UNIVERSITI PUTRA MALAYSIA

ADSORPTION OF QUARTERNIZED PALM KERNEL SHELL FOR FLUORIDE REMOVAL

AYU HASLIJA BT ABU BAKAR

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By

AYU HASLIJA BT ABU BAKAR

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

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DEDICATION

TO:

MY DEAREST BELOVED PARENT:
ABU BAKAR BIN HUSSAIN & HASNAH BT ABDUL RAHMAN

MY HUSBAND:
SAIFUL MUNIR BIN MOHD. SAAD

MY CHILDREN:
SYAUQEE HARRAZ
SYIFA' HANNAN
SYATHIR HAFFAZ
SYAMINA HANNAH

MY FAMILY:
AYU HASWIDA
ABU HASWANDY
ABU HASANIF
AYU HASLELA
ABU HASWIRA

MY FRIENDS
ALL WHO ALWAYS PRAY FOR ME AND SUPPORT ME IN ALL STAGES OF MY PHD JOURNEY.

LOVE YOU ALL & MAY ALLAH BLESS YOU ALWAYS.

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

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AYU HASLIJA BT ABU BAKAR

April 2018

Chair : Professor Luqman Chuah bin Abdullah, PhD
Faculty : Engineering

The excess concentrations of fluoride in water for human consumption may cause severe health problems. Among several treatment technologies applied for fluoride removal, adsorption process has been explored widely and proven as an efficient method. An agricultural waste, palm kernel shell (PKS) was quartenized in order to improve the adsorption efficiency as an adsorbent for adsorbing fluoride from waste water by batch and fixed bed column process. Commercial palm kernel shell activated carbon (PKSAC) was used as a comparison to the quaternized palm kernel shell (QPKS). Effect of various factors on the fluoride removal was investigated, such as pH, initial concentration, adsorbent dosage and contact time. Adsorption capacity increased with the increased of adsorbent dosage and contact time. Optimum parameters which resulted in maximum adsorption capacity of 1.7 mg/g by QPKS and 1.3 mg/g by PKSAC was achieved at pH 3 with initial concentration of 20 mg/L, an adsorbent dosage of 8 g/L with contact time of 4 h. The adsorption behavior was further investigated using equilibrium isotherms. In batch process, isotherms such as Langmuir, Freundlich, Redlich-Peterson, and Sips were studied, in which Redlich-Peterson, Langmuir and Freundlich fit well with a coefficient correlation (R^2), ranged from 0.95 to 0.99. Kinetic studies, such as pseudo first and second order, Boyd's model, Elovich model, Double Exponential model and Intraparticle Diffusivities model, were investigated and showed parallel transports exist in the adsorption process and intraparticle diffusion is the rate limiting step for both adsorbents. In fixed bed column process, breakthrough time was affected by bed height and initial fluoride concentration and kinetics studies investigated were Adam-Bohart, Thomas and Yoon-Nelson Model. Regeneration study showed that QPKS performance decreased by 63% compared to PKSAC which decreased by 80% after four cycles of adsorption-desorption. These results suggest that quaterrnized palm kernel shell (QPKS) has the potential to serve as a low-cost adsorbent for fluoride removal from aqueous solutions.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah.

PENJERAPAN TEMPURUNG ISIRONG KELAPA SAWIT YANG TELAH DIKUARTERNISASI UNTUK PENYINGKIRAN FLUORIDA

Oleh

AYU HASLIJA BT ABU BAKAR

April 2018

Pengerusi : Professor Luqman Chuah bin Abdullah, PhD
Fakulti : Kejuruteraan

Kepekatan fluorida yang berlebihan di dalam air untuk penggunaan manusia boleh menyebabkan masalah kesihatan yang teruk. Di antara beberapa teknologi rawatan yang digunakan untuk penyingkiran fluorida, proses penjerapan telah diterokai secara meluas dan terbukti sebagai kaedah yang cekap. Sisa pertanian tempurung isirong kelapa sawit telah dikuaternisasikan untuk meningkatkan kecekapan penjerapan sebagai satu bahan penjerap untuk menjerap fluorida daripada air sisa buangan secara proses kelompok dan proses berterusan. PKSAC telah digunakan sebagai perbandingan kepada QPKS. Kesan daripada pelbagai faktor penyingkiran fluorida telah dikaji seperti pH, kepekatan larutan permulaan, dos bahan penjerap dan masa penjerapan. Kapasiti penjerapan meningkat dengan peningkatan dos bahan penjerap dan masa penjerapan. Parameter optimum yang menghasilkan kapasiti maksimum penjerapan 1.7 mg/g oleh QPKS dan 1.3 mg/g oleh PKSAC telah dicapai pada pH 3 dengan kepekatan awal larutan fluorida 20 mg/L, dos bahan penjerap 8 g/L dengan masa penjerapan 4 jam. Mekanisma aktiviti penjerapan dikaji menggunakan isoterma keseimbangan. Dalam proses kelompok, isoterma Freundlich, Redlich-Peterson, Langmuir, dan Sips telah dikaji dan menunjukkan Redlich-Peterson, Langmuir dan Freundlich sepadan dengan baik dengan nilai R^2 daripada 0.95 hingga 0.99. Kajian kinetik seperti model pertama dan kedua Pseudo, model Boyd, model Elovich, model Double Exponential dan model Intraparticle Diffusivities telah dikaji dan pergerakan selari wujud dalam proses penjerapan dan penyebaran intrapartikel adalah kadar yang membataskan langkah untuk kedua-dua bahan penjerap. Dalam proses berterusan hasil penyingkiran fluorida dipengaruhi oleh ketinggian turus dan kepekatan awal larutan fluorida. Kajian kinetik yang digunakan adalah model Adam-Bohart, Thomas dan Yoon-Nelson. Kajian penjanaan semula menunjukkan bahawa selepas empat pusingan penjerapan-penyahjerapan, prestasi QPKS menurun sebanyak 63% berbanding dengan PKSAC yang menurun sebanyak 80%. Keputusan ini mencadangkan bahawa QPKS mempunyai potensi untuk menjadi bahan penjerap berkos rendah bagi penyingkiran fluorida daripada larutan akueus.

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

Luqman Chuah Abdullah, PhD
Professor
Faculty of Engineering
Universiti Putra Malaysia
(Chairman)

Thomas Choong Shean Yaw, PhD
Professor, Ir
Faculty of Engineering
Universiti Putra Malaysia
(Member)

Mohsein Nourozi, PhD
Senior Lecturer
Department of Environment
Islamic Azad University Isfahan
(Member)

Ma'an Alkhatib, PhD
Associate Professor
Department of Biotechnology Engineering
International Islamic University Malaysia
(Member)

ROBIAH BINTI YUNUS, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

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Name of Chairman of
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Signature: ______________________
Name of Member of
Supervisory Committee: Prof. Ir. Dr. Thomas Choong Shean Yaw

Signature: ______________________
Name of Member of
Supervisory Committee: Dr. Mohsein Nourozi

Signature: ______________________
Name of Member of
Supervisory Committee: Assoc. Prof. Dr. Ma'an Alkhatib

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LIST OF NOTATIONS/ SYMBOLS

AC	Activated carbon
C_o	Initial concentration of solute in solution
C_e	Concentration of solute in solution at equilibrium
CHMAC	N-(3-chloro-2-hydroxypropyl)trimethylammonium chloride
EFB	Empty fruit bunch
FFB	Fresh fruit bunch
PKS	Palm kernel shell
PKSAC	Palm kernel shell activated carbon
QPKS	Quaternized palm kernel shell
q_e	Amount of adsorbate adsorbed per gram of adsorbent at equilibrium
q_m	Maximum adsorption capacity per gram of adsorbent
q_t	Amount of adsorbate adsorbed per gram of adsorbent in time *t*.
R^2	Correlation coefficient

CHAPTER 1

INTRODUCTION

1.1 Background

Fluoride, a salt of the element fluorine, occurs mainly as sellaite (MgF_2), fluorspar (CaF_2), cryolite (Na_3AlF_6), and fluorapatite [$3Ca_3(PO_4)_2$ $Ca(F,Cl_2)$]. It is an essential constituent for both humans and animals depending on the total amount ingested or its concentration in drinking water. Fluoride in drinking water is known for both beneficial and detrimental effects on health. An appropriate concentration of fluoride in drinking water is required to prevent dental cavities but long-term ingestion of water that contains more than a suitable level of fluoride causes bone disease and mottling of the teeth.

The presence of fluorine in drinking water, within permissible limits of 0.5–1.5 mg/L, is beneficial for the production and maintenance of healthy bones and teeth. Meanwhile, excessive intake of fluoride causes dental or skeletal fluorosis, which is a chronic disease manifested by mottling of teeth in mild cases, softening of bones, and neurological damage in severe cases (Liu, Guo, & Shan, 2010). In fact, there has been an escalation in daily fluoride intake via the total human food and beverage chain (Roy & Dass, 2013). Carbonated soft drinks have considerable amounts of fluorides. Fluoride is also present in most of everyday needs; for example, toothpaste, drugs, cosmetics, chewing gums, mouthwashes (Tikki, 2014).

Recently, an increase in industrial activities and water bodies with excess levels of fluoride has become a matter of great concern. Besides, high fluoride level wastewater is produced every day from industries using hydrofluoric acid as a cleaning agent such as the semiconductor, solar cell or metals manufacturing industries or as a reactant or catalyst in the plastics, pharmaceutical, petroleum refining, and refrigeration industries. Untreated high fluoride level wastewater is also one of the key contributors to groundwater and surface water pollutions (Malakootian, Fatehizadeh, Yousefi, Ahmadian, & Moosazadeh, 2011).

Fluoride contamination in groundwater also has been recognised as one of the serious problem worldwide. Fluoride is classified as one of the contaminant of water for human consumption by the World Health Organisation (WHO), in addition to arsenic and nitrate, which cause large-scale health problems (WHO, 2006). Elevated fluoride concentrations in the groundwater occur in various parts of the world such as Kenya, Poland, China, Tanzania, Mexico, and Argentina (Bhatnagar, Kumar, & Sillanpää, 2011). Furthermore, fluoride is widely distributed in the geological environment and generally released into the groundwater by slow dissolution of fluorine-containing rocks. Various minerals; e.g., fluorite, biotites, topaz, and their corresponding host rocks such as granite, basalt, syenite, and shale contain fluoride that can be released into the groundwater. Thus, groundwater is a major source of fluoride intake among humans.

In addition, Hanumantharao (2011) reported that in Nalgonda District, Andhra Pradesh, India, maximum fluoride content in the groundwater was found to be 4.5 mg/L. This high concentration of fluoride affected the villagers which most of the residents suffer from dental discoloration, early tooth decay and bone deformations.

The difference between desirable and toxic doses of fluoride is ill-defined, and fluoride may, therefore, be considered as an essential mineral with a narrow margin of safety (WHO, 2011). The fact that the problems associated with the excess fluoride in drinking water are highly endemic and widespread in the third world countries has prompted many researchers to explore quite a good number of organic and inorganic materials by adopting various processes from coagulation, precipitation through adsorption, and ion exchange. Some are good under certain conditions, while others are good in other conditions.

1.2 Health Effects and Toxicology of Overdose Fluoride Intake

The standards prescribed by various regulatory bodies for fluoride concentration in drinking water are different according to their climatic conditions. According to WHO, the standard prescribed for fluoride ion concentration in drinking water is 1.5 mg/L. Fluoride in smaller doses (0.8-1.0 mg/L) helps to prevent dental caries particularly among children below eight years of age. Fluoride in higher concentration causes dental fluorosis (1.5-2.0 mg/L) and skeletal fluorosis (>3.0 mg/L) (WHO, 2011). Table 1.1 shows the effect of prolonged exposure to higher fluoride concentrations from dental fluorosis progresses to skeletal fluorosis.

Table 1.1: Effects of fluoride in water on human health (Meenakshi & Maheshwari, 2006).

F^{-1} concentration, (mg/L)	Effects
<1.0	Safe limit
1.0-3.0	Dental fluorosis (discoloration, mottling and pitting of teeth)
3.0-4.0	Stiffened, brittle bones and joints and skeletal fluorisis
4.0-6.0 and above	Deformities in knee and hip bones and finally paralysis making the person unable to walk or stand in straight posture, crippling fluorosis

Chemically, fluorine is the most electronegative element and is always present in a combined state as fluoride due to its high chemical reactivity. Fluoride is a great calcium-seeking element and can affect the calcified structure of bones and teeth in the human body at higher concentration, resulting in dental fluorosis or skeletal fluorosis. Fluoride toxicity can also cause non-skeletal diseases like aches and pain in the joints, non-ulcer dyspepsia, Polyurea (tendency to urinate more frequently) and polydipsia (excessive thrust), muscle weakness, fatigue, and anemia with very low haemoglobin levels (Roy & Dass, 2013).

1.3 Methods of Fluoride Removal

Over the years, many techniques and processes have been developed and used in the treatment and removal of fluoride from the contaminated water effluent. These techniques include coagulation and flocculation, chemical precipitation, the use of membranes for membrane separation, aerobic and anaerobic degradation using various microorganisms, chemical oxidation, ion exchange, electrodialysis, reverse osmosis, foam flotation, electrolysis, and adsorption (Onyango & Matsuda, 2006). Some of these techniques have been proven to be effective, although they displayed some limitations such as the excess amount of chemical usage or accumulation of highly concentrated sludge causing disposal problems, lack of effective fluoride reduction, and sensitivity towards various wastewater inputs (Santhy & Selvapathy, 2006).

Amongst the processes mentioned above, the use of adsorption has been the most prominent and widely used because of its cost-effectiveness, efficiency, and technology readiness due to the fact that it produces effluents containing very low levels of dissolved organic compounds (Chandra, Mirna, Sudaryanto, & Ismadji, 2007). In addition, many adsorption techniques have been employed for the treatment of drinking water as reviewed in the work reported by Tikki (2014).

1.4 Problem Statement

Source of fluoride and several health problems caused by fluoride has been discussed in detail in previous section. As conclusion, it can be stated that high concentrations of fluoride ions in water mainly affected by natural minerals and industrial activities. Lv et al. (2007) reported that concentration of fluoride in the wastewater from Zhejiang Juhua Fluorine Chemical Co. Ltd. exceeded 1000 mg/L (pH = 5-7). Meanwhile, one of the wastewater treatment plant in Malaysia produced 1.35 mg/L of fluoride from its boiler effluent which exceeded Malaysian Drinking Water Quality Standard, in which the acceptable limit is 0.4 - 0.6 mg/L, as shown in Appendix A2. According to Ruan et al. (2017), most natural rocks and minerals contain large quantities of fluoride which are released as fluoride ions into water, thus, contributing to levels of fluoride concentrations rise in water that exceed the acceptable limit set by WHO, 1.5 mg/L. Therefore, fluoride content in wastewater and drinking water should be reduced in order to improve the health quality.

In order to solve the excess of fluoride concentration in water, adsorption process is chosen due to the cost-effectiveness and its efficiency as stated by Chandra et al. (2007). In adsorption process, activated carbons are the most widely used adsorbents due to their excellent adsorption abilities for organic pollutants. Activated carbon has a high-surface-area, pore volume, and porosity which resulted in higher adsorption capacities. Many researchers have shown that activated carbon is an effective adsorbent for removing pollutants. However, its high initial cost resulted from the thermal activation process that consumes high energy making it less economical as an adsorbent (Ahmaruzzaman, 2008; Robinson, McMullan, Marchant, & Nigam, 2001). Reflecting to this issue, a more economic and efficient technique, which lead to the application of chemically-treated agricultural waste as adsorbents, is favored. The advantage of chemically-treated adsorbents is of their low production cost in terms of energy saving which will reduce the total production cost as compared to the production of activated carbon.

Palm kernel shell waste from oil palm mill was chosen as the adsorbent in this study because it is a locally available as abundant material. Since millions of kilograms of palm kernel shells are produced annually, the production of chemically-treated palm kernel shell to produce high value added adsorbent has become an attractive waste reduction solution. Chemical modification on palm kernel shell, such as quaternization to produce adsorbent, is considered. Only few researchers were reported in studying the chemically-treated adsorbent specifically through quaternization process on palm kernel shell for anion removal. Koay, et al. (2014) quaternized PKS to remove reactive dye and Bashir, et al. (2015) quaternized PKS to remove fluoride and nitrate. In their study, potassium hydroxide (KOH) was used instead of sodium hydroxide (NaOH) in mercerization process. Moreover, different ranges of operation parameters are applied from current study.

1.5 Objectives

This study aims to synthesise and analyse quaternized palm kernel shell (QPKS) as an adsorbent to remove fluoride from aqueous solution and commercial palm kernel shell activated carbon (PKSAC) as the control adsorbent.

The specific objectives of this work are described as follows:

1. To synthesise quaternized palm kernel shell as an adsorbent via quaternization process using N-(3-chloro-2-hydroxyproply) trimethylammonium chloride (CHMAC) as quaternization agent.

2. To investigate the effect of initial pH, the dosage of PKSAC and QPKS and initial fluoride concentration in batch process of fluoride removal and reusability of QPKS and PKSAC.

3. To evaluate the adsorption isotherm and kinetics for removal of fluoride from aqueous solution by both PKSAC and QPKS.

4. To investigate the adsorption process of fluoride removal using QPKS in a fixed bed continuous column with different bed height and initial concentration.

1.6 Scope of Research

The scope of this research covered the chemical modification process of the adsorbent which is the palm kernel shell (PKS). PKS was first mercerized using NaOH then chemically modified using quaternizing agent, N-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride (CHMAC) to produce quaternized palm kernel shell (QPKS). In order to verify the QPKS efficiency, batch and continuous (column) adsorption processes by removing fluoride from the solution were done in UPM laboratories. Parameters such as pH, contact time, adsorbent dosage, initial concentration, and bed height were varied. Data obtained from the experimental work were analysed using isotherm models such as Langmuir, Freudlich, Redlich-Peterson, Sips, Adam-Bohart, Yoon-Nelson, and Thomas. Meanwhile, kinetic studies were analysed using models of Pseudo First and Second Order, Weber-Morris, Elovich, Boyd's, Double Exponential and Intraparticle Diffusivity. The regeneration of the adsorbent was also studied to analyse the reusability of the adsorbents.

All results for QPKS were compared with control adsorbent which was Palm PKSAC, a commercial activated carbon originated from Palm Kernel Shell.

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