ADSORPTION OF TOLUENE FROM AQUEOUS SOLUTION ONTO DODECYL DIMETHYL-3-AMMONIO-1-PROPANE SULFONATE (DPS) SURFACTANT MODIFIED NATURAL ZEOLITE

[1]MARVITA, OLIVIA FEBRI, [2]SUTARNO, [3]SUYANTA

[1,2,3]Department of Chemistry, Universitas Gadjah Mada, Special Region of Yogyakarta, Indonesia
E-mail: [1]olivia.f@mail.ugm.ac.id, [2]sutarno@ugm.ac.id, [3]suyanta@ugm.ac.id

Abstract - This study focuses on increasing the ability of natural zeolite adsorption by modifying it with DPS (Dodecyl Dimethyl-3-Ammonio-1-Propane Sulfonate) surfactants for adsorption of toluene as nonpolar organic compounds from aqueous solution. This study started with natural zeolite (ZR) from Klaten-Central Java of Indonesia being activated using acid (HCl) and then zeolite modified with two times DPS surfactant (ZD). The success of ZR activation and modification of natural zeolite is characterized by infrared spectroscopy, x-ray diffraction, surface area and pore analysis and cation exchange capacity. Adsorption of toluene ion determine using UV-Vis spectrophotometer. This study adsorption begins with variation of several pH and times of toluene adsorption on ZD. Then, study of toluene concentration variation on ZD and ZR. The results showed that toluene (optimum pH 2) has a higher adsorption capacity in ZD than ZR because DPS surfactant contain nonpolar sites from its carbon chain that can interact better with nonpolar toluene, not like ZR. The adsorption of toluene in ZD following the Freundlich isotherm because correlation constant (R^2) is larger and close to 1 than Langmuir models. This Freundlich isotherm occurs cooperativelydue to its 1/n value > 1. The adsorption strength (K_f) of ZD of toluene is 1.88×10^{-32} mg/g. Thus, toluene adsorption is better on adsorbentsZD> ZR.

Index Terms - Zeolite, Adsorption, Surfactant, Toluene, Isotherm, Kinetic.

I. INTRODUCTION

Wastewater contamination in aquatic environments is particularly worrying because of the toxic effects on ecosystems, especially for humans. Toluene is a benzene derived compound in which one of its hydrogen atoms is substituted methyl and become an important solvent in the chemical industry [1]. In other side, toluene is also dangerous because if it get inside our body in excess amount, it can cause neurotoxic, it has ability to soluble in fat (lipophilic), so it can also penetrate one of the tissues in the nervous system, causing disturbances in the central nervous system and peripheral nerves [2].

Toluene are some from waste water that require remediation in an appropriate way. Remediation using chemical treatments proved to be very much done because of its cheaper, easier, and efficient techniques[3]. One type of chemical remediation is adsorption. Adsorption is the attachment of molecules to a surface; the substance that adsorbs is the adsorbate and the underlying material is the adsorbent or substrate[4]. Zeolite is a highly porous aluminosilicate mineral and widely used as an adsorbent. It has negative charge on its surface because substitution of Si atoms by Al atoms in some of the $[SiO_4]^{4-}$tetrahedron which is converted into the tetrahedron $[AlO_4]^{5-}$ interconnected with other $[SiO_4]^{4-}$that connected in one oxygen atom used together[3]. Because this negative charge zeolite often used as cation waste, like heavy metal [5][6][7].

In order to increase the affinity of zeolite toward nonpolar compounds or anion waste, several researchers have developed an amphiphilic adsorbent by adsorption the cationic surfactants like hexadecyltrimethylammonium (HDTMA) [8] cetyltrimethylammoniumbromide (CTAB) [9] and tetraethylammoniumand tetramethylammonium[10]onto its external surface. Unfortunately, the use of zwitterion surfactants is still small and still need to be developed in order to know its effect in adsorption.

This present work aims to utilize the natural zeolite of Indonesia from Central Java, to be modified by using one of zwitterion surfactant DPS (Dodecyl Dimethyl-3-Ammonio-1-Propane Sulfonate)become DPS surfactant modified zeolite having adsorption capacity of toluene nonpolar compound from aqueous solution

II. DETAILS EXPERIMENTAL

2.1 Materials and Procedures

A natural zeolite sample was taken from Klaten, Central Java of Indonesia. After being crushed and then pass through a 200-mesh sieve, the sample was soaked with distilled water for 24 hours at room temperature. Then afterwards filtered using regular filter paper. After filtration, the zeolite is heated using an oven at 120°C for 24 hours, this sample called ZR. Next, 50 g of ZR was activated by stirring 100 mL solution of HCl 37% (1:1) for 30 minute, and then ZR being filtration again and washed with distilled water until the sample was neutral, and heated at 80°C.

After activated, 20 g of ZR was modified with DPS, this first modification hasa correlation amount of DPS with the one of Cation Exchange Capacity (CEC) value of 102,56 meq/100 g from ZR after activated. The calculation of DPSamount added to ZR is:

20 g of ZR x 1.0256 meq/g = 0.020512 mol, (1)
0.020512 mol x 335.55 g/mol = 6.883 g DPS(2)

20 gr of ZR was modified stirring for 24 hours with 100 mL of DPS solution in room temperature. After this, the solution being filter and washwith distilled water, and then heated at 80°C. Next,this first modification sample was analyzing its CEC, the value is 97,22 meq/100 g then with the same calculation above the 15 g sample first modification was modified again with DPS (4,893 g) and same method as before. This second modified sample was called ZD.

2.2 Characterization of Material

The crystalline phase(s) inthe materials were identified by powder X-ray diffraction (XRD) analysis instrument (Miniflex,Rigaku) with Cu Ka filtered radiation (45 kV, 200 mA). The elemental compositions of the materials were determined by X-ray fluorescence (XRF) (Minipal 4, PANalytical Company). The Fourier Transform Infrared (FTIR) spectra were recorded with an FT-IR spectrophotometer (SHIMADZU IR) using the KBr method. The specific surface area was determined from micrometrics by fitting the amount of N_2 adsorbed at -196.15^{O}C for the BET equation after preliminary heating at 200°C.The amount of residual toluene after being adsorb by ZR and ZD was measured by UV-Vis Spectrophotometer in the wavelength 261.1 nm.(SHIMADZU UV-1700 (E) 230VCE).

2.3 Batch Adsorption Studies

ZD was used to adsorb aqueous solution of toluene in batch method. Adsorption was done with 0,1 g of ZD for each variable with 20 mL of adsorbate. This experimental adsorption is started from variation of pH 1, 2, 4, 5, 7, and 9 for 200 mg/L of toluene solution.From this variation we will get the optimum pH. Continue with variation of time that done with the optimum pH. The times begin from 1, 5, 15, 30, 60, 90, 120, and 150 minute in order to get the optimum time too. This variation of time will be fitted to pseudo-first (Eq.3) and second order (Eq.4) rate kinetic equation. Where k_1 (/min) and k_2 (g/mg min) are the rate constants of the pseudo-first-order and pseudo-second-order rate equations, respectively.

$$\log(q_t - q_e) = \log q_e - k_1 \frac{t}{2{,}303} \qquad (3)$$

$$\frac{t}{q_t} = \frac{1}{(k_2 q_e^2)} + \frac{t}{q_e} \qquad (4)$$

Optimum pH and time were using in variation of concentration toluene solution in ZR and ZD adsorbent. Concentration using for toluene solution is 30, 50, 100, 150, and 200 mg/L. This variation of concentration next will be fitted to equation of Langmuir and Freundlich Adsorption Isotherm.The maximum adsorption capacity was calculated byfitting the experimental plots with the Langmuir adsorptionisotherm model in the form of Eq. (5):

$$\frac{C_e}{q_e} = \frac{1}{Q_{max} K_L} + \frac{C_e}{Q_{max}} \qquad (5)$$

where q_e is the amount of adsorbate adsorbed onto the sorbent, mg/g;C_e is the adsorbate concentration at equilibrium, mg/L; Q_{max} ismaximum adsorption capacity, mg/g; and K_L (L/mg) is the Langmuirequation constant. The experimental data were also fitted using theFreundlich adsorption equation in the following form:

$$\log q_e = \log K_f - \frac{1}{n} \log C_e \qquad (6)$$

where q_e (mg/g) and Ce (mg/L) have the same meanings with thoseof Eq. (5); K_f and n are the Freundlich equation constants.

III. RESULTS AND DISCUSSION

3.1 Characterization of ZR and ZD

The mineral contents of ZR and ZD samples is depicted in Fig.1. It shows that ZR is kinds of mordenite $(Na_2,Ca,K_2)_4(Al_8Si_{40})O_{96}.28H_2O$ JCPDS code 6-239 but mixed with quartz also, JCPDS code 5-0490. The sharp and high pattern of XRD shows that this mineral of zeolite has high crystallinity. ZR has a sharper and also higher pattern than ZD that means some of Aluminum oxides has release from the framework of zeolite due to acid activation process. It confirms also from the contain of quartz (SiO_2) is increase in ZD than in ZR, and also from the contain of element Al in XRF analyzer that increase (Table.1).

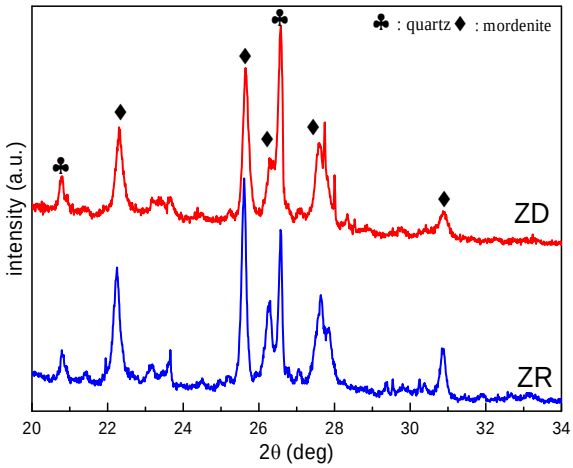

Fig.1: XRD pattern of ZR and ZD

FTIR is used for detect the functional groups from zeolite and surfactant that attached in the zeolite and FTIRis very useful to probe the structure and organization of surfactantmolecules in the interlayer space of layered silicates[11]. In the Fig.2 we see there are four typicalabsorption bands for zeolite that appear on the FTIR spectrum at the wavenumber

3700-3400; 1640-1630; 1250-950; and 800-500 cm^{-1}. Overlap vibration of symmetry and asymmetry of the -OH group with hydroxyl groups present in the zeolite framework is shown in the wave number 3700-3400 cm^{-1}[12][13]. This vibration is followed by a bent vibration of H-O-H that exhibits zeolite water in 1640-1630 cm^{-1}[14]. 1250-950 cm^{-1}shows the asymmetric stretching vibration of the TO4 (T=Al/Si) O-Si-O & O-Al-O internal zeolite[15], whereas on the external frame of TO4 O-Si-O & O-Al-O is shown at 800-500 cm^{-1}. In addition to the four absorption bands above, there are 3 other bands that characterize the presence of surfactants in ZD. Bands at 2900 and 2800 cm^{-1} show vibrations asymmetry and symmetry of C-H on surfactant CH_2 chain[11], while 1400 wave number indicates scissoring vibration CH_2[16]. The narrow and small bands in 2924 and 2854 cm^{-1}indicate that the surfactant already modified in ZR in thegauche conformation not all-trans conformation,due to small amount of adsorbed surfactant[11].

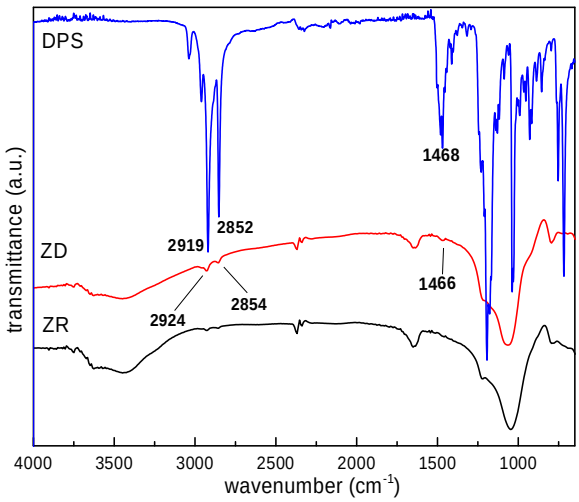

Fig.2: FTIR spectra of ZR, ZD and DPS surfactant

The exact value that proves the DPS already modified in the ZR is the contain of Sulfur as one of element in structure of DPS (Table.1). This value shows that from ZR sample, there no sulfur detects in the sample, but after modification the sulfur detects 1% from the chemical analyzer. Beside the contain of sulfur, we may know the mole Si/Al ratio of ZR and ZD from this result. Si/Al ratio of ZR 5.891 and ZD 9.539. The increase of Si/Al ratio will inform us that dealumination has happened when activation or modification, and increase the acidity of ZD and probability capacity of its adsorption.

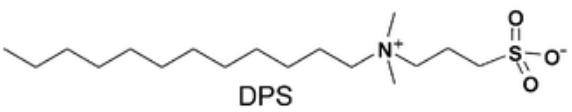

Fig.3: Structure of DPS surfactant

BET method was using to know the specific surface area of the sample ZR and ZD. From this method(Table.2) we see surface area of the ZD decrease from ZR. This decrease is probably due to the presence of DPS that covers the surface of the ZD sample. This decrease in surface area is also followed by decrease of monolayer volume and total volume of pores. As well as the average size of pore diameter increased 3 times from ZR in ZD.

Table.1 Chemical composition of ZR and ZD

Element	Mass Unit (%)	
	ZR	ZD
Al	9.10	7.1
Si	55.8	70.5
S	-	1.0
K	3.74	4.21
Ca	13.1	4.33
Ti	1.26	1.44
V	0.055	0.05
Cr	0.06	-
Mn	0.26	-
Fe	15.7	5.86
Cu	0.11	0.081
Zn	0.03	-
Sr	0.40	-
Eu	0.20	-
Re	0.20	-

This increase in pore indicates that the observed pore is a interstitial pore, i.e. pores from the combined of bulk material that joins one and the other in the sample. We can imagine like a pile of oranges fruits stacked forming a pyramid, where the holes formed in the orangesslit are interstitial pores. It also confirms that the coating of zeolites is getting bigger on ZD. The larger the surfactant layer formed causes the interstitial pores even greater.

Table.2 Results of N_2 adsorption analysis with BET method

Sample	S_{BET}	$V_{Total\ pore}$	$d_{pore\ mean}$	$V_{monolayer}$
	$[m^2/g]$	$[cm^3/g]$	[nm]	$[cm^3/g]$
ZR	27.134	0.089	13.084	6.234
ZD	9.569	0.075	31.324	2.199

3.2 Adsorption of Toluene in ZD and ZR

This pH variation is necessary in the early stages of adsorption, since the adsorbent used has a functional group which is susceptible to a particular pH range. In addition, pH variation is expected to provide information about the adsorption of toluene in ZD under different environmental conditions, whether acidic, alkaline, or neutral. From the pH variation, it was found that the optimum pH of toluene adsorption of the ZD adsorbent was at pH 2. From the data it was found that, toluene adsorption showed lower data

at higher pH, and tended to greater adsorption at lower pH (Fig.4). The adsorption of toluene at optimum pH 2 is supported by Dastjerdi et al. (2017) which also adsorbs toluene in the form of a aqueous solution using Manganese Oxide [17].From this optimum pH we know, this kind of adsorbent is good adsorb in acidic environmental condition.

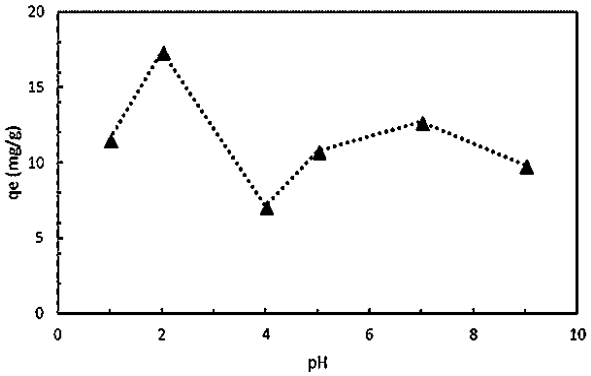

Fig.4: Toluene adsorption in variation of pH

After obtaining optimum pH of toluene adsorption at pH 2, a variation of time on ZD adsorbent was conducted to determine the equilibriumtime of toluene adsorption-desorption at ZD which is called optimum time of toluene adsorption onto ZD. From the results of this adsorption, it is found that the optimum time of toluene adsorption is in the minute of 90 (Fig.5). From fitting the results to kinetics assessment, it is found that the pseudo-second-order rate kinetic equation is an appropriate adsorption model for toluene in ZD adsorbent, because the value of R^2 is close to 1. Conversely on the pseudo-first-order kinetic equation the value of R^2 represents small from one. From Table.3it was found that k_2 of toluene adsorption in ZD according to pseudo-second-order kinetics was 0.0237 g/mg min with adsorption capacity when the equilibrium reached 19.305 mg/g which was almost equal to the experimental equilibrium adsorption capacity with value 19.02 mg/g.

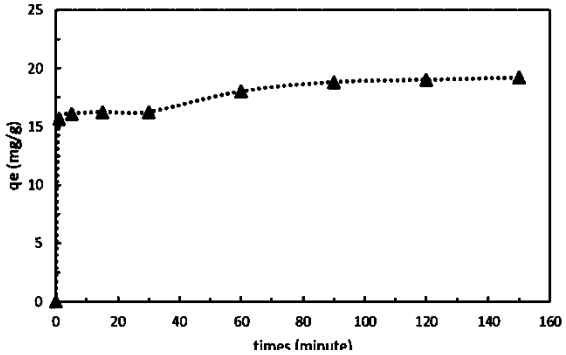

Fig.5: Toluene adsorption in variation of time

After get the optimum pH and time, we did some adsorption with various concentrations of toluene with ZD and ZR adsorbent.It was found that the ability of ZD to adsorb toluene reached almost 16 mg/g at the highest concentration of toluene given was 200 mg/g.

Table.3 Constants and regression coefficient for the kinetic models

Pseudo-first-order rate kinetics	k_1 (/min)	0.01312
	q_e (mg/g)	4.4187
	R^2	0.5677
Pseudo-second-order rate kinetics	k_2 (g/mgmin)	0.0237
	q_e(mg/g)	19.305
	R^2	0.9988

When compared with ZR, the ZD adsorption ability reached 4 times that of ZR which is only capable of adsorbing about 4 mg/g of toluene from 200 mg/g of toluene given. Although ZR is capable of adsorbing toluene as well even it has no nonpolar sites, it is expected only because ZR has sufficient pores for toluene to be absorbed and interact weakly on the internal surface of ZR. ZD has surfactants on the surface so that, interactions between toluene and nonpolar carbon chain surfactants can make toluene uptake greater than ZR.

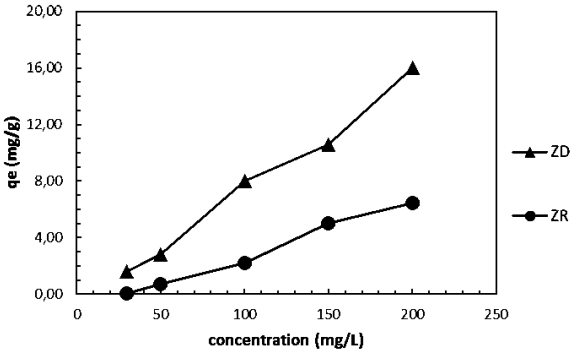

Fig.6: Toluene adsorption in variation of concentration

This variation of concentration data then fitted to the Isotherm equation. In ZD, large R^2has found in Freundlich Isotherm, indicates that Freundlich isotherm model is more suitable to describe the toluene adsorption process in ZD. ZR adsorbent tends to follow Freundlich isotherm model too because its R^2 value tends to be higher in Freundlich isotherms than on Langmuir isotherms, even the value is still far to one (Table.4).

From this Freundlich isotherm it is known that the ability to adsorb toluene, especially in ZD is generated due to the heterogeneous adsorbent, and the adsorption process that forms many layers on the surface of ZD. In Table.4, the value of $K_f$of Freundlich equation is very low, this low K_f means the lower adsorption strength. However, low K_f may be advantageous for toluene desorption process which has been absorbed, so the adsorbent that has been used and saturated with toluene can be reused. While for the value 1/n> 1, means adsorption occurs cooperatively, whereby adsorption occurs in multiple layers, with the first layer only having interaction

between the adsorbate and the adsorbent, while the second layer presents both adsorbate-adsorbent and adsorbate- adsorbate interactions[18].

Table.4 Constants and regression coefficient for Isotherm models

Adsorbent	Langmuir Isotherm			Freundlich Isotherm		
	q_{max}(mg/g)	K_L (L/mg)	R^2	K_f (mg/g)	1/n	R^2
ZD	-2.229	-0.025	0.9238	$2.95x10^{-9}$	3.1344	0.9946
ZR	-0.248	-0.009	0.4225	$1.36x10^{-13}$	3.0928	0.8574

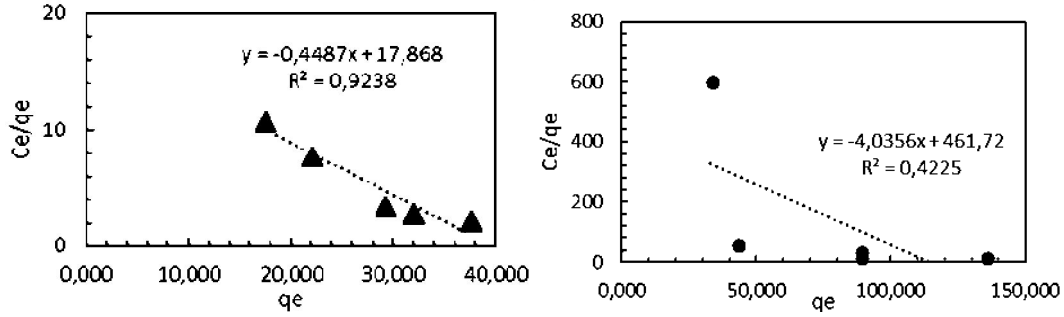

Fig7: Graph of Langmuir isotherm model for (▲=ZD) and (●=ZR) in toluene adsorption

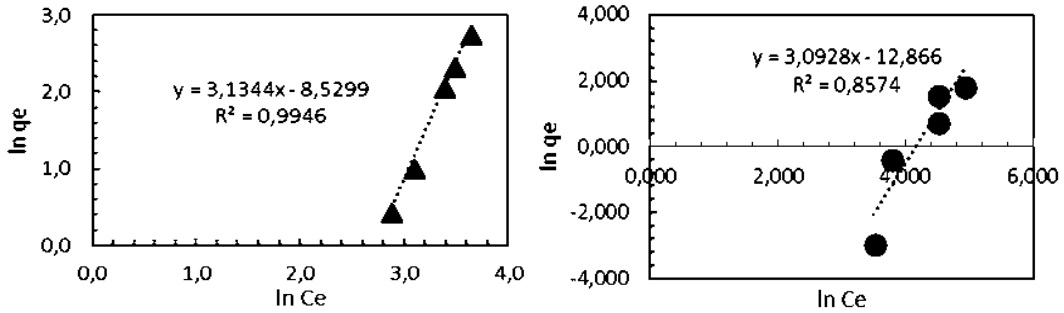

Fig8: Graph of Freundlichisotherm model for (▲=ZD) and (●=ZR) in toluene adsorption

CONCLUSION

The study gives the toluene adsorption ability from aqueous solution and adsorption processof ZD adsorbent. DPS was using as zwitterion surfactant to modified the surface of natural zeolite to make the zeolite more amphiphilic because it has nonpolar carbon chain to adsorb toluene as nonpolar compound too. This study adsorption begins with analyze the effect of pH, time and then variation of concentration. The sorption kinetics followsthe pseudo-second-order rate equation and the calculated qe valueis in good agreementwith the experiments.The adsorption isothermsfit the Freundlich model better, where adsorption of toluene happened cooperatively due to value of 1/n.Besides that, when the adsorption happened its predict that multilayer has formed with lower energy adsorption, so if we do more development in this research this adsorbent will be good in desorption to reuse again.

ACKNOWLEDGMENTS

The authors express gratitude to the Universitas Gadjah Mada (UGM) Yogyakarta, Indonesia, UGM Integrated Research and Testing Laboratory (LPPT), and Indonesian Education Fund Management Institution (LPDP) which has provided overall funding so that this research can be carried out.

REFERENCES

[1] H. Hindarso, S. Ismadji, F. Wicaksana, Mudjijati and N. Indraswati, "Adsorption of Benzene and Toluene from Aqueous Solution onto Granular Activated Carbon," J. Chem. & Eng. Vol. 46, No. 4,, pp. 788-791, 2001.

[2] Ferdianto, Studi Deteksi Toksisitas Pajanan Toluena pada Saraf Optik Tikus Wistar Jantan, Jakarta: Universitas Indonesia, 2013.

[3] D. Singh, Fly Ash Zeolite : Innovation, Aplication and Directions, Springer, 2016.

[4] P. Atkins and J. Paula, Physical Chemistry, Ninth Edition, Great Britain: Oxford University Press, 2010.

[5] J. Castañeda, E. Martha and M. Dora, "Use of Surfactant-Modified Zeolites and Clays for the Removal of Heavy Metals from Water.," Water, p. 235, 2017.

[6] Gaffer, A. Kahlawy and D. Aman, "Magnetic zeolite-natural polymer composite for adsorption of chromium (VI)," Egypt. J. Petroleum Volume 26, Issue 4,, pp. 995-999, December 2017.

[7] H. Merrikhpour and M. Jalali, "Comparative and competitive adsorption of cadmium, copper, nickel, and lead ions by Iranian natural zeolite," Clean Tech. & Environ. Policy, p. 303–316, 2013.

[8] H. Tran, P. Viet and H. Chao, "Surfactant modified zeolite as amphiphilic and dual-electronic adsorbent for removal of cationic and oxyanionic metal ions and organic compounds," Ecotoxicology and Environmental Safety , vol. 147, pp. 55-63, 2018.

[9] L. Zhu, B. Chen and X. Shen, "Sorption of phenol, p-nitrophenol, and aniline to dual cation organobentonite from water," Environ. Sci. Technol., Vols. 34 (3), , p. 468–475, 2000.

[10] M. Park, S. Ahn, C. Nicholas, G. Lewis and S. Hong, "Charge density mismatch synthesis of zeolite beta in the presence of tetraethylammonium, tetramethylammonium and sodium ions: influence of tetraethylammonium decomposition," Microporous Mesoporous Mater., vol. 240, pp. 159-168, 2017.

[11] Q. Xie, J. Xie, Z. Wang, D. Wu, Z. Zhang and H. Kong, "Adsorption of organic pollutants by surfactant modified zeolite as controlled by surfactant chain length," Microporous and Mesoporous Materials 179, p. 144–150, 2013.

[12] J. Groen, T. Sano, J. Moulijn and J. Pérez-Ramírez, "Alkaline-mediated mesoporous mordenite zeolites for acid-catalyzed conversions," J. of Catalysis, pp. 251, 21-27., 2007.

[13] W. Mozgawa, M. Krol and K. Barczyk, "FT-IR studies of zeolites from different structural groups.," Sci. Tech, vol. 65, pp. 667-674., 2011.

[14] W. Song, T. Shi, D. Yang, J. Ye, Y. Zhou and Y. Feng, "Pretreatment effects on the sorption of Cr(VI) onto surfactant modified zeolite: Mechanism Analysis," J. of Environ. Management 162, pp. 96-101, 2015.

[15] F. Pechar and D. Rykl, "Infrared spectra of natural zeolites of the stilbite group," Chem. of Materials, pp. 2, 189-202, 1980.

[16] R. Viana, A. Silva and A. Pimentel, "Infrared Spectroscopy of Anionic, Cationic, and Zwitterionic Surfactants," Adv. in Phy. Chem., 2012.

[17] M. Dastjerdi, G. Habibagahi, A. Ghahramani and K. Ayoub, "Removal of dissolved toluene in underground water with nanowires of manganese oxide," Adsorp. Sci & Tech. Vol. 36(1–2), pp. 393-407, 2017.

[18] K. Foo and B. Hameed, "Insights into the modeling of adsorption isotherm systems," Chem. Eng. J. 156, vol. 156, pp. 2-10, 2010.

[19] M. Bouraie and A. Masoud, "Adsorption of phosphate ions from aqueous solution by modified bentonite with magnesium hydroxide Mg(OH)2," App. Clay Sci. 140, p. 157–164, 2017.

[20] X. Huang, G. Foster, R. Honeychuck and J. Schreifels, "The Maximum of Phosphate Adsorption at pH 4.0: Why It Appears on Aluminum Oxides but Not on Iron Oxides," Langmuir , vol. 25(8), p. 4450–4461, 2009.

★★★