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Application of ozonation process for treatment of organic compounds of landfill leachate from Kieu Ki site

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Abstract
This paper presents several results of treatment of organic compounds from landfill leachate from Kieu Ki landfill site in Viet Nam by using ozonation processes to determine some suitable conditions in Vietnam. Before treating by Ozone, landfill leachate was pre-treated by coagulation. pH range between 5 and 10, reaction time between 20 and 120 min were selected by ozonation process in this research. As the result, the optimums was achieved at pH of 8 and reaction time of 80 min, COD was removed from 2,109 mg l^{-1} to 1,043 mg l^{-1} and color between 2,012 and 333 Pt-Co in this study.

1. Introduction

Today, landfill sites in Vietnam have generated large amounts of leachate containing highly toxic and non-biodegradable organic chemicals due to sources of solide waste and high natural moisture, rain and biochemical processes (Khanh, 2007). If leachate is not properly treated, it will pollute surface and ground water, causing serious environmental contamination. It is a challenge to environmental scientists.

The use of ozonation process to treat landfill leachate will have high performance because ozone oxidizes strongly organic compounds in the leachate. However, because of its high pollution levels, leachate needs to be pre-treated to reduce the amount of organic compounds. Talebi Amir et al, (2009) based on application of coagulation-flocculation with ferrous sulfate and anionic polymers, w concluded that the optimum conditions for pH and coagulant dosage are 11.7 and 10 g/l, respectively, resulted in 21.54% COD reduction (influent: 3520 mg/l, effluent: 2762 mg/l), 41.84% apparent color removal. Advanced Oxidation Processes (AOPs) were used to oxidize organic matters in wastewater (Teel et al. 2001). According to Aken et al. (2011), the oxidation with an ozone dosage of 1.3 g O_3 g^{-1} COD in 2 hours and pH value of 9 achieved COD reduction of 30%. COD removal reached up 70% for 240g O_3l^{-1} of leachate. The percentages for COD and colour removals at ozone dosage of 400 $mgl^{-1}hr^{-1}$ and pH of 9 were found to be 50% and 90%, respectively (Ratanatamskul et al. 2009).

In Viet Nam, coagulation processes are used to reduce suspended solids, organic matters of wastewater through agglutination and settling out (Khanh, 2007; Phuoc and Cuong, 2007). Chemical oxygen demand (COD) and color are the most difficult items for leachate treatment, in long time halogenated organic compounds with high molecular weight can be generated and endanged environment once they fall out surrounding soil and water (Phuoc and Cuong, 2007).

The objective of this research investigate the application of ozonation process to remove both COD and color from leachate of landfill sites in Vietnam. There is not researcher focusing on the amount of COD to assess COD and color removal. Therefore, in this research, all effects of factors on coagulation and ozonation process are considered to treatment organic matters in leachate.

2. Materials and Methods

2.1. Landfill Leachate

Leachate was taken from Kieuki landfill site in Hanoi, Vietnam. It has been operated over 10 years to treat solid waste for Gialam district, Hanoi city. Solid waste is collected from domestic and industrial waste... Leachate samples were taken from the pond between September and Octorber 2011. The characteristics of landfill leachate from Damai site: pH: 8.0 – 8.5; COD: 2,109 – 2,208 mg L^{-1}, Color: 2,012 – 2,333 Pt-Co.

2.2. Coagulation Processes

Coagulation was used to treat leachate in experiments with coagulants: PAC, $(Al_2(SO_4)_3.18H_2O$, $Fe_2(SO_4)_3.7H_2O$ and H_2SO_4, NaOH.

2.3. Analytics

pH and COD were analyzed by Standard Methods (APHA, 2005). Color was analyzed by spectrum method with Pt-Co color at 420 nm (APHA, 2005).

2.4. Experimental Apparatus

Coagulation experiments were performed in the Jar-test apparatus (model: JLT6 Jar test/Flocclulator, made in Italy) equipped with 6 backers showed in Fig. 1.

Fig 1. *Jar-test equipment.*

2.5. Experiments

Pre-treatment experiments of leachate were carried out with three types of coagulants: Polyaluminium Chloride (PAC), aluminum sulfate $(Al_2(SO4)_3.18H_2O)$ and ferric sulfate $(Fe_2(SO_4)_3.7H_2O)$. 5 mg L^{-1} of coagulant auxiliary A110 (sodium acrylates Acrylamic copolime) was added to increase coagulation process.

The experiments were investigated the effects of concentration of coagulants on treatment efficiency, followed by the concentration of which will be suitably determined for coagulation process and advantage for the next stage.

The experiments were conducted at room temperature (20±2°C). In each of the tests, coagulants (with calculated ratio) were added into a reaction beaker containing 500 mL of leachate. The concentration of coagulants were varied from 500; 1,000; 1,500; 2,000; 3,000; 4,000 to 5,000 mg L^{-1}. Quick phases took place in 3 min at a speed of 150 revolutions per minute and then added coagulants Auxiliary (A110) at the last minute of rapid stirring time. After that, stirring speed was reduced to 50 revolutions per min for 10 min. After slow stirring process, samples were settled out from 30 to 60 min.

2.6. Ozonation Processes

After coagulation, leachate was treated in the batch-type ozonation apparatus showed in Fig. 2, type reaction with working volume of 15 liters, consisting of a mica column with a heigh of 120 cm and internal diameter of 10 cm. The pre-treated leachate sample was pumped into a reactor with volume of 5 liters. Ozone is generated by ozone generator (model: OR-15-C). It was purchased from Miyamoto Corporation, Japan. The capacity of ozone is generated 24 mg h^{-1} (with flow rate: 4 L min^{-1}). The air containing ozone was then pumped into the reactor with determining time period, air flow rate was 4 L min^{-1}.

The experiments were performed to determine the optimum of pH, reaction time and the amount of COD. Initial pH was varied from 5, 6, 7, 8, 9 to 10 by sulfuric acid and sodium hydroxide for landfill leachate. The reaction time was varied from 20, 40, 60, 80, 100 to 120 min. There are the change of the amount of COD from 3; 6; 9 to 12 kg. COD and color were then investigated to identify optimun of pH, reaction time and the amount of COD.

3. Results and Discussion

3.1. Coagulation

Figure 3 showed that performance of COD concentration removal increased with increasing concentration of coagulants (performance with PAC: 17-38%, $Al_2(SO_4)_3.18H_2O$: 14-34% and $Fe_2(SO_4)_3.7H_2O$: 3-30%). The COD concentration decreased after coagulation at concentrations from 1,500 mg L^{-1}. The COD concentration decreased from 2,798 mg L^{-1} to 1,740 mg L^{-1} when coagulants reached from 3,000 mg L^{-1} or higher. Reaction might be saturated. The PAC was found to give higher efficiency of removal of organic matters than others with its concentration from 500 to 3,000 mg L^{-1}. After that, it was not increased even with increasing concentration of coagulant. However, COD removal reduced when increasing concentration of ferric sulfate.

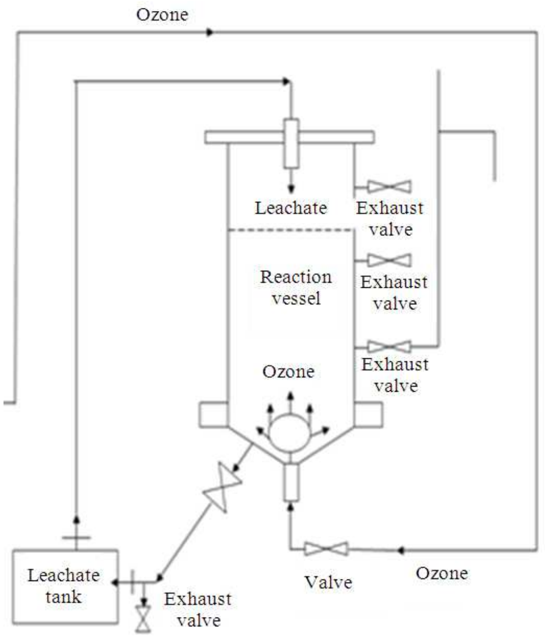


Fig 2. *Schematic of the ozonation apparatus.*

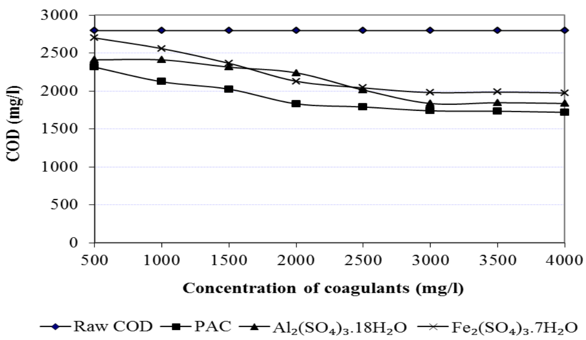


Fig 3. *Effect of concentration of coagulant on COD removal.*

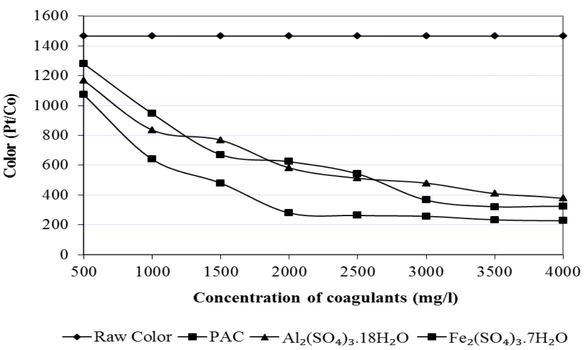


Fig 4. *Effect of concentration of coagulant on color removal.*

Color removal by using coagulation process increased quickly with increasing their concentrations from 500 to 2,000 mgL^{-1}. The result is showed in Fig. 4. It was increased mostly in amounts of coagulants of 1,000 to 2,000 mg L^{-1} and then remains constant. PAC was one of the three chemicals that had the highest performance of coagulation for these experiments. Color removal by $Al_2(SO_4)_3.18H_2O$ is similar to $Fe_2(SO_4)_3.7H_2O$. Color went down quickly from 1,512 to 280 (81%) at PAC concentration of 2,000 mg l^{-1} it then is not significantly reduced. It decreased down to 480 and 360 (68 and 76% respectively) at 3,000 mg L^{-1} of $Al_2(SO_4)_3.18H_2O$ and $Fe_2(SO_4)_3.7H_2O$, respectively. However, it was still high after coagulation. Because persistent organics of leachate such as humic, benzen and phenol affect highly on pretipication and adsorption of coagulants, their concentrations were required higher than other that of wastewater.

The effect of coagulation process with ferrous sulfate on COD, apparent color and turbidity was researched for the pre-treatment of mature landfill leachate of the Pulau Burung Sanitary Landfill, Malaysia (Abbas *et al*., 2009). The results showed that at the optimum setting for coagulant dosage was 10 g L^{-1} and pH 11.7, resulted in maximum of (22%) in COD, (42%) in apparent color and (31%) in turbidity. The coagulation of leachate samples was accomplished by addition of different coagulants including ferric chloride, aluminum sulphate, ferrous sulphate and poly-aluminum chloride in various coagulant and pH values, respectively (Jamali *et al*., 2009). Results of these tests showed that among traditional coagulants the best coagulant for treatment of the leachate is ferric chloride in combination with an anionic polyelectrolyte (Magnafloc LT25). Maximum COD and color removal rates for 41 and 70% had been achieved by addition of 2.5 g lG of ferric chloride as Fe. These results were slighly difference with our findings because landfill leachate in Vietnam is more complex than that of previous studies. Landfill sites consist of municipal and industrial solid waste as well as hospital solid waste without classifying from sources. So leachate characteristics are very complex, including high organic compounds (humic and fulvic acid, lignin, phenol and macromolecular compound...) and high toxic compounds from solid waste of industry and hospital.

The objective of pre-treatment is COD and color removals of about 30%, therefore, the PAC with 1,500 mg L^{-1} was suitable for this research with pH value from 7 to 8. Because the cost of $Fe_2(SO_4)_3.8H_2O$ is much higher than that of PAC, it is not to choose for this research.

4.2. Ozonation Process

4.2.1. Effect of pH

Before ozonation process, the leachate was treated by coagulation with PAC without adjusting pH (after adding coagulants, pH dropped from 8.5 to 7.9) and with concentration of 1,500 mg L^{-1}.

The leachate was pre-treated by coagulation with PAC at 1,500 mg l^{-1} with initial pH of landfill leachate.

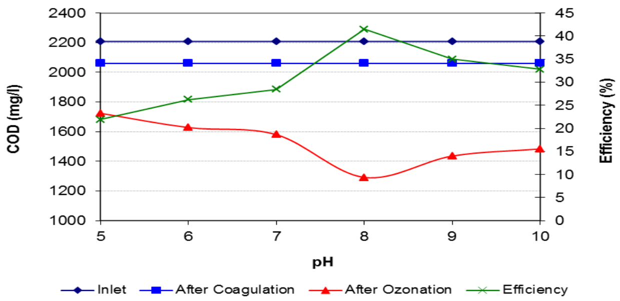


Fig 5. *The effect of pH of leachate on COD by ozonation process.*

Experiment condition: input airflow: 4 l/min, reaction time: 60 min and not change for all experiments of pH effect; leachate sample for each experiment: 5 liters. Figure 5 showed that with pH range from 5 to 10, optimal performance for this research was: pH 8 (COD removal from 2,208 mg l^{-1} to 1,292 mg l^{-1}(41%).

Figure 6 showed that color removal was similar when changing the pH of the leachate. Color removal was not clearly different between pH from 9 to 10. It is from 77 to 84% at pH range 8 – 9 and reaching to the highest at pH 8 and 9 (84%). Therefore, the optimal efficiencies of COD and color removals were achieved at pH 8. in the next stage, pH value of leachate was set at 8.

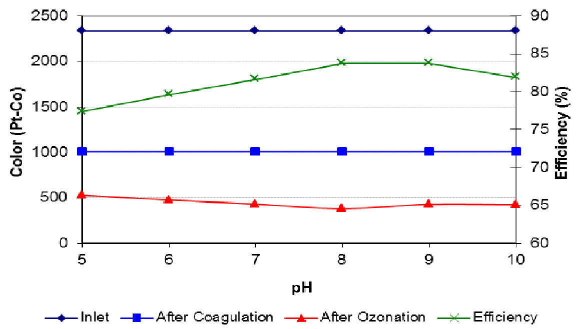


Fig 6. *Effect of pH of leachate on color by ozonation process.*

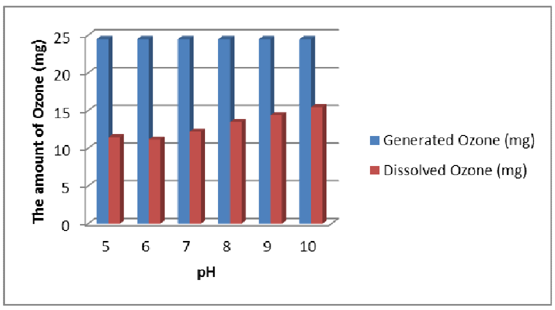


Fig 7. *The amount of dissolved ozone for experiment of pH change.*

The amount of ozone was consumed for each experiment of effect of reaction time is showed in the Fig. 7. For time of 60 minutes, the amount of ozone was generated lowly (about 24.48 mg) but it was not dissolved completely to react with organic matters because ozone is difficult to dissolve in water and wastewater.

Under acidic condition, organic compounds were oxidised directly by molecular ozone. The direct oxidition ($M + O_3$) of organic compound by ozone is a selective reaction with slow reaction rates, typically being in the rang of $k_D = 1.0 – 10^3\ M^{-1}s^{-1}$ (Gottschalk et al. 2000). The result of this research was similar to that of Staehlin and Hoigié's research (1983). In high pH (alkality condition), the decay of ozone to form secondary oxidants sach as hydroxyl radicals ($OH^{\bullet}$).

$$O_3 + H_2O \rightarrow 2HO^{\bullet} + O_2$$

Oxidation of organic compounds by hydroxyl free radicals produced during the decomposition of ozone. Thus, under conditions favoring hydroxyl free radical production, the hydroxyl oxidation starts to dominate (Hoigjé and Bader, 1977). However, $OH^{\bullet}$ can be destroyed by anions of Cl^-, CO_3^{2-}, HCO_3^- of leachate.

$$OH^{\bullet} + CO_3^{2-} \rightarrow CO_3^{\bullet -} + HO^-$$
$$OH^{\bullet} + HCO_3^- \rightarrow HCO_3^{\bullet} + OH^-$$
$$OH^{\bullet} + Cl^- \rightarrow ClOH^{\bullet -}$$

These inhibitors often terminate the chain reaction and ihibit ozone decay (Gottschalk et al. 2000). Therefore, in this research, the efficiency of COD and color removal decreased with high pH of leachate. The result of this research is different to several authors such as Kasprzyk-Hordern et al., 2003, the optimun of pH was achieved at 11; Pieter et al., 2011, the pH value of 9 achieved. However, the result of this research was similar to Hien's research on leachate in Vietnam, 2012, with pH of 7.5 was determined at the highest efficiency.

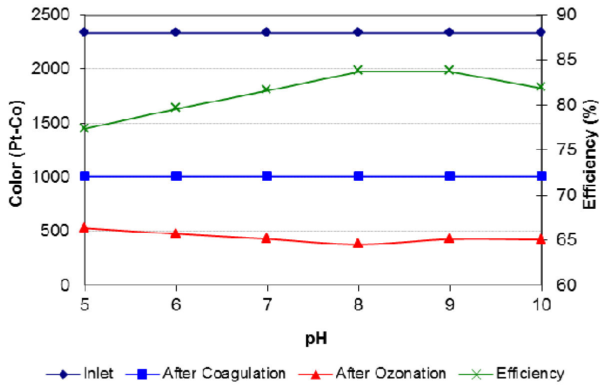
4.2.2. Effect of Reaction Time

The experiments below followed these selected parameters: pH = 8, airflow to 4L min^{-1}. Reaction time was ranging from 20-120 min.

The results of experiments to determine the reaction time of leachate was represented in Fig. 8: COD and color removal is higher and higher by increasing reaction time and the highest decline is after 80 min, reduced from 2,109 mg l^{-1} to 1,043 mg l^{-1} (51% for coagulation and Ozonation processes). It then remains at the constant if reaction time continued to 120 min. That is caused by reaction between ozone and organics of leachate reaches saturated rate.

Similar to COD, color removal was achieved well after ozonation process, raw landfill leachate was gray but it changed to black green after coagulation. It is presented in Fig. 9. After ozonation process, color also reduces quickly from 20 min to 120 min. It decreased from 2,012 to 701 Pt-Co after 20 min of reaction (65%). After 100 and 120 min it reached 88% and 90%, respectively.

The amount of ozone was dissolved for each experiment of effect of reaction time is showed in the Fig. 10.



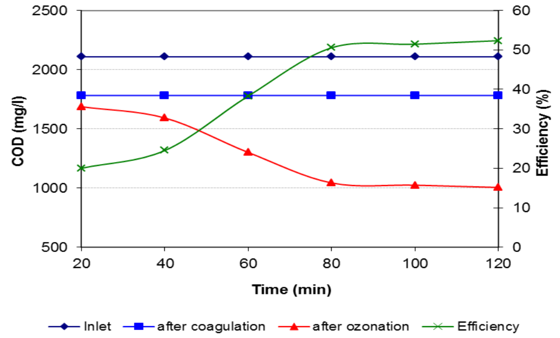


Fig 8. *The effect of reaction time of ozone and leachate on COD removal.*

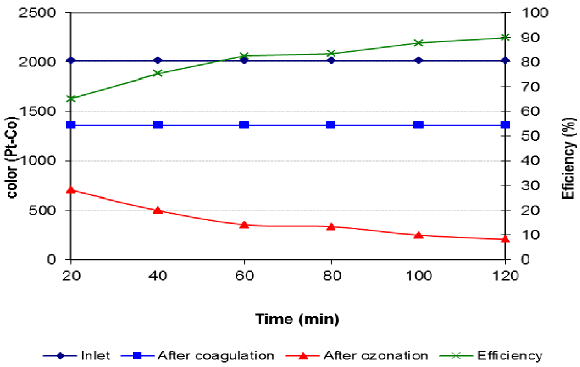


Fig 9. *The effect of reaction time of ozone and leachate on color removal.*

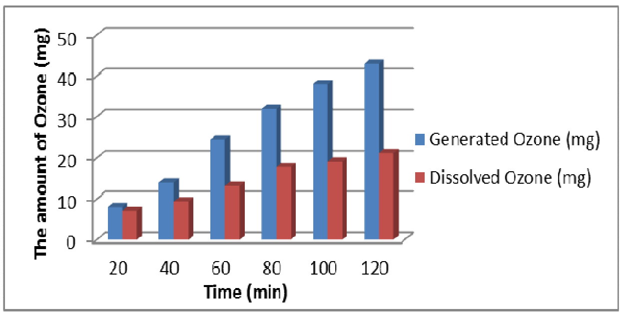


Fig 10. *The amount of dissolved ozone for experiment of reaction time.*

The amount of dissolved ozone increased with time from 20 to 80 min. Thus, the efficiency of COD and color removal and dissolved ozone in leachate slightly increased with rised reaction. The cost can be higher when increasing reaction time. So, reaction time of 60 min is suitable for this research.

4. Conlusion

Using ozonation processes to treat organic matters from leachate brings high effeciency. From this study, pH 8 and reaction time of 80 min were optimal, COD and color efficiency is 51% and 88% respectively. Ozonation process can be used to remove no-biodegradable organic compounds before bio-treatment.

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