



Competitive Adsorption of Cu(II) and Zn(II) from Binary Heavy Metal Solutions by 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 SZ and SOL 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.

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ABSTRACT

Adsorption process has been proven to be one of the best water treatment technologies globally and activated carbon is undoubtedly considered a universal adsorbent for the removal of a variety of pollutants from water. However, widespread use of commercial activated carbon is often times restricted due to its higher costs. Attempts have been made to develop inexpensive adsorbents utilizing numerous agro-industrial and municipal waste materials. Use of waste materials as low-cost adsorbents is attractive due to their contribution in the reduction of costs or waste disposal, therefore, contributing to environmental protection. In this article was investigated the adsorption behavior of coffee waste when exposed to both single and binary metal component solutions under varying initial concentrations (1000, 500, and 250 ppm) and contact time (3 and 24 hrs.) It is

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evident from the literature that various low-cost adsorbents have shown good potential for the removal of various pollutants. However, there are few issues and drawbacks on the use of low-cost adsorbents in water treatment that have been discussed in this paper. Additionally, more research is needed to find the practical utility of low-cost adsorbents such as waste coffee on a commercial scale. After the exposure times, the residual concentrations of each heavy metal was determined by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), using EPA Method 6010. Results suggest that the percentage of adsorption of Cu and Zn decreases as the initial metal concentration increases. The coffee waste also has a higher affinity for Cu than Zn ion. The percentages for metal ion removal from the single metal solution are 250 ppm (73.47%), 500 ppm (46.45%), 1000 ppm (27.69%) for copper and 250 ppm (55.08%), 500 ppm (32.78%), and 1000 ppm (21.22%) for zinc. For the competitive metal removal from the binary Cu-Zn solutions, the percentages are 125 ppm (85.67%), 250 ppm (68.93%), and 500 ppm (46.62%) for copper and 125 ppm (49.67%), 250 ppm (7.73%), and 500 ppm (4.59%) for zinc, respectively.

Keywords: Competitive adsorption; heavy metal; coffee waste; metal adsorption; remediation; waste water.

1. INTRODUCTION

Pollution of water sources by heavy metals such as copper and zinc has been recognized as a global public health problem [1]. They are not biodegradable and persist in the environment for a long time. Thus, their uptake, transport, accumulation, and propagation by plants and animals into the food chain exacerbate their toxic health effects. Copper and zinc pose very harmful and serious problems to human health and the fauna and flora of these bodies of water [2]. 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 [3-4]. Zinc and copper like other heavy metals, gain entry into the human body through inhalation, skin absorption, and ingestion [5]. They are among the most common metals discharged into wastewater from textile, dyeing, metal finishing, electroplating, mining, tanning, and smelting industries [6]. Excessive exposure to zinc may initiate oxidative damage, brain cell death, respiratory disorder, gastrointestinal tract problems, and elevated risk of prostate cancer [2,5-10]. Chronic and acute exposure to copper results in its accumulation and toxicity in the body including liver cirrhosis, neurological, and brain disorders as well as skin, pancreatic, hepatic, renal, and heart diseases, including death [5-7,11-12]. Not only does exposure to excessive copper and zinc pose serious human health risk, they also have deleterious effect on fish, wildlife, and invertebrates [13-14]. Consequently, there is a need to mitigate zinc and copper concentrations in water and waste water below exposure limit. A wide range of methods exist for the removal of heavy metal

ions from aqueous solutions, waste water, and industrial effluents. These methods include chemical precipitation [15-17], electro-chemical treatment [18], ion exchange, adsorption using activated carbon [19-20], and modified biomaterials [21-22]. Unfortunately, some of these processes are either expensive or may introduce potential secondary impacts such as introduction of toxic chemical reagents or transformation products, that may need additional remediation. The response to the ever growing need for cheap, safe, and effective techniques for water clean-up has led to the emergence of a number of alternative processes.

In recent years, a wide range of agricultural or biological materials have been used as sorbents for the removal of heavy metals from contaminated water [23-29]. Coffee waste has been used for the removal of copper [30-31] and zinc [32-33] 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 [32-33]. Thus, this study examined the selectivity in copper and zinc adsorption onto coffee waste from a binary metal (Cu-Zn) aqueous solution at high concentration (1000 ppm).

2. MATERIALS AND METHODS

2.1 Preparation of Coffee Waste Adsorbent

The coffee waste was collected from a local PJ's Classic Roast Coffee shop in New Orleans. The coffee waste was stored in a plastic bag and brought to the laboratory. The coffee waste was

washed three times with deionized water and it was dried in a laboratory Oven Model 40 GC for 24 hr at 125°C. The dried coffee waste was pulverized using a blender followed by sieving using a 500 µm sieve. Nine sets of triplicate samples of 2 g. coffee waste samples were weighed into separate labeled reaction tubes for treatment with 250, 500, and 1000 ppm solutions of each metal. The tubes for copper, zinc, and copper/zinc mixture were labeled as follows:

For single ion system:

Cu250, Cu500, Cu1000; Zn250, Zn500, and Zn1000

For the binary metal (Cu/Zn) system:

Cu-Zn125, Cu-Zn250, and Cu-Zn 500, Cu-Zn1000

The corresponding tubes for the controls for copper, zinc and copper-zinc solution samples for 250, 500, and 1000 ppm were also labelled as:

Cu250-control, Cu500-control, Cu1000-control, Zn250-control, Zn500-control, Zn1000-control, Cu-Zn125-control, Cu-Zn250-control, and Cu-Zn 500-control, Cu-Zn1000 control

2.2 Preparation of Copper Nitrate (1000 ppm of Cu²⁺) Solution

The 1000 ppm copper (II) ion solution was prepared by dissolving 3.73 g of Cu (NO₃)₂·2.5 H₂O from Fisher Scientific (Lot 143404), 98.8% purity, with deionized water in a 500-mL beaker. The mixture was transferred into a 1000 ml volumetric flask and diluted with water to get a 1000 ml solution. A magnetic stirring bar was slowly lowered into the flask and the mixture was stirred to thoroughly mix. The 500-125 ppm solutions were prepared by dilution.

2.3 Preparation of the 500, 250, 125 ppm of Zinc Nitrate (Zn²⁺ ion) Solutions

Following the procedure used to prepare the Copper (II) ion solutions, the 1000 ppm zinc ion solution was diluted serially to prepare the desired concentration.

2.4 Preparation of Mixed Metal Solution of Cu²⁺ and Zn²⁺ (1:1) Solution

A 1:1 v/v of zinc and copper solutions for each concentration were mixed to give the

corresponding Cu (II)-Zn(II) ion solutions. For example, 250 mL of 500 ppm of copper (II) ion solution was mixed with 250 mL of 500 ppm of zinc(II) ion solution in a volumetric flask and stirred well to give the corresponding binary Cu²⁺-Zn²⁺ ion solution of about 250 ppm of Cu(II) ion and 250 ppm of Zn(II) ion.

2.5 Treatment of the Single Metal Solutions with the Adsorbent

To each respective set of triplicate labeled tubes containing the coffee waste, 40 mL of 1000, 500, 250 ppm of copper and zinc ion solutions prepared above was added. The corresponding 40 mL solutions for each metal solution for each concentration were respectively placed into empty labelled control tubes without the waste coffee adsorbent. Each tube and its content were hand shaken, vortexed, placed in a shaker and agitated for 3 hr at room temperature. One set of experimental tubes was allowed to agitate for 24 hours.

2.6 Treatment of the Binary Metal (Copper-Zinc) Solutions with the Adsorbent

For each concentration, 20 ml of copper and 20 mL of zinc solutions were poured into the respective triplicate labelled sample tubes. The appropriate and corresponding controls were also prepared in a similar manner. Each tube was hand shaken, vortexed, and placed on a shaker and agitated for 3 hours.

2.7 Sample Preparation and Analysis

After the 3 hours of agitation, the shaker was stopped, and the tubes with their content were centrifuged for 10 minutes at 3000 rpm. The supernatants were transferred into other labeled tubes. The samples were sent to a commercial analytical laboratory, PACE Analytical Services, Inc. for copper and zinc ion analysis using EPA Method 6010 (Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES)).

3. RESULTS AND DISCUSSION

3.1 Residual Cu(II) and Zn(II) after Treatment with Coffee Waste

Table 1 and Fig. 1 illustrate the residual copper and zinc in their respective single metal solution after treatment with coffee waste compared to

control. At the end of the experiment, the residual Cu ion concentrations were 69, 284 and 771 ppm respectively. Residual zinc concentrations were 117, 378, and 861 ppm for 250, 500, and 1000 ppm solutions, respectively.

Table 1. Residual [Cu] and [Zn] after treatment with coffee waste in single metal solutions

	Concentration of Cu and Zn ions in PPM					
	Copper			Zinc		
	250 ppm	500 ppm	1000 ppm	250 ppm	500 ppm	1000 ppm
Control	261	530	1067	261	562	1093
Coffee waste treated	69	284	771	117	378	861
STDev	73.47	47	27.69	55.08	32.78	21.22

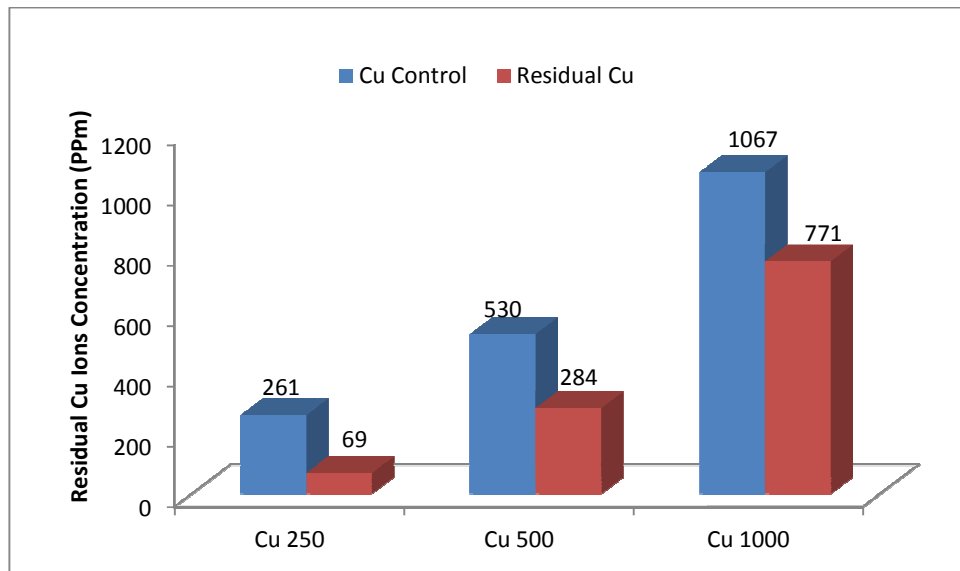


Fig. 1. Copper removal by coffee waste compared to control - single metal solution

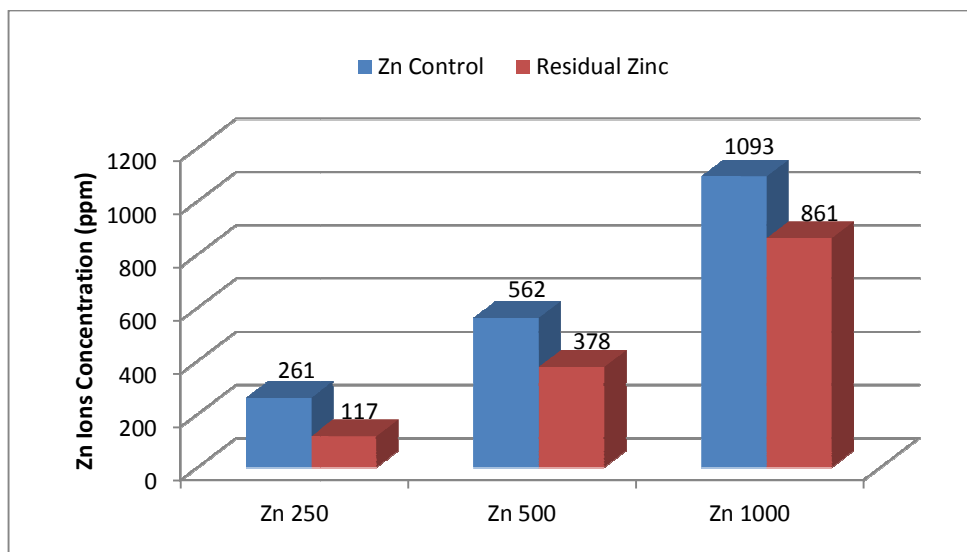


Fig. 2. Zinc removal by coffee waste compared to control - single metal solution

Fig. 2 illustrates the residual concentration of zinc in solutions after treatment with coffee waste compared to control (zinc solution without coffee waste) for single metal solutions. In all concentrations the coffee waste was able to adsorb Zn ions.

3.2 Percent Cu and Zn Ions Adsorbed from Single and Binary Metal Solutions

Table 2 and Fig. 3 show the percentage of adsorption of Cu and Zn by coffee waste from single metal solutions. For copper ion, the percentages of adsorption were 73%, 47%, and 28% from 250 ppm, 500 ppm, and 1000 ppm solutions, respectively while for zinc ion, the percentages of adsorption are 55%, 33%, and 21% from 250 ppm, 500 ppm, and 1000 ppm, respectively.

The adsorption of Cu and Zn ions decreased as the initial metal concentration was increased. At all metal ion concentrations, more copper was adsorbed than zinc.

Table 3 and Fig. 4 showed that copper has a higher tendency to adsorb to the adsorbent

across all metal concentrations used. It is worthy to note that the percent of copper ion adsorbed from the single Cu and the binary Cu-Zn solutions were very close: For the 250 ppm metal ion concentration, 73% of copper was removed from copper solution while 69% of copper was removed from Cu-Zn solution. Similarly, for the 500 ppm metal solution, 47% of copper was removed from both the 500 ppm single copper and the 1000 ppm binary Cu-Zn solutions. However, this was not the case with zinc. The adsorption of zinc decreased drastically from single to binary solutions. For example, at the 250 ppm metal concentration, zinc adsorption went from 55% from the single metal solution to 8% from the binary solution. Similar observation has been reported by Tan [34]. However, the work reported here clearly shows that the adsorption of zinc is repressed by the presence of copper.

Probably, the electron configuration of the two ions could be playing a role in their adsorption whether it is the surface adsorption or intra particle diffusion. At constant adsorbent dose, metal adsorption decreased for both copper and zinc as metal ion concentration increased.

Table 2. % Cu(II) and Zn (II) ions adsorbed from single metal solutions by coffee waste

	Cu(II) 250 ppm	Cu(II) 500 ppm	Cu(II) 1000 ppm	Zn(II) 250 ppm	Zn(II) 500 ppm	Zn(II) 1000 ppm
Average %	73	47	28	55	33	21
STDev	1.57	0.53	0.64	2.92	1.84	2.6

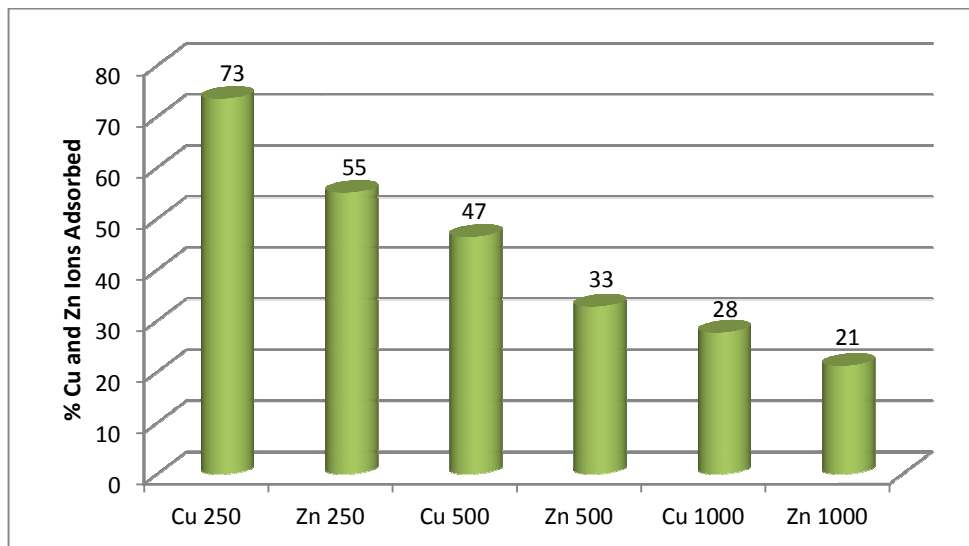


Fig. 3. Percent copper and zinc removed by coffee waste - single metal solution

Table 3. % Cu(II) and Zn (II) ions adsorbed by coffee waste from binary metal solutions

Samples	CuZn 250 ppm	CuZn 500 ppm	CuZn 1000 ppm	ZnCu 250 ppm	ZnCu 500 ppm	ZnCu 1000 ppm
Average %	86	69	47	49	8	5
STDev	0.58	4.1	4.7	4.0	0.58	1.5

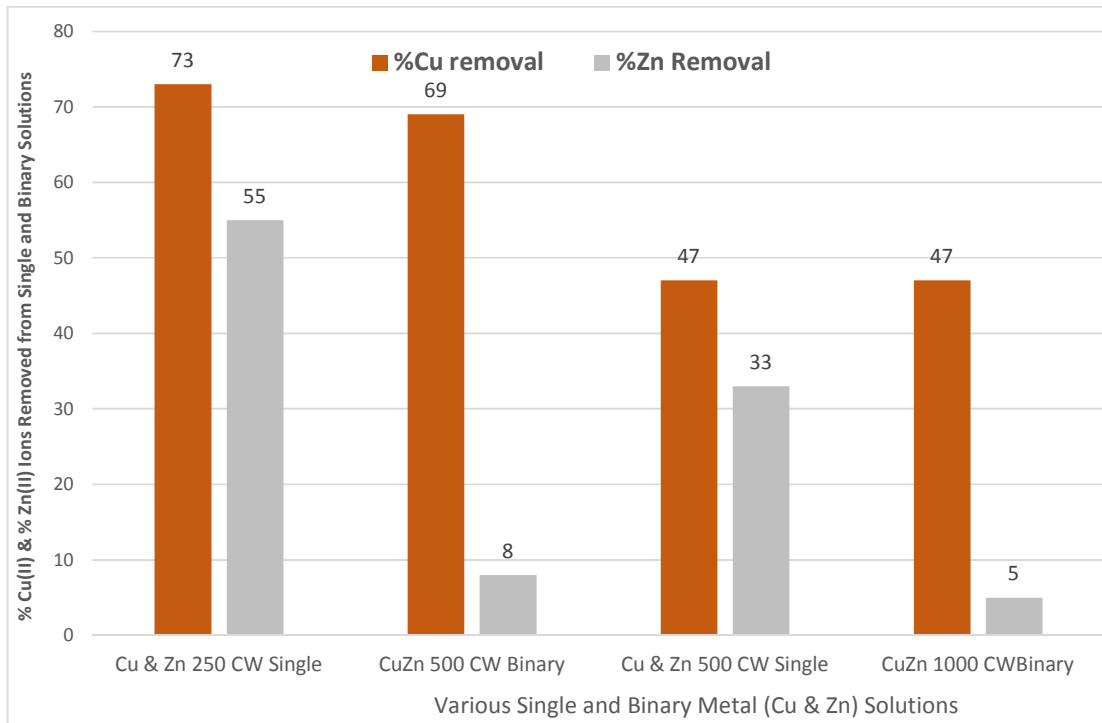


Fig. 4. Comparison of percent copper and zinc removed from single and binary metal solutions

3.3 Effect of Exposure Time on Copper and Zinc Adsorption by Coffee Waste

Separate but similar reactions were carried out with 500 ppm of (a) single metal component copper ion solution (b) single metal component zinc ion solution, and (c) binary metal component (copper-zinc ion) solution. Each solution was agitated with coffee waste for 24 hr. The results were compared with those with 3hr contact time as shown in Fig. 5. Increasing the contact times from 3 to 24 hours, the percent adsorption from single metal solutions increased 1.1 and 1.2 times for copper and zinc, respectively while for binary metal solutions, the adsorption increased 1.2 and 7.3 times for Cu and Zn, respectively.

3.4 Selective or Competitive Site Adsorption

The percent copper adsorption by coffee waste from single metal solution mirrors that from

binary metal solution for any given metal concentration.

For an example, copper adsorptions from 250 ppm of single and binary metal solutions are 73% and 69%, respectively while at 500 ppm metal concentrations, 47% adsorption was observed from both single and binary metal solutions. However, for zinc, the adsorption from 250 ppm of single and binary metal solutions are 55% and 8% while for the 500 ppm solutions, 33% and 5% adsorption were observed. The fact that the percent adsorption ratio between single and binary solutions for copper is near unity at all concentrations suggests that (a) copper is not competing for its adsorption site with zinc, (b) coffee waste may have a specific high affinity site for copper compared to the affinity it has for zinc at another site. On the other hand, the drastic seven fold decline in zinc adsorption from the binary metal solution may suggest that copper acts as a competitor for zinc's adsorption site across all concentrations studied. Thus, it could

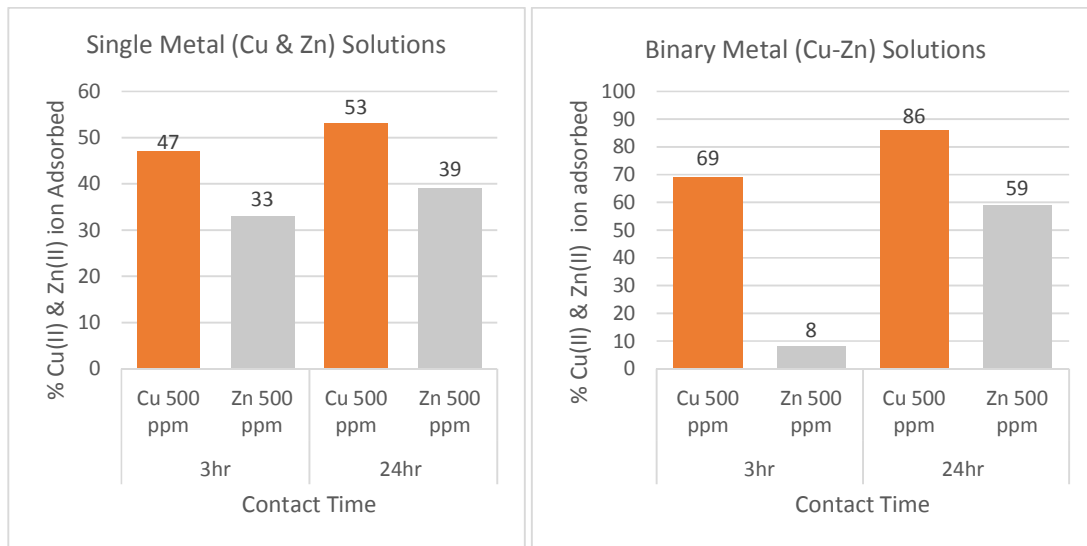


Fig. 5. Effect of contact time and metal type on the adsorption of Cu and Zn by coffee waste

be that the adsorption of a metal by an adsorbent may depend on several factors such as (a) metal types (b) ability of a metal to participate in intra-particle diffusion into the pores of the adsorbent (c) initial metal concentration, (d) the type/s of functional groups at the adsorbent sites/s (e) the affinity of these groups to bind to a specific metal and (f) contact time, etc. [17,35-36].

4. CONCLUSIONS

The results of this project unequivocally demonstrated that coffee waste has a higher specific binding affinity site for copper than zinc. This could be that the zinc acts as an impurity in the copper-zinc solution as reported by Sdiri [37] that impure limestone adsorbed more metals than pure limestone. 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. This is in agreement with the findings reported by Sdiri [38] and Agwaramgbo [39]. These 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.

Finally, this paper provides a fundamental but important information that must be considered

when developing techniques for the cleanup of multi-metal contaminated water sources.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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