Faculty of Resource Science and Technology

Melia azedarach Activated Carbon for Heavy Metals Removal: Isotherm, Kinetic and Response Surface Methodology Study

Muhammad Imran Shaukat

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Muhammad Imran Shaukat

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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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Signature

Name: Muhammad Imran Shaukat

Matric No.: 18010054

Faculty of Engineering

Universiti Malaysia Sarawak

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ABSTRACT

Excessive heavy metals discharge into the environment has become a great concern worldwide and needs an effective long-term solution. *Melia azedarach* tree is a member of the *Meliaceae* family and is used as a source of hard wood; however, the leaves and twigs are burnt due to lack of industrial applications. In this study, biomass from *Melia azedarach* leaves and twigs was used to prepare activated carbons via molten salt synthesis with $ZnCl_2$ as activator, for the removal of Cu(II), Pb(II) and Ni(II) ions from aqueous medium. Both activated carbons were characterised, evaluated for batch adsorption and fitness with the kinetic and isotherm models. The central composite design (CCD) was applied to optimise the removal of Cu(II), Pb(II) and Ni(II) by relating the mutual interactions of the factors including adsorbent dosage, initial metal concentration and contact time. The surface area of activated carbon from *Melia azedarach* leaves (121.592 m^2g^{-1}) and twig (91.423 m^2g^{-1}) was substantially larger than the feedstock leaves (1.02 m^2g^{-1}) and twigs (0.485 m^2g^{-1}). The batch adsorption from both activated carbons for Pb(II) and Ni(II) removal followed the Freundlich isotherm, while Cu(II) adsorption followed the Temkin isotherm. Applying central composite design in response surface methodology, the optimised removal efficiency for Cu(II), Pb(II), and Ni(II) using *Melia azedarach* leaves activated carbon as adsorbent was determined to be 98.63%, 99.52% and 88.18% respectively while optimised adsorption capacity was found to be 192.12 mgg^{-1}, 170.94 mgg^{-1}, 160.77 mgg^{-1}. On the other hand, the optimised removal efficiency for Cu(II), Pb(II), and Ni(II) using *Melia azedarach* twigs activated carbon as adsorbent was found to be 99.66%, 95.05% and 97.53% respectively while optimised adsorption capacity was determined to be 172.32 mgg^{-1}, 254.59 mgg^{-1}, 232.16 mgg^{-1} , optimised through central composite design in response surface methodology. The activated carbon derived from *Melia azedarach* biomass has demonstrated the capacity to be a value-added product as an adsorbent capable of adsorbing heavy metals from aqueous medium.

Keywords: Agricultural and horticultural wastes, biomass utilisation, green adsorbents, response surface methodology, water pollution

Melia azedarach *Karbon Teraktif untuk Penyingkiran Logam Berat: Kajian Metodologi Permukaan Isoterma, Kinetik dan Gerak Balas*

ABSTRAK

Pelepasan logam berat yang semakin meningkat ke alam sekitar telah menjadi kebimbangan besar yang memerlukan penyelesaian yang boleh dipercayai dan jangka panjang. Berikutan sintesis garam lebur dengan $ZnCl_2$ *sebagai pengaktif, biojisim daripada daun dan ranting* Melia azedarach *digunakan untuk menyediakan karbon teraktif untuk penyingkiran ion Cu(II), Pb(II), dan Ni(II) daripada medium akuas. Kedua-dua karbon teraktif telah dicirikan, dinilai untuk penjerapan kelompok, dan kesesuaian dengan model kinetik dan isoterma. Reka bentuk komposit pusat (CCD) digunakan untuk mengoptimumkan penjerapan kelompok dengan mengaitkan interaksi bersama faktor termasuk dos penjerap, kepekatan logam awal dan masa sentuhan. Luas permukaan karbon teraktif daun* Melia azedarach *(121.592* m^2g^{-1}*) dan ranting (91.423* m^2g^{-1}*) jauh lebih besar daripada daun (1.02* m^2g^{-1}*) dan bahan suapan ranting (0.485* m^2g^{-1}*). Penjerapan kelompok oleh kedua-dua karbon teraktif untuk penyingkiran Pb(II) dan Ni(II) mengikuti isoterma Freundlich, tetapi penjerapan Cu(II) mengikuti isoterma Temkin. Pada pembolehubah proses yang dioptimumkan, penyingkiran optimum Cu(II) 99.50%, Pb(II) ialah 100%, dan Ni(II) ialah 89.17% oleh karbon teraktif daun* Melia azedarach. *Manakala kapasiti penjerapan optimumnya didapati ialah 189.44* mgg^{-1} *untuk Cu(II), 171.83* mgg^{-1} *untuk Pb(II) dan 158.56* mgg^{-1} *untuk Ni(II). Dengan karbon teraktif ranting* Melia azedarach, *penyingkiran optimum ialah 99.50% Cu(II), 100% Pb(II), dan 89.17% Ni(II). Manakala kapasiti penjerapan optimum ranting* Melia azedarach *didapati 189.44* mgg^{-1} *untuk Cu(II), 171.83* mgg^{-1} *untuk Pb(II) dan 158.56* mgg^{-1} *untuk Ni(II). Kajian ini penting kerana karbon teraktif yang diperoleh daripada biojisim* Melia azedarach *telah menunjukkan kapasiti untuk menjadi* *produk nilai tambah sebagai penjerap yang mampu menyerap logam berat daripada medium akueus.*

. **Kata kunci:** *Sisa pertanian, penggunaan biojisim, penjerap hijau, metodologi permukaan tindak balas, pencemaran air*

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AC	Activated carbon
ANOVA	Analysis of variance
BET	Brunauer-Emmett-Teller
CCD	Central composite design
CGS	Centre for Graduate Studies
CHNS	Carbon, Hydrogen, Nitrogen, Sulphur
DOE	Design of Experiment
EDX	Energy Dispersive X-Ray
EPA	Environmental Protection Agency
FAAS	Flame atomic absorption spectrometer
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier Transform Infrared
LAC	Leaves Activated Carbon
HM	Heavy Metal
IUPAC	International Union of Pure and Applied Chemistry
MSS	Molten Salt Synthesis
RLP	Raw leaves powder
RMSE	Root Mean square error
RTP	Raw twigs powder
TAC	Twig Activated Carbon
UNIMAS	Universiti Malaysia Sarawak
2FI	Two Factor interaction

CHAPTER 1

INTRODUCTION

1.1 Study Background

Heavy metals contamination of the surface and groundwater has rapidly become an environmentally growing worldwide issue and threatening to human health (Razak et al., 2020). Sources of heavy metals contamination in the environment include industries like metallurgies, ceramics (Ngaini et al., 2021), paints, adhesives (Ghasemi et al., 2020), electroplating, mining, battery manufacturing (Wang & Wang, 2018), printing, fuels (Venkateswarlu et al., 2019), petroleum refineries, computer and television screens, roof and stained glass windows production (Kaya et al., 2020) and pesticides (Ullah et al., 2020). In addition to these, coal combustion and household wastes (Sen et al., 2018), typically contain significant amounts of metals with the potential to be poisonous, demanding extensive waste treatment (Adenuga et al., 2019).

Heavy metals like copper, lead and nickel, can accumulate in living tissues through the food chain, which eventually: causing damage to biosphere (Razak et al., 2020). In humans, heavy metal poisoning can cause high blood pressure, nausea, vomiting, disorientation, liver failure, brain haemorrhage, heart and renal disorders (Amin et al., 2019). According to the United States Environmental Protection Agency (US-EPA), the maximum contamination level in drinking water for Pb(II) is 0.05 mgL^{-1} (Aboli et al., 2020) and 0.25 mgL^{-1} for Cu(II) (Razak et al., 2020). While, based on World Health Organisation (WHO) guidelines, the limit for Ni(II) is 0.02 mgL^{-1} (Guo et al., 2020). In tandem to US-EPA guidelines, the permissible limits for Pb(II), Cu(II) and Ni(II) in wastewater are 0.01 mgL^{-1}, 2.5 mgL^{-1} and 2 mgL^{-1} respectively (Biswas et al., 2019). In order to preserve a healthy ecosystem, it is necessary to treat the heavy metal contaminated wastewater, before being released into water bodies (Taşar & Özer, 2020).

Several techniques have been employed for the removal of heavy metals from wastewater from either via physical (i.e. evaporation-condensation, reverse osmosis, membrane filtration) or chemical methods (i.e. ion exchange, chemical precipitation, solvent extraction) (Ibrahim et al., 2020). These traditional methods, nevertheless, have significant drawbacks (Herrera-Barros et al., 2020) such as solvent extraction restrictions, higher preparation costs, several phases involved and poor quality discharge (Adenuga et al., 2019; Crini & Lichtfzsouse, 2019). The coagulation and flocculation methods have several drawbacks, including insufficient heavy metal removal, high chemical use and increased sludge generation (Jin et al., 2020; Surendran & Baral., 2018).

Chemical methods which involve chemical precipitation is a slow process involving different chemicals in large quantities; and huge amounts of sludge that needs further treatment (Sen et al., 2018; Zamora-ledezma et al., 2021). While, ion-exchange process involves high capital involvement and high operation cost, suitable for low concentrations only, highly sensitive to effluents pH and requires physiochemical pre-treatment to avoid damage to beads of organic matters (Adenuga et al., 2019; Siong et al., 2021). Meanwhile, the physical approaches, which involve a process based on membrane-based technologies, has several limitations such as high energy requirements, higher operation and maintenance costs, and limited flowrates (Siong et al., 2021; Wang et al., 2018). Electrochemical technologies involves huge capital investments, high operation costs due to electricity supply; and ineffective at lower metal ion concentrations (Chen et al., 2020; Zamora-ledezma et al., 2021).

Adsorption is one of the versatile and efficient approaches often employed for the treatment of heavy metal-contaminated wastewater due to its operational simplicity, sludge-free operation and adsorbent reusability in long-term applications (Cao et al., 2019). Commercial activated carbon has been utilised for decades due to its qualities including high surface area, adsorption capacity, ion selectivity, thermal stability, resistance to transportation losses, ease of activation and regeneration (Ghasemi et al., 2020). However, its high cost is the principal obstacle to the industrial application for wastewater treatment (Ansari et al., 2018). Therefore, it is worthwhile to conduct extensive research on the preparation of low-cost adsorbents with specific properties and their utilisation for the removal of various pollutants in aqueous media (Georgieva et al., 2020). Agricultural and horticulture waste materials render prospective adsorbents for heavy metals removal from wastewater and an economical alternate to comparatively expensive activated carbon with comparable qualities by utilising widely available free resources (Hashem et al., 2020). Adsorbents made from agricultural and horticulture wastes have been demonstrated to be fairly effective in extracting heavy metals from wastewater even at very low concentrations (Surendran & Baral, 2018).

1.2 *Melia azedarach*

Melia azedarach tree is found all over the world including Asia, Europe, north and south America however it is native to India, Pakistan, Australia and south east Asia (Majid et al., 2021). A few previous studies have utilised various parts of *Melia azedarach* biomass