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Research Article

Assessment of Modified Rice Husk and Sawdust as Bio-adsorbent for Heavy Metals Removal Using Nano Particles in Fish Farm

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Abstract

Background and Objective: Improving water quality in fish farms is essential key factor for maintaining the fish health and its productivity. This study was designed to assess the quality of pond's water and the effectiveness of bio-adsorbent materials (sawdust and rice husk) and modify these materials using silver nanoparticles (AgNPs) to enhance the adsorption capacity for removal of lead, cadmium and improving physicochemical parameters in different water sources used in fish farm. **Materials and Methods:** A total number of 150 representative water samples were collected from five pond's water to assess hygienic water quality. The physicochemical parameters [pH, alkalinity (mg L^{-1}), electrical conductivity ($\mu\text{S cm}^{-1}$), ammonia (NH_3) (mg L^{-1}), nitrite (NO_2) (mg L^{-1}), nitrates (NO_3) (mg L^{-1}) and total hardness (mg L^{-1})] were determined before and after using bio-adsorbent materials and some heavy metals (Pb and Cd) in pond's water were determined using atomic absorption spectrometer. Bio-adsorbent materials and its modified forms were prepared using silver nanoparticles (AgNPs). The morphology and size of nano particles were characterized by transmission electron microscopy. Data were recorded using the Microsoft excel spreadsheet then prepared for analysis using one-way ANOVA and Duncan's multiple range testes at significance level $p < 0.05$. **Results:** Modified rice husk was significantly effective on the mean values of alkalinity, ammonia, nitrite, total hardness, heavy metals as Pb and Cd at $p < 0.01$ in fish pond of agriculture wastewater as compared to modified sawdust. Furthermore, the effectiveness of modified rice husk on the same water quality parameters in freshwater ponds was significantly high as compared to rice husk and sawdust. **Conclusion:** Using modified rice husk has higher adsorption capacity than modified sawdust in removal of heavy metal contaminants (Pb and Cd) from both freshwater and agriculture wastewater source and helping in improving of water quality parameters in examined fish farm.

Key words: Modified bio-adsorbent, agriculture waste, fish farms, silver nano particles, water quality parameters

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

The health of fish and its productivity is directly influenced by water quality¹ where quality of water is essential aspect in sustaining the fish life along with all the other organisms in the aquatic environment² in addition to there is various physicochemical and biological factors in water may directly or indirectly affect its quality and consequently its suitability for the distribution and fish production³.

In Egypt, heavy metals contaminant represents a serious problem in the aquatic environments⁴. It has drawn particular attentions due to their toxicity, persistence, biological accumulation and the most anthropogenic sources of metals are sewage disposal, industrial and petroleum contamination⁵. Heavy metals can simply enter the food chain thus controlling the toxic heavy metals concentrations in the aquatic environments is necessary to avoid progressive poisonous effects with gradual accumulation in living organisms over their life span⁶.

In recent years, by products of agricultural waste materials are used as bio-adsorbent for removal of heavy metal from aqueous solutions such as orange peel, leaf, wheat shell, rice husk and sawdust of various plants^{7,8}. There is no doubt that effective use of biomass wastes materials became a future promising for treatment of heavy metals due to their nature of environmentally friendly, more economic, more efficient and the low cost⁹.

Rice husk consists of large amounts of hemicelluloses, cellulose and lignin. These compounds can provide binding sites for heavy metals¹⁰. Some studies proved that using the modified rice husk for heavy metal removal such as Cu and Pb from aqueous solutions is a useful material. As well as its adsorption capacity makes it a very attractive alternative adsorption material¹¹. Meanwhile, other studies clarified that sawdust is a promising effective material for heavy metals removal^{12,13}. Furthermore, Fayemiwo *et al.*¹⁴ found that sawdust adsorbent is highly efficient for heavy metals removal as compared to rice husk.

At recent days, with the rapid development of nanotechnology, it has become possible to fabricate, characterize and specially tailor the functional properties of nano particles for different applications¹⁵. No doubt that the application of nanoparticles became widespread in various field and it posed new challenges to synthesis of new composite for controlling of metal contaminants¹⁶. The current study aimed to assess the hygienic quality of pond's water and the effectiveness of bio-adsorbent materials (sawdust and rice husk) and its modified forms using silver nanoparticles (AgNPs) before and after water treatment. With a view to enhance their adsorption capacity for removal of

lead and cadmium ions then improving the physicochemical parameter of water in different water sources used in examined fish farm.

MATERIALS AND METHODS

Study site and period: This study was conducted on a private fish farm located in Beni-Suef district (coordinates: 29°04'N31°05'E), Egypt throughout a period from July, 2016 until August, 2017. Fish farm contains four earthen ponds with average size of 180×52 ms and depth 1.6 m. Fish fed on commercial pellet ration contains 25% protein and pyrogens as feed additives for improving its productivity. Pond water was exchanging twice/month. Two water sources of different qualities were used, freshwater and agriculture wastewater whereas *Tilapia niloticus* was the only species cultured.

Study design: A cross sectional study was carried out to assess hygienic quality of pond's water in fish farm and investigate the effectiveness of sawdust and rice husk as a bio-adsorbent materials and its modified forms using silver nanoparticles (AgNPs) to enhance the adsorption capacity for Pb and Cd ions from pond's water, improve water quality parameters and observe the morphology and size of synthesized nanoparticle. Water samples were collected and examined for physicochemical parameters and heavy metals (Pb and Cd) before and after using of bio-adsorbent materials and its modified forms. The AgNPs was synthesized by chemical reduction method. The morphology and nanoparticles size of AgNPs were clarified by transmission electron microscopy (TEM).

Water sampling: About 150 representative water samples were collected weekly from five pond's water in sterile glass bottles of 1 L capacity from each pond, with three sampling points included pond inlet, outlet besides pond center. During sampling, the containers were rinsed three times with water sample before filling. After collection, water samples were transported in a cool box containing ice packs to the laboratory for physicochemical and heavy metals analyses. All samples were stored at 4°C and analyzed within 48 h of samples collection¹⁷. The physicochemical parameters such as pH, alkalinity (mg L⁻¹), electrical conductivity (µS cm⁻¹), ammonia (NH₃-N), nitrite (NO₂-N), nitrates (NO₃-N) (mg L⁻¹), total hardness (mg L⁻¹) were measured. Meanwhile, some heavy metals concentration as lead (pb) and cadmium (Cd) were determined using atomic absorption spectrometer (AAS) (Thermo electron Ltd., Solar House Cambridge, United Kingdom, Solar, M., 6A.A.Spectrometer) according to AOAC¹⁸.

Analyses of physicochemical parameters: Water quality parameters as pH of the pond's water were determined *in situ*, using pH meter (Model Digital pH meter 335). Calibration of the apparatus was done according to the instruction of the manufacturer. Electrical conductivity of water was measured with the help of conductivity meter (Model Inolab Cond 720). Meanwhile, alkalinity (CaCO_3) values are measured using the colorimetric method, reagent kit (HI93755-01). Ammonia ($\text{NH}_3\text{-N}$ MR) was measured using Nessler method, reagent kit (HI93715-01). Nitrite ($\text{NO}_2\text{-HR}$) was measured using ferrous sulphate method, reagent kit (HI93708-01). Nitrates ($\text{NO}_3\text{-N}$) were measured using cadmium reduction method, reagent kit (HI93728-01) and results are displayed in mg L^{-1} on the instruments screen. Total hardness in water samples was measured using calm augite method, reagent kit (HI93720-01), EDTA method, reagent kit (HI93719-01) using HI-83200Hanna® Instruments (multi parameter photometer).

Assessment of rice husk, sawdust and its modified forms:

The effectiveness of both rice husk and sawdust as a bio-adsorbent of agriculture waste materials were evaluated in an experimental trial to investigate its role for removal of each Pb and Cd from pond's water and improving pond's water quality in fish farm then trying to enhance the bio-adsorbent capacity of these materials using silver nanoparticles (AgNPs). Water quality parameters and heavy metals were analyzed before and after using the bio-adsorbent materials and its modified forms.

Method of preparation of rice husk and sawdust: Rice husk were collected from agricultural areas (Delta district, Egypt) while sawdust was obtained from a carpenter working shop (Beni-Suef district, Egypt). *In vitro*, the bio-adsorbent materials were washed with distilled water, cut into small pieces then dried in hot air oven at 80°C for 72 h and finally were grinded to suitable size. Sixty milliliters of water samples were mixed with definite amount of the bio-adsorbents (1.5 g of sawdust while 4 g of rice husk). The mixture was shaken on a reciprocating shaker at 225 rpm then the solution was left for 20 min. Fifty milliliters of the mixture was gently digested with 3 mL HNO_3 and 2 mL HCL then the mixture heated and filtrated, after that the filtrate was analyzed for water physicochemical parameters and heavy metals (Pb and Cd) as a method described by Fayemiwo *et al.*¹⁴ with some modification in the temperature and time of dried in oven.

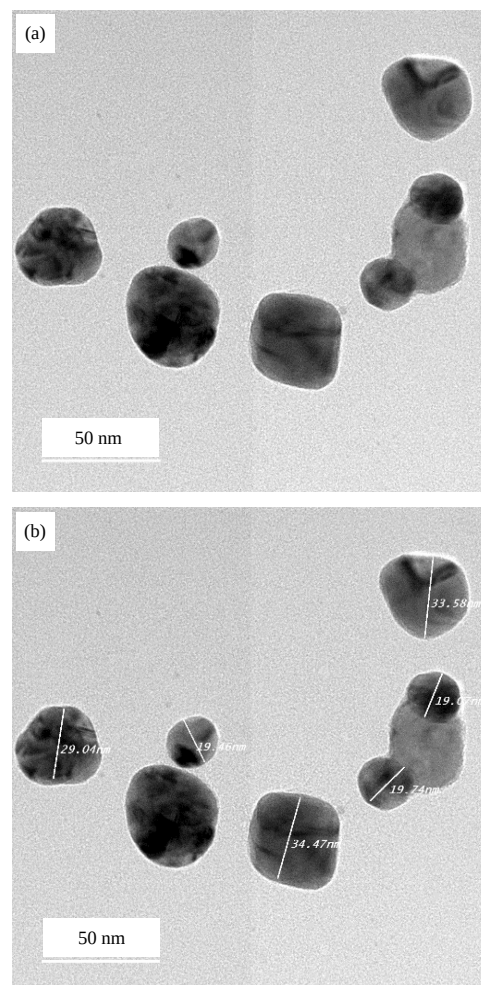


Fig. 1(a-b): Transmission electron microscope (TEM) image of silver nanoparticles (AgNPs), (a-b) TEM photographs, clarified the morphology and internal diameter of the singly silver nano particle (NP) is ranged between 19.07-34.47 nm

Preparation of its modified forms: For modified bio-adsorbents, silver nanoparticles was prepared using chemical reduction method as described by Sileikaite *et al.*¹⁹. All step of sawdust and rice husk preparation are repeated as before. About 100 mg L^{-1} of prepared silver nanoparticles was added to 50 mL of both sawdust and rice husk filtrates then putting them on high speed shaker for 2 h to avoid settle down of nano particles after that the composites were added to different pond's water samples for water quality parameters and heavy metals analysis. The morphology and size of AgNPs were clarified by TEM in National Research Center (NRC), Egypt. The TEM photographs showed that the diameter of silver nano particle is ranged between (19.07-34.47 nm) as shown in (Fig. 1).

Statistical analysis: Data were recorded using the Microsoft excel spreadsheet then prepared for analysis using one-way ANOVA and Duncan's multiple range tests. The statistical analyses were calculated, using Statistical Package for Social Sciences (SPSS) software (version 22.0 for Windows, SPSS Inc., Chicago, IL.). The data values were expressed as mean concentration $\pm$ standard error (SE). The accepted significance level was $p < 0.05$.

RESULTS AND DISCUSSION

Water quality parameters in different pond's water: The present data revealed that pH values in different pond's water showed no significant changes in the four studied fish ponds either before or after water treatment and its value was within the permissible levels (Table 1-4). Meanwhile, it was observed that the agriculture wastewater ponds exhibited a significant increase in most values of physicochemical parameters including alkalinity, ammonia, nitrite and total hardness at $p < 0.01$ when compared with acceptable limits of WHO²⁰ and these physicochemical parameters values were gradually decreased after water treatment with rice husk or that treated with AgNPs loaded rice husk in Table 1 as compared to sawdust and AgNPs loaded sawdust. On the other hand, in freshwater ponds that treated with AgNPs loaded rice husk showed a significant decrease in the values of physicochemical parameters as alkalinity, ammonia, nitrite and total hardness at $p < 0.01$ in (Table 2) as well as in Table 3 and 4 whereas, those water quality parameters became within recommended guide line standard as compared to pond's water before any treatment, water that treated with sawdust and AgNPs loaded sawdust.

Using modified bio-adsorbent materials for removal of heavy metals from pond's water: Results in Table 4 clarified that the estimated heavy metals (lead and cadmium) in the different pond's water were found in higher concentration than the prescribed permissible limits of WHO²⁰ in Table 5. Meanwhile, after using of rice husk and its modified form (AgNPs loaded rice husk) in water treatment, it has been found that significant decrease in concentrations of both lead and cadmium at $p < 0.05$ in pond's water 2, 3 and 4 which became within the acceptable level as compared to water before treatment and sawdust use. From the obtained data the highest efficient methods for water treatment in fish ponds to improve both physicochemical parameters and heavy metals concentration were AgNPs loaded rice-husk > rice-husk > AgNPs loaded sawdust > sawdust.

Effectiveness of modified bio-adsorbents on water quality parameters in fish ponds:

In the current study, using of bio-adsorbent materials (modified rice husk and sawdust) for improving water quality parameters and removal of heavy metal contaminants were proved their effectiveness on the hygienic quality of pond's water from different water sources used in examined fish farm. Thus the recent research studies towards to using bio-adsorbent materials of byproduct of agriculture waste. Those materials are environmentally friends and the low cost alternatives to commercially available materials. In this study, the physicochemical parameters of different pond's water in fish farms were estimated to evaluate its hygienic quality before and after using bio-adsorbent materials and its modified forms. Moreover, in agriculture wastewater pond (Table 1) the mean values of different parameters as alkalinity, ammonia, nitrite and total hardness were significantly exceeded the permissible limits, while pH and electrical conductivity values were within acceptable limit standard of WHO²⁰. These results agreed with Kumar *et al.*²¹, who recorded that pH value ranged from 7.1-8.0 in fish pond. This value was within the values for optimum fish survival²². Regarding, the values of alkalinity in examined fish pond was exceeding the permissible limit (100 mg L^{-1}). Whereas, Krishnan *et al.*²³ clarified that variation in the water alkalinity is due to the presence of some salts as bicarbonate, carbonate and hydroxide of calcium, sodium and potassium. On the other hand, total hardness value in pond water was exceeded 300 mg L^{-1} and there were correlated with high alkalinity values. Bhatnagar *et al.*²⁴ found that the total hardness values higher than 200 mg L^{-1} would cause stress. Furthermore, an optimum value of $75\text{-}150 \text{ mg L}^{-1}$ with a lethal value of $>300 \text{ mg L}^{-1}$ ²⁵. The highest level of ammonia and nitrite in water pond 1 might be attributed to presence of contaminant with fecal matter as well as the intensive use of nitrogenous fertilizers contain (ammonia, urea and nitrate) in agriculture land at the study area.

Concerning, the freshwater ponds in the examined fish farm, the estimated physicochemical parameters exhibited that there are obvious effect of bio-adsorbent materials and its modified forms on water quality parameters in Table 2-4, where the mean values of alkalinity, ammonia, nitrite, nitrate and total hardness were significantly decreased and became within the recommended guideline of WHO²⁰ specially after using AgNPs loaded rice husk as compared to rice husk, sawdust and AgNPs loaded sawdust. Chuah *et al.*²⁶ recorded that rice husk contains about 20% silica, in addition to cellulose, hemicelluloses and lignin which makes it a good adsorbent material for water treatment. In current study,

Table 1: Mean values of physicochemical parameters ($\pm$ SE) in examined fish pond 1

Water source		After using of bio adsorbent materials				
Agriculture wastewater	Water parameters	Before	Sawdust	Rice husk	AgNPs loaded sawdust	AgNPs loaded rice husk
	pH	7.80 $\pm$ 0.25	7.60 $\pm$ 0.10	7.58 $\pm$ 0.08	7.86 $\pm$ 0.27	7.71 $\pm$ 0.25
	Alkalinity (mg L ⁻¹)	411.20 $\pm$ 24.5 ^a	315.00 $\pm$ 20.89 ^a	282.80 $\pm$ 19.24 ^{ab}	292.80 $\pm$ 28.63 ^a	220.00 $\pm$ 33.29 ^b
	Electrical conductivity (μ S cm ⁻¹)	989.76 $\pm$ 14.59 ^a	985.76 $\pm$ 17.42 ^a	979.12 $\pm$ 11.64 ^b	982.28 $\pm$ 13.33 ^a	976.60 $\pm$ 11.77 ^b
	Ammonia (mg L ⁻¹)	2.50 $\pm$ 0.01 ^a	2.23 $\pm$ 0.01	2.31 $\pm$ 0.04	2.26 $\pm$ 0.06	0.51 $\pm$ 0.08 ^b
	Nitrite (NO ₂) (mg L ⁻¹)	1.01 $\pm$ 0.01 ^a	1.02 $\pm$ 0.01	0.76 $\pm$ 0.01 ^b	1.11 $\pm$ 0.01	0.54 $\pm$ 0.0 ^b
	Nitrate (NO ₃) (mg L ⁻¹)	28.65 $\pm$ 0.0	32.50 $\pm$ 0.0	29.60 $\pm$ 0.0	30.10 $\pm$ 0.0	28.56 $\pm$ 0.0
	Total hardness (mg L ⁻¹)	375.60 $\pm$ 19.15 ^a	375.80 $\pm$ 17.66 ^a	285.20 $\pm$ 11.18 ^{ab}	367.80 $\pm$ 23.73 ^a	273.00 $\pm$ 20.19 ^c

^{a,b,c}Within the same row, proportions with different superscript letters differ significantly at p<0.01, Acceptable limit of parameters, pH: 6.0-9.0, Alkalinity: 100 mg L⁻¹, Electrical conductivity: 2000 μ S cm⁻¹, Ammonia: 0.05 mg L⁻¹, Nitrite: 0.02 mg L⁻¹, Nitrate: 0-45 mg L⁻¹ and Total hardness: 75-150 mg L⁻¹, WHO²⁰

Table 2: Mean values of physicochemical parameters ($\pm$ SE) in examined fish pond 2

Water source		After using of bio adsorbent materials				
Freshwater	Water parameters	Before	Sawdust	Rice husk	AgNPs loaded sawdust	AgNPs loaded rice husk
	pH	7.60 $\pm$ 0.18	7.80 $\pm$ 0.13	7.50 $\pm$ 0.05	7.80 $\pm$ 0.20	7.60 $\pm$ 0.21
	Alkalinity (mg L ⁻¹)	308.20 $\pm$ 24.5 ^a	251.00 $\pm$ 8.19 ^b	200.40 $\pm$ 11.21 ^{ab}	212.80 $\pm$ 14.23 ^b	105.00 $\pm$ 13.10 ^c
	Electrical conductivity (μ S cm ⁻¹)	1008.26 $\pm$ 10.59 ^a	1005.76 $\pm$ 15.42 ^a	989.11 $\pm$ 14.31 ^b	1007.28 $\pm$ 13.33 ^a	987.40 $\pm$ 8.37 ^b
	Ammonia (NH ₃) (mg L ⁻¹)	0.52 $\pm$ 0.02 ^a	0.32 $\pm$ 0.01	0.21 $\pm$ 0.04 ^b	0.24 $\pm$ 0.03	0.05 $\pm$ 0.03 ^{ab}
	Nitrite (NO ₂) (mg L ⁻¹)	1.53 $\pm$ 0.02 ^a	1.02 $\pm$ 0.01	0.90 $\pm$ 0.03	0.98 $\pm$ 0.01	0.34 $\pm$ 0.0 ^b
	Nitrate (NO ₃) (mg L ⁻¹)	15.32 $\pm$ 0.0	15.45 $\pm$ 0.2	14.38 $\pm$ 0.0	15.11 $\pm$ 0.04	14.76 $\pm$ 0.01
	Total hardness (mg L ⁻¹)	335.60 $\pm$ 11.13 ^a	235.80 $\pm$ 16.51 ^b	205.20 $\pm$ 10.14 ^{ab}	227.80 $\pm$ 13.32 ^b	200.00 $\pm$ 12.17 ^c

^{a,b,c}Within the same row, proportions with different superscript letters differ significantly at p<0.01, Acceptable limit of parameters, pH: 6.0-9.0, Alkalinity: 100 mg L⁻¹, Electrical conductivity: 2000 μ S cm⁻¹, Ammonia: 0.05 mg L⁻¹, Nitrite: 0.02 mg L⁻¹, Nitrate: 0-45 mg L⁻¹ and Total hardness: 75-150 mg L⁻¹, WHO²⁰

Table 3: Mean values of physicochemical parameters ($\pm$ SE) in examined fish pond 3

Water source		After using of bio adsorbent materials				
Freshwater	Water parameters	Before	Sawdust	Rice husk	AgNPs loaded sawdust	AgNPs loaded rice husk
	pH	8.60 $\pm$ 0.31	8.30 $\pm$ 0.16	7.90 $\pm$ 0.27	8.50 $\pm$ 0.92	8.60 $\pm$ 0.11
	Alkalinity (mg L ⁻¹)	220.20 $\pm$ 18.5 ^a	205.00 $\pm$ 11.15 ^b	150.40 $\pm$ 21.11 ^{ab}	172.30 $\pm$ 10.21 ^b	110.00 $\pm$ 12.11 ^c
	Electrical conductivity (μ S cm ⁻¹)	1075.23 $\pm$ 12.34	1075.16 $\pm$ 13.12	1073.11 $\pm$ 14.31	1071.14 $\pm$ 11.23	1071.40 $\pm$ 8.37
	Ammonia (NH ₃) (mg L ⁻¹)	0.92 $\pm$ 0.01 ^a	0.62 $\pm$ 0.03	0.31 $\pm$ 0.01 ^b	0.36 $\pm$ 0.02	0.06 $\pm$ 0.0 ^{ab}
	Nitrite (NO ₂) (mg L ⁻¹)	1.21 $\pm$ 0.02 ^a	0.91 $\pm$ 0.01	0.50 $\pm$ 0.03	0.61 $\pm$ 0.02	0.04 $\pm$ 0.0 ^b
	Nitrate (NO ₃) (mg L ⁻¹)	0.00 $\pm$ 0.0	0.00 $\pm$ 0.0	0.00 $\pm$ 0.0	0.00 $\pm$ 0.0	0.00 $\pm$ 0.0
	Total hardness (mg L ⁻¹)	250.40 $\pm$ 17.10 ^a	200.60 $\pm$ 13.11 ^a	165.20 $\pm$ 11.15 ^{ab}	185.80 $\pm$ 16.12 ^a	151.00 $\pm$ 10.12 ^c

^{a,b,c}Within the same row, proportions with different superscript letters differ significantly at p<0.01, Acceptable limit of parameters, pH: 6.0-9.0, Alkalinity: 100 mg L⁻¹, Electrical conductivity: 2000 μ S cm⁻¹, Ammonia: 0.05 mg L⁻¹, Nitrite: 0.02 mg L⁻¹, Nitrate: 0-45 mg L⁻¹ and Total hardness: 75-150 mg L⁻¹, WHO²⁰

Table 4: Mean values of physicochemical parameters ($\pm$ SE) in examined fish pond 4

After using of bio adsorbent materials						
Water source	Water parameters	Before	Sawdust	Rice husk	AgNPs loaded sawdust	AgNPs loaded rice husk
Freshwater	pH	8.60 $\pm$ 0.31	8.30 $\pm$ 0.16	7.90 $\pm$ 0.27	8.50 $\pm$ 0.92	8.60 $\pm$ 0.11
	Alkalinity (mg L ⁻¹)	135.40 $\pm$ 13.5 ^a	128.20 $\pm$ 12.10	105.30 $\pm$ 11.14 ^{ab}	110.50 $\pm$ 10.21 ^b	100.00 $\pm$ 10.01 ^c
	Electrical conductivity (μ S cm ⁻¹)	982.21 $\pm$ 10.23	987.10 $\pm$ 13.12	985.01 $\pm$ 12.31	986.15 $\pm$ 17.40	983.12 $\pm$ 16.33
	Ammonia (NH ₃) (mg L ⁻¹)	0.62 $\pm$ 0.01 ^a	0.51 $\pm$ 0.01	0.31 $\pm$ 0.01	0.33 $\pm$ 0.03	0.06 $\pm$ 0.0 ^b
	Nitrite (NO ₂) (mg L ⁻¹)	1.61 $\pm$ 0.02 ^a	0.86 $\pm$ 0.01 ^a	0.50 $\pm$ 0.02 ^b	0.41 $\pm$ 0.04 ^b	0.03 $\pm$ 0.0 ^b
	Nitrate (NO ₃) (mg L ⁻¹)	15.00 $\pm$ 0.03	15.5 $\pm$ 0.04	14.6 $\pm$ 0.0	15.00 $\pm$ 0.01	13.80 $\pm$ 0.01
	Total hardness (mg L ⁻¹)	216.40 $\pm$ 12.10 ^a	216.50 $\pm$ 10.21 ^a	178.2 $\pm$ 10.13 ^a	191.80 $\pm$ 11.02 ^a	156.00 $\pm$ 11.15 ^b

^{a,b,c}Within the same row, proportions with different superscript letters differ significantly at $p < 0.05$, Acceptable limit of parameters, pH: 6.0-9.0, Alkalinity: 100 mg L⁻¹, Electrical conductivity: 2000 μ S cm⁻¹, Ammonia: 0.05 mg L⁻¹, Nitrite: 0.02 mg L⁻¹, Nitrate: 0-45 mg L⁻¹ and Total hardness: 75-150 mg L⁻¹, WHO²⁰

Table 5: Mean values of heavy metals ($\pm$ SE) estimated in different examined fish ponds

After using of bio adsorbent materials						
Examined pond	Bio adsorbent material	Before	Sawdust	Rice husk	AgNPs loaded sawdust	AgNPs loaded rice husk
Pond 1	Cd	0.070 $\pm$ 0.02 ^a	0.04 $\pm$ 0.01 ^a	0.020 $\pm$ 0.03	0.003 $\pm$ 0.07	0.001 $\pm$ 0.0 ^{ab}
	Pb	0.086 $\pm$ 0.04 ^a	0.071 $\pm$ 0.02	0.041 $\pm$ 0.01 ^b	0.050 $\pm$ 0.03	0.020 $\pm$ 0.05 ^{ab}
Pond 2	Cd	0.093 $\pm$ 0.05 ^a	0.091 $\pm$ 0.14 ^a	0.003 $\pm$ 0.08 ^b	0.006 $\pm$ 0.11 ^b	0.002 $\pm$ 0.230 ^{ab}
	Pb	0.032 $\pm$ 0.11 ^a	0.030 $\pm$ 0.31	0.027 $\pm$ 0.23	0.025 $\pm$ 0.12	0.011 $\pm$ 0.0 ^b
Pond 3	Cd	0.005 $\pm$ 0.11 ^a	0.005 $\pm$ 0.08 ^a	0.002 $\pm$ 0.05 ^b	0.003 $\pm$ 0.12 ^b	0.001 $\pm$ 0.0 ^{ab}
	Pb	0.022 $\pm$ 0.03 ^a	0.021 $\pm$ 0.05	0.017 $\pm$ 0.01 ^b	0.019 $\pm$ 0.20	0.010 $\pm$ 0.1 ^{ab}
Pond 4	Cd	0.003 $\pm$ 0.01 ^a	0.003 $\pm$ 0.1	0.002 $\pm$ 0.0 ^b	0.002 $\pm$ 0.03	0.000 $\pm$ 0.0 ^{ab}
	Pb	0.039 $\pm$ 0.12 ^a	0.037 $\pm$ 0.23	0.032 $\pm$ 0.10	0.027 $\pm$ 0.13 ^b	0.015 $\pm$ 0.16 ^{ab}

^{a,b}Within the same row, proportions with different superscript letters differ significantly at $p < 0.05$, Acceptable limit of heavy metals, Cd: 0.003 mg L⁻¹, Pb: 0.01 mg L⁻¹, WHO²⁰

AgNPs loaded rice husk was the most effective bio-adsorbent material for improving of both physico-chemical parameters and heavy metals concentration in water compared to AgNPs loaded sawdust > sawdust. Seo *et al.*²⁷ and Padervand *et al.*²⁸ pointed to silver nanoparticles (AgNPs) have been widely used as adsorbent either as it is or doped with other adsorbing materials to prepare a more effective adsorbent for the removal of various pollutants.

Heavy metals estimation and bio-adsorbent capacity of modified used materials:

Removal of the poisonous lead and cadmium ions from pond's water was possible using modified rice husk and sawdust as bio-adsorbent materials. The present data revealed that the estimated values of lead and cadmium ions in agriculture wastewater (pond 1) and freshwater ponds (2, 3 and 4) before treatment were significantly exceeded the permissible limits as compared to after treatment using rice husk and its modified form followed by AgNPs loaded sawdust. Furthermore, water samples treated with AgNPs loaded rice husk showed a significant decrease in concentrations of both lead and cadmium which became within the acceptable limits. These results are agreed with Chockalingam and Subramaniam²⁹, who confirmed that the utility of rice husk as a good metal adsorbent for many toxic and heavy metal ions removal from agriculture and industrial waste effluents. Abdel-Ghani *et al.*³⁰ showed that used different low-cost adsorbents such as rice husks, sawdust and maize cobs in the removal of lead (Pb) from wastewater. Moreover, AgNPs as specific adsorbents for heavy metals in wastewater and amended environmental quality. Nonetheless, these nanoparticles generally exist as one or ultrafine particles³¹. The most crucial element in the removal of pollutants using adsorption approach would be to find the most suitable adsorbent. It should significantly remove various types of pollutants from a contaminated water system, economical, efficient and easily available. On contrast, Ghaedi *et al.*³² clarified that using of silver nanoparticles and zinc oxide nanorods loaded on activated carbon (Ag-NP-AC and ZnO-NR-AC) were effective in the removal of lead and cadmium from fish pond's water.

CONCLUSION

From the comparative statistical analysis, it has been concluded that the effectiveness of modified rice husk using AgNPs was obvious on water quality parameters and heavy metal contaminants removal in fish ponds whereas the mean

values of alkalinity, ammonia, nitrite, total hardness, lead (Pb) and cadmium (Cd) were closed to permissible limits in both water qualities, agriculture wastewater and freshwater ponds followed by rice husk as compared to sawdust and its modified form. The AgNPs participate in furthermore, it is recommended to compare adsorption system utilizing sawdust and rice husk under different conditions and their economic justification. This study found that locally available modified materials represent an effective and environmentally clean utilization of waste matter. Further studies on using of AgNPs as adsorbent material in pond's water are essential for improving the ecosystem in fish farms.

SIGNIFICANCE STATEMENT

This study discovered the low cost bio-adsorbent materials such as sawdust and rice husk and its modified forms using silver nanoparticles can be beneficial for heavy metal removal in pond's water and helping for improving of water quality in fish farms. Furthermore, silver nanoparticles which loaded on bio-adsorbent materials led to enhancement the bio-adsorbent capacity of used materials. This study help the researchers to uncover the critical areas of using nanotechnology for improving water quality parameters and contaminants removal in fish farms in addition to maintaining the fish health and its productivity that many researchers were not able to explore. Thus a new theory on those bio-adsorbent materials and possibility to modify it may be arrived at.

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