



Reduction of seawater salinity by natural zeolite (Clinoptilolite): Adsorption isotherms, thermodynamics and kinetics



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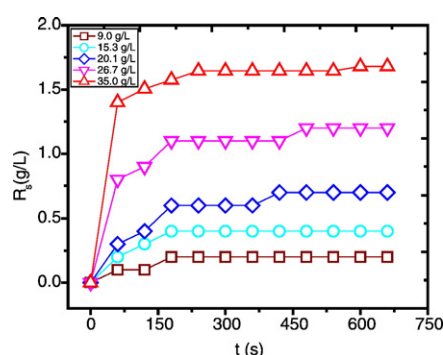
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HIGHLIGHTS

- Adsorption characteristics of salt ion onto zeolite were presented.
- The isotherm of adsorption was identified.
- Thermodynamic parameters of adsorption were determined.
- A kinetic model of adsorption was identified.

GRAPHICAL ABSTRACT



The reduction of seawater salinity as function of time after treated by zeolite at different initial concentration.

ARTICLE INFO

Article history:

Received 25 August 2016

Received in revised form 16 January 2017

Accepted 18 January 2017

Available online 28 January 2017

Keywords:

Natural zeolite

Salinity

Isotherm

Thermodynamics

Kinetics

ABSTRACT

We have investigated the adsorption isotherms, thermodynamics and adsorption kinetics of salt onto zeolites. The adsorption isotherm was studied using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models. The separation factor, $R_L = 0.588$, indicates the nature of adsorption process is favorable. The adsorption is physical as indicated by high adsorption intensity ($n > 1$) and small mean free energy ($E < 20$ kJ/mol). The negative ΔG° (-13.33 to -13.44 kJ/mol) indicates the spontaneous nature of adsorption. The negative ΔH° (-16.71 kJ/mol) confirms the exothermic nature of adsorption process, whereas the negative ΔS° (-0.0116 kJ/mol K) suggests the configuration of the adsorbate on the zeolite surface, whereas random. Pseudo-second-order kinetic model well fits to the experiment data. Based on the characteristics of the adsorption isotherms, thermodynamic and adsorption kinetics, zeolite is potential for seawater desalination process.

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1. Introduction

Nowadays, a number of desalination technologies have been used to produce fresh water from seawater or contaminated water. At recent decade, reverse osmosis (RO), electro dialysis (ED), multi-stage flash distillation (MSF), multiple effect distillation (MED), and vapor

compression distillation (VCD) are common desalination technology used in the world [1]. Indeed, these technologies are able to produce immense quantity of fresh water. Unfortunately, the cost of construction, maintenance and operation are still expensive. Besides, these technologies are considered less friendly to the environment [2]. Therefore, an affordable desalination technology that environmentally acceptable is needed.

Desalination using sorbent material is considered as eco-desalination technology due to low operational cost as well as more friendly to

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the environment [3–6]. In this process, undesirable substances are adsorbed by sorbent material. Although the concentration of undesired elements is slightly reduced, by repeating the flow of feed water into the sorbent material, a great reduction of undesirable substances might be obtained [7].

Low cost materials such as carbon active, fly ash, clay and natural zeolites have been investigated for their potential application as sorbent materials [8–12]. Among these materials, natural zeolites are the most promising material for the removal of heavy metal ions from water and wastewater with adsorption methods [13–15].

Zeolite is a hydrate aluminosilicate with fascinating sorption ability [16,17] and has ion-exchange property [18–19] of alkaline and earth alkaline metal. The porous structure of zeolite with many channels and cavities makes zeolite becomes one of potential sorbent materials with highly surface area [20–22]. Another important property such as non-toxic, abundance, economically and environmentally acceptable make zeolite has more attention to be developed as an outstanding sorbent material in wide range application [2–22]. Various studies has been carried out on the utilization of natural and synthesis zeolites in water purification process [23–25], waste water treatment [26–29] and radioactive waste desalination [19]. The effectiveness of zeolite in adsorbing various kinds of pollutants and toxic substances in water, either in the form of metal ions, organic or inorganic pollutants has also been reported by many authors [30–34].

Clinoptilolite is the most abundant natural zeolite, owing high thermal stability and high selectivity for many cations [11–15]. The Si/Al ratio of clinoptilolite can also be increased through various pathways such as thermal activation, acid or basic activation and treatment with appropriate surfactants [35–37]. The increase of Si/Al ration leads to the increment of adsorption capacity [5]. Besides, clinoptilolite is non-toxic material with economically and environmentally acceptable [15,16]. Therefore, among the most often studied natural zeolite, clinoptilolite has been gaining more interest by scientists and researchers for outstanding adsorbent with wide range applications.

Yousef et al. have reported the use of Jordanian zeolite for phenol removal from aqueous solutions. They reported that the maximum adsorption capacity of zeolite reach 32.6 mg/g for solution at temperature of 25 °C [5]. Inglezakis et al. reported the use of clinoptilolite for Mn^{2+} , Zn^{2+} , and Cr^{3+} removal trough batch methods. They obtained the maximum adsorption capacity for Mn^{2+} , Zn^{2+} , and Cr^{3+} are 15.8 mg/g, 26.9 mg/g and 14.4 mg/g, respectively [11]. Günay et al. have used clinoptilolite for lead removal from aqueous solution with relatively high maximum adsorption capacity (79.323 mg/g) [12]. Widiastuti et al. have used natural zeolite for removal of ammonium from grey water. They reported that the maximum adsorption capacity of zeolite on ammonium adsorption is 6.3012 mg/g [25]. Ates and Akgul have modified natural zeolite from Turkey with NaOH for removal of manganese in drinking water. They showed that the maximum adsorption capacity of zeolite increases from 7.1 mg/g to 66.1 mg/g after modification with 1.5 M NaOH.

Wajima et al. have used modified natural zeolite from Fukushima Japan for removal of NaCl from seawater [7]. Modification was done by heated powder zeolite at 60 °C for 12 h then treated by $AgNO_3$ reagent. 43% NaCl reduction was achieved after 10 times repeating the flow of seawater into fresh modified zeolite. Therefore, 4.3% reduction was occurred for single step of adsorption experiment. Different with Wajima et al., we reduced salinity of seawater using Indonesian zeolite (clinoptilolite). We have activated zeolite with more simple process. Activation zeolite was done by thermal process without utilize any reagent. In our work, powder zeolite was heated at 225 °C for 3 h at atmospheric pressure by using furnace. We obtained 4.8% reduction of salinity for single batch process that equal to 51.43 mg/g. This value is higher than the result of Wajima et al. and it is comparable to the adsorption capacity of various sorbent materials that were previously reported.

Continuing our study, in current work, we investigated the adsorption characteristics of salt ions onto Indonesian zeolite. The adsorption characteristics are identified from the adsorption isotherm, thermodynamic and kinetic [38–44]. Many important information can be obtained from the adsorption isotherm such as the nature of adsorption either favorable, unfavorable or irreversible; the type of adsorption either physical or chemical process; the maximum adsorbent capacity and mean free energy of adsorbate-adsorbent interactions. From thermodynamic aspect, the changes in standard free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°) can be determined. ΔG° specifies the adsorption occurs spontaneously or not, ΔH° shows the adsorption is endothermic or exothermic, while ΔS° measures the degree of disorder of adsorbate distribution on the adsorbent. Meanwhile, the adsorption kinetic describes how adsorbate interacts with adsorbent under certain conditions, such as contact time, variation of initial concentration and variation of solution temperature.

Numerous studies have been conducted to investigate the adsorption characteristic of sorption systems. Chakraborty et al. conducted the adsorption study for the removal of a basic dye by hardwood saw dust. They have reported the adsorption process is spontaneous and endothermic in nature which is indicated by negative value of ΔG° and positive value of ΔH° , respectively [3]. Yousef et al. reported the adsorption of phenol onto natural zeolite was favorable, spontaneous, exothermic and physical adsorption [5]. Kyziol-Komosinska et al. reported that the adsorption of Cu(II) ion onto natural and synthetic zeolite is physical adsorption [10]. Spontaneous process of adsorption was also reported by Günay et al. on the study of lead removal from aqueous solution by natural and pretreated clinoptilolite [12]. Kumar et al. reported that the adsorption characteristics of dye from aqueous solution by cashew nut shell were feasible, spontaneous, exothermic and chemical adsorption [38].

Although there are numerous authors have reported the adsorption characteristic at any adsorption systems, but the adsorption characteristic for specific case of salt ion onto zeolite has not been reported yet. Meanwhile, each adsorption systems (adsorbate-adsorbent interaction) are likely has different adsorption characteristics. In this study we investigated the adsorption isotherm, thermodynamic and kinetic so the adsorption characteristic of salt ion onto zeolite can be obviously described.

2. Material and methods

2.1. Preparation of natural zeolite as sorbent

We used natural zeolite from Buah Batu, Bandung, West Java, Indonesia with average grain size of (10.64 ± 0.21) mm [45]. Prior to activation, the zeolite has been prepared into a fine powder by using mechanical mortar to increase the surface area as well as to promote the activation process. After fining process, the average size of grain is around (17.66 ± 0.13) μm . The zeolite powers obtained from the milling process were then put in alumina crucibles and heated at 255 °C for 3 h by using furnace in atmospheric condition.

2.2. Characteristic of natural zeolite

X-Ray Diffraction (XRD PW1710) was used to identify the type of zeolite. Energy Dispersive X-rays Spectroscopy (Jeol JSM-6510LA) was applied to determine the characteristic of Si/Al ratio of zeolite. The specific surface area of zeolite was determined by N₂-physisorption (Quanta Chrome NovaWin software version 10.01) using multi point BET, while the pore volume and pore diameter were estimated by BJH Desorption. Delsa™ Nano C (Beckman Coulter) was used to measure zeta potential of zeolite in seawater, while Atomic Absorption Spectrophotometer (AAS type GBC Avanta P) was used to determine the concentration sodium and chloride in seawater. The properties of natural zeolite used in this study are presented in Table 1,

The adsorption-desorption characteristic of zeolite has been investigated by using N₂-physorption and the result is presented in Fig. 1. We observed that the adsorption and desorption trends are highly similar and nearly close each other. It indicates that this processes are reversible, therefore the amount of adsorbed ions on zeolite surface are possibly removed so that zeolite can be potentially reused. Before it can be reused, activation process of saturated zeolite may be needed. Reactivation can be conducted through regeneration process [25].

To prove reusability of zeolite on reducing salinity of seawater, we have conducted sequential experiment by using recycling zeolite. The experiment procedures are similar with the previous work. Regeneration was done by washing saturated zeolite using distilled water then heating washed zeolite at 225 °C for 1 h by using furnace. These parameters are the optimal condition for regeneration in our work. After reactivation, zeolite was reused for reducing seawater salinity. Reusability performance of zeolite on reducing seawater salinity is shown in Fig. 2. We have observed that the reduction ability of reused zeolite is acceptable for four times of recycling. Further recycling leads to significant decreasing zeolite performance. It is proven that zeolite is reusable; it can be reactivated and reused for salt ions adsorption.

2.3. Reduction of salinity by using natural zeolite

The thermally activated zeolites were dispersed into the seawater with different salinity (concentration of salt) from (9.1 ± 0.05) g/L to (40.2 ± 0.05) g/L to determine the effectiveness in reducing the salinity of seawater. The initial pH of seawater is 8.3 ± 0.05 . In order to study the adsorption isotherms, (3.50 ± 0.01) g of zeolites were dispersed into 100 mL seawater in transparent bottles followed by mechanically shaking. Measurement of salinity was conducted 48 h after mixing process using Salinometer (Mettler Toledo SG7-FK2) to ensure the equilibrium condition has been obtained (at room temperature (25 °C) and atmospheric pressure). The reduction of salinity (R_s) was calculated using Eq. (1).

$$R_s = C_i - C_e \quad (1)$$

with C_i (g/L) is the initial salinity and C_e (g/L) is the final salinity (equilibrium solution). The amount of solute adsorbed on the adsorbent, q_e (mg/g) was determined by Eq. (2).

$$q_e = R_s \frac{V}{m} \quad (2)$$

with V is volume of the solution (L) and m is mass of adsorbent (g).

2.4. Modeling

Selected adsorption models i.e. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich were fitted to the experimental data (q_e versus C_e). These standard models were commonly used to identify the characteristic of adsorption isotherm of various adsorption systems. The thermodynamic parameters such as the changes in standard free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°) were

Table 1
Characteristics of natural zeolite used in this work.

Parameters	Characteristics
Type	Clinoptilolite
Particle size	$17.66 \pm 0.13 \mu\text{m}$
Specific surface area	$33.628 \text{ m}^2 \cdot \text{g}^{-1}$
Pore volume	$0.089 \text{ cm}^3 \cdot \text{g}^{-1}$
Pore diameter	3.811 nm
Si/Al ratio	4.61
Thermal conductivity	$0.05\text{--}6.0 \text{ W m}^{-1} \text{ K}^{-1}$
Zeta potential in seawater (35.0 g/L, 25 °C)	$-0.53 \pm 0.014 \text{ mV}$

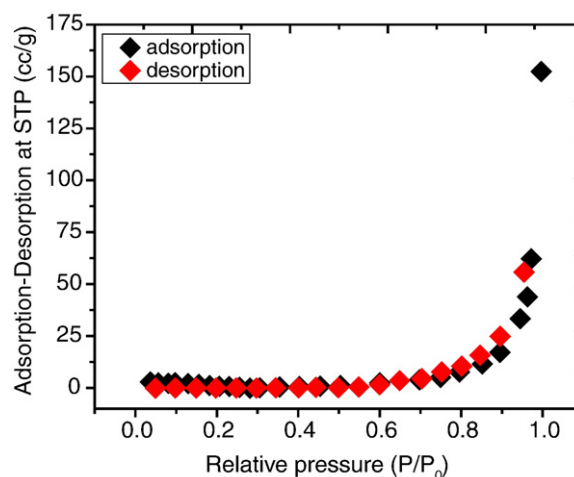


Fig. 1. Adsorption-desorption characteristic of zeolite. Adsorbate: nitrogen, temperature: 77.35 K, sample weight: 0.19472 g, outgas time: 3 h.

determined by conducting the experiments at different temperature of solution (25 °C, 30 °C and 35 °C). Pseudo-first-order model and pseudo-second-order model were used to determine the adsorption kinetic of salt ions onto zeolite, while the adsorption mechanism was described by using electrical double layer theory.

3. Results and discussion

3.1. Adsorption isotherms

The adsorption isotherm describes the relationship between the amounts of solute (adsorbate) adsorbed on the adsorbent (q_e) to the adsorbate concentration at equilibrium condition (C_e) at constant temperature [9,11]. In this model, the equilibrium isotherm becomes essential for understanding the characteristic of adsorption systems. It is due to the equilibrium isotherm provide some important information of the physicochemical data of adsorption process [38,43]. The reduction of seawater salinity after treated by natural zeolite at different initial concentration of solution is presented in Table 2. In order to identify the adsorption characteristic of salt ion onto zeolite, this adsorption data was linearly fitted by using selected adsorption isotherm models and the plots are presented in Fig. 3.

3.1.1. Langmuir model

The Langmuir model was developed based on assumption that the adsorption occurs on a homogeneous surface which each molecule own constant enthalpies and sorption activation energy [38] without interaction between adsorbed molecules [41]. Besides, the adsorption is

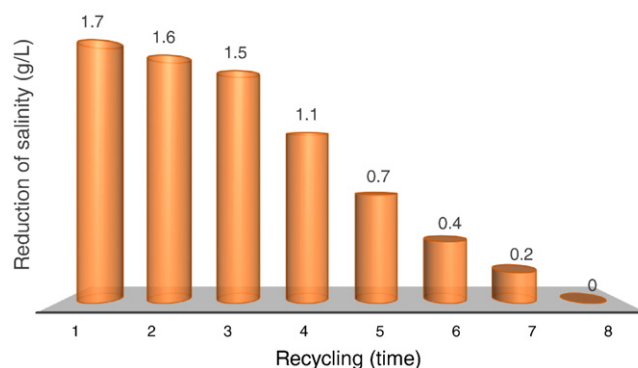


Fig. 2. Reusability of zeolite for reducing seawater salinity. Initial concentration: 35.0 g/L, pH: 8.3, contact time: 24 h, temperature: 25 °C, experimental error: ± 0.05 g/L.

Table 2

Reduction of seawater salinity after treated by natural zeolite at different initial concentration of solution.

C_i (g/L)	C_e (g/L)	R_s (g/L)	q_e (mg/g)
9.0 ± 0.05	8.8 ± 0.04	0.2 ± 0.04	5.71
15.3 ± 0.05	14.9 ± 0.04	0.4 ± 0.04	11.43
20.1 ± 0.05	19.4 ± 0.05	0.7 ± 0.05	20.00
26.7 ± 0.05	25.5 ± 0.04	1.2 ± 0.04	34.28
35.0 ± 0.05	33.3 ± 0.05	1.7 ± 0.05	48.57
40.2 ± 0.05	38.4 ± 0.05	1.8 ± 0.05	51.43

considered as monolayer adsorption i.e. the adsorption layer is one molecule in thickness with no migration of the adsorbate in the surface of adsorbent [39]. The Langmuir isotherms model is given by Eq. (3), while the linear form is expressed in Eq. (4).

$$q_e = \frac{k_L C_e q_{\max}}{1 + k_L C_e} \quad (3)$$

$$\frac{1}{q_e} = \frac{1}{k_L q_{\max}} \frac{1}{C_e} + \frac{1}{q_{\max}} \quad (4)$$

with k_L refers to equilibrium constant of Langmuir model and q_{\max} (mg/g) refers to maximum adsorption capacity. The obtained data of Langmuir parameters are presented in Table 2. By using this data the

separation factor (R_L) as a dimensionless constant that refers to the nature of adsorption can be calculated by using Eq. (5).

$$R_L = \frac{1}{1 + k_L C_i} \quad (5)$$

From the value of R_L , the adsorption isotherms can be classified into unfavorable if $R_L > 1$, linear if $R_L = 1$, irreversible if $R_L = 0$ and favorable if $0 < R_L < 1$. The Langmuir parameters obtained in this work are $q_{\max} = 27.174$ mg/g, $k_L = 0.021$ L/mg and $R_L = 0.571$ with $R^2 = 0.989$. The value of R_L confirmed that the adsorption of salt ion onto zeolite surface was favorable.

3.1.2. Freundlich model

The Freundlich isotherm model assumes that the adsorption occurs on a heterogeneous surface with interaction between adsorbed molecules [12]. The adsorption is not restricted to the formation of monolayer adsorption so it can be applied to the multilayer adsorption [39]. In addition, this model suggests that adsorption energy is not constant but exponentially decrease upon the completion of adsorption process [38]. This model is an empirically equation and expressed by Eq. (6) while the linear form is given by Eq. (7).

$$q_e = K_f C_e^{1/n} \quad (6)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (7)$$

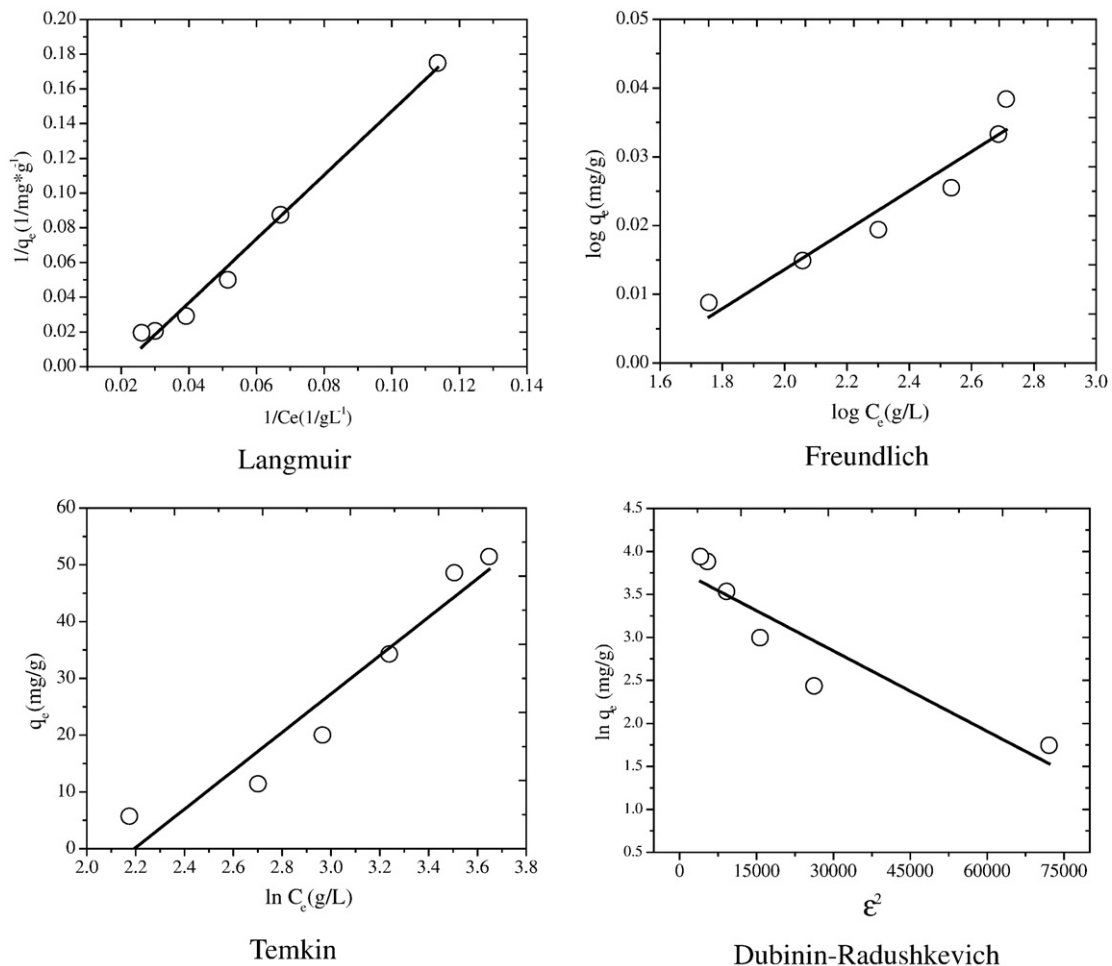


Fig. 3. Linear fitting of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich adsorption isotherms model used in this study.

with K_f is Freundlich isotherm constant that is an approximation indicator of adsorption capacity and n is adsorption intensity that measure the deviation from linearity of adsorption [46]. If $n = 1$, the adsorption is linear; if $n < 1$, the adsorption is a chemical process; if $n > 1$, the adsorption is a physical process [40]. The heterogeneity factor is expressed by $1/n$, the smaller of $1/n$, the greater of expected heterogeneity [46]. The Freundlich parameters obtained in this work are $K_f = 1.105$ mg/g and $n = 34.965$, $1/n = 0.029$ with $R^2 = 0.912$. Based on this result we know that the adsorption of salt ion onto zeolite surface was not chemical process but it was physical process so this adsorption phenomenon was consider as physisorption with heterogeneous process of adsorption.

3.1.3. Temkin model

Temkin isotherm model was established based on assumption that the decrease in the heat of adsorption of all the molecules in the surface layer is linear and the adsorption is characterized by a uniform distribution of binding energies [12]. The derivation of this model assumes that the fall in the heat of adsorption is linear rather than logarithmic such as Freundlich model [38]. This model is described by Eq. (8) and its linear form is given by Eq. (9). The heat of adsorption constant (B_T) can be calculated by using Eq. (10). This constant is used to estimate the type of adsorption mechanism [5].

$$q_e = B_T \ln (A_T C_e) \quad (8)$$

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (9)$$

$$B_T = \frac{RT}{b_T} \quad (10)$$

with A_T is an equilibrium binding constant, b_T is a Temkin isotherm constant, T is the absolute temperature and R is the gas constant (8.314×10^{-3} kJ/K mol). From the linear plot of Temkin model shown in Fig. 3, we obtained the Temkin parameters are $A_T = 8.974$ L/g and $B_T = 33.827$ J/mol. We obtained that the value of B_T was lower than 8 kJ/mol, indicated that the heat of adsorption of salt ion onto zeolite is physical adsorption process [10]. This result support the obtained result from Freundlich model.

3.1.4. Dubinin-Radushkevich model

Dubinin-Radushkevich model was used to express the adsorption mechanism with Gaussian energy distribution onto a heterogeneous surface [10,17]. In this model, the adsorption process are classified in to physical adsorption if $E < 8$ kJ/mol and chemical adsorption if $8 < E < 16$ kJ/mol, with E refers to energy per molecule of adsorbate i.e. energy is needed for removing a molecule from its location on the surface of adsorbent to the infinity [39]. Dubinin-Radushkevich isotherm model is expressed by Eq. (11) and its linear form is given by Eq. (12).

$$q_e = q_s \exp(-\beta \varepsilon^2) \quad (11)$$

$$\ln q_e = \ln q_s - (\beta \varepsilon^2) \quad (12)$$

with q_s refers to theoretical isotherm saturation capacity, β refers to Dubinin-Radushkevich isotherm constant and ε refers to the Polanyi potential (J/mol). The Polanyi potential is given by Eq. (13), while the energy, E can be calculated by Eq. (14).

$$\varepsilon = RT \ln \left[1 + \frac{1}{C_e} \right] \quad (13)$$

$$E = \frac{1}{\sqrt{2\beta}} \quad (14)$$

From the linear fitting of Dubinin-Radushkevich model as shown in Fig. 2, the obtained the Dubinin-Radushkevich parameters are $q_s = 43.789$ mg/g, $\beta = 3.12 \times 10^{-5}$ mol²/kJ² and $E = 0.127$ kJ/mol with $R^2 = 0.851$. Based on the value of E , we can justify that the mechanism of adsorption is physical process [5,9]. Again, this result confirmed that the adsorption of salt ions onto zeolite surface refers to physical adsorption, similar to the results obtained from Freundlich and Temkin isotherm models.

3.1.5. Comparison of adsorption isotherms model

The linear form of adsorption data after fitted to the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models are presented in Fig. 3. From this linear fitting, some parameters of each model can be determined and the results are presented in Table 3. From the Langmuir isotherm model, the maximum monolayer adsorption capacity and the nature of adsorption of zeolite to the salt ions can be predicted. We found that the adsorption of salt ion onto zeolite surface is favorable process due to the value of $R_L = 0.571$ (favorable if $0 < R_L < 1$), with monolayer adsorption capacity is 27.174 mg/g. Freundlich model shows that the adsorption refers to physical adsorption ($n > 1$). The heat of adsorption constant (B_T) obtained from Temkin model is 0.034 kJ/mol, it also indicates that the mechanism of adsorption is physical process. The value of energy per molecule of adsorbate (E) from Dubinin-Radushkevich model (0.127 kJ/mol) is another evidence that the adsorption process refers to physical adsorption.

In physical adsorption (physisorption), the adsorption mechanism is governed by electrical interaction between adsorbate and adsorbent, while monolayer adsorption occurs when the electric field of adsorbent was not strong enough induces the ions beyond the first layer to create the sequence layers. In this work, we obtain the monolayer adsorption capacity of Langmuir model was significantly different to the experiment value. The adsorption capacity of zeolite from experiment result (51.43 mg/g) is obviously higher than monolayer adsorption capacity from Langmuir model (27.174 mg/g). It indicated the adsorption of salt ions onto zeolite surface under the experimental conditions was not monolayer adsorption. It can be considered that beyond the first layer (monolayer), salt ions are also adsorbed and constructed another layer. Therefore, the adsorption of salt ions onto zeolite may be well described by electrical double layer theory [47,48].

Different maximum adsorption capacity of various sorbent materials has been reported by many authors. Qin et al. reported that Ca-selective zeolite that is activated by hydrothermal method has q_e value of 39.59 mg/g [2]. Bakatula et al. reported that q_e value of modified natural zeolite for Cr adsorption is 50 mg/g [49]. Ates and Akgul reported that q_e values of modified natural zeolite with NaOH for removal of Mn^{2+} in drinking water are varied from 7.1 mg/g to 66.1 mg/g [50]. Pawar et al. reported that q_e value of activated bentonite for Cu(II) and Pb(II) are 9.793 mg/g and 21.359 mg/g, respectively [51]. Very low adsorption

Table 3
Models of adsorption isotherms.

Model	Parameters	Value
Langmuir	q_{\max} (mg/g)	27.174
	K_L (L/mg)	0.021
	R_L	0.571
	R^2	0.989
	n	34.965
Freundlich	$1/n$	0.029
	K_f (mg/g)	1.105
	R^2	0.912
	B_T (J/mol)	33.827
Temkin	A_T (L/g)	8.974
	R^2	0.927
	q_s (mg/g)	43.789
Dubinin-Radushkevich	β (mol ² /kJ ²)	3.12×10^{-5}
	E (kJ/mol)	0.127
	R^2	0.851

capacity (4.831 mg/g) of cashew nut shell for adsorption of dye from aqueous solution was reported by Kumar et al. [38]. In this work, the maximum adsorption capacity of thermally activated zeolite to the salt ions is 51.43 mg/g. This value is comparable to the adsorption capacity of various materials that were previously reported.

Similar phenomenon of physisorption (physical adsorption) was also reported by other researchers. The adsorption of Cu(VI) from aqueous solution onto *Agave lechuguilla* biomass [9], the adsorption of phenol from aqueous solution onto natural zeolite [5] and the adsorption of acid dyes in aqueous solutions by shells of bittim [40] were reported as physisorption. On the other hand, the adsorption of Cu(II) onto various zeolites (clinoptilolite, Na-P1 and Na-X) [10], the adsorption of dye from aqueous solution by cashew nut shell [38] and lead removal from aqueous solution by clinoptilolite [12] were reported as chemisorption (chemical adsorption).

3.2. Thermodynamic

Thermodynamically, the energy of an isolated system is constant. It cannot be gained or lost and the entropy change is the only driving force [38]. In order to determine which process will happen spontaneously, both energy and enthalpy factors must be considered [5]. The thermodynamic parameters that must be considered to determine the adsorption processes are the changes in standard free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°). The thermodynamic parameters, ΔG° , ΔH° and ΔS° can be determined by substituted Eq. (15) to Eq. (16).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (15)$$

Eq. (15) is well known equation i.e. formulation of free energy change at constant temperature, while Eq. (16) express the relationship between free energy change and the equilibrium constant, K_c .

$$\Delta G^\circ = -RT \ln K_c \quad (16)$$

with T is the absolute temperature and R is the gas constant. In some references [9,25,38], the value of $K_c = q_e/c_e$ can be approximated by the Langmuir equilibrium constant, K_L so that Eq. (16) can be expressed as following.

$$\ln K_c = \ln K_L = -\frac{\Delta G^\circ}{RT} \quad (17)$$

$$\ln K_L = -\frac{(\Delta H^\circ - T\Delta S^\circ)}{RT} \quad (18)$$

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (19)$$

Eq. (19) is a linear form used to determine ΔH° and ΔS° .

In order to obtain the adsorption data that is used to determine the value of K_L , three set experiments at different temperature of solutions (25 °C, 30 °C and 35 °C) were conducted. The adsorption data at different temperature solutions are presented in Fig. 4. Then, the data in Fig. 4 is linearly fitted by using Langmuir isotherm model based on Eq. (4) as shown in Fig. 5. The obtained Langmuir parameters are listed in Table 4. Based on Eq. (19), we plot $\ln K_L$ versus reciprocal temperature ($1/T$) as shown in Fig. 6, then ΔH° and ΔS° values are calculated from the slop and intercept of the plot.

From Fig. 4 we see the adsorption capacity of zeolite decrease with the increase of solution temperature. Similar phenomenon was also reported by other researchers [5,12]. It is mainly due to the decrease surface activity indicating that adsorption of salt ion onto zeolite surface was an exothermic process [38]. However, there are some researchers reported the opposite phenomenon, the increase of solution temperature increase the adsorbent capacity [3,43,44]. Therefore, we notified

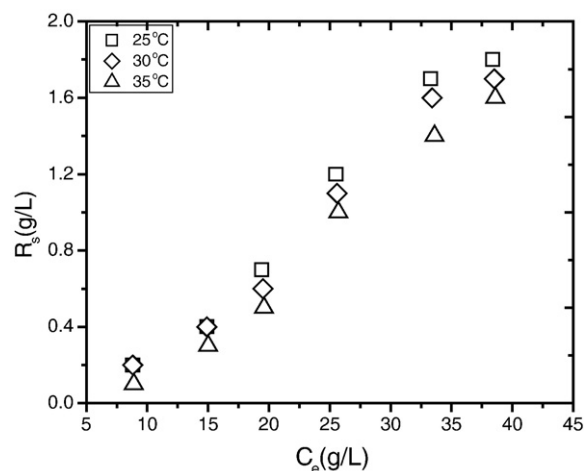


Fig. 4. Reduction of salinity after treated by natural zeolite at different temperature of solutions (25 °C, 30 °C and 35 °C).

that the effect of the increase of temperature to the adsorbent capacity depends on the characteristic of adsorbate-adsorbent interaction. Both phenomena, either exothermic or endothermic are possible occurred on adsorption processes.

Table 5 shows the obtained values of ΔG° , ΔH° and ΔS° as thermodynamic parameters that are used to identify the characteristic of adsorption process. The ΔG° value of adsorption process at 25, 30 and 35 °C are -13.44 , -13.39 , -13.33 kJ/mol, respectively. The negative value of ΔG° indicates the spontaneous nature of adsorption of salt ion onto zeolite surface at given experiment conditions. We can see that the ΔG° value change from more negative to less negative with the increase of temperature. This indicated the adsorption process at room temperature (25 °C) is more feasible and favorable than at higher temperature (30 and 35 °C). Therefore the reduction of salinity (R_s) at 25 °C is highest followed by at 30 and 35 °C as shown in Fig. 2. The favorable adsorption process at temperature of 25 °C rather than at other temperatures can also be identified from R_L values that are listed in Table 4. The R_L values of adsorptions were conducted at 25, 30 and 35 °C are 0.571, 0.588 and 0.649, respectively. It can be seen that the R_L value at 25 °C is lowest, indicated the most favorable adsorption process, while higher value of R_L at 30 and 35 °C refer to less favorable process, even though the all processes lay in favorable category ($0 < R_L < 1$).

We can see that ΔH° value obtained in this work is also negative, i.e. -16.71 kJ/mol. The negative value of ΔH° indicates the exothermic nature of this adsorption process. In general, the value of ΔH° lies in the range of 2.1 to 20.9 for physical adsorption and 80–200 kJ/mol for chemical adsorption [52]. Therefore based on the ΔH° value, the adsorption of salt ion onto zeolite surface is refers to physical adsorption. This result is in agreement with obtained results from all isotherm models were used here. In addition, the negative value of ΔS° (-0.0116 kJ/mol K) indicates the configuration of the adsorbate on the zeolite surface is less random [5,38]. It likely due to the adsorption process was governed by physical process rather than chemical process. Hence, the adsorption of salt ion onto zeolite surface is considered as electrical charge driven process.

Previous works with negative value of ΔG° , ΔH° and ΔS° were also reported by other researchers such as lead removal from aqueous solution by clinoptilolite [12], adsorption of dye from aqueous solution by cashew nut sell [38] and phenol removal from aqueous solution by natural zeolite. Nevertheless, some researchers also reported the adsorption process with positive of ΔH° and ΔS° [3,9]. Chakraborty et al. reported the adsorption of a basic dye from aqueous solution by hardwood saw dust produce positive ΔH° and ΔS° . Moreover, the positive ΔH° and ΔS° of the adsorption of Cr(VI) from aqueous solution onto *Agave lechuguilla* biomass was reported by Romero-Gonzalez et al.

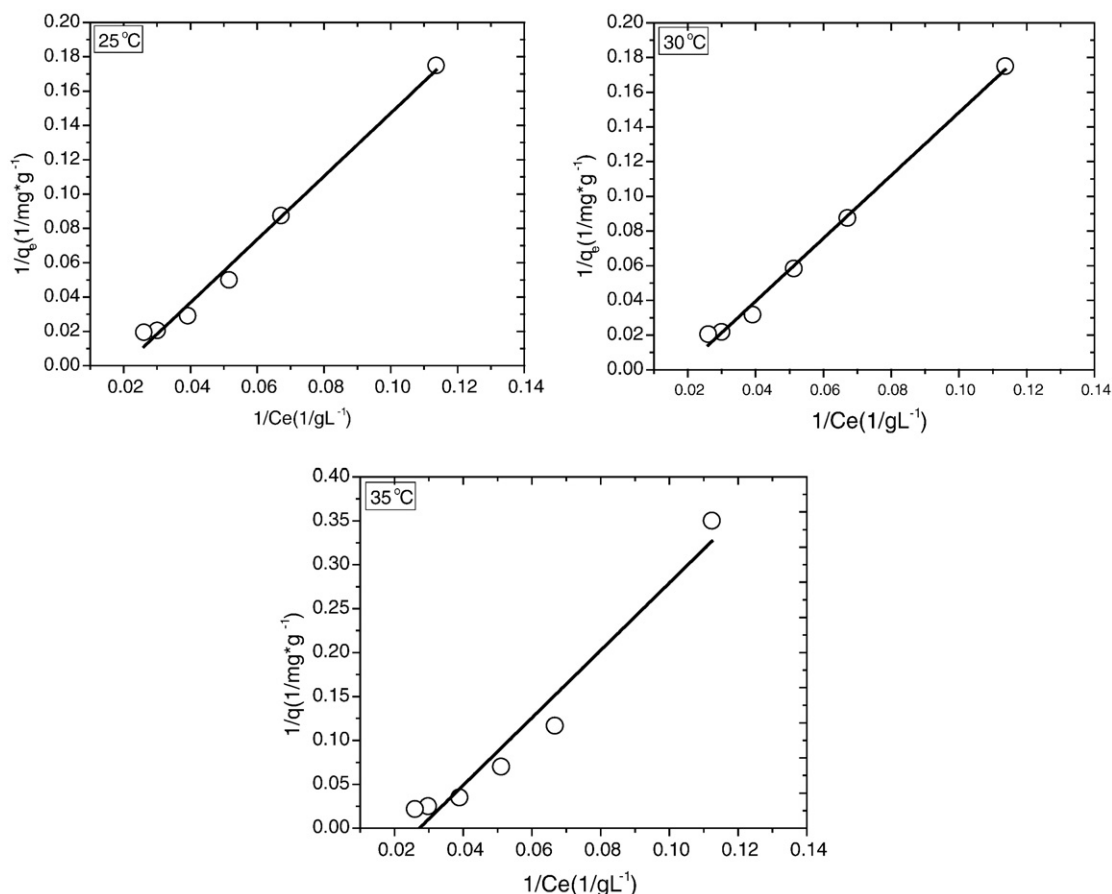


Fig. 5. Linear fitting of Langmuir isotherm model at different temperature of solutions (25 °C, 30 °C and 35 °C).

In this work, the nature of adsorption process of salt ions onto zeolites surface are favorable ($R_L = 0.588$). The spontaneous nature of physical adsorption was designated by the negative value of ΔG° and the small value of the adsorption energy ($E < 20$ kJ/mol). The negative value of ΔH° specified that the adsorption process was exothermic. Thus, for seawater desalination purposes, the use of additional energy for heating the salt solutions are not needed. The adsorption process can be conducted at room temperature, makes the use of zeolite as sorbent becomes much more economically viable. Based on the adsorption characteristic and the thermodynamic parameters that were obtained, we notified the use of zeolite as sorbent is highly potential for seawater desalination application.

3.3. Kinetics

Adsorption kinetic describes the rate of adsorption, which is the change of adsorbed concentration or solution concentration with time. In order to investigate the adsorption kinetics of salt ion onto zeolite, five sets experiment using different seawater salinity (9.0, 15.3, 20.1, 26.7 and 35.0 g/L) were conducted at temperature of 25 °C. Salinity of seawater as function of time was measured and the results are presented in Fig. 7. Pseudo-first-order model and pseudo-second-order model

were used to fit the experiment data for adsorption kinetics identification.

Pseudo-first-order kinetic model is given by Eq. (20), while its linear form is presented in Eq. (21) [1,3,5].

$$q_t = q_e (1 - e^{-k_1 t}) \quad (20)$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (21)$$

with q_t , q_e and k_1 are the amount of salt ion adsorbed on the zeolite surface at any time t (mg/g), the amount of salt ion adsorbed on the zeolite surface at equilibrium (mg/g), and the rate constant of adsorption

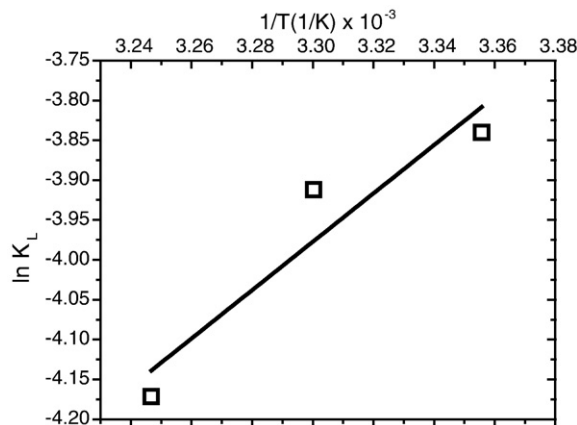


Fig. 6. Plot of $\ln K_L$ versus reciprocal temperature ($1/T$).

Table 4
Langmuir parameters at different temperature of solutions (25 °C, 30 °C and 35 °C).

Langmuir parameters	25 °C	30 °C	35 °C
K_L (L/mg)	0.018	0.020	0.027
R_L	0.571	0.588	0.649
R^2	0.989	0.987	0.959

Table 5
Thermodynamic parameters.

ΔH° (kJ/mol)	ΔS° (kJ/mol K)	ΔG° (kJ/mol)		
		25 °C	30 °C	35 °C
–16.71	-1.16×10^{-2}	–13.44	–13.39	–13.33

kinetic (1/s), respectively. The linear plots of experiment data are shown in Fig. 8 and the obtained parameters are presented in Table 6.

Some adsorption processes have been reported follow pseudo-first-order model, such as the uptake of cadmium(II) on beech leaves [53], the sorption of lead(II) on cypress leaves [54], the adsorption of a basic dye from aqueous solution by hardwood saw dust [3], the adsorption of Cu(VI) from aqueous solution onto *Agave lechuguilla* biomass [9], the adsorption of phenol from aqueous solution onto natural zeolite [5] and the adsorption of acid dyes in aqueous solutions by shells of bittim [40].

Pseudo-second-order kinetic model is given by Eq. (22) and the linear form is expressed by Eq. (23) [55–57].

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (22)$$

$$\frac{t}{q_t} = \frac{1}{q_e^2 k_2} + \frac{t}{q_e} \quad (23)$$

with k_2 is the rate constant of pseudo-second-order kinetic (g/mg·s). The fitting of experiment data by using Eq. (23) are shown in Fig. 9, while the results are tabulated in Table 6.

Table 6 shows the obtained values of adsorption kinetic parameters for salt ions onto zeolite according to pseudo-first-order model and pseudo-second-order model. It can be seen that the correlation coefficients (R^2) of pseudo-second-order model is higher than pseudo-first-order model. R^2 values of pseudo-second-order model in the range of 0.999 to 1, while for pseudo-first-order model are 0.799 to 0.971. The calculated values ($q_{e, cal}$) for pseudo-second-order model is closer to the experimental value ($q_{e, exp}$) than ($q_{e, cal}$) for pseudo-first-order model. These results indicate that pseudo-second-order model better describes the adsorption kinetic of salt ions onto natural zeolite than pseudo-first-order model. Similar trends were also reported by numerous authors such as adsorption of phenol onto natural zeolites [5], adsorption of dye from aqueous solution by cashew nut shell [38], adsorption of reactive dyes on activated carbon [8], removal of Mg^{2+} and Ca^{2+} ions by mesoporous LTA zeolite [56] and removal of Cu(II) and Pb(II) from aqueous solution by activated bentonite [51].

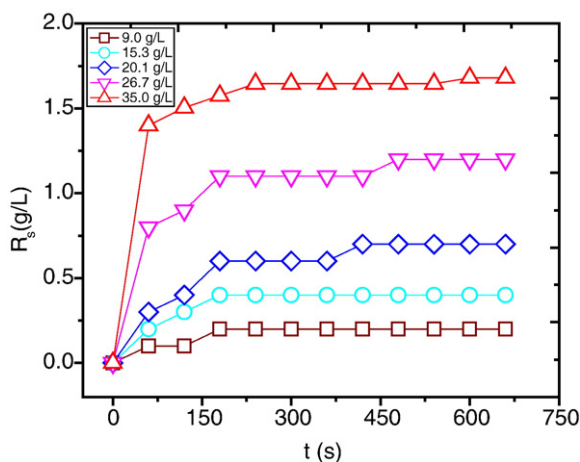


Fig. 7. The reduction of seawater salinity (R_s) as function of time (t) after treated by zeolite powder at different initial salinity.

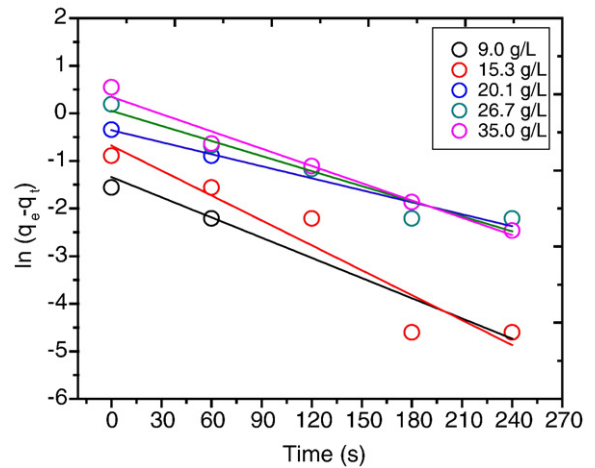


Fig. 8. Linear plot for adsorption data of salt ions onto zeolite according to pseudo-first-order model (Eq. (21)).

3.4. Adsorption mechanism

Base on the previous results (adsorption isotherms and thermodynamics), the adsorption of salt ions onto zeolite was considered as physical adsorption. It has been known that the negative charges of zeolite surface arise due to imbalance of the charges of Si^{4+} and Al^{3+} as the main element of zeolite framework [56,57]. These negative charges appear on the AlO_4^- groups [2]. As a result, zeolite possesses ability to attract the positive ions and repulse the negative ions that are located in the area of zeolite potential. Due to physical process, we explain the adsorption mechanism of salts ion onto zeolite surface by using electrical double layer (EDL) theory [47,48].

Based on EDL theory, therefore, when zeolite particles are dispersed in the seawater, an electrical double layer exists around each particle zeolite. First layer is occupied by strongly bound ions (stern layer), while second layer is occupied by less decisively bound ions (diffuse layer). In this condition, zeolites surface would attract positive ions through Van der Waals attraction and reject the negative ions through electrostatic repulsion. As a result, the positive ions are adsorbed on the surface of zeolite then create a strongly bound layer. If the electric charge of zeolites is still strong enough to attract free ions, the adsorption process will be continued. Meanwhile, after adsorb a number of positive ions, the electric charge of zeolites are decayed so a repulsive force that counter to the negative ions are also declined. As a result, the adsorbed ions on the second layer are not only composed by positive ions but also a small amount of negative ions are possible included. It's because the negative ions obtain the attraction force from positive ions in the stern layer. In this second layer, the positive ions are attracted by zeolite charge (negative) but obtain repulsive force from the adsorbed ions in first layer. Conversely, the negative ions are repulsed by zeolite charge but attracted by positive ions in first layers. In addition, the second layer is located outside the first layer (further away from the zeolite

Table 6
Fitting kinetics parameters of adsorption of salt ions onto zeolite according to pseudo-first-order model and pseudo-second-order model.

C_i (g/L)	R_s (g/L)	$q_{e,exp}$ (mg/g)	Pseudo-first-order model			Pseudo-second-order model		
			$q_{e,cal}$ (mg/g)	k_1 (1/s)	R^2	$q_{e,cal}$ (mg/g)	k_2 (g/mg·s)	R^2
9.0	0.2	5.71	7.48	0.014	0.799	5.72	0.606	0.999
15.3	0.4	11.43	14.48	0.017	0.881	11.44	0.545	0.999
20.1	0.7	20.00	20.04	0.008	0.912	20.04	0.089	0.999
26.7	1.2	34.29	30.10	0.010	0.926	34.32	0.087	1
35.0	1.7	48.57	40.39	0.012	0.971	49.07	0.041	0.999

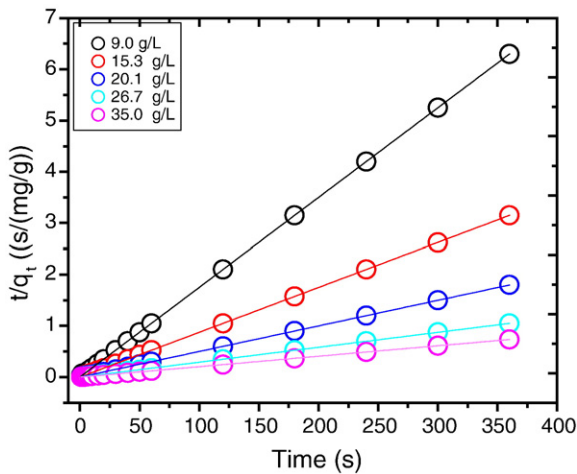


Fig. 9. Linear plot for adsorption data of salt ions onto zeolite according to pseudo-second-order model (Eq. (23)).

surface) therefore the ions in the second layer is gaining weaker electric potential than the ions in first layer. Consequently, the ions in the second layer undergo weaker bounding than the adsorbed ions in the first layer. The greater the electrical charge of zeolite, then the diffusion layer will be wider so that more ions are possible adsorbed then leads to greater reduction of salinity. Illustration of the adsorption mechanism of salt ions onto zeolite surface is shown in Fig. 10.

The binding process of salt ions will continue as long as the attraction potential (V_A) is greater than the repulsion potential (V_R) so that the total potential of adsorbate-adsorbent ($V_T = V_A + V_R$) is negative; otherwise the binding processes are vanished and adsorption process will be disappeared. As a result no longer reduction of seawater salinity is occurred. Outside diffuse layer, the salt ions behave as free ions while the ions and zeolite particles inside the diffuse layer form a stable entity. When zeolite particle moves due to external force (gravity or electrical field for example), ions within the boundary move with it while ions beyond the boundary do not travel with the particle [47]. This national boundary is called as slipping plane or hydrodynamic surface, while

the value of the electric potential at this plane is called as zeta potential which is foremost parameter in the theory of interaction of colloidal particles [48].

From measurement, we obtain zeta potential of zeolite in seawater (35.0 g/L, pH 8.3 and 25 °C) is (-0.53 ± 0.014) mV. The negative value of zeta potential indicates that zeolite surface groups are electro-negative in seawater [58], while small value of zeta potential (below ± 30 mV) indicates instability of the dispersion of zeolite particles [59]. Small value of zeta potential was also reported by Kuzniatsova et al. for zeolite Y in seawater [60]. It has been known that, in colloidal system with negative and small value of zeta potential, the repulsive force among particles is too weak. Therefore, when zeolite particles are dispersed in seawater they would not be stably dispersed. But, zeolite particles will be deposited in the bottom due to sedimentation. During this process, zeolite particles adsorb some amount of salt ions so that the reduction of seawater salinity is occurred. In this work, the reduction salinity of seawater (35.0 g/L) after treated by zeolite reaches 1.7 g/L.

We performed AAS characterization to confirm the reduction of positive and negative ions in seawater after treated by zeolite was actually occurred. We measured sodium and chloride concentrations as two dominant ions so the change of ions concentration can be easily detected. Indeed, we found that concentration of sodium decreases from 9680 ppm to 8837 ppm, while concentration of chloride decreases from 17,839 ppm to 17,318 ppm. It can be seen that, total reduction concentration of sodium and chloride are 1364 ppm or 1.364 g/L. This value is slightly lower than the reduction salinity of seawater (1.7 g/L); but it is reasonable. It because this AAS results are not present concentration of all dissolved ions, but it only calculate two major ions in seawater.

We observed that the amount of adsorbed ions on zeolite surface is dependent on the solution concentration. Fig. 11 shows the dependency of the sorption ability of zeolite to the solution concentration. At low concentration, the sorption ability of zeolite is low, while at higher concentration the sorption ability of zeolite is higher. It can be seen that the reduction salinity of zeolite at concentration of 15.3 g/L, 26.7 g/L and 35.0 g/L are 0.5 g/L, 1.0 g/L and 1.8 g/L, respectively. At high solution concentration, the density of salt ions is high. Therefore the distance of adjacent ion is small. As a result, the amount of salt ions that are located in the zeolite potential are high. In contrast, at low solution concentration, the distance of adjacent ion is far so that the amount of salt ions that are located in the zeolite potential are also small. In addition, in solution with high ion density, the collision probability between salt ions to the surface of zeolite particle is greater than in low solution concentration [61]. Therefore, the binding process of salt ions on zeolites is easily occurred in high solution concentration. Zeolite will possess high sorption ability in high concentration of solution and low sorption

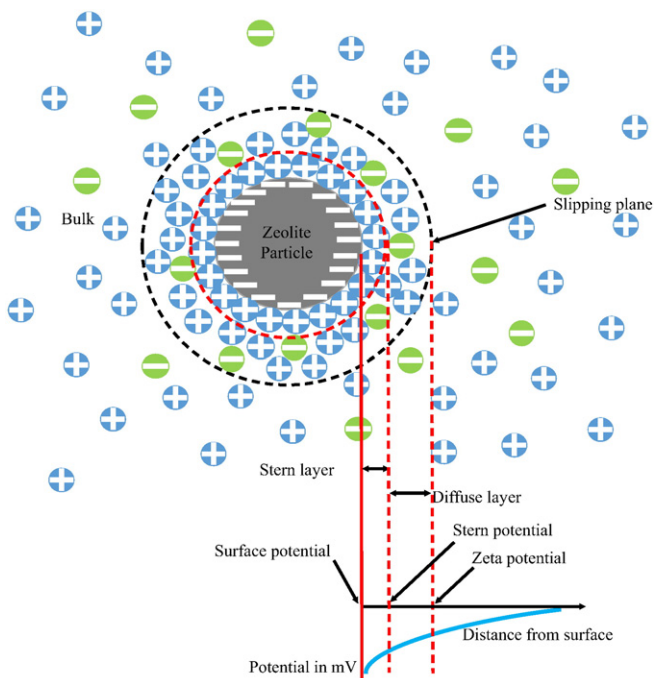


Fig. 10. Illustration of the adsorption mechanism of salt ions onto zeolite surface.

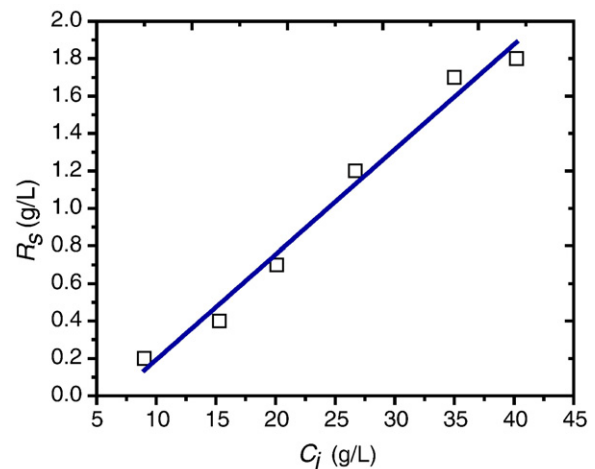


Fig. 11. Reduction of seawater salinity after treated by zeolite at different initial concentration of solution. Contact time: 24 h, temperature: 25 °C, experimental error: ± 0.05 g/L.

ability in low concentration of solution. Consequently, a significant reduction salinity is occurred in high concentration of solution, while in low concentration the reduction salinity of zeolite becomes meaningless.

It can be observed that the increment of reduction salinity is proportional to the increase of solution concentration. Thus, this condition meets:

$$\Delta R_s \approx \Delta C_i \quad (24)$$

By taking $\Delta C_i \rightarrow 0$, Eq. (24) turns into the following differential form:

$$dR_s = \xi dC_i \quad (25)$$

By integrating both of side with boundaries conditions $R_s = 0$ to $R_s = R_s$ and $C_i = C_o$ to $C_i = C_i$, Eq. (25) turns into Eq. (26) and the general solution can be expressed by Eq. (27).

$$\int_0^{R_s} dR_s = \xi \int_{C_o}^{C_i} dC_i \quad (26)$$

$$R_s = \xi C_i - \chi \quad (27)$$

with $\chi = \xi C_o$, ξ is a constant that refers to the capacitance of zeolite and C_o refers to the threshold of solution concentration. By substitute Eq. (2) to Eq. (27), the general solution becomes

$$q_e = \xi C_i - \chi \quad (28)$$

Eq. (28) stated linearity relationship between concentrations of the solution to the amount of adsorbed ions on zeolite. From Eq. (28), it can be shown that the high reduction of salinity (adsorption of salt ion onto zeolites) depends on the concentration of the solution where the adsorption capacitance of zeolite is constant that is independent to the concentration of the solution. In addition, there is a threshold concentration of adsorption. The adsorption process occurs above the threshold value. We obtain adsorption capacitance of zeolite and threshold concentration are 1.603 mgL/g² and 6.6 g/L, respectively. Below threshold concentration (low concentration), the density of salt ions are so low therefore these ions are far away distributed. As a result, the electric field of zeolite is not strong enough to bind the salts ions then the adsorption processes were not occurred. Theoretical and experimental values of q_e are expressed in the Table 7. It can be seen that both values are close each other.

4. Conclusions

We have investigated the sorption characteristics of salt ions onto natural zeolite (clinoptilolite). We have observed that the nature of adsorption process of salt ions onto zeolites surface is favorable, which is indicated by value of $R_L < 1$. The adsorption refers to physical process. The spontaneous nature of physical adsorption was indicated by the negative ΔG° and the small value of the men free energy ($E < 20$ kJ/mol).

Table 7

Theoretical and experimental value of q_e (contact time: 24 h, temperature: 25 °C, experimental error: ± 0.05 g/L).

C_i (g/L)	q_e (mg/g)	
	Experiment	Theoretical
9.0 \pm 0.05	5.71	3.92
15.3 \pm 0.05	11.43	14.01
20.1 \pm 0.05	20.00	21.71
26.7 \pm 0.05	34.29	32.29
35.0 \pm 0.05	48.57	45.59
40.2 \pm 0.05	51.43	53.93

The negative ΔH° (−16.71 kJ/mol) suggested that the adsorption process was exothermic, while the negative ΔS° (−0.0116 kJ/mol K) indicates the configuration of the adsorbate on the ductzeolite surface is less random. The adsorption kinetic well fits to the pseudo-second-order model. Reusability of zeolite on reducing salinity of seawater has been confirmed. Based on the characteristics of the adsorption isotherms, thermodynamic and adsorption kinetics, we suggest that zeolite is potential adsorbent for seawater desalination.

Acknowledgement

This work was financially supported by the Ministry of Research and Higher Education, Republic of Indonesia (Grant No. 310y/I1.C01/PL/2015 and Grant No. 105/SP2H/PPM/II/2016).

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