

Investigation of the Effect of Mixed Anion and Mixed Metal on Heavy Metal Removal from Contaminated Aqueous Solutions

ABSTRACT

Aims: To investigate the effect of variation of metals (Cu vs Zn) and anions (nitrate vs sulfate) in heavy metal remediation by charcoal and coffee waste from contaminated water.

Study design: Aqueous solution of single and mixed nitrate and sulfate salts of copper and zinc were respectively treated with charcoal and coffee waste for 12 hr and the residual metal concentration and percent metal removal were determined.

Place and Duration of Study: The experiments were conducted in the Chemistry Department at Dillard University between January 2021 and November 2021

Methodology: Coffee waste (2 grams) and charcoal (2 grams) were respectively mixed with 40 ml of 500 parts per million (ppm) of each of the following combination of metal solutions: $\text{Cu}(\text{NO}_3)_2$; CuSO_4 ; $\text{Zn}(\text{NO}_3)_2$; ZnSO_4 ; $\text{Cu}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2$; CuSO_4 and ZnSO_4 ; $\text{Zn}(\text{NO}_3)_2$ and ZnSO_4 ; $\text{Cu}(\text{NO}_3)_2$ and CuSO_4 ; $\text{Cu}(\text{NO}_3)_2$ and ZnSO_4 ; $\text{Zn}(\text{NO}_3)_2$ and CuSO_4 . Each solution was agitated for 12 hours at room temperature. The mixtures were centrifuged at 3000 rpm for 10 minutes and residual copper and zinc were analyzed.

Results: The results showed that copper was preferentially adsorbed by waste coffee compared to zinc in all binary metal (copper-zinc) solutions.

Conclusion: Metal type can affect the extent of metal removal from a mixed metal solution. In this research, the copper was more effectively removed from the mixed metal solutions than from a single metal-single anion solutions. In addition, zinc removal is suppressed in binary metal salt solutions. The anion type does not influence the percentage of metal removed from solution to any appreciable extent.

Keywords: Metal Adsorption, Heavy Metal Contamination, Agricultural Waste, Mixed-Metal, Mixed Anion Solutions

1. INTRODUCTION

Heavy metals are known for their highly toxic properties. In fact, in areas affected by humans copper and zinc concentration is 20 times greater than in unpolluted regions not directly impacted by human activity [1-2]. Despite the laws enacted to limit pollution, excess copper and zinc still exists in many bodies of water, making it imperative that we find ways to safely remove them. A number of approaches have been studied for the development of cheaper and more effective adsorbents for metal removal from several

sources such as water and soil. Many non-conventional low-cost adsorbents, including natural materials, and waste materials have been proposed by several researchers [3-5]. Most of the adsorbents studied include agricultural wastes, industrial waste products, and bio adsorbents [6]. Although tiny amounts of copper are essential for human health, excess amounts can cause adverse health effects [7]. Excess zinc in the body can cause harmful effects on human health [8]. Natural materials available in large amounts and several waste products can be considered as effective and alternative technologies for the remediation of heavy metals. Instead of using commercial activated carbon, researchers have worked on inexpensive materials, such as charcoal, corn cob, tea and coffee waste which are locally available [9-11]. Low-cost adsorbents are imperative for local communities with contaminated water sources. Furthermore, many studies have concentrated on single metal [12] or binary metals with the same counter anion [13]. Therefore, this project reported in this paper investigates the effect of mixed metals and mixed anions on the efficiency of metal removal from contaminated aqueous solutions using coffee waste as an adsorbent.

2. METHODOLOGY

2.1 Preparation of the Adsorbent (Coffee Waste)

PJ's Classic Roast Coffee waste was obtained, washed several times with deionized water (DI water). The washed coffee waste was patted dry with a paper towel and placed in a Model 40 GC Laboratory oven to dry for 24 hours at 120 °C. Once dried, the waste was ground in a kitchen blender and in a mortar. The ground coffee waste was sieved using a 300 µM mesh sieve.

2.2 Preparation of the Adsorbent (Charcoal)

Activated Charcoal was obtained from Aldrich Chemicals and was used as is.

2.3 Preparation of 500 PPM of Cu (II) ion solution from Copper Nitrate (labelled as CuN)

A standard solution of 500 ppm of copper (II) ion was prepared by dissolving 1.83 g of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5 \text{H}_2\text{O}$ from Fisher Scientific (Lot 143404), 98.8% purity in enough deionized (DI) water to give a 1000 ml of solution. The solution was then stirred to mix before use.

2.4 Preparation of 500 PPM of Cu(II) ion solution from Copper Sulfate (labelled as CuS)

A standard solution of CuSO_4 was prepared using 1.96g of $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ and following the process above.

2.5 Preparation of 500 PPM of Zn (II) ion solution from Zinc Nitrate (labeled as ZnN)

A standard solution of 500 ppm of zinc (II) was prepared by dissolving 2.3 g $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ from Fisher Scientific (Lot 138261), 98.0% pure is dissolved in a 500 ml beaker with small amount of DI water and then transferred into the 1000 ml volumetric flask. DI water was added to fill the 1000 ml flask to the mark. The solution was then stirred to mix before use.

2.6 Preparation of 500 PPM of Zn (II) ion solution from Zinc Sulfate (labelled as ZnS)

A standard solution of 2.2g of $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ was dissolved in a 500 ml beaker with a small amount of DI water and then transferred into the 1000 ml volumetric flask. DI water was added to fill the 1000 ml flask to the mark. The solution was then stirred to mix before use.

2.7 Preparation of 250 PPM of Various Mixed Metal ion Solutions

250 ppm salt solutions of single metal-mixed anion, mixed metal-single anion and mixed metal-mixed anion were prepared from a 1:1 volume ratio of the solutions prepared above and labelled as CuNCuS, ZnNZnS, CuNZnZ, CuSZnS, CuNZnS, and CuSZnN.

2.8 Agitation of Coffee Waste with Varying Heavy Metals and Anions

Respectively, 2 g of waste coffee was added to 40 ml of each set of metal contaminated solutions into triplicate centrifuge tubes. Controls were prepared following the same procedure except coffee waste was not added. Each mixture was vortexed and placed in the shaker for 12h at room temperature. All the samples were centrifuged at 3000 rpm for 10 minutes then decanted into new tubes. All samples were then analyzed for residual copper and zinc following EPA method 6010 (Inductively Coupled Plasma-Atomic Emission Spectrometry (ICPAES)).

3. RESULTS AND DISCUSSION

3.1 Residual Copper and Zinc concentrations in Single Metal-Single Anion Solutions after Treatment with Coffee Waste & Charcoal

Figure 1 shows the percentage of copper and zinc removed from single metal-single ion solutions. It further suggests that the solutions treated with charcoal showed at least 99.8% percent metal removal while those treated with coffee waste had about 35-45% metal removal. However, copper removal was higher than zinc removal from both single metal-single anion and from mixed metal-mixed anion salt solutions.

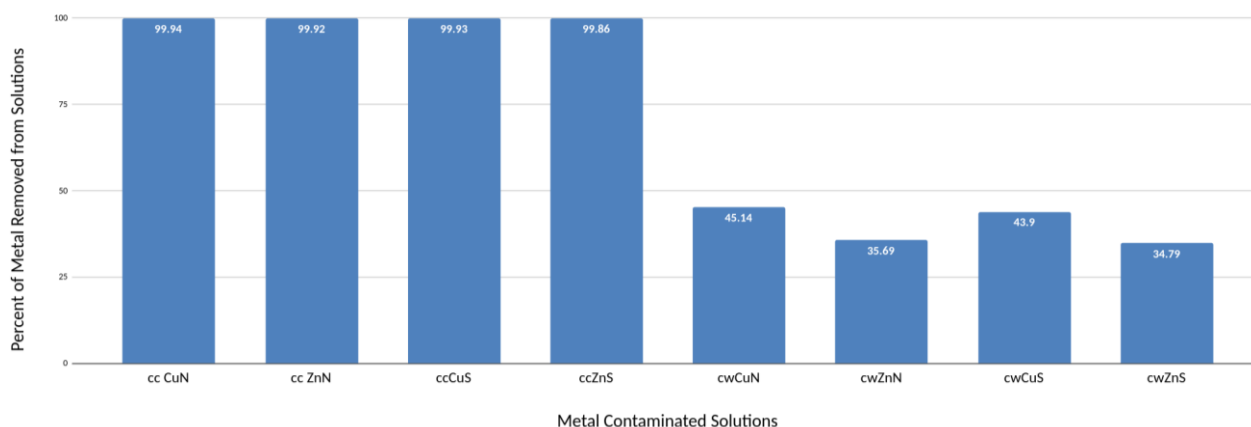


Figure 1: Percent Copper and Zinc from Single Metal and Single Anion Solutions

Table 1: Percent Copper and Zinc Removal from Single Metal and Single Anion Solutions

ADSORBENT	CuN	CuS	ZnN	ZnS
CHARCOAL WASTE	99.9	99.9	99.9	99.9
COFFEE WASTE	45.1	43.9	35.7	34.9

3.2 Residual Copper and Zinc in Mixed Metal-Mixed Anion Solutions after Treatment by Coffee Waste and Charcoal

Table 2 shows the residual concentration of copper and zinc from each reaction tube for mixed metal-mixed anion and mixed metal-single anion after each salt solution was treated with coffee waste for 12 hr compared to control samples.

Table 2: Residual Metal Concentrations after Treatment with Coffee Waste

Samples (mg/L)	Ctr ZnSCuN	WC CuNZnS	Ctr ZnNCuS	WC CuSZnN	Ctr ZnCuS	WC CuSZnS	Ctr ZnCuN	WC CuNZnN
1: Cu	260	86.4	265	76.4	231	89.2	265	87.1
1: Zn	272	190	280	196	306	213	265	200
2: Cu	274	115	262	108	254	92.8	268	87.1
2: Zn	284	187	282	205	283	217	266	195
3: Cu	265	92.1	263	62	248	97.1	263	81
3: Zn	275	198	281	190	282	242	262	195
Average (Cu)	266	97.8	263	82.1	244	93	265	85.1
Average (Zn)	277	191.7	281	197	290	224	264	196.7

Table 3: Residual metal concentrations after treatment of mixed metal-mixed anion and mixed metal-single anion salt solutions with Charcoal

Samples (mg/L)	Ctr ZnSCuN	CC CuNZnS	Ctr ZnNCuS	CC CuSZnN	Ctr ZnCuS	CC CuSZnS	Ctr ZnCuN	CC CuNZnN
1: Cu	260	0.532	265	265	231	0.205	265	0.178
1: Zn	272	87	280	280	306	80.9	265	42.9
2: Cu	274	0.246	262	262	254	0.109	268	0.167
2: Zn	284	88.9	282	282	283	56.8	266	48.8
3: Cu	265	0.044	263	-	248	0.167	263	0.155
3: Zn	275	72.4	281	-	282	63.5	262	54.6
Average (Cu)	266	0.274	263	263.5	244	0.16	265	0.167
Average (Zn)	277	82.8	281	281	290	67.1	264	48.8

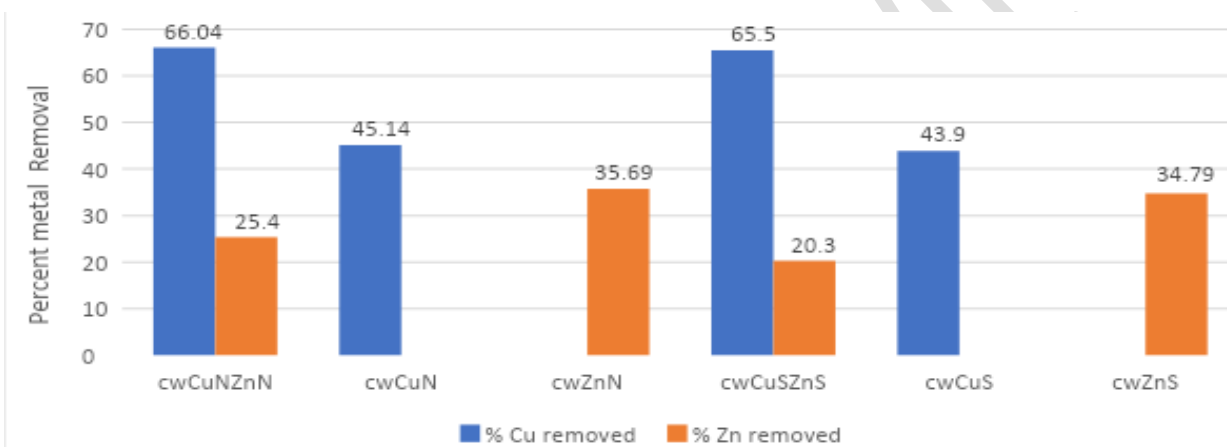
3.3 Cu and Zn metal removal from single metal-mixed anion and mixed metal-mixed anion salt solutions.

Figure 2 below compares Zn and Cu removal by coffee waste from single metal-single anion and mixed metal-single anion salts solutions. It is interesting to note that copper removal from $\text{CuSO}_4\text{-ZnSO}_4$ solution (a mixed metal-single anion salt solution) is 65.5% while that of Zinc is 20.3% suggesting a three-fold removal preference of copper over zinc. Similarly, in the $\text{Cu}(\text{NO}_3)_2\text{-Zn}(\text{NO}_3)_2$ solution (another mixed

metal-single anion salt solution), the copper removal (66.04%) is 2.59 times greater than zinc removal (25.4%).

Furthermore, percent metal removal from mixed metal-single anion salt solution is greater than metal removal from single metal-single anion salt solutions. Compare the 66.04% Cu removal from $\text{Cu}(\text{NO}_3)_2\text{-Zn}(\text{NO}_3)_2$ solution to the 45.14% Cu removal from $\text{Cu}(\text{NO}_3)_2$ solution and the 65.5% Cu removal from $\text{CuSO}_4\text{-ZnSO}_4$ solution to 43.9% Cu removal from CuSO_4 . The data further suggest that metal removal from mixed metal-single anion is greater than metal removal from single metal-single anion solutions. The opposite is the opposite with zinc. In $\text{Cu}(\text{NO}_3)_2\text{-Zn}(\text{NO}_3)_2$ solution, zinc removal was 25.4% compared to the 35.69% zinc removal from $\text{Zn}(\text{NO}_3)_2$ and the 20.3% zinc removal from $\text{CuSO}_4\text{-ZnSO}_4$ solution compared to the 34.79% zinc removal from ZnSO_4 . The data may suggest that zinc may constitute a catalyst for copper removal in the mixed metal-single anion solutions.

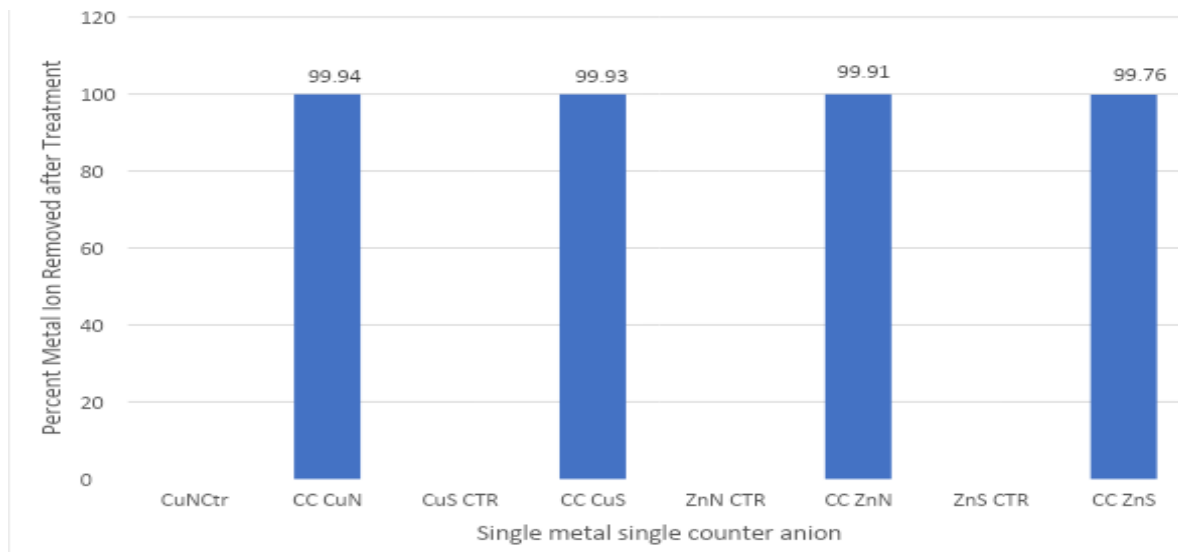
Figure 2: Comparison of Zn and Cu removal from single metal-single anion and mixed metal-single anion salts solutions by coffee waste.



3.4. Comparison of Zn and Cu removal from single metal-single anion salt solutions by charcoal.

Copper and Zinc removal from single metal-single anion salt solutions ($\text{Cu}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2$, CuSO_4 , and ZnSO_4) by Charcoal. The data in Figure 3 below showed that percent copper and zinc removal by charcoal from single metal-single anion salt solutions were greater than 99% irrespective of the metal or anion ($\text{Cu}(\text{NO}_3)_2$ (99.94%); $\text{Zn}(\text{NO}_3)_2$ (99.91%); CuSO_4 (99.93%) and ZnSO_4 (99.76%)

Figure 3: Percent Cu and Zn removal from single metal-single anion salt solutions by Charcoal

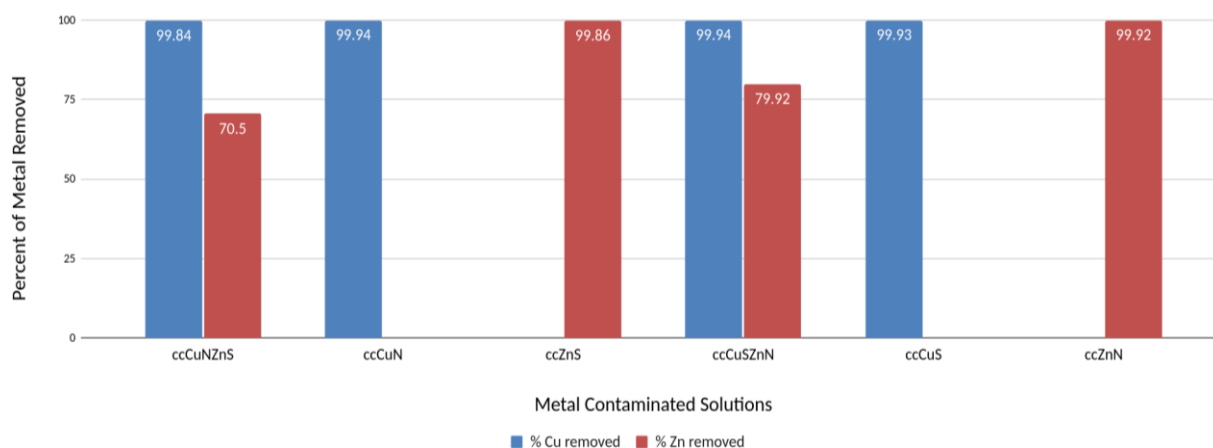


3.5. Effect of Mixed Metal and Mixed Anion on Metal Removal by Charcoal

Figure 4 below compares percent metal removal by charcoal from single metal-single anions and mixed metal-mixed anion salt solutions. In both types of solutions, copper removal was about the same, greater than 99.8% irrespective of metal and anion.

Thus, in the single metal-single anion salt solutions, Zinc and copper were equally removed by charcoal adsorbent: $\text{Cu}(\text{NO}_3)_2$ (99.94%); CuSO_4 (99.93%); $\text{Zn}(\text{NO}_3)_2$ (99.92%); and ZnSO_4 (99.86%) while in the mixed metal-mixed anion salt solutions, Zinc removal by charcoal was severely reduced when compared to zinc removal from single metal-single anion salt solutions: $\text{CuNO}_3\text{-ZnSO}_4$ (70.5%) versus ZnSO_4 (99.86%) and $\text{CuSO}_4\text{-ZnNO}_3$ (79.92%) versus $\text{Zn}(\text{NO}_3)_2$ (99.92%).

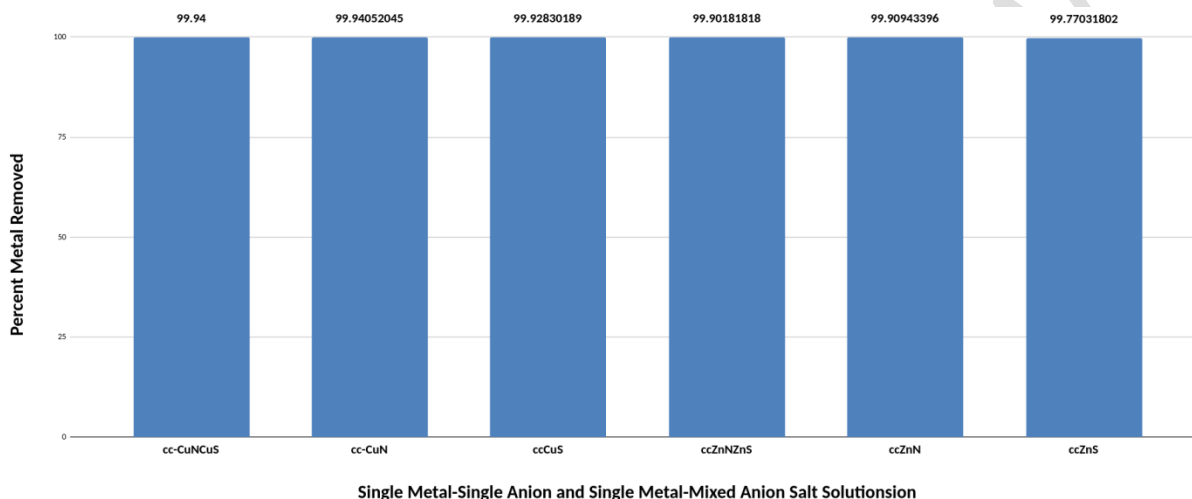
Figure 4: Comparison of Percent Metal Removal from Single Metal-Single Anions and Mixed Metal-Mixed Anion Salt Solutions



3.6. Effect of Mixed Anion on Metal Removal from Single Metal-Mixed Anion Salt Solutions by Charcoal.

Figure 5 below suggests that metal removal from both single metal-single anion and mixed metal-single anion salt solutions were very equal at $\geq 99.93\%$ for copper removal from $\text{Cu}(\text{NO}_3)_2\text{-CuSO}_4$ and 99.94% from $\text{Cu}(\text{NO}_3)_2$ and CuSO_4 . However, for zinc removal more zinc was removed from $\text{Zn}(\text{NO}_3)_2\text{-ZnSO}_4$, (99.9%) and $\text{Zn}(\text{NO}_3)_2$ (99.91%) than from ZnSO_4 (99.86%).

Figure 5: Comparison of metal removal from single metal-single anion and single metal-mixed anion salt solutions.



3.7 Selective or Competitive Site Adsorption

Data on Figures. 2 and 4 unequivocally showed that copper was preferentially removed from all solutions (single metal-single anion; mixed metal-single anion (Fig 2) and mixed metal-mixed anion (Fig 4) salt solutions. The results could be explained in part by the functional groups in coffee waste, and the affinity of these groups to bind to copper [14]. Another explanation for the selectivity of copper removal by coffee waste could be that the binding sites in coffee waste prefer copper to zinc [15]. Finally, the solubility product of the copper-adsorbent complex may be smaller than that of the zinc-adsorbent complex, thus, allowing more zinc in solution than copper.

3.8 Effect of Particle Size on Adsorption of Copper and Zinc Ions by Coffee Waste

In the residual concentration of copper and zinc in the copper-zinc mixtures, we can observe by the graph of Fig. 5 that more copper is removed than zinc by a factor of 3. We can conclude that anion type did not have a major effect on metal removal or adsorption. Instead, the results suggest that particle size contributed in part to the efficiency of the adsorbent. The zinc ions are larger than the copper, therefore making it easier for copper to enter the pores of the coffee waste particles [16]. Thus, in adsorption involving copper and zinc using agricultural waste, the copper removal is favored over zinc more than zinc [17-18].

3.9. Solubility and Solubility Product of the Adsorbent-Metal Complex

It is possible that the solubility and solubility product (KSP) of coffee waste-zinc complex is higher than that of copper. Thus, forcing more copper to be drawn out of the solution than zinc. In another

experiment where $\text{Cu}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2$ were treated with Na_2HPO_4 , more copper was removed than zinc which is attributed in part due to the low solubility and KSP (1.4×10^{-37}) of CuHPO_4 compared to the KSP of 9×10^{-33} for ZnHPO_4 .

4. CONCLUSION

The results of this investigation led us to conclude the following clearly provided the following conclusions: (1) metal type can affect the extent of metal removal from a mixed metal solution. Copper removal by coffee waste from $\text{CuSO}_4\text{-ZnSO}_4$ and CuSO_4 were 65.5% and 43.9%, respectively while zinc removal from $\text{CuSO}_4\text{-ZnSO}_4$ and ZnSO_4 were 20.3% and 34.79%, respectively. Similarly, copper removal from $\text{Cu}(\text{NO}_3)_2\text{-Zn}(\text{NO}_3)_2$ and from $\text{Cu}(\text{NO}_3)_2$ were 66.04% and 45.14%, respectively while the Zinc removal from $\text{Cu}(\text{NO}_3)_2\text{-Zn}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2$ were 25.4 and 35.69%. In each of the mixed metal solutions, three times more copper is removed than zinc. (2) More copper is removed in a mixed metal solution than from a single metal-single anion solution which suggests that zinc may be catalyzing copper removal. (3) Anion type does not appear to influence metal removal to an appreciable extent. In both $\text{Cu}(\text{NO}_3)_2\text{-Zn}(\text{NO}_3)_2$ and $\text{CuSO}_4\text{-ZnSO}_4$ the ratio of % copper to % zinc removal is about 3. However, in single metal single anion salt solutions, more metals are removed from metal nitrate salt solutions than from metal-sulfate salt solutions as shown in Figure 2. (4) Zinc removal from mixed copper-zinc salt solutions is suppressed by the copper as shown in Figure 4 ($\text{CuSO}_4\text{-ZnSO}_4$ (70.5%), $\text{Cu}(\text{NO}_3)_2\text{-Zn}(\text{NO}_3)_2$ (79.9%) when compared to its removal from ZnSO_4 (99.86%) or $\text{Zn}(\text{NO}_3)_2$ (99.92%).

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8. REFERENCES

1. Zhang X., Yang L., Li H., Li Y, Wang W.5., Ye B. Impacts of lead/zinc mining and smelting on the environment and human health in China. Environmental monitoring and assessment. 2011; 184 (4): 2261-2273.
2. Leal, P.P., Hurd, C.L., Sander, S.G. et al. Copper pollution exacerbates the effects of ocean acidification and warming on kelp microscopic early life stages. Sci Rep 8, 14763 (2018). DOI:10.1038/s41598-018-32899-w
3. Zvinowanda, C. M., et al. "A novel adsorbent for heavy metal remediation in aqueous environments" International Journal of Environmental Science; Technology 6.3 (2009): 425-434.
4. Tripathi A., Ranjan M.R. Heavy metal removal from wastewater using low-cost adsorbents. J. Bioremed. Biodeg. 2015; 6(6): 315.
5. George Z. Kyzas. Commercial coffee waste as materials for adsorption of heavy metals from aqueous solutions. Materials. 2012; 5: 1826-1840. DOI:10.3390/ma5101826
6. Kartal, S. Nami, Coskun Kose, B. Tarakanadha, and Yuji Imamura. "Adsorption of Copper, Chromium, and Arsenic from Chromated Copper Arsenate (CCA) Treated

- Wood onto Various Adsorbents," *The Open Waste Management Journal* 1.1 (2008): 11-17. Web.
7. Janet Y. Uriu-Adams, Carl L. Keen, Copper, oxidative stress and human health. *Molecular Aspects of Medicine*. 2005; 26 (4-5): 268-298.
 8. L.M. Plum, L. Rink, H.L. Haase, "The essential toxin: Impact of zinc on human health," *Int. J. Environ Res Public Health*, 2010, Vol. 7, No. 4, pp. 1342-1365.
 9. Mohammed, Rafie Rushdy. "Removal of Heavy Metals from W[aste Water Using Black Teawaste." *Arabian Journal for Science and Engineering* 37.6 (2012): 1505-520. Web.
 10. Lavecchia, Roberto, Alessio Pugliese, and Antonio Zuurro. "Removal of lead from aqueous solutions by spent tea leaves." *Chemical Engineering Transactions* 19 (2010): 73-78.
 11. Kang Myung Yang, David. "Removal of Copper (II) Ions from Contaminated Water by Encapsulation of Peppermint Tea Leaves in Alginate Beads," *AMNH. American Museum of Natural History*, n.d. Web. 07 Dec. 2014.
 12. M. Larakeb, L. Youcef, S. Achour, "Removal of Zinc from Water by Adsorption on Bentonite and Kaolin," *Athens Journal of Sciences*, 2017, 4(1):47-58.
 13. Barbooti, M.M. Simultaneous Removal of Chromium and Lead from Water by Sorption on Iraqi Montmorillonite. *Journal of Environmental Protection*, 2015. 6, 237-249.
 14. Pankaj Pandey, Sambhi SS, Sharma SK, Surinder Singh. Batch adsorption for the removal of Cu (II) Ions by zeolite-NaX from aqueous stream. *Proceedings of the World Congress on Engineering*; 2009.
 15. L. Agwaramgbo, R. Cardoso, T. Matos, "Copper and Zinc Removal from Contaminated Water Using Coffee Waste, " *Journal of Scientific Research & Reports*, 2016, 12(6):1-9.
 16. Seniūnait, Jurgita, Rasa Vaiškūnait, and Violeta Bolutien. "Coffee grounds as an adsorbent for copper and lead removal from aqueous solutions," (2014).
 17. Sdiri A.T., Higashi T., Jamoussi F. Adsorption of copper and zinc onto natural clay in single and binary systems. *Int. J. Environ. Sci. Technol.* 2014; 11: 1081-1092. DOI:10.1007/s13762-013-0305-1
 18. Putra WP, et al. Biosorption of Cu (II), Pb (II), and Zn (II) Ions from aqueous solutions using selected wastes materials. Adsorption characterization studies. *Journal of Encapsulation and Adsorption Sciences*. 2014; 4: 25-35.