

# Adsorption and desorption of lead in Iranian acid and alkaline soils amended with sewage sludge-derived biochar

Hamed Fathi Dokht,\*<sup>1</sup> Esmail Dordipour,<sup>2</sup> Seyed Alireza Movahedi Naeini<sup>3</sup>

1. Ph.D Student, Department of Soil Sciences, Gorgan University of Agricultural Sciences and Natural Resources, Gorgan, Iran
2. Associate Professor, Department of Soil Sciences, Gorgan University of Agricultural Sciences and Natural Resources, Gorgan, Iran
3. Associate Professor, Department of Soil Sciences, Gorgan University of Agricultural Sciences and Natural Resources, Gorgan, Iran

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## ABSTRACT

The effective management of sewage sludge materials in an environmentally and economically acceptable way is through the pyrolytic conversion of the sludge to biochar and its use for agricultural purposes. The aims of this work were: (1) to assess the effect of biochar prepared from sewage sludge at two different temperatures (350 °C and 650 °C) on the adsorption/desorption capacity of Pb (II) in two different Iranian soils (acidic and alkaline soils), and (2) to investigate the adsorption/desorption isotherm. The results indicated that with increasing pyrolysis temperature, the soil pH, ash content, aromaticity, BET, and total heavy metal concentration increased. On the other hand, the pyrolysis yield, percentages of H, N and O, atomic ratios, CEC and polarity of biochar decreased. The adsorption and desorption of Pb was more accurately described by the Langmuir isotherm than the Freundlich isotherm. The maximum adsorption capacity of biochars increased for alkaline and acidic soils when pyrolysis temperatures increased, suggesting that high temperature pyrolysis led to the biochars having high Pb adsorption capacity. The desorption of pre-adsorbed Pb (II) by NaNO<sub>3</sub> decreased in soils incorporated with biochars.

**Keywords:** soils, sewage sludge, environmentally

## Introduction

Sewage sludge is a residual material from wastewater treatment process. Iran currently produces more than 25 million tons of sewage sludge (moisture of 80%) from wastewater treatment plants, thereby entailing a great environmental responsibility for plant owners and local officials.<sup>1</sup> High concentrations of heavy metals in soils may pose long term risks to ecosystems and humans. Heavy metals introduced into soils are persistent and difficult to remove or decompose. In addition, pollution of heavy metals (e.g., Pb-II) is also of great concern due to their adverse effects on human

and aquatic life.<sup>1</sup> Lead (II) is a toxic metal ion present in acid mine drainage, and its management and remediation from soils is a research focus of many environmental communities.<sup>2</sup> Many techniques have been developed to remediate soils polluted by heavy metals.<sup>3</sup> Lime and red-mud,<sup>4</sup> and chicken manure compost,<sup>5</sup> which are reported as adsorbents of heavy metals, can have large surface areas, many functional groups or high pH values, and thus can effectively fix heavy metals in contaminated acid soils. For example, importation of modifiers,<sup>6</sup> electro kinetic remediation (a recently used method for remediation),<sup>7,8</sup> biological remediation,<sup>9,10</sup> and combination of remediation technologies.<sup>11</sup> Modifiers operate quickly to change the properties of heavy metals or soils, and thus decrease the mobility and bioavailability of metals. Accordingly, the effects of minerals and organic matter as modifiers of mobility and

✉ Hamed Fathi  
hamed\_fathi\_dokht@yahoo.com

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bioavailability of heavy metals have been studied extensively.<sup>6</sup> The pyrolysis process tends to reduce the volume of biosolids, eliminate pathogens, and change the organic matter into bio-fuel, bio-oil and biochar.<sup>12</sup> The biochar pyrolyzed from sewage sludge is rich in elemental carbon, nutrients and surface adsorption sites, and it is proved to be effective in removing contaminants from wastewater<sup>13</sup> and improve soil fertility.<sup>14,15</sup> The pyrolysis process of sewage sludge and the sludge-derived biochar are gaining more and more attention.<sup>16</sup> In the partial or total absence of oxygen, the thermal decomposition of plant-derived biomass (oxygen-limited pyrolysis) can be manipulated to yield a solid carbon-rich residue generically referred to as biochar, in addition to gaseous components including carbon dioxide, combustible gases, volatile oils and tarry vapors.<sup>17</sup> Biochar can also be obtained from the by-products of bio-oil production.<sup>18</sup> Biochar has many positive properties as an adsorbent: large specific surface area, microporous structure, and active functional groups.<sup>19</sup> Biochar has considerable adsorption capacity for heavy metals, such as Cu(II) and Pb(II),<sup>20-22</sup> and can be used to remove heavy metals from waste water.<sup>23</sup> In recent years, the adsorption of Cu (II), Pb (II) and Cd (II) by biochar has been investigated by several authors.<sup>24-26</sup> The adsorption mechanisms for these metals by biochar comprise electrostatic attraction, formation of complexes between metals and functional groups on biochar, and precipitation on biochar.<sup>16, 27</sup> Fourier transforms infrared spectroscopy (FTIR), equilibrium and kinetic adsorption data showed that the black carbon derived from wheat residue has a high affinity for heavy metals.<sup>28</sup> Pyrolytic biochar has a large adsorption capacity for copper [Cu (II)], lead [Pb (II)] and cadmium [Cd (II)] from aqueous solutions, and can be used to remove these metals from water.<sup>20, 22</sup> Adsorption of heavy metals such as Cu (II) from soils was also enhanced by the incorporation of biochar via cation exchange mechanisms and the complexation of Cu (II) with surface functional groups.<sup>29</sup> In weathered acidic soils, the stabilization ability of heavy metals, especially

Cu (II) and Pb (II), was directly correlated with the amount of oxygen functional groups in biochars.<sup>30</sup> The aims of this work were (1) to assess the effect of biochar prepared from sewage sludge at two different temperatures (350 °C and 650 °C) on Pb (II) adsorption/desorption capacity in two different Iranian soils (acidic and alkaline soils), and (2) to investigate the adsorption/desorption isotherm.

## Materials and Methods

### Soil characterization

Two composite soil surface samples (0-30 cm soil depth) were taken from Gorgan (alkaline soil) and Lahijan (acidic soil) located in northern Iran. The soil samples were taken to the laboratory, air-dried, and passed through a 2-mm sieve. The pH and electrical conductivity (EC) were determined in a 1:2.5 (g/mL) soil: water ratio using a pH meter (Mettler Toledo Delta 320)<sup>31</sup> and electrical conductivity meter (DDS-307A),<sup>31</sup> respectively. The cation exchange capacity (CEC) was determined by using NH<sub>4</sub>OAc/NaNH<sub>4</sub>OAc at 7.0.<sup>32</sup> The organic matter (OM) was determined with the Walkley-Black method.<sup>33</sup> Finally, the soil texture was determined by using the Bouyoucos method.<sup>34</sup> All the analyses were performed in parallel and in triplicates, and the results are listed in Table 1.

### Sewage sludge and biochar preparation and characteristics

The sludge used for pyrolysis treatment in this study was collected from the Kordkuy sewage sludge treatment plant (Golestan Province, Iran). The biochar was produced by pyrolyzing the biomass at various temperatures under O<sub>2</sub>-limited conditions. The dried sewage sludge was collected from Gorgan, and the sewage sludge was pyrolyzed in a closed ceramic pot under O<sub>2</sub>-limited conditions at 350 °C and 650 °C for 3 hours.<sup>35,36</sup> The pH, EC, and CEC of the biochar and sewage sludge were determined and analyzed with the same methods as mentioned above for soil testing. The total C, N, hydrogen (H), and oxygen (O) content of the sewage sludge and biochars were determined

using the EA3000 Element Analyzer (Euro Vector, Italy). The yield of biochar was determined as follows:  
 Biochar yield (%) =  $(W_2/W_1) * 100$  (1)  
 where  $W_1$  is the dry weight of the sewage sludge

sample prior to pyrolysis, and  $W_2$  is the biochar weight. The biochar yield was calculated by subtracting the chemical reagent weight from the produced biochar mass.

Ash was separated by placing the biochar or

Table 1. Some selected characteristics of the studied soils

Location	pH	EC (dS m <sup>-1</sup> )	CEC (cmol <sub>(+)</sub> kg <sup>-1</sup> )	Clay (g kg <sup>-1</sup> )	Silt (g kg <sup>-1</sup> )	Sand (g kg <sup>-1</sup> )	FC (% vol)	OM (%)
Lahijan (Acidic soils)	4.1	0.1	35	550	220	230	35.2	5.2
Gorgan (Alkaline soil)	7.8	0.88	20	339	461	200	37.5	1.8

sewage sludge sample in a nickel crucible and heating it at 700 °C for 2 hours under air.<sup>37</sup> The ash content was calculated as follows:

Ash content (%) =  $(M \text{ Ash}/M \text{ Biochar or sewage sludge}) * 100$  (2)

where M Ash was the mass of ash, and M Biochar or sewage sludge was the mass of biochar or sewage sludge. Finally, the surface area of the biochar and sewage sludge was measured using the Brunauer, Emmett, and Teller (BET) method that measured N<sub>2</sub> gas sorption (0.162 nm<sup>2</sup>) at 77 K. Approximately, 200 mg of ground biochar was outgassed at 120 °C for 16.5 hours, and then analyzed by an Autosorb-1 Surface Area Analyzer (Quantachrome Instruments). Five data points with relative pressures of 0.05–0.3 were used to calculate the surface area.<sup>37</sup> Based on ASTM D2216-98,<sup>38</sup> the moisture content was found by oven drying the sewage sludge at 110 °C until fixed weight. All the analyses were performed in triplicates and in parallel, and the results are listed in Table 2.

#### Determination of heavy metals contents in sludge and biochar

Aqua regia (a mixture of HF, HClO<sub>4</sub>, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub> acids in the same ratio) was used to determine the total content of heavy metals.<sup>39</sup> The heavy metal content of the digestate was then measured with an atomic absorption spectrophotometer equipped with a graphite furnace (Analytik Jena, AAS6 Vario). This experiment determined the Cd, Cu, Ni, Pb, Cr, Co, and As contents of the sludge and the biochar. All the analyses were performed in triplicates, and the results are listed in Table 4.

#### Incubation experiments

Air-dried soil samples of 200 g were placed in polythene cups, and then biochar was added

at 0%, and 5% w/w rates. The biochar was thoroughly incorporated into the soil, and then wetted with distilled water up to 70% of field capacity (FC) (pressure plate method). All the cups were covered with a plastic lid, and a small hole was made to allow gas exchange as well as to minimize moisture loss, and then incubated at a constant temperature of 25±1 °C. The cups were weighed after every five days, with water added to maintain constant moisture content throughout the incubation period. After 90 days of incubation, the soil samples were removed from the cups.<sup>40, 41</sup> Then, the samples were air-dried and ground to pass through a 60-mesh sieve for the adsorption experiments.

#### Batch adsorption and desorption experiments

A stock solution containing Pb(NO<sub>3</sub>)<sub>2</sub> 0.1 M was prepared by using reagent-grade Pb(NO<sub>3</sub>)<sub>2</sub>. A 1000-mL aliquot of NaNO<sub>3</sub> 1 M<sup>40,42</sup> solution as well as appropriate quantities of 0.1 M Pb(NO<sub>3</sub>)<sub>2</sub> solution and deionized water were added into 1000-mL volumetric flasks to obtain a mixed solution with 0.001 M NaNO<sub>3</sub> and various concentrations of Pb(NO<sub>3</sub>)<sub>2</sub> (0, 25, 50, 100, 250, 500, 1000 or 1500 mg/l for the isotherm experiments). These concentrations were selected on the basis of the severity of lead pollution of the soils in the country.<sup>40, 41</sup> NaNO<sub>3</sub> (0.01 M) was used as the supporting electrolyte to maintain a constant ionic strength in the adsorption experiments. The solution pH was adjusted to the target values with either HNO<sub>3</sub> or NaOH. Samples of 1.0 g of soil in duplicates were weighed in 80-mL polyethylene bottles. Each bottle with a soil sample was weighed as  $W_1$  (g). Then, 25 mL of the Pb(NO<sub>3</sub>)<sub>2</sub> solution with varying concentrations was added into each bottle. The suspensions were shaken in a constant-temperature water bath at 25 ± 1 °C for

1 hour, and then allowed to stand overnight to reach reaction equilibrium. The supernatant was then separated from the solid phase by centrifugation at 4500 rpm for 5 minutes. The bottle, containing the soil sample and the residual solution together, was then weighed as  $W_2$  (g). To desorb the pre-adsorbed Pb(II), 25 mL of  $\text{NaNO}_3$  1.0 M was added into each bottle.<sup>42</sup> The suspensions were shaken for 1 hour, and the solutions were then separated by centrifugation at 3000 rpm for 10 minutes. The Pb(II) concentration in the solutions was determined by using atomic absorption spectroscopy (AAS).<sup>43</sup> The Pb(II)-containing solutions were diluted appropriately with  $\text{HNO}_3$  to make a final  $\text{HNO}_3$  concentration of 0.08 M. The standard Pb(II) solution series (0.01–0.05 mM) were similarly prepared with  $\text{Pb}(\text{NO}_3)_2$ . The amount of adsorbed Pb(II) was calculated from the difference between the total amount added and the amount remaining in the bulk solution. The amount of Pb(II) desorbed by  $\text{NaNO}_3$  [i.e. (Pb(II)<sub>des</sub>)] was calculated by the following equation:

$$\text{Pb(II)}_{\text{des}} (\text{mg kg}^{-1}) = \{ \text{Pb(II)}_{\text{Na}} \times (25 + W_2 - W_1) - \text{Pb(II)}_{\text{ad}} \times (W_2 - W_1) \} \times 1000 \quad (4)$$

where  $\text{Pb(II)}_{\text{Na}}$  is the concentration of Pb(II) in the equilibrium solutions after desorption (M),  $\text{Pb(II)}_{\text{ad}}$  is the concentration of Pb(II) in the equilibrium solution after adsorption (M),  $W_1$  (g) is the total weight of the soil sample and the bottle, and  $W_2$  (g) is the total weight of the soil sample and the bottle together with the residual solution after the adsorption experiment.

## Results and Discussion

### *Sewage sludge and biochars characterization*

The properties of the sewage sludge and biochars, including yield, ash content, pH, CEC, moisture, hydrophobicity, EC, and BET, are summarized in Table 2. The biochars yield decreased with increasing pyrolysis temperature from 48.1 % at 350 °C to 28.5 % at 650 °C, which was in accordance with the results obtained by Mendez et al., 2013.<sup>36</sup> In contrast to the biochar yield, the biochar ash content increased with increasing pyrolysis temperature. This was in line with findings of other studies.<sup>36</sup>  
<sup>44</sup> The percentage of ash content increased from

59.45 % for sewage sludge to 64.2%, and 68.5% for biochar pyrolyzed at 350 °C and 650 °C, respectively. Pyrolysis also increased the pH as a result of the polymerization/condensation reactions and the acidic surface groups released during the pyrolysis process.<sup>36</sup> The EC, a parameter used to estimate the amount of total dissolved salts in a sample, was 4.2  $\text{dS m}^{-1}$  for the raw sewage sludge, while it decreased with pyrolysis to 2.4 and 1.9  $\text{dS m}^{-1}$  for the biochar at 350 °C and the biochar at 650 °C, respectively.<sup>36</sup> With respect to CEC, its value decreased with the pyrolysis temperature from 23.1  $\text{cmol}^{(+)} \text{kg}^{-1}$  for sewage sludge to 21.2 and 18.5  $\text{cmol}^{(+)} \text{kg}^{-1}$  for the biochar at 350 °C and the biochar at 650 °C, respectively. These results are in agreement with those obtained by Mendez et al., 2013.<sup>36</sup> The decrease in CEC with the pyrolysis temperature could be due to the release of functional groups during the pyrolysis process.<sup>36</sup> The SSA (specific surface area) is one of the important parameters to evaluate if adsorption is involved in the distribution of pore structure.<sup>45</sup> It was seen that the BET surface area of the biochar increased as the pyrolysis temperature increased, as reported by others.<sup>36</sup>  
<sup>46</sup> The BET surface area of the biochar obtained at 650 °C (65.3  $\text{m}^2/\text{g}$ ) was larger than that of the biochar at 350 °C (34.2  $\text{m}^2/\text{g}$ ). The elemental content changes in C, H, O and N are listed in Table 4.

As expected from the pyrolytic process for the biochar, the C content increased, while the H, N and O contents decreased with increasing pyrolytic temperature. The increase in carbon content with temperature is due to the increasing degree of carbonization. However, the decline in O and H elements may be attributed to the breaking of weaker bonds in the biochar structure and highly carbonaceous materials with increased temperature. The N content of biochars reduced with increased temperature, which may be attributed to the volatilization of nitrogen during pyrolysis.<sup>45</sup> The calculated atomic ratio of O/C, H/C and (O+N)/C are presented in Table 3. The atomic ratio of elements, which estimates the aromaticity (H/C) and polarity (O/C, (O+N)/C) of the biochars and

sewage sludge, were affected by the pyrolysis temperature.<sup>37</sup> The results revealed that sewage sludge had the highest values of these ratios, whereas these ratios tended to decrease with the pyrolysis temperature. The decline in the O/C ratios with temperature is due to dehydration reactions, and result in less hydrophilic biochar surface.<sup>46,47</sup> In addition, the decrease in the H/C ratio is associated with the degree of carbonization. The lowest H/C ratio (0.019) at 650 °C suggests that the biochar is highly carbonized, indicating the highest aromaticity in the biochar at 650 °C compared to the biochar at

350 °C and the sewage sludge. These results are in agreement with those obtained by.<sup>47</sup> The molar (O+ N)/C ratio, similarly to the tendencies of O/C and H/C, decreases with increasing pyrolysis temperature, suggesting that the surface functional group of the biochars has reduced (46). The highest ratio of the (O + N)/C and polarity were found for the sewage sludge compared to the biochar at 350°C and the biochar at 650 °C, suggesting an increase in aromaticity and a decrease in polarity of the biochar produced at a temperature of 650 °C.<sup>47</sup>

Table 2. Basic characterization of the sewage sludge and biochars pyrolyzed at 350 and 650 °C

Treatments	Moisture (%)	Yield (%)	Ash (%)	pH	EC (dSm <sup>-1</sup> )	C (%)	O (%)	H (%)	N (%)	CEC cmol <sup>(+)</sup> (kg <sup>-1</sup> )	BET (m <sup>2</sup> /g)
Sewage sludge	84.1	-	44.45	6.3	4.2	25.23	19.48	5.14	5.70	23.1	1.1
Biochar (350 °C )	-	48.1	60.2	7.9	2.4	26.42	8.3	1.1	3.98	21.2	34.2
Biochar (650 °C)	-	28.5	68.5	8.8	1.9	27.24	0.81	0.53	2.92	18.5	65.3

Table 3. Effect of pyrolysis temperature on the atomic ratios of biochar

Treatments	Atomic ratios		
	O/C	H/C	(O+N)/C
Sewage sludge	0.77	0.203	0.90
Biochar (350 °C)	0.31	0.041	0.465
Biochar (650 °C)	0.029	0.019	0.136

### Heavy metal content of sewage sludge and biochars

The heavy metal contents of the sewage sludge and the biochars are presented in Table 4. In the present study, due to the domestic origin of the sludge, the amount of trace elements was less than the EPA thresholds for sewage sludge land application.<sup>48</sup>

Table 4. Heavy metal analysis of the sewage sludge and biochars

	Heavy metals (mg/kg)						
	Cd	Cu	Ni	Pb	Cr	As	Co
Sewage sludge	2.2	54.4	62	92.1	28.9	<sup>a</sup> BDL	<sup>a</sup> BDL
Biochar (350 °C)	3.9	99.5	113	158.7	53	<sup>a</sup> BDL	<sup>a</sup> BDL
Biochar (650 °C)	4.15	125.8	155.4	227.8	65	<sup>a</sup> BDL	<sup>a</sup> BDL
US EPA., 1993	85	4300	420	840	3000	75	50

<sup>a</sup> BDL stands for "Below Detection Limit"

### Sorption/desorption isotherm studies

The simulation of sorption isotherms of Pb(II) on the two biochars derived from different pyrolysis temperatures and two soils were based on the Langmuir and Freundlich models. The Langmuir model reflects the standard equilibrium process behavior assuming that the adsorbent has a constant number of adsorption sites, and that the sorption on the (mg/L) is the equilibrium solution concentration of the adsorbate, Q (mg/g) is the maximum

adsorbent surface is a monolayer. It also assumes that the adsorbent surface is homogeneous, and there is no interaction between the adsorbed molecules. The Langmuir model is described by Equation (5):

$$q_e = \frac{Q}{1+bC_e} \quad (5)$$

where  $q_e$  (mg/g) is the amount of metal adsorbed per unit weight of the adsorbent,  $C_e$

amount of adsorbed metal ions needed to form a monolayer on an adsorbent surface, and  $b$

(L/mg) is the Langmuir adsorption constant related to binding energies. On the other hand, the Freundlich model assumes that the adsorbent surface is heterogeneous, and that the sorption on its surface is multilayer (Equation. (6)).

$$q_e = K C_e^{1/n} \quad (6)$$

where  $q_e$  (mg/g) is the amount of metal adsorbed per unit weight of the adsorbent,  $C_e$  (mg/L) is the equilibrium solution concentration of the adsorbate,  $K$  ((mg/g) (l/mg)<sup>1/n</sup>) is a

constant related to the adsorbent's maximum adsorption capacity, and  $1/n$  is a constant measuring the strength of adsorption.

The linear adsorption isotherm equations of the Langmuir and Freundlich models were fitted to the measured adsorption data. The corresponding constants and correlation coefficients of the Langmuir and Freundlich equations are shown in Table 5. All the sorption isotherms were of L-type (Figure 1).<sup>49</sup>

Table 5. The adsorption isotherm models and its coefficients

Treatments	Langmuir model			Freundlich model		
	Q	b	r <sup>2</sup>	k	n	r <sup>2</sup>
Acidic soils- control	5	0.0103	0.96	779.8	3.87	0.95
Acidic soils- Biochar (350 °C)	16	0.0357	0.98	1288	2.237	0.97
Acidic soils- Biochar (650 °C)	20	0.0416	0.99	1698	2.241	0.97
Alkaline soils- control	10	0.0106	0.98	1095	3.85	0.96
Alkaline soil- Biochar (350 °C)	20	0.045	0.99	1864	2.467	0.98
Alkaline soil- Biochar (650 °C)	22	0.083	0.99	2328	2.340	0.95

The linear desorption isotherm equations of the Langmuir and Freundlich models were fitted to the desorption data. The corresponding

constants and correlation coefficients of the Langmuir and Freundlich equations are shown in Table 6.

Table 6. The desorption isotherm models and its coefficients

Treatments	Langmuir model			Freundlich model		
	Q	b	r <sup>2</sup>	k	n	r <sup>2</sup>
Acidic soils- control	16.5	0.05	0.97	616.5	2.79	0.79
Acidic soils- Biochar (350 °C)	20	0.0116	0.97	357.27	2.553	0.95
Acidic soils- Biochar (650 °C)	33	0.0069	0.92	23.1	1.364	0.95
Alkaline soils- control	3.3	0.125	0.97	645.6	3.14	0.81
Alkaline soil- Biochar (350 °C)	16.6	0.0231	0.99	371	1.94	0.84
Alkaline soil- Biochar (650 °C)	25	0.021	0.99	158.1	1.91	0.82

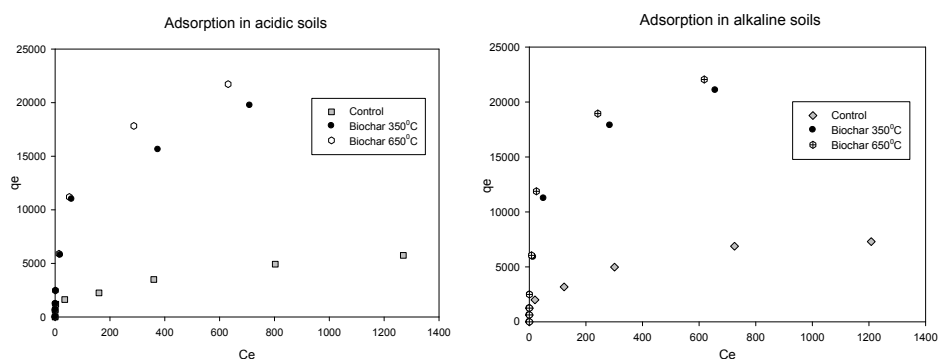


Fig. 1. The relationship between the amounts of  $q_e$  (mg g<sup>-1</sup>) of the adsorbed Pb onto the soils and their concentration in the equilibrium solution  $C_e$  (mg/L) for studying soils.

### ***Isotherms of Pb adsorption***

As shown in Figure 1, the amount of

adsorbed Pb increased with the increase in its initial solution concentrations, but this trend was

most pronounced for the biochar at 350 °C and the biochar at 650 °C probably due to the high affinity of Pb to adsorb onto the biochar surface. As shown in Table (5), the adsorption of Pb onto different biochars and soils are well described by the Langmuir and Freundlich models. The results indicated that the Langmuir model ( $r^2 = 0.96$  to  $0.99$ ) fitted the adsorption data slightly better than that of the Freundlich model ( $r^2 = 0.95$  to  $0.98$ ), implying a monolayer coverage of Pb on the surface of the biochars.<sup>50</sup> The Langmuir maximum adsorption capacity  $Q_0$  of the biochars increased for the alkaline and acidic soils when the temperatures for biochar production increased, suggesting that the high temperature pyrolysis induced the biochar with a capacity for high Pb adsorption. These results are in agreement with,<sup>46</sup> who found higher sorption capacities of Cu and Zn from aqueous solution in corn straw biochar produced at 600 °C compared to that of hard wood biochar at 450 °C. This result could be attributed to the higher surface area, pH, aromaticity and porosity of the biochar formed at the higher temperature.

### ***Isotherms of Pb desorption***

As shown in Table 6, the Pb desorption from different incorporated biochars and soils were well explained by the Langmuir and Freundlich models. The results indicated that the Langmuir model ( $r^2 = 0.97$  to  $0.99$ ) fitted slightly better than the Freundlich model ( $r^2 = 0.79$  to  $0.95$ ).

### ***Effect of biochars on adsorption***

The adsorption of Pb (II) on both soils increased significantly with biochar incorporation for initial Pb (II) concentration >100 mg/l, and the Pb (II) adsorption capability of biochar increased with an increase in production temperature (Table, 7). For Pb (II) 1000 mg/l, the adsorption in the alkaline soil was 27%, 70.14% and 75.13% in the control, for the biochars at 350°C and 650°C treatments,

respectively. The adsorption of Pb (II) in the acidic soil was 19.7%, 62.5% and 71% in the control, for the biochars at 350 °C and 650°C treatments, respectively. Biochar has many functional groups (e.g.  $-\text{COO}_-$  and  $-\text{OH}$ ) on its surface.<sup>51</sup> The functional groups can form surface complexes with Pb (II), and hence increase the specific adsorption of Pb (II) in soils incorporated with biochar. This is consistent with previous observations reported for Pb (II) adsorption by biochars derived from different feedstocks.<sup>52, 27</sup> The sorption of metal ion from soil is generally governed by the surface chemistry and surface area of the sorbent or by the precipitation reactions.<sup>20</sup> The Pb sorption capacity of the biochar at 650 °C was the highest among all the other treatments (Table 5) despite its lowest CEC (Table 2), suggesting that the Pb sorption by the biochar was controlled by its surface area and pH.

### ***Effect of biochars on desorption***

The desorption of the pre-adsorbed Pb (II) by 1.0 mole  $\text{l}^{-1}$   $\text{NaNO}_3$  also decreased in soils incorporated with biochars (Table 8). For instance, for an initial Pb(II) concentration of 1500  $\text{mg L}^{-1}$ , the desorption in alkaline soil were 53.9 %, 25.74 % and 16.78 % in the control, for the biochars 350 °C and 650 °C treatments, respectively. The desorption of Pb (II) in acidic soil were 40.4%, 27.7% and 19.57 % in the control, for the biochars at 350 °C and 650 °C treatments, respectively. Obviously, the soil incorporated with biochars (obtained at 350 °C) exhibited a greater desorption of the pre-adsorbed Pb (II) than with biochars produced at 650 °C. This is consistent with previous observations reported for Pb (II) desorption on bagasse biochar.<sup>53</sup> This result could be attributed to the higher surface area, pH, aromaticity and porosity of the biochar formed at the higher temperature.

### ***Effect of acidic and alkaline soils on adsorption/desorption***

Soil pH is a major factor that affects the

adsorption/desorption of heavy metals in with increasing soil pH. The increase in pH reduces the solubility of most Pb minerals, and increases the adsorption affinity of Pb (II) for organic matter, iron oxides and other adsorptive surfaces. This increases the retention of cationic heavy metal on soil surfaces via adsorption, inner-sphere surface complexation, precipitation, and multinuclear type reaction.<sup>21</sup> The effects of acidic and alkaline soils on Pb (II) adsorption and desorption of the pre-adsorbed Pb (II) from both soils are presented in Tables 7 and 8. The results indicated that the adsorption capacity of

soils. The adsorption of Pb (II) increases the alkaline soil was higher than that of the acidic soil (Table 5). This is consistent with previous observations reported for Pb(II) adsorption in biochars derived from different feedstocks.<sup>52,27</sup> The desorption amount of Pb II for acidic soil followed the order: control > biochar 350 °C > biochar 650 °C treatments. Similar results were observed for the alkaline soil.<sup>41</sup> This suggests that the Pb adsorption/desorption by the biochar was controlled by its surface area and pH.

Table 7. The percentage of adsorption Pb (II) on two soils

Treatments	Different initial concentration of Pb II (mg/L)							
	0	25	50	100	250	500	1000	1500
Acidic soils- control	-	98.6	95	65	36	28	19.7	15.3
Acidic soils- Biochar (350 °C)	-	98	98	97	92	87	62.5	52.6
Acidic soils- Biochar (650 °C)	-	99.6	99.5	99.5	96	95	75	58.8
Alkaline soils- control	-	99	99	80	50.4	39	27	19.4
Alkaline soil- Biochar (350 °C)	-	99	99	98	94	89	71	56
Alkaline soil- Biochar (650 °C)	-	99	99	99	96	95	75	58.8

Table 8. The percentage of desorption Pb (II) from two soils

Treatments	Different initial concentration of Pb II (mg/L)							
	0	25	50	100	250	500	1000	1500
Acidic soils- control	-	5	6.5	8.9	15.7	38.9	43.2	53.9
Acidic soils- Biochar (350 °C)	-	3.6	4.4	4.55	5.47	12.76	19.11	27.72
Acidic soils- Biochar (650 °C)	-	2.2	2.23	2.34	2.92	5.007	12.40	19.57
Alkaline soils- control	-	4.4	5.6	6.8	10.9	26.6	30.2	40.4
Alkaline soil- Biochar (350 °C)	-	3.12	3.25	3.16	3.88	8.9	16.2	25.74
Alkaline soil- Biochar (650 °C)	-	1.67	1.95	2.05	2.69	4.26	10.43	16.78

## Conclusion

Pyrolysis temperature has a significant effect on the chemical and physical properties of the biochar produced from sewage sludge. The results indicated that increasing the pyrolysis temperature, increased the pH, ash content, BET, aromaticity, and total concentration of heavy metals. On the other hand, the pyrolysis yield, percentages of H, N and O, atomic ratios and polarity of biochars, decreased. Furthermore, the adsorption potential of both soils increased with the application of biochars. The adsorption and desorption of Pb was better described by the Langmuir equation than the Freundlich equation. The biochar produced from sewage sludge offers a solution for

minimizing waste volume as well as producing potentially valuable biochar adsorbents. The environmental risk of sewage sludge biochar can be minimized and managed by controlling the source of feedstock and pyrolysis temperature. Further studies are underway to test the impact of the best-selected biochar on metal adsorption and soil amelioration.

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## References

1. Fahiminia M, Farzadkia M, Jafari Mansoorian H,



- Majidi G, Mirzabeygi Arhany M, et al.. The status of wastewater management in Shokuhieh industrial park (A case study of Qom province). *Environ. Health Eng Manage J.* 2015; 2(4): 165-171.
2. Cheng S, Jang JH, Dempsey BA, Logan BE. Efficient recovery of nano-sized iron oxide particles from synthetic acid-mine drainage (AMD) water using fuel cell technologies. *Water Res* 2011;45(1); 303-307.
  3. Dawson J. Barrier containment technologies for environmental remediation applications. *Journal of Hazardous Materials.* 1996;51(1-3):256.
  4. Gray CW, Dunham SJ, Dennis P G, Zhao FJ, McGrath SP. Field evaluation of in situ remediation of a heavy metal contaminated soil using lime and red-mud. *Environ Pollut* 2006; 142(3):530-539.
  5. Liu L, Chen H, Cai P, Liang W, Huang Q. Immobilization and phytotoxicity of Cd in contaminated soil amended with chicken manure compost. *J. Hazard. Mater* 2009; 163(2): 563-567.
  6. Querol X, Alastuey A, Moreno N, Alvarez-Ayuso E, Garcia-Sánchez A, Cama J, Simón M. Immobilization of heavy metals in polluted soils by the addition of zeolitic material synthesized from coal fly ash. *Chemosphere* 2006; 62(2): 171-180.
  7. Acar YB, and Alshwabkeh, AN. Principles of electrokinetic remediation. *Environ. Sci. Technol* 1993; 27(13): 2638-2647.
  8. Mulligan CN, Yong RN, Gibbs BF. Remediation technologies for metal-contaminated soils and groundwater: an Evaluation. *Engin Geo.* 2001; 60(1): 193-207.
  9. Lovley, D. R., Coates, J. D. Bioremediation of metal contamination. *Curr. Opin. Biotechnol* 1997; 8(3): 285-289.
  10. Gavrilescu, M. Removal of heavy metals from the environment by biosorption. *Eng Life Sci* .2004; 4(3): 219-232.
  11. Zhou DM, Hao XZ, Wang YJ, Dong YH, Cang L. Copper and Zn uptake by radish and pakchoi as affected by application of livestock and poultry manures. *Chemosphere.* 2005;59(2): 167-175.
  12. Domínguez A, Menéndez J A, Inguanzo M, Pis J J. Production of bio-fuels by high temperature pyrolysis of sewage sludge using conventional and microwave heating. *Bioresurse Technol.* 2006; 97(10): 1185-1193.
  13. Smith KM, Fowler GD, Pullket S, Graham ND. Sewage sludge-based adsorbents: a review of their production, properties and use in water treatment applications. *Water Res.* 2009; 43(10):2569-2594.
  14. Hossain MK, Strezov V, Chan KY, Nelson PF. Agronomic properties of wastewater sludge biochar and bioavailability of metals in production of cherry tomato (*Lycopersicon esculentum*). *Chemosphere.* 2010; 78(9): 1167-1171.
  15. Hossain MK, Strezov V, Chan KY, Ziolkowski A, Nelson PF. Influence of pyrolysis temperature on production and nutrient properties of wastewater sludge biochar. *J Environ Manage.* 2011; 92(1): 223-228.
  16. Dong X, Ma LQ, Li Y. Characteristics and mechanisms of hexavalent chromium removal by biochar from sugar beet tailing. *J. Hazard. Mater.* 2011; 190(1): 909-915.
  17. Sohi SP, Krull E, Lopez-Capel E, Bol R. A review of biochar and its use and function in soil. *Adv Agron.* 2010; 105: 47-82.
  18. Mohan D, Pittman CU, Steele PH. Pyrolysis of wood/biomass for bio-oil: a critical review. *Energy fuels,* 2006; 20(3): 848-889.
  19. Chen JP, Lin M. Equilibrium and kinetics of metal ion adsorption onto a commercial H-type granular activated carbon: experimental and modeling studies. *Water Rese.* 2001; 35(10):2385-2394.
  20. Cao X, Ma L, Gao B, Harris W. Dairy-manure derived biochar effectively sorbs lead and atrazine. *Environ. Sci. Technol.* 2009; 43(9): 3285-3291.
  21. Ma L, Xu R, Jiang J. Adsorption and desorption of Cu (II) and Pb (II) in paddy soils cultivated for various years in the subtropical China. *J. Environ. Sci.* 2010; 22(5): 689-695.
  22. Tong XJ, Li JY, Yuan JH, Xu RK. Adsorption of Cu (II) by biochars generated from three crop straws. *Chem. Eng. J.* 2011; 172(2): 828-834.
  23. Tong X, Xu R. Removal of Cu (II) from acidic electroplating effluent by biochars generated from crop straws. *J. Environ. Sci,* 2013;25(4): 652-658.
  24. Park J, Choppala G, Bolan N, Chung J, Chuasavathi T. Biochar reduces the bioavailability and phytotoxicity of heavy metals. *Plant and Soil.* 2011;348(1-2):439-451.
  25. Inyang M, Gao B, Yao Y, Xue Y, Zimmerman AR, Pullammanappallil P, Cao X. Removal of heavy metals from aqueous solution by biochars

- derived from anaerobically digested biomass. *Bioresour. Technol.* 2012; 110: 50-56.
26. Suppadit T, Kitikoon V, Phubphol A, Neumnoi P. Effect of quail litter biochar on productivity of four new physic nut varieties planted in cadmium-contaminated soil. *Chil J Agr Res.* 2012; 72(1): 125-132.
  27. Lu H, Zhang W, Yang Y, Huang X, Wang S, Qiu R. Relative distribution of Pb<sup>2+</sup> sorption mechanisms by sludge-derived biochar. *Water Research.* 2012;46(3):854-862.
  28. Peng X, Ye LL, Wang CH, Zhou H, and Sun B. Temperature-and duration-dependent rice straw-derived biochar: Characteristics and its effects on soil properties of an Ultisol in southern China. *Soil Tillage Res.* 2011; 112(2): 159-166.
  29. Uchimiya M, Klasson KT, Wartelle LH, Lima IM. Influence of soil properties on heavy metal sequestration by biochar amendment: 1. Copper sorption isotherms and the release of cations. *Chemosphere,* 2011; 82(10): 1431-1437.
  30. Uchimiya M, Klasson KT, Wartelle LH, Lima IM. Influence of soil properties on heavy metal sequestration by biochar amendment: 2. Copper desorption isotherms. *Chemosphere,* 2011; 82(10): 1438-1447.
  31. Thomas GW, Sparks DL, Page AL, Helmke PA, Loeppert RH, Soltanpour, et al. Soil pH and soil acidity. *Methods of soil analysis. Part 3-chemical methods.* 1996: 475-490.
  32. Sumner M, Miller WP, Sparks DL, Page AL, Helmke PA, et al. Cation exchange capacity and exchange coefficients. *Methods of soil analysis. Part 3-chemical methods.* 1996 : 1201-1229.
  33. Nelson DW, Sommers L. Total carbon, organic carbon, and organic matter. *Methods of soil analysis. Part 2. Chemical and microbiological properties, (methodsofsoilan2),* 1982: 539-579.
  34. Bouyoucos GJ. Hydrometer method improved for making particle size analyses of soils. *Agron. J* 1962; 54(5): 464-465.
  35. Lu H, Zhang W, Wang S, Zhuang L, Yang Y, Qiu R. Characterization of sewage sludge-derived biochars from different feedstocks and pyrolysis temperatures. *J. Anal. Appl. Pyrol* 2013;102 :137-143.
  36. Méndez A, Terradillos M, Gascó G. Physicochemical and agronomic properties of biochar from sewage sludge pyrolysed at different temperatures. *J. Anal. Appl. Pyrol* 2013; 102: 124-130.
  37. Mukome FN, Zhang X, Silva LC, Six J, Parikh SJ. Use of chemical and physical characteristics to investigate trends in biochar feedstocks. *J Agric Food Chem,* 2013; 61(9): 2196-2204
  38. Standard Test Method for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass, ASTM, USA.2005.
  39. EPA Method 3051 A, Microwave Assisted Acid Digestion of Sediments, Sludges and Oils US EPA Office of Solid Waste, Washington DC. 2007.
  40. Rajabi B, Khodaverdilo H, Samadi A, and Rasouli SM. Sorption and Desorption of Lead in some calcareous soils of western Azerbaijan province. *J Water Soil.* 2012; 25(6) : 1287-1298.(In Persian)
  41. Khodaverdiloo H, and HamzenejadTaghliabad R. Sorption and Desorption of Lead (Pb) and Effect of Cyclic Wetting-Drying on Metal Distribution in Two Soils with Different Properties. *Water Soil Sci.*2011; 21(1): 149-163. (In Persian)
  42. Jiang TY, Jiang J, Xu RK, and Li Z. Adsorption of Pb (II) on variable charge soils amended with rice-straw derived biochar.*Chemosphere,* 2012; 89(3): 249-256.
  43. Yuan J, Xu R. The amelioration effects of low temperature biochar generated from nine crop residues on an acidic Ultisol. *Soil Use and Management.* 2010; 27(1):110-115.
  44. Zieli ska A, Oleszczuk P, Charmas B, Skubiszewska-Zi ba J, Pasieczna-Patkowska S. Effect of sewage sludge properties on the biochar characteristic. *J. Anal. Appl. Pyrol* 2015; 112: 201-213
  45. Oh TK, Choi B, Shinogi Y, Chikushi J. Characterization of biochar derived from three types of biomass. *J Faculty Agric, Kyushu University.* 2012; 57(1): 61-66.
  46. Chen T, Zhang Y, Wang H, Lu W, Zhou Z, Zhang Y et al. Influence of pyrolysis temperature on characteristics and heavy metal adsorptive performance of biochar derived from municipal sewage sludge. *Bioresour. Technol.* 2014; 164:47-54.
  47. Al-Wabel MI, Al-Omran A, El-Naggar AH, Nadeem M, Usman AR. Pyrolysis temperature induced changes in characteristics and chemical composition of biochar produced from conocarpuswastes. *Bioresour. Technol.* 2013; 131: 374-379.

48. US EPA, Standards for the use or disposal of sewage sludge, Federal Register 58 .1993. 9248–9415.
49. Giles CH, Smith D, and Huitson A. A general treatment and classification of the solute adsorption isotherm. I. Theoretical. *J. Colloid Interface Sci.*, 1974; 47(3): 755-765.
50. Hawari AH, and Mulligan CN. Biosorption of lead (II), cadmium (II), copper (II) and nickel (II) by anaerobic granular biomass. *Bioresour. Technol*, 2006; 97(4): 692-700.
51. Yuan JH, Xu RK, Zhang H. The forms of alkalis in the biochar produced from crop residues at different temperatures. *Bioresour. Technol*, 2011; 102(3): 3488-3497.
52. Kołodyska D, Wntrzak R, Leahy JJ, Hayes MHB., Kwapiński W, Hubicki Z. Kinetic and adsorptive characterization of biochar in metal ions removal. *Chem. Eng. J.* 2012; 197: 295-305.
53. Inyang M, Gao B, Ding W, Pullammanappallil P, Zimmerman A, Cao X. Enhanced Lead Sorption by Biochar Derived from Anaerobically Digested Sugarcane Bagasse. *Separation Science and Technology*. 2011; 46(12):1950-1956.