PHYCOREMEDIATION OF HEAVY METAL POLLUTANTS IN WATER SAMPLES FROM ASA DAM RIVER, ILORIN, KWARA STATE, NIGERIA

ABSTRACT

This study aimed to evaluate the effectiveness of phycoremediation using algae to reduce heavy metal contamination in the Asa Dam River. The heavy metals analyzed were lead (Pb), nickel (Ni), manganese (Mn), cadmium (Cd), and cobalt (Co). Mn had the highest concentration (0.1774 mg/l) and Co the lowest (0.0828 mg/l), with Co, Cd, and Pb exceeding WHO standards. Phycoremediation treatments at pH levels 5 and 8 were conducted. The study examined contact time, algae dosage, and pH effects on removal efficiency. Results indicated longer contact times enhanced adsorption, while higher biosorbent dosages decreased it, with optimal adsorption at 10 mg. Higher pH levels improved adsorption efficiency. The Heavy Metal Evaluation Index (HMEI) and Heavy Metal Toxicity Index (HMTI) showed significant reductions in these metals post-treatment, though Co showed minimal reduction. These results highlight phycoremediation's potential for mitigating heavy metal pollution in water bodies, with specific limitations for cobalt.

Keywords: Phycoremediation, Heavy Metals, Asa Dam River, Environmental Contaminants, Adsorption.

INTRODUCTION

Globally, the removal of environmental pollutants, organic pollutants, and heavy metals in aquatic ecosystems is essential due to the threat they pose to the life of plants and animals. Bioremediation, which involves using biological systems (such as bacteria, algae, fungi, and plants), living or dead, is a sustainable, eco-friendly, cheap, and scalable method compared to conventional physicochemical treatment methods (Yuvraj, 2022). Bioremediation technologies include various approaches such as phytoremediation, Phycoremediation, bioventing, bioattenuation, biosparging, composting, landfarming, thermal desorption, vitrification, air stripping, bioleaching, rhizofiltration, and soil washing. The primary goal of bioremediation is to remove or reduce harmful compounds to enhance soil and water quality (Canak *et al.*, 2019).

Heavy metals, which are metallic elements characterized by their density (> 4gcm^{-3}), atomic weight (> 23), or atomic number (>20), are found throughout the earth crust in water bodies, soil, and other ecosystems. Some heavy metals such as copper (Cu), selenium (Se), zinc (Zn), and iron (Fe) have essential biological and technological significance. Others, such as mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Ta), Manganese (Mn), and lead (Pb), exert toxic effects on biological systems even at low concentrations (Koller and Saleh, 2018).

The presence of heavy metals such as Pb, Co, Cd, Hg, As, Mn, etc., in aquatic ecosystems poses a potential risk to human health and associated ecosystems due to their toxicity, bioaccumulation, non-biological degradation, and indefinite persistence in the environment. (Koller and Saleh, 2018).

Heavy metals are primarily released into the environment and aquatic ecosystems from human and industrial activities such as mining, electroplating, metal processing, smelting, combustion textile, battery manufacturing, tanneries, petroleum refining, paint manufacture, pesticides, paper, pigment manufacture, printing and photographic industries, among others (Olguın and Sanchez-Galvan, 2012).

Conventional physicochemical methods used to remove heavy metal ions from industrial wastewater, such as chemical precipitation, chemical oxidation or reduction, electrochemical treatment, evaporative recovery, filtration, ion exchange, and membrane technologies, have drawbacks including incomplete removal, production of toxic secondary sludge, high costs, high-energy requirements, and eco-unfriendliness. Moreover, they may be ineffective when the metal concentration in the water is high (Ayele, Suresh and Benor, 2021). Biological methods such as bioremediation, and specifically phycoremediation, is a promising alternative for the removal of heavy metal ions.

Phycoremediation is the use of algae to bioremediate wastes or wastewaters, and it is a potential tool to eliminate excess toxic heavy metal and organic contaminants from the aquatic system. Algae have high photosynthetic efficiency, grow quickly, and are considered important primary producers in aquatic ecosystems (Phang, Chu and Rabiei, 2015).

The mechanism for the removal of heavy metals through algae works on the principle of adsorption onto the cell surface through energy-mediated transport of metal ions through the cell membrane (Ahmad *et al.*, 2020). Their ability to adsorb and metabolize heavy metals is associated with their large surface/volume ratios, the presence of high-affinity, metal-binding groups on their cell surfaces, and efficient metal uptake and storage systems (Phang, Chu and Rabiei, 2015). This study aims to explore the use of phycoremediation in the removal of heavy metals from the aquatic environment, focusing on a case study of Asa Dam River, Ilorin, Kwara State, Nigeria.

MATERIALS AND METHODS

Cultivation, Harvesting and Preparation of Micro-algae

Neosdesmus pupukensis MG257914 previously isolated in the laboratory in the Department of science laboratory technology, (LAUTECH), Ogbomosho, Oyo state was cultured in a Blue Green II (BG II) medium. The culture flask was incubated under natural light for photosynthesis and the flask was shaken twice daily to allow uniform penetration of light. The algae biomass was harvested on the 21st day using a centrifuge at 5000/rpm for 15 minutes. The biomass of the algae was washed with sterile distilled water thrice to remove the culture medium that was present in the cell. The algae powder was obtained by oven drying the filtrate at 70 °C. The resulting flake was ground using mortar and pestle, and sieved with a laboratory sieve to achieve uniform particle size.

Collection of Water sample from Asa Dam

Samples collection, preservation, digestion and analysis were carried out following the standard protocol to ensure quality control and quality assurance as described by Adeyinka et al. (2023).

Evaluation of Heavy metals in Wastewater

The presence and concentration of heavy metals present in the wastewater was determined using induced coupled plasma mass spectroscopy (ICP-MS).

Bio-adsorption Experiment

The bio-adsorption of heavy metals for the wastewater was investigated at different concentrations of dried biomass of NP (10 mg, 20 mg and 40 mg) also the pH was also varied at 5 and 8while the contact time for the experiment was set as 6hrs, 12hrs, and 18hrs. After the addition of the biomass to the wastewater, the mixture was manually agitated for 20min to enhance interaction between the biomass and the metallic concentration in the wastewater. At the expiration of each contact time, the solution was filtered using Whattman No1. Filter paper to separate the adsorbent from the solution. The solution was then subjected to ICP-MS to determine the concentration of the heavy metals.

Heavy Metal Evaluation Index (HMEI) and Heavy Metal Toxicity Index (HMTI)

Both the Heavy Metal Toxicity Index (HMTI) and the Heavy Metal Evaluation Index (HMEI) could provide information on the overall water quality related to heavy metal contamination. According to Singh et al. (2012), the HMEI is used to assess the level of heavy metal contamination in surface water. A result of less than 1.0 indicates that the water is "fit" for domestic use, whereas a value greater than 1.0 indicates that the water is "unfit." A heavy metal pollution level is considered low if the HEI value is less than 40, and medium contamination is suggested by a HEI value between 40 and 80. A high amount of heavy metal contamination is indicated by HEI values more than 80, which presents a serious concern to the quality of water and possibly human health (Edet and Offiong, 2002). The HMEI was determined using Equation 1.

$$HMEI = \sum_{i=1}^{n} \frac{H_{Conc}}{H_{MPC}} \quad (1)$$

Where HMEI is Health metal evaluation Index, H_{Conc} = the measured concentration of a given heavy metal and H_{MPC} = the maximum permissible concentration of the heavy metal.

The Agency for Toxic compounds and Disease Registry's priority list of hazardous compounds' toxicological profiles were used to calculate the HMTI by multiplying the overall score by the product of the individual contents measured at the research site (ATSDR, 2019). When assessing the level of hazardous heavy metals in surface water that are impacted by human activity, the HMTI that is acquired is a crucial instrument (Zakir *et al.*, 2020). HMTI was determined using Equation 2.

$$HMTI = \sum_{i=1}^{n} H_{conc} \times TS_{HM} \quad (2)$$

Where HMTI is Health metal toxicity Index, H_{conc} is the concentration of each heavy metal, and TS_{HM} is the total score of the same heavy metal by ATSDR.

RESULTS AND DISCUSSION

Concentration of heavy metals in Asa-Dam River Ilorin, Kwara State, Nigeria

The amount of some heavy metals in Asa-Dam River was presented in Figure 1. The result showed that Asa-Dam contains some heavy metals such as lead (Pb), Nickel (Ni), Manganese (Mn), Cadmium (Cd) and Cobalt (Co). Mn was the highest of all the heavy metals with the concentration 0.1774 mg/l and Co has the lowest concentration with the value 0,0828 mg/l. The concentrations of the heavy metals were in the order Mn > Pb > Cd > Ni > Co. The value obtained in this study is related to the result of Olawale *et al.* (2016), who reported the presence of Cd (0.0175 mg/l), Pb (0.1275 mg/l), Mn (0.3350 mg/l) and Cr (0.1875 mg/l) in dry season in Asa-dam river, Ilorin, Kwara State Nigeria. The result obtained in this research was compared with the WHO standard as shown in Figure 2. The result showed Cobalt (Co), Cadmium (Cd) and Lead (Pb) have higher concentration compare to their WHO standard. Cd and Pb have poisonous effect to human at high concentration. High blood pressure, kidney, tissue and red blood cells damage are effect of Cd toxicity. Acute Pb poisoning in human causes, kidney, liver, brain and central nervous system dysfunction (Olawale, Adeloju and Abdulkareem, 2016). The concentration of Nickel (Ni) and Manganese (Mn) were below the WHO standard. Nickel and Manganese are considered to be an essential trace element for human and animal health.

Reduction of Heavy Metals concentration through phycoremediation

Due to the high amount of toxic heavy metals such as Cadmium, Lead and Cobalt in the river. Removal of the heavy metals is inevitable before consumption. This research studied the removal of the heavy metals through phycoremediation by green algae. The trend of the change in the heavy metal concentration in the Asa-dam river sample after phycoremediation with 10 mg algae dosage at pH 5 and pH 8 was shown in Figure 3 and Figure 4 respectively. The result showed that there is decrease in the concentration of the heavy metals after treated with the algae for 6 hours, 12 hours and 18 hours. At pH 5 (Figure 3), there was a significant decrease in the concentration of Mn and Cd after 6 hours, however the decrease was insignificant for Pb, Ni and Co. After treatment at increased contact time, the reduction in the heavy metal concentration was well observed for Mn and Pb. There was a slight decrease in Ni, Cd and Co. This implies that at pH 5, Manganese and Leads' concentration reduced effectively with time. The trend of the concentration of the heavy metals at pH 8 (Figure 4) also showed a significant reduction after treatment with time. The result showed that there was a significant decrease in the concentration of all metals after treated for 6 hours. However, there was no significant decrease after treated further for another 6 hours i.e. 12 hours. After 18 hours of treatment of the water sample, there was a further reduction in the heavy metal concentration. The reduction was well pronounced for Pb and Mn and was minute for Co, Ni and Cd. From the observations from both pH 5 and 8, the concentration of Mn and Pb reduced significantly in the water sample after treatment by phycoremediation. There was also reduction in Co, Ni and Cd but the change in concentration was well pronounced at pH 8 and after treatment for 6 hours.

The amount of heavy metal adsorbed at contact time 6 hours, 12 hours and 18 hours with algae dosage of 10 mg, 20 mg and 40 mg at pH 5 and pH 8 were presented in Table 1. Using Table 1, the characteristics effect of some factors affecting the removal of heavy metals such as contact time, algae dosage and pH were presented.

Effect of Contact time on the amount of heavy metals adsorbed.

The effect of contact time on the amount of heavy metals adsorbed was presented in Figure 5(a-f). Figure 5a expressed the effect of contact time at pH 5 and algae dosage 10 mg. The result showed that for all metals, there was an increase in the amount of heavy metals adsorbed as the contact time increased. This indicates that at these conditions, the phycoremediation of the heavy metals in the Asa-dam river sample is effective. At 20 mg dosage (Figure 5b) the amount of metal adsorbed does not increase linearly with time. There was a decrease after 6 hours for Pb, Ni, and Co, however, Mn and Cd amount increased. All the metals have highest adsorption at 18 hours except Cd which had its highest at 12 hours. At 40 mg dosage, only cadmium, Cd adsorption increased with time. Ni and Co had their optimum time at 6 hours and 18 hours when treated with 40 mg dosage at pH 5 as shown in Figure 5c. Mn had its own at 6 hours. Optimum time is the time where the increment of adsorption stops and the equilibrium state is reached where a fixed or reduction in adsorbed heavy metal is observed. Lead, Pb had its optimum adsorption at 12 hours at this dosage.
A similar effect was not observed for the amount of heavy metals adsorbed at pH 8 (Figure 5d-f). At all dosages, there was an increase in the amount of adsorption of the metals with increase in contact time. However, the degree of increment is different. Figure 5d shows the effect at 10 mg dosage, showing an increase in all the heavy metals with time. There was a higher degree of adsorption in Pb than other metals. There was a pronounced increase in the lead Pb adsorbed after 12 hours. Ni, Co, and Mn had a small gradual increment with contact time while the increment was modest in Cd. At 20 mg dosage (Figure 5e), Co and Cd showed a gradual increase in the amount

adsorbed with time. Mn and Ni showed insignificant increases in adsorption with time as the amount of adsorbed at all contact time is almost the same. The result showed a decrease in the Pb adsorption from 6 hours to 12 hours then there was a very high adsorption at 18 hours. This indicated that the optimum contact time for Pb adsorption is 18 hours at pH 8 and a dosage of 20 mg. The result revealed a pronounced increase in the adsorption of Cd, Ni, and Pb with time at 40 mg dosage. However, the was a slight decrease in Ni adsorption from 6 hours to 12 hours after which a well-pronounced increment was observed at 18 hours. The same effect was observed for Mn though, the decrease from 6 hours to 12 hours was extensive. This indicates that Ni and Mn showed optimum adsorption at 18 hours. Overall, the observations from this study showed that more heavy metals are adsorbed at higher contact times. However, this effect was not observed for all the metals at all conditions, this may be due to the nature and interaction of the heavy metals with the algae adsorbents affecting the mechanism of adsorption.

Effect of algae biosorbent dosage on amount of heavy metals adsorbed.

The efficiency of heavy metals adsorbed also depends on the dosage of the adsorbent. In this study, the effect of the algae biosorbent dosage on the amount of some heavy metals adsorbed during phycoremediation process at different pH and contact time were expressed in Figure 6(a-f). The results in Figure 6a-c showed the effect at pH 5, contact time 6, 12, and 18 hours. At 6 hours (figure 6a) contact time, the results showed a significant decrease in the amount of cadmium (Cd) and Manganese (Mn) as time increase while it increased slightly in cobalt (Co). In Lead (Pb) and Nickel (Ni), the amount adsorbed increases when the dosage increases from 10 mg to 20 mg when it decreases gradually till 40 mg.

This indicates that there is an increase in the adsorption of Pb and Ni metal till an equilibrium or optimum state is reached, at this point, a constant or reduction in adsorbed heavy metal may be observed. The optimum dosage for Pb and Ni is 20mg. For other heavy metals, their optimum dosage is 10 mg. At contact time 12 hours (Figure 6b) and 18 hours (Figure 6c), there was a decrease in the amount of heavy metals adsorbed as dosage increased from 10 mg to 40 mg. There was a significant decrease observed for Cadmium (Cd) and manganese (Mn) compare to Co, Ni, and Pb which shows a smaller decrement.

Figure 6d, 6e, and 6f show the amount of heavy metals adsorbed at dosages 10mg, 20 mg and 40 mg at adsorption conditions of pH 8, contact time 6, 12, and 18 hours respectively. The result in Figure 6d shows there is a decrease in the adsorbed metals for all the analyzed heavy metals. Manganese, Mn and Cadmium Cd show a high decrease after treatment at 10 mg. The fall in amount adsorbed continues greatly as the dosage increase. A linear but smaller decrease was observed for Nickel, Ni and lead, Pb compare to Mn and Cd. However, the reduction in amount of cobalt was very small and insignificant. This shows that at all the heavy metals' optimum dosage is 10 mg, albeit the degree of reduction after the optimum state is reached differs.

At contact time 12 hours (figure 6e), the same effect was observed as the amount adsorbed decrease as the dosage increase from 10 mg, 20 mg to 40 mg for all metals. Although, there was a slight difference for Pb, there was a decrease in the amount adsorbed from 10 mg to 20 mg, then, at 40 mg there was no further decrease the amount of lead metal adsorbed remains constant. This indicated an equilibrium state where the adsorption remains constant is reached. The same effect is observed for all the heavy metals at 18 hours. At this condition, the amount of all the heavy metals decreases significantly after treatment with 10 mg to 20 mg, they then decrease slightly afterward. Ni and Co show insignificant decrease steadily.

Overall, the amount of the heavy metals adsorbed reduces as the dosage of the biosorbent increases. This indicates that the heavy metals reach their optimum condition at lower dosage of 10 mg. However, this effect is not well pronounced in the adsorption condition of pH 5, contact time 6 hours and pH 8 contact time 18 hours.

Effect of pH on Heavy Metal Adsorption

The pH of solution during the adsorption process is an important parameter that controls the efficiency of the process. Acidity and alkalinity of the contact solution affect the adsorption capacity of the adsorbent. In this study the effect of pH at acidic (pH 5) and alkaline (pH 8) was expressed as shown in Figure 7-9. Figure 7 showed the effect of pH on the amount of heavy metals adsorbed at dosage 10 mg. The result showed that the amount of all the heavy metals adsorbed is higher at pH 8 than at pH 5. For all the heavy metals, the amount at pH 8 increased with almost half of the amount at pH 5. This indicates that the adsorption capacity increases with increase in the pH. Acidity decreases adsorption capacity. These can be attributed to the conflict between metal ions and hydrogen ions as well as the variation in metal ion hydrolysis products with pH (Cozmuta *et al.*, 2012).

At dosage 20 mg (Figure 8), the same effect was observed as the amount of heavy metals adsorbed at pH 8 is higher. However, effect on the amount of each metals adsorbed differs. Though the amount of cobalt (Co) adsorbed at pH 8 is higher, the difference between the amount at pH 5 and pH 8 is very small. Nickel (Ni) adsorbed at pH 8 is more than twice as much as amount at pH 5. Cadmium (Cd), Manganese (Mn) and lead (Pb) show more adsorption about double of the amount at pH. Overall, at acidic condition, the adsorption capacity reduces and increases at alkaline state, however, the increment is smaller in cobalt (Co) unlike other metals (Ni, Cd, Mn and Pb) where the increment is well pronounced.

Figure 9 shows the effect of pH at dosage 40 mg. Just like at other dosage there is an increase in the adsorption capacity of the heavy metals at alkaline conditions, pH 8. The increase is higher in manganese (Mn) than in the other heavy metals (Figure 9). All the heavy metals have a well pronounced increase in their adsorption at pH 8. The amount adsorbed at pH 8 is about 4 times higher than that of pH 5. This indicates that at higher dosage there are more interactions between hydrogen ion and the adsorbent hindering the adsorption of the heavy metals. Lead (Pb), Nickel (Ni) and cobalt (Co) also have an increment more than twice of the amount adsorbed at pH 5. Cadmium (Cd) has the least increment but it was about 30% increase.

Overall, pH of the solution affects the adsorption capacity. Increase in pH increases the adsorption efficiency due to more interactions between the heavy metal and the adsorbent as the hydrogen ion concentration decreases.

Heavy Metal Evaluation Index

The Heavy Metal Evaluation Index (HMEI) was utilized to assess the water quality of the Asa Dam River both prior to and following treatment with dried biomass (Table 3). According to the HMEI, water quality is classified as having low heavy metal pollution if the HMEI value is below 40. A medium level of contamination is indicated by values ranging from 40 to 80, and a high level of contamination is indicated by values exceeding 80. These thresholds represent significant risks to water quality and potentially to human health (Edet and Offiong, 2002). In this study, the overall HMEI values indicated that the Asa Dam River exhibited a low degree of heavy metal pollution, both before and after treatment, as the HMEI values were below 40 in all samples. However, the contamination levels of individual heavy metals varied. Metals with HMEI values below 1.0 were classified as low-level contaminants, whereas values above 1.0 indicated high contamination (Singh *et al.*, 2017). Before treatment, all evaluated heavy metals, except manganese (Mn) with an HMEI of 0.4435, were high-level contaminants with HMEI values greater than 1. Post-treatment analysis revealed a significant reduction in the contamination levels of the water. All heavy metals exhibited a substantial decrease in contamination levels, except cobalt (Co). Cobalt's HMEI values remained high, decreasing only slightly from 8.28 before treatment to 6.37 after treatment, indicating persistent high-level contamination. In the treated water sample, cadmium (Cd) had an HMEI of 1.27, while lead (Pb) had a value of 1.064, indicating a low-level contamination around the threshold level. The HMEI values for manganese (Mn) and nickel (Ni) were 0.083 and 0.579, respectively which indicate a significant low-level contamination. These results demonstrate the efficacy of phycoremediation using the adsorbent in significantly reducing the contamination levels of Cd, Mn, Ni, and Pb, while proving ineffective for Co.

Heavy Metal Toxicity Index

The toxicity impact and status of the toxic heavy metals in the Asa Dam River, both before and after treatment, were assessed using the Heavy Metal Toxicity Index (HMTI). Table 4 presents the HMTI values for each heavy metal. The data demonstrate that HMTI values decreased following treatment, indicating a reduction in toxicity; however, the percentage reduction varied, reflecting differences in adsorption efficiency. Lead (Pb) exhibited the highest toxicity levels in both treated and untreated samples, with HMTI values of 209.75 and 81.45, respectively. Cobalt (Co) had the lowest toxicity before treatment, with an HMTI value of 84.04, while manganese (Mn) had the lowest toxicity post-treatment, with an HMTI value of 26.61. The phycoremediation process resulted in a 61.17% reduction in Pb toxicity. Nickel (Ni), cadmium (Cd), and manganese (Mn) also showed substantial reductions in their toxicity indices, with decreases of 43.40%, 69.25%, and 81.23%, respectively. In contrast, cobalt exhibited a minimal reduction in toxicity, with a decrease of only 23.07%. These results indicate that the phycoremediation process significantly reduced the toxicity of most heavy metals evaluated in the Asa Dam River. However, cobalt's minimal reduction suggests that the treatment was less effective for this particular metal.

CONCLUSION

This study assessed the concentration and toxicity of selected heavy metals—lead (Pb), nickel (Ni), manganese (Mn), cadmium (Cd), and cobalt (Co)—in the Asa Dam River before and after treatment with phycoremediation using dried biomass. Mn was found to be the most prevalent metal at 0.1774 mg/l, whereas Co had the lowest concentration at 0.0828 mg/l. The heavy metal concentrations followed the order: Mn > Pb > Cd > Ni > Co. Notably, the concentrations of Co, Cd, and Pb exceeded the World Health Organization (WHO) standards, posing potential health risks. Phycoremediation was conducted using various algae dosages at pH levels 5 and 8. The study observed an increase in heavy metal adsorptions at pH 8, indicating pH sensitivity in the adsorption process. Key factors influencing heavy metal removal, such as contact time, algae dosage, and pH, were thoroughly evaluated. The findings indicated that extended contact times improved heavy metal adsorption. Conversely, increasing the dosage of biosorbent resulted in reduced adsorption, suggesting that optimal heavy metal removal occurred at lower dosages of around 10 mg. Additionally, higher pH levels enhanced adsorption efficiency, attributed to increased interactions between heavy metals and the adsorbent. The evaluations using the Heavy Metal Evaluation Index (HMEI) and Heavy Metal Toxicity Index (HMTI) demonstrated that phycoremediation significantly reduced the contamination and toxicity levels of Cd, Mn, Ni, and Pb. However, this method was less effective for Co, indicating the need for alternative or supplementary treatments for complete remediation. The study confirms that phycoremediation is a viable and effective method for mitigating heavy metal pollution in the Asa Dam River, with specific limitations in addressing cobalt contamination. Future research should focus on optimizing conditions and exploring additional methods to enhance the removal efficiency for all heavy metals present.

Acknowledgments

The authors wish to acknowledge the Management of the Federal University of Health Sciences, Ila-Orangun, Osun State, Nigeria, Mangosuthu University of Technology, South Africa, Ladoke Akintola University of Technology, Ogbomoso, Oyo State, Nigeria. For providing the enabling environment for this research work.

Conflict of Interest

All authors declare no conflicts of interest in this paper

REFERENCES

Adeyinka, G.C., Afolabi, F. and Bakare, B.F. (2023) 'Evaluating the fate and potential health risks of organochlorine pesticides and triclosan in soil, sediment, and water from Asa Dam River, Ilorin Kwara State, Nigeria', *Environmental Monitoring and Assessment*, 195(1), pp. 1–14. Available at: https://doi.org/10.1007/s10661-022-10783-5.

Ahmad, S. *et al.* (2020) 'Phycoremediation : Algae as Eco-friendly Tools for the Removal of Heavy Metals from Wastewaters', in R.N. Bharagava and G. Saxena (eds) *Bioremediation ofIndustrial Waste for Environmental Safety*. Singapore: Springer Nature Singapore Pte Ltd., pp. 53–76. Available at: https://doi.org/https://doi.org/10.1007/978-981-13-3426-9_3.

Ayele, A., Suresh, A. and Benor, S. (2021) 'Phycoremediation of Heavy Metals, Factors Involved and Mechanisms Related to Functional Groups in the Algae Cell Surface – A Review', in J.

Aravind et al. (eds) *Strategies and Tools for Pollutant Mitigation - Avenues to a Cleaner Environment*, pp. 269–289. Available at: https://doi.org/https://doi.org/10.1007/978-3-030-63575-6.

Canak, S. *et al.* (2019) ‘Bioremediation and green chemistry’, *Fresenius Environmental Bulletin*, 28(4), pp. 3056–3064.

Cozmuta, L.M. *et al.* (2012) ‘The influence of pH on the adsorption of lead by Na-clinoptilolite: Kinetic and equilibrium studies ’, *Water SA* . scieloza , pp. 269–278.

Edet, A.E. and Offiong, O.E. (2002) ‘Evaluation of water quality pollution indices for heavy metal contamination monitoring. A study case from Akpabuyo-Odukpani area, Lower Cross River Basin (southeastern Nigeria)’, *GeoJournal*, 57(4), pp. 295–304. Available at: https://doi.org/10.1023/B:GEJO.0000007250.92458.de.

Koller, M. and Saleh, H.E.-D.M. (2018) ‘Introducing Heavy Metals’, in H.E.-D.M. Saleh and R.F. Aglan (eds) *Heavy Metals*. First. London, United Kingdom: IntechOpen, pp. 3–11.

Olawale, S.A., Adeloju, E. and Abdulkareem, A. (2016) ‘Concentrations of heavy metals in water , sediment and fish parts from Asa River , Ilorin , Kwara state’, *Imperial Journal oof Interdisciplinary Research of Interdisciplinary Research (IJIR)*, 2(4), pp. 142–150.

Olguın, E.J. and Sanchez-Galvan, G. (2012) ‘Heavy metal removal in phytofiltration and phycoremediation : the need to differentiate between bioadsorption and bioaccumulation’, *New Biotechnology*, 30(1), pp. 3–8. Available at: https://doi.org/10.1016/j.nbt.2012.05.020.

Phang, S., Chu, W. and Rabiei, R. (2015) ‘Phycoremediation’, in D. Sahoo and J. Seckbach (eds) *The Algae World, Cellular Origin, Life in Extreme Habitats and Astrobiology*. 26th edn. Springer Science+Business Media Dordrecht, pp. 357–389. Available at: https://doi.org/10.1007/978-94-017-7321-8.

Singh, R. *et al.* (2017) ‘Assessment of potentially toxic trace elements contamination in groundwater resources of the coal mining area of the Korba Coalfield, Central India’, *Environmental Earth Sciences*, 76(16). Available at: https://doi.org/10.1007/s12665-017-6899-8.

Yuvraj, S. (2022) ‘Microalgal Bioremediation: A Clean and Sustainable Approach for Controlling Environmental Pollution’, in *Innovations in Environmental Biotechnology*, pp. 305–318. Available at: https://doi.org/doi : 10.1007/978-981-16-4445-0_13.

APPENDIX

LIST OF FIGURES

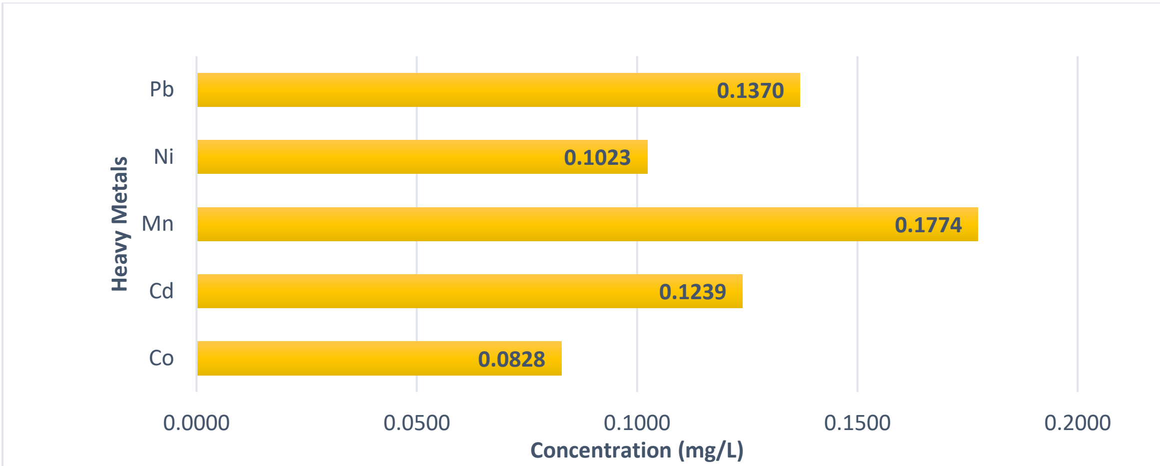


Figure 1: Concentration of some heavy metals in Asa-Dam River

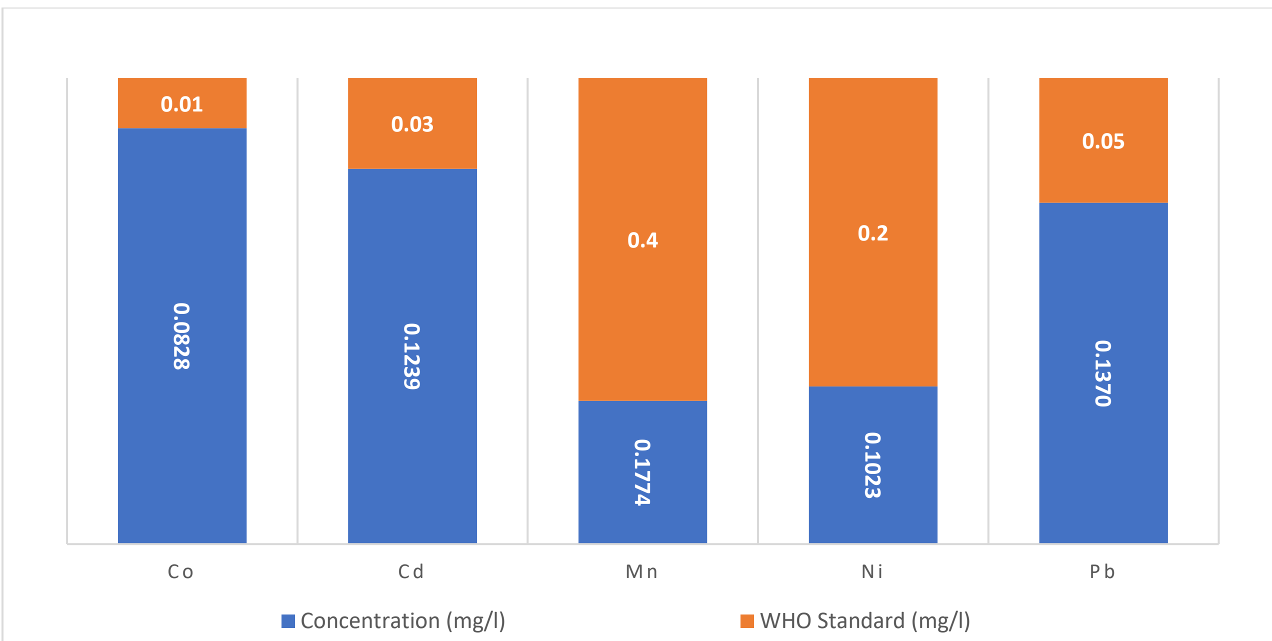


Figure 2: Comparison of heavy metal concentration with WHO standard

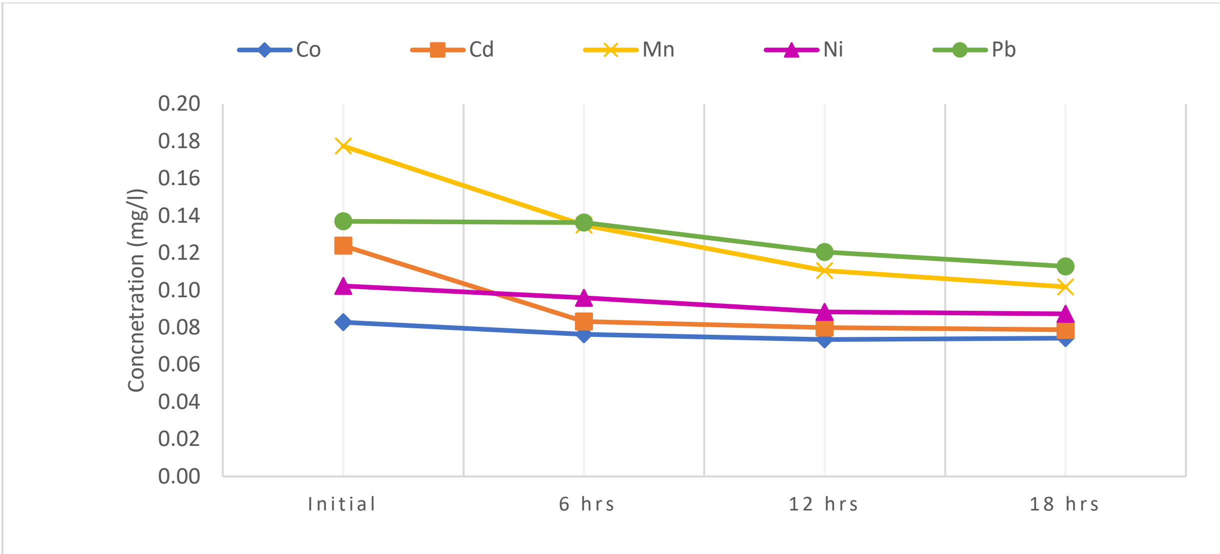


Figure 3: Change in concentration of heavy metals with 10 mg algae at pH 5

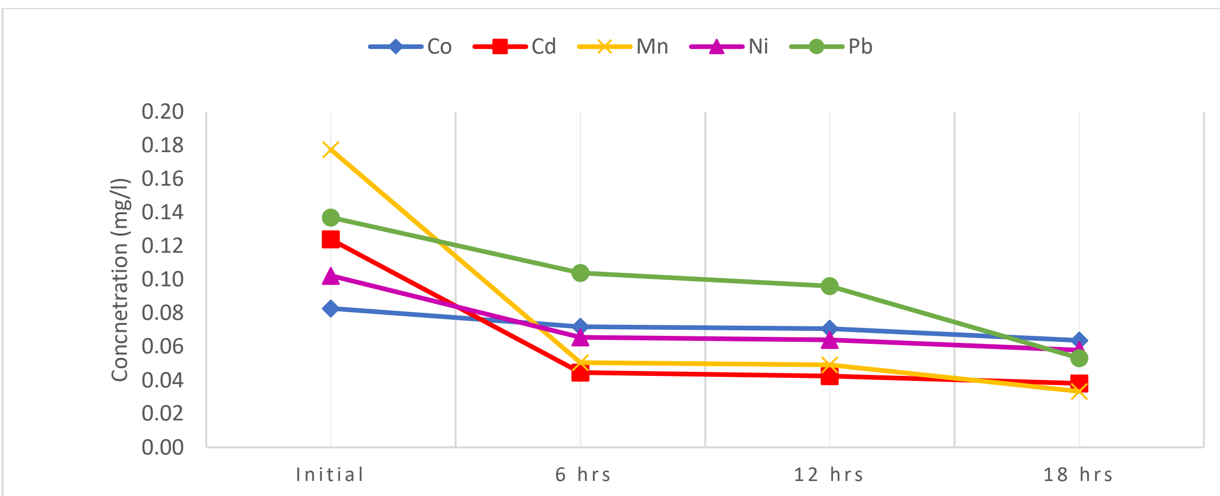
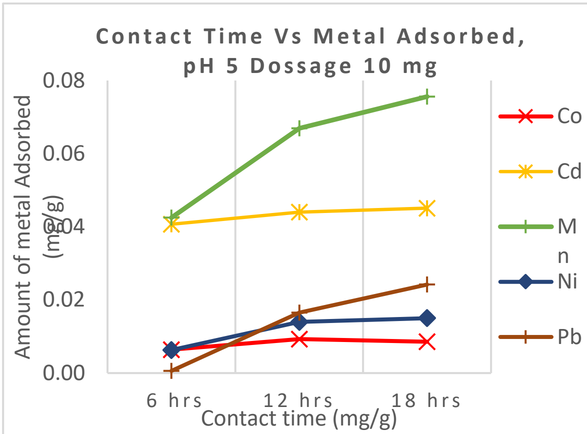
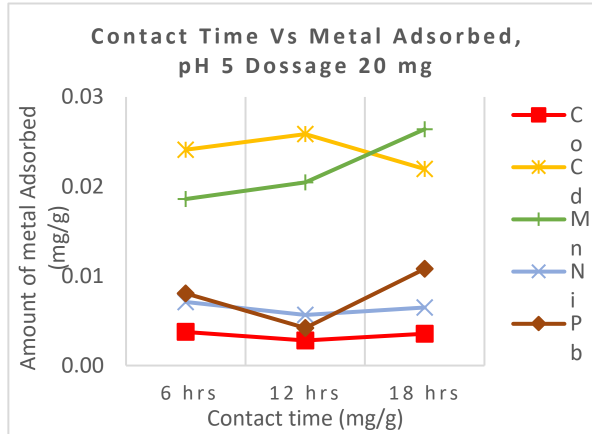


Figure 4: Change in concentration of heavy metals with 10 mg algae at pH 8



(a)



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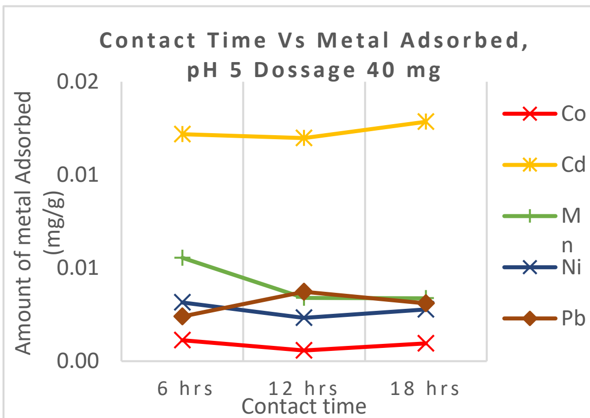

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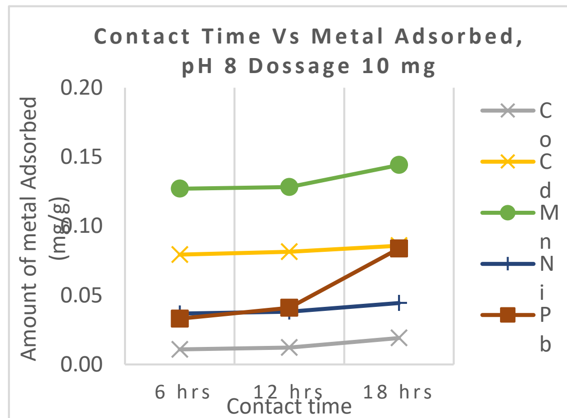
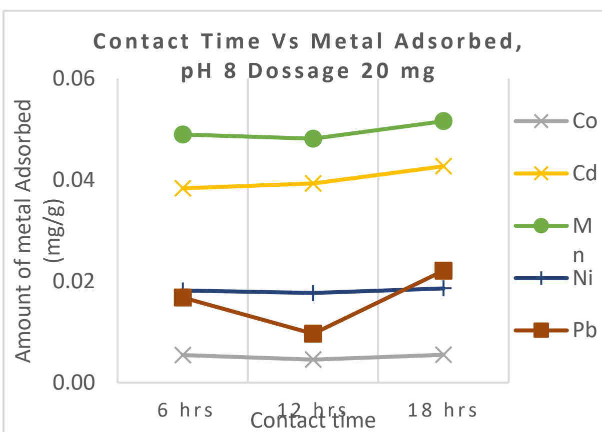
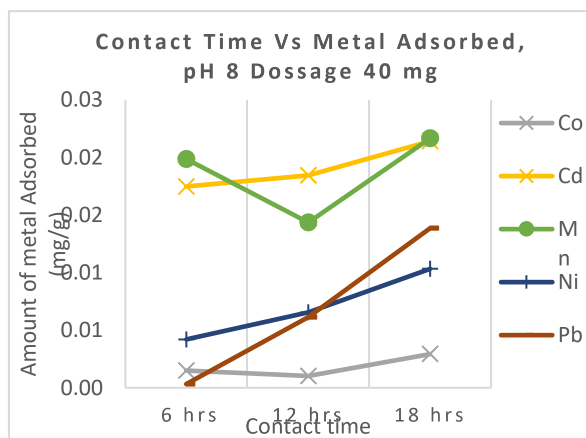


(d)



(e)



(f)

Figure 5: Amount of heavy metal adsorbed with contact time (a) pH 5, dosage 10 mg (b) pH 5, dosage 20 mg (c) pH 5, dosage 40 mg (d) pH 8, dosage 10 mg (e) pH 8, dosage 20 mg (f) pH 8, dosage 40 mg

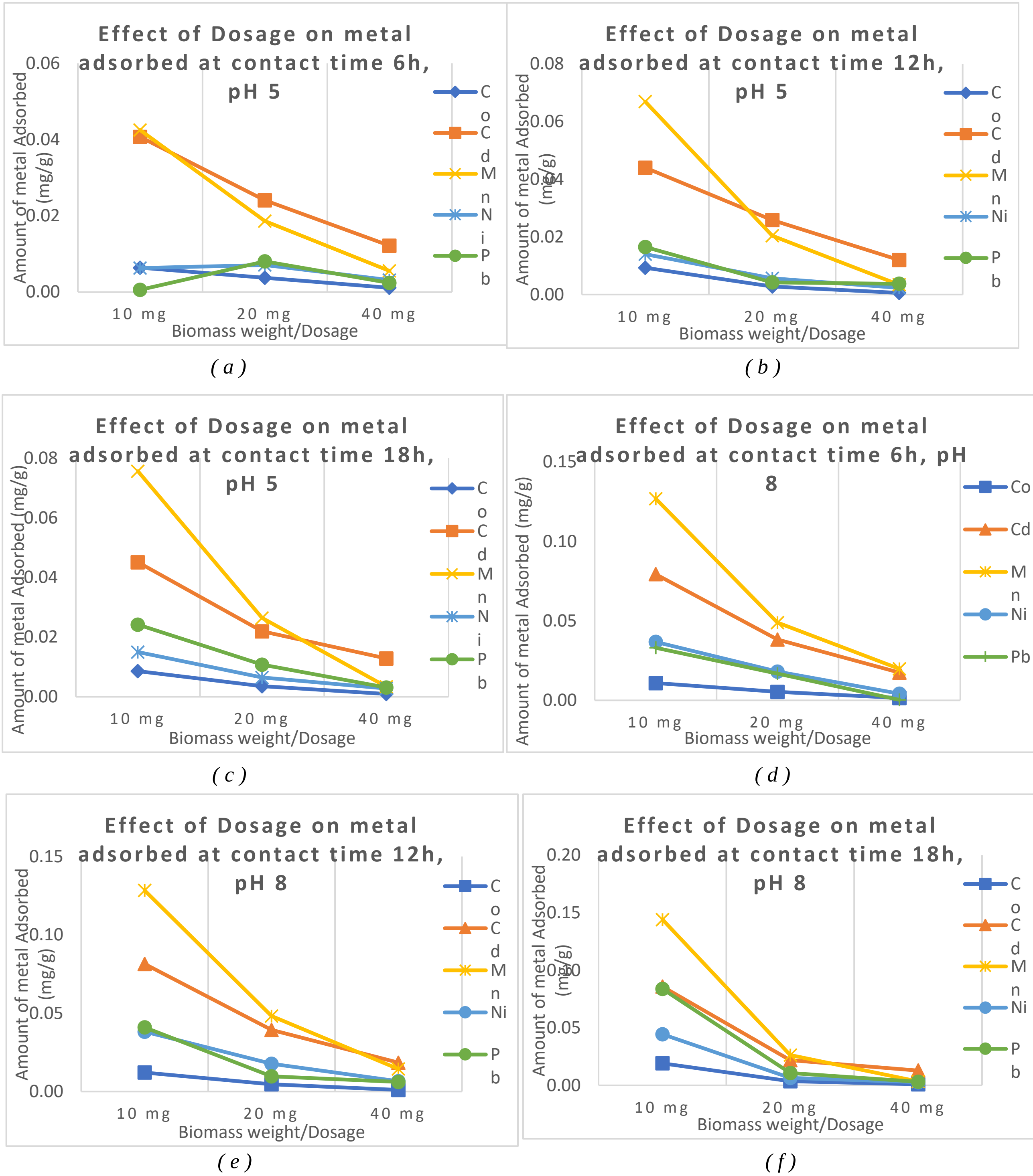


Figure 6: Effect of dosage of algae biosorbent on heavy metal adsorbed at (a) pH 5, 6 hours (b) pH 5, 12 hours (c) pH 5, 18 hours (d) pH 8, 6 hours (e) pH 8, 12 hours (f) pH 8, 18 hours

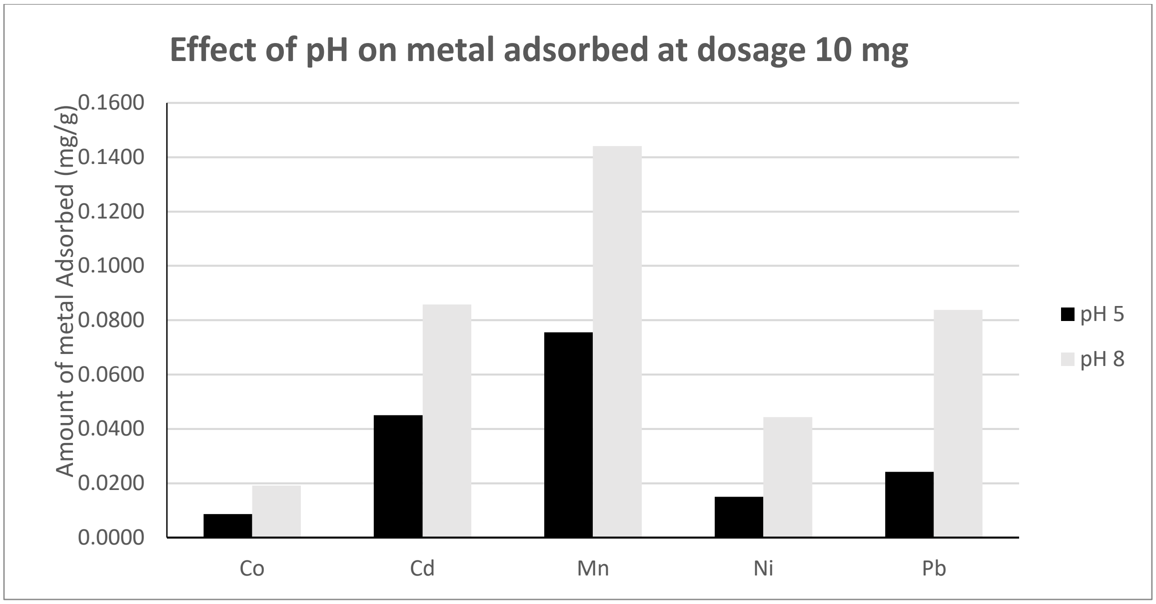


Figure 7: Plot of amount of metal adsorbed at pH 5 and 8 for dosage 10mg

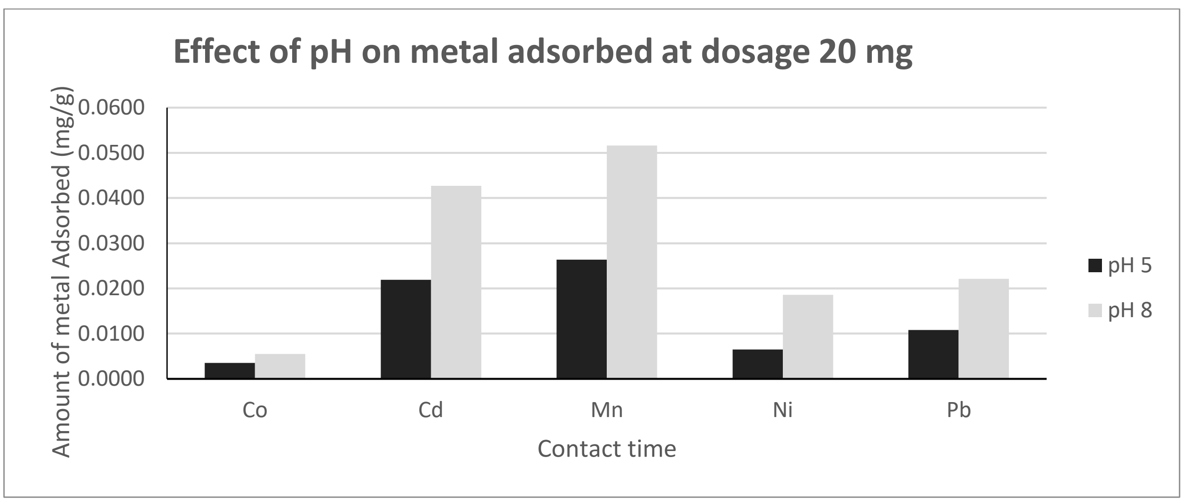


Figure 8: Plot of amount of metal adsorbed at pH 5 and 8 for dosage 20mg

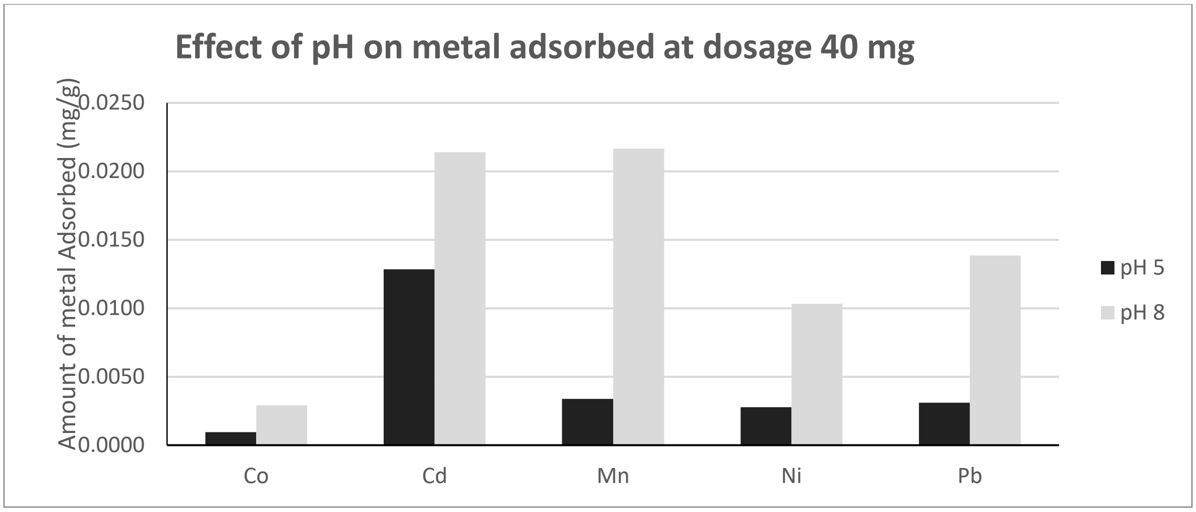


Figure 9: Plot of the amount of metal adsorbed at pH 5 and 8 for dosage 40mg

LIST OF TABLES

Table 1: Amount of heavy metal adsorbed after treatment at pH 5 and pH 8.

Heavy metal	Dosage (mg)	6 hours (mg/g)		12 hours (mg/g)		18 hours (mg/g)	
		pH 5	pH 8	pH 5	pH 8	pH 5	pH 8
Co	10	0.0064	0.0109	0.0093	0.0121	0.0086	0.0191
	20	0.0038	0.0055	0.0028	0.0046	0.0036	0.0055
	40	0.0011	0.0015	0.0006	0.0010	0.0009	0.0029
Cd	10	0.0407	0.0794	0.0440	0.0814	0.0451	0.0858
	20	0.0241	0.0384	0.0259	0.0394	0.0220	0.0427
	40	0.0122	0.0175	0.0120	0.0184	0.0129	0.0214
Mn	10	0.0425	0.1270	0.0669	0.1283	0.0756	0.1441
	20	0.0186	0.0490	0.0205	0.0482	0.0264	0.0516
	40	0.0056	0.0199	0.0034	0.0144	0.0034	0.0217
Ni	10	0.0063	0.0368	0.0140	0.0382	0.0150	0.0444
	20	0.0071	0.0182	0.0057	0.0177	0.0065	0.0186
	40	0.0032	0.0042	0.0023	0.0066	0.0028	0.0103
Pb	10	0.0006	0.0331	0.0165	0.0409	0.0242	0.0838
	20	0.0081	0.0168	0.0042	0.0097	0.0108	0.0221
	40	0.0024	0.0003	0.0037	0.0061	0.0031	0.0139

Table 2: Concentration of heavy metals in Asa-dam river Ilorin, Kwara State

Heavy Metal	**Initial Concentration (mg/l)**	**WHO Standard (mg/l)**
Co	0.0828	0.01
Cd	0.1239	0.03
Mn	0.1774	0.4
Ni	0.1023	0.2
Pb	0.1370	0.05

Table 3: Heavy Metal Evaluation Index of the initial and final concentration of wastewater after treatment at optimum conditions.

	Initial Concentration	**final Concentration**	**HMEI(initial)**	**HMEI(final)**
Co	0.0828	0.0637	8.28	6.37
Cd	0.1239	0.0381	4.13	1.27
Mn	0.1774	0.0333	0.4435	0.08325
Ni	0.1023	0.0579	1.023	0.579
Pb	0.137	0.0532	2.74	1.064
		∑HMEI	**16.6165**	**9.36625**

Table 4: Heavy Metal Toxicity Index of the initial and final concentration of wastewater after treatment at optimum conditions.

	Initial Concentration	**final Concentration**	**Toxicity Score (**ATSDR, 2019)	**HMTI(initial)**	**HMTI(final)**	**% Efficiency**
Co	0.0828	0.0637	1015	84.04	64.66	23.07
Cd	0.1239	0.0381	1317	163.18	50.18	69.25
Mn	0.1774	0.0333	799	141.74	26.61	81.23
Ni	0.1023	0.0579	994	101.69	57.55	43.40
Pb	0.137	0.0532	1531	209.75	81.45	61.17
			∑HMTI	**700.39**	**280.44**	**59.96**