Ammonia Removal from Aqueous Solution Using Organic Acid Modified Activated Carbon

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Abstract: The study was conducted to identify the potential use of organic acid modified activated carbon (AC-RCOONa) to remove ammonia from an aqueous solution using a batch and fixed-bed column adsorption. The optimum conditions for adsorption in the batch study occurred at pH range of 8 to 9 and contact time of 30 min. The Langmuir isotherms corresponded slightly better than Freundlich isotherm for both organic acid modified activated carbon (AC-RCOONa) and pristine activated carbon (AC). The Langmuir adsorption capacities for ammonia on AC-RCOONa and pristine AC were 19.34 mg/g and 4.50 mg/g respectively. The overall rate of the ammonia adsorption processes onto AC-RCOONa appears to be dominated by chemisorptions process. Fixed bed column adsorption indicated the higher performance of AC-RCOONa for ammonia removal compare to pristine AC in terms of chemical adsorption (for the first 40 minutes) and biological treatment (after 100 minutes). Ammonia removal performance of regenerated AC-RCOONa was comparable with fresh AC-RCOONa and better than pristine AC for the first 40 minutes of breakthrough time.

Key words: Ammonia removal • Modified activated carbon • Adsorption

INTRODUCTION

Nitrogen compounds such as ammonia, nitrite and nitrate are often present in different types of waters and wastewater can end up in lakes, rivers and drinking water reservoirs with effluent discharges. 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 [1]. Ammonia removal from water and wastewater are important in the alleviation of environmental problems, including eutrophication, corrosion and fouling [2]. High concentration of ammonia nitrogen in drinking water or industrial water is a potential cause of pipe corrosion and they complicate the chlorination process due to formation of chloramines. Chloramines can severe damage to human health, are toxic for fish and can deteriorate taste and odor of water.

Various studies to remove ammonia in water by adsorption methods have been carried out [3-9]. Among the adsorbents for ammonia removal are clay and zeolite [2, 9], limestone [6] and carbon-zeolite composite [10]. Activated carbon (AC) has been known as an alternative to biological and physicochemical methods in wastewater treatment due to their good adsorptive ability [11]. AC is unique and versatile adsorbents because of their extended surface area, micro-porous structure, high adsorption capacity and high degree of surface reactivity [12]. Despite the usefulness of AC as adsorbent in wastewater treatment, its utilization has been restricted due to costly maintenance [13]. AC also does not have enough adsorption capacity for ammonia due to their non-polar surfaces, which causes poor interactions between some of the polar substances [5, 14-15]. Surface modification is recognized as an attractive approach for enhancement of AC adsorption properties [16].
In general, the surface modification of AC is carried out after the activation step. The modification can be categorized into three classes: chemical modification, physical modification and biological modification. The chemical modification may further be divided into two broad groups, those resulting in acidic and basic surface. The third type of chemical modification is the surface impregnation of AC with active metals and their oxides. It is well known that depending upon the presence on the surface functional groups; the AC surface can show acidic, basic or neutral behaviour. For the removal of heavy metals from water, acidic functional groups (i.e., oxygen functional groups containing proton donors) on carbon surfaces have been examined and found to be highly favourable because metal ions have a tendency to form metal complexes with the negatively charged acid groups. One of the chemical modification methods is attachment of carboxylic acid functional group on AC surfaces [17]. The purpose of this study is to compare the adsorption properties of carboxylic acid modified AC and pristine AC in terms of ammonia removal.

**MATERIALS AND METHODS**

**Batch Adsorption Study:** Batch adsorption study can be divided into three parts starting with determination of optimum parameters, adsorption isotherm study and adsorption kinetic study. Batch adsorption experiment was conducted by placing a series of nine 250 ml conical flask each with 5 g adsorbent media and 100 ml synthetic leachate solution. This flask was then placed on an orbital shaker at 200 rpm for 120 minutes at 25°C (room temperature). All the mixture solution with adsorbent will then be filtered with 50 mm in diameter Whatman filter paper. The range of initial concentrations of ammonia was 685-735 mg/l throughout the study.

The effect of pH for ammonia removal was studied by adjusting the pH of solutions, in the range of 4-10 using 37% HNO$_3$ and 1 M NaOH. Optimum pH was obtained by the highest percentage of ammonia removal. Optimum contact time was determined by fixing in certain time intervals of the conical flasks were removed from the shaker one at a time after 1, 2, 5, 8, 10, 15, 20, 30, 45, 60 and 75 min. The optimum time was investigated from analysis concentrations of ammonia where no changes of concentration been noted after equilibrium time.

Dosage study was conducted by preparing series of the conical flask for two types of adsorbents; new composite adsorbent and conventional activated carbon. This experiment was operated in optimum condition obtained from the optimum parameters test for pH and contact time. The final concentration of ammonia removal will then be compared for fresh organic acid modified activated carbon (AC-RCOOH), regenerated AC-RCOOH and bare activated carbon (bare-AC) as a control experiment.

Adsorption isotherm has been carried out based on the experiment of dosage study; by varying the amount of adsorbents. The most common models used for this isotherm study are Langmuir and Freundlich isotherms. The isotherm constants and least square's correlation coefficients ($R^2$) of both models were in comparison to determine the best of a fit isotherm model in this study. This isotherm study has been applied to three types of adsorbent; Rice husk composite adsorbent, activated carbon and regenerated rice husk composite adsorbent respectively.

Adsorption kinetic was studied based on four kinetic models; pseudo first-order, pseudo second-order, Elovich model and intra-particle model. Kinetic data were obtained from the determination of contact time at equilibrium. The kinetic constants and least square's correlation coefficients ($R^2$) of four models were in comparison to determine the best of a fit kinetic model in this study.

**Column Adsorption Experiments:** Columns used are made from polyvinyl chloride (PVC), 80 cm height and 10 cm of diameter. Modified and untreated sand was packed in columns. The weight of adsorbent added were 996 g, which is 700 ml of volume. Before being used in experiments, 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. Samples were collected at various time intervals and analyzed for ammoniacal nitrogen using the Nesslerization colorimetric method [18].

**Regeneration Studies:** The exhausted column was subjected to desorption to regenerate the composite adsorbent using a regeneration solution, which was composed of 1.0 M 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 determination of ammonia.
RESULTS AND DISCUSSION

The optimum pH for ammonia removal was at pH 8.9. For ammonia, the properties of ammoniacal nitrogen in aqueous solution explain the result; the existence of two types of elements, ammonia, NH₃, and ammonium ions, NH₄⁺. Therefore, the removal of ammonia is supposed to be higher at low pH and vice versa, due to the cation exchange mechanism in aqueous solution (Demir et al., 2002). However, ammonia removal dramatically decreases at pH < 5 because of H⁺ competition. COD components were contributed by organic acids in synthetic leachate, which can be in two forms: acidic (R- COOH) and basic (R- COO-) (Fig. 1).

**Adsorption Isotherm:** Adsorption isotherm was an equilibrium plotted of solid phase (qₑ) versus liquid phase concentration (Cₑ). Two isotherm models are Langmuir model with linear plotted 1/qₑ versus 1/Cₑ and the equation:

\[
\frac{1}{qₑ} = \frac{1}{qₘ} + \frac{1}{KₗqₘCₑ}
\]

Where qₑ is the equilibrium adsorbate concentration in solution, qₑ the maximum adsorption capacity and Kₗ is Langmuir constant in L/mg.

Freundlich model with linear plotted log qₑ versus log Cₑ shown in the following equation:

\[
\log qₑ = \log K_f + \frac{1}{n} \log Cₑ
\]

Where K_f is, roughly, an indicator of the adsorption capacity and 1/n is the adsorption intensity. A linear form of the Freundlich expression will yield the constants K_f and 1/n.

The results indicated that the removal of ammonia was conorming more to Langmuir model due to highest R² value for all adsorbents used (Table 1). Langmuir adsorption isotherm model describes that the surface as homogeneous assuming all the adsorption sites have the equal adsorbate affinity and that adsorption at one site does not affect adsorption at an adjacent site [19]. This model based on the assumption made on maximum adsorption, which is related to monolayer formation of adsorbate onto adsorbent surfaces involving chemically adsorption process; i.e. cations exchange.

![Fig. 1: pH effect on ammonia removal](image1)

![Fig. 2: Langmuir isotherm plot for ammonia adsorption onto AC-RCOONa](image2)

<p>| Table 1: Langmuir and Freundlich isotherm constant for adsorption of ammonia onto AC-RCOONa and pristine AC. |
|-------------------------------------------------|-------------------------------------------------|</p>
<table>
<thead>
<tr>
<th>AC-RCOONa</th>
<th>Pristine AC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Langmuir</strong></td>
<td></td>
</tr>
<tr>
<td>R²</td>
<td>0.9951</td>
</tr>
<tr>
<td>Kᵢ (l/g)</td>
<td>0.00104</td>
</tr>
<tr>
<td>Q (mg/g)</td>
<td>19.34</td>
</tr>
<tr>
<td><strong>Freundlich</strong></td>
<td></td>
</tr>
<tr>
<td>R²</td>
<td>0.9843</td>
</tr>
<tr>
<td>Kᵢ (mg/g)(mg/l)ⁿ</td>
<td>0.0269</td>
</tr>
<tr>
<td>n</td>
<td>1.0928</td>
</tr>
</tbody>
</table>

The comparison of Langmuir constant, i.e. maximum adsorption capacity, qₑ, indicated that higher value noted for organic acid modified AC (19.34 mg/g) compared to bare activated carbon (4.50 mg/g). These qₑ values were derived from the intercept of the linear graphs obtained. The differences between these two adsorbent media were probably due to the higher cation exchange mechanism towards organic acid modified AC during ammonium adsorption compared to bare activated carbon (Fig. 2). It is found that the coefficients of determination obtained (R²) from the Freundlich model were lower than Langmuir model as given in Table 2. Freundlich isotherm model is widely used but does not provide the information on the monolayer adsorption capacity (Fig. 3).
Table 2: Kinetic models constants for adsorption of ammonia onto AC-RCOONa

<table>
<thead>
<tr>
<th>Kinetic Model</th>
<th>$R^2$</th>
<th>$k_1$ (min$^{-1}$)</th>
<th>$q_e$ (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo first order</td>
<td>0.7611</td>
<td>0.1186</td>
<td>2.9276</td>
</tr>
<tr>
<td>Pseudo Second order</td>
<td>0.9800</td>
<td>0.0435</td>
<td>3.075</td>
</tr>
<tr>
<td>Elovich</td>
<td>0.9003</td>
<td>0.5267</td>
<td>1.6458</td>
</tr>
<tr>
<td>Intra-particle</td>
<td>0.8433</td>
<td>0.2023</td>
<td>2.3988</td>
</tr>
</tbody>
</table>

Fig. 3: Freundlich isotherm plot for ammonia adsorption onto AC-RCOONa

Fig. 4: Effect of contact time on ammonia removal

**Kinetic Study:** Figures 4 show the effect of shaking time on the ammonia adsorption by the organic acid modified AC. This figure clearly indicates that the uptake of ammonia increases with increasing shaking time and attains equilibrium after 20 minutes.

Adsorption kinetic was conducted to study the kinetic and adsorption mechanism of ammonia removal onto organic acid modified AC. In order to analyze the adsorption kinetics for these adsorbent, the pseudo first-order, pseudo second-order, Elovich models and intra-particle kinetic models were used to analyze the experimental data.

The pseudo first-order linear equation, describes the kinetics of the adsorption process as follows [20];

$$\ln(q_e - q_t) = \ln(q_e) - k_1t$$

Where $q_e$ (mg/g) and $q_t$ (mg/g) are the amount of adsorbate adsorbed at equilibrium and at $t$ time respectively and $k_1$ is the rate constant of this first order model.

Pseudo second-order equation can be written in linear form as follows [21];

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

Where the slope and intercept of $(t/q_t)$ versus $t$ are used to calculate the pseudo second-order rate constant, $k_2$ and adsorbate adsorbed at equilibrium, $q_e$. This model used to explain the probability of overall adsorption properties was suited to chemically adsorption mechanism. Chemically, adsorption process usually involves monolayer adsorption because of specific bonding between adsorbates and the surface of adsorbent [22].

Elovich equation has been assumed that the real media surfaces are heterogeneous base on their energy, which used to explain the pseudo second-order kinetic [10]. The linear equation form as follows;

$$q_t = \frac{1}{\beta} \ln(\alpha \beta) + \frac{1}{\beta} \ln t$$

Where $\alpha$ and $\beta$ are the Elovich coefficients representing initial sorption rate and desorption constants, respectively.

The intra-particle diffusion model used to show the adsorptions are by intra-particle mixing. Linear equation for intra-particles diffusion model as follows;

$$q_t = k_i t^{0.5} + c$$

Where $k_i$ is the intraparticle diffusion constant and $c$ is intercept.

The kinetic study results show that the adsorption of ammonia was suited to pseudo second-order kinetic model by possessing the highest $R^2$ (0.98) (Table 2).
This strongly suggests that the ammonia uptake process was mainly due to chemisorptions or ion exchange process. Organic acids attached on the surface of the AC act as ion exchange sites and ion exchange process occurs as follows;

\[
\text{AC-RCOOH} + \text{NaOH} \rightleftharpoons \text{AC-RCOONa} + \text{H}_2\text{O} \\
\text{AC-RCOONa} + \text{NH}_4^+ \rightleftharpoons \text{AC-RCOONH}_4^- + \text{Na}^+
\]

**Fixed Bed Adsorption Study:** Continuous ammonia adsorption tests with organic acid modified AC were conducted by fixed bed column adsorption.

Ammonia removal using AC-RCOONa was higher than the pristine AC with AC-RCOONa successfully removed ammonia ranged from 20.04 % to 94.30 % for the first 40 minutes of breakthrough time (Figure 5) as opposed to the removal of ammonia ranged from 10.13 % to 64.05% for the latter. Ammonia removal gradually increases after 40 minutes of breakthrough time and attained constant removal at 56.7 % after 100 minutes for AC-RCOONa. However, ammonia removal for pristine AC and regenerated AC were drop as low as 5.78 % and slightly increase and attained constant at 28 % after 160 minutes of breakthrough time. These results indicated the higher performance of AC-RCOONa for ammonia removal compare to pristine AC in term of chemical adsorption (for the first 40 minutes) and biological treatment (after 100 minutes). High ionic strength and extremely alkali (1M NaCl at pH 12) in regeneration solution during desorption process was reduced microbiological activity on AC-RCOONa as lower ammonia removal indicated by regenerated AC-RCOONa after 40 minutes of breakthrough (Fig. 6). However, the ammonia removal performance of regenerated AC-RCOONa was comparable with fresh AC-COONa and better than pristine AC for the first 40 minutes.

**CONCLUSION**

AC-RCOONa was able to remove ammonia in aqueous solution more efficiently as opposed to pristine AC. results of isotherm study show that ammonia Langmuir adsorption capacity for AC-RCOONa (19.34 mg/g) was higher than pristine AC (4.50 mg/g). The kinetic adsorption study found that the adsorption of ammonia onto AC-RCOONa obeyed the pseudo-second-order model \(R^2 = 0.98\). These results reveal that chemical adsorption or ion exchange mechanism have been dominant in ammonia adsorption on AC-RCOONa. Continuous ammonia adsorption test using fixed bed column indicated that ammonia removal for AC-RCOONa was higher for the first 40 minutes of breakthrough time and remain constant at higher removal after 100 minutes of breakthrough time compare to pristine AC. Column efficiency for ammonia removal was slightly lower when regenerated AC-RCOONa was used than the fresh AC-RCOONa but higher than pristine AC.

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**REFERENCES**


