

Assessing the loading capacity of walnut peels as a nanobiomass for the biosorption of certain heavy metals from wastewater

Sarah Adnan Khalaf¹, Sufyan Mohammed Shartoo^{2*} , Mayada Abdullah Shihan³

¹ Biology Department, College of Science, University of Anbar, Ar-Ramadi, Iraq

* Corresponding author's e-mail: dralwaisi@uoanbar.edu.iq

ABSTRACT

Bio-removal of heavy metal pollution remains a major challenge in environmental biotechnology. This paper focuses on the potential of carbon nanoparticles for biosorption of zinc, copper, and cadmium ions from aqueous solutions, employing economical and environmentally sound plant wastes. Walnut peels were washed by distilled water, mixed with KOH, burned at 650 °C, and treated ultrasonically to obtain carbon nanoparticles. Standard solutions of the heavy metals under study were prepared based on calculations of the molecular weights of the relevant metal salts Zn, Cu, and Cd, the metal ions were estimated in both treated and wastewater sample. The experiment included evaluating the effect of some environmental factors on the process of biosorption of heavy metals from wastewater to choose the optimal conditions for the adsorption process. These environmental factors included the initial metal concentration, pH, temperature, retention time, and biomass. The optimum conditions of initial metal concentration, pH, temperature, retention time, and biomass were recorded as 100 mg/l, pH of 7, 45 °C., 60 min., 0.2 g respectively. These results were supported by XRD examination, which indicated the presence of two Bragg diffraction peaks in the carbon nanoparticles, and TEM results also indicated the presence of inhomogeneous particles, as well as the irregular shape of the surface of the carbon nanoparticles with a large surface area, according to SEM examination. However, the optimal adsorption conditions were applied in a laboratory treatment unit, which showed its efficiency in removing heavy metal ions from wastewater. Carbon nanoparticles derived from walnut shells can be employed as excellent adsorbents for removing heavy metal ions from aqueous solutions.

Keywords: heavy metals, walnut, biosorption, SEM, XRD.

INTRODUCTION

Water is considered as the most essential source of life and important part of our natural resources, around 80% of the world population is now facing water supply and security threat. In fact, about 2% of planet water is fresh and only 0.036% of water is accessible for use [1]. Waste water pollution with heavy metals is accelerating worldwide due to industrial and population growth, notably in countries having poor environmental laws, resulting in many diseases such as cancer [2, 3]. However, heavy metals which had a density above 5 g/cm³ – in wastewater come from industries and municipal sewage, and they are one of the main causes of water and soil pollution [4, 5]. Accumulation of these metals in wastewater depends on many local factors such

as type of industries in the region, people's way of life and awareness of the impacts done to the environment by careless disposal of wastes without treatment [6] metals can be divided into four major categories: Toxic heavy metals, strategic metals, precious metals, and radionuclides [7]. These contaminants include rare earth elements, arsenic, lead, cadmium, chromium, copper and other related effluents from the electronic, textile, agricultural, hospital wastes and pharmaceutical industries [8–10]. Biosorption has been suggested as being cheaper and more effective than chemical (precipitation) or physical (ion exchange and membrane) technologies [11, 12]. Biosorption involves the use of biological materials that form complexes with metal ions using their ligands or functional groups [13–15]. The advantage of biosorption is that growth-independent, non-living

biomass is to toxicity limitation of cells. No requirement of costly nutrients required for the growth of cells in feed solutions [16]. Therefore, the problems of disposal of surplus nutrients or metabolic products are not present also [17]. Because of non-living biomass behave as an ion exchanger; the process is very rapid and takes place between few minutes to few hours, since metal loading on biomass is often very high, leading to very efficient metal uptake [18]. Yet, a review is presented of the literature data concerning the effects induced by carbon nanoparticles on the biological environment and the importance of these effects in human and animal health. Using of walnut peel to prepare carbon has great potential for the preparation of composites because of its unique laminar structure and surface characteristics, wide availability, cost effectiveness and simple synthetic procedure [19]. In addition, it may be easily dispersed in water or other polar solvents because of its good hydrophilic characteristics [20]. Nevertheless, carbon nano-particles (CNPs) used for removal of heavy metals from industrial wastewater leads to the biggest challenge nowadays [19]. To reduce environmental problems, the CNPs are promising candidates for the adsorption of heavy metals due to their unique properties such as chemical stability, mechanical and thermal stability, and the high surface area, which leads to various applications including hydrogen storage, protein purification and water treatment [6, 21, 22]. The aim of the study is to examining the ability of carbon nano particles that prepared using walnut peel in the biosorption of pollutant from industrial wastewater.

MATERIALS AND METHODS

Prepared of carbon nano-particles CNPs from walnut peel

Walnut peel which collected from local market were mixed with KOH in a ratio of 1:1.5 (w/w), then heated at 600 °C for two hours, the formed material (carbon) was washed with distilled water to remove the residues of KOH, metallic components, and contaminants until and pH was adjusted to 7, next dried at 50 °C using the oven for 6 hrs. then the formed carbon that produced treated ultrasonically by ultra sonic device at 20 kh for 1 hour [23], as it seen in Figure 1.

Preparing of standard solutions

Heavy metal ion standard solutions were prepared depending on molecular weight calculations by dissolving 2.2 g of Zn (NO₃) for Zn standard solution, 3.218 g of Cd(NO₃)₂·4H₂O for Cd standard solution, and 0.77 g of Cu (NO₃) for Cu standard solution, all in 500 ml of deionized distilled water DDW and pH was adjusted to 7.

Evaluating the effect of environmental factors on biosorption

Initial concentration, pH, retention time, temperature, and biomass were examined as biosorption potential environmental factors. Further biosorption techniques required such tests to determine the best conditions. Such tests were performed in order to identify the optimum conditions for the later processes of biosorption. In all these experiments the



Figure 1. Walnut peels (A) that mixed with KOH to prepare CNPs (B)

white tubes which contain the heavy metal solution mixed with walnut peel powder were incubated in shaker incubator then filtrate with filter paper in a size of 0.45 μm , and determined the residual concentration of Cu, Zn, and Cd metals in supernatant, where pH was adjusted To7 [24].

Effect of initial concentration of metal ions on biosorption

The ideal starting concentration of the heavy metal solution was determined using seven values: 10, 20, 30, 50, 75, 100, and 250 mg/L, with the pH set to 7. At a starting dose of 100 mg/L, five different pH values (4, 5, 6, 7, and 8) were used to evaluate the effect of pH on biosorption. In order to determine the effect of contact duration, the study used six different retention durations (1, 5, 15, 30, 60, and 120 minutes) with an initial concentration of 100 mg/L and a pH of 7. A range of weights was used to evaluate the effect of bio-sorbent mass: 0.01, 0.025, 0.05, 0.1, and 0.2 mg. In addition, 25, 35, 45, and 55 $^{\circ}\text{C}$ were the five temperature values used for each metal ion to find the ideal temperature [25].

X-ray diffraction (XRD)

The idea behind this technique is that materials will scatter and absorb any radiation that is directed on. The scattered radiation can be used to identify materials based on the diffraction pattern of their crystalline or ordered structure using XRD analyzer (Panalytical 'X' Pert Pr, UK)[26].

Scanning electron microscopy

Scanning electron microscopy (SEM) (Zeiss Sigma VP/Germany) was used as a crucial tool for the development of nanotechnology and the characterization of materials with nanostructure, which is among the most adaptable tools for examining and analyzing the morphology and chemical composition of microstructures that is currently accessible [27].

Transmission electron microscope

Transmission electron microscopy (TEM) has been widely applied to characterize morphology, crystalline structure, and elemental information of membrane materials using Zeiss LEO 912 AB/Germany TEM [28].

Biosorption laboratory treatment unit

Continuous biosorption experiments were carried out using jacketed Pyrex column reactor packed with CNPs biomass (Figure 2). The inner diameter, height and bed volume of column were 1.2 cm, 27 cm and 30.5 ml, respectively. The column was equilibrated with 10 bed volumes and effluent pH was monitored to ensure that the column was continuously at the optimal pH of 7. A flow rate of 2 ml per minute was used to pass the biomass via Zn, Cu and Cd ions which were pumped downward through the column packed with biomass. Effluent liquid overflowed from an outlet port at the end of the bioreactor, maintaining a constant level inside the column. The temperature of the system was maintained at 45 $^{\circ}\text{C}$ by circulating constant temperature water from a circulator bath through the biomass column. The contact time of metal ions through the column was 60 min. this experiment was continued until a constant Zn, Cu and Cd ion concentration was obtained. After applying the optimum conditions on the column by inter sample of Euphrates water within the column, the percentage of removal of Zn, Cd and Cu was 100%.

Calculations

The following equations were used to calculate the biosorption process[26]:

$$\begin{aligned} \text{Biosorbed metal concentration (mg/l)} &= \\ &= C_0 - C_f \end{aligned} \quad (1)$$

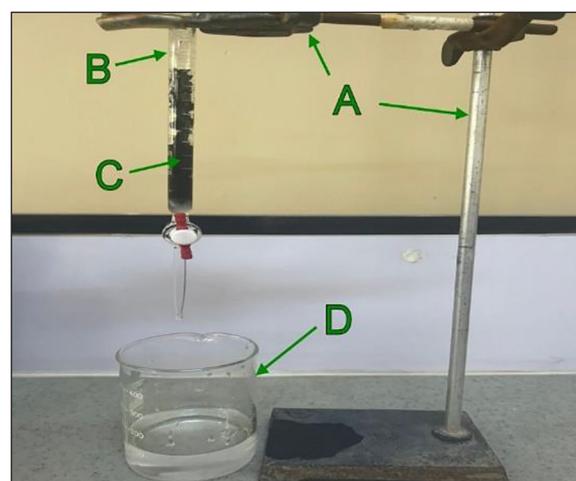


Figure 2. Laboratory treatment unit, where A: holder, B: Pyrex column reactor, C: Biosorbent CNPs, and D: collecting flask

$$\text{Biosorption\%} = (C_0 - C_f) / C_0 \times 100 \quad (2)$$

where: C_0 – the initial metal concentration, C_f – the final concentration.

Statistical analysis

All experiments data were subjected to various statistical tests for the significant differences such as; analysis of variance (F test) and least significant differences test (LSD test) [29].

RESULTS AND DISCUSSION

Factors effect on biosorption process

Effect of initial metals concentration

It seems that the highest mean value (85.14 ± 5.86 mg/l) of Cd concentration biosorbed from aqueous solution was recorded in case of initial Cd solution contains 100 mg/l at temperature of 45 °C whilst the lowest mean concentration (9.77 ± 1.1 mg/l) was found in solutions having initial concentration of 10 mg/l at temperature of 10 °C.

However, the rest solution temperature again with Cd content of 100 mg/l gave mean values of biosorbent ion concentration varying from 62.3 ± 5.17 mg/l at 35 °C to 67.95 ± 6.05 mg/l at 55 °C (Fig. 3). Regarding Cu ions, it seems that the highest mean value (97.92 ± 4.08 mg/l) of Cu concentration biosorbed from aqueous solution was recorded in case of initial Cu solution contains 100 mg/l at temperature of 45 °C while the lowest mean concentration (8.34 ± 2.74 mg/l) was found in solutions having initial concentration of 10 mg/l at temperature of 10 °C. However, the rest solution temperature again with Cu content of 100 mg/l gave mean values of biosorbent Cu ion concentration varying from 77.46 ± 3.38 mg/l at 55 °C to 87.32 ± 3.66 mg/l at 25 °C (Fig. 4).

For Zn ions, it seems that the highest mean value (85.20 ± 4.92 mg/l) of Zn concentration biosorbed from aqueous solution was recorded in case of initial Zn solution contains 100 mg/l at temperature of 45 °C whilst the lowest mean concentration (8.79 ± 2.17 mg/l) was found in solutions having initial concentration of 10 mg/l at temperature of 10 °C. However, the rest solution

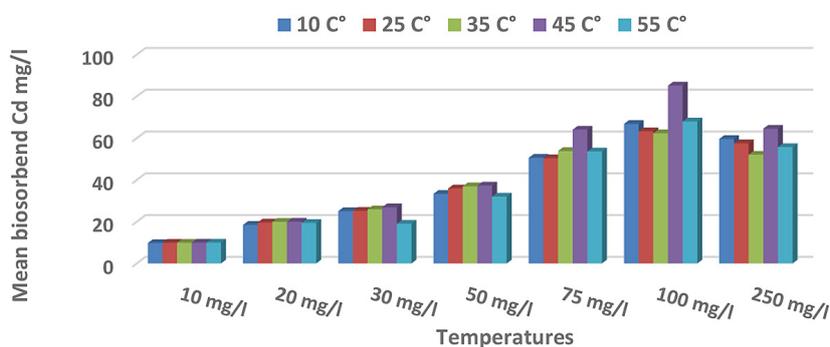


Figure 3. Mean Cd concentration biosorbed from aqueous solution by walnut shells at various initial Cd concentrations under different temperatures

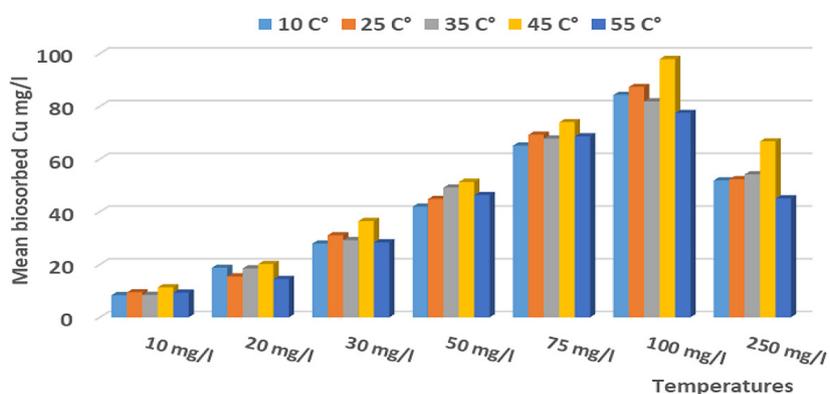


Figure 4. Mean Cu concentration biosorbed from aqueous solution by walnut shells at various initial Cu concentrations under different temperatures

temperatures again with Zn content of 100 mg/l gave mean values of biosorbent Zn ion concentration varying from 66.5 ± 2.15 mg/l at 55 °C to 75.06 ± 3.62 mg/l at 35 °C (Fig 5).

Effect of pH

Apparently, the highest mean value of 92.4 ± 3.54 mg/l of Cd ion biosorbed by walnut shells from aqueous was recorded at solution pH 7 but again with solution temperature of 45 °C while the lowest mean value of 55.7 ± 2.55 mg/l was detected at pH of 4 with solution temperature of 55°C (Fig. 6). For Cu, the highest mean value of 99.8 ± 3.02 mg/l of Cu ion biosorbed by walnut shells was recorded at solution pH 7 but again with temperature of 45 °C whereas the lowest mean value of 55.24 ± 2.12 mg/l was detected at pH of 4 with temperature of 10 °C (Fig. 7). While, it seems

very obvious that the highest mean value (94.39 ± 4.63 mg/l) of Zn ion biosorbed by walnut shells was recorded at solution pH 7 but again with temperature of 45 °C and the lowest mean value of 60.44 ± 2.48 mg/l was detected at pH of 4 with temperature of 55 °C (Fig. 8). Interestingly, solution pH of 7 has given the highest mean values of ions biosorbed by walnut shells from aqueous solutions at all examined temperatures while the lower mean values have been recorded at solution pH of 4 followed by values found at pH 5 and finally by those recorded at pH 6. However, these findings suggest that increased solution pH from 4 to 8 has resulted in increased ion biosorption at various temperatures. On the other hand, solution temperatures have shown fluctuated change on the biosorption process and this means that solution pH variable plays obvious impact on such heavy metal ions biosorption process.

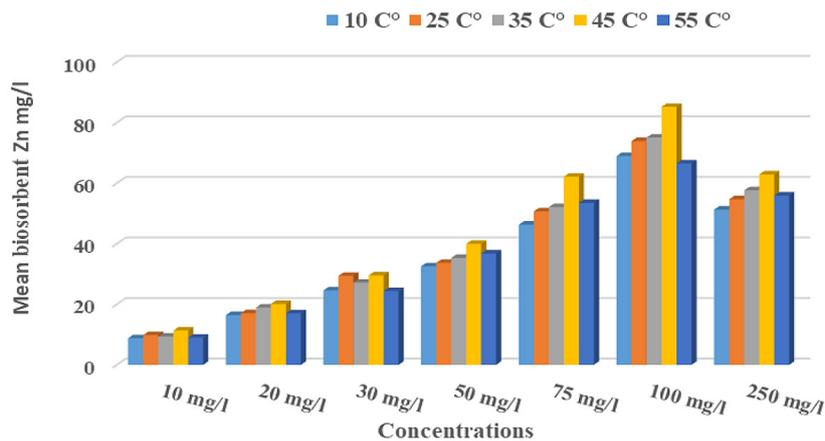


Figure 5. Mean Zn concentration biosorbed from aqueous solution by walnut shells at various initial Zn concentrations under different temperatures

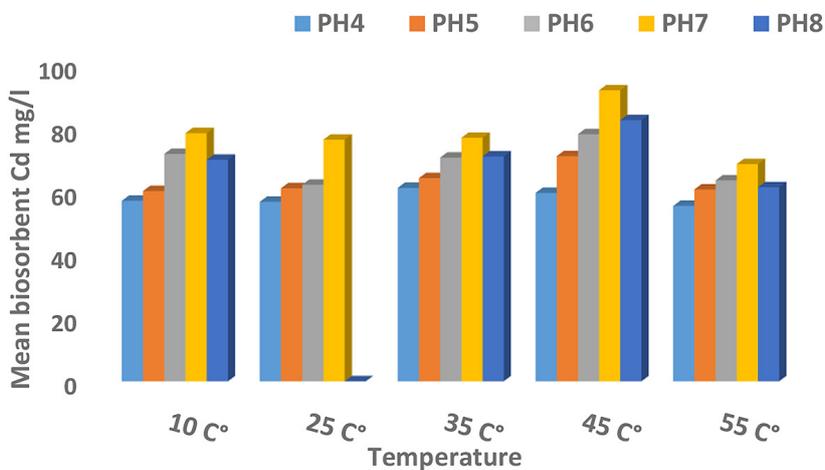


Figure 6. Mean Cd concentration biosorbed from aqueous solution by walnut shells at various solution pH with different temperatures

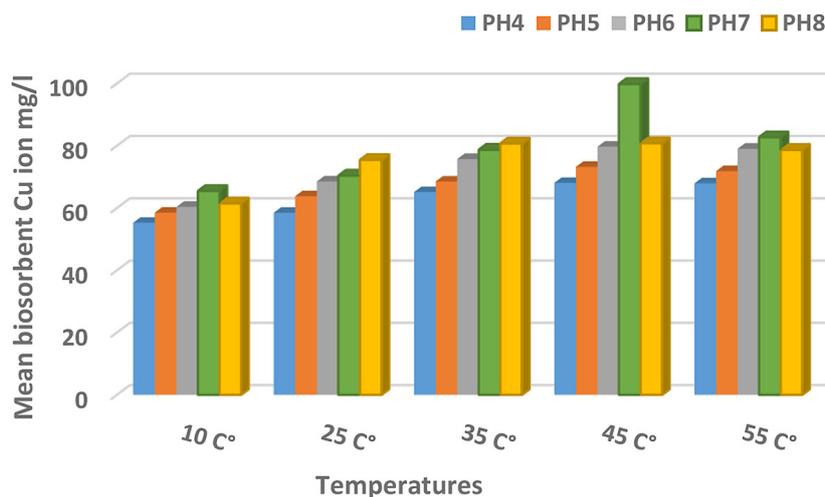


Figure 7. Mean Cu concentration biosorbed from aqueous solution by walnut shells at various solution pH with different temperatures

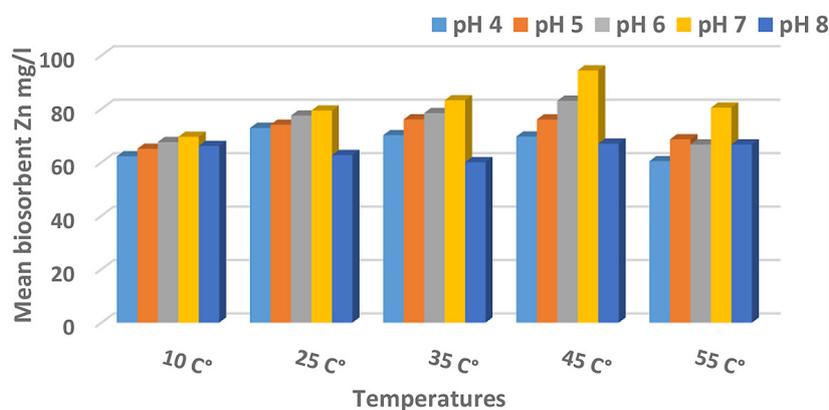


Figure 8. Mean Zn concentration biosorbed from aqueous solution by walnut shells at various solution pH with different temperatures

Effect of biosorbent mass

This test has found that the highest mean value of Cd ions biosorbed by walnut shells from all examined aqueous solutions was 97.85 ± 3.08 mg/l occurred by 0.2 g at solution temperature again of 45 °C whilst the lowest mean value was 44.72 ± 2.78 mg/l was detected in case of 0.01 g biomass weight with solution temperature of 55 °C. However, 0.1 g biomass weight has shown mean values following those given by 0.2 g with all examined solution temperatures (Fig. 9).

Cu ion solution test has found that the highest mean value of Cu ions biosorbed by walnut shells from all examined aqueous solutions was 99.73 ± 3.77 mg/l found for biomass weight of 0.2 g at solution temperature again of 45 °C whilst the lowest mean value was 68.22 ± 2.48 mg/l was detected in case of 0.01 g biomass weight with solution

temperature of 35 °C. However, 0.1 g biomass weight has shown mean values following those given by 0.2 g with all examined solution temperatures. Furthermore, 0.01 g biomass weight has shown the lowest mean values of biosorbed Cu ions under all examined solution temperature (Fig. 10). The experiment of Zn ion solution has found that the highest mean value biosorbed by walnut shells from all examined aqueous solutions was 86.0 ± 4.34 mg/l by biomass weight of 0.2 g at solution temperature again of 45 °C, whereas the lowest mean value was 63.72 ± 3.26 mg/l was detected in case of 0.01 g biomass weight with solution temperature of 10 °C. However, these results were followed by those of 0.1 g biomass weight values were recorded at solution temperatures of 10, 25 and 35 °C but at 55 °C, slight higher mean of Zn ions biosorbed was achieved by 0.025 g (Fig. 11). Additionally, this is consistent with the literature

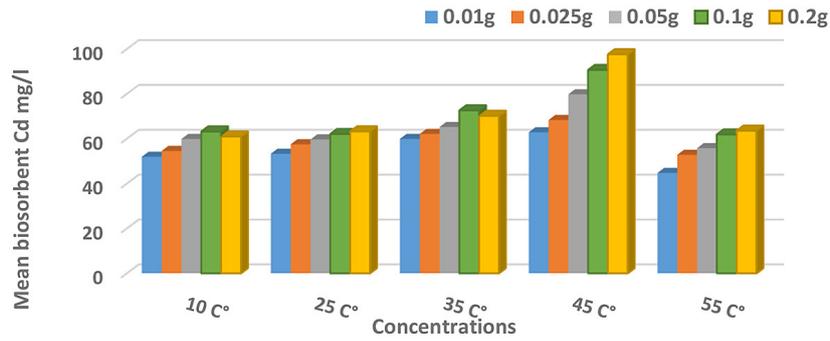


Figure 9. Mean Cd concentration biosorbed from aqueous solution by walnut shells at various biomass weight with different temperatures

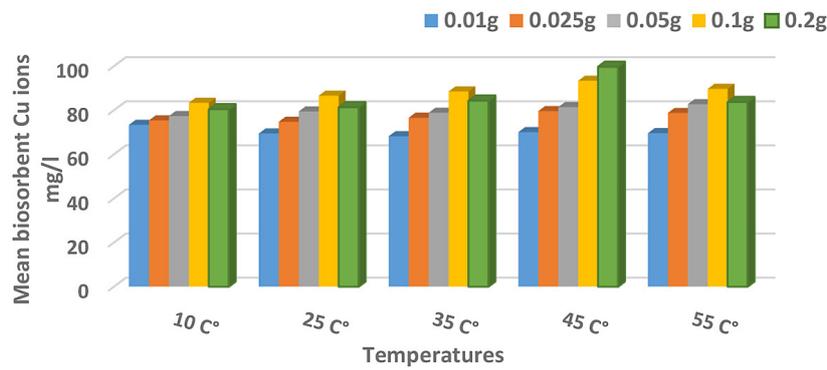


Figure 10. Mean Cu concentration biosorbed from aqueous solution by walnut shells at various biomass weight with different temperatures

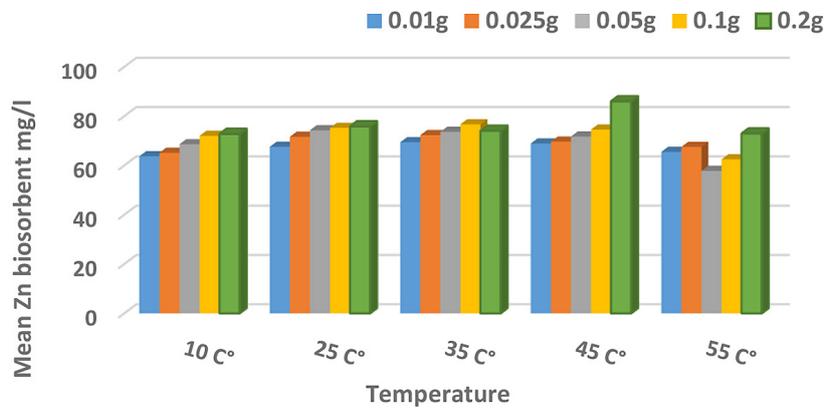


Figure 11. Mean Zn concentration biosorbed from aqueous solution by walnut shells at various biomass weight with different temperatures

once the smaller the particle sizes of the sorbents are, the greater the rate of adsorption, because of the shorter mass transfer zone, causing a faster rate of adsorption [30]. Also, larger particles with spherical shapes, in general, present higher external mass transfer than smaller particles and adsorption from these particles is attributed to mass transport inside the sorbent particles. When higher metal adsorption is verified on smaller particles, as observed

with this study materials, the main process of metal adsorption onto solid adsorbents are those based on adsorption on the particle surface [31].

Effect of contact time

The quantity of total biosorption is determined by the contact time of the biosorbents seems clearly that the best mean value of Cd ion biosorbed by walnut shells from examined aqueous solutions

was 96.1 ± 3.97 mg/l was found in case of contact time of 60 min and at solution temperature of 45°C while the lower mean value of 52.4 ± 3.28 mg/l at temperature of 10°C (Fig. 12). For Cu ion results, it obviously clear that the best mean value of Cu ion biosorbed by walnut shells from examined aqueous solutions was 95.79 ± 3.99 mg/l was found in case of contact time of 60 min and at

solution temperature of 45°C but, the lower mean value of 53.98 ± 2.96 mg/l at temperature of 55°C (Fig. 13). Obviously, the highest mean values of Zn ions biosorbed by walnut shells from aqueous solutions were recorded at solution temperature of 45°C for all examined contact times followed by those at 35°C again for all contact times (Fig. 14), while remaining solution temperatures

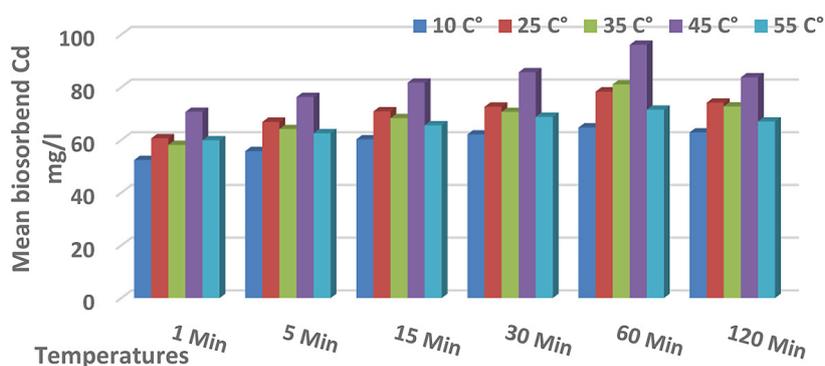


Figure 12. Mean Cd concentration biosorbed from aqueous solution by walnut shells at various contact times with different temperatures

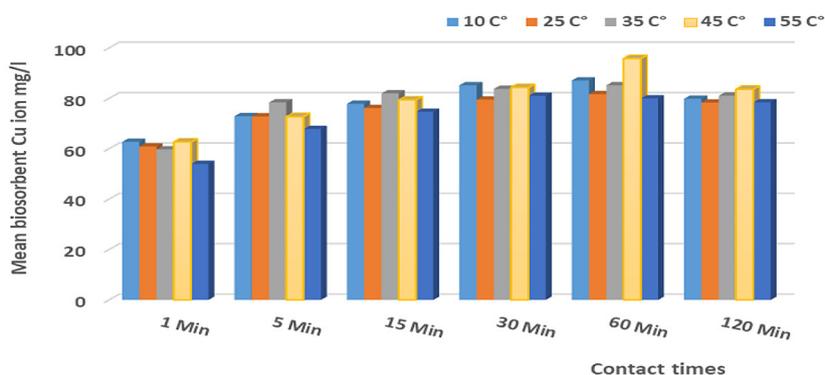


Figure 13. Mean Cu concentration biosorbed from aqueous solution by walnut shells at various contact times with different temperatures

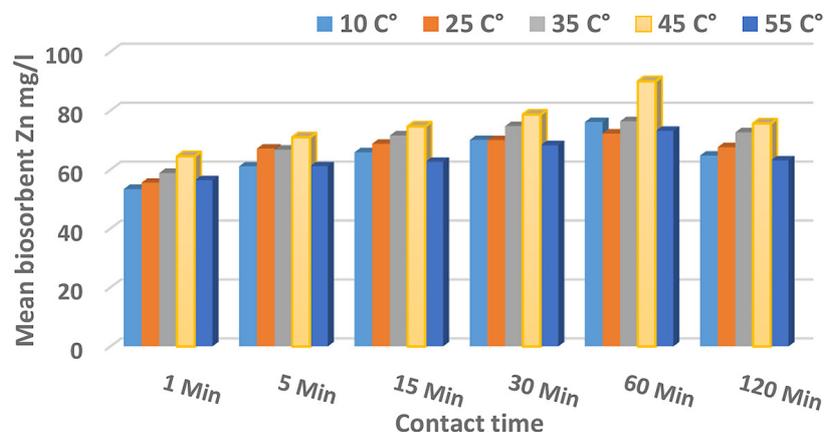


Figure 14. Mean Zn concentration biosorbed from aqueous solution by walnut shells at various contact times with different temperatures

gave fluctuated results of biosorbed Zn ions. However, such higher mean values were recorded for temperature of 45 °C with all contact times, but on the other hand, the lower mean values were found in case of solution temperatures of 10 °C of all examined contact times. Clearly, best contact time values were 60 min.

Metal ions biosorption comparison

From these results, it seems clearly that the highest mean values of all examined heavy metal ions at various variables were recorded at solution temperature of 45 °C as a follows; Initial heavy metal concentration of 100 mg/l, Solution pH is 7, Contact time of 60 minutes, and Biomass weight of 0.2 g as it seen in (Fig. 15).

Regarding this variable, this study has found that highest mean biosorbed concentration (97.92 ± 4.08 mg/l) was recorded for Cu ions, whereas the mean of biosorbed concentration of both Cd and Zn were almost the same and they were 85.14 ± 5.86 and 85.20 ± 4.92 mg/l respectively. In case of solution pH, it was found that the highest mean value of biosorbed metal ion

by walnut shells was detected again for Cu ions where it was 99.8 ± 3.02 mg/l followed by that of Zn ion having mean value of 94.39 ± 4.63 mg/l, whereas Cd ions had the lowest mean value which was 92.4 ± 3.54 mg/l. For contact time factor, it seems very clear that both Cd and Cu ions gave almost highest similar mean value of ions biosorbed by walnut shells which were 96.1 ± 3.97 and 95.79 ± 3.99 mg/l respectively, while Zn ion has recorded lower mean value of 89.94 ± 4.64 mg/l. Regarding biomass weight, this work has recorded highest mean biosorbed mean value of 99.73 ± 3.77 mg/l was for Cu ions whereas, it was 97.85 ± 3.08 mg/l for Cd ion while the lowest value was detected for Zn ion having mean value of 87.0 ± 4.34 mg/l.

X-ray diffraction

X-ray powder diffractometric analysis of carbon nanoparticles was carried out to identify their crystal structure. The XRD spectrum of carbon nanoparticles in Figure 16 shows that there are two Bragg diffraction peaks at near 2θ = 8.9o and 16.01 [32].

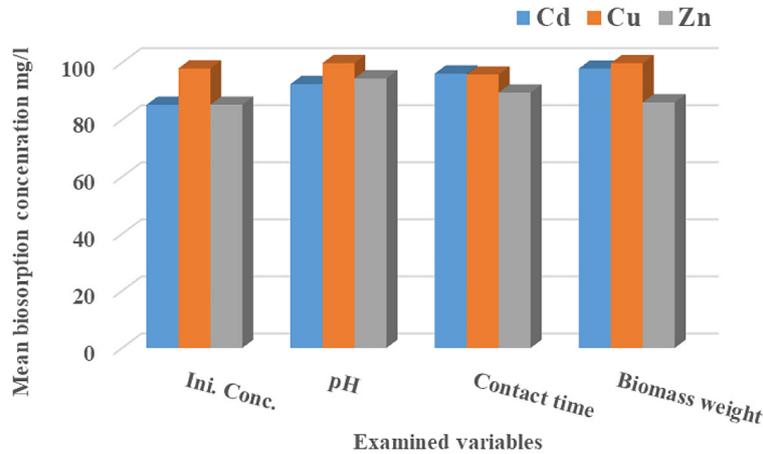


Figure 15. Mean values of all examined heavy metal ions ± standard deviation biosorbed from aqueous solution by walnut

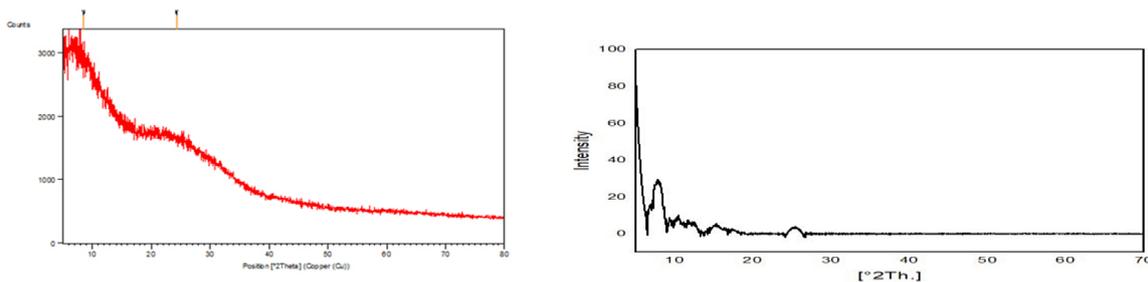


Figure 16. The XRD spectrum of walnut peel nano

Scanning electron microscopy (FE-SEM)

The SEM analysis was done to follow up the changes made to walnut peel nano production process affected the surface morphology. Figure 17 show that the carbon consist of irregular shaped particles having rough surface and caves.

Transmission electron microscopy

TEM images of walnut peel nanoparticles prepared via 2.2 indicates that nanoparticles were producing particles with diameter less than 3.5 nm.

Laboratory treatment unit

With regard to the laboratory treatment unit, this system was designed for the purpose of treating heavy metal ions present in the water of the Euphrates River, where samples were collected from the river water in three replicates from selected sites such as the site of the teaching hospital in the city of Ramadi within Anbar Governorate, it was revealed that there are different concentrations of heavy metal ions whose amounts exceed the internationally permissible limits, given that most of the hospitals located on the banks of the river throw their wastewater directly into the river water without any treatment. This water usually contains different concentrations of heavy metals generated from patient lobbies, radiology clinics, drug residues, and other dangerous pollutants that find their way directly into the river water, which increases the environmental burden of such pollutants in the river water, causing a deterioration in the quality of this water and determining its various uses. However, the concentration of heavy metal ions was measured in the river water, which included the elements of (Zn, Cu, and

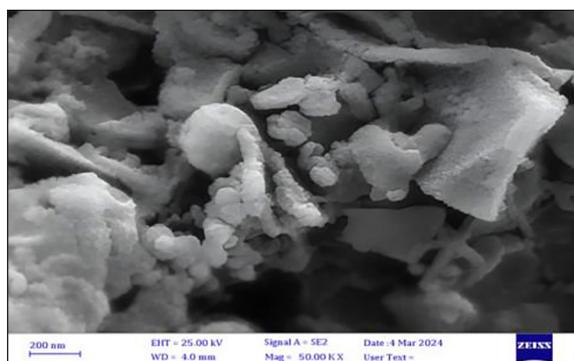


Figure 17. Fe-SEM image of walnut peel Nano-particles

Cd), where the concentrations reached 0.09 ± 0.01 , 1.08 ± 0.2 , and 0.03 ± 0.01 mg/l, respectively. Yet, these values disappeared for all elements when treated with the laboratory treatment unit under the same optimal conditions that the study found. Pollution of water with heavy metals have great concern, the utilization of walnut shell as biomass for heavy metals removal due to its availability, very effecting use and cheap. Biosorption of heavy metals from aqueous solutions is a relatively alternative technology for treatment of domestic wastewater [33]. Walnut shell have great ability to adsorb heavy metals from aqueous solutions. This study was done to obtain optimum conditions for biosorption of heavy metals by walnut shell, it is clear that the results of factors effecting biosorption of heavy metals were:

- initial concentration of metals = 100 ml/l, at this initial concentration the mean value was the highest whereas the lowest mean value was in the case of initial concentration = 10 ml/l of Cd, Cu and Zn is may due to the biosorption process of metals ions increases with the increase in the number of ions competing for the available binding sites in the biomass until it reaches at optimal concentration =100 ml/l but in case of greater concentration levels such as (250 ml/l) there are no binding sites available within biomass for the complexation of Cd, Cu, and Zn ions according to absorvation the Figures (3, 4, 5) [34, 35].
- pH = 7, the effect of pH on biosorption is shown in Figures (6, 7, 8) the highest mean value was recorded at pH = 7 while the lowest mean value was at pH = 4, that mean the biosorption increases with increase pH, this may be attributed to the increase in pH (7) which resulted in increasing the negative charge on the surface of the peels favoring electrochemical attraction and adsorption of metal and the increase in adsorption capacity at higher pH values can be attributed to the weak inhibitory effect of H_3O^+ ions. While at low pH = 4 more H_3O^+ ions will be available to compete with Cu, Zn and Cd ions for the adsorption sites of the biosorbents. In addition, at low pH most of the functional groups are protonated. This will reduce the number of binding sites available for the adsorption of metal ions [35],
- biomass weight = 0.2 g the highest mean value was obtained at mass = 0.2 g while the lowest mean value was recorded at mass of 0.01g due to an increase in the weight of biomass may

account for the overall improvement in the initial rate of metal removal by increasing the number of active sites on the surface available for adsorption while at mass of 0.01g there are no available binding sites for adsorption of metal ions from aqueous solutions as noted in Figures 9–11 [36].

- contact time = 60 minutes followed by that of 30 minute, Figures (12, 13, 14) whereas contact times gave increased under study ions biosorbed by walnut shells from the aqueous solution were started with one min (lowest mean value) up to 60 min (highest mean value), No further increase in the level of bounded Cu, Zn and Cd after 60 min. Therefore, 60 min was selected as equilibrium time for biosorption process at all examined temperatures then declined to value almost similar to that biosorbed at 15 min for all heavy metal ion solutions. Nevertheless, biosorption rises with increasing contact time until it reaches the optimal contact time, when all points stays practically constant, as all active sites are occupied, thus, the biomass becomes saturated, resulting in an equilibrium that identical to study of Nacke [37]. As observed in Figure 15 the highest mean biosorbed concentration was noted by Cu Followed by cd and Zn respectively therefore it can be said that the reason behind is the presence of affinity between the adsorbent and the heavy metal ion [38].

X-ray diffraction, scanning electron microscopy and transition electron microscopy examinations for walnt shell were done, the result of XRD was the peak at near $2\theta = 8^\circ$ indexed as (002)

is an indication of the presence of large amounts of amorphous material in association with multi-walled carbon nanotubes and the peak at near $2\theta = 14.5^\circ$ indexed as (101) plane is an indication of the low quality of carbon nano-materials, It has also been reported that the peak at near $2\theta = 23.4^\circ$ indexed as (101) plane is an indication of the presence of hexagonal graphite lattice, In the present study, the peaks at near $2\theta = 17^\circ$ were indexed as (002) planes which correspond to the presence of large amounts of amorphous carbon nano-materials, in association with hexagonal graphite lattice [31].

The SEM The results depicted in Figure 17 reveal that the walnut peel has irregularly shaped particles with a rough surface and cavities, suggesting a high specific surface area. This occurs as the walnut shell chains are destroyed when combined with potassium hydroxide (KOH) and subjected to combustion through a small aperture at temperatures exceeding 600°C , while the results of the TEM analysis reveal the production of nanoparticles with diameters less than 3.5 nm [39].

TEM examination indicated the existence of inhomogeneous particles (Figure 18), potentially attributable to inadequate temperature in the inner zone. The dimensions of the walnut peel generated differed among samples, suggesting that heating temperature may be the principal factor influencing their sizes [39]. The efficacy of the laboratory treatment unit was evaluated for the elimination of heavy metals (Zn, Cu, and Cd) in water from various sites along the Euphrates River, including Ramadi Hospital. The concentrations of Zn, Cu, and Cd were measured at 0.09 ± 0.01 , $1.08 \pm$

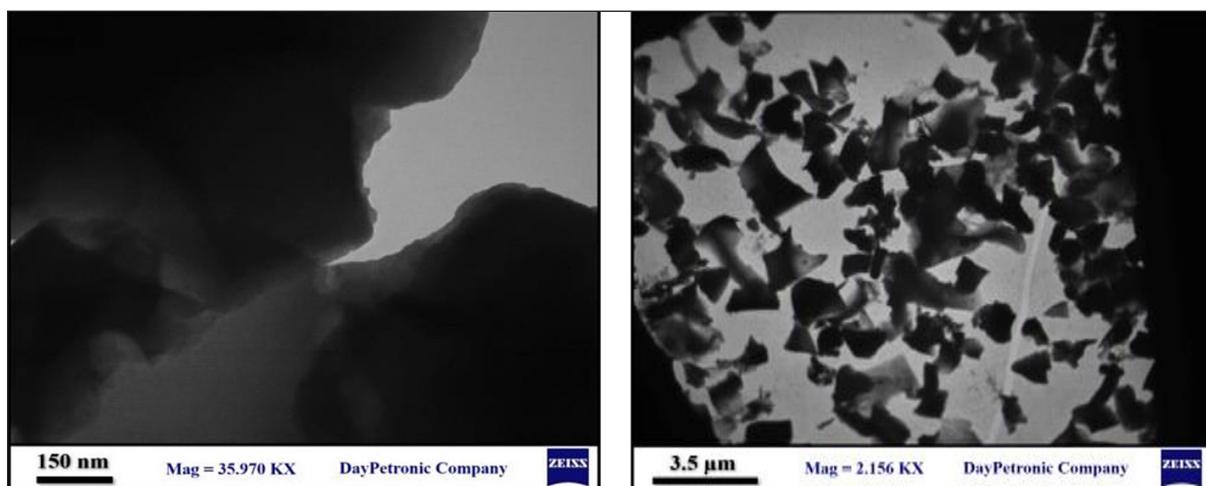


Figure 18. TEM of carbon nanoparticles

0.2, and 0.03 ± 0.01 mg/l, respectively. Following treatment under optimal laboratory conditions, the removal efficiency reached 100%, indicating the system's high effectiveness in treating wastewater contaminated with heavy metals.

As a result of the significance of nanoparticles, it was utilized in a variety of biological domains in general [40–42].

CONCLUSIONS

One useful use for walnut peels is as a plant waste product that can remove or reduce the concentration of heavy metal ions in water, particularly when those ions are in their nano carbonic form. Under ideal conditions – which included an initial concentration of 100 mg/l, a retention time of 60 minutes, a temperature of 45 °C, a pH of 7, and a peel weight of 0.2 grams – these plant byproducts biosorptionally removed cadmium, copper, and zinc ions at a rate of 90%. The XRD, SEM, and TEM results, however, supported this. To sum up, walnut shell-derived carbon nanoparticles are excellent adsorbents for heavy metal ion removal from water.

Acknowledgments

The authors would like to thank the staff of both Biology and Chemistry departments, College of Science, University of Anbar for their help and for supporting this work.

REFERENCES

1. Jayaswal, K., Sahu, V., & Gurjar, B.R. (2018). Water pollution, human health and remediation. *Water Remediation*, 11–27.
2. Ahamed, M.I., & Lichtfouse, E. (2021). *Water pollution and remediation: Heavy metals*. Springer.
3. Gahlout, M.; Prajapati, H., Tandel, N., and Patel, Y. (2021). Biosorption: An EcoFriendly Technology for Pollutant Removal. *Microbial Rejuvenation of Polluted Environment*, 207–227. https://doi.org/10.1007/978-981-15-7455-9_9
4. Al-Jobory, M.B., Al-Thwaini, A.N., Najeeb, L.M. (2018). Using sesame oil to treat the infection of hemorrhagic E. *Coli* o157: H7 bacteria isolation in Baghdad: Molecular and histological study. *Plant Archives*, 18(1), 627–637.
5. Al-Aarajy, N.A.R., Turki, A.M., Alalousi, M.A. (2022). Assessment of Silver Nanoparticle as Anti-Salmonella Agent: Phenotypic and Genotypic Study. *AIP Conference Proceedings*. 2400, 030003.
6. El-Bondkly, A.M., and El-Gendy, M.M. (2022). Bioremoval of some heavy metals from aqueous solutions by two different indigenous fungi *Aspergillus* sp. AHM69 and *Penicillium* sp. AHM96 isolated from petroleum refining waste water. *Heliyon*, 8(7): e09854. <https://doi.org/10.1016/j.heliyon.2022.e09854>
7. Taha, A., Hussien, W. and Gouda, S.A. (2023). Bioremediation of heavy metals in wastewaters: a concise review. *Egypt. J. Aquat. Biol. Fish.*, 27(1): 143–166. <https://doi.org/10.21608/ejabf.2023.284415>
8. Hussain, S.A., Hasan, N.K., Al-Abodi, E.E. (2021). *Biosorption to removing heavy metals from wastewater*. Journal of Physics: Conference Series 1853: 012012 IOP Publishing. <https://doi.org/10.1088/1742-6596/1853/1/012012>
9. Radhi, A.B., Shartooh, S.M., Al-Heety, E.A. (2021). Heavy metal pollution and sources in dust from primary schools and kindergartens in Ramadi City, Iraq. *Iraqi Journal of Science*. 62(6): 1816–1828.
10. Xie, Sh. (2024). Biosorption of heavy metal ions from contaminated wastewater: an eco-friendly approach. *Green Chemistry Letters and Reviews*, 17(1): 2357213, <https://doi.org/10.1080/17518253.2024.2357213>
11. Elwakeel, K.Z., Ahmed, M.M., Akhdhar, A., Alghamdi, H.M., Sulaiman, M.G.M., Hamza, M.F., Khan, Z.A. (2023). Effect of the magnetic core in alginate/gum composite on adsorption of divalent copper: cadmium, and lead ions in the aqueous system. *Int. J. Biol. Macromol.* 253: 126884. <https://doi.org/10.1016/j.ijbiomac.2023.126884>
12. Ungureanu, E.L., Mocanu, A.L., Stroe, C.A., Panciu, C.M., Berca, L., Sionel, R.M., Mustatea, G. (2023). Agricultural byproducts used as low-cost adsorbents for removal of potentially toxic elements from wastewater: a comprehensive review. *Sustainability*, 15(7): 5999. <https://doi.org/10.3390/su15075999>
13. Escudero, L.B., Quintas, P.Y., Wuilloud, R.G., & Dotto, G.L. (2019). Recent advances on elemental biosorption. *Environmental Chemistry Letters*, 17, 409–427.
14. Mishra, S. (2023). Biomedical impact of heavy metal ions on human health. *Int. J. Biochem. Physiol.* 8(1). <https://doi.org/10.23880/ijbp-16000215>
15. Zhao, S., Sun, K., Xie, P., Zhang, S., Zhang, J., Zhu, Y., Sun, Z. (2024). Mercury Removal from Coal Combustion Flue Gas by S. XIE 18 Mechano-chemically Sulfur Modified Straw Coke and its Mercury Stability. *Fuel* 355, 129498. <https://doi.org/10.1016/j.fuel.2023.129498>
16. Buhani, L., Dewi, J.S., Fajriyah, N.S., Rilyanti,

- M., Suharso, Sumadi, Elwakeel, K.Z. (2023). Modification of non-activated carbon from rubber fruit shells with 3-(Aminopropyl)- Triethoxysilane and its Adsorption Study on Coomassie Brilliant Blue and Methylene Blue in Solution. *Water Air Soil Pollut.* 234(9). <https://doi.org/10.1007/s11270-023-06506-2>
17. Pohl, A. (2020). Removal of heavy metal ions from water and wastewaters by sulfur-containing precipitation agents. *Water Air Soil Pollut.* 231(10). <https://doi.org/10.1007/s11270-020-04863-w>
 18. Fang, R., Dhakshinamoorthy, A., Li, Y., & Garcia, H. (2020). Metal organic frameworks for biomass conversion. *Chemical Society Reviews*, 49(11), 3638–3687.
 19. Liu, H., Zheng, Z., Qian, Z., Wang, Q., Wu, D., & Wang, X. (2021). Lamellar-structured phase change composites based on biomass-derived carbonaceous sheets and sodium acetate trihydrate for high-efficient solar photothermal energy harvest. *Solar Energy Materials and Solar Cells*, 229, 111140.
 20. Elanthamilan, E., Meena, B.C., Renuka, N., Santhiya, M., George, J., Kanimozhi, E.P., Ezhilarasi, J.C., & Merlin, J.P. (2021). Walnut shell derived mesoporous activated carbon for high performance electrical double layer capacitors. *Journal of Electroanalytical Chemistry*, 901, 115762.
 21. Singh, V., Singh, N., Rai, S.N., Kumar, A., Singh, A.K., Singh, M.P., Sahoo, A., Shekhar, S., Vamanu, E., Mishra, V. (2023). Heavy Metal contamination in the aquatic ecosystem: toxicity and its remediation using eco-friendly approaches. *Toxics* 11(2), 147. <https://doi.org/10.3390/toxics11020147>
 22. Samawi, M.Kh., Alsalihi, A.A., Suleiman, A.A. (2024). Use of Citrullus colocynthis callus for green synthesis of silver nanoparticles and their activity against biofilm-producing. *Journal of Communicable Diseases*, 56(2); 94–99.
 23. Li, S., Han, K., Li, J., Li, M., & Lu, C. (2017). Preparation and characterization of super activated carbon produced from gulfweed by KOH activation. *Microporous and Mesoporous Materials*, 243, 291–300.
 24. Priya, A.K., Gnanasekaran, L., Dutta, K., Rajendran, S., Balakrishnan, D., & Soto-Moscoso, M. (2022). Biosorption of heavy metals by microorganisms: Evaluation of different underlying mechanisms. *Chemosphere*, 307, 135957.
 25. Yildirim, A., Baran, M.F., & Acay, H. (2020). Kinetic and isotherm investigation into the removal of heavy metals using a fungal-extract-based biosorbent. *Environmental Technology & Innovation*, 20, 101076.
 26. Khan, N., Wahid, F., Sultana, Q., Saqib, N., Rahim M. (2020b). Surface oxidized and un-oxidized activated carbon derived from Ziziphus jujube Stem, and its application in removal of Cd (II) and Pb(II) from aqueous media. *SN Applied Sciences*. 2: 753.
 27. Mohammed, A., & Abdullah, A. (2018). Scanning electron microscopy (SEM): A review. *Proceedings of the 2018 International Conference on Hydraulics and Pneumatics—HERVEX, Băile Govora, Romania, 2018*, 7–9.
 28. Tang, C.Y., and Yang, Z. (2017). Transmission electron microscopy (TEM). In *Membrane characterization* 145–159. Elsevier.
 29. Webster, R., & Lark, R.M. (2018). Analysis of variance in soil research: let the analysis fit the design. *European Journal of Soil Science*, 69(1), 126–139.
 30. Mavinkattimath, R.G., Shetty Kodialbail, V., & Srinikethan, G. (2023). Continuous fixed-bed adsorption of reactive azo dye on activated red mud for wastewater treatment-Evaluation of column dynamics and design parameters. *Environmental Science and Pollution Research*, 30(19), 57058–57075.
 31. Hegazy, G.E., Soliman, N.A., Ossman, M.E., Abdel-Fattah, Y.R., Moawad, M.N. (2023). Isotherm and kinetic studies of cadmium biosorption and its adsorption behaviour in multi-metals solution using dead and immobilized archaeal cells. *Sci. Rep.* 13(1). <https://doi.org/10.1038/s41598-023-29456-5>
 32. Preethi, G., Jeyanthi, J. (2023). Biosorption of heavy metals using Gracilaria edulis seaweed – batch adsorption, kinetics and thermodynamic studies. *Global NEST Journal*. 25(10).
 33. Dodbiba, G. ergj, Ponou, J., & Fujita, T. (2015). Biosorption of heavy metals. *Microbiology for Minerals, Metals, Materials and the Environment*, 409–426. <https://doi.org/10.4018/978-1-5225-8903-7.ch077>
 34. Xu, S., Xing, Y., Liu, S., Hao, X., Chen, W., & Huang, Q. (2020). Characterization of Cd²⁺ biosorption by Pseudomonas sp. strain 375, a novel biosorbent isolated from soil polluted with heavy metals in Southern China. *Chemosphere*, 240, 124893.
 35. Chellaiah, E.R. (2018). Cadmium (heavy metals) bioremediation by Pseudomonas aeruginosa: a minireview. *Applied Water Science*, 8(6), 154.
 36. Nacke, H., Gonçalves Jr, A.C., Campagnolo, M.A., Coelho, G.F., Schwantes, D., dos Santos, M.G., Briesch Jr, D.L., & Zimmermann, J. (2016). Adsorption of Cu (II) and Zn (II) from water by Jatropha curcas L. as biosorbent. *Open Chemistry*, 14(1), 103–117
 37. Shamsollahi, Z., & Partovinia, A. (2019). Recent advances on pollutants removal by rice husk as a bio-based adsorbent: A critical review. *Journal of Environmental Management*, 246, 314–323.
 38. Wibawa, P.J., Nur, M., Asy'ari, M., & Nur, H. (2020). SEM, XRD and FTIR analyses of both ultrasonic and heat generated activated carbon black microstructures. *Heliyon*, 6(3). e03546.
 39. Li, X., Xu, X., Zhou, Y., Lee, K.-R., & Wang, A. (2019). Insights into friction dependence of carbon

- nanoparticles as oil-based lubricant additive at amorphous carbon interface. *Carbon*, 150, 465–474.
40. Al-Saadi, H.K., Awad, H.A., Saltan, Z.S., Hasoon, B.A., Abdulwahab, A.I., Al-Azawi, K.F., & Al-Rubaii, B.A. (2023). Antioxidant and antibacterial activities of allium sativum ethanol extract and silver nanoparticles: <http://www.doi.org/10.26538/tjnpr/v7i6.5>. *Tropical Journal of Natural Product Research (TJNPR)*, 7(6), 3105–3110.
41. Al-saidi, M., Al-Bana, R.J.A., Hassan, E., & Al-Rubaii, B.A.L. (2022). Extraction and characterization of nickel oxide nanoparticles from Hibiscus plant using green technology and study of its antibacterial activity. *Biomedicine*, 42(6), 1290–1295.
42. Saleh, T.H., Hashim, S.T., Malik, S.N., & AL-Rubaii, B.A.L. (2019). Down-regulation of flil gene expression by Ag nanoparticles and TiO₂ nanoparticles in pragmatic clinical isolates of *Proteus mirabilis* and *Proteus vulgaris* from urinary tract infection. *Nano Biomed. Eng.*, 11(4), 321–332.