Effect of pH, Dosage and Concentration on the Adsorption of Congo Red onto Untreated and Treated Aluminium Dross

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Abstract. The adsorption of congo red onto aluminium dross was studied in batch process. The objective of this study is to adsorption capacity between untreated and treated aluminium dross in the removal of congo red. Aluminium dross was leached with 250 ml of 1% of NaOH and precipitated with 30% H2O2. The treated aluminium dross being calcined at 600°C for 3 hours. The surface area for untreated and treated aluminium dross was 10.06 m2/g and 79.80 m2/g respectively. Then the adsorption process was carried out on an orbital shaker at 200 rpm for 4 hours. In the effect of pH, it was found that untreated removes more congo red compared to the treated while in the effect of concentration solution and dosage of adsorbent, treated aluminium dross removes more congo red. In conclusion, this adsorbent was found to be effective and economically viable in the removal of congo red in waste water treatment.

1. Introduction
Aluminium dross is a solid waste from aluminium smelting industry. It is an unavoidable by products that formed on the surface of molten aluminium. According to David & Kopac, (2012), dross can be classified into three categories which is based on the metal content. The three categories are white dross, black dross and salt cake. Hwang et al., (2006) stated that white dross contain 15-70% of recoverable metallic aluminium, while black dross contain 12-18% of recoverable metallic aluminium and salt cake contains only 3-5% residual metallic aluminium. According to Sultana et al., (2013) aluminium dross contain Al2O3, MgF2, SiO2 and MgO. According to Petavratzi, (2007), 95% of it usually being disposed of in a landfill. This could create the environmental problems because of landfill will act as a reactor where complex chemical reaction will occur. According to David & Kopac, (2012), when buried aluminium make contact with water with pH greater than 9 in a landfill, it will create an exothermic reaction that can retard the microbial activity in the soil. According to Murayama et al., (2012), some of this waste recycled as a deoxidizer in steel making and Petavratzi, (2007) stated that this waste can be used as a filler in a concrete. Industries looked at this as a problem due to the management cost of this waste and improper management of this waste could create the environmental problem. In this study, aluminium dross will be the raw material as an adsorbent that can remove of congo red dye in waste water. Dye is a major pollutants that contributes in a wastewater pollution. Industries such as textiles, printing, plastics and food colouring are the common industries that pollutes wastewater with pollution. It was estimated that 106 from 107 kg of dye end up in the effluent streams worldwide Debnath et al., (2014). Liu et al.,(2015)and Namasivayam & Kanchana, (1993) stated that some of dyes hard to treat in wastewater due to the resistance for biological treatment. Mane & Babu, (2013) stated that congo red it is a benzidine based anionic disazo dye with stabile structure that make it hard to biodegrade.
According to Namasivayam & Kanchana, (1993), the colour could remain for a long distances in streams, reduce the re-aeration capacity of the stream and retards the photosynthetic activity. Debnath et al., (2014) stated that when react with water, it can metabolize to benzidine which is carcinogen to human. Membrane separation, photocatalysis and adsorption are the methods that has been developed to overcome this problem. Zhang & Jia, (2016) and Mall et al., (2005) mentioned that adsorption is the best method since it is a simple method, low cost and stable in the treatment. There are various methods which have been employed for removal of dyes from effluent for example activated carbon (Mane & Babu, 2013). Most of these methods are expensive. The good adsorbent is an adsorbent that have a large capacity in the removal of dyes, inexpensive and do not required pre-treatment before being used that makes the adsorption process more economically. Some of the adsorbents has been discovered from waste such as fly ash (Acemioglu, 2004), bentonite (Toor et al., 2015), saw dust (Mane & Babu, 2013), bottom ash (Saleh et al., 2012) and banana pith (Namasivayam & Kanchana, 1993).

This study is to explore the possibility of utilizing aluminium treated with sodium hydroxide for the removal of hazardous congo red from aqueous solution in a batch experiment. The effect of factors such as adsorbent dosage, contact time, initial concentration and initial pH was investigated.

2. Experimental Methods

2.1. Activation of Aluminium Dross and Surface Area Determination

Aluminium dross was collected from aluminium smelting industry, Press Metal Company located in Samalaju Industrial Park, Bintulu, Sarawak. At first, aluminium dross was leached with 250 ml of 1% concentration of sodium hydroxide and stirred for 15 minutes. After 15 minutes, samples was filtered and precipitate with 250 ml of 30% hydrogen peroxide and stirred for 30 minutes. For the last step, aluminium dross filtered and washed for several times before being calcined at 600°C for 3 hours. The surface area of raw and treated aluminium dross were determined using BET equation to nitrogen gas adsorption (Quantachrome Instruments Co. Ltd.). The chemical composition of raw and treated aluminium dross were analysed using X-ray Fluorescence spectroscopy equipment (Bruker S4 EXPLORER X-Ray Fluorescence). The efficiency and effectiveness of raw and treated aluminium dross as an adsorbents was measured on the adsorption of congo red.

2.2. Preparation of Congo Red

1000 mg/L (stock solution) was prepared by dissolving 1 g of congo red in 1 Liter of distilled water. 20, 40, 70 and 100 ppm solution prepared by dilution from the stock solution.

2.3. Batch Study Experiment

A batch experiment was conducted in 100 ml of congo red solution. The parameters involved in this study was adsorbent dosage, pH and initial concentration. The adsorbent dosage was varied from 0.1 to 1.0 gram, the pH of the solution was varied from pH 6 to 9 and the initial concentration of congo red was varied from 20 ppm to 100 ppm. The pH was adjusted with 0.1 M HCl and 0.1 M NaOH. Few drops of 0.01 M of NaCl was used to maintained the ionic strength of the solution. The temperature of the process maintained at room temperature. For the samples measurement, 10 minutes interval within the first hour, 30 minutes for the second hour and subsequent 1 hour sampling until the adsorption process reach equilibrium. The final concentration of congo red solution was measured using UV-Vis spectrophotometer with 500 nm wavelength absorbance. The amount of congo red adsorbed by aluminium dross was calculated according to equation 1:

\[ q = \frac{q_0 - q_e}{m} \]

Where, \( q \) (mg/g) = amount of congo red adsorbed per unit gram of aluminium dross; \( C_0 \) and \( C_e \) (mg/l) is the initial and final concentration of congo red; \( V \) (l) is the solution volume and \( m \) (g) is the dosage of aluminium dross.
3. Results and Discussion

3.1. Surface area of aluminium dross
The untreated and treated aluminium dross being analysed with nitrogen adsorption-desorption measurements to determine the surface area of both samples. It was found that the surface area for untreated and treated aluminium dross was 10.06 m$^2$/g and 79.80 m$^2$/g respectively.

3.2. Effect of pH on the adsorption of congo red onto untreated and treated aluminium dross

| Table 1. Effect of pH on the adsorption of congo red onto 0.1 gram of untreated and treated aluminium dross |
|-----------------------------------------------------------|
| Percentage removal (%)                                      |
| Untreated aluminium dross       | Treated aluminium dross        |
| pH 6                         | 51.45                          | 82.51                          |
| pH 8                         | 65.62                          | 82.05                          |
| pH 9                         | 97.58                          | 67.21                          |

From table 1, it shows that for the untreated aluminium dross, the percentage removal increases as the pH increases while for the treated aluminium dross, the percentage removal decreases as the pH increases. According to Bhat et al., (2015), the solubility of metal ions, concentration of counterions on the functional groups of adsorbent and the degree of the ionization of the adsorbate were affected by pH. Aluminium dross majority comprises of Al$_2$O$_3$ that creates a positive charged when dissolved in water. Therefore, electrostatic attraction occur between the positively charged of treated aluminium dross with negatively charged of congo red dyes. When the pH of congo red solution increases, it shows that the adsorption of congo red decreases due to the positive charge on the active sites of aluminium dross decreases. It is because when the pH increases, more –OH ions will released and there is a competition between the –OH ions and the anionic of congo red dye for the binding process on the positive charge active sites on aluminium dross. According to Kosmulski, (2001), the pH point zero charge (pHpzc) for alumina was pH 8.6. When the pH of congo red solution above 8.6, the surface of aluminium dross will become a negative charge and repulsion of electrostatic charge between congo red and aluminium dross will occur. While, for the untreated aluminium dross, the percentage removal increases as the pH increases. This is because of the positive charged on the active sites of untreated aluminium dross was no effected by pH. In addition, it contains sufficient of positive charged sites for the removal of 20 ppm of congo red concentration.

3.3. Effect of concentration on the adsorption of congo red onto untreated and treated aluminium dross

| Table 2. Effect of concentration of congo red on the adsorption onto 0.1 gram of untreated and treated aluminium dross |
|-----------------------------------------------------------|
| Percentage removal (%)                                      |
| Untreated aluminium dross       | Treated aluminium dross        |
| 20 ppm                        | 51.45                          | 82.51                          |
| 40 ppm                        | 29.36                          | 69.22                          |
| 70 ppm                        | 25.20                          | 67.19                          |
| 100 ppm                       | 19.52                          | 42.34                          |
Table 2 shows the removal of different concentration on congo red onto 0.1 gram of untreated and treated aluminium dross at pH 6 solution. Both of the adsorbent shows that the percentage removal decreases as the concentration increases. This is because of the availability of the active sites of the adsorbent. When the concentration increases, the negative ions of dye solution dissociated also increases. The availability of active sites for the removal of congo red are limited for the high concentration of congo red.

3.4. Effect of dosage of adsorbent on the adsorption of congo red onto untreated and treated aluminium dross

| Percentage removal (%) |
|-------------------------|
| Untreated aluminium dross | Treated aluminium dross |
| 0.1 g | 51.45 | 82.51 |
| 0.4 g | 80.68 | 88.90 |
| 0.6 g | 92.56 | 69.90 |
| 0.8 g | 94.36 | 90.73 |
| 1.0 g | 96.44 | 90.96 |

The table shows that percentage removal increases as the adsorbent dosage increases. Increase in the dosage of adsorbent, it will promote more active sites that participates in the adsorption of congo red. Bhat et al., (2015) stated that when the dosage increases, the competition between the anionic dyes for binding sites decreases. From the result, it was found that the highest removal of congo red was the 1.0 gram of adsorbent dosage with high surface aluminium dross.

4. Conclusion
In this study, the adsorption of congo red was conducted with untreated and treated aluminium dross. The surface area for untreated and treated aluminium dross was 10.06 m²/g and 79.8 m²/g respectively. In the effect of pH, it was found that untreated remove high percentage of congo red compared to the treated aluminium dross. While in the effect of initial concentration and adsorbent dosage, treated aluminium dross remove high percentage of congo red compared to the untreated aluminium dross. From this study, it can be concluded that aluminium dross that has no value can be effectively used for the adsorption of congo red.

5. Acknowledgement
The authors acknowledge the research grant provided by the UNIMAS under Ministry of Higher Education Fund grant (RAGS/c(14)/948/2012(49).

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