

Removal of Ammoniacal Nitrogen from Synthetic Wastewater Using Granular Activated Carbon and Limestone

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Abstract:

Background: Discharging high concentrations of nitrogen compounds in industrial effluent such as those from fertilizer manufacturing plants can cause various environmental problems like eutrophication. **Objective:** to investigate the efficacy of the granular activated carbon (GAC) and limestone (LS) as low cost media in removing ammonium ions from aqueous solution. **Methods:** Batch experiments were conducted to evaluate the efficacy of GAC and different ratios of GAC and LS mixture in the removal of ammoniacal nitrogen. The investigated parameters included contact time, initial ammonium ion concentration, pH, and amount of adsorbent. The adsorption isotherm and adsorption kinetic of ammonium ions by a mixture of GAC and limestone (LS) was studied. **Results:** The experiments showed that the efficacy of GAC alone on the adsorption of $\text{NH}_4\text{-N}$ was 95% at shaking time 150 min, agitation speed 210rpm, temperature 22°C and pH 9. The efficacy of a mixture ratio LS: GAC (30:20) on the removal of $\text{NH}_4\text{-N}$ was 75%. **Conclusions:** The study concluded that the removal percentage of ammoniacal nitrogen by a mixture of lime stone and GAC increase with the increase of agitation time and decrease with the increase of initial concentration while alkaline pH was more favorable for the adsorption of ammoniacal nitrogen.

Keywords: Adsorption, Ammoniacal nitrogen, Granular activated carbon, Lime stone, Waste water

INTRODUCTION

Ammoniacal-nitrogen (NH_4N), nitrite (NO_2^-) and nitrate (NO_3^-) are present in industrial effluents such as those discharged from fertilizers manufacturing plants. These nitrogen compounds can end up onto rivers through effluent discharge, causing eutrophication which disrupt aquatic ecosystems in a severe manner.^(1,2)

The ammonium ion and ammonia can coexist in an aqueous solution according to equation(1) $\text{NH}_4^+ \leftrightarrow \text{NH}_3(\text{aq}) + \text{H}^+$ (equation 1) The equilibrium presented in equation⁽¹⁾ depends on pH and temperature.

The release of ammonia can promote the growth of algae and decrease the dissolved oxygen required for aquatic life if the concentration of $\text{NH}_4\text{-N}$ exceeds 0.3–0.5 mg/L.⁽³⁾ Nitrifying bacteria

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(Nitrosomonas and Nitrobacter) tend to oxidize ammonium ions (NH_4^+) to nitrite (NO_2^-) and nitrate (NO_3^-) ions. However, these ions are removed by aquatic plants, algae and bacteria by assimilating them as a source of nitrogen. ⁽⁴⁾ Studies on the toxicity of nitrate on aquatic animals indicated that nitrate reacts with hemoglobin shortage of oxygen in their body (methaemoglobin) and finally death. In human intestine, nitrate is also converted into nitrite under anaerobic conditions that may lead to methaemoglobinaemia in infants. Moreover, cancers of the gastrointestinal tract system may be induced by formation of nitrosoamines from nitrite.⁽⁵⁾

The removal of $\text{NH}_4\text{-N}$ from wastewater is important in the alleviation of environmental problems including eutrophication, corrosion and fouling.⁽⁶⁾ Conventional wastewater treatment technologies including coagulation, filtration, chlorination, and ozone treatment

are not enough for ammoniacal nitrogen and nitrate ions removal. $\text{NH}_4\text{-N}$ removal can be accomplished by biological, physical, chemical, or a combination of these methods. Such technologies include adsorption, chemical precipitation, membrane filtration, reverse osmosis, ion exchange, air stripping, breakpoint chlorination and biological nitrification and denitrification.⁽⁷⁾ Among these, adsorption offers an efficient and economically feasible technology for the removal of contaminants from wastewaters. Selective adsorption utilizing mineral oxides and activated carbon or polymer resins has become of great interest.

Activated carbon has been utilized as an efficient sorbent for odor removal, solvent recovery, decolorization, dechlorination, ozone annihilation, filtration, fuel gas cleaning, industrial wastewater treatment, drinking water conditioning, etc. The highly porous nature and high adsorption capacity resulting from high

surface area of the activated carbon surface made it extensively used in practice^(7,8). In spite of this, activated carbon is expensive and its regeneration results in 10-15% loss of the activated carbon. Previous studies have investigated the effectiveness of a variety of low cost materials for ammonia removal^(9,10) such as clay⁽¹¹⁾ and zeolite^(12,13,14) and limestone.^(15,16)

The aim of the present study was to investigate the efficacy of the granular activated carbon (GAC) alone and its mixture with limestone (LS) as a low cost adsorbent in the removal of ammoniacal nitrogen from wastewater.

MATERIAL AND METHODS

Study setting:

The present study was an experimental study performed at laboratory of Faculty of Engineering, Pharos University in Alexandria, PUA, Egypt

Study design:

An experimental study was employed

Analyses:

Synthetic wastewater was prepared as follows:

Stock solution of ammonium chloride (500 mg/L N-NH₄) was diluted with deionized water to prepare test samples of ammoniacal nitrogen concentrations of 5, 10, 15, 20, 30, 40 mg/l. Samples of ammoniacal nitrogen were analyzed using ultraviolet (UV) Spectrophotometer (UV-, Shimadzu), measured by phenate method 4500-NH₃ set at 640 nm wavelength, according to the Standard Methods for the Examination of Water and Wastewater.⁽¹⁷⁾

Limestone and granular activated carbon

The Limestone (LS), CaCO₃, samples used in this study were obtained from the Al- Mokattam area in Cairo (Egypt). The samples were crushed and sieved to obtain a uniform size of 0.6-1.8mm. The sample contained 97% calcite (CaCO₃) and 3% dolomite (MgCO₃)

The samples were dried for 2 h in an oven at 125 °C, packed into stoppered

bottles and stored in a desiccator for use. Prior to adsorption experiments the activated carbon was sieved to obtain particle size 0.6-1.8 mm and dried at 110°C overnight. The moisture content was 4.136% and the iodine value was 880mg/g. GAC was then packed into stoppered bottles and stored in a desiccator for use.

Batch adsorption studies

Batch adsorption experiments were conducted using total volume of media mixture (LS- GAC) 50 ml with 100 ml of solutions of ammoniacal nitrogen of concentrations 5mg/l, in 250 ml stoppered conical flasks. The LS and GAC mixture (v/v) by volume(ml) were 40:10, 30:20, 20:30, 10:40 and 0:50 and by mass(g) 104:13, 78:26, 52: 39, 26:52, 0:65 respectively .

The glass-stoppered flasks were then placed in a water bath-shaker and shaken at agitation speed of 210 rpm at constant temperatures (20±2 °C).

The effectiveness of ammoniacal nitrogen adsorption on shaking time was

examined in the initial study to determine the equilibrium time. The study was performed by concentration of ammoniacal nitrogen of 5mg/l with different mixture ratios of granular activated carbon and limestone for different intervals of time ranging from 30 min to 210 min. The effectiveness of ammoniacal nitrogen adsorption was examined by different concentrations of ammoniacal nitrogen of 5mg/l, 10mg/l, 15mg/l and 20mg/l with a desired mixture ratio of granular activated carbon and limestone for different intervals of time ranging from 30 min to 210 min.

Samples were adjusted to pH 3, 5, 7, 9 and 11 (with 0.1 M HCl or 0.1MNaOH) to determine the effect of pH on NH₄-N removal at different mixture ratios. The effect of adsorbent dosage by volume on the removal efficiency was studied .The effect of initial concentration of ammoniacal nitrogen on the removal efficiency was investigated by using different concentrations of NH₄N i.e. 5, 10, 20, 30, 40 and 50 mg/L.

The ammonium removal percentage was calculated by equation (2):

$$\text{Removal \%} = \frac{(C_0 - C_t)}{C_0} \quad (\text{equation 2})$$

In adsorption isotherm studies, solutions with different initial concentrations were added, the pH was not adjusted, and the equilibrium time was set according to the preliminary experiments. The uptake of the adsorbate at equilibrium, q_e (mg/g), was calculated by equation (3) :⁽⁷⁾

$$q_e = \frac{V \times (C_0 - C_e)}{m} \quad (\text{equation 3})$$

Where C_0 , C_t and C_e are the initial, final and equilibrium concentrations of the ammoniacal nitrogen (mg/L) in solution, respectively; V is the volume of the solution (L) and m is the weight of the adsorbent (g).

The kinetic studies were performed following a similar procedure at 23 °C, the initial concentration was set as 20mg/L for ammoniacal nitrogen, and the samples were separated at predetermined time intervals. The uptake of the adsorbate at any time q_t (mg/g) was calculated by equation (4)

$$q_t = \frac{V \times (C_0 - C_t)}{m} \quad (\text{equation 4})$$

Where C_t (mg/l) is the concentration of ammonical nitrogen at any time t (min).

Statistical study:

Each run of the experiments of the studied parameters were performed three times and each sample was analysed in duplicates. The resulting data were represented as the average mean, and the percentages removal were calculated and were plotted on graphs. The R^2 values were determined from polynomial equations.

RESULTS

Effect of shaking time on ammoniacal nitrogen removal using different LS:

GAC ratios

The experiments were carried out with different LS: GA mixture ratios of 0:50, 10:40, 20:30, 30:20, 40:10 (v:v) of 100 ml solution of 5mg/l ammoniacal nitrogen at 20°C solution temperature. The removal percentage of ammonia increased rapidly by increasing the time at the beginning

then followed by slight increase in the percentage removal of ammoniacal nitrogen (figure 1). It was observed that at time 150 min the percentage removal of ammoniacal nitrogen achieved was

90%,78%, 75% with adsorbent LS:GAC mixture of 0:50, 20:30, 30:20 respectively. The optimum mixture ratio was then determined to be 30:20 to decrease the cost of GAC.

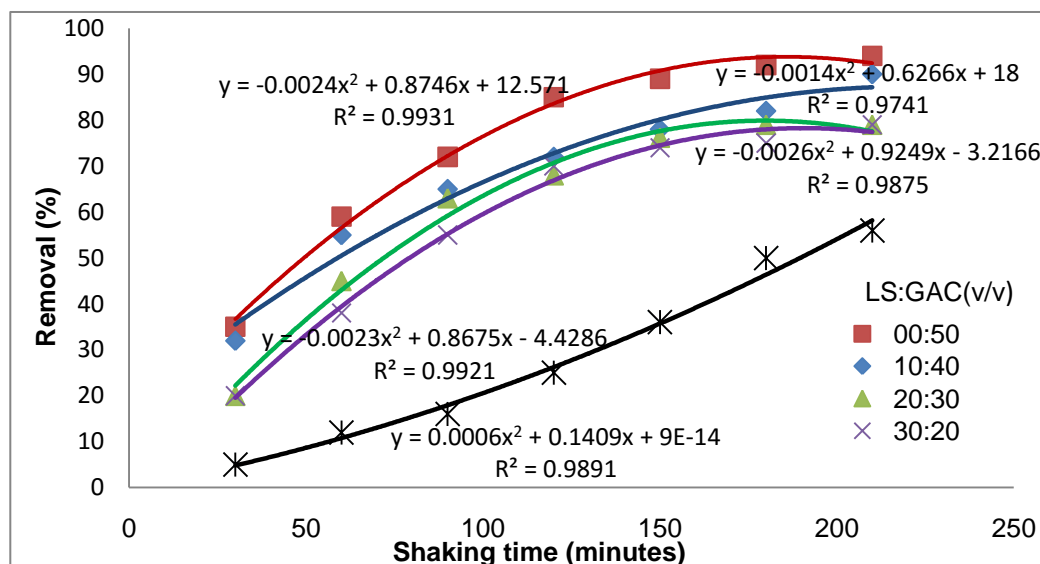


Figure 1: Effect of the shaking time on NH_4N removal using different LS:GAC mixture ratios

Effect of shaking time on ammoniacal nitrogen removal using different concentrations of NH_4N

The experiments were carried out with a LS: GAC mixture ratio of 30:20(v:v) of 100 ml solution at 20°C solution temperature. The pH of the solution was

used without any adjustment. Figure (2) showed the effects of shaking time on the removal of ammoniacal nitrogen at different concentration of ammoniacal nitrogen. It was observed that the adsorption of ammoniacal nitrogen increased with the increase in shaking time and attained an

equilibrium faster for solutions with lower initial concentrations (5mg/l) and at earlier contact. The equilibrium time of 150 min was needed for solutions of 5 mg/l initial

concentrations. However, for higher initial concentrations of 20 mg/l, longer time was required for the system to reach equilibrium, which was 210 min.

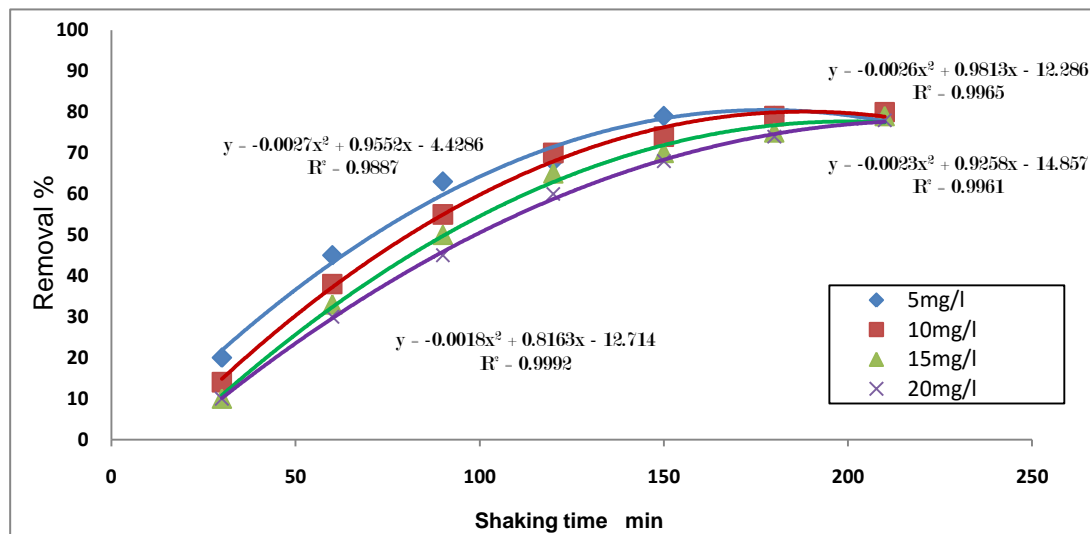


Figure2: Effect of shaking time on adsorption of NH₄N at various initial concentrations

Effect of solution pH on ammoniacal nitrogen removal

Figure (3) shows the effect of solution pH on the removal of ammoniacal nitrogen on different mixture ratio of lime stone and granular activated carbon. From this figure, the percentage removal of ammoniacal nitrogen was found to increase with

increase in the solution pH. The highest ammoniacal nitrogen removal (85%) was achieved at pH 11 with GAC at initial concentration of 5 mg/l. The ammoniacal nitrogen removal was 67% at pH 11 achieved with the mixture ratio of limestone and granular activated carbon 30:20(v:v)

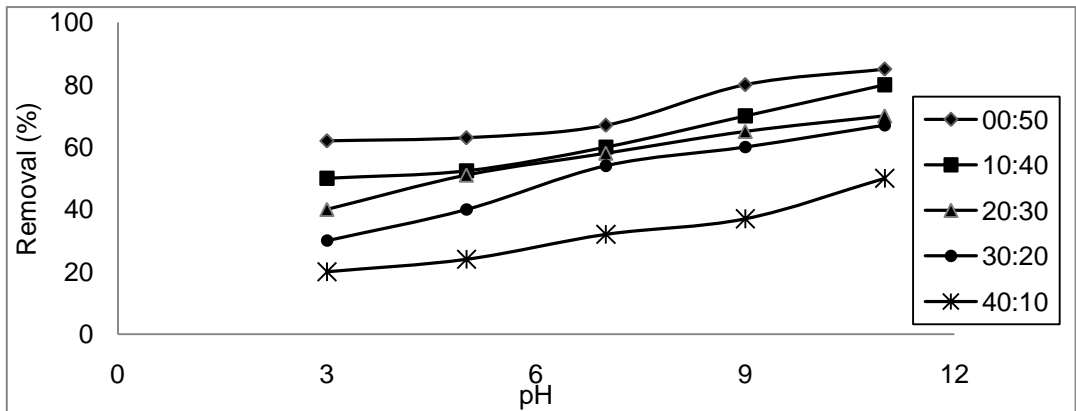


Figure 3: Effect of solution pH on the removal of NH₄N at different mixture ratios

Effect of initial concentration on ammoniacal nitrogen removal

The experiments were carried out to determine the effect of varying the initial concentration at the equilibrium time 150 min and adsorbent mixture limestone and

granular activated carbon 30:20(v/v) on the removal of ammoniacal nitrogen. The percentage removal for initial concentrations 5, 20, 30, 50 mg/l was 76%, 73%, 69% and 58% respectively (fig (4)).

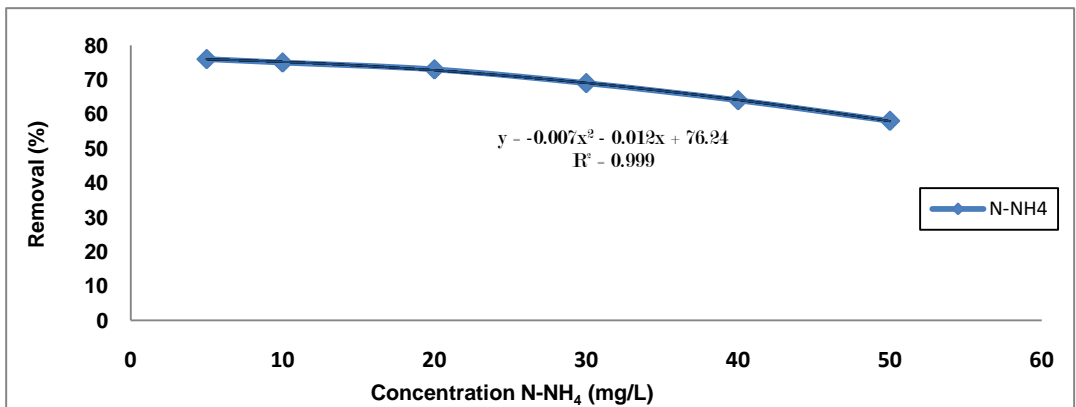


Figure 4: Effect of various initial concentrations on the removal of NH₄N

Effect of adsorbent dosage on ammoniacal nitrogen removal

The optimum dosage of the adsorbent reached 40 mL corresponding to 80 g of

adsorbent mixture. The percentage removal of ammoniacal nitrogen on GAC (0:50) and a mixture ratio of limestone and GAC 30: 20 was 90% and 84% respectively fig (5).

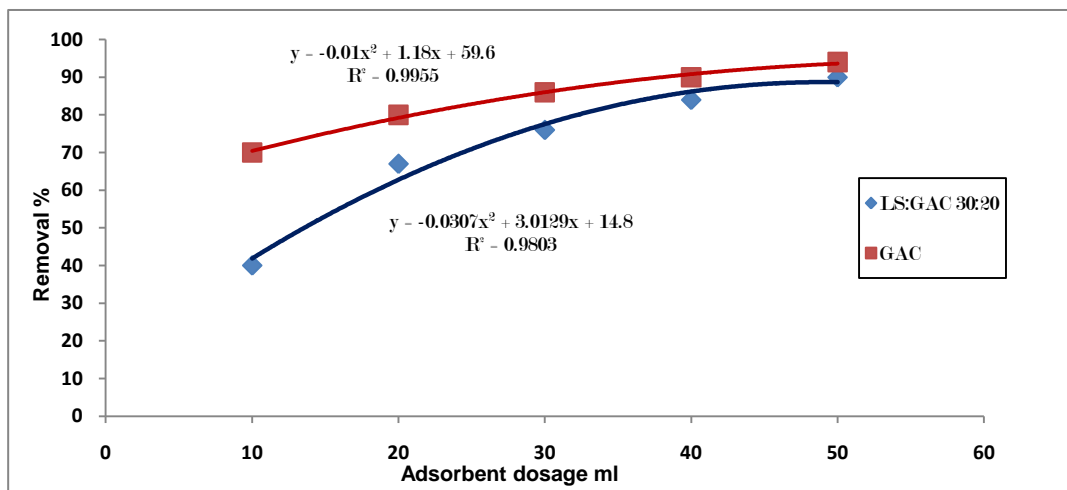


Figure 5: Effect of adsorbent dosages on the removal of NH₄N

Equilibrium isotherm model

The adsorption isotherms of ammoniacal nitrogen on mixture ratio of adsorbents LS-GAC (30:20) 40ml equivalent to 80g were studied by varying the initial concentration of ammoniacal nitrogen. The adsorption isotherm behaves Freundlich mode figure (6) The Freundlich isotherm fits according to equation (5):

$$q_e = K_F C_e^{1/n} \quad \text{(equation 5)}$$

Where q_e is the amount sorbed per specified amount of adsorbent (mg g^{-1}), K_F the constant related to the sorption capacity (mg L^{-1})⁻¹, C_e the equilibrium concentration in solution (mg g^{-1}), and n is the empirical parameter related to the intensity of sorption, which varies with the

heterogeneity of the material. The model parameters (K_F and $1/n$) can be determined from the linear plots of q_e and C_e . The K_F was 0.004 and n was 1.4. The value of $0 < 1/n < 1$ exhibits the favourability of adsorption onto activated carbons.

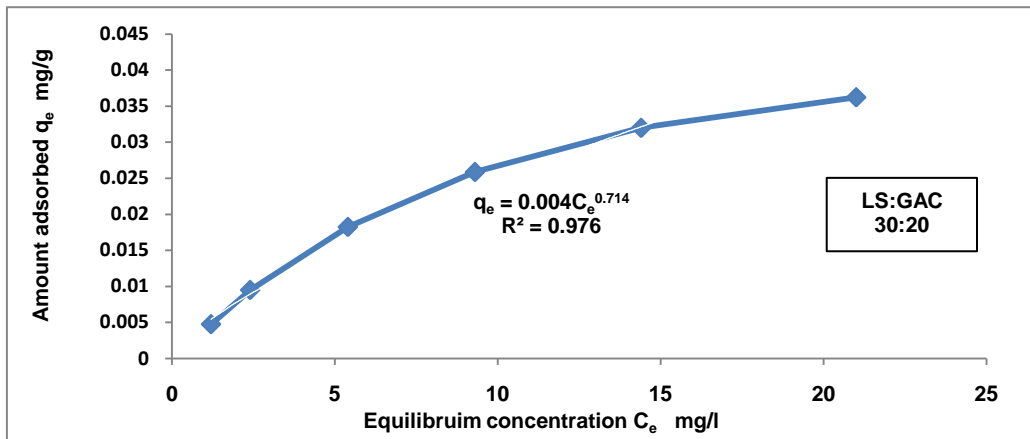


Figure 6: Freundlich Isotherm of ammoniacal nitrogen on adsorbent mixture ratio LS:GAC (30:20) at 22 °C

Adsorption Kinetic

The pseudo-first-order kinetic model has been widely used to predict sorption kinetics. The model given by Langergren⁽²⁵⁾ is defined as in equation (6):

$$\frac{dq}{dt} = k_1(q_e - q) \quad \text{(equation 6)}$$

Integrating Eq. (6) with respect to boundary conditions $q=0$ at $t = 0$ and $q = q_e$ at $t = t$, Eq. (6) becomes as shown in equation (7):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad \text{(equation 7)}$$

Where q_e and q_t (mg/g) are the amounts of adsorbate adsorbed at equilibrium and at any time, t (h), respectively, and k_1 (h^{-1}) is the adsorption rate constant. The plot of $\ln(q_e - q_t)$ versus t gave the slope of k_1 and intercept of $\ln q_e$. As shown in fig (7) the values of k_1 obtained were 0.024, 0.029, 0.02 for ammonia initial concentration of 5, 10, 20 mg/l respectively. The R^2 values

were 0.9, 0.963, 0.96 for ammonia initial concentration of 5, 10, 20 mg/l respectively. Furthermore, the experimental q_e values did not agree with the calculated values obtained from the linear plots.

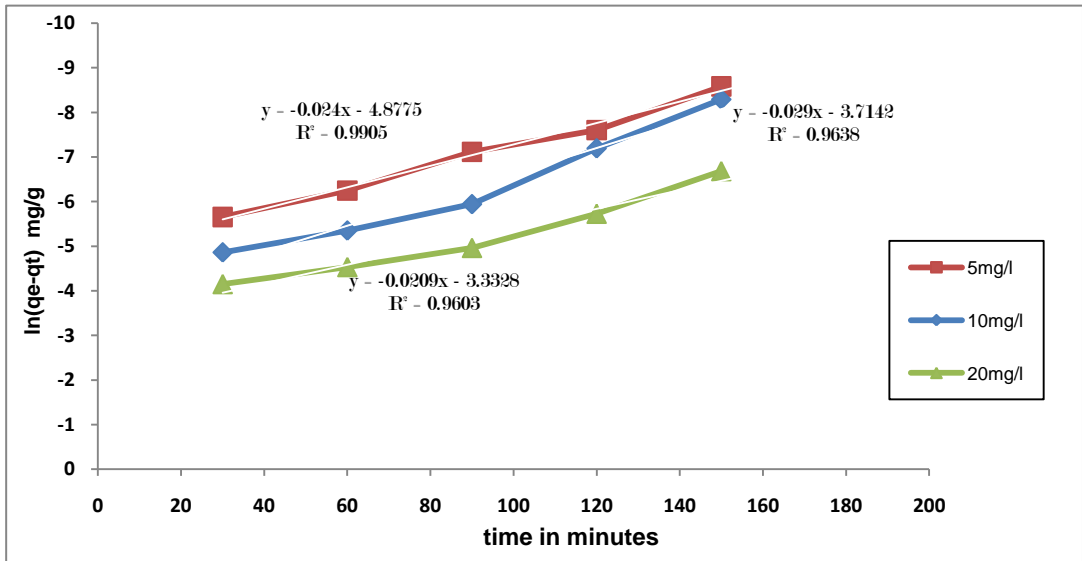


Figure 7: Adsorption kinetics of ammoniacal nitrogen on adsorbent mixture ratio LS: GAC (30:20) at 22 °C

Adsorption mechanism

The plots of figure (8) showed that the initial sharp rise portion represents the intra-particle diffusion process, and the plateau portion corresponds to the final equilibrium process. The plots do not pass through the origin.

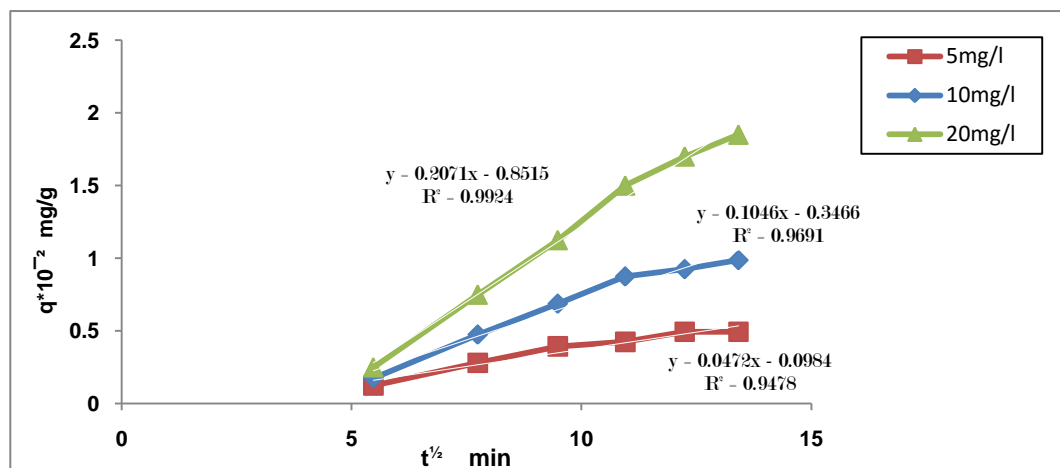


Figure 8: Intra-particle diffusion model fitting of the adsorption kinetics.

DISCUSSION:

Effect of shaking time

The effects of shaking time and different mixture ratio of limestone–granular activated carbon on the removal of ammoniacal nitrogen showed a sharp increase in ammoniacal nitrogen removal with the high dosage of activated carbon (fig.1). That was due to the fact that the adsorption capacity of activated carbon was higher than limestone.^(15,16) The adsorption of ammoniacal nitrogen increased with an increase in shaking time and attains equilibrium faster for solutions with lower

initial concentrations (5mg/l) and at earlier contact (fig.2). This phenomenon was due to the fact that a large number of vacant active surface sites were available for adsorption during the initial stage, and after a lapse of time, the remaining vacant surface sites were difficult to be occupied due to clogging of the pores and less active site remained.⁽¹⁸⁾ For solutions of 5 mg/l initial concentrations the equilibrium time of 150 min was needed. While for higher initial concentrations of 20 mg/l, the equilibrium time of 210 min was

needed (fig.2).

Effect of solution pH

The highest ammoniacal nitrogen removal (85%) was achieved at pH 11 with GAC at initial concentration of 5 mg/l (Figure 3). At pH 5 ammonia was largely in ionized (NH_4^+) form and was removed by adsorption but at $\text{pH} \geq 7$ a substantial part of it was also in the molecular ammonia (NH_3) form, which was subject to gradual removal by ammonia stripping.^(19,20)

Effect of initial concentration

The percentage removal for initial concentrations 5, 20, 30, 50 mg/l was 76%, 73%, 69% and 58% respectively (fig. 4). The increase of initial concentration led to decrease the removal efficiency as pore sites were occupied by the molecule of ammoniacal nitrogen. These results agree with previous studies.^(18,21,22)

Effect of adsorbent dosage

The results of the present work showed that the increase in adsorbent dosage increased the percentage removal

of $\text{NH}_4\text{-N}$, due to the increase in adsorbent surface area, whereas the increase in the amount of GAC increased $\text{NH}_4\text{-N}$ removal.^(15,16) The optimum dosage of the adsorbent reached 40 mL corresponding to 80 g of adsorbent mixture. The percentage removal of ammoniacal nitrogen by GAC (0:50) and a mixture ratio LS: GAC 30:20 was 90% and 84% respectively (fig. 5).

Isotherm model:

The adsorption isotherm behaves Freundlich model as shown in figure (6). Freundlich model is an empirical equation based on sorption on a heterogeneous surfaces or surfaces supporting sites of varied affinities. It is assumed that the stronger binding sites are occupied first and that the binding strength decreases with the increasing degree of site occupation.⁽²³⁾ When $1/n$ values are in the range $0.1 < 1/n < 1$, the sorption process is favourable. This model is valid for heterogeneous surfaces and predicts an increase in the concentration of the ionic

species sorbed onto the surface of the solid with increasing concentrations of said species in the liquid phase.⁽²⁴⁾

Adsorption mechanism:

The intraparticle diffusion model proposed by Weber and Morris⁽²⁶⁾ is applied to study the adsorption process, as in equation (8):

$$q_t = k_{id}t^{1/2} + C_i \quad (\text{equation 8})$$

Where: k_{id} is the intraparticle diffusion rate constant and is obtained from the slope of the straight line of q_t versus $t^{1/2}$ (Fig. 8). C_i , the intercept of stage i , gives an idea about the thickness of boundary layer, i.e., the larger the intercept, the greater the boundary layer effect.⁽²⁷⁾ The adsorption process of the adsorbate molecules from the bulk liquid phase onto the adsorbent surface is presumed to involve three stages: (1) mass transfer of the adsorbate molecules across the external boundary layer; (2) intraparticle diffusion within the pores of the adsorbent; (3) adsorption at a site on the surface.⁽²⁸⁾

The existence of an external layer diffusion process could be deduced by the fact that these plots do not pass through the origin.^(29, 30)

CONCLUSION:

Adsorption of **NH₄N** on a mixture of LS and GAC was found to increase with increase of agitation time and decrease with the increase of initial concentration while alkaline pH was more favourable for the adsorption of **NH₄N**. The experiments showed that the efficacy of GAC alone on the adsorption of **NH₄-N** was 95% at shaking time 150 min, agitation speed 210 rpm, temperature 22°C and pH 9. The results showed that the efficacy of LS: GAC mixture ratio (30:20) on the removal of **NH₄-N** was 75%. The increase of adsorbent dosage increased the percentage of removal of **NH₄-N** on the adsorbent. The increase of the concentration of **NH₄-H** decreased the percentage removal on adsorbent. Equilibrium data were fitted to Freundlich

isotherm models adsorption capacity of 0.004 mg/g at 22 °C. The kinetics of the adsorption process were found to follow the pseudo-first -order kinetic model. Intra-particle diffusion model was applied to identify the adsorption mechanism. It was found that adsorption of NH₄N on the adsorbent LS: GAC mixture ratio (30:20) was mainly governed by particle diffusion.

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