Research paper

The rationale for alternative fertilization: Equilibrium isotherm, kinetics and mass transfer analysis for urea-nitrogen adsorption from cow urine

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Abstract

In an effort to minimize the loss of urea-N through volatilization and concurrently recover urea in a usable form from cow urine, adsorption experiments using bamboo-based activated carbon were performed. Batch studies were undertaken to evaluate the effect of initial concentration, sorption time and temperature on the variation in urea uptake capacity of the prepared carbon. Equilibrium data were tested against various isotherms, kinetics and mass transfer models. The Langmuir monolayer sorption was found to be 146.12 mg.g^{-1} with nearly 90% urea recovery attained. The process was found to be reversible as seen through regeneration experiments. Thermodynamic parameters indicated that urea sorption was physical, spontaneous and exothermic in nature. Kinetic studies revealed that the rate of urea uptake was limited by both surface adsorption and intra-particle diffusion. It was concluded that the mass transfer of urea molecules over the activated carbon was governed by film diffusion at all concentrations examined.

1. Introduction

Animal husbandry, and in particular, livestock wastes are a major source of ammonia (NH_3) in the atmosphere [1,2]. In recent years, the use of such nitrogenous sources in agriculture has increased, due to the ability of animal manure to supply plant-required nutrients to crops [3]. An impetus toward the use of these fertilizers is seen in organic farming where crop nutrients are exclusively supplied from such nitrogen (N) sources. Efficient manure management calls for the application of these wastes to arable land as a means for improving soil fertility and crop productivity. Cow urine is a rich source of nutrients; feedlot cattle is known to retain less than 20% of N from its diet resulting in more than 80% being lost in excretion [4]. Moreover, as Mobley et al. [5] point out, cow urine contains more than 90% of the excreted urea-N. While the use of urine as a liquid fertilizer has been encouraged over the years, especially in contemporary organic farming settings [6], several studies have indicated that this approach could have considerable shortcomings. When added directly to soils, urine undergoes hydrolysis within a few days of application and volatilizes as ammonium-N [7]. Various investigations on NH_3 volatilization indicate that more than 50% of feedlot-N is lost to the atmosphere following the application of urine [8,9]. In addition, externalities in the form of eutrophication [10] and reduced soil N-fixing ability have also been recognized [11].

Although the rationale for recycling resources (plant-required) back to agricultural systems is justified for our resource-scare society to continue to move toward its goal of ensuring food security, there is also an equally important need to address the shortcomings of our current efforts and look for alternative avenues. This investigation focuses on physical separation techniques (adsorption) as an effective strategy to recover urea-N from cow urine while addressing the limitations of previous research in this area [1–3,9]. Through our previous studies we have demonstrated that urea recovery could be realized using activated carbon [12,13]. This research examines the

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potential of bamboo shoots toward the recovery of urea-N from urine while simultaneously minimizing the loss of ammonium-N to the atmosphere. Specific emphasis has been extended to the equilibrium kinetics, isotherm and mass transfer analysis of the sorption to document the favorability of the investigated procedure vis-à-vis current alternatives. Urea-N recovery from cow urine through the procedure investigated here could offer insights into the discourse surrounding sustainable fertilization, resource recovery and recycling of organic wastes back to agricultural fields.

2. Methods and materials

2.1. Urine

Urine was collected from three Indian dairy cows (diet made up exclusively of grazed grass) in sterile polyethylene containers for a consecutive period of four days. The specimens were collected while the animals were indoor for milking. Following the collection all samples were immediately transferred to the laboratory and stored until further use at −18 °C. Tests indicated that no loss of urea-N occurred during storage and refrigeration although *ca* 17% of the total N was observed to transform into ammonium-N when stored at room temperature (23 ± 2 °C). Kjeldahl analysis of urine allowed for determination of total N and urea-N to be 6.28 g.L^{-1} and 4.92 g.L^{-1}, respectively. Urea-N thus constituted 78.3% of the total N content in urine. Kool et al. [14] reported similar observations in their study. Hence, initial urea concentration in urine was analyzed to be 10.5 g.L^{-1}. Prior to the experimental runs all the samples were thawed, mixed uniformly and utilized immediately for sorption.

2.2. Activated carbon

Bamboo shoots procured from Lakimpur, Assam, India were initially washed with distilled water thoroughly to remove surface impurities, oven-dried for 24 h at 105 °C and crushed in a roll mill to particle size of 10 mm. Following this, the shoots were microwave activated at 180 W for 10 min of irradiation time based on preliminary studies (CE104VD – Samsung, Malaysia). Subsequently, the activated precursors were placed in a porcelain boat and carbonized in a muffle furnace at heating rate of 24 °C.min^{-1} and temperature of 500 °C for 1 h. The carbon was allowed to cool in a desiccator to room temperature (25 ± 1 °C) and consequently size-reduced to 100 mesh (0.149 mm) in a ball mill (Deepthi Enterprise, Bangalore) at 80 rev.min^{-1}.

The activated carbon abbreviated as "BAC" throughout the manuscript was stored in air-tight polyethylene containers until further use. BAC was characterized for its surface and textural properties viz., surface area (BET): 911 m^2.g^{-1}; pore volume: 0.2609 cm^3.g^{-1} and percentage moisture (ASTM D2867-09): 3.85. The iodine number (ASTM D4607-94) was determined using a 0.1 N standard iodine solution as 972 mg of iodine/g of carbon^{-1}. The apparent density (ASTM D2854-09) was found to be 0.425 kg.m^{-3}, the porosity was 79.8%, average particle diameter 149 μm, and total yield of the carbon was observed to be 28.5%. All reagents and chemicals utilized in the experi-

ments were purchased from Sigma Aldrich Chemicals, Mumbai, India and were of analytical grade.

2.3. Sorption experiments

Urine (50 mL) at various initial concentration (20% – 2.1 g.L^{-1}; 40% – 4.2 g.L^{-1}, 60% – 6.3 g.L^{-1}; 80% – 8.4 g.L^{-1} and 100% – 10.5 g.L^{-1}) was prepared through dilution with deionized water in Erlenmeyer flasks (250 mL). Sorption experiments were performed in an electric thermo-stated incubator shaker (Orbitek LT, Scigenics Biotech, India) at 150 rpm to determine the effect of initial concentration until the establishment of equilibrium by adding 3 g of BAC to 25 mL of the prepared urine solutions and studied at room temperature (25 ± 1 °C). Moreover, to understand the effect of temperature on the sorption, further experiments were performed at 30 and 35 °C at various initial urea concentrations (20–100%) with constant adsorbent loading of 3 g and shaker speed of 150 rpm.

At various time intervals 1 mL aliquots of urine were withdrawn, filtered through a 0.45 μm syringe (Sartorius Stedim Boitech S.A., Germany) and monitored for change in concentration by observing the corresponding change in absorbance (at 430 nm) using a UV-Vis Spectrophotometer (Shimadzu UV-1601, Japan). The procedure documented by With et al. [15] was followed to monitor the urea concentration at various time intervals. Sorption experiments were carried out in triplicate and the deviations were less than 5%. MATLAB® was used to perform all statistical analyses. In all graphical representations, average values have been reported. Eq. (1) was used to calculate the urea adsorption at equilibrium (q_e; mg.g^{-1}) or urea uptake capacity [16]. C_0 and C_t (mg.L^{-1}) are urea concentration initially and at time 't', respectively (min), V (mL) is the volume of urine used and W (g) is amount of BAC added.

$$q_e = \frac{(C_0 - C_t)V}{W} \tag{1}$$

Following the sorption, it becomes vital to subject the saturated carbon to regeneration for recovering the sorbate as well as to allow reutilization of BAC. Conventional regeneration of carbon is carried out through the application of high temperature thermal processes. However, these processes are unfeasible when it comes to recovery of volatile organics like urea. Chemical regeneration offers a promising approach but suffers from the risk of reaction of the reagent with the sorbate compounds and consequent generation of undesirable by-products thus necessitating post-regeneration separation. The present work thus investigates the efficacy of using deionized water as the desorption media for urea recovery. Regeneration experiments were performed by stirring 3 g of exhausted BAC in 150 mL of deionized water in a reciprocating shaker at 45 °C and 150 rpm for 2 h (conditions were arrived at based on preliminary studies). Following this, the carbon was air dried at 105 °C overnight and used for five additional sorption runs to evaluate its reusability potential over time.

3. Results and discussion

3.1. Effect of initial concentration, time and sorption temperature

As seen in Fig. 1, initial concentration affected the urea uptake capacity of BAC. At room temperature (25 ± 1 °C) increasing inlet urea concentration (20–100%) causes a corresponding increase in uptake (30 to 158 mg.g^{-1}). Increasing the urea concentration increases the probability of collisions between urea and BAC and allows urea molecules to overcome the mass transfer resistance between the solid and aqueous phases [17]. Moreover, with increasing concentration difference the percentage removal of urea varied as: 86.5, 87.1, 87.8, 88.05 and 90.2 when concentration was varied as 20, 40, 60, 80 and 100%, respectively. The curves obtained at all concentration were continuous and smooth pointing toward the possibility of monolayer urea adsorption onto BAC [18,19]. The time required for the sorption to reach equilibrium was 120 min. Fig. 1 reveals that majority of the urea sorption occurred by the first 50 min beyond which further stirring only allows for establishment of equilibrium and little urea uptake. The higher urea uptake capacity during the initial phase of the sorption could be explained by the availability of higher internal surface area over BAC that gets saturated with time. It can be assumed that urea forms a one-molecule thick layer over BAC (monolayer adsorption) until 50 min following which the rate of sorption is controlled by the rate of transfer of urea from the exterior to interior parts of BAC. Similar observations have been made in studies on removal of carboxylic acids [20], dyes [21], and heavy metals [22] using activated carbon.

Since adsorption is spontaneous, an increase in urea uptake must occur with decreasing sorption temperature as expected in the uptake of organic molecules by activated carbon [23]. Fig. 2 shows the effect of temperature on urea sorption onto BAC at various initial concentrations. As seen here, equilibrium urea
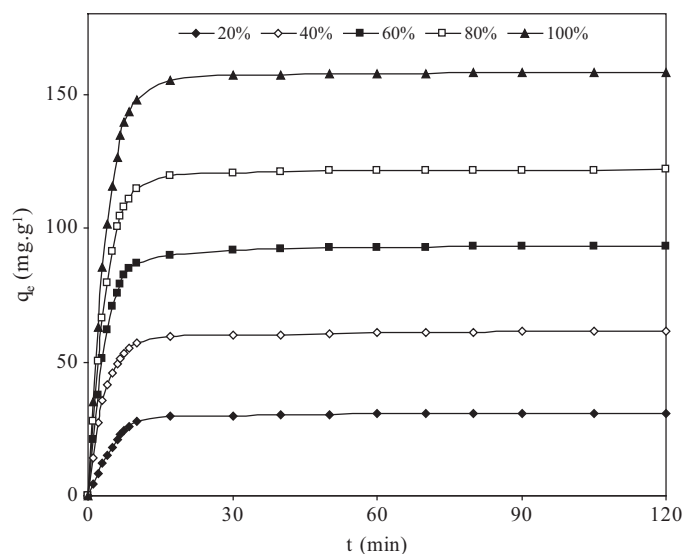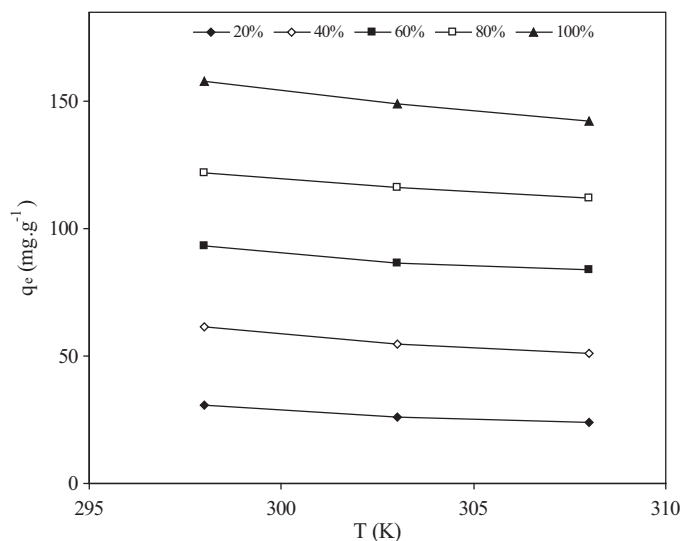

Fig. 2. Variation in urea sorption examined at various temperatures and initial concentration (BAC loading: 3 g; Sorbent volume: 50 mL; Shaker speed: 150 rpm).

uptake is higher at lower temperatures. At 100% urea concentration, equilibrium urea sorption was 158.12, 148.88 and 142.36 mg.g^{-1} at 25, 30 and 35 °C, respectively. Across all the concentrations studied, the average reduction in urea sorption was 8.2% (30 °C) and 13.5% (35 °C) as against a sorption temperature of 25 °C. This observation follows the corollary that increase in kinetic energy of urea molecules with temperature causes a corresponding increase in sorption entropy which decreases the ability of urea molecules to aggregate over the BAC surface. Similar conclusions have been drawn in literature concerning activated carbon for adsorption of phenolic compounds [24], volatile organic compounds [25] and heavy metals [26].

Regeneration studies on the saturated carbon performed using deionized water at 45 °C revealed that the uptake capacity decreased by 2.25, 3.86, 4.41, 5.96 and 7.28 mg.g^{-1} by the end of 5 consecutive adsorption-regeneration cycles. Hence, the decrease in urea sorption at equilibrium was less than 5% despite the continuous use of BAC over time pointing toward its reusability. More than 95% urea was easily eluted by deionized water indicative of the reversible nature of urea sorption onto BAC. In order to recover the concentrated urea eluted by deionized water two pathways are suggested: (i) direct application as a liquid fertilizer by further diluting the eluant with water to achieve required nutrient application rates for arable land and/or (ii) drying-crystallization operations for the urea-deionized water solution to produce solid urea; this could also ease its storage and transportation. It is acknowledged that the purpose of the regeneration experiments were to demonstrate the reuse potential of BAC and provide insights on pathways for urea recovery. Given the non-selective nature of any physical adsorption process, further purification would be required in order to meet regulatory standards or market specifications for use as fertilizers.

Previous studies on minimizing NH$_3$ volatilization losses have focused on approaches such as dietary manipulation

Fig. 1. Effect of initial concentration on urea uptake capacity of BAC studied at 25 °C, 150 rpm stirrer speed, 3 g BAC loading and 50 mL sorbate volume.

[27,28] or use of inhibitors [2,29]. These studies although promising have emphasized on the reduction of loss of urea N via ammonia volatilization and failed to provide ways in which these resources could be potentially utilized. Likewise, the drawbacks in the direct application of cattle urine such as increased soil salinity, acidity and conductivity and in some cases, crop losses have been well documented [30,31]. Hence, the present work emphasizes on an alternative strategy to inhibit such emissions while simultaneously adding value by recovering urea N from cattle urine for subsequent use as fertilizer. Based on results of the present work and similar investigations in the past by our group [12,13,32], it is evident that adsorbents prepared from renewable biomass such as bamboo, walnut and coconut shells indeed have potential for application in resource recovery setups.

3.2. Equilibrium isotherm analysis

For designing a sorption system, it is important to ascertain a suitable correlation with the equilibrium curves. Isotherm analysis through mathematical modeling of correlations allows for optimizing process operating conditions, and provides insights into sorbent capacity and its surface properties [33]. Accordingly, the experimental data were investigated against Langmuir, Freundlich, Flory–Huggins, Dubinin–Radushkevich and Tempkin two-parameter models. Foo and Hameed [34] provided a detailed review on isotherm modeling and their characteristic significance. The linearized forms of all the isotherm models were used on the sorption data and have been presented in Table 1. In addition to the correlation coefficient (R^2), goodness of fit was also evaluated by determining the normalized deviation and normalized standard deviations through Eqs. (2) and 3, respectively [36].

$$Normalized\ Deviation = \frac{100}{N} \sum \left| \frac{q_{e(exp)} - q_{e(pred)}}{q_{e(exp)}} \right| \quad (2)$$

$$Normalized\ Standard\ Deviation = 100 \sqrt{\frac{\sum \left(q_{e(exp)} - q_{e(pred)} / q_{e(exp)} \right)^2}{N}} \quad (3)$$

The use of the Langmuir isotherm has extended beyond its original approach to describe gas-solid phase sorption with the model assuming: (i) equal affinity of all sorbent sites toward the sorbate molecules (ii) adsorbed layer is one-molecule thick (monolayer) and (iii) no lateral interaction between adsorbed, adjacent sorbate molecules [35]. The Langmuir model constant (K_L) which represents the affinity between urea and BAC was further used to compute the dimensionless separation factor (R_L) using Eq. (4). Since R_L was found to be 0.43 ($0 < R_L < 1$) it was established that the sorption of urea onto BAC was favorable [19]. Further, the value of the separation factor was observed to decrease with increasing concentration signifying that the sorption was more favorable at higher urea concentration [41].

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

The Freundlich isotherm has been extensively applied to describe the sorption of organics over activated carbon and assumes a heterogeneous, reversible and non-ideal sorption

Table 1
Isotherm model constants, correlation coefficients and deviations for urea sorption onto BAC at 25 °C.

Isotherm model	Reference	Parameter	Value
Langmuir isotherm $\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{K_L q_m C_e}$	[19,34,35]	R^2	0.9863
		q_m (maximum monolayer saturation capacity; mg.g^{-1})	146.12
		K_L (Langmuir isotherm constant; L.mg^{-1})	0.0012
		R_L (separation factor)	0.4361
		Normalized deviation	4.4155
		Normalized standard deviation	5.0468
Freundlich isotherm $log(q_e) = log K_F + \left(\frac{1}{n}\right) log C_e$	[24,36,37]	R^2	0.9435
		K_F (Freundlich isotherm constant; mg.g^{-1}.(L.mg^{-1})$^{1/n}$)	0.2251
		n (adsorption intensity)	1.1983
		Normalized deviation	10.563
		Normalized standard deviation	12.223
Flory–Huggins $log \frac{\theta}{C_e} = log(K_a) + m log(1 - \theta)$	[35,38,39]	R^2	0.7282
		K_a (Flory–Huggins isotherm constant; L.g$^{-1} \times 10^4$)	4.5151
		ΔG (Gibbs free energy change; J.mol^{-1})	-19084
		Normalized deviation	30.069
		Normalized standard deviation	37.948
Dubinin–Radushkevich $ln(q_e) = ln(q_s) - K_{ad}\varepsilon^2$	[28,35,40]	R^2	0.8463
		q_s (theoretical isotherm saturation capacity; mg.g^{-1})	132.36
		K_{ad} (Dubinin–Radushkevich isotherm constant; mol^2.kJ^{-1})	0.0146
		Normalized deviation	16.257
		Normalized standard deviation	17.165
Tempkin $q_e = B ln(A) + B ln(C_e)$	[28,35]	R^2	0.8613
		B (Tempkin isotherm constant)	76.965
		A (isotherm equilibrium binding constant; L.g$^{-1} \times 10^{-3}$)	5.2835
		Normalized deviation	18.541
		Normalized standard deviation	27.778

process [24]. Although the Freundlich model fits the experimental data well ($R^2 > 0.94$), the correlation was poor in the later stages of the sorption at concentrations greater than 80%. Nonetheless, evaluation of the adsorption intensity (n) confirmed that sorption was indeed favorable reaffirming the conclusions drawn from R_L values.

The Flory–Huggins isotherm was evaluated to consider the degree of surface coverage characteristic of urea onto BAC and evaluate sorption thermodynamic parameters. The Flory–Huggins model constant (K_a) was used to determine the Gibbs free energy change ($\Delta G°$) through Eq. (5) and standard enthalpy ($\Delta H°$) and entropy changes ($\Delta S°$) through Eq. (6) [38].

$$\Delta G° = RTln\left(K_a\right) \tag{5}$$

$$log\left(K_a\right) = \frac{\left(\Delta S^0\right)}{2.303R} - \frac{\left(\Delta H^0\right)}{2.303RT} \tag{6}$$

The Gibbs free energy change evaluated at 25, 30 and 35 °C were calculated to be −19.12, −15.22 and −13.41 kJ.mol^{-1}, respectively. Negative $\Delta G°$ values affirm that the sorption is spontaneous in nature. Moreover, given that $\Delta G°$ values lie in the range 0–20 kJ.mol^{-1} it can be assumed that physisorption of urea molecules onto BAC occurs [42]. The van't Hoff equation (Eq. (6)) allowed determination of enthalpy to be −18.95 kJ.mol^{-1} and entropy change as 0.5753 kJ.mol^{-1}. The negative value for enthalpy shows urea adsorption is exothermic and this is in agreement with experimental observations where, uptake was found to decrease with increasing sorption temperature. As pointed out by Liu [39], since $2.1 < \Delta H° < 20.9$ kJ.mol^{-1}, it can be affirmed that physical sorption is the mechanism for urea uptake by BAC. The positive value for $\Delta S°$ suggests that aggregation of urea molecules over the surface of activated carbon was random although, the extent of this is minimal judging by its low value [37].

The maximum monolayer uptake (q_m) from the Langmuir model was 146.12 mg.g^{-1} while the saturation capacity (q_s) evaluated through the Dubinin–Radushkevich isotherm was 132.36 mg.g^{-1} and both agree closely with the experimental results. Further, the mean free energy for urea sorption was calculated using the Dubinin–Radushkevich isotherm constant (K_{ad}; mol^2.kJ^{-1}) through Eq. (7) and computed to be 5.85 kJ.mol^{-1} suggesting physisorption as the mechanism for urea removal from urine [43]. Moreover, based on the correlation coefficients, normalized and standard normalized deviations, the best fit for the adsorption data was found in the Langmuir isotherm suggesting homogeneous, monolayer uptake of urea by BAC.

$$E = \frac{1}{\sqrt{2K_{ad}}} \tag{7}$$

3.3. Sorption kinetics and mass transfer analysis

As described earlier, rapid urea uptake onto BAC was observed within 50 min. In order to determine the rate limiting step the experimental data were tested against the first-order, second-order and intra-particle diffusion kinetic models for
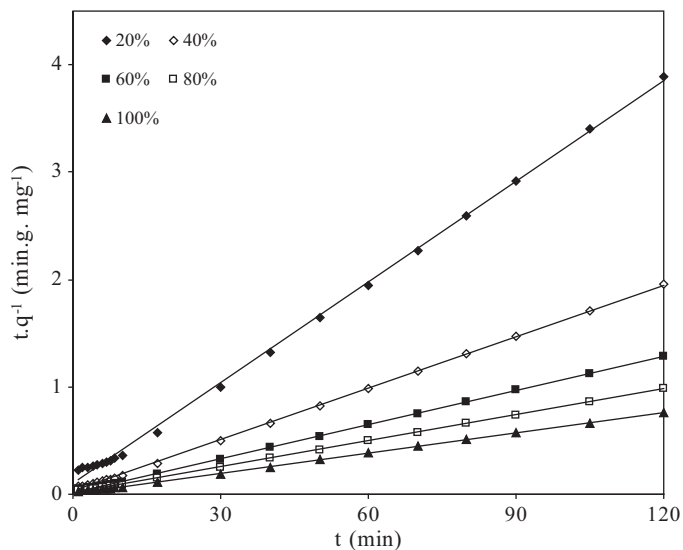

Fig. 3. Second-order kinetic fit for urea sorption on BAC at various initial concentrations.

various initial urea concentrations (20–100%). The first-order model as described by the Lagergren kinetic equation [44] was used in its linear form (Eq. (8)). Log (q_e-q_t) versus sorption time was plotted to determine the first-order constant (k_1; min^{-1}). The second-order kinetic model [45] was used as in Eq. (9). A plot of t/q versus time (Fig. 3) allowed estimation of the second-order kinetic constant k_2 (mg.g^{-1} min^{-1}). In order to examine if intra-particle diffusion was another rate limiting step the equation proposed by Webber and Morris [46] was used as described by Eq. (10). To determine the intra-particle diffusion constant (k_{id}: mg.g^{-1} min$^{-1/2}$), a plot of urea uptake (q_t) versus t$^{1/2}$ was obtained. As seen in Table 2, second-order kinetic fit was more appropriate in describing the urea sorption. The second-order rate constant followed a linear relationship with urea concentration although this was not strictly proportional to the second power of concentration.

$$log\left(q_e - q_t\right) = log\left(q_e\right) - k_1t \tag{8}$$

$$\frac{t}{q} = \frac{1}{k_2q_e^2} + \frac{t}{q_e} \tag{9}$$

$$q_t = \left(k_{id} \times t^{1/2}\right) + C \tag{10}$$

The intra-particle diffusion plots (Fig. 4) at various concentrations demonstrated multi-linearity and indicated that three consecutive steps occurred in the urea sorption process [47]. The first section of the curve describes the boundary layer diffusion of urea from the solution onto the external surface of BAC. The second section (4–10 min) is attributed to intra-particle diffusion to limit the rate of urea sorption while the third (the plateau) describes the attainment of equilibrium where intra-particle diffusion is seen to slow down due to low concentration of urea left in the sorbate [40]. The k_{id} values were seen to vary from 0.36 to 0.18 mg.g^{-1} min$^{-1/2}$ when concentration increased from 20 to 100%. Moreover, the linear lines for

Table 2
Kinetic model constants, correlation coefficients and deviations from experimental urea uptake capacity.

Kinetic model	Parameters			
First-order model	C_0	R^2	k_1	$q_{e(pred)}$ [a]
	20	0.9841	0.0989	35.318
	40	0.9578	0.0917	47.951
	60	0.9979	0.1224	94.776
	80	0.9985	0.1247	125.89
	100	0.9978	0.1224	161.42
Normalized deviation	–	–	–	8.7838
Normalized standard deviation	–	–	–	11.961
Second-order model	C_0	R^2	$k_2 \times 10^3$	$q_{e(pred)}$
	20	0.9987	9.5717	32.051
	40	0.9998	9.1428	62.513
	60	0.9971	6.1251	95.238
	80	0.9669	4.9331	123.45
	100	0.9896	3.5593	161.29
Normalized deviation	–	–	–	2.2925
Normalized standard deviation	–	–	–	2.4671
Intra-particle diffusion model	C_0	R^2	k_{id}	$q_{e\,(pred)}$
	20	0.9639	0.3618	26.758
	40	0.9624	0.7156	53.152
	60	0.9636	0.1086	80.721
	80	0.9642	0.1421	105.68
	100	0.9643	0.1845	137.14
Normalized deviation	–	–	–	13.282
Normalized standard deviation	–	–	–	13.285

[a] $q_{e(pred)}$: predicted values for urea sorption at equilibrium evaluated by respective models.

the intra-particle diffusion did not pass through the origin indicative of the fact that this was not the only rate limiting step. Hence, urea sorption onto BAC is governed and limited by both, surface adsorption and intra-particle diffusion.

$$ln\,\frac{C_t}{C_0} - \frac{1}{1+mK} = ln\,\frac{mK}{1+mK} - \frac{1+mK}{mK} \cdot \beta_L S_s t \quad (11)$$
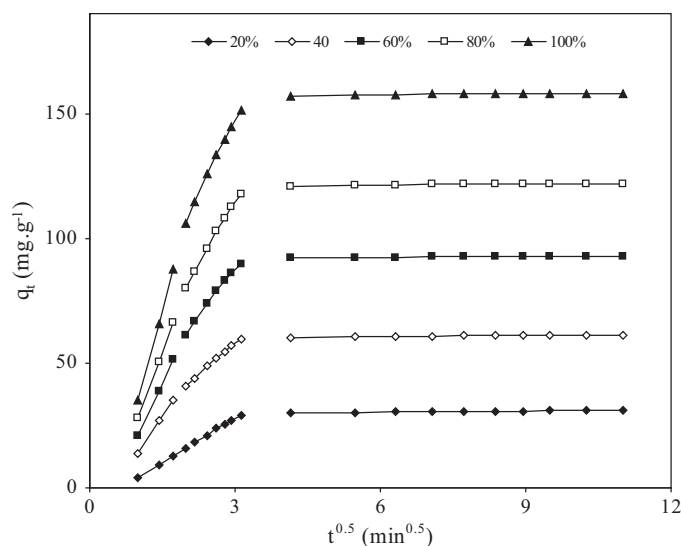

Fig. 4. Plot for intra-particle diffusion of urea onto BAC at various initial concentrations.

Table 3
Mass transfer coefficients at various urea concentrations.

Initial concentration (%)	β_L (cm.s^{-1})
20	2.6541E-05
40	4.2758E-05
60	4.6401E-05
80	4.9563E-05
100	5.5109E-05

The mass transfer of urea onto BAC was analyzed through Eq. (11) as described by McKay et al. [40]. Here, K is a dimensionless parameter evaluated by multiplying the Langmuir constant (K_L) and monolayer saturation capacity (q_m), S_s is outer BAC surface per unit volume of particle-free sorbate (cm^{-1}), m is the amount of BAC per unit volume of particle-free sorbate solution (g.L^{-1}) and β_L is the mass transfer coefficient (cm.min^{-1}). Plots of $ln((C_t/C_0)-1/(1 + mK))$ versus time were obtained for three initial urea concentrations at 25 °C. The mass transfer coefficients as evaluated through the slopes of the linear plots for all the initial concentrations are presented in Table 3. The values of the coefficient once again confirm the influence of concentration difference to overcome mass transfer limitation in the sorption. Further, to determine the steps that govern the urea sorption onto BAC, the mathematical procedure put forward by Boyd et al. [48], Reichenberg [49], and Helfferich [50] was employed through Eq. (12). The three consecutive steps involved in the sorption of organics onto an adsorbent are as follows;

1. Film diffusion: adsorbate transport to the external surface of the sorbent;
2. Particle diffusion: adsorbate transport within the pores of the sorbent; and
3. Adsorption of the sorbate molecules on the external surface of the sorbent.

As pointed out by Helfferich [50], there is consensus that the third step is extremely rapid and is not likely to determine the uptake of organic compounds. The fractional attainment of equilibrium (F) expressed as the ratio of uptake (q_t) at time t and maximum uptake capacity (q_m) were calculated and used to determine the values of Bt using Reichenberg's table [49]. The time constant (B) is influenced by the effective diffusion coefficient (D_i; m^2.min^{-1}) and the radius of BAC (r_0) which is assumed to be spherical. Linear plots of Bt versus sorption time (figure not shown for brevity) were obtained and did not pass through the origin for all initial concentrations. This indicated that film diffusion dominated and governed the overall urea adsorption onto BAC. The effective diffusion coefficient calculated from the slope of the Bt plots and Eq. (13) were found to be 1.322E-09, 2.351E-09, 2.461E-09 increasing as urea concentration was varied as 20, 60 and 100%, respectively.

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-n^2 Bt\right) \quad (12)$$

$$B = \frac{\pi^2 D_i}{r_0^2} \tag{13}$$

4. Conclusions

1. Carbon prepared from the microwave activation and carbonization of bamboo shoots was demonstrated as an effective adsorbent for the removal of urea from cow urine with more than 90% urea recovery attained at 100% initial concentration (50 mL sorbate volume), 150 rpm shaker speed, 25 °C and 3 g BAC loading.

2. Isotherm analysis indicated both Langmuir and Freundlich models could describe the sorption adequately although it was concluded through the calculation of normalized deviations that Langmuir offers better correlation with the experimental data. Thermodynamic parameters pointed to the spontaneity and favorability of the process.

3. Urea adsorption onto BAC followed a second-order kinetic fit with intra-particle diffusion being an additional rate limiting step. The significance of initial concentration was established through mass transfer analysis where further conclusion on film diffusion governing the overall sorption was also drawn.

4. The process investigated here demonstrates that ammonia volatilization from cattle manure could be minimized if coupled with urea recovery by employing physical separation operations such as adsorption onto activated carbon. It is acknowledged that although this study chose to employ bamboo shoots as the precursor; other suitable renewable agro-forestry or agro-waste material could be examined for its affinity toward urea removal.

5. With circular pathways, the topic currently under research points out the potential pathway for recycling nutrients like urea back to agricultural areas. As recommendation for further research, it would be interesting to compare such processes in literature against conventional manufacturing processes for fertilizer production to better understand economic and manufacturing considerations.

Abbreviations

A	Tempkin equilibrium binding constant (L.g^{-1})
B	Tempkin isotherm constant (J.mol^{-1})
C_e	equilibrium liquid-phase urea concentration (mg.L^{-1})
C_t	liquid-phase urea concentration at time t (mg.L^{-1})
C_0	Initial liquid-phase urea concentration (mg.L^{-1})
D_i	Effective diffusion coefficient (m^2.min^{-1})
E_s	Mean sorption energy (kJ.mol^{-1})
K_a	Flory–Huggins isotherm constant (L.g^{-1})
K_{ad}	Dubinin–Radushkevich isotherm constant (mol^2.kJ^{-1})
k_{id}	intra-particle diffusion rate constant (mg.g^{-1}.min$^{-1/2}$)
k_1	first order rate constant (min^{-1})
k_2	second order rate constant (g.mg^{-1}.min^{-1})
K_F	Freundlich isotherm constant (mg.g^{-1}.(L.mg^{-1})$^{1/n}$)
K_L	Langmuir isotherm constant (L.mg^{-1})
n	adsorption intensity
q_e	equilibrium urea uptake or sorption capacity (mg.g^{-1})
q_m	maximum monolayer urea sorption (mg.g^{-1})
q_s	Dubinin–Radushkevich theoretical maximum sorption capacity (mg.g^{-1})
q, q_t	amount of urea adsorbed at time t (mg.g^{-1})
R_L	separation factor
Ss	outer adsorbent surface per unit volume of particle-free sorbate (cm^{-1})
t	adsorption time (min)
T	absolute temperature (K)
V	volume of urine (L)
W	mass of dry adsorbent used (g)
β_L	mass transfer coefficient (cm.sec^{-1})
ε	Polanyi potential
θ	Degree of surface coverage

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