

Adsorption study of Ammonia Nitrogen by watermelon rind

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Abstract. The utilization of fruit waste for low-cost adsorbents as a replacement for costly conventional methods of removing ammonia nitrogen from wastewater has been reviewed. The adsorption studies were conducted as a function of contact time and adsorbent dosage and it were carried out on four different adsorbents; fresh watermelon rind and modified watermelon rind with sodium hydroxide (NaOH), potassium hydroxide (KOH) and sulphuric acid (H₂SO₄). Adsorbents were tested for characterization by using zeta potential test and all samples shows negative values thus makes it favourable for the adsorption process. The batch experimental result showed that adsorption process is rapid and equilibrium was established within 40 minutes of contact time. The ammonia nitrogen removal rate amounted in range of 96% to 99%, and the adsorption capacities were in range of 1.21 to 1.24 mg/g for all four different types of adsorbents used.

1. Introduction

High levels of ammonia nitrogen (NH₃-N) in water can be toxic to some aquatic organisms and leads to eutrophication [1]. Hence, it is important to remove the NH₃-N from waterways and the traditional processes of it are nitrification de-nitrification [2], air stripping [3] and chemical precipitation [4]. However, extensive studies have been made to identify new economically feasible and environmentally friendly treatment alternatives, of which adsorption have received significant attention.

Adsorption is inexpensive, universal nature and ease of operation. Adsorption can remove soluble and insoluble organic pollutants due to its removal capacity may be up to 99.9% [5]. The use of fruit peels based adsorbent for removing various pollutants from wastewater offers many attractive features such as the outstanding adsorption capacity and the fact that these materials are low-cost, non-toxic and biocompatible[6]. Watermelon biomass can be categorised into three main components; the flesh, seed and rind. The flesh constitutes approximately 68% of the total weight, the rind approximately 30%, and the seeds approximately 2% [7]. In this study, watermelon rind was used as potential low-cost adsorbent. The skin of fully ripened watermelon contain approximately 20% cellulose, 23% hemicellulose, 10% lignin, 13% pectin, 7 mg/g silica and 12% silica free minerals[8].

Many studies have been conducted to investigate the ability of watermelon rind (WR) as an adsorbent and the results shows great rate of removal of various pollutants such as dye [9] and heavy

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metals [10]. Therefore, this study was intended to evaluate the effect of contact time and adsorbent dosage on the adsorption of $\text{NH}_3\text{-N}$ by using four different types of WR adsorbents; fresh WR, modified WR with sodium hydroxide (NaOH), potassium hydroxide (KOH) and sulphuric acid (H_2SO_4).

2. Materials and Methods

2.1 Preparation of the adsorbent

Watermelon rinds were collected from Kota Kinabalu area. The collected biomaterials were washed thoroughly using tap water and distilled water to remove any impurities such as soil or fertilizers that may exist on the surface of it. Next, the rind was cut into small pieces (around 1 to 2 mm^2) and dried in an oven at 40°C for 48 hours [11].

Watermelon rind was used as the raw material for the preparation of the chemically modified adsorbent. WR was chemically modified by pre-treatment with NaOH, KOH and H_2SO_4 solution in order to improve the capacity of ammonium (NH_4^+) ions uptake. WR with mass of 20g was treated in each of 1 L of NaOH solution (20 mmol/L), KOH solution (20 mmol/L) and of H_2SO_4 solution (20 mmol/L) respectively for 24 h [12]. Finally, the modified WR was dried in an oven at 40°C for 48 h.

2.2 Preparation of ammonia nitrogen solution

Ammonium chloride salt (NH_4Cl) with calculated weight and distilled water were used for the preparation of a stock $\text{NH}_3\text{-N}$ solution of 50 mg/L. The initial pH was adjusted to 7.0 using dilute solutions of NaOH (0.1 N) [13]. The pH of the $\text{NH}_3\text{-N}$ was constant throughout the experiments.

2.3 Characterization of adsorbent

Zeta potentials of the adsorbent were performed in three runs by using Malven model zetasizer 2010 zeta potential analyser.

2.4 Batch equilibrium studies

Batch equilibrium studies were carried out by adding 20g of watermelon rind adsorbent into 1000mL of ammonium nitrogen solution at room temperature for 40 minutes. Each experiment consisted of two runs and the average value from both experiments was taken. The effects of contact time and adsorbent dosage on the adsorption process for all four types of adsorbents were studied. All samples were adjusted to the optimum pH prior to the addition of the adsorbent. Sample solutions were withdrawn at certain intervals in order to determine the residual concentration by using UV-vis spectrophotometer with HACH Spectrophotometer DR2010 brand at maximum wavelength of 425 nm[14]. The amount of $\text{NH}_3\text{-N}$ adsorbed at equilibrium, q_e (mg/g) was calculated as followed:

$$t = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e (mg/L) are the liquid-phase concentrations of initial adsorbate and equilibrium, respectively. V is the volume of the solution (L) and W is the weight of the adsorbent (g).

2.5 Ammonia nitrogen ($\text{NH}_3\text{-N}$) analysis

The analysis was carried out using Nessler Method of HACH Spectrophotometer DR2010 Procedures Manual. A calibration graph was plotted in order to calculate the concentration of the residual.

3. Result and discussions

3.1 Characterization of adsorbent

3.1.1 Zeta potential of the adsorbent

The characterization of WR adsorbent was evaluated by using zeta potential and the results obtained at different pH conditions are shown in Figure 1. The unmodified and modified WR adsorbent exhibits negative zeta potential over the pH range from 4.9 to 7.0. The zeta potential values decrease significantly with increase of pH. Negative zeta potential values recorded by all four types of adsorbent should be favourable to the attraction between active sites and NH_4^+ ions [15]. Zeta potentials of unmodified or fresh WR were higher than those of modified WR with NaOH, KOH, and H_2SO_4 at different pH values. This indicates that fresh WR adsorbent has more active sites and able to adsorb more NH_4^+ ions than modified WR adsorbents do.

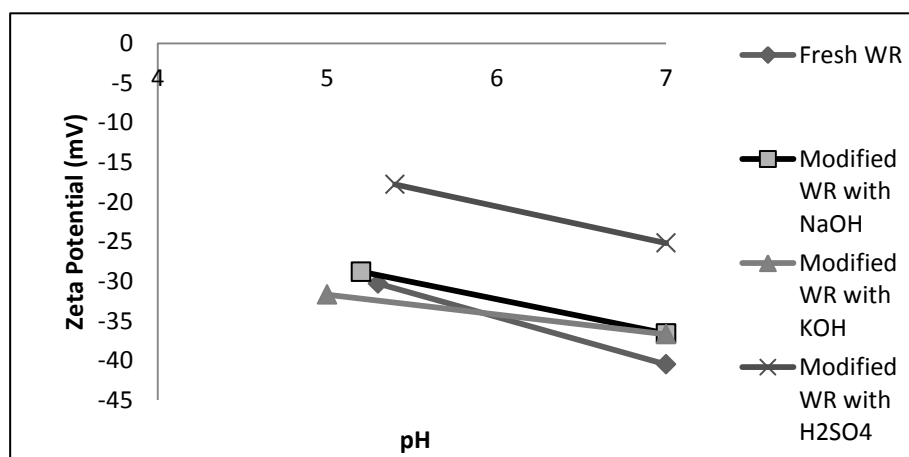


Figure 1. Zeta potentials of adsorbents

3.2 Effect of adsorbent dosage

The dependence of $\text{NH}_3\text{-N}$ adsorption on adsorbent dose was studied by varying the amount of adsorbent used (10g, 20g, 30g, 40g) while keeping initial concentration (50 mg/L) and pH value constant. Based on Figure 2, final concentration of $\text{NH}_3\text{-N}$ left in solution decreased from 1.2 mg/L to 0.4 mg/L as the mass of WR adsorbent increased from 10g to 20g. This indicates that the surface area and availability of adsorption sites increased as the adsorbent dose increased. However, for mass of adsorbent greater than 20 g, the NH_4^+ ions uptake decreased and final concentration left in solution were in range of 0.9 to 1.2 mg/L. This reduction may related to overlapping of adsorbent as the mass of adsorbent increased on which prevent good contact between the NH_4^+ ions and sorption sites[16] and thus decreasing the adsorption capacity of the adsorbent. It can be concluded that 20g of WR adsorbent is the optimum dosage for the adsorption process of $\text{NH}_3\text{-N}$ in this study.

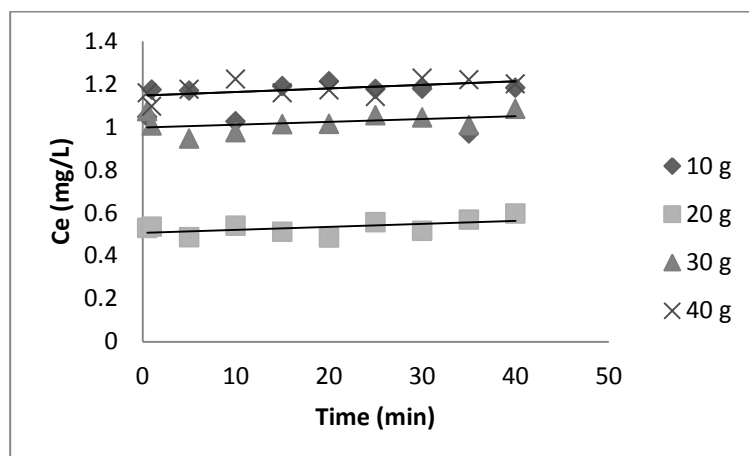


Figure 2. Effect of adsorbent dose on ammonia nitrogen adsorption

3.3 Effect of contact time

The evolution of the transfer ammonium ions from liquid phase to solid phase at certain time can be observed by studying the effect of contact time on adsorption capacity of adsorbent. Figure 3 and 4 shows the final concentration of adsorbate and the adsorption capacity along 40 minutes of contact time respectively. Based on the preliminary experiment results, the adsorption of $\text{NH}_3\text{-N}$ onto adsorbent is rapid and equilibrium is established within 40 min. Thus a contact time of 40 min was fixed for this study in order to optimize the contact times for the maximum uptake of ammonium ions.

Figure 3 shows a fast rate of ammonia nitrogen sorption during the contact time of adsorbent-adsorbate. However, fresh WR adsorbent record the lowest final concentration of $\text{NH}_3\text{-N}$ left in solution with values range from 0.4 to 0.6 mg/L compared to other three modified WR adsorbents (0.9 to 1.5 mg/L). The rate of $\text{NH}_3\text{-N}$ removal is higher in the beginning due to the fact that more active sites of adsorbent are available and gradual occupancies of active sites in later stage resulting slower rate of adsorption [10].

The adsorption capacity of fresh WR adsorbent was slightly higher compared to other three modified WR adsorbents as shown in Figure 4. The adsorption capacity of fresh WR was in range of 1.235-1.237 mg/g. As for modified adsorbents, the adsorption capacities were in range of 1.210-1.225 mg/g. The adsorption capacity of adsorbent decreased after 40 minutes of contact time and this may due to the presence of other co-cation and complex forming anions in the solution [17].

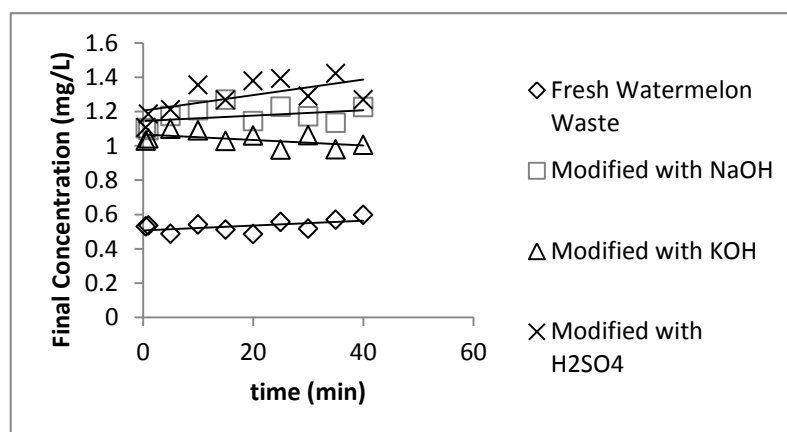


Figure 3. Effect of time on ammonia nitrogen adsorption

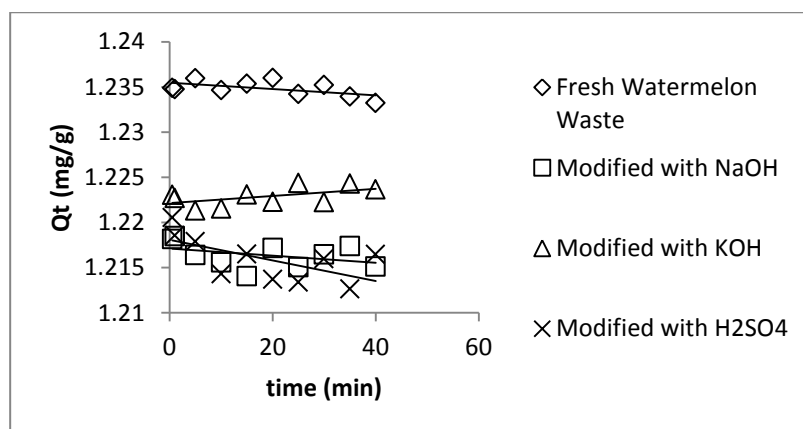


Figure 4. Adsorption capacity against contact time

4. Conclusion

The adsorption behaviour of $\text{NH}_3\text{-N}$ onto fresh WR, modified WR with NaOH, KOH, and H_2SO_4 adsorbent were evaluated as a function of contact time and adsorbent dosage. The $\text{NH}_3\text{-N}$ showed a fast rate of sorption and adsorbents were able to remove the pollutant along 40 minutes of contact time. 20g of adsorbent is the optimum dosage for removal process of $\text{NH}_3\text{-N}$ in this study. The adsorption capacity shows not much difference for all four types of adsorbent. The adsorption capacity obtained shows not much difference between all four types of adsorbents used where all lie in range of 1.2 mg/g. the adsorption capacity of fresh WR (1.230-1.235 mg/g) is slightly higher compared to other three modified WR adsorbent (1.210-1.237 mg/g). Thus, it can be assured that WR have great potential to be used as low-cost adsorbent in ammonia nitrogen removal process.

5. References

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