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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 (Frišták 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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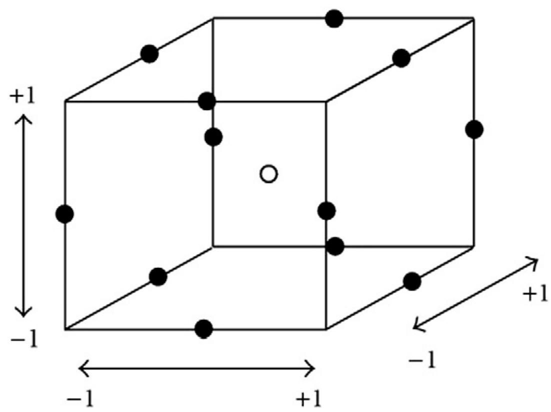

Fig. 1. Geometry of Box–Behnken design for optimization of three parameter process.

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 μS 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.) (μg g^{-1})	Q_{eq}(prEd.) (μg g^{-1})	Q_{eq}(exp.) (μg g^{-1})	Q_{eq}(pred) (μg 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

Table 3
Analysis of variance (ANOVA) of RSM regression analysis.

Source	Q_{eq} Cd SS	DF	F-value	p-Value Prob > F	Q_{eq} Cu SS	DF	F-value	p-Value Prob > F
Model	26013.49	9	89.71	<0.0001	15502.26	9	26.10	<0.0001
Lack of fit	2029.75	3	–	–	4157.75	3	–	–
Pure error	0.00	4	–	–	0.000	4	–	–
Total (cor total)	$2.361 \cdot 10^5$	16	–	–	$1.437 \cdot 10^5$	16	–	–

Methodology (RSM). Concretely, the model of Box–Behnken Design (BBD) (Fig. 1) was used to identify the relationship between the response variable (equilibrium sorption capacity of artificially aged biochar for cadmium and copper) and the experimental variable (concentration of oxidation agent, reaction time and temperature).

The statistical software tools Statgraphics Centurion XV (StatPoint Inc., USA) and Design expert 6.0 (Stat-Ease, USA) were used for the experimental design, data analysis, quadratic model building, graph plotting (three-dimensional response surface and contour plots) and for estimating the responses of oxidation agent concentration, reaction time and temperature. The range of experimental variables, their units and notation are indicated in Table 1. A total of 17 runs were used for optimization of the process parameters. Each experiment was performed in triplicate.

The response variable Q_{eq} (equilibrium sorption capacity of artificial aged biochar for cadmium and copper) can be expressed as a function of the independent experimental variables according to the following RSM second-order polynomial model (Eq. (1)):

$$Q_{eq} = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ij} {x_i}^2 + \sum_{i \le i \le j}^{k} \beta_{ij} x_i x_j + \varepsilon \quad (1)$$

where Q_{eq} is the predicted response (equilibrium sorption capacity of artificial aged biochar for cadmium and copper); β_i, β_{ii}, and β_{ij} present linear, quadratic and interaction effects; β_0 is the constant coefficient; x_i, x_j, …x_k are the input variables ($C_{H_2O_2}$; t; T) which affect the Q_{eq} value; ε represents the error.

In the optimization procedure we studied the response of the statistically designed combinations, estimated the coefficients by fitting the experimental data to the response functions and predicted the response of the fitted model. The adequacy of the model and statistical significance of the regression coefficients were checked using the analysis of variance (ANOVA).

2.3. Design of sorption processes

The sorption process of Cd and Cu from a single component system was studied using a batch equilibration method according to our previous paper (Frišták et al., 2015a). 1 g of chemically aged biochar-based sorbent and unaged biochar as a control were suspended in polypropylene centrifuge tubes filled with 20 ml of 0.01 $mol \cdot L^{-1}$ of $CaCl_2$ (pH = 5.65) and placed on a horizontal shaker for 24 h (200 rpm). The solution of $CaCl_2$ was used to facilitate phase separation and to keep ionic strength similar to natural soil solutions. Deionised water (<0.4 μS cm^{-1}), spiked with Cd or Cu in the form of $CdCl_2$ and $CuCl_2$, was added to each tube, resulting in concentrations of 60 $mg \cdot L^{-1}$ and pH = 7.0 ± 0.1. The solution pH was adjusted for each experiment using 0.01 $mol \cdot L^{-1}$ of HCl or 0.01 $mol \cdot L^{-1}$ NaOH. The biochar-solution ratio was 1:30. After agitation for 24 h, tubes were centrifuged (38,400 *g*, 15 min) and the supernatant was filtered through a 0.45 μm pore size membrane filter (Schleicher and Schuell, Germany) to remove colloids from the solution. Filters were tested for retention of metals before use. Concentration of Cd and Cu in liquid phase was measured by atomic absorption spectrometry with flame atomization (FAAS, AA 400, Perkin Elmer, USA). Sorptions of cadmium and copper were calculated according to Eq. (2):

$$Q_{eq} = (C_0 - C_{eq}) \times V/m \quad (2)$$

where: Q_{eq} is the cadmium or copper uptake ($mg \cdot g^{-1}$), C_0 is the initial liquid-phase concentrations of cadmium or copper (mg L^{-1}), C_{eq} is the equilibrium liquid-phase concentrations of cadmium or copper (mg L^{-1}), V is the volume (L) and m is the amount of aged biochar (g).

3. Results and discussion

3.1. Unaged biochar-based sorbent characterization

Biochar-based sorbent produced from garden green waste residues showed representative contents of C (80.0%), N (0.7%) and H (1.6%). Comparable values were reported previously (Frišták et al., 2015a). The important role surface areas of carbon-based sorbents in sorption processes was described by Rajec et al. (2015). Value of SA was determined as 32.25 m^2 g^{-1}. The determination of pH showed alkaline character of biochar-based sorbent (9.05). Measurement of electroconductivity of biochar water extract revealed EC = 1.70 mS cm^{-1}. Comparable values of pH and EC were found by Kloss et al. (2012). Total Cd concentration determined by aqua regia digestion and spectral analyses was lower than 2 $\mu g \cdot g^{-1}$ and total Cu concentration was 21 $\mu g \cdot g^{-1}$. Readily soluble forms of Cd and Cu were not detected.

Table 4
Analysis of variance (ANOVA) for polynomial expressions of response surface quadratic model (RSM) focusing on Cd sorption capacity of aged biochar. Level of significance α = 0.05.

Source	Sum of squares	DF	F-value	p-Value Prob > F
A	1.794	1	618.70	<0.0001
B	6216.13	1	21.44	0.0024
C	4656.13	1	16.06	0.0051
AB	2500	1	8.62	0.0218
AC	1.00	1	$3.449 \cdot 10^{-3}$	0.9548
BC	0.25	1	$8.622 \cdot 10^{-4}$	0.9774
A^2	40334.8	1	139.10	<0.0001
B^2	1500.07	1	5.17	0.0571
C^2	29.01	1	0.10	0.7610

Table 5
Analysis of variance (ANOVA) for polynomial expressions of response surface quadratic model (RSM) focusing on Cu sorption capacity of aged biochar. Level of significance α = 0.05.

Source	Sum of squares	DF	F-value	p-Value Prob > F
A	67712.00	1	114.00	<0.0001
B	5886.12	1	9.91	0.0162
C	4186.13	1	7.05	0.0327
AB	2352.25	1	3.96	0.0869
AC	15500.25	1	26.10	0.0014
BC	5184.00	1	8.73	0.0213
A^2	31322.37	1	52.73	0.0002
B^2	5764.21	1	9.70	0.0170
C^2	556.84	1	0.94	0.3652

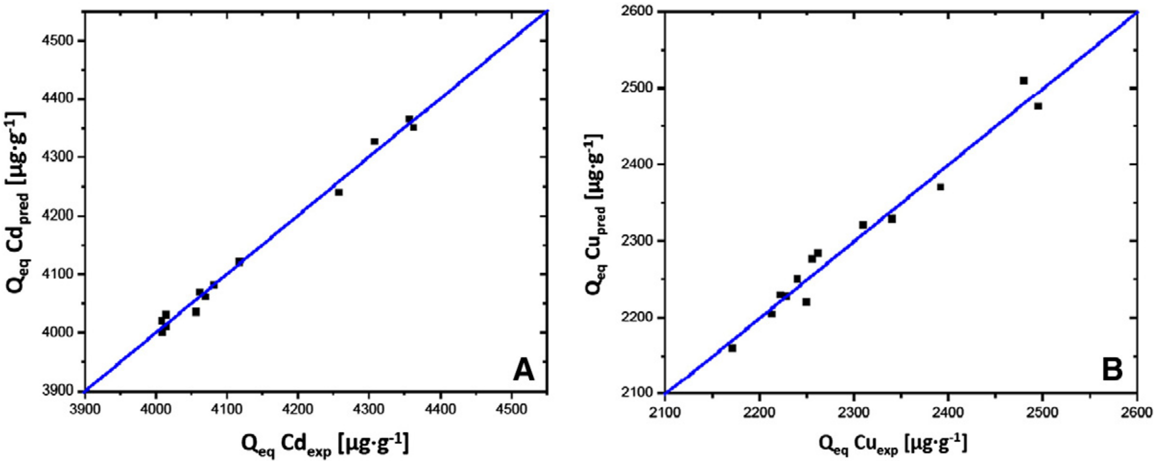

Fig. 2. Comparison of measured and predicted values of aged biochar sorption capacity for Cd (A) and Cu (B).

3.2. Optimization of ageing process

The determination of the empirical model expression as a simulation of the system response to the variation of the input variables is the main step in the RSM-based optimization (Cretescu et al., 2015). In this paper, the Box–Behnken experimental design (BBD) has been applied for developing the polynomial regression relation between the metal sorption capacity of aged biochar and the artificial ageing factors. For the optimization of selected conditions of biochar oxidation process three parameters were studied (concentration of oxidation agent, reaction time and temperature).

Our previous studies (Frišták et al., 2012, 2015b) have revealed the effectiveness of BBD under RSM for optimizing environmental processes. Central points of model were selected on the basis of other studies (Xue et al., 2012) that have focused on the application of hydrogen peroxide as a tool for screening the long-term stability of biochar. The work of Cross and Sohi (2013) confirmed this lab-scale method for providing an analogue of the oxidative degradation (ageing) of biochar incorporated into soil matrix. The sorption capacities of aged biochar for Cd and Cu obtained from the experiments designed by BBD are summarized in Table 2. Based on the obtained results by using multiple regression analysis, a second order polynomial model was gained (Eqs. (2) and (3)) which characterizes the relation between equilibrium sorption capacity of aged biochar for Cd and Cu and studied variables.

$$Q_{eq}\ Cd = +4082.00 + 149.75 \times A + 27.88 \times B - 24.13 \times C + 25.00 \times A \times B - 0.50 \times A \times C + 0.25 \times B \times C + 97.87 \times A^2 - 19.88 \times B^2 + 2.63 \times C^2 \quad (2)$$

$$Q_{eq}\ Cu = +2228.00 - 92.00 \times A - 27.12 \times B + 22.88 \times C + 24.25 \times A \times B - 62.25 \times A \times C - 36.00 \times B \times C + 86.25 \times A^2 + 37.00 \times B^2 - 11.50 \times C^2 \quad (3)$$

where A, B and C represent the coded values for concentration of oxidizing agent, reaction time and temperature.

Analysis of variance (ANOVA) as a statistical technique subdividing the total variation in a set of data into components associated with specific sources of variation to the test hypotheses on the parameters of the model, was used for evaluation of the model equation significance and the accuracy of fit (Tables 3–5). Statistical significance (adequacy) of BBD quadratic model was tested by Fisher's *F*-test and assessed by monitoring of obtained *F*- and *p*-values. According to Myers and Montgomery (1995), a high *F*-value indicates that most of the variation

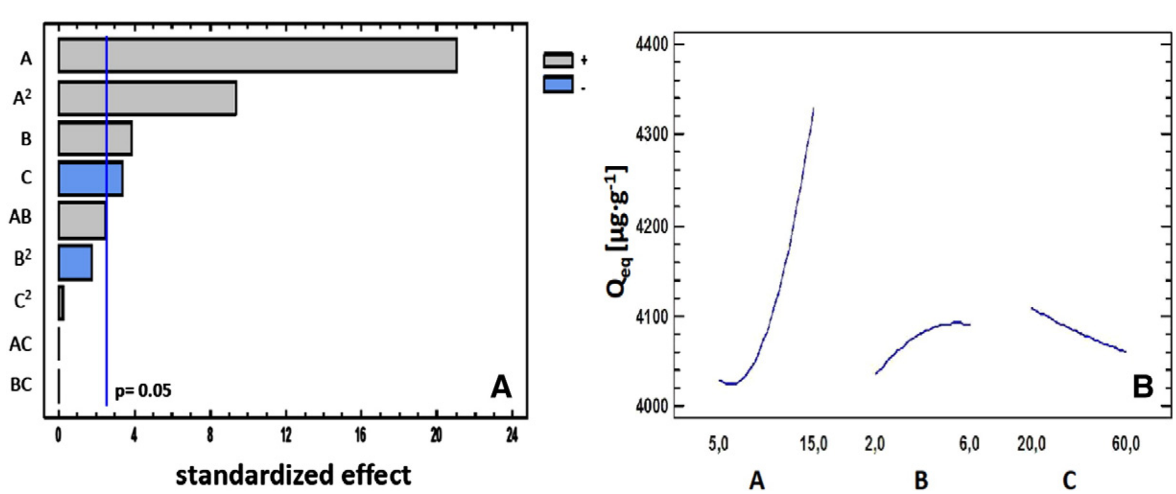

Fig. 3. Standardized Pareto chart (α = 0.05) showing the effects of the analysed factors and their combined impact on aged biochar sorption capacity for Cd (A) and interaction plot of parameters A: concentration of oxidizing agent (5–15%), B: reaction time (2–6 h), C: temperature (20–60 °C) for Cd sorption process (B).

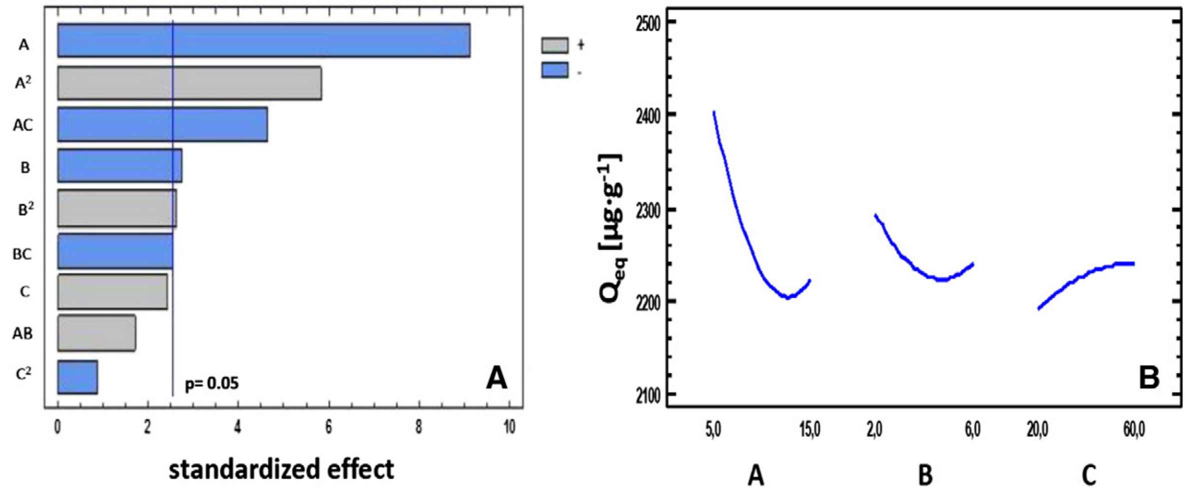

Fig. 4. Standardized Pareto chart (α = 0.05) showing the effects of the analysed factors and their combined impact on aged biochar sorption capacity for Cu (A) and interaction plot of parameters A: concentration of oxidizing agent (5–15%), B: reaction time (2–6 h), C: temperature (20–60 °C) for Cu sorption process (B).

can be explained by a regression equation whereas a low *p*-value (<0.05) indicates that the model is considered to be statistically significant. The coefficients of determination (COD) indicate that the generated model can explain more than 99% variation in the response for Cd sorption capacity of aged biochar (COD = 0.991) and 97% for Cu sorption capacity of aged biochar (COD = 0.972). Values of COD close to 1 indicate a high correlation of experimental and predicted data (Garg et al., 2008). The model *F*-value 26.10 and value of $p < 0.0001$ also indicate the statistical significance of the applied quadratic model. On the basis of these results, the relationship between the independent variables (concentration of oxidation agent, reaction time and temperature) and the response (equilibrium sorption capacity of artificial aged biochar for cadmium and copper) can be explained according to the regression model.

Good correlation and agreement between predicted and experimentally obtained data are shown in Fig. 2A for equilibrium sorption capacity of artificially aged biochar for cadmium and in Fig. 2B for copper. From the evaluation of the ANOVA outputs for both responses (Tables 4–5) the significance of each coefficient based on *p*-values was determined. The obtained results for equilibrium sorption capacity of artificially aged biochar for cadmium as a response demonstrate the statistical significance of linear coefficients: A ($F = 618.70$, $p < 0.0001$), B ($F = 21.40$, $p = 0.0024$) and C ($F = 16.06$, $p = 0.0051$); quadratic coefficient A^2 ($F = 139.10$, $p < 0.0001$) and interaction coefficient AB ($F = 8.62$, $p = 0.0218$).

Other quadratic forms as B^2, C^2 and interaction forms AC and BC did not reach statistical significance at the 5% level (Table 4). Figs. 3 and 4 illustrate the main effect of studied parameters A, B and C on the response of aged biochar sorption capacity for Cd and Cu respectively. The Pareto chart shows the standardized effects of the independent variables and their interactions on the dependent variable (sorption capacity of aged biochar for Cd and Cu). The effect of each parameter as well as the level of its effect on sorption capacity of aged biochar for Cd and Cu is expressed by the length of its bar in the Pareto chart (Remenárová et al., 2014). Fig. 3 illustrates a significantly positive effect of linear factor A (concentration of oxidizing agent), its quadratic form A^2 and linear factor B (reaction time) on sorption capacity of aged biochar for Cd. On the other hand, the negative effect of linear factor C (temperature) reached statistical significance at $\alpha = 0.05$. Other quadratic and interaction parameters had statistically insignificant effects on the studied response.

A different behaviour of Cu sorption is shown in Fig. 4. The linear factor A (concentration of oxidizing agent), linear factor B (reaction time) and the interaction factor AC (concentration of oxidizing agent × temperature) exerted a significantly negative effect on the sorption capacity of aged biochar for Cu. The positive effects of quadratic factors A^2 and B^2 were statistically significant at a level of $\alpha = 0.05$. Other linear, quadratic and interaction parameters had no statistically significant effects on the studied response.

For simplification of interaction interpretation three-dimensional plots were used (Figs. 5–6). These charts provide useful information about the behaviour of the reaction system within the experimental design frame and facilitate an assessment of the effects of the experimental parameters on the responses (Ahmad and Hameed, 2010). Fig. 5 illustrates the strong and significant effect of the oxidizing agent concentration as dominant factor for artificial ageing effects on biochar metal sorption capacity. In the case of subsequent sorption of Cd by aged biochar, we observed an increase of Q_{eq} values with increasing concentration of H_2O_2.

The effects of the contact time of biochar with the oxidizing agent and the temperature of the reaction system were of minor importance. With increasing reaction temperature in the range 20–60 °C the decrease of Q_{eq} values was shown (Fig. 5A). In our previous study (Frišták et al., 2015a) it was concluded that biochar-based sorbents bind the free Cd ions from aqueous solution mainly through exchange active sites of surface structures. Fraction analyses showed that most sorbed Cd represents the easily soluble fraction that is removable by weak acids. The effect of H_2O_2 as a chemical agent affecting sorption capacity of pyrolysis materials for heavy metals was described by Xue et al. (2012). The oxidation process by hydrogen peroxide could be established as a screening method for the determination of biochar C stability (Cross and Sohi, 2013). The effect of this oxidation agent can be explained by the creation of new oxygen-based functional groups and altering in porosity of material. Gan and Wu (2008) showed similar modifications during the oxidation process of biosorbents.

On the other hand, the sorption process of Cu by aged biochar-based sorbent was inverse to Cd uptake. From Fig. 6A it is clear that increasing concentrations of hydrogen peroxide caused decreasing sorption of Cu by the aged biochar-based sorbent. We recorded a slightly negative effect of contact time on sorption efficiency of aged biochar in the range from 2–6 h (Fig. 6B) and a positive effect of reaction temperature on Q_{eq} for Cu. In our previous work we have reported that Cu ions are mainly bound by the organic matter fraction and sulphides present in this type of biochar-based sorbent. The process of biochar oxidation apparently removes residual organic matter at the surfaces of the pyrolyzed material. The results of this study confirmed the effect of hydrogen peroxide to reduce the abundance of biochar binding sites for Cu, resulting in a decrease of sorption capacity for this metal. Naisse et al. (2013)

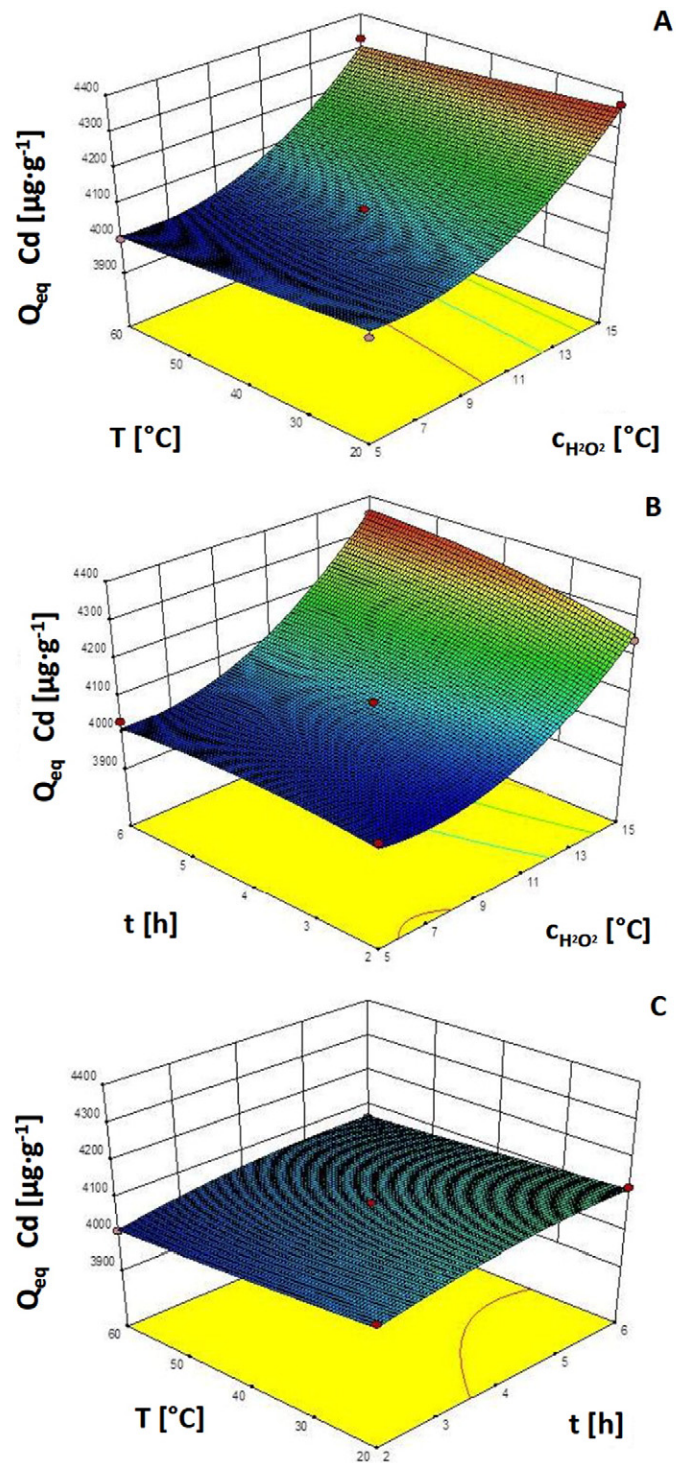

Fig. 5. Three-dimensional surface plots of the combined effect of the temperature (°C) and concentration of H_2O_2 (%) at contact time 4 h (A), contact time (h) and concentration of H_2O_2 (%) at temperature 40 °C (B), temperature (°C) and contact time (h) at concentration of H_2O_2 10% (C) on sorption capacity value of aged biochar for Cd (c_0 60 mg·L^{-1} $CdCl_2$, 24 h, 22 °C).

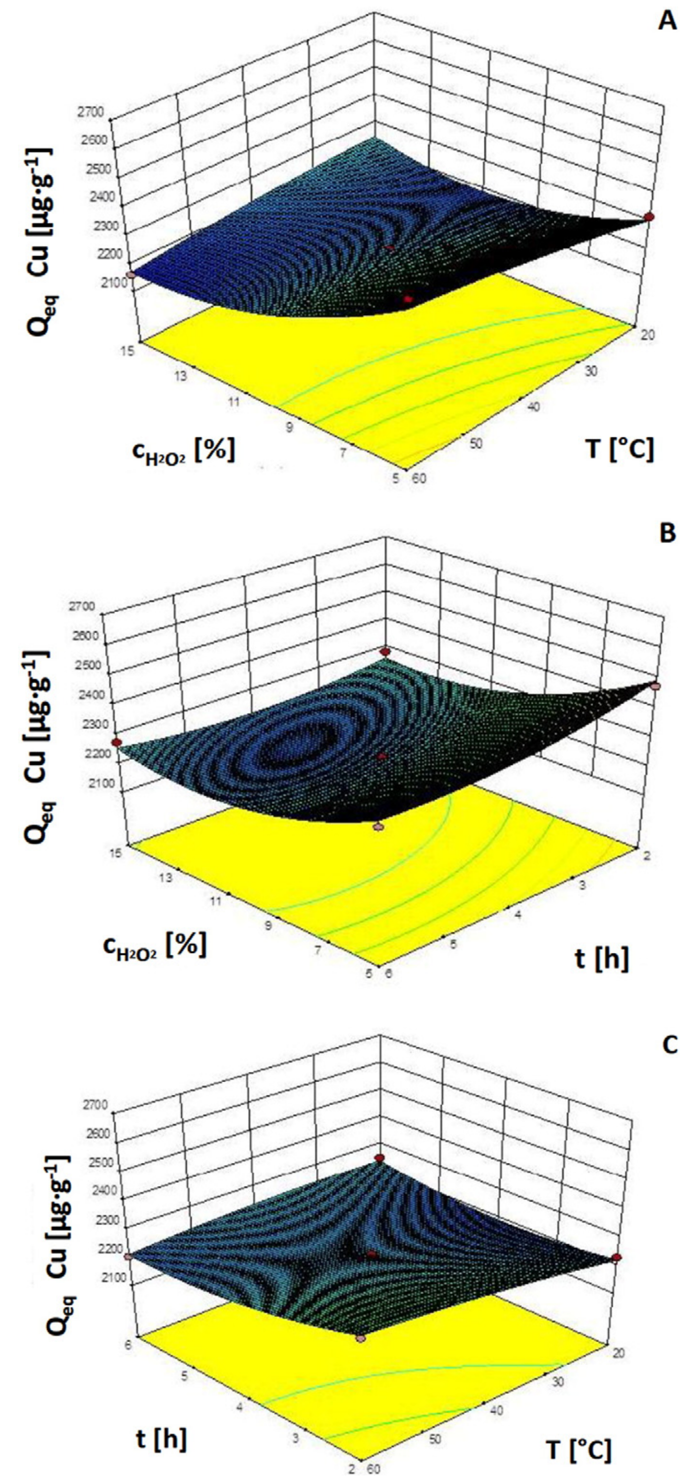

Fig. 6. Three-dimensional surface plots of the combined effect of the temperature (°C) and concentration of H_2O_2 (%) at contact time 4 h (A), contact time (h) and concentration of H_2O_2 (%) at temperature 40 °C (B), temperature (°C) and contact time (h) at concentration of H_2O_2 10% (C) on sorption capacity value of aged biochar for Cu (c_0 60 mg·L^{-1} $CuCl_2$, 24 h, 22 °C).

described in detail the most significant impacts of various reaction parameters for biochar ageing modelling. Based on process optimization by BBD under RSM we determine the optimal conditions of individual oxidation parameters (concentration of oxidizing agent, reaction time, temperature) at which the output variables (Q_{eq} Cd and Q_{eq} Cu) had maximum values (Table 6).

4. Conclusions

The effect of ageing process to carbon-based sorption material — biochar can be studied by different methods. Artificial ageing of biochar via oxidation by H_2O_2 represents a potential tool for understanding the changes in sorption behaviour of this pyrolysis product. The ageing

Table 6
Optimized values of studied parameters (concentration of oxidizing agent, reaction time, temperature) for maximum of aged biochar Q_{eq} values for Cd and Cu.

Parameter	Cd sorption process	Cu sorption process
$C_{H_2O_2}$ (%)	14.9997	5.05
t (h)	5.99998	2.00
T (°C)	20.0	59.5

process was simulated and optimized using Response Surface Methodology (RSM) based on Box–Behnken Design (BBD). The results confirm a good agreement between predicted and experimental values of Q_{eq} for Cd and Cu. The analysis of variance (ANOVA) suggests the peroxide agent concentration as the most significant variable influencing the ageing process in the case of both metals. For Cd biochar-sorption response a positive and Cu biochar-sorption response negative effect was detected. The values of R^2 and p of studied model confirmed the accuracy of analyses. The RSM method appears as a promising method to optimize a wide range of simulated biological processes such as artificial ageing of biochar-based sorbent.

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