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**RESEARCH ARTICLE**

# Removal of ammonia nitrogen from rubber industry wastewater using zeolite as adsorbent

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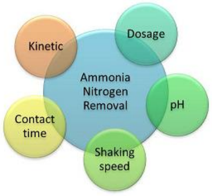
**Graphical abstract**

Zeolite



**Abstract**

Rubber industry wastewater contains high concentration of nitrogen, organic compound and another contaminant. If an elevated level of ammonia and nitrogen is discharged to water bodies, it could contribute to undesirable eutrophication and lead to death of some aquatic organisms. This experiment was designed to investigate the efficiency of zeolite as adsorbent in removing ammonia nitrogen from rubber wastewater. In this study, wastewater samples were collected directly from the wastewater discharge point of a manufacturer in Kluang, Malaysia. The optimum of dosage, pH, shaking speed and contact time for ammonia nitrogen removal were determined. Result indicated the optimum dosage, pH, shaking speed and contact time respectively was 4g, pH 7, 150 rpm and 90 minutes based to the adsorption of ammonia nitrogen by zeolite. The zeolite resulted in 87.2% of ammonia removal efficiency.

***Keywords*****:** Rubber wastewater, wastewater, adsorption, ammonia nitrogen, zeolite

## INTRODUCTION

In Southeast Asian countries, natural rubber is one of the most valuable agricultural product; however, the natural rubber processing industry has cause many environmental impact include water, air and odour pollutions (Watari *et al.*, 2016; Tekasakul & Tekasakul, 2006). Large quantities of wastewater were produced from the processing of raw natural rubber since it required huge amount of water for its operation (Rosman *et al.*, 2014). This wastewater contains high concentration of ammonia, nitrate, BOD, COD, total solids and phosphorus (Watari *et al.*, 2016; Rosman *et al.*, 2014). The discharge of this wastewater to water bodies could contribute to undesirable eutrophication and affect the aquatic life in the water (Nasir & Daud, 2014; Rosman *et al.*, 2013).

Several system have been developed to treat this wastewater such as anaerobic cum facultative lagoon system, anaerobic aerated lagoon system, aerated lagoon system and oxidation ditch system (Rosman *et al.*, 2013). Despite these systems being inexpensive, it required longer effluent treatment period, large space, odour problems, as well as high maintenance and operating costs (Rosman *et al.*, 2014; Rosman *et al.*, 2013).

Adsorption has been shown to be very effective for removal of pollutants from aqueous solutions (Adeleke *et al.*, 2016). Activated carbon (AC) is the most commonly used adsorbents due to its high capability to adsorb organic compound (Latiff *et al.*, 2016). Unfortunately, activated carbon is still considered an expensive adsorbent and the higher the quality, the superior the cost (Daud *et al.*, 2016; Bashir, *et al.*, 2014). This has led to the search for low cost materials. In the last twenty years, many investigators have studied the feasibility of inexpensive, commercially available materials, that are easy to regenerate and reutilized as many times as possible (Mohammed *et al.*, 2012).

Application of adsorbents based on zeolite has particular advantages over conventional methods that were applied for the industrial wastewater treatment. Natural zeolite is a highly porous material. It has natural negative charge which gives it the capacity to adsorb cations (Lakdawala & Patel, 2015). Zeolite also has high cation exchange capacity (CEC), and thus higher potential to be applied in the removal of ammonia nitrogen from wastewater (Mojiri, 2011). The use of natural zeolite for the removal of ammonia nitrogen is considered to be a competitive and effective treatment method due to its low cost and relative simplicity of application and operation (Huang *et al.*, 2010).

Natural zeolite (clinoptilolite) has a three-dimensional crystal structure and its typical cell formula is given as $Na_6[(A_lO_2)_6(SiO_2)_30]•_{24}H_2O$ (Ozdemir *et al.*, 2009). They contain exchangeable alkaline and alkaline-earth metal cations such as as $K^+$, $Na^+$, $Ca_2^+$ and $Mg_2^+$ that maintain charge neutrality. The microporous crystalline structure of zeolites enable the exchange ionic species with diameters that fit through the entry ports of internal zeolite framework, while larger species are excluded, giving rise to ion sieving properties that are exploited in a wide range of commercial applications (Calvo *et al.*, 2009).

This study aimed to investigate the effectiveness of zeolite as adsorbent size on removal of ammonia nitrogen on treatment of rubber wastewater. Optimum dosage, optimum pH, optimum shaking time and contact time was also study. The optimization of these features may significantly enhance the compentency of the process.

## EXPERIMENTAL

### Preparation of zeolite

The natural zeolite (clinoptilolite) was supplied by PT Prima Zeolita, Jakarta, Indonesia. Zeolite were milled and sieved to a size ranging from 106 to 150 µm. It was then dried in the oven at 105°C for 24 h to remove excess moisture, and then kept in a desiccator (to exclude atmospheric moisture) until tested. Zeolite materials were characterized by X-ray fluorescence spectroscopy (XRF), scanning electron microscope (SEM).

### Wastewater sampling

Wastewater was collected from discharge point of a plant located in natural rubber factory at Kluang, Johor, Malaysia. The samples were immediately transferred to the laboratory prior to being preserved in a refrigerator at a temperature of below 4 °C to avoid further biodegradation. The characteristics of the sampled wastewater were analyzed according to the Standard Methods for Examination of Water and Wastewaters (APHA, 2012).

### Adsorption studies

Batch experiments were conducted using the batch method to determine the range of the process variable which includes dosage, pH, shaking speed and contact time. Each of the process variables that require optimization was investigated and monitored separately. Experiment performed by using zeolite as a media and 100mL of natural rubber wastewater in a 250mL Erlenmeyer flask. The flask lid was wrapped with laboratory film (Parafilm M, USA) to ensure proper agitating process. The prepared flask was agitated with orbital shaker (Sartorius, Germany). Then the flask was removed and allowed to settle a bit before the supernatant was withdrawn for analysis of ammonia nitrogen (Nasir & Daud, 2014).

### Adsorption kinetic

In order to investigate the adsorption of ammonia nitrogen on the surface of zeolite, different kinetic models are used to examine the controlling mechanism of adsorption process. In this study, pseudo-first-order kinetic model and pseudo-second-order kinetic model are investigated to find the best fitted model for the experiment.

## RESULTS AND DISCUSSION

### Characteristics of adsorbent

The composition of zeolite was analyzed using X-ray Fluorescence (XRF), as shown in Table 1. Silica ($SiO_2$) and alumina ($Al_2O_3$) is also the main compound zeolite, respectively 64.5% and 15%. Zeolite was characterized by poor sodium and magnesium content and higher calcium and potassium content (Katsouet al., 2011). Figure 1 exhibits the microstructure of zeolite determined by means of SEM. Zeolite is characterized by a rough texture with opened cavities and a three dimensional framework structure composed of $Al_2O_3$ octahedra and $SiO_2$ tetrahedra (Lim et al., 2016; Jin et al., 2014).

**Table 1** XRF analysis data of zeolite.

| Formula | Concentration |
|---|---|
| Original (g) | 7 |
| Added (g) | 3 |
| SiO2 | 64.5 % |
| Al2O3 | 15% |
| K2O | 3.55% |
| CaO | 3.23% |
| Fe2O3 | 0.94% |
| C | 1% |
| Na2O | 0.8% |
| MgO | 0.7% |
| TiO2 | 0.16% |
| SrO | 0.12% |

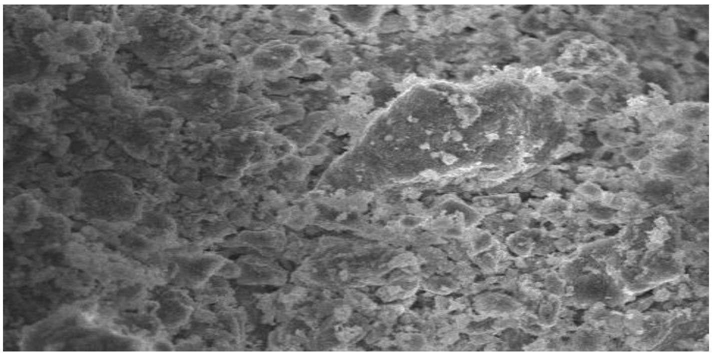


**Fig. 1** Morphology of zeolite.

According to Ismail et al., (2013) zeolites naturally occurring crystalline aluminosilicate that have a three-dimensional structure; aluminum, silicon and oxygen which are arranged in a regular structure of ($SiO_4$) and ($AlO_4$) tetrahedral units that form a framework with small pores (also called tunnels, channels or cavities) of about 0.1 to 2 nm diameter running through the material. In these small channels, solid, liquid, and gaseous substances can be trapped (Ismail, *et al.*, 2013).

### Chemical Analysis of Natural Rubber Wastewater

The photodegradation efficiency was calculated using the Eq. (3). Table 2 shows the characteristics of the wastewater as follows $BOD_5$ 3350, COD 5260 mg/L, suspended solids 500 mg/L, ammonia nitrogen 55 mg/L, colour 345 Pt.Co, turbidity 87 NTU and pH 9.3. These values are high as compared to Department of Environment Malaysia; Environmental Quality (Industrial Effluents) Regulations 2009 under standard A and standard B (Mokhtar *et al.*, 2015). Treatment of this wastewater is required before its discharge into any surface water body. On the other hand, the reading of heavy metals as shown in Table 2 is below the allowed standard.

**Table 2** Characteristics of natural rubber wastewater.

| Characteristics | Unit | Value |
|---|---|---|
| Biological Oxygen Demand (BOD) | mg/L | 3350 |
| Chemical Oxygen Demand (COD) | mg/L | 5260 |
| Total Suspended Solids | mg/L | 500 |
| Ammoniacal Nitrogen | mg/L | 55 |
| Color | Pt.Co | 345 |
| Turbidity | NTU | 130 |
| Zinc | mg/L | 0.266 |
| Iron | mg/L | 0.08 |
| Cu | mg/L | 0.05 |
| pH | | 9.3 |

## Adsorption studies

### Effect of dosage

Dosage is a significant factor in investigating the quantitative uptake of pollutants. The effect of adsorbent dosage (varying from 0 g to 6.0 g) on the percentage removal of the ammonia nitrogen is presented in Figure 2. The ammonia nitrogen removal efficiencies increase with the increase of the dosage from 0.5 to 4 g. The best result obtained was 4g of zeolite dosage with 79.4 % removal efficiency.

Thereafter, further increment in adsorbent dosage did not exert an appreciable increase in the removal efficiency because almost all ammonia nitrogen in natural rubber wastewater were adsorbed when the adsorbent dosage was increased to 4.5 g. Rapid increase in adsorption with the increase in adsorbent amount can be attributed to greater surface area and availability of more adsorption sites (Daud *et al.,* 2017; Rida *et al.,* 2013).

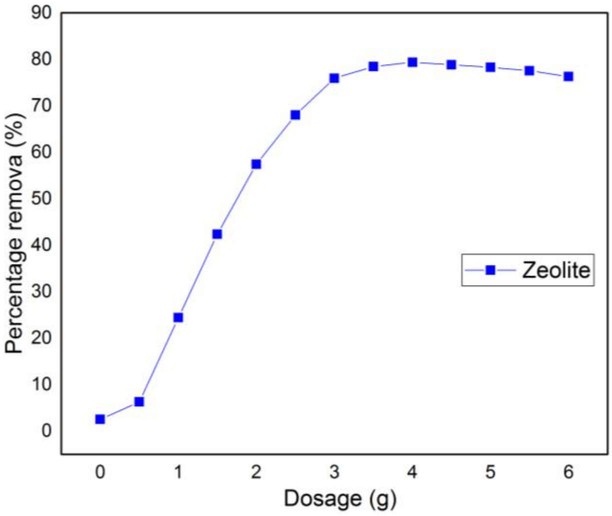


**Fig. 2** Effect of dosage on adsorption.

### Effect of pH

The initial pH of the natural rubber wastewater is an important parameter, which can control the adsorption process, particularly the adsorption capacity. Figure 3 show the effect of pH values ranging between 2 to 12 for removal of ammonia nitrogen using zeolite as adsorbent. From this study, it is shown that as solution pH increase, the removal efficiency of ammonia nitrogen increases gradually and reaches a maximum value of 81.6% at pH 7. When pH increases to 9, the removal efficiency starts to decrease. This finding tallies with the observation other researcher (Huang *et al.,* 2010).

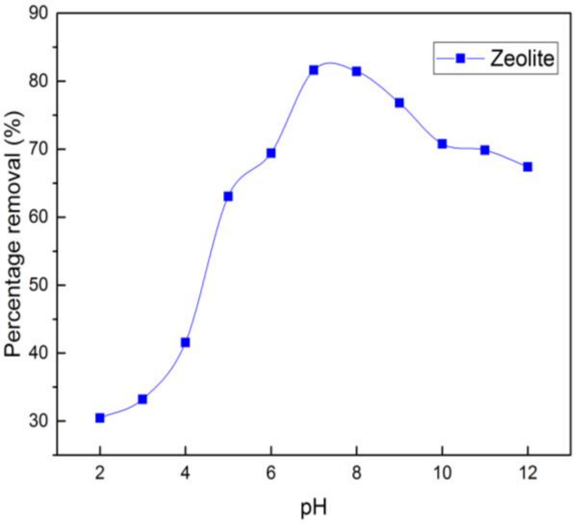


**Fig. 3** Effect of pH on adsorption.

According to Huang *et al.,* (2010) this behavior can be clarified by the fact that at pH values above 8 partial dissolution of the natural zeolite occurs, and it is also likely that $NH_4^+$ is converted into $NH_3$ specimen. Although, at pH values below 8, the $NH_4^+$ ion concentration in solution rises when pH decreases which results in a decline towards removal efficiency, as the $H^+$ ion concentration subsequently rises with the decrease in pH and intensifies the competition for exchange sites.

### Effect of shaking speed

Shaking speed is an important parameter in adsorption phenomena since it influences the distribution of the solute in the bulk solution and the rate of formation of the external boundary film (Daud *et al.,* 2017; Rida *et al.,* 2013). Figure 4 shows the percentage removal of ammonia nitrogen using zeolite at different shaking speed (50, 100, 125, 150 and 175rpm). From the Figure 4 it is observed that optimum shaking speed obtained from the experiment was 150 rpm with the removal efficiency ammonia nitrogen of 81.0%

The increase in percentage of removal can be explained by the fact that increasing shaking speed reduced the film boundary layer surrounding of particles, thus increasing the external film transfer coefficient, and hence the percentage ammonia nitrogen removal (Nandi *et al.,* 2009).

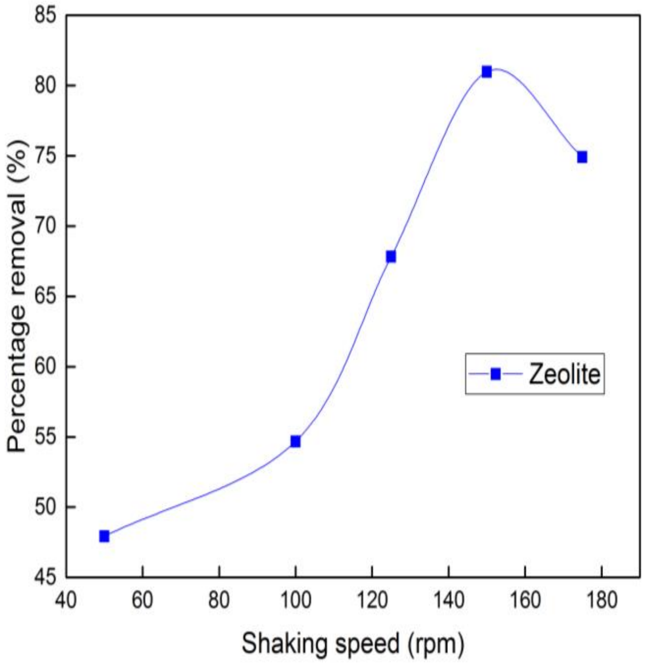


**Fig. 4** Effect of shaking speed on adsorption.

### Effect of contact time

The effect of contact time on the percentage removal of ammonia nitrogen is presented in Figure 5. The effect was studied using 100 mL of natural rubber wastewater, 3 g of ammonia nitrogen, 150 rpm of shaking speed and contact time varied from 0 - 300 minutes. From Figure 5 it can be seen that ammonia nitrogen was removed significantly in the first 5 min. After 5 min, the removal of ammonia nitrogen increases until it reached the equilibrium which is 87.2%. From the result obtained, the adsorption of ammonia nitrogen onto zeolite reached the equilibrium after shaking for 100 minutes.

This phenomenon occurs because there are ample of empty surface sites available for adsorption during the early stage and after some time the remaining empty surface sites are difficult to be occupied because of the repulsive force between the solute molecules on the solid surface and in bulk phase (Daud *et al.,* 2018).

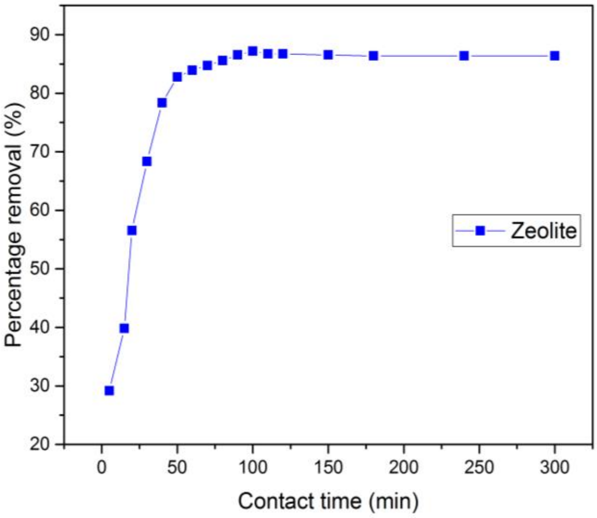


**Fig. 5** Effect of contact time on adsorption.

## Kinetic studies

Adsorption kinetic models were applied to the experimental data in order to analyze the rate of adsorption and possible adsorption mechanism of ammonia nitrogen unto zeolite. The kinetic models applied in this study are the pseudo-first order and pseudo-second order.

Pseudo-first-order kinetic model used to assumed that the rate of solute uptake with time was directly proportional to difference in saturation concentration and the adsorbed amount (Nandi *et al.*, 2009). The pseudo-first order kinetic model equation is expressed as (Lagergren, 1898):

$$\log(q_e - q_t) = \log q_e - \left(\frac{K_I t}{2.303}\right) \qquad (1)$$

where $q_t$ and $q_e$ are the amounts of ammonia nitrogen adsorbed at time *t* and at equilibrium in (mg/g), respectively. $K_I$ is the pseudo-first order adsorption rate constant ($\text{min}^{-1}$). The slope and intercept of the plots of log ($q_e - q_t$) versus *t* were used to determine the rate constant ($K_I$) and $q_e$, and the values are show in Table 3.

**Table 3** Kinetic model's parameter for ammonia nitrogen adsorption onto zeolite.

| Parameter | | Ammonia nitrogen |
|---|---|---|
| Experiment (Exp) | $q_e$, exp (µg/g) | 1.76 |
| Pseudo-First-Order | $K_1$ (1/min) | 0.0310 |
| | $q_e$,cal (µg/g) | 60.0 |
| | $R^2$ | 0.6386 |
| Pseudo-Second-Order | K2 (g/(µg.min) | 0.1031 |
| | $q_e$,cal (µg/g) | 1.78 |
| | $R^2$ | 0.998 |

From Table 3, it is seen that the pseudo-first order equation did not provide a good fit to the experimental data as can be seen from the low regression ($R^2$) values of 0.6386. The pseudo-second order kinetic model is based on the assumption that chemisorption is the rate determining step and is given as (Ho & McKay, 1998):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (2)$$

where $k_2$ is the equilibrium rate constant of pseudo-second order adsorption (g/mg min). The values of qe and $k_2$ were calculated from the slope and intercept of the linear plot of t/qt against t and the values are show in Table 3. From Table 3, it is shown that the pseudo second order provided a good fit to the experimental data of adsorption of ammonia nitrogen from natural rubber wastewater. This is indicated by the high values of their linear regression ($R^2$) close to 1. The high values of $R^2$ means that the adsorption kinetics of the parameter is well defined by the model (Bashir *et al.*, 2014).

From Table 3, it can be deduced that the maximum adsorption capacities ($q_e$) determined from the pseudo-second-order equation was closed to the experimental value. From the value obtained, it can be concluded that the pseudo-second-order kinetic model gave a good correlation for the adsorption of ammonia nitrogen onto the zeolite.

## CONCLUSION

From this study, it is proven that the zeolite is a low-cost and environmentally friendly material capable to remove ammonia nitrogen with more than 80% efficiency from natural rubber wastewater. The kinetics data was best described by pseudo-second-order kinetics model as the $R^2$ was closed to unity which was 0.998. However, further research is necessary to ascertain the effectiveness of the zeolite for the removal of other contaminants in natural rubber wastewater such as suspended solids, COD, and others.

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