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Effect of biochar artificial ageing on Cd and Cu sorption characteristics

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ABSTRACT

The present investigation was carried out to optimize the artificial ageing process of biochar by the hydrogen peroxide method. For the optimization of three oxidation parameters (concentration of oxidizing agent, reaction time, temperature) the Box–Behnken Design under Response Surface Methodology was effectively applied. As a response, the sorption capacity of aged biochar for Cd and Cu was studied. The results demonstrate the crucial effect of hydrogen peroxide concentration on sorption capacity for both studied metals. For Cd sorption capacity a positive effect was detected whereas the sorption efficiency of aged biochar for Cu decreased with increasing concentration of the oxidizing agent. The effects of reaction time and temperature had lower statistical significances. Differences in sorption mechanism of Cd and Cu by biochar-based sorbent were detected. ANOVA analysis as well as 3D surface plots revealed that maximum sorption capacity of aged biochar-based sorbents for Cd was obtained at $C_{H_2O_2} = 14.9997\%$, $t = 5.99998$ h, $T = 20.0$ °C and for Cu at $C_{H_2O_2} = 5.05\%$, $t = 2.00$ h, $T = 59.5$ °C. The results confirm that RSM represents an excellent tool for predicting optimal parameters of chemical engineering processes like the hydrogen peroxide oxidation of biochar to optimize its sorbent behaviour. The application of BBD under RSM could reduce the number of required experiments from 39 to 17.

1. Introduction

Biochar as a pyrolysis product and porous material contains a wide range of reactive functional groups on sorption surfaces (Kumar et al., 2011). These characteristics suggest that biochar is a promising low-cost sorbent for removing toxic metals and other xenobiotics from liquid wastes or contaminated water solutions (Kolodynska et al., 2012). In a previous paper (Frišťák et al., 2015a) the potential of the sorption capacity for heavy metal removal was highlighted. Our results have confirmed the usability of biochar in metal sorption separation from aqueous solutions which recommends a more widespread application as environmental technology tool. Utilization of biochar as a soil amendment in heavy metal contaminated areas and mine sites represents a new step in remediation strategy. However the affinity of heavy metal (Cd, Zn, Pb, Cu) to incorporated biochar-amendment is affected by several parameters and depends on wide range of environmental factors. Biochar can be characterized by various important physic-chemical properties, such as high ion exchange capacity, water holding capacity, surface area, low bulk density, rich porosity and sorption capacity which play decisive roles in a wide range of biochar remediation applications (Lehmann and Joseph, 2009). Although all these biochar properties are stable in the short-term after production, they still may undergo long-term changes depending on the environmental conditions (Guo et al., 2014). Additionally, sorption capacity of biochar-derived sorbents depends on input material characteristics and process parameters during carbonization. The factor time is an additional modifier of abiotic and biotic processes on biochar surfaces therefore ageing affects the main characteristics and the strength of element sorption. Biological, chemical and physical ageing represent the core of artificial and natural ageing processes (Hale et al., 2011). Guo et al. (2014) highlighted that biochar ageing occurs mainly on the surface of pyrolysis products. Physic-chemical ageing or weathering can be simulated by chemical treatment of biochar with specific ligands and can lead to changes in the density of sorption sites. Additionally, the reactivity of biochar produced by thermal pyrolysis may be assessed by its resistance to various oxidizing and hydrolyzing agents (Calvelo-Pereira et al., 2011; Cross and Sohi, 2013; Nocentini et al., 2010). Naisse et al., 2013 showed the application of acid dichromate as a powerful oxidant for the determination of black carbon, while acid hydrolysis proved to be similarly effective for determining recalcitrant organic C. Proposed chemical modifications can affect the physic-chemical properties and sorption capacity of biochar (Xue et al., 2012). Main biochar properties can be altered in the process of simulated ageing by chemical modification with oxidizing agents such as ammonium persulfate, nitric acid or hydrogen peroxide. This ageing simulation can alter the structural properties of biochar and also create new acidic oxides (carboxylic, phenolic, lactonic) and alkaline groups (pyrone-like groups) on the sorbent surfaces (El-Sheikh, 2008). Utilization of hydrogen peroxide as a tool for oxidative depolymerisation can lead to a new biochar product with higher sorption activity at its surfaces and consequently to an increased sorption potential. The process of heavy metal sorption separation by

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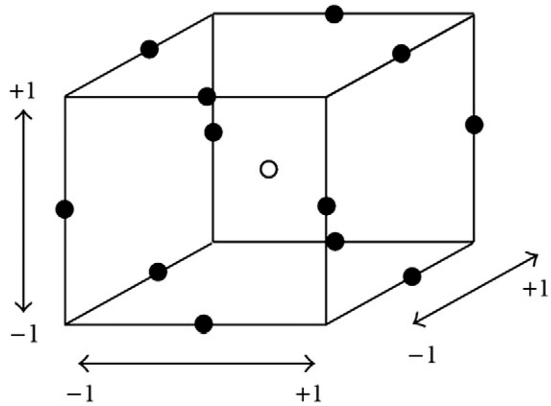

Fig. 1. Geometry of Box–Behnken design for optimization of three parameter process.

biochar is controlled mainly by interactions between metal ions in the reaction solution and oxygen-containing functional groups on the sorbent surfaces (Liu and Zhang, 2009). Consequently oxidation processes of biochar can increase the concentration of reactive surface functional groups, such as carboxyl and hydroxyl groups, for heavy metal sorption. Mainly surface chemistry, oxygen content and textural properties of biochar play a role in modified separation efficiency for sorbing certain metal species.

Usually the optimization of chemical processes is being carried out by monitoring the effect of one factor at a time on the experimental response (Bezerra et al., 2008). This one-variable-at-a-time method has several disadvantages such as the omission of interactive effects among the variables studied and increment in number of experiments. Based on these scenarios, multivariate statistical techniques for process optimization should be applied. One of the most effective methods is response surface methodology (RSM) as a collection of mathematical and statistical techniques useful for analysing the effects of several independent variables on the response (Box and Draper, 1987). RSM has important applications in process design and optimization of existing designs (Frišták et al., 2012). This methodology is more practical, compared to theoretical models as it arises from experimental methodology which includes interactive effects of the variables and, eventually, it depicts the overall effects of the parameters on the process (Bas and Boyaci, 2007). RSM as an optimization tool has recently found applications in a wide range of chemical processes such as: extraction processes (Frišták et al., 2015a; Li et al., 2015; Saikia et al., 2015; Zhang et al., 2015), biofuel production (Betiku and Taiwo, 2015), processes of agent microencapsulation (Ko et al., 2015), bioconversion (Mangayil et al., 2015), enzyme production (Singh et al., 2014), pyrolysis (Kumar and Singh, 2014), oxidation (Saldaña-Robles et al., 2014) and xenobiotic sorption removal (Frišták et al., 2012; Remenárová et al., 2012; Trakal et al., 2014). Additionally, Garba and Rahim (2014) effectively applied RSM for optimization of preparation conditions for modified activated carbon production. As was mentioned above, RSM as a statistical approach can provide a valuable information for evaluation of studied parameters of physical, chemical and biological processes.

This paper is aimed at investigating the potential of hydrogen peroxide as oxidizing agent for biochar artificial ageing with optimization of process parameters (agent concentration, reaction time and temperature) by Box–Behnken Design (BBD) and using the Response Surface Methodology (RSM). As an experimental response the sorption capacities of aged biochar for Cd and Cu as models of heavy metals with different physico-chemical properties were studied. The results of this research work shall support the development of a new method as a combination of in situ and in silico analysis for prediction of biochar sorption properties under ageing process and of innovative biochar sorbent materials for heavy metals with optimized sorption characteristics.

Table 1
Experimental range and levels of independent variables for simulation of artificial ageing using Box–Behnken design.

Independent variables	Symbols	Unit	Coded levels		
			−1	0	+1
$C_{H_2O_2}$	A	%	5	10	15
t	B	h	2	4	6
T	C	°C	20	40	60

2. Materials and methods

2.1. Biochar production and characterization

Biochar samples were produced in a slow pyrolyses process from garden green waste residues. Biomass had been pyrolyzed at a highest treatment temperature of 500 °C and residence time 120 min in a rotary furnace. For ensuring inert and uniform heating conditions, nitrogen was used as flush gas. The obtained biochar was ground and sieved to particles with size 0.5–2 mm. The sorbent was pretreated by rinsing with deionised water (conductivity $<0.4\ \mu S\ cm^{-1}$) to remove the ash impurities. Basic physical and chemical parameters were determined in the following way. The value of pH was determined in suspension after shaking sample with deionised water and 0.01 KCl solution (ratio 1:10) for 2 h by pH metre (inoLab pH level 2P, Weilheim, Germany). The electrical conductivity (EC) of biochar was measured in water suspension (ratio 1:10) after 24 h of shaking (inoLab pH level 2P, Weilheim, Germany). The total carbon (C), hydrogen (H) and nitrogen (N) concentrations were determined by an elemental analyser (CHNS-O EA 1108, Carlo Erba Instruments, Italy). The total cadmium (Cd) and copper (Cu) concentrations in biochar were measured after aqua regia digestion protocol by ICP-MS (Perkin Elmer, Elan DRCe 9000). The readily soluble Cd and Cu concentrations in biochar were determined after extraction with deionised water (24 h, ratio 1:30) by GFAAS, AA 400, Perkin Elmer, USA.

2.2. Simulation and optimization of artificial ageing

For better understanding of the sorbent ageing effect the method of biochar pre-treatment with H_2O_2 according to Hale et al. (2011) was applied. The conditions of the chemical ageing process and the effects of these parameters on the sorption capacity of biochar-based sorbents for Cd and Cu were optimized by application of Response Surface

Table 2
Box–Behnken design matrix, the experimental and predicted values of specific sorption capacity Q_{eq} of aged biochar for Cd and Cu. A. concentration of oxidizing agent (%); B. reaction time (h); C. temperature (°C).

Run	Coded levels			Y_1 (Q_{eq} Cd)		Y_2 (Q_{eq} Cu)	
	A	B	C	Q_{eq}(exp.) ($\mu g\ g^{-1}$)	Q_{eq}(prEd.) ($\mu g\ g^{-1}$)	Q_{eq}(exp.) ($\mu g\ g^{-1}$)	Q_{eq}(pred) ($\mu g\ g^{-1}$)
1	1	−1	0	4258	4241	2262	2284
2	−1	0	1	4009	4000	2480	2510
3	0	−1	−1	4062	4070	2222	2230
4	0	0	0	4082	4082	2228	2228
5	0	0	0	4082	4082	2228	2228
6	0	0	0	4082	4082	2228	2228
7	0	1	1	4070	4062	2213	2205
8	−1	−1	0	4008	4021	2495	2475
9	0	0	0	4082	4082	2228	2228
10	−1	1	0	4014	4031	2392	2370
11	1	0	1	4308	4328	2171	2160
12	0	1	−1	4118	4121	2240	2250
13	0	0	0	4082	4082	2228	2228
14	0	−1	1	4014	4010	2340	2329
15	1	0	−1	4357	4366	2250	2220
16	1	1	0	4363	4351	2256	2276
17	−1	0	−1	4056	4036	2310	2321