Ammonium Ion Removal using Activated Zeolite and Chitosan

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Abstract. Studies have previously been done on efficacies of chitosan and zeolite in ammonium ion (NH_4^+) removal. However, no study compares the adsorption performance of natural zeolite and activated natural zeolite with high and low molecular weight chitosan. Hence, this study investigates the potentials of natural zeolite (NZ), activated natural zeolite (ANZ), low molecular weight chitosan (LMWC) and high molecular weight chitosan (HMWC) in NH_4^+ removal. The characteristics of NZ, ANZ, LMWC, and HMWC such as functional groups, surface morphology, elemental composition, zeta potential and particle size were also investigated. The deposition of NH_4^+ on the surface of NZ and ANZ was confirmed with the absence of nitrogen by the adsorption spectrum of EDX and supported by the presence of an FTIR stretching band at ~3500-3300 cm^{-1}, as well as broader and less intense bands ~1600 cm^{-1} after the adsorption for all the adsorbents. The particle size of LMWC, HMWC, NZ and ANZ were 98, 813, 22354 and 9826 nm, respectively. Meanwhile, after the activation process, the composition of O, Si, Al, Fe, Ca and Na were reduced. NH_4^+ batch adsorption was also studied. HMWC, NZ, and ANZ reached adsorption equilibrium at 15 h, meanwhile for LMWC, the equilibrium reached at t = 20 h. The adsorption capacity of LMWC, HMWC, NZ, and ANZ at an initial concentration of 50 mg/L were 0.769 mg/g, 0.331 mg/g, 2.162 mg/g and 2.937 mg/g respectively. ANZ had the highest adsorption capacity, which might be related to the reduction of cationic elements such as Fe, Ca and Na after the activation has increased the unbalanced negative charge within the crystal lattice of ANZ that can be neutralized by NH_4^+ hence led to higher adsorption. HMWC has the lowest adsorption capacity that may be due it is positively

charged at pH 7 which would favor the adsorption of negatively charged species instead of positively charged species, NH_4^+.

Keywords: Ammonia; nitrogen; adsorption; natural; zeolite; chitosan

1. Introduction

NH_4^+ has been the cause of nitrogen pollution in recent years, originating from municipal and industrial effluent caused by human activities such as surface runoff from farmland and residential areas. In turn this causes nutrient enrichment which lead to serious eutrophication in urban drainage, wastewater, and groundwater sources. Water pollution is linked to 14, 000 deaths daily, which NH_4^+ toxic contaminants are a contributor to [1]. The hazard posed by consuming NH_4^+ has led to stringent water quality standards; as nitrate in drinking water from surface water shall not exceed 10 mg/L, nitrite levels in drinking water usually below 0.1 mg/L and the allowable concentration for treated effluent is 5 mg/L [2–4]. This has led to the necessity to have a competent wastewater treatment in which can remove NH_4^+ to below the allowable limit.

There are many wastewater treatment methods available. Biological processes, such as conventional activated sludge treatment, anaerobic-anoxic-oxic, sequencing batch reactor, and oxidation ditch are reported to be less efficient in nitrogen removal due to inability to meet the stringent nutrients discharge standards, instability treatment effect and time consuming process [5]. Ammonia stripping, electrodialysis, bioelectrical treatment suffer from drawbacks such as regular maintenance, higher capital and operating expenses and lack of technology access and experts [6]. On top of that, adsorption has gained extensive attention in NH_4^+ removal due to its low-cost, high affinity towards NH_4^+, efficiency and simplicity of application as well as environmental friendliness [7–9]. Processes based on the use of natural, locally available adsorbents are considered to be more accessible for developing countries, have lower investment cost and lower environmental impact [10].

Recently, natural zeolites have been upgraded to a commodity of great capabilities such as being used for the removal of NH_4^+ from municipal, industrial or agricultural waste and drinking

water [11]. Natural zeolites consist of three-dimensional frameworks of aluminosilicates where oxygen, aluminium, and silicon are covalently bonded in a tetrahedral structure. Each aluminium (Al^{3+}) atom substitution for silicon (Si^{4+}) atom in the zeolite framework which will generate one negative charge within the pores that will be balanced by positively charged ions (cations) such as Na^+, K^+, $Ca^{2+,}$ and Mg^{2+} on the external surface of natural zeolite with weak electrostatic bonds that caused the ability to be exchanged with other cations in solutions such as NH_4^+ [12–14]. Although natural zeolites are available in abundance, their relatively small adsorption capacities for NH_4^+ (10 mg/g or less) [9] and lower efficacy as compared to synthetic zeolite which is reported to have greater adsorption capacity due to higher proportion of higher specific area, bigger total pore volume and lower average pore size has led to modification of natural zeolite [15,16].

Natural zeolite, such as fly ash, Australian natural zeolite and Chinese natural zeolite, have been previously investigated but low adsorption capacity was recorded [14,16–18]. Several pre-treatments have been done on natural zeolite, activated natural zeolite and commercial zeolite including acid, base, salt, and organic surfactant treatments, before being used in NH_4^+ removal [16,18–20]. Heat treatment is known to be the best pre-treatment due to the morphological structure changes which do not require any chemicals. The pore size decreases, but the content of cations will also greatly reduce, opening up more sites for the attachment of NH_4^+ [18,21]. The temperature used during heat treatment plays an important role. Heat treatment at 400 ^oC and lower have a positive impact as the adsorption capacity will improve compared to non-treated natural zeolite. However, according to Zhang et al. [22], who studied activation temperature of 500 ^oC to 700 ^oC, reported that high heat treatment reduced the adsorption of NH_3-N due to the degradation of an important element, O, changing the isoelectric point.

Other than natural zeolite, chitosan, a non-toxic natural carbohydrate polymer derived from the chitin component of crustacean exoskeletons such as shrimp, crab, crawfish, etc., was reported to be an excellent adsorbent material because it contains hydroxyl (-OH) and amino (-NH_2) groups that serve as binding sites [23]. The mechanism of adsorption of ion on the surface of chitosan was

explained by Zhang and Bai [24]. Chitosan has been used in heavy metals removal [25] and dye adsorption [26].

Many studies have been done on chitosan and zeolite separately as suitable adsorbents for NH_4^+ but no study compares adsorption performance of natural zeolite, activated natural zeolite with high and low molecular weight chitosan. For instance, Kołodyńska et al. [17] reported the comparison of modified natural zeolite with different molecular weights of chitosan, but those were used to treat methylene blue and copper, Cu (II) ion instead of NH_4^+. Yang et al. [18] compared only one molecular weight of chitosan with natural zeolite. Teimouri et al. [27] compared chitosan with commercial zeolite instead of natural zeolite for nitrate ion (NO_3^-) removal. Haseena et al.[28] studied hybrid commercial zeolites such as zeolite Y and bentonite clay with no modification but no comparison was made with chitosan. Hence, this paper fills in these gaps by reporting studies of the capability of natural adsorbents: natural zeolite, modified natural zeolite, low molecular weight chitosan and high molecular weight chitosan whose characterizations and ammonium ion adsorption capacities were investigated.

2. Methodology

2.1. *Materials*

The natural zeolite originated from Indonesia. The chemical composition of natural zeolite from supplier was (SiO_2: 65.5 %, Al_2O_3: 12.5 %, Fe_2O_3: 1.35 %, CaO: 2.6 %, MgO: 1.22 %, Na_2O: 0.63 %, K_2O: 1.6 %, TiO_2: 0.01 % and cationic exchange capacity (CEC): 1.40 meq/g). LMWC (50,000 – 190,000 Da, 75-85% deacetylated) (Sigma Aldrich) and HMWC (310000 – 375000 Da, > 75 % deacetylated) (Sigma Aldrich, USA). It was used directly without further purification. Nessler reagent was used to analyze NH_4^+ which consisted of a Nessler reagent, mineral stabilizer and polyvinyl alcohol dispersion, range of detection limit: 0.02 – 2.5 mg/L (Hach, USA).

2.2. *Preparation of adsorbents*

The natural zeolite was washed and dried at 104 ºC overnight. The activated natural zeolite was prepared by using the method by Taaca et al. [29]. Firstly, the natural zeolite was broken down into

fine powders using mortar and pestle before the treatment procedure. The particles were washed with distilled water and filtered twice. The slurry was dried at 105° C for 2 h and active treatment followed at 120 °C for 6 h. All solids were stored in a dry place to avoid moisture. Low molecular weight chitosan, high molecular weight, natural zeolite, and activated natural zeolite were denoted as LMWC, HMWC, NZ, and ANZ.

2.3. *Functional groups identification*

The functional groups present in LMWC, HMWC, natural zeolite and activated natural zeolite before and after the adsorption were recorded by using Fourier transform infrared (FTIR) spectrometer (Perkin Elmer Spectrum-100). The spectra were recorded in the wavenumber range from 4000 to 400 cm^{-1}.

2.4. *SEM-EDX*

The detailed surface morphology of LMWC, HMWC, NZ, and ANZ before use were obtained by using a scanning electron microscope (SEM, S-3400 N, Hitachi) coupled with energy dispersive X-ray (EDX) spectrometer with 10.0 kV acceleration voltage with a magnification range of 180 until 13 k. The samples were coated with gold by a sputter coater Q150RS before analysis to increase the conductivity of the samples. The approximation of pore size and the sizes of flakes were done for all the adsorbents.

2.5. *Zeta potentials and particle size*

0.1 g NZ, ANZ, LMWC, and HMWC was suspended in 100 g of distilled water, followed by stirring at 200 rpm for 24 h. Before the analysis, each sample was distributed into the vials. The pH values were adjusted to 7 by addition of 0.1 M HCl or 0.1 M NaOH solution. Dynamic light scattering (DLS) was used to measure the hydrodynamic diameter (diameter in nanometer range in (d.nm) and laser Doppler anemometry (LDA) was used to measure the zeta potential in (mV) [30]. DLS and LDA were performed using a Zetasizer Nano ZS instrument (Malvern Panalytical Ltd. UK).

2.6. *Batch adsorption*

Equilibrium tests were conducted to determine the equilibrium adsorption capacity for LMWC, HMWC, NZ, and ANZ. For the reaction, 500 g of NH_4Cl solution with an initial concentration of 50 mg/L was poured inside a 1000 mL beaker. 5 g of NZ and ANZ were used. Meanwhile, 1 g of LMWC and HMWC were used for the adsorption. pH was adjusted to 7 by the addition of 0.1 M NaOH or 0.1 M HCl stock solutions. The temperature was set to 30 ^oC (room temperature), with a stirring speed of 700 rpm. 2.5 mL of solution was pipetted out for 30 min, 1 h, 2 h, 6 h, 12 h, and 24 h. Three replicates were done per adsorbent type. The samples were then analysed using a Jasco UV-vis 650 Bio-spectroscopy with a maximum wavelength of 425 nm. Before analysis, Nessler reagent was used for ammonia nitrogen compound detection by following the standard USEPA Nessler Method No.8038. The concentration of ammonium ion adsorbed at equilibrium was calculated as in equation (1).

$$q_e = \frac{(C_o - C_e)V}{W} \quad (1)$$

3. Results and discussions

3.1. *Characterizations of adsorbents*

3.1.1. Functional groups identification

The FT-IR spectra for NZ, ANZ, LMWC and HMWC for before and after the adsorption reaction are depicted in figure 1. All adsorbents showed stretching vibrations at ~3500-3300 cm^{-1}. Both O-H and N-H stretch at wavenumbers above 3100 cm^{-1}, but O-H will show a more intense band than N-H [27,31]. NZ, ANZ, LMWC, and HMWC had shown an intense peak at range ~3500-3300 cm^{-1} but the band showed medium and broad shape after the adsorption which indicated the presence of N-H bond. This has confirmed the attachment of NH_4^+ after the adsorption process.

Before the adsorption, HMWC and LMWC had shown stretching vibration with medium peak intensity at 3300 – 2700 cm^{-1} which is for the C-H compound [31,32]. This has been confirmed with

the formation of band at ~1380 cm^{-1} which is the indication of methyl group. The compound has fewer than four adjacent methylene groups because there is no absorption band at ~720 cm^{-1}.

There are bands at the range of ~ 2260 – 2100 cm^{-1} shown by ANZ, HMWC, LMWC, NZ before and after the adsorption which indicated for the presence of triple bond of C and triple bond of C and N. N-H bending vibrations also occur at ~1600 cm^{-1} and absorption at that wavelength does not always indicate a C=C bond. However, absorption bands resulting from the N-H bend tend to be broader (due to hydrogen bonding) and more intense due to being more polar) than those caused by C=C stretches [31].

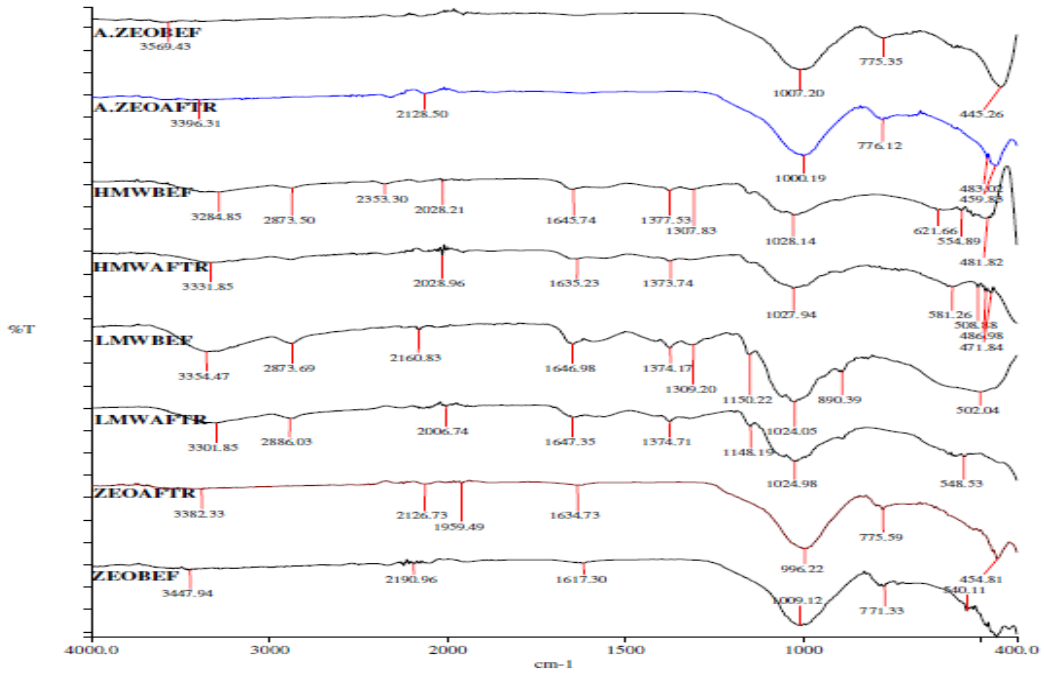


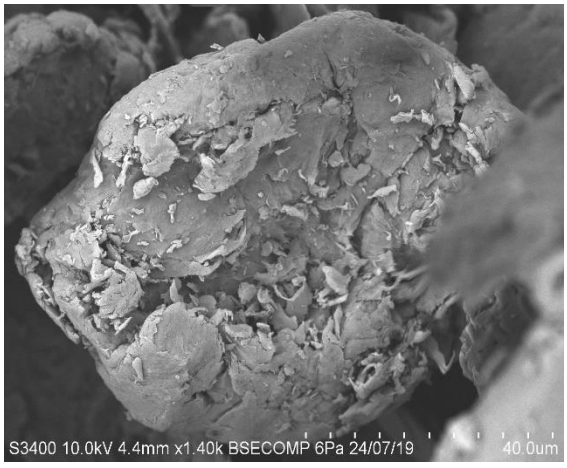
Figure 1. FTIR analysis.

Band around ~1000.14 cm^{-1} is a bending vibration of Si-O [33] and ~1018 stretching vibrations of the Y zeolite structure framework [27] which have been shown by both NZ and ANZ.

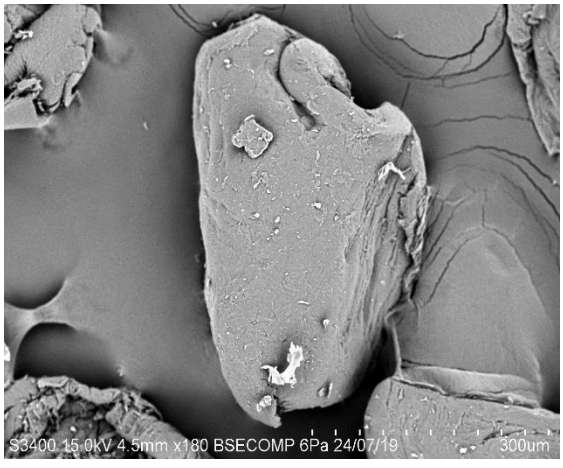
The major peak at 1023 cm^{-1} and 1015 cm^{-1} justifies Si-O-Si asymmetric stretching and bending respectively [34]. NZ and ANZ showed bands at 775.35 cm^{-1} - 776.12 cm^{-1} and 775.59 cm^{-1} - 771.33 cm^{-1} were due to the quarts or amorphous SiO_2 stretching vibration and Si-O-Si bending mode [32].

3.1.2. Morphological structure

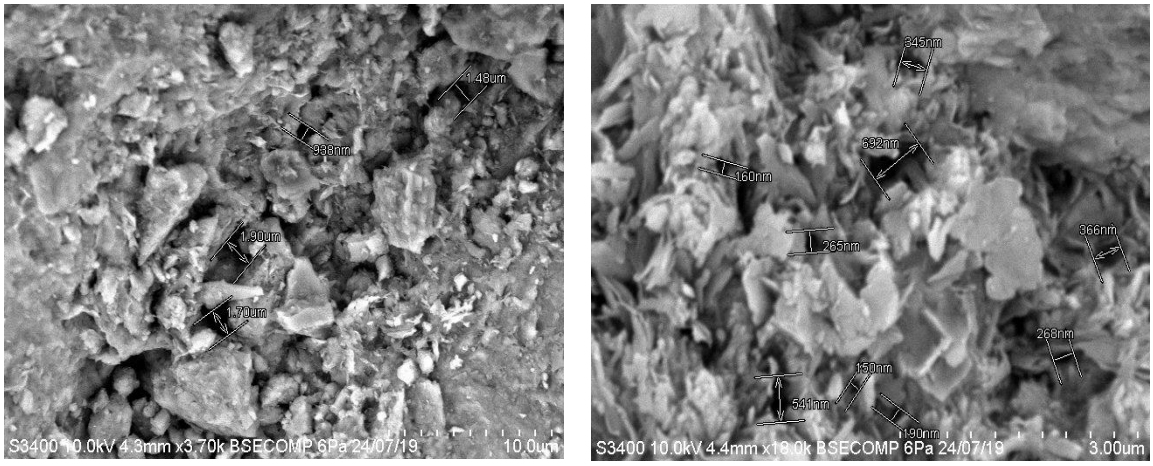
The surface morphological structures of LMWC, HMWC, NZ, and ANZ are depicted in figure 2 (a)-(d). In SEM analysis, the surface morphology was taken at an acceleration voltage of 10kV and with magnifications 180 until 13 k. From the results, rough surface was noticed for HMWC, LMWC, NZ, and ANZ. As shown in figure 2 (a) and (b), an irregular shape of flakes like structure with no distinctive pore was observed for both LMWC and HMWC. This was also being observed by Cui et al.[35] in the commercial chitosan. Meanwhile, irregular pores for NZ and ANZ were noticed as illustrated in figure 2 (c) and (d). Powder like structure was observed for NZ but not for ANZ, as the structure changed to flakes like structure with more pores were observed. Furthermore, irregular cracks have also being noticed on the ANZ surface in figure 2 (d). The estimated pore size of NZ and ANZ was 1153.8 µm and 825. 32 µm respectively. It was noted that the activation had caused the pore size to decrease.



(a)



(b)



(c) (d)

Figure 2. SEM analysis (a) LMWC, (b) HMWC, (c) NZ, (d) ANZ.

3.1.3. Elemental Analysis

As presented in Table 1, the elemental composition of LMWC, HMWC, NZ, and ANZ before the adsorption test were studied using the EDX. The elements of C, O, and N were detected for LMWC and HMWC. These elements are the common elements present in most chitosan due to the presence of free amine, carboxyl and hydroxyl groups that functions as active sites during the adsorption process [25].

The presence of the elements Si, Al, O, Na, Ca and Fe were detected due to the natural zeolites which are composed of three dimensional frameworks of aluminosilicate where the aluminium and silicon structure atoms are bound by covalent bond over shared oxygen atoms to form interconnected cages and channels. These will form pores and is where most of the cations are present and ion exchange processes occur [14,36]. It was noticed that after the activation, the composition of O, Si, and Al had decreased. The decrease of element O is suspected to be due to the loss of H_2O. The decrease of exchangeable cations such as Na, Ca, Fe by 12 %, 47 %, and 10 % respectively.

Table 1. EDX analysis.

Adsorbent	Element composition (wt. %)							
	C	O	N	Si	Al	Na	Ca	Fe
HMWC	53.250	21.223	9.215	-	-	-	-	-
LMWC	50.975	21.905	8.9075	-	-	-	-	-
NZ	1.548	41.130	0	34.278	9.130	0.603	3.513	3.933
ANZ	7.510	38.418	0	30.280	8.450	0.503	1.855	3.550

3.1.4. Zeta Potentials

The measured zeta potentials of NZ, ANZ, HMWC, and LMWC at pH 7 are shown in table 2. As can be seen, LMCW, HMCW, NZ, and ANZ have zeta potentials of -46.8 mV, 6.4 mV, -36.7 mV and 34.9 mV respectively. The particle size of LMCW, HMWC, NZ and ANZ were 98, 813, 22354 and 9826 nm, respectively. The size of LMWC is smaller than HMWC. From Table 2, NZ has larger particle size compared to ANZ. This has shown that the heat pretreatment has reduced the particle size of NZ. The reduction of particle size has proven that the activation process has occurred.

Table 2. Zeta potentials and particle sizes

Adsorbent	Zeta Potentials (mV)	Particle size (nm) (This study)	Particle size (nm) (Other study)
LMCW	-46.8	98.41 DD : 77 %, MW: 131 kDa	308.4[37] DD : 90.4 %, MW : 66.3 kDa
HMWC	6.4	813.57 DD : > 75 %, MW : 343 kDa	543.8[37] DD : 90.2 %, MW : 316 kDa
NZ	-36.7	22354	17660 [38]
ANZ	-34.9	9826	4580 [38]

3.2. *Ammonia nitrogen batch adsorption*

Figure 3 illustrates the concentration of NH_4^+ adsorbed on the surface of LMWC, HMWC, NZ, and ANZ as a function of the contact time. HMWC, NZ, and ANZ reached adsorption equilibrium at 15 h, whereas for LMWC, the equilibrium was reached at t = 20 h. LMWC required more time to reach equilibrium which is due to its lower deacetylation degree (DD) which lowers its stability during the reaction [39].

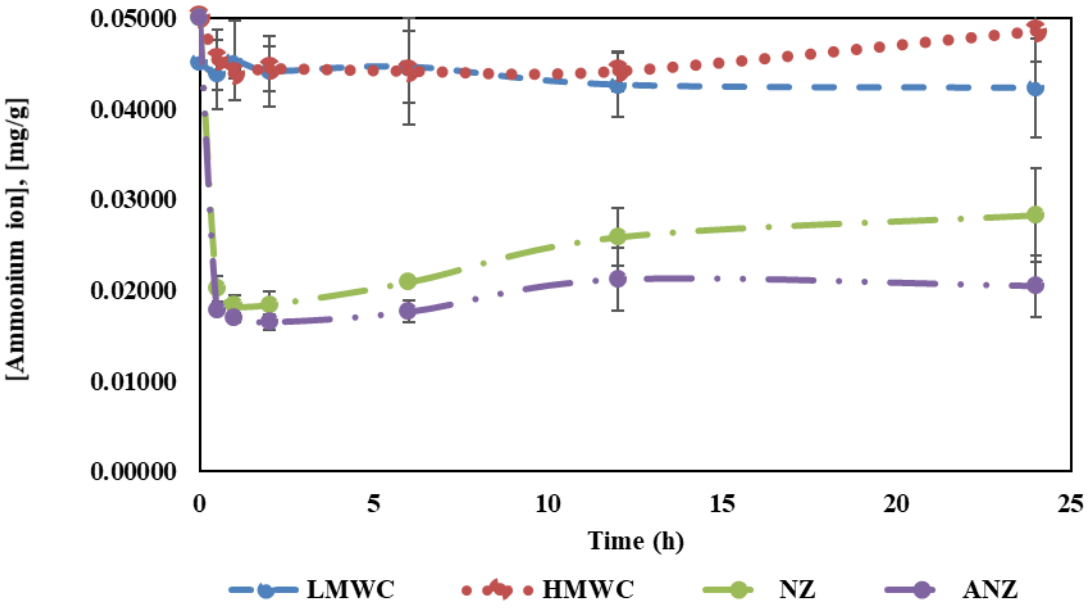


Figure 3. Adsorption of ammonium ion at different time intervals using LMWC, HMWC, NZ, and ANZ.

The adsorption capacity of LMWC, HMWC, NZ, and ANZ at an initial concentration of 50 mg/L were 0.769 mg/g, 0.331 mg/g, 2.162 mg/g and 2.937 mg/g respectively. ANZ had the highest adsorption capacity compared to LMWC, HMWC, and NZ. This was due to the decrement of cationic species Na, Ca and Fe which was detected by EDX analysis for ANZ, which contributed to the higher unbalanced negative charge within the crystal lattice of ANZ that can be neutralized by NH_4^+ hence led to higher adsorption [18,20,21]. This is also supported by the findings of Yang et al. [18] who reported that the activation using heat treatment caused the adsorption capacity of natural zeolite to improve due to the decrease of exchangeable cations. Furthermore, the reduction of particle size from 22354 nm to 9826 nm after the activation process has also contributed to higher sorbent performance because a fresh surface is exposed, and the total outer surface area is increased [38,40].

The effect of the molecular weight of chitosan and DD has been studied on the adsorption of NH_4^+. In this study, HMWC with higher DD (>75 %) contains higher amino groups which were confirmed by EDX analysis which showed that it has higher nitrogen content compared to LMWC

(DD: 75-85 %). It was found that HMWC has a lower adsorption capacity compared to LMWC. Li et al. [41] also observed that the adsorption capacity of chitosan with lower DD was higher compared to chitosan that has high DD. The same founding has also being observed by Chung et al. [42] where low molecular weight has higher removal for ammonia (NH_3) compound compared to high molecular weight chitosan.

Based on the zeta potentials tabulated in Table 2, LMWC, NZ, and ANZ are negatively charged at pH 7 that may enhance the adsorption of NH_4^+, hence, higher adsorption capacity recorded except for HMWC which is positively charged at pH 7. From the electrostatic interaction point of view, the positive zeta potentials would favour the adsorption of negatively charged species instead of positively charged species, NH_4^+ which may lower the adsorption capacity [43]. Chitosan acts as a weak base at lower value of DD and the cationicity aa well as pKa of the chitosan will importantly increase at DD over 80 % due to the presence of amino groups of glucosamine which responsible for cationic nature and net positive charge of chitosan under acidic or neutral condition [44–46]. DD determines the number of acetamide groups (C_2H_5NO) that randomly distributed along the C2 atoms along the chitosan chain which will affect the conformational charge of chitosan when in a solution and solubility. Furthermore, there is a possibility of hydrogen bonds (intra or intermolecular bonds) that reduced the number of accessible free amines for the cations uptake [47].

The second factor that may attribute to the low adsorption capacity of HMWC is due to it has a bigger particle size compared to LMWC as tabulated in Table 2. The particle sizes of HMWC and LMWC are 813.57 nm and 98.41 nm respectively. In research reported by Guibal et al.[48], the adsorption capacity was found to be lower, which was attributed to the larger particle size of the flakes. The large particle size of HMWC will occupy large volume in the reactor that leads to less mobility of adsorbents during the reaction, meanwhile, LMWC which is smaller in size has lesser resistance towards flow and hence higher exposed surface area [49]. Even though LMWC is more negative and has smallest particle size among NZ and ANZ, however, the reactions may be hindered brought about by the number of acetyl groups and formation of hydrogen bond between the other

LMWC and water compounds as well as the effect of swelling may contribute to the low adsorption capacity [50,51].

However, based on Figure 3, there is an increasing trend of adsorption at 24th h for all adsorbents used in this study. The same trend was observed by Zahrim & Hilal [52] for dye removal, Bernardi et al. [53] in removal of total ammonia using chitosan and Masheanne et al.[54] in nitrate removal using chitosan. There is probability of desorption since this can perhaps be explained by the fact that the process involves several mechanisms such as physico-chemical adsorption, ion-exchange, precipitation or complexation as controlling step that can act simultaneously during batch adsorption using chitosan [54–56].

4. Conclusion

This work shows the characterization and adsorption capacity of natural zeolite (NZ), activated natural zeolite (ANZ), low molecular weight chitosan (LMW) and high molecular weight chitosan (HMWC). Based on the FTIR and EDX analysis, it was confirmed there was attachment of NH_4^+ to the surface of NZ, ANZ, LMW, and HMWC. The activation on natural zeolite had caused the pore size, particle size as well as the composition of O, Si, Al, Fe, Ca and Na to be decreased. HMWC, NZ, and ANZ reached adsorption equilibrium at 15 h, meanwhile for LMWC, the equilibrium reached at t = 20h. The adsorption capacity of LMWC, HMWC, NZ and ANZ at initial concentration 50 mg/L were 0.769 mg/g, 0.331 mg/g, 2.162 mg/g and 2.937 mg/g respectively. ANZ employed the highest adsorption capacity due to the vacant sites for ion exchange to occur after the activation process. Meanwhile, HMWC recorded the lowest adsorption capacity because it is positively charged and as such favours negatively charge ions instead of positively charged species, such as NH_4^+.

5. References

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