Adsorption capacity study of ethanol-water mixture for zeolite, activated carbon, and polyvinyl alcohol

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Abstract. Global energy issue is no longer a new topic. The expansion of energy production proven to show significant influence is the fossil fuel modification by blending it with liquid renewable fuel, such as bioethanol. Bioethanol must achieve fuel-grade standard to qualify as gasoline, one of the specification is to have moisture content of 1.0% v/v or less, as regulated by ASTM D4806. This parameter is a challenging one to achieve, because water-ethanol mixture will encounter the azeotrope phenomenon when the mixture undergoes a common distillation process and reach 95.6% v/v of ethanol. One of the dehydration method that use less energy is adsorption. One of the efficiency consideration of bioethanol dehydration with adsorption is its adsorption capacity. Adsorption capacity is influenced by the material of adsorbent, operational temperature and time. The material being tested in this research is poly vinyl alcohol (PVA), zeolite, and activated carbon. This research will analyze the dependency and influence of mixture's initial concentration and operational temperature condition towards the final concentration of ethanol and adsorption capacity utilizing a Langmuir model. The result of this study showed that the activated carbon has the highest parameter capacity, which is twice as much than zeolite and three times larger than PVA. Whereas the result of selectivity study between the three prove that zeolite has better selectivity.

Nomenclature

V_S	initial stock volume of ethanol	K_L	Langmuir constant
C_S	initial stock concentration of ethanol	q_e	quantity of adsorbate in adsorbent when reaching an equlibria state
V_B	blended volume of ethanol	C_e	concentrationwhen reaching an equlibria state
C_B	concentration of ethanol after blending	D_{water}	dipole moment or polarity of water
C_0	initial concentration	D_{EtOH}	dipole moment or polarity of ethanol
V_0	initial sample volume	ΔV_t	adsorbed volume at a given time
t	time variables in minutes	V_{TP}	total pore volume in sample
m	mass of adsorbent	V_{pore}	pore volume in every gram of adsorbent
V_t	volume of sample after a particular time	ε_{water}	relative permittivity of water
C_t	concentrationafter a particular time	ε_{EtOH}	relative permittivity of ethanol
T	temperature	S_{BET}	BET surface area
q_m	maximum adsorption capacity	AD	adsorption degree

1. Introductions

The use of bioethanol (CH_3CH_2OH) as a substitute for fossil energy is quite promising [1]. The natural and renewable sources of it are relatively abundant yet the production process is rather simple. The local prospect of its market in Indonesia is especially supported by the blueprint of national energy policy (Presidential regulation No 5 of 2006) in which stated that the percentage of biofuel role in national energy mix must reach 5% by 2025 [2].

The ethanol that may alternate the use of fossil fuel must fulfill a standard set in ASTM D 4806-16a. Based on the standard, fuel grade ethanol is ethanol with minimum content of water, 1.0% v/v or 1.26 m/m (measured at the temperature of 60ºF) at most [3]. To fulfill this requirement, the distillation procedure is not sufficient to separate the water from ethanol because when the water-ethanol mixture reach 3.37:95.63 (in % b/b, or 2.80:97.20 in % v/v) an azeotrope phenomenon occurred. Thus, the vapor of this composition has the same proportions of constituents as the unboiled mixture, and hence the composition cannot be altered by simple distillation anymore [4]. Therefore, the bioethanol produced by fermentation must undergo extra steps after being distilled from the beer product in order to dehydrate the water content.

The dehydration of water-ethanol azeotrope mixture can be done by several options, such as pervaporation, extraction, distillation, adsorption, or the combination of the available options, but the high-energy cost associated to dehydration is known as a major challenge [1].

A review by Frolkova and Raeva (2009) stated that adsorption by molecular sieves are most efficient for water removal from solutions with low water content, and if the process is carried in vapor phase the adsorption would excludes the wetting of molecular sieves and reduce heat and energy consumption required in desorption drying of the sieves. Despite its advantages, this method is not usually employed in large-scale ethanol dehydration [1]. The present day commercial-scale process utilized for water dehydration by adsorption is aadsorber-desorber complex of Pressure Swing Adsorption (PSA). The pressure swing adsorption (PSA) process is attractive for the final separation since it requires little energy input and is capable of producing a very pure product [5]. The adsorbent employed in PSA is currently being researched to determine which adsorbent possess the largest capacity and best kinetic properties to support the dehydration of water from water-ethanol solutions.

Various kind of zeolite and activated carbon are investigated. The recent research objectives vary from the raw material, activation factor, throughout the kinetics of various zeolite and activated carbon. Zeolite 3A is proven to be one of the best zeolite to be applied in water adsorption process, because the size of its sieve (3 nm) is only slightly bigger than average water molecule (0.28 nm), and smaller than the size of ethanol molecule (0.4 nm) [6].

Carbon is another efficient water adsorbent. It could dehydrate water–ethanol vapor mixtures containing 1.6–50.9% water. Carrying out the process in an adiabatic carbon adsorber demonstrated that the adsorbent is stable over 85 adsorption–desorption cycles using hot air or nitrogen (80–120°C) [1].

PVA, a hydrophilic polymer, is known to have irregular hydroxyl groups which may easily bonded with another functional group. It is non-toxic, non-carcinogenic, and known to be able to adsorb water in high quantity (up to 12 times its own mass). PVA is an uncommon water adsorbent for water removal from water-ethanol system, but its potential is promising enough to be inspected further due to the high number of hydroxyl groups content [7].

There has been a growing interest for utilizing adsorption in the means of ethanol dehydration, and the need to compare the available and/or new adsorbent arise. The effects of adsorption capacity of adsorbent towards the adsorption process is important, because its influence in the efficiency of the process is clear: the smallest required amount for an adsorption process with the highest capacity will minimize the energy requirement thus increase the economic and time efficiency. The selectivity of adsorbent must be considered too due to the adsorption process may not only take a target adsorbate from the mixture, and thus in the case of water-ethanol mixture dehydration, adsorbent must have adsorbed water rather than ethanol. This research aims to compare the capacity of PVA, activated

carbon, and zeolite as water adsorbent for dehydration from ethanol-water system by the adsorption capacity (q_m and K_L) of the Langmuir adsorption isotherm, and then analyze the selectivity of each adsorbent.

2. Materials and method

2.1. Materials

The ethanol (>>95% v/v) was obtained from CV Harum Kimia, while aquadest water was attained from local water which processed by a reverse osmosis (NESCA^{TM} YDO 6800). The stock ethanol was then diluted in the aquadest to provide ethanol with four variations of concentration in addition to the original stock; 88%, 90%, 92%, and 94%. The dilution was done by blending stock ethanol and aquadest together.

There were three kind of adsorbent being tested in this research:80 mesh pellet activated carbon bought from Ajax Chemicals, 40 mesh natural zeolite from Yogyakarta, and 14 mesh fully hydrolyzed polyvinyl alcohol (EMD Millipore Corporation, MW 145,000). Pellet carbon and zeolite was activated using Thermolyne 46200 high temperature furnace in gradually increasing room temperature up to 150ºC and then held for 2 hours. Afterwards, the temperature increased by 10ºC/minutes up to 800ºC and then held for 4 hours. Subsequently, the cooling down process was done in 10ºC/minutes. Both pellet activated carbon and zeolite kept in a desiccator at all times outside experiment usage.

After activation was done to pellet carbon and zeolite, each adsorbent was characterized using Fourier Transform InfraRed (FTIR), Brunauer, Emmett and Teller Surface Area Analysis (BET), Scanning Electron Microscopy with Energy Dispersive X-Ray Analysis (SEM EDX), and Hydroxyl Test (ASTM E222, Test Method B) [8]. Iodine Number Test (ASTM D4607) was also done as a standard measure for liquid phase applications characterization for activated carbon.

FTIR characterizations was recorded by Shimadzu FTIR Spectrophotometers in Research Center for Chemistry LIPI, PUSPIPTEK, Serpong, to determine the functional groups existing in each adsorbent. The BET analysis was done utilizing Micromeritics' TriStar II 3020 in Research Center for Chemistry LIPI, PUSPIPTEK, Serpong, using N_2 as analysis adsorptive in -195.850ºC to characterize the surface and pore structure of adsorbent. SEM EDX 6510 (LA) instrument in Engineering Faculty of Universitas Negeri Jakarta with 20kV accelerating voltage was used to characterize the morphology of the adsorbents.

2.2. Method

The adsorption experiment was done in batch system, utilizing New Brunswick Scientific controlled environment incubator shaker set in 100 rpm. Each of the adsorbent was tested at the temperature of 30ºC.The initial concentration of ethanol (C_0) was varied to the prepared five; 88%, 90%, 92%, 94%, and 95%.

One experiment run is defined for the adsorption process of ten 100ml Schott's Duran bottles inside an incubator with one temperature variation. Each bottle contained an amount of adsorbent, and a volume of one initial concentration variation poured right before the bottles was settled inside the incubator. Every two minutes, one bottle was taken out of the incubator as sample. The volume after particular adsorption contact time is measured. The concentration of ethanol in sample after adsorption contact time is measured Kyoto KEM Densito/Specific Gravity Meter DA-640.

The mass of PVA for each sample is 3.75gr and 25ml of ethanol with a particular C_0. Meanwhile, AC and zeolite experiment prepare 7.5gr of the adsorbent, and 50ml of ethanol with a particular C_0.

2.3. Experimental adsorption capacity calculation

The calculation of adsorption capacity was evaluated with experimental data based on the process mass balance. Applying the assumption that $q_0 = 0$, obtained:

$$q = \frac{(V_0 C_0 - V_t C_t)}{m} \tag{1}$$

From the experimental data, the q_e was also calculated by equation (1), determined for each experiment as the highest q achieved. q_e is defined as the highest amount of adsorbatein the surface an adsorbent for an experiment run, typically achieved when the adsorption process reach the equilibrium state. The concentration of water measured and the q_e was then used in the Langmuir adsorption isotherm to determine the q_m and K_L.The Langmuir isotherm is an adsorption isotherm with a theoretical or rational basis, given by:

$$q_{\mathrm{mod}} = \frac{q_m K_L C_e}{(1 + K_L C_e)} \tag{2}$$

Where q_m and K_L are empirical constant, and considered as Langmuir capacity parameters. After adsorption experiments were carried out to determine which adsorbent gave the highest q_e in solution, the adsorbent with highest selectivity of water-to-ethanol adsorption was determined.

The adsorption selectivity of adsorbents was determined by adsorbed percentage comparison of water to the adsorbed percentage of ethanol, by considering the moment dipole and relative permittivity of each. The adsorbed volume percentage must include a correction factor of adsorbate dielectric constant or relative permittivity. Permittivity is a property of material corresponds to the coulomb force between two point charges in the material. The relative permittivity is the permittivity factor itself which decreased relative to vacuum. ε_{water} is 78.4 and ε_{EtOH} is 26.6[10]. By considering relative permittivity, the selectivity comparison in percentage was transformed into a comparison of molecule adsorbed degree (AD), determined by the equation below:

$$AD_{water} = \frac{\Delta V_{t\,water}}{C_{0\,of\,water} V_0} D_{water} \varepsilon_{water} \tag{3}$$

$$AD_{EtOH} = \frac{\Delta V_{t\,EtOH}}{C_{0\,of\,EtOH} V_0} D_{EtOH} \varepsilon_{EtOH} \tag{4}$$
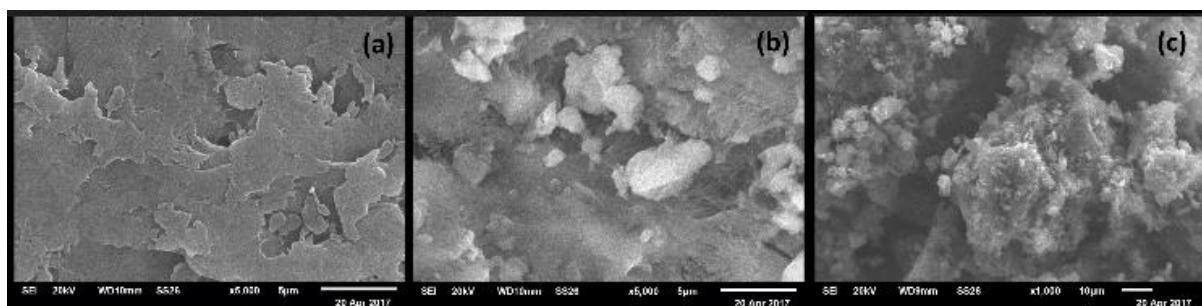
3. Results and discussion

3.1. Characteristics of the adsorbents

3.1.1. Surface morphology and element composition of adsorbent. The summary of SEM EDX element characterization results for each adsorbent is shown below in Table 1, while the SEM EDX visual result can be seen in Figure 1. Figure 1 shows distinctive surface morphology of each adsorbent. The micrographs of zeolite and activated carbon shows visible pores, while the PVA micrographs invisible. SEM image of PVA shows a fairly smooth surface topology, with few skin epidermis-like layers, thus differentiate it from the rough looking surface of zeolite and activated carbon. However, less impurities are shown in PVA image rather than activated carbon and zeolite. The image is consistent to the element reading of SEM EDX in, which confirms the existence of various impurities in activated carbon and zeolite. The element reading also shows that the ratio of Si:Al in zeolite is 6.4, thus considered hydrophilic.

Table 1. Element reading by SEM EDX result.

AC		Zeolite		PVA	
Element	Mass %	Element	Mass %	Element	Mass %
C,	97.87%	Si,	39.44%	C,	85.78%
Cu,	0.82%	O,	30.91%	O,	10.77%
Ca,	0.40%	Ca,	14.73%	Au,	3.19%
Si,	0.32%	Al,	6.14%	Na,	0.26%
Mg,	0.30%	Au,	3.78%		
S,	0.29%	Cl,	2.78%		
		K,	1.17%		
		Na,	1.05%		

Figure 1. SEM micrographs of (a) PVA (5,000x); (b) Zeolite (5,000x); and (c) Activated carbon (1,000x).

3.1.2. Functional groups of the adsorbents. The FTIR results in table 2 shows that the sample examined in this study contains O-H groups in various forms. The result of this characterization corresponds with what bond the adsorbent might form with the adsorbate. The existence of OH in every adsorbent indicates that all three adsorbents is able to adsorb water, because the oxygen in OH will form a bond with both water and ethanol molecule to form a hydrogen bond. Water molecule interact by means of hydrogen bonding, because their own hydrogen atom is attached to a highly electronegative element and this hydrogen atom able to bound with the electronegative atom of a neighboring molecule, forming a hydrogen bridge. The FTIR characterization results also confirms the essentials functional groups of each adsorbent, such as Si-O and Al-O in zeolite.

The existence of OH groups is then affirmed by the hydroxyl value test, along with the determination of the unbounded hydroxyl group. Hydroxyl value (HV) in analytical chemistry is defined as the number of milligrams of potassium hydroxide (KOH) necessary to neutralize the acetic acid taken up on acetylation of one gram of sample that contains free hydroxyl groups.[4] It measures the content of free hydroxyl groups in the sample in units of the mass of KOH in milligrams equivalent to the hydroxyl content of one gram of the sample.

The HV value measurement of PVA result is 893.23 mg KOH/gr PVA, the highest compared to zeolite (100 mg KOH/gr zeolite) and activated carbon (156.06 mg KOH/gr activated carbon). The comparison between each adsorbent's HV shows that PVA has almost 9 times more free or unsubstituted hydroxyl groups than zeolite, and almost 6 times more than activated carbon. This may indicate that PVA have a better hydrophilic property than those of activated carbon or zeolite.
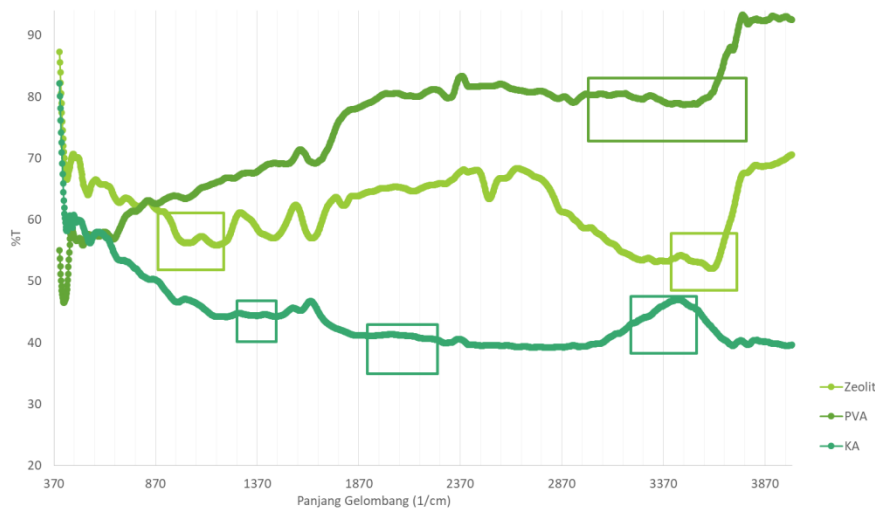
Figure 2. FTIR characterization results summary.

3.1.3. Surface area and pore volume. The BET characterization results in S_{BET} and pore volume of each adsorbent, shown in Table 2. The S_{BET} and pore volume may correspond to the amount of adsorbate that the adsorbent can adsorbs, because the nature of adsorption as an interface reaction in which adsorbate attached to the surface of adsorbent. The BET test show that activated carbon has the largest surface area and pore volume, followed by zeolite and then PVA. This result agrees to the particle diameter of each adsorbent, which is 80 mesh for activated carbon, 40 mesh for zeolite, and 14 mesh for PVA.

Table 2. Characterization result of BET.

Measurement	AC	Zeolite	PVA
S_{BET} (m²/g)	1149.644	12.9068	0.1209
Pore Volume (cm³/gr)	0.33028	0.003708	0.00002

Iodine number is a parameter used to characterize activated carbon performance, which measures activity level, where higher number indicates higher degree of activation. This characterization measures the microspore content of the activated carbon (0 to 20 Å, or up to 2 nm) by adsorption of iodine from solution, and is equivalent to surface area of carbon between 900 m²/g and 1100 m²/g. Iodine number of the carbon utilized in this research is reported as 2209.67 mg/g, higher than the typical range of 600–1450 mg/g.[5] Corresponding to the result of BET analysis, the surface area of the activated carbon results at 1149.64 m²/g is also higher than the typical 1100 m²/g.

3.2. Equilibrium adsorption capacity
The equilibrium adsorption capacity of each experiment is determined in each experiment run by calculating the q_e using equation (1), and then the result is presented below in Table 3.

Table 3. Results of q_e determination for each experiment run.

Temperature (°C)	C_0 of water (% v/v)	q_e (mlof water/gr of adsorbent)		
		AC	Ze	PVA
	12.00	0.1807	0.1519	0.0977
	10.00	0.1799	0.1256	0.0800
30°C	8.00	0.1372	0.0943	0.0651
	6.00	0.0745	0.0743	0.0514
	5.00	0.0669	0.0561	0.0415

The q_e obtained by each adsorbent ranged differently; q_e for activated carbon is ranged 0.0669-0.1807ml/gr, 0.0561-0.1519ml/gr for zeolite, and 0.0415-0.0977ml/gr for PVA. The highest q_e obtained by activated carbon with initial concentration of 12.0%, while the lowest is shown by PVA with initial concentration of 5.0%. A decreasing trend of q_e as the C_0 decreases is shown in all adsorbent variant. The decreasing trend of q_e in all adsorbent is consistent to the theory of mass transfer. When the initial concentration increased, the mass transfer driving force would become larger, hence resulting in higher adsorption capacity.

The adsorption capacity is typically increase as the initial water concentration increase, until it reaches an optimum concentration. If the initial water concentration is above the optimum, the adsorption capacity will either be the same as the adsorption capacity produced by the optimum initial water concentration or lower. The data in table 4 shows that the largest adsorption capacity produced by 12.0%, thus the C_0 12.0% is the more optimum initial water concentration for zeolite, activated carbon, and PVA compared to the lower C_0. An extended research to observe higher concentration than 12.0% may be conducted to see whether if the higher concentration is more optimum.

The value of adsorption capacity in activated carbon is larger than zeolite or PVA. This is a valid prove that activated carbon has the largest adsorption capacity compared to PVA and zeolite. This prove is supported by the pore volume comparison in which activated carbon is indeed have the largest pore volume and surface area, as shown in BET test. Zeolite also have larger pore volume and surface area compared to PVA, while PVA compared to the other two is only better in the hydroxyl value comparison. The surface area and pore volume is correlated to the physisorption adsorption mechanism while the number of free hydroxyl groups is correlated to chemisorption mechanism. This means that the water adsorption is more influenced by physisorption rather than chemisorption.

3.3. Isotherm adsorption model

The adsorption data can be represented well by Langmuir model, with average absolute deviation percentage of 7.72%. A comparison of adsorption data and the Langmuir model is presented in figure 3 for all adsorbent. The Langmuir model parameters are obtained, as presented in Table 4.

The model curve comparison shows that as seen in figure 3and table 5, activated carbon has the highest q_m value, followed by zeolite, and then PVA as the smallest q_m between the three adsorbents. This comparison is identical with the adsorption capacity resulted from the experiment.

Table 4. Adsorption capacity constant obtained from Langmuir model.

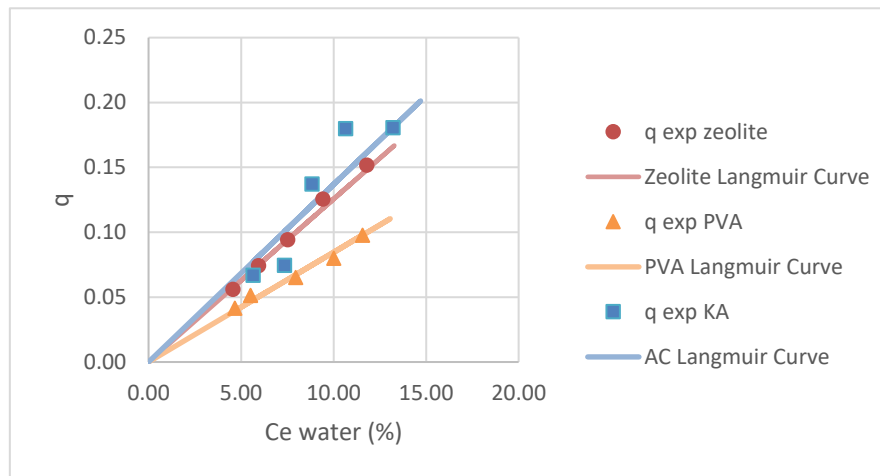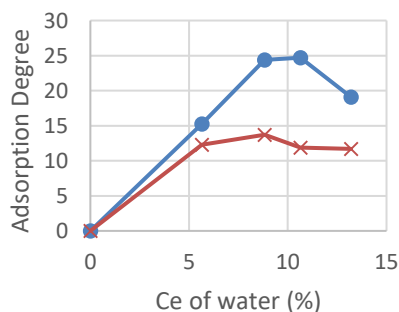| Adsorbent	q_m	K_L	%AAD
PVA	0.0093	9.6878	4.63
Zeolite	0.0138	10.0107	2.23
AC	0.0158	6.5553	16.30
Average			7.72

Figure 3. Comparison of adsorption capacity experimental data and the Langmuir model.
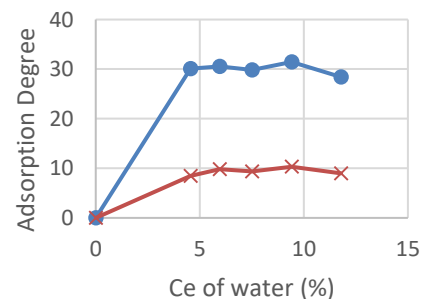
3.4. Adsorbent selectivity

A selectivity evaluation is done to the data obtained in the experiment with operational temperature of 30ºC. The comparison between adsorbed water and ethanol is shown in figure 4 (a) for activated carbon, (b) for zeolite, and (c) for PVA.

The graph of adsorbed percentage for adsorbent with good selectivity for water adsorption ideally shows that the water adsorbed percentage is higher than the ethanol adsorbed percentage. All of the adsorbent researched in this study shows that the water adsorbed degree is higher than the ethanol adsorbed percentage at all times. The good comparison amount of adsorbed water and ethanol is clearly better in zeolite and PVA than activated carbons. Zeolite shows an average of 20 degree higher water adsorption than ethanol and PVA shows 13 degree average difference, while activated carbon only show only 8 degree.
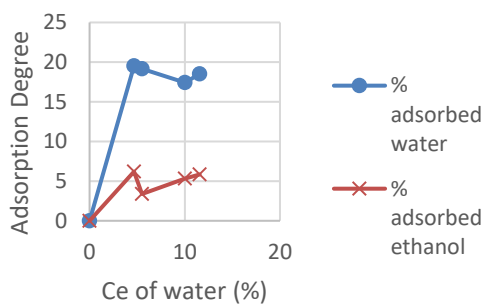
The selectivity of zeolite may be supported by its molecular shieving structure, which is more selective to the larger sized water molecules rather than the smaller ethanol. The pore structure in activated carbon is rather irregular and consist of smaller sized pores. These pore may have bind ethanol molecule first, and leaving less space for water in its surface. Meanwhile, PVA is more selective because the tendency of hydrogen bridge formation from the free hydroxyls found in PVA with water.

(a)

(b)

(c)

Figure 4. Adsorben selectivity graph of (a) activated carbon; (b) zeolite; and (c) PVA.

4. Conclusions

The data of adsorption can be represented by Langmuir model. This research has shown that activated carbon has a higher adsorption capacity compared to PVA and zeolite, which is 20% more than zeolite and 89.21% larger than PVA. Even though activated carbon has the largest capacity, the selectivity of zeolite is better than activated carbon or PVA. PVA potential as adsorbent that mainly apply chemisorption mechanism is proven, but did not cause its adsorption capacity to be larger than activated carbon nor ethanol. The initial concentrations of ethanol also affect the adsorption capacity of adsorbent, as the initial concentration increase, the adsorption capacity will decrease.

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