Faculty of Resource Science and Technology

Chemically Modified Palm Kernel Shell Biochar for Methylene Blue Removal: A Response Surface Methodology Approach

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DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Malaysia Sarawak. Except where due acknowledgements have been made, the work is that of the author alone. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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ABSTRACT

Biochar has emerged as a prominent adsorbent in reducing the bioavailability of organic pollutants in water bodies due to its properties such as large surface area, porous structure, enhanced surface functional groups, and inorganic components. However, these properties can be further enriched and improved to increase the removal efficiency of contaminants to develop biochar as a better adsorbent. Further enhancement of biochar properties can be accomplished via chemical modification. This study focuses on the development and characterization of chemically modified palm kernel shell (PKS) biochar using ethanol (EtOH), methanol (MeOH), and magnesium (Mg) for the removal of methylene blue (MB) from aqueous solution. Characterization of chemically modified biochar, such as ultimate analysis, proximate analysis, SEM analysis, BET analysis, and FTIR analysis, were also investigated. Based on the results, both SEM and BET analysis revealed a notable increase in the size and amount of pores on the surface of biochar and its surface area where Mg-treated PKS displayed the highest surface area of 674 m^2g^{-1}. Batch adsorption was conducted at different initial concentrations and contact times. Mg-treated PKS biochar was chosen for optimization study via the Response Surface Methodology (RSM) approach since it gave the highest removal efficiency in both batch experiments. RSM was conducted to study the effects of pH of the solution (pH 4-10), contact time (30-90 min), and adsorbent dosage (0.1-0.5 g). The optimal conditions for the adsorption of MB onto Mg-treated PKS biochar were found to be at a pH value of 10 with a contact time of 30 minutes and a dosage of 0.5 gram with a percentage removal of 98.50%. All chemically modified PKS biochar are proven to be successful in removing MB from an aqueous solution compared to untreated PKS biochar.

Keywords: Biochar, chemical modification, characterization, methylene blue, response surface methodology

Bioarang Kernel Kelapa Sawit Terubahsuai secara Kimia untuk Penyingkiran Metilena Biru: Pendekatan Kaedah Gerak Balas Permukaan

ABSTRAK

Bioarang telah muncul sebagai penyerap yang menonjol dalam mengurangkan bioavailabiliti bahan pencemar organik di badan air kerana mempunyai sifat-sifat seperti luas permukaan yang besar, struktur berliang, kumpulan fungsi permukaan yang lebih baik dan komponen mineral. Ciri-ciri ini, bagaimanapun, dapat diperkayakan dan ditingkatkan lagi untuk meningkatkan kecekapan penyingkiran bahan cemar dengan tujuan untuk menjadikan bioarang sebagai penyerap yang lebih baik. Peningkatan selanjutnya terhadap sifat bioarang boleh dicapai melalui pengubahsuaian kimia. Kajian ini memberi tumpuan kepada perkembangan dan pencirian bioarang kernel kelapa sawit (PKS) yang diubahsuai secara kimia menggunakan etanol (EtOH), metanol (MeOH) dan magnesium (Mg) untuk penyingkiran metilena biru (MB) daripada larutan akueus. Pencirian bioarang terubahsuai secara kimia seperti analisis muktamad, analisis proksim, analisis SEM, analisis BET dan analisis FTIR juga disiasat. Berdasarkan keputusan pencirian, kedua-dua analisis SEM dan BET menunjukkan peningkatan yang ketara dalam saiz dan jumlah liang pada permukaan bioarang serta luas permukaannya di mana bioarang magnesium PKS mempamerkan luas permukaan tertinggi iaitu 674 m^2g^{-1}. Pendekatan kaedah gerak balas permukaan (RSM) dijalankan berdasarkan kepekatan awal yang berbeza dan masa sentuhan. Bioarang-Mg PKS yang dirawat telah dipilih untuk kajian pengoptimuman melalui RSM kerana ia memberikan kecekapan penyingkiran tertinggi dalam kedua-dua eksperimen secara kumpulan. RSM dijalankan untuk mengkaji kesan pH larutan (pH 4-10), masa sentuhan (30-90 min) dan dos penjerap (0.1-0.5 g). Keadaan optimum untuk penjerapan MB ke bioarang-Mg PKS telah didapati pada nilai pH 10 dengan masa sentuhan 30 minit dan dos 0.5 gram *dengan peratus penyingkiran sebanyak 98.50%. Semua bioarang PKS yang diubahsuai secara kimia terbukti berjaya dalam menyingkirkan MB daripada larutan akueus berbanding dengan bioarang PKS yang tidak dirawat.*

Kata kunci: *Bioarang, pencirian, pengubahsuaian kimia, metilena biru, kaedah gerak balas permukaan*

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LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
BET	Brunauer-Emmett-Teller
CCD	Central Composite Design
CHN	Carbon-Hydrogen-Nitrogen
EtOH	Ethanol
FTIR	Fourier Transform Infrared
g	gram
HCl	Hydrochloric acid
MB	Methylene blue
MeOH	Methanol
Mg	Magnesium
min	minutes
O	Oxygen
PKS	Palm kernel shell
ppm	Parts per million
RSM	Response Surface Methodology
S	Sulfur
SEM	Scanning Electron Microscopy

CHAPTER 1

INTRODUCTION

1.1 Study Background

The lack of attention given to the discharge of environmental contaminants has resulted in the deterioration of surrounding ecosystems, especially to surface water (Kooh et al., 2017). As microbial pathogens bring immediate harm to human health, various organic contaminants such as dyes, pesticides, phenolics, antibiotics, and polynuclear aromatics also affect surface water condition (Kearns et al., 2014). The accumulation of harmful organic contaminants in natural water bodies have raised concerns around the world. Long-term exposure to organic contaminants is reported to cause cancer, endocrine and reproductive disease, liver, kidneys, or central nervous system damage (Kearns et al., 2014).

Each year, over 100,000 commercial dyes have been produced, with the total production exceeding 700,000 metric tons (Jawad et al., 2016). Around 90% of the total dyes produced are used in fabrics, whereas the remaining ratio is used in paper, plastic, leather, and chemical industry (García et al., 2018). Consequently, around 10–15% used from these industries have been discharged into waste streams as industrial effluent annually (Vikrant et al., 2018). The concentration of chemicals and color in wastewater from the textile industry is high; thus, proper treatment is needed to cease environmental problems. Colored water prevents solar radiation from entering water sources, inhibiting the photosynthesis of aquatic biota (Jia et al., 2018).

Dyes can be categorized into two categories, which are natural dyes and synthetic dyes. Natural dyes consist of pigment or colorants found in animals, particularly insects and vegetables, with no chemical handling (Yusuf et al., 2015). Alternatively, synthetic dyes are colorants that are made by humans. Recently, the growth of synthetic dyes production is a result of their economic low-cost synthesis process and a diverse selection of color choices (Ngoh et al., 2015). Dyes can be grouped as cationic, anionic, and non-ionic dyes (Vikrant et al., 2018).

Carbonaceous materials have been applied for many years as adsorbents for organic and inorganic pollutants in water and soil (Salih et al., 2011). Recently, biochar has emerged as an ameliorant to lower the bioavailability of pollutants in the water bodies (Ahmad et al., 2014). Activated carbon is currently the most frequent carbon material used as an adsorbent, but it is costly to make (Ahmad et al., 2014). Alternatively, biochar requires less investment and is renewable (Mohan et al., 2014). Biochar possesses specific properties that fit sorbent materials such as large specific surface area, porous structure, enhanced surface functional groups, and mineral components (Tan et al., 2015).

Today, various technologies such as adsorption, ion exchange, reverse osmosis, precipitation, and solvent extraction have been created and introduced to remove pollutants such as heavy metals, organic contaminants, and dyes from wastewaters (Igwe & Abia, 2007; Karaer & Kaya, 2016). However, most of the methods mentioned have a few drawbacks, such as incomplete pollutant removal, requires high energy and cost, and toxicity, which involves careful disposal (Al-Homaidan et al., 2014). Among these methods, adsorption is the most preferred technique in removing organic contaminants from aqueous solution. It has been proven to be effective, low cost, and gives high removal capacity (Liao et al., 2012).

The purpose of this study is to offer a few amounts of knowledge, insight, and understanding into the ability of chemically modified PKS biochar in the removal of MB from an aqueous solution. The chemicals used in the modification of biochar were ethanol (EtOH), methanol (MeOH), and magnesium (Mg). The characterization of raw PKS, untreated PKS biochar, EtOH-treated PKS biochar, MeOH-treated PKS biochar, and Mg-treated PKS biochar were also investigated. The optimization of MB adsorption was conducted under optimized parameters such as pH, contact time, and adsorbent dosage.

1.2 Problem Statement

Organic contaminants such as dyes, phenolic, pesticides, pharmaceutical residues, and polynuclear aromatics can impact the safety of surface waters, thus threatening human health. Many types of research have been done to study the uses of biochar for the removal of contaminants from aqueous solutions. Due to its fiscal and ecological benefits, biochar is an excellent adsorbent for water contaminants treatment. Biochar displays the great potential to remove contaminants due to its pore size distribution, surface area, and ion-exchange capacity. Furthermore, a great deal of modification onto biochar has been carried out to improve its sorption ability, including acid/base treatment, amination, carboxylation, magnetic modification, and surfactant modification. However, gaps exist in applying EtOH, MeOH, and Mg as the appropriate chemicals for modification of biochar since the most commonly used chemicals are acids and bases. Moreover, the amount of information and studies that have been conducted regarding the removal of MB from aqueous solution by EtOH, MeOH, and Mg modified biochar is very limited. This issue indicates that further research is needed to promote the benefits of these chemically modified biochars as an adsorbent for organic contaminant treatment.

1.3 Objectives

The objectives of this research are as follows:

i. To produce and characterize EtOH-treated, MeOH-treated, and Mg-treated PKS biochar

ii. To investigate the adsorption efficiency of the modified biochars with different chemical modification techniques

iii. To optimize the factors of adsorption of MB by Mg-treated PKS biochar

1.4 Scope of the Study

In the present study, chemical modification of biochar was carried out by using EtOH, MeOH, and $MgSO_4.7H_2O$. Then, EtOH-treated PKS biochar, MeOH-treated PKS biochar, and Mg-treated PKS biochar were characterized based on ultimate analysis, proximate analysis, surface area, surface morphology, and functional groups. The efficiency of EtOH-treated PKS biochar, MeOH-treated PKS biochar, and Mg-treated PKS biochar to remove MB from an aqueous solution was also investigated. Adsorption of MB onto these chemically modified biochars was studied in batch experiments under initial concentration and contact time parameters. Besides, RSM was utilized to determine the combined effects of variables (pH, contact time, adsorbent dosage) on the removal efficiency of MB using Mg-treated PKS biochar.

CHAPTER 2

LITERATURE REVIEW

2.1 Biochar

Biochar is a black carbon product produced by pyrolysis or heating biomass with limited or no access to oxygen and at relatively low temperatures (Nartey & Zhao, 2014). The term 'black carbon' refers to the solid by-product, which contains a high carbon concentration (Spokas et al., 2012). Feedstock such as coconut shell, sugarcane bagasse, empty fruit bunches of oil palms, rubber-wood sawdust waste, rice straw, bamboo, rice husk, maple wood, switchgrass, corn cobs, palm kernel shells, maize cobs, and cassava waste have been used in biochar production.

Different types of feedstock may affect the physicochemical properties of the biochar. For example, woody biomass usually has high contents of hemicellulose, cellulose, and lignin contents (Lupoi & Smith, 2012). It was found that the high content of lignin in plant biomass will increase the biochar yield (Ahmad et al., 2014). This further proves that feedstock types may affect the surface characteristics of biochar as well as their potential environmental applications (Wang et al., 2015).

The properties of biochar such as large surface area, porous structure, enriched surface functional groups, negative surface charge, and charge density have increased the biochar's ability to expand its capacity and stability in soils, exhibiting the potential to be utilized as an adsorbent to eradicate contaminant from soils and also an aqueous solution (Tan et al., 2015). Furthermore, biochar contains a non-carbonized fraction that can interact with soil and water pollutants (Ahmad et al., 2014). The surface functional groups in biochar,