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# DYE ADSORBENT BY PINEAPPLE ACTIVATED CARBON: $H_3PO_4$ AND NaOH ACTIVATION

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## ABSTRACT

Dye has becomes an indispensable tool for a variety of industries. More than 100000 types of dyes were produced exceeding 150 metric tons per year. They are used extensively in many industries which make the research on the color production more important. Despite that, dye can cause major environmental problems due to its toxicity and carcinogenic properties. So, it is important for the dyes to be treated before being disposed into the environment. In this study, activated carbon derived from different pineapple wastes namely pineapple crown, core and peel which prepared by chemical activation by using phosphoric acid ($H_3PO_4$) and sodium hydroxide (NaOH) were utilized to adsorb methylene blue and malachite green dyes. The results indicated that the activated carbon derived from pineapple crown shows maximum adsorption of methylene blue (99.48%) and malachite green (98.94%). This research was also used to determine the appropriate activation method between acid ($H_3PO_4$) and base activation (NaOH) by comparing the percentage of adsorption by both activation methods. Results obtained shows that the acid activated carbon serves as the best activated carbon with highest adsorption value of 99.48%. This study shows a benefit of transforming agriculture waste to value added product and also helps to solve over the abundance pineapple waste problem.

**Keywords:** pineapple waste, activated carbon, adsorption, methylene blue dye, malachite green dye.

## INTRODUCTION

Water covers about 70% of the earth's surface and earth is the only planet that has water in abundance on its surface. Human being, animal and plants require water for survival and to carry out daily routines, thus making water essential for all living forms to maintain continuity of their lives. The water on earth moves continually through the water cycle via several processes such as evaporation, transpiration, condensation, precipitation and runoff. The amount of water on earth is immense, where 97% consists of ocean which is unfit for human consumption and 2% is in the form of icecaps while the rest exists as fresh water. Above all, clean water supply is necessary but water sources and supplies are currently being tremendously polluted. This is due to increasing world population, unsustainable consumption of water and aggravated development [1]. Specifically, the following sectors namely agriculture, industrial and domestic respectively consumes 70%, 22% and 8% of available fresh water. Thus, it results in generation of large quantity of wastewater [2].

Dye manufacturing, textile and other fabric finishing releases massive amounts of dye into the wastewater [3]. Textile industry is a complex unit consisting of bleaching, dyeing, printing and stiffening of textile products and the entire process is well known to discharge pollutants especially wastewater. The textile waste water contains organic dyes, chemicals, auxiliaries, salts, surfactants, heavy metals, mineral, oil and others [4]. The dyes from textile wastewater are highly resistant to light, pH and microbial attack that makes them to remain in the environment for a longer period of time [5].

Commercially, there are more than 100000 types of dyes such as acid, reactive, disperse, vat, metal complex, mordant, direct, basic and sulphur dyes in which their production exceeds 150 metric tons per year [5]. Among them, azo dyes are the major group of synthetic dyes and makes up 70% of all commercial dyes [6].

As a result, major environmental issues arise due to the toxicity and carcinogenic property of the dyes. The carcinogenic property is caused by the presence of carcinogens such as benzidine, naphthalene and other aromatic compounds [7]. In addition, increasing demand for water supply had caused polluted water to be recovered and reused. Thus, several methods such as activated carbon, sorption, chemical coagulation, ion exchange, electrolysis and chemical treatment have been developed for removing dye from wastewater prior to release into the environment. According to [8], the effective method to remove dyes and pigments is activated carbon sorption. Activated carbon sorption is regarded as a better option for adsorption due to its large surface area and pore volume. Coal based activated carbon has been used widely, but cost and generation acts as a limitation. Therefore, non-conventional and low cost adsorbents from bottom ash, fly ash, coir pith, cassava peel, cotton, orange peel, bagasse fly ash, cellulose-based wastes, sewage sludge, kaolinite, zeolite, wheat straw, sawdust, char fines, and oil mill waste have been used [9]. Since commercial carbon activation method is expensive, thus production of activated carbon from agricultural waste can be less costly and environmental friendly as well.

Malaysia is one of the successful and potentially leading countries in pineapple industry. Pineapple (Ananas comosus) holds the third rank in the world tropical fruit production after banana and citrus [10]. Pineapple is the edible member of the family Bromeliaceae. Pineapple industry in Malaysia was started in1888 by an European from Singapore. It was then brought to Malaysia, particularly Johor and later spread to Selangor and Perak. According to the data provided by the Malaysia Pineapple Industry Board (1992), the species of pineapple found in Malaysia are Maspine, Sarawak, Yankee, Gandul, Moris Gajah, Josapine, N36, MD2 and Moris. Due to the massive production of pineapples, wastes generated are not exception with the production of residual pulp, peels, stems and crowns.

Pineapple wastes are generally disposed in the open environment due to the costly proper disposal method. This eventually causes serious environmental problems as pineapple waste requires high biochemical oxygen demand (BOD) and chemical oxygen demand (COD) to degrade. To overcome the disposal problem, currently pineapple waste is utilized in various manners namely as bromelain, ethanol, antioxidant, organic acid, acids, anti-dyeing agent, fiber, removal of heavy metal, animal feed, and energy and carbon source [11].

Besides that, pineapple waste can be used in the removal of dye due to the adsorbent produced from pineapple waste is of low cost, prevents disposal cost and off-site burning issues [4]. Based on these reasons, pineapple waste namely pineapple crown, peel and core were chosen for this study to produce activated carbon for the adsorbent of dyes. The objective of this study was to investigate the most suitable waste of pineapple that enables to produce the best activated carbon for dye adsorption.

## MATERIALS AND METHODS

### Preparation of raw material

The materials that are used in this research were pineapple crown, pineapple peel and pineapple core. Pineapples were bought at local markets in Jeli, Kelantan. The pineapple peel, crown and core were cut into small pieces and washed thoroughly with deionized water and dried in oven for 2 to 3 hours at 105 °C [4]. The dried pineapple crown, peel and core were then grinded and sieved by using 300µm siever.

### Preparation of adsorbate

About 0.5g of dye was weighed by using a weighing balance and pour into 250ml beaker. Then, about 20ml deionized water was poured into the beaker and was stirred by using a glass rod to ensure complete dissolving of the dye. Next, the dye solution was poured into 100ml volumetric flask and mad up to the mark with deionized water. The dye solution was then filtered by using 0.45 µm Whatman filter paper. Later, about 5ml of the dye solution was pipetted into 50ml volumetric flask and made up to the mark with deionized water. The dye sample was stored in 50ml polypropylene bottle and labelled before being analyzed [12].

### Preparation of adsorbent using phosphoric acid ($H_3PO_4$)

Oven dried pineapple crown, peel and core were soaked in a boiling solution of 40% phosphoric acid for 1 hour [13]. Later, the pineapple crown, peel and core were subjected to oven at 100 °C for 24 hours to dry the raw materials [8]. Then, the pineapple peel, crown and core were kept at room temperature for 24 hours [13]. The air dried pineapple peel, crown and core were carbonized in a furnace at 500 ºC for 1 hour [8]. Later, the pineapple peel, crown and core were washed with hot deionized water, cold deionized water and dried at 120 °C for 2 hours [14] and stored in tight lid container [13].

### Preparation of adsorbent using sodium hydroxide (NaOH)

Oven dried pineapple crown, peel and core were stirred in 4% sodium hydroxide solution (NaOH) for 1 hour in the ratio of 1:20. Then, it is kept overnight [1] before oven dried at 300 °C for 3 hours [15]. Then, they were carbonized in furnace at 200 °C for 60 minutes and washed with 0.5M hydrochloric acid solution. Later, the carbonized materials were washed with hot deionized water until the pH reaches 5 to 8 and rewashed with cool deionized water. The washed samples were dried in oven at 120 °C for 2 hours and stored in tight lid container [16].

### Testing pure adsorbate in spectrophotometer

The prepared pure dye, methylene blue and malachite green were placed on spectrophotometer HACH DR 5000 to identify their initial optical density prior to treatment with activated carbon from pineapple peel, crown and core. The initial optical density was determined by the wavelength of 668nm for methylene blue and 659nm for malachite green [5]. Spectrophotometer HACH DR 5000 operates on principles of UV light absorption by dye being tested. Untreated methylene blue and malachite green contain a higher percentage of color pigments that absorbs the UV light produced in the Spectrophotometer HACH DR 5000. Thus, the absorber detects higher optical density as the color pigments in the dye absorb the UV radiation indicating the concentration of color is high. However, vice versa should occur in which lower optical density or zero optical density value should be recorded for treating methylene blue and malachite green. It indicates a lower percentage or absence of color pigments after treatment with activated carbon.

**Adsorption process**

About 50ml of methylene blue and malachite green were treated with 1g of activated carbon. The mixture was placed in a shaker and stirred for 2 hours at 150rpm [1]. Then, the supernatant liquid (treated dye) was filtered by using 0.45µm Whatman filter paper [1]. The treated dye was then tested with spectrophotometer HACH DR 5000 at the wavelength of maximum absorbance of 668nm and 650nm for methylene blue and malachite green respectively to identify the optical density of the adsorbed dye by the activated carbon [5]. The percentage removal of dye is defined as the difference in dye concentration before and after adsorption, and was calculated by using the Equation. (1):

$$\% \text{ Removal} = \frac{(C_o - C_t)}{C_o} \times 100\% \qquad (1)$$

where Co is the adsorbance value before the dyes are treated (pure treated) with different activated carbon while Ct is the adsorbance value after the dyes are treated (treated dye).

**RESULTS AND DISCUSSIONS**

The raw materials used in this research were pineapple wastes comprising of pineapple crown, peel and core. The nature of pineapple is acidic due to its citric acid content in the fruit. Theoretically, it is believed that base activation method supposed to produce the best activated carbon compared to acid activated carbon. This is where the acidic raw material will produce the best base activated carbons while basic raw materials will produce best acidic activated carbons [17].

Generally, base such as potassium hydroxide and sodium hydroxide are chosen as activating agents in carbon activation [18]. However, in this research sodium hydroxide was chosen as an activating agent. Sodium hydroxide is an etching material that promotes defect in the structure of the carbon material in which this causes and improves porosity of carbon material. The cation in the hydroxide in this case which is the sodium ion ($Na^+$) is responsible to determine the size and number of pores in the activated carbon [19]. Sodium lies above potassium in the periodic table which explains the size of sodium ion ($Na^+$) is far smaller compared to potassium ion ($K^+$). The size of ion plays a major role in carbon activation due to the smaller size of cationic ions such as sodium, which capable of penetrating more deeply into the carbon structure to develop a high number of smaller pores [20].

Besides that, sodium hydroxides are the strong base in nature dissociates completely in water to produce hydroxide ions (-OH). This further increases the active sites in active carbon produced by base activation, since the number of hydroxyl functional group present in the cellulose and hemicelluloses of pineapple waste will be enhanced by the hydroxyl groups in the sodium hydroxide. The increase in hydroxyl group should increase the adsorption capacity of dyes. Despite the facts discussed above, the adsorption of methylene blue and malachite green dye for activated carbon produced from sodium hydroxide (NaOH) activation shows lower adsorption compared to activated carbon produced from acid activation ($H_3PO_4$). The highest adsorption occurs in acid ($H_3PO_4$) activated carbon for both methylene blue and malachite green dye adsorption in which the adsorption was 99.48% and 98.94% respectively. Table-1 shows the highest percentage of adsorption between acid and base activation.

**Table-1.** Percentage adsorption for acid and base activation (%).

| **Dyes** | **Acid activation ($H_3PO_4$)** | **Base activation (NaOH)** |
|---|---|---|
| Methylene Blue (MB) | 99.48 | 98.80 |
| Malachite Green (MG) | 98.94 | 98.17 |

Highest adsorption of dyes for acid and base activated carbon was by activated carbon produced by the pineapple crown. By comparing the results obtained in Table-1, acid activated carbon serves as the best activated carbon for adsorption of dyes compared to base activated carbon. The experimental results contradict with the theoretical context may due to several events that occurs during the preparation of activated carbon via base activation.

Sodium hydroxide and potassium hydroxide are corrosive and deleterious chemicals [18]. The corrosiveness of sodium hydroxide used in this research may cause the structure of pineapple waste to be corroded during chemical activation. Thus, the surface area of the pineapple waste had been reduced even before it was carbonized causing reduced uptake of dye pigments.

The complete dissociation of sodium hydroxide in water causes sodium ion ($Na^+$) to be freely available, and compete with the cationic dyes for the active sites in activated carbon [21]. A major portion of the active sites on activated carbon may be taken up by sodium ions ($Na^+$), even before the activated carbon is used to treat dyes which causing limited active sites for the uptake of cationic dye pigments.

In addition, the formation of salt and its competitive effect may also be another reason for lower adsorbance of dyes by sodium hydroxide (NaOH) activated carbon. The formation of salt may take place during the washing process as well where activated carbon in base activation has washed with 0.5M of hydrochloric acid. The reaction of sodium hydroxide and hydrochloric acid results in the formation of sodium chloride, as shown in Equation. (2).

$$NaOH + HCl \longrightarrow NaCl + H_2O \quad (2)$$

The formation of sodium chloride (NaCl) salt may deposit in the porous structure of activated which supposed to be available for the uptake of cationic dye pigments. Hence, the treatment of base activated carbon could not adsorb dye pigments as the surface of the activated carbon was lined with sodium chloride salt. Besides the deposit of sodium chloride salt, the deposition of sodium carbonate ($Na_2CO_3$) might take place as well and reduced the adsorption capacity of base activated carbon. It assumes that sodium hydroxide was reduced to metallic sodium during the carbonization process, in which the sodium hydroxide reacted with the carbon to produce sodium carbonate as shown in Equation. (3).

$$6NaOH + 2C \longrightarrow 2Na + 3H_2 + 2Na_2CO_3 \quad (3)$$

## CONCLUSIONS

The adsorption of methylene blue and malachite green dyes by using acid and base treated pineapple wastes namely pineapple crown, peel and core were investigated. From this study, it shows that the removal of methylene blue and malachite green dyes by adsorption utilizing activated carbon derived from pineapple waste to be useful in controlling water pollution. It can be concluded that acid treated pineapple crown activated carbon was an effective adsorbent for adsorption of methylene blue and malachite green dyes as compared to base with treated activated carbon. Pineapple waste is easily available and has the potential to be used for small industries that releases dye as effluent. The information collected from this study may be informative to design an economically inexpensive treatment process for removal of dye effluent.

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