UNIVERSITI PUTRA MALAYSIA

ADSORPTION OF BORON USING MODIFIED MULTIWALLED CARBON NANOTUBES

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ADSORPTION OF BORON USING MODIFIED MULTIWALLED CARBON NANOTUBES

By

NIMA ZOHDI

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

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Specially dedicated to

My mother, my father and my sisters Neda and Yalda who are the most beloved persons in my life, for their love, understanding, endless patience and encouragement when it was most needed.

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

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Chairman Thomas Choong Shean Yaw, PhD

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Boron is mostly used in the form of boric acid and borates in various industries. However, due to its toxicity to animals and plants, discharge of boron contained waste must be controlled at sustainable and safe level. In order to remove boron from the water to a desirable level to meet the requirement set by the legislation, multi walled carbon nanotubes (MWCNT) was used and modified by using three different chemicals which are glucose, sorbitol and tartaric acid. Surface chemistry of modified-MWCNT (m-MWCNT) was studied through Boehm technique to evaluate the quantity of oxygen containing functional groups. The results showed that tartaric acid m-MWCNT contained the highest amount of oxygen containing functional groups. Also, Fourier Transform Infrared Spectroscopy (FTIR) confirmed that carboxylic groups were formed on the surface of the m-MWCNT. Brunire Emmett Teller (BET) results showed no significant increase in surface area after modification of MWCNTs with these three organic chemicals comparing to the unmodified-MWCNTs.

Boron adsorption characteristic of m-MWCNT samples was investigated under different pH, dosage of m-MWCNT, initial boron concentration, contact time and temperature. The tartaric acid m-MWCNT adsorbed the maximum amount of 1.97 mg/g of boron from contaminated water at pH of 6, temperature of 25 °C, contact time of 60 min and dosage adsorbent of 0.4 g/l. At the same condition glucose m-MWCNT and sorbitol m-MWCNT adsorbed around 1.53 and 1.14 mg/g of boron respectively. The isotherm study of the adsorption revealed that adsorption behavior was best described by Freundlich model for all three modified samples. Lagergren-first-order, Pseudo-second-order and Intraparticle diffusion models were applied to determine the kinetics of the adsorption process. Pseudo-second order results showed higher coefficient of determination (R^2) values for all three modifications comparing to the Lagergren-first-order.

Sample with the highest adsorption capacity from the adsorption experiments was MWCNT modified with tartaric acid. It was selected for solid-liquid separation study where it was impregnated with magnetic property. Magnetized m-MWCNT was characterized by using FTIR, X-ray differactometer (XRD), SEM and EDX. The change in boron adsorption behavior of magnetized tartaric acid m- MWCNTs was also studied. Boron adsorption capacity of m-MWCNTs decreased very slightly from 1.97 mg/g to 1.91 mg/g. Separation of used m-MWCNT was carried out successfully by using a simple magnet. The quantitative analysis showed that only 0.03% of magnetized MWCNT was not adsorbed by the magnet.

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

PENJERAPAN BORON MENGGUNAKAN TIUB-TIUB NANO KARBON MULTIWALLED DIUBAH SUAI

Oleh

NIMA ZOHDI

Mei 2013

Pengerusi **Thomas Choong Shean Yaw, PhD**

Faculti **Fakulti kejuruteraan**

Boron secara kerapnya digunakan dalam industri dalam bentuk asid boric dan borates. Walau bagaimanapun pengeluaran sisa boron harus dikawal pada tahap kelestarian yang selamat. Untuk mengeluarkan boron daripada boron pada tahap yang dikehendaki bagi memenuhi keperluan yang ditetapkan oleh perundangan. Tiub nano karbon dinding pelbagai (MWCNT) telah diubahsusi oleh tiga bahan kimia yang berlainan iaitu glukosa, sorbitol dan asid tartarik. Permukaan kimia yang diubahasuai-MWCNT telah dikaji melalui teknik Boehm untuk menilai kuantiti oksigen yang mengandungi kumpulan berfungsi. Hasil kajian menunjukkan bahawa asid tartarik m-MWCNT mengandungi jumlah oksigen yang tertinggi dalam kumpulan berfungsi. Selain itu, Spectroskopi inframarah transformasi fourier (FTIR) juga mengesahkan bahawa kumpulan karboksilik terbentuk di atas permukaan MWCNT. Keputusan daripada analysis Brunire Emmet Teller (BET) menunjukkan bahawa tidak terdapat peningkatan

ketara pada luas permukaan pada MWCNT yang dimodifikasi dengan tiga jenis bahan kimia organic ini berbanding MWCNT yang tidak dimodifikasi.

Ciri-ciri penjerapan boron oleh m-MWCNT sampel telah dikaji di bawah pH, kepekatan awal boron dan masa penjerapan yang berlainan. Dalam keadaan yang optimum, asid tartarik m-MWCNT menunjukkan penjerapan boron yang maksimum (1.97 mg / g) daripada air yang tercemar pada pH 6, suhu 25°C, masa penjerapan 60 min dan dos adsorben 0.4g / l. Dalam keadaan operasi yang sama glukosa m-MWCNT dan sorbitol m-MWCNT terjerap 1.53 dan 1.14 mg / g boron. Penyelidikan ini mendedahkan bahawa ciri-ciri penjerapan isoterma mengikuti model Freundlich untuk ketiga-tiga sampel yang diubahsuai. Lagergren-order-pertama, Pseudo-order-kedua model penyerapan intra partikel telah digunakan untuk menentukan proses kinetik. Keputusan menunjukkan nilai R^2 yang lebih tinggi bagi ketiga-tiga pengubahsuaian membandingkan kepada order pertama Lagergren. Sampel dengan keupayaan penjerapan iaitu asid tartarik m-MWCNT telah dipilih untuk kajian pemisahan pepejal bendalir melalui teknik permagnetan. m-MWCNT yang telah melalui permagnetan telah dicirikan dengan menggunakan FTIR, X-ray differactometer (XRD) dan EDX. Perubahan dalam tingkah laku penjerapan boron oleh tartarik asid-m MWCNT yang dimagnet juga dikaji. Kapasiti penjerapan boron oleh sampel termagnet menurun sedikit daripada 1.97 mg / g kepada 1.91 mg / g. Pemisahan m-MWCNT terguna melalui teknik pemagnetan yang mudah telah dijalani dengan berjaya. Keputusan secara kuantitatif menunjukkan bahawa hanya 0.03% MWCNT bermagnet yang tidak terjerap oleh magnet.

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

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DECLARATION

I hereby declare that the thesis is my original work expect for quotations and citations which have been duly acknowledged. I also, declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institutions.

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NIMA ZOHDI

Date: 14 May 2013

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LIST OF ABBREVIATIONS

1/n	Freundlich exponent
AC	Activated Carbon
Å	Angstrom
B	Boron
°C	Degree centigrade
C	Concentration
C_{Ae}	Amount of adsorbate on the adsorbent
C_e	Equilibrium concentration of adsorbate in solution after adsorption
C_f	Final concentration
C_i	Initial concentration
CHNS-O	Carbon, Hydrogen, Nitrogen, Sulfur - Oxygen
cm	Centimeter
cm^{-1}	Reciprocal centimeter
CNT	Carbon Nanotube
EDTA	Ethylenediaminetetraacetic acid
EDX	Electron Dispersive X-ray
FT-IR	Fourier transform infra red
g	Gram
g/l	Gram per litter
h	Hours
h (mg/g min)	Sorption rate
HCl	Hydrochloric acid
K	Degree Kelvin
k_1	Lagergren first-order rate constant
k_2	Rate constant for pseudo-second-order

K_c	Equilibrium constant
K_f	Empirical Freundlich constant or capacity factor
K_L	Empirical Langmuir constant
k_p	Intraparticle diffusion rate constant
KBr	Potassium bromide
KNO_3	Potassium nitrate
KOH	Potassium hydroxide
L	Litter
l/g	Litter per geram
m-MWCNT	Modified-MWCNT
mmol/g	Mili mole per gram
mg	Milligram
mg/g	Miligeram per geram
mg/l	Milligram per litter
min	Minutes
ml	Milliliter
MWCNT	Multiwalled Carbon Nanotube
Na_2CO_3	Sodium carbonate
$NaHCO_3$	Sodium bicarbonate
NaOH	Sodium hydroxide
nm	Nanometer
pH_f	Final Ph
pH_I	Initial pH
pH_{pzc}	pH of point of zero charge
q	Adsorption
q_0	Empirical Langmuir constant which represents maximum adsorption capacity
q_{cal}	Calculated adsorption

q_e	Amount adsorbate adsorbed per unit weight of adsorbent at equilibrium
q_{exp}	Experimental adsorption
q_t	Adsorption capacities at time t
R	Universal gas constant (8.314 J/mol-K)
R^2	Correlation coefficient
SWCNT	Single Wall Carbon Nanotube
UV/Vis	Ultra Violet Visible spectroscopy
wt%	Weight percentage
XRD	X-Ray Diffractometer
ΔpH	pH_i - pH_f
ΔG	Mtandard free energy change
ΔH	Standard enthalpy change
ΔS	Standard entropy change

CHAPTER 1

INTRODUCTION

1.1 Background

Water pollution happens when lakes, rivers, oceans, aquifers, ground water or other bodies of water become contaminated. Pollutants that are directly or indirectly released into the water bodies will cause water pollution. These contaminating pollutants will negatively affects the plants and organisms, damaging not only to individual species and populations, but also to the natural biological communities that exists in and around the polluted water bodies.

Some examples of water pollutant elements are: metals, metalloids and heavy metals such as Nickle (Ni(II)) (Yang et al., 2009), Zinc (Zn(II)) (Lu, 2007), Lead (Pb(II)) (Atieh et al., 2010), Arsenic (As) (Tawabini et al., 2011), Cu(II) (Kuo, 2009) and boron (B) (Chong et al., 2009); dyes such as methylene blue (Ai et al., 2011) and methyl orange (Yao et al., 2011); inorganic materials such as dioxin (Long and Yang, 2001), diuron and dichlobenil (Chen et al., 2011). Among all contaminants as mentioned above, boron (B) and its removal from water solution is the target of this investigation. High boron concentrations can be found in wastewater from some industries including semiconductor (May and Costas J, 2006), ceramic (Chong et al., 2009), borosilicate glass (Stevie et al., 1991) and detergent manufacturers (Vengosh et al., 1994).

Excessive consumption of boron will cause the lethal if it is more than the dosage of 640 mg per kg body weight (WHO, 2009). According to the legislation requirement of Department of Environment (DOE), Malaysia, the boron concentration should be reduced to below 1 and 4 mg/L for effluent discharge standards A and B (Environmental Quality Act, 1974) respectively. Standards A and B are related to the upstream and the downstream region of the water catchment area respectively.

Numerous investigations has been done for boron removal from water and wastewater by different methods such as coagulation, co-precipitation (Turek et al., 2007), adsorption, ion exchange using cation exchangers (Popat et al., 1988) , selective ion-exchange resins (Badruk et al., 1999), solvent extraction (Matsumoto et al., 1997), and membrane operations (Redondo, 2003). In water treatment different adsorbents were employed, such as activated carbon (Kluczka et al., 2007), fly ash (Chong et al., 2009), resins (Ersan and Pinarbasi, 2011), metal oxides (Prodromou, 2003), clay minerals (Draoui et al., 1999) and composite magnetic particles (Liu et al., 2009).

Multi-walled carbon nanotubes (MWCNTs) is an effective adsorbent for removing contaminants from water and wastewater due to large surface area, fibrous shape with high aspect ratio and well developed mesopores. MWCNTs showed a very good potential for removing metals and heavy metals, dyes and inorganic materials from aqueous solutions (Lv et al., 2011; Yao et al., 2011).

1.2 Problems statement

Release of wastewater into water could result to the spoil of drinking and ground water quality. Among the contaminants, boron (B) is one of the important elements that can be cause to lethal more than 640 mg/kg body weight by oral intake according to the World Health Organization (WHO) report 2009.

Many adsorbents have been used to remove boron from water and wastewater such as activated carbon, fly ash, resins, metal oxides, clay materials and composite magnetic particles. However, the removing costs like filtration or precipitation processes are the main disadvantages of using these materials as an adsorbent (Chong et al., 2012). The fine and small particles need to be removed from the solution easily and efficiently.

MWCNTs as an adsorbent showed a very good potential adsorption properties for removing contaminations such as metals and heavy metals (Tawabini et al., 2011; Yang et al., 2009), dyes (Ai et al., 2011; Yao et al., 2011) and inorganic materials (Chen et al., 2011; Long and Yang, 2001) from water-based solutions. However, the advantage of using MWCNTs which makes them unique adsorbents to remove contaminants from solution is the ability to remove easily from solution. Comparing other common adsorbents, magnetizing MWCNTs is known as a promising method for removal of contaminated MWCNTs from solution after the adsorption process and it has been suggested by numerous works (Ai et al., 2011; Gong et al., 2009; Madrakian et al.

2011). Through acid elution (Srivastava, 2013) and also exposure to acidic environment at different contact times (Kosa et al., 2012).

In current study the potential efficiency of MWCNT for boron removal from synthetic solution was studied in batch system as is considered as the usual system for adsorption of boron (Çelik et al., 2008; Chong et al., 2012; Kluczka et al., 2007).

1.3 Objectives of work

The objectives of this research are listed as follows:

1) Modification of MWCNTs surface by using tartaric acid, sorbitol, and, glucose for increasing the boron adsorption capacity of MWCNTs.

2) Investigation of the effect of various parameters which include pH, dosages of adsorbent, initial boron concentration and different contact time on boron adsorption behaviour of m-MWCNTs to find the optimal conditions for highest boron adsorption capacity.

3) Evaluate the m-MWCNTs-liquid separation efficiency by magnetizing the surface of the used MWCNTs.

1.4 Scopes of work

In this study, the surface of MWCNTs was modified with tartaric acid, sorbitol and glucose to increase the potential adsorption capacity of MWCNTs. Characterization of the surface of MWCNTs and modified MWCNTs (m-MWCNTs) was done through CHNS-O elemental analysis, Boehm surface chemistry technique, Brunauer ±Emmett± Teller (BET), thermo gravimetric analysis (TGA) and fourier transform infrared spectroscopy (FTIR).

The adsorption behavior of boron on m-MWCNTs was studied under different pH, dose of adsorbent, contact time and temperature by using batch adsorption study. The isotherm models (Langmuir and Freundlich) and also the kinetics of the adsorption behavior of samples were also investigated by using regression analysis.

The sample of m-MWCNTs with the highest adsorption property was selected for magnetic impregnation by modifying the surface with iron oxide particles. The m-MWCNT was added to a solution of ammonium iron (II) sulfate hexahydrate and hydrazine followed by sonicating and refluxing the mixture for 2 hours. Magnetized MWCNTs were characterized by using the FTIR, X-ray diffractometer (XRD), electron dispersive X-ray analysis (EDX) and scanning electron microscopy (SEM). Adsorption property of magnetized m-MWCNTs was also studied under the optimal conditions obtained from the second objective. Then the separation of spent adsorbent was studied by using a simple magnetic technique.

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