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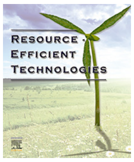

Research paper

On the behaviour, mechanistic modelling and interaction of biochar and crop fertilizers in aqueous solutions

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Abstract

Although the benefits of applying biochar for the purposes of soil conditioning and crop productivity enhancement have been demonstrated, relatively few studies have elaborated on its causal mechanisms, especially on the biochar–fertilizer interaction. Thus, in the present study, the ex-situ adsorptive potential of base activated biochar (BAB) towards plant nutrient immobilization and removal from aqueous solutions was investigated. Napier grass (*Pennisetum purpureum*) was utilized as the precursor to prepare slow vacuum pyrolysed char and its affinity towards adsorption of urea was examined at various process conditions. Low sorption temperatures, moderate agitation speeds and high initial concentration were seen to favour greater urea uptake by BAB. The sorption was exothermic, physical, spontaneous and had a pseudo-second order kinetic fit. Both surface and intra-particle diffusion governed the removal and immobilization of urea. Furthermore, process mass transfer was limited by film diffusion of urea to the external surface of the BAB. Equilibrium studies suggested that Dubinin–Radushkevich is the most appropriate model to describe the urea-BAB behaviour with maximum uptake, estimated to be 1115 $mg\cdot g^{-1}$. Through such ex-situ analysis, it could be possible to have prior knowledge, quantification and differentiation of the potential of chars manufactured from various feedstocks. This could then be used as an effective screening step in designing appropriate biochar–fertilizer systems for soil conditioning and help reduce the time and effort spent otherwise in long-term field studies.

Keywords: Soil fertility; Adsorption; Soil management; Sustainable agriculture; Fertilizer; Adsorption kinetics

1. Introduction

Biochar is a highly carbonaceous charred organic material that is deliberately applied as a soil conditioner with the intent to improve soil quality and associated environmental services [1]. Its preparation requires pyrolysis of plant-derived biomass under limited or no oxygen to promote the thermal degradation of the precursor. Several studies have pointed out that the application of biochar for soil conditioning, fertilization and amendment is a ‘multiple-win’ strategy [2] with the most touted benefits being carbon sequestration, waste disposal, enhanced plant nutrient uptake, pollutant immobilization and simultaneous biofuel production [3]. Nonetheless, biomass pyrolysis is not a new technology as it has conventionally been applied to maximize bio-liquid production for renewable energy capture. Moreover, with the char derived from the process potentially attaining energy contents as high as 30 $MJ\cdot kg^{-1}$ [4], any process that favours the char over the fuel represents an opportunity cost [5].

On the contrary, it is also evident today that immediate and effective adaptation measures need to be implemented for human society to address as well as mitigate the consequences of anthropogenic-induced radiative forcing and climate change. The causal linkage between agriculture and climate change has been shown to result in a net radiative forcing of 13.5% with crop production related land-use change accounting for a further 17.4% [6]. Additionally, the continuous intensification of agricultural practices in the hope of attaining global food security has caused extensive deterioration of soil quality and fertility [7]. It is therefore imperative that workable and implementable technologies are adopted that simultaneously

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Nomenclature

C_e	liquid-phase concentration of urea at equilibrium (mg·L^{-1})
C_t	liquid-phase concentration of urea at any time t (mg·L^{-1})
C_0	liquid-phase concentration of urea at t = 0 (mg·L^{-1})
D_i	effective diffusion coefficient (m^2·min^{-1})
F	fractional attainment of equilibrium expressed as a ratio of q_t to q_{max}
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})
S_s	BAB surface area per unit volume of particle-free adsorbate (cm^{-1})
m	BAB loading per unit volume of particle-free adsorbate
n	number of experimental observations
q_e	urea uptake capacity of BAB at equilibrium (mg·g^{-1})
$q_{e(exp)}$, $q_{e(pred)}$	experimental and predicted urea uptake capacity of BAB at equilibrium (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 by BAB at any time t (mg·g^{-1})
R_L	separation factor, Langmuir model
Ss	outer adsorbent surface per unit volume of particle-free sorbate (cm^{-1})
t	sorption time (min)
T	absolute temperature (K)
V	volume of adsorbate solution (L)
W	mass of BAB used (g)
β_L	mass transfer coefficient (cm·sec^{-1})
ε	Polanyi potential
θ	degree of surface coverage

provide pathways for improving (or restoring) soil health and mitigating climate change. Lehmann [8] estimated that carbon abatement to the (realistic) extent of 1 GtC·year^{-1} can be achieved through the addition and concentration of carbon within soils as biochar; this stems from our understanding that biochar could act as permanent C sinks (half-life of 100–1000 years) due to their chemical persistence within soils [8]. In addition, the co-benefits of biochar soil amendment include improved nutrient retention, augmented soil-moisture holding capacity, reduced emissions of CH_4 and N_2O, higher cation exchange capacity, etc. [9,10].

In particular, several investigations into the agronomic value of biochar addition have indicated an increase in crop yield following soil conditioning [11–14]. However, this increase in crop productivity was the combined interactive effect of biochar and externally added N fertilizers. For instance, Chan et al. [12] observed that there was no significant effect of biochar addition on productivity in the absence of N fertilizers. The same authors also demonstrated a corresponding increase in productivity as biochar addition was increased in the presence of N fertilizers. Similar observations on the inherent dependency of biochar on external fertilizer additions for augmenting crop growth have been made by Van Zwieten et al. [15] in their studies on wheat and radish biomass yields. However, little research exists on the causal mechanisms that govern and determine the much acclaimed benefits of biochar and its ability to immobilize plant available N. Particularly, few studies have evaluated the ex-situ adsorptive potential of biochar towards nutrient adsorption. While the benefits of biochar addition to soils are well-recognized today, there is a dearth of literature that seeks to qualitatively and quantitatively distinguish various feedstock derived biochar. Ex-situ understanding and quantification of the potential of different chars to adsorb soil nutrients could act as a screening process for identifying a good combination of biochar and crop fertilizer for improving soil health. Therefore the objective of the present work is to investigate the adsorptive characteristics of biochar to elucidate its relative affinity towards nitrogenous fertilizers. Through the analysis of urea (fertilizer) sorption from aqueous solutions onto a plant biomass derived char, the processes behaviour, rate controlling mechanisms, mass transfer and establishment of equilibrium have been described. Such quantification could potentially allow for designation of the agronomic values of biochar derived from various feedstocks and lead to their large scale application.

2. Materials and methods

2.1. Biochar preparation and characterization

Napier grass (*Pennisetum purpureum*) was utilized as the precursor for biochar production and was obtained from Kirloskar Oil Engines Ltd., Pune, India. Initially, the grass was uniformly ground to a particle size of 1–1.5 mm in an electric mixer and oven dried at 105 °C until constant weight was obtained. Subsequently, 50 g of the oven dried grass was fed to a SS 316 batch reactor and vacuum pyrolysed at 400 °C (based on initial experiments). A pressure gauge (1–15 bar) and a thermostat (K-type sensor) were attached to the reactor to monitor the pyrolysis. The obtained biochar was further washed with KOH (1:2) and activated at 500 °C as per the procedure described by Tseng and Tseng [16] in order to enhance its sorption capacity. Finally, it was acid washed (0.1 M HCl) to a pH of ca. 6–7 and dried in oven at 105 °C. The obtained biochar (BAB) was stored in air-tight polypropylene containers for further use and analysis.