Adsorption of Ammonia Nitrogen in Aqueous Solution Using Zeolite A

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Abstract. The capacity of alternative adsorbents including rice straw, delignified rice straw and zeolite A for ammonia nitrogen removal from aqueous solution was investigated. The adsorption experiments were carried out in batch system with initial ammonia nitrogen concentration of 0.5 mg-N/l, 1000 ml ammonia nitrogen solution for 1 g of adsorbent. Experimental data indicated that rice straw and delignified rice straw cannot adsorb ammonia nitrogen. However, zeolite A provided rapidly adsorption capacity for ammonia nitrogen removal. The amount of ammonia nitrogen adsorbed by zeolite A was 0.256 mg/g at 1 minute after the experiment was initially conducted and slightly stable at 0.275 mg/g after 10 minutes. The adsorption experiments were carried out at 0.25, 0.5, 1.0, 2.0, 4.0, and 8.0 mg-N/l of ammonia nitrogen concentration. The results indicated that zeolite A had the adsorption capacity of 0.102, 0.294, 0.551, 1.153, 2.303, and 3.897 mg/g respectively at equilibrium time. The Langmuir and Freundlich adsorption models were applied to describe the equilibrium isotherms. Based on R^2, Freundlich model was more promising to represent the adsorption data than Langmuir model.

1. Introduction

Ammonia is widely used in the chemical industries as a bleaching agent in the production of fertilizers, plastics and explosives. The discharge of ammonia from wastewater treatment and industrial processes has been an important environmental issue and has been gained major worldwide concerns. Besides, the production of commercial fertilizers and other industrial applications, natural sources of ammonia include the decomposition of organic waste matters, human and animal wastes, and food scraps from aquatic lives. Ammonia does not only cause pollution of lakes and seas, but its excess level from the recommended limit dangerously harms aquatic lives and other animals. Therefore, it is necessary to remove ammonia from wastewater before discharge to environment.

Various methods have been employed to eliminate ammonia from wastewater including physical methods such as reverse osmosis and distillation, chemical methods such as chemical precipitation. However, these methods have some limitations and disadvantages. Reverse osmosis method requires large amount of energy input to provide hydraulic pressure driving water through the membrane.
Moreover, semi-permeable membrane can be easily damaged since suspended solids in wastewater are high. Distillation method requires large amounts of energy and water during the removal process. Chemical precipitation method requires working with corrosive chemicals, increasing operator safety concerns. Adsorption is one of the treatment processes which is a highly-efficient technique and has been gained considerable attention for treating ammonia from aqueous solution due to low initial cost, flexibility and simplicity of design. In recent years, most of attention has been considered and focused on the use of alternative adsorbents to replace the conventional adsorbents. Various unwanted plant wastes such as rice husk, water hyacinth and waste tea.

Rice straw is an agricultural waste, low cost, abundance, reliability, and availability. The surface of rice straw normally contains a lot of pores. Thus, rice straw has the potential to be used as an adsorbent. Zeolite A has been reported as an adsorbent used to remove cations from aqueous solution. Zeolite A can be synthesized from silica extracted from local rice straw using a simple extraction method. In this work, rice straw, delignified rice straw, and zeolite A was considered as an adsorbent for ammonia removal process and the adsorption isotherm was studied.

2. Experiment methods

2.1. Adsorbents Preparation and Characterization

The rice straw was boiled in distilled water at 80 °C for 3 hours and was extracted in acetone at 50 °C for 3 hours. Then it was placed in oven to dry 24 hours at 100 °C. The sample was milled to pass through a 8 mesh screen. The rice straw was immersed in 1.4% acidified NaClO₂ (250 ml), with pH adjusted to 4 by CH₃COOH, at 70 °C for 5 h to dissolve lignin. The delignified rice straw washed and dried. Silica extracted from rice straw was used as silica source for Zeolite A synthesis. 1 g of NaOH dissolved in 100 ml of distilled water was added to 4 g of silica (from rice straw). Then sodium silicate solution was heated at 80 °C until clear solution. 6 g of sodium aluminate and 3.4 g of NaOH dissolved in 100 ml of distilled water was stirred until clear solution. The sodium silicate solution was dropped into the mixture of sodium aluminate and stirred for 1 hour. The mixture was refluxed for 1 hour at 250 °C. Centrifugation at 2000 rpm was used to separate the precipitate and the liquid phase was removed by filtration. The precipitate was dried at 100 °C for 24 hour. Analysis by X-ray diffractometer (XRD) revealed major crystalline phases in Zeolite A.

2.2 Ammonia Nitrogen Adsorption

1 g of adsorbent was added in to 50 ml of ammonia solution (0.25, 0.5, 1.0, 2.0, 4.0, and 8.0 mg-N/l). The sample was stirred with speed 200 rpm at room temperature by various contact time. After stirring, the adsorbent was removed and ammonia nitrogen concentration was determined by spectrophotometer according to Phenolypochlorite Method [1]. The adsorption capacity was defined as the amount of ammonia nitrogen adsorbed onto unit mass of adsorbent (mg/g).

3. Results and Discussion

3.1 Adsorbents Characterization

The overall crystalline phases of zeolite A were determined by XRD measurement. The XRD pattern in Figure 1 indicated that the presence of peak with 2θ = 7.14, 10.12, 12.40, 16.06, 21.62, 23.94, 27.06, 29.90, and 34.14 respectively matching with the data base of zeolite A [2]. Therefore, it could be confirmed that the sample characterized by XRD was zeolite A.
Figure 1. The XRD pattern of zeolite A

Figure 2. Ammonia adsorption capacity of rice straw, delignified rice straw and zeolite A

3.2 Ammonia Nitrogen Adsorption

Ammonia nitrogen removal of different adsorbents is presented in Figure 2. Preliminary experiments were carried out to initially investigate the efficiency of rice straw, delignified rice straw, and zeolite A adsorbents for ammonia removal with initial ammonia nitrogen concentration of 0.5 mg-N/l, 1000 ml ammonia nitrogen solution for 1 g of adsorbent. The result showed that ammonia nitrogen concentration remained constant after adsorption process using rice straw and delignified rice straw adsorbents. However, the amount of ammonia nitrogen adsorbed by zeolite A was 0.256 mg/g at 1 minute after the experiment was initially conducted and slightly stable at 0.275 mg/g after 10 minutes. The high efficiency of zeolite A adsorbent is due to the high surface area of adsorption sites and the capacity to enhance the cation exchange with NH$_4^+$ from ammonia solution [3, 4].

3.3 Effect of Initial Concentrations

The adsorption experiments onto zeolite A adsorbent were carried out at 0.25, 0.5, 1.0, 2.0, 4.0, and 8.0 mg-N/l of ammonia nitrogen concentration considering removal capacity at 1, 3, 6, 10, 15, 20, 30, 60, 90, and 120 minutes, using 1 g/l of zeolite A adsorbent. The rate of ammonia nitrogen removal was very rapid during the initial 1 minute and remained nearly constant thereafter for every initial concentration due to the number of vacant sites on the adsorbent were much available to adsorb the adsorbate molecules in the solution. As shown in Figure 3, the results indicated that zeolite A had the adsorption capacity of 0.102, 0.294, 0.551, 1.153, 2.303, and 3.897 mg/g respectively at equilibrium time. Differences of initial ammonia concentration clearly showed that a gradual increase in the ammonia nitrogen concentration led to high adsorption capacity using zeolite A adsorbent since the more increased of ammonia nitrogen molecule in the solution, the higher driving force of ammonia nitrogen molecules adsorbed onto available sites of the zeolite A particles [5].

Figure 3. Effect of ammonia concentration on adsorption capacity using zeolite A adsorbent

Figure 4. Adsorption isotherm of ammonia nitrogen using zeolite A adsorbent
3.4 Adsorption Isotherms

The amount of ammonia nitrogen adsorbed onto unit mass of zeolite A adsorbent at equilibrium time \( (q_e) \) and the ammonia nitrogen concentration at equilibrium time \( (C_e) \) were calculated and correlated for the adsorption isotherm as shown in Figure 4. The correlation of adsorption capacity with equilibrium ammonia nitrogen concentrations after adsorption process conducted at different initial concentrations indicated that the ammonia nitrogen removal capacity of zeolite A increased with the increased of ammonia nitrogen concentration. The maximum capacity of ammonia nitrogen adsorbed onto unit mass of zeolite A adsorbent was about 3.897 mg/g.

The adsorption isotherms can be represented by several numerous theoretical models where Langmuir and Freundlich models have been commonly used to fit experimental data. The equilibrium experimental data for the adsorption of ammonia nitrogen from aqueous onto zeolite A adsorbent was compared using Langmuir and Freundlich models as shown in Figures 5. and Figures 6. respectively.

![Figure 5. Langmuir plots for adsorption of ammonia nitrogen onto zeolite A adsorbent](image)

![Figure 6. Freundlich plots for adsorption of ammonia nitrogen onto zeolite A adsorbent](image)

The model parameters are tabulated in Table 1. The Regression coefficients \( (R^2) \) were 0.9723 and 0.9917 for Langmuir and Freundlich model, respectively. Based on \( R^2 \), Freundlich model was more promising to represent the ammonia nitrogen adsorption data than Langmuir model. It is evident from these data that the adsorption sites occurring between zeolite A and ammonia nitrogen molecules are multilayer adsorption. Charge on the surface of zeolite A is a determining factor of ammonia nitrogen removal efficiency. Ammonium ion \( (\text{NH}_4^+) \) which has a positive charge will attract negative charge on the surface of zeolite A adsorbent [6].

![Table 1. Equation and R² value of Langmuir isotherm and Freundlich isotherm](image)
4. Conclusion

The presented study was carried out to investigate the adsorption capacity of rice straw, delignified rice straw, and zeolite A as alternative adsorbents for ammonia nitrogen removal. The experimental results clearly indicated that zeolite A was an effective adsorbent for the removal of ammonia nitrogen from aqueous solution. However, rice straw and delignified rice straw were not able to provide the adsorption capacity of ammonia nitrogen. The influence of ammonia nitrogen concentration had significant effect on the removal capacity of zeolite A. The rate of ammonia nitrogen removal was rapid after adsorption processes conducted due to the high surface area of adsorption sites and the capacity to enhance the cation exchange with $\text{NH}_4^+$ from ammonia solution. For Langmuir and Freundlich isotherm, the experimental results showed that the Freundlich model gives the best correlation coefficient value based on the obtained determination coefficients ($R^2$) of Freundlich model gives the highest value. Therefore, it employed to describe the adsorption sites between zeolite A and ammonia nitrogen are multilayer adsorption. Zeolite A provides the application potentials for effective ammonia nitrogen removal and may display the advantages of adsorption capacity for other hazardous pollutants from aqueous solution.

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