COMPARISON OF PB^{2+} ADSORPTION AND DESORPTION BY SEVERAL CHEMICALLY MODIFIED BIOCHARS DERIVED FROM STEAM EXPLODED OIL-RAPE STRAW

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Abstract. To deal with lead (Pb^{2+}) contamination, four engineered biochar materials: NaOH modification of biochar (BC_{Na}), $KMnO_4$ impregnation of biochar (BC_{Mn}), hydroxyapatite modified biochar (BC_{HA}), and chitosan modification of biochar (BC_C), were compared for their adsorption and desorption capabilities. Steam exploded oil-rape straw was selected as the biomass material. Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) examination of biochars revealed that the modified adsorbents surface was covered by the respective modifying mineral. Adsorption and desorption studies were executed to examine the properties of adsorbents and the focal adsorption/desorption mechanism. The findings revealed that Mn oxides and hydroxyapetite nano-particles were conceded well within the biochar structure and formed inner sphere complexes perhaps with oxygen bearing functional groups. The extra adsorption sites formed by the impregnated respective minerals play the crucial roles in Pb^{2+} adsorption in an aqueous solution. Pb^{2+} adsorption isotherm experiments by BC_{Mn} was well determined by the Langmuir model with the highest adsorption capacity of BC_{Mn} being 70.92 mg g^{-1} followed by the BC_{HA} (49.26 mg g^{-1}). While, the adsorption kinetics of Pb^{2+} by all adsorbents were well determined by pseudo-second-order kinetics with the highest adsorption capacity of BC_{Mn} being 22.61 g (mg h)$^{-1}$. $KMnO_4$ and hydroxyapatite modified biochars exhibited very promising physicochemical and adsorptive properties for adsorbing divalent metal Pb^{2+} and might thus have high potential as a soil amendment and an alternative adsorbent for environmental remediation.
Keywords: *biochar, modification, heavy metals, kinetics, isotherms*

Introduction

Lead (Pb^{2+}) is considered as one of the most deleterious environmental pollutants because of its persistence and non-degradability nature in the terrestrial ecosystem (Wang et al., 2015a). Pb^{2+} contamination of soil and water is reputed all over the world as one of the key substantial problem in our ecosystem (Arshadi, 2015). Heavy metals including Pb^{2+} in aquatic system has also been revealed in Russia (Snakin and Prisyazhnaya, 2000), the USA (Triantafyllidou et al., 2014), India (CPCB, 2008), France (Ayrault et al., 2012), China (Li et al., 2012), Argentina (Kohn et al., 2001), Korea (Lee et al., 2005) and numerous other countries. A huge amount of Pb-contained waste-water is inescapably discharged from mining-related industries annually in China, as it is one of the key producer and consumer of Pb^{2+} in the world (Zhang et al., 2012). Pb^{2+} also can be espoused and concerted in organisms (Mohan et al., 2014a) and proposes deleterious effects on living organisms (Lu et al., 2012). Furthermore, Pb toxicity has serious implication on human health including damage of

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the reproductive and central nervous system, hypertensive toxicity which ultimately leads towards fatality (Zhang et al., 2019).

Numerous conservative and modern practices have been passed on for Pb^{2+} removal, for instance; ion exchange, electrocoagulation, membrane filtration, precipitation and adsorption (Malamis et al., 2010). Adsorption has been identified to be an influential, meek and efficient methodology for Pb^{2+} removal (Inyang et al., 2012). There is still a crucial requirement for designing an environment friendly and low-cost adsorbent for reducing Pb^{2+} pollution in terrestrial environment. Biochar as one of the biosorbents has recently gained increasing attention in removal and bioavailability decrement of heavy metals in soil and water medium as well (Wang et al., 2015b; Rechberger et al., 2017). Bundles of novel measures have been established for improving biochar adsorption capacity for heavy metals through improving surface characteristics (Mejias Carpio et al., 2014), effective functional groups (Becidan et al., 2017), hydrophobic/hydrophilic characters (Chen et al., 2014) and surface charges etc. (Samsuri et al., 2013). In addition, the use of diverse engineering approaches in biochar production, such as treatment of biomass or modification of biochar surface has ensued in numerous great proficiencies and efficient novel modified biochars with adsorption capacities equivalent to or even better than that of a few commercially available activated carbons.

The pristine biochar can be significantly modified with impregnation approaches; metal salts/oxides of minerals can be mixed with biochars (BCs) to expedite physical/chemical bonding of metal ions in the porous structure of biochars. To further improve the metal adsorption/sorption proficiency of biochars, these biosorbents have been pretreated or modified prior to pyrolysis process. The distinct improvement of divergent biochar materials has been revealed in previous studies (Rajapaksha et al., 2016; Sizmur et al., 2017), where improvement of metal adsorption has been analytically proved. To further improve the adsorption of biomass-derived biochars, biomass pretreatment is led to increase porosity because biomass fractionation process is beneficial for the succeeding activation process (Harun and Danquah, 2011; Rizwan et al., 2020).

In the current years, several technical innovations and applications of steam explosion were reported (Jia et al., 2013; Chen and Peng, 2014; Liu et al., 2014; Huang et al., 2015; Chen et al., 2019a). Steam explosion consequences in the hemicelluloses being hydrolyzed, the cellulose and lignin is marginally depolymerised, which aid in binding particles collectively during the densification process. Our previous group study (Chen et al., 2019a) revealed that steam explosion could remarkably change the physicochemical properties of typical agricultural feedstocks such as oil-rape, wheat, rice, maize and cotton straws and their derived biochars. In the current study, the most effective feedstock of oil-rape straw was selected for further mineral impregnation and biochar modification as well. It was hypothesized that chemical modification following steam explosion would fabricate the novel biochar with satisfactory adsorption and desorption properties. Apparently, this is the first study on modification of biochar/biomass following steam explosion of oil-rape straw. The particular objectives of the present study were thus (1) to quantify the adsorption and desorption characteristics of the engineered biochars for Pb^{2+}, (2) and then to recommend a measure for preparing the novel engineered biochar.

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Materials and methods

Oil-rape straw pretreatment and biochar production

Oil-rape straw residues were collected from Shang Zhuang experimental station, China Agricultural University, Beijing (40.14°N, 116.18°E). The details of the steam explosion (SE) pretreatment and biochar synthesis were described previously in Chen et al. (2019a). Briefly, oil-rape straw was steam-exploded for 2 min at 210°C and 2.5 MPa using a QB-200 platform, in Hebei Heavy-Duty Mechanical Factory. The steam exploded straw was distributed into two bulks. One bulk of steam exploded oil-rape straw was kept in a stainless steel reactor and heated in a muffle furnace at 500℃ for 2 h under N_2 flow (10 psi). The solid residues in the reactor were obtained and denoted as BC.

Synthesis of engineered biochars

The above described prepared biochar (BC) was further modified with chitosan and NaOH. The detailed protocol for the preparation of engineered biochars was described in our previous study (Chen et al., 2019b). Briefly, three g of chitosan was initially dissolved in 180 mL acetic acid (2%) solution, and further mixed with 3 g BC while stirring for 30 min at a rotatary shaker. The obtained suspension was then drop-wise added into a 900 mL NaOH (1.2%) solution and further retained for 12 hours. The obtained biochar material (named as BC_C) was further washed with deionized water to eliminate the surplus sodium hydroxide till the pH value became neutral and afterwards the obtained product was oven dried at 70℃ for 24 h (Zhou et al., 2013).

The NaOH-modified biochar (BC_{Na}) was synthesized according to Li et al. (2017). Briefly, 10 of the BC were mixed with 100 mL of 2 M NaOH solution with vigorous stirring for 12 h at 100℃. The biochar was oven-dried as described above followed by washing 3 times with 0.01 M $NaHCO_3$ solution to remove impurities and further 3 times washing with deionized water until the pH value reached pH 7.

Second bulk of steam exploded oil-rape straw was used for further modification. A nano-hydroxyapatite suspension solution was prepared by adding two grams of nano-hydroxyapatite mineral powder to 500 mL deionized water followed by the ultra-sonication of the mixture for 30 minutes. Ten grams of steam exploded oil-rape straw were agitated with the nano-hydroxyapatite suspension for 1 h, then oven dried at 60℃ for 24 hours. The hydroxyapatite-pretreated straw was kept in a quartz tube and then slowly pyrolized as described above (Yao et al., 2014; Yang et al., 2016). The solid residue was denoted as BC_{HA}.

One hundred grams of the SE oil-rape straw were vigorously agitated with 1000 ml 2% $KMnO_4$ solution at 80℃ for 3 h and then ultra-sonicated for 20 min, then oven-dried at 105℃ for overnight. The straw was slowly pyrolized as described above. The collected biochar (denoted as BC_{Mn}) was rinsed 3 times with 0.01 M $NaHCO_3$ solution and further 3 times with deionized water (Li et al., 2017). The details and study circumstances of studied biochars are given in *Table 1*.

Adsorption kinetics and isotherm studies

Adsorption isotherms were determined for Pb^{2+} by using the identical protocol as described in a previous study (Wang et al., 2015a), with minor modifications. A range of Pb^{2+} (25 mL, 1–250 mg L^{-1}) sorbate concentrations of solution and 24 hours contact time period was set in the adsorption isotherms study. Nitrate salts were used for

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preparing all solutions. Concisely, 0.1 g of biochar in a 25 mL Pb^{2+}, three drops of phenol were added in each sample to prevent microbial growth. Hence, the sorbent concentrations were 2.5 g L^{-1} for all treatments. In addition, to prevent metal precipitation, the initial pH values of the Pb^{2+} solutions were adjusted to 5 in all cases, by using 0.01 M HCl and 0.01 M NaOH solutions. In a former study (Li et al., 2017) it was revealed that the highest adsorption capacities were obtained at pH 5.0, hence this pH was used in the current study. The isotherms and kinetics tests were executed in triplicates and mean values were used for further data analysis.

Table 1. *Tested biochars and study circumstances are given as:*

Tested Biochar	Abbreviation	Study circumstances
Pristine Oil-rape straw biochar	BC	Oil-rape straw was pyrolyzed at 500℃ for 2 h under N_2 flow (10 psi).
Steam Exploded-Pretreated	BC_{SE}	Oil-rape straw was steam-exploded for 2 min at 210°C and 2.5 MPa.
$KMnO_4$-Impregnated	BC_{Mn}	Hundred grams of steam exploded rape straw was mixed with 1000 ml 2% $KMnO_4$ solution prior to biochar production.
NaOH-Modified	BC_{Na}	Ten grams of biochar was mixed with 100 ml of 2M NaOH solution, stirred vigorously at 100℃ for 12 h.
Hydroxyapatite-Modified	BC_{HA}	Two grams of hydroxyapatite powder was dissolved in 500 ml deionized (DI) in ultrasonic condition. Ten grams of steam exploded oil-rape straw were agitated with the nano-hydroxyapatite suspension for 1 h (prior to biochar production).
Chitosan-Modified	BC_C	Three grams of chitosan was first dissolved in 180 ml of acetic acid (2%), and 3 g of the as-is biochar was added to this solution.

Investigation of Pb^{2+} (50 mg L^{-1}) adsorption kinetics by biochars was carried out following the methods described above. Batch adsorption tests were conducted in triplicates using 50 ml centrifuge tubes on a rotatory shaker at 180 rpm. At each sampling time (0-24 h), the suspensions were collected and promptly filtered by using 0.22 ml pore size nylon membrane filters (GE cellulose nylon membrane). The Pb^{2+} ions concentrations in the resulting supernatant were determined by using inductively coupled ICP-OES (Optima 2300, Perkin-Elmer SCIEX, USA).

Desorption study

Desorption experiments were executed to examine, if biochar adsorption of Pb^{2+} was reversible and the Pb^{2+} immobilization aptitude of biochar was assessed. For desorption experiment, all Pb^{2+} loaded biochar samples were shaken for 24 h with 0.01 M HNO_3 (background electrolyte at pH = 5.00); (Trakal et al., 2014b), 0.01 M $CaCl_2$ (solution simulating ‘‘bioavailable form’’ of metal; Houba et al., 1996); and finally 0.01 $NaNO_3$ (solution exhibiting ‘‘geochemically active form’’ of metals; Tipping et al., 2003) to assess potential metal desorption. The aqueous solution phase was then separated from the sorbent using a centrifuge and promptly filtered by using 0.22 ml pore size nylon membrane filters. The residual concentrations of Pb^{2+} ions in the resulting supernatant were then determined using ICP-OES.

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Calculations

The adsorption amount (q_t) was determined according to the equation given below:

$$q_t = \frac{(C_0 - C_t)\,V}{m} \qquad \text{(Eq.1)}$$

Here, q_t denotes the maximum adsorption quantity of metal ions at a specific time t (mg/g), m represents the mass of biochar used (g), V denotes the volume of solution used (dm^3), and C_0 and C_e represents the initial and equilibrium concentration of the Pb^{2+} ions (mol/dm^3), respectively. The Langmuir model is expressed as (Langmuir, 1916; Aksu and Isoglu, 2005):

$$q_e = \frac{q_0 K_L C_e}{1 + K_L C_e} \qquad \text{(Eq.2)}$$

Here, q_e denotes the maximum adsorption capacity at equilibrium stage (mg/g), and C_e represents the concentration of Pb^{2+} ions at equilibrium (mg/dm^3). While, q_0 (mg/g) and K_L are constant of the Langmuir equation (dm^3/mg) and both these constants can be calculated from its linear form. The Freundlich model can be expressed as below (Freundlich, 1906; Zhang et al., 2011):

$$q_e = K_F C_e^{1/n} \qquad \text{(Eq.3)}$$

Pseudo second order model can be given as the following equation (Blanchard et al., 1984; Ho and McKay, 1998).

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} - \frac{t}{q_e} \qquad \text{(Eq.4)}$$

Pseudo first order kinetic model equation can be expressed as:

$$log(q_e - q_t) = log(q_e) - \frac{k_1 t}{2.303} \qquad \text{(Eq.5)}$$

Here, q_e and q_t represent quantities of Pb^{2+} ions adsorbed at equilibrium stage and at specific time t, respectively. k_1 and k_2 are the pseudo-first and second-order rate constants for the adsorption process.

Data analysis

All the tests were carried out in triplicates and the mean data was reported to plot adsorption kinetics and isotherms. The obtained data was examined statistically by using Statistics 8.1 software. The variability in the data was determined as the standard deviation and threshold of significance was $p < 0.05$.

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Results

Morphological characteristics of the studied biochar

To investigate the surface morphology characteristics of the studied biochars, SEM-EDS images of the pristine and numerous engineered biochars used in this study were obtained (*Figs. 1, 2 and 3*). The results displayed that porous structure exists on the biochar that sustains the disordered pattern of the pristine oil-rape straw cell morphology. As it is evident from the SEM images there is deposition of Mn, Na and Ca/ P on BC_{Mn}, BC_{Na} and BC_{HA} respectively. On the other hand, there is no obvious deposition on pristine and SE biochars (*Fig. 1a,b*). Furthermore, pristine biochar structure was disturbed, fragmented, and even shattered after SE pretreatment, which had a substantial impact on the structure of the corresponding biochars.

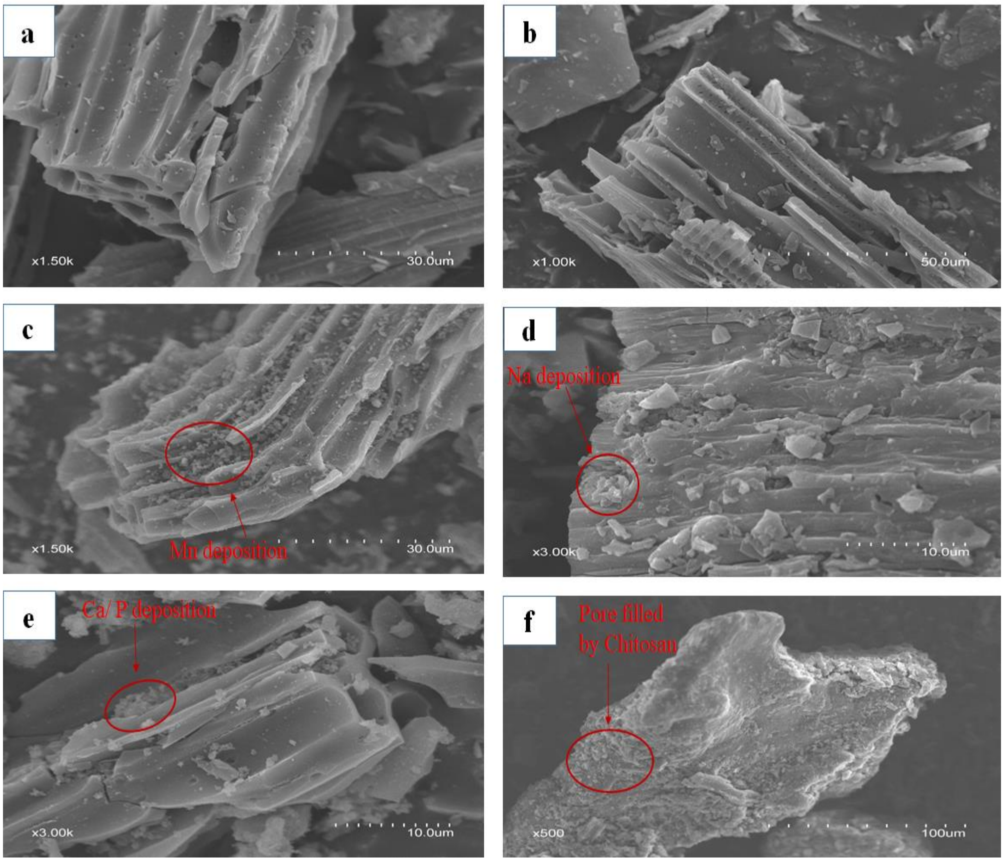

Figure 1. *SEM analysis of the biochars derived from pristine (BC) (a), SE pretreated (BC_{SE}) (b), $KMnO_4$-impregnated (BC_{Mn}) (c), NaOH- (BC_{Na}) (d), hydroxyapatite (BC_{HA}) (e), and chitosan (BC_C) (f)*

Additionally, the findings of surface elemental examination by using the EDS spectra obviously confirmed the higher concentration of respective various mineral contents in terms of weight and atomic percentages (*Figs. 2 and 3*). After modification, the higher concentration of these minerals depicts that these minerals were successfully impregnated on the respective biochar surface. Moreover, EDS elemental composition analysis of biochars further affirmed that biochars not just have greater amounts of oxygen and carbon, yet they additionally contain substantial amounts of slag

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components such as P, Cl, P and K amongst others (*Figs. 2 and 3*). The accumulation of Mn oxides on the BC_{Mn} surface, which was further confirmed by SEM-EDS analysis and these could provide more adsorption sites for Pb^{2+}. SEM-EDS analysis of studied BCs also confirmed the significant concentration of potassium and chlorine in the respective biochar. The SEM images of BC_{HA} is identical to that of BC, with the exemption that the amounts of P and Ca elements enhanced on the surface of biochar.

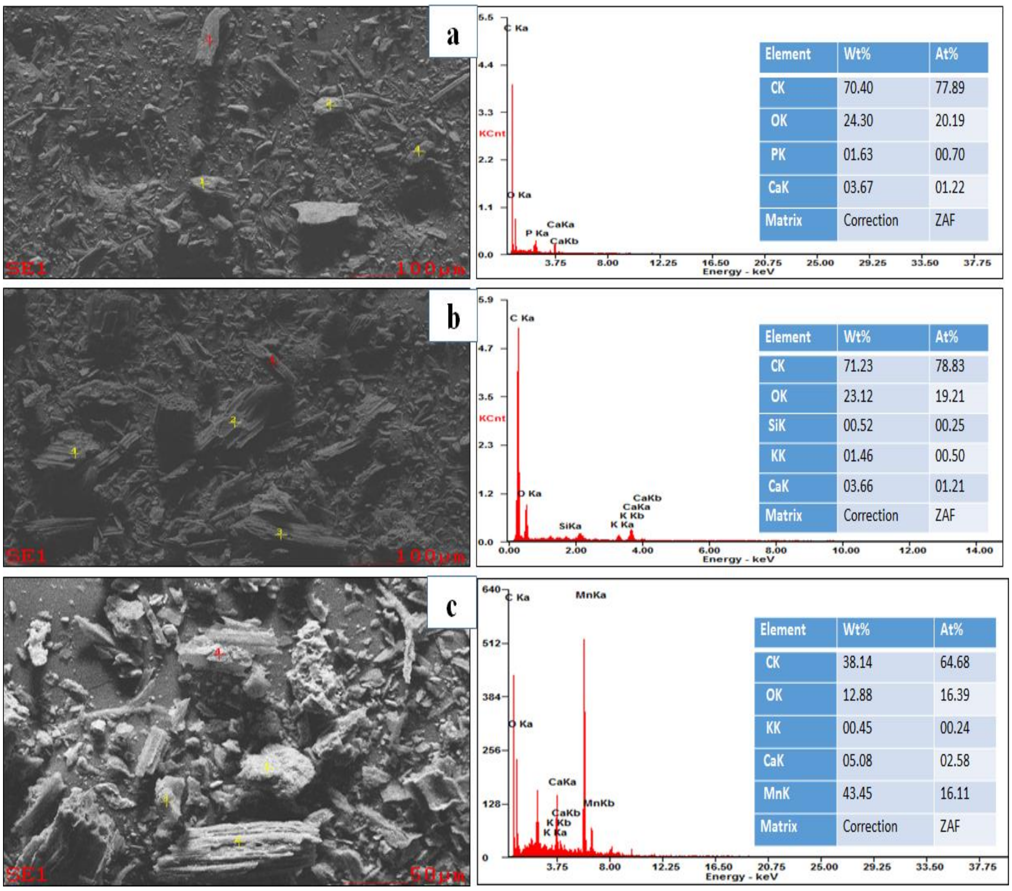

***Figure 2.** EDS analysis of the biochars derived from pristine (BC) (a), SE pretreated (BC_{SE}) (b), and $KMnO_4$-impregnated (BC_{Mn}) (c), and their corresponding EDS spectra with atomic elemental ratio*

Adsorption isotherms

In order to check the distribution of the adsorbate molecules between the liquid and the solid phases in equilibrium state, the adsorption equilibrium isotherm is necessary (Almeida et al., 2009). We performed Pb^{2+} batch adsorption experiment and the obtained experimental data was fitted in Langmuir and Freundlich models. In the present study linear forms of isotherm models were being employed instead of non linear forms as 95 % of liquid-phase adsorption studies used non linear forms (*Fig. 4, Table 2*). The data obtained from isotherm models was well fitted by using Langmuir models and 0.99 R^2 value was obtained for approximately all samples (*Table 2*). The Pb^{2+} adsorption hiked dramatically when the equilibrium solution concentration of Pb^{2+} was less than 30 mg L^{-1}.

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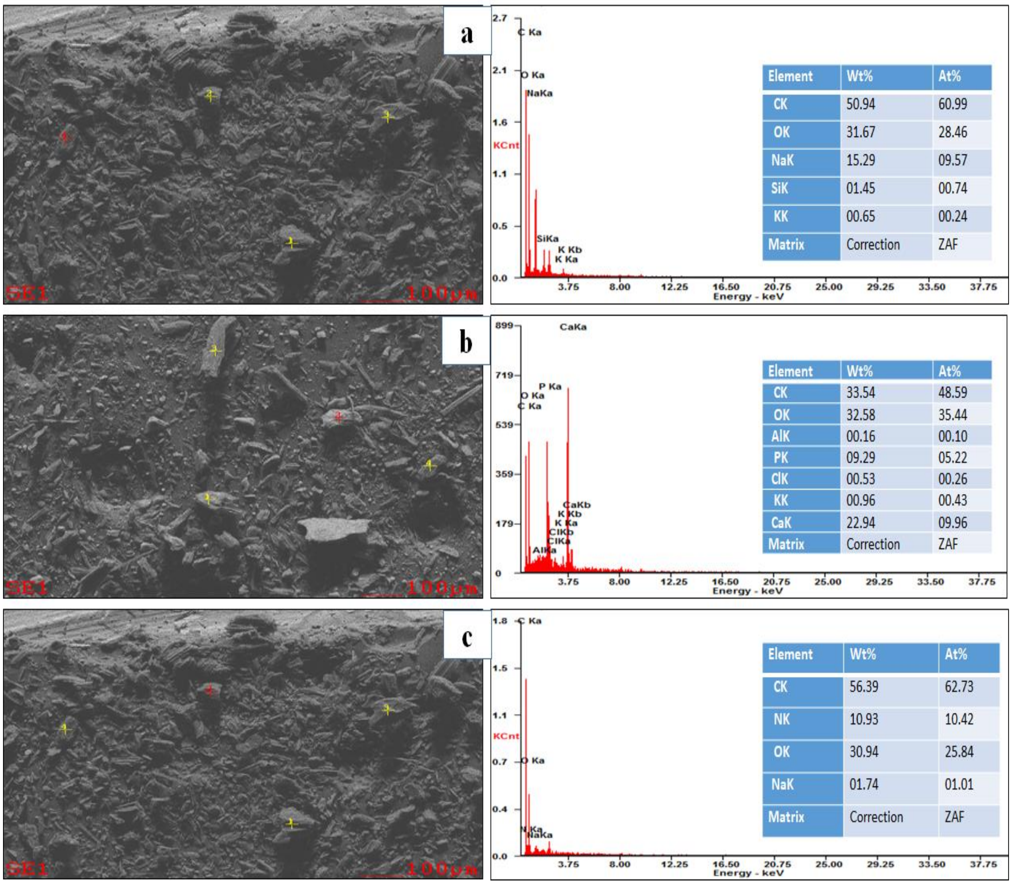

Figure 3. *EDS analysis of the biochars derived from NaOH- (BC_{Na}) (a), hydroxyapatite (BC_{HA}) (b), and chitosan (BC_C) (c) and their corresponding EDS spectra with atomic elemental ratio*

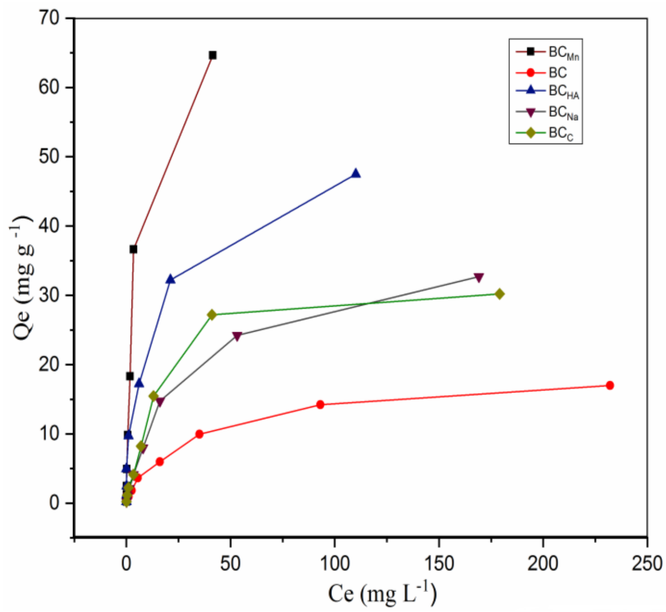

Figure 4. *Adsorption isotherms for Pb^{2+} on pristine (BC), $KMnO_4$- (BC_{Mn}), hydroxyapatite- (BC_{HA}), NaOH- (BC_{Na}) and chitosan-modified (BC_C) biochars (Qe is the adsorbed Pb^{2+} per unit mass of biochar, Ce is the equilibrium solution concentration)*

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Table 2. *The isothermal parameters calculated from both Langmuir and Freundlich equations for Pb^{2+} adsorption by pristine (BC), $KMnO_4$- (BC_{Mn}), hydroxyapatite- (BC_{HA}), NaOH- (BC_{Na}) and chitosan-modified- (BC_C) biochars*

Biochars	Langmuir			Freundlich		
	Q_{max}	K_L	R^2	1/n	K_F	R^2
BC	18.32	0.05	0.99	0.56	1.11	0.98
BC_{Mn}	70.92	0.24	0.98	0.71	9.92	0.89
BC_{Na}	37.04	0.04	0.99	0.67	1.6	0.98
BC_{HA}	49.26	0.18	0.99	0.49	6.37	0.75
BC_C	32.89	0.07	0.99	0.65	1.94	0.96

Q_{max} is the maximum adsorption capacity (mg g^{-1}). K_L is the Langmuir constant related to the sorption energy (L mg g^{-1}). 1/n is the Freundlich constant associated to surface heterogeneity. K_F is the Freundlich constant associated to sorption capacity ($mg^{(1-n)}$ L^n g^{-1})

In contrast the Pb^{2+} adsorption inclined to plateau when equilibrium concentration of Pb^{2+} was more than 30 mg L^{-1}. Adsorption capacities (q_e, mg g^{-1}) of the engineered biochars were raised significantly, as compared with the pristine biochar at this concentration. The results are consistent with a previous study (Foo and Hameed, 2010). The adsorption capacity of BC_{Mn}, BC_{HA}, BC_{Na} and BC_C is 287.12%, 168.89%, 102.18%, and 79.53%, respectively, much higher than BC. The maximum adsorption capacities of the biochars were observed in the following order: BC_{Mn} > BC_{HA} > BC_{Na} > BC_C > BC.

Table 2 shows the correlation coefficient, Langmuir and Freundlich models parameters. It is obvious that marginally better fits were attained by the use of the Langmuir model as compared to those attained from the Freundlich model, proposing that Pb^{2+} adsorption on these biochar was more constant with the Langmuir model rather than with the Freundlich model. Consequently, it was presumed that the adsorption happened mainly in monolayers, or occurred through fixed number of equal and energetically corresponding sites on the surface of biochar. In particular, Mn-modified biochar (BC_{Mn}) revealed the highest potential for Pb^{2+} adsorption, in which Q_{max} and K_L values were 3.87 times and 4.8 times (respectively) as high as those of virgin biochar.

Adsorption kinetics

Kinetic models were used to access the effect of contact time on the quantity of adsorbed Pb^{2+} on biochar and all the parameters of kinetic equations are given in *Table 3*. In the initial hours, the adsorption rate was very high. The rate of adsorption subsequently declined with the loom in equilibrium concentrations. Twenty-four hours were considered enough to confirm that the adsorption has reached equilibrium stage. Pseudo first order and pseudo second order models were used to evaluate the adsorption mechanism, (*Table 3*). The obtained regression coefficients (R^2) after using pseudo first order were 0.79-0.96 and the fitted model perceived a poor fit in the experimental data (*Table 3*). The pseudo second order equation fitted the kinetics data well and the regression coefficient of most samples was more significant (*Table 3*). The calculated q_e accorded the experimental data well, specifying the Pb^{2+} adsorption on engineered biochars follows the pseudo second order model which presumes chemisorption mechanism.

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Table 3. *Fitting parameters for the kinetic equations that describe Pb^{+2} adsorption on pristine (BC), $KMnO_4$- (BC_{Mn}), hydroxyapatite- (BC_{HA}), NaOH- (BC_{Na}) and chitosan-modified (BC_C) biochars*

Biochars	Pseudo-first-order model			Pseudo-second-order model		
	q_e	K_1	R^2	qe	K_2	R^2
BC	8.32	0.037	0.91	11.78	0.03	0.95
BC_{Mn}	18.93	1.24	0.79	22.61	0.78	0.96
BC_{Na}	11.04	0.42	0.89	13.67	0.36	0.91
BC_{HA}	14.26	0.18	0.81	16.49	0.37	0.96
BC_C	10.89	0.08	0.90	12.65	0.05	0.92

Where, q_e is calculated data, (mg g^{-1}). K_1 is the rate constant for pseudo-first-order adsorption (L h^{-1}). While, K_2 is the rate constant for pseudo-second-order (g (mg h)$^{-1}$)

The Pseudo second-order equation determined the adsorption of Pb^{2+} on the surfaces of BC, BC_{Mn}, BC_{HA}, BC_{Na} and BC_C as well (*Table 3*). Adsorption rate constant (K) for various chars was in the following orders: BC_{Mn} > BC_{HA}> BC_{Na} > BC_C > BC. The rate constant is higher for BC_{Mn} (0.78 g (mg h^{-1}) than for BC (0.03 g (mg h^{-1}), suggesting the rapid adsorption of Pb^{2+} to BC_{Mn} (*Table 3*).

Desorption capacity

A post desorption test was piloted to examine the stability of the adsorbed metals onto/into these adsorbents (closely related with variable adsorption mechanism of each biochar). In the beginning, all the loaded Pb^{2+} was desorbed from every examined biochar and most of the adsorbed Pb^{2+} was detached from BC_{Mn}, BC_{HA}, BC_{Na}, BC_C and BC using the 0.1 M HNO_3. The desorption aptitude of all the biochars was much higher with HNO_3 extractant (*Fig. 5*). As 98.31%, 89.42%, 91.56%, 93.98% and 95.71% of metal desorption occurred in BC, BC_{Mn}, BC_{HA}, BC_{Na}, and BC_C, respectively. While, 9-11% of pre-loaded Pb^{2+} in BC_{Mn}/ BC_{HA} could be fixed in the studied biochars after desorption is anticipated to expose the ‘‘geochemically active form’’ of metals (Tipping et al., 2003).

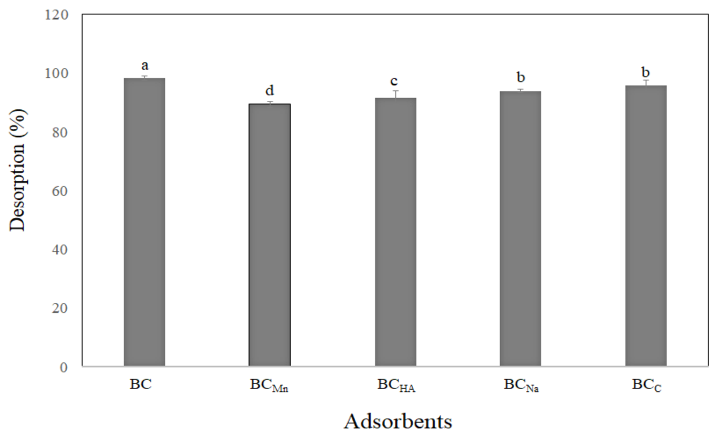

Figure 5. *Pb^{2+} desorption capacity by pristine (BC), $KMnO_4$- (BC_{Mn}), hydroxyapatite- (BC_{HA}), NaOH- (BC_{Na}) and chitosan-modified (BC_C) biochars by using 0.1 N HNO_3 solution. Experimental conditions: pH 5.0, initial concentration 50 mg/L, agitation rate 180 rpm, temperature 25°C, contact time 24 h*

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Next, metal desorption was carried out using 0.01 M $CaC1_2$ for the assessment of bioavailable metal forms (Houba et al., 1996), and desorption is variable for all the studied biochars (*Fig. 6*). Pb^{2+} was desorbed at lower rate (2.67%-4.34%) in all types of biochars. Obviously, BC has much desorption capacity (4.34%) and BC_{Mn} has the lowest one (2.67%). Finally, background electrolyte of 0.1 M $NaNO_3$ having pH 5.00 was used for desorption of Pb^{2+} from biochars (*Fig. 6*). Results exhibited that Pb-desorption was trivial in all cases (<1.83%), which was caused by the contrasting behaviour of Pb^{2+} (higher stability and affinity to organic matter in Pb^{2+} at a specific pH) and by variable metal adsorption mechanisms.

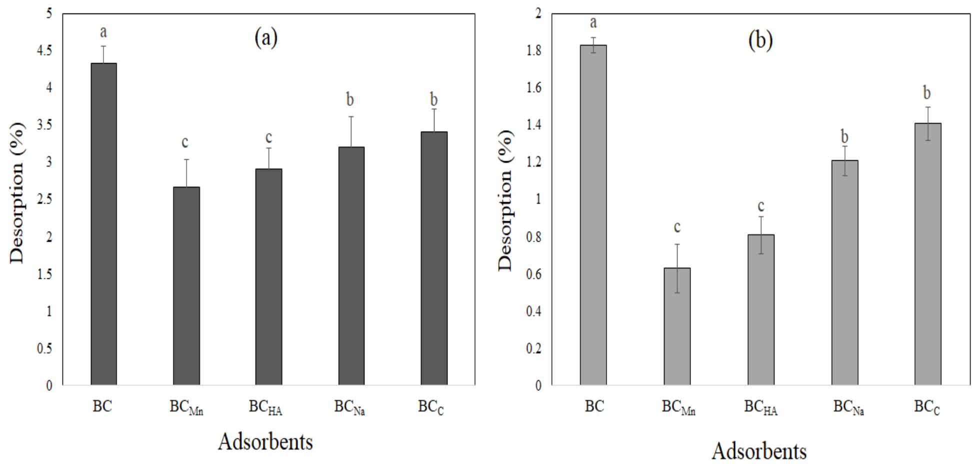

Figure 6. *Pb^{2+} desorption capacity by pristine (BC), $KMnO_4$- (BC_{Mn}), hydroxyapatite- (BC_{HA}), NaOH- (BC_{Na}) and chitosan-modified (BC_C) biochars by using 0.1 N $CaCl_2$ (a) and 0.1 M $NaNO_3$ (b). Experimental conditions: pH 5.0, initial concentration 50 mg/L, agitation rate 180 rpm, temperature 25°C, contact time 24 h*

Discussion

Our results revealed that the surface of biochars derived from SE-treated feedstock became coarser, compared to the smooth surface, clear anatomy, and distinctive pore structure in the biochars derived from the pristine feedstock. Our results are consistent with a previous study (Chen et al., 2019a). The accumulation of small particles on the BC_{Mn} surface is very obvious in SEM-EDS images, and is probably due to potassium permanganate. Due to Mn oxides formation, the porous structure was obstructed by these Mn oxide particles that are formed during pyrolysis (Petit et al., 2010). Various compounds of Mn oxides with various phases like β-MnO_2, δ-MnO_2, and MnO_2- coated sand have been reported to have strong affinity for various divalent metal cations (Tripathy and Kanungo, 2005). This might enhance the surface area of respective biochar and expose additional adsorption sites for Pb^{2+} (Chia et al., 2015).

All the four modified biochars had significantly greater maximum adsorption capacities (Q_{max}) and K_L values than the pristine biochar, which could direct that both feedstock pretreatment and biochar modification significantly increase the adsorption capacity of Pb^{2+}. The Langmuir model, presumes that the adsorptions of metal happened on a homogenous surface by monolayer adsorption deprived of any interaction between the adsorbed ions and has been used efficiently in many monolayer adsorption processes. Whereas, the Freundlich model presumes that the adsorption of metal ions

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took place on heterogeneous surfaces and sorption was multilayer. As evident from *Table 2* the adsorption isotherms are well described by the Langmuir model, suggesting that adsorption could be mono-molecular. As cited earlier, the adsorption/sorption efficiency differed not merely amongst tested metals, but usually differed among all the studied biochars. This might be because of the diverse adsorption mechanisms of respective metals on the studied biochars. As it is reported ion exchange, complexation and physical adsorption are liable for adsorption and sorption of metal on the surface of biochar (Sohi et al., 2010; Lu et al., 2012; Ahmad et al., 2014). However, these metal ions adsorption mechanisms are different for different kinds of biochars.

The adsorption proficiency of Pb^{2+} by these five adsorbents enhanced with time and then plateaued when equilibrium was attained. In the early stages adsorption capacity of Pb^{2+} by the pristine and modified biochars was much faster, probably because adsorption mainly took place on the external surfaces of biochars (Li et al., 2017). Pb^{2+} diffused into the carbon pores with the passage of time and further reacted with interior active sites of the carbon skeleton, where the adsorption process is comparatively slow (Babel and Kurniawan, 2003). BC_{Mn} and BC_{HA} adsorbed Pb^{2+} faster than BC and reached the equilibrium stage within only four hours. On the other hand, BC, BC_{Na} or BC_{C} needed eight hours to attain adsorption equilibrium. The aptitude of BC_{Mn} to grasp fast and proficient adsorption equilibrium which is extensively employed for the treatment of heavy metals contaminated water particularly in emergency conditions. Results of our investigation are in accordance with those of Ofomaja et al. (2010) who indicated that the sorption kinetics of heavy metals is considerably dependent on the physiochemical properties of biochar.

Solute-uptake rate is determined by adsorption kinetics which in turn governs the time of adsorption process (Ofomaja et al., 2010; Betts et al., 2013). Validation of the sorption kinetics model and the potential rate controlling steps was checked by pseudo first (Lagergren, 1898) and pseudo second order models (Ho and McKay, 2000). These parameters are beneficial for the selection of the optimal operating conditions. Furthermore, the adsorption capacities attained from pseudo-second-order model fitting are reconcilable with the experimental data, along with a chemisorption rate-controlling mechanism, where the limiting step is a physicochemical sorption or adsorption process including valence forces through the sharing or exchange of electrons between the sorbent and the sorbate (Vijayaraghavan and Yun, 2008). Findings of the current study are also in line with the observation of Li et al. (2017). Thus, this study speculated that these modified biochars may have higher potential for adsorption of pollutants as compared to pristine biochar. In addition, oil-rape straw might be suitable to SE pretreatment for preparing novel biochar for waste-water treatment and other environmental applications.

Following the results of an earlier study (Anastopoulos et al., 2015), 0.1 N HNO_3 was perceived as the best desorbing solution among numerous solutions. This proposes a dominant role for exchange sites in determining the adsorption properties of the various adsorbents. It is presumed that higher concentration of protons (H^+) of 0.1 N HNO_3 solution triggered intense competition of the H^+ between the metal ions for the adsorbent's exchange sites throughout the ion exchange process, and to the resultant desorption of Pb^{2+} ions adsorbed on exchange sites of the adsorbents surface (Anastopoulos et al., 2015). Obtained results of desorption study are most probably because of the predominant weak Pb π-bindings with poly-organic chains, e.g. physical adsorption and, in contrast, due to the stronger fixing of metals into the engineered

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biochar structures caused mostly by the cation release (particularly for BC_{Mn}). These results support the findings about the very strong fixation of Pb^{2+} to the structure of BC_{Mn}, BC_{HA}, BC_{Na} and BC_C (ion exchange adsorption mechanism). This partial desorption of adsorbed Pb^{2+} in the biochar after all extractions might be described by surface complexation reactions (Namgay et al., 2010). The current study, recommends that this often perceived partial extraction using $NaNO_3$ and $CaCl_2$ might be the result of strong bonds to biochar surfaces that would make adsorbed Pb^{2+} unavailable. So our study recommends that Pb^{2+} adsorption is not entirely reversible using $CaCl_2$ and $NaNO_3$ regardless of modifying agents, in contrast, it can be accomplished with HNO_3 as an extractant. Our findings are in accordance with previous studies (Trakal et al., 2014; Anastopoulos et al., 2015). Thus the current study, may reveal that the adsorbed Pb^{2+} was much more stable on the modified biochar with a lower desorption rate, as compared to the pristine biochar.

Conclusion

To summarize, $KMnO_4$ and nano-hydroxyapatite modification significantly improved the adsorption capacities of biochar for Pb^{2+}. The highest adsorption capacity for Pb^{2+} was exhibited by Mn and nano-hydroxyapatite modified biochars (70.92 and 49.26 mg g^{-1}, respectively), as compared to pristine biochar. Additional adsorption sites on engineered biochars appeared to play more significant role in Pb^{2+} adsorption instead of specific surface area of biochars. It can be concluded that cation-π bonding and cation exchange are the key mechanisms responsible for the highest adsorption capacities of studied biochars. Surface precipitation, surface electrostatic attraction and surface complexation are responsible for higher adsorption capacity in BC_{Na}. Conversely, BC_C exhibiting lower adsorption capacity might be caused by plenty of protons that obstructed the approach of Pb^{2+} ions, prompting to the decreased adsorption of Pb^{2+}. Thus, the manganese oxide impregnated biochar might provide an efficient way to elevate Pb^{2+} removal from aqueous medium. Although, various metal removal mechanisms are involved in the current study, but ion exchange mechanism is a crucial one among others. Furthermore, ion exchange mechanism revealed solid binding of adsorbed metal as affirmed by the post desorption of fully metal loaded biochars. To conclude, these biochars showed much promising adsorptive properties for divalent metals and might thus have a high potential as a soil amendment and an alternative adsorbent for environmental remediation. Further competitive adsorption and desorption studies are necessary in order to accurately estimate the heavy metal adsorption/desorption capabilities of biochar in natural environments.

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