

SORPTION BEHAVIOR OF ZEOLITE P AND ITS MODIFIED FORMS IN THE
REMOVAL OF SOME HEAVY METALS AND OXYANIONS FROM
AQUEOUS MEDIA

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*To Jesus Christ, my Lord, Savior and Provider,
And
My Parents, Sis, and Nanny.*

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ABSTRACT

Due to their toxicity and persistence, hazardous metal ions such as lead (Pb^{2+}), cadmium (Cd^{2+}) and zinc (Zn^{2+}) as well as oxyanions like selenite, Se (IV) and selenate, Se (VI) pose a worrying threat to the environment and human health when released into water resources as constituents of waste. This study covers the synthesis, characterizations and analytical works on the development of an inexpensive and excellent inorganic sorbent, i.e. zeolite Na-P2 which was synthesized using local rice husk ash as the raw material. The product was well characterized with various sophisticated techniques and further modified into its nearly-homoionic sodium and calcium form zeolite through ion exchange in order to investigate the sorption behaviors of these cationic form zeolite samples towards the selected hazardous metal ions. The sorption of selected metals such as Pb^{2+} , Cd^{2+} and Zn^{2+} was proven to be ion-exchange process through batch adsorption studies. The removal efficiencies of these zeolite species were investigated via several variables such as time, concentration, pH and competition within the solutes. The binary ion-exchange isotherms were constructed using thermodynamic equilibrium model and the standard free energies of exchange were calculated as well. The selectivity sequence of zeolite Na-P2 was as $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Na}^+ > \text{Zn}^{2+}$ whereas for Ca-exchanged garronite which denoted as Homo-Ca, the selectivity sequence was $\text{Pb}^{2+} > \text{Ca}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$. The multicomponent exchange of zeolite was also investigated. On the other hand, the original zeolite Na-P2 was loaded with aluminium ions using aluminium sulfate post desilication in order to investigate its capability in the removal of selenite and selenate species in water. Different variables of the selenium species adsorption onto aluminium-loaded zeolite Na-P2 such as time, concentration and ionic strength were also studied. The results showed that the aluminium-loaded zeolite Na-P2 (sample 10Al-P) performed well in the removal of selenium oxyanions from water compared to other materials. As conclusion, zeolite Na-P2 and its modified forms can be used as excellent metal-removing agents in the water purification process.

ABSTRAK

Disebabkan oleh ketoksikan dan kekekalan yang wujud, ion-ion logam merbahaya seperti plumbum (Pb^{2+}), Kadmium (Cd^{2+}) and Zink (Zn^{2+}) serta oksianion seperti selenit, Se (IV) and selenat, Se (VI) memaparkan sebagai ancaman terhadap alam sekitar dan kesihatan manusia apabila mereka dilepaskan ke dalam sumber-sumber air sebagai bahan sisa. Penyelidikan ini merangkumi kerja-kerja sintesis, pencirian dan analisis ke atas pembangunan suatu penjerap tak organik yang murah dan cekap, iaitu zeolit Na-P2 di mana ia disintesis dengan menggunakan abu sekam padi tempatan sebagai bahan mentah. Produk itu dicirikan dengan pelbagai jenis teknik yang canggih dan seterusnya ia dimodifikasi kepada bentuk natrium dan kalsium hampir-homoionik agar dapat mengkaji tabiat penjerapan bagi sampel zeolit yang berbentuk kationik ini terhadap ion-ion logam merbahaya terpilih. Penjerapan ion-ion logam terpilih seperti Pb^{2+} , Cd^{2+} and Zn^{2+} telah dibuktikan sebagai proses penukargantian ion melalui kajian penjerapan berkelompok. Kecekapan penyingkiran bagi spesies-spesies zeolit ini telah dikaji melalui beberapa pembolehubah seperti masa, kepekatan, pH and persaingan di antara bahan terjerap. Isoterma penukargantian ion binari telah dibina dengan menggunakan model keseimbangan termodinamik dan tenaga bebas piawai bagi penukargantian juga telah dikira. Susunan kepilihan bagi zeolit Na-P2 adalah $Pb^{2+} > Cd^{2+} > Na^+ > Zn^{2+}$ manakala bagi garronit tertukarganti kalsium yang dilabel sebagai Homo-Ca, susunan kepilihannya adalah $Pb^{2+} > Ca^{2+} > Cd^{2+} > Zn^{2+}$. Penukargantian komponen multi bagi zeolit Na-P2 juga dikaji. Di samping itu, zeolit Na-P2 asal dimuatkan dengan menggunakan aluminium sulfat selepas penyingkiran silika untuk mengkaji kecekapannya dalam penyingkiran spesies selenit and selenat dalam air. Pembolehubah bagi penjerapan spesies-spesies selenium ke atas zeolit Na-P2-termuat-aluminium seperti masa, kepekatan dan kekuatan ionik juga telah dikaji. Keputusan menunjukkan zeolite Na-P2-termuat-aluminium (sampel 10Al-P) mempunyai prestasi yang baik berbanding dengan bahan-bahan lain dalam penyingkiran oksianion selenium daripada air. Sebagai kesimpulannya, zeolit Na-P2 dan bentuk-bentuk terubahsuai dapat digunakan sebagai agen penyingkiran logam yang cekap dalam proses penulenan air.

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LIST OF SYMBOLS

$^{\circ}\text{C}$	-	Celsius degree
K	-	Kelvin degree
C_0	-	Initial concentration
C_e	-	Equilibrium concentration
C_t	-	Concentration, after a prescribed duration
cm	-	Centimeter
g	-	Gram
kg	-	Kilogram
L	-	Liter
m	-	Meter
μm	-	Micrometer
nm	-	Nanometer
M	-	Molar
mA	-	Miliampere
λ	-	Wavelength
meq	-	Miliequivalent
mg	-	Miligram
μg	-	Microgram
h	-	Hour
min	-	Minute
s	-	Second
μs	-	Microsecond
mL	-	Mililiter
mm	-	Milimeter
mmol	-	Milimol
N	-	Normal

q_t	-	Sorbate uptake after a prescribed duration
q_e	-	Sorbate uptake at equilibrium
q_{\max}	-	Maximum uptake capacity
K_A	-	Thermodynamic equilibrium constant
t	-	Time
V	-	Volume of solution
\AA	-	Angstrom
2θ	-	2-Theta value in X-ray diffraction
%T	-	Percent transmission
KHz	-	Kilohertz
MHz	-	Megahertz
k_1	-	Equilibrium rate constant of pseudo-first-order sorption
k_2	-	Equilibrium rate constant of pseudo-second-order sorption
r^2	-	Correlation coefficient
k_{id}	-	Rate constant of intraparticle diffusion
ΔH_{hydr}	-	Enthalpy of hydration
C	-	Concentration or activity of free metal in solution according to Langmuir and Freundlich model
S	-	Quantity of the metal ions sorbed according to Langmuir and Freundlich model
M	-	Maximum sorption capacity of the sorbent according to Langmuir model
b	-	Coefficient related to bonding energy according to Langmuir model
K_F	-	Freundlich empirical constant which related to adsorption capacity
n	-	Freundlich empirical constant which related to intensity of adsorbent
z_i	-	Valency of ion i
M	-	Molar concentration
W	-	Zeolite mass
γ	-	Solution-phase activity coefficient
I	-	Ionic strength of solution

a_i	-	Ion size parameter
A and B	-	Constants in the Debye-Hückel term
ρ_o	-	Density of water
ϵ	-	Dielectric constant of water
T	-	Temperature
ΔG°	-	Gibbs standard free energy
ΔH°	-	Standard enthalpy
ΔS°	-	Standard entropy

LIST OF ABBREVIATIONS

FAO	-	Food and Agriculture Organization of the United Nations
XRD	-	X-ray diffraction
FTIR	-	Fourier-transform infrared spectroscopy
MAS/NMR	-	Solid- state nuclear magnetic resonance spectroscopy under magic angle spinning
WDXRF	-	Wavelength dispersive x-ray fluorescence spectroscopy
FAAS	-	Flame atomic absorption spectroscopy
SEM	-	Scanning electron microscopy
TG-DTA		Thermogravimetric-differential thermal analysis
EDAX		Energy dispersive x-ray microanalysis
Pb	-	Lead
Cd	-	Cadmium
Zn	-	Zinc
Se	-	Selenium
GIS	-	Gismondine
IUPAC	-	International Union of Pure and Applied Chemistry
DNA	-	Deoxyribonucleic acid
RNA	-	Ribonucleic acid
FIAM	-	Free ion activity model
HDL	-	High density lipoprotein
LDL	-	Low density lipoprotein
HgbA1C	-	Glycated hemoglobin
SLI	-	Staring-lighting-ignition

CNS	-	Central nervous system
PKC	-	Protein kinase C
AC	-	Alternate current
DC	-	Direct current
ELM	-	Emulsion liquid membrane
EC	-	Electrocoagulation
ETS-10	-	Engelhard titanosilicate-10
SBU	-	Secondary building units
ANA	-	Analcime
TLM	-	Triple layer model
IIS	-	Ibnu Sina Institute for Fundamental Science Studies
LOI	-	Loss of ignition
H ₂ SO ₄	-	Sulfuric acid
HF	-	Hydrofluoric acid
NaOH	-	Sodium hydroxide
NaAlO ₂	-	Sodium aluminate
DDW	-	Distilled-deionized water
NaNO ₃	-	Sodium nitrate
KCl	-	Potassium chloride
Ca(NO ₃) ₂		Calcium nitrate
NH ₄ NO ₃		Ammonium nitrate
rpm		Revolution per time
KBr		Potassium bromide
CRM		Certified standard material
PP		Polypropylene
C ₂ H ₂		Acetylene
HCL		Hollow cathode lamp
EDL		Electrodeless-discharged lamp
QCS		Quality control sample
RHA		Rice husk ash
PDF		Powder diffraction file
Ori-P		As-synthesized zeolite Na-P2
Homo-Na		Nearly-homoionic zeolite Na-P2

Homo-Ca	Calcium exchanged zeolite Na-P2 (corresponded to garronite)
CEC	Cation exchange capacity
H ₂ SeO ₃	Selenious acid
10Al-P	Desilicated zeolite Na-P2 loaded with 10 mmol/L aluminium sulfate
NaCl	Sodium chloride
n.v	Negative value

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

The presence of hazardous metals such as lead, zinc, cadmium as well as some metalloids like selenium and arsenic in the environment particularly in water have been drawing more and more public concern due to their toxicity and acute impacts to the human health. Pollution of the environment and the human exposure to these metallic or semi-metallic elements may occur naturally (e.g. erosion of surface deposits of metal minerals and natural weathering of rock), or from anthropogenic activities (mining, smelting, fossil fuel combustion and industrial application of metals).

Concerned for sustaining healthy water resources, public are calling for more and more environmental restriction. Consequently, industries and scientists are searching for economic and efficient methods in protecting water resources from pollution. Using the sorption process for the removal of harmful metals from wastewater has a relatively shorter history if compared to other water purification processes. In 1785, Lowitz observed that charcoal would decolorize many liquids. This is the earliest documented use of carbon for the removal of impurities in solutions [1]. Nowadays adsorption on activated carbon is a recognized method for the removal of harmful metals from wastewater while the high cost of activated carbon production and application limits its use in adsorption. A search for low cost

and easily available adsorbent has led to the investigation of materials of agricultural and biological origin as potential metal sorbents [2].

Mineralogists have studied zeolites for two and half centuries beginning with the first member, stilbite, which was discovered in 1756 [3]. However their spectacular applications in industry have been developed only in the last 50 years. The openness of the anionic frameworks ensures the easier mobility both of cations in ion exchangers and of water molecules or other guest species. Additions and removals of guest species can be fully reversible, and so zeolites may be excellent sorbents for gases, vapors and liquids.

Considering the operation cost and efficiency, natural mineral zeolites such as chabazite, clinoptilolite, mordenite etc. with high exchange capacity and specific selectivity towards certain metal cations, have been utilized widely in water purification [4-9]. Nevertheless, an unavoidable problem of the utilization is the coexistence of the considerable impurities with the zeolitic tuffs, which interferes the exchange behavior of natural zeolites with the toxic elements. As an alternative, synthetic zeolites which usually possess higher exchange capacity, controlled and known physicochemical properties relative to that for natural zeolites [10], have been emphasized. Since the cost effectiveness is still the main consideration, low cost and locally available natural materials should be the first priority in the zeolite synthesis attempts.

Among the available local natural materials, rice husk which contains high percentage of silica has drawn attention of researchers worldwide. Rice husk is an agricultural waste material generated as by-product of rice refining process. According to the Food and Agriculture Organization of the United Nations (FAO), the annual world rice production amounts to 614,654,895 metric tons in the year of 2005 [11], of which 10-23% is husk [12]. The big amounts of rice husk produced are treated as waste, causing disposal and pollution problem.

Silica is one of the basic raw materials in zeolite synthesis. Many authors [13-15] have characterized and concluded that rice husks are outstanding source of high-grade amorphous silica, approximately 92%-97% in the ash from the

combustion of this material at moderate temperature. The utilization of rice husk ash as silica source in the synthesis of zeolite were well investigated by H. Hamdan et al. [16]. They showed that that amorphous silica extracted from the rice husk by the physical combustion with controlled temperature contains only $^*Si(OSi)_4$ tetrahedral units and is the most reactive silica source in the synthesis of zeolite Y.

P.K. Bajpai and his co-workers [17-18] were the first group in the past who has successfully synthesized mordenite-type zeolite using rice husk ash as silica source. Later, Ajay K. Dalai and his group [19] have synthesized sodium X zeolite by using this silica source for the first time. The syntheses of other zeolite species with silica source from rice husk ash were carried on by other researchers. For instance, zeolite P_c (cubic P), HS (hydroxysodalite), Z-21 (unknown structure, like Linde-N), analcime, ZSM-5, ZSM-48 etc. were attempted to be produced in last two decades [20-22]. Obviously, rice husk ash is suitable for low cost zeolite synthesis, and this advantage certainly decreases the cost needed in the water purification process, especially for drinking water resources.

The superior selectivity properties of the zeolites and their modified forms towards hazardous substances deserve wide and further exploration and development. In general, it must be recognized that relatively less attention has been given in the beginning to study the sorption behavior of synthetic zeolites toward d- and p-block metals and metalloids if compared to aspects of synthesis, gas separation and catalysis. The comparative neglect was clearly biased since the incorporation of zeolite with metals is often an essential component in the preparation and/or manufacturer of zeolites for use either as sorbents or catalysts. This has been motivating worldwide researchers to investigate the sorption behavior of zeolites including ion exchange and adsorption since the past two decades.

1.2 Research Description and Objectives

With the view of long-term bioaccumulation risk of trace level harmful metals to the livings' health, the aim of this research is to compare several types of

modified sorbents, originated from a known extremely good water softener called low silica zeolite P in the removal of some selected toxic metals and inorganic oxyanions from water. The whole experimental design was based on the comparison basis in which sorption behavior of the sorbents were interpreted according to their batch sorption kinetic and equilibrium data in various conditions.

The study was mainly divided to three major component including material development and characterization, cation exchange studies of the materials with some metallic cations as well as adsorption of one of its modified form with selenium oxyanions. Considering the cost efficiency factor, the original low silica zeolite P was synthesized directly from the extremely low cost material, namely rice husk ash as the silica source. The synthesis conditions were investigated and optimized in the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$. Factors affecting the formation of products such as composition of starting materials, heating temperature and crystallization period were also studied.

The as-synthesized zeolite P was converted to nearly homoionic sodium and calcium forms through exhaustively exchange with high concentration sodium and calcium salt solution. The original zeolite was also partially loaded with aluminium sulfate post modification step called desilication. Controlled desilication is an advanced technique where the framework silica of the zeolite is partially removed in basic medium. This technique has been introduced as an effective approach to create significant extraposity in various zeolites [23-24] and increase cation exchange capacity [25-26].

The zeolite samples were well characterized with appropriate techniques including structural analysis with x-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FTIR), solid state NMR under magic angle spinning (MAS); elemental analysis either by wavelength dispersive x-ray fluorescence spectroscopy (WDXRF) or atomic absorption spectroscopy (AAS) post sample decomposition; morphological study with scanning electron micrography (SEM) and surface study with nitrogen adsorption analysis.

Comparisons of the metallic cation sorption behaviors were done among the nearly homoionic sodium and calcium form of the zeolites with the as-synthesized zeolite P. Meanwhile, the aluminium-loaded zeolites P were tested and compared with the original one in the removal of inorganic metalloid species. Divalent lead (Pb), cadmium (Cd), zinc (Zn) and inorganic species of selenium, i.e. Se (IV) and Se (VI) as well were chosen as the target adsorbates due to their toxicity and persistency in the aqueous environment.

Batch mode studies were conducted throughout the whole research instead of column studies. This is the most commonly used technique because of its ease of laboratory operation and ease of data handling. This technique involves placing the known quantity of sorbent and solution containing the known concentration of the metals into a vessel and mixing the samples for a prescribed time. The sorbent and/or solution phases are then analyzed by an accurate elemental analyzer (e.g. atomic absorption spectrophotometry or inductively coupled plasma emission spectrometry), after separation of the mixture with centrifugation and/or filtration.

The goal of this research is to examine the interaction of rice husk ash-synthesized zeolite P and its modified forms with various ions in solutions under ranging conditions to elucidate the mechanism of sorption and ion exchange. The specific objectives of this research are to:

- Optimize the synthesis of zeolite P with gismondine (GIS) framework by using local available rice husk ash as the silica source.
- Investigate the physical and chemical changes of zeolite P after modification with different solid-state techniques.
- To understand the sorption behavior of the as-synthesized and modified zeolites including exchange rate, equilibrium, and selectivity towards selected metallic elements and metalloids under different conditions.
- To evaluate the performance of as-synthesized and modified zeolites in the removal of selected toxic metals and metalloids from aqueous media.

1.3 Organization of Thesis

This thesis consists of six chapters. Chapter 1 presents the general research background, research description, objectives and the thesis organization. Chapter 2 introduces the general nature of zeolites as well as metallic elements and metalloids as contaminants. The following description emphasizes on the materials under study, i.e. gismondine (GIS) group zeolites generally and zeolite P particularly. This chapter also presents extensive review of research relevant to the present study. Chapter 3 describes the synthesis method of material, characterization techniques and the experimental conditions employed in this work. Discussions on the synthesis condition and characterization are the main body in chapter 4 whereas the sorption behaviors of the materials toward the hazardous metals and metalloid oxyanions are focused in chapter 5. The last chapter contains the concluding remarks and also some recommendations for future studies.