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Comparative Study of the Efficacy of Metal Removal from Contaminated Aqueous Solutions by Solid Bidentate Ligands & Liquid Plant Materials

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Abstract: Heavy metal contaminated water sources pose serious health risks for humans, animals, and plants. Exposure to and ingestion of heavy metals have been associated to liver, kidney, and brain function. Objective: The aim of this research is to comparatively examine the metal removal efficacy of three solid bidentate chemicals and four plant materials. Study Design & Methods: Standard solutions of zinc (II) and lead (II) ions with concentrations of 1,000 ppm were respectively treated with OA (Oxalic Acid), dibasic bidentate ligands (sodium hydrogen phosphate and sodium carbonate). Then, the solutions were placed on a shaker for 15 h, centrifuged, and the supernatant was analyzed using ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry). Results: All the solid bidentate adsorbents were very effective in removing zinc and lead (> 90%). However, more lead than zinc was removed across all adsorbents except for lemon where equal percent of zinc and lead (49%) were removed. OA and Na_2HPO_4 removed about equal amount of lead (> 99%). The plant materials (SP (Spinach), bell pepper and GBP (Green Bell Pepper)), respectively and preferentially removed more lead (98.9%, 98.3%, 81.5%) than zinc (91.7%, 46%, 46%). Conclusion: Although plant materials have gained attraction for the remediation of heavy metal, however, some bidentate chemical ligands such as OA, sodium carbonate and sodium hydrogen phosphates are even more effective in removing these metals from contaminated water. Furthermore, heavier metals are preferentially removed than lighter metals.

Key words: Organic acids, OA, remediation, chelation, ligands, heavy metal contamination.

1. Introduction

Heavy metal poisoning of soil and water is a major global environmental concern due to their causative factors and their negative effects on ecosystems and human health [1-4]. Heavy metals such as lead (Pb), cadmium (Cd), mercury (Hg), and arsenic (As) are persistent contaminants that can accumulate in soil and water as a result of numerous industrial, agricultural, and home activities [2, 3, 5]. These metals are hazardous because they are non-biodegradable, poisonous, and can accumulate in the chain of food production, resulting in severe health problems such as brain damage, cancer, gastrointestinal and kidney dysfunction, nervous system disorders, birth defects, etc. [1-5]. Phytoremediation [1, 6-8] is widely seen as an environmentally friendly technology for the removal of heavy metals from contaminated soil [1, 6-8]. However, it has its drawbacks and limitations. Thus, use of adsorption method using cheap and readily available agricultural waste materials and biomaterials began to gain traction [9-11]. Some of these agricultural wastes and biomaterials include SP (Spinach), coffee, tea [12], corn and palm husks [13], walnut, almond, and hazelnut, and pistachio shells [14] and other agricultural and industrial wastes [15, 16].

Emerging remediation methods are using water soluble ligands such as sodium carbonates and

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phosphates to remove heavy metal from contaminated water [3, 17] and low molecular weight organic acids to leach out heavy metals from contaminated soils [18-21]. Due to limited research report on the use of low molecular organic acid ligands to treat heavy-metal contaminated water, the project reported here examines not only the efficacy of OA (Oxalic Acid) to remove heavy metals from contaminated water but also compares such efficacy with those of sodium carbonate, phosphate and plant materials.

2. Materials and Methods

Standard solutions of 1,000 ppm of Pb (II) and Zn (II) ions were prepared with the corresponding salts for each. Equivalent amounts of each salt were dissolved in 1,000 mL of solution. Duplicate samples of about 40 mL for each metal contaminated solution were put into centrifuge tubes. The duplicate samples were treated with about 4 g of each of the solid dibasic (Na_2HPO_4, Na_2CO_3), 2 g of solid OA, and 20 mL of the supernatant of each plant material (SP, RBP (red bell pepper) and GBP (Green Bell Pepper)) prepared by blending 100 g of the plant material with 200 mL of deionized water. The samples were vortexed to mix and placed into a shaker for 12 h at room temperature. Then, all the samples were centrifuged at 3,000 rpm for 10 min. The supernatant of each sample was decanted into a new centrifuge tube. The resulting samples were analyzed for residual metal ion concentration using the EPA Method 6010 (ICPAES (Inductively Coupled Plasma-Atomic Emission Spectrometry)).

3. Results and Discussions

Fig. 1 demonstrates that the three solid bidentate ligands (oxalic acid, Na_2CO_3 and Na_2HPO_4) were highly effective in removing >90% of lead and zinc

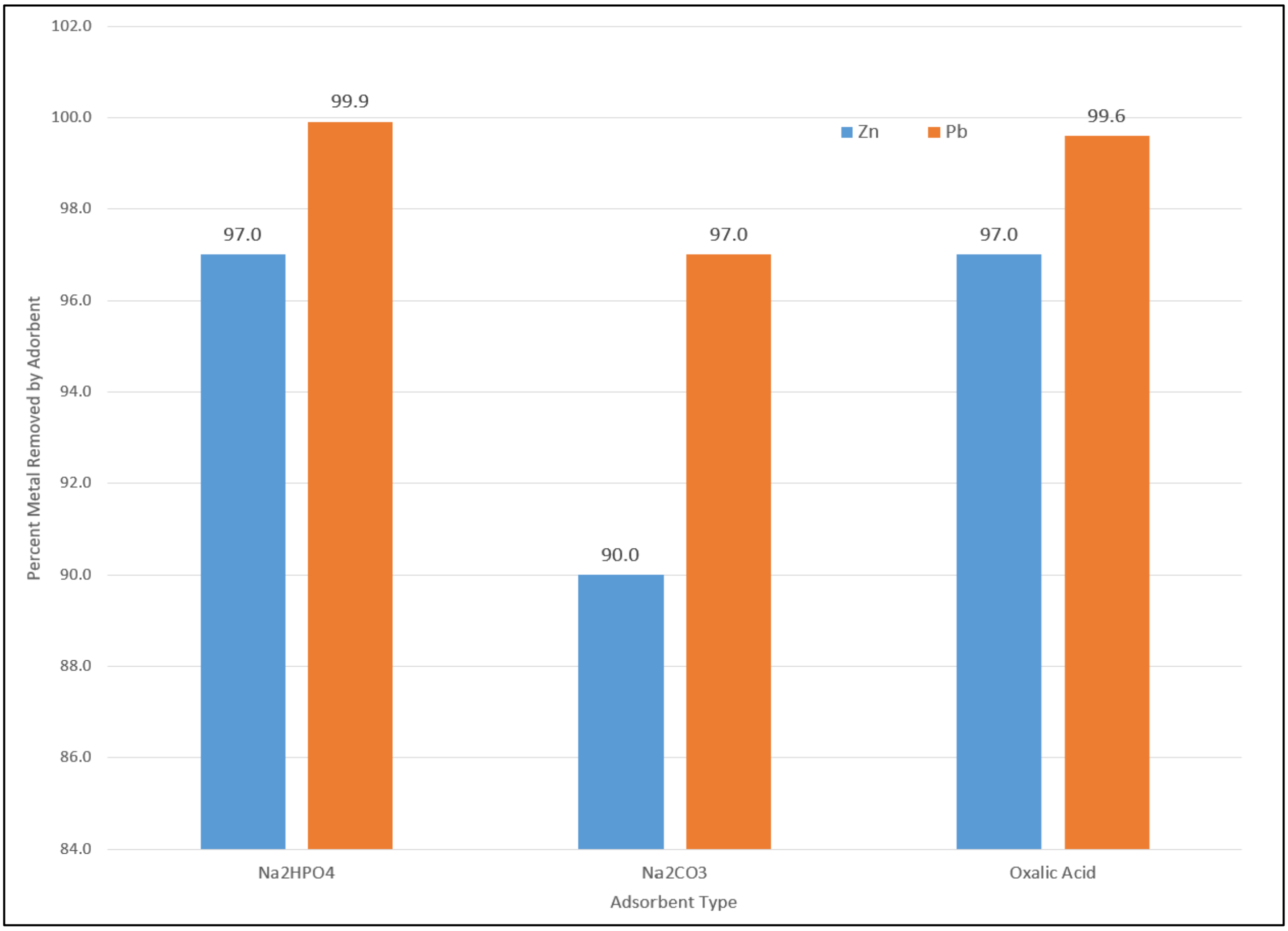

Fig. 1 Comparative metal removal efficacy of bidentate OA, Na_2HPO_4 and Na_2CO_3.

from contaminated aqueous solutions. It is also worthy to note that although only 2 g of oxalic acid was used, it removed more lead and zinc from the contaminated water (99.6%, and 97%) than 4 g of Na_2CO_3 (97% and 90%) and about equal amount of each metal as 4 g of Na_2HPO_4 (99.9% and 97%).

Fig. 2 showed that the liquid spinach extract has equal efficacy for lead removal from contaminated water at about 99.0% when compared to the efficacy of the three solid bidentate compounds (oxalic acid (99.6%), Na_2HPO_4 (99.9%) and Na_2CO_3 (97%)). Agwaramgbo [22] reported that charge clearly plays a role in the efficiency of the adsorbent in metal removal. He reported that metal removal efficacy of dibasic sodium phosphate and sodium carbonate was greater than those of mono basic phosphate and carbonate and that the -2-charged ligands had higher affinity for the +2-charged metals. Interestingly, uncharged neutral bidentate ligand like oxalic acid had the same level of metal removal efficacy as charged bidentate like sodium hydrogen phosphate. This observation could be attributed to the fact that through resonance, the oxalic acid can have two partial negative charges on two carbonyl oxygen basic sites.

Surprisingly, red bell pepper had similar efficacy as spinach, oxalic acid, Na_2HPO_4 and Na_2CO_3 for lead removal (see Figs. 2 and 3). However for zinc removal, all plant materials with the exception of spinach had about 46% removal efficiency.

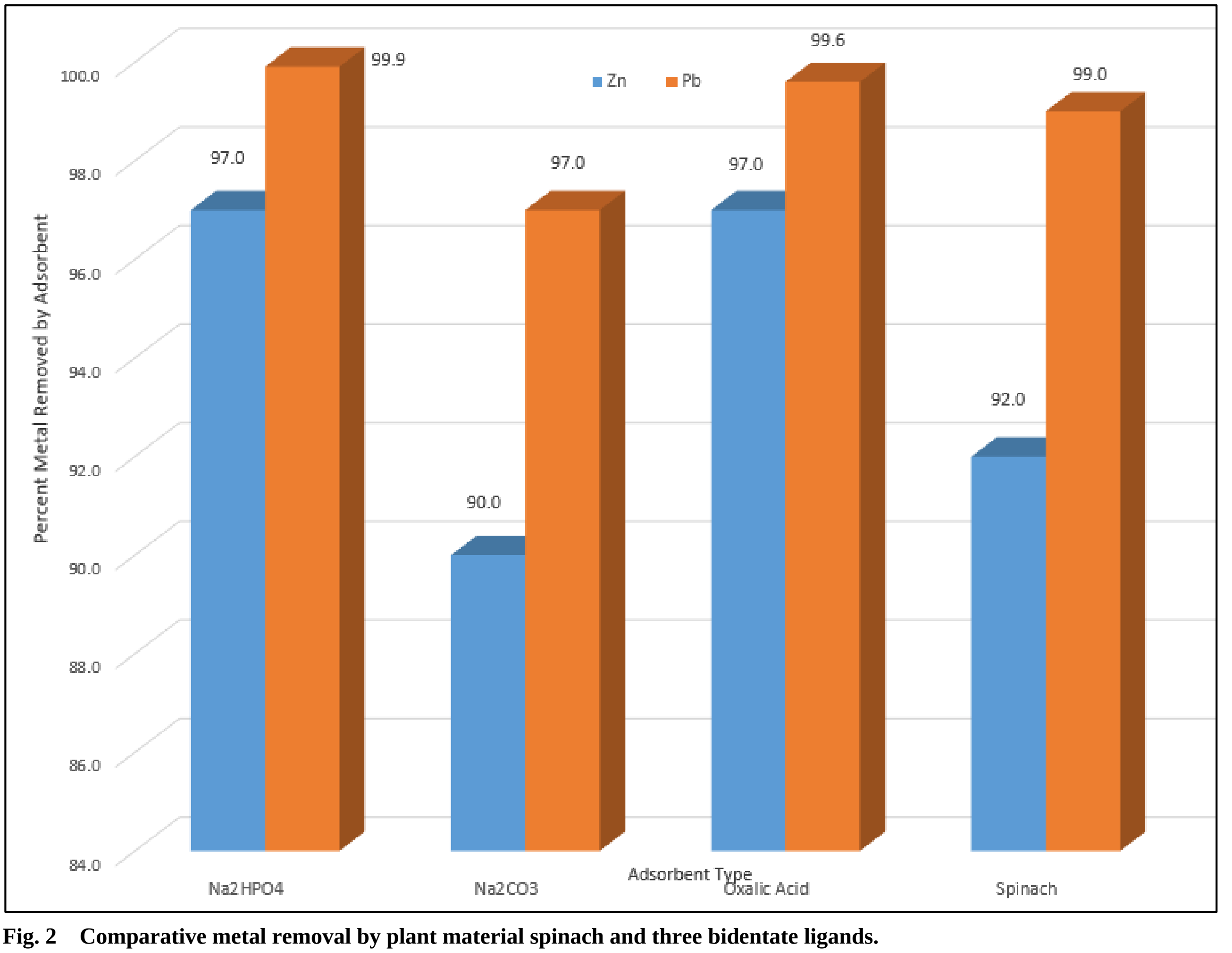

Fig. 2 Comparative metal removal by plant material spinach and three bidentate ligands.

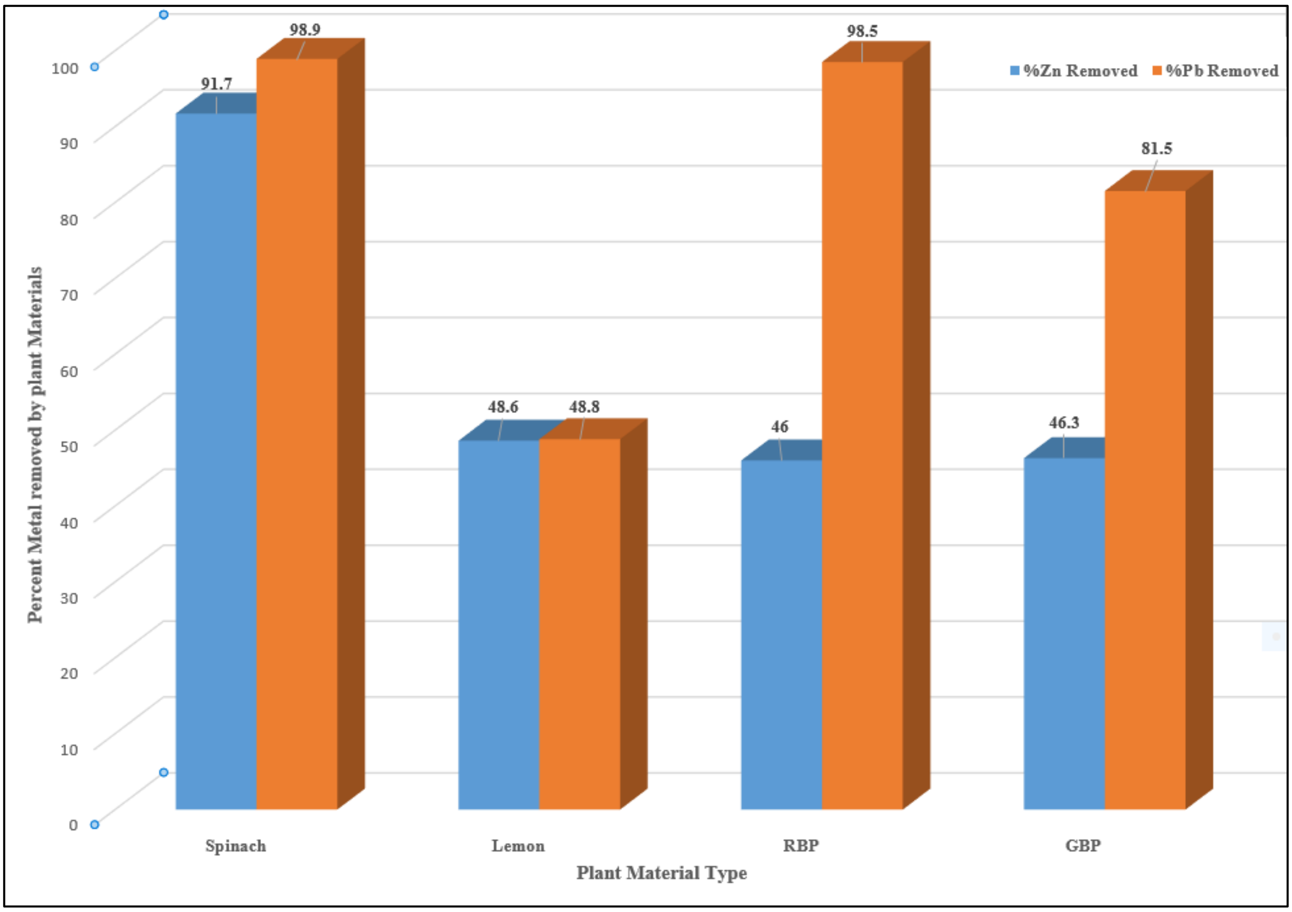

Fig. 3 **Comparative metal removal by plant materials: spinach, lemon juice, green and red bell pepper.**

4. Conclusion

Although oxalic acid is a neutral bidentate with half dose as Na_2HPO_4 and Na_2CO_3, it none-the-less removed equal amount of lead and zinc as Na_2HPO_4 but removed more lead and zinc than Na_2CO_3. Thus oxalic acid, a soluble biodegradable compound is a major contender for heavy the remediation of heavy metals from contaminated water. That spinach removed more metals than other plant materials could be attributed to the fact that it contains more oxalic acid than the other plant materials. Finally, the fact that lemon juice removed equal amount of lead and zinc could mean that the enzymes are the main players in metal removal and once the enzyme is depleted, no more metal is removed.

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