Adsorption of Ammonium Ion Using Zeolite, Chitosan, Bleached Fibre and Activated Carbon

N N Safie, A Y Zahrim*, M Rajin, N M Ismail, S Saalah, S M Anisuzzaman, A D Rahayu, H Huslyzam, R Jennisha, T T H Calvin
Faculty of Engineering, Universiti Malaysia Sabah, Jalan UMS, 88400 Kota Kinabalu
E-mail: zahrim@ums.edu.my

Abstract. Several materials have been studied for the adsorption of ammonium ion from synthetic solution. Zeolite is having the highest adsorption capacity (3.160 mg/g) with fast reaction time followed by chitosan (2.5770 mg/g). Activated carbon derived from Tarap (Artocarpus odoratissimus) and rice husk shows better performance than the low cost bleached fibres.

1. Introduction
Ammonium is the most basic form of nitrogen and commonly present in the waterways due to the discharge from urban runoff, industrial discharges and untreated sewage discharge[1]. Several pollution cases due to NH$_4^+$ has been recorded in Malaysia river [1] indicating the needs for proper treatment. To minimise the discharging of ammonium ion into the river, gross pollutant trap can be coupled with specific adsorbent for ammonium ion removal. Agricultural waste has been used as low-cost bio sorbents since it is low cost, renewable, wide range of sources as well as contain functional groups such as carboxyl group and hydroxyl group that bind with contaminants during adsorption [2].

Biopolymer such as chitosan has being used because it is natural, biodegradable, reusable and non-toxic polysaccharide from crustacean shells such as shrimps and crabs [6]. Fibers are known to be rich in lignocellulosic materials that comprised of three main components namely lignin, cellulose and hemicellulose that contain functional groups responsible for the adsorption process to occur [7]. In this study, zeolite, chitosan, bleached fibres from coconut coir, water hyacinth, empty fruit bunch (EFB) and activated carbon from rice husk and tarap (Artocarpus odoratissimus) skin have been tested to remove ammonium ion by adsorption.

2. Materials and methods
Zeolites and high molecular weight chitosan were purchased commercially. Banana stems, coconut coir, water hyacinth, tarap skin and rice husk were obtained from Kota Kinabalu, Salut Commercial Centre, Tuaran river, Papar and Kilang Padi Sri Keranahan, Kota Belud respectively. Activated carbon from rice husk and tarap skin were prepared according to the method by Binanipuram and Kerala [8] and Wang et al. [9] respectively. Zeolite, high molecular weight chitosan, rice husk activated carbon, tarap skin activated carbon, bleached EFB, bleached water hyacinth, bleached coconut coir and...
bleached banana stem are denoted as zeolite, HMWC, RHAC, TSAC, EFB, WH, CC and BS respectively.

The NH₄Cl stock solution was prepared from a 99.5% pure anhydrous solid by dissolution in distilled water. NH₄Cl solution with a concentration of 0.05 mg/g was used for the batch adsorption experiment. The samples were then analysed using it was analysed using Jasco UV-vis 650 Bio-spectroscopy with maximum wavelength of 425 nm. Prior to analysis, Nessler reagent was used for NH₃-N compound detection by following the standard USEPA Nessler Method No.8038. The concentration of ammonium ions adsorbed at equilibrium was calculated using Equation (1).

\[ q_e = \frac{(C_o - C_e)V}{W} \]  

where \( q_e \) (mg/g), \( C_o \) (mg/L), \( C_e \) (mg/L), \( V \) (dm³) and \( W \) (g) are the concentration of ammonium ions adsorbed at equilibrium, liquid-phase concentrations of initial adsorbate and equilibrium, volume of solution and mass of activated carbon used, respectively.

3. Results and Discussions

As shown in Figure 1 is the concentration of NH₃-N being adsorbed by BS, EFB, WH, CC, zeolite and CC against time in minute. Based on the results summarized in Table 1, zeolite has the highest adsorption capacity followed by HMWC, RHAC, TSAC, BS, EFB, CC and the lowest was WH with values of 3.160 mg/g, 2.577 mg/g, 2.269 mg/g, 0.409 mg/g, 0.317 mg/g, 0.258 mg/g and 0.018 mg/g respectively. Zeolite has reached equilibrium in 2 minutes. Research regarding the sorption kinetics studies that the ammonium ion removal using zeolite occurred very rapidly and equilibrium was reached within few minutes ranging between 10 min and 90 min[10][11]. High selectivity and reasonable adsorption capacity of zeolite can be attributed to their unique structural chemistry, for instance, Si/Al ratio, pore size and high specific surface area [12]. Natural zeolite used by Beebe et al. [13] recorded adsorption capacity of 5.02 mg/g but required longer time to reach equilibrium contact time. This behaviour may be ascribed to the quick utilization of the most readily available adsorbing sites of the zeolite used in this work that has contributed to fast diffusion and attainment of rapid equilibrium[10]. Also, the CEC of zeolite used in Beebe et al. [13] was higher 180–195 meq/100 g compared to CEC zeolite used in this work, 140 meq/100 g which explains that it can absorb more cation (NH₄⁺). MCW has higher adsorption capacity compared to bleached fibers and activated carbon and reached equilibrium in 1 minute. HMCW has high deacetylation degree and carries more positive charges that exhibit better performance in removing pollutants[14].

Activated carbon from rice husk and tarap recorded higher adsorption capacity compared to the bleached fibers but with longer time to reach equilibrium. The chemical and activation process has enhanced its porous structure and surface area which attributes to higher adsorption capacity as compared to raw bleached fibers[15]. TSAC has lower adsorption capacity since higher activation temperature was used, 800 °C compared to rice husk 300°C. The lower temperature biochar described by Gaskin et al.[16] was shown to have a higher degree of oxygen surface functional groups. The content of silica in most rice husk may greatly enhance the surface area of rice husk compared to tarap skin[17]. Bleached fibers used in this investigation namely BS, EFB, WH and CC with adsorption capacity 0.4085 mg/g, 0.3171 mg/g, 0, 0176 mg/g and 0.2577 mg/g respectively. Bleached fibers recorded the lowest NH₃-N adsorption capacity compared to activated carbon, zeolite and HMWC. Nevertheless, unbleached EFB done by Zahrim et al. [18] recorded higher adsorption capacity, 0.828 mg/g at the same initial concentration and 94-97 % NH₃-N removal when used as the medium in filtration [19].
Figure 1. Adsorption of ammonia nitrogen against time using BS, EFB, WH, CC, zeolite and HMWC

Table 1. Total time to reach equilibrium, adsorption capacity and comparison with other authors for zeolite, HMWC, BS, EFB, WH, CC, TSAC and RHAC

| Type (s) of adsorbent | Equilibrium contact time (min) | Adsorption capacity (mg/g) | Initial conc. (mg/L) | Ref. |
|----------------------|-------------------------------|---------------------------|----------------------|------|
| Zeolite              |                               |                           |                      |      |
|                      | 2                             | 3.160                     | 50                   | This study |
|                      | 60                            | 1–6                       | 100-500              | [20] |
|                      | -                             | 2.8                       | 200                  | [21] |
|                      | 2880                          | 5.03                      | 40                   | [13] |
|                      | 1440                          | 1.9                       | 10                   | [22] |
| HMWC                 | 1                             | 2.5770                    | 50                   | This study |
|                      | 180                           | 6.933                     | 7.35                 | [6]  |
| Bleached fibers      |                               |                           |                      |      |
| BS                   | 30                            | 0.4085                    | 50                   | This study |
| EFB                  | 10                            | 0.3171                    | 50                   | This study |
|                      | 40                            | 0.828                     | 50                   | [18] |
| WH                   | 30                            | 0.0176                    | 50                   | This study |
| CC                   | 20                            | 0.2577                    | 50                   | This study |
| Activated Carbon     | TSAC                          | 1.8750                    | 50                   | This study |
|                      | RHAC                          | 1.8154                    | 50                   | This study |
|                      | 24                            | 0.87 – 2.20               | 5                    | [17] |

4. Conclusion
The adsorption capacity of zeolite, high molecular weight chitosan, bleached fibers and activated carbon have been investigated. Zeolite recorded the highest adsorption capacity of 3.160 mg/g and reached equilibrium in two minutes. Carbon activation using KOH on tarap peels and rice husk may influence its porosity that contributed to higher adsorption capacity compared to bleached fibers.

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