AMMONIA REMOVAL FROM SEWAGE WASTEWATER USING CHEMICALLY MODIFIED SAND

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Abstract. The study was conducted to observe the effectiveness and the efficiency of the adsorption method to remove ammonia from sewage water. The experimental design involves fixed-bed column, desorption and regeneration study. The results showed that the modified sand performed better in removing ammonia from sewage compared with pristine sand and regenerated used modified sand. The experimental data showed a better fit to the Thomas and Yoon-Nelson adsorption models. We found that the modified sand removed ammonia up to 99% and remained 80% of removal after 50 minutes compared to the pristine sand that was only 78.51% and gradually dropped to 10% after 50 minutes. Modified sand recorded the maximum adsorption capacity of 0.014 mg/g compared to 0.0033 mg/g for pristine sand and 0.0087 mg/g for regenerated used modified sand. Modified sand was able to be reused using a relatively low cost regenerating solution (NaCl).
Keywords: *fixed bed adsorption, wastewater treatment, nitrogen, X-ray diffraction, column experiment, regeneration*

Introduction

Nitrogen compounds such as ammonia, nitrite and nitrate are often present in wastewater and can end up in lakes, rivers and drinking water reservoirs (AWWA, 1990). In many developed countries, consent levels for the amount of ammonium contained in the final effluent invariably dictates the need for a nitrogen treatment step to be included as part of the wastewater treatment process (Pearce et al., 2000). Ammonia removal from water and wastewater is vital especially in environmental protection as ammonia can lead to problems such as eutrophication, corrosion and fouling (Rožić et al., 2000).

Various conventional methods are capable of removing ammonia from aqueous solutions, which include air stripping, breakpoint chlorination, ion exchange and biological nitrification-denitrification. Adsorption using various types of adsorbents is an important method due to its ease of operation and relatively low cost. Various studies to remove ammonia in water by adsorption methods have been carried out (Rožić et al., 2000; Halim et al., 2012; Aziz et al., 2004; Lei et al., 2008; Halim et al., 2010; Sarioglu, 2005). Among them are clay and zeolite (Rožić et al., 2000; Sarioglu, 2005; Celik et al., 2001), limestone (Aziz et al., 2004), carbon-zeolite composite (Halim et al., 2009) and silica-carbon-calcium carbonate (Aguilar et al., 2002). This study was done to modify silica sand as an alternative adsorbent which is of lower cost than other conventional adsorbents.

The application of sand in water treatment has been reported previously (Ehret et al., 2001). It has been used to filter particulate matter and to reduce turbidity. Sand as a filter was also used to remove bacteria (Ellis and Wood, 1985; Ellis, 1987). A previous study found that sand modified with aluminum hydroxide was able to filter

microorganism effectively (Farrah and Preston, 1985). Sand surface coated with ferric oxide is capable of removing uncomplexed and ammonia-complexed cationic metals (copper, cadmium, lead, nickel and zinc) as well as some oxyanionic metals (SeO_3 and AsO_3) from simulated and actual waste streams over a wide range of metal concentrations (Benjamin et al., 1996). The adsorbent was stable during backwashing and regeneration operations, releasing most metals quantitatively. This composite media is inexpensive, easy to prepare and can serve as the basis of a useful metal removal and possibly metal recovery process in a variety of settings.

Therefore, the aim of this study was to investigate the fixed bed adsorption capability of both chemically modified sand and pristine sand to remove ammonia from sewage wastewater. In addition, this study reported the regeneration and desorption processes for identifying the ability of chemically modified sand to be reused.

Research methods

Modification of sand surface

Commercial sand with the size in the range of 0.5-1.0 mm was used in this study. The modification of the sand surface was done using sodium aluminates ($NaAlO_2$) and sodium hydroxide (NaOH). The sand was washed with distilled water before soaking into the chemical solution. The optimum concentration ratios of $NaAlO_2$ over NaOH were determined in various concentration of $NaAlO_2$ (0.125M, 0.25M, 0.5M, 1.0M, 2.0M and 3.0M) and fixed concentration of NaOH (4M). Then, the sand was soaked in this chemical solution and heated at 80^oC for 30 minutes. A sufficient solution was poured to completely cover the sand. The sand was left overnight, rinsed and stored at room temperature.

X-Ray Diffraction (X-RD)

This test was done using an X-ray diffraction spectrometer (model D-5000, Siemens, Germany). The purpose of this test was to determine the mineral content present in the new chemically modified sand adsorbent.

Column adsorption study

Columns were made of Perspex with a dimension of 80 cm height and 10 cm internal diameter. Modified and pristine sand was packed in columns. The weight of adsorbent added was 996 g with a measured volume of 700 mL. Before being used, deionized water was passed through the columns to ensure the column effluents were clear and free of precipitates. A Masterflex peristaltic pump was employed to feed the stock solution to the column at 20 mL/min of flow rate. Fixed bed column adsorption experiment was perform at pH 7 as suggested by a previous researcher, which was the optimum pH for ammonia adsorption (Halim et al., 2011). Samples were collected at various time intervals and analyzed for ammoniacal nitrogen using the Nesslerization colorimetric method (APHA, 1995).

Regeneration study

The exhausted column was subjected to desorption to regenerate the adsorbent using a 1.0 M NaCl solution at pH 12 (adjusted using sodium hydroxide) (Celik et al., 2001).

To regenerate the column, NaCl was pumped through the adsorbent in the up flow mode and the breakthrough solution was collected for determination of ammonia content.

Results and discussion

X-Ray Diffraction (X-RD)

From the X-RD test (*Fig.1*), the obvious change of spectra was obtained for microline minerals, $Na^+[AlSi_3O_8]^-$, which was detected at $2\theta = 27.48$. The presence of this mineral may increase the number of cation exchange sites, thus increasing the cation exchange capacity during wastewater treatment.
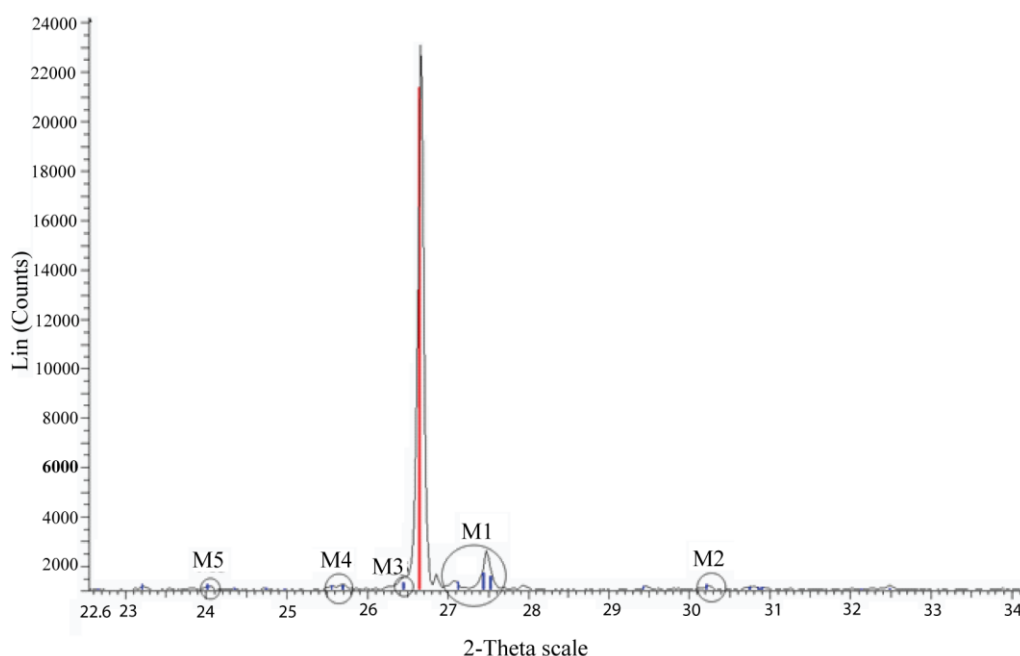

***Figure 1.*** *X-ray diffraction spectra for chemically modified sand*

Fixed bed adsorption

As indicated in *Fig. 2*, ammonia removal was more successful by using chemically modified sand. The modified sand removed ammonia up to 99% and remained 80% of removal after 50 minutes. Maximum removal of ammonia by pristine sand was only 78.51% and gradually dropped to 10% after 50 minutes. A statistical test (Mann-Whitney) found that ($P<0.05$) there was a significant difference in the rate of adsorption for both types of adsorbents. The regenerated modified sand also performed well as the removal percentage of ammonia was more than 80%.

Ammonia adsorption activity is based on the ion-exchange process of $Na^+>K^+>Ca^{2+}>Mg^{2+}$ where Na^+ has higher affinity towards ion exchange with ammonia compared with other cations. The process of ion exchange involves replacement of ions on the solid phase with the ions from the liquid phase (Lei, 2008). The reaction occurred can be represented by the equation 1:

$$S\text{-}Na^+(s) + NH_4^+(aq) \longleftrightarrow Na^+ (aq) + S\text{-}NH_4^+ (s) \qquad \text{(Eq.1)}$$
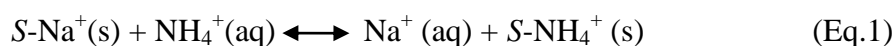
Where, *S* refers to the sand surface. The ammonium desorption process for used modified sand was perform using 1.0M NaCl at pH 12 (adjusted using NaOH, at flow rate 10 ml/min) as shown in *Fig. 3*. Desorption process was almost complete at 2.91 of bed volume.
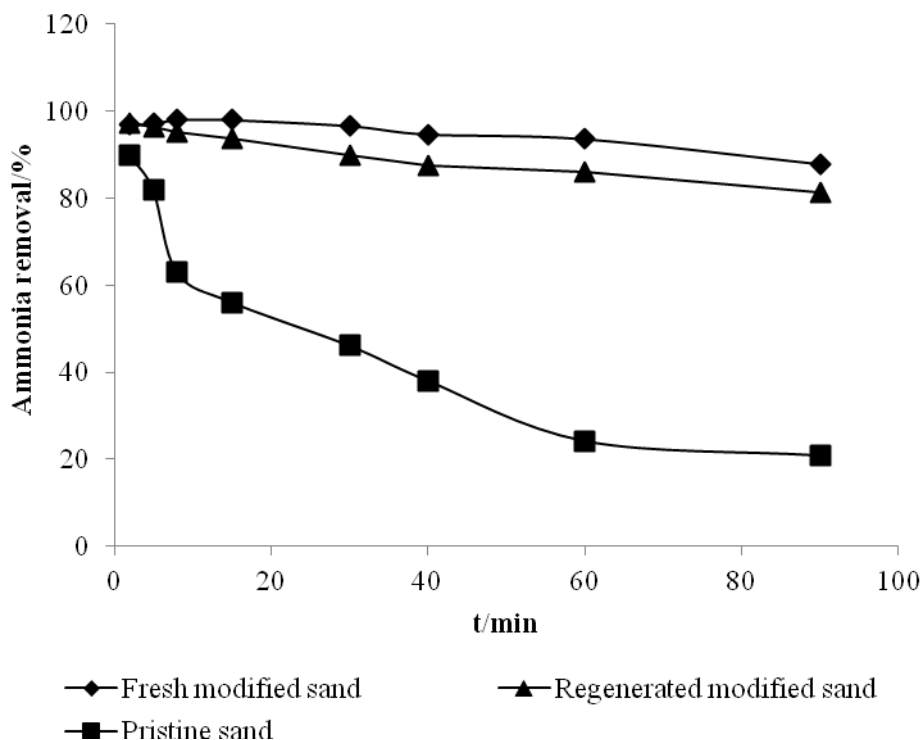
Figure 2. *Comparison of pristine sand with fresh modified sand and regenerated modified sand (regenerated from used modified sand) in term of ammonia removal in column adsorption study*
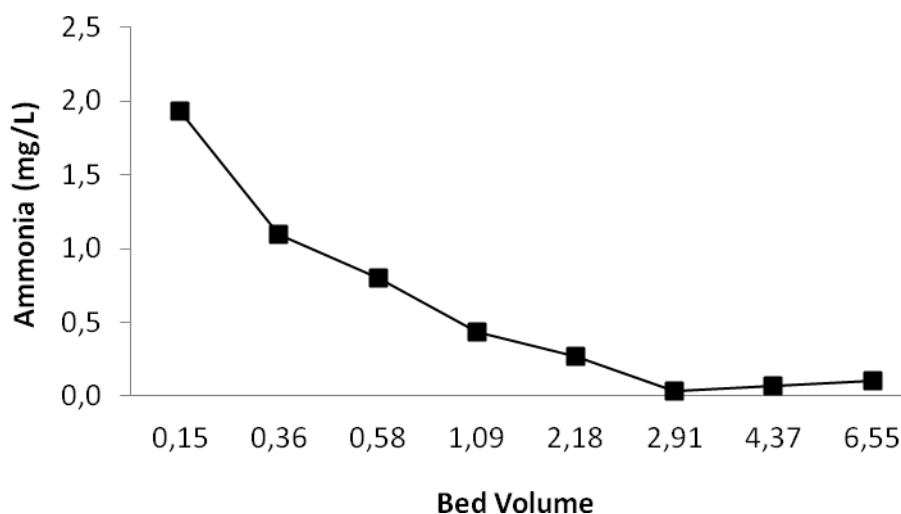

Figure 3. *Ammonia desorption from used modified sand vs. bed volume of a 1.0 M NaCl solution at pH 12 (adjusted using sodium hydroxide) at 10 ml/min flow rate*

Modeling of fixed bed column adsorption

Thomas and Yoon-Nelson mathematical models were applied in this study for evaluation of efficiency and applicability of column models for a large-scale operation (Thomas, 1944; Yoon and Nelson, 1984). Thomas model was adapted from the first order of the kinetic adsorption model. It can be expressed by the equation 2 below:

$$ln\left(\frac{C_o}{C_t} - 1\right) = \frac{k_T q_o m_c}{Q} - k_T C_o t \qquad \text{(Eq.2)}$$

Where k_T (mL/min mg) is the Thomas rate constant, q_o (mg/g) is the maximum capacity of ammonia adsorption; C_o (mg/L) is the initial concentration of ammonia in the sewage; C_t (mg/L) is the concentration of ammonia adsorption at the end of time t; Q (mL/min) is the flow rate of solution, m_c is the weight of adsorbent (g) and t is time (min). Linear graph was plotted to identify the values of k_T and q_o as shown in *Fig. 4A* and *Fig. 4C*. As shown in *Table 1*, the value of q_o for modified sand is higher than the untreated sand. Modified sand showed the maximum adsorption capacity of 0.014 mg/g compared with 0.0033 mg/g for pristine sand.
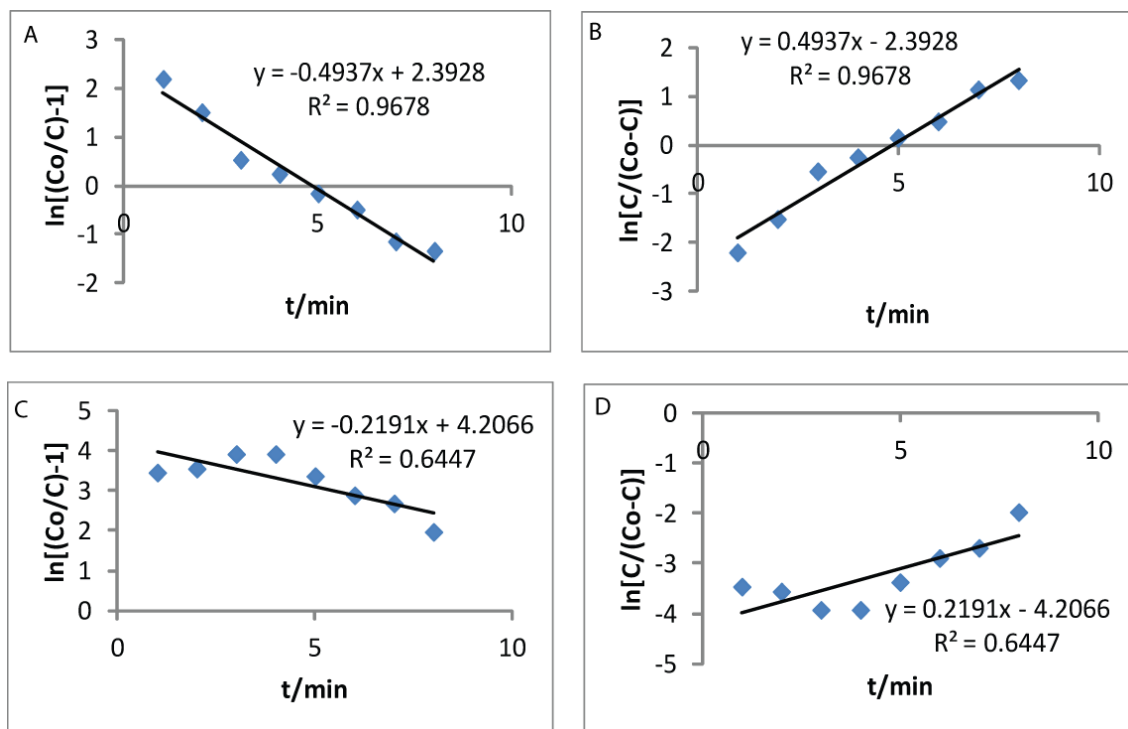
Figure 4. Fixed bed column adsorption modeling for pristine sand (A and B) and modified sand (C and D) using Thomas equation (A and C) and Yoon-Nelson equation (B and D)

Table 1. Maximum adsorption capacity

Sand	k_T (mL/mg/min)	R^2	q_o (mg/g)
Pristine sand	0.0411	0.9675	0.0033
Modified sand	0.0183	0.6442	0.014
Regenerated used modified sand	0.0252	0.988	0.0087

Principally, Yoon and Nelson model was used to estimate the possible decrease of adsorption rate, which is directly proportional to its adsorption action. This model can be expressed by the equation 3:

$$ln\frac{C}{C_o-C} = k_{YN}t - t_{0.5}k_{YN}$$ (Eq.3)

Where, k_{YN} (L/min) is the rate constant and $t_{0.5}$ (min) is the breakthrough curve for 50 % of ammonia being absorbed by adsorbent. A plot of $ln\ C/(C_o-C)$ versus t gives a straight line with a slope of k_{YN} and intercept of $t_{0.5}k_{YN}$ as shown in *Fig. 4B* and *Fig. 4D*. Based on *Table 2*, the values of breakthrough for 50 % of ammonia absorbed by modified sand and pristine sand were 59.56 and 24.11 min, respectively. For a given bed, the adsorption capacity of Yoon-Nelson model (q_{oYN}) for a given weight of adsorbent can be calculated using the equation 4 (Sivakumar and Palanisamy, 2009):

$$q_{oYN} = \frac{C_oQt_{0.5}}{1000X}$$ (Eq.4)

Based on Yoon-Nelson model, adsorption capacity, q_{oYN} of modified sand had increased to 0.014 mg/g compared to 0.03 mg/g for pristine sand.

Table 2. Adsorption capacity

Adsorbent	k_{YN} (t/min)	R^2	$t_{0.5}$ (min)	q_{oYN} (mg/g)
Pristine sand	0.4933	0.9678	4.85	0.0033
Modified sand	0.2191	0.6447	20.54	0.0141
Regenerated used modified sand	0.303	0.9885	12.75	0.0087

Regeneration

The ability of modified sand to be reused was determined by regeneration or desorption studies. The result from the first desorption at flow rate 10 mL/min using 1.0 M NaCl at pH 12.3 indicated that 2.91 BV (bed volume) of NaCl solution was sufficient for ammonium elution from used modified sand. Increasing flow rate needed a higher volume of regenerating solution to remove ammonium from modified sand surfaces. The reaction occurred on the sand surface between Na$^+$ (from NaCl solution) and ammonium can be summarized by the following ion exchange process:

$$S\text{-}NH_4^+ + Na^+ \leftrightarrow Sand\text{-}Na^+ + NH_4^+$$ (Eq.5)
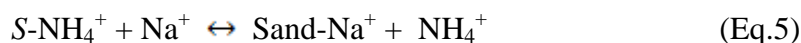
Desorption process was performed in alkali condition (pH = 12.3) to convert ammonium ion to ammonia as shown in the equation 6:

$$NH_4^+ + OH^- \leftrightarrow NH_3 + H_2O$$ (Eq.6)

Maximum adsorption capacity, q_o for regenerated modified sand was slightly lower than fresh modified sand as indicated in *Table 1*. This indicated that by using NaCl

solution, the regeneration of the column could be done repeatedly without loss of ammonium adsorption capacity.

Conclusions

Modified sand performed better in removing ammonia from sewage compared with pristine sand. The experimental data showed a better fit to the Thomas and Yoon-Nelson adsorption models. Hence, these models can be used to describe the behaviour of the adsorption of ammonia in a continuous column. Modified sand was able to be reused using a relatively low cost regenerating solution (NaCl).

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