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BIOAVAILABILITY OF METALS IN THE FUNTUA TEXTILE WASTEWATER, NORTH WESTERN NIGERIA

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ABSTRACT

Textile wastewater pose a significant threat to surface water especially the water bodies closer to the textile industry locations. The study investigated the bioavailability of cobalt (Co), copper (Cu), lead (Pb), nickel (Ni) and chromium (Cr) in wastewater from ten sampling points including wastewater from point of effluent discharge in Funtua textile across Funtua region. The trends in the metal bioavailability (mg/L) among the fractions were; Zn Cu: total> mobile > dissolved > particulate; Pb: total> particulate > mobile> dissolved; Ni: total> particulate > dissolved> mobile; Cr: total > particulate > mobile > dissolved, respectively. All the concentrations of the metal ions were above the WHO (2006) and USEPA (2000) tolerable limits across the sites, with the exception of Co which was not detected in all the fractions. While lead and chromium was detected in S1, S2 and S1, S10, respectively. The order of the metals bioavailability was; total>mobile>dissolved>particulate, with more than 50% found in the bioavailable phase. Hence, the surface waters within the vicinity of the textile industry were greatly at risk of being polluted by these toxic metals and subsequently affecting the inhabitants who use the water for agricultural and other domestic activities untreated, through the food chain transfer. The health implications associated with the toxic metals include an irreversible damage to nervous system, gastric and intestinal disorder, heart disease, liver, brain damage, mental retardation and teratogenic effects. Key words: Metals, wastewater, surface water, textile industry, North western Nigeria.

INTRODUCTION

The pollution of surface waters is significant, though on a local scale. However, it has been steadily increasing recently. Today, a number of small and large companies that are into activities such as textile, tanning, and paint industries are dispersed throughout, mostly close to the villages that rely on this surface water for agriculture and survival. Because there are no centralized sewage systems, industrial effluents from companies are typically dumped untreated into streams, rivers, and other bodies of water (Olade, 1987). This has resulted in high alarming levels of lead (Pb), nickel (Ni), copper (Cu), and chromium (Cr) in some localized areas.

Funtua is an agrarian community with farming activities ranging from crop cultivation to animal husbandry being practiced. The location of a textile industry around this area has led to constant release of untreated wastewater into the environment thereby resulting to deterioration of water quality in Funtua. Heavy metal pollution of water has serious consequences because it may poison both terrestrial and aquatic life, induce disease owing to the presence of some dangerous substance that may affect the water quality, and severely impede economic activity (Asonye et al., 2007). The presence of various metals, such as chromium, nickel, copper, manganese, mercury, cadmium, and lead, as well as metalloids, such as arsenic, antimony, and selenium, in the natural environment, is a major concern (Adriano, 1986), especially in close proximity to textile sites, landfills, tanning areas, and impoundments, as well as in urban areas and industrial hubs. Due to past industrial operations, which may have resulted in the development of the more bioavailable forms of certain elements, water in these places may contain greater than usual abundances of these elements.

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The percentage of total elements abundances in water that are bioavailable must be determined in order to quantify effects and potential dangers connected with elevated elemental concentrations caused by industrial activities. Metal bioavailability does not always match total metal concentrations. However, knowledge of the chemical speciation of metals in solution, or the specific physicochemical forms that are a component of the total concentration of metal in solution, may be necessary for a more thorough understanding of the cycling of heavy metals in the environment (Martnez et al., 2006).

According to the U.S. Environmental Protection Agency (EPA), the following metals are of particular relevance in bioavailability studies: Al, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Se, and Sb (McKinney and Rogers, 1992). Due to their potential for human exposure and elevated health risk, these metals were chosen. Humans may suffer negative effects from the biota's bioaccumulation of metals in surface water. Due to the pollution created by wastewater utilized in the textile industry, there is growing worry regarding the potentially dangerous consequences of textile wastewater on aquatic biota and humans as a result of the alarming increase of various types of industrial toxicants (Talouizte et al., 2020). Heavy metals in textile effluents typically have a high structural diversity noticeable and indicate ecotoxicological consequences when textile wastewater is released at a considerable concentration level (Talouizte et al., 2020). Environmental exposure to toxic metals may result in bioaccumulation and biomagnification (Tiwari et al., 2016). Therefore, the focus of this study is on assessing the bioavailability of metals in Funtua Textile wastewater as well as the dangers to human health and the environment posed by the discharge of textile wastewater into surface waters.

MATERIALS AND METHODS The Study Area

The study area of this research is the Funtua textile industry and its environments where irrigation are carried out. The textile industry is located at Funtua local government area, Katsina state, Nigeria. The textile industry was established in 1978 and is located between latitude $11^{\circ}34'$ N and longitude $7^{0}14'$ E.

Sample Collection and Pre-treatment

Water samples for analysis was collected in 120mL container which was initially washed with detergent and then rinsed with distilled water. The sample containers were finally rinsed with 10% HNO₃ before sampling. The first sample

(S1) was collected inside the textile industry at the point of effluent discharge, while other water samples (S2-S10) were collected at various point of surface waters where the wastewater is emptied into giving 1km gap for each point.

Chemical Fractionation of Water sample

Chemical fractionation of water samples was carried out on the principle proposed by B"ackstr" om *et al.*, (2003) in duplicate. Samples were subjected to extraction using 2% nitric acid separately. The extraction was aimed at differentiating fractions in three stages as follows.

Fraction I (dissolved): 50mL was decanted from the sampling vessel and filtered through 0.50μ m Teflon filters before acidification with 2% nitric acid.

Fraction II (mobile): 50mL was decanted from the sample vessel and acidified with 2% nitric acid followed by filtration through 0.50μ m Teflon filters after 24hrs.

Fraction III (total): 2% nitric acid was added directly into the sample vessel and shaken rigorously to suspend all particulate matters. The solution was filtered after 24hrs through 0.50μ m Teflon filters. The particulate concentration was calculated as the difference between Fraction III and Fraction I.

Analysis of Cu, Ni, Pb, Co and Cr was performed on an atomic absorption spectrophotometer (AAS). The validation of the procedure for metal determination and efficiency of AAS was conducted by spiking a sample with multi element standard solution containing all metals analysed (APHA, 2005).

Samples analysis

The digests of the samples were analysed for Cu, Ni, Pb, Co and Cr using AAS-650 (variant double beam) and the validation of the procedure for metal determination was conducted by spiking samples with multielement standard solutions containing 5 mg/L of the metals. Spiked samples were used under the same experimental conditions as the procedural blanks (APHA, 2005).

Statistical analysis

The data were expressed as means \pm standard deviation. To show whether there is significant difference between the mean concentrations of the metals across the sites, one way analysis of variance (ANOVA) was used and Pearsons Correlation was used to establish the degree of relationship among the fractions of the analysed metal ions across the fractions using a statistical software package for social science (SPSS version 20).

BAJOPAS Volume 15 Number 1, June, 2022 RESULTS AND DISCUSSION

Tables 1 to 5 shows the percentage bioavailability of Pb, Cu, Ni and Cr in the fractionated wastewater samples across the sampling sites and on these tables the concentrations of various fractions in mg/L were shown. The highest total extractable fraction of Pb in Table 2 was 100 at the bioavailable phase. The order of bioavailable fractions across the sites followed this trend: S2 > S1 while S3 to S10 were below detection limit as shown in Table 2. Furthermore, Table 3 shows elevated levels of copper recorded across the sites with extractable fractions predominantly found in the

bioavailable phase across the sampling sites with exception to S3 and S8 samples which was > 90. The highest bioavailable Cu was recorded at S4. The order of mobility recorded in Table 3 showed the concentration of Cu in the fractionated wastewater samples in this range: S4 > S7 > S2 > S6 > S10 > S5 > S9 > S1 > S3 > S8.

Similarly, Table 4 shows the concentration of Ni in the fractionated water samples in which the lowest bioavailable fraction at S10 was recorded as 50. However, at S7, the highest value recorded for the bioavailable Ni was 100.

Symbol	Description	Unit	limit (WHO, 2006)
Ι	Dissolved fraction	mg/L	Depends on the metal
II	Mobile fraction	mg/L	Depends on the metal
III	Total fraction	mg/L	Depends on the metal
IV	Particulate fraction	mg/L	Depends on the metal
Pb	Lead	mg/L	0.01
Со	Cobalt	mg/L	0.07
Cu	Copper	mg/L	1.0
Ni	Nickel	mg/L	0.02
Cr	Chromium	mg/L	0.05
Bioavailable	(Bv) Equal to the sum of	of dissolved and mobile phas	se's %

Table 1 Fractions	descri	ptions and	WHO	limits.

Table 2 Concentrations (mean ± SD) mg/L of Lead in the fractionated wastewater.

					Sites					
Fraction	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10
I	0.03±0.01	0.00 ± 0.00	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
II	0.38±0.03	0.96±0.00	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
III	0.52±0.00	0.96±0.00	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
IV	0.49±0.00	0.96±0.00	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Bv(%)	65.49	100.00	-	-	-	-	-	-	-	-

Table 3 Concentrations (mean ± SD) mg/L of Copper in the fractionated wastewater.

Fra	action	Sites								
	S1	S2	S 3	S4	S 5	S 6	S7	S 8	S 9	S10
Ι	59.27±0.75	0.45±0.00	0.05±0.01	0.07±0.01	0.07±0.00	0.33±0.01	0.34±0.01	0.21±0.00	0.19±0.01	0.08±0.00
Π	77.11±9.73	0.41±0.01	0.07±0.00	0.07±0.00	0.07±0.01	0.29±0.00	0.30 ± 0.01	0.20±0.00	0.17±0.04	0.09±0.01
III	80.65±2.91	0.48±0.01	0.14±0.00	0.07±0.00	0.08±0.01	0.35±0.00	0.35±0.00	0.48±0.01	0.16±0.00	0.09±0.00
IV	21.38±0.00	0.03±0.01	0.09±0.00	0.00 ± 0.00	0.01±0.01	0.03±0.00	0.01±0.00	0.28±0.01	0.04±0.00	0.01±0.00
<u>Bv</u> ((%) 91.03	97.10	74.29	100.00	95.65	97.00	98.88	76.07	92.86	96.29

Table 4 Concentrations (mean ± SD) mg/L of Ni in the fractionated wastewater.

Fr	action Sites										
	S1	S2	S 3	S4	S 5	S 6	S7	S 8	S 9	S10	
Ι	0.41±0.06	0.00±0.00	0.00±0.00	0.00±0.00	0.12±0.03	0.21±0.08	0.12±0.10	0.00±0.00	0.14±0.10	0.05±0.05	
Π	1.00 ± 0.08	0.00 ± 0.00	0.25±0.25	0.00±0.00	0.06±0.06	0.00±0.00	0.00 ± 0.00	0.01±0.01	0.09±0.09	0.00 ± 0.00	
III	1.11±0.01	0.00 ± 0.00	0.14±0.00	0.15±0.00	0.00 ± 0.00	0.14±0.05	0.00 ± 0.00	0.08±0.00	0.05±0.05	0.00 ± 0.00	
IV	0.71±0.41	0.00 ± 0.00	0.14±0.04	0.12±0.00	0.07±0.00	0.12±0.09	0.00±0.00	0.07±0.00	0.07±0.02	0.05±0.00	
<u>Bv</u>	(% <u>) 78</u> .	-	73.58	55.56	72.00	74.47	100	56.25	30.00	50.00	

BAJOPAS Volume 15 Number 1, June, 2022 Table 5 Concentrations (mean \pm SD) mg/L of Chromium in the fractionated wastewater.

	Sites									
Fraction	S1	S2	S 3	S4	S5	S6	S7	S8	S9	S10
Ι	0.01 ± 0.00	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.09±0.09
II	0.01 ± 0.00	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
III	0.01 ± 0.00	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.11 ± 0.00
IV	0.01 ± 0.00	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.11 ± 0.01
Bv(%)	75.00	-	-	-	-	-	-	-	-	-

The bioavailable trend across the sampling sites was: S7 > S9 > S1 > S6 > S3 > S5 > S8 > S4 > S10 and BDL for S2.

Furthermore, Table 5 shows the bioavailable fractions of Cr across the sampling sites. Bioavailability of Cr was only recorded for S1 and S9 while Cr was not detected in samples S2, S3, S4, S6, S7, S8 and S10.

Generally, it was observed that the levels of metals obtained in all the analysed samples were well above the WHO (2006) limit both across the sites and among the fractions with exception for Pb and Cr, at S3 to S10 and S2 to S9, respectively. Co was not detected on all the wastewater samples. Pb is reckoned as the least mobile heavy metal and this could be ascribed to Pb complexation with organic matter, chemisorption on oxides and silicate clays, and precipitation as carbonate, hydroxide, or phosphate that are all favored at higher pH (McBride, 1994).

The distribution trend among fractions in this study was in this order: total > mobile > dissolved > particulate. This is in agreement with similar work carried out by Uba *et al.*, (2013).

On comparing the results obtained for total concentration of Cu with standard limits (USEPA, 2000; WHO, 2006), S1 was contaminated (concentration > 1 mg/L) with Cu. Thus, the Cu in the analysed wastewater samples was readily bio-available to the environment, contaminating especially the surface water due to water percolation (Uba et al., 2013). Cu being an essential element, acute toxicity of Cu results in hypertension, coma, and death (WHO, 1999). Overall, the total fractions had the highest concentrations of the total extractable Cu across the sites. The concentrations recorded were lower than the values of 85 to 105 mg/L reported by Aiyesanmi and Imoisi., (2011) in a similar work conducted in Benin City for the total elemental analysis of leachates and Vicente-Martorell et al., (2009) in Spain. However, lower values of 0.001 to 1.39 were reported by Uba et al., (2013) in Kaduna and 1.5 mg/L reported by Ikem et al., (2002) in Lagos in similar studies. The difference might be attributed to the different composition of the analysed wastewater. The distribution pattern among the

fractions was Cu: total> mobile > dissolved > particulate. When the concentrations (total extractable) across the sites were compared with those of the international standard (WHO, 1999) the concentrations were all within the tolerable limit of 0.05 mg/L with the exception of the fractions at S1 where it was below. The total extractable fractions of Pb were higher compared to the WHO (2006) standard limits of 0.01 mg/L (WHO, 2006) for S1 and S2 respectively. Pb levels were found to be lower than mean concentration range of 2.05-9.0 mg/ L reported for polluted and unpolluted sites in a similar study in Nigeria (Uzairu et al., 2014) and higher than 0.02-0.032 reported by Asonye et al., (2007 and 0.23- 0.39 reported by Uba et al., (2013). The distribution for Pb pattern among the fractions was: total> particulate > mobile> dissolved. As identified from various literatures, main source of Pb is the alkyl derivatives in petroleum which is gradually phasing off. Also, it comes from other sources like metal manufacturing sewages, paints, fertilizer, pesticides, and ashes (Dumann et al., 2007). Cytogenetic alteration such as kidney and brain damage or birth defects results especially when ingested through the food chain or drinking water (Aiyesanmi and Imoisi., 2011).

The extractable fractions of Ni were compared with the WHO (2006) standard limits of 0.02 mg/L, overall, the results showed higher values with few exceptions. The distribution pattern among the fractions of Ni were: total> particulate > dissolved> mobile. The recorded concentrations in this study were below the ranges of 3.62 to 8.15 mg/L reported by Ahlberg et al., (2006) in Sweden, and higher than the range 0.02 to 0.24 mg/L reported by Aiyesanmi and Imoisi, (2011) in Benin City, Nigeria. Accumulation of Ni and nickel compounds in the body through chronic exposure may be responsible for a variety of adverse effects on the health of human beings, such as lung fibrosis, kidney and cardiovascular diseases and cancer of the respiratory tract (Genchi et al., 2020)

The levels of Cr recorded were significantly high, quiet above the WHO tolerable limit in S1 and S10, while it was below detection limit for the other wastewater samples, and equal amount

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was found in all the fractions. The levels of Cr recorded in this study were lower than > 1.5mg/L reported by Ikem et al., (2002) in Lagos and 0.31-7.10 mg/L reported by Uzairu et al., (2014) in a similar study carried out in Kano. The distribution pattern for Cr among the fractions was: total > particulate > mobile > dissolved. Cr being a major constituent of chemicals use in dyeing industries in this area may explain reason for the high level of Cr. Thus the metal can be readily leachable into the nearby surface water resulting to serious health problems such as chromosomal segregation, disruption and inhibition of cell division. Though Cr is an essential trace nutrient and a vital component for the glucose tolerance factor, Cr toxicity damages the livers and lungs and causes organ hemorrhages (Goyer and Cherian, 1995).

Statistical Treatment of Data

One way ANOVA test revealed that there was significant difference at $P \leq 0.05$ (at 95% confidence limit) for Pb, Cu and Ni in fraction I, II, III and IV across the sampling points with exception of Ni in fraction IV as reflected in Table 6, while no significant difference was

observed for Cr in fraction I, II, III and IV and Ni in fraction IV.

This implies that the water samples across the sampling points have different source of pollution. The Cu concentrations recorded suggest that there was a common source of pollution by the metal ions as significant difference among the fractions was observed at p < 0.05.

Table 7 showed the degree of association of the metal ions, the variables showed significant positive correlations with each other and with different metal ions while strong negative correlations were equally recorded. Cu was positively correlated with the Pb, this implies that as the concentration of Cu increases, Pb concentration also increases. However, negative correlation of the metal ion was recorded between Cu, Cr, Ni and Pb, revealing an inverse relationship. The high concentrations recorded in the sample might not be unconnected to textile wastewater constituents where copper containing waste formed part of the constituents and the total fraction was significantly not different at p < 0.05.

ANOVA										
		Sum of Squares	Df	Mean Square	F	Sia.				
PbI	Between	0.001	9	0.000	31.360	0.000				
	Groups									
	Within Groups	0.000	10	0.000						
	Total	0.001	19							
PbII	Between	1.776	9	0.197	1173.106	0.000				
	Groups	0.000	10	0.000						
	Within Groups	0.002	10	0.000						
DATT	I Otal Botwoon	1.//8	19	0.060	2250 216	0.000				
PDIII	Groups	0.536	9	0.000	2256.510	0.000				
	Within Grouns	0.000	10	0 000						
	Total	0.538	19	0.000						
PbIV	Between	0.481	9	0.053	267289.000	0.000				
	Groups									
	Within Groups	0.000	10	0.000						
	Total	0.481	19							
CuI	Between	6281.251	9	697.917	6201.246	0.000				
	Groups									
	Within Groups	1.125	10	0.113						
CUIT	l otal Batuaan	6282.377	19	1102 471		0.000				
Cull	Between	10651.240	9	1183.4/1	62.503	0.000				
	Within Crouns	100 2/7	10	10 025						
	Total	109.347	10	10.955						
CuIII	Between	11637 429	9	1293 048	763 453	0.000				
Culli	Groups	110571125	5	12551010	, 001100	01000				
	Within Groups	16.937	10	1.694						
	Total	11654.366	19							
CuIV	Between	818.619	9	90.958	259545.276	0.000				
	Groups									
	Within Groups	0.004	10	0.000						
	Total	818.622	19							
Nil	Between	0.305	9	0.034	4.895	0.010				
	Groups	0.000	10	0.007						
	Total	0.069	10	0.007						
NiTT	Retween	1 730	9	0 192	12 089	0.000				
14111	Groups	1.750	5	0.152	12.005	0.000				
	Within Groups	0.159	10	0.016						
	Total	1.889	19							
NiIII	Between	2.044	9	0.227	292.532	0.000				
	Groups									
	Within Groups	0.008	10	0.001						
	Total	2.052	19							
NiIV	Between	0.749	9	0.083	2.292	0.106				
	Groups	0.060	10	0.000						
	Within Groups	0.363	10	0.036						
Crī	Total	1.112	19	0.001	0.000	0 502				
CII	Groups	0.015	9	0.001	0.969	0.502				
	Within Grouns	0.014	10	0.001						
	Total	0.027	19	0.001						
CrII	Between	0.000	9	0.000	2.469	0.088				
	Groups									
	Within Groups	0.000	10	0.000						
	Total	0.000	19							
CrIII	Between	0.020	9	0.002	0.982	0.506				
	Groups									
	Within Groups	0.022	10	0.002						
C=T) (lotal	0.042	19	0.000	0.070	0 570				
CLIA	Between	0.028	9	0.003	0.878	0.573				
	Within Groups	0 026	10	0.004						
	Total	0.030	19	0.004						
	10001	0.001	17							

BAJOPAS Volume 15 Number 1, June, 2022 Table 6 **Analysis of variance for bioavailable fractions**

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	JUITEIali	un mau		Javallab		5115						
Fractio	Ni2I	Ni3I	Ni4I	Ni5I	Ni6I	Ni8I	Ni9I				Cr1II	Cr9II
n	V	V	V	V	V	V	V	Cr1I	Cr8I	Cr1II	Ι	Ι
Ni3IV	1.00											
		1										
Ni4IV	-1.00	-1.00	1									
Ni5IV	-1.00	-1.00	1.00	1								
Ni6IV	-1.00	-1.00	1.00	1.00	1							
Ni8IV	-1.00	-1.00	1.00	1.00	1.00	1						
Ni9IV	-1.00	-1.00	1.00	1.00	1.00	1.00	1					
Cr1I	-1.00	-1.00	1.00	1.00	1.00	1.00	1.00	1				
Cr8I	1.00	1.00	1.00	-1.00	-1.00	-1.00	1.00	-1.00	1			
Cr1II	1.00	1.0	-1.00	-1.00	-1.00	-1.00	1.00	-1.00	1.00	1		
Cr1III	-1.00	-1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	-	1	
										1.000		

CONCLUSION

The wastewater samples were heavily polluted by Cu and Ni. Pb and Cr was not detected in most of the analysed wastewater samples in all the fractions of the samples while Co was not detected in all the fractions. Furthermore, significant amounts of the fractionated metals were found in the mobile phase showing a threat to the surface water within the vicinity of

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the wastewater. Overall, more than 50% of the analysed toxic metals were found in the bioavailable fractions (dissolved + mobile fractions) resulting to serious health problems such as typhoid fever, cholera and other water borne related diseases to the residents.

Conflict of Interests

The authors declare that they have no conflict of interests regarding the publication of this paper.

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