Environmentally Friends and Cheap Removal of Some Heavy Metals from Wastewater with Fish Scale Remains

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Abstract: ***Wastewater samples were collected from the sewage treatment plant in Azdinawiyaregion, south of Nasiriyah district. Fish samples were collected from the Euphrates River in Suq Al-Shuyoukh district, where Cyprinus carpiotypes of fish were collected, weighted 1.5 kg. Heavy metals were measured directly after sampling Zn, Cd, Cu and Pb by Flam automatic absorption. A powder was made of fish scales. The scales were ground after cleaning. The scales were filtered by three types of sieves (250µm, 1mm and 2.36 mm). The ability of fish scales powder to adsorption of trace elements from sewage water was tested, where 50 gm of fish scales powder was placed in a burette, and its adsorption capacity was tested in five times (zero time, 12 hours, 48 hours, 72 hours, and 96 hours). The current study showed that fish scales have ability to adsorb heavy metals in wastewater***.

Keywords: Trace Elements, Adsorption, *Cyprinus carpio,* fish scales

1. Introduction

Freshwater scarcity has been one of the world's greatest concerns over the last few decades. The advancement of technology, rapid pace of industrialization, population expansion, agricultural activities, and unplanned urbanization have largely contributed to the severe shortage of freshwater. Furthermore, the small quantity of the available freshwater is constantly being polluted by among others, toxic metal ion containing; discharge of untreated sanitary and toxic industrial wastes, household effluent, and runoff from agricultural fields (Maktoof, 2013 and Kummu*et al.*, 2016).

Alternative water sources have become a major focus for many countries, industries, companies, and researchers (Maktoof, 2020). Reuse and recycling of water are currently employed as ways to curb the situation. Wastewater treatment has become one of the most widely used alternative water sources for most countries' worldwide (Coelho *et al.*, 2020). However, removal of pollutants especially excess toxic heavy metal ions is costly and often employs toxic chemical to the environment. Wastewater containing excess, toxic heavy metal ions such as Lead (II) and Zinc (II) causes detrimental effects to all forms of life upon direct discharge in to the environment (Ayangbenro and Babalola, 2017). In order to reduce the toxic heavy metal environmental pollution, a number of conventional physico-chemical removal methods, such as chemical precipitation, electroplating, membrane separation (Maktoof, *et al.*,2020) evaporation and resin ionic exchange have been employed remove the heavy metal ions from wastewater before use. These methods are expensive and non-environmentally friendly, thus cheaper and environmentally friendly, thus alternative removal methods are sought after the world over (Stevens and Batlokwa, 2017).

For the above reasons in this study, we are employed, fish scales waste remains as an environmentally friendly and cheap method to simultaneously remove some of the heavy metals.

2. Materials & Methods

2.1 Wastewater Samples Collection

Water samples were collected from the collection room in the Al Hindiya plant (used for sewage treatment in Al-Nasiriyah city) located near Al-Zaraa on the road leading to Ur city / Al-Nasiriyah city in southern Iraq. The plant treats sewage that comes from the city center through the line containing sewage produced by homes, restaurants, and industry. The samples were taken during the autumn of 2020, and the samples were kept in plastic containers (polyethylene), and the samples were transferred to the Advanced Pollution and Environment Laboratory at the College of Science / Thi-Qar University.

2.2 Fish Sample Collection and Preparation Powder for Adsorption

Fish samples were collected from the Euphrates River in Suq Al-Shuyoukh district, Thi-Qar province, after which the scales were removed from the fish and washed in water several times to remove sediments and left exposed to sunlight to dry for one month, after which the scales and bones were collected. It was placed in the oven at a temperature (70 ºC) for an hour until the crusts became crispy. Then the scales were ground by the electric mill, where three different sizes of sieves filtrated then 250 µm,1mm, and 2.36 mm. Then 5 gm of each sample was taken and placed in a 100 ml burette containing medical gauze at the top and bottom where the form is in the middle, and 50 ml of water was added to it sewage. The samples were then incubated five times (0, 12 hours, 48 hours, 72 hours and 96 hours). It has been upgraded to wild head cap (Srividya and Mohanty, 2009).

2.2.1 Determination of Heavy Metal Concentrations in Wastewater

The concentrations of heavy metals in sewage water were estimated based on the given method Csuros *et al.*, (2018).

2.2.2 Adsorption of Heavy Metals from Scales

The Heavy metals were measured by the following equation

$$\text{Heavy Metals Adsorption} = \frac{(Ci - Cf)}{Ci} * 100$$

C_i= Heavy metals before adsorption
C_f= Heavy metals after adsorption

3. Statistical Analysis

The current study data were analyzed by using SPSS (Statistical Package of Sociot Science version 26) and independent t test. The difference is considered to be significant whenever p. value less than 0.05.
3- Results:

3.1 Removal of Cd by using scales *Cyprinus carpio*1.5 kg according to Time of Adsorption

The result of the current study by noted the higher Cd element removing in 48 hours 88.054 %, while the lowest Cd metal removing in 12 hours 58.993 %. The results also recorded a significant difference in Cd removing by scales in different time of adsorption categories.

Table 1: Removal of **Cd** by using scales according to time

Cadmium according to Time		Mean + SD	Mean difference	Adsorption in %	p. value
In zero Time	Before	1.49 ± 0.01	0.896	60.134	< 0.05
	After	0.60 ± 0.07			
In 12 H	Before	1.49 ± 0.01	0.879	58.993	< 0.05
	After	0.61 ± 0.11			
In 48 H	Before	1.49 ± 0.01	1.312	88.054	< 0.05
	After	0.18 ± 0.02			
In 72 H	Before	1.49 ± 0.01	1.187	79.664	< 0.05
	After	0.31 ± 0.04			
In 96 H	Before	1.49 ± 0.01	1.195	80.201	< 0.05
	After	0.30 ± 0.04			

3.1.1 Removal of Cd by using scales *Cyprinus carpio*1.5 kg according to Sieve Size

The result of the current study by illustrated the higher Cd metal removing in sieve size 250μm 74.966 %, while the lowest heavy metal removing in 2.36 mm72.416 %. The results also recorded a significant difference in Cd removing by scales in different sieve size categories.

Table 2: Removal of **Cd** by using scales according to sieve size

Cadmium according to sieve size		Mean + SD	Mean difference	Adsorption in PTT	p. value
250μm	Before	1.49 ± 0.01	1.117	74.966	< 0.05
	After	0.38 ± 0.06			
1 mm	Before	1.49 ± 0.01	1.085	72.819	< 0.05
	After	0.41 ± 0.10			
2.36 mm	Before	1.49 ± 0.01	1.079	72.416	< 0.05
	After	0.41 ± 0.09			
	After	0.45 ± 0.18			

3.2 Removal of Zn by using scales *Cyprinus carpio*1.5 kg according to Time of Adsorption

The result of the current study by noted the higher Zn element removing in zero time 77.014%, while the lowest Zn metal removing in both 12 and 48 hours 61.754%. The results also recorded a significant difference in Zn removing by scales in different time of adsorption categories.

Table 3: Removal of **Zn** by using scales according to time

Zinc according to Time		Mean + SD	Mean difference	Adsorption in %	p. value
In zero Time	Before	2.11 ± 0.01	1.625	77.014	< 0.05
	After	0.49 ± 0.08			
In 12 H	Before	2.11 ± 0.01	1.303	61.754	< 0.05
	After	0.81 ± 0.24			
In 48 H	Before	2.11 ± 0.01	1.438	61.754	< 0.05
	After	0.67 ± 0.12			
In 72 H	Before	2.11 ± 0.01	1.518	71.943	< 0.05
	After	0.59 ± 0.05			

In 96 H	Before	2.11 ± 0.01	1.595	75.592	< 0.05
	After	0.52±0.13			

3.2.1 Removal of Zn by using scales *Cyprinus carpio*1.5 kg according to Sieve Size

The result of the current study by illustrated the higher Zn metal removing in sieve size 250µm72.464%, while the lowest heavy metal removing in both 1 and 2.36 mm70.095%. The results also recorded a significant difference in Zn removing by scales in different sieve size categories.

Table 4: Removal of **Zn** by using scales according to sieve size

Zinc according to sieve size		Mean + SD	Mean difference	Adsorption in %	p. value
250µm	Before	2.11 ± 0.01	1.529	72.464	< 0.05
	After	0.58 ± 0.12			
1 mm	Before	2.11 ± 0.01	1.479	70.095	< 0.05
	After	0.63 ± 0.11			
2.36 mm	Before	2.11 ± 0.01	1.479	70.095	< 0.05
	After	0.63 ± 0.05			
	After	0.70 ± 0.11			

3.2.2 Removal of Cu by using scales *Cyprinus carpio*1.5 kg according to Time of Adsorption

The result of the current study by noted the higher Cu element removing in 48-hourtime 74.29 %, while the lowest Cu metal removing in both 12 hours 57.38 %. The results also recorded a significant difference in Cu removing by scales in different time of adsorption categories.

Table 5: Removal of **Cu** by using scales according to time

Copper according to Time		Mean + SD	Mean difference	Adsorption in %	p. value
In zero Time	Before	0.42 ± 0.01	0.264	62.86	> 0.05
	After	0.16 ± 0.04			
In 12 H	Before	0.42 ± 0.01	0.241	57.38	< 0.05
	After	0.18 ± 0.01			
In 48 H	Before	0.42 ± 0.01	0.312	74.29	< 0.05
	After	0.11 ± 0.01			
In 72 H	Before	0.42 ± 0.01	0.296	70.48	< 0.05
	After	0.12 ± 0.01			
In 96 H	Before	0.42 ± 0.01	0.279	66.43	< 0.05
	After	0.14 ± 0.02			

3.2.3 Removal of Cu by using scales *Cyprinus carpio*1.5 kg according to Sieve Size

The result of the current study by illustrated the higher Cu metal removing in sieve size 2.36 mm 78.17 %, while the lowest heavy metal removing in 250µm63.10 %. The results also recorded a significant difference in Cu removing by scales in different sieve size categories.

Table 6: Removal of **Cu** by using scales according to sieve size

Copper according to sieve size		Mean + SD	Mean difference	Adsorption in %	p. value
250µm	Before	0.42 ± 0.01	0.265	63.10	< 0.05
	After	0.15 ± 0.03			
1 mm	Before	0.42 ± 0.01	0.287	68.33	< 0.05
	After	0.13 ± 0.02			
2.36 mm	Before	0.42 ± 0.01	0.283	78.17	< 0.05
	After	0.14 ± 0.03			
	After	0.23 ± 0.05			

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3.2.4 Removal of Pb by using scales *Cyprinus carpio*1.5 kg according to Time

The result of the current study by noted the higher Pb element removing in 72-hourtime 63.39 %, while the lowest Pb metal removing in both 12 hours 36.36 %. The results also recorded a significant difference in Pb removing by scales in different time of adsorption categories.

Table 7: Removal of **Pb** by using scales according to time

Lead according to Time		Mean + SD	Mean difference	Adsorption in %	p. value
In zero Time	Before	1.65 ± 0.01	0.965	58.48	< 0.05
	After	0.68 ± 0.18			
In 12 H	Before	1.65 ± 0.01	0.600	36.36	> 0.05
	After	1.05 ± 0.27			
In 48 H	Before	1.65 ± 0.01	0.905	54.85	< 0.05
	After	0.74 ± 0.23			
In 72 H	Before	1.65 ± 0.01	1.046	63.39	< 0.05
	After	0.60 ± 0.01			
In 96 H	Before	1.65 ± 0.01	0.836	50.67	< 0.05
	After	0.81 ± 0.09			

3.2.5 Removal of Pb by using scales *Cyprinus carpio*1.5 kg according to Sieve Size

The result of the current study by illustrated the higher Pb metal removing in sieve size 1 mm 62.61 %, while the lowest heavy metal removing in 2.36 mm44.97 %. The results also recorded a significant difference in Pb removing by scales in different sieve size categories.

Table 8: Removal of **Pb** by using scales according to sieve size

Lead according to sieve size		Mean + SD	Mean difference	Adsorption in %	p. value
250µm	Before	1.65 ± 0.01	0.836	50.67	< 0.05
	After	0.81 ± 0.23			
1 mm	Before	1.65 ± 0.01	1.033	62.61	< 0.05
	After	0.61 ± 0.10			
2.36 mm	Before	1.65 ± 0.01	0.742	44.97	< 0.05
	After	0.91 ± 0.22			
	After	0.93 ± 0.18			

4. Discussion

The current study showed that the highest removal of Cd, Cu, Zn and Pb according to time were after (48 hours at 88.054 %, 48 hours at 74.29 %, zero time at 77.014%, and 72 hours at 63.39 % respectively), while the lowest removal of Cd, Cu, Zn and Pb according to time were after (12 hours at 58.993 %, 12 hours at 57.38 %, in both 12 and 48 hours at 61.754 % and 12 hours at 36.36% respectively) and there were significant differences between all-time categories at p. value < 0.05%.

Also, the current study showed that the highest removal of Cd, Cu, Zn and Pb according to sieve size was (250µm 74.966%, 2.36mm 78.17 %, 250µm 72.464 %, and 1mm 62.61 % respectively), while the lowest removal of Cd, Cu, Zn and Pb according to sieve size were (2.36mm 72.416 %, 250µm 63.10 %, in both 1mm and 2.36mm 70.05 %, and 2.36mm 44.97 % respectively) and there were significant differences between all sieve size categories at p. value < 0.05%.

Based on these results it can be concluded that fish scales are green biomass and an effective alternative for removing heavy metals from aqueous solutions due to their good biological absorption capacity, renewable nature and low cost. Also, fish scales have been shown to be a potential environmentally friendly biosorbent for heavy metals in wastewater samples, and these results are consistent with the results of a water demineralization study using fish scales by (Cunnigham and Shahan, 2019).

Under the best optimum adsorption conditions, Cu was the best removed heavy metal in wastewater, and this is consistent with the results presented in a study conducted by Kwaansa *et al*., (2019) in Ghana, where Cu was the best removed heavy metal ions in both surface water reservoirs. At the same time, Zayadi and Othman results in Malaysia showed that 92.3% of zinc could be isolated under the best absorption conditions, and this result is consistent with the result of zinc removal in our current study.

In India, a study was conducted by Prabu *et al*., in (2012) for the biological absorption of heavy metal ions from aqueous solutions using fish scales, where it was found through the Indian study that fish scales have a high ability to absorb heavy metals from water and this is in line with our current study.

A study conducted in Malaysia by Alif *et al*., (2020) for the removal of zinc using a fish scale, showed that the maximum removal percentage was 93.52% of the zinc ion and this is fully consistent with the present results.

Also, Eletta and Ighalo, (2019) in Nigeria, fish scales have been found to have very good adsorption capacity for heavy metals with excellent removal efficiencies (50-100% for heavy metals. Relying on this study and previous studies, it was found that the adsorption time, the surface area of fish scales and the type of fish used in the biological treatment had a major role in influencing the removal of heavy metals from wastewater. Also, another potential role that contributed to the removal of heavy metals was the microbes in fish scales, where found in a study by Mustafiz *et al*. (2003) that microbes were responsible for removing heavy metals using fish scales as a biosorbent.

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