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Comparison of Adsorbents for Ammonia Removal from Mining Wastewater

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***Abstract*—**Ammonia in mining wastewater is a significant problem, and treatment can be especially difficult in cold climates where biological treatment is not feasible. An adsorption process is one of the alternative processes that can be used to reduce ammonia concentrations to acceptable limits, and therefore a LEWATIT resin strongly acidic H+ form ion exchange resin and a Bowie Chabazite Na form AZLB-Na zeolite were tested to assess their effectiveness. For these adsorption tests, two packed bed columns (a mini-column constructed from a 32-cm long x 1-cm diameter piece of glass tubing, and a 60-cm long x 2.5-cm diameter Ace Glass chromatography column) were used containing varying quantities of the adsorbents. A mining wastewater with ammonia concentrations of 22.7 mg/L was fed through the columns at controlled flowrates. In the experimental work, maximum capacities of the LEWATIT ion exchange resin were 0.438, 0.448, and 1.472 mg/g for 3, 6, and 9 g respectively in a mini column and 1.739 mg/g for 141.5 g in a larger Ace column while the capacities for the AZLB-Na zeolite were 0.424, and 0.784 mg/g for 3, and 6 g respectively in the mini column and 1.1636 mg/g for 38.5 g in the Ace column. In the theoretical work, Thomas, Adams-Bohart, and Yoon-Nelson models were constructed to describe a breakthrough curve of the adsorption process and find the constants of the above-mentioned models. In the regeneration tests, 5% hydrochloric acid, HCl (v/v) and 10% sodium hydroxide, NaOH (w/v) were used to regenerate the LEWATIT resin and AZLB-Na zeolite with 44 and 63.8% recovery, respectively. In conclusion, continuous flow adsorption using a LEWATIT ion exchange resin and an AZLB-Na zeolite is efficient when using a co-flow technique for removal of the ammonia from wastewater. Thomas, Adams-Bohart, and Yoon-Nelson models satisfactorily fit the data with R^2 closer to 1 in all cases.

***Keywords*—**AZLB-Na zeolite, continuous adsorption, LEWATIT resin, models, regeneration.

I. Introduction

INCREASING ammonia concentrations in mining wastewater (MW) has become a critical issue resulting from industrial activities. To reduce ammonia concentrations to acceptable levels, ion exchange and adsorption may be an effective process to remove ammonia in this type of wastewater treatment [1]. There are many advantages to using ion-exchange such as high treatment loading and removal efficiency, low cost, and fast kinetics [2]. Many techniques have been used in the past for the ammonia removal such as: air stripping, biodegradation, catalytic oxidation, ion-exchange adsorption by a cation exchanger, and membrane separation, but in this research, an adsorption process using resins/zeolites was chosen because it is easy to maintain and operate, low cost relative to air stripping and appropriate for a cold environment on the contrary of biodegradation as well as ammonia removal and treatment capacity are high and kinetics are fast [3]. Studies of the ammonia removal by adsorption using resins/zeolites were investigated by many researchers including: 60% removal of ammonia at high-concentration within 150-4000 ppm using zeolites [4], 80% removal of ammonia at 80 ppm using clinoptilolite zeolites [5], removal of ammonia at the low-concentration of 8.8 ppm using natural zeolites [6], removal of ammonia from a 1000 ppm solution using zeolites [7], [8] and removal of ammonia at the low-concentration range of 2-10 ppm using various-types of Na-form zeolites using a flow system in different range of temperature [9]. Our research focuses on studying an AZLB-Na zeolite and a LEWATIT resin for removing ammonia concentrations of 22.7 mg/L or ppm in MW to examine their removal efficiencies using different-size columns (Mini & Ace). The AZLB-Na 14×50 mesh zeolite used in this study was an anhydrous sodium aluminosilicate obtained from St. Cloud^{TM} Mining [10]. The advantages of a AZLB-Na zeolite are that it can be hydrated, it forms regular structures, it is resistant to high pressures, it has large open pores and high melting temperatures, and it is very stable, insoluble in water and organic solvents, and it does not oxidize in air [11], [12]. Commonly mined zeolites including chabazite, clinoptilolite, and mordenite are very useful in water purification because they can exchange positively charged ions already in their structure with positively charged ions in the water whose removal is desired. They are very often used as water-softeners whose purpose is to remove ions such as magnesium and calcium and they have been used to remove ammonia from water [13]. The LEWATIT Lanxess Monoplus S108, used in these studies is a strongly acidic in the Na form with beads of uniform size based on a styrene-divinylbenzene copolymer [14] Commercially prepared ion- exchange resins consist of an organic polymer cross-linked backbone with different functional groups such as sulfonic acids, quaternary amino groups, carboxylic acid groups, or primary, secondary, and tertiary amino groups. These groups are either strongly acidic, strongly basic, weakly acidic, or weakly basic, respectively, with their functions specific to the type of resin. These materials are either spheres or granules with specific

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sizes depending on the desired application. They can be designed to exchange cations or anions in water based applications and their adsorption of ammonia in water has been studied [15]-[17]. Commonly, ion-exchange resins are like zeolites in their functions although they are polymer based materials rather than natural materials such as the zeolites [18].

TABLE I
SYMBOLS' DEFINITION

Symbol	Unit	Definition
C_e	(mg/L)	Ammonia concentration as nitrogen of MW at equilibrium
C_o	(mg/L)	Initial ammonia concentration as nitrogen of MW
C_t	(mg/L)	Ammonia concentration as nitrogen of MW at time
k_{AB}	(L/mg.min)	Rate constant of the Adams-Bohart model
k_{Th}	(L/mg.min)	Rate constant of Thomas model
k_{YN}	(1/min)	Rate constant of the Yoon-Nelson model
m	(g)	Mass of the adsorbent
N	(-)	No. of increments of the volume added in the continuous adsorption
N_o	(mg/L)	Saturation concentration of the Adams-Bohart model
Q	(L/min)	Volumetric flow rate of MW
q_{max}	(mg/g)	Maximum adsorption capacity
q_t	(mg/g)	Experimental adsorption capacity at time
t	(min)	Time
τ	(min)	Time required to reach 50% breakthrough
U_o	(cm/min)	Superficial velocity of MW
V	(L)	Volume of the adsorbate
Z	(cm)	Bed depth of the packed-bed column

II. Adsorption Analysis

For the adsorption experiments, analysis was conducted using a UV-Visible spectrophotometer (HP8452A diode array) and high-range Hach kits for ammonia. The Hach kits were used to determine the ammonia concentration as nitrogen (NH_3 as N). The Hach kits are meant to be field test kits with a reported accuracy of approximately 95% with some interferences. To find the ammonia (NH_3) concentration, the NH_3 as N concentration must be multiplied by 1.2159 (Ratio between molecular weights of NH_3 and Nitrogen (N)).

III. Continuous Adsorption

Two types of the columns were used in the continuous adsorption as follows:

A. Mini Column

As shown in Fig. 13, the mini column was constructed of a 32-cm long x 1-cm inner diameter piece of glass tubing sealed at one end using duct tape with a piece of 5 µm Whatman filter. The resin/zeolite masses were placed into the mini-column and MW was passed through the column in increments of 30 - 120 ml until breakthrough of the ammonia was observed. Using the mini column, one ion-exchange resin (LEWATIT Monoplus), and one zeolite (St. Cloud ALZB-Na) were tested at three (3, 6, and 9 g) and two masses (3, and 6 g), respectively. The procedure for using a mini column to test adsorption of ammonia with the adsorbents (resins/zeolites) was as follows: 3, 6, or 9 g of the adsorbent was added to the column and the heights of the adsorbent measured. A sample of the mining water was collected before adding to the column and the NH_3 as N was measured using a Hach kit. A clamp and vertical bar stand were used to hold the column upright in a 100-ml graduated cylinder. 30 ml of the mining water was poured into the column and a timer started. This operation was performed in volume increments of either 30, 60, or 120 ml until the total volume increment had drained down to the top of the adsorbent, each specific volume increment was collected in the graduated cylinder then poured into a plastic container and a sample collected for Hach analysis of the ammonia after which the waste was discarded into a waste bucket. This procedure was repeated until 300 ml had been passed through the column for a 3-g adsorbent sample, 600 ml for a 6-g adsorbent sample, and 900 ml for a 9-g adsorbent sample. When testing was completed, the taped filter circle was removed, and DI water was passed through the column until all the adsorbent has been dislodged.

B. Ace Column

As shown in Fig. 14, the Ace chromatography column was constructed of a 60-cm long x 2.5-cm inner diameter piece of glass tubing with taped threaded glass ends, and threaded Teflon endcaps. Appropriate tubing was connected to an adjustable-headed peristaltic pump (10.6" x 5.3" x 6.0") using 1/4'' and 1/8" ID plastic tubing with duct tape [19], [20] to deliver water into the column at a rate of approximately 5.7-105.14 ml/min or 1-10 according to the pump setting by connecting Using the Ace column, the LEWATIT Monoplus ion-exchange resin and ALZB-Na zeolite were tested at masses of approximately 131.4 and 38.5 g, respectively, while the mining water was passed through the column until the experiment was terminated or breakthrough of the ammonia was observed. The procedure for ammonia adsorption in the Ace column using the adsorbents was as follows: The desirable masses of the adsorbent were weighed and then added into the column and the bed depth measured. DI water was poured into the column to remove the adsorbent from the column wall and ensure the entire mass filled the column to the selected height. The valve was opened to drain the DI water in the column until the height of the water was 1 to 2 cm above the adsorbent. A peristaltic pump was connected to the column at the top by the appropriate tubing (as described above) and the speed was adjusted to the desired setting. A 500-ml or 1-L beaker was placed under the bottom of the column to collect the water. The pump was activated and the valve opened at the bottom to let the water drain out of the column at a speed equaling the speed of the water entering the column. The valve was opened and closed as required to try to maintain the water level at a mark approximately 1 cm above the height of the bed. A stopwatch was turned on to monitor the time. Samples were collected when either the desired time or volume was reached for testing the ammonia removal and then the residual water was discarded in a waste bucket. This procedure was repeated until breakthrough. After the breakthrough point has been achieved, samples were collected to monitor the rise in the NH_3 as N in the adsorption sample

volume. When the experiment was complete, the adsorbent was regenerated. The percentage of the NH_3 removal was calculated using (1). The ratio $C_t/C_o$was plotted vs. time and the accumulative NH_3 mass calculated using (2).

$$\%\, NH_3 removal = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

$$\text{Acc. } NH_3 \text{ mass} = \int_0^v (C_o - C_t)dv \simeq V \sum_1^N C_o - C_t \quad (2)$$

where C_o is the initial NH_3 as N of MW (mg/L) and C_t is the NH_3 as N of MW at time t (mg/L), N is the no. of increments of the volume added, V is the volume (L), and t is time (min).

IV. Adsorbents' Regeneration

Two methods were performed to regenerate adsorbents depending on its nature. Regeneration of the LEWATIT Monoplus resin and ALZB-Na zeolite was attempted using 5% (v/v) and 10% (w/v) solution of HCl and NaOH respectively. In these tests, the resin or zeolite was retained in the column after the previous experiments, drained of the mining water, then filled with the acid or base, and up to 2500 ml of the acid or base subsequently passed through the resin or zeolite, in 200 to 600 ml increments, until a sample collected from the acid or base passed through the column measured < 0.5 mg/L NH_3 as N. This 5% HCl solution was prepared in in one-liter batches in the fume hood by adding approximately 70 ml of concentrated acid to one-liter DI water. 10% NaOH solution was prepared in one-liter batches in the fume hood by adding approximately 100 g of NaOH pellets to one-liter DI water in a one-liter beaker and mechanically stirring until all the pellets had dissolved. Instructions for regenerating the LEWATIT Monoplus resin & ALZB-Na zeolite using the Ace column were as follows: 5% HCl and 10% NaOH solution were prepared for a strong acid (H+) Monoplus resin and the ALZB-Na zeolite, respectively. To regenerate, the Monoplus resin & the ALZB-Na zeolites were first drained of the remaining water. With the valve closed, HCl or the NaOH was added to a level 1 or 2 cm above the LEWATIT resin or ALZB-Na zeolite. After 400-500 ml has been collected in the beaker, a sample was taken and analyzed for NH_3 as N. If the value was higher than 50 mg/L (the maximum limit of the Hach kits), a dilution (2:1; 5:1 or 10:1 depending on the concentration) was required for accurate analysis. The acid or base was added to the column in 400-500 or 200 ml increments until < 1 mg/L NH_3 as N is detected in the beaker. When finished regenerating, the acid or base was drained from the rein/zeolite and DI water was added to remove any residual acid from the column.

V. Models

Three flow models were used to describe behavior of the continuous ammonia adsorption in the column flow using the LEWATIT resin & ALZB-Na zeolite as follows:

A. Thomas Model

The Thomas model is one of the widely used models for a packed bed adsorption process [21]. Its non-linear and linear forms are in (3) and (4) respectively:

$$\frac{C_t}{C_o} = \frac{1}{1+exp\left(k_{Th}q_o\left(\frac{m}{Q}\right) - k_{Th}C_o t\right)} \quad (3)$$

$$ln\left(\frac{C_o}{C_t} - 1\right) = k_{Th}q_{max}\left(\frac{m}{Q}\right) - k_{Th}C_o t \quad (4)$$

where C_o is the initial NH_3 as N of MW (mg/L), C_t is the NH_3 as N of MW at time t (mg/L), m is mass of the adsorbent (g), k_{Th} is the Thomas rate constant (L/mg.min), q_{max} is the maximum concentration (mg/g), Q is the volumetric flow rate of MW (L/min) and t is time (min). Plotting $ln\left(\frac{C_o}{C_t} - 1\right)$ vs. t produces a slope and intercept in which k_{Th} and q_{max} can be determined by applying $\frac{slope}{C_o}$ and $\frac{intercept}{k_{Th}}\left(\frac{Q}{m}\right)$ respectively.

B. Adams-Bohart Model

This model was derived by [22] which is also one of the widely used models in a packed bed adsorption process. Its non-linear and linear forms are in (5) and (6) respectively:

$$\frac{C_t}{C_o} = exp\left(-k_{AB}N_o\left(\frac{Z}{U_o}\right) + k_{AB}C_o t\right) \quad (5)$$

$$ln\left(\frac{C_t}{C_o}\right) = -k_{AB}N_o\left(\frac{Z}{U_o}\right) + k_{AB}C_o t \quad (6)$$

where C_o is the initial NH_3 as N of MW (mg/L), C_t is the NH_3 as N of MW at time (mg/L), k_{AB} is the Adams-Bohart rate constant (L/mg.min), N_o is the saturation concentration (mg/L), U_o is the superficial velocity of MW (cm/min), t is time (min) and Z is the bed depth (cm). Plotting $ln\left(\frac{C_t}{C_o}\right)$ vs. t produces a slope and intercept in which k_{AB} and N_o can be determined by applying $\frac{slope}{C_o}$ and $\frac{intercept}{k_{AB}}\left(\frac{U_o}{Z}\right)$ respectively.

C. Yoon-Nelson Model

This model, derived by [23], [24], is also one of the widely used models in a packed bed adsorption process. Their non-linear and linear forms are in (7) and (8) respectively:

$$\frac{C_t}{C_o} = \frac{exp(k_{YN}t - \tau k_{YN})}{1+exp(k_{YN}t - \tau k_{YN})} \quad (7)$$

$$ln\left(\frac{C_t}{C_o - C_t}\right) = k_{YN}t - \tau k_{YN} \quad (8)$$

where C_o is the initial NH_3 as N of MW (mg/L), C_t is the NH_3 as N of MW at time t (mg/L), k_{YN} is the Yoon-Nelson rate constant (1/min), t is time (min) and τ is the time required to reach 50% breakthrough (min).

VI. Results and Discussions

A. Mini Column

Mini-column tests were meant to see if breakthrough could be achieved in a reasonable amount of time and how that might differ with resin mass. It was interesting to note that the

calculated flow rate was initially fast (12, 17.3, and 14.6 ml/min respectively) for the 3, 6, and 9 g of LEWATIT resin and it slowed down to a relative steady state (5.7, 5.7, and 5.3 ml/min respectively) as the tests progressed. For the 3 and 6 g AZLB-Na zeolite, the flow rate was relatively stable throughout the experiment, ranging from 3.9 to 7.2 ml/min once the mass loading had reached a certain level. As shown in Fig. 1 and Table II, The LEWATIT adsorption results demonstrated that once approximately 3.4, 6.5, and 15.3 mg of NH_3 as N had been adsorbed onto the resin, breakthrough progressed rapidly. There was some leakage through the column as evidenced by the fact that the ammonia concentration in the filtrate never reached 0 and some separation of the resin was observed. A plot of the breakthrough masses versus the resin mass appears to be quite linear, suggesting that for 131.4 g of resin, as was used for the Hatch chromatography column, it is possible that breakthrough might occur once approximately 214 mg of NH_3 as N had been adsorbed. As shown in Fig. 2 and Table II, the AZLB-Na adsorption results demonstrated that breakthrough started to occur once approximately 2.0 mg and 6.8 mg of NH_3 as N had been deposited onto the zeolite, respectively, on 3 and 6 g of zeolite. From these results, it was estimated that approximately 58.3 g of NH_3 as N would adsorb to 38.5 g of zeolite before breakthrough occurred.

B. Ace Column

As shown in Fig. 3 and Table II, The Ace column was set up in the same manner and a LEWATIT resin (131.4 g) was added to the column using DI water as the carrier. The height of the resin was approximately 29.5 cm. The DI water was drained until approximately 2.5 cm above the resin. The peristaltic pump was operated at the same setting, which was approximately 38.5 ml/min. However, during the experiment, the time to collect the bulk samples prior to grab sampling indicated an average flow rate of 41.7 ± 1.5 ml/min. The bulk sample volume collected over the experiment was increased from 345 ml to 530 to 960 to 1540 to 2100 ml as the experiment progressed to speed up the breakthrough. 19 samples were collected in total. The estimated breakthrough for the LEWATIT in the Ace column was calculated to be approximately 214 mg, according to the graph plotted with the data from the mini-column. According to the breakthrough results obtained for the 131.4 g LEWATIT in the Ace column, the breakthrough occurred at approximately 226 mg. So, the breakthrough of ammonia adsorption is generally linear according to mass of resin used for this range of resin masses. As shown in Fig. 4 and Table II, The Ace column test using the AZLB-Na zeolite was conducted using the same setup as with the LEWATIT resin, only with 38.5 g of the zeolite. This was due to a limited amount of mining water remaining. The volumes of mining water extracted from the column, increased from 200 to 600 ml as the experiment progressed. Breakthrough progressed rapidly after approximately 44.8 mg of NH_3 as N had been delivered to the column. This is slightly less than the 58.3 mg predicted.

C. Adsorbents Regeneration

For the LEWATIT resin as in Fig. 5, a total of 1805 ml in increments of 420, 470, 465, and 450 ml was delivered in the first test to the LEWATIT resin at an average flow rate of approximately 90 ml/min, yielding 76.0, 22.7, 0.7, and 0.2 mg of NH_3 as N in the volumes collected. For the total volume collected, this produced a total of 99.6 mg from an expected 226 mg adsorbed (44% recovery) and a combined filtrate with a concentration of approximately 55.2 mg/L compared to the original 22.7 mg/L mining water concentration. Since only 44% of the ammonia adsorbed was recovered, it was decided to remove the resin from the column, leave it overnight in an acidic solution, mix it around, re-introduce it to the column, slow the flow rate, and try again. In the second test, a total of 1000 ml of 5% HCl was used in 430 and 470 ml increments at an average flow rate of 33.4 ml/min. No ammonia was recovered in either volume. For the AZLB-Na zeolite as in Fig. 6, a total volume of 1000 ml of the 10% NaOH regenerating liquid was introduced in increments of 200 ml at an average flow rate of 40 ml/min. The amount of ammonia recovered was 12.2, 6.5, 4.1, 2.9, and 2.6 mg NH_3 as N for the respective volumes for a total of 28.4 mg out of an expected 44.8 mg adsorbed (63.8% recovery), however, this is a slightly low estimate as the test was not continued until the filtrate registered 0 mg NH_3 as N. The filtrate concentration for the total ammonia in the 1000 ml was 28.58 mg/L compared to the 22.7 mg/L NH_3 as N in the original mining water.

D. Models

Figs. 7 & 8 showed plots of the models using 3 & 6 g of LEWATIT respectively in a mini-column while Figs. 9 & 10 showed plots of the models using 3 & 6 g of AZLB-Na respectively. Fig. 11 showed plots of the models using 141.5 g of LEWATIT in an Ace column while Fig. 12 showed plots of the models using 38.5 g of AZLB-Na. The constants of the models were calculated using the intercepts and slope of those figures and applying (4), (6), and (8). It can be observed that the constants of the models are approximately the same in using different masses of both LEWATIT and AZLB-Na as in Table III. In each figure, plots of the models looked like the same, but in fact, they are not. Firstly, the y-axis of each plot is not the same: $ln\left(\frac{C_o}{C_t}-1\right)$, $ln\left(\frac{C_t}{C_o}\right)$ and $ln\left(\frac{C_t}{C_o-C_t}\right)$ are y-axises of the Thomas, Adams-Bohart, and Yoon-Nelson models respectively. Secondly, the slopes and intercepts of each plot are not the same as shown in (4), (6), and (8). Thirdly, the rate constant of each plot is not the same as in Table III.

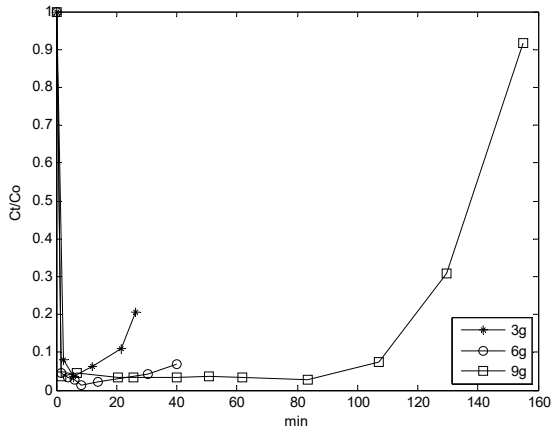


Fig. 1 Relative ammonia concentration using 3, 6 & 9 g of LEWATIT in a mini column

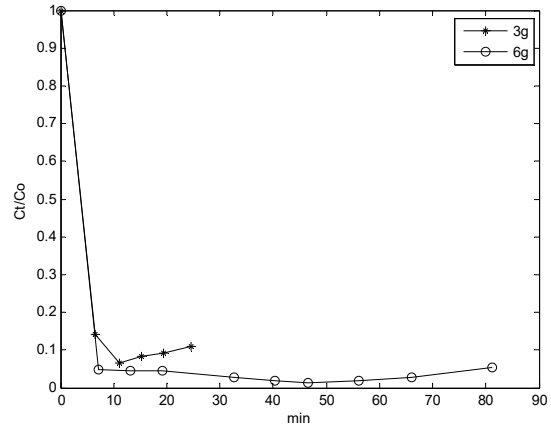


Fig. 2 Relative ammonia concentration using 3 & 6 g of AZLB-Na in a mini column

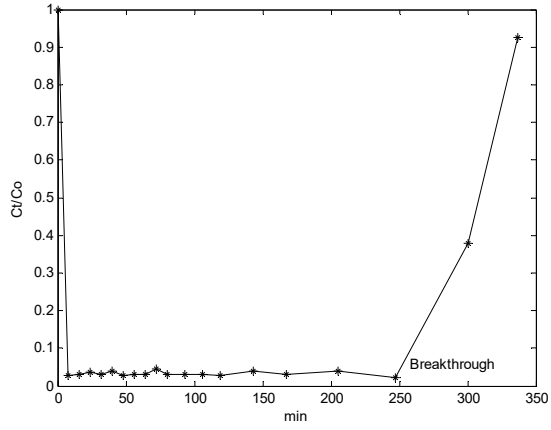


Fig. 3 Relative ammonia concentration using of LEWATIT in an Ace column

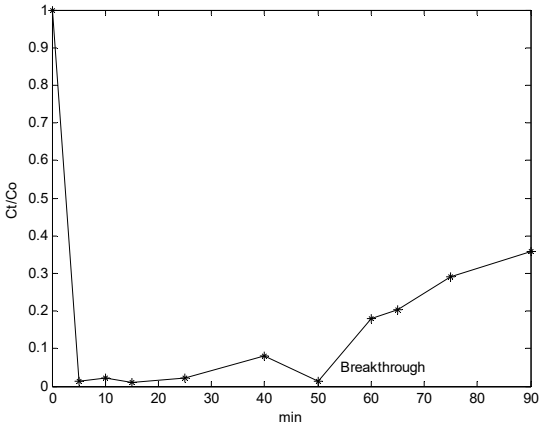


Fig. 4 Relative ammonia concentration using of AZLB-Na in an Ace column

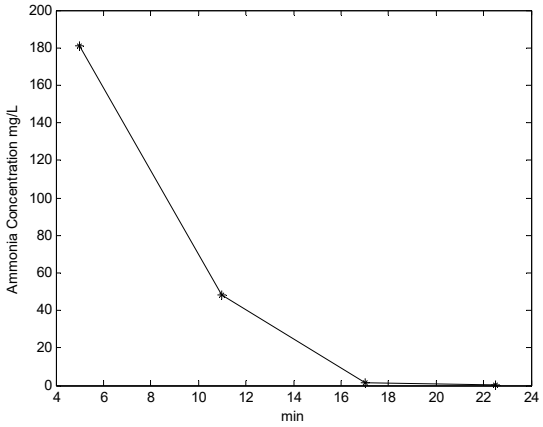


Fig. 5 Regeneration of a LEWATIT resin using 5% HCL in an Ace column

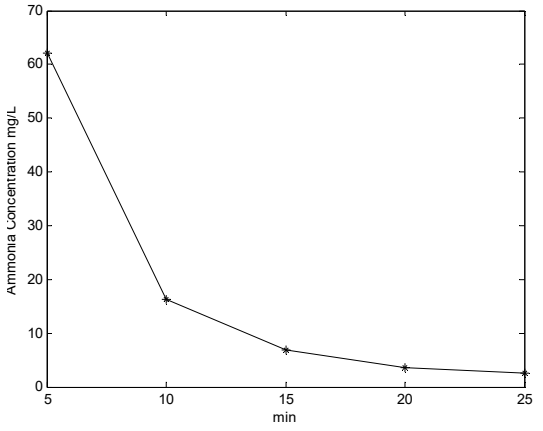
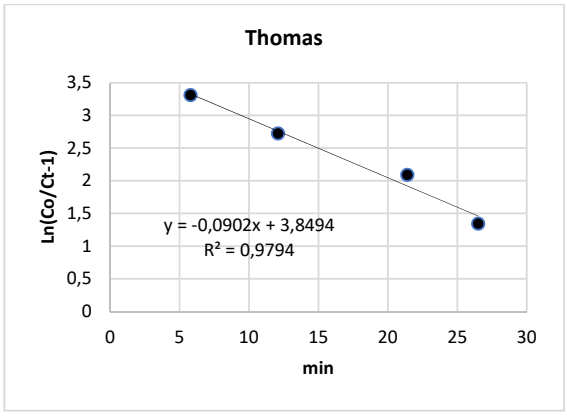
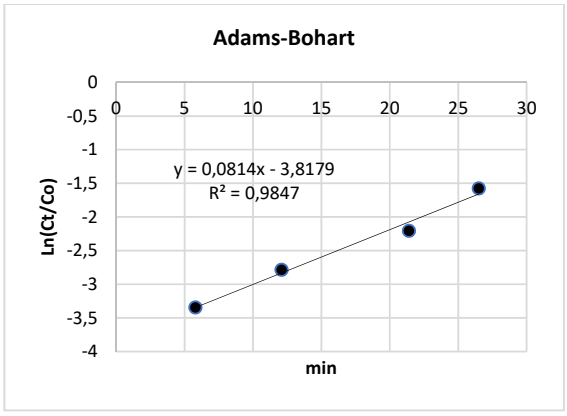


Fig. 6 Regeneration of an AZLB-Na zeolite using 10% NaOH in an Ace column





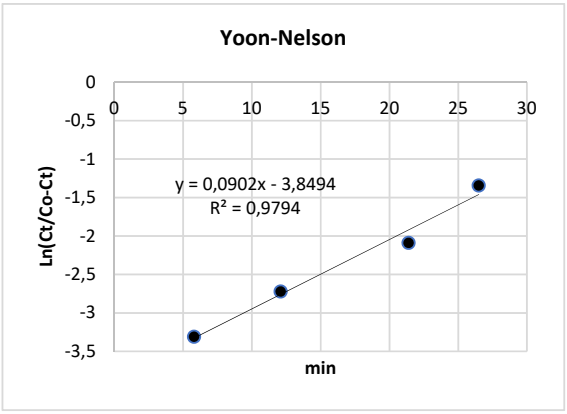
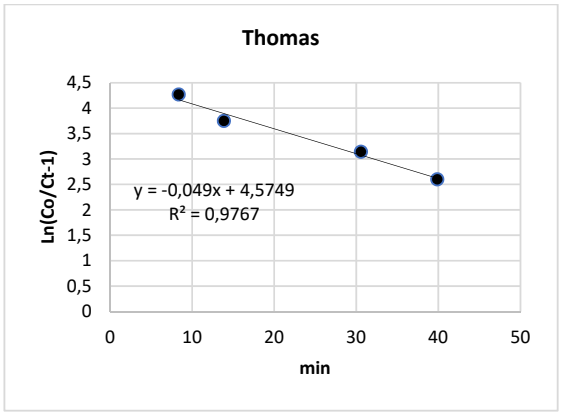
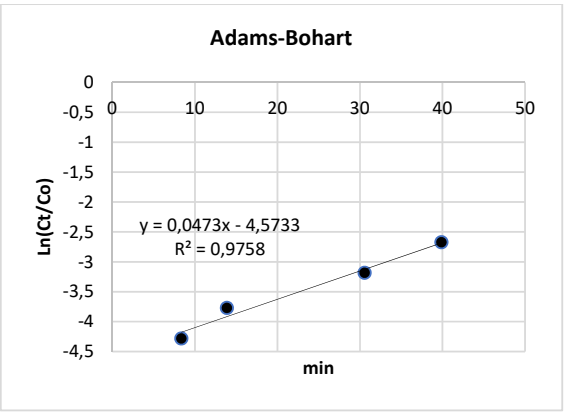


Fig. 7 Plots of the mini-column models using 3 g of LEWATIT





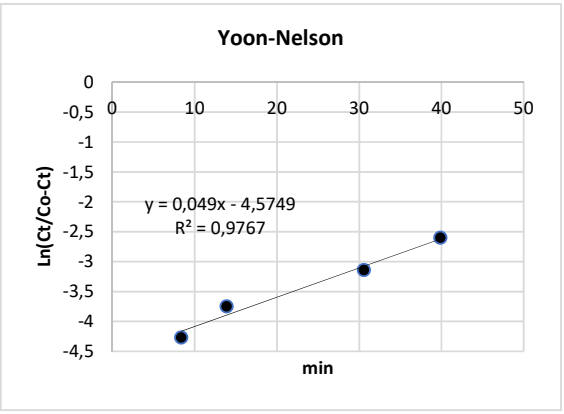


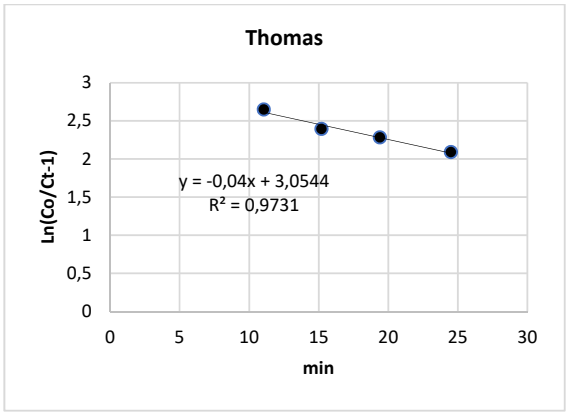
Fig. 8 Plots of the mini-column models using 6 g of LEWATIT

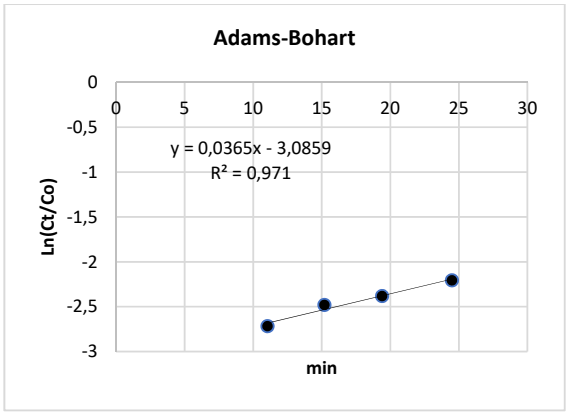
TABLE II
ADSORPTION TEST DETAILS OF LEWATIT AND AZLAB-NA USING MINI AND ACE COLUMNS

Column Type	Mass, g	Height, cm	Rate, ml/min	Velocity, cm/min
	LEWATIT			
Mini	3	5	5.6	6.3
	6	10	5.6	6.3
	9	15	5.6	6.3
Ace	131.4	29.5	38.5	7.6
	AZLB-Na			
Mini	3	7	5.3	6.7
	6	14	5.3	6.7
Ace	38.5	9	38.5	7.6

TABLE III
CONSTANTS OF THOMAS, ADAMS-BOHART AND YOON-NELSON MODELS USING LEWATIT AND AZLAB-NA

Column Type	Thomas		Adam-Bohart		Yoon-Nelson	
	k_{Th} L/mg.min	q_{max} mg/g	k_{AB} L/mg.min	N_o mg/L	k_{YN} 1/min	τ min
	LEWATIT					
3-g Mini	0.0039	1.81	0.0036	1354.1	0.09	42.6
6-g Mini	0.0021	1.97	0.0021	1390.3	0.05	93.3
Ace	0.0030	2.1	0.0018	2017.6	0.07	303
	AZLB-Na					
3-g Mini	0.0017	3.062	0.0016	1849.3	0.040	76.3
6-g Mini	0.0018	3.037	0.0017	3387.1	0.041	151.5
Ace	0.0014	2.426	0.0010	592.7	0.031	106.8





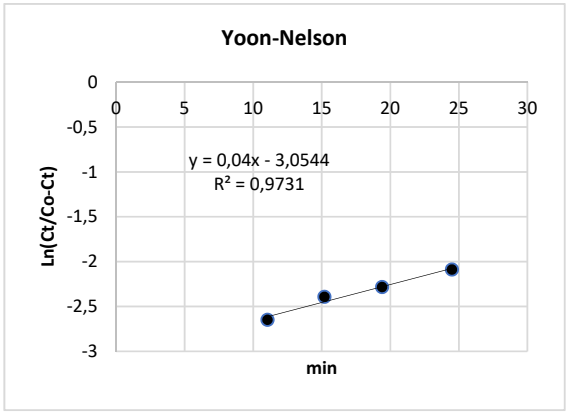
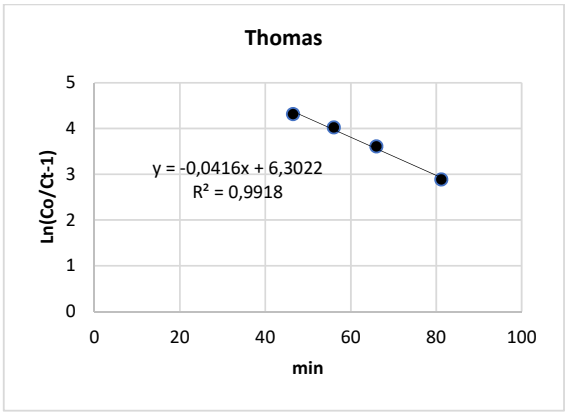
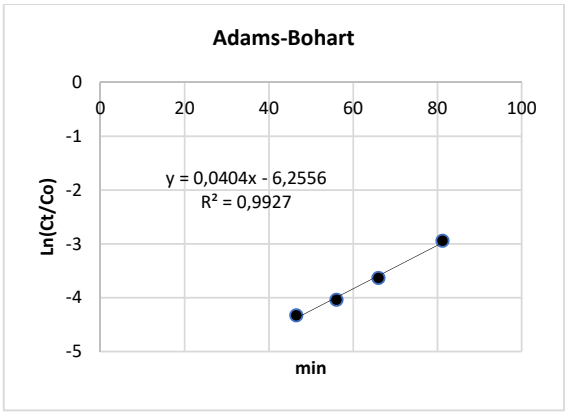


Fig. 9 Plots of the mini-column models using 3 g of AZLB-Na





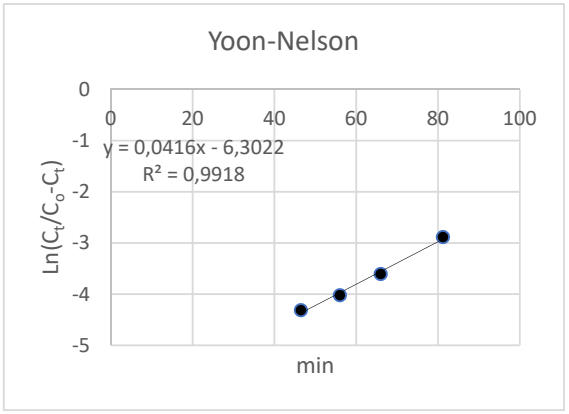
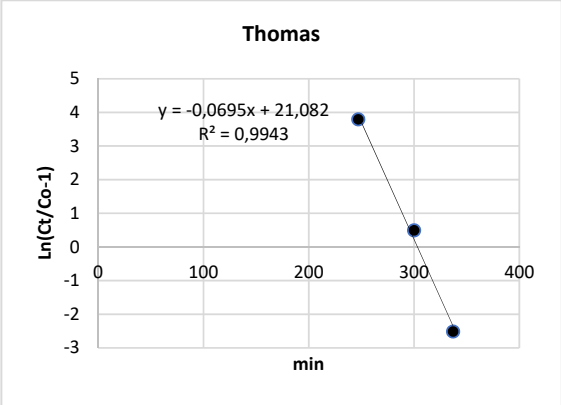
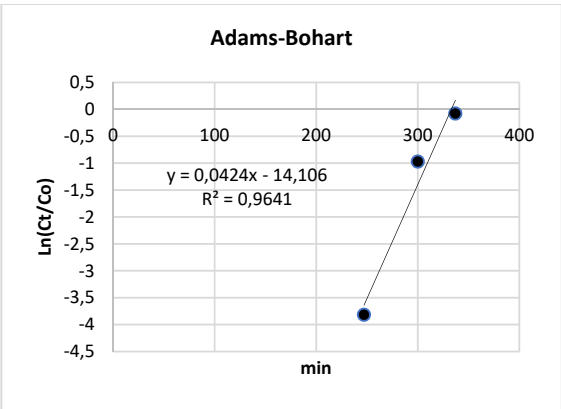


Fig. 10 Plots of the mini-column models using 6 g of AZLB-Na

VII. Conclusion

The results obtained from the experiments conducted for this research study allow for the following simple conclusions to be made thus far about the efficiencies of this technique tested to remove ammonia from MW. 1. An adsorption of the ammonia using ion-exchange resins or zeolites is more effective for the acidic resins than for the basic zeolites. 2. Using 5% HCl and 10% NaOH for regenerating a LEWATIT resin and an AZLB-Na zeolite was only 44 and 63.8%, respectively, efficient when using a co-flow technique. 3. Thomas, Adams-Bohart, and Yoon-Nelson models satisfactorily fit the data with R^2 is closer to 1 in all cases.





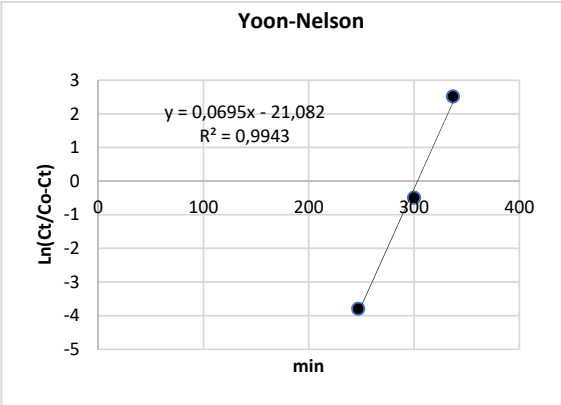
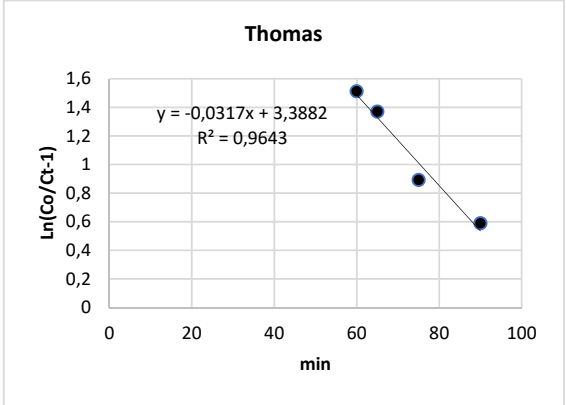
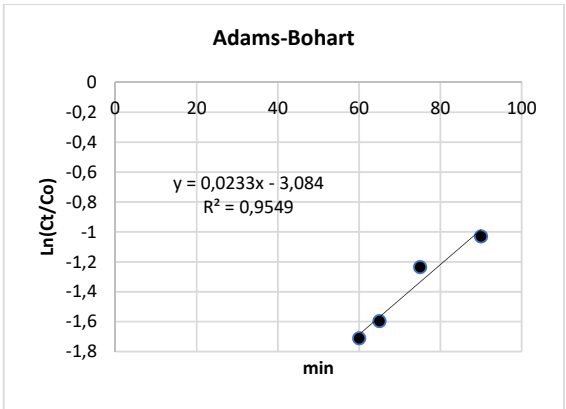


Fig. 11 Plots of the Ace column models using LETTWET





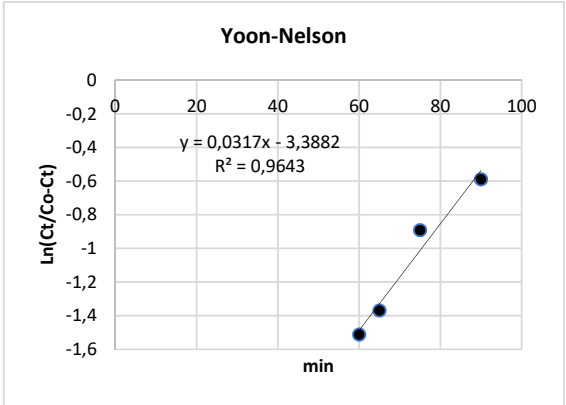


Fig. 12 Plots of the Ace column models using AZLB-Na

APPENDIX

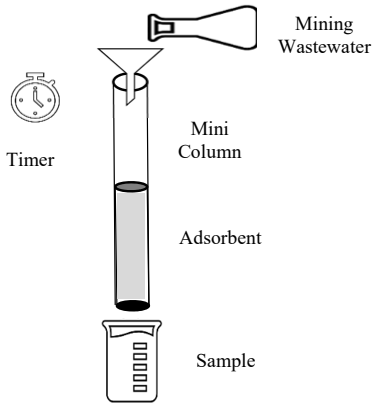


Fig. 13 A systematic diagram of the flow process using the mini-column

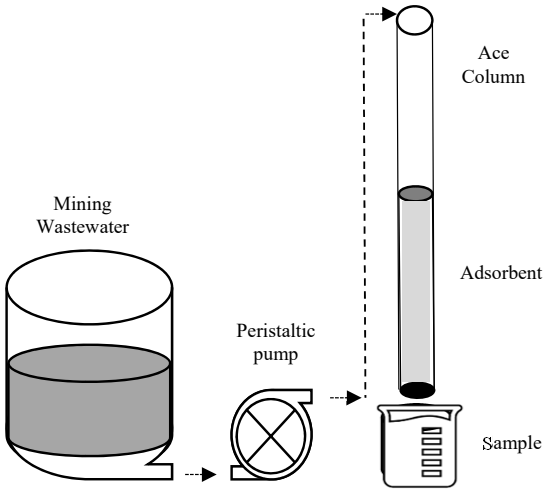


Fig. 14 A systematic diagram of the flow process using the Ace column

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