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Simultaneous resource recovery and ammonia volatilization minimization in animal husbandry and agriculture

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Abstract

The study demonstrates that the minimization of ammonia volatilization and urea recovery could be coupled through the use of physical adsorption processes in continuous packed-bed columns. The potential of using microwave activated coconut shell based activated carbon toward the recovery of urea from cattle urine was investigated. The prepared carbon was immobilized onto etched glass beads to investigate the effect of initial concentration, flow rate and size of carbon support in a continuous, down-flow mode packed column. Further, to describe the sorption behavior, the experimental data were tested against different kinetic models. The analysis of the breakthrough curves allowed identification of the favorable operating parameters as: sorbate flow (8 $L \cdot h^{-1}$), initial urea concentration (60%) and glass bead support size (ϕ 1.5 cm). An equilibrium sorption of 802.8 $mg \cdot g^{-1}$ and up to 80% urea recovery was observed. Regeneration studies allowed for nearly 95% urea recovery with sorbent capacity decreasing by 5% over seven cycles of sorption/desorption.

Keywords: Cattle urine; Microwave activated carbon; Sustainable agriculture; Immobilized column adsorption; Waste management; Breakthrough

1. Introduction

It has long been recognized that there are certain physical limits on the global availability of economically-valuable natural resources underlying their potential exhaustibility [1]. However, for effective stewardship of earth's resources, it is evident that the economy–environment interaction must acknowledge these ecological constraints. Despite this understanding, our industrial activities seem to operate contrary to what is required for them to be sustainable. This phenomenon is clearly evident in the procurement of minerals and resources by the fertilizer industry which has tripled its output since the 1960s [2]. While technological modernization of agriculture has allowed its intensification commensurate with synthetic fertilizer use bringing the obvious benefits of increased food production, the ecological degradation accompanying this has been extensive and well-documented [3–5]. On the other hand, sustainability, a human construct, has seen its comprehension and applicability to various circumstances evolves continuously over time. Sustainability in agricultural production systems is now being seen through the lens of resource recovery where enhancing crop productivity through resources recovered from wastes is seen as a potential solution to ensure food security [6–9].

Cattle urine is one such resource where nutrient recovery would be beneficial. Feedlot cattle is known to retain less than 20% of dietary nitrogen (N) indicating that more than 80% of it finds its way in cattle excreta [10]. Although 60–80% of this N is excreted as urine, it undergoes rapid conversion thereafter to result in ammonia volatilization. This loss of ammonia to the environment contributes to its increased atmospheric concentration as ammonium sulfate ($(NH_4)_2SO_4$), ammonium nitrate (NH_4NO_3) and ammonium chloride (NH_4Cl) that are subsequently removed by dry and/or wet acid deposition [11]. Atmospheric mobilization and deposition of NH_3 have disturbed the nutrient balance of natural ecosystems [12], induced acute toxicity and secondary metabolic changes in vegetation [13], and

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Nomenclature

A	Area under break through curve [m^2]
C_{ads}	Adsorbed urea concentration [$g \cdot L^{-1}$]
C_b	Breakthrough concentration [$mg \cdot L^{-1}$]
C_o	Inlet sorbate concentration [$g \cdot L^{-1}$]
C_t	Outlet sorbate concentration [$g \cdot L^{-1}$]
$EBCT$	Empty bed contact time [min]
k_{AB}	Adams–Bohart kinetic constant [$L \cdot mg^{-1}\,min^{-1}$]
k_{Th}	Thomas rate constant [$L \cdot mg^{-1}$]
k_{YN}	Yoon–Nelson rate constant [min^{-1}]
K_a	Rate constant [$L \cdot mg^{-1}\,min^{-1}$]
m_{total}	Total amount of urea fed to the column [mg]
N	Number of sorption runs
N_0	Saturation concentration [$mg \cdot L^{-1}$]
q_c	Column capacity [mg]
q_{eq}	Equilibrium uptake or maximum column capacity [$mg \cdot g^{-1}$]
q_{exp}	Experimental uptake or maximum column capacity [$mg \cdot g^{-1}$]
q_{pred}	Predicted uptake or maximum column capacity [$mg \cdot g^{-1}$]
q_0	Maximum solid-phase concentration of the solute [$mg \cdot g^{-1}$]
Q	Flow rate [$mL \cdot min^{-1}$]
R^2	Coefficient of determination
t_b	Breakthrough time [min]
t_e	Bed exhaustion time [min]
t_{total}	Total flow time [min]
U_0	Linear velocity from Adams–Bohart model [$cm \cdot min^{-1}$]
v	Flow rate [$mL \cdot min^{-1}$]
V	Velocity [$cm\ min^{-1}$]
Δt	Mass transfer zone [min]
t or τ_{exp}	Time required for 50% of adsorbate break-through [min]
X	Total mass of adsorbent in the column [g]
Y	Linear velocity [$cm\ min^{-1}$]
Z	Bed height [cm]
Z_m	Length of the mass transfer zone [cm]

caused adverse effects on human health [14], and also represent a continued economic loss to the farmer as unavailable soil nutrients.

Indeed, several studies have been performed on developing pathways to minimize these losses; they have focused on dietary manipulation [15–18], use of inhibitors [19,20] and in-situ soil amendment with charcoal/biochar following the application of urine [21,22]. The objective of these studies has either been restricted to reducing ammonia volatilization or increasing the availability of ammonia-N subsequent to urine application in soils. However, the direct application of cattle urine, a fast acting fertilizer, has its downsides of increased soil salinity, acidity and conductivity and in some cases, crop losses [23,24]. Enclosure experiments in various studies have indicated that 4–41% of the N applied from cattle urine may volatilize following its application on arable soils [25,26]. Hence, this study argues that an alternative strategy to inhibit such emissions while simultaneously recovering urea-N from cattle urine (ex-situ) for subsequent use as fertilizer could be through the use of physical adsorption processes.

Biosorption using activated carbon (AC) prepared from renewable agro-waste can be seen as a promising method for urea recovery [27–30]. In our earlier investigations, batch experiments were performed to demonstrate the efficiency of AC toward urea recovery from urine [31–33]. The principal objective of the present study was to demonstrate a continuous process to recover urea from cattle urine through adsorption using AC prepared from coconut shells. To perform this, we focus on cyclic sorption/desorption that employs packed-bed column which makes effective utilization of concentration difference, adsorbent capacity and, hence, results in better quality effluent streams [34]. Moreover, a continuous packed-bed column also has process engineering advantages of ease in scale-up of the investigated procedure and can treat high volumes of influent streams using a definite quantity of adsorbent. On the contrary, earlier studies have shown that regeneration of AC and the cost of the sorbent is relatively high, which subsequently limits its application. To this effect, immobilization of AC onto a supporting material offers an efficient solution to the problems involved in separation processes [35]. Given their low cost, mechanical strength, and ease of surface modification, this study uses etched glass beads as the support material [36]; indeed, glass beads have found application as a support material for several other immobilization studies [36–39]. In particular, immobilization is well suited for non-destructive recovery of substances and is relatively resistant in chemical environment [35,40–42]. Hence, this study employs immobilization of the prepared AC onto etched glass beads to ease post-experimental recovery of the adsorbed urea.

2. Materials and methods

2.1. Urine: collection and characterization

The urine specimen was collected from four Indian dairy cows (diet consisted exclusively of grazed grass) while the animal was indoor for milking. Collection was carried out two to three times per day for a period of 7 consecutive days using polyethylene buckets. The urine was immediately transferred to the laboratory in sterile polypropylene containers and stored at −15°C until required. Following the period of collection, all samples were thawed, thoroughly mixed and immediately utilized in the adsorption column. Initially, the urine was characterized for its total-N and urea-N concentrations.

2.2. Sorbent preparation

2.2.1. Activated carbon

Activated carbon (AC) was prepared from coconut shells as described in an earlier study [31]. Initially, coconut shells were washed with distilled water, air dried at 110°C for 24 h in a tray dryer and crushed in a roll mill to particle size fractions of