A Review on Current Development of Animal Bone-Based Sorbent for Heavy Metals Removal from Contaminated Water and Wastewater

Sri Martini^{a,*}, Kiagus Ahmad Roni^b, Dian Kharismadewi^c, Erna Yuliwaty^d

Chemical Engineering Department, Universitas Muhammadiyah Palembang, Palembang, Indonesia

^asri_martini@um-palembang.ac.id, ^bkgs_a.roni@um-palembang.ac.id, ^cdian_kharismadewi@um-palembang.ac.id, ^derna_yuliwati@um-palembang.ac.id

Keywords: Heavy metals, Biosorption, Chicken bone, Cow bone, Carbonization

Abstract. This review article presents the usage of various animal bones such as chicken bone, fish bone, pig bone, camel bone, and cow bone as reliable biosorbent materials to remove heavy metals contained in contaminated water and wastewater. The sources and toxicity effects of heavy metal ions are also discussed properly. Then specific insights related to adsorption process and its influential factors along with the proven potentiality of selected biosorbents especially derived from animal bone are also explained. As the biosorbents are rich in particular organic and inorganic compounds and functional groups in nature, they play an important role in heavy metal removal from contaminated solutions. Overall, after conducting study reports on the literature, a brief conclusion can be drawn that animal bone waste has satisfactory efficacy as effective, efficient, and environmentally friendly sorbent material.

Introduction

The increasing rate of industrialization and population globally has impacted the environmental sustainability regarding the increase in contaminated water and wastewater containing hazardous pollutants [1, 2]. To date, more research has focused on minimizing the threats posed by various pollutants including heavy metals in order to avoid their harmful effects [3-5]. Massive industrial activities have been the main factor of an increasing amount of contaminated water and wastewater containing heavy metals. Their existence is posing negative consequences to human health and other living creatures due to their carcinogenic and non-biodegradable characters [4, 6]. In accordance with this phenomenon, the effective and efficient treatment method to purifying wastewater in the first stage is an avoidable option.

Several available techniques including ion exchange, adsorption, filtration, membrane filtration and membrane bioreactor, sedimentation, electrodialysis, advanced oxidation processes, biological processes or integrated treatment system can be selected and applied to separate those heavy metals from wastewater solution [7-11]. Each of those techniques has its own advantageous and disadvantageous aspects. However, when it comes to several important targets like lower energy consumption, modest operation procedure, high removal efficiency, and environmentally friendly method, adsorption is one of the best candidates [12, 13].

To date, there are various types of adsorbents such as activated carbon, metal oxide, carbonbased materials, and metal organic framework that can be applied for trapping targeted pollutants contained in contaminated water and wastewaters. The increasing interest in circular economic perspective and keeping environmental sustainability has then led to better awareness of using organic materials derived from plant and animal wastes to be further reused as biosorbent [14]. Despite several articles already reviewed sorbent derived from low-cost materials, to the best of our knowledge, there is less specific discussion on the removal of heavy metals from contaminated water and wastewater using sorbent derived from animal bone. Therefore, this review article then corroborates the current usage of animal bone for heavy metals removal.

Heavy Metals

In the last decades, there has been an increasing attention to health and environmental damage caused by hazardous pollutants including heavy metals. These substances can penetrate the groundwater polluting water and soil [15, 16]. Beyond their permissible levels, heavy metals will cause damaging impact on human health and other living organism. Most of heavy metals contaminating environment are produced by various industries such as mining, pulp and paper, battery, textile, fertilisers, paints, pigments, steel and glass manufacturers, then followed by certain natural factors such as atmospheric reactions and volcanic eruptions [4, 17]. Water and wastewater contaminated by heavy metals must be sufficiently treated before they are disposed to open environment. Several harmful heavy metals along with their allowable values and toxicity effects are tabulated in Table 1 [4, 17-23].

| Heavy | Permissible limit (mg/L) | Toxicity effect |
|---------|---------------------------|---|
| metal | | |
| Mercury | 0.01 mg/L by EU, 2 mg/L | Liver lung, paralysis, loss of memory, blindness, weak |
| | by EPA | immunity |
| Lead | 0.05 mg/L by WHO, | Brain damage, anaemia, anorexia, vomiting, nervous |
| | 0.1 mg/L by EPA | systems and mental illness |
| Arsenic | 0.01 mg/L by WHO | Lung, melanosis, keratosis, bladder, and kidney cancer, |
| | | neurological disorder, liver |
| Copper | 1.3 mg/L by USEPA, | Liver damage and lung cancer, insomnia, osteoporosis, |
| | 1.0 mg/L by EPA | heart disease, cancer |
| Cadmium | 0.003 mg/L by WHO, | Bronchitis, lung cancer, anemia, kidney failure, lung |
| | 0.005 mg/L by EPA | fibrosis, emphysema |
| Chro- | <5 mg/L by WHO (Cr(III)), | Necrosis, cancer, lung tumour, gastrointestinal, |
| mium | 0.1 mg/L by EPA (Cr(VI)) | teratogenic, severe diarrhoea |
| Nickel | 0.015 mg/L by USEPA | DNA damage, dermatitis, cancer, chronic bronchitis, |
| | 1 mg/L by EPA | eczema |

| Table 1. | Heavy | metals | sources | and | toxicit | v effect |
|----------|-------|--------|---------|-----|---------|----------|
| | _ | | | | | |

Adsorption Process

Adsorption process involves atoms, ions or, solid particles accumulating onto sorbent surface and forming a typical layer of the pollutant particles named sorbates. It takes place continuously until equilibrium condition is established. The quantification of sorbate-sorbent interactions is important to examine targeted pollutant uptake expressed as batch equilibrium isotherm related to mechanistic models or empirical equations [24, 25]. There are two main models commonly used to analyze isotherm mechanism including Freundlich and Langmuir. Freudlich model assumes that the adsorption occurs on the heterogeneous surface having unequal available sites with different adsorption energies. In contrast, Langmuir describes that the adsorption happens onto an ideal homogeneous uniform surface where all of the sites on the adsorbent surface are equivalent. Regarding the kinetic modelling, it may follow pseudo-first order, pseudo-second order, intra particle diffusion, or Elovich models [26].

Biosorbent Preparation and Comparative Analysis on Their Performance

The performance of biosorbent in adsorption process is affected by certain sorbent properties including surface area, pore structure, surface chemistry, particle size, along with the nature of sorbate like polarity, molecular weight, and molecular structure. Other than that, several operating and physicochemical conditions such as sorbent dosage, solution pH, contact time, temperature, initial sorbate concentration, and the existence of other ions are also considerable aspects influencing pollutant removal efficiency [4, 6]. Furthermore, several preparation modes such as drying, carbonization, pyrolysis, calcination, chemicals impregnation or hybrid activation systems can also be implemented to modify the characteristics of the sorbents for increasing their

performance to enable higher adsorption capacity [7, 14, 17, 27]. A study reported that the effect of initial preparation on the biosorbent performance was significant. Compared to its raw version, calcinated and mineralized pig bone, for example, was found more effective for Pb(II) ions removal due to the increase in the adsorption capacity from 96.1 mg/g to 312.5 mg/g [28]. Other than that, the comparative assessment on the performance of biosorbent derived from animal bone with other prominent sorbent materials also shows interesting outcomes. While the adsorption capacity values of zeolite and cauliflower leaves-based sorbent were found to be 109.89 mg/g, 57.80 mg/g, and 177.82 mg/g, 53.96 mg/g for adsorbing Pb(II) and Cu(II) ions, respectively, cow bone-based activated carbon could have around 558.88 mg/g and 287.58 mg/g of adsorption capacity for adsorbing the same metals, respectively [29-31]. Therefore, it is worthy to utilize the potentiality of various animal bones abundantly available for being alternative materials to remove heavy metals and other recalcitrant pollutants contained in contaminated water and wastewater.

Biosorbent Derived from Animal Bone

Based on the estimation, there are millions of tons of bone waste that are produced each year by the meat industry. The increasing amount of its production could be expected around 40 million metric tons within the next decade resulting in a significant increase in bone waste globally [32]. The waste has been considered as organic waste disposed in landfills or rendering plants. It is then worthy to further valorize the bones. Along with carbon and other components, the existence of hydroxyapatite containing apatite calcium phosphate as an inorganic material present in all vertebrates bones has enabled the use of the bones as sorbent material [33]. This substance has unique features such as great biocompatibility, high biodegradability and ionic exchange properties. Therefore, many researchers have reported the use of animal bone for wastewater treatment, especially regarding its ability to remove heavy metal ions from aqueous solutions. Table 2 displays several findings on bone waste-based sorbent for heavy metals removal reported on the literature.

| Material | Metal | Activation | Removal efficiency | Isoterm | Kinetics | Pef |
|----------------|---------|--------------------------|---------------------|-----------|------------------------|------|
| Waterial | Wictai | Technique | (9/)/ and Comparity | model | Killeties | Kel. |
| | | rechnique | (70)/ ads. Capacity | model | | |
| | | | (mg/g) | | | |
| Chicken | Cr(VI) | Pyrolysis 350°C | 58.195 mg/g | Langmuir | Elovich | [34] |
| bone | Pb | Pyrolysis 600°C | 263 mg/g | Langmuir | - | [35] |
| | Cd(II) | Fe and Mg coating | 97% | - | Pseudo-first order | [36] |
| Mutton bone | Cr(VI) | Calcination 650°C | 93.85% | Langmuir | Pseudo-second order | [37] |
| Sheep | As(III) | Pyrolysis 900 °C | >4 mg/g | Freudlich | Pseudo-first | [38] |
| bone | AS(V) | 5 5 | >53 mg/g | | order | |
| Cow | Cd(II) | Pyrolysis 600°C | 165.77 mg/g | Langmuir | Pseudo-second | [29] |
| bone | Cu(II) | | 287.58 mg/g | C | order | |
| | Pb(II) | | 558.88 mg/g | | | |
| Fish | Cd(II) | Carbonization | >140 mg/g | Langmuir | - | [39] |
| bone | . / | 500°C | | C | | |
| Camel | Cd(II) | Pyrolysis 800°C | 99.4% | Langmuir | Pesudo-second | [40] |
| bone | Pb(II) | 5 5 | 99.89% | 8 | order | |
| | Pb(II) | Pyrolysis 500°C + | 344.8 mg/g | Langmuir | Pseudo-second | [41] |
| | Cd(II) | magnetization by | 322.6 mg/g | C | order | |
| | Co(II) | co-precipitation | 294.1 mg/g | | | |
| | Cu(II) | NaOH/activation 900°C | 200 mg/g | Freudlich | - | [42] |
| Pig bone | Cd(II) | Pyrolysis 500°C | 73.5 mg/g | Langmuir | Pseudo-second order | [43] |

Table 2. The use of bone waste-based sorbent for heavy metals removal

Summary

In this current work, assorted biosorbents derived from animal bone to remove heavy metals have been presented. Comprehensive literature related to the sources and toxicity effects of those heavy metals on human health is also explained. The existence of environmentally friendly wastewater treatment technology is one of critical solutions. Therefore, biosorption can be great alternative to numerous treatment methods like membrane filtration, biological technique, and advanced oxidation processes. Eventually, biosorption process using organic natural materials including animal bones seems still well considered due to its high uptake, lower cost, abundant choices and availability. When it comes to comparative analysis with other natural based sorbents commonly used for heavy metals removal, the performance of animal bone-based sorbents are inclined to have better output. To conclude, implementing modification techniques on the animal bones materials as well as finding the optimum operating conditions could noticeably enhance their adsorption capacity and metals removal efficiency.

References

- [1] C. Bhattacharjee, S. Dutta, V.K. Saxena: A Review on Biosorptive Removal of Dyes and Heavy Metals from Wastewater using Watermelon Rind as Biosorbent, Environ. Advan. Vol. 2 (2020), p. 100007
- [2] S. Mishra, L. Cheng, A. Maiti: The Utilization of Agro-biomass/byproducts for Effective Bio-Removal of Dyes from Dyeing Wastewater: A comprehensive review, J. of Environ. Chem. Eng. Vol 9 (2021), 104901
- [3] H. Esmaeili, S. Tamjidi, M. Abed: Removal of Cu (II), Co (II) and Pb (II) from Synthetic and Real Wastewater Using Calcified Solamen Vaillanti Snail Shell, Desalin. Water Treat. Vol. 174 (2020), p 324-335
- [4] R. Chakraborty, A. Asthana, A.K. Singh, B. Jain, A.B.H. Susan: Adsorption of Heavy Metal Ions by Various Low-Cost Adsorbents: a Review, Inter. J. of Environ. Analytical Chem. Vol. (2020), p. 1-38
- [5] S. Martini: Pengolahan Limbah Cair Minyak Kanola Menggunakan Kombinasi Adsorpsi dan Membran Ultrafiltrasi Polimer, Kinetika Vol.10 (2019), p. 36-41
- [6] S. Afroze, T.K. Sen, A Review on Heavy Metal Ions and Dye Adsorption from Water by Agricultural Solid Waste Adsorbents, Water, Air, & Soil Pollut. Vol. 229 (2018), p. 225.
- [7] S. Martini, S. Afroze, K. Ahmad Roni: Modified Eucalyptus Bark as a Sorbent for Simultaneous Removal of COD, Oil, and Cr(III) from Industrial Wastewater, Alexandria Eng. J. Vol. 59 (2020), p. 1637-1648
- [8] S. Martini, H.M. Ang: Hybrid TiO2/UV/PVDF Ultrafiltration Membrane for Raw Canola Oil Wastewater Treatment, Desalin. and Water Treat. Vol. 148 (2019), p. 51-59
- [9] S. Martini, H.M. Ang, H. Znad: Integrated Ultrafiltration Membrane Unit for Efficient Petroleum Refinery Effluent Treatment, CLEAN Soil, Air, Water Vol. 45 (2017), 1600342
- [10] J. Willner, A. Fornalczyk: Application of Biological Method for Removing Selected Heavy Metals from Sewage Sludge, Physicochemical Problems of Mineral Processing, 56 (2020).
- [11] S. Martini, E. Yuliwati: Membrane Development and Its Hybrid Application for Oily Wastewater Treatment: A Review, J. of Appl. Membrane Sci. & Technol. Vol. 25 (2020), p. 57-71

- [12] S. Tamjidi, H. Esmaeili: Chemically Modified CaO/Fe3O4 Nanocomposite by Sodium Dodecyl Sulfate for Cr (III) Removal from Water, Chem. Eng. & Technol. Vol. 42 (2019), p. 607-616
- [13] J. Feng, J. Zhang, W. Song, J. Liu, Z. Hu, B. Bao: An Environmental-friendly Magnetic Bioadsorbent for High-efficiency Pb (II) Removal: Preparation, Characterization and Its Adsorption Performance, Ecotoxicology and Environ. Safety Vol. 203 (2020), 111002.
- [14] A. Agarwal, U. Upadhyay, I. Sreedhar, S.A. Singh, C.M. Patel: A Review on Valorization of Biomass in Heavy Metal Removal from Wastewater, J. of Water Proc. Eng. Vol. 38 (2020), 101602.
- [15] V. Masindi, K.L. Muedi: Environmental Contamination by Heavy Metals, Heavy Metals Vol.10 (2018), p. 115-132
- [16] X. Luo, J. Guo, P. Chang, H. Qian, F. Pei, W. Wang, K. Miao, S. Guo, G. Feng: ZSM-5@ MCM-41 Composite Porous Materials with a Core-shell Structure: Adjustment of Mesoporous Orientation Basing on Interfacial Electrostatic Interactions and Their Application in Selective Aromatics Transport, Sep. and Purif. Technol. Vol. 239 (2020), 116516.
- [17] S. Tamjidi, B.K. Moghadas, H. Esmaeili, F.S. Khoo, G. Gholami, M. Ghasemi: Improving the Surface Properties of Adsorbents by Surfactants and Their Role in the Removal of Toxic Metals from Wastewater: A Review Study, Proc. Safety and Environ. Protec. Vol. 148 (2021), p. 775-795
- [18] E. Bibaj, K. Lysigaki, J. Nolan, M. Seyedsalehi, E. Deliyanni, A. Mitropoulos, G. Kyzas: Activated Carbons from Banana peels for the Removal of Nickel Ions, Intern. J. of Environ. Sci. and Technol. Vol. 16 (2019), p. 667-680
- [19] S. Pavithra, T. Gomathi, S. Sugashini, P.N. Sudha, H.H. Alkhamis, A.F. Alrefaei, M.H. Almutairi: Batch Adsorption Studies on Surface Tailored Chitosan/Orange Peel Hydrogel Composite for the Removal of Cr(VI) and Cu(II) Ions from Synthetic Wastewater, Chemosphere Vol. 271 (2021), 129415.
- [20] P. Mishra, R. Patel: Removal of Lead and Zinc Ions from Water by Low Cost Adsorbents, J. of Hazard. Mater. Vol. 168 (2009), p. 319-325
- [21] M. Ahmaruzzaman, V.K. Gupta: Rice Husk and Its Ash as Low-cost Adsorbents in Water and Wastewater Treatment, Indust. & Eng. Chem. Res. Vol. 50 (2011), p. 13589-13613
- [22] F.-L. Mi, S.-J. Wu, F.-M. Lin: Adsorption of Copper (II) Ions by a Chitosan–oxalate Complex Biosorbent, Inter. J. of Bio. Macromolecules Vol. 72 (2015), p. 136-144
- [23] C.-S. Zhu, L.-P. Wang, W.-b. Chen: Removal of Cu (II) from Aqueous Solution by Agricultural By-product: Peanut Hull, J. of Hazard. Mater. Vol. 168 (2009), p. 739-746
- [24] B. Volesky: Biosorption and Me, Water Res. Vol. 41 (2007), p. 4017-4029
- [25] S. Afroze, T.K. Sen, M. Ang, H. Nishioka: Adsorption of Methylene Blue Dye from Aqueous Solution by Novel Biomass Eucalyptus Sheathiana Bark: Equilibrium, Kinetics, Thermodynamics and Mechanism, Desalin. and Water Treat. Vol. (2015), p. 1-21
- [26] M.A. Ahsan, S.K. Katla, M.T. Islam, J.A. Hernandez-Viezcas, L.M. Martinez, C.A. Díaz-Moreno, J. Lopez, S.R. Singamaneni, J. Banuelos, J. Gardea-Torresdey, J.C. Noveron: Adsorptive Removal of Methylene Blue, Tetracycline and Cr(VI) from Water Using Sulfonated Tea Waste, Environ. Technol. & Innovation Vol. 11 (2018), p. 23-40

- [27] M. Om Prakash, G. Raghavendra, S. Ojha, M. Panchal: Characterization of Porous Activated Carbon Prepared from Arhar Stalks by Single Step Chemical Activation Method, Materials Today: Proceedings Vol. 39 (2020), p. 1476-1481
- [28] Y. Zhou, D. Chang, J. Chang: Preparation of Nano-structured Pig Bone Hydroxyapatite for High-efficiency Adsorption of Pb2+ from Aqueous Solution, Intern. J. of Appl. Ceramic Technol. Vol. 14 (2017), p. 1125-1133
- [29] J. Xiao, R. Hu, G. Chen: Micro-nano-engineered Nitrogenous Bone Biochar Developed with a Ball-milling Technique for High-efficiency Removal of Aquatic Cd(II), Cu(II) and Pb(II), J. of Hazard. Mater. Vol. 387 (2020), 121980.
- [30] I.V. Joseph, L. Tosheva, A.M. Doyle: Simultaneous Removal of Cd (II), Co (II), Cu (II), Pb (II), and Zn (II) Ions from Aqueous Solutions via Adsorption on FAU-type Zeolites Prepared from Coal Fly Ash, J. of Environ. Chem. Eng. Vol. 8 (2020), 103895.
- [31] Z. Ahmad, B. Gao, A. Mosa, H. Yu, X. Yin, A. Bashir, H. Ghoveisi, S. Wang: Removal of Cu (II), Cd (II) and Pb (II) Ions from Aqueous Solutions by Biochars Derived from Potassium-rich Biomass, J. of Clean. Prod. Vol. 180 (2018), p. 437-449
- [32] O.f.E. Co-operation, Development: OECD-FAO Agricultural Outlook 2018-2027, OECD Publishing, 2018.
- [33] S. Sathiyavimal, S. Vasantharaj, M. Shanmugavel, E. Manikandan, P. Nguyen-Tri, K. Brindhadevi, A. Pugazhendhi: Facile Synthesis and Characterization of Hydroxyapatite from Fish Bones: Photocatalytic Degradation of Industrial Dyes (Crystal Violet and Congo Red), Prog. in Org. Coatings Vol. 148 (2020), 105890.
- [34] T. Yang, C. Han, J. Tang, Y. Luo: Removal Performance and Mechanisms of Cr (VI) by an Insitu Self-improvement of Mesoporous Biochar Derived from Chicken Bone, Environ. Sci. and Pollut. Res. Vol. 27 (2020), p. 5018-5029
- [35] J.-H. Park, J.J. Wang, S.-H. Kim, S.-W. Kang, J.-S. Cho, R.D. Delaune, Y.S. Ok, D.-C. Seo: Lead Sorption Characteristics of Various Chicken Bone Part-derived Chars, Environ. Geochem. and Health Vol. 41 (2019), p. 1675-1685
- [36] S.S. Alquzweeni, R.S. Alkizwini: Removal of Cadmium from Contaminated Water Using Coated Chicken Bones with Double-Layer Hydroxide (Mg/Fe-LDH), Water Vol. 12 (2020), 2303.
- [37] S. Pawar, T. Theodore: Development of Hydroxyapatite from Waste Mutton Bones and its Application for Hexavalent Chromium Removal from Aqueous Solutions-Adsorption Isotherms and Kinetics Study, in: AIP Conference Proceedings, AIP Publishing LLC, 2020, pp. 030001.
- [38] S.S.A. Alkurdi, R.A. Al-Juboori, J. Bundschuh, L. Bowtell, S. McKnight: Effect of Pyrolysis Conditions on Bone Char Characterization and Its Ability for Arsenic and Fluoride Removal, Environ. Pollut. Vol. 262 (2020), 114221.
- [39] N.A. Medellín-Castillo, S.A. Cruz-Briano, R. Leyva-Ramos, J.C. Moreno-Piraján, A. Torres-Dosal, L. Giraldo-Gutiérrez, G.J. Labrada-Delgado, R.O. Pérez, J.P. Rodriguez-Estupiñan, S.Y. Reyes Lopez, M.S. Berber Mendoza: Use of Bone Char Prepared from an Invasive Species, Pleco Fish (Pterygoplichthys spp.), to Remove Fluoride and Cadmium(II) in Water, J. of Environ. Management Vol. 256 (2020), 109956.
- [40] M.N. Rashed, A.A.-E. Gad, N.M. Fathy: Adsorption of Cd (II) and Pb (II) Using Physically Pretreated Camel Bone Biochar, Advan. J. of Chem. Sec. A Vol. 2 (2019), p. 347-364

- [41] A.A. Alqadami, M.A. Khan, M. Otero, M.R. Siddiqui, B.-H. Jeon, K.M. Batoo: A Magnetic Nanocomposite Produced from Camel bones for an Efficient Adsorption of Toxic Metals from Water, J. of Clean. Prod. Vol. 178 (2018), p. 293-304
- [42] H.S. Abd-Rabboh, K.F. Fawy, N.S. Awwad: Removal of copper (II) from Aqueous Samples Using Natural Activated Hydroxyapatite Sorbent Produced from Camel Bones, Desalin. Water Treat, 164 (2019) 300-309.
- [43] J.-H. Park, J.-J. Yun, S.-W. Kang, S.-H. Kim, J.-S. Cho, J.J. Wang, D.-C. Seo: Removal of Potentially Toxic Metal by Biochar Derived from Rendered Solid Residue with High Content of Protein and Bone Tissue, Ecotoxic. and Environ. Safety Vol. 208 (2021), 111690.