

Biosorbent From Uncharred Dry Leaves of *Ficus Nota* (Blanco) Merr. For Nickel (II) Removal in Wastewater

^{*1)} Joshua B. Bufi ²⁾ Samuel Omar S. Gerio ³⁾ Manuel Bayani S. Bukas ⁴⁾ Maria Teresa M. Mina
¹⁾Kalinisan Chemical Corp., Cavite, Philippines ²⁾Camarines Norte, Philippines ³⁾A THPAL Nickel Corp. Surigao Del Norte, Philippines ⁴⁾ Bicol University College of Engineering, Legazpi City, Albay, Philippines

*email: bufi.joshuabejo@gmail.com, geriosamuelomars@gmail.com, manuelbukasjr16@gmail.com, mtmmina@bicol-u.edu.ph

Abstract

The mining sector is facing increasing demands to adopt environmentally-friendly practices due to growing concerns about the negative impacts of its operations on the environment and local communities. As a result, the industry is actively exploring ways to reduce water usage and improve the handling of wastewater. This situation has led to the development of improved mineral processing techniques and the integration of innovative approaches to treating wastewater.

The utilization of biosorbent, derived from uncharred dry leaves of *Ficus nota* (blanco) merr, has been found to be a proficient adsorbent for the elimination of nickel (II) from polluted water. It was found that in this study the adsorption process is most efficient at pH 4.5 based on the one-factor graph. Percent removal is decreasing beyond pH 7 because of the presence of nickel hydroxide precipitation. It was discovered that a high amount of sorbent dosage increases the percent removal of nickel in the aqueous solution. It was also found that as the initial concentration increases, the percent removal of nickel decreases because the capacity of the treatment process to remove nickel from the wastewater becomes overwhelmed as the concentration of nickel increases.

This study examines the feasibility of using biosorbent made from uncharred dry leaves of *Ficus nota* (blanco) merr. to remove Nickel (II) from wastewater. The researchers aim to find a different use for uncharred dry leaves of *Ficus nota* (blanco) merr as a means of reducing waste disposal. The study offers potential solutions to combat Nickel (II) pollution in mining wastewater, while also promoting sustainable waste management practices.

Keywords: biosorbent, *ficus nota*, adsorption

1. Introduction

The issue of water pollution is putting the people's health at risk, and it is a significant problem affecting many areas. The number of people who die each year from consuming unsafe water is higher than the casualties from war and all other types of violence combined. Additionally, the sources of potable water are limited, with less than 1% of the world's freshwater being easily accessible, and the situation is projected to worsen by 2050, as the global need for freshwater is anticipated to be one-third higher than it is now.

Chemicals and heavy metals from industrial and municipal wastewater are the main contributors in contaminating the water. These contaminants are toxic to aquatic life—most often reducing an organism's life span and ability to reproduce. They make their way up the food chain as predators eat prey. "Heavy metal" describes any metal element that is dense and can be harmful in small amounts. There are plenty of heavy metals that can contaminate the waters, and one of the alarming types of it is Nickel. Nickel compounds are hazardous at high concentrations, yet they are frequently insoluble in water, limiting the potential for harm. Nickel tetracarbonyl, for example, is water insoluble but poisonous and carcinogenic nonetheless. Higher amounts of nickel frequently cause vomiting, resulting in quick removal from the body.

The retrieval of heavy metals from industrial wastes and wastewater has become a crucial concern for the environment. Ni has many useful applications but it is harmful if discharged into natural water resources. The wastewater from industries such as silver refineries, electroplating, zinc base casting and storage battery industries contain Ni(II). When present in higher amounts, Ni(II) can lead to the development of lung, nasal, and bone cancer. Dermatitis (Ni itch) is the most frequent effect of exposure to Ni, such as coins and costume jewelry. Exposure to Ni carbonyl [Ni(CO)₄] at 30 ppm for 30 minutes is estimated to be deadly in humans. Ingesting a large amount of Ni(II) can result in immediate symptoms such as headache, dizziness, nausea, and vomiting. Other signs include chest pain, tightness, a dry cough, and difficulty breathing, leading to rapid respiration, weakness, cyanosis, and extreme fatigue. Hence, it is essential to remove Ni(II) from industrial wastewaters before mixing with natural water sources.

Typical techniques used to eliminate Ni(II) from wastewater involve processes such as chemical precipitation, ion exchange, filtration, chemical reduction, electrodeposition, and adsorption using activated carbon. But due to operational demerits and high cost of the treatment, some new technologies have been tried for a long time. Among them less expensive non conventional adsorbents are being investigated.

Activated carbon is a popular choice for use as an adsorbent, but it is costly. Therefore, contemporary researchers are seeking alternative, more affordable adsorbents, particularly bioadsorbents due to their greater availability, low cost as compared to activated carbon and eco-friendly. *Ficus nota* (Blanco) Merr. (*Moraceae*) plant, also called "tibig" or "tabog" in the Philippines, is native to the country. This particular fig species is highly valued for its medicinal properties and is among the valuable trees cultivated and cared for by rural families in Leyte province. "Tabog-tabog" Fig tree is also known for its antimicrobial, antioxidant, and free radical scavenging properties that makes it an interesting raw material to be studied especially for treating wastewater and making sure that the quality of water is good.

Ficus nota (Blanco) Merr. leaves contain cellulose, hemicellulose, lignin, pectin, and other extractives such as waxes. Metal ions tend to stick to certain types of molecules in plants, such as carboxylic, phenolic, hydroxyl, and carbonyl groups, which can be found in hemicellulose, pectin, cellulose, and lignin. The goal of this study focuses on the production and application of biosorbent made from uncharred dried leaves of *Ficus nota* (Blanco) Merr. to remove nickel ions in water and be able to have cleaner and safer waters.

2. Materials and Methods

2.1 Materials

Dry fallen leaves of *Ficus nota* were collected from sacking trees at Brgy. Pawa, Tabaco City. These leaves were washed thoroughly with distilled water three to four times to remove dust and particulate matter from their surface. Washed leaves were dried at 105 °C for 1-2 hours in a hot air oven. The dried leaves were pulverized. It was then sieved using a 100-mesh screen. The pulverized leaves were treated with 1M HCl for 1 hour on a shaker at 100 rpm to activate the surface functional groups. The digest was repeatedly washed with distilled water to remove the excess acid then filtered using Whatman Filter Paper, dried in shadow and stored in air tight containers until further use. This sample was designated as *Ficus nota* biomass (FNB).

2.2 Characterization of the Adsorbent

Analysis of particle size and physical properties of the adsorbent was done through Scanning Electron Microscope (SEM) analysis.

2.3 Determination of Equilibrium Contact Time

To establish the experimental conditions in which the batch adsorption operations will be carried out, the equilibrium contact time should be known. In this experiment, eight (8) 50 mL samples

of nickel solution with 100 ppm Ni (II) were treated at 0.25, 0.5, 1, 2, 3, 4, 5, and 6 hours, respectively with 3.0 grams of FNB and were stirred continuously at 200 rpm using a magnetic stirrer. The pH of the samples was set at 4.25.

2.4 Batch Adsorption Experiments

2.4.1 Preparation of Ni (II) Solution

For biosorption experiments, stock nickel solution of 1000 ppm was prepared by dissolving 0.023214 g of nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$) in 1000 mL deionized distilled water (DDW). Ni (II) solutions at different concentrations were prepared by adequate dilution of stock solution with DDW. All the glassware and polypropylene flasks used in the experiments were immersed overnight in 10% (v/v) HNO_3 nitric acid and rinsed several times with DDW.

2.4.2 Ni (II) Determination Method

The Ni (II) determination was done using UV-Vis Spectroscopy. The 200 ppm Nickel solution was used to measure the lambda max of 200.1 nm. The five samples of 100-500 ppm were subjected to the maximum wavelength to measure each absorbance. This data was used for the calibration curve of the molar absorptivity. The Ni (II) concentration of the treated sample was determined using UV-Vis Spectrophotometry. The Ni (II) removal efficiency (Ni (II) RE) was calculated using the following equation:

$$\text{Ni(II) RE (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100$$

where C_0 and C_e are the initial and final Ni (II) (mg/L), respectively.

2.4.3 Experimental Design and Optimization

The effects of pH, dosage and initial Nickel concentration of the samples were optimized by using Response Surface Methodology (RSM). Box Behnken Design was used in RSM. The independent variables and the coded levels are shown in Table 3.1. The experiential runs were conducted at room temperature. The pH of the solution was adjusted using 0.1 M HCl and 0.1 M NaOH solution. The solutions were stirred continuously at 200 rpm in a magnetic stirrer until the determined equilibrium time was reached.

Table 2.1 Design of experiment for Ni removal using treated *Ficus nota* Biomass

Factors	Units	Low	High
pH		2	7
Adsorbent Dosage	g	1.5	7
Nickel Concentration	ppm	50	150

The data for Box-Behnken was evaluated using analysis of variance (ANOVA) and with the use of Design Expert Version 13. The design was performed with a total of 17 experimental runs. The runs are composed of two level and three factorial runs.

3. Results and Discussion

3.1 Characterization of the Biosorbent

The Scanning Electron Microscopy (SEM) has been widely used in characterizing the surface morphology of various materials, including plant samples. In this study, *Ficus nota* Blanco Merr. before and after treatment were subjected to SEM analysis to examine its surface morphology at different magnifications. The aim of this investigation is to provide a comprehensive understanding of the structural features of *Ficus nota* Blanco Merr. using SEM, and to determine how these features may

relate to its adsorption capability as a potential biosorbent in treating Nickel in wastewater. Figure 3.1 (a and b) shows the SEM image of the *Ficus nota* biomass before and after treatment.

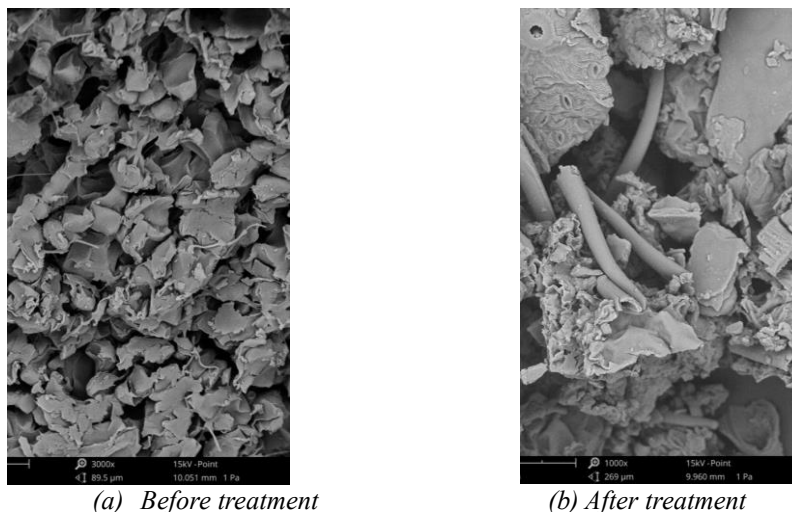


Figure 3.1 SEM Images of FNB

3.2 Determination of Equilibrium Contact Time

As shown in the graph, it can be observed that after a contact time of 5 hours, there is no significant increase in the Ni(II) RE. It is important to note the sudden increase of Nickel removal efficiency after 1 hour. After that there is an almost minute increase in efficiency until it reaches the contact time. This shows that the equilibrium of the adsorption process had already been attained. Therefore, this contact time was used in the succeeding batch adsorption experiments.

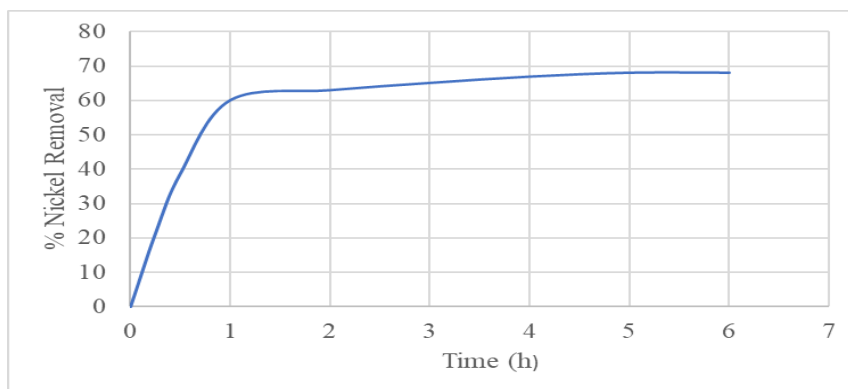


Figure 3.2 Plot of Contact Time vs Ni (II) Removal

3.3 Modeling

Response Surface Methodology was utilized in order to analyze the effects of the independent variables and their interaction on the Ni(II) removal efficiency.

Among the probable models, the quadratic model was suggested since it gave the maximum and yet closest, Adjusted R-Squared and Predicted R-Squared of 0.9799 and 0.9035, respectively. The actual response versus the predicted response is shown in Figure 3.3, which shows the general fit of the actual data to the predicted Ni removal efficiency.

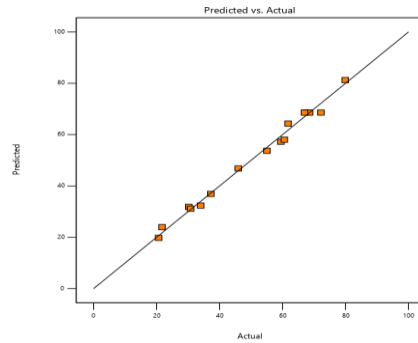


Figure 3.3 Predicted Response vs Actual Response

3.4 Response Surface

The response surface to the Ni removal of the synthetic wastewater using *Ficus nota* as adsorbent are shown in Figures 3.4 to 3.7. The curvatures of the surface demonstrate the behavior of the quadratic model and the results further demonstrate that the Ni RE of the nickel solution is strongly affected by the pH and initial concentration.

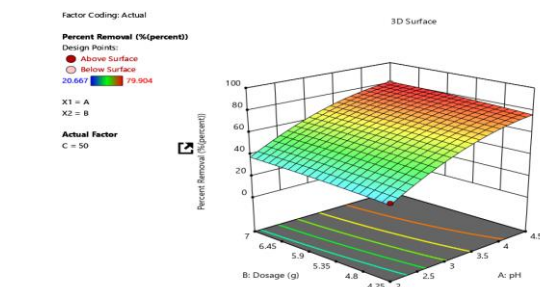


Figure 3.4 Response surface showing the effect of dosage and pH

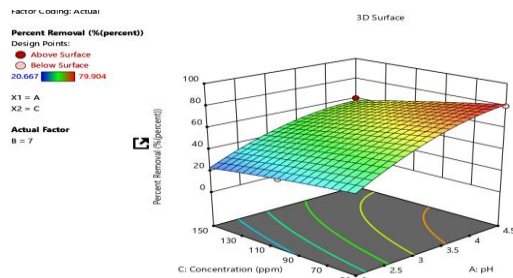


Figure 3.5 Response surface showing the effect of concentration and pH

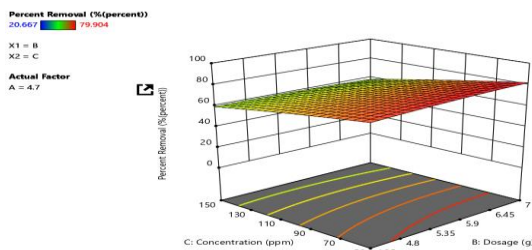


Figure 3.6 Response surface showing the effect of concentration and dosage

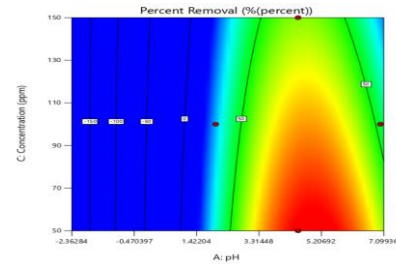


Figure 3.7 Contour Plot for the Effect of Interactions between initial nickel concentration and pH

3.5 Optimization of Parameters

Necessary constraints are set to obtain the optimum value of the adsorbent dosage, initial nickel concentration, and pH to achieve the highest percent removal, and table 3.1 below summarizes them.

Table 3.1 Optimum Values for Operating Variables

pH	Adsorbent Dosage	Concentration	Percent Removal
4.12044	1.51992	50.0003	65.28

To verify the validity of the model generated in explaining the behavior of the adsorption of nickel, experimental runs were performed using the optimum values. Table 3.2 gives the percent removal of nickel with an experimental error of 2.6166%, showing that the model adequately links the response variable to the operational parameters.

Table 3.2 Predicted and Observed Percent Degradation under Optimal Conditions

Run no.	Predicted Percent Removal of Nickel	Actual Percent Removal of Nickel	% Error
1	67.0321	65.284	2.6777
2	66.9523	65.284	2.5555
Average			2.6166

4. Conclusion

Ficus Nota Biomass (FNB) Biosorbent was successfully produced from uncharred dry leaves of Ficus Nota (Blanco) Merr. activated by Hydrochloric acid. It was identified as a highly efficient low-cost biosorbent that can remove nickel (II) from aqueous solution of wastewater.

The effect of operating parameters, namely the pH, adsorbent dosage and initial nickel concentration were evaluated on the removal of nickel (II) in wastewater. It was found that the adsorption process is most efficient at pH 4.5. Percent removal is decreasing beyond pH 7 because of the presence of Nickel hydroxide precipitation. A high amount of adsorbent dosage increased the percent removal of nickel in the aqueous solution as it provided a larger surface area for adsorption. However, there is a limit to how much adsorbent can be added before it becomes saturated. The initial nickel concentration in wastewater also had a significant effect on the percent removal of nickel. As the initial concentration increased, the percent removal of nickel decreased because the capacity of the treatment process to remove nickel from the wastewater became overwhelmed as the concentration of nickel increased.

Scanning Electron Microscopy (SEM) Analysis of the FNB Biosorbent showed that the average particle size of the treated and untreated Ficus nota biomass was small and very acceptable since small particle size provides large surface area for adsorption. The SEM images also showed an average porous surface of the treated biomass, which is a characteristic of a subpar adsorbent since adsorbates will adhere on these micropores.

The Response Surface Model (RSM), implemented in Design Expert, was utilized to identify the optimal operating conditions for the parameters of pH at 4.5667, adsorbent dosage of 1.922 g, and initial nickel concentration of 50.0059 ppm which led to the maximum possible percent removal efficiency of nickel (II) in the aqueous solution. The ideal situation displays 66.8956% maximum removal of nickel using the optimized parameters specified. Predicted percent removal value from RSM vs Actual Percent removal of nickel value from confirmatory experiment shows a percent error of 1.8676 % which means the values are relevant with one another proving that the biosorbent is effective.

References

- [1] McCarty, P. L. (2012). What Is Wastewater? Water & Wastes Digest. Retrieved from <https://www.wwdmag.com/wastewater-treatment/wastewater-treatment/article/>
- [2] Lenntech. (n.d.). Heavy Metals. Retrieved from
- [3] Lee, Y., Kim, M. K., & Kim, H. (2005). Heavy metal contamination and health risk assessment in the vicinity of the abandoned Songcheon Au-Ag mine in Korea. Environmental Geochemistry and Health, 27(2), 79-89. <https://doi.org/10.1007/s10653-004-6014-4>
- [4] Osman, A. G. M., & Al-Reasi, H. A. (2009). Heavy metals pollution in water and sediments of

- The River Nile at Sohag Governorate, Upper Egypt. *Water Science and Technology*, 60(4), 921-932. <https://doi.org/10.2166/wst.2009.447>
- [5] Nakayama, S. M. M., Serikawa, Y., Kurishima, K., & Nakamura, M. (2001). Solvent extraction of heavy metals from incineration fly ash: the possibility of metal recovery and the removal of toxicity. *Separation and Purification Technology* 22-23, 543-549. [https://doi.org/10.1016/S1383-5866\(01\)00149-6](https://doi.org/10.1016/S1383-5866(01)00149-6)
- [6] Rahman, M. A., & Saha, N. (2018). Environmental risk assessment of heavy metals in water and sediment of Karnaphuli River, Bangladesh. *Marine Pollution Bulletin*, 131, 236-243. <https://doi.org/10.1016/j.marpolbul.2018.04.023>
- [7] Manginsay, J., & Paltiyon, A. (2021). Potential Use of Magnetic Nanoparticles in the Treatment of Wastewater. *IOP Conference Series: Materials Science and Engineering*, 225(1), 012105. <https://doi.org/10.1088/1757-899X/225/1/012105>
- [8] de Castro, M. A. F., Trinidad, L. C., & Fernandez, J. J. M. (2020). Adsorption Efficiency of Coated Sand for Phosphates and Nitrogen Nutrients from Aquaculture Wastewater. *Philippine Agricultural Scientist*, 103(2), 212-222. <https://doi.org/10.46937/1032020>
- [9] de Padua, L. S., & Bunye, V. M. (n.d.). Tibig. Retrieved from <http://www.stuartxchange.org/Tibig>
- [10] Sulistyowati, D., Kartika, N. F., & Fadilah, N. (2018). Total Phenolic and Flavonoid Contents and Free Radical Scavenging Components of *Ficus nota* Merr. (Moraceae) Ethanolic Leaf Extract. *Indonesian Journal of Chemistry*, 18(3), 498-503. <https://doi.org/10.22146/ijc.27802>
- [11] Limpin, M. D. C., de la Torre, R. A., & Trajano, V. N. A. (2018). Antibacterial, Histochemical, and Phytochemical Screening and Cytotoxicity Activity of Tubog (*Ficus nota* Blanco Merr.) Leaf and Fruit Extracts. *Journal of Pharmacy and Biological Sciences*, 13(4), 50-57. <https://doi.org/10.9790/3008-1304015057>
- [12] Solis, N. R. (2016). Issues and Challenges in the Management of Municipal Solid Waste in a Philippine Coastal City. *Philippine Journal of Science*, 145(2), 139-151. <https://doi.org/10.3860/pjs.145.2.07>
- [13] Burac, C. P., Laroza, E. P., & Baldrias, J. C. (2018). Chemical Composition and Antibacterial Activity of Essential Oil of *Lantana camara* L. Leaves against Selected Pathogenic Bacteria. *Research in Molecular Pharmacology*, 4(1), 1-9. <https://rmrj.usjr.edu.ph/rmrj/index.php/RMRJ/article/view/107>
- [14] Taguba, Y. L. T., & Japitana, R. M. (2018). Antibacterial, Histochemical, and Phytochemical Screening and Cytotoxicity Activity of Tubog (*Ficus nota* Blanco Merr) Leaf and Fruit Extracts. *Journal of Pharmacognosy and Phytochemistry*, 7(2), 2276-2280. https://www.researchgate.net/publication/326972720_Antibacterial_Histochemical_and_Phytochemical_Screening_and_Cytotoxicity_Activity_of_Tubog_Ficus_nota_Blanco_Merr_Leaf_and_Fruit_Extracts
- [15] Eusebio, R. M. B., Pama, G. L., & Reyes, R. G. B. (2013). Evaluation of the Chemical Constituent and Biological Activities of Selected Philippine Medicinal Plants. In 2013 DLSU Research Congress (Vol. 4, pp. 139-155). De La Salle University.
- [16] Dizon, J. R. C., & Carreon, M. C. (2017). Antibacterial Activity of the Ethanolic Extract of Tarragon (*Artemisia dracunculus* L.) Leaves against Selected Pathogenic Bacteria. *Journal of Advanced Chemical Sciences*, 3(1), 24-28. <https://www.jacsdirectory.com/journal-of-advanced-chemical-sciences/articleview.php?id=184>
- [17] Fajardo, A. C., & Navarro, P. M. R. (2018). Antimicrobial Activities of Selected Plant Extracts against Selected Food Pathogens. *Journal of Environmental Science and Management*, 21(1), 1-11. [https://neptjournal.com/upload-images/\(36\)B-3673.pdf](https://neptjournal.com/upload-images/(36)B-3673.pdf)
- [18] Paraguya, R. K. M., & de Guzman, A. B. (2017). Antibacterial Activity of Selected

- Philippine Medicinal Plants against *Staphylococcus aureus* and *Escherichia coli*. *Journal of Environmental Science and Management*, 20(1), 1-11.
- [20] Marques, M., & Pinheiro, J. P. (2009). Adsorption of heavy metals from mining wastes by low-cost natural and modified materials. *Journal of Hazardous Materials*, 163(2-3), 768-775. <https://doi.org/10.1016/j.jhazmat.2008.07.084>
- [19] Kwon, Y. N., & Yun, Y. S. (2009). Removal of anionic surfactants from aqueous solution by activated carbons and carbon nanotubes. *Journal of Hazardous Materials*, 164(2-3), 1139-1143. <https://doi.org/10.1016/j.jhazmat.2009.01.019>
- [20] Liu, J., Shi, R., Zhang, Y., Chen, L., Chen, X., & Chen, H. (2018). Adsorption behavior and mechanism of Zn^{2+} on Al_2O_3 particles in aqueous solution. *Environmental Science and Pollution Research*, 25(32), 32415-32424. <https://doi.org/10.1007/s11356-018-2963-7>
- [21] Chaudhuri, M., & Das, D. (2008). Heavy metal pollution and its control through green adsorption technology. *Chemical Engineering Journal*, 143(3), 141-149. <https://doi.org/10.1016/j.cej.2008.05.029>
- [22] Bayongan, E. C., & de Guzman, M. R. T. (2018). Antibacterial, histochemical, and phytochemical screening and cytotoxicity activity of tubog (*Ficus nota* Blanco Merr.) leaf and fruit extracts. *Journal of Nature Studies*, 17(1), 17-25. <https://www.ukdr.uplb.edu.ph/journal-articles/3976/>
- [23] Zhang, H., Chen, J., Zhao, G., Guo, X., Liu, G., & Wang, X. (2015). Efficient removal of heavy metal ions using porous magnetic Fe_3O_4 /graphene oxide composites. *Journal of Hazardous Materials*, 283, 484-492. <https://doi.org/10.1016/j.jhazmat.2014.09.075>
- [24] Hua, M., & Xu, C. (2022). Recent advances in heavy metal removal from wastewater by biochar. *Frontiers in Sustainability*, 2, 765592. <https://doi.org/10.3389/frsus.2022.765592>
- [25] Wang, Q., Qu, J., & Cheng, Y. (2021). Comprehensive review on the removal of heavy metal ions from wastewater by adsorption. *Nature Reviews Materials*, 6, 618-640. <https://doi.org/10.1038/s41578-021-00311-1>
- [26] Netsol Water Solutions Pvt. Ltd. (2021). How are heavy metals removed from wastewater? NetsolWater. <https://netsolwater.com/how-are-heavy-metals-remove-from-wastewater>
- [27] Shah, S. S., & Adil, S. (2017). Adsorption basics, part 1. *Chemical Engineering Progress*, 113(7), 26-33. <https://doi.org/10.1002/cep.10400>
- [28] Aslam, M. Z., Ramzan, N., Naveed, S., & Feroze, N. (n.d.). Ni(II) removal by BIOSORPTION using *Ficus religiosa* (peepal) leaves. *Journal of the Chilean Chemical Society*. Retrieved April 27, 2023, from https://www.scielo.cl/scielo.php?script=sci_arttext&pid=S0717-97072010000100019
- [29] Environmental Management Bureau. (2019). DENR Administrative Order No. 2016-08: Water quality guidelines and general effluent standards of 2016. Retrieved from https://emb.gov.ph/wp-content/uploads/2019/04/DAO-2016-08_WATER-QUALITY-GUIDELINES-AND-GENERAL-EFFLUENT-STANDARDS.pdf