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Research Article

Premilinary Investigation of Sorption Kinetics of Nitrate on Poultry and Swine Biochar and Charcoal

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Abstract

Rate of nitrates (NO_3^-) lost from the soil is alarming. This study was carried out to monitor the extent to which biochar made from poultry manure, swine manure and charcoal can adsorb NO_3^- thus reducing wastage. The experiment was carried out in the Soil Science Laboratory of Faculty of Agriculture, Obafemi Awolowo University, Ile-Ife. 25 ml of 0.01M of urea fertilizer solution was added to 0.5g of each biochar in a 50 ml plastic tube and subjected to mechanical shaking. Duplicate samples were removed every 4 hours (0h, 4h, 8h, 12h, 16h, 20h, 24h). NO_3^- and the filterate was analyzed using UV Spectrometer and the amount of NO_3^- per time was fit in pseudo-first and pseudo-second kinetic models. The rate of NO_3^- sorbed with time was in agreement with pseudo-second order kinetic model for all the biochar used indicating the presence of many functional groups on adsorption sites peculiar to polyfunctional materials like biochar. The rate of adsorption obtained for these biochar materials were 497.47, 221.52 and 396.108 mmol of NO_3^- per gram of poultry biochar, swine biochar and charcoal per hour. Thus, indicating the capability of these biochar materials in reducing the rate of release of NO_3^- from the soil and enhancing the nitrogen use efficiency of urea.

Keywords: *Nitrates; Biochar; Sorption; Kinetics and Efficiency*

Introduction

Nitrogen (N) is an essential nutrient needed in large quantity for optimal plant growth [1]. It is a major constituent of all proteins and nucleic acids [2] and readily available to crops as either Nitrate ion (NO_3^-) or ammonium ion (NH_4^+) depending on the aerating system of the soil [3]. It is the most limiting essential nutrients for plant growth globally due to its great loss (denitrification, volatilization, leaching, erosion and continuous cropping) in the soil system [2].

Moreover, N is very low in Nigerian soils due to its kaolinitic nature (low activity clay), low organic matter content and low CEC [4], therefore the need to apply Nitrogenous fertilizer is important. Urea is the commonest N-fertilizer applied by Nigerian farmers [5], but about 20 - 30% N is greatly loss from urea due to the low nutrient holding capacity of the soil.

Biochars has been discovered to be a good organic material with high adsorbing capacity. Several studies carried out in advanced countries confirms its ability to sorb nutrients such as Phosphate ions, Nitrate ions and ammonium ions [6-8]. However, there is little information available about the potential of biochar to adsorb NO_3^- from soil in Nigeria. Therefore, this study was carried out to investigate the rate at which biochar made from different organic materials (Poultry biochar-PB, Swine biochar-SB and charcoal-CC) can sorb NO_3^- in the soil thus reducing its removal from the soil.

Methodology

Materials

Dry poultry and swine manure were obtained from poultry and swine unit of the Teaching and Research Farm Obafemi Awolowo University, Ile-Ife and were pyrolysed for 5 hours with the use of local pyrolyser at Department of Mechanical Engineering at the University of Ibadan. Urea and charcoal were obtained from local markets.

Determination of selected elemental composition of poultry and swine biochar and Charcoal

pH Determination

Ten grammes (10g) of these air-dried biochars were weighed into 2 pieces of 50 ml pH cups respectively. 0.01M $CaCl_2$ was added to each cups in ratio 1:2 sample-solution. The pH was determined using pH meter after being buffered at pH 4 and pH 7.

Organic matter content determination

This was determined using the chromic acid digestion method [9].

Sorption kinetics experiment

0.5 gramme of PB, SB and CC were placed in various vessels and 25 ml of 0.01M urea solution was added. These mixtures were subjected to vigorous shakings, duplicate samples were removed every four hours until 24 hours (which was considered to be the equilibration time). Duplicate sets were not shaken and used as control experimental [7]. Supernatant was filtered off with the use of Whatman No 42 filter paper and NO_3^- in the filtrates was determined by the use of UV spectrometer (wavelength - 275 nm) at the Central Science Laboratory at OAU Ile-Ife.

NO_3^- sorbed was calculated by the equation

$$Q_{e/t} = \frac{[Ci - Cf] X V}{Wb}$$

Where; C_i and C_f (mg/L) are the initial and final NO_3^- concentrations in solution respectively, Q_e (mg/g) was the amount of NO_3^- at equilibrium, V (L) was the volume of solution used and W_b (g) the mass of biochar.

Determination of sorption kinetics

The rate at which NO_3^- was adsorbed with time was analyzed using the regression fit model of pseudo-first order and pseudo-second order equations [6].

$$\log(Qe - Qt) = \log Qe - \frac{k1}{2.303} t \qquad (1)$$

$$\frac{t}{Qt} = \frac{1}{K2Qe2} + \frac{t}{Qe} \qquad (2)$$

Where Q_e and Q_t are the amounts of nitrate sorbed (mg/g) at equilibrium and at time t (hours), k_1 and k_2 are the sorpion rate constants of pseudo-first order and pseudo-second order, respectively.

Results and Discussion

Selected properties of poultry biochar

pH values obtained for different biochars were 11.9 (PB), 12.4 (SB) and 10.7 (CC) respectively, showing a very strongly alkaline nature of the materials, thus making them useful liming materials for soil amended with N fertilizer.

Organic matter content of PB (7.72%) and SB (6.74%) were higher than CC (2.03%). It is an indication that biochar will improve soil organic matter, thereby improving the C.E.C. Biochar obtained from animal manure proves a better soil amendment compared to Charcoal obtained from plant sources.

Ppt	Values		
	PB	SB	CC
pH (0.01 M $CaCl_2$)	11.9	12.4	10.7
Organic matter (%)	7.722	6.74	2.026

Table 1: *Selected chemical properties of poultry biochar.*
PB: Poultry Biochar; SB: Swine Biochar; CC: Charcoal.

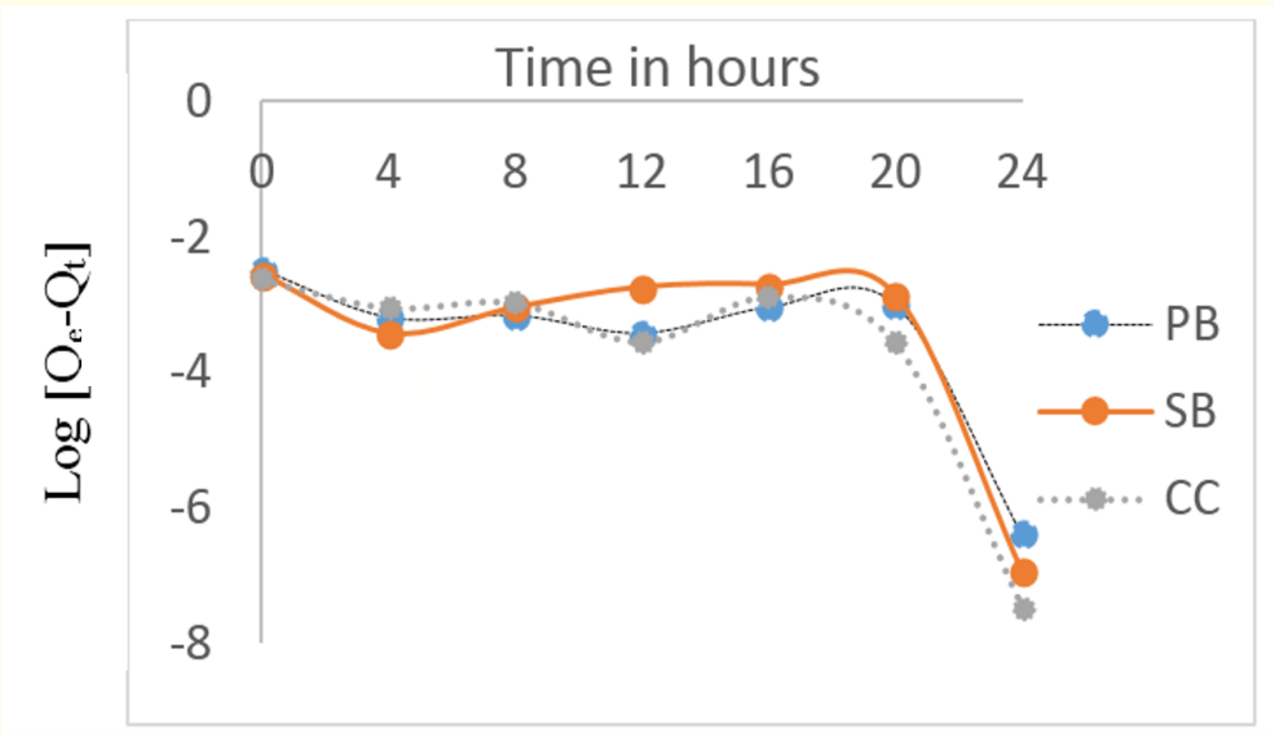

Figure 1: *Plots for the pseudo-first order kinetic model.*

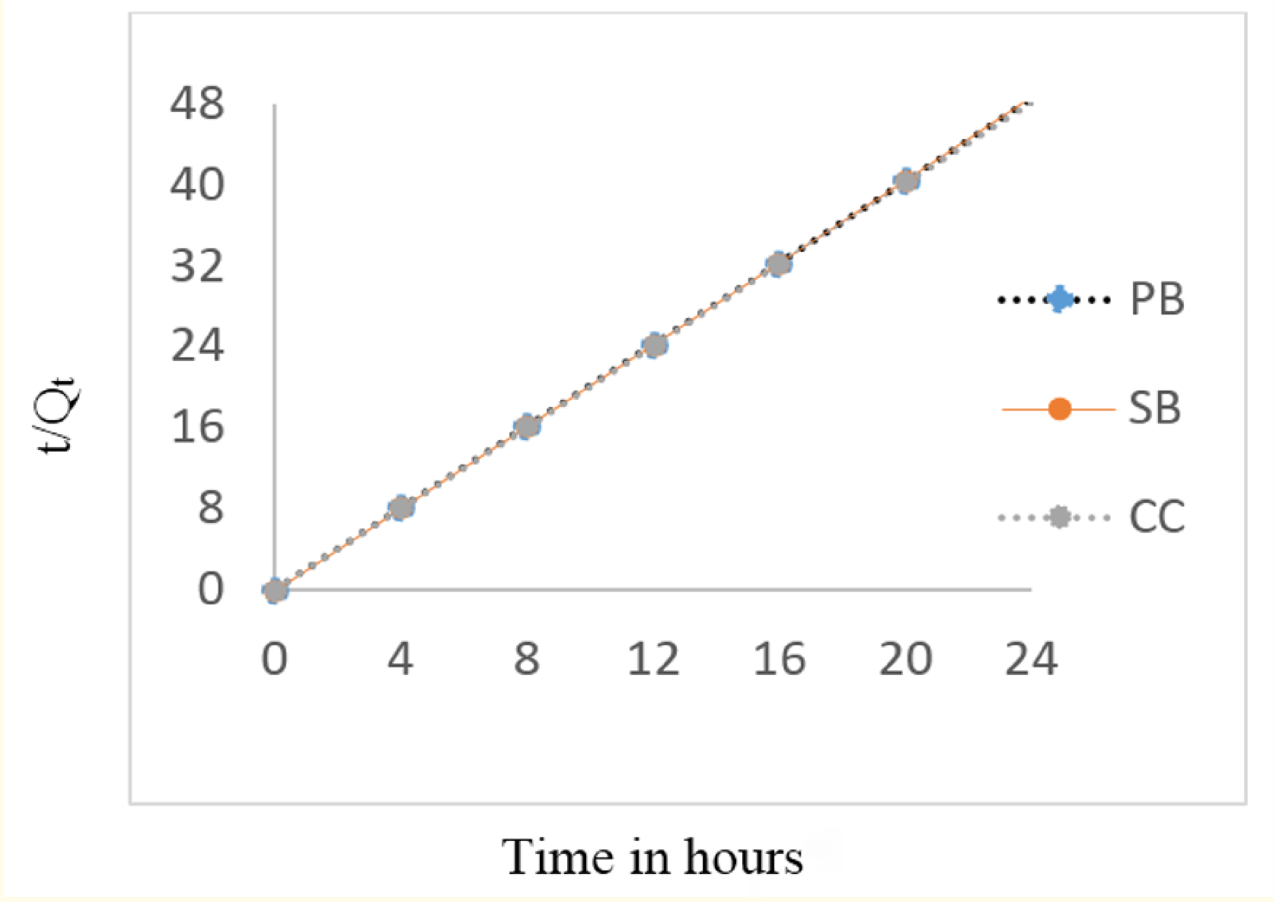

Figure 2: *Plots for the pseudo-second order kinetic model.*

Kinetic models used to monitor the rate of reaction

The Q_e (amount of NO_3^- sorbed) observed with time was subjected to both pseudo-first order and pseudo-second order equations. The graph generated were presented in figures 1 and 2 respectively.

The values determined from the pseudo-first order equation were different from those obtained experimentally in such a way that the Q_e obtained were far smaller with values: 4.65E-03 (PB), 6.03E-03 (SB), 8.38E-03 (CC) compared to the Q_e determined experimentally after 24 hours which were 0.4947 (PB), 0.4946 (SB) and 0.4979 (CC) respectively. K_1 obtained was 0.2315 h^{-1} (PB), 0.2407 h^{-1} (SB) and 0.3178 h^{-1} (CC) respectively. The regression coefficients obtained from the graph were 0.4471 (PB), 0.3359 (SB) and 0.5037 (CC) respectively.

However, values determined from pseudo-second order equation were in close uniformity with those obtained experimentally. Q_e obtained from the equation were 0.4951 mmol/g (PB), 0.4953 mmol/g (SB) and 0.4975 mmol/g (CC) respectively and the rates of adsorption (K_2) were 497.47, 221.52 and 396.108 mmol of NO_3^- per gram of poultry biochar, swine biochar and charcoal respectively per hour. The regression coefficients obtained from the graph was 1.000 for all biochars used. The data obtained agreed with pseudo-second order kinetic model because of the closeness of values obtained from the equation compared to experimental values and because the regression coefficient obtained was > 0.95 [10]. This shows a chemisorption mechanism confirming the presence of multiple adsorption sites on biochar [11-14].

Conclusion

The result of this experiment revealed the presence of multiple adsorption sites on various biochar materials used, thus confirming their potential as good adsorbents - hence reducing NO_3^- loss from the soil and enhancing N use efficiency of urea.

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