



Ammonium-Nitrogen Removal in Wastewater Through Adsorption Utilizing Bio-Sorbent Matrix

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Abstract

Adsorption is one of the effective methods for removing nutrients from effluent. Adsorbent such as chitosan and various formed of activated carbon such as granulated, maize cob and bamboo were used in nitrogen-rich wastewater treatment. An alternative to the aforementioned adsorbent is bio-sorbent, a biological material that could adsorb desired substances from aqueous solution. Eggshell, with calcium carbonate as the main composition, is a waste and readily available biological material for the adsorbent matrix development. This study aimed to develop an effective and economical alternative adsorbents matrix with eggshell incorporated for the adsorption of nitrogen for the treatment of effluent from aquaculture. Eggshell was collected and washed with distilled water several times and dried in the oven at 105°C overnight, then, ground into different sizes of 250-151, 150-75, and less than 75 μm . Batch experiments were performed under a simulated influent condition with ammonium sulfate concentration of 1 to 10 gL^{-1} . The ammonium removals were ranged from 20 to 44 percent. Formed eggshell matrixes with bentonite was also tested for ammonium nitrogen adsorption, the adsorption efficiency were ranged from 20 to 41 percent. This study reaffirms that eggshell matrix could be used as bio-sorbent for ammonium nitrogen removals. However, the treatment cost of eggshell is needed to be considered.

Keywords : eggshell; bio-sorbent; nitrogen removal; ammonium-nitrogen; adsorption

Introduction

Wastewater, especially wastewater from aquaculture, can contain a high level of nutrients such as nitrogen (N). Especially, in many aquaculture systems, ammonium-nitrogen, a by-product of the digestion of high protein feeds and density, poses threats towards the aquaculture system [1]. In agriculture, nitrogen fertilizer such as ammonium sulfate, and potassium nitrate are used to increase the output of crops such as rice, cotton, wheat, and soybean [2-5]. Industry factories, landfilled, and piggery farms usually contain excess ammonium-nitrogen of up to 2.8 gL^{-1} [6, 7]. The runoff and the wastewater leakage can also contribute to excess nutrients in water-body nearby. High levels of nutrients in the aquatic system can adversely affect water quality, leading to the deterioration of the water body, and eutrophication [8]. Nutrients removal is essential to the aquaculture industry because nutrients removal protects receiving water bodies from excess nutrients, and eutrophication. At the same time, this process allowed the treated water to be reused and recirculated in the aquaculture system [9]. The current processes of ammonium-nitrogen removal from wastewater are nitrification-denitrification, air stripping, chemical precipitation, and adsorption and ion-exchange. Among these, adsorption and ion-exchange offer many advantages such as economically feasible and environmentally friendly treatment alternatives, and simple-to-operate basis [6].

Due to variation in nutrient removal efficiency ranging from 40 to 100 percent nitrogen removal, adsorbent such as chitosan and various formed of activated carbon such as granulated, maize cob, and bamboo were used in aquaculture wastewater treatment [10-12]. An alternative to the aforementioned adsorbent is bio-sorbent. A bio-

sorbent matrix is defined as biological material that could adsorb desired substances from aqueous solution [13, 14]. Eggshell consists of biomineralized calcite crystals embedded in an organic framework of protein fibers with macropore structure contains open voids with a total volume of $0.006 \text{ cm}^3 \text{ g}^{-1}$ and specific surface area that ranges between 0.84 to $1.3 \text{ m}^2 \text{ g}^{-1}$ [15-17]. The pore volume as well as specific surface area contributed the adsorption properties of eggshell. Eggshell, with calcium carbonate as the main composition, permitted the process of adsorption as well as ion-exchange [18]. After uses for adsorption, the eggshell material can be applied in field as nutrient source. Thus, eggshell is a cheap and readily available biological material for the adsorbent matrix development [19]. Global egg production is expected to increase by more than 90 tons by 2030, and so would the eggshell waste generate from consumption [20]. In order to develop the matrix, bentonite was selected as a binding material. Bentonite is a clay rock, generally consisting mostly of hydrated aluminum silicate with permanent negative charges on its interlamellar sites. The advantageous of bentonite includes high ion exchange capacity, ion selectivity and ability to regenerate, make bentonite uses as adsorbent in many applications for wastewater treatment [21]. The bentonite structure enables the material to be intercalated by inorganic and organic cations such as cadmium, and ammonium, with high specific-surface-area relative to its size [22, 23]. Bentonite with macropore structure contains open voids with a total volume of $0.11 \text{ cm}^3 \text{ g}^{-1}$ and specific surface area of approximately $97 \text{ m}^2 \text{ g}^{-1}$ with ammonium-nitrogen adsorption capacity of 46.90 mg g^{-1} [23].

This study aimed to evaluate the potential of eggshell as effective adsorbents in removing high concentration of ammonium-nitrogen from

wastewater. Another objective was to examine the potential of bentonite and eggshell matrix as adsorbent for ammonium-nitrogen removal from simulated solution. The adsorption of ammonium-nitrogen by eggshell of different sizes, and bentonite with eggshell matrix were evaluated by adsorption isotherms.

Methodology

Preparation of the eggshell as adsorbents

Eggshells were collected from the Faculty of Social Sciences and Humanities Canteen, Mahidol University, Nakhonpathom, Thailand. The eggshells were washed with tap water multiple times to remove eggshell membrane, then rinsed with deionized water thrice to remove other contaminants and impurities. The eggshells were then dried at 105°C overnight in an electric oven. The dried eggshells were grinded and sieved through three different sieve size: number 50, number 100, and number 200. The eggshells were categorized according to sieve size into 250-151 μm sieved eggshell (EGGPOW >150), 150-75 μm sieved eggshell

(EGGPOW 150-75), and less than 75 μm sieved eggshell (EGGPOW <75) before use as adsorbents (Figure 1).

Preparation of the matrix as adsorbents

Different types of eggshell matrixes were formed with the combination of three different categories of sieved eggshell and bentonite. The ratio of sieved eggshell to bentonite were determined using trial and error method with the goal of maximizing the eggshell component and minimizing bentonite. The ratio of eggshell to bentonite mixture were 95:5, 90:10, 85:15, 80:20, 75:25, 70:30, and 65:35. Deionized water was slowly added to the combination of eggshell and bentonite until spherical matrix with diameter of 10 millimeter could be formed using handheld tablet press. The formed matrixes were dried in oven at 155-160°C for 3 hours, then, tempered in electric furnace at 450°C for 1 hour and at 950°C for 1 hour. The matrixes were left to cool in the furnace overnight (Figure 2). The matrix would be categorized based on sieved eggshell size into sieved eggshells of 250-151 μm with bentonite (MATRIX >150), 150-75 μm sieved eggshell with



Figure 1 Preparation of eggshell

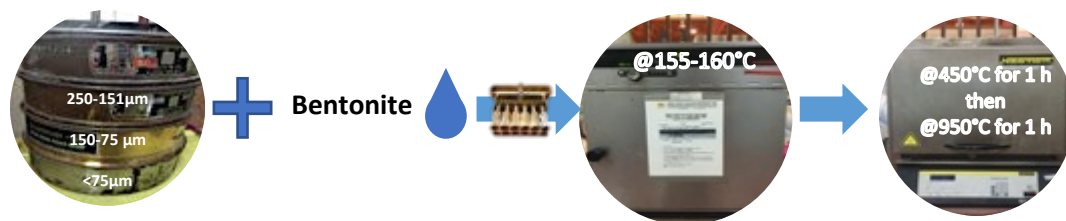


Figure 2 Formation of eggshell with bentonite matrix

bentonite (MATRIX 150-75), and less than 75 μm sieved eggshell with bentonite (MATRIX <75). The matrixes underwent tablet hardness test (Diligent HP-500N Hand screw type max 500N Res 0.1 N., China). The matrixes with highest ratio of the eggshell and withstanding 30 Newtons, which is average the force from hand-crushing, were selected to be use as adsorbents.

Characteristic of adsorbents

The pH of adsorbents provides information about the acidity and basicity of the surface. Approximately 1.0 g of the initial and exhausted adsorbents was added to 75 mL of deionized water. The solution was stirred using magnetic stirrer overnight, then pH was recorded. Surface area and total pore volume of the particle distribution of the developed matrix adsorbent were analyzed with Brunauer- Emmett-Teller (BET) (BELSORP-max series, Japan).

Preparation of adsorbate

Ammonium sulfate was dried in oven at 105°C for 6 hours and left in desiccator to cool. The stock solution of $(\text{NH}_4)_2\text{SO}_4$ (10 gL^{-1}) was prepared by dissolving 10.0 g dried $(\text{NH}_4)_2\text{SO}_4$ in deionized water. The experimental solutions being used to simulate effluent condition were prepared by diluting the stock solution with deionized water.

Batch experiments

The adsorption experiments were performed using the batch equilibrium method. Experiments were performed in triplicates and the averages were reported. In this experiment, 100 mL of different concentration of $(\text{NH}_4)_2\text{SO}_4$ solution was added in a 250 mL conical flask inside a shaking incubator operating at 125 rpm and room temperature and pressure. The adsorbents, namely, EGGPOW >150, EGGPOW 150-75, EGGPOW <75, MATRIX >150, MATRIX 150-75, and MATRIX <75 were added at approximately 5 g with variation of less than 5 percent in the experiments. To assess the effects of initial ammonium-nitrogen concentration, a $(\text{NH}_4)_2\text{SO}_4$ concentration range of 1 to 10 gL^{-1} was at equilibrium time. To assess the effects of contact time, kinetic studies were carried out where the samples were shaken from 1 h to 72 h, and the initial $(\text{NH}_4)_2\text{SO}_4$ concentrations were 2.5 gL^{-1} . The concentration of ammonium ions in this experiment was analyzed using the titrimetric method with the determination limit of ammonium-nitrogen of 50-100 mgL^{-1} [24]. Serial dilution was performed when the concentration of sample exceeded the determination limit using equation (1) below:

$$C_1V_1 = C_2V_2 \quad (1)$$

where C_1 (mgL^{-1}) is the initial concentration, V_1 (L) is the initial volume, C_2 (mgL^{-1}) is the final concentration, and V_2 (L) is the final volume. The ammonium-nitrogen adsorption rate was calculated using equation (2), and the ammonium-nitrogen adsorption capacity was calculated using equation (3) below:

$$\text{Adsorption percentage} = (C_0 - C_e)/C_0 \times 100 \quad (2)$$

$$q = (C_0 - C_e) \times V \text{ M}^{-1} \quad (3)$$

where q (mgg^{-1}) is the ammonium-nitrogen adsorption capacity, C_0 (mgL^{-1}) and C_e (mgL^{-1}) are the initial and equilibrium ammonium-nitrogen concentrations in the solution respectively, V (L) is the solution volume, and M (g) is the mass of adsorbent.

Langmuir and Freundlich models are used to describe the equilibrium isotherm. Langmuir model usually describes monolayer adsorption. The linearized form of Langmuir model can be expressed as shown in equation (4) and (5) below:

$$q_e^{-1} = (C_e K_L q_{\text{max}})^{-1} + q_{\text{max}}^{-1} \quad (4)$$

$$R_L = (1 + K_L q_{\text{max}})^{-1} \quad (5)$$

where q_{max} (mgg^{-1}) is the maximum adsorption capacity of adsorbent, K_L (Lmg^{-1}) is the Langmuir constant, and R_L is the adsorption energy coefficient. The Freundlich model usually describes multilayer adsorption and the adsorption on heterogeneous surfaces. Its linearized form is as equation (6) below:

$$\log q_e = \log K_F + n^{-1} \log C_e \quad (6)$$

where K_F (Lmg^{-1}) is the Freundlich constant, and n is the heterogeneity factor, and a constant

related to adsorption intensity or surface heterogeneity.

Two types of kinetic models were used to describe kinetics of adsorption and reaction in a batch system: pseudo-first order and pseudo-second order rate laws. The pseudo-first order, also termed as the Lagergren's equation was introduced initially by Lagergren (1898).

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (7)$$

with q_t is the amount of adsorbed solute in mgg^{-1} at time t , q_e is the amount adsorbed value at equilibrium in mgg^{-1} , k_1 is the pseudo-first order rate constant (min^{-1}), and t is the time in minutes. Based on adsorption equilibrium capacity, the pseudo-second order equation may be expressed in the linearized form shown below:

$$t q_t^{-1} = t q_e^{-1} + (k_2 q_e^2)^{-1} \quad (8)$$

where k_2 is the pseudo-second order rate constant ($\text{gmg}^{-1} \text{min}^{-1}$); q_t is the amount of adsorbed solute in mgg^{-1} at time t ; q_e is the equilibrium adsorption in mgg^{-1} ; and t is the time in minutes

Results and Discussions

Effect of eggshell powder sizes on matrix formation

Different types of eggshell matrixes were formed with the combination of three different categories of sieved eggshell; EGGPOW >150, EGGPOW 150-75, and EGGPOW <75 with bentonite at a different ratio. The effect of powdered sizes and ratio of sieved eggshell powder to bentonite were shown in Figure 3. The ratio of 65 to 35 of sieved eggshell to bentonite was selected from the results of the hardness test. The sizes of eggshell powder also contributed to the hardness factor of the matrix

formation. EGGPOW >150 with bentonite, regardless of the ratio, could not be formed into the functional matrix as the combination would break apart at less than 5 N of force (Figure 3). EGGPOW 150-75 with bentonite (MATRIX 150-75), and EGGPOW <75 with bentonite (MATRIX <75) that could withstand the force of more than 30 N, demonstrated that particle size affects the hardness of the matrix and, thus, affects the viability of matrix formation. MATRIX 150-75, and MATRIX <75 were selected for further study.

Characteristic of matrix adsorbents

In this study, the initial pH of MATRIX 150-75, and MATRIX <75 adsorbents were found to be approximately 7.8 to 8.1, and the pH of exhausted MATRIX 150-75, and MATRIX <75 adsorbents were 9.6 to 10.8 respectively. The pH

of MATRIX 150-75, and MATRIX <75 showed that the surface is basic. The initial condition of the experiment was adjusted to the initial pH of the matrixes using sodium hydroxide and sulfuric acid, which was also the pH range for optimal ammonium adsorption capacities [21].

The surface area and total pore volume of MATRIX 150-75, and MATRIX <75 were investigated. Results showed that the MATRIX <75 had the highest surface area and total pore volume of $8.17 \text{ m}^2 \text{ g}^{-1}$ and $0.0443 \text{ cm}^3 \text{ g}^{-1}$ respectively. Similarly, MATRIX 150-75 had the surface area and total pore volume of $8.05 \text{ m}^2 \text{ g}^{-1}$ and $0.0416 \text{ cm}^3 \text{ g}^{-1}$ respectively (Figure 4). The surface area and total pore volume of adsorbents affect the performance of adsorbents, in general, the higher the surface area and total pore volume, the higher the adsorption sites and effectiveness of the adsorbents.

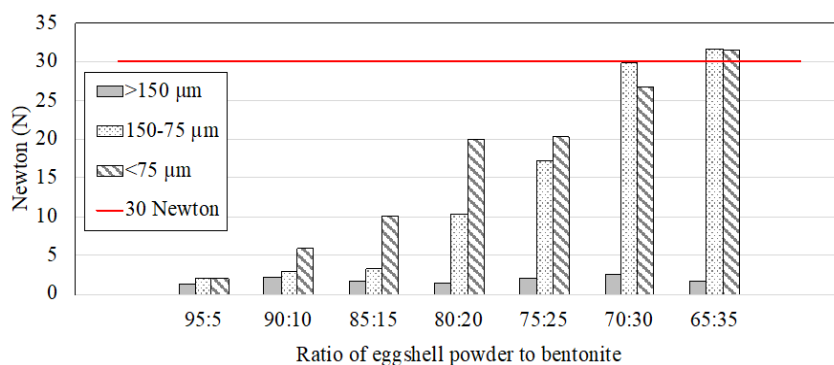


Figure 3 Effect of different ratio of eggshell powder to bentonite on hardness of matrix adsorbent

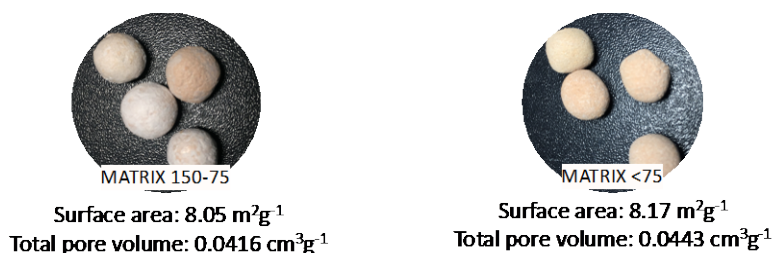


Figure 4 Surface area and total pore volume of MATRIX 150-75 and MATRIX <75

Effect of contact time

The effect of contact time on the adsorption of ammonium nitrogen was studied with an initial concentration of $(\text{NH}_4)_2\text{SO}_4$ at 2.5 gL^{-1} . The ammonium adsorption by the sieved eggshell powder and matrixes with contact times from 2 to 72 hours. The results showed that the adsorption rate of ammonium nitrogen by all types of adsorbents rose sharply from 2 hours to 6 hours due to the availability of adsorption sites (Figure 5).

After the contact time of 6 hours, there is decrease in ammonium-nitrogen adsorption rate in experiments with EGGPOW >150, EGGPOW 150-75, EGGPOW <75, and MATRIX 150-75 adsorbents. The decrease in ammonium-nitrogen adsorption rate could be attributed to the desorption of ammonium from adsorbents as well as pseudo-second-order kinetics biosorption [25]. The decreased rate of ammonium-nitrogen adsorption with increasing contact time was due to the filling of the adsorption site by ammonium ions. As seen in Figure 5 the higher the contact time, the higher the adsorption of ammonium-nitrogen percentage. From the experiment, the adsorption equilibrium was reached at 24 hours.

Effect of initial concentrations

In order to analyze the effect of the initial ammonium-nitrogen concentrations, experiment was performed using $(\text{NH}_4)_2\text{SO}_4$ concentration range of 1 to 10 gL^{-1} was at equilibrium time of 24 hours as determined in the earlier experiment with adsorbents at 5 g. The results showed that the initial ammonium-nitrogen concentration had a significant influence on the ammonium-nitrogen adsorption by the adsorbents. There was also a significant different in adsorption percentage between sieved eggshell powder and matrixes form from sieved eggshell, and bentonite. It was observed, at 10 gL^{-1} , that the ammonium-nitrogen adsorption percentage is highest at 5.2 mgg^{-1} for MATRIX 150-75 and slightly less than 5 mgg^{-1} for MATRIX <75 in comparison to ammonium-nitrogen adsorption percentage of EGGPOW >150, EGGPOW 150-75, and EGGPOW <75 at 4.1 mgg^{-1} , 4.4 mgg^{-1} and 4.6 mgg^{-1} respectively (Figure 6). The ammonium-nitrogen adsorption rate by MATRIX 150-75 was higher than observed results of MATRIX <75. This could be the effects of bentonite material in MATRIX. Therefore, this performance was not significant.

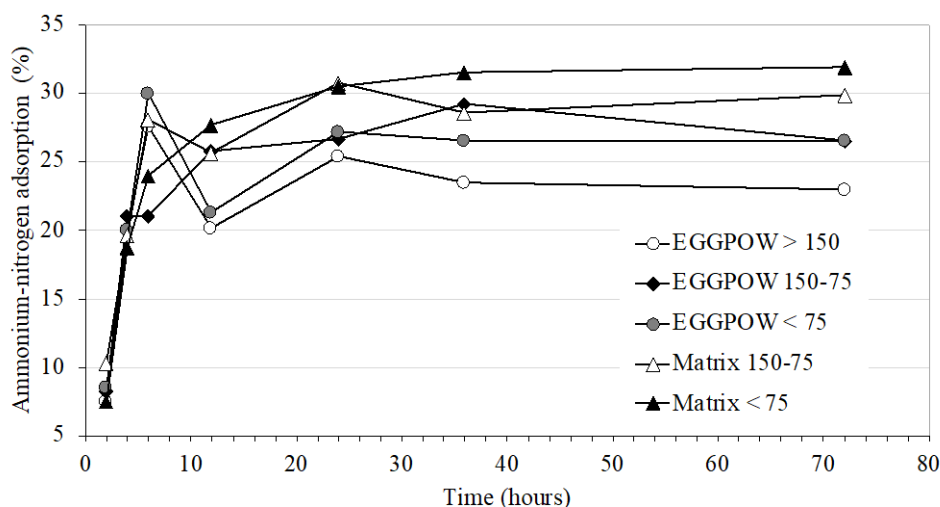


Figure 5 Effect of contact time in hours on the adsorption of ammonium-nitrogen

Overall, the increases in initial concentration of ammonium-nitrogen affected the ammonium nitrogen adsorption by the adsorbents. With the increase in initial ammonium-nitrogen concentration, the ammonium-nitrogen adsorption amount of all adsorbents increases sharply from $(\text{NH}_4)_2\text{SO}_4$ concentration of 1.0 gL^{-1} to 2.5 gL^{-1} (Figure 6). The increases in adsorption amount could be attributed to high concentration of initial ammonium-nitrogen concentration, it was expected that with the same surface area and total pore volume of adsorbents, a higher initial ammonium-nitrogen concentration would result in a stronger driving force generating from the higher concentration gradient on the adsorbent. As a result of the concentration gradient, there was a drive on amount of ammonium nitrogen adsorption for higher concentration of initial condition as seen in Figure 6 at the $(\text{NH}_4)_2\text{SO}_4$ concentration of 1.0 to 10.0 gL^{-1} [26]. The shallow increases in the amount of ammonium nitrogen adsorption per gram of adsorbents from 5.0 gL^{-1} to 10 gL^{-1} $(\text{NH}_4)_2\text{SO}_4$, in contrast to the amount of ammonium nitrogen adsorption per gram of adsorbents from 2.5 gL^{-1} to 5.0 gL^{-1} $(\text{NH}_4)_2\text{SO}_4$, could be attributed to the filling up of sorption site on the adsorbents. Then, results from conducting adsorption tests at lower concentration

might not differentiate the adsorption capacity of sorbent.

Adsorption isotherms

To access the ammonium-nitrogen adsorption of EGGPOW >150, EGGPOW 150-75, EGGPOW <75, MATRIX >150, MATRIX 150-75, and MATRIX <75 from simulated wastewater, the isotherm of the adsorbents was studied. Langmuir and Freundlich models were used to fit the experimental data. Based on the experiment, two isotherm parameters of Langmuir model and Freundlich model were determined as shown in Table 1. The correlation for Langmuir model (R^2) was within acceptable range of more than 0.972 for all types of adsorbents. This implied that the adsorption reaction occurs as a monolayer on the matrixes surface with a finite number of adsorption sites. R_L of EGGPOW >150, EGGPOW 150-75, EGGPOW <75, MATRIX 150-75, and MATRIX <75 were between 0.98 to 0.99, which is less than 1 and more than 0. Therefore, there are four probabilities for the R_L value, for favorable adsorption, $0 < R_L < 1$; for unfavorable adsorption, $R_L > 1$; for linear adsorption, $R_L = 1$; for irreversible adsorption, $R_L = 0$ [14]. In this case, R_L obtained from experiment showed that adsorption of ammonium ions on the adsorbents was favorable.

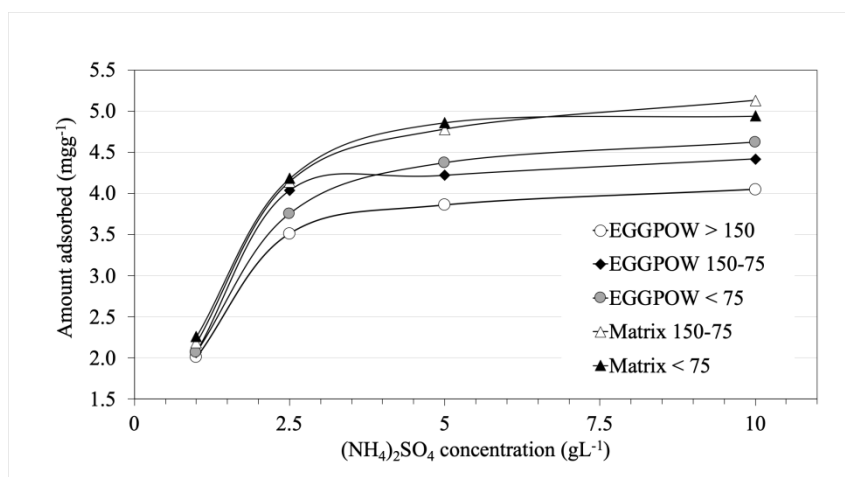


Figure 6 Effect of initial $(\text{NH}_4)_2\text{SO}_4$ concentration on the amount of ammonium-nitrogen adsorption

Table 1 Langmuir and Freundlich isotherm parameters for ammonium-nitrogen adsorption onto different types of eggshell and matrixes

Adsorbents	Langmuir Isotherm				Freundlich Isotherm		
	q_{\max} (mgg^{-1})	K_L (Lmg^{-1})	R_L	R^2	n^{-1}	K_F (Lmg^{-1})	R^2
EGGPOW > 150	19.0	0.0005	0.99	0.999	0.9588	0.0251	0.998
EGGPOW 150-75	25.0	0.0003	0.99	0.975	0.9909	0.0214	0.996
EGGPOW < 75	36.2	0.0002	0.99	0.984	0.9627	0.0245	0.999
MATRIX 150-75	20.1	0.0007	0.98	0.990	0.9989	0.0197	0.998
MATRIX < 75	16.4	0.0009	0.98	0.972	0.9986	0.0201	0.999

From correlation comparison, it was concluded that the Freundlich model provided a more consistent fit to the data comparing with the Langmuir model. Freundlich model based on the sorption onto a heterogeneous surface was applicable with R^2 of 0.99. The empirical parameter value of n^{-1} which was smaller than 1 was implied favorable adsorption conditions [14]. From the results, both Langmuir and Freundlich model are applicable, should be considered for further application.

Adsorption kinetics

The pseudo-first order and pseudo-second order models are applied to the experimental data to study the adsorption of the ammonium nitrogen by the adsorbent. The correlation coefficients, R^2 for pseudo first-order equation were 0.127, 0.198, 0.170, 0.391, and 0.502 for the adsorption of ammonium nitrogen onto EGGPOW >150, EGGPOW 150-75, EGGPOW <75, MATRIX 150-75, and MATRIX <75 respectively (Table 2). The R^2 indicated that the kinetic of the experiment data in this study did not fit under the pseudo first-order condition. However, the experimental data satisfied the pseudo second order linear regression. The correlation

coefficients, R^2 for pseudo first-order equation were 0.9646, 0.9705, 0.9096, 0.9506, and 0.7402 for the adsorption of ammonium nitrogen onto EGGPOW >150, EGGPOW 150-75, EGGPOW <75, MATRIX 150-75, and MATRIX <75 respectively.

From the data and R^2 analysis, the values of pseudo second-order rate constants (k_2) for the adsorption ammonium nitrogen onto EGGPOW >150, EGGPOW 150-75, EGGPOW <75, MATRIX 150-75, and MATRIX <75 were $0.0015 \text{ mgg}^{-1} \text{ min}^{-1}$, $0.0011 \text{ mgg}^{-1} \text{ min}^{-1}$, $0.0008 \text{ mgg}^{-1} \text{ min}^{-1}$, $0.0197 \text{ mgg}^{-1} \text{ min}^{-1}$, and $0.0201 \text{ mgg}^{-1} \text{ min}^{-1}$ respectively (Table 2). The pseudo-equilibrium adsorption coefficient of the second-order regression for the adsorption ammonium nitrogen onto EGGPOW >150, EGGPOW 150-75, EGGPOW <75, MATRIX 150-75, and MATRIX <75, q_e were 3.32 mgg^{-1} , 3.82 mgg^{-1} , 3.54 mgg^{-1} , 4.53 mgg^{-1} , and 5.75 mgg^{-1} , respectively (Table 2). In this case, the calculated q_e values showed similar value to the amount adsorbed shown in Figure 6. As a result, the pseudo second-order kinetic model can be used to quantify the adsorption kinetics of EGGPOW >150, EGGPOW 150-75, EGGPOW <75, MATRIX 150-75, and MATRIX <75.

Table 2 Pseudo-first order and pseudo-second order parameters for ammonium-nitrogen adsorption onto different types of eggshell and matrixes

Adsorbents	Pseudo-first order			Pseudo-second order		
	q_e (mgg^{-1})	k_1 (min^{-1})	R^2	q_e (mgg^{-1})	k_2 ($\text{gmg}^{-1}\text{min}^{-1}$)	R^2
EGGPOW > 150	27.4	0.0002	0.127	3.32	0.0015	0.965
EGGPOW 150-75	18.9	0.0004	0.198	3.82	0.0011	0.971
EGGPOW < 75	24.5	0.0004	0.170	3.54	0.0008	0.910
MATRIX 150-75	10.7	0.0006	0.391	4.53	0.0197	0.951
MATRIX < 75	21.2	0.0007	0.502	5.75	0.0201	0.740

Conclusion

The experimental results showed both eggshell and eggshell matrix could potentially be utilized as a bio-sorbent for ammonium-nitrogen adsorption. For further application, a cost-benefit analysis of the preparation sieved eggshell, and matrixes should be calculated to access the feasibility of a large-scale treatment application. The MATRIX 150-75 also showed the potential of ammonium-nitrogen with maximum ammonium-nitrogen adsorption of 41%, which was higher than EGGPOW >150, EGGPOW 150-75, and EGGPOW <75. The surface area and total pore volume of adsorbents affected the performance of adsorbents as observed from sieved eggshell of different sizes. The results also showed that the initial ammonium-nitrogen concentration and contact time had a significant influence on the ammonium-nitrogen adsorption by the adsorbents. The experimental data were fitted by both the Langmuir and Freundlich model to characterized the adsorption model, of which the Freundlich model is more applicable. From linear regression, the adsorption kinetics of EGGPOW >150, EGGPOW 150-75, EGGPOW <75, MATRIX 150-75, and MATRIX <75 conformed to the pseudo second-order kinetic. However, there are other forms of nitrogen, such as nitrite and nitrate presence in wastewater,

that adversely affect the environment. Further research is required to understand the efficiency of eggshells and eggshell matrixes to remove other forms of nitrogen from the wastewater.

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