Adsorption of Heavy Metals (Cu, Mn, Fe and Ni) from Surface Water using Oreochromis Niloticus Scales

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Abstract: Surface water contains a large number of pollutants, particularly human pathogens, organic toxicants and heavy metals. Due to the toxic nature of heavy metals towards marine organisms, its removal from the environment has been a growing issue. The biosorption of heavy metal ions from surface water using fish scales has emerged as an environmentally friendly technique. This study assessed the degree of heavy metals accumulation in the scales of Oreochromis niloticus and determining its efficiency as a bioindicator for Cu, Mn and Fe ions removal in the environment of Wewe and Owabi rivers. This study shows that the levels of Cu, Mn, Fe adsorbed from the Owabi river were 685.70 ± 16.51, 247.06 ± 50.46 and 892.90 ± 96.29 mg/kg, respectively. Moreover, the levels of Cu, Mn and Fe adsorbed from Wewe river were 501.60 ± 77.78, 300.89 ± 54.61 and 413.04 ± 9.92 mg/kg, respectively. Under best optimum adsorption conditions, Cu was the best removed heavy metal ions in both surface water reservoirs. Multivariate analysis showed that Cu and Mn showed association in Owabi river, while Mn and Fe were correlated in Wewe river signifying their similarities to a common anthropogenic activity. The Fourier–transform infrared spectrum revealed the existence of a nitro, amine, and carbonyl groups in the biosorption process. This study highlighted that Oreochromis niloticus scales was an efficient bio–sorbent in removing Cu, Mn and Fe ions from Owabi and Wewe rivers.

Keywords: Anthropogenic activity; Fish scales; Multivariate analysis; Bioindicator

INTRODUCTION

The global fish consumption has increased due to its vital source of vitamins, protein, essential omega–3 fatty acid and minerals (Medeiros et al., 2012; Mziray & Kimirei, 2016). Nonetheless, human activities in and around rivers draining into oceans/estuaries as well as near coastal waters can affect the quality of water via trace/heavy metals contamination (Govers et al., 2014; Mziray & Kimirei, 2016). Moreover, fish species located at the top of the food chain may accrue more trace/heavy metals from food, water and sediments (Cuí et al., 2011; Zhao et al., 2012). The accumulation of trace/heavy metals in fish may cause several adverse effects to human and aquatic health (Castro-González & Méndez-Armenta, 2008) and this includes cardiovascular diseases, liver damage and renal failure (Al-Busaïdi et al., 2011). To this effect, several approaches have been used to evaluate the quality of fish for consumption and health implication to human and the aquatic ecosystem (Meche et al., 2010).

Heavy metals, including both non–essential and essential elements are toxic above some threshold levels in the

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ecosystem (Ebrahimpour & Mushrifah, 2010) due to their long perseverance, toxicity, biomagnification and bioaccumulation in the food chain (Yousafzai et al., 2010). Heavy metals in the marine ecosystem may come from either anthropogenic or natural sources (Mendil et al., 2005). Fish can accrete heavy metals by direct consumption of water via their skin, gill surface, gut tract wall, non–food particles and contaminated food particles (Jabeen & Chaudhry, 2010). Consequently, the heavy metals then flow via the bloodstream and are carried to either the liver or the storage point and accumulate into their tissues. The heavy metals are biotransformed and defecated or taken up by the food chain to consumers and this can induce either chronic or acute diseases (Weber et al., 2013). Fish are commonly used as bioindicators of heavy metal pollution in the ecosystem because fish are easily identified, large in size, and at the top of the aquatic food chain (Kumolu-Johnson et al., 2010). The accumulation of heavy metals in fish relies on environmental factors, trophic level, sampling location, age/life span, fish species, swimming patterns, pollutant type, and feeding habits (Asuquo et al., 2004; Weber et al., 2013; Zhao et al., 2012).

The removal of heavy metals from the aquatic environment has several approaches including adsorption on activated carbon, membrane technologies, electrochemical treatment, and chemical precipitation have been designed to remove heavy metals contaminants from surface water. Nonetheless, these methods are often ineffective owing to their production of large quantities of wastes and high operating costs (Othman et al., 2006). Recently, bio–sorption approach offers a high efficiency of wastewater treatment with a higher possibility of metal recovery and low heavy metal concentrations due to their easy operation and low pollution (Othman et al., 2006). Palm shell, peanut shell, algae–yeast, pecan nutshell, crab carapace, rice bran, mandarin peels, seashells, and others have been used as a natural bio–sorbent to remove heavy metals (Abdul Kadir et al., 2013; Witek-Krowiak et al., 2011). Moreover, the cell wall surface of each fish scales contains several functional groups including amine, nitro, and carbonyl groups and this may offer a good adsorption of heavy metal ions on its surface (Vieira et al., 2012). Recently, scales of several fishes had been used as a bio–sorption of heavy metal ions (Othman et al., 2015; Othman & Juki, 2011; Rahaman et al., 2008; Srividya & Mohanty, 2009; Zayadi & Othman, 2013a). However, there are no reports on the use of Nile Tilapia scales (Oreochromis niloticus) as a biosorption of heavy metals removal from Owabi and Wewe rivers. Therefore, this study aims to evaluate the unexploited property of Oreochromis niloticus scales as a suitable bio–sorbent to eliminate the targeted heavy metals (Cu, Mn, Fe and Ni ions) sedimentation from surface water.

**MATERIALS AND METHODS**

Fourteen (14) commercial *Oreochromis niloticus* were purchased from local fishermen located in Owabi and Wewe rivers. The *Oreochromis niloticus* fish species are economically important and represent different biotops. Immediately, the fish samples were conserved in an ice chest and transported to the laboratory and kept frozen in a refrigerator prior to analysis. The scales were detached from the fish skin and then soaked in 10% HNO₃ for 24 hours to remove any soluble impurity and adhering dust, as well as improving the hydrophilic nature of the surface of the fish scales. The scales were further rinsed with distilled water and then dried in an oven at 60 °C until constant weight was attained. The dried fish scales were ground with a mechanical grinder (blender) into powdery forms. The powdered samples were then kept in a clean, dry container and made ready for use.
About 10 g of the powdered fish scales was weighed into a digestion tube (El-Sheikh & Sweileh, 2008). A 10 mL of Conc. HNO₃ was added to the fish scales sample and the mixture was allowed to stand overnight. The mixture was then subjected to heat until the evolution of the brown fumes ceased. The solution was allowed to cool to room temperature and then filtered into a 100 mL volumetric flask using a medium filter paper. The sample solution was analyzed for the levels Fe, Mn and Cu using the Flame Atomic Adsorption Spectrophotometer (FAAS). To check for background contaminant by the apparatus and reagents used, blank experiments were run and the concentrations obtained were subtracted from the analyte. An external standard curve approach was adopted to measure the concentration of the heavy metals. The analysis was performed in duplicate and the results were expressed in mg/kg. Precision and accuracy were verified using a DORM-2 certified reference material (CRM) provided by the National Research Council of Canada. The average recoveries of the targeted heavy metals in the DORM-2 CRM were between 94 and 104.7 %.

About 100 mL of surface water from Wewe and Owabi rivers were measured separately into two different 250 mL conical flask and 10 g of the powdered fish scales was added to each conical flask. The samples were shaked at room temperature (25°C) for 10 minutes to ensure a uniform mixture and later allow to stand for 48 hours and then filtered with a Whatman filter paper. The solutes were dried in an oven at 60°C to obtain a constant weight and digested using a 10 mL of Conc. HNO₃ and analyzed using the FAAS to obtain the final concentrations of the targeted Mn, Fe, Cu, and Ni in the powdered fish scales.

A small portion of the powdered fish scales sample was analyzed using the FTIR spectroscopy to evaluate the functional groups present in the fish scales that are responsible for the adsorption of heavy metal ions the Wewe and Owabi reservoirs.

**RESULTS AND DISCUSSION**

The concentration of Cu was below the detection limits for both river samples. This may be attributed to the fact that Cu concentrations in both surface water samples were so low before adsorption. The Mn and Fe concentrations were found to be 183.94 ± 23.64 and 409.57 ± 55.05 mg/kg, respectively, while the corresponding concentrations in Wewe river 197.57 ± 23.89 and 319.28 ± 18.52 mg/Kg (Table 1).

However, the mean concentrations of Cu, Mn, and Fe recorded in the fish scales samples after the adsorption process with the Owabi sample were 685.70 ± 16.51, 247.06 ± 50.46 and 892.90 ± 96.29 mg/Kg, respectively. Similarly, the mean levels of Cu, Mn, and Fe recorded in the fish scales samples after the adsorption process in the Wewe surface water sample were 501.60 ± 77.78, 300.89 ± 54.61 and 413.04 ± 9.92 mg/kg, respectively. The increase in heavy metal concentrations in the fish scales after adsorption confirms that the fish scales are capable of adsorbing heavy metals from surface water, see Fig. 1 for the percentage (%) removal of heavy metals ions from Wewe and Owabi rivers.

<table>
<thead>
<tr>
<th>Surface water</th>
<th>Heavy metal concentrations ± standard deviation (mg/Kg)</th>
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<tbody>
<tr>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td><strong>Before adsorption</strong></td>
<td></td>
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<tr>
<td>Owabi river</td>
<td>BDL</td>
</tr>
<tr>
<td>Wewe river</td>
<td>BDL</td>
</tr>
<tr>
<td><strong>After adsorption</strong></td>
<td></td>
</tr>
<tr>
<td>Owabi river</td>
<td>685.70 ± 16.51</td>
</tr>
<tr>
<td>Wewe river</td>
<td>501.60 ± 77.78</td>
</tr>
</tbody>
</table>

BDL – Below Detection Limit
Copper is an important micronutrient, which is vital to all forms of life, particularly in the embryonic growth, regulation of haemoglobin levels, mitochondrial respiration, neuronal and hepatocyte functions (Gao et al., 2014). Nevertheless, excessive consumption of Cu can cause severe mucosal corrosion and irritation, central nervous system irritation, hepatic and renal damage. Severe gastrointestinal disorder and necrotic changes in the kidney and liver can also occur (Jiwan, 2011). Copper concentrations were reported to be $6.54 \pm 2.92 \, \mu g/g$, in the scales of *Labeo rohita* from the Bhagwanpur Fish Pond, India (Negi & Maurya, 2015) and $0.51 \pm 0.20 \, \mu g/g$ in wastewater from Nyalanda Wastewater Lagoons, Kenya (Orata & Birgen, 2016). Iron is an essential element for most living organisms with direct involvement in vast metabolic processes, such as electron transport, Deoxyribonucleic acid synthesis and oxygen transport (Gupta, 2014; Jiwan, 2011). Fe also facilitates the appropriate myelination of the white matter of cerebellar fold in the brain and spinal cord (Soetan et al., 2010). However, excessive intake of Fe tends to cause health disorders (Giripunjie et al., 2016). Under the optimum condition of Zn ion, Fe levels removal from wastewater using fish scales of *Mozambique tilapia* and *Tilapia Mossambica* have been reported in the range of 781.96 - 875.94 $\mu g/g$ (Othman et al., 2006) and 313.54 – 624.99 $\mu g/g$ (Zayadi & Othman, 2013b) from Malaysia. Moreover, Mn is a vital element (Anim et al., 2011) and is homeostatically controlled and non-toxic to the marine environment (Wiener & Giesy Jr, 1979). However, overexposure can cause an adverse effect on the central nervous system (Soetan et al., 2010). Magnesium concentrations have been reported in $124.4 \pm 5.2 \, mg/kg$ in sewage Sediments of El-Shekh pond, Egypt (Ibrahim et al., 2016).

Comparisons of the mean Cu, Mn, and Fe analysed indicated significant differences ($p < 0.05$) for the fish species analysed. The one-way ANOVA analysis revealed that the observed levels of Cu, Mn, and Fe recorded in the fish scales samples after the adsorption process differed from each other ($p < 0.05$). The Shapiro–Wilk normality revealed that the levels of Cu, Mn and Fe were normally distributed ($p > 0.05$) in the analysed surface water. Two principal components with eigenvalues greater than 1 with a total contribution of 100% were extracted to identify the likely sources of heavy metals in both surface water (Fig. 2).

The loading plot showed that Cu and Mn had a similar source of pollution in Owabi river, while Mn and Fe were

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**Fig. 1.** A graphical representation of percentage (%) removal of heavy metals ions from surface water collected from Owabi and Wewe rivers.

**Kwaansa- Ansah, E. E. et al.**
correlated in Wewe river. This indicated that human activities including improper waste disposal and agricultural practices in and around Owabi and Wewe catchment might influence the levels of Cu, Mn and Fe in both surface water.

Functional groups including amide, hydroxyl, and carboxyl are responsible for the biosorption of heavy metal ions (Arıca & Bayramoğlu, 2005; Jain et al., 2009). These functional groups act as potential adsorption sites for heavy metals, and their uptake of heavy metal ions relies on several factors including the affinity between the heavy metal ions and adsorption site (Prabu et al., 2012). The FTIR spectroscopy is a vital analytical technique, which measures the vibration characteristics of several functional groups on the adsorbent surface (Prabu et al., 2012). The FTIR spectra of Oreochromis niloticus scales is given in Fig. 3.

The represented functional groups in the FTIR spectrum are shown in Table 2.

**Fig. 2.** Principal component analysis biplot of heavy metals in (a) Owabi and (b) Wewe rivers

**Fig. 3.** FTIR spectrum of Oreochromis niloticus scales

**Table 2.** FTIR spectrum of Oreochromis niloticus scales

<table>
<thead>
<tr>
<th>S. No</th>
<th>Band position (cm⁻¹)</th>
<th>Functional groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3300 – 3200</td>
<td>N–H stretch</td>
</tr>
<tr>
<td>2</td>
<td>1640 – 1630</td>
<td>C=O stretch</td>
</tr>
<tr>
<td>3</td>
<td>1450 – 1375</td>
<td>C–H bending (symmetric and asymmetric bending)</td>
</tr>
<tr>
<td>4</td>
<td>1080 – 1000</td>
<td>C–O stretch</td>
</tr>
<tr>
<td>5</td>
<td>560 – 550</td>
<td>N–H stretch</td>
</tr>
</tbody>
</table>
According to Table 2, the bands of *Oreochromis niloticus* at 3284 cm\(^{-1}\) signify an amine group (N–H stretching vibrations). Moreover, the bands at 1635 cm\(^{-1}\) represent a carbonyl group (C = O stretch). Besides, the peaks in the region of 1450 to 1375 cm\(^{-1}\) are representative of C–H band bending. The spectra also show N–H stretch in the region of 560 to 550 cm\(^{-1}\). The FTIR spectroscopic analysis showed that the functional group in the cell walls of the fish scales was amide compound.

**CONCLUSION**
The concentrations of Cu, Mn, and Fe adsorbed from the Wewe river were 501.60 ± 77.78, 300.89 ± 54.61 and 413.04 ± 9.92 mg/kg, respectively. Similarly, the mean concentrations of Cu, Mn, and Fe recorded in the fish scales samples from Owabi river after adsorption process were 685.70 ± 16.51, 247.06 ± 50.46 and 892.90 ± 96.29 mg/Kg, respectively. Multivariate analysis revealed the association of heavy metals to a similar source of contamination, where anthropogenic activities were the likely source of heavy metal pollution within the Owabi and Wewe catchments. The FTIR spectrum revealed the presence of the nitro, amine and carbonyl group in the biosorption process. This study shows the promising biosorption of Cu, Mn and Fe ions from surface water using *Oreochromis niloticus* fish as biosorbent. The findings in this study confirmed the strong binding of Cu ions to *Oreochromis niloticus* as compared with the other heavy metal ions. In summary, *Oreochromis niloticus* fish scales have the ability to adsorb heavy metal ions from surface water.

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