Sorption and Ion Exchange Behaviour of Natural Zeolite Packing

Chandra Wahyu Purnomo
Department of Chemical Engineering, Engineering Faculty, Universitas Gadjah Mada, Yogyakarta 55281, Indonesia, chandra.purnomo@ugm.ac.id

Bernice Lenora
Department of Chemical Engineering, Engineering Faculty, Universitas Gadjah Mada, Yogyakarta 55281, Indonesia

Wiratni Budhijanto
Department of Chemical Engineering, Engineering Faculty, Universitas Gadjah Mada, Yogyakarta 55281, Indonesia

Hirofumi Hinode
Department of International Development Engineering, Tokyo Institute of Technology, Meguro, Tokyo 152-8550, Japan

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Chandra Wahyu Purnomo[1,2*], Bernice Lenora[1], Wiratni Budhijanto[1,2], and Hirofumi Hinode[3]

1. Department of Chemical Engineering, Engineering Faculty, Universitas Gadjah Mada, Yogyakarta 55281, Indonesia
2. Center for Advanced Materials and Mineral Processing CAMMP, Department of Chemical Engineering, Universitas Gadjah Mada, Yogyakarta 55281, Indonesia
3. Department of International Development Engineering, Tokyo Institute of Technology, Meguro, Tokyo 152-8550, Japan

*e-mail: chandra.purnomo@ugm.ac.id

Abstract

It is well known that zeolite is an efficient metal ions adsorbent. The excess charge of the zeolite building blocks i.e. $(AlO_4)^{-5}$ and $(SiO_4)^{-4}$ creating a negative surface charge that attract metal cations. Beside the surface charge, zeolite also has three dimensional pore structure and reasonably large surface area which also can be used as adsorption sites. Ease of cation uptake make it suitable for many process with adsorption and desorption application. This study was conducted to observe the sorption and ion exchange behaviour of zeolite-betonite rings toward iron and cobalt cations. The results shows that the adsorption patterns follow Langmuir isotherm with the highest uptake capacity is 59,9 mg/g for Fe(II) and 57. 8 mg/g for Co(II).

Abstrak

Perilaku Penyerapan dan Pertukaran Kation Bahan Isian dari Zeolit Alam. Telah banyak diketahui bahwa zeolite adalah material yang baik untuk menyerap ion-ion logam. Kelebihan muatan dari gugus penyusun zeolit yaitu $(AlO4)^{-5}$ dan $(SiO4)^{-4}$ mengakibatkan permukaan zeolite bermuatan negatif yang dapat menarik kation logam. Selain muatan di permukaan, zeolite juga memiliki stuktur pori tiga dimensi dan juga luas permukaan yang cukup besar untuk keperluan adsorpsi. Kemudahan dalam mengambil kation menjadikan zeolit banyak dipakai di berbagai proses yang mengaplikasikan prinsip adsorpsi dan desorpsi. Penelitian ini dilakukan untuk mengamati perilaku penyerapan dan penukaran kation bahan isian zeolit berbentuk cincin terhadap kation logam besi dan kobalt. Hasil pengamatan menunjukkan bahwa pola adsorpsi mengikuli persamaan Langmuir dengan kapasitas penyerapan 59,9 mg/g untuk ion Fe dan 57.8 mg/g untuk ion Co.

Keywords: cation adsorption, cation exchange capacity, zeolite packing

1. Introduction

In a conventional biogas reactor, organic wastewater is flown into an air-tight chamber to undergo anaerobic digestion by microorganism for reducing the organic content while producing biogas. The introduction of fresh feed in the same time removing the digested substance out from the reactor. It is often in a high wastewater flowrate, the outflow of the reactor carry out a significant amount of the essential microbial consortium (washout) which will hamper the reactor efficiency.

To solve the problem, solid media is added inside the reactor for microbial immobilization. The immobilizat ion on a support media provides many advantages which are maintain high concentration of microorganism for enhancing the efficiency of the process and avoid washout problem during a high substrate flow rate operation [1]. On the other hand, the solid support properties can be adjusted to provide a suitable environment for the microbial consortium. The modification could be done by incorporating a suitable cations as the surface micro-nutrientin the solid mediafor enhancing the attachment of microbial film on the support [2-4].

Zeolite as abundantly available natural resources is considered as one of potential support since it has high porosity and ease of modification. The zeolite structure consists of three-dimensional frameworks of SiO_4 and AlO_4 that are linked to each other. The combination of

tetravalent silicon and trivalent aluminium creates a net negative charge that is counterbalanced by the presence of naturally occurred cations (Ca^{2+}, Na^+ and K^+) which are exchangeable with other cations [5]. It was reported that modification of natural zeolite by several metals (Ni^{2+}, Co^{2+} and Mg^{2+}) could increase the biogas production [2]. Meanwhile, bentonite is an aluminium phyllosilicate (clay) consisting mostly of montmorillonite. Similar with zeolite, due to the replacement of tetravalent silicon with trivalent aluminium the layer charge becomes negative andis mostly neutralized by hydrated cations in the interlayer space which are bonded by electrostatic forces to the internal surfaces and can be exchanged with other cations [6].

In this study, a mixture of natural zeolites with bentonite as a binder is shaped into Raschig rings and impregnated with Co^{2+} or Fe^{2+} after calcination. The aim of this study is to understand the sorption and desorption profile of the packing to the cations. The proper amount of the cation is necessary to the biogas application since very high concentration of the specific ion could be harmful to the microorganism. By shaping the solid media into rings, it is suitable for continuous application such as in a packed bed anaerobic filter.

2. Methods

During the zeolite packing preparation,water was added gradually into a specific mixture of zeolite and bentonite powder under continuous manual mixing to produce an extrude-able paste. The variation of zeolite:bentonite ratio were 50:50 and 60:40. The mixture then extruded to produce a hollow tube with the outer diameter of 2.5 cm and hole diameter of 1,0 cm, and then carefully cut into ring shape of 3 cm in length. The rings then oven dried and calcined at 700 ^{o}C for 1 hour. The solid materials was analysed using XRD Multiflex Rigaku and Surface Area Analyzer Nova Micromeritics.

Before impregnation of the targeted cations, the rings was homoionized to become Na-zeolite/bentonite rings. Each different bentonite:zeolite ratio was separated into four parts which each part consists of 4 rings (Table 1). Then, each part rings was immersed into 200 ml NaCl 1M solution for 2 days. After the sodium ion exchange, the packings was removed and soaked into deionized water for 1 day to remove excess Na ions before oven dried and stored in a sealed container. Na concentration after immersion step was measured as well as in the washing solution for calculating Na ion retained inside the solid which is provided in Table 1.

Cation impregnation after the packing has been homo-ionized by Na cations, a part of the rings will be immersed in $CoCl_2$ solution to exchange the Na with Co, and the other part in $FeCl_2$ solution (Figure 1). The concentration of each solution was varied from 0.15 to

Table 1. Packing ID and Na Ion Retained

ID	zeolite:bentonite	weight (g)	ion retained (mg/g)
1a	60:40	25.85	38.03
1b		25.30	110.01
1c		25.40	79.13
1d		25.10	166.51
2a	50:50	31.30	36.26
2b		30.94	109.14
2c		30.50	35.12
2d		31.70	41.98

Figure 1. Zeolite/bentonite Rings under Cation Exchange

0.05 M. The concentration of each ion involved in the impregnated solution before and after immersion was always analysed using ICP-OES Optima 8300 Perkin Elmer.

The initial concentration of the selected ion in the solution before immersion of the rings is C_0 (ppm), while C_s (ppm) is the concentration in equilibrium after immersion. Thus the difference of the two concentration (C_a) can be used for determining how much the uptake of the cation by the media in gram of cation (x) by immersion in a specific volume V (l) of cation solution (Eq.(2)).

$$C_a = C_0 - C_s \qquad (1)$$

$$x = \frac{v \cdot c_a}{1000} \qquad (2)$$

Then by knowing x, and also the weight of media (m) the cation sorption can be modelled using well known equation of Langmuir (Eq.(3)) and Freundlich (Eq.(4)).

$$\frac{C_s}{x/m} = \frac{1}{k \left(\frac{x}{m}\right)_m} + \frac{C_s}{\left(\frac{x}{m}\right)_m} \qquad (3)$$

$$Log \left(\frac{x}{m}\right) = log\,K + \left(\frac{1}{n}\right) log\,Cs \qquad (4)$$

Total cation sorption in here is the combination of physical adsorption and also cation exchange mechanism. Even though the sorption mechanism on the

zeolite and bentonite surface is complex, but the equilibrium often can be sufficiently modelled by a simple equilibria equation of Langmuir and Freundlich isotherm [7].

3. Results and Discussion

Table 1 shows the nomenclature and dry weight of each batch of packing prior NaCl immersion and washing. Each batch contain the same number of rings (four) with the similar size and shape. It is clearly seen that the weight of higher bentonite content rings is larger. It is interesting to note that capacity in storing Na ion is varied among the batch with the same ratio. It could be due to the variation of zeolite and bentonite properties as natural products. Meanwhile, the general trend shows the higher zeolite content packing (1a-1d) has larger capacity of 98.42 mg/g in average, compared with lower zeolite rings (2a-2d) of 55.62 mg/g in average. It can be said that zeolite is better in retaining Na^+ than bentonite. This figure can also represent cation exchange capacity (CEC) of the packing.

Analysis of solid media before and after calcination was done using XRD and some solids were characterized using surface area analyzer. As shown in Table 2, the surface area of zeolite and bentonite mixture is much higher than bentonite alone. Micropore of zeolite mixture is also larger that allows for higher available adsorption site for ionic moieties. From Table 1 and 2 show that bentonite rich rings are not favourable for sorption and ion exchange. However, significant bentonite content is necessary for gaining sufficient mechanical integrity of the packing.

For XRD analysis (Figure 2), the natural zeolite diffraction is match with mordenite pattern thus the natural zeolite contain mostly mordenite crystal structure. Mordenite has better ion exchange capacity then common natural zeolite crystal structure i.e. clinoptillolite. Then, the calcination step does not alter any pattern instead of intensifying and sharpening the peak. It can be said that the heat treatment increase the crystallinity of the solids.

Meanwhile, bentonite diffraction pattern shows montmorillonite structure peaks which also improved after calcination. The zeolite/bentonite mixture after calcination pattern shows a combination between mordenite and montmorillonite peaks. It is confirmed that the

mixture is only a physical mixture without any chemical or structural transformation.

For Fe^{2+} impregnation, the adsorption and desorption behaviour of the media in different $FeCl_2$ concentration is shown in Figure 3. Similar to the sodium ion sorption capacity in Table 1, the uptake of Fe(II) also higher for packing with more zeolite (1a-1d). The difference of the performance is larger for lower concentration. The profile of sorption at the high concentration region is still increasing, thus the packing does not reach saturation yet.

The desorption of Fe ion during washing is relatively small due to strong attraction of the negative surface of the packing to the cations especially in low concentration. At high concentration the desorbed ion is observable due to weaker attraction of the surface which is already occupied by cation layer.
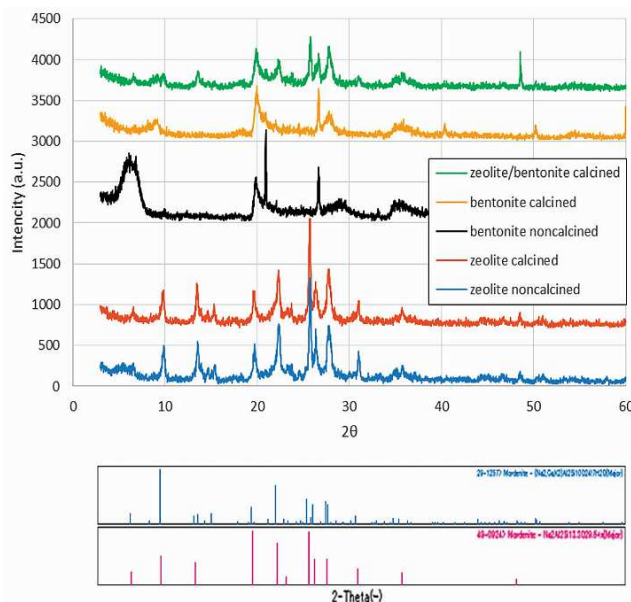

Figure 2. XRD Pattern of the Solids
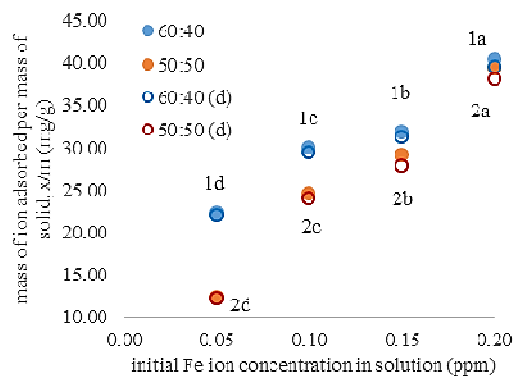
Figure 3. Sorption Profile of Fe in Various Concentration (d) Indicate Desorption

Table 2. Porosity Profile of Selected Samples

Zeolite:bentonite	Porosity		
	B.E.T (m^2/g)	Total vol. (cc/g)	Micropore vol. (cc/g)
50:50	26.1	0.076	0.0123
0:100	10.3	0.032	0.0042

The superiority of packing with more zeolite is also shown in Co sorption (Figure 4). However, the Co^{2+} sorption profiles are nearly steady in the high initial concentration region which indicates saturated condition. The desorption of Co(II) is observable at high concentration, similar to the Fe(II) isotherm profiles.

From Table 3, it can be said that Langmuir equation is well fitted with the isotherms due to lower R squared value than Freundlich isotherm. It indicates that the attracted cations cover the available surface of zeolite-bentonite packing in a monolayer arrangement.
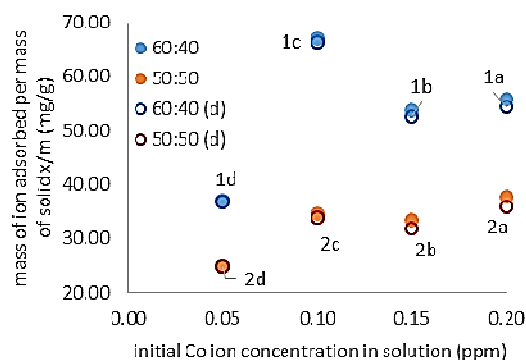
Figure 4. Sorption Profile of Co in Various Concentration (d) Indicate Desorption

Table 3. Isotherm Model Fitting

Cation	Ratio	R^2	
		Langmuir	Freundlich
Fe	60:40	0.944	0.853
	50:50	0.890	0.860
Co	60:40	0.975	0.840
	50:50	0.988	0.860

Table 4. Result Comparison

Ref	Materials	Shape and treatment	Ions	Max. capacity (mg/g)
[8]	cement kiln dust; zeolite; bentonite	Raschig rings, calcined	Pb(II)	85.0
[9]	Bentonite	Powder, acid treated	Cu(II) Pb(II)	3.8 6.5
[10]	mordenite	Powder, Na-homoionized	Ni (II)	5.3
[11]	Kaolinit; montmorillonite	Powder, calcined	Fe(III) Co(II) Ni(II)	28.9 28.6 28,4
This study	Zeolite; bentonite	Raschig rings, calcined	Fe(II) Co(II)	59.9 57.8

Table 4 shows the comparison of the maximum cations uptake capacity of materials from several previous experiments with this study. It is shown that the prepared packing from this study has relatively high maximum capacity compared with the others. Meanwhile, the rings of cement dust with zeolite and bentonite have the highest capacity due to a synergetic effect among the three components [8]. However to prepare the packing, it requires more ingredients and longer processing stages than this study. Table 4 also confirms that bentonite only has relatively low uptake capacity toward the ions that can be improved by mixing with high surface area and ion exchange capacity materials such as zeolites.

4. Conclusion

The prepared packing of zeolite and bentonite shows a good sorption capacity of metal ions which is suitable for essential nutrient storage in the bacterial immobilized application. The storage capacity can be altered by varying the zeolite content inside the packing.

Acknowledgement

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