



## Investigation of the Effect of Lead Adsorption on Surface Modified Fish Bones

Bayram Kızılkaya<sup>1</sup>  • Evren Tan<sup>2</sup> 

<sup>1</sup> Çanakkale Onsekiz Mart University, Faculty of Marine Sciences and Technology, Department of Aquaculture, Çanakkale, Turkey, bayram342001@yahoo.com

<sup>2</sup> Çanakkale Onsekiz Mart University, Graduate School of Natural and Applied Sciences, Department of Aquaculture, Çanakkale, Turkey, evrentantr@gmail.com

✉ Corresponding Author: bayram342001@yahoo.com

### Please cite this paper as follows:

Kızılkaya, B., Tan, E. (2020). Investigation of the Effect of Lead Adsorption on Surface Modified Fish Bones. *Acta Natura et Scientia*, 1(1): 56-60.

## ARTICLE INFO



**Received:** 16.08.2020

**Accepted:** 13.10.2020

### Keywords

Surface modification

Fish bone

Apatite

Lead

## ABSTRACT

This study investigates lead (Pb) elimination of surface modified fish bones as a biogenic apatite source. Surface modification was performed with 4-Aminohippuric acid (MBA<sub>1</sub>) and 2-Thiophenecarboxaldehyde (MBA<sub>2</sub>). In this study, different methods were used for surface modification. Apart from that, lead elimination was performed by the method of adsorption in aqueous solution. It is detected that both of the modified materials eliminate as 7.16 mg/g in 50 mgL<sup>-1</sup> lead solution. It was determined that MBA<sub>1</sub> and MBA<sub>2</sub> materials removed 99.9% of the lead in solution. In conclusion, it is seen that waste fish bones, which are regarded as worthless, can be applied to the chemical modifications and they can be transformed into useful materials. It is possible to say that transforming them into economic, efficient, qualified and useful materials can contribute environment.

## INTRODUCTION

It is known that environmental pollution has increased seriously due to the increasing population, technological developments, and uncontrolled industrialisation. It is also seen that natural resources rapidly extinct in order to supply the needs of world population. Moreover, most of the wastes of human being,

industry and technology are disposed unhealthily. As the potable and available water resources lessen, it is seen that pollution has reached a hazardous level for human being and environment. Although active carbon is an efficient adsorbent, it is not used very often as it is expensive. (Baccar et al., 2009; Mahmoodi et al., 2011). There are various methods of

disposing waste; yet, it is evident that most of these methods are expensive and inadequate. In recent years, most of the studies focus on recycling waste and transforming them into qualified materials and essential studies exist for this purpose.

Hydroxyapatites are used as an important material as they have ion exchange property and hydroxyl groups ( $-OH$ ). As the bones have biogenic and natural hydroxyapatite resources, they can be used efficiently. Fish bones are generally composed of 30% organic compound of fibrous protein and collagen and approximately 70% inorganic hydroxyapatite  $Ca_{10}(PO_4)_6(OH)_2$  (HAP) (Dimovic et al., 2009; Kizilkaya et al., 2010). This study aims to research the effect of chemical modification of waste fish bones in lead adsorption.

## MATERIAL AND METHODS

### Preparation of Fish Bones

Tuna fish bones provided from Dardanel Onentas Gıda Sanayi AS (Çanakkale, Turkey) were used as waste fish bones. Firstly, purification and milling and then homogenization were applied to the waste fish bones provided. The most efficient way for cleansing is using alkali solutions (Kizilkaya et al., 2010). Accordingly, unprocessed fish bones were treated with mechanic mixer in  $60^{\circ}C$  with NaOH solution until they were purified from contamination. Finally, the waste fish bones were dried in the incubator and pulverized with the aid of homogenizer and grinder.

### Functionalization of Bone Surfaces with 4-Aminohippuric Acid and 3-Aminopropyl-Triethoxysilane

Fish bones have been modified with 4-Aminohippuric acid and 2-thiophenecarboxaldehyde (Tan et al., 2014; Kizilkaya et al., 2016). Esterification reaction occurs in acidic environment by extracting a molecule of  $H_2O$  via hydroxyapatite-OH group and carboxyl group ( $-COOH$ )-OH. In brief, fish bone was refluxed with 4-Aminohippuric acid (**MBA<sub>1</sub>**) in boiling point inert atmosphere (Tan et al., 2014). Firstly, fish particles were silanized with 3-aminopropyl-triethoxysilane, and then stirred with magnetic stirrer with 2-thiophenecarboxaldehyde (**MBA<sub>2</sub>**) in room temperature (Kizilkaya et al., 2016). All modified solid phase was dried at  $45^{\circ}C$  in incubator.

### Lead Elimination and Adsorption

The elimination and adsorption experiments were performed in aquatic environment with the interference of lead solution and modified fish bones. Lead adsorption and elimination of the materials achieved from the experiments were investigated.  $Pb(NO_3)_2$  (Acros Organics, 211565000) were used for the experiments. The solution was prepared in  $50\text{ mgL}^{-1}$  concentration and each material was adsorbed with 1:200 adsorbent/solvent proportions during 30 hours and then the liquid phase taken from the solution was filtered with  $0.45\text{ }\mu\text{m}$  syringe, analysed with AAS-Flame and finally the lead amount adsorbed were determined. Photron (HGC0358, in Australia)

halogen cathode ray tube was used for lead analysis.

The removal capacities of fish bone as milligram per gram of bone (mg/g fish bone) were calculated with Equation (1) (Kaushal & Tiwari, 2010; Kizilkaya et al., 2010; Rafatullah et al., 2010)

$$q_{e.exp} = \frac{(C_0 - C_t)}{W} \times V \quad (1)$$

$C_0$  is the initial concentration of dye (mg/l),  $C_t$  is the dye concentration after sorption time  $t$  (mg/L).  $V$  is the volume of dye solutions (ml) and  $W$  is the weight of bone (g).  $q_{e.exp}$  is experimental adsorption capacity (mg/g).

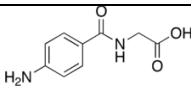
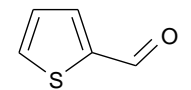
## RESULTS AND DISCUSSION

4-Aminohippuric acid and 2-Thiophenecarboxaldehyde technical information and  $q_e$  and  $A$  (Absorption) % of the lead removal of the materials achieved were given in Table 1. The materials achieved were interacted with lead solutions in  $50 \text{ mgL}^{-1}$  concentration. Lead elimination for  $\text{MBA}_1$  and  $\text{MBA}_2$  were detected as  $7.16 \text{ mg/g}$ . Atomic

number of lead is 82 and atomic mass of it is  $207 \text{ g/mol}$ . It is known that the atomic mass of it is higher than the other metals. Bones are natural resources of ion exchange. Ion exchange takes place with calcium which exists in metals and apatite structure. The molecule magnitude and the atomic mass of lead in ion exchange can be inferred as approximate results in both of the modified materials.

There are various methods of elimination of heavy metals in water resources such as neutralisation, chemical precipitation, adsorption, ion exchange, reverse osmosis, phytoextractum, or extraction of membrane and solvent. (Bailey et al., 1999; Donat et al., 2005). Among these methods, it is known that ion exchange, chemical precipitation, membrane processes and solvent extraction are expensive and insufficient for low metal involving water and waste water resources. Therefore, adsorption process can be offered as the cheapest and the most efficient way of eliminating heavy metals such as lead in water and waste water resources.

**Table 1.** Information and lead (Pb) elimination of modification chemicals

	Molecule	$M_A$	Pb	
			$q_e \text{ (mg/g)}$	%A
<b>MBA<sub>1</sub></b>	4-Aminohippuric acid 	<b>194.19</b>	7.16	99.96
<b>MBA<sub>2</sub></b>	2-Thiophenecarboxaldehyde 	<b>112.15</b>	7.16	99.95

Studies on natural bones focus especially on metal adsorption. In this context; cobalt (Dimovic et al., 2009), zinc (Banat et al., 2000), chrome (Chojnacka, 2005), copper and nickel (Alasbeb et al., 1999) eliminations and

adsorptions are investigated. It is seen that Hydroxyapatite is applicable in the elimination and adsorption of heavy metals thanks to its low-resolution in water, high stability in degradation and oxidation, high surface space

and buffer capacity. In this field, synthetic HA was synthesized with cobalt (Smiciklas et al., 2006), lead (Janga et al., 2008), and copper (Corami et al., 2008), cadmium (Zhu et al., 2008) and their eliminations were also studied.

## CONCLUSION

As it is known, waste products are supplied from several fields. It is known that the precautions are expensive and insufficient in disposing these wastes. Therefore, several researchers study upon transforming these wastes into useful materials. In this study, it is investigated that waste fish bones can be used after chemical processes. In this context, the surfaces of fish bones were modified with chemicals 4-Aminohippuric acid and 2-Thiophenecarboxaldehyde. The materials achieved after the modifications were interacted with the lead ions in aqueous solutions. It is detected that both of the modification products cleanse 99.9% of the lead solution in 50 mgL<sup>-1</sup> concentration.

## ACKNOWLEDGEMENTS

This study was supported by TÜBİTAK Project No: 213M200. The authors acknowledge TÜBİTAK and also wish to thank Merve Nihal TAN for her help in English proofreading. Lab experiments were carried out in the laboratory of Biochemistry; and laboratory of Feed and Food Analysis, Faculty of Marine Sciences and Technology, Çanakkale Onsekiz Mart University.

## COMPLIANCE WITH ETHICAL STANDARDS

### Authors' Contributions

Both authors made contributions in the necessary fields during preparation of samples, the experiments, the evaluating of the results and the writing of the article.

### Conflict of Interest

The authors declare that there is no conflict of interest.

### Ethical Approval

For this type of study, formal consent is not required.

## REFERENCES

- Alasbeeb, S., Banat, F., & Mobai, F. (1999). Sorption of copper and nickel by spent animal bones. *Chemosphere*, 39(12), 2087-2096. [https://doi.org/10.1016/S0045-6535\(99\)00098-3](https://doi.org/10.1016/S0045-6535(99)00098-3)
- Baccar, R., Bouzid, J., Feki, M., & Montiel, A. (2009). Preparation of activated carbon from Tunisian olive-waste cakes and its application for adsorption of heavy metal ions. *Journal of Hazardous Materials*, 162(2-3), 1522-1529. <https://doi.org/10.1016/j.jhazmat.2008.06.041>
- Bailey, S., Olin, T. R., & Dean, M. A. (1999). A review of potentially low-cost sorbents for heavy metals. *Water Research*, 33(11), 2469-2479. [https://doi.org/10.1016/S0043-1354\(98\)00475-8](https://doi.org/10.1016/S0043-1354(98)00475-8)
- Banat, F., Asheh, S. A., & Mohai, F. (2000). Batch zinc removal from aqueous solution using dried animal bones. *Separation and Purification Technology*, 21(1-2), 155-164. [https://doi.org/10.1016/S1383-5866\(00\)00199-4](https://doi.org/10.1016/S1383-5866(00)00199-4)
- Chojnacka, K. (2005). Equilibrium and kinetic modelling of chromium (III) sorption by animal bones. *Chemosphere*, 59(3), 315-320. <https://doi.org/10.1016/j.chemosphere.2004.10.052>

- Corami, A., D'Acapito, F., Mignardi, S., & Ferini, V. (2008). Removal of Cu from aqueous solutions by synthetic hydroxyapatite: EXAFS investigation. *Materials Science and Engineering B*, 149(2), 209–213. <https://doi.org/10.1016/j.mseb.2007.11.006>
- Dimovic, S., Smiciklas, I., Plecas, I., Antonovic, D., & Mitric, M. (2009). Comparative study of differently treated animal bones for  $\text{Co}^{2+}$  removal. *Journal of Hazardous Materials*, 164(1), 279–287. <https://doi.org/10.1016/j.jhazmat.2008.08.013>
- Donat, R., Akdogan, A., Erdem, E., & Cetisli, H. (2005). Thermodynamics of  $\text{Pb}^{2+}$  and  $\text{Ni}^{2+}$  adsorption onto natural bentonite from aqueous solutions. *Journal of Colloid and Interface Science*, 286(1), 43–52. <https://doi.org/10.1016/j.jcis.2005.01.045>
- Janga, S. H., Jeonga, Y. G., Mina, B. G., Lyoob, W. S., & Leea, S. C. (2008). Preparation and lead ion removal property of hydroxyapatite/polyacrylamide composite hydrogels. *Journal of Hazardous Materials*, 159(2-3), 294–299. <https://doi.org/10.1016/j.jhazmat.2008.02.018>
- Kaushal, M., & Tiwari, A. (2010). Removal of rhodamine-B from aqueous solution by adsorption onto crosslinked alginate beads. *Journal of Dispersion Science and Technology*, 31(4), 438–441. <https://doi.org/10.1080/01932690903210135>
- Kizilkaya, B., Tekinay, A. A., & Dilgin, Y. (2010). Adsorption and removal of Cu (II) ions from aqueous solution using pretreated fish bones. *Desalination*, 264(1-2), 37-47. <https://doi.org/10.1016/j.desal.2010.06.076>
- Kizilkaya, B., Ucyol, N., & Tekinay, A. A. (2016). Surface modification of biogenic hydroxyapatite particles with 2-thiophenecarboxaldehyde. *Environmental Science: An Indian Journal*, 12(7), 1-10.
- Mahmoodi, N. M., Salehi, R., & Arami, M. (2011). Binary system dye removal from colored textile wastewater using activated carbon: Kinetic and isotherm studies. *Desalination*, 272(1-3), 187-195. <https://doi.org/10.1016/j.desal.2011.01.023>
- Rafatullah, M., Sulaiman, O., Hashim, R., & Ahmad, A. (2010). Adsorption of copper (II) onto different adsorbents. *Journal of Dispersion Science and Technology*, 31(7), 918–930. <https://doi.org/10.1080/01932690903224003>
- Smiciklas, I., Dimovic, S., Plecas, I. & Mitric, M. (2006). Removal of  $\text{Co}^{2+}$  from aqueous solutions by hydroxyapatite. *Water Research*, 40(12), 2267–2274. <https://doi.org/10.1016/j.watres.2006.04.031>
- Tan, E., Kizilkaya, B., Ucyol, N., Ormanci, H. B., & Oral, A. (2014). Surface modification with P-aminohippuric acid on biogenic apatite (fish bones) particles. *Marine Science and Technology Bulletin*, 3(2), 45-50.
- Zhu, R., Yu, R., Yao, J., Mao, D., Xing, C. & Wanga, D. (2008). Removal of  $\text{Cd}^{2+}$  from aqueous solutions by hydroxyapatite. *Catalysis Today*, 139(1-2), 94–99. <https://doi.org/10.1016/j.cattod.2008.08.011>