



شبكة المعلومات الجامعية
التوثيق الإلكتروني والميكروفيلم

بسم الله الرحمن الرحيم



MONA MAGHRABY



شبكة المعلومات الجامعية
التوثيق الإلكتروني والميكروفيلم



شبكة المعلومات الجامعية التوثيق الإلكتروني والميكروفيلم



MONA MAGHRABY



شبكة المعلومات الجامعية
التوثيق الإلكتروني والميكروفيلم

جامعة عين شمس

التوثيق الإلكتروني والميكروفيلم

قسم

نقسم بالله العظيم أن المادة التي تم توثيقها وتسجيلها
علي هذه الأقراص المدمجة قد أعدت دون أية تغيرات



يجب أن

تحفظ هذه الأقراص المدمجة بعيدا عن الغبار



MONA MAGHRABY



**Ain Shams University
Faculty of Science
Chemistry Department**

Preparation of Synthetic Zeolite from Aluminum and Silicon Based Secondary Resources

**A Thesis
Submitted by**

Reham Mohamed Abdelhameed

**B.Sc. (Chemistry), 2004
M.Sc. (Chemistry), 2010**

**For the Requirement of Ph. D. Degree
of Science in Chemistry**

**To
Department of Chemistry
Faculty of Science
Ain Shams University**

2021



Preparation of Synthetic Zeolite from Aluminum and Silicon Based Secondary Resources

Thesis submitted

By

Reham Mohamed Abdelhameed

B.Sc. (Chemistry) 2004

M.Sc. (Chemistry) 2010

Under the supervision of

Prof. Dr. Mohamed Abd Elhay Ahmed

Professor of physical Chemistry Faculty of Science, Ain Shams
University

Prof. Michel Fahmy Abdel Messih

Professor of physical Chemistry Faculty of Science, Ain
Shams University

Prof. Dr. Ibrahim Ahmed Ibrahim

Professor of Chemical and Electrochemical processing Department,
Mineral Technology Division, Central Metallurgical Research and
Development Institute (CMRDI)

Assoc. Prof. Fatma Emam Farghaly

Associate Professor of Chemical and Electrochemical Processing
Department, Minerals Technology Division, Central Metallurgical
Research and Development Institute (CMRDI)

To

Department of Chemistry
Faculty of Science, Ain Shams
University for Philosophy Degree
(Ph. D.) Chemistry
(2021)



APPROVAL SHEET FOR SUBMISSION



Title of Thesis:

**"Preparation of Synthetic Zeolite from Aluminum and Silicon
Based Secondary Resources"**

Name of candidate:

Reham Mohamed Abdelhameed

This Thesis has been approved for submission by the supervisors:

Signature

1- Prof. Dr. Mohamed Abd Elhay Ahmed

2- Prof. Dr. Michel Fahmy Abdel Messih

3- Prof. Dr. Ibrahim Ahmed Ibrahim

4 Assoc. Prof. Fatma Emam Farghaly

Head of Chemistry Department

Prof. Dr. Ayman Ayoub Abdel-Shafi

Acknowledgement

Above all, praise to **ALLAH**, the lord of the world, by whose grace this work has been completed and never leaving me during this stage.

My deep thanks also to **Prof. Dr. Mohamed Abd Elhay Ahmed**, Professor of physical Chemistry, Faculty of Science, Ain Shams University and **Prof. Michel Fahmy Abdel Messeh** Associate Professor of physical Chemistry Faculty of Science, Ain Shams University for continuous guidance, support and kind advice over the whole duration of the study.

The author is also greatly indebted to **Prof. Dr. El-Sayed Ali Abdel-Aal**, Professor in Chemical and Electrometallurgy Dep., Central Metallurgical R & D Institute (CMRDI), **Prof. Dr. Ibrahim Ahmed Ibrahim**, Professor of Chemical and Electro Metallurgy, Mineral Technology Department, Central Metallurgical Research and Development Institute (CMRDI) and **Assoc. Prof. Fatma Emam Farghaly**, Associate Professor of Chemical and Electro-Processing Department for valuable and fruitful comments and discussions and kind help during the experimental work and theoretical calculation. I express my sincere gratitude for their supervision, during the progress of this work.

I would like to appreciate **Prof. Dr. Mohamed Abdel khalek**, Professor of minerals technology, for his kind help, assistance and fruitful discussions. Many thanks are also directed to all staff members of the Chemical and Electrochemical Dep., (CMRDI)

I would like to express my sincere gratitude to my mother, husband and my kids, sisters and brothers for their patience, support and encouragement especially to my inspiration and my continuous support for Mom for her patience, prayers and support while this work in progress and to my biggest support one ever, my husband, for his encouragement to be always the best one.

Reham Mohamed

Received July 15, 2020; reviewed; accepted October 22, 2020

Exploitation of industrial solid wastes for preparing zeolite as a value-added product and its kinetics as adsorbent for heavy metal ions

R.M. Abdel-Hameed ¹, F.E. Farghaly ¹, E.A. Abdel-Aal ¹, I.A. Ibrahim ¹, M.A. Ahmed ², M.F. Abdel-Messih ², M.A. Abdel Khalek ¹

¹ Central Metallurgical Research and Development Institute (CMRDI), P.O. Box 87 Helwan 11421, Cairo, Egypt

² Chemistry Department, Faculty of Science, Ain shams University, Cairo, Egypt

Corresponding author: rehamabdelhamed81@gmail.com (R.M. Abdel-Hameed)

Abstract: Aluminum and fumed silica as solid industrial wastes were converted to zeolite NaP as a value-added product without any template. The hydrothermal process was optimized using static autoclave. The crystallization was carried out at 100, 120 and 150°C for 24, 48 and 72 h. The prepared zeolite of Si:Al ratio of 1.2 was characterized using X-ray Diffraction (XRD), Scanning Electron Microscope (SEM) provided with Energy Dispersive Spectroscopy (EDS), Surface Area, Fourier Transmitted Infra-Red (FTIR) and Thermal Analysis (TG-DSC). The crystalline phase was formed at 100°C after 72 hours and at 120°C after 48 hours, while it was formed after 24 h only at 150°C. Increasing temperature and time lead to the conversion of the prismatic gibbsite crystals into plate-like structure of zeolite which is then formed cauliflower-like structure. The prepared zeolite was employed as adsorbent for Ni²⁺ and Cu²⁺ ions from aqueous solution. The kinetic studies of adsorption processes were performed.

Keywords: zeolite P, aluminum wastes, hydro-thermal process, metal ion removal, aluminum waste

1. Introduction

Aluminum is one of the most commonly used metals in most forms of everyday life. It is produced from bauxite ore in the primary industry and from scraps in the secondary industry (Tsakiridis et al., 2013). Both industries generate wastes as slag or dross. They contain ultra-fine particle size, which is not a marketable product due to its lower aluminum content (Galindo et al., 2015a). Aluminum waste is considered as hazardous waste due to its risk to the environment and to human health (Galindo et al., 2015b). The European Waste Catalogue classifies it as a hazardous waste. The black dross and ball mill dust is highly flammable able to release toxic gases such as ammonia, methane and hydrogen sulfide. The main negative impacts come from its very fine grain size and its heterogeneous chemical composition (Mahinroostaa and Allahverdi, 2018; López-Delgado et al., 2020). The aluminum content (as oxide) in the most aluminum wastes is approximately 53-81% by weight. Also, the amount of silica fume generated from ferrosilicon alloys and silicon metal industries about 1,000,000 tons. About 25,000 tons of silica fume are produced each year by the Egyptian Ferroalloys Co. (EFACO) from its ferrosilicon plant located in the Edfu City (xalinyuan, 2020). So, they must be used as a “secondary” raw material for the production of added-value materials. (López-Delgado and Tayibi, 2012).

Zeolite is microporous, alumino-silicate mineral. Its importance arises from its structure. It has a three-dimensional tetrahedral structure with negative surface charge. It is generated as a result of isomorphous substitution of Si⁴⁺ by Al³⁺. It may be balanced by alkali and alkali-metal cations and water molecules. It has a general formula of M_{2/n}OAl₂O_{3x}SiO_{2y}·H₂O where M is alkali or alkaline earth element, n is the valence charge on that element, x varies from 2 to 10 and y varies from 2 to 7 (Corma, 1997; Cundy and Cox, 2005; Moliner et al., 2013; Cejka et al., 2016; Visa, 2016). The flexibility of Si-O-Si bond explains its 200 structure forms (Meftah et al., 2008). Zeolite is characteristic of high surface area,

micro porosity, high ion-exchange capacity and high stability (Larsen, 2007; Garcia, et al., 2016). Thus, it is applied in ion exchange, catalysis, chemical separation and membranes (Cao et al., 2008; Huang, 2010).

It is reported that, the Zeolite could be synthesized by different methods. The most common methods are sol-gel, hydrothermal synthesis and microwave heating synthesis (Zubowa et al., 2008). The hydrothermal method includes also the zeolite crystallization from aqueous systems (Vartuli et al., 2000; Boukadir et al., 2002; Hu and Liu, 2003; Aguado et al., 2004). They are prepared by using organic structure-directing agents (OSDAs) (Lobo et al., 1995). However, there are a limited number of zeolites that can be synthesized by OSDA-free routes (Oleksiak and Rimer, 2014). The OSDA-free crystallization of zeolites is not easy to control (Navrotsky et al., 2009; Maldonado et al., 2013; Oleksiak et al., 2016). Although, all zeolites have the same formula and geometric structure, but the SiAl ratio, Na content and hydration is difficult to determine. This is attributed to high flexible of the SiAl link (Hansen et al., 1993; Meier and Olsen, 1996).

There are three polymorphs of zeolite Na-P: cubic (Na-P1), tetragonal (Na-P2) and more rarely orthorhombic (Na-P3). Na-P1 has been described as a body-centred tetragonal with a unit cell of pseudo-cubic geometry (Baerlocher and Meier, 1972; Gottardi and Galli, 1985; Rodrigues et al., 2016). Gismondine framework of zeolite (GIS) and other framework types have proven to be excellent materials for small liquid or gas molecule separation, the removal of radioactive and toxic waste species from wastewaters, and water softening in detergents (Adams et al., 1997; Huo et al., 2012). Zeolite synthesis occurs at temperatures from 70 to 250°C. Some conditions of extreme importance, such as SiAl ratio, crystallization time and temperature (Delgado et al., 2014).

This work aims to develop the hydrothermal process to prepare zeolite from aluminum and silica fume as waste materials without using any template. Then the produced zeolite will be investigated as absorber for copper and nickel ions from aqueous solutions.

2. Materials and methods

2.1. Materials

Ultra-fine aluminum powder waste is supplied by Alumisr Co., for the aluminum industry, Helwan, Egypt. Silica waste and fumed silica were supplied by ferrosilicon Co., Egypt. The particle size is less than 0.074 mm and they are employed as raw materials for zeolite preparation without further treatment. Sodium hydroxide pellets, as a source of alkali was supplied by Sigma Aldrich. Copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and Nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) of reagent grade, Merck Chemicals GmbH are used for preparation of Cu^{2+} and Ni^{2+} ions solutions.

2.2. Methods

2.2.1. Zeolite synthesis

The calculated amount of sodium hydroxide is dissolved in a small amount of pure water. The solution is divided into two portions. Silica waste is added to the first portion and the aluminum waste is added to the second portion. The two solutions were mixed together for 1 h and left for another 1h for aging. Then, it is transferred to a Teflon-lined autoclave reactor. The product is quenched in water, filtered and washed with distilled water till pH 9 and it is dried at 100°C for 24 h.

2.2.2. Characterization of zeolite

The prepared zeolite are characterized using BRUKER X-Ray Diffractometer (Germany) Model AXS D8 with Cu-target ($\lambda=1.540 \text{ \AA}$ and $n=1$) at 40 kV potential and 40 A was used for characterization of the crystal structure of synthesized zeolite. The diffraction data were recorded for 2θ values between 10° and 80° and the scanning rate was 3° min^{-1} or $0.02^\circ/0.4 \text{ sec}$. Micro-pore and BET specific surface area are measured using nitrogen adsorption-desorption isotherms using BEL (Japan) nitrogen adsorption apparatus. A sample is degassed at 120°C prior to BET measurements. The BET specific surface area (SBET) is determined by a multipoint BET method using the adsorption data in the relative pressure P/P0 range of 0.05–0.25. The surface morphology and microstructure of gold coated synthesized zeolite

were identified by JEOL instrument (Japan) model JSM-5410 scanning electron microscope (SEM) at 15 kV of excitation potential. Mattson 1000, series LC operating, issue I (0791) spectro-photometer was used for Fouriertransform infrared (FTIR) measurement in the transmission mode, with a wave number range of 4000-400 cm^{-1} . The spectrum of the sample is carried out in KBr powder using a resolution of 4 cm^{-1} . Standard software (Omic ESP, version 5.1) was used for data acquisition and analysis. The wastes were analyzed using X-Ray Fluorescence, XRF (Axios Advanced WDXRF analytical, Netherland). Energy Dispersive X-Ray spectroscopy EDX attachment with Bruker AXS-Flash Detector 410-M, Germany, is used for characterization. The atomic absorption AAnalyst 200, was used for elemental analysis of digested sample in 20% hydrofluoric acid solution.

2.2.3. Adsorption procedure

An attempt was made to use the zeolite for removal of Ni^{2+} and Cu^{2+} ions aqueous solutions. A 0.05 g of Zeolite is added to 25 ml of synthetic solution and stirred at 200 rpm for different time intervals at the desired pH and temperature.

The removal percent and the sorption capacity of adsorbent were calculated by Eqs. (1) & (2), respectively (Mohora et al., 2012).

$$\text{Removal}(\%) = \frac{C_i - C_t}{C_i} \times 100 \quad (1)$$

where C_i and C_t are the ion concentration (mg/l) at time zero and t, respectively.

$$q_e = \frac{(C_i - C_t)V}{M} \quad (2)$$

where q_e is the sorption capacity of adsorbent at time t, (mg/g), V is the solution volume (liter) and M is the adsorbent weight (g).

3. Results and discussion

3.1. Characterization of silica and aluminum wastes

XRF of fumed silica shows that it is composed of 96.18% SiO_2 with low impurities, Table 1. The relative density of silica fume is 2.14 g/cm^3 . XRD indicated that the main phase of silica fume waste is amorphous silicon dioxide. SEM photograph showed that the silica particles are almost spherically agglomerated, Fig. 1. It is composed of fine vitreous particles with a surface area 20 m^2/g .

XRF of aluminium waste (Table 2) shows that it has high aluminum content ($\text{Al}_2\text{O}_3 = 59\%$) with $\text{SiO}_2 = 1.36\%$ and $\text{Na}_2\text{O} = 2.12\%$. Also, minor MgO , P_2O_5 , Fe_2O_3 , CuO , ZnO , PbO and SO_3 are detected.

The XRD pattern showed that it is mainly composed of gibbsite (aluminum hydroxide) - Fig. 2. FTIR scan confirms the gibbsite composition - Fig. 3 (Rodrigues et al., 2016). Morphology and EDS show hexagonal and prismatic gibbsite crystals with chamfered faces of different sizes (Huo et al., 2012) - Fig. 4.

Table 1. Chemical analysis of the applied silica fume

Item	SiO_2	CaO	TiO_2	K_2O	MnO	Al_2O_3	Fe_2O_3	P_2O_5	Na_2O	MgO	L.O.I.	Total
%	96.19	0.321	0.003	0.159	0.036	0.511	0.231	0.005	0.012	0.016	2.080	99.56

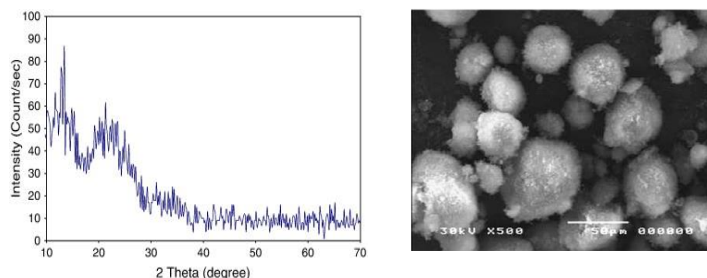


Fig. 1. XRD pattern and SEM photograph of silica fume

Table 2. Chemical analysis of Alumisr aluminum waste

Item	Al ₂ O ₃	SiO ₂	Na ₂ O	MgO	P ₂ O ₅	Fe ₂ O ₃	CuO	ZnO	PbO	SO ₃	CaO	L.O.I	Total
%	59.04	1.36	2.12	0.473	0.072	0.717	0.045	0.104	0.013	0.327	1.54	34.17	99.98

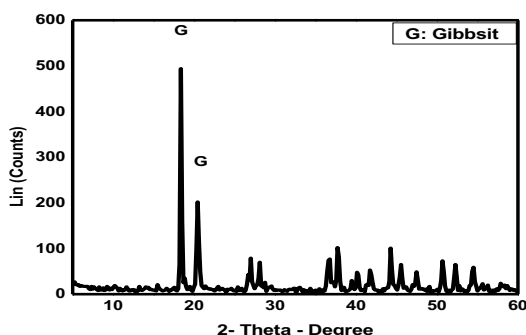


Fig. 2. XRD pattern of Aluminum waste

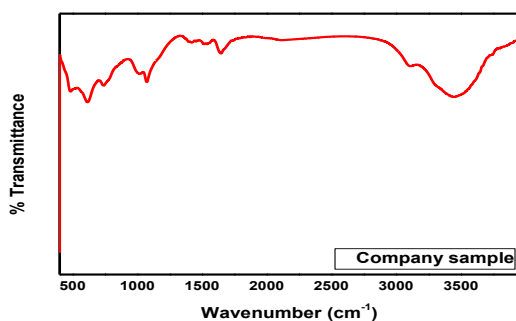


Fig. 3. FTIR spectra of Aluminum waste

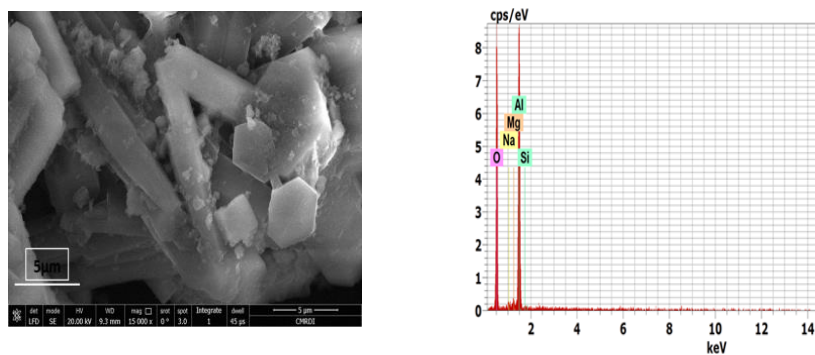


Fig. 4. SEM and EDX of Aluminum waste

3.2. Zeolite preparation

As stated in latter studies the molar ratio of Si/Al is the most important parameter that controls crystallization and morphology of zeolite (Huo et al., 2012). The most appropriate ratio of Si/Al reported in literature where high-silica, cubic NaP₆ (Si/Al = 3.38) and NaP₂ (Si/Al = 4.6) (Larsen, 2007) are required is 1.2. Thus, the preparation is carried out with the most favourable silicon and aluminum ratio (1.2) which obtains the maximum yield. Because the crystal growth and zeolite type depend on the crystallization time and temperature (Mohora et al., 2012), both factors were investigated.