

The Utility of Rice Husk Ash from Biomass Power Plant: Synthesis of Na-A and Na-X Zeolites Using the Two Step Method Hydrothermal

Chawikarn Santasnachok¹, Winarto Kurniawan¹, Chris Salim², and Hirofumi Hinode¹

¹Tokyo Institute of Technology/Department of International Development Engineering, Tokyo, Japan

²Surya University/Department of Environmental Engineering, Banten, Indonesia

Email: {santasnachok.c.aa, kurniawan.w.ab, hinode.h.aa}@m.titech.ac.jp, chris.salim@surya.ac.id

Abstract—Rice husk ash (RHA), a solid waste from biomass power plant was used as a raw material to synthesize Na-A and Na-X zeolites. In fact, high silica content of this material opens a possibility for it to be used as a potential zeolite precursor. In this study, a medium size particle of RHA has been reused to prepare zeolite with high purity. After segregation by mechanical sieving, the medium size particle fraction of RHA was subjected to alkali fusion treatment followed by dissolution and then residue separation to produce clear silicate supernatant as the silica source for preparing the low-silica zeolites. High purity Na-A and Na-X zeolites were prepared using hydrothermal treatment by optimizing the process condition, curing time, hydrothermal temperature and Si/Al molar ratio in the reaction mixture. The utilization of zeolite for adsorption of cadmium using batch technique was investigated. The effect of time, dosage and initial concentration of solutions on the adsorption was investigated. The result showed that adsorption capacity of Na-A zeolite was much higher than that of Na-X zeolite. The equilibrium data were fitted by the Langmuir model. Na-A and Na-X zeolites synthesized with the optimal condition possessed a maximum value of cation exchange capacity (CEC) of 470 meq/100 g and 503 meq/100g, respectively.

Index Terms—zeolites, fly ash, hydrothermal treatment, adsorbent.

I. INTRODUCTION

Currently there is increasing interest in synthesizing zeolite from by-products such as oil shale ash [1], bagasse fly ash [2], coal fly ash [3], [4], and rice husk ash [5]–[7]. Rice husk is one of the agriculture milling by-products of rice and one of the important by-products of biomass available in Thailand as well as globally. It is used as a major energy source to generate electricity which produces ash as its major solid waste. Majority of the rice husk ash is dumped or used in low-valued methods such as using as a land-fill material, soil improvement, and raw materials in cement production [6]. Initially, it was found that when rice husk is burnt, the

resulting black ash contains silica. It is similar to raw materials typically used in zeolite synthesis.

Zeolites are crystalline microporous aluminosilicates with very well-defined structures that consist of a framework formed by tetrahedra of SiO_4 and AlO_4 . The isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedra results in a negative charge on the zeolite framework that can be balanced by exchangeable cations. Hence, zeolites can exchange cations but not anions. It has been demonstrated that the cationic surfactants have a great affinity to this negative charge. Zeolites have high cation exchange ability as well as molecular sieve properties. It shows special importance in water and gas purification, catalysts for hydrogenation, alkylation, isomerization and sorbents for the removal of contaminants such as heavy metals, toxic gases, dyes and organic pollutants [8]. The most common method used for zeolites synthesized were involves a hydrothermal process. There are two main methods for zeolite synthesis using solid wastes as the silica-alumina source. The methods are widely recognized as single step and two step method. The single step method aims to utilize whole part of the silica containing solid waste for zeolite production without any separation. Usually this method employs hydrothermal treatment in a single pot for all preparation sequences, i.e. dissolution of silica and alumina from the bulk solid in alkali solution and then re-crystallization of the two components into zeolites covering the un-dissolved solid. By employing this method there will be no leftover residue, however particles irregularities and crystal variety in the zeolite end products become the major drawbacks of this method. On the other hand, the two step method requires solid residue separation after most of silica and alumina content have been dissolved in the alkali solution. The residue removal increases the possibility in producing desired type of zeolite with high purity and particle regularity (shapes and sizes) but leaving a new solid waste along with very low production yield. Meanwhile, for eliminating any waste generation, a combination between the two methods has been proposed to produce high purity zeolite from the supernatant and

also low grade zeolite from the mixture of the solid residue and the spent reaction time [2].

It has been known that heavy metal in industrial wastewater represents an important source of environmental pollution [9]. Heavy metals like cadmium is an element that occurs naturally in the earth's crust and is found to be associated with zinc minerals [8], [10]-[12]. Mae-Sot District in Tak Province of Thailand is contaminated with high cadmium levels. O. Krissanakriangkrai, *et al.*, 2009 have found the high concentration of cadmium in water, sediment, fish and shellfish [13]. The major sources come from industrial process which is released to the environment then become a water pollutant such as electroplating, cadmium-nickel battery, phosphate fertilizers, mining, pigments, stabilizers and alloys manufacturing [8], [14]. Cadmium is one of the most toxic metal ions as it is a non-essential and non-biodegradable metal ion. It is harmful for human and animal since it can be accumulated in the blood causing a variety of symptoms such as high blood pressure, kidney damage, and destruction of red blood cells [9]. The permissible limit for cadmium as described by the World Health Organization (WHO) is 0.01 mg/L [15]. There are varieties of water treatment for contaminated cadmium such as filtration, reverse osmosis, flocculation, activated carbon, ion-exchange, chemical precipitation or coagulation, ultrafiltration and electrochemical. However the aforementioned techniques are not economically feasible for small or medium industries and rural area or developing countries. Recently, the adsorption processes using agricultural waste products or biosorption are becoming the new alternative for waste water treatment and suitable for small or medium industries and rural area or developing countries as well.

This study was aimed to investigate the effect of reaction condition in hydrothermal treatment of supernatant (Silica extraction solution) such as alkali concentration for silica extraction method, treatment temperature, treatment time and amount of sodium aluminate added for zeolite preparation method. Then zeolites with a better result would be used to study the effectiveness of cadmium ion adsorption process by determining the maximum adsorption capacity of cadmium by batch experiment. The kinetic or rate of adsorption based on pseudo-first order, pseudo-second order and adsorption isotherms were also studied.

II. MATERIALS AND METHODS

A. Materials

The rice husk ash after combustion (650°C) from Roi-Et Green power plant in the Northeastern of Thailand was used as raw material. The sample was then sieved to remove dirt and was dried in an oven at 100°C overnight. The particle fraction was separated from the bulk rice husk ash by mechanical sieving using standard sieve of 25 meshes (particle size less than 0.710 mm).

All the chemicals were obtained from Wako Pure Chemical Industries, Ltd., Japan. Stock solutions of

cadmium were prepared by dissolving cadmium nitrate tetrahydrate, 99.9% in deionized water.

B. Silica Extraction from Rice Husk Ash

The first preparation step was the extraction of silicon and aluminum content from medium RHA particles proposed by Purnomo *et al.* (2012) [2]. 10 g of ash was mixed with sodium hydroxide powder (Waco; 97 wt.% NaOH) with different weight ratios of RHA:NaOH (1:1 and 1:2) and heated at different temperature of 100, 200, 300, 400 and 500°C for 1 and 2 hours. The mixture was then cooled to room temperature and milled for several minutes. The obtained powder was mixed with deionized water with weight ratio of powder to water of 1:5 followed by aging for 2 hours with agitation at room temperature. Then solid in the mixture were filtered to obtain a clear supernatant by using WhatmanTM filter paper 540 hardened ashless. The concentrations of silicon, aluminum and sodium in the supernatant were measured with Inductively Couple Plasma-Atomic Emission Spectroscopy (ICP-AES) method using SPS 7800 (SII).

C. Zeolite Preparation

The synthesis of zeolite was prepared from silicon and aluminum in the supernatant after its concentration measured by ICP-AES. A mixture of zeolites were synthesized from the high silica supernatant mixed with sodium aluminate solution from dissolution of sodium aluminate powder (Waco; 0.77M ratio of Al/NaOH) into deionized water for preparing the reaction mixture with Si/Al molar ratio of 0.5 to 2.0. The mixture were stirred in ultrasonic bath for 5 minutes then stirred for 1 hour with magnetic stirring machine, after that the mixture was mixed thoroughly and treated at 90° and 120°C for 10 to 24 hour in TeflonTM – lined stainless steel vessels of 15 mL capacity without agitation. The final procedures were filtering, washing and drying of the precipitates. For identification, zeolite sample names follow this rule: ZR_xT_yz where x is the Si/Al molar ratio in the parent solution, y is the hydrothermal temperature in °C and z is the hydrothermal time in hours.

D. Cation Exchange Capacity (CEC)

The cation exchange capacity (CEC) of zeolites synthesized was measured using sodium acetate method to exchange all the cations in the material with sodium using sodium acetate and then extract all of them using ammonium acetate [16]. The extracted sodium ions will then be analyzed using ICP-AES.

E. Preparation of Synthetic Waste Water

Cadmium Nitrate Tetrahydrate: Cd(NO₃)₂·4H₂O was used to prepare a stock solution of 1000 mg/L of Cd(II). The solution was diluted from this stock solution in the following step.

F. Adsorption Experiment

Batch adsorption experiments were carried out in series of volumetric flasks (100 mL) and covered with cap to prevent contamination. The effect of contact time (0 – 3 hours), initial concentration of solution (10 – 250 mg/L and adsorbent dosage (0.5 – 3.0 g/L) on the

adsorption of cadmium on zeolites was investigated. All adsorption experiments were carried out on a shaker at 100 rpm in the same temperature (30°C). After adsorption, the solution was filtered and analyzed with ICP - AES.

The percentage removal (1) and equilibrium concentration (2) on the adsorbent has been calculated for all the studied parameters using the following equation.

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

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

where C_i and C_e are initial and equilibrium of heavy metal ion concentration in (mg/L), respectively. V is the volume of solution in (L), M is the amount of zeolite in solution in (g), and q_e is the mass of heavy metal adsorbed per unit mass of zeolite at time t in (mg/g).

G. Characterizations

The elements of Si, Al, Na, Mg, K, Fe and others in the raw material was analyzed using ICP-AES. N_2 adsorptions of synthesized materials were carried out using Autosorb 1 (Quantachrome) and the specific surface areas were calculated using BET method. X-ray diffraction (XRD) analyses using Multiflex (Rigaku) with Cu-K α radiation were carried out to determine the crystalline type of zeolites produced. Scanning electron microscopy using JSM-5310LV (JEOL) was conducted to observe the surface morphology and FT-IR analysis of zeolites was performed using Perkin Elmer spectrophotometer.

III. RESULTS AND DISCUSSIONS

A. Characterization of Rice Husk Ash and Supernatant after Silica Extraction

The chemical compositions of the rice husk ash from power plant was as follow: Si was 27.05 wt.%, Al was 5.03 wt.%, Na was 41.59 wt.%, Mg was 0.87 wt.%, K was 0.42wt.%, Fe was 0.11wt.%, the others were 24.93 wt.% and the loss of ignition (LOI) was 5.15%. The surface area of RHA was 17.13 m²/g. The XRD pattern of rice husk ash showed in Fig. 1, confirms the main composition of SiO₂ with crystalline type of quartz and cristobalite. The broad peak between 2 θ of 21 – 32° implied the presence of amorphous phase of carbon and silica.

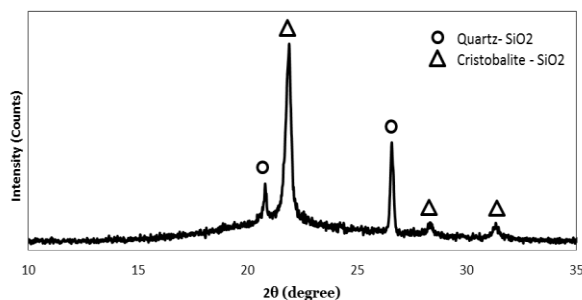


Figure 1. XRD pattern of rice husk ash from power plant at 650°C.

The composition of supernatants obtained from RHA extractions with different conditions were listed in Table II. at RHA:NaOH ratio of 1:1 and heating time of 1 hour, the change of temperature from 500°C to 400°C and 300°C resulted in the change of silicon content from 21400 mg/L to 23809 mg/L and 23333 mg/L, respectively and the change of aluminum content from 500 mg/L to 952 mg/L and 476 mg/L, respectively.

For the condition of heating time of 2 hours, RHA:NaOH ratio of 1:2, temperature of 300°C, the silicon and aluminum dissolved were 24286 mg/L and 952 mg/L, respectively.

For heating time of 2 hours with RHA:NaOH ratio of 1:1 and temperature of 200°C, the amount of silicon has been changed to 22857 mg/L and heating time of 2 hours with RHA:NaOH ratio of 1:2 and temperature of 100°C, the amount of silicon and aluminum have been changed to 6667 mg/L and 476 mg/L, respectively. The supernatant extracted at RHA:NaOH of 1:1, heating temperature of 300°C and heating time of 1 hour was used in the next step of hydrothermal treatment of the supernatant

B. The Effect of Si/Al Molar Ratio, Hydrothermal Heating Time and Temperature

Adjusting the ratio of Si/Al in the reaction mixture prior to undergoing crystallization by hydrothermal treatment is the most important aspect in determining crystal structure of the end zeolite product. Because the supernatant has very low aluminum content, sodium aluminate solution was added to increase its concentration in the mixture.

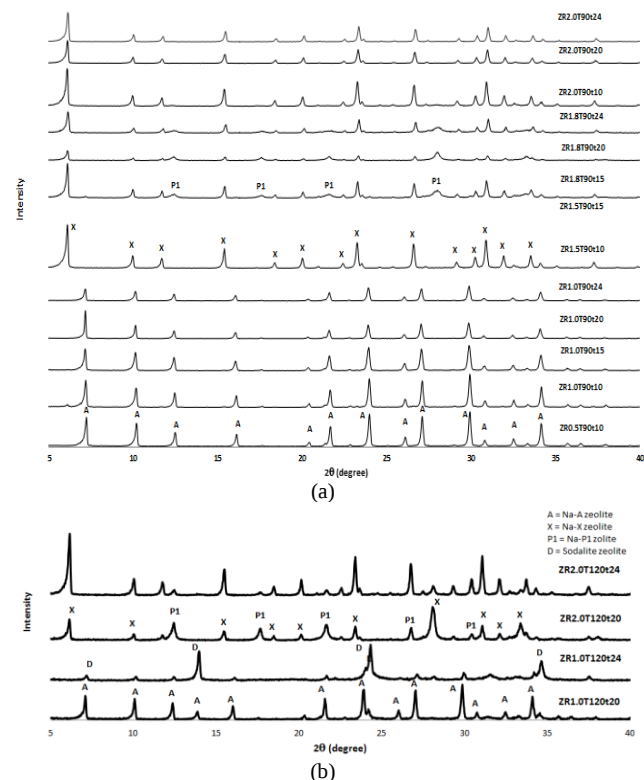


Figure 2. XRD pattern of produced zeolite by hydrothermal treatment at 90°C (a) and 120°C (b) in different Si/Al ratio, heating time and temperature.

Fig. 2 (a), the heating temperature of 90°C, Si/Al molar ratio of 1.5, and heating time of 10 hours was critical ratio to prepare pure zeolite X (PDF 38-0237: $\text{Na}_2\text{Al}_2\text{Si}_{2.5}\text{O}_9 \cdot 6.2\text{H}_2\text{O}$) named ZR1.5T90t10. Increase the ratio higher than 1.5 and heating time higher than 10 hours, the mixture of zeolite Na-X and Na-P1 (PDF 39-0219: $\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32} \cdot 12\text{H}_2\text{O}$) was formed in the name of ZR1.8T90t15, ZR1.8T90t20 and ZR1.8T90t24, while when the Si/Al molar ratio increased to 2.0 and heating time from 10 to 24 hours in the name of ZR2.0T90t10, ZR2.0T90t20 and ZR2.0T90t24, the pure zeolite Na-X was formed. On the other hand, using lower Si/Al ratio (1.0 and 0.5) zeolite Na-A (39-0222: $\text{Na}_{96}\text{Al}_{96}\text{Si}_{96}\text{O}_{384} \cdot 216\text{H}_2\text{O}$) was formed and they are named ZR0.5T90t10, ZR1.0T90t10, ZR1.0T90t15, ZR1.0T90t20, and ZR1.0T90t24.

Fig. 2 (b) shows the zeolite prepared at heating temperature of 120°C. The Na-A zeolite was formed at the Si/Al ratio of 1.0 with heating time of 20 hours (ZR1.0T120t20). Increase in the heating time to 24 hours (ZR1.0T120t24) caused the sodalite zeolite to form instead. Higher Si/Al ratio at 2.0 results in the mixture of Na-X and Na-P1 zeolites (ZR2.0T120t20 and ZR2.0T120t24). It could be concluded that heating temperature of 120°C pure product could not be achieved due to sodalite and aluminosilicate impurity.

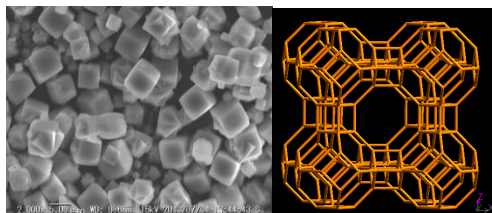


Figure 3. Unit cell structure [18] and crystal morphology of Na-A zeolite synthesized from $\text{Na}_{96}\text{Al}_{96}\text{Si}_{96}\text{O}_{384} \cdot 216\text{H}_2\text{O}$.

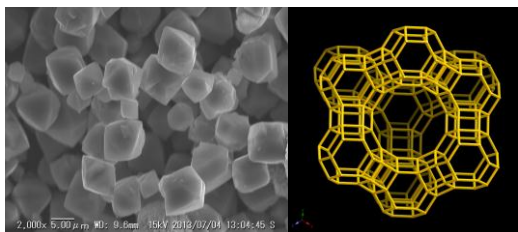


Figure 4. Unit cell structure [18] and crystal morphology of Na-X zeolite synthesized from $\text{Na}_2\text{Al}_2\text{Si}_{2.5}\text{O}_9 \cdot 6.2\text{H}_2\text{O}$.

The purity was also confirmed by SEM images of the two main zeolite types. It can be seen that the building unit of Na-A zeolite was in cubic shape, developed from the connection of sodalite cage (β -cage or T24 unit) along the cube axes through double T4-rings showed in Fig. 3. Zeolite X (Fig. 4), which belongs to Faujasite (FAU) family, has a three-dimensional framework built up of small sodalite cages linked by means of hexagonal prisms or doublet-six rings. The large cages (β -cages) thus formed possess an internal diameter of 13Å and the supercages are interconnected mutually by 12-membered rings [17], [18]. The inner diameter of the sodalite cages and supercages, with the charge compensating cations

placed inside, amount to 0.26 and 0.9 nm, respectively, while their entrance apertures amount to 0.22 and 0.74 nm, respectively [19], [20]. The surface area, pore size and the cation exchange capacity (CEC) of the synthesis Na-A zeolite: ZR1.0T90t15 was 134.7 m^2/g , 0.50 and 470 meq/100g, respectively. On the other hand, the surface area, pore size and the cation exchange capacity (CEC) of the synthesis Na-X zeolite: ZR2.0T90t20 was 703.2 m^2/g , 0.49 and 503 meq/100g, respectively. The IR spectra of absorption bands due to the formation of structural unit during zeolite crystallization are shown in Fig. 5. All of the band assignments of rice husk ash, zeolite A and X follow the work pioneered by Flanigen *et al.* [21]. The formation of rice husk ash after combustion at 650°C from biomass power plant was showing the presence of absorptions at 459, 792 and 1090 cm^{-1} . The band at 459 and 792 cm^{-1} are due to the S4R T-O-T (where T = Si or Al) symmetric stretching, while the absorption at 1090 cm^{-1} is due to siloxane bonds; Si-O-Si. The spectrum of Na-A zeolite exhibited absorptions at 459, 554 and 1001 cm^{-1} . The 1001 cm^{-1} band was due to the Si-O-Si siloxane bond. The band at 554 cm^{-1} was attributed to the D6R T-O-T symmetric stretching. On the other hand, the spectrum of Na-X zeolite exhibited absorptions at 456, 554, 670, 753 and 974 cm^{-1} . The 974 cm^{-1} band was due to the Si-O-Si siloxane bond. The 753 cm^{-1} band was due to the S4R T-O-T symmetric stretching while the absorption at 670 cm^{-1} was attributed to the Si-O-Al symmetric stretching. The 554 cm^{-1} and 456 cm^{-1} bands were due to the D6R T-O-T symmetric stretching and S4R T-O-T symmetric stretching, respectively.

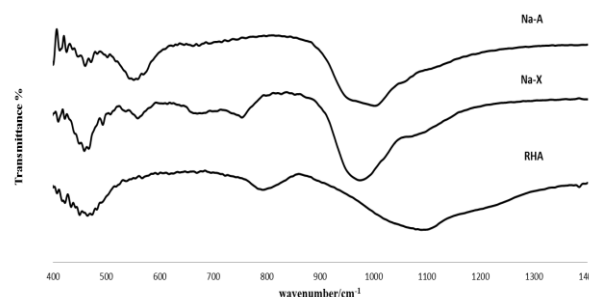


Figure 5. FTIR spectra of rice husk ash (RHA), Na-A and Na-X zeolites.

C. The effect of Initial Concentration and Time on Cadmium Removal onto Na-A and Na-X Zeolites

The adsorption capacity of cadmium ion (Cd^{2+}) on zeolites was tested by varying initial concentration of cadmium solution from 50, 100 and 150 mg/L, adsorbent dosage of 0.5 g/L at pH 7 solution. The concentration of cadmium was measured at regular interval of time from 5 to 180 min. Both synthesized Na-A and Na-X zeolites were investigated as shown in Fig. 6.

In the first 5 min, 50 mg/L cadmium ion solution was completely adsorbed onto both zeolites while adsorption for 100 mg/L solution onto Na-A and Na-X zeolites was 80% and 47%, respectively. Adsorption of 150 mg/L cadmium ion solution onto Na-A and Na-X zeolites was

34% and 27%, respectively. Then after 3 hours, percentage adsorption of 100 mg/L Cd^{2+} onto Na-A and Na-X zeolites was increased to 80% and 47%, respectively. It showed the same trend with 150 mg/L Cd^{2+} onto Na-A and Na-X zeolites where adsorption was increased to 72% and 64%, respectively. The cadmium adsorption increased with increasing adsorption time. On the other hand, the adsorption capacity was decreased with increasing cadmium concentration solution and Na-A zeolite has a better adsorption capacity than Na-X zeolite.

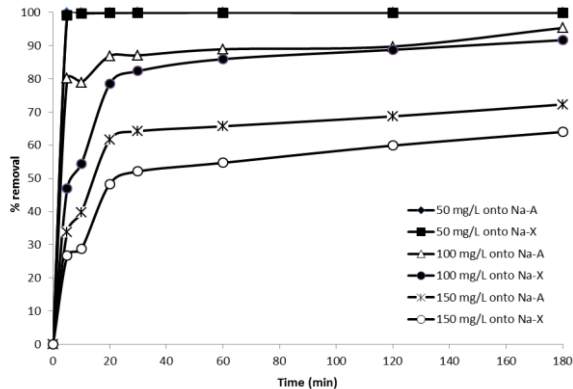


Figure 6. Effect of time on the adsorption of cadmium ion solution for different initial concentration.

D. Adsorption Isotherms

For both type of zeolites, Langmuir and Freundlich adsorption models were applied and studied to describes the interaction between adsorbate and adsorbent material [22], [23]. The adsorption experiment was carried out by contacting 50 mL solution of Cd^{2+} (concentration: 30, 50, 100, 150, 200, and 250 mg/L) with 0.5 g/L of adsorbent for 3 hours. The Langmuir isotherm was described by the following equation;

$$\frac{C_e}{q_e} = \frac{1}{bQ^0} + \frac{C_e}{Q^0} \quad (3)$$

where q_e is the mass of heavy metal adsorbed per unit mass of zeolite at time t in (mg/g), C_e is the equilibrium of heavy metal ion concentration in (mg/L), Q^0 is the maximum adsorption capacity (mg/g) and b is the Langmuir constant (L/mg). Q^0 and b can be determined from the slope and intercept of the linear plot of $\frac{C_e}{q_e}$ against C_e , respectively.

The Freundlich isotherm was described by the following equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where K_F is the Freundlich constant (mg/g) and $\frac{1}{n}$ is an empirical constant. K_F and $\frac{1}{n}$ can be determined from

the slope and intercept of the linear plot of $\log q_e$ against $\log C_e$, respectively.

Adsorption data with Langmuir and Freundlich isotherms are shown in Fig. 7 and Fig. 8, respectively, and their corresponding isotherm parameters are listed in Table I. Comparison of experimental data with Langmuir isotherms showed R^2 value closer to unity than those with Freundlich isotherms.

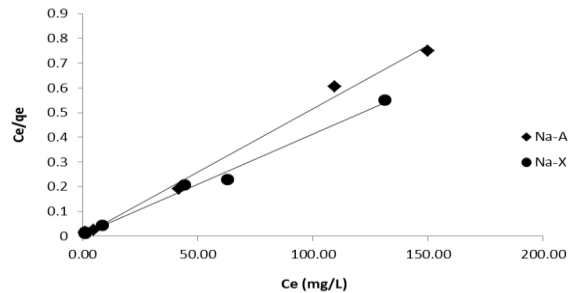


Figure 7. Adsorption isotherm of adsorbent Na-A and Na-X zeolites for Langmuir isotherm, condition adsorption: dosage 0.5 g/L, conc. 30 -250 mg/L, 30°C, pH 7.

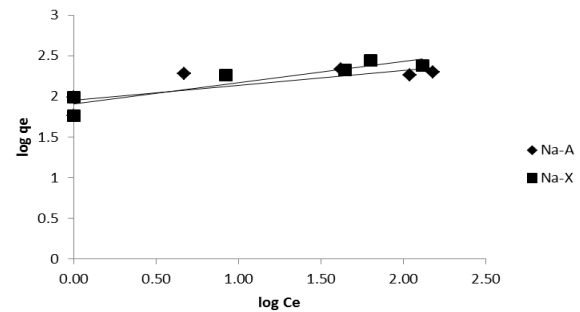


Figure 8. Adsorption isotherm of adsorbent Na-A and Na-X zeolites for Freundlich isotherm, condition adsorption: dosage 0.5 g/L, conc. 30 -250 mg/L, 30°C, pH 7.

TABLE I. LANGMUIR AND FREUNDLICH PARAMETER FOR ADSORPTION OF CADMIUM ION ON ADSORBENT ZEOLITES

Zeolite types	Langmuir isotherm			Freundlich isotherm		
	b (L/mg)	Q_0 (mg/g)	R^2	K_F	1/n	R^2
Na-A	3.71	192.31	0.995	7.07	5.43	0.639
Na-X	2.93	243.93	0.992	6.73	3.83	0.848

It can be seen from correlation coefficient (R^2) that the Langmuir model is better than Freundlich model in simulation of the adsorption isotherm. This result is same as W. Chunfeng *et al.*, (2009) [24] which studied the zeolites from fly ash for heavy metals adsorption. The agreement of the Langmuir model with the experimental results suggests that a monolayer coverage of Cd^{2+} ion on the outer surface of both zeolites. The maximum equilibrium adsorption capacity obtained for Cd^{2+} onto Na-A and Na-X zeolites is 192.2 and 243.93 mg/g, respectively.

IV. CONCLUSIONS

The rice husk ash waste from power plant in Thailand can be used for synthesized a pure Na-A and Na-X

zeolites by using it as silica source by employing alkali fusion and then extraction with residue removal followed by hydrothermal treatment. Zeolite A was formed at 90°C hydrothermal temperature for 10 to 24 hours by varying Si/Al molar ratio from 0.5 to 1.0. On the other hand, Na-X zeolite were formed in the same hydrothermal heating time as zeolite A by varying Si/Al ratio from 1.5 to 2.0 with heating time of 10, 20, and 24 hours, respectively. Zeolite P1 was formed together with zeolite X at the ratio of 1.8 with heating time of 15 to 24 hours. Na-A and Na-X zeolites synthesized with the optimal condition possessed a maximum value of cation exchange capacity of 470 meq/100 g and 503 meq/100g, respectively. The comparative studies showed that Na-A zeolite was more effective in removing metal ion (Cd^{2+}) compared to Na-X zeolite. Adsorption isotherms studies showed that the adsorption process could be best fitted by the Langmuir equation. Overall, both zeolites were able to reduce cadmium ion concentration to meet the criteria of 0.01 mg/L set by the WHO.

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Chawikarn Santasnachok graduated from department of Chemical Engineering, Burapha University, Thailand in 2007 for her undergraduate degree, and obtained her master degree from Department of Chemical Engineering, De La Salle University, Philippines in 2009. Her master thesis was on the effects of process parameters in the removal of arsenic using treated laterite as adsorbent.

She worked at Burapha University, Thailand as a lecturer in Chemical Engineering Department for 2 years and currently she is studying a Ph.D. degree at Tokyo Institute of Technology, and her main topic of research is utilization of rice husk ash from biomass power plant in Thailand.



Winarto Kurniawan graduated from department of Gas and Petrochemical Engineering, University of Indonesia in 2000 for his undergraduate degree, and obtained his master and doctoral degree from Department of International Development Engineering, Tokyo Institute of Technology in 2006 and 2009, respectively. His doctoral thesis was on the utilization of Indonesian natural zeolite for soot oxidation catalyst.

He worked at Kureha Corporation for 4 years and mainly he was assigned in the Carbon Product Department where his research topic was on the quality improvement of lithium-ion battery anode materials. Currently he is working as assistant professor at Tokyo Institute of Technology, and his main topic of research are environmental catalysis and utilization of waste materials.



Hirofumi Hinode graduated from Department of Chemical Engineering, Tokyo Institute of Technology in 1978 for his undergraduate degree, and obtained his master and doctor degree from Department of Chemical Engineering, Tokyo Institute of Technology in 1980 and 1983, respectively. His doctoral thesis was “Equilibrium Study and Crystal Chemistry in Compounds in the Fe-Nb-S System”.

After graduation, he worked as assistant professor at Tokyo Institute of Technology on April 1983, and promoted to Full Professor on January 2000.

His research topics are (1) Environmental Catalysis (air pollution control and water pollution control) and (2) Utilization of waste material.



Chris Salim was born in Medan, Indonesia, on December 25, 1976. He graduated from the doctoral program in Tokyo Institute of Technology on March 2005 earning Ph.D. degree in Engineering.

His first employment experience was as an assistant professor at the same university from April 2005 until June 2013. Then, he returned to his home country, Indonesia, to continue his academic work as a lecturer at Surya University in Tangerang. From the same institution, he was also entrusted to lead one of the research centers, Indonesia Center for Clean Water Technology, as the director.

His fields of specialization include environmental technology and material, and separation process.