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# Recovering urea from human urine by bio-sorption onto Microwave Activated Carbonized Coconut Shells: Equilibrium, kinetics, optimization and field studies

Mahesh Ganesa Pillai *, Prithvi Simha, Ashita Gugalia

*Mass Transfer Laboratory, Chemical Engineering Division, School of Mechanical and Building Sciences (SMBS), VIT University, Vellore 632014, Tamil Nadu, India*

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ABSTRACT

Microwave Activated Carbonized Coconut Shell (MACCS) was used to recover urea from human urine. Batch adsorption studies were conducted to evaluate the effect of initial adsorbate concentration (25%–100%), contact time, carbon loading (1–3 g) and shaking speed (150–200 rpm) on the removal of urea at 30 °C. Microwave activation was performed at 180 W (microwave output power) for 10 min. The sorption data were fitted to Langmuir, Freundlich, Tempkin, Flory–Huggins and Dubinin–Radushkevich isotherm models. Results showed that the maximum monolayer adsorption capacity of the MACCS powder was 256.41 mg $g^{-1}$. The Flory–Huggins model was found to best describe the urea uptake process since it demonstrated the minimum deviations from the experimental data. The kinetic data was fitted to pseudo-first-order, pseudo-second-order and intra-particle diffusion models, and was found to follow closely the pseudo-first order kinetic model. Based on the Central Composite Rotary Design, a five factor interaction model and a quadratic model were respectively developed to correlate the adsorption variables to the adsorption capacity. Field studies were conducted to determine the percentage biomass increase and relative agronomic effectiveness for soil treated with the urea adsorbed MACCS powder. Microwave activated carbonized coconut shell was shown to be a promising adsorbent for recovery and removal of urea from human urine solutions.



## Introduction

The objective of any sanitation system is to protect and promote human health by breaking the cycle of disease. Most of the existing sanitary systems prevent exposure of humans to harmful pathogens found in the excrement. These systems carry the waste, remove pathogens and pollutants, and finally release the contents back into the nature, often in large volumes of diluted wastes, which leads to eutrophication. By shifting away from today's paradigm which focuses on what must be removed from wastewater, to a new paradigm focusing on what can be recovered sanitation systems may begin to be described as Resource Recovery Systems [1].

The key role of inorganic fertilizers (NPK) in the phenomenal growth of food grain production is well established [2]. However, majority of the nitrogen is made from natural gas which is subject to price change and availability of methane, whilst, the global potassium and phosphorous mines are set to run out in less than a century [3]. Besides, the regular usage of inorganic fertilizers contributes to a progressive increase in soil acidity. These factors have made many farmers switch over to organic farming. However, the progress of organic farming has been very slow due to rapid decline in organic raw materials such as animal wastes, crop residues and green manure [4]. The application of fresh human urine as a source of plant nutrient is rapidly growing in agricultural practices, and has already been successfully exploited in many countries for cultivating a wide variety of crops [5–7]. The results validated that the crops grown using human urine, recorded a higher yield with greater nutritional value and taste similar to crops grown in normal soil. In addition, they do not pose any significant hygienic threat or leave any distinct flavor in food products.

In particular, the use of human urine can help achieve a "closed loop fertility system" that can re-circulate nutrients from human beings back to agricultural fields. The initial phase of this system involves separating urine from the waste stream, keeping the excrement dry and speeding up the decomposition of pathogens, while the latter phase involves recovery of valuable nutrients from the source separated urine [8]. Though extensive research has already been carried out on urine diversion systems, studies on the recovery of nutrients (urea) are relatively few; particularly separation of urea from urine has not been adequately investigated [9]. Although conventional methods such as reverse osmosis, chemical precipitation, electro-chemical process and ion exchange can be used for the removal of urea from urine, strict operating

* Corresponding author. Tel.: +91 97902 99447; fax: +91 4162243092.
*E-mail addresses:* maheshgpillai@vit.ac.in, clickonmag@yahoo.co.in (M.G. Pillai).

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**Nomenclature**

| | |
|---|---|
| $A$ | Tempkin isotherm equilibrium binding constant ($L\ g^{-1}$) |
| $B$ | Tempkin isotherm constant ($J\ mol^{-1}$) |
| $B_{ac}$ | biomass of plants in absolute control (g) |
| $B_{DAP}$ | biomass of plants in di-ammonium phosphate (g) |
| $B_t$ | biomass of plants in treatment (g) |
| $C_e$ | equilibrium liquid-phase concentration of urea ($mg\ L^{-1}$) |
| $C_0$ | initial liquid-phase concentration of urea ($mg\ L^{-1}$) |
| $E_s$ | mean sorption energy ($kJ\ mol^{-1}$) |
| $k_{ad}$ | 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 ($g\ mg^{-1}\ min^{-1}$) |
| Ka | equilibrium constant of adsorption |
| $K_f$ | Freundlich isotherm constant related to adsorption capacity ($mg\ g^{-1}$) ($L\ g^{-1}$)$^n$ |
| $K_L$ | Langmuir isotherm constant ($L\ mg^{-1}$) |
| LoD | limit of detection ($mg\ L^{-1}$) |
| LoQ | limit of quantitation ($mg\ L^{-1}$) |
| $n$ | adsorption intensity |
| $q_e$ | amount of urea adsorbed at equilibrium ($mg\ g^{-1}$) |
| $q_m$ | maximum adsorption capacity for the solid phase loading ($mg\ g^{-1}$) |
| $q_s$ | theoretical maximum capacity ($mg\ g^{-1}$) |
| $q$, $q_t$ | amount of urea adsorbed at time $t$ ($mg\ g^{-1}$) |
| $R$ | universal gas constant ($8.314\ J\ mol^{-1}\ K^{-1}$) |
| $R_L$ | separation factor |
| $t$ | adsorption time (min) |
| $T$ | absolute temperature (K) |
| $V$ | volume of the urine solution (L) |
| $W$ | mass of dry adsorbent used (g) |
| $\theta$ | degree of surface coverage |
| $\varepsilon$ | Polanyi potential |
| $\Delta G^\circ$ | Gibbs free energy of sorption ($kJ\ mol^{-1}$) |

conditions, high cost, long periods and bad impact from shock loads make them undesirable to be used in practical industrial applications [10]. Compared to these methods, adsorption has drawn more attention by researchers due to its feasibility, high safety and low cost [11].

Biomaterials have the potential to be used as low cost eco-friendly adsorbents because of the unused resources that are widely available [12]. Coconut (*Cocos nucifera*) generates a huge amount of solid waste, mostly in the form of fiber and shell. It has been reported that the processing of coconut shells into granular activated carbon of sufficient density, hardness and porosity, can potentially provide an inexpensive and renewable adsorbent [13,14]. Hence, the feasibility of employing activated carbon prepared from coconut shell toward the removal of urea from human urine was analyzed. The study attempts to: (i) enhance the surface area of coconut shell under microwave irradiation before carbonization; (ii) investigate the effect of contact time, initial concentration of adsorbate and adsorbent dosage on urea adsorption capacity; (iii) analyze the adsorption equilibrium and kinetics; (iv) characterize the Microwave Activated Carbonized Coconut Shell (MACCS) powder; and (v) optimize the process variables, using Response Surface Methodology (RSM) for the particular batch adsorption system.

## Materials and methods

### *Raw materials*

The adsorbate used for the studies was urine obtained from ten healthy young male volunteers (early twenties) with a well-balanced diet. Fresh urine samples collected in air-tight containers were immediately put on ice and stored at −20 °C for two days until the start of batch tests. The urine samples were thawed just before the investigation. Urine samples were characterized to calculate its major constituents and results have been summarized in Table 1. The coconut shells utilized for the preparation of activated carbon were obtained locally. The shells of the fruit were washed with distilled water to remove dirt from its surface and dried at 105 °C for 24 h. Subsequently, the shells were crushed to a size of 1–2 cm. Proximate analysis of the raw coconut shells used in this study by ASTM-1762 standards revealed the following; moisture content (5.64%), volatile matter (73.44%), fixed carbon content (20.29%) and ash content (0.63%). All chemicals used in the study were purchased from Nice Chemicals Pvt. Ltd, Cochin, India and were used without further purification.

### *Preparation and characterization of MACCS powder*

The sieved coconut shells were exposed to microwave irradiation at an output power of 180 W for 10 min (selected as the heating period, based on preliminary runs) before carbonization. The samples were placed in porcelain boats and heated in a furnace at a rate of 24 °C per min from room temperature to 500 °C, and maintained at this temperature for 1 h. The carbon thus obtained was cooled to room temperature, ground using a mortar, sieved to 100 mesh size (0.149 mm) and stored in tightly closed bottles for further analysis. The surface texture and the development of porosity for the precursor and the prepared activated carbon were analyzed using Scanning Electron Microscopy (FE-SEM, SUPRA 55, Carl Zeiss) with a 20 kV electron source. The surface organic structures of the samples were detected using Fourier Transform Infra-Red spectroscope (IRAffinity-1, Shimadzu) recorded at 4 $cm^{-1}$ of resolution and 60 scans $min^{-1}$ between 4000 and 400 $cm^{-1}$. The pore texture was characterized by $N_2$ adsorption at 77 K using a BET surface area analyzer (Micromeritics ASAP 2020). Prior to adsorption, the carbon was degassed at 300 °C in a vacuum condition for 2 h. The BET surface area was calculated from the $N_2$ adsorption isotherm using the Brunauer–Emmett–Teller (BET) equation [15]. The samples were characterized for their total pore volume, pore size, and specific surface area [16]. Iodine Number (mg iodine/g carbon) was determined by using a 0.1 N standardized Iodine solution and by extrapolating to 0.02 N by an assumed isotherm slope using the standard method.

**Table 1**
Major constituents and their concentration in the urine samples.

| S. No. | Constituents in urine | Concentration ($mg\ L^{-1}$) |
|---|---|---|
| 1 | Urea | 19,800 |
| 2 | Creatinine | 980 |
| 3 | Chlorides | 5945 |
| 4 | Sodium | 3195 |
| 5 | Potassium | 1480 |
| 6 | Sulfates | 810 |
| 7 | Phophates | 685 |
| 8 | Ammonium | 512 |
| Total solutes | | 33,407 |