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Removal of some heavy metals from wastewater using planiliza abu 65 gm waste remains

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***Abstract*---**Wastewater samples were collected from the sewage treatment plant in the Azdinawiya City, south of Nasiriyah district, and fish samples were collected from the Euphrates River in Suq Al-Shuyoukh district, where three types of fish were collected, each with two different weights Planiliza abu 65 gm, heavy metals were measured directly after sampling (Zn, Cd, Cu and Pb) by automatic instrument. A powder was made of fish scales and bones. The scales and bones were ground after cleaning. The scales were filtered by three types of sieves (250µm, 1mm and 2.36 mm). The chemical elements were measured by a scanning electron microscope before and after adsorption. The scales and bones adsorbed the following chemical elements from the wastewater. The ability of fish scales and bones powder to adsorption of trace elements from sewage water was tested, where 50 gm of fish scales and bones 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 was showed that fish scales have more ability to adsorb trace elements in wastewater from the bones.

***Keywords*---**heavy metals, adsorption, planiliza abu.

Introduction

Freshwater scarcity has been one of the world's greatest concern 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

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wastes, household effluent, and runoff from agricultural fields (Kummu et al., 2016). The pollutants are hazardous to the environment due to their toxicity and strong tendency to concentrate in the environment and in food chains (Mishra et al., 2019). The expansion in the production of huge amounts of chemical materials, and the increase in these materials annually are due to the global industrial development, especially of the chemical industries like petrochemicals, paper industry, paints, plastics and electric instrument industries, but these lead to environmental crease identifying by environmental pollution (Krausmann et al., 2017).

Alternative water sources have now become a major focus for many countries, industries, companies and researchers (Tate et al., 2012). 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 source for most countries around the world (Coelho et al., 2020) but the 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 Lead (II) and Zinc (II) causes detrimental effects to all forms of life upon direct discharge 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 (Gunatilake, 2015), 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 alternative removal methods are sought after the world over (Stevens and Batlokwa, 2017). It is for the above reasons that in this study, we are employing, fish scales waste and bones remains as an environmentally friendly and cheap method to simultaneously remove some of heave metals.

Materials and Methods

Wastewater sample collection

Water samples were collected from the collection room in Al Hindiya plant (used for sewage treatment in Al-nasiriyah city). The samples were taken during the end 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.

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 and bones were removed from the fish and washed in water several times for removing sediments and left exposed to sunlight for drying for a period of one month, after which the scales and bones were collected. It was placed in the oven at a temperature (70 °C) for an hour until the crusts became crispy, then the scales were ground by the electric mill, where they were filtered by 3 different sizes of sieves (250 µm,1mm and 2.36 mm), while the bones were only filtered by one size of sieves 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 at five different times (0 time, 12 hours, 48 hours, 72 hours and 96 hours). Where has been upgraded to wild head cap (Srividya and Mohanty, 2009).

Statistical analysis

The data of the current study was analyzed by using SPSS independent t test and using below question for measuring adsorption heavy metals.

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

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

Results

Removal of Cd by using scales *Planiliza abu* 65 GM according to time

The result of the current study by noted the higher Cd element removing in 96 hours 86.11%, while the lowest Cd metal removing in 48 hours 34.36%. The results also recorded a significant difference in Cd removing by scales in different time of adsorption categories with except zero time.

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	0.941	63.15	< 0.05
	After	0.55 ± 0.04			
In 12 H	Before	1.49 ± 0.01	0.932	62.55	< 0.05
	After	0.56 ± 0.017			
In 48 H	Before	1.49 ± 0.01	0.512	34.36	< 0.05
	After	0.98 ± 0.08			
In 72 H	Before	1.49 ± 0.01	1.216	81.61	< 0.05
	After	0.28 ± 0.07			
In 96 H	Before	1.49 ± 0.01	1.283	86.11	< 0.05
	After	0.21 ± 0.02			

Removal of Cd by using scales *Planiliza abu* 65 gm according to Sieve Size

The result of the current study by showed the high adsorption in sieve size 250µm 69.73 %, in contrast the lowest adsorption in 2.36 mm 62.62 %. In bone Cd removing the result recorded a lowest stage in removing 54.70 % compare with scales extract.

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

Cadmium according to sieve size		Mean + SD	Mean difference	Adsorption in %	p. value
250μm	Before	1.49 ± 0.01	1.039	69.73	< 0.05
	After	0.45 ± 0.03			
1 mm	Before	1.49 ± 0.01	0.979	65.70	< 0.05
	After	0.51 ± 0.09			
2.36 mm	Before	1.49 ± 0.01	0.933	62.62	< 0.05
	After	0.56 ± 0.01			
In Bone	Before	1.49 ± 0.01	0.815	54.70	< 0.05
	After	0.68 ± 0.09			

Removal of Zn by using scales *Planiliza abu* 65 GM according to time

The result of the current study by noted the higher Zn element removing in 72 hours 72 hours 61.80 %, while the lowest Zn metal removing in zero time 29.81 %. The results also recorded a significant difference in Zn removing by scales in different time of adsorption categories with except zero time.

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	0.629	29.81	< 0.05
	After	1.48 ± 0.11			
In 12 H	Before	2.11 ± 0.01	1.066	50.52	< 0.05
	After	2.11 ± 0.13			
In 48 H	Before	2.11 ± 0.01	1.080	51.18	< 0.05
	After	1.03 ± 0.07			
In 72 H	Before	2.11 ± 0.01	1.304	61.80	< 0.05
	After	0.81 ± 0.04			
In 96 H	Before	2.11 ± 0.01	1.122	53.18	< 0.05
	After	0.99 ± 0.11			

Removal of Zn by using scales *Planiliza abu* 65 gm according to Sieve size

The result of the current study by showed the high adsorption in sieve size 2.36 mm 51.28 %, in contrast the lowest adsorption in 250μm 46.26 %. In bone Zn removing the result recorded a highest stage in removing 54.70 % compare with scales extract.

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	0.976	46.26	< 0.05
	After	1.14 ± 0.25			
1 mm	Before	2.11 ± 0.01	1.063	50.38	< 0.05
	After	1.05 ± 0.30			
2.36 mm	Before	2.11 ± 0.01	1.082	51.28	< 0.05
	After	1.03 ± 0.22			
In Bone	Before	1.65 ± 0.01	1.514	71.75	< 0.05
	After	0.60 ± 0.08			

Removal of Cu by using scales *Planiliza abu* 65 GM according to time

The result of the current study by noted the higher Cu element removing in 96 hours 81.67%, while the lowest Cu metal removing in 96 hours 48 hours 56.19 %. The results also recorded a significant difference in Cu removing by scales in different time of adsorption categories with except zero time.

Table 5
Removal of Cu by using scales according to time

Copper according to Time		Mean + SD	Mean difference		p. value
In zero Time	Before	0.42 ± 0.01	0.322	76.67	> 0.05
	After	0.10 ± 0.006			
In 12 H	Before	0.42 ± 0.01	0.294	70.00	< 0.05
	After	0.13 ± 0.06			
In 48 H	Before	0.42 ± 0.01	0.236	56.19	< 0.05
	After	0.18 ± 0.02			
In 72 H	Before	0.42 ± 0.01	0.314	74.76	< 0.05
	After	0.11 ± 0.01			
In 96 H	Before	0.42 ± 0.01	0.343	81.67	< 0.05
	After	0.08 ± 0.01			

Removal of Cu by using scales *Planiliza abu* 65 gm according to Sieve size

The result of the current study by showed the high adsorption in sieve size 2.36 mm 71.19%, in contrast the lowest adsorption in 250µm 67.38 %. In bone Cu removing the result recorded a second stage in removing 54.70 % compare with scales extract.

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	0.283	67.38	< 0.05
	After	0.14 ± 0.05			
1 mm	Before	0.42 ± 0.01	0.288	68.57	< 0.05
	After	0.13 ± 0.02			
2.36 mm	Before	0.42 ± 0.01	0.299	71.19	< 0.05
	After	0.12 ± 0.02			
In Bone	Before	0.42 ± 0.01	0.288	68.57	< 0.05
	After	0.13 ± 0.04			

Removal of Pb by using scales *Planiliza abu* 65 gm according to time

The result of the current study by noted the higher Pb element removing in 48 hours 57.94 %, while the lowest Pb metal removing in zero time hours 40.0 %. The results also recorded a significant difference in Pb removing by scales in different time of adsorption categories with except zero time.

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	0.660	40.00	< 0.05
	After	0.99 ± 0.18			
In 12 H	Before	1.65 ± 0.01	0.867	52.55	< 0.05
	After	0.78 ± 0.17			
In 48 H	Before	1.65 ± 0.01	0.956	57.94	< 0.05
	After	0.69 ± 0.10			
In 72 H	Before	1.65 ± 0.01	0.827	50.12	< 0.05
	After	0.82 ± 0.13			
In 96 H	Before	1.65 ± 0.01	0.707	42.85	< 0.05
	After	0.94 ± 0.14			

Removal of Pb by using scales *Planiliza abu* 65 gm according to Sieve size

The result of the current study by showed the high adsorption in sieve size 250µm 49.33 %, in contrast the lowest adsorption in 2.36 mm 48.12 %. In bone Pb removing the result recorded a lowest stage in removing 42.97 % compare with scales extract.

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	0.814	49.33	< 0.05
	After	0.83 ± 0.14			
1 mm	Before	1.65 ± 0.01	0.802	48.61	< 0.05
	After	0.85 ± 0.06			
2.36 mm	Before	1.65 ± 0.01	0.794	48.12	< 0.05
	After	0.85 ± 0.27			
In Bone	Before	1.65 ± 0.01	0.709	42.97	< 0.05
	After	0.94 ± 0.16			

Discussion

The current study showed that the highest removal of Cd, Cu, Zn and Pb according to time were after (96 hours at 86.11 %, 96 hours at 81.67 %,72 hours at 61.80 %, and 48 hours at 57.94% respectively) , while the lowest removal of Cd, Cu, Zn and Pb according to time were after(48 hours at 34.36 %, 48 hours at 56.19 %, zero time at 29.81 % and zero time at 40.00% 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 were (250µm 69.73%, 2.36mm 71.19 %, 2.36mm 51.28 %, and 250µm 49.33 % respectively), while the lowest removal of Cd, Cu, Zn and Pb according to sieve size were (2.36mm 62.62 %, 250µm 67.83 %, 250µm 46.26%, and 2.36mm 48.12 % respectively) and there were significant differences between all sieve size categories at p. value < 0.05%. Through the results of the present study, it was found that the highest percentage of Cd, Cu, Zn and Pb removal from wastewater using fish scales were 92.282%, 93.810%, 90.806%, and 73.03% respectively, while the lowest removal were 30.40 %, 26.19 %, 29.81 %, and 36.36% respectively. 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 (Cunningham 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 adsorb 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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