SYNTHESIS, CHARACTERIZATION AND SORPTION PROPERTIES OF MICROPOROUS TITANOSILICATE ETS-10 FROM RICE HUSK ASH

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To my love one

Wong Hon Loong

To my beloved parents

Jei Mok Choon and Wong Mai Yin

To my beloved brother and sister

Jei Jenn Ning and Jei Chien Fong

For their love that made me firm and resolute

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PREFACE

This thesis is the result of my work carried out in the Department of Chemistry; Universiti Teknologi Malaysia between July 2005 to December 2006 under supervision of Assoc. Prof. Dr. Mustaffa Shamsuddin. Part of my work described in this thesis has been reported in the following publications or presentations:

1. Jei, C. Y., Sulaiman, A. and Shamsuddin, M. Synthesis and Characterization of Microporous Titanosilicate, ETS-10 from Agricultural Waste. *Proceeding of 1st Penang International Conference of Young Chemists.* Universiti Sains Malaysia. 2006.

2. Jei, C. Y., Sulaiman, A. and Shamsuddin, M. Physicochemistry Analysis of ETS-10 Derived from Rice Husk Ash. Poster presentation at the *19th Simposium Kimia Analisis Malaysia (SKAM-18).* Universiti Teknologi Malaysia, *2006.*

ABSTRACT

A new class of nano-sized microporous titanosilicate ETS-10 has been prepared through hydrothermal synthesis route in the absence of ETS-4 and organic template agent. Local agriculture waste – rice husk ash (RHA) has been used as the silica source and commercial titanium oxide namely P25 as titanium source. For comparison, the colloidal silica source, LUDOX-30 was also used as a silica source to synthesize the ETS-10. The influence of some synthesis parameters such as synthesis time and heating temperature on the crystallization of ETS-10 and the gel oxides composition have also been investigated. The physico-chemical characterization of these synthesized materials have been carried out by X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), UV-Vis spectroscopy (UV-VIS), Field Emission Scanning Electron Microscopy (FESEM), Solid State Nuclear Magnetic Resonance (NMR), nitrogen adsorption-desorption analysis and Raman spectroscopy. The best ETS-10 sample was successfully obtained under heating at 220°C for 52 hours using the following molar ratio TiO_2 : $3.75SiO_2$: 1.5NaOH : 0.54KF : $21.25H_2O$. The ability of the synthesized ETS-10 as adsorbents for heavy metal ion such as Pb^{2+}, Cd^{2+} and Cu^{2+} was investigated. The study of equilibrium and adsorption isotherm at 298 K was conducted using batch mode. The uptake rates for these heavy metal ions were extremely fast and fitted well with the pseudo-second order model and Langmuir equation with an affinity order of $Pb^{2+} > Cd^{2+} > Cu^{2+}$, with values of 1.86, 1.51 and 1.45 mmol/g respectively, which are the highest adsorptive capacities of the heavy metal ions on zeolite materials reported so far. This indicates that ETS-10 is a very promising adsorbent for divalent heavy metals.

ABSTRAK

Titanosilikat ETS-10 mikroliang bersaiz nano telah disintesis melalui tindak balas hidroterma tanpa ETS-4 sebagai benih dan agen organik. Abu sekam padi yang merupakan sisa buangan pertanian tempatan telah digunakan sebagai sumber silika dan titanium oksida komersil (P25) digunakan sebagai sumber titanium. Untuk tujuan perbandingan, silika koloid (LUDOX-30) juga digunakan sebagai sumber silika dalam sintesis ETS-10. Parameter yang mempengaruhi proses sintesis ETS-10 dan komposisi oksida gelnya seperti masa dan suhu tindak balas juga dikaji. Hasil daripada sintesis telah dicirikan menggunakan pembelauan sinar-X (XRD), spektroskopi infra-merah transformasi Fourier (FT-IR), spektrokopi ultra lembayung-nampak (UV-VIS), mikroskopi elektron imbasan pancaran medan (FESEM), spekstroskopi resonans magnet nuklear keadaan pepejal (RMN), analisis penjerapan dan penyahjerapan nitrogen and spektroskopi Raman. Sampel ETS-10 yang paling tulen didapatkan dengan menggunakan nisbah molar TiO_2 : $3.75SiO_2$: 1.5NaOH : 0.54KF : $21.25H_2O$ pada suhu 220°C selama 52 jam. Sampel ETS-10 tulen ini kemudiannya digunakan dalam proses penjerapan untuk tujuan penyingkiran ion logam berat, terutamanya Pb^{2+}, Cd^{2+} dan Cu^{2+}. Dalam kajian ini, keseimbangan dan penjerapan isoterma pada suhu 25°C telah dijalankan melalui kaedah berkelompok. Kadar penjerapan untuk logam berat tersebut sangat pantas dan mematuhi dengan baik model pseudo tertib kedua dan model isoterma Langmuir dengan urutan $Pb^{2+} > Cd^{2+} > Cu^{2+}$ dengan nilai keupayaan penjerapan 1.86, 1.51 and 1.45 mmol/g masing-masing yang merupakan muatan penjerapan paling tinggi berbanding dengan zeolit lain yang dilaporkan setakat ini. Ini membuktikan bahawa ETS-10 adalah penjerap yang paling berpotensi terutamanya untuk penjerapan logam berat dwivalen.

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LIST OF SYMBOLS

°C	-	Degree Celsius
C_o	-	Initial concentration
C_e	-	Equilibrium concentration
cm	-	Centi meter
g	-	Gram
kg	-	Kilo gram
kV	-	Kilo Volt
L	-	Liter
m	-	Meter
M	-	Molar
meq	-	Mili equivalent
mg	-	Mili gram
MHz	-	Mega Hertz
mL	-	Mili Liter
mm	-	Mili meter
mmol	-	Mili mol
mW	-	Mili Watt
N	-	Normal
nm	-	Nano meter
ppm	-	Part per million
Å	-	Angstrom
μL	-	Micro Liter
μm	-	Micro meter
λ	-	Lambda
δ	-	Delta
θ	-	Theta

LIST OF ABBREVIATIONS

ETS-4	-	Engelhard titanosilicate-4
ETS-10	-	Engelhard titanosilicate-10
AAS	-	Atomic Absorption Spectroscopy
BET	-	Brunauer, Emmet, and Teller
CEC	-	Cation Exchange Capacity
FAAS	-	Flame Atomic Absorption Spectroscopy
FAU	-	Faujasite
FESEM	-	Field Emission Scanning Electron Microscopy
FTIR	-	Fourier Transform Infrared
h	-	Hour
ICP-MS	-	Inductively Coupled Plasma Mass Spectrometry
FTIR	-	Fourier Transform Infrared
NMR	-	Nuclear Magnetic Resonance
RHA	-	Rice Husk Ash
rpm	-	Revolution per minute
TEACl	-	Tetraethylammonium chloride
TMACl	-	Tetramethylammonium chloride
UV-Vis	-	Ultra Violet-Visible
XPS	-	X-ray photoelectron spectroscopy
XRD	-	X-Ray Diffraction
XRF	-	X-Ray Flourescence
V	-	Volume

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CHAPTER 1

INTRODUCTION

1.1 Research background

Due to the modern life nowadays, a lot of new technologies bring us to the easier life but at the same time it also brings the worst effects to the environment. Heavy metals such as lead (Pb), copper (Cu) and cadmium (Cd) which are released into aquatic environments largely from various anthropogenic activities are serious concern for human health and the environment. Therefore, removal of the heavy metal pollutants from aqueous systems has received a considerable amount of attention in order to control wastewater into an acceptable level according to the environmental regulations worldwide.

There are many water treatment processes such as chemical precipitation [1], adsorption [2], reverse osmosis [3], electro-dialysis [4], ultra-filtration [5,6] and ion-exchange [7,8] that are currently available for removal of heavy metals. Among them, the sorption process including ion-exchange and adsorption are the attractive ones, due to their relatively simple and safe process. Ion exchange for cation removal is often competitive with the classical chemical methods as it exhibits good performances, reasonable costs and sometimes metal recovery ability [9]. Hence, the good performances adsorbent has been investigated widely for this purpose.

Since its first introduction for heavy metal removal, it is undoubted that activated carbon has been the most and widely used adsorbent in wastewater treatment applications throughout the world. In spite of its prolific use, activated carbon remains an expensive material since higher the quality of the activated carbon, the higher it cost. Therefore, this situation makes it no longer attractive to be widely used in the small-scale industries due to cost inefficiency. Until currently, there are still many researchers working on inexpensive materials in search of the low-cost adsorbents for heavy metal removal. As a result, the low-cost adsorbents which have high adsorption capacity and locally available are desired. It is evident from the literature survey of about 100 papers that low-cost adsorbents have demonstrated outstanding removal capabilities for certain metal ions as compared to activated carbon [10].

In the past few decades, both natural and synthetic zeolites have been studied for heavy metal removal [11]. With increasingly stringent environmental regulations for heavy metal presence in drinking water and wastewater, novel zeolite ion exchangers with fast ion exchange rates and high uptake capacities are desired. Natural zeolites gained a significant interest among scientists due to their ion-exchange capability to preferentially remove unwanted heavy metals such as strontium and cesium [10]. This unique property makes zeolites favourable for wastewater treatment. However, the abundance of natural zeolites, an unavoidable problem of the utilization is the coexistence of the considerable impurities within the zeolitic tuffs, which interferes the exchange behavior of natural zeolites with heavy metals. As a result, synthetic zeolites which usually posses higher exchange capacity, easily controlled and known physico-chemical properties relative to that natural zeolites, have been preferred [12].

Currently many researches are being carried out on the synthesis of zeolite or microporous and mesoporous materials for the better heavy metal removal. In 1989, a new class of microporous titanosilicate molecular sieves zeolite with octahedral coordinated titanium framework known as (Engelhard Titanosilicate-4), ETS-4 with pore size 0.3 – 0.4 nm and ETS-10 with pore size 0.49 – 0.76 nm were discovered by Kuznicki [13-15]. This new family of microporous titanosilicates have been shown to possess zeolite-like properties such as catalysis, separation, absorption and ion exchange [16].

The ETS-10 comprises of corner-sharing $[SiO_4]^{4-}$ tetrahedra and $[TiO_6]^{8-}$ octahedra linked through oxygen atoms, forming a three-dimensional 12-membered ring network with pore-opening size of about 0.8 nm [17]. In ETS-10 the titanium (IV) is found in the centre of the corner-sharing octahedral and the silicon in the centre of corner sharing tetrahedral. This produces an anionic framework whereby, whenever titanium is present in the structure, there is an associated two minus charge which is compensated by extra-framework cations (Na^+ and K^+ in as-synthesised ETS-10) [18]. Such a unique framework property has been demonstrated to display unusual adsorption properties towards heavy metal ions in aqueous solution [19]. Unlike conventional aluminosilicate zeolites which are chemically constituted from SiO_4 and AlO_4 tetrahedrals giving rise to one negative charge for each AlO_4 tetrahedron balanced by an ion-exchangeable cation like Na^+. Therefore the associated two minus charge in ETS-10 structure make it a very interesting and suitable material for extremely fast ion exchange especially for divalent heavy metal cations removal compared with the zeolites which only has one minus charge in the structure.

Since the first report of ETS-10, many titanium sources have been used to synthesize ETS-10. $TiCl_3$ was used as the Ti source in the initial report of synthesis of ETS-10 by Kuznicki [13]. Due to the relatively expensive of $TiCl_3$, the search for alternative Ti source had been carried out. Thus, organotitanium compounds, $TiCl_4$ and TiF_4 had been used as Ti precursor to prepare ETS-10. However, the commercial pure anatase TiO_2 and commercial nano-sized TiO_2 (commercially known as P25) is of particular interest for the synthesis of ETS-10 because they are commercially readily available and do not bring any unwanted guest anions like Cl^- and F^-.

Silica is one of the basic raw materials in synthesizing ETS-10. Many researchers have used Ludox to synthesize the ETS-10. At present, there is still no report of the rice husk ash being used as silica source to synthesize the ETS-10. Since the rice husk is an agricultural waste material and locally available with high percentage of silica, it becomes very suitable for low cost ETS-10 production. These advantages make it an important material for water purification process, especially in drinking water and waste water treatment. This will lead to an improved water quality for healthier life and green environment in Malaysia.

1.2 Scope of Study

In the research, the synthesis of ETS-10 was carried out using locally produced rice husk ash as the silica source and titanium dioxide (namely P25) as the titanium source in different molar oxide gel ratio. During the synthesis of ETS-10, optimisation of the experimental conditions such as pressure, heating temperature, pH, duration of stirring and reaction time were investigated. The structure and of the synthesized ETS-10 from rice husk ash will be compared with the ETS-10 synthesized from colloidal silica source, LUDOX-30.

Modification of the ETS-10, will also be carried out where a novel method called desilication will be applied to the synthesized ETS-10. In this method, some silicon will be selectively removed from the ETS-10 framework in order to create an extra ion exchange capacity. The desilication process toward ETS-10 will be optimized systematically by altering the temperature, time and concentration of the modifier. The original ETS-10 and desilicated ETS-10 will then be modified with $NaNO_3$, KNO_3 and NH_4NO_3 to produce the sodium, potassium loaded ETS-10 and protonated ETS-10 in order to use it as an ion-exchanger.

All the synthesized ETS-10, desilicated ETS-10 and modified ETS-10 were characterized by Fourier transform infrared spectroscopy (FTIR), Raman spectroscopy, UV-Vis spectroscopy (UV-Vis), X-ray diffraction (XRD), solid state nuclear magnetic resonance (NMR), field emission scanning electron microscopy (FESEM), thermogravimetric analysis and simultaneous differential thermal analysis (TG-SDTA), nitrogen adsorption-desorption study for surface area analysis and cation exchange capacity for the ion-exchange capacity analysis (CEC).

The sorption properties of the RHA synthesized ETS-10 were tested using water samples containing toxic heavy metals such as Pb^{2+}, Cd^{2+} and Cu^{2+} under single, binary or ternary systems. The selectivity, kinetics and equilibrium, efficiency and ion exchange capacity of the ETS-10 were determined by Flame Atomic Absorption Spectroscopy (FAAS).

For comparison purpose, the LUDOX synthesized ETS-10 and RHA synthesized zeolite such as Zeolite A, Zeolite X and Zeolite Y samples were tested using water samples containing toxic heavy metals such as Pb^{2+}, Cd^{2+} and Cu^{2+} under single metal ion system. The selectivity, kinetics and equilibrium, efficiency and ion exchange capacity of this LUDOX synthesized ETS-10 and zeolite will be determined by Flame Atomic Absorption Spectroscopy (FAAS).

1.3 Objective of Study

(i) To synthesize the microporous titanosilicate 10 (ETS-10) using rice husk ash as a silica source.

(ii) To modify the synthesized ETS-10 by desilication and ion-exchange methods.

(iii) To characterize the physico-chemical properties of the synthesized and modified ETS-10.

(iv) To study the sorption properties of the synthesized and modified ETS-10 as an ion exchanger for Pb^{2+}, Cd^{2+} or Cu^{2+} in aqueous samples.

(v) To compare the sorption properties of ETS-10 and zeolite under single metal ion system toward the removal of Pb^{2+}, Cd^{2+} or Cu^{2+} in the aqueous samples.