USE OF BIOCHAR GENERATED FROM SPENT COFFEE GROUNDS FOR THE REMOVAL OF Zn(II) FROM AQUEOUS SOLUTIONS

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ABSTRACT

The main focus of this study is to evaluate five types of biochar as adsorbents for Zn(II) removal from aqueous solutions. Five different biochar samples (CB300, CB400, CB500, CB600 and CB700) were prepared through pyrolysis of spent coffee grounds (SCG) at 300, 400, 500, 600 and 700 °C, respectively.

Materials characterization was carried out with respect to pH, elemental composition, higher calorific value and point of zero charge (pHpzc). Adsorption studies included assays to determine the effect of initial pH, agitation period, adsorbent dose and initial metal concentration on Zn(II) removal. Adsorption kinetics and isotherms were also studied, through these experiments.

The optimum conditions for Zn(II) removal using SCG-derived biochars resulted: an initial pH=5, an agitation period of 4 h and an adsorbent dose of 25 g/L. The materials produced at 600 and 700 °C were provided the best results regarding Zn(II) adsorption, having no significant differences from each other.

Fitting the experimental data to mathematical models showed that the pseudo-second order model best described the adsorption kinetics, suggesting chemisorption as that the limiting step. Furthermore, for what concerns adsorption equilibrium each biochar was best fitted by different isotherms. Specifically, the linear isotherm best fitted the data for CB300 and CB600, the Freundlich isotherm described best the data for CB700, while the Langmuir model was better for CB400 and CB500.

Keywords: biochar, adsorption, pyrolysis, coffee, metals

1. Introduction

Metals are known to potentially have negative effects on the environment and on human health. That is the case when these substances are found in elevated concentrations. For this reason, environmental contamination by metals constitutes a major issue of concern and research (Houben *et al*., 2013; Salam *et al*., 2012; Sheela *et al*., 2012).

Zinc, when present in the environment in trace amounts acts as a micronutrient, while if its concentrations exceed the permissible limits that may lead to serious health and ecological problems (Bhattacharya *et al*., 2006). The maximum acceptable zinc concentration recommended by the World Health Organization (WHO) for drinking water is 5.0 mg/L (Li *et al*., 2010).

Adsorption is an effective method for metal removal from water and wastewater (Bhattacharya *et al*., 2006; Sheela *et al*., 2012). In the last years the use of biochar as an adsorbent has been gaining interest. Biochar production is relatively inexpensive considering not only the process used (pyrolysis) but also the fact that it can be derived from everyday household waste (Houben *et al*., 2013). Biochar's composition is highly heterogeneous, containing both stable and labile components (Bruun, 2011), while its large surface area and high cation exchange capacity make it suitable for sorption of organic and inorganic contaminants. The specific characteristics

of this product are determined both by the feedstock material and the production temperature (Beesley *et al*., 2011).

In this study five different types of biochar were used as potential adsorbents to remove Zn(II) from aqueous solutions. The materials were produced by means of pyrolysis at five different temperatures, namely 300, 400, 500, 600 and 700 °C, using spent coffee grounds as the source material. In order to determine the optimum conditions for Zn(II) removal, batch adsorption experiments were carried out.

2. Materials and methods

2.1. Raw material and biochar preparation

The Spent Coffee Grounds (SCG) sample used in this study was a mixture of materials originating from university and local cafeterias, and coffee capsules from households. The composite SCG sample was initially dried at 105°C for 24 h and subsequently subjected to pyrolysis under oxygen-limited conditions for biochar production. In brief, porcelain crucibles were initially filled to capacity with SCG, then covered with a fitting lid and finally introduced in a muffle furnace. The five target temperatures (300, 400, 500, 600 and 700 °C) for biochar production were achieved within 1 h, while pyrolysis lasted for 2 h. The resulting materials were then washed with deionized water (DW) for excess ash removal, separated by vacuum filtration, once again rinsed with DW and finally dried and gently ground in an agate mortar.
SCG and the five biochar samples (CB300, CB400, CB500, CB600 and CB700) were characterized regarding pH (solid/liquid ratio of 1/10 g/mL in DW and KCl 1N), point of zero charge (pH_{PZC}) (pH 'drift' method), Higher Calorific Value (HCV) and C, H and N contents.

2.2. Batch adsorption experiments

Batch adsorption experiments were carried out, through which the effect of pH (2–10), agitation period (15–1440 min), adsorbent dose (2.5–100 g/L) and initial zinc concentration (0.1–5 mM) on the adsorption process was investigated. Zn(II) concentration in the aqueous phase was determined using Atomic Absorption Spectrometry (AAS).

3. Data analysis

The following equations were used for data analysis:

$$q_e=((C_0-C_e)\cdot V)/m \quad (1)$$

$$\log(q_{e,exp}-q_t)=\log(q_{e,calc}) - (k_1/2.303)\cdot t \quad (2)$$

$$t/q_t=1/(k_2\cdot q_e^2) + t/q_e \quad (3)$$

$$q_t=k_{id}\cdot t^{1/2} + C \quad (4)$$

$$q_e=K_d.C_e \quad (5)$$

$$C_e/q_e=1/(b\cdot Q) + C_e/Q \quad (6)$$

$$\log(q_e)=\log(K)+(1/n)\cdot\log(C_e) \quad (7)$$

where t is time, q_e and q_t are the adsorption rates (mmol/g), at equilibrium and at time t respectively, C_0 and C_e are Zn(II) concentrations (mM), initially and at equilibrium, respectively, V is the solution volume (L) and m is the mass of adsorbent used (g), k_1, k_2 and k_{id} are the rate constants for the pseudo-first order, the pseudo-second order and the intraparticle diffusion kinetic models, respectively, C is an intraparticle diffusion constant and $q_{e,exp}$ and $q_{e,calc}$ are the adsorption rates, at equilibrium, obtained experimentally and from the fitting to the pseudo-first order model, respectively, K_d is the linear adsorption coefficient (L/g), Q is the maximum metal uptake (mmol/g), b is a Langmuir parameter (L/mmol) and K (L/g) and n are Freundlich constants related to the adsorption capacity of adsorbent and adsorption intensity, respectively. Equations 2, 3 and 4 refer to the pseudo-first order, pseudo-second order and intraparticle diffusion kinetic models, respectively (Sheela *et al*., 2012; Tang *et al*., 2009), while Equations 5,

6, and 7 refer to the linear, the Langmuir and the Freundlich isotherm models, respectively (Nasir et sl., 2007; Pellera *et al*., 2012; Tang *et al*., 2009).

4. Results and discussion

4.1. Characterization

As it is shown in Table 1, biochar yield decreases with increasing pyrolysis temperatures. Morever, biochars produced at higher temperatures are characterized by higher pH values, while it is made obvious that the pyrolysis process caused the pH to shift from acidic to alkaline, with the exception of CB300. The same general trend is also observed for the pH_{PZC} values. This behavior can be explained by the fact that when biomass is pyrolyzed at temperatures above 300 °C, the carbon present in it, is converted into ash, while separation of alkali salts from the organic structure takes also place (Meng *et al*., 2013; Cao and Harris, 2010). The conversion of SCG to biochar generally leads to higher HCVs, with higher temperatures resulting in lower values. Elemental analysis indicates that increasing pyrolysis temperature leads to increased carbon contents, and decreased hydrogen contents. Nitrogen contents are comparable and do not follow a specific trend.

Table 1: Physicochemical characteristics of SCG and biochars

Properties	Samples					
	SCG	CB300	CB400	CB500	CB600	CB700
Biochar yield (%)	-	43.6	28.1	23.3	21.5	20.0
			pH			
Deionized Water	4.52	7.22	8.65	9.55	9.58	9.95
KCl	4.13	5.84	7.22	8.70	9.13	9.44
pH_{PZC}	4.75	7.00	7.50	8.40	8.25	8.60
HCV (cal/g)	5047	7079	7087	6846	6922	6679
			Elemental Analysis (%)			
C	50.94	74.61	75.87	78.71	82.60	83.38
N	2.16	3.54	4.11	3.14	2.26	3.13
H	7.56	5.96	4.03	2.72	1.87	1.12

4.2. Batch adsorption experiments

As seen in Figure 1a with increasing pH values, increased Zn(II) adsorption rate is observed. This can be explained by the competition between metal cations and H+ for binding sites on the adsorbents (Kolodynska *et al*., 2012). A plateau is observed between pH 5 and 7, while above this value an increase and a slight decrease are noticed to follow. Since in the pH range 1–7 almost 100% of zinc is present in the Zn(II) form (Kolodynska *et al*., 2012), pH 5 was considered as the optimum value for subsequent experiments.

Figure 1b presents the effect of agitation period on adsorption rate. The adsorption process appears to follow two steps for almost every material. In the first one, between 15 and 240 min, there is a more intense increase of Zn(II) adsorption, while in the second it seems to approach a steady state. This probably is due to the progressive saturation of active sites on the biochars' surface, with time (Pellera *et al*., 2012). An agitation period of 4 h (240 min) was considered acceptable for carrying out the remaining assays, since after that time an almost steady behavior was observed.

Figure 1c shows a decreasing trend of the adsorption rate with higher adsorbent dose. This is most probably attributed to the greater availability of binding sites on the biochars' surface, as well as to the progressive saturation of these binding sites (Bhattacharya *et al*., 2006; Pellera *et al*., 2012). The optimum adsorbent dose of 25 g/L was selected in all subsequent experiments, since above this dose there are no significant changes in the obtained values.

According to the results shown in Figure 1d, increasing Zn(II) concentration from 0.1 to 5 mM at a constant pH of 5, caused an increase in the adsorption rate. This phenomenon is related to the increase in the metal-ion/adsorbent ratio in the solution as the metal concentration increases. More specifically, at higher metal concentrations saturation of the higher energy sites

takes place and adsorption begins on lower energy sites. This results in decreased adsorption efficiency (Bhattacharya *et al*., 2006).

4.3. Adsorption modeling

The results derived from modelling of the adsorption process indicated that the pseudo-second order model best described the Zn(II) adsorption kinetics for all tested materials (Table 2). The description of the adsorption kinetics by the pseudo-second order model, indicates that the limiting stage of the adsorption mechanism is chemical adsorption (Tang *et al*., 2009; Ding *et al*., 2006; Gupta *et al*., 2010; Salam *et al*.; 2012).

The obtained equilibrium parameters presented in Table 4 show that the linear isotherm best described the adsorption equilibrium for CB300 and CB600, with high correlation coefficients values (R^2). On the other hand, the Freundlich isotherm best fitted the experimental data for CB700 and the Langmuir isotherm gave the best fit for CB400 and CB500.

Table 2: Adsorption kinetics parameters

Samples	$q_{e,exp}$ (mmol/g)	Pseudo-first order model			Pseudo-second order model				Intraparticle diffusion model		
		k_1 (min^{-1})	$q_{e,cal}$ (mmol/g)	R^2	k_2 (g/mmol·min)	q_e (mmol/g)	$h=k_2 \cdot q_e^2$ (mmol/min·g)	R^2	k_{id} (mmol/g·$min^{1/2}$)	C	R^2
CB300	0.0242	0.0030	0.0009	0.2025	11.058	0.0242	0.006	0.9998	0.00005	0.0230	0.5310
CB400	0.0300	0.0009	0.0042	0.1082	3.885	0.0259	0.003	0.9988	0.00004	0.0258	0.0519
CB500	0.0416	0.0002	0.0130	0.1514	0.354	0.0417	0.001	0.9749	0.00040	0.0253	0.7323
CB600	0.0343	0.0007	0.0089	0.4291	0.640	0.0345	0.001	0.9926	0.00030	0.0235	0.7819
CB700	0.0468	0.0014	0.0197	0.4452	0.300	0.0474	0.001	0.9818	0.00060	0.0234	0.7821

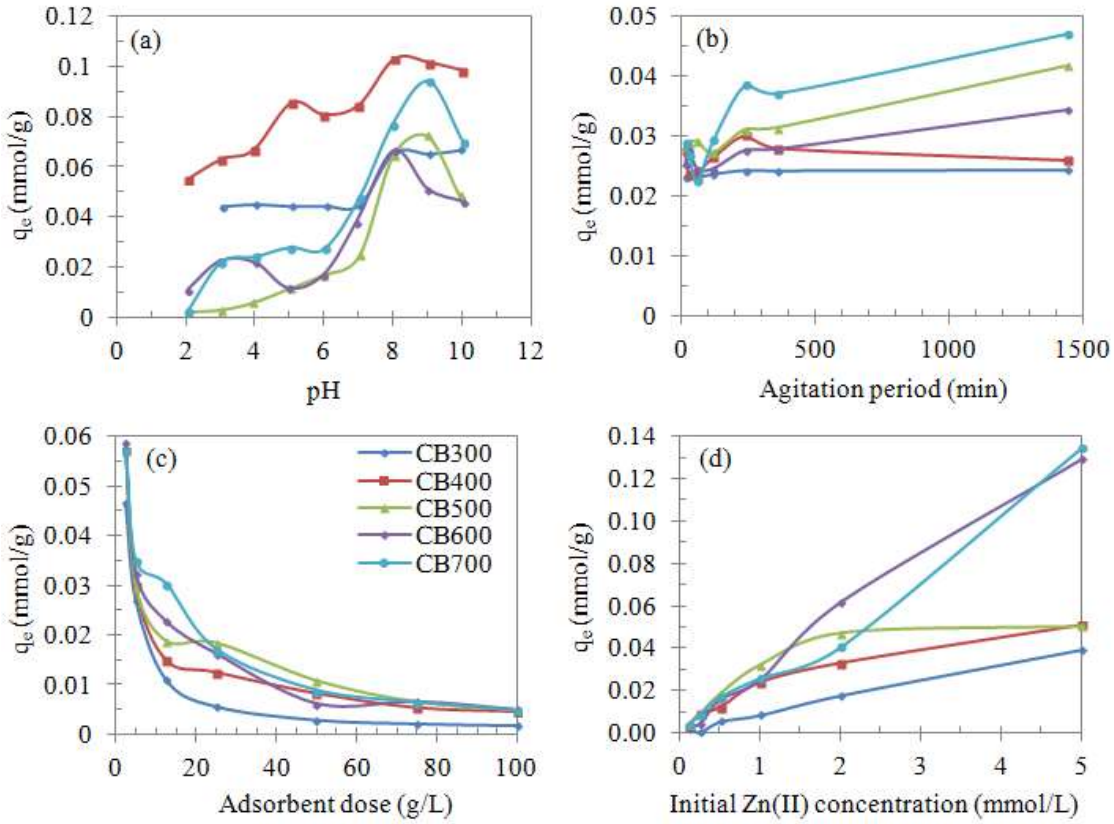

Figure 1: Effect of (a) initial pH, (b) agitation period, (c) adsorbent dose and (d) initial Zn(II) concentration on Zn(II) adsorption rate

Table 3: Adsorption equlibrium parameters

Samples	Liner isotherm		Freundlich isotherm				Langmuir isotherm		
	K_d (L/g)	R^2	K (L/g)	n	1/n	R^2	Q (mmol/g)	b (L/mmol)	R^2
CB300	0.0096	0.9881	0.0096	1.0284	0.9724	0.7053	-0.041	-0.127	0.0456
CB400	0.0115	0.8608	0.031	2.2447	0.4455	0.9698	0.056	0.641	0.9699
CB500	0.01	0.5568	0.0403	2.8106	0.3558	0.9311	0.052	0.977	0.9961
CB600	0.0716	0.9374	0.0601	1.6348	0.6117	0.7573	0.526	0.053	0.0195
CB700	0.069	0.8860	0.0626	1.8005	0.5554	0.9267	0.117	0.272	0.4344

5. Conclusions

From the results obtained in this study, it was concluded that the biochars' properties are significantly affected by their production temperature. Optimal Zn(II) adsorption, for all five biochars was achieved after 4 h of agitation with an adsorbent dose of 25 g/L and at pH = 5. Higher sorption was obtained using the biochars produced at 600 and 700 °C. The pseudo-second order model described best the adsorption kinetics overall, while for equilibrium modeling a different isotherm was associated with each biochar.

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