

# Bio Removal of Copper (Cu<sup>+2</sup>) and Cobalt (Co<sup>+2</sup>) by *Chlorella Vulgaris* From Aqueous Solutions

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## Abstract:

The biological removal of the two elements copper and cobalt was studied in this paper. *Chlorella vulgaris* (*C.vulgaris*) algae was used for the removal process. CHU-10 medium was used to cultivation this algae. It was observed that algae has the ability to remove more copper than cobalt due to the strong affinity of the cell membrane to bind to copper and increase the process of adsorption of this element. It was concluded that there is a good benefit to using algae in removing copper and cobalt from polluted water.

**Keywords:** Bioremoval, *Chlorella vulgaris*, copper and cobalt, elements, adsorption

## 1-Introduction

All living things depend on water, which also serves as a great solvent. Heavy metals and other toxic chemicals found in water may have a devastating effect on aquatic ecosystems.(1).Because of their high toxicity and limited degradability in Nature, heavy metals pose a significant hazard to human and environmental health as a component of industrial effluent. Hence, water contaminated with metal ions must be cleaned thoroughly before being returned to the natural environment (2,3). Heavy metals may be found in wastewaters produced by industries (4). Industry and agriculture facilities , as well as home sewage, are the primary contributors to heavy metal contamination of waterways. In addition to human activity, natural processes like soil disrobing may contribute to the introduction of harmful metals into the ocean (5)

Some negative effects may result from direct and prolonged exposure to the heavy metal bioaccumulation that plagues natural food systems.

Urbanization and industrialization are the primary contributors to the contamination of aquatic habitats, which in turn leads to the buildup of pollutants in aquatic ecosystems. (6).

There is species variation in how sensitive microalgae are to harmful compounds (7). Consequently, only a few species of freshwater microalgae, such as *Chlorella vulgaris*, are used as examples. There are three essential needs that are met by this species: This single-celled organism is sensitive to pollutants but does not aggregate under laboratory conditions of cultivation and testing. And there's the added hazard of a compound's combined toxicity

(8). Estuaries are home to a wide variety of algae, including both prokaryotic and eukaryotic forms; these algae are beneficial to the ecology because of their capacity to thrive in water tainted with harmful elements (9, 10,11). Numerous studies highlight the potential of algae(both macro- and microalgae)to effectively remove harmful heavy metals from water (12,13).

Microalgae are able to withstand heavy metal poisoning thanks to cell absorption systems (14,15). In addition, it has been shown that hazardous metal ions can adsorb to the functional groups of microalgae cell walls (16). While ion exchange, reverse osmosis, electrodialysis, and ultra-filtration are all viable chemical and physical procedures for removing heavy metals from wastewater, biological treatment has intrigued scientists for years due to its high economic and operational efficiency (17,18). Bioremediation is the operation of utilising targeted microbes to degrade potentially hazardous contaminants in soil or water (19,20).

The microalgae's advantageous biomass output, low-cost culture, and efficient biological treatment make it a suitable technique. *Chlorella vulgaris* is a kind of microalgae that is particularly well-suited to this (21,22,23). Even though it's important to human existence and health, copper has been linked to negative impacts on the environment. Copper has been linked to gastrointestinal upset, renal damage, and anemia in humans (24,25). Some industries are major contributors of copper in industrial wastewaters. Copper ion concentrations in such wastewaters have been found to exceed 1000 mg/l (26). In aqueous solutions, chemicals and ions may easily move through the permeable cell walls of the *Chlorella vulgaris* algae. The cell wall provides a rich source of ligands with a variety of functional groups that can bind certain metal ions. Live or deactivated, these cells provide use (27).

Cobalt, a part of B12 vitamin that aids in the production of red blood cells, is also present in nature (28). Cobalt compounds are utilised in a variety of applications, including paints, medicine, agriculture, and industrial applications like grinding and cutting tools, the rise of cobalt levels is lead to poisonous (29). Eliminating or significantly reducing its environmental presence requires a biological approach. As a practical solution, algae's biosorption or resistance to cobalt might be used to control cobalt levels and stop water contamination (30).

## 2- Experimental Study:

### 2-1-*C.vulgaris* Growth:

We got the *C. vulgaris* strain of freshwater green microalgae from the Environmental Laboratory at the College of Science at the University of Babylon in Iraq for cultivation. Precultures of microalgae were established in CHU-10 medium (31)

Before planting the seeds in 5 L tubes, *Chlorella vulgaris* was grown in flasks in a growth chamber at 60-80 micromol m<sup>-2</sup> s<sup>-1</sup> and 28 + 2 C for 7 days. Microalgae utilized in bio removal tests were grown from seeds taken from the culture.

### 2-2-Determination of Algal Growth

*C. vulgaris* was grown in CHU-10 at 25 +1C and 16h:8h light:dark with 100-120 mol/m<sup>2</sup>/s intensity from a 5 mL starting volume in 1 L flasks with capacity of 800 mL in a growth chamber. Last but not least, Optical Density techniques at 540 nm were used to quantify algal growth after each 24 hour period.

## 2-3- Heavy metal processing

Deionized water was used to prepare all solutions used in this study. Copper and Cobalt solutions were prepared from reagent-grade metal of hydrated copper sulfate and hydrated Cobalt nitrate respectively. The solution pH was adjusted using reagent grade of HCl or diluted NaOH.

## 2-4- Experiment of Bioremoval method

To conduct the study, 100 ml of algal media containing microalgal cells with  $\text{Co}^{2+}$  and  $\text{Cu}^{2+}$  ions concentrations (1,1.5&3) mg/L was prepared (Kaplan, 2013 ;Colagar et al., 2011). The concentrations of each ions (before and after treatment) were measured by Atomic Absorption spectroscopy. . The concentrations were compared to blank controls.

$$\text{Algal Removal Efficiency} = \frac{(C_b - C_a)}{C_b} * 100$$

where:

$C_b$ : Concentration before treatment

$C_a$ : Concentration after treatment

## 3-Results and Discussion:

The current study explain that the initial concentrations for copper were (1,1.5&3)  $\text{mg.L}^{-1}$ . After bioremoval by *C.vulgaris* the final concentrations were (0.07, 0.05&0.13)  $\text{mg.L}^{-1}$  respectively.(Fig.1).

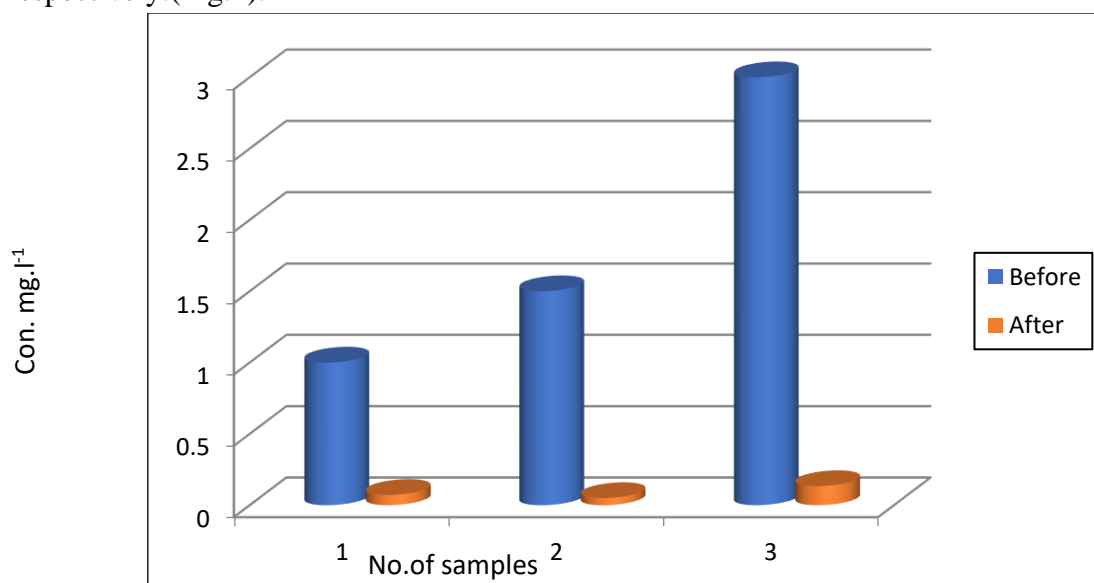


Fig.1. Copper Concentrations before and after removal by *C.vulgaris*

The Removal Efficiency % for Copper was (92.80, 96.67&95.54) Fig.3

It is anticipated that the biosorption of copper on algal cells is the result of a mixture of ion exchange, electrostatic relationships, surface complexation, and a minor contribution from intraparticle diffusion mechanisms(32).The findings suggested that the biomass of *C. vulgaris* is an extremely effective and eco-safe sorbent for the bioremoval of Copper from aqueous solutions, which may be applied on a large scale in industrial settings(33).

The results of the sorption experiment confirm *C.vulgars* is a good sorbent for the element copper than it does for nickel(34).

For Cobalt the initial concentrations were (1,1.5&3)  $\text{mg.L}^{-1}$  and the final concentrations were (0.02, 0.12&0.35)  $\text{mg.L}^{-1}$  respectively.(Fig.2).

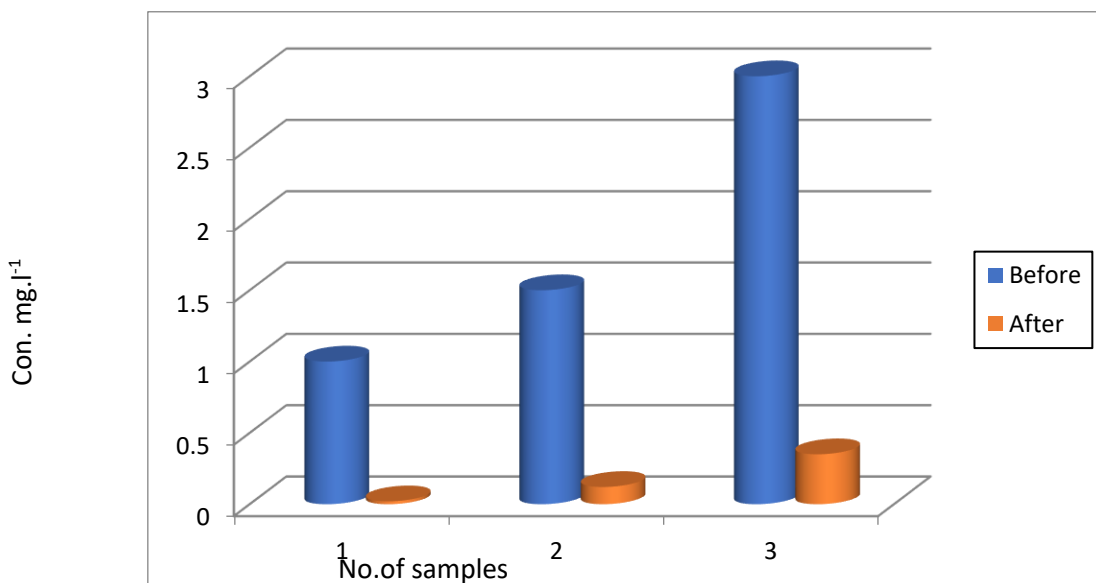


Fig.1. Cobalt Concentrations before and after removal by *C.vulgaris*

The Removal Efficiency % for Cobalt was (92.80, 96.67&95.54) Fig.3

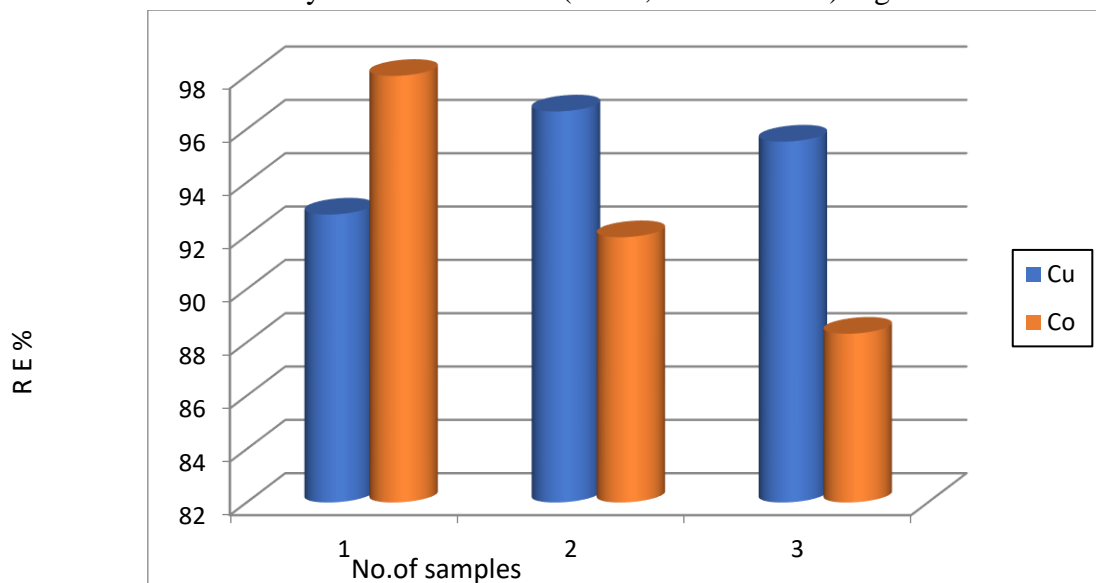


Fig.3 The Removal Efficiency % for Copper and Cobalt

Isolated from the surrounding environment, the *C. vulgaris* bacterium has the potential to function as reduction of  $Co^{+2}$  ions in solution or for the biosorption of these ions. The capacity for the bioremoval of Cobalt was reported to be 87% by *C. vulgaris* under conditions that were optimal for the removal of  $CO_2^{+}(35)$ . The algal biomass was successfully utilised as a sorbent for the purpose of bioremoval of Heavy metals from some solutions(36).

When compared to the traditional technologies of wastewater treatments, phytoremediation is the technology that offers the greatest potential for environmental preservation. Heavy metals cannot be broken down by the natural processes that occur in the environment, making them a threat not only to people but also to plants and animals. The primary contributor of oxygen to the atmosphere of aquatic environments is algae, which also play a role in the hyperaccumulation of heavy metals in these environments. These species generate a substantial quantity of biomass, which has

multiple applications, including environmental cleanup and the production of cutting-edge goods such as biodiesel, biomethane, organic fertilisers, feedstock, nanoparticles, and pharmaceutical items(37).

## References

1. Abrar, M.; Hussain, Z.; Akif, M.; Sok, K.; Muhammad, A.; Khan, A.; Khan, M. Textile effluents and their contribution towards aquatic pollution in the Kabul River (Pakistan). *J. Chem. Soc. Pak.* **2011**, 24, 106.
2. Mishra, S., Cheng, L., & Maiti, A. (2021). The utilization of agro-biomass/byproducts for effective bio-removal of dyes from dyeing wastewater: A comprehensive review. *Journal of Environmental Chemical Engineering*, 9(1), 104901.
3. Martini, S., & Roni, K. A. (2021, April). The existing technology and the application of digital artificial intelligent in the wastewater treatment area: a review paper. In *Journal of Physics: Conference Series* (Vol. 1858, No. 1, p. 012013). IOP Publishing.
4. Chakraborty, R., Asthana, A., Singh, A. K., Jain, B., & Susan, A. B. H. (2022). Adsorption of heavy metal ions by various low-cost adsorbents: a review. *International Journal of Environmental Analytical Chemistry*, 102(2), 342-379.
5. Foday Jr, E. H., Bo, B., & Xu, X. (2021). Removal of toxic heavy metals from contaminated aqueous solutions using seaweeds: A review. *Sustainability*, 13(21), 12311.
6. Masindi, V., & Muedi, K. L. (2018). Environmental contamination by heavy metals. *Heavy metals*, 10, 115-132
7. Eldridge, R.; Hanson, M. and de Jourdan, B.(2003)." Toward the development of a new toxicity test with the Arctic alga *Nitzschia frigida*". *Marine Pollution Bulletin*,188.
8. Expósito, N.; Carafa, R.;Kumar, V.; Sierra, J.; Schuhmacher, M.; Papiol, G.G. Performance of *Chlorella Vulgaris* Exposed to Heavy Metal Mixtures: Linking Measured Endpoints and Mechanisms. *Int. J. Environ. Res. Public Health* **2021**, 18,1037.
9. Hammouda, O., Abdel-Raouf, N., Shaaban, M., Kamal, M., Plant, B. S. W. T., 2015. Treatment of mixed domestic-industrial wastewater using microalgae *Chlorella* sp. *Am. J. Sci.* 11(12), 303-315.
10. Singh, J. S., Kumar, A., Rai, A. N., Singh, D. P., 2016. Cyanobacteria: a precious bio-resource in agriculture, ecosystem, and environmental sustainability. *Front. Microbiol.* 7, 529.
11. Al-Homaidan, A. A., Al-Qahtani, H. S., Al-Ghanayem, A. A., Ameen, F., Ibraheem, I. B., 2018. Potential use of green algae as a biosorbent for hexavalent chromium removal from aqueous solutions. *Saudi J. Biol. Sci.* 25, 1733-1738.
12. Ayangbenro, A. S., Babalola, O. O., 2017. A new strategy for heavy metal polluted environments: a review of microbial biosorbents. *Int. J. Environ. Res. Public Health.* 14, 94.
13. Ubando, A. T., Africa, A. D. M., Maniquiz-Redillas, M. C., Culaba, A. B., Chen, W. H., Chang, J. S., 2020. Microalgal biosorption of heavy metals: a comprehensive bibliometric review. *J. Hazard. Mater.* 402, 123431.
14. Petrovič, A., Simonič, M., 2016. Removal of heavy metal ions from drinking water by alginate-immobilised *Chlorella sorokiniana*. *Int. J. Environ. Sci. Technol.* 13,1761-1780.

15. Dulla, J. B., Tamana, M. R., Boddu, S., Pulipati, K., Srirama, K., 2020. Biosorption of copper (II) onto spent biomass of *Gelidiella acerosa* (brown marine algae): optimization and kinetic studies. *Appl. Water Sci.* 10, 1-10.
16. Kumar, K. S., Dahms, H. U., Won, E. J., Lee, J. S., Shin, K. H., 2015. Microalgae—A promising tool for heavy metal remediation. *Ecotox. Environ. Saf.* 113, 329-352.
17. Wang LK, *et al.* Environmental bioengineering. Springer Science & Business Media 2010; Vol. 11.
18. Wang J, Chen C. Biosorbents for heavy metals removal and their future. *Biotechnol Adv* 2009; 27(2): 195-226.
19. Eslami A, Nemati R. Removal of Heavy metal from aqueous environments using Bioremediation technology—review. *Journal of Health in the Field* 2017; 3(2).
20. Dwivedi S. Bioremediation of heavy metal by algae: current and future perspective. *Journal of Advance Laboratory Research in Biology* 2012; 3(3): 229-33.
21. Daliry S, *et al.* Investigation of optimal condition for *Chlorella vulgaris* microalgae growth. *Global Journal of Environmental Science and Management* 2017; 3(2): 217-30.
22. Scarsella M, *et al.* Study on the optimal growing conditions of *Chlorella vulgaris* in bubble column photobioreactors. *Chem Eng* 2010; 20: 85-90.
23. Kong W, *et al.* The characteristics of biomass production, lipid accumulation and chlorophyll biosynthesis of *Chlorella vulgaris* under mixotrophic cultivation. *Afr J Biotechnol* 2011; 10(55): 11620-30.
24. Kandah M, Abu Al-Rub FA, Al-Dabaybeh N. Competitive adsorption of copper-nickel and copper-cadmium binaries on SMW. *Eng Life Sci* 2002;8:237–43.
25. Kandah M, Abu Al-Rub FA, Al-Dabaybeh N. The aqueous adsorption of copper and cadmium ions on sheep manure. *Adsorpt Sci Technol* 2003;21:501–9.
26. Figueira MM, Volesky B, Ciminelli VST, Roddick. Biosorption of metals in brown seaweed biomass. *Water Res* 2000;34:196–204.
27. Abu Al-Rub FA, El-Naas MH, Benyahia F, Ashour I. Biosorption of nickel on blank alginate beads, free and immobilized algal cells. *Proc Biochem* 2004;39:1767–73.
28. Leyssens, L., Vinck, B., Van Der Straeten, C., Wuyts, F., Maes, L., 2017. Cobalt toxicity in humans-A review of the potential sources and systemic health effects. *Toxicol.* 387, 43-56.
29. Kalisińska, E., 2019. Human Population Increase and Changes in Production and Usage of Trace Elements in the Twentieth Century and First Decades of the Twenty-First Century. Mammals and Birds as Bioindicators of Trace Element Contaminations in Terrestrial Environments. Springer, pp. 3-20.
30. Sen, B., Alp, M. T., Sonmez, F., Kocer, M. A. T., Canpolat, O., 2013. Relationship of algae to water pollution and waste water treatment. 14, 335-54.
31. Chu, S. P.(1942).The influence of the mineral composition of the medium on the growth of planktonic algae. Part I. Methods and culture media. *J. Ecol.*, 30, 284-325.
32. Al-Rub, F. A., El-Naas, M. H., Ashour, I., & Al-Marzouqi, M. (2006). Biosorption of copper on *Chlorella vulgaris* from single, binary and ternary metal aqueous solutions. *Process Biochemistry*, 41(2), 457-464.)

33. Goher, M. E., AM, A. E. M., Abdel-Satar, A. M., Ali, M. H., Hussian, A. E., & Napiórkowska-Krzebietke, A. (2016). Biosorption of some toxic metals from aqueous solution using non-living algal cells of *Chlorella vulgaris*. *Journal of Elementology*, 21(3).
34. Mehta, S. K. and Gaur, J. P.(2001). Removal of Ni and Cu from single and binary metalsolutions by free and immobilized *Chlorella vulgaris*. 37( 3), 261-271.
35. Abdel-Raouf, N., Sholkamy, E. N., Bukhari, N., Al-Enazi, N. M., Alsamhary, K. I., Al-Khiat, S. H. A., & Ibraheem, I. B. M. (2022). Bioremoval capacity of Co<sup>2+</sup> using *Phormidium tenue* and *Chlorella vulgaris* as biosorbents. *Environmental research*, 204, 111630.
36. Kızılkaya, B., Doğan, F., Akgül, R., & Türker, G. (2012). Biosorption of Co (II), Cr (III), Cd (II), and Pb (II) ions from aqueous solution using nonliving *Neochloris Pseudoalveolaris* Deason & Bold: equilibrium, thermodynamic, and kinetic study. *Journal of Dispersion Science and Technology*, 33(7), 1055-1065.
37. Chugh, M., Kumar, L., Shah, M. P., & Bharadvaja, N. (2022). Algal Bioremediation of heavy metals: An insight into removal mechanisms, recovery of by-products, challenges, and future opportunities. *Energy Nexus*, 100129.