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NEW BIOFILTER MEDIA FOR HEAVY METALS REMOVAL FROM AQUACULTURE WASTEWATER

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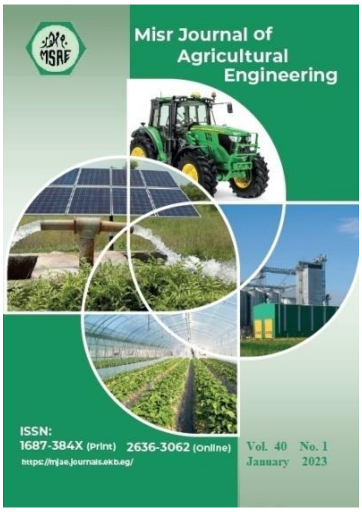


Keywords:
Aquaculture; Biological Filter; Activated carbon; Rice straw; Heavy metals removal.

ABSTRACT

It will be necessary to provide about 40 million additional tons of fish by 2030 to keep the per capita share constant. Fish from aquaculture contribute about 50% of the total fish production around the world. It has become common to treat water from fish farms using the biological method, because it is one of the best methods comparinet to the physical and chemical methods. Although ammonia (NH_3) is one of the most important pollutants produced by fish farms, several heavy metals have serious effects on fish and the environment. In this experiment, a treatment unit consisting of two stages was designed, the mechanical filter stage as a primary treatment and then the biological filter as the main treatment stage. Gravel was used as a mechanical filter medium, while activated carbon (AC) and rice straw (RS) were used as biofilter media. The AC and RS effects on the heavy metals removal from the water were studied. Changing the pH value on ammonia removal efficiency was also produced to determine its effect. The concentrations of lead (Pb), tin (Sn), iron (Fe), arsenic (As), copper (Cu), nickel (Ni), boron (B), zinc (Zn) and cadmium (Cd) were measured for wastewater and treated water. The best efficiency of AC and RS was to remove copper (Cu) by 65.80 and 84.68%, respectively, and the lowest efficiency was to remove lead (Pb) by 31.50 and 43.20%, respectively. The best pH of AC and RS was 8 with ammonia removal efficiency of 85 and 68%, respectively.

1. INTRODUCTION

The scarcity of resources and the increase in population are the most important problems facing the world today. Therefore, aquaculture appeared to provide a source of protein for the population **(Turcios and Papenbrock, 2014; Abdelbary, 2016)**. In recent decades, the fish farming field has witnessed significant growth **(Nghia et al., 2009)**. Through aquaculture, fish are produced in quantities close to fish that are produced from natural sources **(Verma et al., 2012; Abdelbary, 2017)**. Aquaculture currently produces nearly 50% of the total fish production in the market **(Emenike et al., 2021; Abdelfatah et al., 2022)**.

Recently, fish production is required to be increased with high quality to meet the expected increase in the population which is estimated by 10 million in 2050. The products of aquaculture must be treated to get rid of pollutants and heavy metals **(Emenike et al., 2021)**. Therefore, the objectives of this research were to, 1-preserve natural water sources from pollution as a result of the wastewater being disposed of without treatment, and 2- Provide an additional source of water that produce by recycling water from the biological treatment **(Nicula et al., 2022)**.

Residues from fish farms contain dissolved carbon, uneaten food, feces and nitrogenous and phosphorous components, which accumulate in production units. The most important criterion by which the quality of fish farm water is judged is ammonia (NH_3). The presence of a high percentage of protein in the fish feed leads to increase the percentage of NH_3 in the water of fish farms, which accumulates very quickly in the water. Ammonia can be removed in two stages: converting ammonia to nitrite and then converting nitrite to nitrate **(Erbanová et al., 2012; Godoy-Olmos et al., 2019; Abdelfatah et al., 2022).**

Ammonia is the main harmful product of fish farming and is toxic to fish in its non-ionized form. One of the effective ways to remove NH_3 is the process of adsorption to solid surfaces. The fish farming sector is one of the fastest-growing sectors in the world. Considering the increased demand for fish, it was necessary to follow the intensification system in production. Therefore, the amount of waste generated from those systems increased. To improve the aquaculture system, water quality and quantity must be monitored. However, ammonium is the main product of fish and is a highly soluble gas. Ammonium may arise from nitrogen fertilizers, fish secretion, phytoplankton death, and decomposition of organic matter, but mainly from fish feeds which contain large amounts of protein **(Zadinelo et al., 2015; Musyoka, 2016).**

There are several factors that can be used to determine the performance of the biofilter which is used to get rid of ammonia from fish farms. These factors are organic matter, hydraulic loading, temperature and pH **(Schroeder et al., 2015; Godoy-Olmos et al., 2019).** The water pH is the most important factor that affects the nitrification process, where a decrease in the efficiency of the nitrification process results from the low pH. An improper pH in the recirculating aquaculture systems (RAS) leads to a high concentration of total ammonium nitrogen (TAN) and greater fluctuations in pH level. This is because of the lack of stability in microbial activity which leads to damage to fish. Therefore, it is necessary to know the appropriate pH of the RAS **(Summerfelt et al., 2015)**.

Heavy metals are elements that have an atomic density greater than 5 gm/cm^3 and an atomic number greater than 20 **(Raychaudhuri et al., 2021)**. Essential and non-essential heavy metals are the two basic categories into which heavy metals can be divided. These elements hold a noticeably high density in contrast to the imitation of water **(Kinuthia et al., 2020)**. In addition, the amounts of chromium (Cr), thallium (Tl), cadmium (Cd), nickel (Ni), lead (Pb) and mercury (Hg) are probably hazardous to fish. Moreover, they are pretty soluble within aquatic environments and may keep drowned readily via living organisms permanency.

Recirculating aquaculture system (RAS) is the most environmentally friendly method used for fish production. However, heavy metals may accumulate in these systems because of low water exchange rates. The intensive system is usually used to produce fish to meet the required quantities of fish. This intensive system consequently leads to an increase in the quantities of water required and an increase in the generated waste. Reusing wastewater after the removal of heavy metals is one of the most promising solutions to meet the required quantities of water, and to protect the environment from pollution. In a wastewater recycling system, heavy metals accumulate in the water as well as in the tissues of fish **(Martins et al., 2011)**.

To control environmental pollution, heavy metals from fish farms must be monitored and removed. The discharge of wastewater containing these minerals into natural drains without a treatment procedure leads to damage to those sources and human health. The very dangerous effect of heavy metals may not appear at the same time, but their negative effects appear after several years. Cadmium (Cd) and lead (Pb) are among the most important heavy metals. Lead is considered the first environmental poison among heavy metals, which causes great harm to human health **(Kumar et al., 2011; Olusola et al., 2012)**.

Because heavy metals happen in small concentrations in biological systems, they are known as trace elements **(Md et al., 2016; Sonone et al., 2020)**. They lead to the deterioration of the aquaculture system, physical distortions of living organisms and pollution of the aquatic environment. They also cause many diseases in fish and thus ultimately affect the food chain because they are long-lasting and can bioaccumulate (**Sultana et al., 2017; Sonone et al., 2020)**. They are usually existed in the form of ions or a compound and are soluble in water and thus be absorbable by fish **(Abdulali, 2011)**. The majority of heavy metals are known to be poisonous and cancer-causing substances. When they exist in wastewater, they pose a substantial risk to both the human population and the flora and fauna of the receiving water bodies **(Srivastava and Majumder, 2008)**. They also cause a lot of diseases that are fatal to all living beings. In this way, wastewater treatment offers a solution that replenishes the planet's decreasing water supply while also protecting it from contamination **(Yadav et al., 2019)**.

There are numerous techniques for removing heavy metal ions from various wastewater sources **(Qasem et al., 2021)**. These techniques could be divided into many treatments based on adsorption, membranes, chemicals, electricity, and photocatalysis. These approaches are thoroughly and critically reviewed and discussed in terms of the used agents/adsorbents, removal effectiveness, operating circumstances, and the advantages and disadvantages of each technique.

Despite all the previous harm to heavy metals, it can be said that living beings need essential heavy metals (HMs) to carry out their basic functions, including growth, metabolism, and the formation of various organs. Plants need a variety of critical heavy metals, such as Cu (copper), Fe (iron), Mn (Manganese), Zn (zinc), and Ni (Nickel). As these metals combine to generate cofactors that are crucial for the structural and functional integrity of enzymes and other proteins **(Raychaudhuri et al., 2021)**.

The sorption method is extensively used for serious metals removal from wastewater due to its low price, obtainability and eco-friendly nature. Industrial adsorbents and bioadsorbents are used for serious metals removal from waste material. Excessive levels of heavy metals frequently have negative consequences on people, other living beings, and the environment **(Madhu and singh, 2017, Balali-Mood, et al., 2021).** Table 1 shows the effect of the most important heavy metals and their safe concentrations **(Kinuthia et al., 2020)**.

Table (1) The effect of the most remarkable heavy metals on human health and their safe concentrations.

Heavy metals	Human adverse health effects	WHO recommended safe limits, ppm	
		Wastewater	Agricultural soils
Mercury, Hg	Carcinogens harm the kidneys, lungs, and brain - harm to growing foetuses high heart rate and blood pressure - diarrhoea, skin rashes, eye discomfort, and vomiting	0.0019	0.05
Cadmium, Cd	lung, kidney, prostate, and stomach cancer development; renal, skeletal, and cardiovascular systems injury	0.003	0.003
Lead, Pb		0.01	0.1
Chromium, Cr	very water soluble, poisonous, and carcinogenic. has a connection to ulcers that heal slowly	0.05	0.1
Nickel, Ni	Skin conditions, allergies, organ disorders, cancer of the lungs, and inhalation cutaneous pathways - elevated Ni levels in human urine and tissues	0.02	0.05
WHO: World Health Organization			

The main goal of this study work is to get rid of the heavy metals present in aquaculture wastewater, in preparation for the reuse of that water again. In addition, the best pH has been determined to have the best ammonia removal efficiency. This is to study the complex relationship between ammonia removal and the effect of the existence of heavy metals and pH.

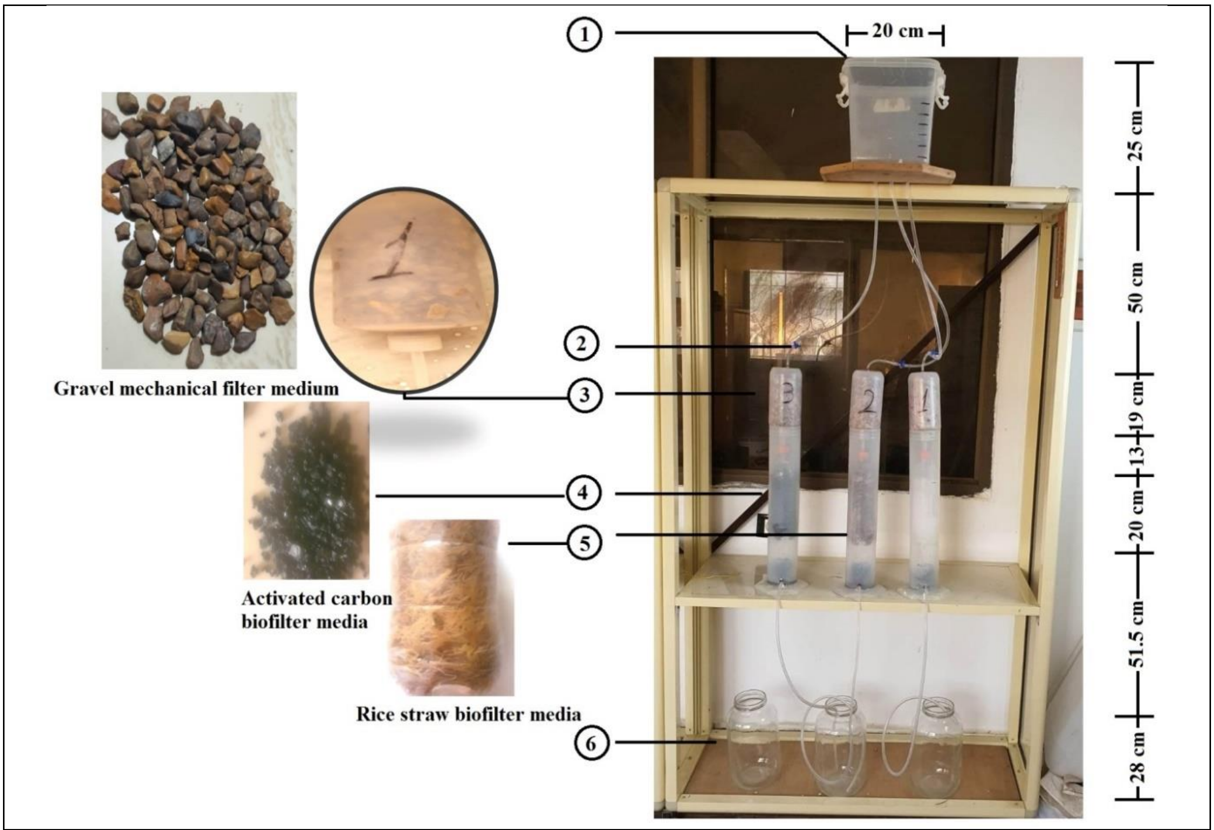
2. MATERIALS AND METHODS

Samples Collection

Samples were collected from a fish farm at Animal Production Dept., Fac. Of Agric., Cairo University. From a pond with a depth of 1.5 m and a surface area of 2.3 m^2 (size of 3.5 m^3). The type of fish is Nile tilapia.

Aquaculture Wastewater Treatment System

Figure 1 illustrates the experimental layout of the treatment system which starts with a 9L wastewater tank. Then a gravel mechanical filter with a volume of 1 liter was used to pass the wastewater through it initially. The gravel used as a medium was with diameter < 6.3 mm and its characteristics were as described in **(Abdelfatah et al., 2022)**.



1	Wastewater vessel.	**4**	Activated carbon biofilter vessel.
2	Flow rate controller.	**5**	Rice straw biofilter vessel.
3	White aggregates mechanical filter.	**6**	Treated wastewater exhaust vessel.

Fig.(1). Schematic diagram of aquaculture wastewater treatment system.

Finally, the wastewater passed through a biofilter with a volume of 0.85 liter. As described previously in detail by **Abdelfatah et al., 2022**, the experiment was carried out using two different types of media, namely activated carbon (AC) and rice straw (RS). Activated carbon was microporous and crushed. While the rice straw was washed and left to dry, then it was cut into pieces with lengths of 2 - 3 cm.

Experimental Design (Experimental Procedure)

As shown in figure 2 wastewater passed through a gravel mechanical filter then two types of media of biofilter were used, activated carbon (AC) and rice straw (RS). The doses were 15 and 20 gm/L wastewater and hydraulic retention times (HRTs) were 20 and 30 min for activated carbon (AC) and rice straw (RS), respectively.

Heavy Metals Elements

The simultaneous detection of several elements using inductively coupled plasma mass spectroscopy (ICPMS) quantitative heavy metal detection method can sometimes go as low as low ppt for various metals. **Binkley and Simpson (2003)** reported that polography and anodic stripping voltimetry are electrochemical methods of detection that can detect several elements, although this method is quite expensive compared to others. They can provide insightful data regarding the availability of metal ions.

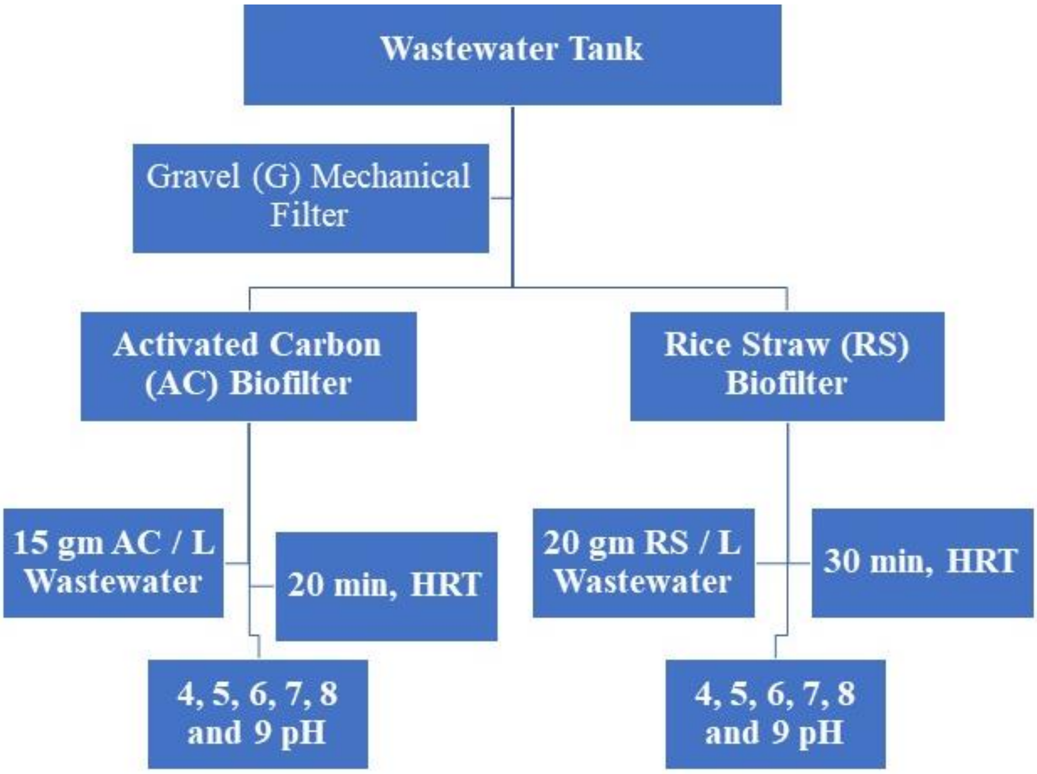


Fig.(2). Experimental design of aquaculture wastewater treatment system.

Multiple elements can be detected using electrochemical detection techniques including polography and anodic stripping voltimetry. They are best suited for research purposes and can also provide useful data regarding the availability of metal ions. The use of conventional chemical reagents for metals is appropriate when the element of interest is known **(Binkley and Simpson, 2003; Kapadnis, et al., 2016).**

Iron (Fe), was measured by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES), Agilent (Cary Series UV-Vis Spectrophotometer) at a wavelength range of 475, (Fig. 3, 4) at Water Pollution Research Lab, National Research Centre.

Fig.(3). UV-Vis Spectrophotometer.

Fig.(4). Preparation of Standards.

Lead (Pb), nickel (Ni), cadmium (Cd), arsenic (As), boron (B), copper (Cu), tin (Sn) and zinc (Zn) were determined by atomic absorption spectrometry, (Perkin Elmer precisely, AAnalyst 400 AA Atomic Absorption Spectrometer (Fig. 5), at Physiology of Plants, Water and Soil Lab, National Research Centre. They were measured for raw wastewater in accordance with **(ECP. 501. (2015); Baird et al., 2017)**, and wastewater treated by activated carbon and rice straw media,

Fig.(5). Atomic Absorption Spectrometer.

<u>Measurements</u>

Hydraulic retention time depends on the volume of the filter and the flow rate. It is calculated according to:

$$HRT = \frac{V_f}{Q}$$

Where:

HRT = Hydraulic retention time (min)
Q = Flow rate (l/min)
V_f = *Biofilter media volume (l)*

Removal efficiency is the percentage of pollutants that are removed after passing through the biofilter, while elimination capacity is the mass of removed pollutants per unit volume of media and per unit of time. Removal efficiency and elimination capacity were calculated according to:

$$R.E = \frac{C_i - C_o}{C_i} * 100$$

$$E.C = \frac{(C_i - C_o) * Q}{V_f}$$

Where:

R.E = The efficiency of removal (%)
E.C = Elimination capacity (mg/l. min)
C_i = *Inlet concentration (mg/l)*
C_o = *Outlet concentration (mg/l)*

3. RESULTS AND DISCUSSION

The methods used to remove heavy metals vary depending on the specific metal(s) involved, the wastewater's chemical composition, the volume that needs to be treated, the composition's unpredictability, the flow of the wastewater, and the degree of treatment needed. In this research, the results of using the aquaculture wastewater treatment system for heavy metals removal efficiency were obtained. Also, pH was changed to determine its effect on ammonia removal.

Heavy Metals Removal

For heavy metals removal, both physical (mechanical filtration) and biochemical techniques (biofiltration) are used. These procedures include ultrafiltration, precipitation, ion exchange, oxidation/reduction (for NH_3, NO_2, NO_3), and ion exchange of the heavy element itself. Sedimentation removes a large portion of the metal associated with particulates during basic treatment. For the removal and recovery of metals, microorganisms provide an alternative to physical and chemical processes. The biomass accumulation performs metal elimination or immobilization.

Heavy metals have detrimental effects on human health; they are ingested through fish intake and eventually make their way into humans. Cooking fish does not reduce the mercury concentration (**Balali-Mood, et al., 2021**). The European Union and the US both base their regulations on the preservation of drinkable water sources on World Health Organization (WHO) recommendations on the maximum allowable concentration of certain priority contaminants. These are intended to guarantee that water for drinking is safe for human consumption.

Constraints on the release of heavy metals into the environment are presented and illustrated by **Binkley and Simpson, (2003)**, in the following table, table (2). Moreover, **El Bahgy et al., (2021)** demonstrated heavy metal concentration (mg/l) in varied sites for water sources (marine inlet, fresh inlet, fish ponds, the main canal, and the mixing pond) in comparison with the United States Environmental Protection Agency (USEPA). They reported that Cd, Cu, Zn, Pb, Fe, and Ni concentrations were 0.003, 0.947, 0,094, 0,050, 0,100 and 0,006 mg/l and values between parenthesis exceed the allowed range.

Atomic Absorption Spectrophotometer was used to examine the levels of heavy metals by **Leonard, et al., (2022)**. Their study's findings showed that the levels of metal traces in fish tissues varied widely. Fish muscles exhibited the lowest levels of heavy metals across all fish species, while fins and guts had the highest percentages of Cr, Zn, Cu, and Pb (African catfish and Nile tilapia).

Resma, et al., (2020) measured heavy metal concentrations using a flame atomic absorption spectrometer and a graphite furnace atomic absorption spectrometer. Metals in meat were concentrated in the following order Zn > Cu > Cr > As > Cd with values of $16.205 \pm 0.303 > 0.874 \pm 0.037 > 0.590 \pm 0.05 > 0.042 \pm 0.003 > 0.004 \pm 0.00$ (mg/kg dw) in T. nilotica.

Heavy metals concentrations were measured for row wastewater and water treated by a treatment system using activated carbon and rice straw biofilter media. The results show that the concentrations of lead (Pb), cadmium (Cd), iron (Fe), nickel (Ni), copper (Cu), zinc (Zn), boron (B), tin (Sn) and arsenic (As) for raw wastewater were 1.965, 0.789, 4.998, 0.098, 0.111, 0.768, 0.023, 0.000 and 0.000 mg/l, 1.345, 0.487, 2.765, 0.045, 0.038, 0.341, 0.012, 0.000 and 0.000 mg/l for activated carbon biofilter and 1.116, 0.167, 1.534, 0.034, 0.017, 0.231, 0.010, 0.000 and 0.000 mg/l for rice straw biofilter, respectively, as illustrated in table (3).

Table (2) Limitations on the discharge of heavy metals entering the environment according to (Binkley and Simpson, 2003).

Heavy metal	EQS[(a)], mgl^{-1}	EU [(b)], mg kg^{-1} dm	EU [(c)], gas $^{-1}y^{-1}$	US [(d)], $mgkg^{-1}$	[(e)], $kgha^{-1}y^{-1}$
Arsenic	**50**	**--**	**--**	**75**	**2.0**
Cadmium	**5**	**20-40**	**150**	**85**	**1.9**
Chromium	**20**	**--**	**--**	**--**	**--**
Copper	**10**	**1000-1750**	**12000**	**4300**	**75**
Iron	**1000**	**--**	**--**	**--**	**--**
Lead	**10**	**750-1200**	**15000**	**840**	**15**
Manganese	**--**	**--**	**--**	**--**	**--**
Mercury, (total)	**1**	**16-25**	**30**	**57**	**0.85**
Molybdenum	**--**	**--**	**--**	**75**	**--**
Nickel	**150**	**300-400**	**3000**	**420**	**21**
Selenium	**--**	**--**	**--**	**100**	**5.0**
Vanadium	**20**	**--**	**--**	**--**	**--**
Zinc	**75**	**2500-4000**	**30000**	**7500**	**140**

EQS[(a)] British EQS (Environmental Quality Standards).
EU [(b)] EU limits for the amount of metals present in sludge.
EU [(c)] EU yearly loading rates for receiving agricultural land MSW(Municipal Sewerage Works) sludge.
US [(d)] US part 501 maximum metals in sludge concentration.
[(e)] Annual loading rates for pollutants.

Table (3) Measured concentrations of heavy metals (in alphabetical order) in both untreated (raw), and treated wastewater.

Heavy metal	Concentrations in untreated (raw) wastewater, mg/l	Concentrations in treated wastewater, mg/l	
		Activated carbon biofilter	Rice straw biofilter
Arsenic, (As)	0.000	0.000	0.000
Boron, (B)	0.023	0.012	0.010
Cadmium, (Cd)	0.789	0.487	0.167
Copper, (Cu)	0.111	0.038	0.017
Iron, (Fe)	4.998	2.765	1.534
Lead, (Pb)	1.965	1.345	1.116
Nickel, (Ni)	0.098	0.045	0.034
Tin, (Sn)	0.000	0.000	0.000
Zinc, (Zn)	0.768	0.341	0.231

Figures 6 and 7 show heavy metals removal efficiency for the treatment system in the case of using activated carbon and rice straw as a biofilter media.

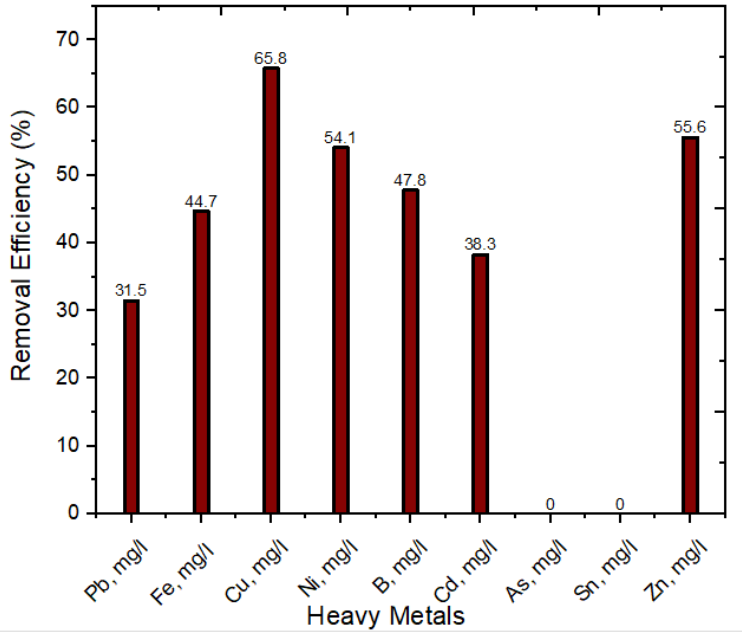


Fig.(6). Heavy metals removal efficiency for activated carbon biofilter medium.

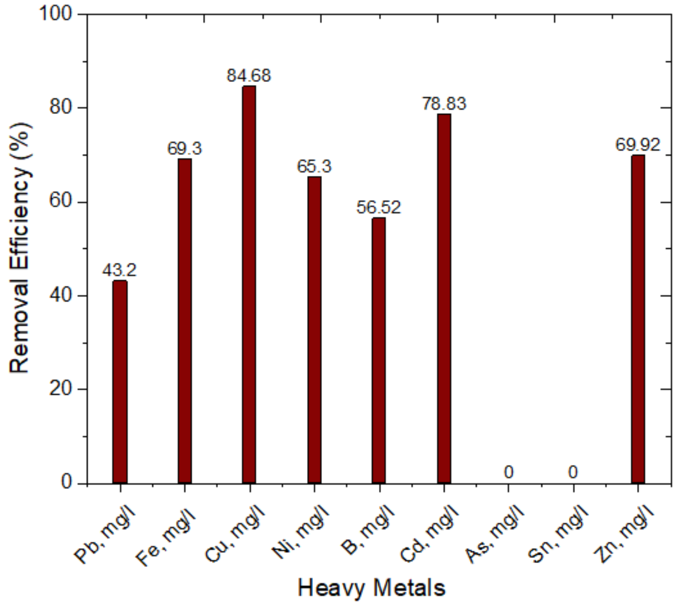


Fig.(7). Heavy metals removal efficiency for rice straw biofilter medium.

It is clear from Figures 6 and 7 that the best removal efficiency in the case of activated carbon and rice straw biofilters was for copper (Cu) with a percentage of 65.8 and 84.68%, respectively. Followed by zinc (Zn) and cadmium (Cd) in the case of activated carbon and rice straw biofilters with a percentage of 55.6 and 78.83%, respectively. It is also clear that the use of the biofilter, whether the medium is activated carbon or rice straw, has an effective effect in removing heavy metals in wastewater, as it affects the ammonia that is also present in an effective manner, and thus leads to an increase in the quality of the treated water and the possibility of using it again.

Toxic Effects of Heavy Metals

Boron, (B): In this experiment, the concentration of boron in raw wastewater was 0.023 and it was reduced to 0.012 and 0.010 for activated carbon and rice straw, respectively. With removal efficiency of 47.8 and 56.5%.

Cadmium, (Cd):- Even though it is uncommon, cadmium (Cd) naturally exists in water, soil, and minerals like sulphate, chloride, carbonate, and hydroxide salts. The presence of Cd in contaminated water may interfere with vital bodily functions and cause short- or long-term illnesses **(Balali-Mood, et al., 2021)**. In ocean water, the typical concentration in surface water and groundwater regularly <1 $\mu g.l^{-1}$, with the average value falling between 5-110 $mg.l^{-1}$ (Garai, et al., (2021). According to the International Agency for Research on Cancer (IARC), cadmium causes human cancer (Group 1). **Ehiemere, et al., (2022)** identified the quantities of cadmium in a fish pond (Clarias gariepinus, African sharptooth catfish, and species of airbreathing catfish of the family Clariidae), they listed the ranges for the mean cadmium contents of 0.733-1.405 mg/kg dry weight. As long as the permissible level of cadmium according to the Environmental Quality Standards (EQS) is 50 mg/l, and since the percentage of cadmium in the raw wastewater used in this research was 0.789 mg/l, it was less than the permissible limits.

Copper, (Cu): Although copper is necessary for cell function and the formation of haemoglobin, its existence in a watery environment may result from the build-up of home and agricultural waste. The high concentration of copper in the ponds may be due to human activity (runoff from agricultural regions, produce feeds, algaecides used in the ponds, and effluents from abattoirs), and it's also possible that the water's interaction with the surrounding soil and rock debris played a role **(Ehiemere, et al., (2022)**. They claimed also that copper content was 7.97 mg/kg, whereas actual copper concentrations ranged from 175.882 to 255.321 mg/kg. **El-Khatib, et al., (2020)** investigated the impact of some heavy metals on the quality of fish produced from these farms, four fish farms were chosen (El-Abbasa, Edko, Mariout, and Bahr El-Baqar). Their results displayed that, the highest average of copper concentration in water was recorded at Bahr El-Baqar fish farm (32.77 ± 3.44µg/l) and the lowest value at El-Abbassa fish farm (5.316 ± 0.43µg/l). The percentage of copper in the raw wastewater used in this experiment was 0.111 mg/l, and it was reduced when activated carbon and rice straw biofilters were used to 0.038 and 0.017 mg/l, respectively, which are percentages that comply with Environmental Quality Standards.

Iron, (Fe): El-Khatib, et al., (2020)'s results showed that El-Abbassa fish farm had the lowest average value of iron content in water (116.59±16.94 µg/l) and Bahr El-Baqar fish farm had the highest average value (863.21 ±67.07 µg/l). At Mariout Fish Farm, the iron concentration peaked in the spring (1043.94± 58.83 µg/l), and at El-Abbassa Fish Farm, it peaked in the summer (92.72 ±38.32 µg/l). According to Environmental Quality Standards, the concentration of iron was within the permissible limits, and its concentration was 4.998 mg/l in raw wastewater used, and it decreased to 2.765 and 1.534 mg/l when using activated carbon and rice straw biofilter, respectively.

Lead, (Pb): A hazardous environmental contaminant called lead has very detrimental consequences on several human organs. Although lead (Pb) is usually absorbed through the stomach and respiratory systems, it can be absorbed through the skin **(Balali-Mood, et al.,**

2021). **El-Khatib, et al., (2020)'s** results revealed that El-Abbassa fish farm had the lowest average lead content in water (0.82± 0.17 µg/l) while Bahr El-Baqar fish farm had the highest average lead concentration in water (28.81± 3.03 µg/l). At Bahr El-Baqar fish farm, the lead concentration peaked in the spring at (33.09± 9.96 µg/l), and peaked at El-Abbassa fish farm in the summer at (0.64 ±0.25 µg/l). The percentage of lead in this experiment decreased from 1.965 mg/l for wastewater to 1.345 and 1.116 mg/l for activated carbon and rice straw biofilter, respectively, while the limit allowed by Environmental Quality Standards was 10 mg/l.

Nickel, (Ni): At low concentrations, nickel is a necessary element for many species, but at excessive concentrations, it is hazardous. The physicochemical characteristics of water, such as pH, the strength of ionic, temperature, hardness, and dissolved organic carbon, affect the toxicity of nickel to fish (DOC) **(Garai, et al., 2021)**. Nickel is a fairly common trace element that is found in combination with oxygen or sulphur in the environment. The environment is exposed to nickel from both natural and human-made sources. When Nile tilapia were exposed to nickel chloride, they exhibited irregular swimming behavior, fast opercular movement, respiratory disorders, and skin lesions **(Garai, et al., 2021)**. When Nile tilapia were exposed to nickel, their blood parameters also changed, with a rise in red blood cell count and a decrease in haemoglobin and white blood cell counts. Freshwater fish exposed to nickel showed histopathological alterations in various tissues, including the gills, kidney, liver, and intestine. The concentration of nickel in the raw wastewater was significantly lower than the limit allowed by Environmental Quality Standards.

Zinc (Zn): One of the most common trace elements and vital micronutrients for all living things is zinc. Multiple physiological illnesses, including poor conception rates, cardiovascular diseases, and cancer, are brought on by zinc deficiency. However, excess zinc can be hazardous **(Garai, et al., 2021)**. Zinc sulphate was revealed Tilapia nilotica displayed sluggish swimming behavior and a loss of body balance. Zinc builds up in fish through their gills and digestive systems. **El-Khatib, et al., (2020)**'s results showed that at the Mariout fish farm, the average zinc concentration in water was found to be the highest (73.72 ± 5.79µg/l), the highest average zinc concentrations in water was recorded at Mariout fish farm (73.72 ± 5.79µg/l), and the least value (22.81 ± 10.32µg/l) at El- Abbassa fish farm. In the spring, zinc concentrations were at their highest (79.12 ± 10.44µg/l) at Mariout fish farm and the summer's lowest concentration was ever observed at El- Abbassa fish farm station (14.10 ± 2.18µg/l).

Arsenic (As): AL Taee, et al., (2020) reported that arsenic permissible concentration in water was 0.01 ppm, fortunately, no traces of both arsenic and tin were observed in the wastewater under study.

<u>pH Changing</u>

The pH was examined, and it was discovered to have a significant impact on the microorganisms' enzyme activity. **Binkley, and Simpson (2003)** believed that the reactive site undergoes protonation of the amino acid and by the heavy metal cation, complexation were responsible for the enzyme's action.

When the pH increases, the efficiency of ammonia removal increases accordingly **(Coelho et al., 2015; Thorarinsdottir et al., 2015)**. 4, 5, 6, 7, 8 and 9 of pH were used to choose the best pH for ammonia removal efficiency. Usually, HCL is used to reduce it or NaOH to increase it. For the activated carbon biofilter medium, the ammonia removal efficiency for 4, 5, 6, 7, 8 and 9 pH was 15, 27.2, 47.6, 76, 85 and 84.6 %, respectively, while for rice straw biofilter medium, the ammonia removal efficiency was 8.4, 18, 41, 58, 68 and 67.8 % for 5, 6, 7, 8 and 9 pH, respectively. Tables 4 and 5 show ammonia concentration, removal efficiency (RE) and elimination capacity (EC) for activated carbon and rice straw biofilters, while figures 8 and 9 show the ammonia removal efficiency for activated carbon and rice straw biofilter. The optimum pH was 8 for activated carbon and rice straw biofilter and increasing it had a reverse effect on ammonia removal.

Ammonia concentration, removal efficiency (RE) and elimination capacity (EC) For biofilter

Some heavy metals have an impact on biological treatment procedures; for instance, Cu, Pb, Cd, Ni, Zn, and Cr have been found to impair anaerobic digestion **(Binkley and Simpson, 2003)**. Microorganisms' ability to breathe is how toxicity is displayed. Generally speaking, heavy metals have a bacteriostatic effect. Mortality increases with concentration. Some bacteria have evolved defenses to deal with high levels of heavy metals in their surroundings.

Microorganisms' metabolic processes and metal biotransformations can cause heavy metals to solubilize, precipitate, chelate, biomethylate, or volatilize. As a result of microbial activity, ammonia may be produced or organic bases may form, can cause insoluble hydroxides of heavy metals to precipitate.

Fortunately, the concentration of ammonia, removal efficiency and elimination capacity) were not affected by the presence of heavy elements, but the performance of the biological filters had an excellent effect in reducing the concentration of ammonia in the wastewater for both activated carbon biofilter and (Table 4 and Fig.8) and rice straw biofilter (Table 5 and Fig.9).

Table (4) Ammonia concentration, removal efficiency (RE) and elimination capacity (EC) For AC biofilter

pH	NH_3 Concentration (mg/l)	Removal Efficiency (RE) (%)	Elimination Capacity (EC) (mg/l. min)
4	21.25	15	0.12
5	18.20	27.2	0.23
6	13.1	47.6	0.40
7	6	76	0.63
8	3.75	85	0.70
9	3.85	84.6	0.704

Table (5) Ammonia concentration, removal efficiency (RE) and elimination capacity (EC) For RS biofilter

pH	NH_3 Concentration (mg/l)	Removal Efficiency (RE) (%)	Elimination Capacity (EC) (mg/l. min)
4	22.90	8.4	0.07
5	20.50	18	0.15
6	14.75	41	0.34
7	10.50	58	0.48
8	8.00	68	0.57
9	8.05	67.8	0.56

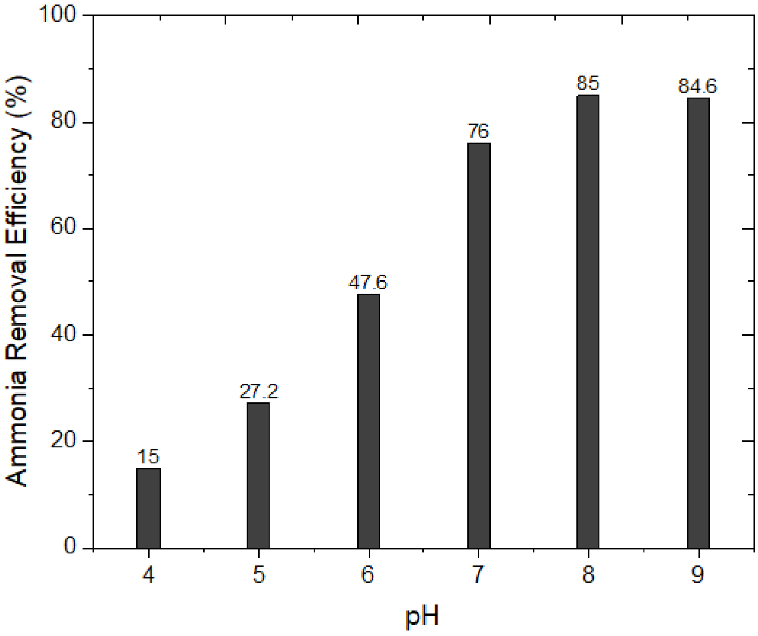


Fig.(8). Ammonia removal efficiency for activated carbon biofilter by different pH.

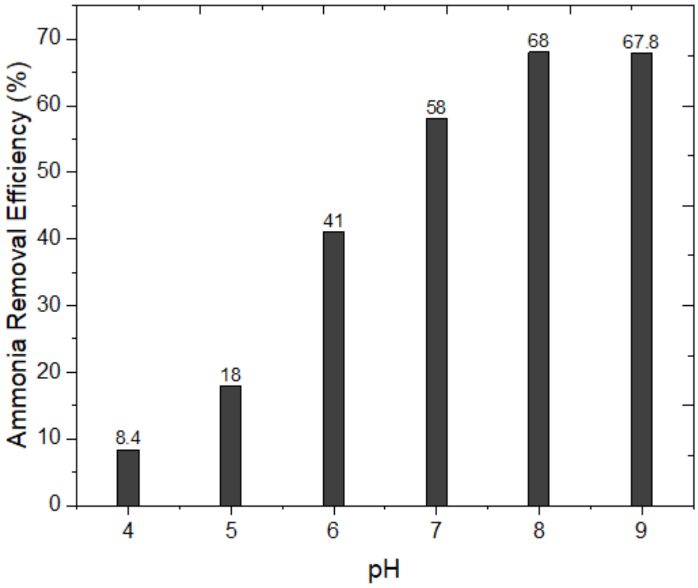


Fig.(9). Ammonia removal efficiency for rice straw biofilter by different pH.

Where, was the highest removal efficiency 85% (pH 8) and 68% (pH 8) for activated carbon and rice straw respectively, where the highest elimination capacity was 0.7 and 0.57 mg/l. min for activated carbon and rice straw respectively also, at pH 8.

You, et al., (2009) used batch experiments to add different combinations of heavy metals (lead (Pb), nickel (Ni), cadmium (Cd), Pb Ni, Ni Cd, Pb Cd, and Pb Ni Cd) at seven concentration levels (0, 2, 5, 10, 15, 25, and 40 ppm) to see which one inhibited nitrogen removal performance, including ammonia and nitrate specific uptake rate.

Their research looked at how these metal ions interacted with each other to affect both nitrification and denitrification. The results of their experiments revealed that Cd had the highest inhibition of the specific nitrate uptake rate, while Ni had the highest inhibition of the specific ammonia uptake rate.

Additionally, introducing even as much as 40 ppm of Pb into the activated sludge did not significantly limit ammonia or nitrate levels. Additionally, no synergistic impact was discovered when several heavy metals were administered simultaneously in various amounts.

4. CONCLUSION

Because they bioaccumulate in the body and have a variety of deleterious impacts on different human tissues and organs, heavy metals have negative consequences on human health. Heavy metals have an impact on apoptosis, differentiation, growth, proliferation, and other biological processes. Heavy metals can be removed by more than one method, and the selection of the suitable method depends on a variety of variables.

In this experiment, an aquaculture wastewater treatment system was designed, starting with the mechanical filter and then the biofilter. Gravel was used as a mechanical filter medium while the activated carbon and rice straw were used as biofilter media. Heavy metals concentrations in the wastewater and treated water were measured to determine the effect of activated carbon and rice straw on the removal efficiency of these heavy metals. The results showed that both activated carbon and rice straw had the best ability to remove copper (Cu) with a removal efficiency of 65.8 and 84.68%, respectively, and the lowest ability to remove lead (Pb) with a removal efficiency of 31.5 and 43.2%, respectively.

Whereas, removal efficiencies were 31.5, 44.7, 54.1, 47.8, 38.3, 0.0, 0,0 and 55.6 % for lead, iron, nickel, boron, cadmium, arsenic, tin and zinc, respectively, in the case of using activated carbon biofilter, and were 43.2, 69.3, 65.3, 56.52, 78.83, 0.0, 0.0, and 69.92 % for lead, iron, nickel, boron, cadmium, arsenic, tin and zinc, respectively, in the case of usage rice straw biofilter. unfortunately, no traces of both arsenic and tin were observed in the wastewater under study. The effect of pH on the ammonia removal efficiency was also determined. It was found that the best ammonia removal efficiency was obtained at a pH of 8.

Maximum removal efficiencies of ammonia were 84.6 % for activated carbon biofilter and 68 % for rice straw biofilter, whereas, ammonia elimination capacities were 0.704 mg/l. min (pH of 9) For AC biofilter and 0.57 mg/l. min (pH of 8) For RS biofilter.

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وسائط ترشيح حيوية جديدة لإزالة المعادن الثقيلة من مياه صرف المزارع السمكية

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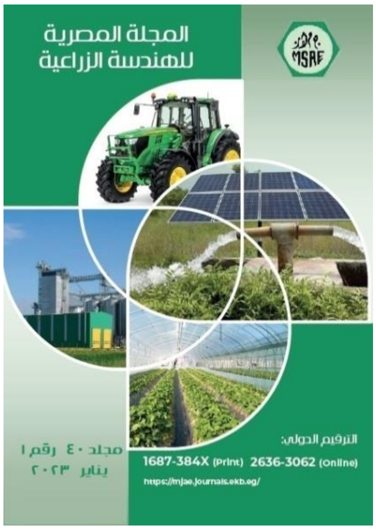

الكلمات المفتاحية:
تربية الأحياء المائية؛ المرشح البيولوجي؛ الكربون المُنشَطْ؛ قش الأرز؛ إزالة المعادن الثقيلة.

الملخص العربى

سيكون من الضروري توفير حوالي ٤٠ مليون طن إضافية من الأسماك بحلول عام ٢٠٣٠ من أجل الحفاظ على نصيب الفرد ثابتًا. تساهم الأسماك الناتجة من المزارع السمكية بحوالي ٥٠٪ من إجمالي إنتاج الأسماك حول العالم. أصبح من الشائع معالجة المياه الناتجة من المزارع السمكية بالطريقة البيولوجية، لأنها من أفضل الطرق مقارنة بالطريقة الفيزيائية والكيميائية. على الرغم من أن الأمونيا (NH_3) من أهم الملوثات التي تنتجها المزارع السمكية، إلا أن هناك العديد من المعادن الثقيلة التي لها تأثيرات سلبية على الأسماك والبيئة. في هذه التجربة تم تصميم وحدة معالجة مكونة من مرحلتين، مرحلة المرشح الميكانيكي كمرحلة معالجة أولية ثم المرشح البيولوجي كمرحلة معالجة اساسية. تم استخدام الحصى كوسط للمرشح الميكانيكي واستخدام الكربون المُنشَطْ (AC) وقش الأرز (RS) كوسائط للمرشح الحيوى. تمت دراسة تأثير الكربون المُنشَطْ وقش الأرز على إزالة المعادن الثقيلة من الماء. كما تم تحديد تأثير تغيير قيمة الرقم الهيدروجيني (pH) على إزالة الأمونيا. تم قياس تركيز الرصاص (Pb) والحديد (Fe) والنحاس (Cu) والنيكل (Ni) والبورون (B) والكادميوم (Cd) والزرنيخ (As) والقصدير (Sn) والزنك (Zn) للمياه العادمة والمياه التي تم معالجتها. أظهرت النتائج أن أفضل كفاءة للكربون المُنشَطْ وقش الأرز كانت لإزالة النحاس (Cu) بنسبة ٦٥,٨٠ و٨٤,٦٨٪ على التوالي، وأقل كفاءة كانت إزالة الرصاص (Pb) بنسبة ٣١,٥٠ و٤٣,٢٠٪ على التوالي. أفضل رقم هيدروجيني للكربون المُنشَطْ وقش الأرز كان ٨ بكفاءة إزالة للأمونيا ٨٥,٠٠ و٦٨,٠٠٪ على التوالي.