Estimation The Efficiency Of Nanoparticles From Some Species Of Blue-Green Algae In The Bio-Sorption Of Heavy Metals From Polluted Water

Khitam Abbas Marhoon , Ebtesam K. Khudher , Ali O. Shaawiat

Abstract: Nanoparticles(NPs) were prepared from Nostoc sp. and Spirulina sp. for the purpose of removing some heavy elements(Pb, Cd, and Cu) from water. An FTIR device was also used to identify an active sites present in the bio-nanoparticles both without adding any elements and when adding elements individually. It was observed that binding bands led to adsorption between the surface of the prepared nanoparticles and the heavy elements due to nanoparticles surface area. Results showed ability of nanoparticles to adsorb HMs from water, with the highest removal percentage with the addition of (1g) of the Spirulina sp. NPs for cadmium, reaching (82.94%), this was followed by lead, which reached (77.81%), and the percentage of removal for copper was (70.89%). While the results indicated lower removal percentages when using Nostoc sp. NPs. compared to Spirulina sp. NPs with percentages (79.8, 74.22, 67.39)% for the three elements at a concentration of 50 ppm respectively.

Keywords: Nanoparticles , blue green algae , Cyanophyta , FTIR

Julian Bongsoikrama (Julian@budiluhur.ac.id)Universitas Budi Luhur, Indonesia
Nexen Alexandre Pinontoan (nexenalexandre.pinontoan@budiluhur.ac.id)Universitas Budi Luhur, Indonesia

Introduction

Water pollution of heavy metals(HMs) is one of the global environment problems, released into water bodies during mining operations, agricultural runoff, and industrial and domestic liquid waste, which has a lasting negative impact on aquatic systems because of its toxic and remained in water, thereby preventing self-purification of the water body [1]. Treatment of polluted water and removal of HMs from the environment is essential, with an urgent need to innovate new methods to effectively solve the pollution problem and increase the availability of usable water by minimizing or eliminating pollutants [2,3].. Many traditional methods have been used to treat water, which have often been limited in effect and economically costly, hence researchers have shifted towards finding modern methods instead of traditional approaches, including bioremediation [4]. Biosorption, as a biological method leveraging the ability of inactive biomass to attract heavy metals in polluted waters. [5,6]. Microalgae have been used in various environmental biotechnological applications, as they have a significant impact on controlling heavy metal concentrations in water bodies due to their high capability for accumulating heavy metals [7]. With the continuous advancement in technology, many techniques were tested to eliminate HMs which pollutes water, including nanotechnology for HMs removal; this technique offers advantages such as ease of preparation, low cost, non-toxicity, and no side effects [8]. The properties and characteristics of NPs are attributed to their size,chemical composition, and structure of surfaces, these properties and physical changes of materials at the nanoscale have led to the development of industrial product properties, resulting in a significant and impactful increase in industrial and medical applications [9]. Algae possess a unique ability to bind with heavy elements, which they have been used in the manufacture of nanoparticles to enhance their efficiency in bioremediation of pollutants [10,11], as well as forming biologically active materials such as proteins, phenolic acids, amino acids, alkaloids, and terpenoids that represented as natural abbreviations and capping factors to facilitate NPs synthesis by stabilising or controlling their shape and size, this makes them ideal particles in the treatment processing [12,13,14,15], and thus algae have become an important factor in the biosynthesis of nanoparticles used for detoxifying from sites polluted with metals in order to maintain a sustainable environment [16]. Many studies that use algae as nanoparticles in the treatment and absorption of heavy metals from water [17,18,19,20,21,22,23]. It has been found that the use of microalgae and macroalgae in removing pollutants from wastewater and eliminating heavy metal ions from aqueous solutions is more efficient than other methods. Additionally, they are low-cost and easy to cultivate, more environmentally friendly, and exhibit higher adsorption capacity and selectivity for heavy metal ions.

Objective of study

This study aim to synthesise nanoparticles from some blue green algae (Cyanophyta) and demonstrate their ability in reducing or removing heavy metals from polluted media.

Materials and Methods

2.1. Prepare extract of algae and $AgNO_3$solution:-

Algal extracts were prepared from adding 100g powdered algae to 200 ml of distilled water in an extraction device for 3 hours, followed by filtration using filter paper.

The silver nitrate was prepared from adding a specific weight $AgNO_3$ to 1000ml deionised distilled water to obtain a 1mm silver nitrate solution ready for use [24].

2.2: Preparation of nanoparticles (NPs) :-

The bio-nanoparticles were prepared from the aqueous extract of algae based on [24].Which involves place $AgNO_3$solution on magnetic stirrer then add the algal extract as drop wise. After 20 minutes, a colour change was observed, indicating the occurrence of the bioreduction of silver by the algae extract. Impurities were then separated using a centrifuge, and dry the residue to obtain silver nanoparticles in powder form. Finally, the prepared nanoparticle powder was placed in a special container to protect it from contamination for use in the experiment. Subsequently, weights of (0.1 - 0.5 - 1)g were prepared, and these weights were obtained using a sensitive balance.

2.3: The detection of bio-nanoparticles:-

Involved FTIR Spectroscopy analysis over at wavelength 500-3500cm^{-1} using FTIR device to elucidate the size of the nanoparticles and reveal the main active groups which important to reduce $AgNO_3$ at biosynthesis process and the stabilization of nanoparticles [25,26].

2.4: Study of the effectiveness of nanoparticles (NPs) in adsorbing heavy metals (HMs):-

Involved preparing solutions of heavy metals (Pb, Cd, Cu) at 50 ppm for each element, and then placed in plastic tubes to which the prepared nanoparticles with weights (0.1, 0.5, and 1)g was added. The mixtures were then placed in a shaker for 15 minutes to ensure homogeneity between the nanoparticles and the metal concentrations, left to sediment for 24 hours. After 24 hours, the solution was filtered using a filtration device, and the tubes were placed in a centrifuge to ensure the separation of the nanoparticles.To determine the amount absorbed, the solution was passed through membrane filters with a pore size of 0.45 µm, to estimate their concentrations using a flame atomic absorption spectrometer [27].

2.5: Removal efficiency percentage of HMs:-

A percentage removal of HMs represented by cadmium, copper, and lead was estimated, according to the following equation [28].

$$Removal\ percentage\ of\ HMs\ \% = (C0 - C1/\ C0) * 100$$

C_0 : Concentration of HMs before treatment.

C_1: Concentration of HMs after treatment.

2.6:Analysis of statically:

By using SPSS program at a significance level of 0.05P ≤, to determine significant differences between the concentrations of the elements after treatment with nanoparticles .

Results and Discussion

The percentage of heavy metal removal from the aqueous solution using algal nanoparticles :-

Tables (1&2) illustrates the concentration and percentage removal when using algal nanoparticles(NPs) , showing that concentrations decreases in aqueous solution with an increase in the amount of NPs from *Spirulina* sp. and the highest removal percentage for cadmium was achieved with the addition of (1g) of the NPs, reaching (82.94%), this was followed by lead, which reached (77.81%), and the percentage of removal for copper was (70.89%). While the results indicated lower removal percentages when using NPs from *Nostoc* sp. compared to NPs from *Spirulina* sp., with percentages of (79.8, 74.22, 67.39)% for the three elements respectively, when (1g) of the NPs was added.

Analysis of statically at $p \leq 0.05$ indicated that the different were non-significant between the algal NPs while recorded significant differences between the weights (0.1, 0.5 and 1)g among each other, with the highest removal percentage for cadmium, followed by lead, and the lowest removal for copper.

The results indicate that the percentage of heavy metal removal is increases with the increase in the amount of nanoparticles due to the increased surface area, which increased NPs active groups that have capacity to adsorb [29]. The low removal of heavy metal ions is attributed to the crowding of ions for algal active sites, resulting in many ions remaining unabsorbed in the solution at high concentrations [30]. The ability of nanoparticles to absorb high concentrations of heavy metals results from the potential for a state of balance between both enzymatic and molecular antioxidants, which increases the activity of secondary metabolite secretion. Additionally, when algae absorb HMs, it may stimulated the production of chelating compounds that surrounding the pollutants and trap them within their vacuoles [6].

From the above, it is clear that the capacity of algal nanoparticles to remove heavy metals, particularly lead and cadmium, is significant, followed by copper, which is an essential element but considered toxic at increased concentrations.

Detection of algal nanoparticles using FTIR before treatment :-

The shape (1&2) represents the infrared spectrum of the NPs from *Spirulina* sp. before treatment with any element, as the results showed the presence of bands at the wavenumbers (3495.78 , 2924.08 ,1578.56 ,1419.63 , and 1016.56) cm^{-1} and a peak of the NPs from *Nostoc* sp. appeared at the wavenumbers (3324.26, 2802.83, 1431.23, 1698.74,and 1048.37) cm^{-1} corresponding to the alcohol group carrying the hydroxyl bond (-OH), alkyl group (-CH), amine group (N-H), (C-O) represented an aromatic ester group, and(S=O) represented sulfoxide group respectively [31,32].The bonds above represent active adsorption groups because of negative charges it carries, which increase the ability of active groups forming physical connections and chemically bonds because of containing one or more lone pair electrons that they can donate or share to form a physical bond or link. [33].

The results of the active sites determination for the accumulated lead(Pb) in *Spirulina* sp. NPs showed broad and significant peaks at(3419, 2959, 2927, 1659, 1546, 1328, and 1153)cm^{-1} and in *Nostoc* sp. NPs showed a peaks at(3426, 2958, 2934, 1666, 1542, 1323, and 1157) cm^{-1}, this indicating the presence of the hydroxyl group (OH) , group in the organic compound(-CH2,and -CH), the carbonyl and carboxyl groups C=O, the amine group (N-H), a weak C-C bond, and the appearance of C-O respectively. shape(3&4).

As for the cadmium (Cd) showed peaks at (3406, 2957, 2929, 1656, 1539, 1327, and 1059) cm-1 for Spirulina sp. NPs and peaks at (3415, 2961, 2931, 1652, 1543, 1323, and 1052) cm-1 for Nostoc sp. NPs, which indicating for a hydroxyl group(OH), and organic compound (-CH2 and –CH) , the carbonyl and carboxyl groups (C=O), an amino group (N-H), a weak C-C and C-O. respectively, shape(5&6).While the FTIR technique for adsorption of copper (Cu), elucided the existence of functional groups as amino acids -NH and hydroxyl-OH, alongside other active groups responsible for the stabilization, adsorption, and reduction of copper. Its absorption was noted across a broad range of (3419-1059)cm-1 for Spirulina sp. NPs and (3417-1051)cm-1 for Nostoc sp. NPs with peaks observed at (1446 and 1442)cm-1 respectively indicating C-N bond of the amino group. The band at (1649 and 1638)cm-1 represented(C=O) group, respectively, and (1059 and 1051)cm-1 respectively, it refers to its connection with C-O, and noting that the infrared spectrum shows a shift in the peaks after the addition of copper and a wide range of absorbance, this indicates the association of the Spirulina sp.NPs and Nostoc sp.NPs with the Cu when the absorbance range reached (1649-461)$cm^{-1.}$ and (1638-459)$cm^{-1.}$, shape(7&8)

Bands extension may result from the extension of the O-H bond in alcohols and phenols during the association of NPs with copper, and a band appearing at the peak of 1539 corresponding to primary amines [33]. It was found that phenolic compounds have a stronger affinity for copper, which may explain that biomolecules can perform two functions: the synthesis and stability of copper in water[10]. Bioremediation of lead and cadmium due to the negatively charged ions on walls of bionanoparticles that attract (uptake) ions of these elements from water, which is due to carboxyl groups (COO). Thus, these negative charges bind with positive charges and prevent them from exiting back to the external growth medium [30]. Alternatively, heavy metals may bind with active groups – the carboxyl and phenolic groups – within the organic matter [20],preventing the accumulation of these elements at the target sites, converting them into inert forms (harmless salt crystals), and storing them in non-sensitive sites such as vacuoles, or converting them into other non-toxic forms that can be redistributed and reused in metabolic processes [34].

Conclusions

The current study demonstrated that bio-nanoparticles are highly efficient in removing heavy metals from aqueous solutions as their concentrations increase because of increase surface area and thus increase the effective groups present on their surface that have the ability to absorb. The most effectively removed element was cadmium, followed by lead and then copper(Cd > Pb > Cu)..

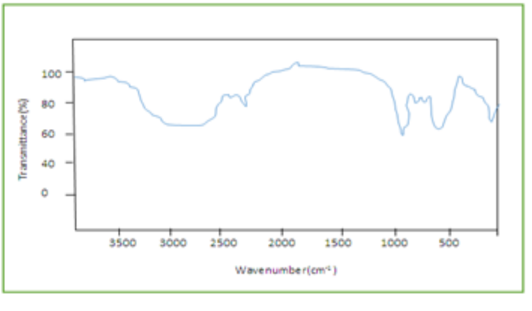
Table 1. The concentration of HMs(ppm) and the removal percentage(%) after add *Spirulina* sp. NPs .

Weight of NPs(g)	concentration of HMs(ppm)			removal percentage%		
	Cd	Pb	Cu	Cd	Pb	Cu
0.1	19.4	22.86	24.04	61.42	54.32	51.29
0.5	12.91	16.2	19.23	74.38	67.46	61.58
1	8.79	11.45	14.54	82.94	77.81	70.89

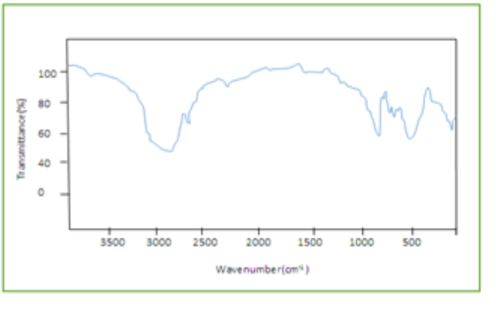
Table 2. The concentration of HMs(ppm) and the removal percentage(%) after add *Nostoc* sp. NPs .

Weight of NPs(g)	concentration of HMs(ppm)			removal percentage%		
	Cd	Pb	Cu	Cd	Pb	Cu
0.1	20.96	24.07	24.91	58.21	51.84	50.24
0.5	14.98	17.81	21.56	70.19	64.45	56.83
1	10.14	12.94	16.34	79.8	74.22	67.39

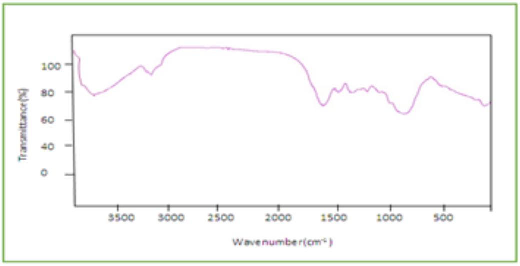
3.3 Investigation of the effectiveness of algal nanoparticles for adsorbing heavy metals:



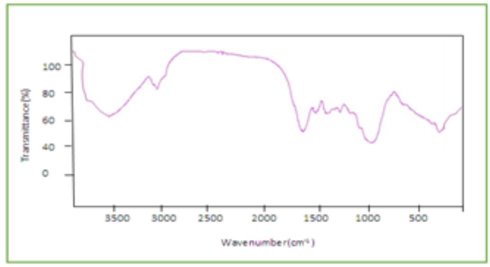
Shape(1): FTIR of Nostoc sp. NPs before treatment with any element



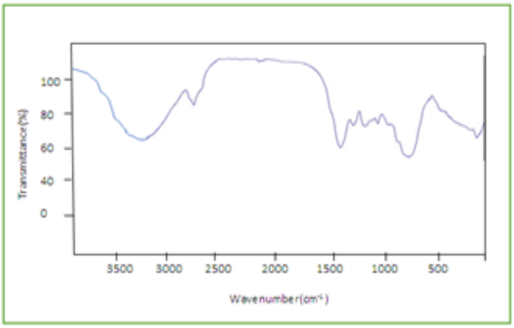
Shape(2): FTIR of Spirulina sp. NPs before treatment with any element



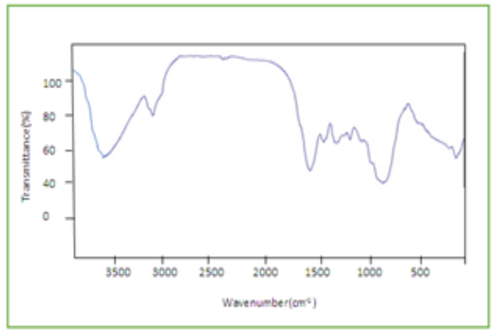
Shape(3): FTIR of Spirulina sp. NPs
that treatment with Pb



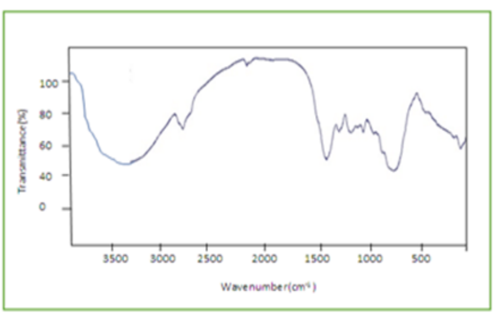
Shape(4): FTIR of Nostoc sp. NPs
that treatment with Pb



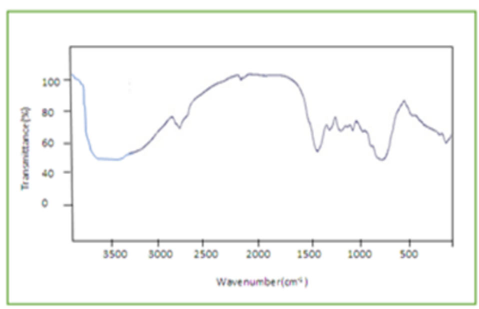
Shape(5): FTIR of Spirulina sp. NPs
that treatment with Cd



Shape(6): FTIR of Nostoc sp. NPs
that treatment with Cd



Shape(7): FTIR of Spirulina sp. NPs
that treatment with Cu



Shape(8): FTIR of Nostoc sp. NPs
that treatment with Cu

References

Alazaiza, M.; Albahnasawi, A.; Ali, G. and Bashir, M. (2022). Natural coagulants for pharmaceutical removal from wastewater. Gomaa., 1-8.

Kumar, V.; Kumar, S.; Américo-Pinheiro, J. H. P.; Vinthange, M. and Sher, F.(2023).

Emerging approaches for sustainable management for wastewater. Frontiers in Environmental Science, 10, 1122659.

Nishat, A.; Yusuf, M.;Qadir, A.; Ezaier, Y; Vambol, V.; Khan, M. I. and Eldin, S. M. (2023). Wastewater treatment: a short assessment on available techniques. Alexandria Engineering Journal, 76, 505-516.

Al-Allaf, M. A.; Al-Rawi, A. M. and AL-Ahmadi, K. K. (2023). Biosynthesis of Iron Oxide Nanoparticles and Using it to Support the Efficiency of Wastewater Filtration System. Rafidain Journal of Science, 32(1), 28-39.

Hopkins, D. and Hawboldt, K.(2020). Biochar for the Removal of Metals from Solution: A Review of Lignocellulosic and Novel Marine Feedstocks. J. Environ. Chem. Eng. 2020, 8 (4), 103975. doi:10.1016/j.jece.2020.103975

Abd Elnabi, M.K.; Elkaliny, N.E.; Elyazied, M.M.; Azab, S.H.; Elkhalifa, S.A.; Elmasry, S.; Mouhamed, M.S.; Shalamesh, E.M.; Alhorieny, N.A.; Abd Elaty, A.E.; Elgendy, I.M.; Etman, A.E.; Saad, K.E.; Tsigkou, K.; Ali, S.S.; Kornaros, M.; Mahmoud, Y.A.-G.(2023). Toxicity of Heavy Metals and Recent Advances in their Removal: A Review. Toxics 2023, 11 (7), 580. doi:10.3390/toxics11070580

Ayşe G. & Saniye T. (2023). The Use of Algae in Removal of Heavy Metal Ions from Wastewater , In book: Pioneer and Contemporary Studies in Agriculture, Forest and Water Issues (pp.107) Publisher: Duvar Publishing , DOI:10.59287/pcsafwi.50.

Xie, S. (2024). Biosorption of heavy metal ions from contaminated wastewater: an eco – friendly approach. Green Chemistry Letters and Reviews.VOL:17.NO:1. https://doi.org/10.1080/17518253.2024.2357213.

Bashir, N.; Afzaal, M.; Khan, A. L.; Nawaz, R.; Irfan, A.; Almaary, K. S. and Ahmed, Z. (2025). Green-synthesized silver nanoparticle-enhanced nanofiltration mixed matrix membranes for high-performance water purification. Scientific Reports, 15(1), 1001.

Chugh, D.; Viswamalya, V. S. and Das, B. (2021). Green synthesis of silver nanoparticles with algae and the importance of capping agents in the process. Journal of Genetic Engineering and Biotechnology, 19(1), 126.

Rathod, S.; Preetam, S.; Pandey, C. and Bera, S. P. (2024). Exploring synthesis and applications of green nanoparticles and the role of nanotechnology in wastewater treatment. Biotechnology Reports, e00830.

Nguyen, N.T.T. Nguyen, L.M.; Nguyen, T.T.T.; Liew, R.K.; Nguyen, D.T.C. and Tran, T.V. (2022). Recent advances on botanical biosynthesis of nanoparticles for catalytic, water treatment and agricultural applications: A review. Science of the Total Environment, 827.154160. doi: https://doi.org/10.1016/J.SCITOTENV.2022.154160.

Salih, A. M.; Al-Qurainy, F.; Khan, S.; Nadeem, M.; Tarroum, M. and Shaikhaldein, H. O. (2022). Biogenic silver nanoparticles improve bioactive compounds in medicinal plant

Juniperus procera in vitro. Frontiers in Plant Science, 13, 962112.

Rani, G.; Bala, A.; Ahlawat, R.; Nunach, A. and Chahar, S. (2025). Recent Advances in Synthesis of AgNPs and Their Role in Degradation of Organic Dyes. Comments on Inorganic Chemistry(1):45:1-29. doi: https://doi.org/10.1080/02603594.2024.2312394.

Bala, A. and Rani, G. (2023). Green synthesis of AgNPs using Delonix regia bark for potential catalytic and antioxidant applications Microscopy Res. Tech. 86: 911– 922. DOI: 10.1002/jemt.24310.

Namasivayam, S. K. R.; Aroma, R.; Samrat, K; Bharani, R. A.; Kavisri, M.; Kadaikunnan, S. and Moovendhan, M. (2024). Heat shock proteins capped biocompatible silver nanoparticles and their notable organic waste pollutants removal efficacy. Journal of Environmental Chemical Engineering, 12(1(111753.

Karaduman, F.R., Turk Culha, S., Horzum, N., (2022). Algal nanofibers: Current status and recent developments, Materials Today Communications, Volume 33, 104248..

Sulaymon, A.H.; Mohammed, A.A.; Al-Musawi, T.J. (2023). Multicomponent Biosorption of Heavy Metals Using Fluidized Bed of Algal Biomass. J. Eng., 19 (4), 469–484. doi:10.31026/j.eng.2013.04.05.

Al-Assaf, Azhar Y.R., Mira A. Al-Katib, Abdulazeez Y.T. Al-Saffawi (2025). The Effectiveness of Bio-Silver Nanoparticles in Treating Wastewater from the Khosar River . Egyptian Journal of Aquatic Biology & Fisheries Vol. 29(3): 555 – 569.

Qader. Muzhda Q. & Shekha .Yahya A. (2023) Role of Microalgae in Environmental Biotechnology to Remove Heavy Metals . Journal of Applied Sciences and Nanotechnology Vol. 3, No. 1 (2023)..

Ordóñez, J.I.; Cortés, S.; Maluenda, P.; Soto, I.(2023). Biosorption of Heavy Metals with Algae: Critical Review of Its Application in Real Effluents. Sustainability 2023, 15 (6), 5521. doi:10.3390/su15065521.

Lucaci, A.-R.; Bulgariu, L. (2024). Biosorption of Technologically Valuable Metal Ions on Algae Wastes: Laboratory Studies and Applicability. Water. (Basel) 2024, 16 (4), 512. doi:10.3390/w16040512.

Mohammed, D. H. and Al-Katib, M. A. (2023). Green Bio-Manufacturing of Silver Nanoparticles Using the Green Microalga Cosmarium sp. (Desmidiaceae) and Assessment of Their Microbial Efficacy. Egyptian Journal of Aquatic Biology and Fisheries, 27(4), 483-494.

Soto, K. M.; Quezada-Cervantes, C. T.; Hernández-Iturriaga, M.; Luna-Bárcenas, G.; Vazquez-Duhalt, R. and Mendoza, S. (2019). Fruit peels waste for the green synthesis of silver nanoparticles with antimicrobial activity against foodborne pathogens. Lwt, 103, 293300.

Kumar, N. and Kumbhat, S. (2016). Unique properties. Essentials in Nanoscience and Nanotechnology; John Wiley & Sons: Hoboken, NJ, USA.

Siddique, I. M. (2024). Exploring Functional Groups and Molecular Structures: A Comprehensive Analysis using FTIR Spectroscopy. development,1,2.

Abada, E.; Mashraqi, A.; Modafer, Y.; Al Abboud, M. A. and El-Shabasy, A.(2024). Review green synthesis of silver nanoparticles by using plant extracts and their antimicrobial activity. Saudi Journal of Biological Sciences, 31(1), 103877

APHA, AWWA and WCPE (2017). "Stand Method for Examination of water and wastewater. American public Health Association, 23 ed ; Washington DC, USA. doi: https://doi.org/10.2105/SMWW.2882.216.

Ismail, G. A.; El-Sheekh, M. M.; Samy, R. M. and Gheda, S. F. (2021). Antimicrobial, antioxidant, and antiviral activities of biosynthesized silver nanoparticles by phycobiliprotein crude extract of the cyanobacteria Spirulina platensis and Nostoc linckia. Bionanoscience, 11, 355-370.

Chakraborty, R. and Mukherjee, S. (2012). Bio-adsorptive removal of Chromium and Lead by aquatic macrophyte, New Horizons PIP, 13(2): 43-48.

Mahdieh, M.; Zolanvari, A. and Azimee, A. S. (2012). Green biosynthesis of silver nanoparticles by Spirulina platensis. Scientia Iranica, 19(3), 926-929.

Kumari, R. M.; Thapa, N.; Gupta, N.; Kumar, A. and Nimesh, S. (2016). Antibacterial and photocatalytic degradation efficacy of silver nanoparticles biosynthesized using Cordia dichotoma leaf extract. Advances in Natural Sciences: Nanoscience and Nanotechnology, 7(4), 045009.

Hamouda, R. A.; Hussein, M. H.; Abo-Elmagd, R. A. and Bawazir, S. S. (2019). Synthesis and biological characterization of silver nanoparticles derived from the cyanobacterium Oscillatoria limnetica. Scientific reports, 9(1), 13071.

Mukherjee, A.; Sarkar, D. and Sasmal, S. (2021).A review of green synthesis of metal nanoparticles using algae. Frontiers in Microbiology, 12, 693899.