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A biosorption of some trace elements from wastewater using fish scales (*Barbus luteus*)

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Abstract

Wastewater samples were collected from the sewage treatment plant in Azdinawiya region, south of Al-Nasiriyah city. *Barbus luteus* fish, weighing 1.15 kg, sampled from the Euphrates River in the Suq Al-Shuyoukh district. Zn, Cd, Cu, and Pb were measured by Flam Automatic Absorption. A powder was made of fish scales. The scales were ground after cleaning. The scales were passed by three types of sieves (250µm, 1mm and 2.36 mm). Test the fish scale powder's capacity to absorb trace elements from sewage water, 50 g of the powder was placed in a burette, and its capacity was tested five times (zero time, 12 hours, 48 hours, 72 hours, and 96 hours). The results showed that highest removal of Cd, Cu, Zn and Pb according to time after (72 hours 91.946 %, 72 hours at 76.19 %,12 hours at 84.360%, and 72 hours at 58.788 % respectively), while the lowest removal of Cd, Cu, Zn and Pb according to time after (48 hours at 81.879 %, 48 hours at 26.19 %, 48 hours at 54.502 % and Zero time at 39.394 % respectively) and there were significant differences between all-time categories at p. value < 0.05%. Fish scales absorb trace elements from wastewater.

Key words: trace elements, biosorption, *Barbus luteus*.

Introduction

The term "biosorption" to the process by which biological materials can absorb heavy metals from water through metabolically mediated or physical-chemical absorption mechanisms (Singh and Kumar *et al.*,

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2020; Maktoof*, et al.*, 2020). The biological components employed in the process are often waste biomass from algae, fungi, or bacteria, which is naturally abundant and affordable dead biomass (Abdi and Kazemi, 2015). Biosorption is advantageous due to the significant energy savings from a more efficient water treatment system operating for hours. Waste biomass is also economically enticing because it is inexpensive and widely accessible (Rajasulochana and Preethy, 2016; Maktoof and AL-Enazi,2020).

Fish scales are one potential adsorbent for heavy metal removal; *Labeo Rohita, Catlacatla*, and *Atlantic Codad* fish scales have all been recorded and have shown encouraging results globally (Vo *et al*., 2020). Therefore, this study will investigate a novel method for removing target heavy metals from water, such as iron, zinc, and aluminum, by taking use of a feature of fish scales (Tilapia). Additionally, it is crucial to research the ideal heavy metal removal conditions, including pH, biosorbent dosage, initial heavy metals concentration, and contact duration (Bakhiet, 2016). Chemical and biological sludge, costs little to operate, and doesn't require additional nutrients (Liu *et al*., 2018). A recent study suggested the scales of the Atlantic cod, Gadusmorhua level of lead, arsenic, and chromium in water (O'Donnell and Sullivan, 2021). Like any other biomaterial, fish scales are made up of both organic and inorganic materials. Because of the nitrogen-containing ligands present, it has been determined from the scales of cod, porgy, and flounder that the proteins and organic component in fish scales seem to be the main factor influencing the adsorption ability (Qin et al., 2022). The adsorption of heavy metals by the scales of *Mozambique tilapia* fish is one method that has gained popularity for eliminating metal from home and industrial effluent (Othman *et al*., 2016). The adsorption isotherm and bio sorption kinetics in synthetic wastewater determine how well fish scale removes zinc ions and iron ions from domestic wastewater. *M. tilapia* fish scale is a potential adsorbent for removing Zn and Fe ions from synthetic and domestic wastewater solutions (Othman *et al*.,2016; Onwordi *et al*., 2019). Since there are no studies in Iraq that deal with removing heavy elements from wastewater using remain fish scales. Because of the lack of studies that relate to the removal of heavy elements from wastewater by using remains a waste of fish, the purpose of this study is to assess the contamination levels of some trace elements, including cadmium, lead, zinc, and copper, from wastewater treatment in Al-Nassiriya at the Al-Hindia plants as well as using freshwater fish scale waste from *Barbus lutes* fish as an affordable and eco-friendly way to remove metal ions by biosorption.

Materials and Methods

Wastewater Samples Collection

Water samples were gathered from the collecting chamber at the Al Hindiya plant on the highway leading to Ur city/Al-Nasiriyah city in southern Iraq (used for sewage treatment in Al-Nasiriyah city). Al Hindiya is not far from this factory. The facility treats sewage that arrives from the city's core through a conduit that also carries sewage from close-by restaurants, shops, and homes. The samples were collected in the Autumn of 2020, placed in polyethylene plastic containers, and transported to the Advanced Pollution and Environment Laboratory at the College of Science at Thi-Qar University.

Fish Sample Collection and Preparation Powder for Adsorption

Fish samples were taken from the Euphrates River in the Suq Al-Shuyoukh area of Thi-Qar province. The fish's scales were removed then they were rinsed in water several times to remove any sediments, and it was put out in the sun to dry for a month before the scales were gathered. The crusts were made crispy and put in the oven for an hour at a temperature (70 °C). Following the electric mill's grinding of the scales, three different-sized sieves—250 m, 1 mm, and 2.36 mm—were used. A 100 ml burette with 50 ml of medical gauze at the bottom and top, where the form is positioned, was then filled with 5 g of each sample of water and sewage added to it. After that, the samples were incubated five times (0, 12 hours, 48 hours, 72 hours and 96 hours) (Srividya and Mohanty, 2009).

Determination of Trace Elements Concentrations in Wastewater

The approach described by Csuros *et al.* (2018), was used to assess the amounts of heavy metals in sewage water.

Adsorption of Trace elements from Scales

The trace elements were measured by the following equation:

$$\text{Trace elements Adsorption} = \frac{(Ci - Cf)}{Ci} * 100$$

C_i= Trace elements before adsorption

C_f= Trace elements after adsorption

Statistical Analysis

Statistical Package for Social Science version 26 was used to analyze the data for the current study, along with an independent t_ test. When the difference has a p-value less than 0.05, it is considered significant.

Results

Removal of Cd by using scales *Barbus luteus* 1.15 kg according to time

The result of the current study showed higher heavy metal removal after 72 hours 91.946 %, follow by zero time 87.919, while the lowest heavy metal removal after 48 hours 81.879 %. The results also recorded a significant difference $p \le 0.05$ in Cd removing by scales in all time categories.

Table 1: Removal of cadmium metal from scales at different times

Cadmium according to Time		**Mean + SD**	**Mean difference**	**Adsorption %**	**p. value**
zero Time	Before	1.49 ± 0.01	1.309	87.919	< 0.05
	After	0.18 ± 0.05			
12 hr	Before	1.49 ± 0.01	1.279	85.906	< 0.05
	After	0.21 ± 0.04			
48 hr	Before	1.49 ± 0.01	1.227	81.879	< 0.05
	After	0.27 ± 0.04			
72 hr	Before	1.49 ± 0.01	1.373	91.946	< 0.05
	After	0.12 ± 0.01			
96 hr	Before	1.49 ± 0.01	1.270	85.234	< 0.05
	After	0.22 ± 0.03			

Removal of Cd by using scales *B. luteus* 1.15 kg according to Sieve Size

The result of the current study recorded the higher heavy metal removal in a sieve size 2.36 mm 88.590%, while the lowest heavy metal removing in sieve size 1 mm 85.234 %. The results also recorded a significant difference in Cd removal by scales in different sieve size categories. In bone Cd removing the result recorded the lowest removing 80.536 % 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	1.282	85.906	< 0.05
	After	0.21 ± 0.06			
1 mm	Before	1.49 ± 0.01	1.272	85.234	< 0.05
	After	0.22 ± 0.06			
2.36 mm	Before	1.49 ± 0.01	1.320	88.590	< 0.05
	After	0.17 ± 0.03			

Removal of Zn by using scales *Barbus luteus* 1.15 kg according to time

The result of the current study illustrated higher Zn removal after 12 hours 84.360 %, followed by zero time 80.569 %, while the lowest heavy metal removal after 48 hours 54.502 %. The results also recorded a significant difference in Zn removal by scales in all- time categories.

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

Zinc according to Time		Mean + SD	Mean difference	Adsorption in %	p. value
zero Time	Before	2.11 ± 0.01	1.703	80.569	< 0.05
	After	0.41 ± 0.06			
12 hr	Before	2.11 ± 0.01	1.785	84.360	< 0.05
	After	0.33 ± 0.05			
48 hr	Before	2.11 ± 0.01	1.148	54.502	< 0.05
	After	0.96 ± 0.22			
72 hr	Before	2.11 ± 0.01	1.619	76.777	< 0.05
	After	0.49 ± 0.10			
96 hr	Before	2.11 ± 0.01	1.229	58.294	< 0.05
	After	0.88 ± 0.16			

Removal of Zn by using scales *B.luteus* 1.15 kg according to Sieve Size

The result of the current study was recorded that the higher heavy metal removal in sieve size 2.36 mm 72.038 %, while the lowest heavy metal removal in both other sizes 71.090 %. The results also recorded a significant difference in Zn removal 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	1.497	71.090	≥0.05
	After	0.61 ± 0.07			
1 mm	Before	2.11 ± 0.01	1.502	71.090	≥0.05
	After	0.61 ± 0.08			
2.36 mm	Before	2.11 ± 0.01	1.525	72.038	≥0.05
	After	0.59 ± 0.14			

Removal of Cu by using scales *Barbus luteus* 1.15 kg according to Time of Adsorption

The result of the current study recorded the higher Cu element removal in 72 hours 76.19%, while the lowest Cu metal removal in 48 hours 26.19%. The results also recorded a significant difference in Cu removal by scales in different time of adsorption categories.

Removal of Cu by using scales *B. luteus* 1.15 kg according to Sieve Size

The result of the current study was recorded the higher heavy metal removal in sieve size 1 mm was 57.143%, while the lowest heavy metal removal in 250µm 52.381%. The results also recorded a significant difference in Cu removal by scales in different sieve size categories. In bone Cu a higher removal 61.905% compared with scales extract.

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	0.289	69.048	> 0.05
	After	0.13 ± 0.04			
12 hr	Before	0.42 ± 0.01	0.227	54.762	< 0.05
	After	0.19 ± 0.008			
48 hr	Before	0.42 ± 0.01	0.114	26.190	< 0.05
	After	0.31 ± 0.05			
72 hr	Before	0.42 ± 0.01	0.324	76.190	< 0.05
	After	0.10 ± 0.001			
96 hr	Before	0.42 ± 0.01	0.191	45.238	< 0.05
	After	0.23 ± 0.02			

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	0.220	52.381	< 0.05
	After	0.20 ± 0.07			
1 mm	Before	0.42 ± 0.01	0.237	57.143	< 0.05
	After	0.18 ± 0.08			
2.36 mm	Before	0.42 ± 0.01	0.226	54.762	< 0.05
	After	0.19 ± 0.06			
	After	0.16 ± 0.04			

Removal of Pb by using scales *Barbus luteus* 1.15 kg according to Time of Adsorption

The result of the current study was noted the higher Pb element removal in 72 hours 58.788 %, while the lowest Pb metal removal in zero time 39.394 %. The results also recorded a significant difference in Pb removal 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
zero Time	Before	1.65 ± 0.01	0.651	39.394	< 0.05
	After	1.00 ± 0.08			
12 hr	Before	1.65 ± 0.01	0.811	49.091	< 0.05
	After	0.84 ± 0.20			
48 hr	Before	1.65 ± 0.01	0.860	52.121	< 0.05
	After	0.79 ± 0.05			
72 hr	Before	1.65 ± 0.01	0.965	58.788	< 0.05
	After	0.68 ± 0.05			
96 hr	Before	1.65 ± 0.01	0.898	54.545	< 0.05
	After	0.75 ± 0.10			

Removal of Pb by using scales *B. luteus* 1.15 kg according to Sieve Size

The result of the current study recorded the higher heavy metal removal in sieve size 2.36 mm at 53.939 %, while the lowest heavy metal removal at 250µm 48.788 %. The results also recorded a significant difference in Pb removal 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	0.805	48.788	< 0.05
	After	0.84 ± 0.21			
1 mm	Before	1.65 ± 0.01	0.890	53.939	< 0.05
	After	0.76 ± 0.10			
2.36 mm	Before	1.65 ± 0.01	0.816	49.455	< 0.05
	After	0.83 ± 0.10			
	After	0.75 ± 0.07			

Discussion

The current study showed that the highest removal of Cd, Cu, Zn and Pb according to time after (72 hours at 91.946 %, 72 hours at 76.19 %,12 hours at 84.360%, and 72 hours at 58.788 % respectively), while the lowest removal of Cd, Cu, Zn and Pb according to time was after (48 hours at 81.879 %, 48 hours at 26.19 %, 48 hours at 54.502 % and Zero time at 39.394 % respectively) and there 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 (2.36mm 88.590%, 1mm 57.143 %, 2.36mm 72.038 %, and 2.36mm 53.939% respectively), while the lowest removal of Cd, Cu, Zn and Pb according to sieve size were (1mm 85.234%, 250µm 52.381%, in both other sizes 71.090 %, and 250µm 48.688 % respectively) and there were significant differences between all sieve size categories at p. value < 0.05%.

Based on these findings, it can be said that fish scales are green biomass with a high biological absorption capacity, are renewable, and are inexpensive, making them a good alternative to other methods for removing heavy metals from aqueous solutions. Additionally, it has been demonstrated that employing fish scales as a biosorbent for
heavy metals in wastewater samples could be environmentally benign, and these findings are in line with those of a study on water demineralization that used fish scales (Cunningham and Shahan, 2019).

This is consistent with the findings of a study conducted in Ghana by Kwaansa et al., (2019), where Cu was the best removed heavy metal ions in both surface water reservoirs. Under the best ideal adsorption circumstances, Cu was the best removed heavy metal in wastewater. The results of Zayadi and Othman in Malaysia at the same time revealed that under the ideal absorption conditions, 92.3 percent of zinc could be isolated, and this result is similar to the zinc removal in our current investigation. 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.

Alif et al., (2020) 's investigation on the removal of zinc using a fish scale in Malaysia revealed that the greatest removal percentage was 93.52 percent of the zinc ion, which is completely consistent with the current findings. Additionally, Eletta and Ighalo (2019) in Nigeria discovered that fish scales have very good heavy metal adsorption capability and outstanding removal efficiency (50–100% for heavy metals). The removal of heavy metals from wastewater was shown to be significantly influenced by the adsorption period, the surface area of fish scales, and the species of fish utilized in the biological treatment, according to this study and earlier research.

Conclusions

The current study concluded the following:

1. Fish scales have a greater ability to adsorb trace elements from wastewater.
2. There is a positive correlation between the quantity and quality of active chemical groups on the surface of fish scales and bones and their ability to adsorb trace elements.

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الامتصاص الحيوي لبعض العناصر النزرة من مياه الصرف باستخدام حراشف اسماك الحمري

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المستخلص

جمعت عينات مياه الصرف الصحي من محطة المعالجة لمياه الصرف الصحي بمنطقة الازديناوية جنوب مدينة الناصرية. الأسماك المأخوذة من نهر الفرات في قضاء سوق الشيوخ هي اسماك الحمري بوزن 1.15 كغم. تم قياس الزنك والكادميوم والنحاس والرصاص عن طريق جهاز الامتصاص الذري الهبي. المسحوق مصنوع من حراشف الاسماك. تطحن الحراشف بعد التنظيف. ثم تمرر الحراشف بثلاثة أنواع من المناخل (250 ميكرومتر ، 1 مم ، 2.36 مم). من أجل اختبار قدرة بقايا حراشف الأسماك على امتصاص العناصر النزرة من مياه الصرف الصحي ، وضع 50 غرام من المسحوق في سحاحة ، وتم فحصها بخمس اوقات (وقت صفر ، 12 ، 48 ، 72 ، 96 ساعة). أظهرت النتائج أن أعلى إزالة للعناصر بعد 72 ساعة بلغت للكادميوم 91.946٪ ، وللنحاس 76.19٪ ، وللزنك 84.360٪ ، وللرصاص 58.788٪ ، بينما كانت اقل إزالة بعد 48 ساعة بلغت كما يلي للكادميوم 81.879 ٪ و للنحاس 26.19٪ و للزنك 54.502٪ وللرصاص 39.394٪ بوقت قدره صفر وكانت هناك اختلافات معنوية تحت مستوى $p < 0.05\%$ بين كل الاوقات. فأن الحراشف قادرة على امتصاص العناصر النزرة من مياه الصرف الصحي.

الكلمات الافتتاحية: العناصر النزرة، الامتزاز ، سمكة الحمري.

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