Fixed-Bed Column sorption of Ammonium from Treated Municipal wastewater using Clinoptilolite

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Abstract

The sorption of ammonium (NH₄⁺) ion was measured in a continuous fixed-bed column via employing a granular natural zeolite (clinoptilolite). The column performances were investigated at influent flow rate of 0.22 mL/min. The experimental data were fitted to well-known sorption models, namely Thomas and Yoon–Nelson. The experimental and theoretical maximum capacity was 3.7±0.3 mg/g.

Keywords: ammonium sorption, zeolite, fixed-bed column, breakthrough curve, resource recovery.

1. Introduction

One of the common form of reactive nitrogen is NH₄⁺ which is mainly found in environments e.g., municipal sewage discharges, fertilizers, and waste leachates (Yang et al. 2018). Appearing of ammonium in water resources probably causes eutrophication, and consequently fast growth of algae that in turn it would deplete dissolved oxygen and harm other aquatic organisms (Liikanen, 2003). A broad variety of treatments including chemical, physical and biological treatments have been implemented to eliminate/recover NH₄⁺ (Hjorth et al. 2011). However, among them, NH₄⁺ sorption with assist of zeolites is gaining on popularity owing to its easy-to-perform and cost-effective operation (Akimkhan 2012). Zeolites are classified as aluminosilicate minerals that can be produced in a highly regular microporous structure and with high affinity to ion exchange in water. They are used as sorbents and specially ion-exchange media in industry and wastewater treatment (Inglezakis,2012). The aim of this study is to determine the zeolite ability in up taking NH₄⁺ ions at flow rate of 0.22 ml/min.

2. Experimental methodology

The applied zeolites in this study were prepared with mixing up the zeolite into Sodium Hydroxide (NaOH) solution (1.0 M, under reflux) on a shaker for 1 h. Then, the prepared samples were packed in a glass column (10 mm inner diameter and 80 mm length). The Schematic diagram of packed-bed column is illustrated in Figure 1. Sorbents were considered saturated when column effluent concentration reached 95% of inlet concentration. Initially, the column was equilibrated with deionized water. The test solution with competing ions was supplied in counter-current through the column. A fraction collector (Gilson FC204) collected samples from the outlet of the column at given time intervals. The overall characteristic of initial samples are listed in the table 1.

Table 1. Overall characteristic of the treated urban Wastewater (Note: Initial concentration (C₀), total solid (TSS) and chemical oxygen demand (COD)).

C ₀ (mg/l)	pH	TSS (mg/L)	COD(mg/L)
70±3	8.7±0.3	120±21	72±13

Figure 1: Schematic diagram of continuous packed bed column system.

3. Ammonium sorption modelling in fixed bed columns

The Thomas model(Thomas 1944), is frequently employed to theoretically defines the breakthrough of a fixed-bed column and also the impact of sorption parameters in a fixed-bed column. This model is based on the second-order law of kinetic reaction with assumption of not considering any axial dispersion even for when the depth of bed was at the minimum and the breakthrough happened very fast after the flow started (Apiratikul, 2008). The Thomas model is formulated in a linearized form, as described in Eq. (1).

$$\ln \left[\frac{C_0}{C_t} - 1 \right] = \frac{K_{Th} q_0 m}{Q} K_{Th} C_0 t \quad (1)$$

In the Thomas model equation, outlet solute concentration at time (mg/L) and mass of sorbent in the column (g) are denoted with C_t and m, respectively. The K_{Th} and q₀ describes the Thomas kinetic coefficient (mL/min mg) and maximum solid phase concentration (mg/g). The value of K_{Th} and q₀ can be calculated through the plot of ln (C₀/C_t - 1) versus t (min).

The Yoon–Nelson model was proposed according to the theory of adsorption and breakthrough of sorbate probability (Pilli, 2012). This model is applicable for a single component system and it is mathematically defined in Eq. (2).

$$\ln \left[\frac{C_0}{C_0 - C_t} \right] = K_{YN} t - \tau K_{YN} \quad (2)$$

The τ and k_{YN} in this equation describe the time required for 50% of sorbate break-through (min) and Yoon–Nelson rate of constant (min^{-1}), respectively. The value of k_{YN} and τ can be obtained from the plot of $\ln(C_t/(C_0 - C_t))$ versus t .

4. Results and Discussion

Figure 2 compares experimental and predicted breakthrough curve using two implemented models of (2A) Thomas model and (2B) Yoon–Nelson model for Ammonium uptake versus time. Experimental data were properly fitted by two models and predicted results can be seen for both employed models. According to the results, the total NH_4^+ removal was $29 \pm 2\%$ while the amount of equilibrium ion uptake sorbed in column was around $4.1 \pm 0.4 \text{ mg/g}$. This value was also obtained by Thomas model which was $3.7 \pm 0.3 \text{ mg/g}$. The Total flow time during the packed bed column was 68 h.

Figure 2: Ammonium removal versus time: Experimental and breakthrough curve modelling using (A) Thomas model and (B) Yoon–Nelson model

5. Conclusion

The wastewater containing NH_4^+ was treated in a continuous fixed-bed column system using flow rate of 0.22 ml/min . In order to further describe the sorption mechanism, the well-known adsorption models were used to describe the experimental data. The Thomas model showed an excellent correlation for the NH_4^+ experimental data. The Yoon–Nelson model also estimated the 50% breakthrough curve with minimal data required and provided the estimate break-through time for the column system.

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References

- Akimkhan, Aiyngul M. 2012. "Structural and ion-exchange properties of natural zeolite." *Ion Exchange Technologies*:261-282.
- Apiratikul, Ronbanchob, and Prasert Pavasant. 2008. "Batch and column studies of biosorption of heavy metals by *Caulerpa lentillifera*." *Bioresource technology* 99 (8):2766-2777.
- Hjorth, Maibritt, Knud Villy Christensen, Morten Lykkegaard Christensen, and Sven G Sommer. 2011. "Solid–liquid separation of animal slurry in theory and practice." In *Sustainable Agriculture Volume 2*, 953-986. Springer.
- Inglezakis, Vassilis J, and Antonis A Zorpas. 2012. *Handbook of natural zeolites*: Bentham Science Publishers.
- Liikanen, Anu, and Pertti J Martikainen. 2003. "Effect of ammonium and oxygen on methane and nitrous oxide fluxes across sediment–water interface in a eutrophic lake." *Chemosphere* 52 (8):1287-1293.
- Pilli, Santhi Raju, Vaibhav V Goud, and Kaustubha Mohanty. 2012. "Biosorption of Cr (VI) on immobilized *Hydrilla verticillata* in a continuous up-flow packed bed: prediction of kinetic parameters and breakthrough curves." *Desalination and Water Treatment* 50 (1-3):115-124.
- Thomas, Henry C. 1944. "Heterogeneous ion exchange in a flowing system." *Journal of the American Chemical Society* 66 (10):1664-1666.
- Yang, Hye In, Kangyi Lou, Anushka Upamali Rajapaksha, Yong Sik Ok, Anthony O Anyia, and Scott X Chang. 2018. "Adsorption of ammonium in aqueous solutions by pine sawdust and wheat straw biochars." *Environmental Science and Pollution Research* 25 (26):25638-25647.