

Ammonia Removal from an Aqueous Solution Using Chemical Surface- Modified Sand

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ABSTRACT: The study was conducted to identify the potential used of chemical surface-modified sand to remove ammonia from an aqueous solution using a fixed-bed column. The study compared the adsorption capacity of modified sand to the untreated raw sand followed by determination of the ability for both adsorbents on regeneration and desorption process. The capacity of adsorption was determined by ammonia removal percentage. Three mathematical modeling for adsorption of fixed-bed column namely Thomas model, Adam Bohart model and Yoon and Nelson model were used. Based on the study, chemically surface-modified sand could remove ammonia higher than raw sand at the flow rate of 20 mL/min more with removing rate of 78.25% to 97% as compared to pure sand at 0.60% to 78.51% only. Modified sand is reusable after the regeneration process. The Thomas model showed the maximum adsorption capacity of ammonia on chemical surface-modified sand was at 16.72 mg/g compared to raw sand at 4.86 mg/g at the flow rate of 20 mL/min.

Keywords: adsorption capacity, ammonia removal, chemical surface-modified sand, regeneration and desorption process

Introduction

Nitrogen compounds such as ammonia, nitrite and nitrate are often present in different types of waters and wastewater; ending up in lakes, rivers and drinking water reservoirs with effluent discharges (Aguilar *et al.*, 2007). 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 (APHA, 1995). Ammonia removal from water and wastewater are important in the alleviation of environmental problems including eutrophication, corrosion and fouling (AWWA, 1990).

Various studies to remove ammonia in water by adsorption methods have been

carried out (AWWA, 1990; Azhar *et al.*, 2009; Azhar *et al.*, 2010a; Azhar *et al.*, 2010; Azhar *et al.*, 2011; Azhar *et al.*, 2004; Bohart and Adams, 1920; Celik *et al.*, 2001; Ehret *et al.*, 2001). Among the adsorbents for ammonia removal are clay and zeolite (Azhar *et al.*, 2011; Aziz *et al.*, 2004; Bohart and Adams, 1920), limestone (Celik *et al.*, 2001), carbon-zeolite composite (Ehret *et al.*, 2001) and silica-carbon-calcium carbonate (Farrah and Preston, 1985). This current study investigates a new alternative adsorbent with enhanced adsorption characteristics at a lower cost compared to conventional adsorbents.

The application of sand in water treatment had been reported since 1804 by John Gibb (Chapman, 1965). Sand has been used to filter particulate matter and to

reduce the turbidity of water. Researchers had used sand filter to remove bacteria (Huisman and Wood, 1974). A study conducted by Farrah and Preston (cited by Lei *et al.*, 2008) also found that sand modified with aluminum hydroxide was able to effectively filter microorganism.

Sand surface coated with ferric oxide was found efficient to remove uncomplexed and ammonia-complexed cationic metals (cuprum, cadmium, lead, nickel and zinc) as well as some oxyanionic metals (SeO_3 , 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, and released most metals quantitatively. This composite media is inexpensive to prepare and could serve as a useful metal removal medium and possibly for metal recovery process in a variety of settings.

Therefore, the aims of this study was to investigate the fixedbed adsorption capability for both chemically surface modified sand and raw sand (untreated). Apart from that, this study investigated the regeneration and desorption process to identify the feasibility of reusing this chemically surface modified sand.

Research method

Modification of sand surface using chemical solution

Commercial sand with an arranged size in the range of 0.5-1.0 mm was used. Sodium aluminates (NaAlO_2) and sodium hydroxide (NaOH) of analytical grades were used for sand surface modification. The sand was washed prior to use. The mass proportions of NaAlO_2 over NaOH used were 2:1 with 80 g of NaAlO_2 being mixed with 40 g of NaOH and dissolved in one liter of distilled water. Then, the clean sand was soaked into the solution mixture and heated at 80°C for 30 minutes.

Sufficient solution was used to completely cover the sand. The sand was left overnight before being rinsed and stored at room temperature until used.

X-Ray Diffraction Test (X-RD)

An X-ray diffraction spectrometer model D-5000 (Siemens, Germany) was used to determine the mineral content present in the new chemically modified sand adsorbent.

Cation Exchange Capacity (CEC)

CEC test on modified and raw sand was conducted using ammonium substitution method (Pearce *et al.*, 2000). This method is performed by removing excess ammonium with 95% ethanol solution and replaced and dissolved ammonium with proton ion, H^+ from aqueous hydrochloric acid.

Batch Study

Batch study was divided into three sections. It began with the determination of optimum parameters, followed by a study of adsorption isotherms and kinetics adsorption. Optimum parameters study was determined using 40 g modified sand adsorbent. 100 mL of synthetic ammonium solution was included in a series of 250 mL flasks.

The flasks were sealed with parafilm to avoid evaporation and placed on an orbital shaker at 150 rpm for two hours. The purpose for using the orbital shaker was to ensure constancy of all the adsorbent mixture of sand and the solution through the process of adsorption. Finally, all mixture of solutions and adsorbents were filtered with filter papers of 50 mm in diameter. The filtrate was kept for content analysis of its ammonium concentration.

Column adsorption experiments

The columns used were made from polyvinyl chloride (PVC), with 80 cm in length and 10 cm in diameter. Modified and untreated sand were packed in separate columns. The weight of adsorbent added was 996 g and was 700 mL of volume. Before being used in experiments, deionized water was passed through the columns to ensure that the column effluents were clear and free of precipitates. A Master flex peristaltic pump was employed to feed the stock solution to the column at a flow rate of 20 mL/min. Samples were collected at various time intervals and analysed for ammonia cal nitrogen using the Nesslerization colorimetric method (Rozic *et al.*, 2000).

Regeneration studies

The exhausted columns were subjected to desorption to regenerate the composite

adsorbent using a regeneration solution, made of 1.0M sodium chloride at pH 12 (adjusted using sodium hydroxide). To regenerate the column, the regeneration solution was pumped through the adsorbent in the up flow mode and the breakthrough solution was collected for the determination of ammonia.

Results and Discussion

X-Ray Diffraction Test (X-RD)

From the X-RD test, the obvious change of spectra was obtained for microline minerals, $\text{Na}^+[\text{AlSi}_3\text{O}_8]^-$. The amount of microline minerals increased as observed from the spectra intensity (**FIGURE 1**). The formation of this mineral was from the treatment of raw sand by sodium hydroxide and sodium aluminate solution.

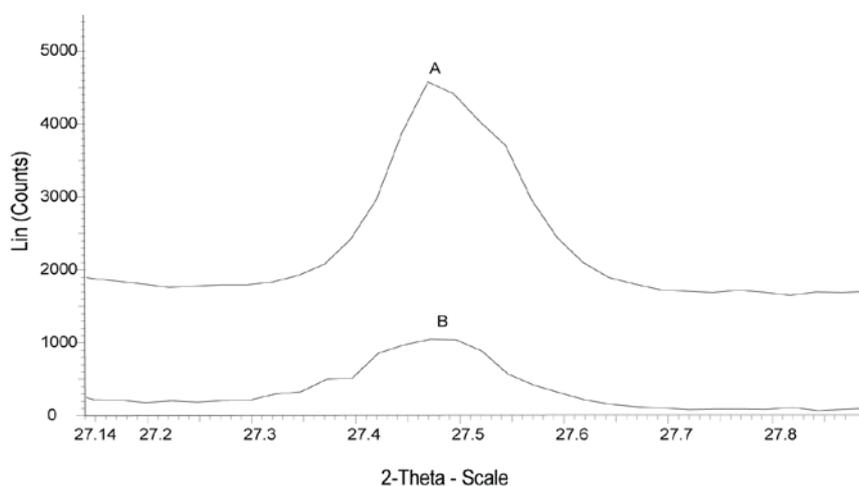


FIGURE 1: XRD spectrum for modified sand (A) and raw sand (B)

Cation Exchange Capacity (CEC)

Based on the test performed on chemical modified-sand and raw sand, the mean of CEC value of chemical modified-sand (0.0047meq/g) was significantly higher

than raw sand (0.00118meq/g). The increase of the amount of microlite minerals on the modified-sand surface increases cationic exchangeable sites, thus increasing its CEC.

Fixed Bed Adsorption

Ammonia removal using chemical modified-sand was higher than the raw sand with modified sand successfully removed ammonia between 78.25% and 97%, as opposed to the removal of ammonia between 0.60% and 78.51% for the latter. The mean percentage of ammonia removal for modified sand was 75.22%, and the raw sand was 53.46%.

A (Mann-Whitney) test found that the value of P=0.000, which is slightly smaller than 0.05 indicating that there was a significant difference in the rate of adsorption for both adsorbents. **FIGURE 2** shows the differences in the percentage of ammonia removal for raw sand, modified sand and regenerated modified sand.

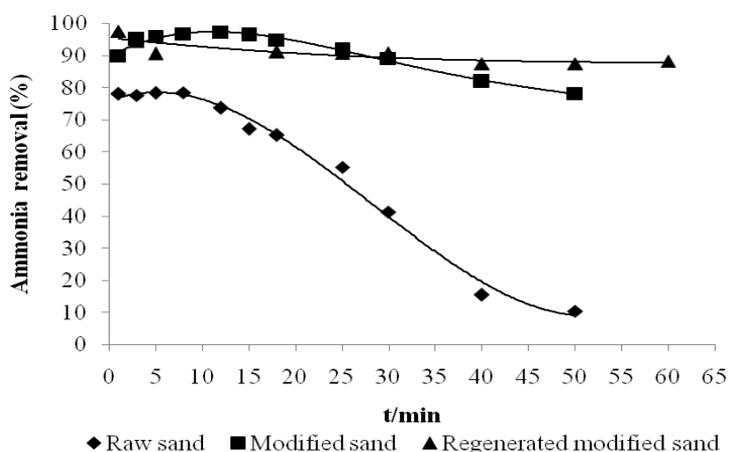


FIGURE 2: Ammonia removal from aqueous solution using raw sand modified sand and regenerated modified sand

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 to the other ions. The process of ion exchange involves the reaction of ion transfer in the solid phase that replaced with the same amount of ions in the liquid phase (Rozic *et al.*, 2000) as follows:



Where, p refers to the solid phase (sand) and aq refers to the liquid phase.

Modeling of Fixed-Bed Column Adsorption

Thomas (Sarioglu, 2005), Bohart-Adam (Thomas, 1944) and Yoon-Nelson (Yoon and Nelson, 1984) mathematical models were applied in this study for the evaluation of efficiency and applicability of column models for large scale operation. Thomas' model was adapted from the first order of kinetic adsorption model. It can be expressed as the **Equation1** below:

$$\ln\left(\frac{c_0}{c} - 1\right) = \frac{k_T q_0 m_c}{Q} - k_T C_0 t \tag{Equation1}$$

Where k_T (mL/min mg) is the Thomas rate constant, q_0 (mg/g) is the maximum capacity of ammonia adsorption, C_0 (mg/L) is the initial concentration of ammonia in the aqueous solution, 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 mass adsorbent and t (min) is time. Linear graph was plotted to identify the value of k_T and q_0 .

As shown in **TABLE 1**, the value of q_0 , maximum concentration of ammonia adsorbed using chemical modified-sand is higher than the raw sand. The modified sand showed the maximum adsorption capacity of ammonia of 16.722 mg/g compared to the untreated sand of 4.8644 mg/g.

The Bohart-Adam model illustrates that the adsorption rate is directly proportional to the capacity and concentration of adsorbent used. The model **Equation 2** is described below:

$$\ln C_t / C_0 = k_{AB} C_0 t - k_{AB} N_0 Z / F \quad \text{(Equation 2)}$$

C_0 and C_t (mg/L) are respectively the initial and concentration at time t , k_{AB} (L/mg min) is the kinetic constant, N_0 (mg/L) is the saturation concentration, Z (cm) is column depth, and F is obtained by dividing the linear velocity of the flow rate with an area of the column. Linear graph was plotted to identify the value of k_{AB} and N_0 . The value of N_0 , the saturation concentration of modified sand is higher than the raw sand. Modified sand showed the value of saturation concentration of 12.627 mg/L compared the raw sand of 7.3319 mg/L (**TABLE 1**).

TABLE 1: Fixed-bed model constant for ammonia adsorption using modified and raw sand

	Thomas model		
	$K_t/L.min^{-1}mg^{-1}$	q_0/mgg^{-1}	R^2
Modified sand	0.00475	16.722	0.962
Raw sand	0.00886	4.8644	0.962
	Bohart-Adam model		
	$K_{AB}/L(mg.min)^{-1}$	N_0/mgL^{-1}	R^2
Modified sand	0.0056	12.627	0.979
Raw sand	0.0041	7.3319	0.991
	Yoon and Nelson model		
	k_{YN}/min^{-1}	$t_{0.5}/min$	R^2
Modified sand	0.073	59.560	0.985
Raw sand	0.089	24.1124	0.962

Principally, the model by Yoon and Nelson estimates the possible decrease of adsorption rate which is directly proportional to its adsorption action. This model can be expressed as the following **Equation 3**:

$$\ln \frac{C}{C_0 - C} = k_{YN} t - t_{0.5} k_{YN} \quad \text{Equation 3)}$$

Where, k_{YN} (1/min) is the rate of constant velocity and $t_{0.5}$ (min) is the breakthrough curve for 50% of ammonia being adsorbed by adsorbent.

Regeneration

The results from the first regeneration using 1.0 M NaCl at pH 12 (NaOH

solution adjusted) indicate that 1.14 BV of NaCl solution is sufficient for ammonium elution from modified sand as shown in **FIGURE 2**. The ability of the modified sand to be reused was determined by regeneration studies which found that the mean percentage removal of ammonia during adsorption studies was 88.63% with the highest percentage removal being 97.58% during the first interval.

Statistical data of Mann-Whitney test gave the value of $P=0.149$, which was higher than 0.05, suggesting that there is no significant difference in percentage removal ammonia during initial and desorption studies. Thus, the chemically modified sand has the ability to be reused. **FIGURE 3** shows the different percentage of ammonia removal during initial and desorption studies:

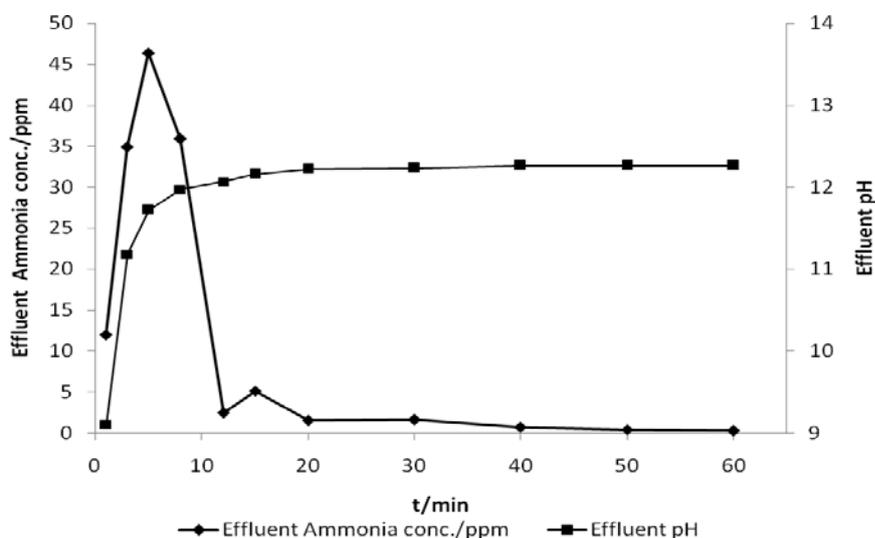


FIGURE 3: Ammonia concentration (ppm) and pH of effluent solution during desorption process

Regeneration studies using raw sand showed a trend of increasing ammonia adsorption. The raw sand was capable of removing ammonia at an average of 90.39% compared to 53.41% during the initial studies. The same results were obtained during a study of adsorption of ammonia using zeolite clinoptilolite. The increase in adsorption rate of ammonia may be due to the presence of organic constituents that reduce the surface tension of liquid phase and thus allow increasing entry of liquid phase into the adsorbent pore (Rozic *et al.*, 2000).

Conclusion

Chemically surface modified sand is able to remove ammonia in aqueous solution more efficiently as opposed to raw sand. In addition, it can also be reused after regeneration process. Thomas model showed modified-sand had a maximum adsorption 16.722 mg/g which is four folds than the maximum capacity of ammonia adsorption using the raw sand.

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