Desalination and Water Treatment
www.deswater.com

1944-3994/1944-3986 © 2012 Desalination Publications. All rights reserved
doi: 10.1080/19443994.2012.672160

43 (2012) 113–117
April

Taylor & Francis
Taylor & Francis Group

Performance and modeling of zeolite adsorption for ammonia nitrogen removal

Jong-Oh Kim[a,]*, Suhan Kim[b], No-Suk Park[c]

[a]*Department of Civil Engineering, Gangneung-Wonju National University, Gangneung Daehangno 120, Gangneung, Gangwon-do, Korea*
Tel. +82 33 640 2420; Fax: +82 33 646 1391; email: jokim@gwnu.ac.kr
[b]*Department of Civil Engineering, Pukyong National University, Yongdang-Dong, Nam-Gu, Busan, Korea*
[c]*Water Management & Research Center, K-water Institute, Jeonmin-Dong, Yusong-Gu, Daejeon, Korea*

Received 25 December 2011; Accepted 10 February 2012

ABSTRACT

This study was conducted to investigate the adsorption characteristics of synthetic zeolite for NH_4^+–N removal in fermentation permeates and to establish a mathematical model for system design. Zeolite with a size of 1.7–2.3 mm, cation exchange capacity 130 meq/100 g-zeolite, gravity 1.7, and micropore surface (product of TOSO Company) was used in this study. This experiment was focused on the following research points: (1) effect of pH on NH_4^+–N adsorption and (2) simulation on space velocity or line velocity as design and operational parameters by adsorption isotherm.

Keywords: Ammonia nitrogen; Zeolite; Fermented suspension; Modeling; Adsorption

1. Introduction

Recent interests in upgrading the anaerobic fermentation process have prompted studies on the anaerobic contact process, the anaerobic filter process, the upflow anaerobic sludge blanket process, two-stage fermentation process, membrane-coupled fermentation process, and others. Although the anaerobic fermentation process has long been popular in the wastewater treatment field, it has been mainly employed to stabilize the suspended organic material and to provide a source of energy as methane recovery [1,2]. Relatively few studies have focused on the acid-phase step of the process. In anaerobic sludge fermentation process, the volatile fatty acids fermentation has some advantages, such as organic materials that generated during the fermentation of sludge can be used usefully as an electron donor necessary for the biological denitrification or phosphorous removal, basic materials of yeast, and to the methane fermentation. More, the quantity of sludge that has to be disposed finally can be reduced through this process. However, recovered permeates or supernatant by anaerobic fermentation contains high concentration of NH_4^+–N as well as soluble organic materials at the same time. Therefore, it is necessary to remove NH_4^+–N in permeates, when it is used as an electron donor for denitrification. Based on the above discussion, this study was mainly focused on the basic characteristics of NH_4^+–N adsorption by zeolite with synthetic substrate and was conducted to establish a mathematical model for the design of zeolite adsorption system.

2. Materials and methods

This study was conducted to investigate the adsorption characteristics of synthetic zeolite for

---

*Corresponding author.

The 4th International Desalination Workshop (IDW4), 16–18 November 2011, Jeju Island, South Korea

NH_4^+–N removal in fermentation permeates. Zeolite with a size of 1.7–2.3 mm, cation exchange capacity 130 meq/100 g-zeolite, gravity 1.7, and micropore surface (product of TOSO Company) was used in this study. The schematic experimental unit is shown in Fig. 1.

This experiment was focused on the following research points: (1) effect of pH on NH_4^+–N adsorption and (2) simulation on space velocity (SV) or line velocity (LV) as design operation parameter by adsorption isotherm. The composition of synthetic wastewater and experimental condition on pH variation are illustrated in Table 1. NH_4^+–N concentration was adjusted by the control of NH_4Cl dosage and the pH was adjusted with HCl and NaOH.

The other experimental condition to find overall mass-transfer coefficient ($k_f a_v$(1/s)) for simulation is shown in Table 2.

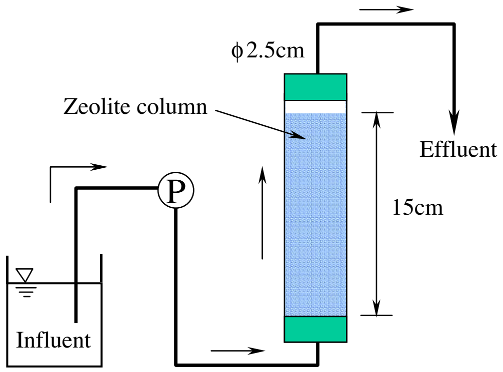

Fig. 1. Schematic diagram of packed zeolite column.

Table 1
The composition of synthetic wastewater and experimental condition on pH variation

Parameter	Run 1	Run 2	Run 3
pH	5.0	7.0	9.0
NH_4^+–N (mgN/L)	470	470	470
CH_3COONa (mgC/L)	1,000	1,000	1,000

Table 2
Experimental condition on SV variation of zeolite column

Parameter	Run 4	Run 5
SV (1/h)	4.8	2.0
LV (cm/h)	72	30
NH_4^+–N (mgN/L)	236	220
DOC (mgC/L)	625	680

Note: Others; volume of zeolite column: 73.9 cm^3, weight of packed zeolite: 59.6 g.

In analysis, targeted measurement items are total organic carbon (TOC), NH_4^+–N, and cation ion concentration. TOC was measured with a TOC analyzer (TOC-5000, Shimadzu, Kyoto) and NH_4^+–N concentration was analyzed by the Indophenol method (Shimadzu UV-1200. Cation ion concentration was measured by ICPU (ICPS4960, Shimadzu, Kyoto).

2.1. Investigation of design and operation parameter

Numerical analytic model prepared by kinetics of fixed bed adsorption process was used to investigate the design and operational parameters in this study. The summaries of numerical analytic model are as follows [3,4].

Mass balance equation:

$$u\frac{\partial C_b}{\partial z} + \varepsilon_b\frac{\partial C_b}{\partial t} + \rho_b\frac{\partial Q}{\partial t} = \varepsilon_b D_b\frac{\partial^2 C_b}{\partial Z^2} \tag{1}$$

Film dispersion:

$$\rho_b\frac{\partial Q}{\partial t} = k_f a_v(C_b - C) \tag{2}$$

Transgranular dispersion:

$$\frac{\partial q}{\partial t} = \frac{D_s}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial q}{\partial r}\right), \quad r \neq 0 \tag{3}$$

$$\left(\frac{\partial q}{\partial t}\right)_{r=0} = 6\frac{D_s}{\delta_r}\left(\frac{\partial q}{\partial r}\right)_{r=\delta r/2} \tag{4}$$

$$\left(\frac{\partial q}{\partial t}\right)_{r=r_p} = \frac{2D_s}{(\delta_r)^2}\left\{q_{r=r_p-\delta_r} - q_s + \frac{k_f\delta_r}{\rho_s D_s}\left(1 + \frac{\partial r}{r_p}\right)(C_b - C_s)\right\} \tag{5}$$

Adsorption isotherm

$$q_s = f(C_s) \tag{6}$$

where C_b (g/cm^3): solute concentration of fixed bed cavity; Q (g/g-zeolite): adsorption quantity of zeolite; U (cm/s): LV; ε_b (–): porosity of fixed bed; ρ_b (g-Zeo/cm^3-bed): charging density of zeolite; D_b (cm^2/s): dispersion coefficient; t (s): time; z (cm): height of fixed bed; q (g/g-zeolite): adsorption quantity in transgranule; q_s (g/g-zeolite): adsorption quantity in surface of particulate ($r = r_p$); C_s (g/cm^3): solute concentration in surface of particulate ($r = r_p$); r (cm): central distance from zeolite particulate; r_p (cm): radius of zeolite particulate; δ_r (cm): micro-distance of radius direction in particulate; ρ_s (g-zeolite/cm^3-zeolite): apparent density of zeolite particulate; a_v (cm^2/cm^3-bed): surface area of zeolite particulate per unit volume of column; k_f (cm/s): film mass-transfer coefficient; D_s (cm^2/s): transgranular surface diffusion coefficient.

Based on the above simultaneous equations, the numerical simulation for design and operation of process was carried out.

3. Results and discussions

3.1. Adsorption characteristic and effect of pH

Fig. 2 shows the result of the effect of pH on adsorption. In case the pH of solution was 5.0 and 7.0, there was not a great difference in adsorption ability. However, in case of the pH 9.0, it was found that the adsorption ability was decreased compared to those of pH 5.0 and 7.0. This may in part be attributed to the decrease of adsorption ability by the transition of NH_4^+ to NH_3 in solution in case of pH 9.0. Because the pH of membrane permeates is usually in the range of 5 .0–6.0, there is no need to think that there is a problem by the pH on adsorption of zeolite. To examine the existence of disturbance for adsorption, the adsorption isotherms in both actual permeate and synthetic wastewater were investigated. Adsorption isotherm is shown in Fig. 3. Equations of *Freundlich* adsorption isotherm were as follows:

$$\text{Actual permeate: } q = 0.607C^{1/1.77} \tag{7}$$

$$\text{Synthetic wastewater: } q = 0.528C^{1/1.69} \tag{8}$$

where q : NH_4^+–N concentration in solid phase (mgN/g-zeolite); C : NH_4^+–N concentration in liquid phase (mgN/L).

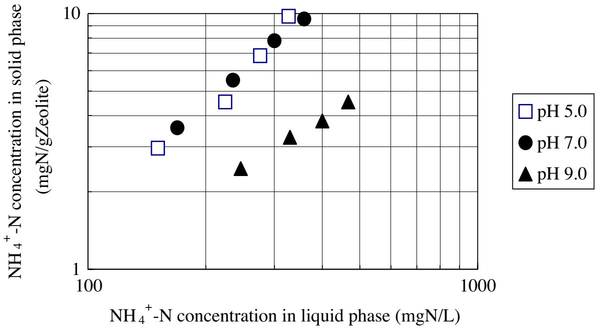

Fig. 2. The effect of pH on NH_4^+–N adsorption of zeolite.

From Fig. 3, the *Freundlich* adsorption isotherms were consistent in both cases of actual permeates and synthetic wastewater. Therefore, it is considered that NH_4^+–N could be effectively removed by zeolite adsorption even in permeates that contain other cations [5,6]. Equilibrium adsorption of ammonia and humic acid onto natural zeolite had the best fitness with the *Freundlich* isotherm at all temperatures ranging from 20 to 50°C [7].

The results of continuous-flow experiment of zeolite column are shown in Figs. 4 and 5. These figures indicate that NH_4^+–N is removed by adsorption of zeolite, while dissolved organic materials are hardly being adsorbed. We can understand that any loss of soluble organics does not occur with the adsorption of NH_4^+–N. This may be attributed that the organic components of fermented suspension are hardly to adsorb by synthetic zeolite. Thus, recovered soluble organics contained in fermented suspension can be returned to the denitrification tank without any adsorption by

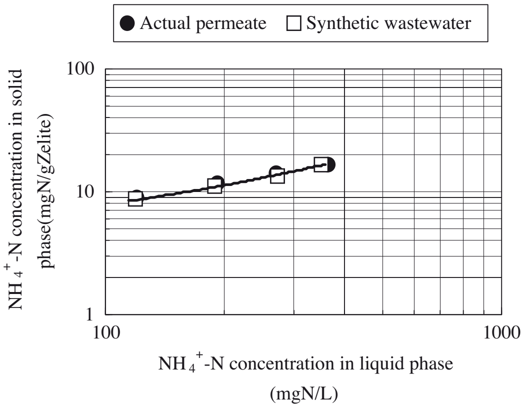

Fig. 3. Adsorption isotherm in case of permeate and synthetic wastewater (pH is controlled of 5.6 in both case, Na, Mg, K, and Ca concentrations were 88, 23, 40, and 127 mg/L, respectively, in actual permeate).

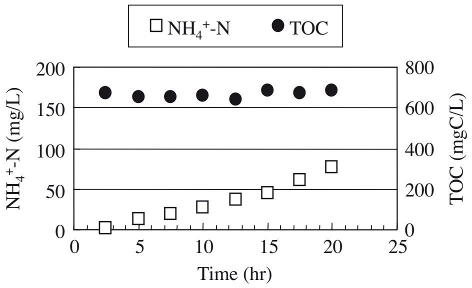

Fig. 4. The breakthrough curve of NH_4^+–N and TOC (SV: 2.0 (1/h)).

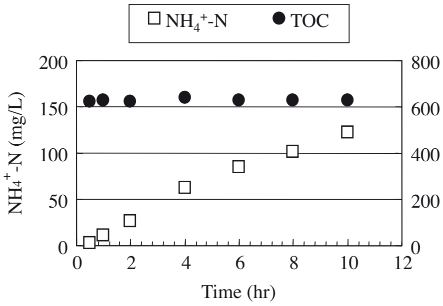

Fig. 5. The breakthrough curve of NH_4^+–N and TOC (SV: 4.8 (1/h)).

zeolite. Reports in the literature are inconsistent on the adsorption of ammonia. Therefore, by comparing the findings of the present study with those of literature, it can be concluded that the adsorption performance of ammonia depends on both the nature of the adsorbents and the selected experimental conditions.

3.2. Design and operational parameters

Parameters and operating conditions used for simulation are listed in Table 3. Measured and calculated values of NH_4^+–N concentration ratio (C/C_o) are illustrated in Fig. 6.

The NH_4^+–N concentration ratio (C/C_o) illustrated that there is a reasonably good agreement between measured data and simulated values. Film mass-transfer coefficient (k_f) and surface diffusion coefficient (D_s) could be obtained by curve fitting from Fig. 6 and the values were 2.5×10^{-4} cm/s and 7.0×10^{-8} cm^2/s, respectively. Based on the coefficient values, breakthrough curve prepared by numerical analysis is shown in Fig. 7 and the relationship between SV and breakthrough time in a certain breakthrough NH_4^+–N concentration is illustrated in Fig. 8.

Table 3
The values of parameter used for simulation

Parameter	Selected value
Coefficient of adsorption isotherm ($q = A \times C^B$)	$A = 0.607$, $B = 0.565$
Influent NH_4^+–N concentration: C_o (mgN/L)	236, 220
LV: u (cm/min)	1.2 (SV: 4.8(1/r)), 0.5 (SV: 2.0(1/h))
Diameter of zeolite: d_p (cm)	0.2
Density: ρ_s, ρ_b (g/cm^3)	$\rho_s = 1.265$, $\rho_b = 0.809$
Height of column: z (cm)	15.0
Porosity of fixed bed: ε_b (–)	0.15
Micro-distance of radius direction in particulate: δ_r (cm)	0.05
Film mass-transfer coefficient: k_f (cm/s)	2.5×10^{-4}
Transgranular surface diffusion coefficient: D_s (cm^2/s)	7.0×10^{-8}

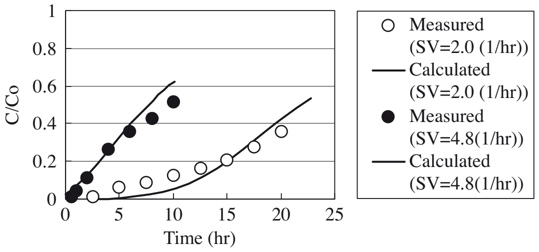

Fig. 6. Measured and calculated values of NH_4^+–N concentration ratio (C/C_o).

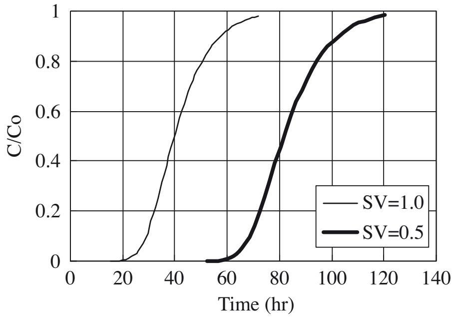

Fig. 7. Breakthrough curve according to SV. (Condition: Influent NH_4^+–N concentration 300 mgN/L.)

From Fig. 7, in case of SV 1.0 and 0.5, breakthrough time was about 29 and 69 h, respectively, under the condition of NH_4^+–N concentration ratio (C/C_o) of 0.1. However, it is said that the break-

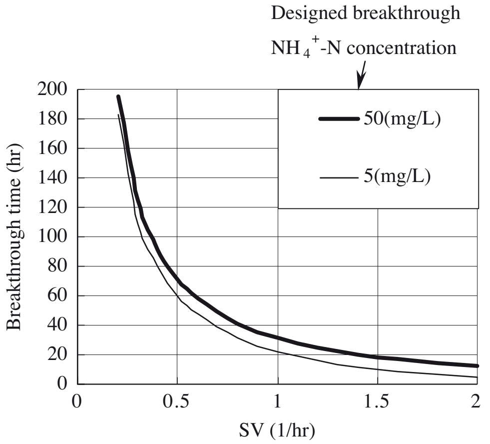

Fig. 8. Relationship between SV and breakthrough time.

through time is necessary to be 3–4 days, at least, when actual treatment is considered. Therefore, to satisfy the breakthrough time of 92 h, we can find that the SV has to be set below 0.4 (1/h) from Fig. 8. Necessary volume of zeolite becomes 2.5Q m^3 when permeate flow rate obtained is put on Q m^3/h, in case of SV 0.4 h. For example, 4,000 m^3/day of membrane permeates could be treated by the zeolite column with a volume of 417 m^3 for 92-h cycle. From the above results, it was confirmed that NH_4^+–N in permeates could be removed stably by zeolite adsorption under certain conditions.

4. Conclusions

On the characteristics of NH_4^+–N adsorption by zeolite, the adsorption capacity decreased compared to those of pH 5.0 and 7.0 in case of the pH 9.0 of solution. NH_4^+–N that could be effectively removed by zeolite adsorption even in permeates that contain other cations and dissolved organic materials is hardly being absorbed. It was confirmed that NH_4^+–N in permeates could be removed stably by zeolite adsorption under certain conditions. In case of SV 1.0 and 0.5, breakthrough time was about 29 and 69 h, respectively, under the condition of NH_4^+–N concentration ratio (C/C_o) of 0.1. To satisfy the breakthrough time of 92 h, the SV has to be set below 0.4 (1/h). Necessary volume of zeolite becomes 2.5Q m^3 when influent flow rate obtained is put on Q m^3/h, in case of SV 0.4 h.

References

[1] J.P. Boisvert, T.C. To, A. Berrak, C. Jolicoeur, Phosphate adsorption in flocculation processes of aluminum sulphate and poly-aluminum-silicate-sulphate, Water Res. 31(8) (1997) 1939–1946.

[2] W. Ghyoot, W. Verstraete, Anaerobic digestion of primary sludge from chemical pre-precipitation, Proceedings of 8th International Conference on Anaerobic, Digestion 1 (1997) 315–322.

[3] A.H. Oren, A. Kaya, Factors affecting adsorption characteristics of Zn^{2+} on two natural zeolites, J. Hazard. Mater. 131 (2006) 59–65.

[4] Sang-Mo Koh., K.G. Joe Boris Dixon, Preparation and application of organo-minerals as sorbents of phenol, benzene and toluene, Appl. Clay Sci. 18 (2001) 111–122.

[5] G.S. Sen, K.G. Bhattacharyya, Adsorption of Ni(II) on clays, Journal of Colloid Interface Science 295 (2006) 21–31.

[6] Taihong Shi., Shiguo Jia, Ying Chen, Yinghong Wen, Du Changming, Huilin Guo, Zhuochao Wang, Adsorption of Pb (II), Cr(III), Cu(II), Cd(II) and Ni(II) onto a vanadium mine tailing from aqueous solution, J. Hazard. Mater. 169 (2009) 838–846.

[7] Gholamreza Moussavi., Sadegh Talebi, Mehrdad Farrokhi, The investigation of mechanism, Kinetic and isotherm of ammonia and humic acid co-adsorption onto natural zeolite, Chem. Eng. J. 171 (2011) 1159–1169.