

Removal of Colour from Semi-aerobic Landfill Leachate by Solar Photocatalytic

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ABSTRACT

Leachate are heavily polluted liquid which may contain large amount of chemical oxygen demand (COD), biological chemical demand (BOD), ammonia (NH_3) and colour. This study was conducted to examine the percentage of colour removal using coagulation as pretreatment, followed by the effects of ZnO, pH, stirring time and solar photocatalytic as final treatment. The duration of photocatalytic reaction occurs after 30 minutes of exposure to sunlight at solar intensity of $0.13 - 0.89 \text{ kW/m}^2$ that is from 11 – 1 p.m. The study showed that, pretreatment of leachate by coagulation at no pH adjustment, at its natural pH 8.68 with addition 10 g/L FeCl_3 as coagulant can remove 67.2% colour. But, 35% colour removal can be obtained by coagulation at pH 5 with addition 1 g/L FeCl_3 . Using 1.0 g/L ZnO at pH 5 capable of removing 97% colour after 120 minutes of exposure.

Keywords: Colour removal, leachate, solar photocatalytic

Introduction

Leachate is defined as the liquid that has percolated through solid waste and has dissolved or suspended material; in most cases water has entered the landfill from external sources. The chemical constituents of leachate can change greatly depending on the age of the landfill and the events preceding the time of sampling. Therefore, the application of the treatment method is very difficult in order to achieve better biodegradability and eventually a complete destruction of the organic pollutants contained in the leachate (Bekbolet et al., 1996).

Leachate produced from landfill contains large quantities of organic and inorganic matters, and heavy metals. For the removal of these matters, heterogeneous photocatalysis could be applied. In photocatalytic process, hydroxyl radicals can be generated when the photocatalyst, such as TiO_2 and ZnO, is illuminated and these ultra-reactive species lead to successful mineralization of pollutants to CO_2 , H_2O and other minerals. The studies in which heterogeneous photocatalysis on TiO_2 was a useful method for the elimination of toxic and non-biodegradable and refractory organic and inorganic components from landfill leachate by their transformation into harmless species, have been reported by Cho et al., (2002).

Therefore, for this study a semiconductor, ZnO and H_2O_2 , was chosen to treat leachate. The parameters that were focused in this study is colour.

Semiconductor, notably zinc oxide is known to be a photocatalyst. Illumination of these oxides will produce excited electrons that will react with water or hydroxyl ions to generate hydroxyl radicals (Saha & Chaudhari, 2002). The hydroxyl radical is the primary oxidizing agent. The hydroxyl radicals react with the leachate, completely mineralizing most compounds, leaving carbon dioxide, water and mineral acids as products (Saha, 2001). Semiconductor photocatalysis has had its usefulness explored as a viable alternative technology to classical 'best' technologies.

Hydrogen peroxide (H_2O_2) is a clear liquid, slightly more viscous than water. It has strong oxidizing properties and is therefore a powerful bleaching agent that has found use as a disinfectant and as an oxidizer. According to Rabindranathan et al., (2003), addition H_2O_2 enhances the rate of TiO_2 catalysed photodegradation of phosphamidon and the combination

efficiency of the catalyst and H_2O_2 is more than the sum of the effect of H_2O_2 and the catalyst. This study focuses on the leachate generated from Pulau Burung Landfill Site (PBLs) which has a semi-aerobic system. The characteristics of raw leachate from old detention pond at Pulau Burung Landfill Site (PBLs) are still very high. So, there must be treatment of leachate before it discharged to surface water.

Literature Review

Leachate is produced when moisture enters the refuse in a landfill extracts contaminants into the liquid phase, and produces moisture content sufficiently high to initiate liquid flow. Leachate composition depends on many factors such as the waste composition, site hydrology, the availability of moisture and oxygen, design and operation of the landfill and its age. There is a considerable number of studies reported in the literature for metals concentrations from full-scale landfills, test cells and laboratory works (Aziz et al., 2004).

Leachate produced from landfill contains large quantities of organic and inorganic matters and heavy metals (Cho et al., 2002). Landfill leachate is a very dark coloured liquid formed primarily by the percolation of precipitation through the cap of the completed site. The decomposition of organic matter such as humic acid may cause the water to be yellow, brown or black (Aziz et al., 2005).

The characteristics of landfill leachates are the combined result of a number of complex factors, including soil properties, weathering conditions, garbage composition, landfill age and landfill operation. The organic matter present in old landfill leachates is usually well stabilized, so biological treatment is ineffective for such effluents. This being the case, the identification of a satisfactory combination of techniques to produce an effluent that will not harm neighboring aquatic systems remains a challenge (Silva et al., 2004). Table 1, shows details of the main characteristics of leachate used in the experiment.

Table 1: The Characteristic of Raw Leachate from Detention Pond at Pulau Burung Landfill Site

Parameter	Value	Standard B*
pH	7.8 - 9.4	5.5 - 9.0
COD (mg/L)	1533 - 3600	100
BOD (mg/L)	48 - 1120	50
Turbidity (NTU)	50 - 450	-
Suspended solid (mg/L)	159 - 1120	100
Colour (PtCo)	2430 - 8180	-
Zinc (mg/L)	0.1 - 1.8	1
Copper (mg/L)	0.1 - 0.4	1
Manganese (mg/L)	0.6 - 1.1	1
Cadmium (mg/L)	< 0.04	0.02
Iron (mg/L)	0.32 - 7.5	5

Source: Aziz et al., 2005

Methods and Materials

Coagulation as Pretreatment Process

Leachate is dark brown or black in colour. So, coagulation was used as pretreatment process

to remove this dark colour first in order to allow for photooxidation to occur. Sample of leachate was taken out from cold room and left for about 1 hour at room temperature. The colour concentration in raw leachate were determined to obtain initial readings. For coagulation process, ferric chloride was chosen as the coagulant. The 10 % ferric chloride stock solution was prepared with 1 g of ferric chloride diluted with 10 mL distilled water. According to Hua (2005) the removal of COD increased when the dosage of ferric chloride increased. A 32 % removal of COD was obtained by the addition of 1000 mg/L ferric chloride at pH 5.

There were two methods that have been done before coagulation. First, adjust pH to 5. 1000 mL raw leachate poured into 1 litre high shape beaker for coagulation. Before coagulation, sulphuric acid (H_2SO_4) is used for pH adjustment raw leachate to pH 5. According to Hua (2005), the highest removal of COD by addition of ferric chloride was at pH 5 which the percentage of removal was 9 %. This is similar with the optimum pH 4.9 found by Amokrane *et al.* (1997) for the removal of 55 % COD in landfill leachate using ferric chloride as coagulant.

Secondly, without pH adjustment. To find optimal coagulant dose, ferric chloride was added to 500 mL raw leachate sample. The coagulant doses of ferric chloride used range from 1 g/L to 15 g/L, at varying increments.

Coagulation studies on leachate were performed with jar test equipment (Jar Tester Model CZ150) comprising six paddle rotors (24.5 mm x 63.5 mm), equipped with 1 beaker of each. A pre-determined concentration of ferric-chloride was added to the conditioned leachate. The initial rapid mixing stage for the both experiments were 1 min at 80 rpm, followed with slow mixing stage for 15 min at 30 rpm. The final gravity settling stage lasted for another 1 hr before sampling.

After 60 minutes of settling time (Song *et al.*, 2004), the colour of the supernatant were determined. The supernatant from this pretreatment step was then removed by using the pipet. 500 mL of this supernatant was taken and kept for the next step.

Treatment of Leachate

Batch studies on different concentration of ZnO and/without H_2O_2

To study zinc oxide-mediated photocatalytic degradation, concentration of leachate was chosen. In each case, one 'light control' (without ZnO) was used. 500mL of the supernatant (without ZnO) from first pretreatment was taken and measured for colour.

Secondly, 500mL of the supernatant were taken in a 1000mL glass beaker to which zinc oxide (ZnO) and/without hydrogen peroxide (H_2O_2) was added and kept in suspension by constant stirring and exposed to sunlight to allow photooxidation to occur in 30 minutes to 2 hours. A 20mL aliquot will be drawn out at every 30 minutes interval and filtered through a 0.45 μ m membrane filter. The filtrate will be diluted 1 in 10 and then tested for colour.

Results and Discussion

Pretreatment by Coagulation-Flocculation using $FeCl_3$

Leachate is dark brown or black in colour. Coagulation-flocculation is to remove this dark colour first in order to allow for photooxidation to occur. Ferric chloride ($FeCl_3$) was chosen as a pretreatment for coagulation-flocculation process. The leachate samples were then adjusted to pH 5 before the addition $FeCl_3$ (1g/L). The amount of colour, ammonia (NH_3) and COD removal were determined after coagulation-flocculation. In the next stage, no pH adjustment was made before the addition $FeCl_3$ (optimal coagulant dose). The amount of colour, ammonia (NH_3), and COD removed were again determined and compared to the first.

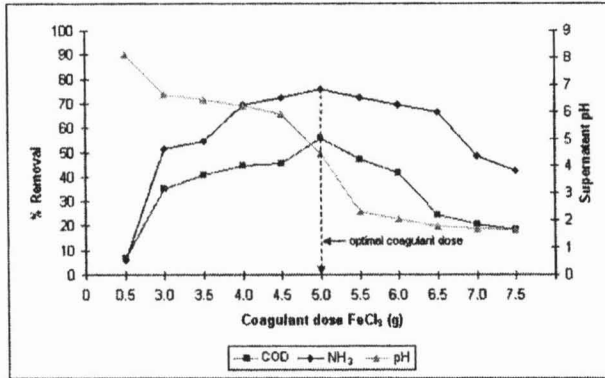


Figure 1: pH of Supernatant and % Removal of COD and NH₃ vs Coagulant Dose (With No pH Adjustment) in 500 ml Leachate

Based from the results, the coagulant dose that gave the highest percentage COD and ammonia removal was chosen as the optimum coagulant dose. The highest removal of COD and ammonia was obtained by addition 10g/L FeCl₃. The percentage removals were 55.8 % and 75.8 % respectively.

The pH for the supernatant decreased continually with increasing coagulant dose and gave a value of 4.43 with optimal coagulant dose of FeCl₃. This pH decrease can be explained by the acidic character of Fe³⁺ (acid of Lewis), when reacting with OH⁻ ions to form iron precipitated in the forms of Fe(OH)₃ (Amokrane et al., 1997).

With increasing coagulant dose, the dark brown colour of raw leachate turned to become clear yellow for the optimal coagulant dose near the optimum coagulant dose. For each coagulant dose tested, the settling times required were 2hrs. These results were similar to that obtained by Amokrane et al., 1997.

Stage 1: Batch Studies on Photooxidation using Different Concentration of Zinc Oxide (ZnO)

Figure 2, the final colour of the leachate dissolved was 120 Pt-Co which means a 97% reduction. It shows that 97% colour removal occurred in 90 minutes with ZnO dose of 1.0g/L and solar intensity of 0.13 – 0.89 kW/m².

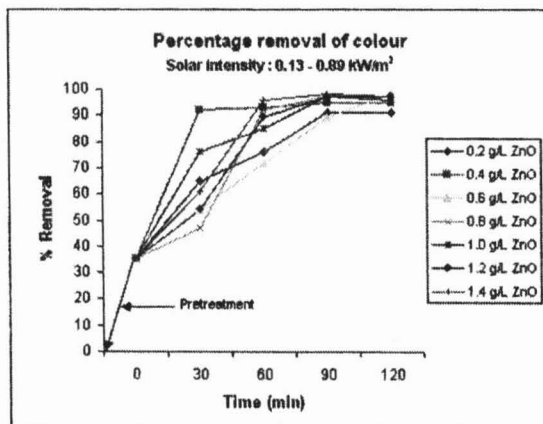


Figure 2: Percent Removal of Colour using Photooxidation and Different Concentration of ZnO

Stage 2(a): Batch Studies using 0.2g/L Zinc Oxide (ZnO) and Different Concentration of H₂O₂

Hydrogen peroxide corresponds to two-electron transformations of oxygen and water. It is formed under photocatalytic conditions. It is also degraded over band-gap irradiated semiconductors even at irradiating energies insufficient for its direct photolysis (Pichat et al., 1995). At neutral or acidic pH, the reduction of superoxide via OH⁻ ions to produce OH radicals is also improbable.

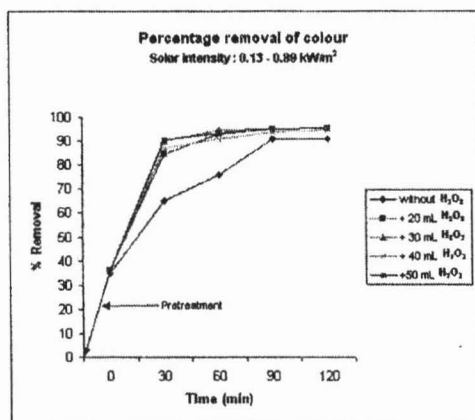


Figure 3: Percentage Removal of Colour using 0.2 g/L ZnO and H₂O₂

From the graph, preliminary studies have shown that addition of H₂O₂ enhances the rate of ZnO catalysed photodegradation of leachate is more than without adding H₂O₂. The final colour of the leachate was 195 Pt-Co – a 95.3 % reduction in 120 minutes when using 50mL/L H₂O₂. If without using H₂O₂ the final results for colour was 91% (310 Pt-Co) reduction in 120 minutes.

Stage 2(b): Batch Studies on 50mL/L H₂O₂ and Different Concentration of Zinc Oxide (ZnO)

From the graphs, it can be seen that when we can see that using 0.2 g/L ZnO and 50 mL/L H₂O₂ gives the best result for removing colour. Figure 4, the final colour of the leachate was 195 Pt-Co. It shows that 95.3 % colour removal occurred in 120 minutes. From Figure 1, the final concentration ammonia was 224 mg/L removal. It show that 84.8 % reduction occurred in 30 minutes

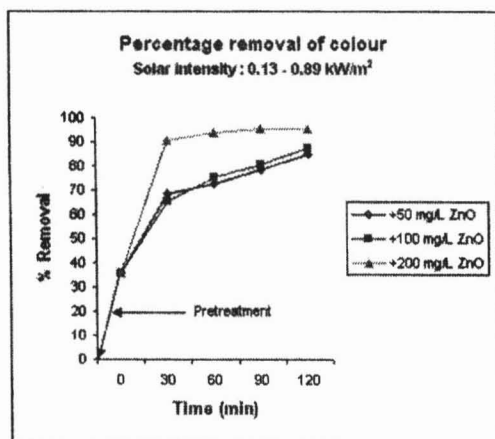


Figure 4: Percentage Removal of Colour using 50 mL/L H₂O₂ and ZnO

- Hua, L. M. (2005). *Removal of chemical oxygen demand (COD) and ammonia in pretreated leachate using granular activated carbon and zeolite mixture*. Universiti Sains Malaysia.
- Rabindranathan, S., Devipriya, S., & Yesodharan, S. (2003). Photocatalytic degradation of phosphamidon on semiconductor oxides. *Journal of Hazardous Materials, B102*, 217-229.
- Saha, A. K. (2001). *Zinc oxide-mediated solar photocatalytic degradation of metal complex azo dyes and treatment of a woolen textile dye house waste*. Indian Institute of Technology.
- Saha, A. K., & Chaudhuri, M. (2003). Solar photocatalytic degradation of metal complex azo dyes and treatment of dye house waste. *Indian Journal of Engineering & Materials Sciences, 10*, 69-74.
- Silva, A. C., Dezotti, M., & Sant'Anna Jr, G. L. (2004). Treatment and detoxification of a sanitary landfill leachate. *Chemosphere, 55*, 207-214.
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