional treatment methods. It is extremely difficult to restore the polluted groundwater to its former state (Kho, 2005).

Over the last few years, great attention has been paid to the use of ultrasound as one of many potential wastewater treatment technologies since this method is easy to operate. Ultrasound is well known that the degradation effect is caused by bubble cavitation which occurs when a high intensity ultrasound wave passes through a liquid. Depending on the physiocochemical properties of organic pollutants, there are two different mechanisms of their degradation: thermal decomposition due to direct pyrolysis inside the cavitation bubbles and decomposition via oxidizing the pollutants by OH radicals formed when the cavitation bubble collapse. It has been recognized that hydrophobic pollutants with high vapor pressure are decomposed according to the first mechanisms, whereas hydrophilic pollutants with low pressure are decomposed mainly by reacting with the OH radicals in the bulk solution and at the interfacial region between the cavitation bubble and liquid (Liang *et al.*, 2007).

However, total mineralization of organic pollutants by means of ultrasound irradiation alone still remains a difficult task especially for refractory organic compounds and thus application of ultrasound for an industrial plant is still impractical. To overcome the limitation of low degradation efficiency, many efforts have been made on investigation of various combined ultrasound systems in order to reach a desired efficiency of substrate and total carbon degradation and reduce the reaction time required for removing the pollutants. These methods include ultrasound coupled with oxidants

such as hydrogen peroxide (H_2O_2) and ozone, electrochemical method, Fenton reagent and photocatalysis (Kim *et al.*, 2007; Sotelo *et al.*, 2002)
In this study, the sonication effect with the addition of activated carbon was also investigated.

2. Objectives

1. To investigate the effect of ultrasonic irradiation on the percentage reduction of COD, TOC
and TSS in landfill leachate at different operating conditions, namely:-

   i. Different power density
   ii. Varying pH
   iii. Varying volume
   iv. Varying concentration
   v. Addition of different types and amounts of catalysts
   vi. Addition of different amounts of PAC

2. To investigate the effect of ultrasonic irradiation and the combination of other treatment
methods on the reduction of COD, TOC and TSS.

   i. Ultraviolet
   ii. Ultrasonic bath

3. To evaluate the effectiveness of PAC addition into the best selected operating conditions.

3. Research methodology

Leachates were collected from an open dumping landfill in Selangor, Malaysia. Samples used in the study were taken from a point just before the discharge of water to the drain and were stored at +4 C until used (Wu *et al.*, 2004). The leachate was immediately characterized according to the Standard methods for examination of water and wastewater for the following parameters: pH, chemical oxygen demand (COD), total organic carbon (TOC), total suspended solid (TSS), total solid (TS), total dissolved solid (TDS), oxidation reduction potential (ORP), temperature and heavy metals (Zn, Ni, Cd, and Hg).

All experiments are performed in a sonoreactor designed for this purpose. Ultrasonic irradiation was performed with 72 W; 20 kHz ultrasonic processor (Model Branson S-450D) from LE equipment equipped with ¼ inch microtip for ½ inch tapped standard horn.

For the experiments, 250 mL of leachate were placed in the reactor and the sonotrode was immersed into the liquid of approximately 1.5 cm from the bottom of the beaker. The irradiations were performed for 30, 60 and 90 min at amplitude of the sonotrode vibration of 50% except for the varied power density. The pH value of the solution was adjusted to a desired level using sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH). The temperature was maintained constantly at 30±2 C. Concentration of COD, TOC and TSS were measured before and after ultrasonic irradiation. The effect of addition of catalyst was assessed by adding appropriate amounts of $FeSO_4$ were added to a 250 mL of leachates.

For reaction of activated carbon addition, 2g of activated carbon was added to the leachate. The best operating conditions selected from the power density, pH and catalysts were then added with activated carbon by turning on the ultrasonic at the same time.

Concentration of COD, TOC and TSS were measured before and after ultrasonic irradiation while the samples that added with activated carbon were left for one night before measured for its COD, TOC and TSS values.

The chemical oxygen demand (COD) was determined by oxidation of the organic compounds with $K_2Cr_2O_7$. The total suspended solids were determined by drying the filtered solids at 105 C and TOC values of the leachate were detected by Shimadzu Total Organic Carbon Analyzer (TOC-V) CSN. pH was measured by a Orion 5 star model pH meter.

4. Results and Discussion

4.1. Effect of power density on COD reduction efficiency

The most important parameters for the application of sonolysis are the power employed in the aqueous solution (Méndez-Arriaga *et al.*, 2008). There is an optimum power for each process using different types of ultrasound and wastewater.

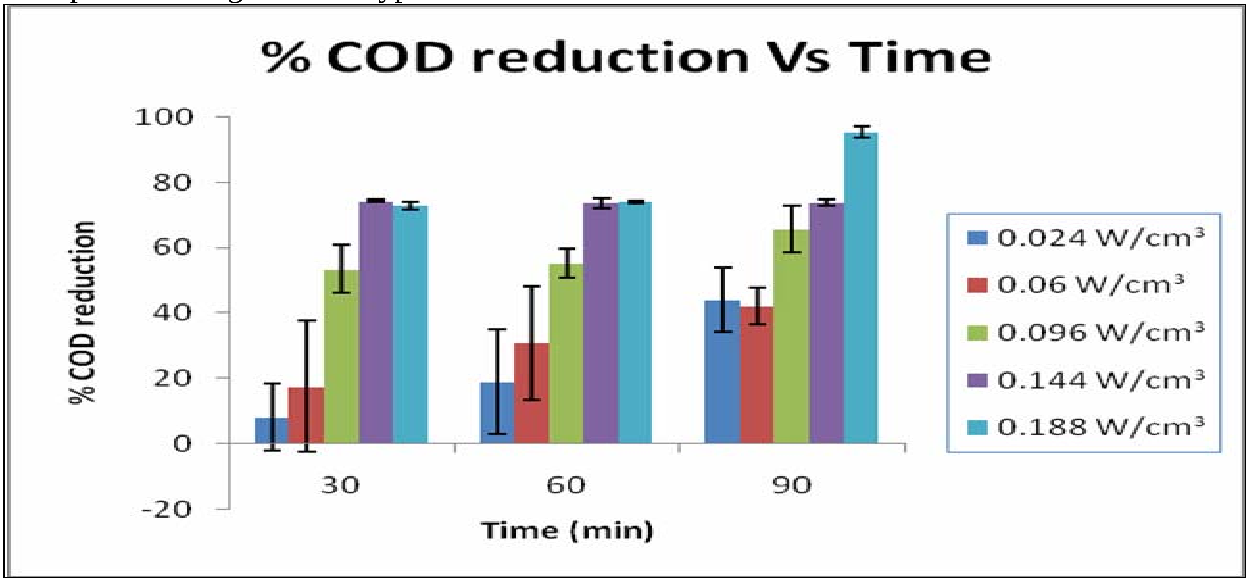

Figure 4.1: Effect of power density on COD reduction efficiency. Error bars represent the standard error of three replicate measurements of the sample.

The enhancement of COD reduction efficiency by ultrasonic irradiation at various power densities and at constant frequency of 20 kHz is presented in Figure 4.1. On the percentage reduction versus time plots, error bars used show the standard error of the average of 3 independent runs. As expected, the higher the sonication power, the higher the COD reduction obtained. The highest reduction of COD can be achieved at 0.188 W/cm^3 at 90 min of irradiation which is 95.55 % followed by 74.30 % at 0.144 W/cm^3, 30 min and 74.00 % at 0.188 W/cm^3, 60 min. The results showed that the power density of ultrasound has a very important role on the degradation process. At higher power density the concentration of hydroxyl radicals and mass transfer are higher which lead to the more degradation of organic matters (Wang *et al.*, 2008). The reduction of COD was low at lower power density might be due to the rate of formation of hydrogen peroxide are lower compared to higher power density which is capable to produce more hydroxyl radical to react with the organic compounds. Similar effects have been observed for the degradation of oxalic acid which is more efficient at higher power density (Dükkanci and Gündüz, 2006).

4.2. Effect of pH on COD reduction efficiency

In wastewater treatment a crucial parameter is the pH because depending on its value the discharged effluent can or cannot be able for subsequent stages in the treatment (Méndez-Arriaga *et al.*, 2008). Solution pH is an important factor in determining the physical and chemical properties of the solution (Ku *et al.*, 1997).

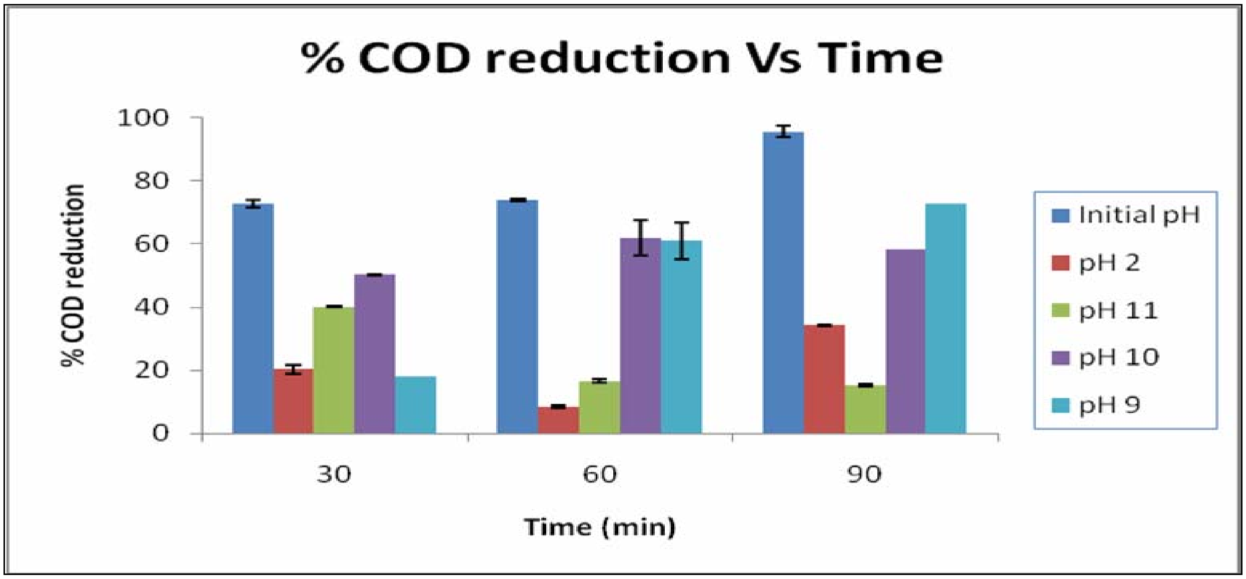

Figure 4.2: Effect of pH on COD reduction efficiency. Error bars represent the standard error of three replicate measurements of the sample.

The experiments of the effect of pH on COD reduction efficiency were carried out at 0.188 W/cm^3 and the results are shown in Figure 4.2. The pH was adjusted from pH 2 to pH 11 using acid sulfuric and sodium hydroxide. As can be seen, COD reduction is strongly depend on the solution pH since the reductions of COD showed differences on acidic and alkaline conditions with the initial pH of the sample under sonication. As clearly seen, pH 7.4 (initial pH) has the best pH for COD reduction with the values 95.55 %, 74.00 % and 72.83 at 30, 60 and 90 min respectively. Since there are many kinds of organic compounds in landfill leachate and the optimal pH is quite different for the sonolysis of different individual organic compound. For example, chlorophenol, at alkaline pH the ionic species dominate and react only with radicals that enter the bulk liquid. The molecular chlorophenol species present at acidic pH diffuse more easily into the interfacial region of the cavitation bubble where the concentration of radicals is high. So, sonochemical degradation of chlorophenols is more efficient at low pH (Ku *et al.*, 1997). Another study conducted by Gaddam and Cheung 2001, they found that 1,1,1-trichloroethane (TCA) is fairly easily treated by ultrasound at pH 10.9. Therefore, the optimal pH of the sonochemical decomposition may vary with leachates of different landfills (Wang *et al.*, 2008).

4.3. Effect of $FeSO_4$ ($FeSO_4$/US system) on COD reduction efficiency

Catalysts such as iron salt should increase the number of cavitational events by way of providing additional nuclei due to the deformities formed on the liquid surface. At the same time, it is expected that the reaction of the iron powder with in situ generated hydrogen peroxide due to ultrasonic irradiation will lead to formation of more hydroxyl radicals (Chakinala *et al.*, 2007).

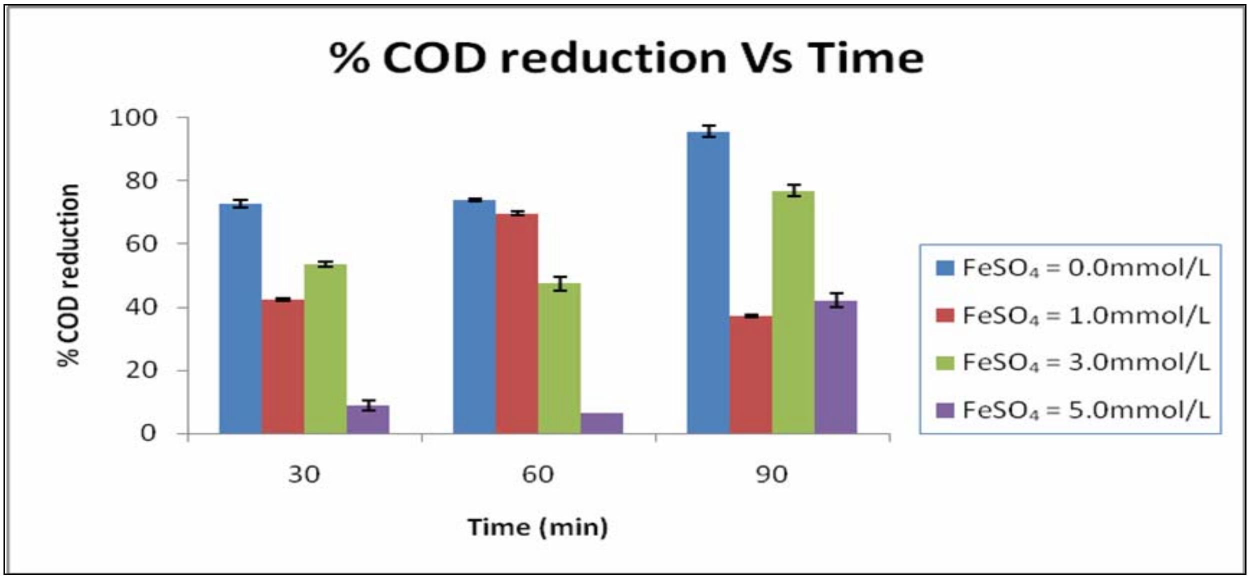

Figure 4.3: Effect of $FeSO_4$ on COD reduction efficiency. Error bars represent the standard error of three replicate measurements of the sample.

For the $FeSO_4$/US system experiments, the $FeSO_4$ was added to the desired target concentration (1.0, 3.0 and 5.0 mmol/L). As shown in the Figure 4.3, the addition of $FeSO_4$ increases the COD percentage reduction. The highest reduction using $FeSO_4$ at each concentration were at 0.0 mmol/L (95.55 %) which is without the addition of $FeSO_4$ followed by 3.0 mmol/L (76.89 %), 1.0 mmol/L (69.64 %) and 5.0 mmol/L (42.12 %). When the results where compared among 1.0, 3.0 and 5.0 mmol/L, the highest reduction can be achieved at 3.0 mmol/L and getting lower when $FeSO_4$ concentration increased to 5.0 mmol/L. It might be due to under neutral pH, reduction by Fenton chemistry does not prevail. Therefore, it is important to maintain acidic conditions for obtaining the synergistic effects (Nagata *et al.*, 2000). The percentage reduction reached its optimum concentration at 3.0 mmol/L due to the fact that the over dose iron would produce too many ferrous ions, which would scavenge hydroxyl radicals (Zhang *et al.*, 2009).

4.4. Effect of $FeSO_4$/PAC/US system on the COD percentage reduction

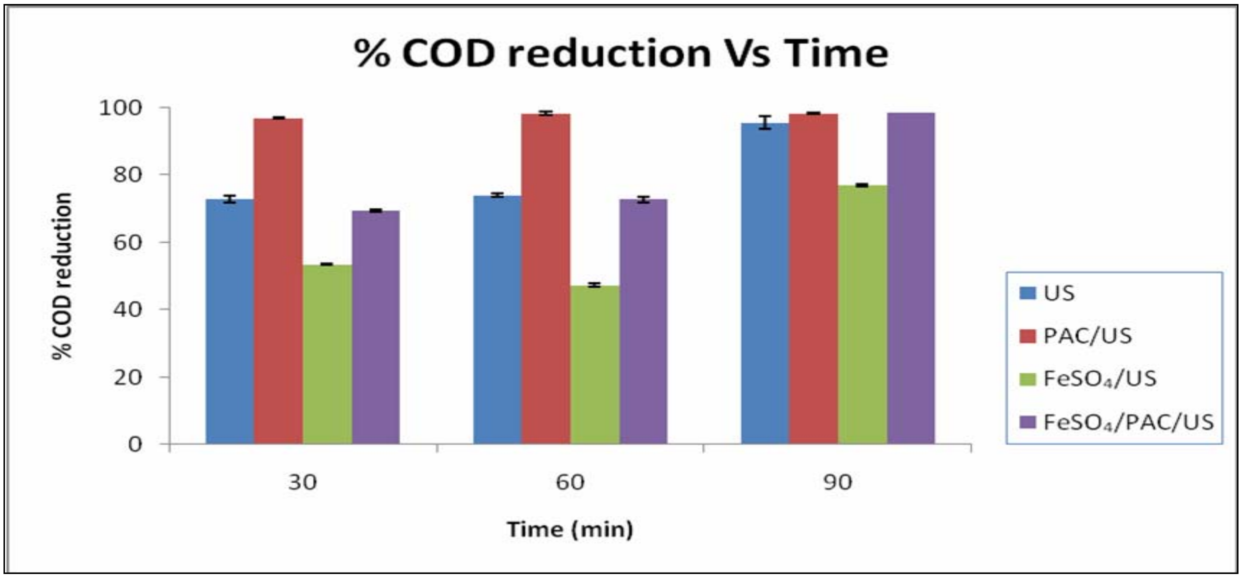

Figure 4.4: Effect of $FeSO_4$/PAC/US system on COD reduction efficiency. Error bars represent the standard error of three replicate measurements of the sample.

As can be seen in Figure 4.4, the highest reduction was 98.52 % after 90 min of ultrasonic irradiation with the combination of $FeSO_4$ and PAC ($FeSO_4$/PAC/US system) would increase the COD reduction efficiently. Generally, insufficient radicals were generated by ultrasonic irradiation. Therefore, the sonochemical process is often supplemented with catalysts or activated carbon. The COD reduction was accelerated via a Fenton-like process. The presence of iron particles leads to an increase in the cavitational intensity as the solid particles act as nuclei for surface cavitation thereby increasing the number of cavitational events occurring in the reactor (Bremner *et al.*, 2008) while activated carbon accelerated the kinetic rate of the ultrasound decomposition through the formation of ·OH radicals in the solution.

5. Significant of Finding

The results of the present study showed that the combination of ultrasonic irradiation and presence of activated carbon (PAC/US system) can be more useful in the reduction of COD in aqueous solution, which present an enhancement in reduction in the treatment time. The reduction of organic compounds increase with the increasing power density. The optimal pH value of the solutions was observed at the initial pH (7.4). Considering that there was not much effect of COD concentration after addition of Fe^{2+} from 1.0 to 5.0mmol/L, it is not a good idea to use Fe^{2+} for landfill leachate.

6. References

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