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Nitrogen adsorption on Biochar: a preliminary study

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Introduction

Worldwide experiences show that the use of biochar could be a bioenergy source, partially avoiding global warming and positioning itself as a tool for promoting agriculture in unproductive zones. Biochar can improve water retention and nutrients availability in soils. In addition, biochar may be used as soil amendment, enhancing some of the chemical properties and improving their fertility. Also, Biochar could be used as support of nitrogen and phosphorous in controlled release fertilizer.

In this work, a preliminary study of a nitrogen source (NH_4Cl) adsorption on biochar is presented, adsorption kinetics and equilibrium isotherms to understand the effect of biochar on NH_4Cl release processes were studied.

Biochar produced by pyrolysis of *Acacia dealbata* wood and a commercial activated carbon, as blank for comparison purposes, were used in the adsorption experiments. Biochar was characterized by their chemical and physical properties.

Total organic carbon (TOC) and inorganic carbon (CI) were determinated by COT-CVSP analyzer. Total nitrogen (TN) was determined by Kjeldahl digestion (Organic Nitrogen) and, NO_2 and NO_3 by KCl extraction of the sample and selective ion determination. The ash and moisture content were determinate by loss of weight at 550 and 105 ºC during 2 h, respectively.

Specific surface area (S_{BET}) and pore volume (V_p) were determined by 1000 NOVA porosimeter. Finally, the particle size distribution was measured by SALD-3101 particle analyzer.

Results and Discussions

Biochar characterization is show in Table 1.

Table 1. Chemical and physical characterization.

chemical						physical			
CO %	CI %	COT %	NT %	ash %	H_2O %	pH	S_{BET} m^2/g	V_p cm^3/g	PS* mm
87	0.1	87.1	0.2	2.6	5.4	8.4	14.4	0.01	<1

*Particle size

As it show in Table 1 biochar has a high content of total carbon (TC), however, this composition does not depend only on the starting wood, also depends of the pyrolysis conditions employed. Specific surface area and pore volume of biochar used in this experiment are very low compared with activated carbon, up to 380 m^2/g and 0.2 cm^3/g for specific surface area and pore volume respectively [1]. Usually, the adsorption capacity of materials is proportional to surface area and pore volume.

The particle size distribution showed the distribution of the cumulative particle size in the sample of biochar, which was in the range between 1 and 1900 µm. Despite the heterogeneity in the particle size, the largest fraction is between 400 and 800 µm.

Once the biochar was characterized, the NH_4Cl adsorption kinetic was carried out. NH_4^+ adsorption kinetics showed an equilibrium at 2 and 1.5 hours for biochar and activated carbon, respectively. Additionally, after 2 h of treatment a marked desorption was observed in both substrates.

Despite of, the higher specific superficial area and pore volume of activated carbon, there were no significant differences regarding to NH_4Cl adsorption biochar, especially at lower concentrations. However, when higher concentrations of NH_4Cl were used activated carbon presented a 13% more adsorption capacity than biochar. This scare difference suggests that the structure of the activated carbon is mainly microporous, therefore is more

difficult to the NH_4^+ molecules penetrate to the inside of the microporous structure.

Once the time to reach the equilibrium of the adsorption was determinated, adsorption isotherms of the NH_4Cl on biochar and activated carbon at various pH values were performed.

From these experiments the adsorption capacities for biochar and activated carbon are show in Table 2, indicating that biochar may act as a NH_4^+ adsorption material, eventually avoiding leaching processes and simultaneously promoting its slow release.

Table 2. Experimental adsorption capacities, q_i,(mg/g) of NH_4Cl on biochar and activated carbon, respectively.

q_i	biochar				activated carbon			
	pH				pH			
	4	6	6.7	8	4	6	6.7	8
q_1	0	0	0	0	0	0	0	0
q_2	16	-	-	-	9	22	13	-
q_3	73	167	192	108	70	153	204	140
q_4	39	300	384	292	170	307	411	260
q_5	357	445	543	362	152	504	610	364
q_6	574	667	541	463	322	412	651	415

As it can be observed in Table 2 the difference in adsorption capacity obtained for biochar and activated carbon is low, considering that biochar specific surface area and pore volume values are smaller than those of activated carbon. The effect of pH was significant for the adsorption process on both materials, showing the highest adsorption capacity at pH values around 6.

Experimental data were adjusted to Freundlich model for biochar and activated carbon (Table 3).

As it can be noted in Table 3 the experimental data were well adjusted to Freundlich model with correlation coefficient (R^2) values up to 99%. Therefore it can be concluded that for both types of materials present heterogeneous adsorption surfaces with sites with different energies.

Table 3. Langmuir and Freundlich parameters

sample	pH	Freundlich		
		k_f	*1/n*	R^2
Biochar	4	2.10	1.18	0.98
	6	6.99	0.97	0.98
	6.7	16.0	0.79	0.95
	8	4.12	1.04	0.96
activated carbon	4	1.47	1.15	0.97
	6	4.38	1.05	0.97
	6.7	12.8	0.87	0.97
	8	10.9	0.80	0.97

On the other hand, from the parameters calculated in Table 3, it can conclude for activated carbon the higher pH value increase adsorbent affinity (1/n). In the case of biochar a similar effect was observed stopping a pH 6.7. Regard this effect; it can suggest that higher pH values increase the Na^+ cations in the solution sample (due to the addition of NaOH to increase pH value), therefore, Na^+ cations would compete for adsorption sites in the adsorbent, nevertheless, other interaction it does not rule out.

Conclusions

Biochar of *Acacia dealbata* wood presented a lower pore size and specific surface area than activated carbon. Despite of, the high surface area of activated carbon, adsorption of NH_4Cl was not improved, most probably due to the small molecular size of this compound.

The Freundlich equation agrees well with adsorption isotherm of ammonia nitrogen onto biochar and activated carbon with different pHs under the entire concentration ranges studied.

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[1]Cheremisinoff, N.P., (1993), Carbon adsorption for pollution control. Prentice Hall (Eds.), Nueva Jersey, pp. 20-24.