CARBON FROM AGRICULTURAL WASTE AS AN ADSORBENT IN THE REMOVAL OF CHROMIUM AND NICKEL IONS FROM AQUEOUS SOLUTION

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by

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DEDICATION

This work is dedicated to my husband, Bazli Azmi for his full support and to my childrens Muhammad Irfan, Muhammad Nabil, Nurul Irdina, Nurul Nabihah and Nurul Hasanah for appreciating and understanding Ummi.

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NOMENCLATURE

Symbol	Description	Unit
C_e	The concentration at equilibrium in solution	mg/L
C_i	The initial concentration in the solution	mg/L
C_t	The concentration at time, t in solution	mg/L
I	The constant of intraparticle diffusion	mg/g
K_a	Langmuir constant	L/mg
K_f	Freundlich constant	L/g
k_1	The rate constant of pseudo-first order adsorption	L/min
k_2	The rate constant of pseudo-second order adsorption	g/mg min
k_{id}	The initial rate intraparticle diffusion	g/mg $min^{1/2}$
M	The mass of adsorbent	g
n	Dimensionless emperical constant	-
q_e	The concentration of solute adsorbed on the solid at equilibrium	mg/g
q_i	The initial concentration of solute adsorbed on the solid	mg/g
q_m	Maximum adsorption capacity	mg/g
q_t	The concentration of solute adsorbed on the solid at time, t (Adsorption capacity at time, t)	mg/g
R	The removal efficiency	%
R_L	Dimensionless constant separation factor	-
T	Time	min
V	Volume of the solution	L

LIST OF ABBREVIATION

Aluminium oxide	Al_2O_3
Ammonium persulphate	$NH_4S_2O_8$
American Society for Testing and Materials Standard	ASTM
Atomic Absorption spectrometry	AAS
Brunauer-Emmet-Teller	BET
Biochemical Oxygen Demand	BOD
Chemical oxygen Demand	COD
Energy Dispersive X-ray	EDX
Environmental Protection Agency	EPA
Fourier Transform Infrared	FT-IR
Granular activated carbon	GAC
Hydrochloric acid	HCl
International Union of Pure and Applied Chemistry	IUPAC
Nickel(II) sulphate-6-hydrate	$NiSO_4.6H_2O$
Phosphoric acid	H_3PO_4
Phosphoric pentoxide	P_2O_5
Potassium dichromate	$K_2Cr_2O_7$
Potassium hydroxide	KOH
Potassium oxide	K_2O
Powder activated carbon	PAC
Rice straw	RS
Rice straw carbon	RSC

Scanning Electron Microscopy	SEM
Silicon dioxide	SiO_2
Sugarcane bagasse	SB
Sugarcane bagasse carbon	SBC
Sodium hydroxide	NaOH
Sulfuric acid	H_2SO_4
Zinc chloride	$ZnCl_2$

Karbon daripada sisa pertanian sebagai penjerap dalam penyingkiran ion-ion kromium dan nikel dari larutan akueus

ABSTRAK

Objektif kajian ini adalah untuk menghasilkan karbon daripada hampas tebu dan jerami padi melalui teknik pirolisis sebagai penjerap kepada nikel(II) dan kromium(VI) dan untuk menentukan keadaan optima bagi hubungan dengan masa sentuhan, pH larutan, dos penjerap, saiz zarah penjerap, kepekatan awal larutan dan suhu. Juga penjerapan garis sesuhu dan kelakuan kinetik penjerapan bagi penyingkiran nikel(II) dan kromium(VI) oleh setiap penjerap akan ditentukan.

Hampas tebu dan jerami padi adalah sisa pertanian tempatan yang murah dan mudah didapati. Bahan-bahan mentah tersebut telah dipirolisiskan pada julat suhu 300 – 700ºC selama 30 minit dengan kadar pembakaran purata 30 ºC/minit.

Penjerap-penjerap itu telah dikaji ciri-ciri seperti hasilan, ketumpatan, pH, kandungan abu, kadungan lembapan, keluasan permukaan dan keliangan dengan menggunakan Penganalisa keluasan permukaan dan keliangan BET, gugusan permukaan dengan menggunakan Pengubah Fourier inframerah, morfologi permukaan dengan menggunakan Elektron mikroskop imbasan dan elemen serta komposisi kimianya dengan menggunakan Serakan tenaga sinar-X.

Penjerapan didapati telah dipengaruhi oleh suhu pirolisis dan luas permukaan. Penjerap-penjerap yang dihasilkan pada suhu 700 ºC telah dipilih untuk kajian penjerapan ini kerana ia menghasilkan peratus penyingkiran yang tertinggi. Keupayaan penyinggiran maksimum Ni(II) ke atas RSC dan SBC adalah masing-masing 85.65% dan 21.79%, dan Cr(VI) ke atas RSC dan SBC pula adalah masing-masing 61.81% dan 76.10%

Operasi parameter-parameter termasuk masa sentuhan (15 – 210 minit), pH larutan (1.0 – 10.0), suhu (25, 30, 45 and 55 ºC), saiz partikel (1.18 mm, 600 µm, 300 µm and 150 µm), dos penjerap (0.04, 0.10, 0.20, 0.40, 0.6 and 1.0 g) dan kepekatan awal larutan (10, 25, 50, 75 and 100 mg/L). Eksperimen-eksperimen telah dijalankan secara berkelompok. Masa sentuhan, banyaknya penjerap, suhu, saiz partikel dan kepekatan awal larutan ion logam berat telah memberi kesan kepada muatan penjerapan, namun begitu yang paling penting keputusannya bergantung kepada pH larutan.

Data telah dianalisis dengan menggunakan persamaan Langmuir dan Freundlich. Kebolehgunaan penjerapan telah ditunjukkan dengan model garis sesuhu Langmuir and Freundlich. Ia menujukkan hahawa model garis sesuhu Langmuir padan data dengan baik bagi nickel(II) and chromium(VI). Nilai koefisien pembetulan R^2 yang tinggi dan factor pemisah tak berdimensi, R_L yang didapati menunjukkan bahawa penjerapan kedua-dua penjerap adalah baik. Model kinetik pseudo tertib pertama, pseudo tertib kedua dan model resapan intrazarah telah digunakan dengan menganalisis data eksperimen kinetik. Ia

menunjukkan kedua-dua penjerap mematuhi kinetik pseudo tertib kedua dengan baik. Kebolehan kedua-dua penjerap menjerap nikel(II) and kromium(VI) juga telah dibandingkan. Ia menunjukkan bahawa muatan penjerapan karbon jerami padi lebih baik bagi penjerapan nikel(II) kerana kehadiran gugusan oksigen permukaan, caj permukaan, tinggi kandungan silica dan sifat-sifat nikel sendiri. Sebaliknya karbon hampas tebu mempunyai muatan penjerapan yang tinggi terhadap kromium(VI) kerana mempunyai keluasan permukaan yang tinggi, caj permukaan dan sifat-sifat kromium itu sendiri.

Carbon from agricultural waste as an adsorbent in the removal of chromium and nickel ions from aqueous solution

ABSTRACT

The objectives of this study were to produce carbon from sugarcane bagasse and rice straw by pyrolysis technique as an adsorbent for heavy metal removal and to determine the optimum condition with respect to contact time, pH of solution, adsorbent doses, particle sizes of adsorbent, initial metal concentration and temperature. Also adsorption isotherm and adsorption kinetic behavior of nickel(II) and chromium(VI) removal by each adsorbent will be determined.

Sugarcane bagasse and rice straw are inexpensive and locally available agricultural waste. The raw materials were pyrolized at different temperatures ranging from 300 – 700 °C for 30 minutes with the average heating rate of 30 °C/minute.

The adsorbents were characterized for the yield, density, pH, ash content, moisture content, surface area and porosity by using BET surface area and porosity analyzer, functional groups by using Fourier Transform Infrared, surface morphology by using Scanning Electron Microscope and element and chemical composition by using Energy Dispersive X-ray.

Adsorptions were found to be effected by pyrolyzing temperature and surface area. The adsorbents that produced at 700 °C have been chosen for this adsorption study because it produced the highest percentage of removal.The maximum removal efficiency of Ni(II) on RSC and SBC as 85.65% and 21.79 %, respectively and Cr(VI) on RSC and SBC as 61.81 % and 76.10 %, respectively.

The operation parameters included contact time (15 – 210 minutes), pH of solution (1.0 – 10.0), temperature (25, 30, 45 and 55 °C), particle sizes of adsorbents (1.18 mm, 600 µm, 300 µm and 150 µm), adsorbents doses (0.04, 0.10, 0.20, 0.40, 0.6 and 1.0 g) and initial concentrations of adsorbates (10, 25, 50, 75 and 100 mg/L). The experimental tests were conducted in batch process. The contact time, amount of adsorbent, temperature, particle size of adsorbent and initial concentration of the metal ions solutions affect the adsorption efficiency but most importantly depended on the pH of solution.

The experimental isotherms data were analyzed by using Langmuir and Freundlich equation. The applicability of adsorption was described by using the Freundlich and Langmuir adsorption isotherm. It was found that Langmuir isotherm model fit well the data for nickel(II) and chromium(VI). The measured high linearity of correlation coefficient, R^2 and the values dimensionless separation factor, R_L indicated a favorable adsorption of both Ni(II) and Cr(VI) onto RSC and SBC, respectively. While, the adsorption kinetics, pseudo-first order model, pseudo second order model and intra-

particle diffusion model were analyzed on the experimental kinetics data. It was found that the pseudo second order kinetic model described the adsorption kinetic of both adsorbent well. The performance of both adsorbent in the removal of nickel(II) and chromium(VI) were also compared. It was found that the adsorption capacity of rice straw carbon on nickel(II) was high may be due to the present of surface oxygen groups, surface charge, high silica content and the properties of nickel. While, the adsorption capacity of sugarcane bagasse carbon on chromium(VI) was high was caused by the high surface area of the adsorbent, surface charge and the properties of chromium..

CHAPTER ONE

INTRODUCTION

1.1 Agricultural waste

Principal sources of agricultural waste are mainly farming activities or agro-industry, such as crops harvesting, abattoirs and tanneries. Waste includes organic sludge effluents, used pesticides and fertilizers, chemical containers and crop residues. Waste is often defined as something unwanted and has no economic value. However, increasingly waste generation may provide a source with certain economic values for another usage. Whereas new products can be generated from various kinds of crop residues with appropriate technology, for examples generation of energy from palm oil waste, production of compost or fertilizer from rice hull and converting rice husk to carbon and etc. Furthermore, waste if not handled properly will effect to human health and the environment (IMPAK, 2006).

Agricultural waste which is available and inexpensive in some places may be a better option for adsorbent production. A few adsorbents that stand out for high adsorption capacities are agricultural waste such as coconut shell and coirpith. These adsorbents are efficient and can be effectively used for inorganic effluent treatment containing metal ions (Babel and Kurniawan, 2004). Recently, various low cost adsorbents derived from agricultural waste, industrial by-products or natural materials, had been investigated intensively for heavy metal removal from contaminated wastewater (Kurniawan *et al*., 2006).