PREPARATION AND CHARACTERISATION OF INTEGRATED BIO-ADSORBENT CHITOSAN/HYDROXYAPATITE/RICE STRAW FROM BY-PRODUCTS FOR HEAVY METALS REMOVAL IN WATER TREATMENT

NORHAFIZA ILYANA BINTI YATIM

Thesis Submitted in Fulfilment of the Requirement for the Degree of Doctor of Philosophy in the School of Marine and Environmental Sciences
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DEDICATION

This work is devoted to

My lovely husband,
Mohd Yusof bin Samsudin

My adorable daughters,
‘Adani Fathonah binti Mohd Yusof,
Amina Syafiyya binti Mohd Yusof,
Annur Hana Tasnim binti Mohd Yusof
&
Aisyah Ainul Mardhiyah binti Mohd Yusof

My beloved parent,
Haji Yatim bin Mohamad
&
Hajjah Asiah binti Awang

Thank you for everything

Abstract of thesis presented to the Senate of Universiti Malaysia Terengganu in fulfilment of the requirement for the degree of Doctor of Philosophy

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NORHAFIZA ILYANA BINTI YATIM

2018

Main Supervisor : Associate Professor Marinah binti Mohd Ariffin, PhD

Co-Supervisor : Sofiah binti Hamzah, PhD

School : School of Marine and Environmental Sciences

The prevention and control of water pollution caused by heavy metals are of great emphasis due to its hazardous effect to the living organism. The revalorization of biowaste materials has led to the main objective of this study; to produce bio-adsorbent from agriculture (rice straw) and marine (hydroxyapatite, HAP) for heavy metal removal in water treatment. In order to produce a high affinity bio-adsorbent heavy metal ion, the surface of alkaline rice straw powders (RSA) was modified by integration with chitosan (CH), hydroxyapatite (HAP), and stabilizing agent (sodium hydroxide, NaOH). Firstly, HAP was synthesized from the bulk seashell via calcination at 1000°C followed by wet precipitation at different reaction times (3, 5, 24, 48, and 72 h). The bio-adsorbent (capable of removing 99.1% of Pb^{2+}) was produced at the reaction time of 48 h (HAP48). In the second stage of the study, equivalent ratios of HAP48 and CH at various composition percentages (5%, 15%, 25%, 35%, and 45%) were mixed prior to incorporation with 3 g of RSA to evaluate its removal capability towards selected heavy metal ions. The 25%CH-HAP48/RSA

bio-adsorbent formulation exhibited the highest heavy metal ions (Pb^{2+}, Fe^{3+}, Cu^{2+}, Mn^{2+}, Zn^{2+} and Ni^{2+} ions) removal capabilities with total adsorption capacity of 21.10 mg/g. This formulation was further modified with a stabilizing agent, NaOH at different molarities (0.1, 0.5, 1.0, 1.5 and 2.0 M) in order to improve the deposition of CH-HAP48 on RSA surfaces. It was found that 1.5 M of NaOH solution effectively stabilized the CH-HAP48 molecules by increasing the removal of multi-metal ions in the aqueous solution (total adsorption capacity = 32.14 mg/g). This was increased the pH within the solution and consequently, the amount of CH-HAP48 deposited was enriched and thus produced an effective bio-adsorbent, namely 25%CH-HAP48/RSA1.5M. The adsorption study showed that the experimental adsorption data were fitted with pseudo-second-order kinetic model. In the equilibrium study, data were fitted with the Langmuir isotherm with high values of R^2 for all metal ions (R^2> 0.9), indicating a homogenous and monolayer adsorption mechanism of the solute. Based on the maximum adsorption capacity, $q_{max,}$ 25%CH/HAP/RSA1.5M adsorbent had the highest adsorption capacity towards Pb^{2+}(75.19 mg/g) followed by Zn^{2+}(47.39 mg/g), Mn^{2+}(22.73 mg/g), Fe^{3+}(19.23 mg/g), Ni^{2+}(15.02 mg/g) and Cu^{2+}(10.72 mg/g). The maximum uptake of heavy metal ions of Fe^{3+}, Pb^{2+}, and Cu^{2+} occurred at pH<7; cations including Mn^{2+}, Zn^{2+}, Al^{3+} and Ni^{2+} showed a maximum uptake nearer to the neutral pH (pH 6.0). In conclusion, a promising green bio-adsorbent was successfully synthesized and applied in real wastewater treatment.

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PENYEDIAAN DAN PENCIRIAN BIO-PENJERAP INTEGRASI KITOSAN/HIDROKSIAPATIT/JERAMI PADI DARI HASIL SAMPINGAN UNTUK PENYINGKIRAN LOGAM BERAT DALAM RAWATAN AIR

NORHAFIZA ILYANA BINTI YATIM

2018

Penyelia Utama : Professor Madya Marinah binti Mohd Ariffin, PhD

Penyelia Bersama : Sofiah binti Hamzah, PhD

Pusat Pengajian : Pusat Pengajian Sains Marin dan Sekitaran

Pencegahan dan pengawalan pencemaran air yang disebabkan oleh logam berat sangat dititikberatkan kerana kesannya yang berbahaya kepada organisma hidup. Penambahbaikan bahan bio-sisa telah membawa kepada objektif utama kajian ini untuk menghasilkan bio-penjerap daripada sisa pertanian (jerami padi) dan laut (hidroksiapatit) untuk penyingkiran logam berat dalam rawatan air. Untuk menghasilkan bio penjerap jerami padi yang berkecenderungan tinggi terhadap ion logam berat, permukaan jerami padi alkali (RSA) telah diubah suai dengan penyepaduan kitosan (CH), hidroksiapatit (HAP) dan bahan penstabil, natrium hidroksida (NaOH). Pada mulanya, HAP telah disintesis daripada cengkerang melalui proses pengkalsinan pada 1000 °C diikuti oleh kaedah pemendakkan basah pada selang masa tindak balas yang berbeza (3, 5, 24, 48, dan 72 j). Bio-penjerap yang (berupaya menyingkirkan 99.1% ion logam Pb^{2+}) telah dihasilkan pada masa tindak balas selama 48 j (HAP48). Pada fasa kedua kajian, nisbah setara HAP48 dan CH pada pelbagai komposisi peratusan (5%, 15%, 25%, 35%, dan 45%) telah dicampur sebelum digabungkan dengan 3 g jerami padi alkali (RSA) untuk menilai keupayaan penyingkiran terhadap ion logam terpilih. Formula 25%CH-HAP48/RSA

bio penjerap mempamerkan ion logam berat tertinggi (Pb^{2+}, Fe^{3+}, Cu^{2+}, Mn^{2+}, Zn^{2+} and Ni^{2+} ion) berupaya disingkirkan dengan jumlah kapasiti penjerapan 21.10 mg/g. Formula ini dibuahsuai dengan bahan penstabil, NaOH pada kemolaran yang berbeza (0.1, 0.5, 1.0, 1.5 dam 2.0 M) bertujuan untuk meningkatkan pemendapan CH-HAP48 molekul pada permukaan RSA. Keputusan yang didapati menunjukkan bahawa 1.5 M larutan NaOH berkesan menstabilkan molekul CH-HAP48 dengan meningkatkan penyingkiran ion multi-logam dalam larutan akues (jumlah kapasiti penjerapan = 32.14 mg/g). Keadaan ini telah meningkatkan pH dalam larutan dan dengan itu jumlah CH-HAP48 termendap telah diperkaya dan menghasilkan bio-penjerap yang berkesan, iaitu 25%CH-HAP48/RSA1.5M. Kajian penjerapan menunjukkan bahawa data penjerapan eksperimen berpadanan dengan model kinetik tertib-kedua. Dalam kajian kesimbangan, data berpadanan dengan isoterma Langmuir dengan nilai R^2 yang tinggi untuk semua logam ion (R^2> 0.9), yang menunjukkan mekanisme penjerapan homogen dan satu lapisan oleh bahan larut. Berdasarkan kepada kapasiti penjerapan maksimum q_{max}, penjerap 25%CH-HAP48/RSA1.5M mempunyai kapasiti penjerapan tertinggi terhadap Pb^{2+}(75.19 mg/g) diikuti oleh Zn^{2+}(47.39 mg/g), Mn^{2+}(22.73 mg/g), Fe^{3+}(19.23 mg/g), Ni^{2+}(15.02 mg/g) dan Cu^{2+}(10.72 mg/g). Penjerapan maksimum ion logam berat Fe^{3+}, Pb^{2+}, and Cu^{2+} berlaku pada pH<7; kation termasuk Mn^{2+}, Zn^{2+}, Al^{3+} dan Ni^{2+} menunjukkan penjerapan maksimum pada nilai pH hampir kepada neutral (pH 6.0). Sebagai kesimpulan, bio-penjerap hijau yang berpotensi telah berjaya disintesis dan digunakan dalam rawatan air sisa yang sebenar.