

Efficient Removal of the Toxic Lead Ions from Contaminated-Sandy Soils using Newly Engineered Carbon Black Nano-adsorbent

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ABSTRACT

Soils contaminated with heavy metals can embarrass a fatal risk to the environment and human life via the direct uptake of the heavy metal-contaminated agricultural crops. Hence, the treatment of metal-contaminated soils is attracting a lot of research activities to reduce the negative impact on the environment. In the current study, I have activated the surface of the carbon black (CB) adsorbent by introducing functional groups capable to efficiently capture the lead (Pb) metal ions from a Pb-contaminated sandy soil. The soil properties (e.g. electrical conductivity, acidity, carbon and nitrogen content, and organic matter) were studied before and after the treatment with the CB adsorbent. I also showed a comprehensive adsorption study in soil-batch extraction experiments, evaluating a series of factors such as the effects of soil pH (pH 3.0 to pH 7.0), Pb concentration into the soil (5-100 mg/L), and the soil temperature (15-50 °C). Furthermore, the recyclability of the adsorbent was highlighted to evaluate adsorption efficiency upon use. The results of the study were remarkable where a 100 % removal efficiency of Pb ions was obtained using only a 40 ppm of the oxidized CB compared to a 60% removal efficiency when using a pristine CB at the same concentration. The adsorption capacity of Pb ions was as high as 100 mg/g at 30 mg/L of oxidized CB adsorbent. The life cycle of oxidized CB adsorbent was also remarkable compared to that of pristine adsorbent. The recyclability data of the functionalized CB has showed an easy regeneration process with an efficient reuse for 5 cycles with 30 % a performance decline of 30 % only from the initial adsorption efficiency.

Keywords: Sandy soils; carbon black; heavy metals contamination; engineering of agricultural materials; removal and adsorption studies.

INTRODUCTION

The liquid wastes discharged from the industrial activities such as manufacturing battery, dyeing of textiles, and metals plating, resulting in the contamination of agricultural soils, crops, and ground water with many heavy metals. Thus, the engineering of new agricultural materials for treating soils contaminated with heavy metal has receiving a great deal of attention, where, soil pollution is one of the most important environmental problems throughout the agriculture field and human health.(Tchounwou et al., 2012; Wu et al., 2014)

Toxic heavy metals are high density metals with high toxicity for living organisms even at very low concentrations. Pb is naturally found in soils at a concentration of 10 to 50 mg/kg.(Madhavan et al., 1989)In urban soils, it often reaches much greater values than normal levels (< 150 mg/kg), due to the widespread use of paints and the other industrial sources.(Aelion et al., 2013) Pb has a high degree of toxicity, and does not degrade over time, however it remains in soils for many of years. (Flora et al., 2012)Hence, Pb-contaminated soils can embarrass a fatal risk to the human body *via* the direct uptake of the Pb-contaminated vegetables and fruits. Typically, Pb causes chronic toxicities, cancer,

disabilities, and even death due to its potential accumulation in different human organisms (bones, muscles, kidney and brain. (Kim et al., 2015) Accordingly, the treatment of Pb-contaminated soils is attracting a lot of research activities to reduce its negative impact on the environment.(Yang et al., 2016). In this regard, different techniques including adsorption, complexation, ion exchange, electro dialysis, precipitation, and reverse osmosis were introduced to remove Pb from wastewater and soils.(Guanxing et al., 2011). For example, Wuana *et al.*,(Wuana et al., 2010) have studied the removal of heavy metals from a contaminated soil using organic chelating acids. This study has showed that the removal efficiency of Pb ions is strongly depending on the nature of the chelates. Thus, engineering and testing new candidate materials for the removal of Pb ions from soils is an issue of interest to improve the removal efficiency of toxic heavy metals.

CB is a nanometer carbon-based material, commercially produced at low-cost by the thermal decomposition or the incomplete combustion of heavy oil or hydrocarbons. CB is receiving a great deal of attention as an adsorbent for the removal of heavy metals from wastewater, (Dong et al., 2017) because it has a form of paracrystalline structure that possesses a high surface area to volume

ratio,(Sebok and Taylor, 2001) a large internal surface area, a highly developed porosity, and a remarkably high mechanical properties.(Biniak et al., 2016; Voet and Aboytes, 1971) However, adsorption properties of CB is affected by its activation process.(Brennan et al., 2002) Thus, researchers have started to modify and update its physical and chemical properties (e.g. surface functional groups, surface charge, specific surface area) to improve its adsorption behavior. (Liu and Cheng, 2019; Suryanto and Zhao, 2016) Polymer grafting of CB is considered one of the most effective techniques to improve the CB properties, where it provides additional functional groups to the CB surface, thus extending its applications. (Tsubokawa, 1992; Wu et al., 2013; Yang et al., 2007) Accordingly, the polymer composite formation of CB is expected to improve the removal efficiency and capacity of heavy metals from wastewater.

In the current study, we engineer and fabricate a recyclable and an efficient adsorbent of CB for agricultural purposes. Typically, we introduce oxygen containing functional groups on the surface of CB through an oxidation process using harsh oxidizing agents (see the details of Figure 1). We discuss the synthesis and the characterization processes of the adsorbent, and also show a comprehensive study about the adsorption properties of the formed material inside a sandy soil, evaluating the synergetic effect on the adsorption behavior. In addition, we illustrate the impact of the fabrication material on soil properties.

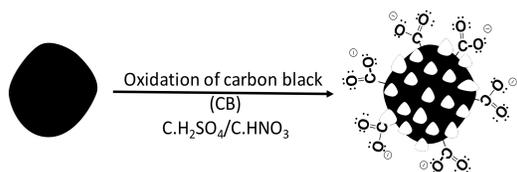


Figure 1: A schematic illustration of oxidation process of CB using harsh oxidizing agents.

MATERIALS AND METHODS

1. Materials

Sulphuric acid, nitric acid, potassium permanganate, hydrogen peroxide, sodium carbonate, sodium hexametaphosphate, ethylenediaminetetraacetic acid (EDTA), lead nitrate, and hydrochloric acid were purchased from El-Gomhouria for Trading Chemicals and Medical Appliances. CB was provided from Denka black Co., Ltd. Deionized water (18.2 MX/cm, produced from Milli-Q) was used to prepare all the solutions used in the study. All the materials used in the study were used as received without further purification steps. The soil used in the study was collected from AlBustan-farm, Damanhour university (latitude 31.03 and longitude 30.46).

2. Activation of CB surface via oxidation

A certain mass of CB was dispersed upon sonication for 2 h in a 100 mL solution of concentrated sulphuric acid/nitric acid mixture (ratio 3:1) which contained a 10.0 g of potassium permanganate. Then, the mixture was magnetically stirred at room temperature for 1 h. The reaction medium was then diluted by adding 400 mL water upon stirring. Finally, the oxidation process was terminated by the addition of 100 mL of hydrogen peroxide (5% w/v). The obtained CB (oxidized form) was washed several times by distilled water, centrifuged, and dialyzed against water till the pH of the medium reached 6.0.(Amornwachirabodee et al., 2018) To show the effect of oxidation process on the structure of CB, a dispersion process of both oxidized CB and pristine CB in water was performed. The dispersed materials were left to stand at room temperature for 1 month.

3. Determination of physical and chemical properties of the soil used in the study

3.1. The electrical conductivity (EC)

One of the important measurements of soils is the EC which is used as an indicator of soil nutrients and fertility. The EC was measured in a soil extract as follows. Typically, a certain weight of the soil was immersed in Milli-Q water with a ratio of 1 to 3. The mixture was sonicated for 10 min using a Branson ultrasonic bath. The suspension was then centrifuged at 10,000 rpm for 10 min. The supernatant was collected and subject to EC measurement using a conductivity meter.(Carmo et al., 2016) The process was repeated twice and an average was recorded in Table 1.

3.2. Soil acidity

Soil pH is a measure of the hydrogen ions concentration in the soil, and it is an indicator of the acidic salts into the soil used for agriculture. To get an ideal pH result, soil samples were oven dried at 90 °C overnight. Then, a soil water suspension of a ratio 1 to 3 was prepared. The suspension was sonicated for 10 min using a Branson ultrasonic bath. The pH of the suspension was then measured using a probe pH-meter.(Carmo et al., 2016) The process was repeated 3 times and an average was reported in Table 1.

3.3. Soil particle size and texture analysis

Soil texture analysis was determined using a hydrometer technique.(Beretta et al., 2014) Prior to measurement, soil sample was ground and sieved to remove soil particles larger than 2 mm in diameter. Then, 50 g of the soil was oven-dried at 90 °C overnight. A solution of 37.5 g of sodium hexametaphosphate and 12.5 g of sodium carbonate was prepared a dispersing agent to help suspension the soil particles. Then, the 50 g dried soil sample was added to a 100 mL of the dispersing agent and the mixture was homogenized for 2 min using a high power mixer. The obtained mixture was then

diluted to a 1 L solution and placed into a 1 L graduated cylinder. The soil mixture into the graduated cylinder was shaken well before recording the hydrometer data. The hydrometer data was recorded at different time intervals to calculate the soil particle size diameters. The particle size analysis yielded an average of 94% sand, 4% clay, and 2% silt. Accordingly, the used soil was classified as a sandy soil through the use of soil-texture triangle. (Dexter, 2004)

3.4. Soil carbon and nitrogen content

Soil carbon and nitrogen content were determined by a drying combustion process using an elemental analyzer (Elementar brand). The carbon and nitrogen contents and their ratio were determined and recorded in Table 1.

3.5. Soil organic matter

Soil organic matter is the fraction of plants or animal tissues found in soil. It is important to evaluate the soil structure, soil water holding capacity, holding capacity of nutrient, and soil infiltration. It was determined through the weight loss on ignition of dried soil sample at 360 °C. (Jensen et al., 2018; Salehi et al., 2011)

4. Soil loading with Pb metal ions

Soil samples were mixed with Pb ions using aqueous solutions of their nitrates. The amount of Pb adsorbed on soil particles was determined as follow. Firstly, the soil was oven dried at 80 °C overnight to reach a constant weight. Then, batches of 10 g of soil samples were added to different concentrations of aqueous Pb solutions (100, 200, 300, 400, 500, and 600 mg/100 mL). The resultant suspensions were shaken for 3 h at room temperature, then was incubated at 30 °C for three week. (Reddy and Chinthamreddy, 2000; Yang et al., 2004) Subsequently, the suspensions were centrifuged at 10000 rpm for 10 min, and the supernatant was carefully decanted and was kept for Pb concentration analysis using atomic absorption spectrometer. The amounts of Pb adsorbed on the soil particles were calculated from the weight difference between the applied Pb concentration and the concentration of Pb in the equilibrium solution. The amount of Pb adsorbed by the soil was found to be 4000 mg/kg. Similar adsorption data was reported by Peter *et al.*, (Peters and Shem, 1992).

5. Pb ions removal from contaminated soil

Batch extraction experiments of the heavy metal from the contaminated soil was done using the activated CB as follows. Typically, different weights of activated CB (5, 10, 20, 30, 40, 50, 60, 70, 80, 90, and 100 mg) were added to 10 mg of contaminated soils. The resultant mixture was dispersed in 100 mL deionized water upon sonication 1 h. (Khodadoust et al., 2005) The CB adsorbent was carefully separated from the reaction mixture by a decantation process after a complete settling down of the sand particles. The

sonication/decantation process was repeated several times to ensure a complete separation of CB from the soil. Subsequently, the CB adsorbent was collected by filtration and oven dried at 80°C overnight.

The adsorption process of Pb metal ions was tested in a series of steps such as the effects of pH on Pb adsorption (from pH 3.0 to pH 7.0), the concentration of Pb (5-100 mg/L), and the soil temperature (15-50 °C). The adsorption process was repeated twice and the average of the data was reported.

6. Pb desorption and recyclability experiments

The Pb loaded-CB was immersed in 100 mL of 1 M HCl/0.1 M EDTA solution and was shaken at 25 °C for 1 h. Then, the mixture was centrifuged at 10000 rpm for 10 min, and the supernatant was carefully decanted and used for Pb concentration detection on an atomic absorption spectrometer. The extracted CB adsorbent was washed several times using a 1 M HCl/0.1 M EDTA solution, followed by Milli-Q water, and finally oven dried for the second run of Pb removal. (Kumar et al., 2018) The recyclability of the adsorbent was thus studied to evaluate its adsorption efficiency.

The removal efficiency (%) and the adsorption capacity (q_e ; mg/g) were calculated using the following equations: (Reddy and Chinthamreddy, 2000).

$$\text{Removal efficiency (\%)} = [(C_i - C_f) / C_i] \times 100$$

$$\text{The adsorption capacity } (q_e) = (C_i - C_f) V / m$$

where: C_i and C_f are the initial and equilibrium concentrations of the metal ion (mg/L), respectively; V is the volume of the metal ion solution (L); and m is the weight of the adsorbent (g).

7. Characterization

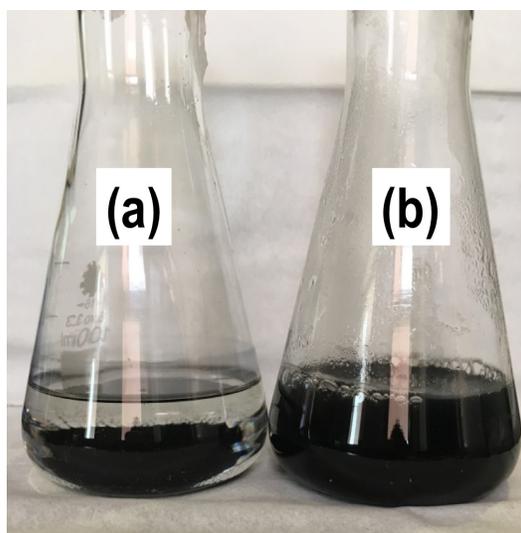
The electron microscope micrographs were captured by a FEI Nova NanoSEM microscope. Atomic absorption spectrometer (Thermo Scientific) was used to determine the concentrations of Pb.

RESULTS AND DISCUSSION

The soil physicochemical properties of the soil used in the study are summarized in Table 1. As notices from the distribution of the soil particles size, a 94% of the soil texture was sand. Thus, the soil used in the study is classified as a sandy soil. (Naga Raju et al., 2017). The soil electrical conductivity of the saturated extract was 120 $\mu\text{s/cm}$, indicating a low ion exchange capacity. The soil pH was 6.3 (slightly acidic), indicating a high nutrient availability which is best for most plants. The soil organic matter was less than 1%, showing a poor soil of living and dead organic based-products. (Naga Raju et al., 2017).

Table 1: Physical and chemical properties of the used soil

Property	Before CB treatment	After CB treatment
EC($\mu\text{s}/\text{cm}$)	120	210
pH	6.3	5.5
Soil texture	94% sand, 4% clay, 2% silt	94% sand, 4% clay, 2% silt
Carbon content(%)	0.8	7.5
Nitrogen content(%)	0.3	0.3
C/N	2.6	25
Organic matter(%)	0.8	0.6

**Figure 2: a** Photo image of CB before (a) and after (b) oxidation process.

The effect of oxidation process on the water dispersibility of CB was evaluated from the photo images of Figure 2. As seen, oxidized CB (image b) has become able to form hydrogen bonds with water molecule (attracted to water molecules) compared to pristine CB. This result indicates the formation of additional ionic functional groups on the surface of CB after the oxidation process.

The scanning electron micrographs of Figure 3 has confirmed the changes of the morphological structure of CB after the oxidation where a rougher and a more hydrophilic surface on oxidized CB was observed (Figure 3 b). (Amornwachirabodee et al., 2018). These results have also revealed the formation of additional cavities onto the surface of CB after the oxidation process due to the use of harsh corrosive and oxidizing reagents. (Wang et al., 2013) The formed CB cavities were highlighted in the schematic illustration of Figure 1. These observations clearly indicate the formation of a highly hydrophilic adsorbent.

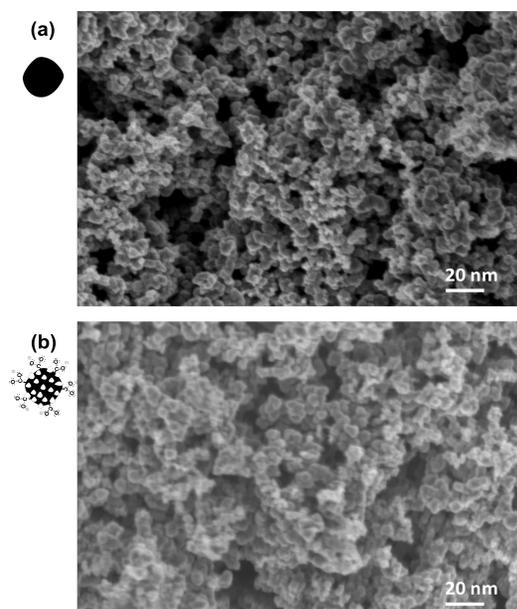
**Figure 3: Scanning electron micrographs of: (a) pristine CB, and (b) oxidized CB.**

Figure 4a shows a photo image of the soil contaminated with Pb ions. The soil particles are being attached to each other probably due to the intermolecular interaction between the soil particles and the Pb ions. (Murray and Quirk, 1990). The amounts of Pb adsorbed on the soil particles were calculated from the weight difference between the applied Pb concentration and the concentration of Pb in the equilibrium solution. The amount of Pb adsorbed by the soil was found to be 4000 mg/kg. Similar adsorption amount of Pb on soil was reported by Peter et al. (Peters and Shem, 1992) Figure 4b shows a schematic illustration of a Pb-contaminated soil. The Pb metal ions are attached to the surface of the soil particles through weak van der waal forces. (Hu et al., 2019; Murray and Quirk, 1990) Figure 4c displays the photo image of the Pb-contaminated soil treated with oxidized CB. As seen, the oxidized CB particles are homogeneously dispersed in the extraction medium due to its hydrophilic character. This property will support and contribute in the removal of the Pb ions from the Pb-contaminated soil. Figure 4d shows a

schematic illustration of how the oxidized CB nanoparticles are being mixed with the soil particles. Since the oxidized CB nanoparticles have a much smaller particle size compared to the particle size of the forces. (Hu et al., 2019; Murray and Quirk, 1990). Figure 4c displays the photo image of the Pb-contaminated soil treated with oxidized CB. As seen, the oxidized CB particles are homogeneously dispersed in the extraction medium due to its

hydrophilic character. This property will support and contribute in the removal of the Pb ions from the Pb-contaminated soil. Figure 4d shows a schematic illustration of how the oxidized CB nanoparticles are being mixed with the soil particles. Since the oxidized CB nanoparticles have a much smaller particle size compared to the particle size of the sandy soil.

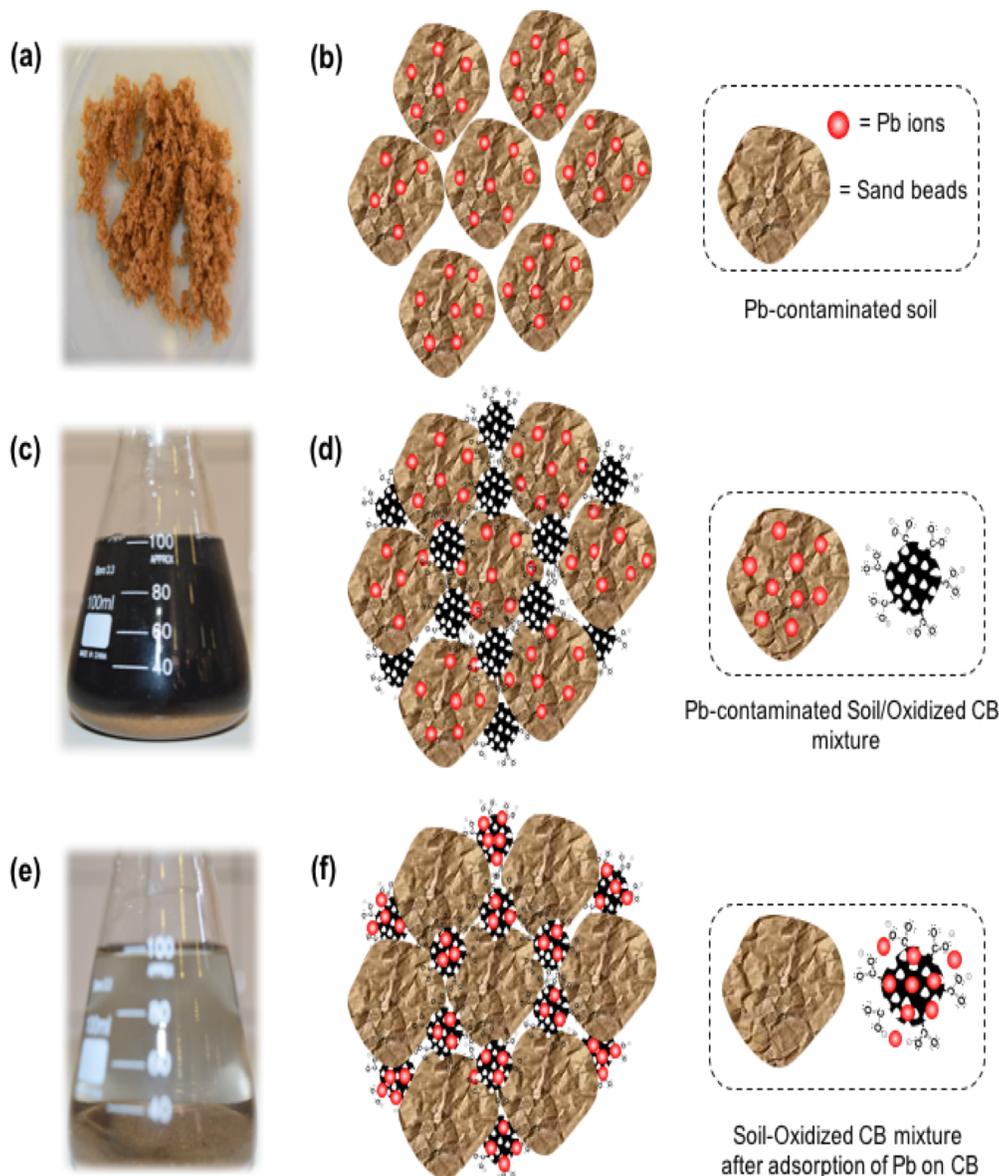


Figure 4: Pb removal process from contaminated soil. (a) A photo image of Pb-contaminated soil. **(b)** A schematic illustration of Pb particles attached to the surface of soil particles. **(c)** A photo image of Pb-contaminated soil mixed with oxidized CB. **(d)** A schematic illustration of oxidized CB nanoparticles attached to the soil particles. **(e)** A photo image of the adsorption medium after the removal of the oxidized CB nanoparticles loaded with the Pb ions. **(f)** The mechanism of how the Pb ions are being adsorbed on the surface of oxidized CB. The rounded rectangle brackets of the figure show the composition of the extraction medium at different stages.

Thus, CB nanoparticles can penetrate in between the soil particles catching efficiently the Pb ions from sandy soil particles which have a low retention capacity for metal ions.(Li, 2006) Hence, the Pb ions can be easily leached out and exchanged during the soil remediation process. Figure 4e shows a photo image of the adsorption medium after the removal of the oxidized CB particles loaded with Pb ions, leaving the soil particles clean. Figure 4f shows the mechanism of how the Pb ions are being adsorbed and attached to the surface of oxidized CB. As seen, the negative ionic groups formed on the surface of the oxidized CB have attracted and attached the Pb positive ions, forming a complex between Pb and CB. The low retention capacity of the sandy soil for Pb ions has also facilitated the exchange process of Pb ions.(Li, 2006; Salmasi and Tavassoli, 2005).

However, soil pH is a key parameter affecting adsorption efficiency of heavy metals.(Ge and Fan, 2011) Thus, the adsorption studies of Pb ions on pristine and oxidized CB were performed in a wide range of pHs. Figure 5 shows the Pb removal efficiency dependence on soil pH. As seen, the Pb ion uptake has increased with the increase of soil pH up to pH 6 in both the pristine and the oxidized CB. The removal efficiency in the case of oxidized CB was higher than that of the pristine CB due to the presence of more carboxylate groups on the surface of oxidized CB. The increase of the removal efficiency with the increase of the soil pH was related to the decrease in the protonation of the carboxylate groups (formation of more negative charges on the surface of CB), leading to an improvement in the interaction between the Pb positive ions and the negative carboxylate groups.(Ge and Fan, 2011) The decrease in the removal efficiency above pH 6 was related to the formation of Pb-hydroxides which decreases the adsorption performance of Pb ions. Table 2. summarizes the collected results of the removal efficiency of the pristine CB and the oxidized CB at different soil pHs.

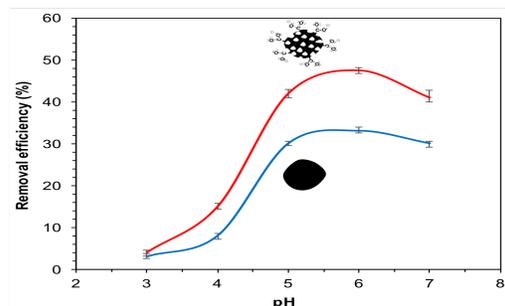


Figure 5: Pb removal efficiency dependence on soil pH treated with: pristine CB (blue curve) and oxidized CB (red curve) using a 20 mg/L Pb aqueous solution at 25 °C.

Table 2: The relation between the solution pH and the removal efficiency of pristine CB and oxidized CB using a 20 mg/L Pb aqueous solution at 25 °C.

Soil pH	Removal efficiency Pristine CB	Removal efficiency Oxidized CB
3.0	3 ± 0.55	44 ± 0.7
4.0	8 ± 0.7	15 ± 0.75
5.0	30 ± 0.5	42 ± 0.85
6.0	33 ± 0.75	47 ± 0.7
7.0	30 ± 0.65	41 ± 1.85

Figure 6 shows the removal efficiency dependence and adsorption capacity dependence on adsorbent doses. As seen, a 50 mg/L of the oxidized CB adsorbent was used to reach a 100% removal of Pb ions from the adsorption medium at pH 6 in room temperature, while a 100 mg/L of the pristine CB adsorbent was used to reach a 100% removal of Pb ions at the same adsorption conditions. The adsorption capacity of Pb ions (q_e) was as high as 100 mg/g at 30 mg/L of oxidized CB adsorbent compared to 60 mg/g for pristine CB adsorbent at the same concentration. This remarkable increase of the Pb ions uptake is attributed to the formulation of a CB adsorbent with a large number of carboxylate groups, which have efficiently captured more Pb ions from the adsorption medium at low concentrations. The adsorption of Pb ions on the oxidized CB adsorbent was schematically illustrated in Figure 7, through a chelation process(Sisombath et al., 2014) between Pb ions and the oxidized CB. Table 3 summarizes the collected adsorption data of oxidized CB and pristine CB adsorbents at different concentrations.

To evaluate the soil temperature effect on the Pb adsorption capacity, the adsorption experiments were done at different soil temperature. As seen from Figure 9 no significant effect on the adsorption behavior of Pb ions was observed with the change of soil temperature.

However, the recyclability of the used adsorbent and recovery of Pb metal ions is one of the most important issues from the environmental and economical point of views.(Manzoor et al., 2019; Niu et al., 2017)Thus, we have performed a life cycle assessment experiments for thepristine and oxidized CBs. The results of Figure 9 have indicated that, after a 5 adsorption/desorption cycles, oxidized CB has showed a 70% adsorption efficiency of Pb ions compared to almost the same ratio for pristine CB. This slight decrease in the adsorption capacity was attributed to the filling of some CB microspheres with Pb ions and the inability of the proposed desorption method to recover these microspheres. These results indicate a good regeneration and reusability of oxidized CB as an efficient adsorbent.

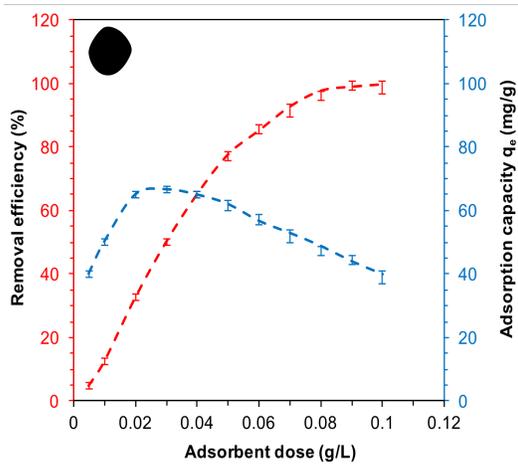
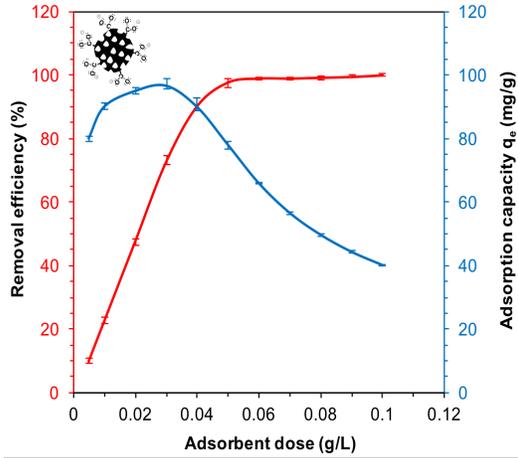


Figure 6: Removal efficiency (red color curves) and adsorption capacity (blue color curves) dependence on adsorbent dose of: pristine CB (lower panel) and oxidized CB (upper panel), measured at pH 6 and temperature 25 °C.

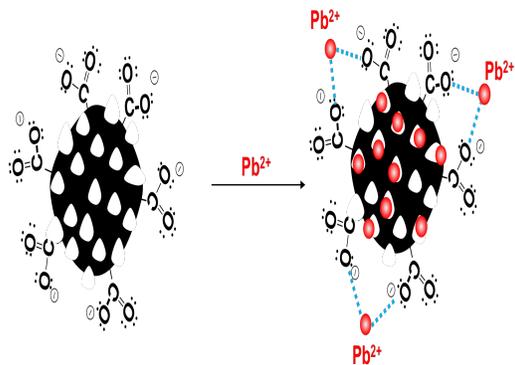


Figure 7: A schematic illustration of the mechanism of capturing Pb ions on oxidized CB.

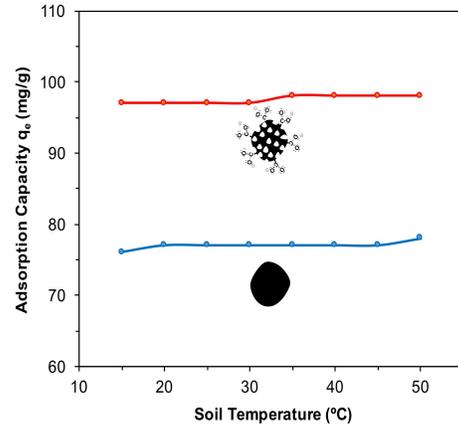


Figure 8: Adsorption capacity dependence on soil temperature of: pristine CB-based adsorption medium (blue color), and oxidized CB-based adsorption medium (red color).

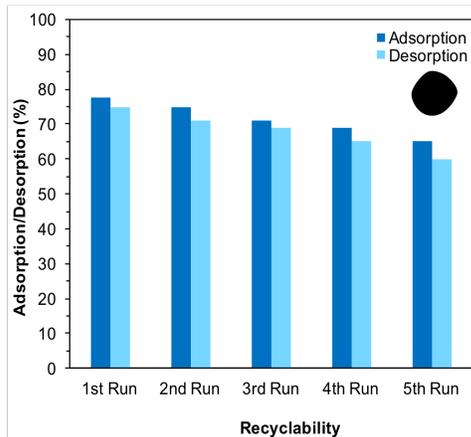
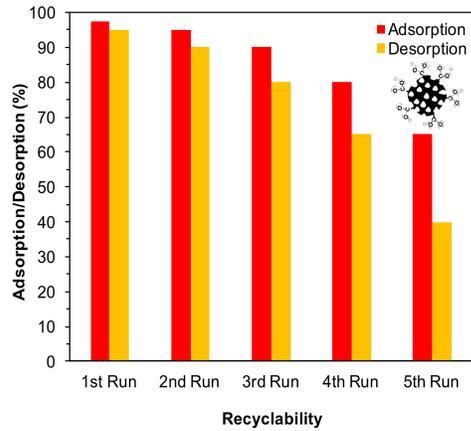


Figure 9: Life cycle assessment of: pristine CB adsorbent (lower panel), and oxidized CB adsorbent (upper panel) for Pb ions removal.

Table 3: Removal efficiency and adsorption capacity data measured at different doses of pristine CB and oxidized CB in a solution of pH 6 and a temperature of 25 °C.

Mass of adsorbent (g)	Pristine CB		Oxidized CB	
	Removal efficiency %	Adsorption capacity q_e (mg/g)	Removal efficiency %	Adsorption capacity q_e (mg/g)
0.005	5.00	40.00	10.00	80.00
0.01	12.50	50.00	22.50	90.00
0.02	32.50	65.00	47.50	95.00
0.03	50.00	66.67	72.50	96.67
0.04	65.00	65.00	90.00	90.00
0.05	77.50	62.00	97.50	78.00
0.06	85.00	56.67	98.50	65.83
0.07	92.50	52.86	98.75	56.43
0.08	97.50	48.75	99.00	49.50
0.09	98.75	43.89	99.25	44.11
0.1	99.50	39.80	99.75	39.90

Table 4: The collected data of adsorption capacity dependence on soil temperature.

Temperature of Soil (° C)	Adsorption capacity of Pristine CB (q_e)	Adsorption capacity of Oxidized CB (q_e)
15.0	76± 0.9	97± 0.1
20.0	77± 0.3	97± 0.2
25.0	77± 0.5	97± 0.5
30.0	77± 0.6	97± 0.75
35.0	77± 0.65	98± 0.05
40.0	77± 0.8	98± 0.15
45.0	77± 0.9	98± 0.6
50.0	78± 0.5	98± 0.7

CONCLUSIONS

We successfully engineered an efficient adsorbent of CB by creating a surface ionic functional groups capable to capture large amounts of the toxic heavy metal Pb from Pb-contaminated sandy soils. The functionalized CB adsorbent has showed an adsorption capacity of 100 mg/g using a 30 mg/L of oxidized CB adsorbent. The recyclability data of the functionalized CB has showed a regeneration and efficient reuse of oxidized CB for 5 cycles with a decline of 30 % only from the initial adsorption efficiency.

REFERENCES

Aelion, C. M., Davis, H. T., Lawson, A. B., Cai, B., and McDermott, S. (2013). Associations between soil lead concentrations and populations by race/ethnicity and income-to-poverty ratio in urban and rural areas. *Environmental geochemistry and health* **35**, 1-12.

Amornwachirabodee, K., Tantimekin, N., Pan-In, P., Palaga, T., Pienpinijtham, P., Pipattanaboon, C., Sukmanee, T., Ritprajak, P., Charoenpat, P., Pitaksajakul, P., Ramasoota, P., and Wanichwecharunguang, S. (2018). Oxidized Carbon Black: Preparation, Characterization and Application in Antibody Delivery across Cell Membrane. *Scientific Reports* **8**, 2489.

Beretta, A. N., Silbermann, A. V., Paladino, L., Torres, D., Bassahun, D., Musselli, R., and García-Lamohte, A. (2014). Soil texture analyses using a hydrometer: modification of the Bouyoucos method. *Ciencia e investigación agraria* **41**, 263-271.

Biniak, S., Pakuła, M., Świątkowski, A., Kuśmierk, K., and Trykowski, G. (2016). Behavior of graphitized carbon blacks in the electrodegradation and sorption of chlorophenoxyacetic acids. *Reaction Kinetics, Mechanisms and Catalysis* **117**, 477-486.

Brennan, J. K., Thomson, K. T., and Gubbins, K. E. (2002). Adsorption of Water in Activated Carbons: Effects of Pore Blocking and Connectivity. *Langmuir* **18**, 5438-5447.

Carmo, D. L. d., Silva, C. A., Lima, J. M. d., and Pinheiro, G. L. (2016). Electrical Conductivity and Chemical Composition of Soil Solution: Comparison of Solution Samplers in Tropical Soils. *Revista Brasileira de Ciência do Solo* **40**.

Dexter, A. R. (2004). Soil physical quality: Part I. Theory, effects of soil texture, density, and organic matter, and effects on root growth. *Geoderma* **120**, 201-214.

Dong, P., Maneerung, T., Ng, W. C., Zhen, X., Dai, Y., Tong, Y. W., Ting, Y.-P., Koh, S. N., Wang, C.-H., and Neoh, K. G. (2017). Chemically treated carbon black waste and its potential applications. *Journal of Hazardous Materials* **321**, 62-72.

- Flora, G., Gupta, D., and Tiwari, A. (2012). Toxicity of lead: A review with recent updates. *Interdisciplinary toxicology* **5**, 47-58.
- Ge, H., and Fan, X. (2011). Adsorption of Pb²⁺ and Cd²⁺ onto a Novel Activated Carbon-Chitosan Complex. *Chemical Engineering & Technology* **34**, 1745-1752.
- Guanxing, H., Jichao, S., Ying, Z., Jingtao, L., Yuxi, Z., Jihong, J., Jincui, W., Haiwei, C., Xi, C., Xiaoping, X., Yuanjing, Z., and Jili, W. (2011). Recent Progress in Research on the Adsorption of Lead in Soil. In "2011 Third International Conference on Measuring Technology and Mechatronics Automation", Vol. 2, pp. 966-969.
- Hu, F., Li, S., Xu, C., Gao, X., Miao, S., Ding, W., Liu, X., and Li, H. (2019). Effect of soil particle interaction forces in a clay-rich soil on aggregate breakdown and particle aggregation. *European Journal of Soil Science* **70**, 268-277.
- Jensen, J. L., Christensen, B. T., Schjønning, P., Watts, C. W., and Munkholm, L. J. (2018). Converting loss-on-ignition to organic carbon content in arable topsoil: pitfalls and proposed procedure. *European Journal of Soil Science* **69**, 604-612.
- Khodadoust, A. P., Reddy, K. R., and Maturi, K. (2005). Effect of different extraction agents on metal and organic contaminant removal from a field soil. *Journal of Hazardous Materials* **117**, 15-24.
- Kim, H.-C., Jang, T.-W., Chae, H.-J., Choi, W.-J., Ha, M.-N., Ye, B.-J., Kim, B.-G., Jeon, M.-J., Kim, S.-Y., and Hong, Y.-S. (2015). Evaluation and management of lead exposure. *Annals of occupational and environmental medicine* **27**, 30-30.
- Kumar, M., Singh, A. K., and Sikandar, M. (2018). Study of sorption and desorption of Cd (II) from aqueous solution using isolated green algae *Chlorella vulgaris*. *Applied Water Science* **8**, 225.
- Li, L. Y. (2006). Retention Capacity and Environmental Mobility of Pb in Soils along Highway Corridor. *Water, Air, and Soil Pollution* **170**, 211-227.
- Liu, C. Y., and Cheng, W. T. (2019). Surface modification and characterization of carbon black through oxidation. *Surface and Interface Analysis* **51**, 316-325.
- Madhavan, S., Rosenman, K. D., and Shehata, T. (1989). Lead in soil: Recommended maximum permissible levels. *Environmental Research* **49**, 136-142.
- Manzoor, K., Ahmad, M., Ahmad, S., and Ikram, S. (2019). Removal of Pb(II) and Cd(II) from wastewater using arginine cross-linked chitosan-carboxymethyl cellulose beads as green adsorbent. *RSC Advances* **9**, 7890-7902.
- Murray, R. S., and Quirk, J. P. (1990). Interparticle Forces in Relation to the Stability of Soil Aggregates. In "Soil Colloids and Their Associations in Aggregates" (M. F. De Boodt, M. H. B. Hayes, A. Herbillon, E. B. A. De Strooper and J. J. Tuck, eds.), pp. 439-461. Springer US, Boston, MA.
- Naga Raju, M., Golla, N., and Vengatampalli, R. (2017). Soil Physicochemical Properties. In "Soil Enzymes: Influence of Sugar Industry Effluents on Soil Enzyme Activities" (N. R. Maddela, N. Golla and R. Vengatampalli, eds.), pp. 5-10. Springer International Publishing, Cham.
- Niu, Y., Li, K., Ying, D., Wang, Y., and Jia, J. (2017). Novel recyclable adsorbent for the removal of copper(II) and lead(II) from aqueous solution. *Bioresource Technology* **229**, 63-68.
- Peters, R. W., and Shem, L. (1992). Adsorption/desorption characteristics of lead on various types of soil. *Environmental Progress* **11**, 234-240.
- Reddy, K. R., and Chinthamreddy, S. (2000). Comparison of Extractants for Removing Heavy Metals from Contaminated Clayey Soils. *Journal of Soil Contamination* **9**, 449-462.
- Salehi, M. H., Beni, O. H., Harchegani, H. B., Borujeni, I. E., and Motaghian, H. R. (2011). Refining Soil Organic Matter Determination by Loss-on-Ignition. *Pedosphere* **21**, 473-482.
- Salmasi, R., and Tavassoli, A. (2005). Using different amendments to reduce heavy metals movement in soils. *International Journal of Environmental Science & Technology* **1**, 295-300.
- Sebok, E. B., and Taylor, R. L. (2001). Carbon Blacks. In "Encyclopedia of Materials: Science and Technology" (K. H. J. Buschow, R. W. Cahn, M. C. Flemings, B. Ilshner, E. J. Kramer, S. Mahajan and P. Veyssi re, eds.), pp. 902-906. Elsevier, Oxford.
- Sisombath, N. S., Jalilehvand, F., Schell, A. C., and Wu, Q. (2014). Lead(II) Binding to the Chelating Agent d-Penicillamine in Aqueous Solution. *Inorganic Chemistry* **53**, 12459-12468.
- Suryanto, B. H. R., and Zhao, C. (2016). Surface-oxidized carbon black as a catalyst for the water oxidation and alcohol oxidation reactions. *Chemical Communications* **52**, 6439-6442.

- Tchounwou, P. B., Yedjou, C. G., Patlolla, A. K., and Sutton, D. J. (2012). Heavy metal toxicity and the environment. *Experientia supplementum* (2012) **101**, 133-164.
- Tsubokawa, N. (1992). Functionalization of carbon black by surface grafting of polymers. *Progress in Polymer Science* **17**, 417-470.
- Voet, A., and Aboytes, P. (1971). Porosity of carbon blacks. *Carbon* **9**, 135-138.
- Wang, Y., Wang, D., and Zhang, H. (2013). Corrosion rate of carbon steel and aluminum alloy in sulfuric acid and hydrochloric acid solutions accelerated by microwave heating. *Asia-Pacific Journal of Chemical Engineering* **8**, 483-493.
- Wu, B., Wang, G., Wu, J., Fu, Q., and Liu, C. (2014). Sources of heavy metals in surface sediments and an ecological risk assessment from two adjacent Plateau reservoirs. *PloS one* **9**, e102101-e102101.
- Wu, X., Qiu, J., Liu, P., Sakai, E., and Lei, L. (2013). Polystyrene grafted carbon black synthesis via in situ solution radical polymerization in ionic liquid. *Journal of Polymer Research* **20**, 167.
- Wuana, R. A., Okieimen, F. E., and Imborvungu, J. A. (2010). Removal of heavy metals from a contaminated soil using organic chelating acids. *International Journal of Environmental Science & Technology* **7**, 485-496.
- Yang, J. Y., Yang, X. E., He, Z. L., Chen, G. C., Shentu, J. L., and Li, T. Q. (2004). Adsorption-Desorption Characteristics of Lead in Variable Charge Soils. *Journal of Environmental Science and Health, Part A* **39**, 1949-1967.
- Yang, Q., Wang, L., Xiang, W.-d., Zhou, J.-f., and Tan, Q.-h. (2007). Preparation of polymer-grafted carbon black nanoparticles by surface-initiated atom transfer radical polymerization. *Journal of Polymer Science Part A: Polymer Chemistry* **45**, 3451-3459.
- Yang, Z., Fang, Z., Zheng, L., Cheng, W., Tsang, P. E., Fang, J., and Zhao, D. (2016). Remediation of lead contaminated soil by biochar-supported nano-hydroxyapatite. *Ecotoxicology and Environmental Safety* **132**, 224-230.

الملخص العربي

إزالة عالية الكفاءة لأيونات الرصاص السامة من الأراضي الرملية الملوثة باستخدام ممتص من حبيبات اسود الكربون متناهية الصغر المهندسة حديثاً

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يمكن أن تسبب التربة الملوثة بالمعادن الثقيلة في احداث خطورة بالغة على البيئة وحياة الإنسان وذلك من خلال تناول المحاصيل الزراعية الملوثة بالمعادن الثقيلة. وبالتالي، تجتذب معالجة التربة الملوثة بالمعادن الكثير من الأنشطة البحثية لتقليل التأثير السلبي على البيئة. في الدراسة الحالية، قمت بتنشيط سطح مادة الكربون الأسود عن طريق إدخال مجموعات وظيفية قادرة على التقاط أيونات الرصاص المعدنية بكفاءة وذلك من تربة رملية زراعية ملوثة. تمت دراسة خواص التربة (مثل التوصيلية الكهربائية، درجة الحموضة، محتوى الكربون والنيروجين، والمواد العضوية) قبل وبعد المعالجة باستخدام ممتزات الكربون الأسود. لقد أظهرتالدراسة أيضاًتقييم سلسلة من عواملالامتزاز مثل آثار درجة الحموضة في التربة (درجة الحموضة من ٣,٠ إلى ٧,٠)، وتركيز الرصاص في التربة (٥-١٠٠ مجم/ لتر)، و درجة حرارة التربة (١٥-٥٠ درجة مئوية). علاوة على ذلك، تم تسليط الضوء على إعادة التدوير للممتزات داخل التربة الرملية لتقييم كفاءة الامتزاز. كانت نتائج الدراسة رائعة حيث تم الحصول على كفاءة إزالة ١٠٠٪ من أيونات الرصاص باستخدام ٤٠ جزء في المليون فقط من الكربون الأسود المؤكسد مقارنة بكفاءة إزالة ٦٠٪ عند استخدام الكربون الأسود البكر عند نفس التركيز. كانت قدرة امتصاص أيونات الرصاص عالية تصل الي ١٠٠ ملغم/ غرام عند ٣٠ ملغم / لتر من ممتزات الكربون الأسود المؤكسد. كانت دورة حياة الامتزازللكربون الأسود المؤكسد أيضاً ملحوظة مقارنةً بدورة حياة الامتزاز للكربون الأسود البكر. أظهرت البيانات التحليلية قابلية إعادة التدوير للكربون الأسود بفعالية لمدة ٥ دورات بنسبة انخفاض ٣٠٪ في الأداء من كفاءة الامتزاز الأولية.