Turnitin Originality Report

RSC Adv., 2015, 5, 83689–83699 by Suryadi Ismadji

From paper 2 (Hippo-hippo 02)

Processed on 16-Feb-2018 14:45 WIB
ID: 916901919
Word Count: 6931

Similarity Index	Similarity by Source	
14%	Internet Sources:	7%
	Publications:	13%
	Student Papers:	5%

sources:

1 2% match (student papers from 20-Jul-2017)
Submitted to Indian Institute of Science, Bangalore on 2017-07-20

2 1% match (publications)
S. Ismadji, S. K. Bhatia. "A Modified Pore-Filling Isotherm for Liquid-Phase Adsorption in Activated Carbon", Langmuir, 2001

3 1% match (publications)
Suwandi, Anita Carolina, Nani Indraswati, and Suryadi Ismadji. "Adsorption of N-methylated diaminotriphenilmethane dye (malachite green) on natural rarasaponin modified kaolin", Desalination and Water Treatment, 2012.

4 1% match (student papers from 22-May-2017)
Submitted to B.S. Abdur Rahman University on 2017-05-22

5 1% match (publications)
Arslan, A.. "Zeolite 13X for adsorption of ammonium ions from aqueous solutions and hen slaughterhouse wastewaters", Journal of the Taiwan Institute of Chemical Engineers, 201205

6 1% match (publications)
Soetaredjo, Felycia E., Alfin Kurniawan, L. K. Ong, Dimas R. Widagdyo, and Suryadi Ismadji. "Investigation of the continuous flow sorption of heavy metals in a biomass-packed column: revisiting the Thomas design model for correlation of binary component systems", RSC Advances, 2014.

7 1% match (publications)
Chen, Jie, Jiangtao Feng, and Wei Yan. "Facile synthesis of a polythiophene/TiO2 particle composite in aqueous medium and its adsorption performance for Pb(ii)", RSC Advances, 2015.

8 < 1% match (student papers from 15-Oct-2009)
Submitted to Asian Institute of Technology on 2009-10-15

9 < 1% match (publications)
Sahmoune, Mohamed Nasser, and Ahmed Reda Yeddou. "Potential of sawdust materials for the removal of dyes and heavy metals: examination of isotherms and kinetics", Desalination and Water Treatment, 2016.

10 < 1% match (Internet from 28-May-2016)
http://fcee.utm.my/aishah/files/2016/04/2015-08-RSC-Advances-20155-37405-Mun.pdf

11 < 1% match (Internet from 23-Jun-2015)

http://www.researchgate.net/publication/222068049_Natural_zeolites_as_effective_adsorbents_in_water_and_wastewater

12 < 1% match (publications)
Soenjaya, Soegiarto Adi, Nova Handoyo, Felycia Edi Soetaredjo, Artik Elisa Angkawijaya, Yi-Hsu Ju, and Suryadi Ismadji. "Preparation of carbon fiber from water hyacinth liquid tar", International Journal of Industrial Chemistry, 2014.

13 < 1% match (publications)
Aydın Temel, Fulya, and Ayşe Kuleyin. "Ammonium removal from landfill leachate using natural zeolite: kinetic, equilibrium, and thermodynamic studies", Desalination and Water Treatment, 2016.

14 < 1% match (publications)
Widiastuti, N.. "Removal of ammonium from greywater using natural zeolite", Desalination, 20110815

15 < 1% match (publications)
Chao Gan, Yunguo Liu, Xiaofei Tan, Shufan Wang, Guangming Zeng, Bohong Zheng, Tingting Li, Zhengjiang Jiang, Wei Liu. " Effect of porous zinc–biochar nanocomposites on Cr( ) adsorption from aqueous solution ", RSC Advances, 2015

16 < 1% match (publications)
Lu, Hongfei, Xueliang Qiao, Wei Wang, Fatang Tan, Zunqi Xiao, and Jianguo Chen. "Facile preparation of mesoporous silica/nano zero-valent iron composite for Pb(II) removal from aqueous solution", Desalination and Water Treatment, 2015.

17 < 1% match (publications)
Ates, Ayten. "Role of modification of natural zeolite in removal of manganese from aqueous solutions", Powder Technology, 2014.

18 < 1% match (Internet from 23-Feb-2016)
http://scialert.net/fulltext/?doi=jest.2016.226.237

19 < 1% match (publications)
Ullah, Zia, Sajjad Hussain, Saima Gul, Sabir Khan, and F.K. Bangash. "Use of HCl-modified bentonite clay for the adsorption of Acid Blue 129 from aqueous solutions", Desalination and Water Treatment, 2015.

20 < 1% match (publications)
NanoScience and Technology, 2016.

21 < 1% match (Internet from 10-Sep-2017)
https://repository.ntu.edu.sg/bitstream/handle/10356/53146/SongXianghua12.pdf?isAllowed=y&sequence=1

22 < 1% match (Internet from 08-Jun-2017)
https://www.intechopen.com/books/microporous-and-mesoporous-materials/the-increase-of-the-micoporosity-and-co2-adsorption-capacity-of-the-commercial-activated-carbon-cwz-

23 < 1% match (publications)
Chen, Yunqiang, Qingkun Zhang, Libin Chen, Hua Bai, and Lei Li. "Basic aluminum sulfate@graphene hydrogel composites: preparation and application for removal of fluoride", Journal of Materials Chemistry A, 2013.

24 < 1% match (publications)
Qiuyan Gan, Weilong Shi, Yanjun Xing, Yu Hou. "A Polyoxoniobate/g-C3N4 Nanoporous Material with High Adsorption Capacity of Methylene Blue from Aqueous Solution", Frontiers in Chemistry, 2018

25 < 1% match (student papers from 13-Sep-2015)
Submitted to University of Mustansiriyah on 2015-09-13

26 < 1% match (publications)
Kurniawan, Alfin, Chintya Effendi, L.K. Ong, Fredi Kurniawan, C.X. Lin, Artik Elisa Angkawijaya, Yi-Hsu Ju, Suryadi Ismadji, and X.S. Zhao. "Preparation of nanoporous carbon microspheres by subcritical water carbonization and electrocapacitive study", Electrochimica Acta, 2013.

27 < 1% match (publications)
Putra, E.K.. "Performance of activated carbon and bentonite for adsorption of amoxicillin from wastewater: Mechanisms, isotherms and kinetics", Water Research, 200905

28 < 1% match (publications)
Zahra Rahmani, Mohammad Taghi Samadi. "Preparation of Magnetic Multi-Walled Carbon Nanotubes to Adsorb Sodium Dodecyl Sulfate (SDS)", Avicenna Journal of Environmental Health Engineering, 2017

29 < 1% match (student papers from 08-Dec-2015)
Submitted to Thapar University, Patiala on 2015-12-08

30 < 1% match (publications)
Kuokkanen, Eveliina, Eveliina Repo, Jolanta K. Warchoł, and Mika Sillanpää. "Ammonium adsorption from synthetic and real mining wastewaters by eight-clay based adsorbents", Desalination and Water Treatment, 2015.

31 < 1% match (publications)
Zhou Qiusheng, Lin Xiaoyan, Qian Jin, Wang Jing, Luo Xuegang. "Porous zirconium alginate beads adsorbent for fluoride adsorption from aqueous solutions", RSC Advances, 2015

32 < 1% match (publications)
Otero, M.. "Adsorptive purification of phenol wastewaters: Experimental basis and operation of a parametric pumping unit", Chemical Engineering Journal, 20050601

paper text:

10**RSC Advances PAPER Cite this: RSC Adv., 2015, 5,** 83689 **Received** 3rd August **2015 Accepted** 24th September **2015 DOI: 10.1039/** c5ra15419g **www.rsc.org/advances**

2**Ammonia removal from water using sodium hydroxide modified zeolite mordenite Jennifer Pieter Soetardji,†** a **Jeannete Cindy Claudia,†** a **Yi-Hsu Ju,** b **Joseph A. Hriljac,** c **Tzu-Yu Chen,** c **Felycia Edi Soetaredjo,*** a **Shella Permatasari Santoso,** b **Alfin** Kurniawanb and **Suryadi Ismadji***

a Natural and modified mordenite zeolites were used to remove ammonium ions from aqueous solution and Koi pond water. The zeolite modification was conducted using sodium hydroxide solutions of different strengths at 75 C for 24 h. Langmuir, Freundlich, Sips, and Toth equations with their temperature dependent forms were used to represent the adsorption equilibria data. The Langmuir and its temperature dependent forms could represent the data better than the other models. The pseudo-first order model has better performance than the pseudo-second order model in correlating the adsorption kinetic data. The controlling

11**mechanism of the adsorption of** NH4+ **from aqueous solution** onto the **natural zeolite and**

the one treated with 6 M sodium hydroxide solution was dominated by physical adsorption. The competition with other ions occurred through different reaction mechanisms so it decreases the removal efficiency of ammonium ions by the zeolites. For the treated zeolite, the removal efficiency decreased from 81% to 66.9%. A Thomas model can represent the experimental data for both adsorption of ammonia from aqueous solution or from Koi pond water. Introduction The presence of ammonia in aquatic environments causes a serious problem for aquatic biota, especially ?sh. In water, the ammonia can be present in the ionized form (NH4+) and un- ionized form (NH3), and both of these substances are present under equilibrium conditions according to the following equation:1 NH3 + H2O 4 NH4+ + OH (1) The total concentration of the ionized ammonia (NH4+) and un-ionized ammonia (NH3) in water is de?ned as the total ammonia nitrogen (TAN), and at a certain concentration the un- ionized ammonia (NH3) is lethal for ?sh. The equilibrium concentration of ammonia in the water is affected by both the pH and temperature. At high pH, the equilibrium condition (eqn (1)) will shi? towards the formation of ammonia, while at low pH the formation of ammonium ion (NH4+) is dominant. For aquatic biota such as ?sh, the ammonium ion is relatively aDepartment of

6**Chemical Engineering, Widya Mandala Surabaya Catholic University, Kalijudan 37, Surabaya 60114, Indonesia. E-mail: felyciae@yahoo.com;** suryadiismadji@yahoo.com; **Fax: +62 31 389 1267; Tel: +62 31 389 1264**

bDepartment

26**of Chemical Engineering, National Taiwan University of Science and Technology, No. 43, Sec. 4, Keelung Rd., Taipei** City 106, **Taiwan,** Republic **of**

China cSchool of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK † These authors contribute equally. non-toxic compared to the ammonia. Ammonia also predomi- nates when temperature is high while the ammonium ion predominates at low temperature. In the aquaculture industry the quality of water is the most important parameter for the continuation of the industry. One of the important parameters for the quality of water is TAN as it is the major nitrogenous waste product of ?sh and also results from the decomposition of organic matter. As a natural byproduct of ?sh metabolism, ammonia can accumulate easily in an aquatic system and it has the tendency to block the transfer of oxygen from gills to the blood nerve system and cause gill damage. The excess ammonia in water also destroys the mucous producing membrane in ?sh and damages the internal intestinal surfaces. The presence of excessive amounts of ammonia in the aquatic environment causes eutrophication. A number of processes are currently available for the removal of TAN from the aquatic environment, and the most widely used process is the adsorption process. This process offers several advantages over other available processes, such as high removal efficiency, the adsorbent can be re-used, it can be applied for a wide range of concentrations, and is a cost effective process. One of the available natural adsorbents which is widely employed for the removal of ammonia from aquatic environ- ment is a zeolite. A zeolite is a microporous aluminosilicate mineral which possesses a structure like a three-dimensional honeycomb with an overall negatively charged

framework. The presence of hydrated alkali and/or alkaline earth cations (Na+, K+, Ca2+, Mg2+) in the pores of the aluminosilicate framework stabilizes the structure, and in the aquatic condi- tion, these cations are also exchangeable with other cations from the solution.2,3 The disadvantage of using a natural zeolite

24**as an adsorbent for the removal of** NH4+ ion **from aqueous solution** is **a**

low adsorption capacity; most have a value less than 10 mg g 1.4–10 The low adsorption capacity and removal efficiency are still the main problem for industrial application

11**of natural zeolites in** aquaculture, **water and wastewater** processes. **In**

order to improve the adsorption capacity, a modi?cation using a chemical treatment processes is necessary such as using an acid, alkali or salt.11–14 Microwave irradiation15 and heat treat- ment16

20**methods have** also **been** employed **to** increase **the adsorption capacity of**

natural zeolites. Leyva-Ramos et al.14 modi?ed natural zeolite chabazite with sodium chloride to remove ammonium from aqueous solution and the result clearly indicates that chabazite enriched with Na+ is more preferentially exchanged by NH4+ than the other alkali cations. The modi?cation using acid solution is seldom used because acid treatment causes de-alumination, the removal of Al3+ ions from the zeolite structure degrades it and decreases the ion exchange capacity.1 In this study a modi?cation of natural mordenite with sodium hydroxide combined with a thermal treatment is investigated. To the best of our knowledge, this is the ?rst of the use of such a modi?ed zeolite as the adsorbent for removal of the ammonium ion from aqueous solution in an aquacul- ture system (Koi pond). Since the ?nal goal of this study was to treat the ammonia from the Koi pond, therefore all of the adsorption experiments were conducted at a pH similar to the water of Koi pond system (6.5). The adsorption isotherms of ammonium ion onto natural and modi?ed mordenite were obtained

2**at three different temperatures (303.15, 308.15, and 313.15 K). The**

3**temperature-dependent forms of** the Lang- muir, **Freundlich, Sips, and Toth** equations **were** used **to correlate the** experimental **adsorption data.**

The adsorption kinetics of ammonium ions onto the natural and modi?ed zeolite was also studied. Well known

15**pseudo ?rst- and second- order** kinetic **models were** employed **to** represent **the kinetic data. The**

removal of ammonium ion from the Koi pond system was conducted in dynamic mode. The breakthrough adsorption performances were correlated by a Thomas equation. Material and method Materials The natural zeolite used in this study was obtained from Ponorogo, East Java, Indonesia. The zeolite was crushed in a mortar and sieved using a Retsch Haan vibrator screener to particle size of about 0.85–1.70 mm (12 + 20 US mesh). All of the chemicals used in this study were obtained as pure analysis reagents from Sigma Aldrich Singapore and used without any further treatment or puri?cation. Modi?ed zeolite preparation The modi?cation of the natural zeolite was performed under alkaline condition using sodium hydroxide solution at concentrations of 1 M, 3 M, and 6 M at 75

20**C for 24 h.** Subse- quently **the** modi?ed **zeolite was**

washed using tap

20**water to remove excess sodium** hydroxide solution. Then, **the**

solid sample was dried at 110 C for 24 h. Characterization of solid samples The characterization of the natural (NatZ) and modi?ed zeolites (1M-Z, 3M-Z, and 6M-Z) used scanning electron microscopy (SEM), X-ray diffraction (XRD), and nitrogen sorption. The SEM analysis was conducted to study the surface topography and texture of the adsorbents. The SEM analysis was conducted

6**on a JEOL JSM-** 6390 **?eld emission SEM** operated **at an**

accelerating voltage of 15 kV.

12**Prior to analysis the samples were coated with** ultra **-thin layer of** conductive **platinum** on the specimens **using an**

auto ?ne coater (JFC-1200, JEOL, Ltd, Japan) for 120 s in an argon atmosphere. The X-ray diffraction analysis was conducted on a Philips PANalytical X'Pert powder X-ray diffractometer with monochromated high intensity Cu Ka1 radiation (l ¼ 0.15406 nm). The diffractograms were obtained at 40 kV, 30 mA and with a step size of 0.05 s 1. The elemental compositions of the adsorbents were analyzed using a Bruker S8 Tiger X-ray ?uorescence spectrophotometer. The pore structures of NatZ, 1M-Z, 3M-Z, and 6M-Z were characterized by nitrogen sorption method. The nitrogen sorption measurements were carried out at boiling point of liquid nitrogen (77 K) on automated Micromeritics ASAP2010 sorption equipment.

19**Prior to the** analysis, **the** solid **samples were degassed at** 473.15 **K for** 24 **h.**

The speci?c surface area of the

25**samples were calculated** by the **Brunauer–Emmett–Teller (BET) method** at a **range of relative** pressure of **0.05** to **0.** 3, while **the total pore volume was determined**

at a relative pressure of 0.995. Adsorption isotherm study The adsorption isotherm study was conducted in batch mode at three different temperatures (303, 308, and 313 K) and pH of 6.5. A known amount of adsorbent (0.1 to 1.0 g) was added in a series of Erlenmeyer ?asks containing 100 mL ammonium chloride solution with a concentration of 10 mg L 1. The ?asks were moved to a Memmert type WB-14 thermostatic shaker

27**water bath. The temperature of** the thermostatic shaker **water bath was**

adjusted to a desired temperature and

15then the system was shaken at 100 rpm for 24 h (equilibrium condition). The equilibrium condition was

determined at temperature of 303 K, pH of 6.5, and initial solution concentration of 10 mg L 1. A?er the equilibrium time was reached, the solid adsorbent was removed from the solution by centrifugation. The concentration of ammonium in the solution was measured quantitatively at maximum wavelength (699.5 nm) based on Nessler method17 using Shimadzu UV/Vis-1700 Pharma Spectrophotometer. The amount of ammonium ion adsorbed by the adsorbent at equi- librium condition

28was calculated by the following equation: qe ¼ ðCo CeÞ V m (2) where qe is the

equilibrium condition (mg g 1),

18Co (mg L 1) and Ce (mg L 1) are the initial and equilibrium concentration of ammonium in the solution, respectively. The amount of adsorbent (g) and the volume of

solution (L) are represented by symbols m and V. The adsorption isotherm experiments were conducted in triplicate. Adsorption kinetic study The adsorptions kinetic of ammonium from aqueous solutions onto natural and modi?ed zeolites were also conducted isothermally

2at three different temperatures (303, 308, and 313 K)

and pH of 6.5. A similar procedure to the adsorption isotherm study was employed for the kinetic study. In the kinetic study, the ?xed amount of adsorbent (1 g) was added to each Erlenmeyer containing 100 mL ammonium solution (10 mg L 1). At

23a certain interval of time (1 h) one of the avail- able ?asks was taken from the

thermostatic water bath. The amount of the ammonium adsorbed by the adsorbent at time t was determined

24by the following equation qt ¼ ðCo CtÞ V m (3) where Ct

21is the concentration of ammonium in the solution at time interval of t. The adsorption

kinetic experiments were conducted in triplicate. Continuous adsorption experiment Continuous adsorption of ammonium ion from aqueous solu- tion and Koi pond onto modi?ed zeolites were conducted as follow: the modi?ed zeolites were packed in glass columns of 1 cm diameter and 16.5 cm height. Synthetic ammonium chloride solution and ?sh pond wastewater were pumped into the column using a Master?ex 7550-62 peristaltic pump. This experiment was performed to obtain breakthrough curves of ammonium from aqueous solution and real aquaculture system (in this case Koi pond). The ?ow rate of the solution entering the column was 6.5 mL min 1 and the height of modi?ed zeolite in the column was 5 cm. The solution was collected at the outlet of the column a?er certain intervals of time and the concentration of ammonium was

measured spectrophotometrically using the Nessler method.17 Results and discussion Characterization of natural and modi?ed zeolite The SEM micrographs of the surface morphology of NatZ and 6M-Z are

7**depicted in Fig.** 1. **It can be seen that the**

modi?cation using a strong sodium hydroxide solution (6 M) did not affect the surface topography of the zeolite. The breakdown of some of the particles from a needle-like shape into smaller and less uniform particles is attributed to the mechanical force used during the grinding of the zeolite. The XRD patterns of NatZ and 6M-Z are given in Fig. 2. The identi?cation of the mineral content by comparing to the Fig. 1 Surface topography of (a) natural zeolite (NatZ), and (b) modi- fied zeolite (6M-Z). Fig. 2 XRD diffractograms of natural zeolite (NatZ) and its modified form (6M-Z) with the pattern reported for mordenite in the ICSD JCPDS database. standard of JCPDS 80-0642 indicates it consists mainly of mor- denite. The modi?cation of the natural zeolite using sodium hydroxide solution did not change or degrade the mordenite as seen in the XRD patterns in Fig. 2. This evidence clearly indi- cates that the sodium hydroxide modi?cation exerted little or no in?uence on the crystallinity of the mordenite. The chemical composition of the natural zeolite and its modi?ed form obtained from XRF analysis are summarized in Table 1. The increase of Na2O composition in modi?ed zeolite indicates

14**Table 1 Chemical composition of natural and** NaOH modified **zeolites**

as determined by XRF % Weight Element NatZ 1M-Z 3M-Z 6M-Z SiO2 60.85 Al2O3 11.78 CaO 2.43 Fe2O3 2.07 Na2O 1.87 K2O 1.05 MgO 0.52 Other 19.43 60.14 62.05 12.03 12.6 1.92 0.93 2.02 2.01 2.34 3.05 0.95 0.92 0.51 0.51 20.09 17.93 58.47 13.41 0.11 1.78 3.85 0.51 0.42 21.45 that the incorporation of exchangeable sodium ions to the natural zeolite occurred during the modi?cation process. Partial exchange of several cations such as Ca2+, K+ and, to a lesser extent, Mg2+ with Na+ was observed. With increasing NaOH concentration, the amount of CaO decrease from 2.43 to 0.11%, while the composition of Na2O increase from 1.87 to 3.85%. The modi?cation using 6 M NaOH almost completely transformed the Ca-zeolite into a Na-zeolite with, as stated earlier, no obvious change in crystallinity. As illustrated in Fig. 3, the modi?cation of the natural zeolite using sodium hydroxide solution improved the porosity. The hysteresis loops in NatZ, 1M-Z, 3M-Z, and 6M-Z con?rms the presence of mesopores in the pore structure. The BET surface area, micropore volume and total pore volume of the zeolites are summarized in Table 2. It can be seen that the micropores did not have signi?cant contribution to the total pore since the values were almost equal to zero. The modi?cation of zeolite using sodium hydroxide at 75 C brought the formation of more mesopores due to the clearing of the pore channels and voids of the natural zeolite. The increased NaOH concentration also increased the formation of pores, leading

7**to the increase of BET surface area and** total **pore**

volume as indicated in Table 2 and Fig. 3. Effect of sodium hydroxide concentration to adsorption capacity Initial adsorption experiments showed that the adsorption of ammonium ions had reached equilibrium a?er 24 h. For subsequent adsorption experiments, 24 h was chosen as the Fig. 3 Nitrogen sorption isotherms of natural and modified zeolites. Table 2 The pore

17**characteristics of natural and modified zeolites Sample** SBET, **m2 g 1** Vmicro, **cm3 g 1** Vtotal, **cm3 g 1**

NatZ 30.2 1M-Z 38.9 3M-Z 49.5 6M-Z 58.6 0.002 0.116 0.002 0.138 0.002 0.153 0.002 0.182 Fig. 4 Removal efficiency

17**of natural and modified zeolites.** equilibrium time. **Fig. 4**

shows the removal

13**efficiency of NH4+ from** the solution **using natural**

and NaOH modi?ed zeolites as the adsorbents. This ?gure clearly indicates that NaOH modi- ?cation effectively improved the adsorption capability of the zeolite for removal of NH4+ from aqueous solution. According to Table 1, the removal efficiency of NH4+ is closely related to the content of Na and Ca; the zeolite with higher Na and less Ca content removed more NH4+. Since the 6M-Z has the highest removal efficiency; this modi?ed zeolite was used for subse- quent adsorption experiments. Adsorption equilibria The equilibrium relation between the ammonium ion

5**on the surface of** the **adsorbent and in** the **solution**

could be related through an adsorption isotherm. Different kind of adsorption models have been developed and are currently used for the interpretation of liquid phase adsorption experimental data. The adsorption of chemical compounds onto the surface of adsorbents is affected by temperature. For physical adsorption, the temperature gives

30**a negative effect on the adsorption** capacity **of** adsorbent, while **for**

chemical adsorption the uptake increases with the increase of temperature. The in?uence of temperature on the amount uptake can be represented in the adsorption models through the inclusion of temperature dependent forms.18–20 In this study, the Langmuir, Freundlich, Sips, and Toth models with their temperature dependent forms were employed to correlate the adsorption equilibria of NH4+ onto NatZ and 6M-Z. The Langmuir equation is one of the most widely used adsorption equations to correlate liquid phase adsorption experimental data of various systems.

21**Based on the** theory **of** the **adsorption on a** ?at **surface,**

Langmuir developed an adsorption model which has the form as follows qe ¼ qmax 1 þ KLCe KLCe (4)

9**where qmax is the maximum amount of adsorbate adsorbed by the adsorbent to achieve complete monolayer coverage of the adsorbent surface (mg g** 1), **and** KL **is the** adsorption **affinity (L mg** 1). **The**

parameters qmax and KL are affected by temperature, and the mathematical forms of these parameters as function of temperature are as follow: qmax ¼ q0max exp(d(T0 T)) (5) KL ¼ KL0 exp RT0 E (6) Parameter q0max represents the maximum adsorption capacity at a reference temperature T0, while temperature coefficient of expansion of the adsorbate is represented by parameter d. The affinity constant of Langmuir equation at reference temperature and heat of adsorption are given by symbols K0L and E, respectively. The second equation used in this study to represent the adsorption equilibria data is the Freundlich isotherm. This equation is the earliest known empirical adsorption equation and widely used for heterogeneous systems and reversible adsorption processes. The Freundlich isotherm has the form qe ¼ KFCe1/n (7)

29**where KF** ((mg **g 1)(** mg L **1) n) and n are parameters** represent **adsorption capacity and** the **adsorption intensity, respectively.** Parameter n **also**

indicates the heterogeneity of the system. The temperature dependent forms of Freundlich equation are KF ¼ KF0 exp aAR0T (8) 1 n ¼ RT A0 (9) where K0F is the adsorption capacity at the reference tempera- ture, a/A0 is a constant. The Sips equation was developed for predicting adsorption in heterogeneous systems, and this

22**model is a** combination **of** the **Langmuir and Freundlich** adsorption isotherm. **The** advantage of **Sips equation is**

it has a ?nite limit. The Sips equation can be

28**written as follows: " # qe ¼ qmax** ðKSCeÞ1=n **1**

þ ðKSCeÞ1=n (10) where KS (L mg 1)n is the adsorption affinity of Sips model, and n characterizes the heterogeneity of the system. When the value of n become unity, eqn (10) reduces to eqn (4). The temperature dependent forms of Sips equation are represented by parameter qmax, KS and n. The temperature dependent of qmax follows eqn (5) while for KS and n are as follow KS ¼ KS0 exp RT0 E 1 T0 T n¼ 1 1 þ h 1 T0 n0 T (11) (12) The parameter K0S

13**is a measure of the affinity between** the **adsorbate and** the **adsorbent**

at the reference temperature, while n0 characterizes the heterogeneity of the system at refer- ence temperature. The parameter h is a constant of Sips temperature dependent form. The last model used in this study is the Toth equation. This equation was developed on the basis of potential theory and provides a good description of many systems with sub- monolayer coverage.21 Similar to Langmuir equation, Toth equation has ?nite saturation limit for high concentration and follows Henry's law at very low concentration.19 qmaxCe qe ¼ KTh þ Cet 1=t (13) The adsorption affinity of the Toth equation is given by parameter KTh (mg L 1)t, and t is a parameter represents the system heterogeneity. Both of these parameters are affected by temperature and can be written as: KTh ¼ KT0h exp RT0 E T 0 T 1 (14) Fig. 5 Effect of temperature on ammonium removal using: (a) NatZ, (b) 6M-Z. t¼t0þh 1 T 0 T (15) where K0Th and t0 are adsorption affinity constant and parameter characterizes system heterogeneity at reference temperature, respectively. Temperature has a pronounced effect on the removal capacity of the zeolite as shown in Fig. 5 for NatZ and 6M-Z. The uptake of NH4+ ions by both of the adsorbents decreased as the temperature increased. The main mechanism of the adsorption of NH4+ ions by the zeolite is ion exchange and the process can be written as NaxZ + xNH4+ 4 (NH4)xZ + xNa+ (16) In most cases, ammonium exchange onto a zeolite is an exothermic process,5,8,22 therefore the increase of temperature will shi? the equilibrium condition towards endothermic, and less NH4+ ions adsorbed by the NatZ and 6M-Z. Fig. 6 and 7 depict the adsorption equilibria of ammonium ions onto NatZ and 6M-Z at three different temperatures. The experimental data were ?tted by

3**temperature dependent forms of Langmuir, Freundlich, Sips, and Toth**

equations. The parameters of each model were obtained by the non-linear least-squares method, and the ? tting was conducted for all the experimental data at various temperatures simultaneously using T0 ¼ 298 K. The Toth equation with its temperature dependent forms failed to correlate the adsorption equilibria data of ammonium onto NatZ. The values of parameters of Langmuir, Freundlich, Sips, and Toth equations obtained

from the ?tting of the adsorption experimental data are summarized in Table 3. Since the Toth equation failed to represent the adsorption equilibria data of ammonium onto NatZ, it will be excluded for further discussions of the validity of the adsorp- tion equations in representing the adsorption experimental data. Visually (Fig. 6 and 7), Langmuir, Freundlich, and Sips isotherm equations could represent the experimental data well with good value of R2 (Table 3). However, the decision of the suitability of the models in representing the experimental data should not be based on the visual appearance of the model or the value of R2 but should be based on the physical meaning of the parameters obtained through the ?tting of the data. The parameter qm0ax in the Langmuir and Sips models and the parameter KF0 in the Freundlich model represent the adsorption Fig. 6 Adsorption experimental data of ammonium ion into NatZ and the model fitted by: (a)

14**Langmuir, (b) Freundlich, and (c)** Sips. Fig. 7 **Adsorption** experimental data **of ammonium**

ion into 6M-Z and the model fitted by:

22**(a) Langmuir, (b) Freundlich, (c) Sips, and (d) Toth.**

capacity of the adsorbent at 298 K. Since the values of adsorp- tion capacity of NatZ and 6M-Z were in the range of the adsorption capacity of common zeolites,15,23 therefore, the value of parameter q0max and K0F of those models were physically consistent and reasonable. The affinity parameter in the Langmuir and Sips models is expressed as K0L and K0S, respectively. This parameter measures how strong the adsorbate (ammonium ion) is attracted to the adsorbent (zeolite) surface. A higher value of the affinity parameter means more adsorbate molecules cover the adsor- bent surface. The experimental results revealed that 6M-Z zeolite has better adsorption capability than NatZ as seen in Fig. 6 and 7. It indicates that 6M-Z zeolite had higher affinity value than NatZ. Based on the affinity parameter values listed in Table 3, all of three model used still capable to correlate the adsorption experimental data. The parameter d in the Langmuir and Sips equations is the temperature coefficient of adsorbate expansion. The value this parameter is speci?c for different component and independent with type of adsorbent.24 From Table 5, the ?tted values of parameter d of ammonium ion obtained from both adsorbents and equations were essentially constant and consistent with the value of most liquids and independent on the type of adsorbent. Therefore, the Langmuir and Sips models still had plausible reason for further discussion. In the Freundlich and Sips models, the heterogeneity of a given system is represented by A0 (Freundlich) and n0 (Sips). The attachment and exchange of the sodium ion into the zeolite framework would increase the system heterogeneity, and therefore increase the A0 and n0 value. The inconsistency of the heterogeneity parameter values with the physical meaning of this parameter is observed as indicated in Table 3. Since both of the Freundlich and Sips models failed to predict a correct value, both of these are excluded in the subsequent discussion. Fig. 6 and 7 show that the temperature

30**had a negative effect on the** amount **of ammonium**

ion uptake by both of NatZ and 6M-Z. This phenomenon indicates that physical adsorption is more dominant than chemisorption. Comparing the heat of adsorption value (E) with adsorption bonding type is necessary to verify the adequacy of Langmuir isotherm model. An adsorption process can be classi?ed into physical adsorption if the adsorption energy is less than 40 kJ mol 1 and chemi- sorption when the adsorption energy is between 40-80 kJ Table 3 The parameters of

3**Langmuir, Freundlich, Sips and Toth** equations as fitted **to the adsorption**

of ammonium onto NatZ and 6M-Z Isotherm model Parameters NatZ 6M-Z Langmuir q0max (mg g 1) d (K 1) KL0 (L mg 1) E (kJ mol 1) R2 Freundlich K0F (mg g 1)(mg L 1) n a/A0 A0 R2 Sips q0max (mg g 1) d (K 1) KS0

32**(L mg 1)** E **(kJ mol 1)**

n0 h R2 Toth q0max

32**(mg g 1)** KT0h **(L mg 1)** E **(kJ mol 1)**

t0 h R2 7.9462 0.00203 0.1111 1.575 0.9851 1.2505 0.029 37.82 0.9835 0.1166 0.00251 4.0834 0.8499 1.4735 0.3281 0.9835 — 53.9169 0.00218 0.4044 18.234 0.9882 1.676 0.0412 36.63 0.9925 0.5633 0.00243 7.0279 10.36 1.333 1.8641 0.9724 528.567 5.3859 31.327 0.4155 2.6879 0.929 mol 1. In physical adsorption, increasing temperature would weaken the interaction between adsorbate and adsorbent therefore less amount of ammonium ion adsorbed onto zeolite. The ?tted adsorption heat value in Langmuir model was found to be consistent with the theory. Accordingly, Langmuir model can represent the adsorption data better than any other models. Adsorption kinetic study The adsorption kinetic information is

14**important for the design of an adsorption system.**

The rate of ammonium ion adsorbed into NatZ and 6M-Z are represented by

23**pseudo-?rst** order25 **and pseudo-second** order26–28 **models. The pseudo-?rst order**

has the form q(t) ¼ qe(1 exp (k1t)) (17) While the pseudo-second order has the following form qek2t qðtÞ ¼ qe 1 þ qek2t (18) While k1 (h 1) and k2 (g mg 1 h 1) are time scaling factor for pseudo-?rst and pseudo second order, respectively. Time scaling factor describes how fast the system reaches the equilibrium. The adsorption kinetic data of NH4+ onto NatZ and 6M-Z are given in Fig. 8 and 9. Fig. 8 depicts the experimental data and plots of

7**pseudo-?rst order** while **the** plots of **pseudo-second order**

are given in Fig. 9. The ?tted parameters of

7**pseudo-?rst and pseudo-second order are** given **in Table**

4. From Fig. 8 Fig. 8

5**Pseudo first order reaction kinetics for the adsorption of NH4+ ion on**

(a). NatZ and (b). 6M-Z. and 9 and Table 4, it can be seen that pseudo-?rst order gave better performance in representing the experiment kinetic data than pseudo-second order. The deviation of qe obtained from the ? tting and experimental data in the pseudo ?rst order is smaller than the pseudo-second order. Based on this evidence, the controlling

11**mechanism of the adsorption of** NH4+ **from aqueous solution**

onto NatZ and 6M-Z was dominated by physical adsorption. Depending on the adsorption mechanism, the time scaling parameter k1 in pseudo-?rst order and k2 in pseudo-second order is also as a function of temperature. At a temperature higher than 30 C, the physical adsorption gave a quite domi- nant effect in the adsorption of NH4+ onto NatZ and 6M-Z. In both kinetic models, the value of this time scaling parameter decreased with increasing of temperature, obviously, the higher temperature of the system, the longer time was needed for the system to reach equilibrium state. Adsorption of ammonia from real aquaculture water

10**In order to** test **the** effectiveness **of the modi?ed**

zeolite for removal of NH4+ from an aquatic environment, an adsorption study using a real aquaculture system, a Koi pond, was also Fig. 9

5**Pseudo second order reaction kinetics for the adsorption of NH4+ ion on**

(a) NatZ and (b) 6M-Z. Table 4 Fitted parameters for

19**pseudo-first order and pseudo-second order for adsorption** kinetic **of** NH4+ **onto**

NatZ and 6M-Z Pseudo-?rst

16**order Pseudo-second order** T (K) **k1 (h 1) qe (mg g 1) R2 k2 (g mg 1 h 1) qe (mg g 1) R2**

Using natural zeolite as adsorbent 303 0.2399 2.9457 0.9785 0.0485 308 0.1929 2.9243 0.9602 0.0335 313 0.1837 2.7522 0.9656 0.0326 Using modi?ed zeolite as adsorbent 303 0.4102 20.7974 0.9796 0.0167 308 0.3764 20.3851 0.9733 0.0147 313 0.3480 20.1977 0.9698 0.0130 4.0609 4.2665 4.0744 25.6145 25.5650 25.7437 0.9691 0.9525 0.9580 0.9644 0.9568 0.9550 conducted. The water capacity of the Koi pond was 2 m3 and it was equipped with a ?ltering and biological system. The number of Koi in the pond was 45 Koi carp with an average weight of 2.0 kg per Koi. With this high density of Koi, the average ammonia concentration in the Koi pond a?er 1 h feeding was 4.2 mg L 1. The pH in the Koi pond was 6.5. The zeolites used for the adsorption of NH4+ from the Koi pond were NatZ, 1M-Z, 3M-Z, and 6M-Z. The adsorption experiments were conducted at 30 C in a batch mode. The water analysis of the Koi pond before and a?er zeolite adsorption is given in Table 5. It can be seen that the adsorption in this real system also involved the adsorption of other ions. The competition with other ions occurred through different reaction mechanisms so it decreases the

5**removal efficiency of ammonium ions** by **the**

zeolites. For 6M-Z zeolite, the removal efficiency decrease from 81% to 66.9%. The comparison of the adsorption capacity of sodium hydroxide modi?ed zeolite mordenite with other zeolite adsorbents toward the ammonium ion

12**is given in Table** 6. **From this table it can be seen that the**

sodium hydroxide modi?ed zeolite mordenite has better ammonium adsorption capacity than other zeolites. Continuous adsorption experiment A breakthrough curve for ammonium provides the performance of adsorption in a packed bed column system. A number of models with different kinds of assumptions have been devel- oped and tested for various adsorption systems. One of the models is the Thomas equation: Ct Co ¼ 1 KThqmaxx (19) 1 þ exp Q KThCot where KTh is Thomas rate constant (mL min 1 mg 1) and qmax is maximum adsorption capacity (mg g 1). The zeolite used for the breakthrough curve experiments was 6M-Z. The breakthrough curves of the adsorption of NH4+ from aqueous solution and from Koi pond water are given in Fig. 10. The

27**symbols represent the** adsorption **data while** the **solid lines represent the** Thomas **model.**

From this ?gure it can be seen that the Thomas model can represent the exper- imental data well for both system. The values of parameters KTh and qmax for adsorption of NH4+ from the aqueous solu- tion are 0.0082 mL min 1 mg 1 and 45.47 mg g 1, respectively, while for the real system (Koi pond water) the values are KTh and qmax of 0.0080 mL min mg and 38.40 mg g 1, 1 1 respectively. The Thomas parameter KTh for both systems is essentially the same, this parameter represents the interaction between adsorbent and adsorbate in a dynamic system. Since the breakthrough experiments for both systems were conducted at the same operating conditions (temperature, initial concen- tration, column diameter, and amount of adsorbent) it is not surprising that the parameter of KTh for both systems should be the same. As mentioned before, the parameter qmax represent the

13**adsorption capacity of the adsorbent, the** ?tted **value of**

qmax for adsorption of NH4+ from aqueous solution is higher than from the Koi pond water. As seen in Table 5, the Koi pond water contains other ions besides NH4+. During the adsorption of NH4+ in the packed bed column the competition for active sites or for exchangeable cations (especially Na+) occurred; therefore less NH4+ could be adsorbed/exchanged on the surface of 6M-Z. The breakthrough condition was achieved a?er 800 min. Table 5 Water analysis report of Koi pond before and after adsorption using zeolites Original NatZ 1M-Z 3M-Z 6M-Z pH Alkalinity total as CaCO3,

8**mg L 1** CO32 **as CaCO3, mg L 1** Fe2+, **mg L 1** Mn2+, **mg L 1** Cl , **mg L 1** SO42 , **mg L 1** NO3 , **mg L 1** Total ammonia, mg **L 1** NO2 , **mg L 1** PO43 , **mg L 1**

6.5 0.0 121 4.1 1.21 0.04 0.12 0.01 0.01 0.0 4.50 0.08 3.74 0.14 0.09 0.0 4.20 0.17 0.01 0.0 0.15 0.01 6.5 0.0 121 3.2 1.21 0.06 0.11 0.01 0.01 0.0 4.42 0.05 3.69 0.10 0.08 0.0 3.91 0.13 — 0.14 0.02 6.5 0.0 120 5.5 1.18 0.05 0.11 0.02 — 4.34 0.07 3.61 0.09 0.07 0.01 3.25 0.20 — 0.12 0.01 6.5 0.0 121 3.8 1.11 0.05 0.08 0.01 — 4.24 0.09 3.43 0.11 0.02 0.0 2.61 0.05 — 0.11 0.01 6.5 119 1.05 0.06 — 4.14 3.11 — 1.39 — 0.08 0.0 2.1 0.03 0.0 0.21 0.23 0.06 0.01 Table 6 Adsorption capacity of sodium hydroxide modified zeolite mordenite and several zeolites samples toward ammonium ion Adsorption Sample capacity, mg g 1 References Zeolite mordenite Sodium hydroxide modi?ed zeolite mordenite New Zealand mordenite Natural calcium rich zeolite Sodium salt modi?ed zeolite NaA zeolite from halloysite Zeolite 13X 7.94 53.91 8.70 9.72 15.44 44.30 8.61 This study This study 7 15 29 30 Fig. 10 Breakthrough curve for NH4+ adsorption from aqueous solution and Koi pond water. Conclusions The modi?cation of natural zeolite from Ponorogo, predomi- nantly mordenite, using NaOH as a modifying agent has been successfully conducted. The natural zeolite and its modi?ed forms were used for the removal of ammonium ions from aqueous solution and Koi pond water. The adsorption and kinetic experiments were conducted at three different temper- atures at static mode conditions.

3**Temperature-dependent forms of Langmuir, Freundlich, Sips, and Toth** adsorption equations **were** used **to** analyse **the experimental data**

and among these models the Langmuir model could best represent the data with

3**reasonable values of the** ?tted **parameters.** For the **kinetic**

study, well-known

31**pseudo-?rst order and pseudo-second order** equations **were used to** represent **the** kinetic **data. Pseudo- ?rst order**

gave better performance than pseudo-second order model. The Thomas model also successfully represents the dynamic adsorption data. Acknowledgements The authors would like to acknowledge ?nancial support for this work provided by Directorate of Higher Education, Indo- nesia Ministry of Research, Technology, and Higher Education through Competency Research Grant with project number 003/SP2H/P/K7/KM/2015. References 1 Canadian Environmental Protection Act, Ammonia in the Aquatic Environment, 1999. 2 A. Arslan and S. Veli, J. Taiwan Inst. Chem. Eng., 2012, 43, 393–398. 3 M. Rozic, S. Cerjan-Stefanovic, S. Kurajica, V. Vancina and E. Hodzic, Water Res., 2000, 34, 3675–3681. 4 R. Malekian, J. Abedi-Koupai, S. S. Eslamian, S. F. Mousavi, K. C. Abbaspour and M. Afyuni, Appl. Clay Sci., 2011, 51, 323–329. 5 K. Saltali, A. Sari and M. Aydin, J. Hazard. Mater., 2007, 141, 258–263. 6 H. Huo, H. Lin, Y. Dong, H. Cheng, H. Wang and L. Cao, J. Hazard. Mater., 2012, 229–230, 292–297. 7 L. Zhou and C. E. Boyd, Aquaculture, 2014, 432, 252–257. 8 A. Alshameri, A. Ibrahim, A. M. Assabri, X. Lei, H. Wang and C. Yan, Powder Technol., 2014, 258, 20–31. 9 G. Moussavi, S. Talebi, M. Farrokhi and R. M. Sabouti, Chem. Eng. J., 2011, 171, 1159–1169. 10 M. Li, X. Zhu, F. Zhu, G. Ren, G. Cao and L. Song, Desalination, 2011, 271, 295–300. 11 Y. P. Zhao, T. Y. Gao, S. Y. Jiang and D. W. Cao, J. Environ. Sci., 2004, 16, 1001–1004. 12 Y. Watanabe, H. Yamada, J. Tanaka and Y. Moriyoshi, J. Chem. Technol. Biotechnol., 2005, 80, 376–380. 13 H. B. Wang, Y. M. Bao, J. Zhang, H. Y. Chen, L. Z. Ma and M. Yang, Energy Procedia, 2011, 11, 4236–4241. 14 R. Leyva-Ramos, J. E. Monsivais-Rocha, A. Aragon-Pina, M. S. Berber-Mendoza, R. M. Guerrero-Coronado, P. Alonso-Davila and J. Mendoza-Barron, J. Environ. Manage., 2010, 91, 2662–2668. 15 Z. Liang and J. R. Ni, J. Hazard. Mater., 2009, 166, 52–60. 16 L. Lei, X. J. Li and X. W. Zhang, Sep. Purif. Technol., 2008, 58, 359–366. 17 APHA, Water Environment Federation, Washington DC, USA, 1998. 18 I. K. Chandra, Y.-H. Ju, A. Ayucitra and S. Ismadji, Int. J. Environ. Sci. Technol., 2013, 10, 359–370. 19 Yesi, F. P. Sisnandy, Y.-H. Ju, F. E. Soetaredjo and S. Ismadji, Adsorpt. Sci. Technol., 2010, 28, 846–868. 20 A. C. Suwandi, N. Indraswati and S. Ismadji, Desalin. Water Treat., 2012, 41, 342–355. 21 D. D. Do, Adsorption Analysis: Equilibria and Kinetics, Imperial College Press, London, UK, 1998. 22 M. Zhang, H. Zhang, D. Xu, L. Han, D. Niu, B. Tian, J. Zhang, L. Zhang and W. Wu, Desalination, 2011, 271, 111–121. 23 V. K. Jha and S. Hayashi, J. Hazard. Mater., 2009, 169, 29–35. 24 S. Ismadji and S. K. Bhatia, Langmuir, 2001, 17, 1488–1498. 25 S. Lagergren, K. Sven. Vetenskapsakad. Handl., 1898, 24, 1–39. 26 Y. C. Sharma, G. S. Gupta, G. Prasad and D. C. Rupainwar, Water, Air, Soil Pollut., 1990, 49, 69–79. 27 M. Essandoh, B. Kunwar, C. U. Pittman Jr, D. Mohan and T. Misna, Chem. Eng. J., 2015, 265, 219–227. 28 C. Gan, Y. Liu, X. Tan, S. Wang, G. Zeng, B. Zheng, T. Li, Z. Jiang and W. Liu, RSC Adv., 2015, 5, 35107–35115. 29 Y. Zhao, B. Zhang, X. Zhang, J. Wang, J. Liu and R. Chen, J. Hazard. Mater., 2010, 178, 658–664. 30 H. Zheng, L. Han, H. Ma, Y. Zheng, H. Zhang, D. Liu and S. Liang, J. Hazard. Mater., 2008, 158, 577–584.

4**RSC Advances Paper Paper RSC Advances RSC Advances Paper Paper RSC Advances RSC Advances Paper Paper RSC Advances RSC Advances Paper Paper RSC Advances RSC Advances Paper** Paper RSC Advances **This journal is © The Royal Society of Chemistry 2015 RSC Adv., 2015, 5,**

83689–83699 | 83689 83690 |

1**RSC Adv., 2015, 5,** 83689–83699 **This journal is © The Royal Society of Chemistry 2015 This journal is © The Royal Society of Chemistry 2015 RSC Adv., 2015, 5,**

83689–83699 | 83691 83692 |

1**RSC Adv., 2015, 5,** 83689–83699 **This journal is © The Royal Society of Chemistry 2015 This journal is © The Royal Society of Chemistry 2015 RSC Adv., 2015, 5,**

83689–83699 | 83693 83694 |

1**RSC Adv., 2015, 5,** 83689–83699 **This journal is © The Royal Society of Chemistry 2015 This journal is © The Royal Society of Chemistry 2015 RSC Adv., 2015, 5,**

83689–83699 | 83695 83696 |

1**RSC Adv., 2015, 5,** 83689–83699 **This journal is © The Royal Society of Chemistry 2015 This journal is © The Royal Society of Chemistry 2015 RSC Adv., 2015, 5,**

83689–83699 | 83697 83698 | RSC Adv., 2015, 5, 83689–83699 This journal is © The Royal Society of Chemistry 2015 This journal is © The Royal Society of Chemistry 2015 RSC Adv., 2015, 5, 83689–83699 | 83699