HYDROTHERMAL SYNTHESIS AND CHARACTERIZATION OF ZEOLITE FROM MALAYSIA'S NATURAL KAOLIN FOR ADSORPTION OF SODIUM ION (Na^+) FROM SEAWATER

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My love and special dedication for my husband, Mohamad Salehin bin Abd Rahim, my daughter, Norsurfina binti Mohamad Salehin, my parents, Sazali bin Kandar & Soliah binti Adinan, and my siblings (Norzalyana, Dr. Norazlianie, Mohamad Suzaime, and Mohamad Suzaidie). Thank you for everything, and I am forever grateful for all of the kindness and encouragement have given throughout my journey in completing this project. May Allah S.W.T repay all of you accordingly. Amin.

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ABSTRACT

Zeolite-A is widely known as aluminosilicate mineral that has been intensively used as an adsorbent in the adsorption process for desalination. Desalination is a technique to eliminate sodium ion and other minerals in the water. Because of the nature of seawater, which is very salty, the main purpose of the removal of sodium ion from seawater is to produce a source of clean drinking water. The capability of zeolite-A as an adsorbent makes it suitable to remove sodium ion from seawater. The raw kaolin from a different location (Perak and Johor) that acts as the main source of silica and alumina has been successfully studied to synthesized and transform into the Zeolite-A. The proposed synthesis of zeolite-A from kaolin has been reduced the cost of using synthetic reagent and high energy utilization. The various operating parameters to synthesis zeolite-A from both low-grade kaolin (Perak and Johor) were investigated to produce high crystallinity of zeolite. The alkaline solution (2-3 M NaOH) was added as a modification method for their conventional hydrothermal synthesis process. The calcination and crystallization process was recognized as an important processing stage for the synthesis. For the metakaolin process, the temperature 650 ^{0}C and time 240 minutes were used. The crystallization time of 12-16 hours with an aging treatment time of 24 hours was selected in the synthesizing of zeolite. The successful of synthesized Zeolite-A was further characterized by XRD, FESEM, FTIR, PSA and BET. The composition percentage of kaolinite from Perak kaolin (84 %) is higher compared to the Johor kaolin (40.6 %). As demonstrated in this work, Perak kaolin was successfully synthesized into Zeolite-A which give higher crystallinity percentage, 72.97 % compared to Johor kaolin, 46.72 % under 24 hours aging, with 2M NaOH and 12 hour crystallization time. The higher percentage of kaolinite from Perak kaolin gives higher crystallinity percentage of synthesizing zeolite-A compared to Johor kaolin. In addition, the BET surface area of Zeolite-A is higher, 5.26 m^2/g compared to natural zeolite, 2.9 m^2/g. The performance of adsorption capacity of sodium ion (Na^+) toward synthesized Zeolite-A was further analyzed by batch adsorption analysis (Isotherm and Kinetic Model) and column adsorption analysis

(Breakthrough curve model). The various parameter was applied to the batch experiment (Zeolite-A dosage, time, initial sodium ion concentration and volume) and column experiment (Zeolite-A dosage, initial sodium ion concentration and flow rate). For batch adsorption analysis, both the Langmuir model and Freundlich model were used to analyze the adsorption of sodium ion toward Zeolite-A. Langmuir isotherm model shows slightly better fitted with the correlation coefficient, R^2 = 0.9074 compared to Freundlich isotherm, R^2= 0.9028. The result from the kinetic model shows the intra particle diffusion model gives better fitted with R^2 value is 0.9117 compared to pseudo first order (R^2= 0.732) and pseudo second order (R^2= 0.8276). In addition, the calculated value of adsorption capacity at equilibrium, q_e, is 88.4 mg/g by intra particle diffusion model gives the closest to the experimental value of q_e, (92 mg/g) compared to pseudo first order (q_e= 205.36 mg/g) and pseudo second order (q_e= 104.1 mg/g). For column adsorption analysis, breakthrough capacity, q_B was increased by increasing the bed height of zeolite-A and initial sodium ion concentration but decrease when increasing the flow rate. The column kinetic model shows the Adam Bohart model slightly better fitted with R^2 range is 0.86-0.95 for flow rate, R^2 = 0.82-0.93 for bed height and R^2 = 0.90-0.95 for initial sodium ion concentration compared to Thomas model, R^2 = 0.84-0.94 for flow rate, R^2 = 0.72-0.89 for bed height and R^2= 0.78-0.88 for initial sodium ion concentration and Yoon and Nelson model, R^2 = 0.84-0.94 for flow rate, R^2 = 0.69-0.89 for bed height and R^2 = 0.78-0.87 for initial sodium ion concentration. It can be concluded that the performance of synthesizing zeolite-A from Perak kaolin was capable of adsorbing sodium ion from seawater solution.

ABSTRAK

Zeolit-A dikenali sebagai mineral aluminosilikat yang telah digunakan secara meluas sebagai bahan penyerap dalam proses penjerapan untuk penyahgaraman. Penyahgaraman adalah teknik untuk menghilangkan ion natrium dan mineral lain di dalam air. Oleh kerana sifat air laut yang sangat masin, tujuan utama penyingkiran ion natrium dari air laut adalah untuk menghasilkan sumber air minuman yang bersih. Keupayaan zeolit-A sebagai penyerap menjadikannya sesuai untuk mengeluarkan ion natrium dari air laut. Kaolin mentah dari lokasi yang berbeza (Perak dan Johor) yang bertindak sebagai sumber utama silika dan alumina telah berjaya dikaji untuk disintesis dan diubah menjadi zeolit-A. Sintesis zeolit-A yang dicadangkan dari kaolin telah dapat mengurangkan kos penggunakan reagen sintetik dan penggunaan tenaga yang tinggi. Pelbagai parameter operasi untuk sintesis zeolit-A dari kaolin gred rendah (Perak dan Johor) disiasat untuk menghasilkan kristal zeolit yang tinggi. Larutan alkali (2-3 M NaOH) telah ditambahkan sebagai kaedah pengubahsuaian untuk proses sintesis hidrotermal konvensional. Proses pembakaran dan penghabluran diakui sebagai peringkat pemprosesan penting untuk sintesis. Untuk proses metakaolin, suhu 650 ^{0}C dan masa 240 minit digunakan. Waktu penghabluran 12-16 jam dengan masa rawatan penuaan 24 jam telah dipilih dalam sintesis zeolit. Kejayaan Zeolit-A yang disintesis telah dicirikan oleh XRD, FESEM, FTIR, PSA dan BET. Peratusan komposisi kaolinit dari kaolin Perak (84 %) adalah lebih tinggi berbanding kaolin Johor (40.6 %). Seperti yang ditunjukkan dalam hasil kerja ini, kaolin Perak berjaya disintesis menjadi Zeolit-A yang memberikan peratusan kristaliti yang lebih tinggi, 72.97% berbanding dengan kaolin Johor, 46.72% di bawah penuaan 24 jam, dengan 2 M NaOH dan masa penghabluran 12 jam. Peratusan kaolinit yang lebih tinggi dari kaolin Perak memberikan keputusan kristalogi yang lebih tinggi untuk mensintesis zeolit-A berbanding kaolin Johor. Di samping itu, luas permukaan BET Zeolite-A adalah lebih tinggi, 5.26 m^2/g berbanding dengan zeolit semula jadi, 2.9 m^2/g. Prestasi kapasiti penjerapan ion natrium (Na^+) terhadap zeolit-A yang disintesis telah dianalisis dengan analisis penjerapan kumpulan (Isoterma dan Model kinetik) dan analisis

penjerapan lajur (Model lengkung terobosan). Pelbagai parameter telah digunakan pada ujikaji kumpulan (dos zeolit-A, waktu, kepekatan awal ion natrium) dan ujikaji lajur (dos zeolite-A, kepekatan ion natrium awal dan kadar aliran). Untuk analisis penjerapan kumpulan, kedua-dua model Langmuir dan model Freundlich digunakan untuk menganalisis penjerapan ion natrium terhadap zeolit-A. Model isoterma Langmuir menunjukkan keputusan sedikit lebih baik dilengkapi dengan pekali korelasi, R^2 = 0.9074 berbanding isoterma Freundlich, R^2 = 0.9028. Hasil daripada model kinetik menunjukkan model penyebaran intra zarah memberikan nilai yang lebih baik dengan nilai R^2 adalah 0.9117 berbanding aturan pertama pseudo (R^2 = 0.732) dan aturan kedua pseudo (R^2 = 0.8276). Di samping itu, nilai kapasiti penjerapan pada keseimbangan, qe, ialah 88.4 mg/g oleh model penyebaran intra zarah memberikan nilai paling hamper dengan eksperimen qe, iaitu 92 mg/g lebih baik berbanding dengan aturan pertama pseudo (qe = 205.36 mg/g) dan aturan kedua pseudo (qe = 104.1 mg/g). Untuk analisis penjerapan lajur, kapasiti penembusan, q_B meningkat dengan peningkatkan ketinggian katil zeolit-A dan kepekatan ion natrium awal tetapi menurun apabila meningkatkan kadar aliran. Model kinetik lajur menunjukkan model Adam Bohart yang sedikit lebih baik dilengkapi dengan nilai R^2 ialah 0.86-0.95 untuk kadar aliran, R^2 = 0.82-0.93 untuk ketinggian katil dan R^2 = 0.90-0.95 untuk kepekatan ion natrium awal berbanding model Thomas, R^2 = 0.84 -0.94 untuk kadar aliran, R^2 = 0.72-0.89 untuk ketinggian katil dan R^2 = 0.78-0.88 untuk kepekatan ion natrium awal dan model Yoon dan Nelson, R^2 = 0.84-0.94 untuk kadar aliran, R^2 = 0.69-0.89 untuk ketinggian katil dan R^2 = 0.78-0.87 untuk kepekatan ion natrium awal. Dapat disimpulkan bahawa prestasi sintesis Zeolit-A dari kaolin Perak mampu menyerap natrium ion dari larutan air laut.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATIONS

BET	-	Brunauer-Emmett-Teller
EDS	-	Energy-dispersive X-ray spectroscopy
FAU	-	Faujisite Topology
FTIR	-	Fourier-Transform Infrared Spectroscopy
FESEM	-	Field Emission Scanning Electron Microscope
ICDD	-	International Centre for Diffraction Data
ICSD	-	Inorganic Crystal Structure Database
IZA	-	International Zeolite Association
LTA	-	Linde Type Alpha
MSF	-	Multi-Stage Flash Distillation
PBU	-	Primary Building Unit
R^2	-	Coefficient of Determination
RO	-	Reverse Osmosis
SBU	-	Secondary Building Unit
SOD	-	Sodalite
T	-	Tetrahedral
TGA	-	Thermogravimetric Analyzer
XRD	-	X-ray Diffraction
q_e	-	Solute adsorbed per mass adsorbent/ adsorption capacity at equilibrium
K_L	-	Langmuir Constant
C_e	-	Concentration of solute at equilibrium
R_L	-	Dimensionless equilibrium factor for Langmuir Model
n	-	Adsorption intensity of Freundlich Model
K_f	-	Freundlich constant
q_t	-	Adsorption capacity at time
K_i	-	Intra Particle Diffusion constant
V_{waste}	-	Volume of waste water
Q	-	volumetric flow rate

q_{total}	-	Maximum capacity of column bed
C_o	-	inlet concentration of solution
Ce	-	Outlet concentration of solution
K_{TH}	-	Thomas rate constant
K_{YN}	-	Yoon and Nelson constant
t	-	time
π	-	pai
τ	-	time for 50% of adsorbate breakthrough
K_{AB}	-	Adam Bohart model constant
N_o	-	saturation concentration of maximum adsorption capacity
Z	-	bed height of column
F	-	Linear flow rate
ppm	-	parts per million
mg/L	-	milligram/litre
cm	-	centimeter
ml/min	-	millilitre/ minute
cm^{-1}	-	centimeter $^{-1}$
N_2	-	Nitrogen
ISE	-	Ion-selective electrode
µm	-	micrometre
SiO_2	-	silicon dioxide
Al_2O_3	-	Aluminium oxide
M	-	Molarity
NaOH	-	Sodium Hydroxide
m^2/g	-	meter square/gram
P	-	Pressure
ml	-	millimetre
g/L	-	gram/litre
mg/g	-	milligram/gram
t_b	-	breakthrough time
q_b	-	breakthrough capacity
meq/g	-	miliequivalent per gram

LIST OF EQUATION

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Research Background

The natural water resource with the most quantity in the world is the seawater. The majority of the earth's surface, approximately about 70%, is covered with water in the form of oceans, seas, and ice at the poles. Unfortunately, for drinking purposes, only about 3% of water is fresh. Therefore, gaining fresh water from other sources is very important. Because of the nature of the seawater, which is very salty, it is not suitable for drinking. The increased awareness of the world towards clean water has led to improved methods for gaining fresh water through ion exchange and desalination. Usually, seawater, wastewater, and brackish water are the sources of water for desalination. Sadly, most desalination techniques require high cost and can produce harmful chemicals as waste products. High cost and maintenance are often the reasons why not many countries in the world use or consider desalination technology [1].

Desalination can be defined as a process of eliminating salt and other minerals from the water. In addition, this process needs to be fitted for suitable uses, such as drinking, industry, aquaculture, and agriculture. There are many methods used for desalination, including distillation, adsorption, evaporation, electrodialysis, freezing, ion exchange, and reverse osmosis.

Issues related to the use of the natural resource of clay have been discussed for many years for sustainability and green approaches. A world has been discussing how these natural sources can keep sustain and exploited them for world development. Countries with abundant natural resources seem to turn to these resources for industrialization. The first discovery of natural zeolite was documented in 1756. But

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