



Desorption of Lead Adsorbed from Contaminated Water by Fishbone and Charred Spinach/Grape

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Authors' contributions

This work was carried out in collaboration between all authors. Lovell Agwaramgbo designed the study, performed the statistical analysis, managed the analyses of the study, wrote the protocol, and wrote the first draft of the manuscript. Ruby Broadway, Shelby Edwards, and Tanesia Patterson conducted the experiments and managed literature searches. All authors read and approved the final manuscript.

Original Research Article

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ABSTRACT

Aims: We have studied the adsorption of lead onto many substrates such as biomaterials and inorganic adsorbents and found these substrates to have very high adsorptive capacities for lead. However, limited studies have reported desorption of lead adsorbed by these substrates under mechanical agitation and neutral pH conditions. The study reported here investigated not only the adsorption of lead from contaminated water by biomaterials such as fishbone from stock, salmon, and drum fish, and charred spinach and grapes) but also the bioavailability via desorption of the adsorbed lead when mechanically agitated with deionized water under neutral conditions.

Place and Duration of Study: School of Science, Technology, Engineering, and Mathematics, Dillard University, Between January 2013 and May 2013.

Methodology: Fishbone and charred spinach and grapes were exposed to 1300 PPM lead solution under stirring at room temperature for 48 hrs. The amount of lead adsorbed by each bio-substrate was calculated by difference between control sample and residual

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lead in the supernatant from each substrate's reaction vessel. Each exposed substrate was mechanically agitated with deionized water for 48 hr at room temperature. The amount of lead desorbed into the water was analyzed using EPA Method 6010 (Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)).

Results: The order of percent lead adsorption is Salmon Fishbone (99.9%) > Drum Fish bone (99.7%), > Stock Stock fishbone (86%)> Charred Grape (82% > Charred Spinach (44%) while the order of desorption is Charred grape (6.4%) > Drum fishbone (2%) ~ Charred Spinach (2%) > Salmon Fishbone (0.06%) > Stock Fishbone (0.017%).

Conclusion: The data suggests that very little desorption of adsorbed lead on various substrates occurred and that there is varying lead-adsorption capabilities for various substrates. Furthermore, charring biomaterials diminishes their ability to adsorb lead from contaminated water.

Keywords: Chemisorption; physisorption; adsorption; desorption; lead; bioremediation.

1. INTRODUCTION

Natural and man-made disasters have been known to expose our environment (air, water, and soil) to organic and inorganic pollutants, specifically, heavy metals such as lead [1-5]. Soil contamination by lead and other heavy metals from various sources present a serious health challenge in many urban cities such as New Orleans [6-8]. Majority of the residential and commercial buildings in New Orleans are more than 39-40 years old and pose the possibility of lead paint contamination. Frequent flooding causes sewage overflow and the transport of sewage, lead paints, and other heavy metal pollutants to non-source points across urban neighborhoods such as New Orleans, Louisiana [7,9-10]. Research studies by Mielke and his collaborators showed high levels and wide distribution of lead across New Orleans neighborhoods. Their studies concluded that lead contamination of US communities such as New Orleans and Minnesota is a function of city size [11-12]. Furthermore, in our soil sampling analysis of several sites in East and West Banks of New Orleans after Hurricane Katrina, the average lead levels was about 1300-1400 PPM.

The concern for the potential exposure of hazardous toxicants such as lead and arsenic to the New Orleans environment was widely assumed to have been exacerbated by the flood water brought by hurricane Katrina [1-3,13]. Residents such as New Orleanians are worried about the safety of their homes and soils because lead is a toxic soil, water, and air contaminant that poses serious human health risks [14-19]. Several studies have demonstrated the ability of many substrates to adsorb lead from contaminated waters: Deligiannakis reported the use of organo-clay [20], Singh on phosphatic clay [21] and Agwaramgbo on Louisiana red clay [22]. Other biomaterials have been studied for their potential in heavy metal remediation via adsorption. These biomaterials used for the adsorption of various heavy metals have been reported by Agwaramgbo [22-26], Igwe [27], Zvinowanda [28], Ma [29], Minamisawa [30], and Venkatesan [31]. Agwaramgbo [22-23] found that charcoal (activated carbon) effectively removed lead from contaminated water far more than uncharred plant materials. It is hoped that if these plant materials are charred, they would remove more lead than the uncharred materials. Furthermore, the bioavailability of soil adsorbed lead can become another pathway for lead contamination and exposure. Very few studies have examined the availability or desorption of adsorbed lead on biomaterials under neutral conditions [13,21,32]. New Orleans is one of the capital cities in US for seafood, such as fish, crawfish, crab, and shrimp to mention a few. The un-edible parts (bone, shell) of these organisms are cheap, abundant, and considered a waste thrown in the

garbage. Furthermore, Hyder examined the use of bone char and bio-char in the sorption of hexavalent chromium [33]. Thus, this study decides to investigate not only the adsorption of lead by fishbone and charred spinach and grape but also if physical or mechanical disturbance of lead that had adsorbed on these substrates could desorb through agitation with clean water.

2. MATERIALS AND METHODS FOR LEAD ADSORPTION

The lead nitrate and charcoal were purchased from Aldrich Chemicals and were used without further purification. Stockfish was obtained from Norway while spinach and grapes were obtained from a local Wal-Mart store.

2.1 Preparation of Lead Nitrate Solution 1300 ppm

Using an analytical balance, 1.3 g of lead Nitrate from Fisher Scientific (L6200) was dissolved in enough deionized water (added incrementally) to give a liter of solution. Then a stirring bar was dropped into the volumetric flask and the mixture was stirred until all the lead was completely dissolved. The flask was wrapped with aluminum foil to avoid much exposure to light while the solution continued to stir at room temperature until it was used.

2.2 Preparation of Charcoal and Solid Substrates

Three 50 mL centrifuge tubes were charged with 4.0 g of charcoal (CC-S) bought from Aldrich chemicals.

2.3 Preparation of Stock Fishbone Substrate

Six-2ft dried stock fishbone from Norway bought from a local store deboned after soaking in water at room temperature for 3 hr. Similarly, salmon and Drum fish bones obtained from local restaurants were deboned after boiling in hot water for 0.5 hr. Each type of fishbone was respectively washed with deionized water and dried in an oven at 50°C for 24 hrs. The dried bones were respectively pulverized using a blender. Three sets of 50-mL centrifuge tubes were charged with 4.0 g of the stock fishbone (SFFB-S), Salmon fishbone (SalFB-S), and Drum fishbone (DFB-S), respectively.

2.4 Preparation of Charred Spinach

Spinach (100 g) bought from local grocery store was washed with distilled water and patted dry with kimwipes. The spinach was put in a metal basket and placed in an oven at 90 °C for 24 hr to dry. The dried spinach was transferred into a 500 mL beaker, covered with a wash glass and heated in an oven at 200 °C until it is charred. The charred spinach material is ground using mortar and pestle. The ground material was sieved using a 250 µm sieve. Three centrifuge tubes were each charged with 4.0 g of the charred spinach and labeled CSP-S.

2.5 Preparation of Charred Grape

Grape (100 g) bought from local grocery store was washed with distilled water and patted dry with kimwipes. The grapes were put in a 500 mL beaker and placed in an oven at 90°C for 24 hr to dry. The dried grapes was transferred into a 500 mL beaker, covered with a

wash glass and heated in an oven at 200°C until it is charred. The charred grape is ground using mortar and pestle. The ground material was sieved using a 250 µm sieve. Three centrifuge tubes were each charged with 4.0 g of the charred grape and labeled CG-S.

3. ADSORPTION AND DESORPTION STUDIES

3.1 Adsorption Reaction of Lead Solution with the Charred Substrates

Into each of the respective triplicate centrifuge tubes containing the substrates was added 50 mL of 1300 ppm of lead nitrate solution prepared above.

The tubes and their contents were vortexed, secured tightly on a heavy duty Eberbach 6000 shaker, and agitated for 48 hr at room temperature.

3.2 Sample Preparation and Analysis

3.2.1 Sample preparation

After 48 hrs, the shaker was stopped and the centrifuge tubes and their contents were centrifuged at 3000 rpm for ten minutes. The resulting supernatant in each tube was transferred into another labeled clean centrifuge tube. The solid adsorbents were stored for the desorption studies while all the labeled centrifuge tubes with the liquid contents were labeled and stored in the refrigerator to be sent to PACE Analytical Services, Inc. for lead analysis. The lead concentration (in ppm) in the liquid from each reaction tube was analyzed using EPA Method 6010 (Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)). Note that PACE Analytical Services, Inc is a commercial environmental laboratory that is accredited in accordance to the National Environmental Laboratory Accreditation Conference (NELAC).

3.3 Desorption Studies using Mechanical Agitation

3.3.1 Desorption of adsorbed lead and sample analysis

To each of the residue samples from the adsorption reaction (SFFB-S, SalFB-S, DFB-S, CC-S, CSP-S, and CG-S) above was added 25 mL of deionized water. The resulting mixture was vortexed and then agitated on a shaker for 48 hr. at room temperature as in adsorption experiment above. After the 48 hrs agitation period, the centrifuge tubes and their contents were centrifuged at 3000 rpm for ten minutes. The resulting supernatant in each tube was transferred into another labeled clean centrifuge tube. The labeled centrifuge tubes with their liquid contents were sent to PACE Analytical Services, Inc. for lead analysis as stated above. The lead concentration in these samples represents the amount of desorbed or available lead under such physical or mechanical agitation and neutral conditions.

4. RESULTS

Data on Table 1 shows residual lead in ppm in each reaction tube after contaminated water was treated with each solid substrate (stock fishbone (SFFB-S); salmon fishbone (SalFB-S); drum fishbone (DFB-S), charcoal(CC-S), charred spinach (CSP-S), and charred grape (CG-S))for 48 hr. Table 2 shows the percent of lead adsorbed by each substrate. Table 3 shows the amount of adsorbed lead by each substrate and desorbed lead, respectively versus the

amount of lead desorbed from each substrate by water after 48 hrs of mechanical agitation on a shaker.

Table 1. Residual lead after 48 hr reaction of aqueous lead solution with biomaterials

Substrate	Control	SFFB-S	SalFB-S	DFB-S	CC-S	CSP-S	CG-S
Reaction 1	1300	173	0.93	2.65	0.25	718	225
Reaction 2	1315	185	0.91	3.1	0.21	726	228
Reaction 3	1295	186	0.93	5.5	0.27	732	215
Average Residual[Pb]	1303	181	0.92	3.75	0.24	725	223
STD. Dev	8.5	5.91	0.01	1.25	0.023	5.74	5.68
SQRT	1.73	1.73	1.73	1.73	1.73	1.73	1.73
STD Err	4.91	3.41	0.005	0.72	0.01	3.31	3.21

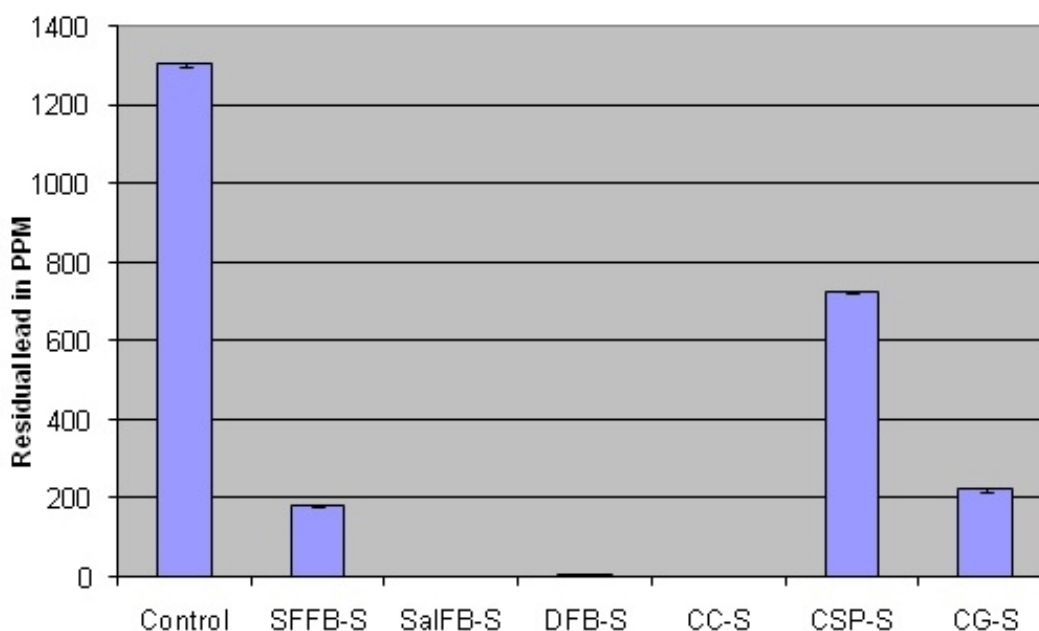


Fig. 1. Residual Lead Concentration after Lead Solution was treated with substrates for 48 hr at 25°C

Table 2. Percent lead adsorbed by each biomaterial calculated as the the difference between the initial concentration before reaction [Pb control] and the residual concentration after reaction control and multiplied by 100; { [Pb Ctr] – [residual Pb]/[Ctr Pb]} X 100

Substrate	Control	SFFB-S	SalFB-S	DFB-S	CC-S	CSP-S	CG-S
% Pb adsorbed	0	86.07	99.93	99.71	99.98	44.35	82.92

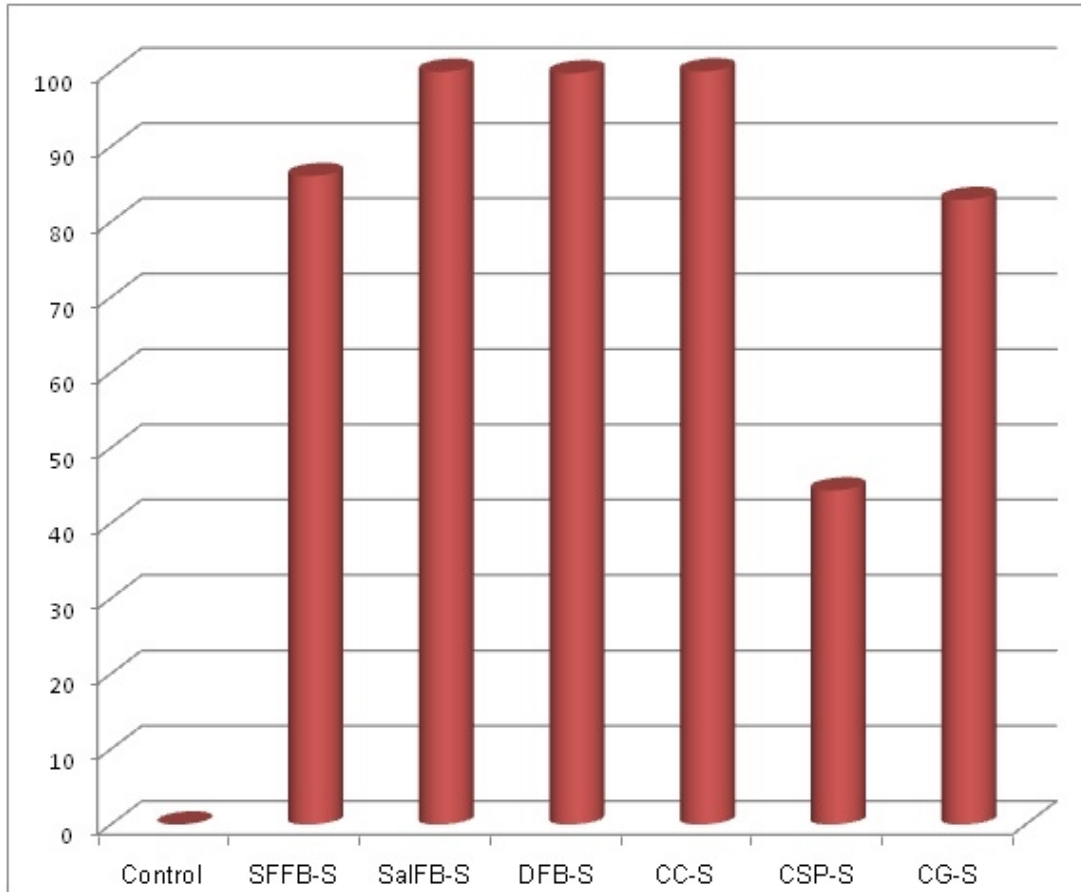


Fig. 2. Percent of Lead Adsorbed by the Substrates

Table 3. Adsorbed versus Desorbed [Pb] by the Biomaterials after 48 hr Mechanical Agitation

Substrate	SFFB-S	SaIFB-S	DFB-S	CC-S	CSP-S	CG-S
Adsorbed lead	1122	1302	1300	1303	578	1081
Desorbed Pb	0.2	0.8	26	0.2	12	69

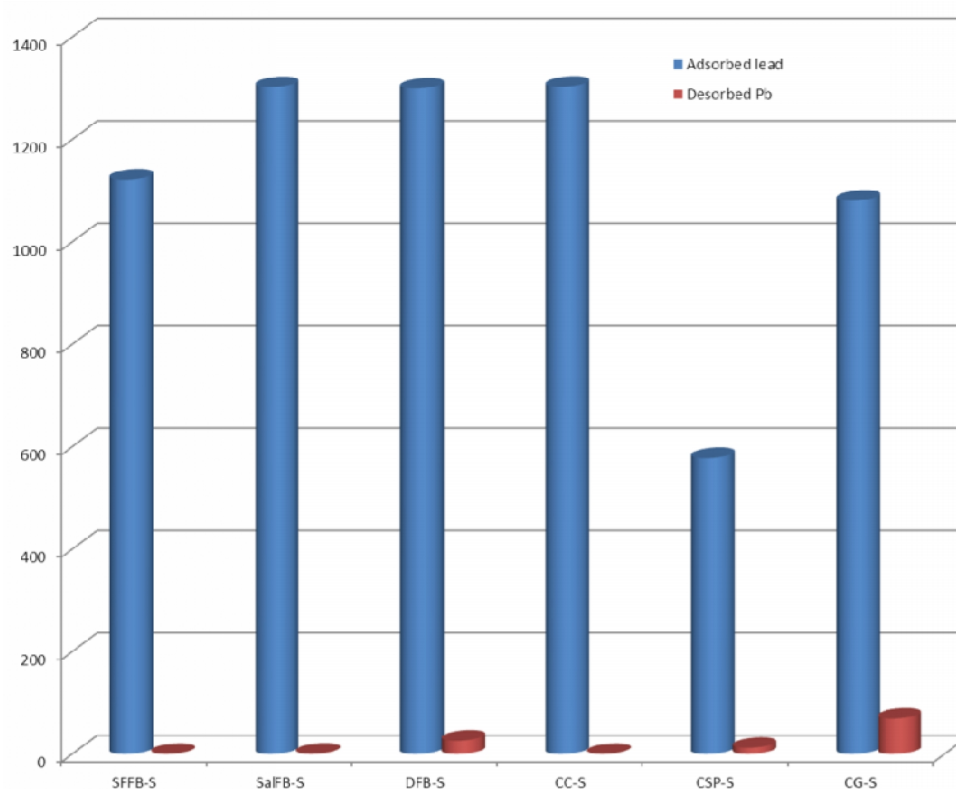


Fig. 3. Adsorbed lead by substrates versus Desorbed lead from substrates

5. DISCUSSIONS

Table 1 and Figs. 1 and 2 clearly suggest that charred spinach and grape adsorbed the least amount of lead when compared to charcoal (activated carbon) or fishbones. However, in previous study in which unheated and uncharred spinach were used, lead adsorption was 98% for spinach and 96% for charcoal [22]. The data in Table 3 and Fig. 3 suggest that charring some biomaterials such as spinach, reduces their adsorption capacity but also increases the desorption of the adsorbed lead. Although the percent of lead adsorbed by stock fishbone (86%) is about the same as charred grape (83%), yet, desorption of lead from charred grape was 345 times the desorption from stock fishbone. These results suggest that fishbone adsorbs lead tighter than the grape or spinach. Agwaramgbo [24] also reported that heating biomaterials degrades their adsorbing strength and capacity. Also, even though charred grape adsorbed twice as much lead as charred spinach, it desorbed 5.7 times more lead than charred spinach. It is interesting to note that charcoal (activated carbon) adsorbed more lead than stockfish, yet equal amount of desorption occurred in both suggesting that both substrates held their adsorbed lead very tightly.

6. CONCLUSIONS

Very little desorption of lead adsorbed by most of the biosorbents under 48 hours of mechanical agitation with deionized water. Lead adsorbed to stock fish and salmon fish

bones did not desorb in any appreciable extent just like in the case of activated carbon. Stockfish and salmon fish bones held the adsorbed lead as tightly as activated carbon. Charring of some biomaterials such as spinach and grapes significantly reduced their lead-adsorbing capacity [24]. Singh [21] in his sorption and desorption behavior in the heavy metal interactions with phosphatic clay suggested that there are several processes and factors that control the sorption of metals as well as their desorption behavior. In either case, the physical, chemical, and biological transformation can minimize or maximize the mobility of metals. Thus, the bioavailability of metals is related to solubility rather than than concentration of adsorbed metal. Furthermore, metal desorption is is dependent on the nature of the extraction solvent (solubility of adsorbed metal , the pH) and the strength of the interaction of metal and the adsorbent such as precipitation, absorption, adsorption, and electrostatic attractive forces. Charring of spinach and grape has a destructive effect on its constituent polyphenols (tannins) [24,34], or oranic matter content [32] and may affect one or more of these processes by degrading one or more constituents responsible for the interactions with metals. Thus, the adsorption and desorption behavior observed with charred spinach and grape is in agreement with observations by Agwaramgbo [24], Singh [21], Vega [32], and England [34]. Thus, Flood water that does not disturb the soil will not be able to desorpd and transport adsorbed lead on biomaterials used in this study except for charred grape.

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COMPETING INTERESTS

Authors declare that there are no competing interests.

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