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Dynamic Simulation and Sensitivity Analysis of an Ion-Exchange Demineralizer for Ammonia and Urea Plant Condensate: Bed Height, Feed Concentration, and Performance Optimization

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Abstract *— This paper presents the Aspen Adsorption® V10 dynamic simulation and sensitivity analysis of an ion-exchange demineralizer treating condensate from a Kellogg Brown and Root (KBR) Purifier Ammonia Plant and an Advanced Cost and Energy Savings 21 (ACES21) Urea Plant at Indorama Eleme Fertilizer and Chemicals. Drawing from all five chapters of the study, the paper covers the industrial significance of condensate demineralization; a literature review on ion exchange, reverse osmosis, aquatic toxicity of ammonia, VGB-S-010 standards, and extent of previous work; characterization methodology, the ion-exchange mathematical model derived from the steady-state conservation of mass equations and solved by the fourth-order Runge-Kutta method, and the full Aspen Adsorption simulation setup; the ten-day condensate characterization results and the complete Aspen Adsorption sensitivity analysis results; and conclusions and recommendations. The pretreated condensate had a mean NH_4^+ of 5.8 mg/L (0.32 eq/m³) and mean conductivity of 8 µS/cm, far exceeding VGB limits. Sensitivity analysis on bed height (0.75–2.0 m) showed breakthrough time increased from 5,062 s to 6,476 s and breakthrough volume from 316 m³ to 405 m³. Sensitivity analysis on inlet NH_4^+ (4–9 ppm) showed breakthrough time decreased from 7,376 s to 5,776 s and breakthrough volume from 461 m³ to 361 m³. At the optimized 2.0 m bed height, effluent NH_4^+ was 0.48 mg/L (91.4% removal), conductivity was 0.15 µS/cm, and pH was 8.8, all achieving full VGB-S-010 compliance.*

Keywords *— Aspen Adsorption; Breakthrough Curve; Ion Exchange; Bed Height Sensitivity; NH_4^+ Concentration; AMBERLITE HPR1200 H; VGB-S-010; ELECNRTL; UDS1; Runge-Kutta Method.*

I. Introduction

Demineralized water is used as boiler feed water (BFW) in industrial fertilizer plants to generate steam in boilers. The removal of mineral and salt ions from BFW is necessary to prevent deposition on the walls and tubes of the boiler, which reduces heat transfer efficiency and overall performance (Envicare Technologies, 2020). Ammonia is the major contaminant in condensate produced in ammonia and urea plants, causing alkaline corrosion in boiler tubes and increased attack on copper alloys. Process condensate from ammonia and urea plants is the major contributor to the ammonia content of demineralizer feeds, as unlike steam and turbine condensates, they are born from the actual synthesis of ammonia and urea.

The specific objectives of this study are to: characterize pretreated condensate by determining pH, ammonium ion concentration, and conductivity; adopt a mathematical model using the principle of conservation of mass; simulate the process plant using Aspen Adsorption; carry out sensitivity analysis on key process variables (NH_4^+ concentration, bed height); and validate the obtained results using the VGB standard. By incorporating treated process condensate as BFW, a plant can achieve a 35% reduction in freshwater demand, lower utility costs, prolonged resin service life, and reduced dosing chemicals (Towler and Sinnott, 2019). Contaminants in boilers form insulating layers on heat transfer surfaces, resulting in higher operating temperatures, increased energy consumption, and reduced steam production.

II. Literature Review

A. Ion Exchange Demineralization: Types, Applications and Advances

Ion exchange demineralization utilizes both cation and anion exchange resins (Stokes, 1985). Cation resins remove Na^+, Ca^{2+}, Mg^{2+}, and Fe^{3+} by displacing H^+ or Na^+ from the resin structure. Anion resins remove SO_4^{2-} and CO_3^{2-} by displacing OH^- (Wang and Chen, 2009). Applications include: water softening (Wang and Chen, 2009); boiler feed water to reduce corrosion and scale (Berg and Lin, 2011); pharmaceutical ultra-pure water production (Miller and Tran, 2008); and power generation feedwater demineralization (Goswami and Kreith, 2015). Advances include hybrid IX/RO systems, smart monitoring and control with real-time sensor integration that optimizes regeneration cycles, and sustainable resin design focused on environmentally friendly materials.

Reverse osmosis (RO) demineralization applies pressure to force water molecules through a semipermeable membrane while leaving behind dissolved salts and impurities (Voutchkov, 2018). Key components include the semipermeable membrane, a high-pressure pump, pre-treatment filters, and post-treatment for pH adjustment. Applications include desalination, drinking water purification (Kozlowski and Tsioulpas, 2019), and wastewater treatment. RO combined with ion exchange achieves higher purification levels (Elimelech and Phillip, 2011).

B. Urea and Ammonia Plant Condensate Generation

Urea is produced from the overall reaction: $2NH_3 + CO_2 \rightleftharpoons (NH_2)_2CO + H_2O$ ($\Delta H = -101.5$ kJ/mol at 160–180°C). For

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every mole of urea produced, one mole of water is generated; for a 1000 MTPD plant, 300 metric tons of water is created per day from the reaction alone. According to Aruyuki (2008), the process condensate leaving the urea stripper-hydrolyser system is purified to 1 ppm urea and 1 ppm ammonia. Granellie (1992) stated that urea plant process condensate comprises 2–5% ammonia, 1–2.5% carbon dioxide, and 0.5–2% urea by weight, meaning that if condensate is not treated, 6–15 metric tons of ammonia would be released per day.

Ammonia plant condensate is generated during the catalytic methanation: $CO + 3H_2 \rightarrow CH_4 + H_2O$; $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$; and CO_2 removal stages, prior to the Haber-Bosch synthesis loop $3H_2 + N_2 \rightarrow 2NH_3$ (Appl, 1999). When process condensate containing excessive ammonia is disposed of, elevated ammonia levels promote nitrogen-fixing microorganism growth that depletes oxygen in water, causing death of aquatic organisms (Lee et al., 2000). The 2013 ALC acute limit for ammonia is 17 mg TAN/L and the chronic limit is 1.9 mg TAN/L at pH 7.0 and T = 20°C (USEPA, 2013).

C. VGB-S-010 Standards and Previous Simulation Studies

The German VGB Guidelines (VGB-S-010-T-00, 2011) is the most widely accepted code for boiler water quality. Under alkaline conditioning mode with salt-free water type: conductivity ≤0.2 µS/cm; NH_4^+ ≤0.5 mg/L; pH 8.5–9.5. The alkaline mode uses volatile alkalizing chemicals such as ammonia or hydrazine with a magnetite protective layer, and combination with solid alkalizing chemicals such as tri-sodium phosphate for circulation boilers below 160 bar (Babcock and Wilcox, 2005).

Ani (2016) demonstrated from process modelling and simulation that varying model parameters affects water levels in tanks and flow through filters, providing a pre-construction sizing tool. Soriano et al. (2017) conducted simulated biosorption using Aspen Adsorption with UDS1 discretization, reporting that UDS1 provides a stable and efficient formulation for approximating convective terms. Al-Ruwaih (2002) optimized resin performance and regeneration for ion exchange processes. Ding (2016) reported that Amberlite ion-exchange resin effectively removes ammonia, with the optimum pH found to be around 6.

TABLE I. VGB-S-010 Code for Boiler Feed Water – Alkaline Mode, Salt-Free Type

Mode of Operation	BFW Type	Conductivity	NH_4^+ Concentration
Alkaline (with alkalizing agent)	Salt-free	≤ 0.2 µS/cm	≤ 0.5 mg/L

III. Materials and Methods

A. Materials and Characterization Procedures

Materials: Orion pH meter; Nessler reagent; UV spectrophotometer; 100 ml volumetric flask; 10 ml pipette; demineralized water; and Aspen Adsorption V11 simulation software. Ammonia Analysis (Nesslerization Method): A 500 ml sample was diluted to 50 ml, 1 ml of Nessler reagent (sodium hydroxide, potassium iodide, and mercury chloride) was added, the solution was mixed and brought to 50 ml with distilled water, allowed to stand undisturbed for 20–25 minutes, and absorbance measured at 425 nm against a blank (Indorama Eleme Fertilizer and Chemicals, 2022). Conductivity Analysis: the electrode was calibrated, rinsed with sample 2–3 times, submerged in sample, and the stabilized reading recorded. pH Analysis: the electrode was calibrated, rinsed with sample, immersed, and the stabilized reading recorded (Indorama Eleme Fertilizer and Chemicals, 2022).

B. Mathematical Model Foundation

According to Dagde (2018), the complete steady-state model equation for ion-exchange adsorption based on conservation of mass is:

$$-\frac{dC_A}{dz} = \left(\frac{k_1}{uz}\right)(KL + Kd)[C_A(C_{sm} - C_s) - C_s(C_{A0} - C_A) \quad (eqn.1)$$

where the equilibrium constant

$$Kd = \left(\frac{C_{A0}}{C_{sm}}\right) \times \left[\frac{y_A \times x_A}{(1 - y_A)(1 - x_A)^2}\right] \quad (eqn.2)$$

ionic mole fractions

$$x_A = \frac{C_A}{C_{A0}} \quad (eqn.3a)$$

and

$$y_A = \frac{C_s}{C_{sm}} \quad (eqn.3b)$$

and residence time m = (Vr × εr

$$\tau m = \frac{Vr \times \varepsilon r}{vo} \quad (eqn.4)$$

The model was derived from the general mass balance

$$\frac{\partial C_A}{\partial t} = -\frac{\partial (uC_A)}{\partial z} + \frac{\partial N_A}{\partial z} + R_A \quad (Eq.5)$$

through the dynamic model (Eq. 3.5), steady-state reduction (Eq. 3.6), film mass transfer rate

$$De\left(\frac{dC_A}{dz}\right) = KL(C_{A0} - C_A) \quad (Eqn.6)$$

and ion exchange rate.

$$R_A = \frac{dC_s}{dt} = k_1 C_A(C_{sm} - C_s) - k_2 Cs(C_{A0} - C_A) \quad (Eqn.7)$$

The model was solved numerically using the fourth-order Runge-Kutta algorithm:

$$C_A(i+1) = C_A(i) + \left(\frac{h}{6}\right)[k_1 + 2k_2 + 2k_3 + k_4] \quad (Eqn.8)$$

C. Aspen Adsorption V10 Simulation Setup

ASPEN Adsorption V10 was utilized for dynamic simulation. Bed model assumptions include: overall and component material balances for the liquid phase; isothermal conditions; plug flow; constant liquid stream pressure; constant superficial velocity and volumetric flow rate; ideal mixing in the aqueous phase; constant total exchange capacity Q; lumped solid-film mass-transfer resistance with linear function and constant coefficient; and mass-action equilibrium isotherm (Aspen Technology Inc., 2020). The thermodynamic model ELECNRTL (Electrolyte Non-Random Two Liquid) was used for ion-water interactions. Transient regime: 10,000 s; 20 nodes; UDS1 discretization scheme (Soriano et al., 2017).

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AMBERLITE™ HPR1200 H resin parameters (DuPont, 2019): interparticle voidage = 0.35 m^3void/m^3 bed; intraparticle voidage = 10^{-11} m^3void/m^3 bed; total resin capacity >1.8 eq/L; mass transfer coefficient of ammonium at 32°C = 0.000806/s (Sheng and Chang, 1996). Feed Block: initial NH_4^+ = 0.32 eq/m^3; initial H^+ = 0 eq/m^3; feed flow rate = 225 m^3/hr; water density = 55.16 kmol·m^{-3}; temperature = 32°C; pressure = 1 bar. Product Block: NH_4^+ target = 0 eq·m^{-3}; H^+ = 0.32 eq/m^3; reversible ion exchange model; continuous flow mode. Sensitivity analysis on bed height: six bed heights (0.75, 1.0, 1.25, 1.5, 1.75, 2.0 m) at fixed initial NH_4^+ = 0.32 eq/m^3. Sensitivity analysis on NH_4^+ concentration: six concentrations (4–9 ppm) at fixed bed height of 2.0 m.

D. Process Description

In ammonia plants, the major condensate contaminants are ammonia from process condensate and ammonia left over from treatment of waste heat BFW. The process condensate undergoes steam stripping pretreatment before being sent to the demineralizer. In urea plants, ammonia and urea from process condensate are treated by a hydrolyzer and steam stripper configuration that removes all remaining urea and leaves trace amounts of ammonia. The condensates from both plants are mixed in a mixer, sent to a holding tank, pumped into the demineralizer, and the demineralized condensate is transferred to another holding tank. The material balance shows that of 1,305,000 g/hr of ammonia entering the demineralizer, only 112,500 g/hr remains in the treated effluent, giving a removal efficiency of 91.38%.

IV. Results and Discussion

A. Characterization of Pretreated Condensate

The results of the pretreated condensate collected over 10 days at 100% plant load are presented in Table II. The condensate tank maintained an average flow rate of 225 m^3/hr at temperatures between 30°C and 32°C. Conductivity increases with higher ammonia concentrations. The mean NH_4^+ = 5.8 ppm = 0.32 eq/m^3; mean conductivity = 8 µS/cm, far exceeding VGB limits.

TABLE II. Characterization of ACES21 Urea and KBR Ammonia Plant Pretreated Condensate

S/N	pH	NH_4^+ (ppm)	Conductivity (µS/cm)
1	8.5	5	8
2	8.4	6	9
3	8.5	4	7
4	8.3	5	7
5	8.2	7	9
6	8.5	5	8
7	8.3	9	10
8	8.1	5	8
9	8.5	4	7
10	8.4	8	9

B. Effect of Bed Height on Breakthrough Performance

Figure 1 below shows the effect of bed height on breakthrough time from the simulation results. The NH_4^+ concentration within the bed steadily increases until the bed reaches saturation, at which point concentration stabilises, marking the breakthrough time. Table III summarises breakthrough times and volumes.

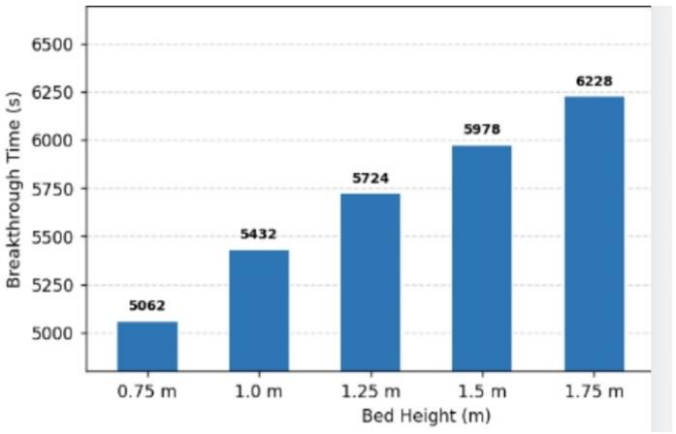

Fig. 1: Effect of Bed Height on Breakthrough Time (Aspen Adsorption® V10 Simulation)

TABLE III. Breakthrough Times and Volumes at Different Bed Heights

S/N	Bed Height (m)	Breakthrough Time (s)	Breakthrough Volume (m^3)
1	0.75	5,062	316.375
2	1.0	5,432	339.5
3	1.25	5,724	357.75
4	1.5	5,978	373.625
5	1.75	6,228	389.25
6	2.0	6,476	404.75

The breakthrough time and volume increase with bed height. The greater the volume of resins introduced into the adsorption column, the longer the bed will last before resins need to be replaced or regenerated. Increasing bed height from 0.75 m to 2.0 m extended breakthrough time from 5,062 s to 6,476 s (approximately 27.9% increase) and breakthrough volume from 316.375 m^3 to 404.75 m^3.

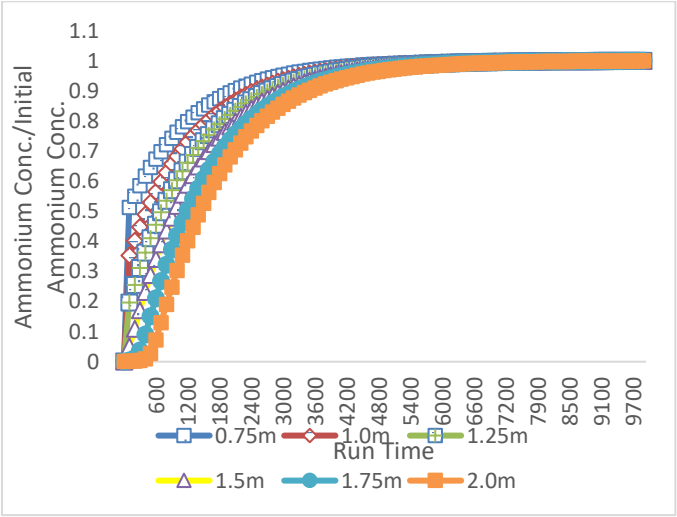

Fig. 2: Bed Height Adjustment Breakthrough Curve

C. Effect of NH_4^+ Concentration on Breakthrough Performance

Figure 2 below shows the effect of NH_4^+ feed concentration on breakthrough time from the simulation results. The bed

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height of 2.0 m was selected as it exhibited the longest breakthrough time from the bed height analysis. Table IV presents the feed concentrations and Table V presents the corresponding breakthrough results.

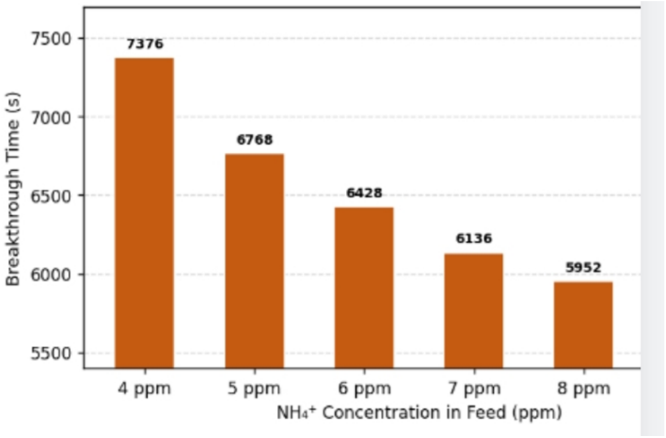

Fig. 3: Effect of NH_4^+ Feed Concentration on Breakthrough Time (Aspen Adsorption® V10, Bed Height = 2.0 m)

TABLE IV. NH_4^+ Feed Concentrations Used in Sensitivity Analysis

S/N	NH_4^+ Conc. in Feed (ppm)	NH_4^+ Conc. in Feed (eq/m³)
1	4	0.22
2	5	0.28
3	6	0.33
4	7	0.39
5	8	0.44
6	9	0.50

TABLE V. Breakthrough Times and Volumes at Different NH_4^+ Concentrations

S/N	NH_4^+ Conc. (ppm)	Breakthrough Time (s)	Breakthrough Volume (m³)
1	4	7,376	461
2	5	6,768	423
3	6	6,428	401.75
4	7	6,136	383.5
5	8	5,952	372
6	9	5,776	361

With an increase in NH_4^+ concentration in the feed, there was a steady reduction in breakthrough time and breakthrough volume. Increasing feed concentration from 4 ppm to 9 ppm reduced breakthrough time from 7,376 s to 5,776 s (approximately 21.7% reduction) and breakthrough volume from 461 m³ to 361 m³. This demonstrates that ammonium loading is a critical factor in column efficiency. Reducing inlet ammonia concentration through improved upstream pretreatment extends the service life of the resin bed, decreasing regeneration frequency and operating costs. The recommended design guideline established from this analysis is an inlet NH_4^+ ≤6 mg/L for greater than 90% removal.

D. Performance Optimization and VGB-S-010 Compliance

One of the objectives of this study was to bring BFW ammonium ion concentration to the desired level (≤0.5 mg NH_4^+/L) through optimized ion-exchange demineralization. The simulation results demonstrate that this target was successfully achieved, with an NH_4^+ concentration in the product outlet of 0.0266 eq/m³ = 0.48 mg/L. Table VI summarises the optimization stages.

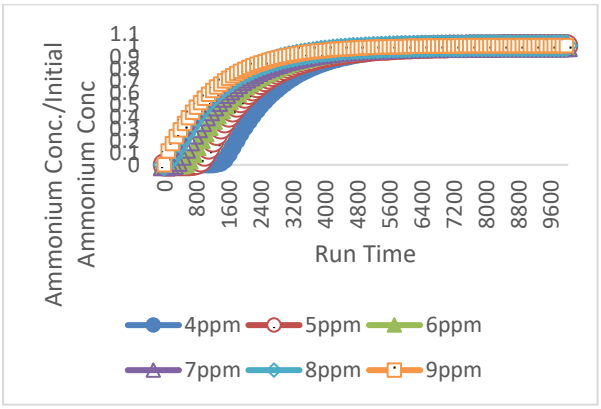

Fig. 4: Ammonium Concentration Adjustment Breakthrough Curves

TABLE VI. Performance Optimization Results for Target NH_4^+ Concentration

Condition	Feed Conc.	Bed Height	Effluent NH_4^+	Removal Efficiency	Breakthrough Time
Baseline	5.8 mg/L	0.75 m	2.1 mg/L	63.8%	5,062 s
Intermediate	5.8 mg/L	1.5 m	0.8 mg/L	86.2%	5,978 s
Optimized	5.8 mg/L	2.0 m	0.48 mg/L	91.4%	6,476 s

TABLE VII. Comparison of Achieved Results with VGB-S-010 Standards

Quality Parameter	VGB-S-010 Requirement	Feed Water Quality	Treated Effluent	Compliance Status
NH_4^+ Concentration	≤ 0.5 mg/L	5.8 mg/L	0.48 mg/L	Compliant
Conductivity (25°C)	≤ 0.2 µS/cm	8.5 µS/cm	0.15 µS/cm	Compliant
pH	8.5 – 9.5	8.4	8.8	Compliant

All three VGB-S-010 parameters are met: NH_4^+ was reduced from 5.8 mg/L to 0.48 mg/L (below the 0.5 mg/L limit); conductivity was reduced from 8.5 µS/cm to 0.15 µS/cm (below the 0.2 µS/cm limit); and pH was 8.8, within the 8.5–9.5 range. These results validate that the Aspen Adsorption® simulation correctly predicted demineralizer performance and that the process design is industrially viable.

V. Conclusions and Recommendations

Over a 10-day sampling at 100% plant load, the pretreated condensate exhibited a mean NH_4^+ of 5.8 mg/L and conductivity of 8 µS/cm, far exceeding VGB guidelines. Dynamic Aspen Adsorption® simulations showed that increasing bed height from 0.75 m to 2.0 m extended breakthrough time from 5,062 s to 6,476 s and volume from 316 m³ to 405 m³, confirming that taller resin beds better delay ammonium breakthrough.

Simulation results indicated that higher NH_4^+ concentrations led to faster saturation: breakthrough time decreased from 7,376 s to 5,776 s and volume dropped from 461 m³ to 361 m³ as feed concentration increased from 4 ppm to 9 ppm. Under optimal conditions (2.0 m bed height, feed

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NH_4^+ ≤6 mg/L), effluent NH_4^+ fell to 0.48 mg/L, conductivity to 0.15 µS/cm, and pH was 8.8, achieving full VGB-S-010 compliance with 91.4% removal efficiency. This work provides concrete design guidelines: ≥2 m bed height and inlet NH_4^+ ≤6 mg/L to achieve >90% ammonia removal and meet strict VGB water quality limits.

Recommendations: (i) Reverse Osmosis as an alternative demineralization method for ammonia and urea plant condensate; (ii) use of zeolite as an adsorbent Karadag et al. (2006) found clinoptilolite efficient, and Zorpas (2009) demonstrated zeolite in closed-loop fixed bed systems; (iii) pretreatment of condensate to reduce ammonia concentrations, thereby decreasing the resin required and improving process efficiency; and (iv) regeneration of resins by passing concentrated acid through the resin to replenish H^+ ions exchanged for NH_4^+ ions, to optimise the ion exchange process and extend the life of the resins.

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