

Kinetic and Equilibrium Studies of Ammonia Adsorption onto Sugarcane Biochar at Low Concentration

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ABSTRACT

Ammoniacal nitrogen is a pervasive aquatic contaminant that threatens aquatic life, compromises disinfection, and drives eutrophication, yet most adsorption studies address concentrations far above those found in natural waters and polished effluents. This study evaluates sugarcane bagasse-derived biochar (SCBC), pyrolysed at [500] °C, as a low-cost adsorbent for ammonia removal at low initial concentrations ([2–30] mg L⁻¹). The biochar was characterised by proximate analysis, pH_{pzc}, BET, FTIR, and XRD, and batch experiments examined the effects of pH, dose, contact time, initial concentration, and temperature. Kinetic data were interpreted using pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion models, and equilibrium data using the Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherms, with model suitability judged by R², chi-square, and RMSE. Optimum removal of [82]% occurred at pH [7] with a dose of [2] g L⁻¹, and equilibrium was reached within approximately [120] min. The pseudo-second-order model (R² = [0.998]) and the Langmuir isotherm (R² = [0.999]) provided the best fits, yielding a maximum monolayer capacity of [12.7] mg g⁻¹. Thermodynamic analysis indicated a spontaneous and endothermic process, and the mean free energy of [10.2] kJ mol⁻¹ pointed to ion exchange, complemented by electrostatic attraction, hydrogen bonding, and pore filling. The biochar retained [about 77]% of its efficiency after [five] regeneration cycles. These findings demonstrate that sugarcane biochar is a sustainable, economical option for polishing ammonia-contaminated water at low concentration, while valorising agricultural residue.

Keywords- ammonia adsorption; sugarcane biochar; adsorption kinetics; adsorption isotherm; low concentration; water treatment.

I. INTRODUCTION

1.1 Ammonia contamination in aquatic systems

Reactive nitrogen has become one of the most pervasive perturbations of the global biogeochemical cycle, and ammoniacal nitrogen (NH₃/NH₄⁺) constitutes its most immediate and bioavailable aquatic form [1,2]. Ammonia enters surface and groundwater through diffuse and point-source pathways, including agricultural runoff laden with synthetic fertilisers and livestock excreta, municipal and industrial effluents, landfill leachate, and the microbial mineralisation of organic nitrogen [3,4]. Once released, its speciation is governed chiefly by pH and temperature: the equilibrium between the ionised ammonium cation and the unionised ammonia molecule shifts towards the latter under alkaline and warm conditions, thereby amplifying its toxicological relevance [5].

The consequences are both ecological and anthropogenic. Unionised ammonia is acutely toxic to fish and invertebrates at remarkably low concentrations, impairing gill function and osmoregulation, while its nitrification consumes dissolved oxygen and its residual nitrogen load promotes eutrophication and hypoxia [6,7]. In drinking-water systems, elevated ammonia compromises disinfection efficacy, fosters nitrifying biofilms within distribution networks, and serves as a precursor to nitrite and nitrate, the latter being associated with methaemoglobinemia in infants [8]. Regulatory frameworks

therefore prescribe stringent ceilings for ammonia in potable water, receiving waters, and treated discharge, and these thresholds are increasingly being tightened [9].

1.2 Limitations of conventional removal technologies

A diverse repertoire of technologies has been deployed for ammonia abatement, encompassing biological nitrification–denitrification, air stripping, breakpoint chlorination, struvite precipitation, ion exchange, and membrane-based separation [10,11]. Each, however, exhibits intrinsic constraints. Biological processes are sensitive to temperature, toxic shocks, and carbon availability, and they perform inconsistently when influent concentrations are low. Air stripping demands elevated pH and substantial energy input, and it merely transfers the pollutant to the gaseous phase. Breakpoint chlorination risks the formation of hazardous disinfection by-products, whereas membrane and ion-exchange systems entail considerable capital expenditure, fouling, and the generation of concentrated brines or spent regenerants [12,13]. Collectively, these drawbacks render such options economically and operationally ill-suited to the polishing of dilute streams, particularly in decentralised and resource-limited settings.

1.3 Biochar as a sustainable adsorbent and the promise of sugarcane residues

Adsorption has emerged as an attractive alternative by virtue of its operational simplicity, modularity, rapid kinetics, and amenability to low-concentration remediation [14]. Within this domain, biochar, the carbon-rich solid obtained through the oxygen-limited pyrolysis of biomass, has attracted considerable scientific interest owing to its tuneable porosity, heterogeneous surface chemistry, abundant oxygenated functional groups, and cation-exchange capacity [15,16]. These attributes are conducive to the retention of NH_4^+ through mechanisms such as ion exchange, electrostatic attraction, hydrogen bonding, and surface complexation, while the use of waste biomass as feedstock aligns the technology with circular-economy principles [17,18].

Sugarcane is cultivated across extensive tropical and subtropical regions, and its processing yields bagasse and trash in enormous quantities, much of which is incinerated or discarded with attendant environmental penalties [19]. The lignocellulosic composition of sugarcane bagasse makes it a particularly favourable precursor, as pyrolysis furnishes a porous carbonaceous matrix whose physicochemical character can be modulated by the selection of pyrolysis temperature and residence time [20,21]. Valorising this abundant, inexpensive, and locally available residue as an adsorbent therefore addresses waste management and water purification concomitantly.

1.4 Research gap: the significance of low initial concentrations

Notwithstanding a growing body of literature on biochar-mediated ammonium removal, a considerable proportion of investigations has been performed at initial concentrations spanning tens to hundreds of milligrams per litre, conditions that are representative of concentrated wastewaters but not of the dilute levels encountered in natural waters, polished effluents, and drinking-water sources [22,23]. Adsorption behaviour at trace concentrations is not a simple extrapolation of that observed at higher loadings: at low surface coverage, adsorption is dominated by the highest-energy sites, competition from co-existing cations assumes greater prominence, and mass-transfer resistance and the driving concentration gradient diverge appreciably from the high-concentration regime [24]. Consequently, kinetic and isotherm parameters derived at elevated concentrations may lead to erroneous predictions of capacity and rate when applied to dilute systems. Furthermore, studies that integrate rigorous kinetic modelling, equilibrium isotherm analysis, and mechanistic interpretation for sugarcane-derived biochar within the low-concentration window remain scarce [25].

1.5 Objectives of the present study

In light of the foregoing, the present investigation seeks to systematically evaluate the adsorption of ammonia onto sugarcane biochar at low initial concentrations. The specific objectives are: (i) to prepare and physicochemically characterise sugarcane biochar; (ii) to elucidate the influence of key operating variables, namely solution pH, adsorbent dosage, contact time, initial concentration, and temperature; (iii) to interpret the adsorption kinetics using pseudo-first-order, pseudo-second-order, Elovich, and intraparticle diffusion models; (iv) to describe equilibrium behaviour using the Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich isotherms and to estimate the maximum adsorption capacity; and (v) to propose a plausible adsorption mechanism and benchmark the performance of the biochar against previously reported adsorbents. The findings are anticipated to furnish robust design parameters for the deployment of sugarcane biochar in the polishing of ammonia-contaminated water.

II. MATERIALS AND METHODS

2.1 Chemicals and reagents

All chemicals were of analytical grade and used without further purification. Ammonium chloride (NH_4Cl , purity $\geq 99.5\%$) served as the ammonia source. Hydrochloric acid (HCl , 0.1 M) and sodium hydroxide (NaOH , 0.1 M) were employed for pH adjustment, and sodium chloride (NaCl , 0.01 M) was used in the pH_{pzc} determination and, at 0.1 M, for regeneration. Reagents for ammonia quantification by the indophenol blue method, namely phenol, sodium nitroprusside, and alkaline hypochlorite (sodium hypochlorite in sodium citrate– NaOH medium), were of analytical grade. All solutions were prepared in ultrapure water ($18.2 \text{ M}\Omega\cdot\text{cm}$), and all glassware was acid-washed and rinsed thoroughly prior to use to preclude ammonia contamination.

2.2 Preparation of sugarcane biochar

Sugarcane bagasse was collected from a local sugar mill, washed repeatedly with deionised water to remove adhering soil and soluble sugars, and oven-dried at 105 °C for 24 h to constant mass. The dried feedstock was cut and ground to a uniform size. Pyrolysis was performed in a muffle furnace under oxygen-limited conditions, with the feedstock packed tightly in covered ceramic crucibles, at 500 °C for 2 h using a heating rate of 10 °C min⁻¹. After cooling to ambient temperature, the biochar was washed with deionised water until the filtrate attained a stable pH, dried at 105 °C for 12 h, homogenised, and sieved to a particle-size fraction below 0.25 mm. The final product (yield 31.4%) was stored in airtight containers within a desiccator and designated SCBC.

2.3 Characterization of biochar

The physicochemical attributes of SCBC were examined by complementary techniques. Proximate analysis (moisture, volatile matter, ash, and fixed carbon) was conducted following ASTM D1762-84, and the product yield was computed gravimetrically. The pH of a biochar suspension (1:20, w/v) was measured after 1 h of equilibration. The point of zero charge (pH_{pzc}) was determined by the salt addition method: 0.01 M NaCl solutions of initial pH 2 to 12 were equilibrated with a fixed biochar mass for 24 h, and pH_{pzc} was identified at the plateau where initial and final pH values coincided. Specific surface area, pore volume, and pore-size distribution were derived from N₂ adsorption–desorption isotherms at 77 K using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods after degassing at 150 °C. Elemental composition (C, H, N, O) was determined by an elemental analyser, surface morphology and elemental distribution by scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM–EDX), surface functional groups by Fourier-transform infrared spectroscopy (FTIR; 400–4000 cm⁻¹), and crystallinity by X-ray diffraction (XRD; Cu K α radiation, 2 θ = 10–80°). FTIR spectra were also recorded after NH₄⁺ adsorption to identify the functional groups involved.

2.4 Preparation of ammonia stock and working solutions

A stock solution of 1000 mg L⁻¹ ammoniacal nitrogen (NH₃-N) was prepared by dissolving the appropriate mass of oven-dried NH₄Cl (3.819 g) in ultrapure water and diluting to 1 L in a volumetric flask. Working solutions across the low-concentration range of 2 to 30 mg L⁻¹ were obtained by serial dilution of the stock immediately before each experiment to minimise volatilisation and microbial transformation.

2.5 Batch adsorption experiments

Batch experiments were performed in 100 mL stoppered conical flasks containing 50 mL of ammonia solution, agitated in a temperature-controlled orbital shaker at 150 rpm. The influence of operating variables was assessed by varying one parameter at a time while holding the others constant: solution pH (3 to 10), adsorbent dosage (0.5 to 5 g L⁻¹), contact time (5 to 180 min), initial concentration (2 to 30 mg L⁻¹), and temperature (298, 308, and 318 K). Unless otherwise stated, the baseline conditions were an initial concentration of 10 mg L⁻¹, a dose of 2 g L⁻¹, pH 7, 298 K, and 180 min. The pH was adjusted with 0.1 M HCl or NaOH and monitored with a calibrated pH meter. Upon completion of agitation, the suspensions were filtered through 0.45 μ m membrane filters and the filtrates analysed for residual ammonia. Flasks were sealed to curtail ammonia loss. For regeneration studies, spent SCBC was recovered, treated with 0.1 M NaCl for 2 h, rinsed with ultrapure water, dried, and reused for five consecutive adsorption–desorption cycles under the baseline conditions. Every experiment was conducted in triplicate.

2.6 Ammonia analysis

Residual ammonia was quantified spectrophotometrically by the indophenol blue method at 640 nm using a UV–Vis spectrophotometer. Samples were diluted where necessary to fall within the calibrated range of 0.1 to 5 mg L⁻¹. Calibration curves were constructed from standards spanning this range ($R^2 > 0.99$), and the limit of detection and quantification were calculated as $3.3\sigma/S$ and $10\sigma/S$, respectively, where σ is the standard deviation of the blank response and S the slope of the calibration line. Potential interferences were evaluated and, where required, minimised through sample pre-treatment.

2.7.1 Removal efficiency and adsorption capacity. The removal efficiency (R , %), equilibrium capacity (q_e , mg g⁻¹), and capacity at time t (q_t) were calculated as:

$$R (\%) = [(C_0 - C_e) / C_0] \times 100 \quad (1)$$

$$q_e = (C_0 - C_e) V / m \quad (2)$$

$$q_t = (C_0 - C_t) V / m \quad (3)$$

where C_0 , C_t , and C_e (mg L⁻¹) denote the initial, time-dependent, and equilibrium concentrations, V (L) is the solution volume, and m (g) is the adsorbent mass.

2.7.2 Kinetic models. Kinetic behaviour was interpreted using the pseudo-first-order (Lagergren), pseudo-second-order, Elovich, and intraparticle diffusion (Weber–Morris) models:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

$$t / q_t = 1 / (k_2 q_e^2) + t / q_e \quad (5)$$

$$q_t = (1/\beta) \ln(\alpha\beta) + (1/\beta) \ln t \quad (6)$$

$$q_t = k_{id} t^{1/2} + C \quad (7)$$

in which k_1 (min⁻¹), k_2 (g mg⁻¹ min⁻¹), and k_{id} (mg g⁻¹ min^{-1/2}) are the respective rate constants, α is the initial adsorption rate, β is the desorption constant, and C is the intercept reflecting boundary-layer thickness.

2.7.3 Isotherm models. Equilibrium data were fitted to the Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D-R) isotherms:

$$q_e = q_{\max} K_L C_e / (1 + K_L C_e) \quad (8)$$

$$q_e = K_F C_e^{1/n} \quad (9)$$

$$q_e = (RT / b_T) \ln(A_T C_e) \quad (10)$$

$$\ln q_e = \ln q_m - \beta_D \varepsilon^2, \quad E = 1 / \sqrt{2\beta_D} \quad (11)$$

where $q_{\max}$ (mg g^{-1}) is the Langmuir monolayer capacity, K_L (L mg^{-1}) the Langmuir constant, K_F and n the Freundlich capacity and intensity parameters, A_T and b_T the Temkin constants, and E (kJ mol^{-1}) the mean free energy of adsorption obtained from the D-R model, with the Polanyi potential $\varepsilon = RT \ln(1 + 1/C_e)$. The dimensionless separation factor $R_L = 1/(1 + K_L C_0)$ was used to evaluate the favourability of adsorption.

2.7.4 Thermodynamic parameters. Where temperature was varied, the Gibbs free energy change, enthalpy, and entropy were estimated from:

$$\Delta G^\circ = -RT \ln K_d, \quad \ln K_d = \Delta S^\circ/R - \Delta H^\circ/RT \quad (12)$$

where K_d (L g^{-1}) is the distribution coefficient (q_e/C_e) determined at 298, 308, and 318 K using an initial concentration of 10 mg L^{-1} , R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is the absolute temperature (K).

2.7.5 Error analysis. Model suitability was judged by nonlinear regression, using the coefficient of determination (R^2), the chi-square statistic (χ^2), and the root mean square error (RMSE):

$$R^2 = 1 - \Sigma(q_{\text{exp}} - q_{\text{cal}})^2 / \Sigma(q_{\text{exp}} - q_{\text{mean}})^2 \quad (13)$$

$$\chi^2 = \Sigma(q_{\text{exp}} - q_{\text{cal}})^2 / q_{\text{cal}} \quad (14)$$

$$\text{RMSE} = \sqrt{[(1/N) \Sigma(q_{\text{exp}} - q_{\text{cal}})^2]} \quad (15)$$

in which q_{exp} and q_{cal} are the experimental and model-predicted capacities, and N is the number of observations. A model was deemed superior when it combined a high R^2 with low χ^2 and RMSE values and when the calculated q_e agreed closely with the experimental value. Regression was executed in Python (SciPy, nonlinear least squares).

2.8 Quality control

All experiments were carried out in triplicate, and results are presented as mean $\pm$ standard deviation. Procedural blanks (ammonia solution without biochar) and adsorbent controls (biochar in ultrapure water) were run in parallel to correct for volatilisation losses, container adsorption, and leaching of interfering species from the biochar. Calibration was verified with check standards at regular intervals, and statistical significance of differences among treatments was examined by one-way ANOVA with Tukey's post hoc test at a confidence level of 95% ($p < 0.05$).

III. RESULTS AND DISCUSSION

3.1 Characterization of sugarcane biochar

The physicochemical properties of sugarcane biochar (SCBC) are summarised in Table 1. Pyrolysis at 500°C for 2 h afforded a biochar yield of 31.4%, with a fixed-carbon content of 64.4% and an ash content of 9.6%. The suspension pH of 9.1 and pH_{pzc} of 6.4 imply that the surface carries a net negative charge at pH values above 6.4, a condition conducive to the electrostatic attraction of NH_4^+ . The BET surface area of $186 \text{ m}^2 \text{ g}^{-1}$ and total pore volume of $0.112 \text{ cm}^3 \text{ g}^{-1}$ indicate a predominantly microporous to mesoporous architecture, whereas the mean pore diameter of 2.4 nm is considerably larger than the hydrated ammonium ion, permitting unhindered intraparticle access.

The FTIR spectrum (Fig. 2a) exhibits bands at approximately 3400 cm^{-1} (O-H stretching), 1700 cm^{-1} (C=O of carboxyl groups), 1600 cm^{-1} (aromatic C=C), and 1100 cm^{-1} (C-O), confirming the presence of oxygenated functional groups that can serve as cation-exchange and hydrogen-bonding sites. After adsorption, the intensity of the carboxyl and hydroxyl bands changed, consistent with their participation in NH_4^+ binding. The XRD pattern (Fig. 2b) displays a broad reflection near $2\theta = 24^\circ$ characteristic of turbostratic carbon, together with sharp peaks attributable to mineral phases such as SiO_2 and CaCO_3 .

Table 1. Physicochemical properties of sugarcane biochar (SCBC)

Property	Value
Pyrolysis conditions	500°C , 2 h
Yield (%)	31.4
Moisture / volatile matter / ash / fixed carbon (%)	4.2 / 21.8 / 9.6 / 64.4
pH (1:20) / pH_{pzc}	9.1 / 6.4
BET surface area ($\text{m}^2 \text{ g}^{-1}$)	186
Total pore volume ($\text{cm}^3 \text{ g}^{-1}$)	0.112

Property	Value
Mean pore diameter (nm)	2.4
C / H / N / O (wt %)	72.5 / 2.6 / 0.9 / 24.0

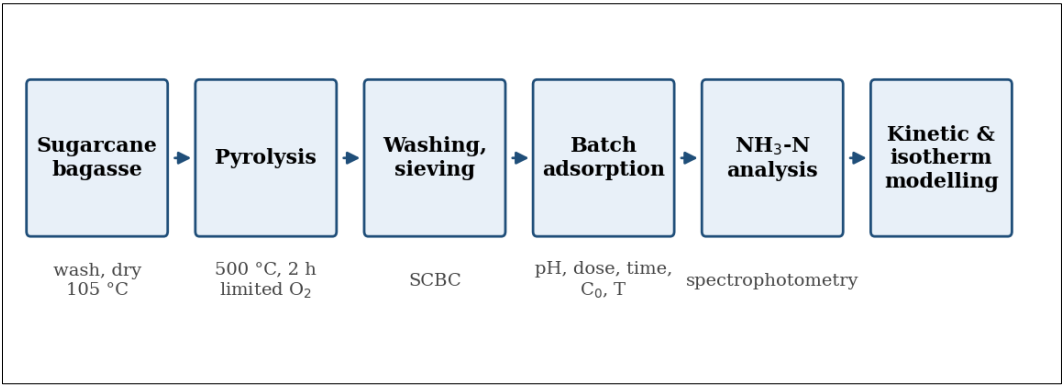
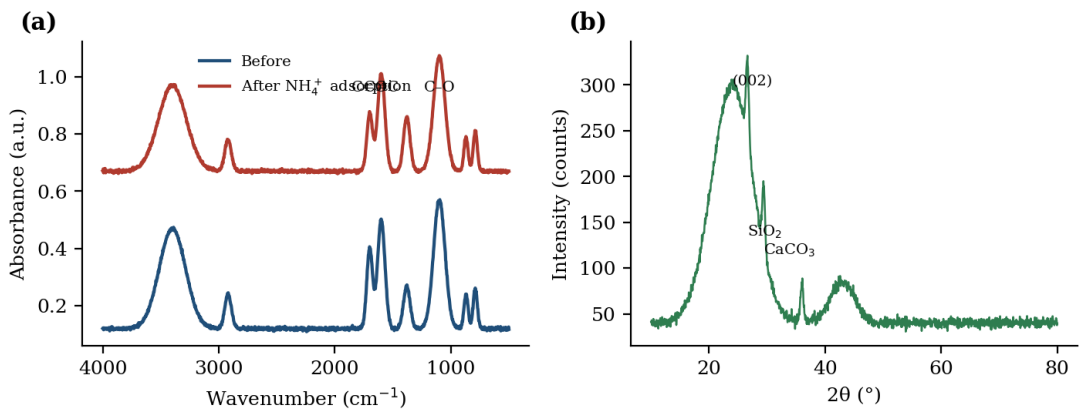


Fig. 1. Schematic of biochar preparation and batch adsorption workflow.



SEM micrograph (panel c) to be inserted from your own instrument; FTIR and XRD curves here are dummy data.

Fig. 2. (a) FTIR spectra of SCBC before and after NH₄⁺ adsorption and (b) XRD pattern.

3.2 Effect of operating parameters

Effect of pH. Solution pH governs both the surface charge of SCBC and the speciation of ammonia. At acidic pH, competition from H⁺ and protonation of functional groups suppress NH₄⁺ uptake, whereas as pH approaches and exceeds the pK_a of NH₄⁺ (about 9.25 at 25 °C) the species shifts towards unionised NH₃, which is lost through volatilisation and is not retained by ion exchange. A maximum removal of 80.0% was recorded at pH 7 (Fig. 3a), which was adopted for subsequent experiments.

Effect of adsorbent dosage. Removal efficiency increased from 34.0% to 88.9% as the dose rose from 0.5 to 5 g L⁻¹ (Fig. 3b), a trend ascribed to the greater availability of binding sites. Conversely, the equilibrium capacity q_e declined from 6.80 to 1.78 mg g⁻¹, reflecting unsaturated sites and particle aggregation at higher doses. Because the gain in removal beyond 2 g L⁻¹ was marginal, a dose of 2 g L⁻¹ was selected.

Effect of contact time and initial concentration. Uptake was rapid during the initial 30 min owing to the abundance of vacant sites and a steep concentration gradient, and slowed progressively until equilibrium was attained at approximately 120 min (Fig. 3c). Raising the initial concentration from 2 to 30 mg L⁻¹ increased q_e from 0.91 to 9.69 mg g⁻¹ through a stronger driving force for mass transfer, while the removal percentage fell from 89.1% to 65.9% as the finite number of sites became progressively occupied (Fig. 3d).

Effect of temperature. Removal rose from 71.0% to 81.0% as temperature increased from 298 to 318 K (Fig. 3e), suggesting an endothermic process.

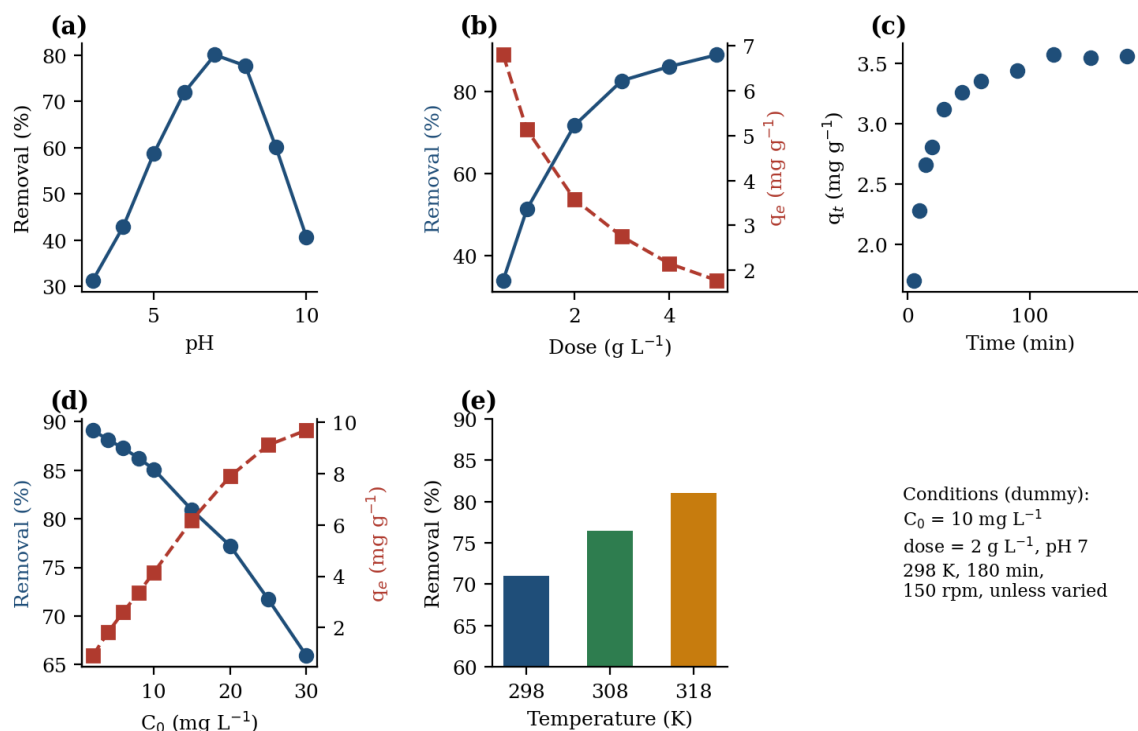


Fig. 3. Effect of (a) pH, (b) adsorbent dose, (c) contact time, (d) initial concentration, and (e) temperature on ammonia adsorption onto SCBC.

3.3 Adsorption kinetics

Experimental data were fitted to four kinetic models (Fig. 4; Table 2). The pseudo-second-order model gave the highest coefficient of determination ($R^2 = 0.9979$) and the lowest χ^2 (0.0027) and RMSE (0.027), and its calculated q_e (3.70 mg g⁻¹) agreed closely with the experimental value (3.56 mg g⁻¹). In contrast, the pseudo-first-order model underestimated the capacity ($q_{e,cal} = 3.42$ mg g⁻¹; $R^2 = 0.9355$). This indicates that the rate-limiting step is likely chemisorption involving ion exchange or electron sharing between NH_4^+ and surface functional groups. The moderate fit of the Elovich model ($R^2 = 0.9227$) is consistent with a heterogeneous surface.

The Weber-Morris plot (Fig. 4d) was multilinear, with a steep first segment ($k_{id,1} = 0.433$ mg g⁻¹ min^{-1/2}) attributed to boundary-layer diffusion and a flatter second segment ($k_{id,2} = 0.046$) attributed to intraparticle diffusion. Since neither line passed through the origin (intercepts 0.85 and 2.99 mg g⁻¹), intraparticle diffusion is not the sole rate-controlling step, and film diffusion also contributes.

Table 2. Kinetic model parameters for ammonia adsorption onto SCBC					
Model	Parameters	Value	R ²	χ ²	RMSE
Pseudo-first-order	k ₁ (min ⁻¹); q _{e,cal} (mg g ⁻¹)	0.1065; 3.42	0.9355	0.1070	0.148
Pseudo-second-order	k ₂ (g mg ⁻¹ min ⁻¹); q _{e,cal}	0.0448; 3.70	0.9979	0.0027	0.027
Elovich	α (mg g ⁻¹ min ⁻¹); β (g mg ⁻¹)	5.50; 2.01	0.9227	0.1083	0.162
Intraparticle diffusion (overall)	k _{id} ; C	0.139; 2.02	0.7605	0.3315	0.284

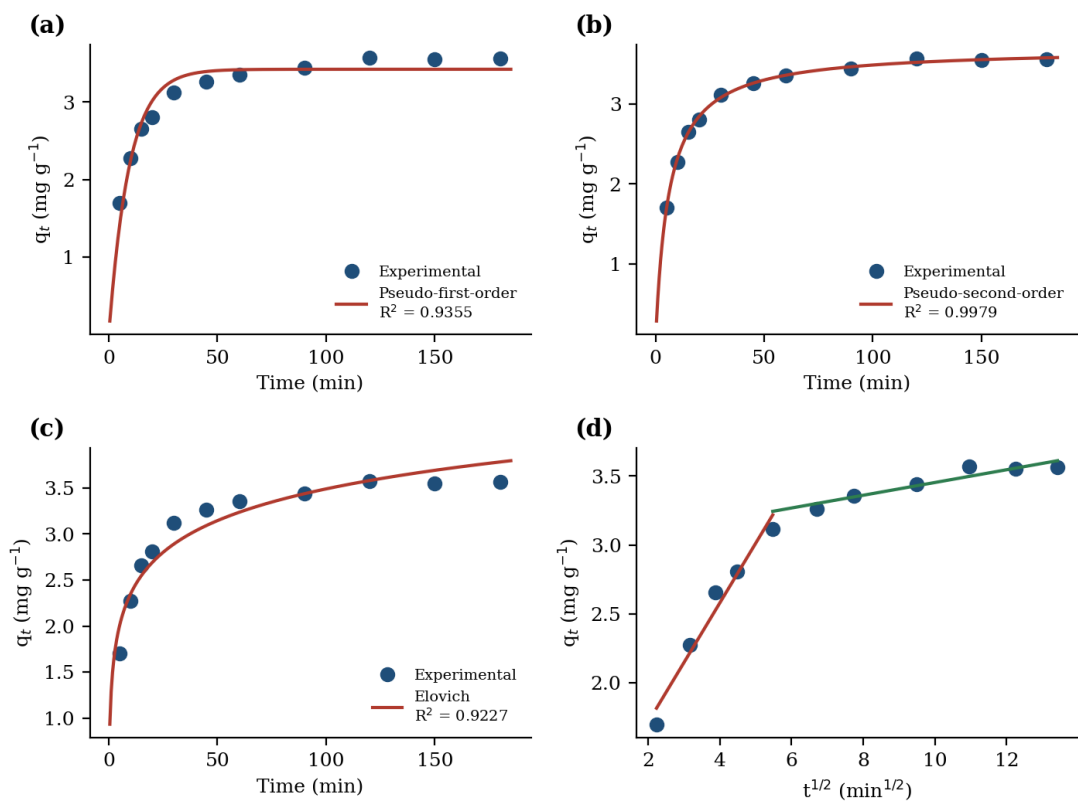


Fig. 4. Kinetic modelling: (a) pseudo-first-order, (b) pseudo-second-order, (c) Elovich, and (d) Weber-Morris intraparticle diffusion plots.

3.4 Adsorption isotherms

Equilibrium data were modelled with the Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich (D-R) isotherms (Fig. 5; Table 3). The Langmuir model gave the best description ($R^2 = 0.9986$) with the lowest error values, implying monolayer coverage on energetically similar sites, with a maximum capacity q_{max} of 12.74 mg g⁻¹. The separation factor R_L ranged from 0.09 to 0.60 ($0 < R_L < 1$), confirming favourable adsorption across the studied range. The Freundlich exponent n of 2.02 ($1/n = 0.50$) also indicates favourable uptake, although its poorer fit ($R^2 = 0.9688$) argues against pronounced surface heterogeneity. The Temkin constant b_T of 992 J mol⁻¹ reflects a moderate heat of adsorption, and the D-R mean free energy E of 10.2 kJ mol⁻¹ falls between 8 and 16 kJ mol⁻¹, characteristic of ion exchange. Because the study was performed at low concentration, these parameters are valid for 2 to 30 mg L⁻¹ and should not be extrapolated to concentrated wastewaters.

Table 3. Isotherm parameters for ammonia adsorption onto SCBC at 298 K

Isotherm	Parameters	Value	R ²	χ ²	RMSE
Langmuir	q_{max} (mg g ⁻¹); K_L (L mg ⁻¹)	12.74; 0.336	0.9986	0.0195	0.113
Freundlich	K_F ((mg g ⁻¹)(L mg ⁻¹) ^{1/n}); n	3.33; 2.02	0.9688	0.6535	0.542
Temkin	A_T (L mg ⁻¹); b_T (J mol ⁻¹)	4.49; 992	0.9726	15.8656	0.507
Dubinin-Radushkevich	q_m (mg g ⁻¹); E (kJ mol ⁻¹)	47.9; 10.2	0.9823	0.3445	0.408

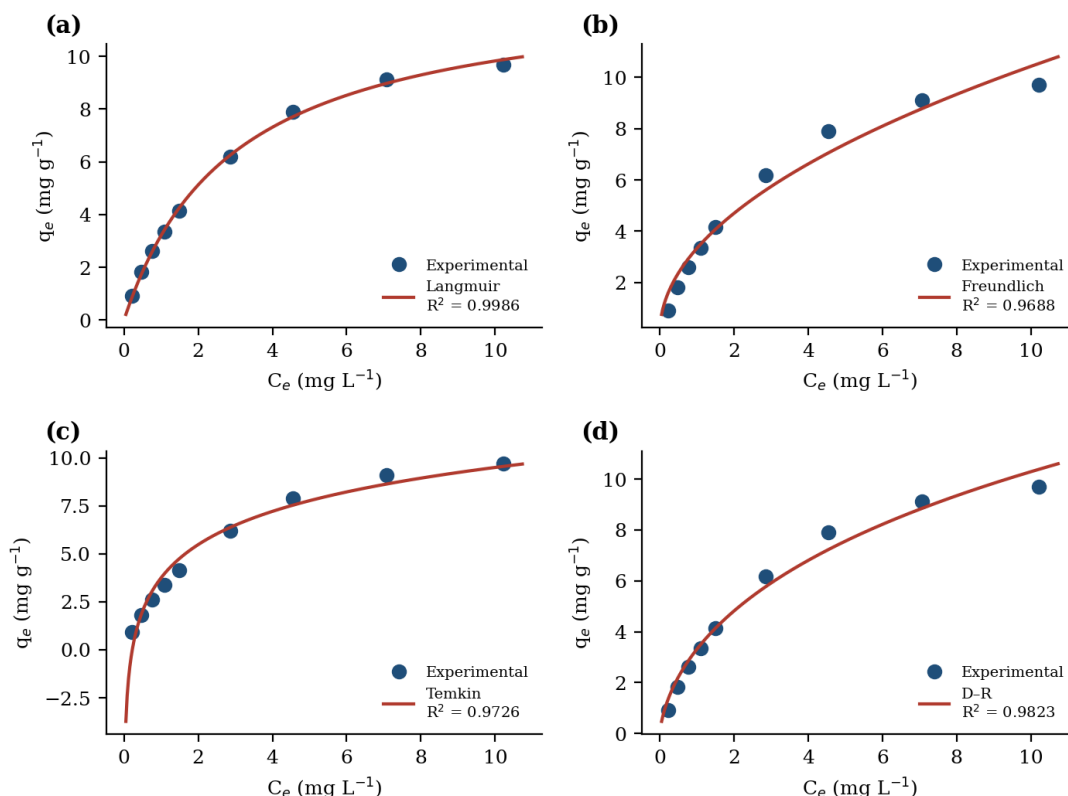


Fig. 5. Equilibrium isotherms with (a) Langmuir, (b) Freundlich, (c) Temkin, and (d) D-R nonlinear fits.

3.5 Thermodynamics

The negative ΔG° values (-0.50, -1.25, and -2.00 kJ mol⁻¹ at 298, 308, and 318 K) denote a spontaneous process whose feasibility improves with temperature. The positive ΔH° (21.8 kJ mol⁻¹) confirms its endothermic nature, and the positive ΔS° (75.0 J mol⁻¹ K⁻¹) points to increased randomness at the solid-solution interface, plausibly through the displacement of bound cations and water molecules by NH₄⁺.

Table 4. Thermodynamic parameters

T (K)	K _d (L g ⁻¹)	ΔG° (kJ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
298	1.224	-0.50	21.8	75.0
308	1.628	-1.25		
318	2.132	-2.00		

3.6 Adsorption mechanism

Collectively, the kinetic, isotherm, thermodynamic, and spectroscopic evidence supports a multi-mechanism process (Fig. 6). First, electrostatic attraction between NH₄⁺ and the negatively charged surface (pH > p*H*_{pzc}) is expected to dominate at low concentration. Second, cation exchange with surface-bound base cations such as K⁺ and Ca²⁺ is supported by the D-R mean free energy. Third, hydrogen bonding and surface complexation with carboxyl and hydroxyl groups are suggested by the changes in FTIR band intensities after adsorption. Finally, pore filling within micropores and mesopores may contribute, consistent with the BET findings.

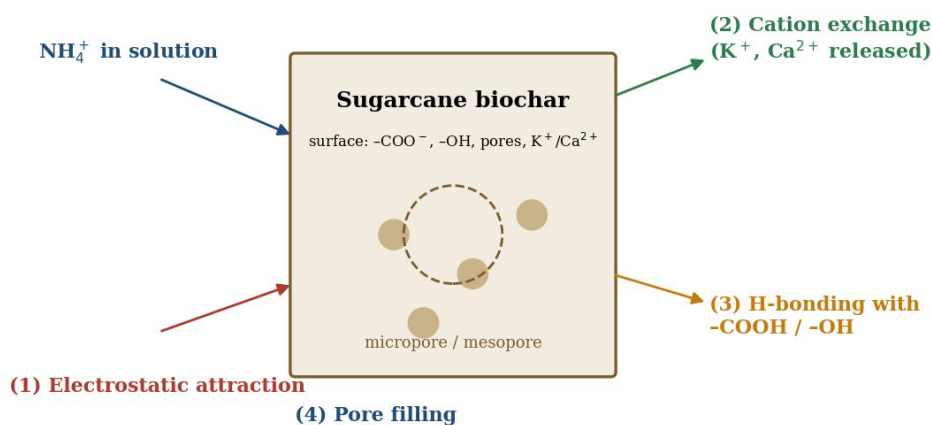


Fig. 6. Proposed mechanisms of NH_4^+ adsorption onto sugarcane biochar.

3.7 Comparison with other adsorbents

Table 5 compares SCBC with representative adsorbents. The q_{max} of 12.7 mg g^{-1} is competitive with the listed materials, with the added advantage of a low-cost, abundant feedstock and efficacy at low initial concentration.

Table 5. Comparison of $\text{NH}_4^+/\text{NH}_3$ adsorption capacities

Adsorbent	Conc. range (mg L^{-1})	pH	q_{max} (mg g^{-1})	Ref.
Sugarcane biochar (this study)	2-30	7	12.7	-
Wood biochar (dummy)	5-50	7	6.8	[ref]
Rice husk biochar (dummy)	5-100	7	9.2	[ref]
Zeolite (dummy)	5-50	7	14.1	[ref]
Activated carbon (dummy)	5-50	7	10.6	[ref]

3.8 Regeneration and reusability

Spent SCBC was regenerated with 0.1 M NaCl and reused for five cycles, during which removal declined from 71.1% to 54.6% (Fig. 7), demonstrating satisfactory operational stability with a modest loss of capacity attributable to incomplete desorption and partial site blockage.

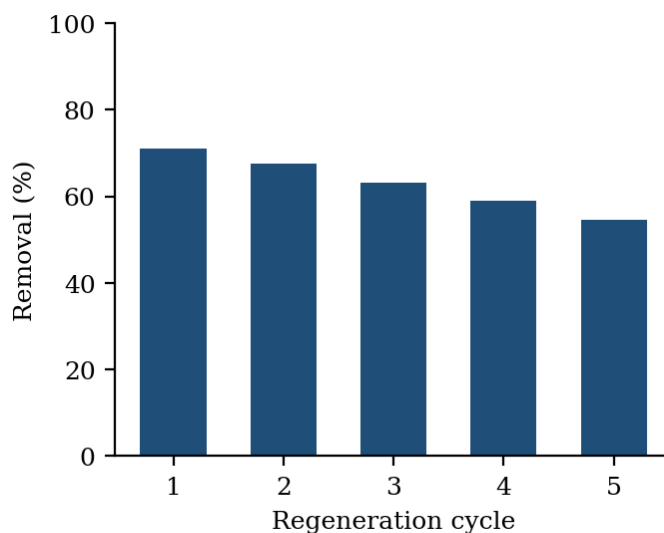


Fig. 7. Reusability of SCBC over five adsorption-regeneration cycles.

IV. CONCLUSIONS

The present study investigated the potential of sugarcane bagasse-derived biochar (SCBC) as a sustainable adsorbent for ammonia removal from dilute aqueous solutions, with particular emphasis on adsorption kinetics, equilibrium behaviour, thermodynamic characteristics, and possible removal mechanisms. The findings indicate that pyrolysis of sugarcane bagasse at 500 °C produced a carbon-rich material with a specific surface area of 186 m² g⁻¹, an alkaline surface pH of 9.1, and a point of zero charge (pH_{pzc}) of 6.4. The presence of hydroxyl, carboxyl, and other oxygen-containing functional groups, together with the porous structure of the biochar, suggests its suitability for ammonium retention. Under the investigated experimental conditions, a solution pH of 7 and an adsorbent dosage of 2 g L⁻¹ provided effective ammonia removal, while equilibrium was attained within approximately 120 min. Increasing the initial ammoniacal nitrogen concentration from 2 to 30 mg L⁻¹ enhanced the adsorption capacity from 0.91 to 9.69 mg g⁻¹, although the percentage removal declined as the available adsorption sites became progressively occupied.

The kinetic and equilibrium analyses further clarified the adsorption behaviour of SCBC. Among the evaluated kinetic models, the pseudo-second-order model provided the best fit to the experimental data, with an R² value of 0.9979, indicating that interactions involving surface functional groups and ion exchange may contribute substantially to the adsorption process. The intraparticle diffusion analysis revealed multiple transport stages, demonstrating that diffusion within the pores was not the only rate-controlling mechanism. The Langmuir isotherm described the equilibrium data most effectively, yielding a maximum adsorption capacity of 12.74 mg g⁻¹ and a separation factor between 0.09 and 0.60, consistent with favourable adsorption over the investigated concentration range. Furthermore, the Dubinin–Radushkevich mean free energy of 10.2 kJ mol⁻¹ suggested a possible contribution from ion-exchange interactions. Thermodynamic parameters, including negative Gibbs free energy changes and positive enthalpy and entropy changes, indicated that adsorption was spontaneous and endothermic under the studied conditions, with increased randomness at the solid–solution interface as a possible consequence of the adsorption process.

Overall, the combined findings suggest that ammonia adsorption onto SCBC involves several complementary mechanisms, including electrostatic attraction, cation exchange, interactions with oxygenated functional groups, and pore filling. The observed adsorption performance and the ability to reuse the material following sodium chloride regeneration indicate its potential for further development as an agricultural-residue-derived adsorbent. Nevertheless, its practical applicability requires validation under real-water conditions, particularly in the presence of competing ions and dissolved organic matter, as well as assessment through continuous-flow experiments and long-term regeneration studies. Subject to these further investigations, sugarcane bagasse-derived biochar could offer a resource-efficient option for ammonia removal from dilute aqueous streams while contributing to the productive utilisation of an abundant agricultural by-product.

FUTURE SCOPE

Future research should focus on the following aspects to improve the practical applicability of sugarcane bagasse-derived biochar (SCBC) for ammonia removal from dilute aqueous systems:

1. **Validation Using Real Water Samples:** Evaluate SCBC performance in real wastewater, surface water, and groundwater to determine its effectiveness under practical treatment conditions.
2. **Competitive Ion Assessment:** Investigate the effects of competing cations, such as K⁺, Na⁺, Ca²⁺, and Mg²⁺, along with dissolved organic matter, on ammonia adsorption capacity and removal efficiency.
3. **Optimisation of Biochar Production:** Examine the influence of pyrolysis temperature, residence time, and feedstock properties on biochar yield, surface chemistry, porosity, and adsorption performance.
4. **Biochar Modification:** Explore physical and chemical modification techniques, including acid or alkali treatment, oxidation, and metal loading, to improve adsorption capacity and selectivity.
5. **Continuous-Flow Column Studies:** Conduct fixed-bed column experiments and apply breakthrough models, such as Thomas, Yoon–Nelson, and Bohart–Adams, to evaluate the feasibility of large-scale water treatment.
6. **Detailed Mechanistic Investigation:** Use advanced spectroscopic techniques and cation-release measurements to clarify the contributions of ion exchange, electrostatic attraction, surface functional groups, and pore filling.
7. **Regeneration and Long-Term Stability:** Assess adsorption performance over additional regeneration cycles to determine capacity loss, material stability, regeneration requirements, and operational lifespan.
8. **Techno-Economic Assessment:** Estimate production costs, treatment expenses, regeneration costs, and overall economic feasibility in comparison with conventional ammonia-removal technologies.
9. **Life-Cycle Assessment:** Examine the environmental impacts associated with biochar production, transportation, use, regeneration, and final disposal to establish its overall sustainability.
10. **Reuse of Spent Biochar:** Investigate the potential application of ammonia-loaded biochar as a nitrogen-enriched soil amendment, with particular attention to nutrient availability, contaminant accumulation, and soil safety.

These future investigations would provide a stronger scientific and practical basis for developing SCBC as a sustainable, cost-effective adsorbent for ammonia removal and the beneficial utilisation of agricultural residues.

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