Fish Bones Proving Their Worth in the De-leadification of Contaminated Water

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Authors’ contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

ABSTRACT

Lead is among the heavy metals that contaminate our soil and water. Chronic exposure to lead has been reported to have serious health implications to humans, animals, and plants as well as our food, soil, and water safety. Adsorption onto biomaterials is one of the most promising processes for heavy metal remediation of contaminated water. In order to assess and compare the efficacy of unmodified and unactivated fish bones, Na₂CO₃, and Na₃PO₄ as sorbents in remediating lead contaminated water, triplicate samples of fish bones from three types of fish and the carbonate and phosphate salts were separately exposed to 1400 PPM lead nitrate solution under stirring at room temperature for 24 hrs. The residual lead after the exposure period was analyzed using EPA Method 6010 (Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)). The percent lead removed from the contaminated aqueous solution by each fish bone, carbonate and phosphate salts were separately exposed to 1400 PPM lead nitrate solution under stirring at room temperature for 24 hrs. The residual lead after the exposure period was analyzed using EPA Method 6010 (Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)). The percent lead was calculated. Lead removal by the fish bone was greater than 99% for each type of fish bone used. The results further suggest that the fish bones removed slightly more lead than sodium carbonate and sodium phosphate. These results suggest that unmodified fish bone is a highly effective biomaterial for removing lead from contaminated water.
Keywords: Fish bone; contaminated water; adsorption; lead; bioremediation; chemisorption.

1. INTRODUCTION

Global appetite for industrial and agricultural activities has led to reoccurring incidences of lead pollution in many urban cities and rural areas. Historically, lead pollution results from a variety of human activities such as past practices of lead related industrial activities by battery, paint, mining, ammunition, plumbing pipe, agricultural fertilizer, insecticide, pesticide, oil and petrochemical industries. Lead contamination of water above permissible levels can cause elevated blood lead levels [1-3], spontaneous abortion [4], infant mortality [5], and fetal death and reduction in birth rates [6]. The potential exposure of hazardous lead to citizens is widely exacerbated in rural areas due to lack of water regulations and treatment [7-8]. The lack of clean water for human consumption and activities will pose a major challenge globally if water management, pollution control, and regulations are not enacted and enforced.

To that end, many researchers across the globe have devoted their efforts towards the development of a variety of methods with wide-ranging degrees of success for lead removal from contaminated water. Traditional methods such as ion exchange, phytoextraction, reverse osmosis, electrodeposition, chemical precipitation, and adsorption have been used to remove heavy metals, including lead from contaminated water, waste water, and aqueous solutions [9,10]. However, many of these remediation processes have some inherent disadvantages such as incomplete remediation in phytoremediation, prohibitive cost in electrodeposition, and introduction of toxic chemical reagents and transformation products that may need additional remediation in chemical precipitation and chelation. Consequently, alternative cheap and safe methods to remove heavy metals from water are needed. Adsorption, a process in which chemical species, in this case, lead ions are adsorbed by the surface of the adsorbent via electrostatic or chemical interaction attracted much attentions because it could be simple, cheap, and safe. Solid sorbents such as clay [11,12], phosphate containing substrates [13], phosphate rock [14], and apatite II [15], molecular sieve, phosphate and carbonate salts [16], and coconut fiber [17] have been used to remove heavy metals from water. Although these sorbents were able to effectively remove heavy metals from contaminated water, however, they are either modified, synthetic, relatively scarce, or expensive. None the less, it is worthy to note that the adsorption of heavy metals using apatite II, phosphate rock and sodium phosphate and sodium carbonate had very high metal removal capacity and could be attributed to stability of metal-phosphate compounds. Since deJong reported in 1926 that fish bone contains calcium phosphate similar to apatite [18], various research work utilizing various forms of fish bone have reported. Some of these research work include but not limited to (a) Cobalt removal by animal bones [9], (b) lead removal by fish bone waste hydroxyapatite powder [19], (c) immobilization of lead with nanocrystalline carbonated apatite present in fish bone [20], (d) anchoring hazardous metal ions using modified fishbone [21], (e) lead removal using unmodified fishbone [22], (f) lead removal using waste fish bone via ion exchange [23], and (g) desorption of lead adsorbed by fish bone [24]. Thus, fish bone has become an attractive cheap and abundant waste for in-situ lead stabilization from contaminated water. Unfortunately, much of the research using fish bone reported above used either chemically modified and activated fish bones or conditions. Results from previous studies demonstrated that sodium phosphate and sodium carbonate effectively removed lead from aqueous solutions at room temperature [16], this project investigates the efficacy of different unmodified and unactivated fish bones (known to contain phosphate and carbonated apatite [20]) for lead removal from contaminated aqueous solutions and compare the results with those of sodium phosphate and sodium carbonate.

2. MATERIALS AND METHODS

2.1 Preparation of Lead Nitrate Solution 1400 ppm

Following the procedure described by Agwaramgbo [16], 1.4 g of anhydrous lead nitrate from Aldrich Chemicals was dissolved in a 1000 ml volumetric flask and enough deionized water was added to the mark to give a liter of solution. The mixture was stirred until all the lead was completely dissolved. The flask was stored in the dark to avoid much exposure to light while the solution continued to stir at room temperature until it was used.
2.2 Preparation of Fishbone Substrates

Dried stock fish from Norway was bought from a local store while the salmon and drum fish were obtained from local restaurants in New Orleans. Enough stock fish (6-3ft stock-fish), waste salmon and drum fish bones from local restaurants were defleshed after boiling in hot water for one hour. 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 and sieved with a 250 µm sieve. Three sets of triplicate 50-ml centrifuge tubes were charged with 4.0 g of each of the fish bones and labeled Stockfish Fish Bone (SFFB), Salmon Fish Bone (SFB), and Drum Fish Bone (DFFB), respectively.

2.3 Preparation of Sodium Carbonate and Sodium Phosphate Substrates

Following the procedure described by Agwaramgbo [16], two sets of triplicate 50-ml centrifuge tubes were respectively charged with 4.0 g of solid sodium carbonate and sodium phosphate purchased from Aldrich Chemicals without further purification.

2.4 Adsorption Experiments

Following the procedure of Kizilkaya, the adsorption studies were carried out in triplicate 50 ml polycarbonate centrifuge tubes containing 4 g of the adsorbent (stock fish bone, Salmon fish bone, drum fish bone, sodium carbonate, and sodium phosphate) and 40 ml of aqueous lead nitrate (Pb(NO$_3$)$_2$) prepared above at room temperature. The mixture in each tube was vortexed for 30 seconds and agitated on a heavy duty Eberbach 6000 shaker for 24hr at room temperature. Triplicate 40 ml samples of the lead nitrate solution prepared above serving as control were not treated with any adsorbent but were similarly vortexed and agitated like the rest of the samples.

2.5 Sample Preparation and Analysis

After 24hrs, 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 and stored in the refrigerator to be sent to PACE Analytical Services, Inc. for lead analysis. The lead nitrate concentration (in ppm) in the liquid from each reaction tube was analyzed using EPA Method 6010 (Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)). Standard errors of the means were calculated and percent lead removed and lead removal capacity for each adsorbent were calculated. The lead adsorbed fish bone, carbonate, and phosphate wastes were picked up and disposed by a state licensed hazardous waste disposal company.

The adsorption capacity (mg/g) for each adsorbent was calculated using the equation q = (V/$W_g$)($C_i$-$C_f$) reported by Kizilikaya [23] where q = adsorption capacity; $C_i$ = initial lead ion concentration in mg/L; $C_f$ = final lead ion concentration after the 48 hr of adsorption time in mg/L; VL = volume of aqueous lead solution used in liters; and $W_g$ = mass of adsorbent in grams.

The lead removal efficiency for each adsorbent was calculated using the formula: $%R = (C_i- C_f)/ C_i * 100$ where $C_i$ = initial lead ion concentration in mg/L; $C_f$= final lead ion concentration after the 48 hr of adsorption time in mg/L.

3. RESULTS AND DISCUSSION

The results from the experiments described in this study and shown in Figs. 1 and 2 clearly demonstrate that waste fish bones efficiently adsorb Pb(II) ion from the contaminated aqueous solution. Furthermore, in comparing the three fish bone adsorbents, it is evident that the difference in their adsorption efficiency and capacity are statistically insignificant under the adsorption conditions. These results are in agreement with the 99% lead removal reported by Ozawa and Kanahara [19] in which lead solution was exposed to fishbone heated at 600ºC for activation. When lead removal by the fish bones were compared to those of sodium carbonate and sodium phosphate, fish bones (99%) are only 2-3% more effective in lead removal than carbonate (97%) or phosphate (96%). Although the chemical composition of the fish bones may differ from that of sodium carbonate or sodium phosphate, they all have phosphate and or carbonate groups. This observation further supports the findings by Giammar that fish bone contains both phosphate and carbonate apatite [20] and the FT-IR results by Kizilkaya which showed FT-IR peaks at 1020 cm$^{-1}$, 963 cm$^{-1}$, 600 cm$^{-1}$ and 558 cm$^{-1}$ for the phosphate group vibrations and peaks at 1413 cm$^{-1}$ and 872 cm$^{-1}$ for the stretching and bending modes for the carbonate groups. Additionally, the results in this
study is buttressed by the findings reported by Agwaramgbo et al. [16] in lead nitrate was exposed to solid chlorides, carbonates, and phosphates of sodium and calcium. The order of percent removal efficiency is NaCl (31%) < CaCl₂ (63%) < Na₂HPO₄ (95.8%) < Na₂CO₃ (97%) < CaCO₃ (99.9%). The results suggest that for both sodium and calcium salt adsorbents, the carbonate was the most efficient. Comparison of the sodium and calcium salt adsorbents, the calcium salts were better adsorbents. Thus, the results are in line with the findings in this study where the three fish bones containing calcium apatite proved to have better lead removal efficiency than sodium carbonate and sodium phosphate.

The Pb to Pb(NO₃)₂ ratio was used to calculate the initial and final (Pb(II) ion concentrations in the aqueous phase for each adsorbent reaction and are reported in Table 1 below.

The adsorption capacity (mg/g) for each adsorbent using the equation \( q = \frac{(V_L/W_g)(C_i-C_f)}{} \) reported by Kizilkaya [23] (where \( q \) = adsorption capacity; \( C_i \) = initial lead ion concentration in mg/L; \( C_f \) = final lead ion concentration after the 48 hr of adsorption time in mg/L; \( V_L \) = volume of aqueous lead solution used in liters; and \( W_g \) = mass of adsorbent used in grams) was simultaneously calculated to be: stock Fish Bone, SFFB (8.70); Salmon Fish Bone, SFB (8.71); Drum Fish Bone, DFFB (8.69); Na₂CO₃ (8.48).

### Table 1. Average residual lead ion concentrations in ppm for control and experimental samples after exposure time, standard deviation, standard error, and percent lead(II) ion removed

| Adsorbent | Ctr | SFFB | SFB | DFFB | Na₂CO₃ | Na₃PO₄ |
|-----------|-----|------|-----|------|--------|--------|
| Rxn.1     | 869 | 0.44 | 1.0 | 0.58 | 19.3   | 34.4   |
| Rxn. 2    | 876 | 1.1  | 0.34| 0.59 | 19.3   | 40.0   |
| Rxn. 3    | 869 | 1.1  | 0.41| 3.8  | 30.6   | 36.3   |
| Average Pb (II) in PPM | 871 | 0.88 | 0.58| 1.66 | 23.0   | 36.9   |
| STD DEV   | 2.95| 0.31 | 0.30| 1.5  | 5.31   | 2.34   |
| SQRT      | 1.7 | 1.7  | 1.7 | 1.7  | 1.7    | 1.7    |
| STD ERR   | 1.73| 0.18 | 0.17| 0.90 | 3.12   | 1.38   |
| Pb (II) Removed | 0  | 870 | 871 | 869.5 | 848 | 834.3 |
| Percent lead (II) ion removed | 0 | 99.9 | 99.9 | 99.8 | 97 | 96 |

Fig. 1. Residual lead concentration after lead solution was treated with substrates for 24 hr at 25°C

Ctr = Control, SFFB = StockFish Fish Bone, SFB = Salmon Fish Bone, DFFB = Drum Fish Bone
4. CONCLUSION

The potential exposure of hazardous lead produced during agricultural and industrial activities poses a major treat to human, food, water, air safety. Based on the results from this study, it can be concluded that fish bone with adsorption efficiency above 90% can be a promising natural biomaterial for the remediation of lead contaminated water. More importantly, it is a local abundant cheap waste which contains natural apatites with calcium phosphate [18,20,25] and carbonate [18,20]) groups. It is worth noting that the fish bone had a higher lead removal efficiency than the two chemical compounds, sodium carbonate and sodium phosphate used in this study.

COMPETING INTERESTS

Authors declare that there are no competing interests.

REFERENCES

1. Edwards M, Triantafyllidis S, Best Dana. Elevated blood lead in young children due to lead-contaminated drinking water: Washington, D.C., 2001-2004; Environ. Sci. Technol. 2009;43(5):16:18-1623. DOI: 10.1021/es802789w.
2. Brown MJ, Raymond J, Homa D, Kennedy C, Sinks T. Association between children’s blood lead levels, lead service lines, and water disinfection. Washington, DC, 1998-2006. Environ. Res. 2011;111(1):67–74.
3. Triantafyllidis S, Edwards M. Lead (Pb) in tap water and in blood: Implications for lead exposure in the United States. Crit. Rev. Environ. Sci. Technol. 2011;42:1297–1352.
4. Borja-Aburto VH, Hertz-Picciotto I, Lopez MR, Farias P, Rios C, Blanco J. Blood lead levels measured prospectively and risk of spontaneous abortion. Am. J. Epidemiol. 1999;105:590 −597.
5. Troesken W. Lead water pipes and infant mortality at the turn of the twentieth century. J. Hum. Resources. 2008;43(3):553–575.
6. Edwards M. Fetal death and reduced birth rates associated with exposure lead-contaminated drinking water. Environ. Sci. Technol. 2014;48(1):739-746.
7. Musa A, Yakasai IA, Ya’u IB. The concentrations of lead in shallow well, borehole and package water samples in Zaria, Nigeria. Int. J. of Pure and Appl. Sci. 2008;2(2):22-27.
8. Kaplan S, Hiar Corbin. How an EPA project backfired, endangering drinking water with lead. NBC News Investigative Reporting Workshop; 2012.
9. Bailey SE, Olin TJ, Bricka RM, Adrian DD. A review of potentially low-cost sorbents...
for heavy metals. Water Research. 1999;33(11):2469-2478.

10. Dimovic S, Smiciklas I, Plecas I, Antonovic D, Mitric M. Comparative study of differently treated animal bones for Co²⁺ removal. J. Hazardous Materials. 2011;164(1):279-287. DOI: 10.1016/j.jhazmat.2008.013.

11. Agwaramgbo L, Agwaramgbo E, Mercadel C, Edwards S, Buckles E. Lead remediation of Contaminated Water by Charcoal, LA Red Clay, Spinach, and Mustard Green. Journal of Environmental Protection. 2011;2(9):1240-1244. DOI:10.4236/jep.2011.29142.

12. Stathi P, Litina K, Gournis D, Giannopoulos TS, Deligiannakis Y. Physicochemical study of novel organoclay as heavy metal ion adsorbents for environmental remediation. Journal of Colloid and Interface Science. 2007;316:298-309. DOI: 10.1016/j.jcis.2007.07.078.

13. Singh SP, Ma LQ, Harris WG. Heavy metal interactions with phosphate clay: Sorption and desorption behavior. J. Environ. Qual. 2001;30:1961-1968.

14. Ma QY, Logan TJ, Traina SJ. Lead immobilization from Aqueous Solutions and Contaminated Soils Using Phosphate Rocks. Environmental Science & Technology. 1995;29:1118-1126.

15. Wright J, et al. PIMS Using Apatite II™: How It Works To Remediate Soil and Water. In: Sustainable Range Management-2004, Hinchee RE, Alleman B, eds. Columbus, OH: Battelle Press (2004). In: Proceedings of the Conference on Sustainable Range Management. New Orleans, LA. 2004;5-8.

16. Agwaramgbo L, Magee N, Nunez S, Mitt K. Biosorption and Chemical Precipitation of Lead using Biomaterials, Molecular Sieves, and Chlorides, Carbonates, and Sulfates of Na & Ca. Journal of Environmental Protection. 2013;4:1251-1257. DOI: org.10.4236/jep.2013.411145.

17. Igwe JC, Abia AA, Ibeah CA. Adsorption kinetics and intraparticulate diffusivities of Hg, As, and Pb ions on unmodified and thiolated coconut fiber. Int. J. Environ. Sci. Tech. 2008;5(1):83-92.

18. Rey C, Combes C, Drouet C, Glimcher MJ. Bone mineral: Update on chemical composition and structure. Osteoporos Int. 2009;20(6):1013-1021. DOI:10.1007/s00198-009-0860-y.

19. Ozawa M, Kanahara S. Removal of aqueous lead by fish-bone waste hydroapatite powder. J. Material Science. 2005;40(2005):1037-1038.

20. Giammar D, Xie L, Pasteris JD. Immobilization of lead with nanocrystalline carbonated apatite present in fish bone. Environmental Engineering Science, 2008;25(5):725-735. DOI: 10.1089/ees.2007.0168008.

21. Zayed EM, Sokker HH, Albishric HM, Farag AM. Potential use of novel modified fishbone for anchoring hazardous metal ions from their solutions. Ecological Engineering. 2013;61(Part A.):390-393.

22. Agwaramgbo L, Lathan N, Edwards S, Nunez S. Assessing lead removal from contaminated water using solid bio-materials: Charcoal, coffee, tea, fishbone, and caffeine. Journal of Environmental Protection. 2013;4(7):741-745. DOI:10.4236/jep.2013.47085.

23. Kizilkaya B, Tekiney AA. Utilization to remove Pb(II) ions from aqueous environments using waste fish bones by ion exchange. Journal of Chemistry. 2014;2014(2014):1-12 ID: 739273. DOI: 10.1155/2014/73927.

24. Lovell Agwaramgo, Shelby Edwards, Tanesia Patterson, Ruby Broadway. Desorption of lead adsorbed from contaminated water by fishbone and charred spinach/grape. British Journal of Applied Science and Technology. 2014;4(10):1566-1575.

25. Freeman KS. Remediating soil lead with fish bones. Environmental Health Perspectives. 2012;120(1):20-21. DOI: 10.1289/ehp.120-a20a.