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REMOVAL OF COPPER (II) IONS BY PHOSPHORIC ACID AND IMINODIACETIC ACID MODIFIED KENAF FIBER

MUHAMMAD RAZNISYAFIQ BIN RAZAK

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MUHAMMAD RAZNISYAFIQ BIN RAZAK

MASTER OF SCIENCE
UNIVERSITI PUTRA MALAYSIA

2014

REMOVAL OF COPPER (II) IONS BY PHOSPHORIC ACID AND IMINODIACETIC ACID MODIFIED KENAF FIBER

By

MUHAMMAD RAZNISYAFIQ BIN RAZAK

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

March 2014

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

REMOVAL OF COPPER (II) IONS BY PHOSPHORIC ACID AND IMINODIACETIC ACID MODIFIED KENAF FIBER.

By

MUHAMMAD RAZNISYAFIQ BIN RAZAK
March 2014

Chair: Nor Azah Yusof, PhD

Faculty: Science

Kenaf fiber can be chemically modified to enhancing their metal-binding ability by introducing new functional groups. The aim of this research was to prepare kenaf fiber (K) modified with phosphoric (K-PA) and iminodiacetic acid (K-IDA). The use of modified fiber for the removal of heavy metals which is Cu^{2+} is reported. The adsorbents is chemically modified with PA and IDA and in order to obtain the additional of functional group and the morphology in modified kenaf fiber, several characterization instruments were used such as Fourier Transform Infrared Analysis (FTIR), Elemental Analysis (CHNS), Scanning Electron Microscopy (SEM), Surface Area and Porosity Analysis (BET).

K-PA and K-IDA show an increase in adsorption capacity of $Cu^{2+}$when compared to the untreated fiber. The adsorption capacity of Cu^{2+} is in the following order: K-PA < K-IDA. Under the optimum conditions of pH 5 and a minimum of 0.1 g of adsorbent, K-PA and K-IDA adsorbsCu^{2+}at amounts corresponding to the maximum adsorption efficiencies with percentages of removal of 90% and 99%, respectively. The adsorption capacity increased with increasing initial Cu^{2+} concentrations and followed the Langmuir model and pseudo second order kinetic mechanism for K-PA and K-IDA. The maximum sorption capacities as calculated from the Langmuir isotherm for K-PA and K-IDA were 64.52 and 91.74 mg g^{-1} respectively. Higher adsorption capacity at higher temperature indicates that the Cu^{2+} sorption process is endothermic for all adsorbents. The free energy changes, $\Delta G°$ for the sorption by K-IDA was negative indicating that the sorption process is spontaneous, while vice versa for K-PA.

In the selectivity study, K_d for Cu^{2+} is higher than other heavy metal ions for K-IDA while K_d for Pb^{2+} is the highest value for K-PA. The foreign ion study showed that the sorption of Cu^{2+} was significantly affected by the presence of Cr^{3+}, Pb^{2+} and Zn^{2+} except while with K-IDA. For the desorption study, it was observed the highest percentage desorption of Cu^{2+} towards K-PA and K-IDA was 95.41%, 99.46% respectively by using 1 M hydrochloric acid. For the reusability study, adsorption

capacity for K-IDA did not vary until 4th cycle. Nevertheless, the adsorption capacity for K-PA suddenly decreases after the 2nd cycle.

Both modified kenaf fibers, K-PA and K-IDA were found to be effective for the removal of Cu^{2+} in real wastewater samples obtained from electroplating waste and wood treatment industries. In conclusion, the modified kenaf fiber has potential to be used as effective heavy metal adsorbent for water treatment.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Master Sains

PENYINGKIRAN LOGAM KUPRUM DENGAN MENGGUNAKAN FIBER KENAF YANG DIUBAHSUAI DENGAN PHOSPHORIK ACID DAN IMINODIACETIK ACID.

Oleh

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Fiber Kenaf boleh diubahsuai secara kimia untuk meningkatkan keupayaan mengikat logam dengan pengenalan kumpulan baru berfungsi. Tujuan kajian ini adalah untuk menyediakan gentian kenaf (K) fungsi dengan asid fosforik (K-PA) dan asid iminodiacetik (K-IDA). Gentian kenaf yang diubahsuai digunakan untuk penyingkiran logam berat seperti Cu^{2+} dilaporkan. Bahan penjerap diubahsuai secara kimia dengan menggunakan PA dan IDA dan untuk mendapatkan penambahan kumpulan baru berfungsi dan morfologi pada bahan penjerap yang diubahsuai, beberapa peralatan telah digunakan seperti Fourier Transform Infrared Analysis (FTIR), Elemental Analysis (CHNS), Scanning Electron Microscopy (SEM), Surface Area dan Porosity Analysis (BET).

K-PA dan K-IDA menunjukkan peningkatan dalam kapasiti penjerapan Cu^{2+} berbanding dengan gentian Kenaf yang tidak diubahsuai. Kapasiti penjerapan terhadap Cu^{2+} berada dalam susunan yang berikut: K-PA $<$K-IDA. K-PA dan K-IDA menjerap Cu^{2+} ion logam berat dalam keadaan optimum pada pH 5 dan 0.1 g berat penjerap minimum dengan maksimum kecekapan penjerapan dengan peratusan penyingkiran adalah 90% dan 99% masing-masing. Kapasiti penjerapan meningkat dengan peningkatan kepekatan awal Cu^{2+} dengan mengikuti model Langmuir dan pseudo kinetic tertib kedua untuk K-PA dan K-IDA. Kapasiti penjerapan maksimum yang dikira dari Isoterma Langmuir untuk K-PA dan K-IDA adalah 64.52 dan 91.74 mg g^{-1}. Kapasiti penjerapan yang lebih tinggi pada suhu yang tinggi menunjukkan bahawa proses penjerapan Cu^{2+} adalah endotermik untuk semua bahan penjerap. Perubahan tenaga bebas, $\Delta G°$ untuk penjerapan oleh K-IDA adalah negatif menunjukkan bahawa proses penjerapan adalah spontan manakala sebaliknya untuk K-PA.

Untuk kajian pemilihan, K_d untuk Cu^{2+} yang lebih tinggi daripada logam berat yang lain untuk K-IDA manakala K_d untuk Pb^{2+}adalah nilai tertinggi bagi K-PA. Kajian ion asing menunjukkan bahawa penyerapan Cu^{2+} telah terjejas dengan ketara

terhadap K-PA dengan kehadiran Cr^{3+}, Pb^{2+} dan Zn^{2+} kecuali K-IDA. Untuk kajian penyahjerapan diperhatikan peratusan penyahjerapan tertinggi Cu^{2+} terhadap K-PA dan K-IDA adalah 95.41% 99.46%, masing-masing dengan menggunakan asid hidroklorik 1 M. Kapasiti penjerapan tidak banyak berubah untuk K-IDA (antara 11.6-10.1 mg/g) bagi setiap penggunaan berulang. Walaubagaimanapun, kapasiti penjerapan untuk K-PA adalah penurunan mendadak selepas kitaran 2.

Akhir sekali, kedua-dua gentian kenaf diubahsuai iaitu K-PA dan K-IDA didapati berkesan untuk menyingkirkan Cu^{2+} dalam sampel air sisa sebenar yang diperolehi daripada sisa penyaduran dan industri rawatan kayu. Kesimpulannya, gentian kenaf yang diubahsuai mempunyai potensi untuk digunakan sebagai penjerap logam berat yang berkesan untuk rawatan air.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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LIST OF ABBREVIATIONS

ppm	Parts per million
q_e	Amount of adsorbate per unit weight of adsorbent in equilibrium
C_e	Equilibrium concentration of the adsorbate
K_L	Langmuir constant
K_F	Freundlich constant
K	Rate constant
q	Amount or sorbate on the surface of adsorbent at any time
q_e	Adsorption capacity
IDA	Iminodiacetic acid
PA	Phosphoric acid
K-PA	Kenaf fiber modified with phosphoric acid
K-IDA	Kenaf fiber modified with iminodiacetic acid
T	Temperature in Kelvin
K_1	Rate constant of sorption for pseudo-first-order
K_2	Rate constant of sorption for pseudo-second-order
V	Volume
m	Mass
k_d	Distribution coefficient
ΔH	Enthalpy
ΔS	Entropy
ΔG	Gibbs Free Energy
R	Coefficient correlation

t	Time in minute
R^2	Correlation of determination
C_f	Final solution
Ci	Initial Concentration
M	Molarity

CHAPTER 1
INTRODUCTION

1.1 Background of Study

Heavy metal ions can be harmful to aquatic world and human health through contaminated water. Heavy metal ions are mainly pollutant to the environment for their mobility in natural water ecosystem and due to their toxicity (Volesky and Holant, 1995). Heavy metal ion cannot be degraded and destroyed, so they can accumulate in the human body (Qaiser*et al.*, 2007). Accumulation in human body can lead to reduction in mental, cognitive, physiological and neurological disorder.Several noted human toxicities for certain heavy metals were listed in Table 1.1 (Davidson, 2010).

Guideline limits value from World Health Organisation’s (WHO) for copper heavy metal in drinking water was 2 mg/L (WHO, 2004). Overall human body contains about 1.4 to 2.1 mg/kg copper and Dietary References intake for copper is quoted as 0.97 to 3.0 mg/day (Davidson, 2010). The main intake is normally through the diet and water consumption. Copper can be found naturally in sunflower seeds, oyster and lobster.

Copper can be found in binary compound such as copper (I) oxide and copper (II) oxide which is red and deep blue colour. Copper ions also essential element for human health in functioning organs and metabolic processes such as blood formation and iron utilization. Elevated levels of copper are associated with body disorder such as liver damage, Wilson disease, insomnia, osteoporosis and leukaemia (Tapiero*et al.*, 2003). In this century, there is exponential growth for production of copper that used in modern industries such as plumbing, electrical, construction and stainless steel industry.

Table 1.1.Toxicities of some heavy metal.

Heavy metal	Toxicities
Arsenic	Gastrointestinal, cardiovascular, nervous system disruption, bone marrow depression, haemolysis, hepatomegaly, melanosis, polyneuropathy and encephalopathy, death
Cadmium	Kidney damage, renal disorder, Itai-Itai, carcinogenic
Chromium	Headache, nausea, diarrhea, vomiting, carcinogenic
Copper	Liver damage, Wilson disease, insomnia
Gold	Autoimmunity
Lead	Autoimmunity, headache, irritability, abdominal pain, various nervous system and psychological disturbances, retardation
Mercury	Tremors, changes in personality, restlessness, anxiety, sleep disturbance, depression, autoimmunity, death
Nickel	Dermatitis, nausea, chronic asthma, coughing, carcinogenic
Zink	Depression, lethargy, seizures, ataxia, thirst

1.2 Problem Statement

Heavy metals have been used in many different areas for thousands of years. For examples, lead and mercury has been used for at least 5000 years as building material and medicine to reduce teething pain in infants. Nowadays, there are increasing in consumption of heavy metal in daily life although health effect of heavy metal towards human body was known (Järup, 2003). Environmental pollution is mainly caused by rapid industrialisation and increase in modern agriculture chemicals in the developing country. One of the environmental pollution was water pollution caused by untreated released of effluent by industries such as cosmetics, electroplating, fuel, plumbing hardware and textile. Thus, it is necessary to study regarding the removal of heavy metal in water sample.

Activated carbon is the most used adsorbent to adsorb heavy metal in wastewater in these recent years, but unfortunately activated carbon is relatively expensive (Gabaldon, 1996). In order to produce cheaper adsorbents, lignocellulosics materials such as sawdust, husks, rice hulls, nut shells, jute, oil palm empty fruit bunch (OPEFB) and kenaf is used as an adsorbent. Kenaf fiber is renewable and biodegradable. Economically, kenaf fiber is good sorbent since it is low cost while commercial activated carbon is expensive. Moreover, kenaf fiber is constituted by a lignocellulosic which enhance the capability to adsorb the heavy metals (Joly*et al.*, 1996; Marcovich*et al.*, 1996). Based on the previous study, although kenaf fiber has been modified for removal of heavy metal in wastewater using different functional groups (Lee and Rowell, 2004; Sciban *et al.*, 2006), the modification did not increase the adsorption capacity very much. Therefore, modification of kenaf fiber using IDA and PA are important to know the adsorption towards heavy metals in wastewater.

1.3 Objectives

The study was carried out to achieve the following objectives:

- To modify and characterise kenaf fibre with chelating compound such as phosphoric acid and iminodiacetic acid.
- To investigate the parameters such as pH, adsorbance dosage, initial metal concentration, temperature and also study regarding kinetic parameter, selectivity, desorption and reusability by utilizing modified kenaf fiber for removal of Cu heavy metal from aqueous solution by the modified kenaf fibre.
- To apply the modified kenaf fibre for removal of heavy metal in waste water.

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