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KINETIC AND THERMODYNAMIC STUDIES OF REMOVAL OF CADMIUM ION ONTO SYNTHETIC PURE ZEOLITE FROM RICE HUSK ASH THAILAND

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Kinetic and Thermodynamic Studies of Removal of Cadmium Ion onto Synthetic Pure Zeolite from Rice Husk Ash, Thailand

Chawikarn Santasnachok ^α, Winarto Kurniawana ^σ & Hirofumi Hinodea ^ρ

Abstract- The rice husk ash (RHA) waste from biomass power plant in Thailand is still underutilized leaving disposal problems. Indeed, this material content high silica inside it has a possibility to become a potential zeolites precursor. In this study, small particle of RHA has been reused to prepare a Na-A and Na-X zeolites with high purity using two step method hydrothermal treatments. First, RHA was submitted to a chemical pre-treatment using NaOH powder and then adjusting the Si/Al molar ratio by adding sodium aluminate solutions, and maintaining the mixture at different temperature and heating time. Pure zeolites used to remove cadmium from aqueous solution concentration ranging from 30 to 500 mg/L and at the temperature of 20, 30 and 40°C using batch technique. The effect of time, initial concentration, pH and temperature on removal process was investigated. The results showed that kinetic data were followed more closely the pseudo-second order model than the pseudo-first order by both zeolites. The adsorption isotherms were described by Langmuir and Freundlich isotherm models, and both model fitted well with both zeolites. The thermodynamic parameters such as, Gibbs free energy changes (ΔG_0), standard enthalpy change (ΔH_0) and standard entropy change (ΔS_0) had been determined. The results show that cadmium ion removed onto Na-A and Na-X zeolites are an endothermic and spontaneous in nature.

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1. INTRODUCTION

Rice husk is well-known as an agriculture byproduct of the rice milling industry. It is the most important agriculture residues in quantity in Thailand. The rice husk can be used as a fuel in the plant's steam boiler to generate hot steam in the power plant [1]. If the remaining ashes from burned husks are not collected and treated properly, they could become air pollutants that affect the environment due to the small particle size and light weight. The utilization of these ashes as raw materials in cement industries or insulator in steel industries has been practiced. The study of rice husk ash showed high content of silica and alumina similar to raw materials typically used in zeolite synthesis [2]. These raw materials can be coal fly ash

[3, 4], oil shale ash [5], bagasse fly ash [6], or rice husk ash [7, 8, 9]. Therefore, rice husk ash is a potential raw material for 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 [10]. 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 [6].

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Heavy metal in industrial wastewater represents an important source of environmental pollution [11]. Heavy metals like cadmium is an element that occurs naturally in the earth's crust and is found to be associated with zinc minerals [10, 12-14]. 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 [15]. 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 [10, 16]. 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 [11]. The permissible limit for cadmium as described by the World Health Organization (WHO) is 0.01 mg/L [17]. 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. The aim of this work is to investigate the effect of reaction condition in hydrothermal treatment of supernatant (silica extraction solution) such as alkali condition for silica extraction method, treatment temperature, treatment time and amount of sodium aluminate added for zeolite preparation method. Zeolite used to study the effectiveness of cadmium ion adsorption process by determining the maximum adsorption capacity of cadmium by batch experiment. Kinetic data can be used to predict the rate at which the target contamination is removed from aqueous solutions and equilibrium adsorption isotherms are used to quantify the adsorptive capacity of a cadmium ion. Thermodynamic studies for the removal of cadmium have been undertaken to understand the process of removal in a better way.

II. EXPERIMENTAL

a) Materials

Rice husk ash (RHA) was corrected directly from electrostatic precipitators of Roi-Et Green power plant, Thailand after combustion at 650°C. This ash was used without any pretreatment and its properties was

characterized by various techniques. Rice husk ash has content of SiO₂ above 90 wt% and other oxides below 3wt%. Quartz and cristobalite were found as the main phases. All the chemicals used in the present studies were obtained from Wako Pure Chemical Industries, Ltd., Japan.

b) Methods

i. Silica extraction from rice husk ash

Rice husk ash was sieved to remove dirt and dried in 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 0.71 mm.). The first preparation step was the extraction of silicon and aluminum content from RHA particles. 10 gram of ash was mixed with sodium hydroxide powder (Waco; 97 wt% NaOH) with different weight ratio of RHA:NaOH (1:1) and heated temperature of 300°C for 1 h. The mixture was then cooled to room temperature. The obtained powder was mixed with deionized water with weight ratio of powder to water of 1:5 followed by aging for 2 h with agitation at room temperature. Then solid in the mixture were filtered to obtain a clear supernatant by using Whatman™ 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).

ii. Zeolites synthesis from rice husk ash

Zeolites synthesis was done by hydrothermal treatment. The synthesis mixture was prepared from the high silica supernatant and sodium aluminate (NaAlO₂) solution from dissolution of sodium aluminate powder (Waco; 0.77M ratio of Al/NaOH) into deionized water with Si/Al molar ratio of 1.0 and 2.0 then, the mixtures were stirred for 1 hour, after that mixed thoroughly and treated at 90°C for 15 and 20 h in Teflon™ – lined stainless steel vessels of 15 mL capacity without agitation to synthesized Na-A and Na-X zeolites, respectively. The final procedures were centrifuging, washing and drying of the precipitates.

c) Characterization of rice husk ash and synthesized zeolites

The chemical composition of rice husk ash was analyzed by using Inductively Couple Plasma-Atomic Emission Spectroscopy (ICP-AES) method using SPS7800 (SII), N₂ adsorptions of synthesized materials were carried out using Autosorb1 (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 microscope (SEM) using Keyence VE-8800 was conducted to observe the surface morphology and FT-IR analysis of zeolites uses

performed using Perkin Elmer Spectrophotometer. 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. The extracted sodium ions will then be analyzed using ICP-AES.

d) Preparation of synthetic waste water

Cadmium Nitrate Tetrahydrate: $Cd(NO_3)_2 \cdot 4H_2O$ was used to prepare a stock solution of 1000 mg/L of Cd(II). The solution was dilute from this stock solution in the following step.

e) Cadmium removal studies

The experiments were conducted in a set of 250 mL volumetric flasks with cover cap to prevent contamination, where solutions of cadmium was carried out to 200 mL with different initial concentrations of 30 – 500 mg/L were added in these flasks. The effect of contact time at 0 – 3 h, pH at 3 – 11, zeolites dosage at 0.3 – 3.0 g/L, and temperature at 293, 303 and 313 K was investigated by placing the flask on a temperature shaker at 100 rpm. After predetermined time intervals, the zeolites were separated from solution by syringe filtration 0.22 μm . The progress of removal was assessed by determining concentration of cadmium left by ICP-AES instrument.

The percentage removal and equilibrium concentration on the removal process has been calculated for all the studied parameters using the following equation;

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

$$q_e = ((C_i - C_e)V) / M \quad (2)$$

Where C_i and C_e are the initial and equilibrium concentrations (mg/L) of cadmium ion in solution, V is the volume (L) and M is the weight (g) of the synthesized zeolites.

III. RESULTS AND DISCUSSION

a) Characterization of raw material and synthesized zeolites

The chemical composition of the rice husk ash from power plant was as follow; SiO_2 was 91.50 wt%, Al_2O_3 was 2.27 wt%, K_2O was 0.48 wt%, MgO was 1.00 wt%, Na_2O was 2.68 wt%, Fe_2O_3 was 0.10 wt% and others was 1.97 wt%. The surface area of rice husk ash was 17.13 m^2/g and the XRD pattern of rice husk ash showed in Figure 1 which confirmed the main composition of SiO_2 with crystalline type of quartz and cristobalite. The broad peak between 2θ of 21 – 32° implied the presence of an amorphous phase of carbon and silica.

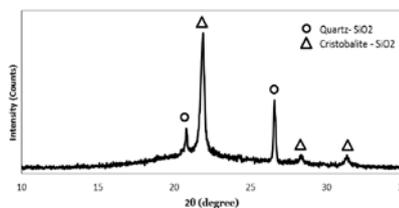


Figure 1 : XRD pattern of rice husk ash from power plant after combustion at 650°C

Fig. 2 shows the XRD patterns of synthesized zeolites to confirm that high purity of zeolite Na-A and pure zeolite Na-X prepared from the reaction mixture with proper Si/Al ratio. Numerous peaks between 2θ of 6 – 34° implied the presence of zeolite -X (PDF card No. 38-0237: $Na_2Al_2Si_{2.5}O_9 \cdot 6.2H_2O$) was formed at the heating temperature of 90°C for 20 h with the SiO_2/Al_2O_3 molar ratio of 2.0. On the other hand, using lower Si/Al ratio of 1.0, zeolite Na-A (39-0222: $Na_{96}Al_{96}Si_{96}O_{384} \cdot 216H_2O$) was formed. Quartz and cristobalite disappeared completely due to the mixing step, because these compounds can easily be dissolved for zeolite formation in the later stage of hydrothermal synthesis.

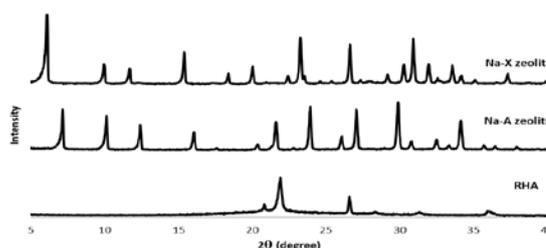


Figure 2 : XRD pattern for comparison between raw rice husk ash and zeolitic materials

The purity was also confirmed by SEM images of the two main zeolite types. It can be seen that typical octahedral particle shape of faujasitic zeolite Na-X and cubic shape of zeolite Na-A are clearly showed in Figure 3a and 3b, respectively. The surface area and CEC of the synthesis Na-A zeolite was 11 m^2/g and 958 meq/100g, respectively. The surface area and CEC of the synthesis Na-X zeolite was 1044 m^2/g and 925 meq/100g, respectively.

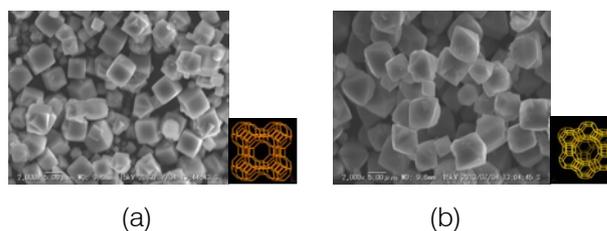


Figure 3 : Unit cell structure and crystal morphology of (a) zeolite A and (b) zeolite X

The IR spectra of synthesized zeolites were taken in the range of 400 – 1400 cm^{-1} the formation of structural unit during zeolite crystallization is shown in Figure 4.

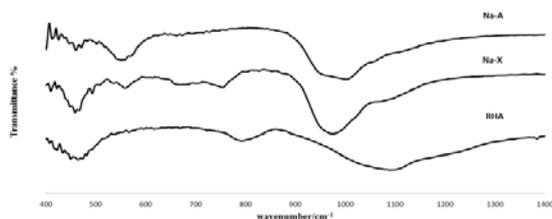


Figure 4 : FTIR spectra of rice husk ash (RHA), Na-A and Na-X zeolites

All of the band assignments of rice husk ash, zeolite A and X follow the work pioneered by Flaningen et al. [18]. 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 zeolite A 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 zeolite X 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.

b) Effect of contact time and initial concentration on Cadmium removal

Figure 5 depicts the effect of time on the removal of cadmium ion at various initial concentrations from 50 – 200 mg/L with 0.5 g/L dosage of zeolites at pH 7 solutions. The concentration of cadmium was measured at regular interval of time from 5 to 180 min. Both zeolite A and X were investigated. In the first time added zeolite onto solution, cadmium ion seems to be removed onto both zeolites above 80%. The percentage removal was decreased with increasing cadmium concentration solution. After 60 minutes cadmium ion was equilibrium by both zeolites.

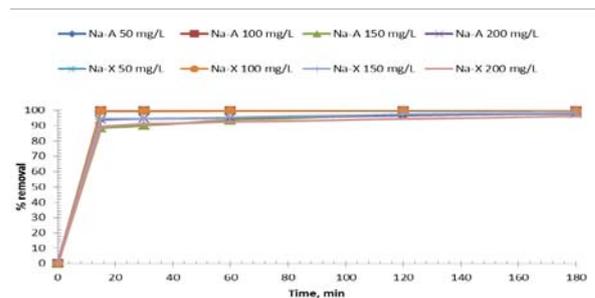


Figure 5 : Effect of time on the removal of cadmium ion solution for different initial concentrations

c) Effect of solution pH on cadmium removal

To study the effect of pH on cadmium removal by using both zeolite A and X, experiments were carried out at fixed zeolite concentration at 0.05 g of zeolite in 100 mL solution by maintaining 150 mg/L cadmium ion concentration using different initial solution pH values, changing from 3 - 13. Figure 6 shows that the cadmium removal was maximum when the initial pH of cadmium solution was in the range of 7 – 9 and cadmium was slightly removed at pH 3 for both zeolites.

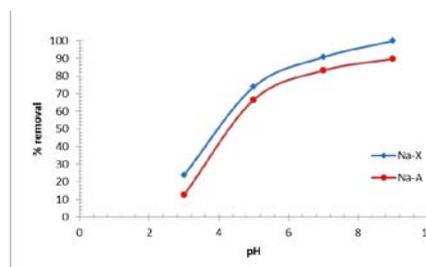


Figure 6 : Effect of solution pH on the removal of cadmium onto zeolite A and X

According to Reed and Matsumoto, 1993 [19] reported that the cadmium ion in aqueous solution can form various species or hydro complexes. The principal species of cadmium ion are formed as the following reactions;

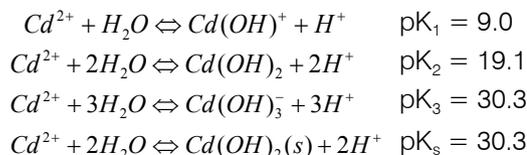


Figure 7 shows a speciation diagram at pH below 7, the cadmium ion predominates and at pH values just below 9, cadmium begins to precipitate out as $\text{Cd}(\text{OH})_2$. At pH 8 the species distribution is approximately 90% Cd^{2+} and 10% $\text{Cd}(\text{OH})^+$. This means that the species occurring at pH values of 8 and below carry a positive charge either as Cd^{2+} or $\text{Cd}(\text{OH})^+$. The point of zero charge (PZC) for the zeolite A and X used was determined at 5.5 and 5.8, respectively. This indicates that at pH lower 5.5 and 5.8, the zeolites are positively charged and the cadmium is present as Cd^+ .

Under these conditions adsorption must be occurring not due to electrostatic attraction but to a chemical interaction with enough energy to overcome the repulsive forces between the positively charged zeolites surface and the cadmium ion, Cd²⁺. At pH greater than 5.5 and 5.8 and less than 9, the zeolite surface becomes negatively charged and the cadmium is present mainly as Cd²⁺. In this case adsorption occurs by electrostatic attraction [20].

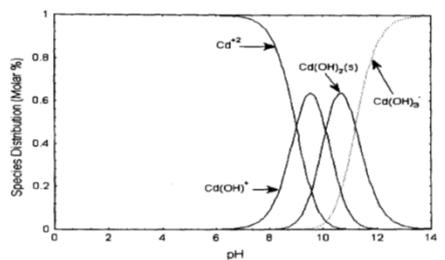


Figure 8 : Speciation diagram for cadmium complexes present in aqueous solutions

d) Effect of temperature on reaction rate

To study the effect of temperature on cadmium removal, temperature is an important parameter was carried out at fixed zeolite dosage at 0.03 g of zeolite 100 mL solution by using 200 mg/L cadmium concentration solution at 293K, 303K, and 313K and pH of the solution was maintained at 7. The removal process was carried out for 3 hours until equilibrium. The effect of temperature shows in Figure 8. The data showed that the amount of Cd²⁺ removed at equilibrium increase with increase in temperature indicating an exothermic nature of the process. Zeolite A could remove cadmium ion from aqueous solution better than zeolite X since zeolite A presented higher CEC than zeolite X due to the lower Si/Al molar ratio from 1.0 to 2.0.

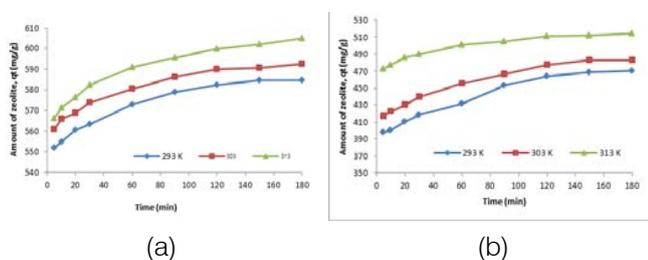


Figure 9 : Effect of contact time on the amount of removal of cadmium ion from aqueous solutions onto zeolite A (a) and zeolite X (b)

The rate constant of metal ion removal from the solution by zeolite A and X were determined using pseudo-first-order and pseudo-second-order rate models, respectively. The pseudo-first-order equation or Langergren's equation describes removal process in solid-liquid systems based on the removal capacity of

solids [21]. It is assumed that one cadmium ion removed onto the zeolite surface:



where B represents an unoccupied sorption site on the synthesized zeolite and k₁ is the pseudo first order rate constant (h⁻¹).

The linear form of pseudo-first-order model can be expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (4)$$

where q_e and q_t (mg/g) are the removal capacities at equilibrium and at time t (min), respectively.

k₁ and q_e, at the temperatures evaluated experimentally, were calculated using the slope and intercept of plots of log(q_e - q_t) versus t as shows in Figure 9 and Table 1. The results show that the experiments fit well with this model at each temperature yielded relatively high R² values.

The pseudo-second-order rate expression, which has been applied form analyzing chemisorption kinetics from liquid solutions [22], is linearly expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (5)$$

where k₂ is the rate constant for pseudo second-order model, (g/mg.min) and k₂q_e² or h (mg/g.min) is the initial adsorption rate.

This model assumes that one cadmium ion is sorbed onto two sorption sites on the zeolites surface:



Figure 10 and Table 1 show the pseudo second-order removal parameters q_e and k₂ in Eq. (6) were determined by plotting t/q_t versus t. The results shown that both zeolite A and X with various temperatures are fitted with this model according to the correlation coefficients (R²) values are 0.99 and 1.0, respectively

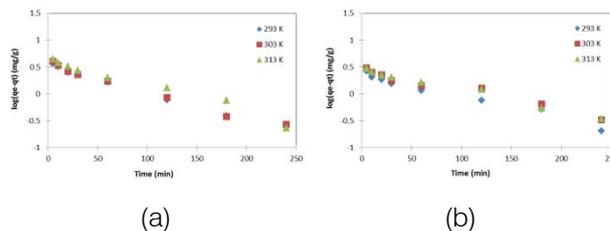


Figure 10 : Pseudo first-order kinetic model fit for Cd²⁺ removal onto synthesized zeolite A (a) and zeolite X (b) at various temperatures

It can be observed that this model is higher than the correlation coefficients derived from pseudo first-order models fits. Given a good agreement between model fit and experimentally observed equilibrium adsorption capacity in addition to the large correlation coefficients, this suggested that cadmium ion removal were removed onto synthesized zeolite A and X surface via chemical interaction. Similar trends have been reported for the adsorption of Cd²⁺ ions aqueous solutions by other adsorbents such as orange waste, activated sludge and so on [23 – 24].

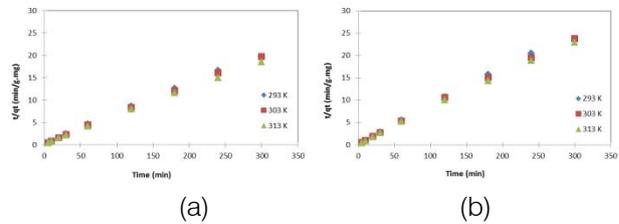


Figure 11 : Pseudo second-order kinetic model fit for Cd²⁺ removal onto synthesized zeolite A (a) and zeolite X (b) at various temperatures

Table 1 : Removal kinetic model rate constants for Cd²⁺ solution on synthesized zeolites at different temperatures

Zeolite A						
Temp (K)	Pseudo first-order			Pseudo second-order		
	k ₁ (min ⁻¹)	Q _e (mg·g ⁻¹)	R ²	k ₂ (g·mg ⁻¹ ·min ⁻¹)	Q _e (mg·g ⁻¹)	R ²
293	2.178E-03	1.70	0.95	0.016	14.599	0.99
303	2.158E-03	1.73	0.94	0.013	15.314	0.99
313	2.114E-03	1.87	0.97	0.010	16.313	0.99
Zeolite X						
Temp (K)	Pseudo first-order			Pseudo second-order		
	k ₁ (min ⁻¹)	Q _e (mg·g ⁻¹)	R ²	k ₂ (g·mg ⁻¹ ·min ⁻¹)	Q _e (mg·g ⁻¹)	R ²
293	1.796E-03	1.44	0.97	0.025	11.710	0.99
303	1.652E-03	1.54	0.96	0.015	12.579	0.99
313	1.571E-03	1.58	0.98	0.014	13.072	0.99

e) Adsorption isotherms

The maximum adsorption capacity of synthesized zeolite A and X for cadmium was investigated over a range of cadmium concentrations at three different temperatures are shown in Figure 11, the plot of the adsorption capacity, q_e (mg/g) versus the equilibrium concentration. The initial pressing sorption gives way to a slow approach to equilibrium at higher ion concentrations.

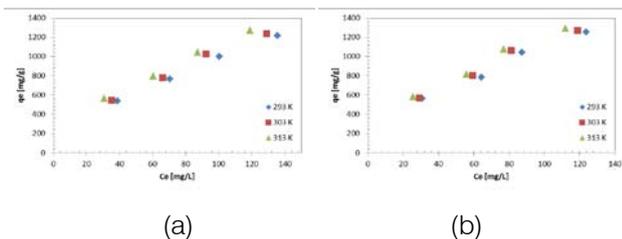


Figure 11 : Effect of temperature on the sorption isotherm of cadmium ion onto synthesized (a) zeolite Na-A and (b) zeolite Na-X

The removal of cadmium ion from aqueous solution in a wide range of concentrations was reflected the efficiency of both synthetic zeolite Na-A and Na-X. The uptake of ion increased with the increase in

temperature thereby indicating the process to be exothermic.

The sorption studies were carried out at 293K, 303K and 313K to determine the sorption isotherms. The Langmuir isotherm is based on the assumption that there are uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface [25]. The linear form of Langmuir adsorption is given by;

$$\frac{C_e}{q_e} = \frac{1}{Q^o b} + \frac{1}{Q^o} C_e \quad (7)$$

where q_e is the amount of solute sorbed per unit weight of adsorbent (mg/g), C_e is the equilibrium concentration of the cadmium in solution (mg/L), Q^o is the monolayer adsorption capacity, and b is the constant related to the free energy of adsorption. Figure 12 shows a linear relationship of C_e/q_e versus C_e using experimental data obtained. Values of Q^o and b calculated from the plot shown in Table 2. The applicability of the model suggests monolayer coverage of the adsorbate at the outer surface of the adsorbent is significant by both synthetic zeolite A and X according to the correlation coefficient (R²).

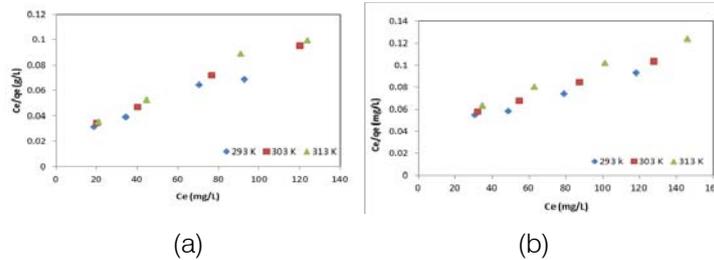


Figure 12 : Langmuir adsorption isotherm of cadmium ion onto synthetic (a) zeolite A and (b) zeolite X

Table 2 : Langmuir isotherm parameters of cadmium ion sorbed onto synthetic zeolite A and X

Temperature (K)	Q ^o (mg/g)		b (L/mg)		R ²	
	Zeolite Na-A	Zeolite Na-X	Zeolite Na-A	Zeolite Na-X	Zeolite Na-A	Zeolite Na-X
293	2232.1	2525.3	0.0098	0.0066	0.92	0.96
303	2227.2	2463.1	0.0109	0.0076	0.94	0.96
313	2141.3	2331.0	0.0129	0.0095	0.93	0.95

The Freundlich isotherm is an empirical equation based on adsorption on a heterogeneous surface suggesting that binding sites are not equivalent and/or independent. The Freundlich isotherm is given as [26];

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \quad (8)$$

where Q_e is an amount adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/L), K_f (mg/g) and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. Figure 13 shows that the sorption of

cadmium ion fit with this model by both synthetic zeolite A and X. The corresponding Freundlich parameters along with correlation coefficient are given in Table 3.

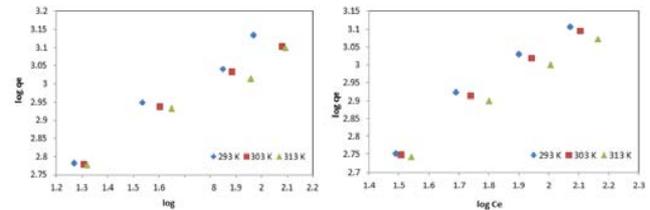


Figure 13 : Freundlich isotherm plots for the sorption of cadmium ion from aqueous solution onto synthetic (a) zeolite Na-A and (b) zeolite Na-X

Table 3 : Freundlich isotherm parameters of cadmium ion sorbed onto synthetic zeolite Na-A and Na-X

Temperature (K)	K _F (mg/g)		n		R ²	
	Zeolite Na-A	Zeolite Na-X	Zeolite Na-A	Zeolite Na-X	Zeolite Na-A	Zeolite Na-X
293	73.91	48.58	1.71	1.53	0.98	0.99
303	78.63	55.65	1.72	1.57	0.99	0.99
313	94.28	70.10	1.81	1.66	0.98	0.99

The Freundlich constant K_F is the relative sorption capacity or sorption power [27]. Value of $n > 1$ represents a favorable adsorption condition and results found that the adsorption of cadmium ion onto both synthetic zeolite A and X was favorable.

f) *Thermodynamic parameters of removal*

The feasibility of the adsorption process was evaluated by the thermodynamic parameters including free energy change (ΔG°), enthalpy (ΔH°), and entropy (ΔS°). ΔG° was calculated from the following equation:

$$\Delta G^\circ = -RT \ln K_d \quad (9)$$

where R is the universal gas constant (8.314 Jmol⁻¹K⁻¹), T is the temperature (K), and K_d is the

distribution coefficient. The K_d value was calculated using following equation:

$$K_d = \frac{q_e}{C_e} \quad (10)$$

where q_e and C_e are the equilibrium concentration of cadmium ion on adsorbent (mgL⁻¹) and in the solution (mgL⁻¹), respectively. The enthalpy change (ΔH°), and entropy change (ΔS°) of adsorption were estimated from the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (11)$$

This equation can be written as:

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (12)$$

The thermodynamic parameters of ΔH° and ΔS° were obtained from the slope and intercept of the plot between $\ln K_d$ versus $1/T$, respectively as shown in Figure 14. The values of ΔG° , ΔH° , and ΔS° for the removal of cadmium ion onto synthetic zeolite Na-A and Na-X at different temperatures are given in Table 4.

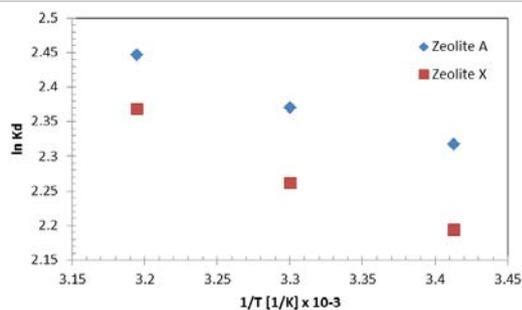


Figure 14 : The plot between $\ln K_d$ versus $1/T$ for obtaining thermodynamic parameters by both synthetic zeolite A and X (pH: 7.0, initial cadmium conc.: 500 mgL⁻¹, zeolite dosage: 0.3 gL⁻¹)

Table 4 : Thermodynamic parameters of the cadmium ion removal onto synthetic zeolite A and X at different temperatures

Temperature (K)	ΔG° (kJ mol ⁻¹)		ΔS° (J mol ⁻¹ K ⁻¹)		ΔH° (J mol ⁻¹)	
	Zeolite Na-A	Zeolite Na-X	Zeolite Na-A	Zeolite Na-X	Zeolite Na-A	Zeolite Na-X
293	-0.153	-0.173	36.12	40.92	4.95	6.66
303	-0.158	-0.179				
313	-0.163	-0.185				

IV. CONCLUSION

Synthesis of Na-A and Na-X zeolite was achieved using rice husk ash carbonized at 650°C from power plant, rice husk ash as the silica source by employing alkali fusion and the extraction with residue removal followed by hydrothermal treatment at 90°C and Si/Al molar ratio at 1.0 after heating time 15 h and 2.0 after heating time 20 h, respectively. The pure zeolite Na-X and Na-A were presented high CEC values as 9.25 and 9.58 meq/g, respectively. The morphology of SEM image for Na-A zeolite is cubic shape. On the other hand, Na-X zeolite is octahedron shape. The result showed that Na-A zeolite was more effective in removing metal ion (Cd²⁺) than Na-X zeolite. The cadmium removal was achieved at pH 7 – 9. The kinetic was studied the removal of cadmium ion onto both zeolites result showed that the pseudo-second order model fitted with experiment more than pseudo-first order model. The increasing of temperature, the amount of Cd²⁺ removed at equilibrium increased. The

Both zeolites show that the standard free energy change (ΔG°) of the process decreases with increase in temperature, which indicates that the process is spontaneous and spontaneity increases with increase in temperature. The positive values of ΔH° suggest endothermic nature of adsorption and cadmium ions are adsorbed more efficiently on cork powder at higher temperatures. The positive values of standard entropy change (ΔS°) shows the increase in randomness at the solid/solution interface during the adsorption of cadmium ion solution.

adsorption isotherms were described by Langmuir and Freundlich isotherm models, and both model fitted well with both zeolites. The experimental equilibrium data indicating that disclosing of heterogeneous and homogeneous distribution in the active sites on the surface of Na-A and Na-X zeolites. The removal capacity on cadmium ion onto Na-A and Na-X zeolites increased with increasing temperature. The negative ΔG° values indicated that the removal of cadmium ion onto both zeolites was feasible and spontaneous. The positive value of ΔH° confirmed the endothermic nature of process. The positive ΔS° suggested the increased randomness at the solid/liquid interface during the removal of cadmium ion onto zeolites. The experimental results indicated that the rice husk ash from biomass power plant can be successfully used for zeolite synthesized and removal of heavy metal such as cadmium ion from aqueous solutions.

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