ACTIVATED CARBON FROM PINEAPPLE WASTE BIOMASS FOR THE REMOVAL OF METHYLENE BLUE

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ABSTRAK

Pencemaran alam sekitar terutamanya air buangan yang mengandungi pigmen pewarna dari sumber industri menjadi perhatian pada masa kini. Teknik rawatan konvensional adalah cekap tetapi tidak sesuai bagi aplikasi berskala besar. Penggunaan sisa biojisim pertanian daripada industri nanas (*Ananas comosus*), menawarkan alternatif untuk menyingkirkan pigmen berdasarkan potensinya untuk ditukarkan menjadi karbon teraktif. Dalam kajian ini, karbon teraktif telah disediakan dengan menggunakan kaedah pirolisis (suhu 500 ^{o}C, 1 jam) sisa biojisim nanas (daun, batang, mahkota) dengan zink klorida ($ZnCl_2$). Karbon teraktif disediakan dengan menggunakan nisbah impregnasi yang berbeza-beza (50 ,100 dan 150 peratus berat) dan ditetapkan sebagai PLAC A, PLAC B dan PLAC C di mana karbon teraktif yang mempunyai luas permukaan yang paling tinggi telah dipilih untuk kajian seterusnya. Kemudiannya, ia dicirikan bagi mengkaji luas kawasan permukaan, kumpulan berfungsi, titik caj sifar, keliangan dan morfologi permukaan. Prestasi penyingkiran pewarna (penjerapan) oleh PLAC disiasat dengan menggunakan metilena biru (MB) dengan mengambil kira parameter berikut; masa sentuhan, kepekatan MB, pH, suhu dan dos PLAC. Selain itu, pengambilan maksimum MB (q_{max}) oleh PLAC ditentukan berdasarkan model-model isoterma penjerapan iaitu *Langmuir*, *Freundlich* dan *Redlich Peterson* serta model kinetik (*pseudo* peringkat pertama dan *pseudo* peringkat kedua). Model isoterma *Langmuir* telah menunjukkan penjerapan yang terbaik dengan nilai r^2 iaitu 0.969 dan q_{max} pada 288.34 mg/g. Kinetik penjerapan menunjukkan dua fasa yang berbeza, penjerapan menunjukkan reaksi *pseudo* peringkat kedua pada kepekatan MB yang tinggi pada 300 hingga 400 mg/L, dan *pseudo* peringkat pertama pada kepekatan MB yang rendah pada 100 hingga 200 mg/L. Berdasarkan data yang diperoleh, dapat disimpulkan bahawa PLAC B mempunyai kapasiti penyingkiran pewarna tertinggi berdasarkan kepada sifat luas permukaan yang tinggi (914.67 m^2/g), pH (6.12) dan kapasiti penjerapan pada 288.34 mg/g. Kajian ini telah menunjukkan bahawa sisa biojisim nanas boleh ditukarkan menjadi bahan penjerap yang boleh digunakan untuk penyingkiran pewarna dalam air buangan.

ABSTRACT

Environmental pollution especially pigment-containing wastewater from industrial sources are of concern nowadays. Conventional treatment techniques are efficient but they are not economically feasible for large-scale application. Utilization of agricultural waste biomass such as from the pineapple (*Ananas comosus*) industry offers an interesting alternative to remove pigment as it can be converted into activated carbon. In this study, activated carbon was prepared from the pyrolysis (500 ^{o}C, 1 hour) of pineapple waste biomass (leaves, stem, crown) impregnated with zinc chloride ($ZnCl_2$). The activated carbon was prepared with different impregnation ratios (50, 100 and 150 wt %) and designated as PLAC A, PLAC B and PLAC C in which the resulting activated carbon with the highest surface area was chosen for subsequent studies. It was characterized for its surface area, surface chemistry, point of zero charge (pH_{pzc}), functional groups, porosity and surface morphology. The dye removal performance of PLACs was investigated using methylene blue (MB) taking into consideration of the following parameters; contact time, initial concentration of MB, pH, temperature and PLAC dosage. In addition, maximum uptake (q_{max}) of MB by PLACs were determined based on goodness-of-fit obtained from mathematical models, including Langmuir, Freundlich and Redlich Peterson adsorption isotherm models as well as kinetic models (*pseudo* first order and second order). The adsorption equilibrium data was best fitted with the Langmuir adsorption isotherm with r^2 of 0.969 and q_{max} at 288.34 mg/g. The adsorption kinetics showed two distinct phases of adsorption indicating a *pseudo* second order reaction at higher MB concentration of 300 to 400 mg/L, and a *pseudo* first order kinetic model at lower MB concentration of 100 to 200 mg/L. Based on the data obtained, it can be concluded that PLAC B has the highest dye removal capacity due to its properties of high surface area (914.67 m^2/g), pH (6.12) and adsorption capacity at 288.34 mg/g. This study has shown that, pineapple waste biomass can be turned into an adsorbent which can be used for dye removal in wastewater.

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Plants and crops such as the oil palm plant, rubber tree, coconut, cocoa, peppers and pineapple has contributed 3.0% towards the nation's Gross Domestic Products (GDP) (amounting to RM58 billion for the year 2013) according to the Economic Planning Unit (2013). Downstream processing of these crops had also resulted in the production of large volume of biomass would which either be burnt or left to rot, leading to environmental concerns such as the deterioration of air quality, contamination of ground water as well the Green House effect (Nor *et al.*, 2013).

Pineapple (*Ananas comosus*) is one of the most popular edible fruit in the world. Malaysia is one of the largest producers of pineapple along with other countries including Thailand, Philippines, Indonesia, Hawaii, Ivory Coast, Kenya, Brazil, Taiwan, Australia, India and South Africa. It is used in various applications ranging from the food industry to the pharmaceuticals industry. In Malaysia, approximately 96,957 metric tons of pineapple fruits were produced for the year 2011 (MPIB 2011) and the state of Johor was the highest producer of pineapple throughout the country with total production volumes of 80,389.22 tonne metric.

1.5 Research Significance

of raw material for the production of activated carbon. The characterization of physic-chemical properties can add to the existing knowledge on the activated carbon produced from agricultural waste biomass. On another note, close collaboration with the industries and local government authorities on the utilization of this pineapple waste biomass may lead to the generation of new income to pineapple farmers as well as alleviating the problem of disposing of this biomass after the harvesting season. Owing to the limited studies reported regarding the utilization of the pineapple waste biomass as a precursor for the production of activated carbon, it adds to the novelty features of this study.

1.3 Objective of the Study

This study was aimed at investigating the potential of pineapple waste biomass as an activated carbon for the removal of dyes. Specific objectives of this study are as follows:

i. To characterize the activated carbon produced via chemical activation method from pineapple waste biomass.
ii. To evaluate the adsorptive properties of the activated carbon produced to remove dye from water.

1.4 Scope of Research

The pineapple leaf obtained from Pusat Penyelidikan Teknologi Tanaman Nanas (PPTTN) Stesen Alor Bukit, Pekan Nenas, Johor was used as the raw material for the preparation of activated carbon. Combination of zinc chloride activation and carbonization was used to prepare the activated carbon. The activated carbon produced was characterized for its chemical and physical properties consisting of surface area, ash content, surface functional group (Fourier Transformed Infrared Spectroscopy, FTIR), surface area (Brunauer Emmet Teller Analysis, BET), surface morphology (Scanning Electron Microscopy, SEM) and point of zero charge (pH_{pzc}). The activated carbons were then investigated for its adsorptive properties (effect of initial concentration, contact time, pH, adsorbent dosage, temperature) in the removal of dye using methylene blue.

1.2 Problem Statement

Due to the harm poised by dyes to the water bodies, the Methylene Blue (MB) dyes itself needed to be removed immediately as it can caused severe environmental problems such as light pollution, disturbances of ecosystem. The dyes itself is toxic and carcinogenic (Kumar *et al,*. 2011; Benadjemia *et al*., 2013). In order to remove MB, there are several methods available such as adsorption, oxidation, Fenton reagents, irradiation, photochemical and membrane filtration (Robinson *et al.*, 2001). However, the adsorption process has an edge over the other methods due to its sludge free operation. For this purpose, activated carbon was used widely due to its high adsorptive capacity, high surface area, chemical and mechanical stability and also high reactivity (Ahmed and Dhedan, 2012; Alam *et al.*, 2009). However, as commercially available activated carbons are expensive (1 kilogram of activated carbon costs RM 51.00), cheaper alternative of turning local agricultural biomass waste into activated carbon was sought (Kumar, 2011; Dias *et al.*, 2011). One of the available agricultural biomass waste is from the pineapple plantations. After the harvesting season, only the pineapple fruit will be collected and a small number of the pineapple plant will be kept for explants. As for the rest of the plant, the plant will be poisoned and burned which would cause severe harm to the environment. Thus, turning these waste into an activated carbon will alleviate the problem of biomass abundance and also the removal of dyes. Furthermore, no studies had reported the usage of pineapple waste into an activated carbon and the results of this study would provide valuable information regarding the sources of activated carbon production in Malaysia.

Amongst the most common strategies employed to counter the biomass abundance problem are burning, leaving it at the plantation for natural degradation or conversion into useful products such as cellulose, hemicellulose, lignin, biofuel, biogas, biofertilizer or activated carbon (Dias *et al.*, 2007). Activated carbon is a form of carbon where its adsorptive capabilities have been increased by physical or chemical treatment from a typical charcoal. It can be produced from any lignocelullosic materials particularly from plant and also from other materials including tyres or even manures (Zaini *et al.*, 2009). Activated carbon has been widely used in many fields, ranging from the health sector as a medicine for poisoning and diarrhoea, water filters, smoke filter, heavy metal adsorption, semiconductors and others (Dias et *al.*, 2007). Besides of its abundances, pineapple waste biomass was chosen as the precursor for the production of activated carbon as it possessed similar lignocellulosic properties with other precursors used and also very limited studies were reported regarding the utilization for this purpose, hence adding to the novelty features of this study.

One emerging area for the application of activated carbon is its application based on its adsorptive properties particularly in the removal of dyes. Dyes have been widely used in industries such as silk, cotton, fabrics, coloured paper and also for the manufacturing of inks. Since most dyes in used today are of synthetic origin, it poses a problem to the environment if it weren't properly removed. Amongst the problems associated with dye contamination includes visible pollution where the presence of dyes would interfere with the extent of light penetrating the water body. This would ultimately interfere with the growth of microorganism that is vital for the survival of water-based organisms such as plants and fishes. In the end, the overall water ecosystem will be disrupted (Ong *et al.*, 2012; Prahas *et al.*, 2008; Kumar *et al.*, 2011). Dyes have also been reported to be mutagenic and carcinogenic where a study by Ratna and Padhi (2012) on human cells has shown on the role of dyes on the newly formed micronuclei, chromosomal breakage (clastogenicity) and aneuploidy. Methylene blue was chosen for this research as it was extensively studied where this would lead to easier comparison with existing precursors of activated carbon (Pezoti *et al.*, 2014; Sharma *et al.*, 2011; Ahmed and Dhedan, 2012; Rozada *et al.*, 2005)

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