International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064
Index Copernicus Value (2015): 78.96 | Impact Factor (2015): 6.391

Sustainable Use of Bioenergy Byproduct: Biochar for Nutrient Removal from Wastewater

A. K. Alva[1], H. Ren[2, 5], Q. Wang[2], T. Bera[3, 6], Y. Li[2], B.Gao[4]

[1]Kuwait Institute for Scientific Research, Environmental and Life Sciences Research Centre, Kuwait

[2]Department of Soil and Water Sciences, Tropical Research and Extension Center, IFAS, University of Florida, Homestead, FL

[3]Indian Agricultural Research Institute, New Delhi, India

[4]University of Florida, Agricultural and Biological Engineering Department, Gainesville, FL

[5]Current Address: Witgang Far East Ltd., Beijing, China

[6]Current Address: University of Florida, Horticultural Sciences Dept., Gainesville, FL

Abstract: ***Biochar, byproduct of pyrolysis for bioenergy production, is a good adsorbent of nutrients and pollutants from wastewater (WW). Efficiency of nutrient removal by biochar is dependent on the feedstock used. Removal of nitrogen (N) and phosphorus (P) from WW was evaluated using a commercial biochar, from Dynamotive company (DY), activated carbon (AC), or biochars produced from peanut hull (PH), bagasse (BG) or hickory wood (HW), at rates 2.5 to 100 g L^{-1} WW. Removal of NH4-N by DY and PH biochars increased significantly with an increase in biochar rate. In the case of BG and HW biochars, the highest removal of NH_4-N was at 25 g L^{-1} rate. Removal of NH_4-N by AC was extremely low, except at 100 g L^{-1} rate. The Ortho-P adsorption from WW increased with increasing rates of biochar, except for PH biochar. This study demonstrated that most of the biochars, except PH biochar, are more effective than AC in removal of NH_4-N and P from wastewater. The N and P enriched biochar can be used as soil amendment to agricultural soils to supply nutrients and enhance carbon sequestration.***

Keywords: biochar, feedstock, pyrolysis, nutrient recycling, wastewater

1. Introduction

Industrial, agricultural or municipal wastewaters (WW) contain high concentrations of nutrients, metals, and other pollutants. Removal of these pollutants from WW is mandatory before the water can be discharged to streams/rivers or pumped to recharge groundwater (USEPA, 2000).Excess loading of nutrients from WW is a significant concern of negative effects on quality of surface water bodies (Smith et al., 1999). The cleanup process of WW is often expensive, but is required to minimize the potential loading of the pollutants to surface or groundwater resources. One of the alternatives is to explore cost effective adsorbent material for removing WW pollutants to make the waste water treatment cost effective (USEPA, 2000).

Biochar, a by-product of bioenergy production through pyrolysis of carbon-rich biomass feedstocks, has been suggested as a potential agent to clean the WW by adsorption of heavy metals and other pollutants, e.g. lead (Cao et al., 2009; Liu & Zhang, 2009; Mohan et al., 2007), arsenic and cadmium (Mohan et al., 2007), naphthalene, 1-naphthol (Chen & Chen, 2009), atrazine (Cao et al., 2009), dye (Qiu et al., 2009), phosphorous (Mortula et al., 2007), copper and zinc (Wilson et al., 2003). The unique characteristics of biochar, i.e. small particle size, large surface area, and negative surface charge, make biochar a good adsorbent for positively charged ions (Liang et al., 2006; Lehmann, 2007). Biochar produced from different agricultural residues also contain calcium (Ca) and magnesium (Mg) carbonates (Yuan et al., 2011), which enable biochar to adsorb negatively charged ions including phosphate (Yao et al., 2011).

Variations in feedstock type and pyrolysis conditions may influence the resulting biochar's characteristics and hence its capacity to remove pollutants from WW (Cantrell et al., 2012; Novak et al., 2009; Singh et al., 2010). The objective of this study was to evaluate the adsorption of N and P from municipal WW by biochars produced from different feedstocks.

2. Materials and Methods

Wastewater and Biochar

Wastewater used in this study was sampled from a municipal wastewater treatment facility at the Tropical Research and Education Center (TREC), University of Florida (UF), Homestead, FL, and stored at 4o C prior to use. The WW was analyzed for the content of NH_4^+-N, NO_3^- -N, Ortho P, F^-, Cl^-, Br^- and SO_4^{2-}.

A commercially produced biochar (DY; DynamotiveEnergy Systems, Canada) and activated charcoal (AC; Fisher Scientific, Pittsburgh, PA) were compared with three additional biochars produced at the University of Florida, Gainesville, FL, by pyrolysis of Peanut Hull (PH), Bagasse (BG), and Hickory wood (HW) inside a furnace (Olympic 1823HE) in N2 environment at 600 ^oC for 6h, 300 ^oC for 24h, and 450 ^oC for 12h, respectively.One gram of each biochar or AC was extracted with distilled water in 1:40 ratio and concentrations of NH_4^+-N, NO_3^--N, Ortho P, F^-, Cl^-, Br^- and SO_4^{2-} were analyzed

Adsorption experiment

The adsorption experiment was conducted by using 40 mL wastewater in 60 mL polypropylene tubes. Biochar or AC was added at 0.1, 0.2, 0.4, 1.0, 2.0, or 4.0 g in 3 replications. These treatments resulted in 2.5, 5.0, 10.0, 25.0, 50.0, or 100.0 g L^{-1} rates. A treatment with no biochar was paralleledas a control. The suspensions were shaken at 100 rpm for 24h, filtered through Whatman No 42 (90 mm) filter paper for analysis of NH_4^+-N, NO_3^--N and Ortho-P using AQ2+ auto-analyzer (AQ-2 Discrete Automated Analyzer, Seal Analytical, Mequon, WI). An aliquot was re-filtered by nylon supported plain 0.45 µm filter film (25 mm) for analysis of concentrations of F^-, Cl^-, Br^-, and SO_4^{2-} using a ion chromatograph (DIONEX AS 40-LC 20-EG 50-CP 25,Dionex, Sunnyvale, CA).

Data Analysis

The concentration of adsorbed ion on the sorbentwas calculated by

$$q = [C_i - C_e] \times V / m \quad \text{(i)}$$

$$\text{Removal rate}\,(\%) = (C_i - C_e)/C_i \times 100 \quad \text{(ii)}$$

Where,

$q(mg/kg)$ = the adsorption capacity of biochar or AC.

$C_i(mg/l)$ and $C_e(mg/l)$ = initial and equilibrium (after 24h shaking) concentrations of N or P in wastewater, respectively.

$V(ml)$ = the volume of wastewater

$m(g)$ = the weight of biochar or AC in the tube (Variable per treatment)

Statistical significance of the treatments was evaluated by Analyses of Variance (ANOVA) test and mean separation between the treatments was analyzed by Duncan Multiple Range test.

3. Results

NH_4^+-N removal

The WW used in this study contained only NH_4^+ form of N (Table 1). The rate of adsorption of NH_4-N by the adsorbents peaked at 2.5 g absorbent L^{-1} of WW, except for HW biochar and AC, and subsequently the adsorption rate decreased with further increase in rate of adsorbent (Fig. 1). For the HW biochar, the rate of NH4-N adsorption peaked at adsorbent rate of 5.0 g L^{-1} WW, remained constant at 10 g L^{-1} rate, and then declined.

For AC, there was some NH_4-N release at the first 3 rates of AC addition. With further increase in AC rates, there was slight adsorption of NH_4-N far lower than that by the other biochar sources. At the highest rate of addition of adsorbent (100 g L^{-1} of WW), the percent removal of NH_4-N decreased in the order:

DY (80%) > PH (66%) > HW (59%) > BG (53%) > AC (36%) (Table 2).

The percent removal of NH_4-N from WW increased with increasing rate of adsorbent addition to WW only for DY, PH, and AC (Table 2). For HW and BG adsorbents, the percent removal of NH_4-N peaked at 25.0 g L^{-1} WW, and declined with further increase in rate of adsorbent. At the 25.0 g L^{-1} rate, the percent removal of NH4-N ranked in the order: HW (72%) > BG (63%) > DY (43%) > PH (29%) > AC (4%).

Ortho- P removal

Ortho-P content of WW was 1.94 mg L^{-1} (Table 1). The Ortho-P concentration of PH biochar 4.7 mg kg^{-1}. Therefore, this biochar was not effective in Ortho-P removal from WW (Table 3). In fact, the data showed Ortho-P released from this biochar into the solution at all rates of PH biochar addition to WW. For the rest of the adsorbents the percent Ortho-P removal increased with increased rate of adsorbent addition. For HW and BG adsorbents the percent P removal peaked at 96 and 98%, respectively, with addition of 10.0 g L^{-1} rate. The percent Ortho-P removal slightly decreased with further increase in rate of biochar addition from 25.0 to 50.0 g L^{-1}. For DY biochar the percent Ortho-P removal peaked (87%) at 50.0 g L^{-1} rate with slight reduction (79%) at 100.0 g L^{-1}. The percent Ortho-P removal increased with each increment in AC addition up to 100 g L^{-1}. The DY, HW, and BG biochars were more effective in Ortho-P removal from WW as compared to that by AC. For the latter, the percent Ortho-P removal was < 7 % with ≤ 10 g L^{-1}, and then increased from 22 to 60% with an increase in rate from 25 to 100 g L^{-1}. The most effective was BG, which removed 98% of Ortho-P from WW with 5 g L^{-1}. To remove 96% and 87% Ortho-P from WW, 100 and 50 g of HW and DY biochar were required, respectively.

The Ortho-P adsorption rate by the BG and HW biochar peaked at adsorbent rate of 2.5 g L^{-1} WW, and then declined with further increase in rate of adsorbent (Fig. 2). For the DY biochar, the rate of Ortho-P adsorption peaked at 10 g L^{-1} and then decreased. The rate of Ortho-P adsorption by AC was much lower than that of BG, HW and DY biochar at 2.5, 5, 10, and 25 gL^{-1} rates. This difference gradually decreased at 50 and 100 gL-1 rates.

4. Discussion

With increase in rate of addition of adsorbent the rate of NH_4-N adsorption per unit weight of adsorbent decreased for most adsorbents. However, the percent removal of NH_4-N from WW increased. This can be attributed to non-proportional increase in active adsorption sites with an increase in total weight of adsorbent or overlapping of active adsorption sites with an increase in weight of adsorbent in fixed volume of WW (Garg et al., 2007). Increase in total number of active adsorption sites accompanied by an increase in surface area appears to be the main factor contributing to an increase in percent NH_4-N removal with an increase of adsorbent weight (Hussain et al., 2006). For BG, the volume of biochar might also be a potential factor influencing the adsorption due to its "sponge characteristics". Excess rate of BG and HW may have caused insufficient contact with WW in the equilibration tube. This, in turn, contributed to decreased percent removal of NH4-N at > 25 g L^{-1} rates.

Among all the adsorbents used, BG biochar was most efficient for removing Ortho-P from WW by adsorption. Due

to the high Ortho-P content of the PH biochar (4.74 mg kg^{-1}), it was not a suitable adsorbent for removal of Ortho-P from WW. Instead, application of this biochar at all rates increased the Ortho-P content in the equilibration solution due to desorption of P from this biochar.

References

[1] Cantrell, K. B., Hunt, P. G., Uchimiya, M., Novak, J. M., Ro, K. S. 2012. Impact of pyrolysis temperature and manure source on physicochemical characteristics of biochar. Bioresource Technology 107:419–428.
[2] Cao, X., L. Ma, B. Gao, W. Harris, 2009. Dairy-manure derived biochar effectively sorbs lead and atrazine. Environmental Science and Technology 43:3285-3291.
[3] Chen, B., Z. Chen, 2009. Sorption of naphthalene and 1-naphthol by biochars of orange peels with different pyrolytic temperatures. Chemosphere 76:127–133.
[4] Garg, U.K., Kaur, M.P., Garg, V.K., Sud, D., 2007 Removal of hexavalent chromium from aqueous solution by agricultural waste biomass. Hazardous Material 140:60-68.
[5] Hussain, S., Aziz, H.A., Isa, M.H., Adlan, M. N., Asaari, F.A.H., 2006. Physico-chemical method for ammonia removal from synthetic wastewater using limestone and GAC in batch and column studies. Bioresource Technology 98:874-880.
[6] Lehmann, J., 2007. Bio-energy in the black. Frontiers in Ecology and the Environment 5:381–387.
[7] Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman,J., O'Neill, B., Skjemstad, J.O., Thies, J., Luizao, F.J., Petersen, J., Neves, E.G. 2006. Black carbon increases cation exchange capacity in soils. Soil Science Societyof America Journal 70:1719–1730.
[8] Liu, Z., and Zhang, F., 2009. Removal of lead from water using biochars prepared from hydrothermal liquefaction of biomass. Journal of Hazardous Material 167:933–939.
[9] Mohan, D., Pittman, C.U. Jr., Bricka, M., Smith, F., Yancey, B., Mohammad, J., Steele, P.H., Alexandre-Franco, M.F., Gómez-Serrano, V., Gong. H., 2007. Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production. Journal of Colloid and Interface Science 310:57–73.
[10] Mortula, M., Gibbons, M., Gagnon, G., 2007. Phosphorus adsorption by naturally-occurring material and industrial by products. Journal of Environmental Engineering and Science 6:157-164.
[11] Novak, J.M., Lima, I., Baoshan, X., Gaskin, J.W., Steiner, C., Das, K.C., Watts, D.W., Busscher, W.J., Schomberg, H., 2009. Characterization of designer biochar produced at different temperatures and their effects on a loamy sand. Annals of Environmental Science 3:195–206.
[12] Qiu, Y., Zheng, Z., Zhou, Z., Sheng, G.D., 2009. Effectiveness and mechanisms of dye adsorption on a straw-based biochar. Bioresource Technology 100:5348–5351.
[13] Singh, B., Singh, B.P., Cowie, A.L. 2010. Characterization and evaluation of biochars for their application as soil amendment. Australian Journal of Soil Research 48:516–525.
[14] Smith, V.H., Tilman, G.D., Nekola, J.C., 1999. Eutrophication: impacts of excess nutrient inputs on freshwater, marine, and terrestrial ecosystems. Environmental Pollution 100:179-196.
[15] USEPA "Environmental Assessment for the Final Effluent Limitations Guidelines, Pretreatment Standards for New and Existing Sources and New Source Performance Standards for the Centralized Waste Treatment," Prepared by Charles Tamulonis (2000).
[16] Wilson, J.A., Pulford, I.D., Thomas, S., 2003. Sorption of Cu and Zn by bone charcoal. Environmental Geochemistry and Health 25:51–56.
[17] Yao, Y., Gao, B., Inyang, M., Zimmerman, A.R., Cao, X.D., Pullammanappallil, P., Yang, L.Y., 2011. Removal of phosphate from aqueous solution by biochar derived from anaerobically digested sugar beet tailings. Journal of Hazardous Material 190:501–507.
[18] Yuan, J. H., Xu, R. K., Zhang, H. 2011.The forms of alkalis in the biochar produced from crop residues at different temperatures. Bioresource Technology 102:3488–3497.

Table 1: Properties of different biochars, activated carbon, and wastewater

	Biochar source / Feedstock				Activated Carbon	Wastewater
	Dynamotive	Hickory Wood	Peanut Hull	Bagasse		
Pyrolysis temperature (°C)	400-450	450	600	300	-	-
	← mg kg^{-1} →					
NH_4_N	0.28±0.04	0.26±0.03	0.18±0.02	0.39±0.03	1.02±0.54	24.40±0.96
NO_3_N	0.04±0.002	0.02±0.02	0.01±0.00	0.06±0.02	0.06±0.05	0.00±0.00
Ortho-P	0.22±0.05	0.12±0.02	4.74±0.13	0.08±0.01	0.04±0.05	1.94±0.07
F^-	1.22±0.43	41.95±0.33	0.09±0.02	BD	0.54±0.30	0.40±0.13
Cl^-	1.56±0.28	22.71±2.62	13.15±0.42	3.61±0.42	16.54±0.95	147.21±3.15
Br^-	50.83±0.75	BD	BD	BD	BD	27.15±0.58
SO_4^{2-}	3.79±1.10	10.90±0.08	44.19±0.64	25.04±0.35	0.20±0.07	2.56±0.96

BD = below detection limit

Table 2: Percent removal of NH4-N from wastewater with addition of different rates of adsorbents

Rate of adsorbent (g L^{-1})	Dynamotive (DY)	Hickory wood (HW)	Peanuthull (PH)	Bagasse (BG)	Activatedcarbon (AC)
2.5	10.4 ± 1.6 e	7.1 ± 1.2 e	3.9 ± 0.8 e	12.5 ± 2.0 f	-3.3 ± 0.4 d
5.0	12.8 ± 0.8 e	16.8 ± 1.8 d	4.9 ± 1.0 e	23.1 ± 0.7 e	-4.7 ± 0.6 d
10.0	22.0 ± 1.9 d	33.6 ± 1.0 c	14.5 ± 2.8 d	44.4 ± 1.6 d	-4.8 ± 0.8 d
25.0	42.9 ± 1.7 c	72.0 ± 0.8 a	28.9 ± 1.5 c	63.1 ± 0.9 a	3.9 ± 2.8 c
50.0	64.0 ± 1.5 b	58.0 ± 1.5 b	44.9 ± 3.2 b	49.8 ± 0.8 c	11.6 ± 1.7 b
100.0	80.4 ± 0.1 a	58.5 ± 1.6 b	65.7 ± 3.7 a	53.8 ± 1.2 b	35.6 ± 1.3 a

Values after ± symbol are the standard error for the respective treatment calculated from 3 replicates.
Means followed by different letters in each column are significantly different according to Duncan's new multiple range test at P≤0.05

Table 3: Percent removal of Ortho-P from wastewater with addition of different rates of adsorbents

Rate of adsorbent (g L^{-1})	Dynamotive (DY)	Hickory wood (HW)	Peanut hull (PH)	Bagasse (BG)	Activated carbon (AC)
2.5	7.5 ± 0.7 e	46.2 ± 2.4 c	-18.5 ± 0.3	78.1 ± 1.7 d	-0.6 ± 0.4 e
5.0	19.4 ± 3.6 d	71.9 ±0.3 b	-31.3 ± 0.8	98.1 ± 0.3 a	1.1 ± 0.6 e
10.0	45.9 ± 2.1 c	95.6 ± 0.3 a	-47.5 ± 3.4	98.1 ± 0.9 a	6.8 ± 1.0 d
25.0	79.0 ± 2.0 b	89.1 ± 2.3 a	-42.8 ± 2.9	95.1 ± 0.3 b	22.0 ± 1.1 c
50.0	87.3 ± 0.5 a	93.6 ± 4.5 a	-42.8 ± 8.4	94.6 ± 0.2 b	41.9 ± 1.4 b
100.0	78.7 ± 0.4 b	91.9 ± 0.7 a	-96.4 ± 4.8	86.0 ± 1.0 c	60.3 ± 0.4 a

Values after ± symbol are the standard error for the respective treatment calculated from 3 replicates
Means followed by different letters in each column are significantly different according to Duncan's new multiple range test at P≤0.05

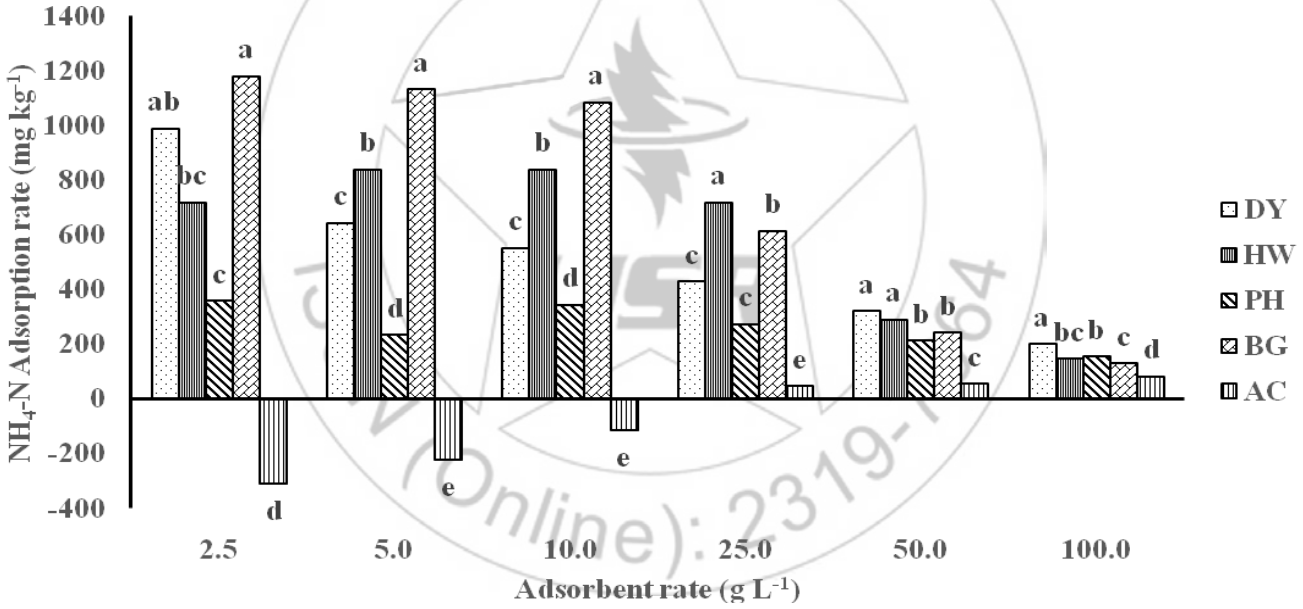

Figure 1: $NH4_{+}$-N adsorption rates with application of different amounts of adsorbents to waste water.

Commercial biochars: DY = Dynamotive; HW = Hickory wood; PH = Peanut hull; BG = Bagasse
AC = Activated carbon. Means followed by different letters in each adsorbent rate are significantly different according to Duncan's new multiple range test at P≤0.05.

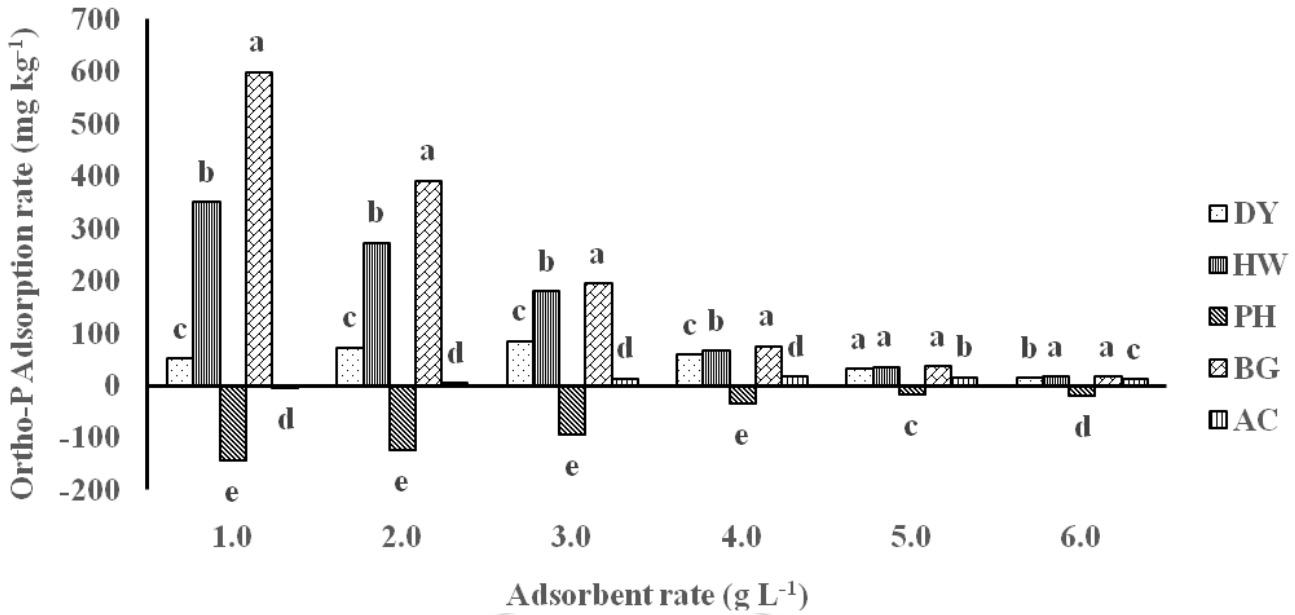

Figure 2: Ortho-P adsorption rates with application of different amounts of adsorbents to waste water

Commercial biochars: DY = Dynamotive; HW = Hickory wood; PH = Peanut hull; BG = BagasseAC = Activated carbon. Means followed by different letters in each adsorbent rate are significantly different according to Duncan's new multiple range test at P≤0.05.