Journal of Scientific Research & Reports
12(6): 1-9, 2016; Article no.JSRR.31118
ISSN: 2320-0227

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Copper and Zinc Removal from Contaminated Water Using Coffee Waste

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Authors' contributions

This work was carried out in collaboration between all authors. Author LOEA designed the study and wrote the protocol of the study and the final draft of the manuscript. Authors RFC and TSM conducted the experiments and wrote the first draft of the manuscript. All authors performed and managed the statistical analysis of the study. All authors managed literature searches, read and approved the final manuscript.

Article Information

DOI: 10.9734/JSRR/2016/31118
Editor(s):
(1) Leszek Labedzki, Institute of Technology and Life Sciences, Kujawsko-Pomorski Research Centre, Poland.
Reviewers:
(1) Ghadir Aly El-Chaghaby, Agricultural Research Center, Egypt.
(2) P. N. Palanisamy, Kongu Engineering College, India.
Complete Peer review History: http://www.sciencedomain.org/review-history/17593

Original Research Article

Received 21st December 2016
Accepted 14th January 2017
Published 24th January 2017

ABSTRACT

Aim: The aim of this research is to evaluate the selectivity in metal removal by coffee waste from binary-metal polluted water from contaminated water.
Place: The work was done at Dillard University in New Orleans, LA, USA.
Duration: The project was carried out between November and December 2014.
There are reports that suggest that there is a steady increase in industrial effluents containing heavy metals that are being dumped into the water. The presence of these heavy metals in water is harmful for the environment, human health, and aquatic life. It is necessary to develop cheap and friendly method such as agricultural waste to remove these metals. These industrial effluents are known to contain more than one heavy metal; thus, the paper presented here examines the effects of dose of adsorbent, metal type, and the presence of another metal on heavy metal removal by coffee waste. Results showed that (1) increasing the dose of coffee waste increases the removal of

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heavy metal from the samples. As the adsorbent dose increased from 1 g - 4 g, the percent metal removal increased from 73-92% for copper and 50-74% for zinc from single-metal solutions and from 26-78% for copper and 18-58% for zinc from binary-metal solutions (2) there is selectivity in favor of copper removal from the binary metal mixture by the coffee waste as shown above (3) ion type effect was observed in that more copper was adsorbed from both mono and binary metal samples (4) the presence of another metal as impurity increased metal adsorption hence, more adsorption occurred from binary metal solution than from the single metal solution.

Keywords: Adsorption; coffee waste; copper; zinc; wastewater; heavy metals; remediation.

1. INTRODUCTION

Globally, contamination by heavy metals such as, copper, and zinc poses very harmful and serious problems to human health, the environment, especially the water sources, and the fauna and flora of these bodies of water [1]. Although zinc and copper are essential elements that the body needs and can regulate their levels, in large doses, they can have harmful and fatal effects for human health. Heavy metals such as zinc and copper can gain entry into the human body through inhalation, skin absorption, and ingestion [2]. Acute exposure to zinc causes brain cell death, respiratory disorder, gastrointestinal tract problems, and elevated risk of prostate cancer [2-5]. Chronic and excessive copper exposure pose great human health risk which can lead to death, renal and hepatic failure liver disease, neurological defects, and alzheimer [6]. Copper toxicity from ingestion of copper polluted drinking water led to outbreak of childhood cirrhosis and even death [7-11]. Not only does exposure to excessive copper and zinc pose serious human health risk, they also have deleterious effect on fish, wildlife, and invertebrates [12-13]. Although many techniques exist for the removal of metals from contaminated water [14-15], however, adsorption method using low cost and readily available agricultural waste materials proved to be very effective in removing metals such as lead, and copper from contaminated water. These agricultural wastes and biomaterials include corn and palm husks [16], spinach [17], coffee and tea [18], groundnut shell [19] and chitin and peat moss [20], walnut, almond, and hazelnut, and pistachio shells [21], rice straw [22], and other agricultural and industrial wastes [23].

Metal adsorbing property of agricultural wastes and biomaterials is affected by their functional groups such as proteins, carbohydrates carboxyl, hydroxyl, sulfate, phosphate, phenolic and amino groups that can bind metal ions [18,24]. Coffee waste has been used for the removal of copper [25-26], zinc [27-28] from single-component metal waste water. Limited studies have examined the removal of metals from binary and ternary component metal solutions by biomaterials at lower concentrations [27-28]. Thus, this study examined the selectivity in copper and zinc adsorption onto coffee waste from a binary metal (Cu-Zn) aqueous solution at high (500 PPM).

2. MATERIALS AND METHODS

2.1 Preparation of Copper Nitrate (1000 ppm of Cu^{2+})

A standard solution of 1000 ppm of copper (II) was prepared by dissolving 3.73 g of $Cu(NO_3)_2.2.5\ H_2O$ from Fisher Scientific (Lot 143404), 98.8% purity in enough deionized water to give weighed and diluted with deionized water to give a 1000 ml of solution. Other copper ion concentrations were prepared by diluting the stock solution.

2.2 Preparation of Zinc Nitrate (1000 ppm of Zn^{2+})

A standard solution of 1000 ppm of Zinc (II) was prepared by dissolving 4.55 g $Zn(NO_3)_2.6H_2O$ from Fisher Scientific (Lot 138261), 98.0% pure in enough deionized water to give 1000 ml of solution. Other zinc concentrations were prepared by dissolving the stock solution.

2.3 Preparation of Mixed Metal Solution of Cu^{2+} + Zn^{2+} (1:1)

A 500 PPM mixed solution of **Cu^{2+}** and **Zn^{2+}** (prepared from a 1:1 volume ratio) were poured into a 500 ml volumetric flask and the mixture was stirred to mix for ten minutes.

2.4 Preparation of Coffee Waste Adsorbent

The coffee waste was collected local PJ's Classic Roast Coffee shop. The coffee waste was stored in a plastic bag inside of styrofoam box. The coffee waste was washed three times with deionized water, and it was dried in the laboratory Oven Model 40 GC for 24 h at 125℃. The dried coffee waste was pulverized using a blender followed by sieving using a 500 μm sieve. Six sets of triplicate samples for respective 1 g, 2 g, and 4 g coffee waste were weighed into separate labeled reaction tubes. The tubes for copper, zinc, and copper/zinc mixture were labeled as follows.

For single ion system:

Cu^{2+}-1g-CW1-3, Cu^{2+}-2g-CW1-3, and Cu^{2+}-4g-CW1-3;
Zn^{2+}-1g-CW1-3, Zn^{2+}-2g-CW 1-3, and Zn^{2+} -4g-CW1-3;
Cu^{2+}/Zn^{2+} - 1g CW1-3, Cu^{2+}/Zn^{2+}- 2g-CW1-3, Cu^{2+}/Zn^{2+}-4g-CW1-3.

Where 1 g-CW1-3 = triplicate samples of copper treated with 1 g coffee waste
Where 2 g-CW1-3 = triplicate samples of copper treated with 2 g coffee waste and
Where 4 g-CW1-3 = triplicate samples of copper treated with 4 g coffee waste

The zinc single metal reaction tubes were labelled following the method for copper.

The binary metal system, Cu/Zn (copper/zinc mixture) was labeled similarly.

2.5 Treatment of the Heavy Metal Solutions with the Adsorbent

For each labeled tube, 40 mL of the respective 500 ppm solution of heavy metal was added. After this step, all tubes containing coffee waste with the respective metal solution were placed in the Shake Table for 3 h.

2.6 Sample Preparation and Analysis

After 3 h, the shaker was stopped, and the test tubes were transferred to a centrifuge for 10 minutes at 3000 rpm. Each supernatant was transferred into other labeled test tubes, and they were sent to a commercial analytical laboratory, PACE Analytical Services, Inc. to analyze the concentration of heavy metals in each of the solutions. The concentration of the heavy metal/s remaining after the exposure period analyzed using EPA Method 6010 (Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)).

3. RESULTS AND DISCUSSION

3.1 Effect of Adsorbent Dose on Metal Removal from Single Metal Solutions

Table 1 below show the residual copper and zinc concentrations after the treatment of each metal solution with various doses of the adsorbent while Figs. 1 and 2 illustrate the percent of copper and zinc removed from respective single metal solution. The data clearly demonstrated that the coffee waste adsorbent has a greater affinity for copper than zinc across all adsorbent doses investigated. This could be explained in part by the possibility that in addition to the adsorption on the outer surfaces on the adsorbent, there could also be intra-particle diffusion from the outer surface into the pores of the adsorbents [29-32]. Thus, the smaller size of copper ion makes it easier for copper ion to diffuse into the adsorbent pores easier than zinc.

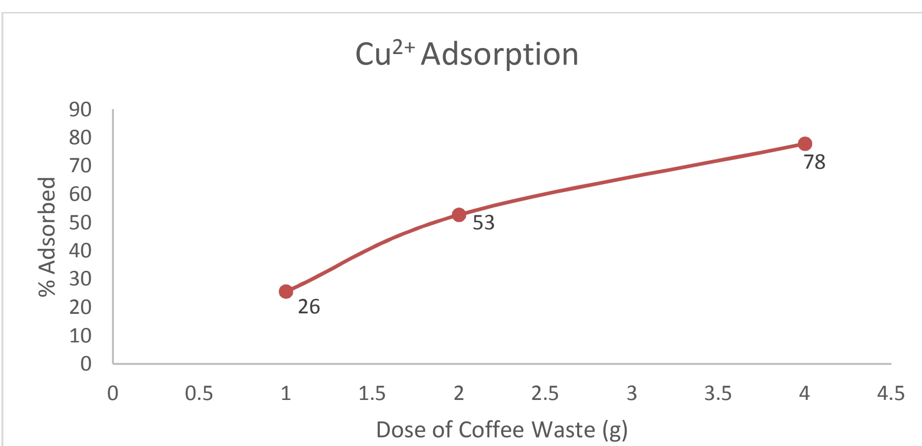

Fig. 1. Percent of copper adsorbed

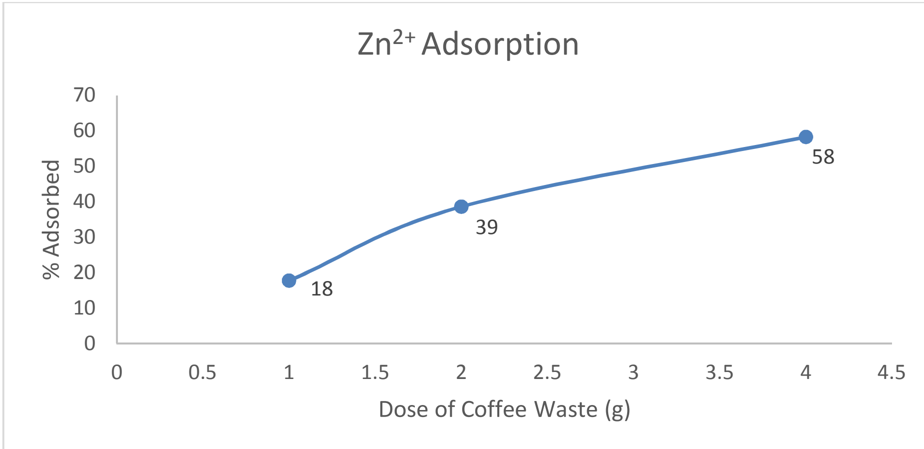

Fig. 2. Percent of zinc adsorbed

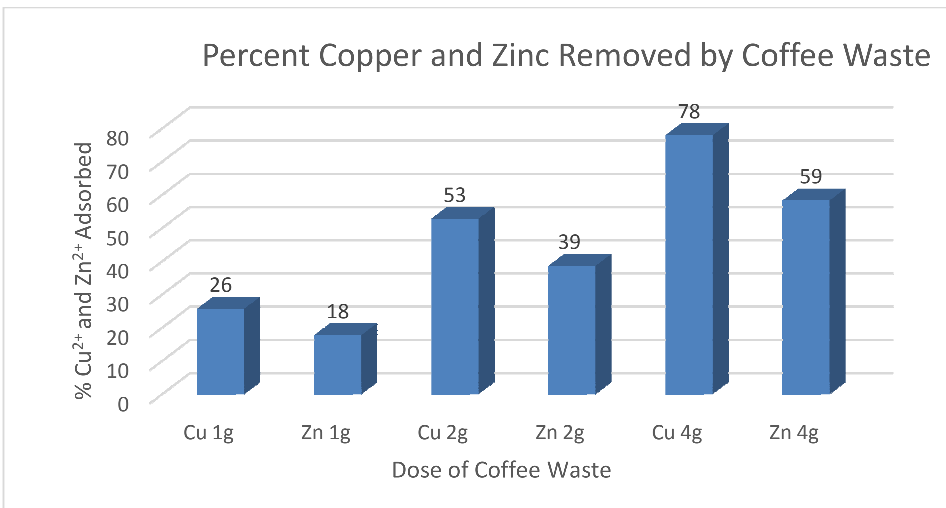

Fig. 3. Comparison of percent copper & zinc adsorbed by different doses of coffee waste

Fig. 3 compared the percent adsorption of copper and zinc form single metal solutions. The data demonstrate that as the dose of coffee waste increases, the percent of metal removed also increases. Furthermore, the graph suggests that more copper is removed from metal solution than zinc.

Figs. 4 and 5 compared residual copper and zinc concentrations after contact with coffee waste and the control solutions. The results suggest that as the dose of coffee waste increases, the concentration of residual metal ion decreases.

The Table 2 shows residual concentrations of copper and zinc from binary metal ion (copper+ zinc) solution after treatment with coffee waste.

It is worthy to note that the data on Table 2 and Figs. 6-9 unequivocally showed that copper was preferentially removed from the binary metal solution than zinc. At adsorbent dose of 2 g and 4 g, copper was removed three times more than zinc. The observed result could be explained by the fact that the major pathway or the slow step in chemical adsorption of metal onto an adsorbent involves intra particle diffusion of metals (initially covalently or ionically adsorbed on the adsorbent surface) into the active sites of the pores of the adsorbent [20,27-32]. Thus, the observed variation and selectivity in adsorption of copper over zinc could be attributed to the larger size of zinc ion which makes it more difficult for it to enter the pores of the coffee waste particles (500 µm mesh) used as adsorbent. It is also interesting to note that more copper was

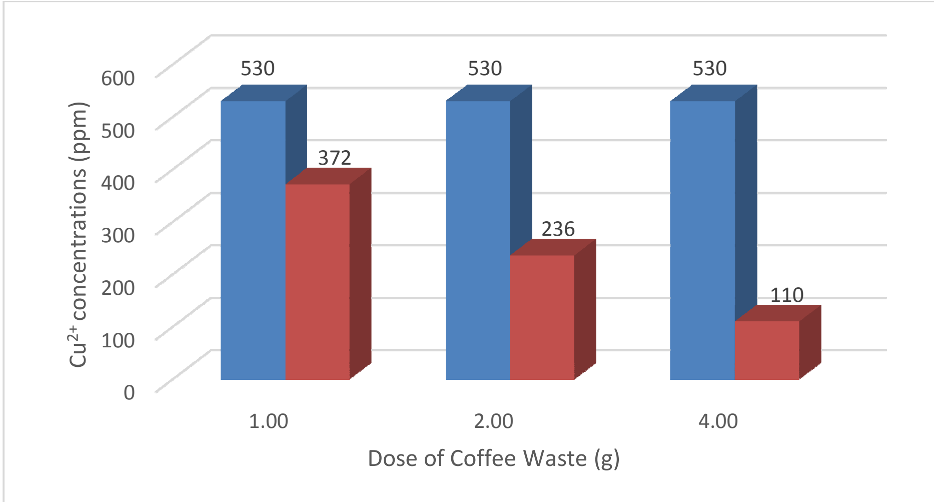

Fig. 4. Residual copper ion after exposure to coffee waste compared to control

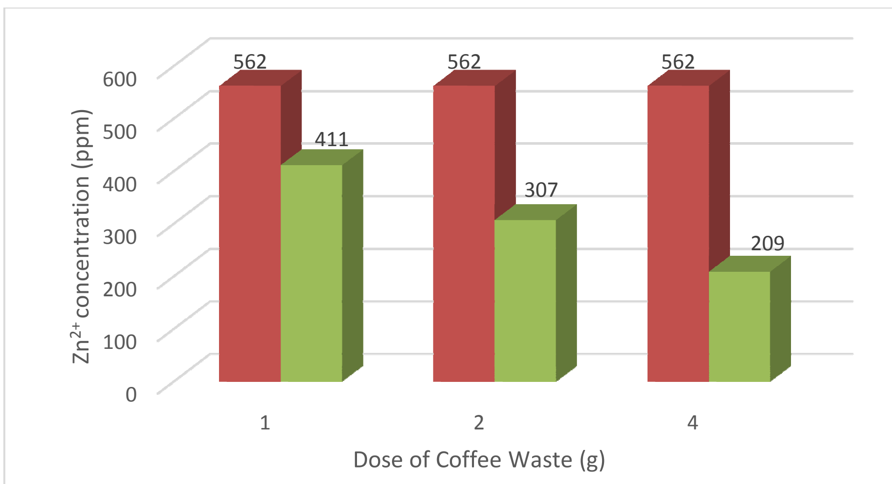

Fig. 5. Residual zinc ion after exposure to coffee waste compared to control

Table 1. Effect of dose of absorbent on 500 ppm of Cu and Zn using coffee waste

Sample	Cu			Zn		
	1 g-CW	2 g-CW	4 g of CW	1 g-CW	2 g of CW	4 g of CW
1	376	236	110	405	308	214
2	369	239	114	407	311	199
3	370	233	107	422	302	213
Average Residual [Metal] in PPM	372	236	110	411	307	209
Standard Deviation	3.8	3	3.5	9	4.6	8
Standard Error	2.2	1.7	2	5	2.6	4.8
% Adsorbed	26	53	78	18	39	58

1 g-CW = 1 g of coffee waste; 2 g-CW = 2 g of coffee waste; 4 g of CW = 4 g coffee waste

removed from the binary metal (Cu + Zn) solution at each of the three doses used (73%, 86%, and 92%) than from the mono copper solution (26%, 53%, and 78%). This could be that the zinc acts as an impurity in the copper solution as reported by Sdiri in his adsorption study heavy metal by limestone in which impure limestone contaminated by silica, iron, aluminum adsorbed more metal than the pure limestone [33].

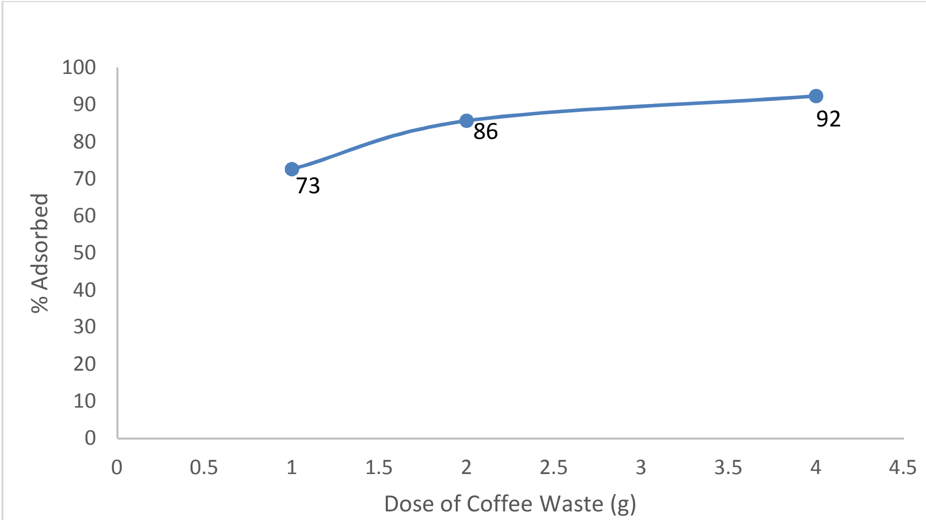

Fig. 6. Percent copper removed from Cu^{2+} Zn^{2+} (1:1) solution

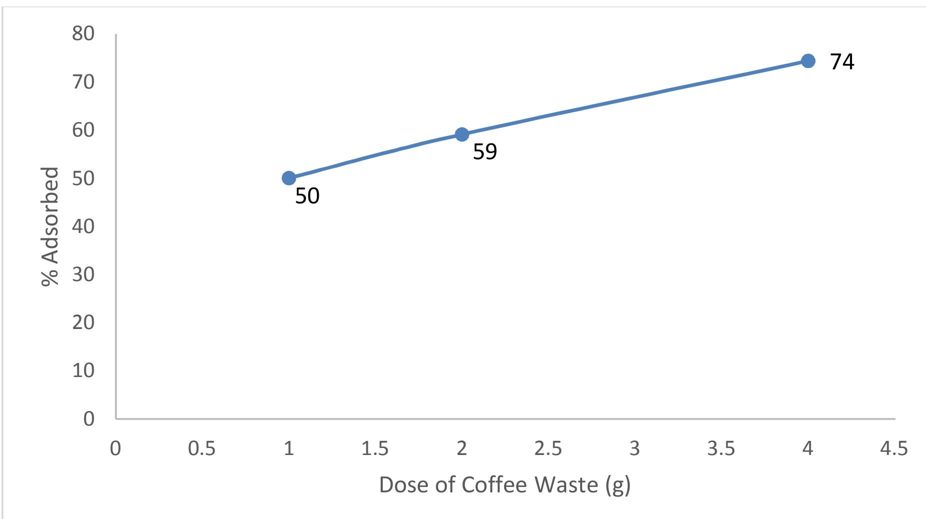

Fig. 7. Percent zinc removed from Cu^{2+} Zn^{2+} (1:1) solutions

Table 2. Effect of coffee waste adsorbent dose on 500 ppm of binary solution of Cu/ Zn

Sample		**Cu^{2+}+ Zn^{2+}**		
		1 g of CW	**2 g of CW**	**4 g of CW**
1	Cu^{2+}	143	68	39
	Zn^{2+}	258	201	133
2	Cu^{2+}	130	76	38
	Zn^{2+}	239	212	125
3	Cu 2+	137	71	38
	Zn 2+	252	200	126
Average Residual [Metal] in PPM	Cu^{2+}	137	71	38
	Zn^{2+}	250	204	128
Standard Deviation	Cu^{2+}	7	4	1
	Zn^{2+}	10	7	4
Standard Error	Cu^{2+}	4	2	0.4
	Zn^{2+}	6	4	3
% Adsorbed	Cu^{2+}	73	86	92
	Zn^{2+}	50	59	74

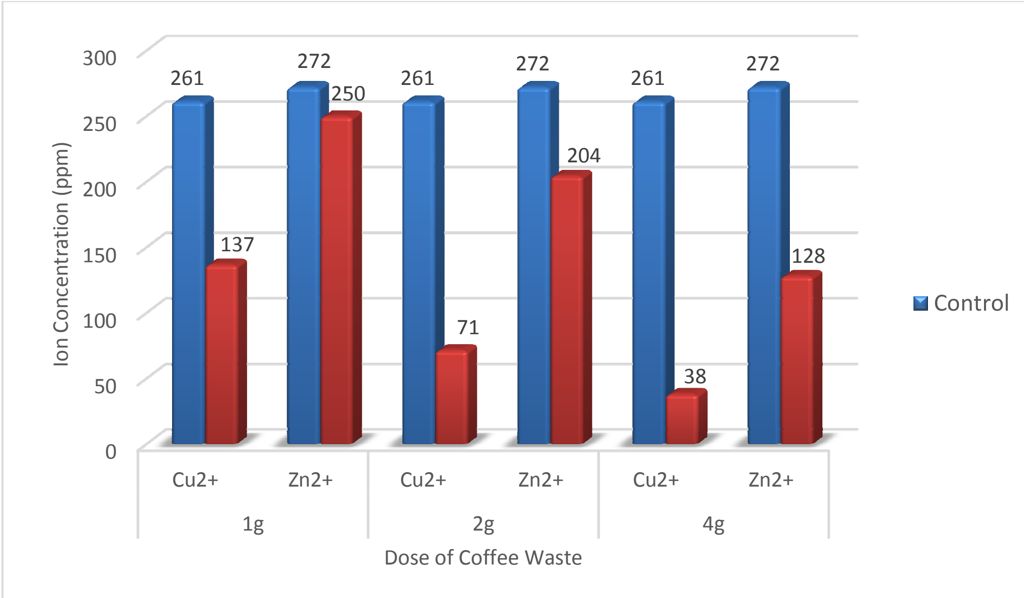

Fig. 8. Concentrations of copper and zinc from binary (1:1 Cu^{2+}: Zn^{2+}) solution compared to controls

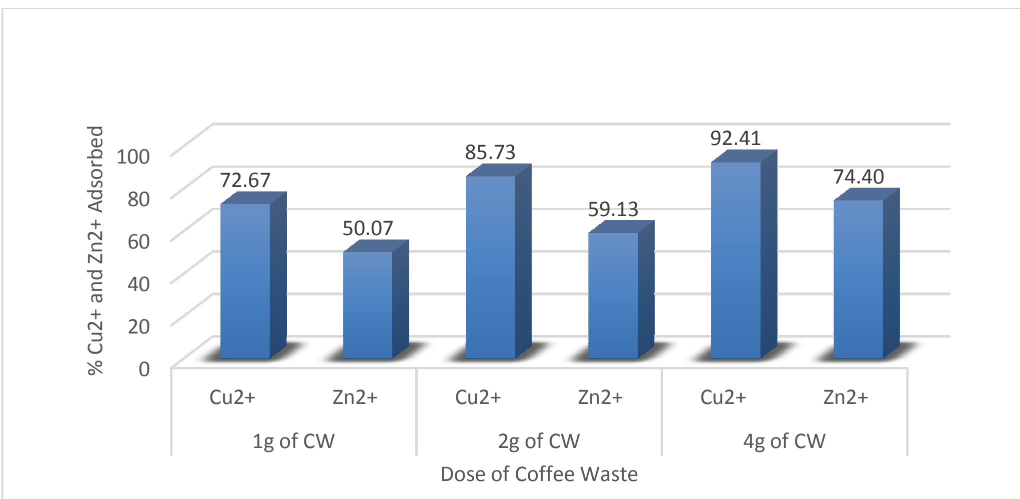

Fig. 9. Comparison of Cu (II) and Zn (II) removed from Cu^{2+} Zn^{2+} (1:1) solutions

The adsorption of a metal by an adsorbent occur in different sites depending on the type/s of functional groups at the sites/s [32]. Thus, metal removal by an adsorbent depends on many factors, such as dose of adsorbent, metal type, and ionic strength, pH, initial metal concentration, etc. The ability of the adsorbent to bind metals depends on the functional groups and the affinity of these groups to bind to a specific metal. Coffee waste showed to be a better adsorbent for copper than for zinc. Another reason for the selective copper removal by the adsorbent could be that the binding sites in the coffee waste prefer copper to zinc. The results of the adsorption involving copper and zinc either in a single or binary metal systems using agricultural waste or biomaterial favor removal of copper more than zinc [27-29,31,33-35].

4. CONCLUSION

Coffee waste is shown to be a suitable adsorbent for the treatment of effluent containing metal ions. However, the adsorption capacity of an adsorbent is dependent on a variety of factors such as the nature and dose of adsorbent, metal ion type, initial metal concentration, exposure time, and number of metal ions. Although copper and zinc ions have the same charge, however, the nature and mode of their interactions with the adsorbent differed greatly as the data suggested. Our results showed that the adsorption of zinc decreased in the binary-metal system than in the single metal system while the adsorption of copper remained fairly steady in both binary and single metal solutions. Furthermore, the results suggest that the nature and mechanism of the adsorption of a specific metal ion from a binary metal solution may change or may be different from that of the single metal system. Additionally, the data presented here-in which suggest competitive and selective metal removal provide fundamental information that must be considered in the development of innovative remediation techniques for the treatment of multi-metal effluents.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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