CHAPTER-6

Revolutionizing Coffee toxicity: Sustainable Heavy Metal Remediation Using Rice Husk Synthesized Silica Nanoparticles and Metal Quantification

6.1: INTRODUCTION

The prevalence of poisonous toxic heavy metals in the soil of the Kerala region has presented a considerable obstacle for those involved in the coffee industry there. These metals not only endanger the taste of the coffee, but they also raise worries about the potential effects they could have on human health. Coffee plants may store heavy metals including Pb, Cd, and As that they absorb from polluted soil [1-3]. This could reduce the quality of the final coffee product that is consumed by humans.

The removal of toxic heavy metal contamination from agricultural systems has been investigated from a number of different angles over the course of many years. The traditional approaches include both physical and chemical treatments, such as washing the soil and precipitation. These treatments can be both expensive and harmful to the environment. As a direct consequence of this, there is an increasing demand for creative and long-term solutions to successfully address this problem [4-7].

The usage of adsorbents made from biomass has gained attention in recent years as a potentially beneficial strategy for the remediation of polluted sites. When it comes to the production of adsorbents, biomass materials, such as waste from agricultural production, offer a resource that is both renewable and economical. RHA is an example of one of these types of biomass waste that is abundantly available in agricultural regions such as North Gujarat. RHA has a high silica content, which enables it to be extracted and converted into nanoparticles with superior adsorption capabilities [8-12].

Investigating the use of SNPs produced from RHA in coffee remediation could have substantial repercussions for the overall quality of coffee as well as the long-term viability of the ecosystem. The prevalence of harmful heavy metals in the soil of Kerala, a state that is well-known for its coffee production, presents the state with a number of unique issues. Utilising the adsorption properties of these SNPs in the indigenous coffee-growing districts of Kerala could provide a long-term and environmentally responsible solution to the problem of heavy metal contamination.

In addition, it is of the utmost significance to investigate the efficacy of RHA-derived SNPs in the context of this discussion. It would not only solve the urgent problem of toxic heavy metal accumulation in coffee plants, but it would also contribute to improving the general quality and safety of the coffee that is produced in the region. This would be a win-win situation. This uncharted territory offers an intriguing prospect for multidisciplinary inquiry and cooperative work among agricultural specialists, environmental scientists, and stakeholders in the coffee sector [13-15].

In this research, we propose a new biomass adsorption method that makes use of RH-synthesized SNPs from the Navsari special variety "GNR-3" to remove potentially toxic heavy metals from Robusta coffee grown in the Kerala region. This strategy uses RH to produce the SNPs. We hope that by utilising the adsorption characteristics of these SNPs, we will be able to give a solution that is both long-term and economical for the problem of enhancing the quality and safety of the coffee that is produced in the area.

6.2: RESULT AND DISCUSSION

6.2.1: SNPs: Their Properties Analysed

In order to assess the synthesised SNPs potential for use in heavy metal removal, a thorough set of analytical methods was used to characterise them. The SNPs atomic structure and atomic phase could be deduced via an XRD analysis. Scanning and transmission electron microscopy were utilised to learn more about the SNPs structure and surface chemistry. We determined the elemental composition of the sample using EDX, and the surface area of the sample was revealed using BET analysis. AFM was applied in order to conduct in-depth research on the topography of nanoparticles.

6.2.2: Heavy Metal Contamination

The essential or harmful nature of toxic heavy metals makes it quite concerning that they are found in food. This is a problem that is of great concern. Here, we assess the concentrations of many metals like Fe, Cu, Zn, Mn, Pb, and Ni in coffee from the Kerala region. The safety of our food supply is crucial to our health and the health of our communities. Even while eating a diversified diet can minimise the risk of certain health problems, the majority of the nutrients we obtain still comes from our regular meals. Half of the world's population, for instance, eats rice as their main staple food. In contrast, rice is more susceptible to toxic heavy metal contamination than other crops. When compared to wheat, it may accumulate heavy metals at a rate almost three times higher. Toxic heavy metals' toxicity, bioaccumulation, and potential health effects are all major causes for alarm. Maximum

Allowable Concentrations (MAC) for heavy metals in rice has been determined by international organisations and national governments in an effort to reduce the severity of the associated health risks. However, there are still potential dangers to human health even at quantities lower than the MAC. According to research, long-term exposure to even relatively low levels of toxic heavy metals can result in non-carcinogenic illnesses such as cancer, hypertension, and neurological issues. Additionally, the hazards of exposure vary depending on factors such as age, body mass, geography, and dietary preferences, which makes vulnerable people more susceptible. Therefore, in addition to adhering to MAC values, health risk assessments should take into consideration numerous aspects such as body weight, age, dietary habits, and long-term consumption patterns in order to conduct an exhaustive analysis of the potential health hazards associated with heavy metal exposure [29-32]. (See Table 2).

Table 2: The impact of SNPs on the elimination of toxic heavy metals

Replication	Adsorbent dose	Co (%)	Ni (%)	Pb (%)	Cr (%)
R-1	1:2 Coffee	2.2319	2.8623	1.0853	3.8175
R-1	1:5 Coffee	1.938	2.1502	1.1267	6.5654
R-1	1:10 Coffee	2.0805	3.3446	1.3641	4.6266
R-2	1:2 Coffee	2.9762	3.0661	2.032	2.8555
R-2	1:5 Coffee	2.9901	3.34	2.2268	3.6661
R-2	1:10 Coffee	2.9827	2.5199	2.1186	3.5165
R-3	1:2 Coffee	3.4652	4.0042	3.3077	1.7528
R-3	1:5 Coffee	3.3086	4.1336	3.3453	1.4516
R-3	1:10 Coffee	3.834	4.551	3.7672	1.0493

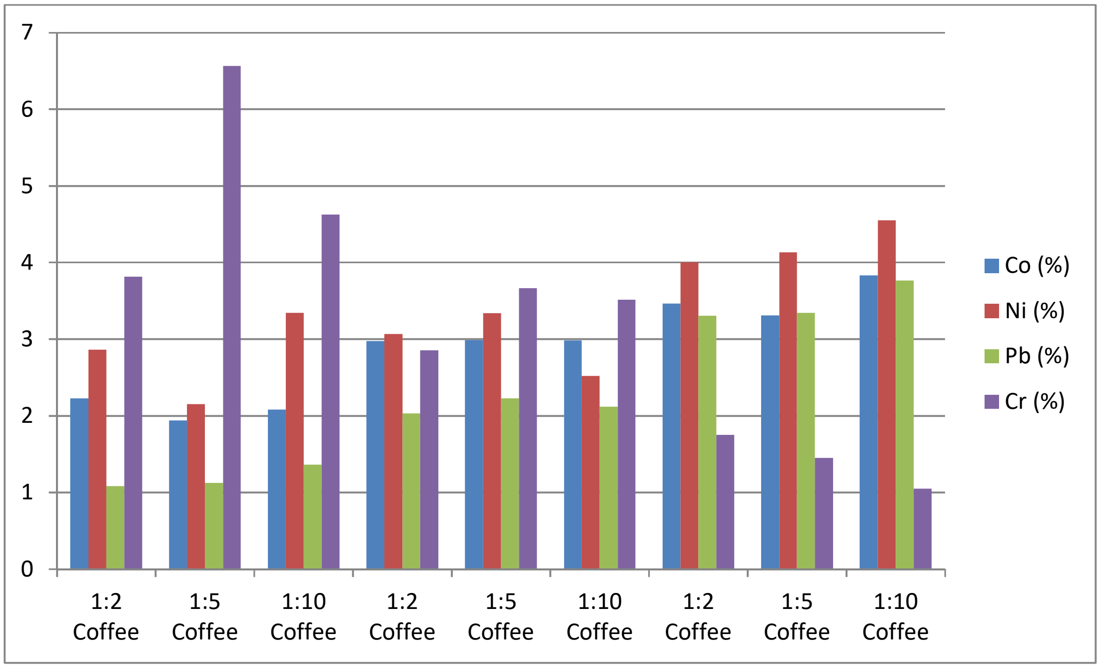


Figure 2: The impact of SNPs on the elimination of toxicheavy metals

The table 2 presented is a summary of research data related to the removal of high concentrations of toxic heavy metals, namely Co, Ni, Pb, and Cr, using varying doses of a Coffee-based adsorbent. The adsorbent doses are denoted as "1:2 Coffee" "1:5 Coffee" and "1:10 Coffee" indicating the ratio of adsorbent to the metal solution applied. For instance, in the case of "1:2 Coffee" the percentages of residual metals are as follows: Co at 2.083%, Ni at 2.786%, Pb at 1.192%, and Cr at 5.003%. Each of these values is accompanied by its standard error, providing a measure of the uncertainty associated with the measurement. The critical difference (CD) is also provided, which is used to determine if the differences between any two values are statistically significant. A higher CD suggests greater significance.

Additionally, the coefficient of variation (CV %) is included, indicating the relative variability in the data compared to the mean. Higher CV% values suggest greater data variability. These results are crucial for assessing the effectiveness of the potato-based adsorbent in removing these heavy metals, which can have significant implications for environmental and health considerations in cases of contamination. Further analysis and interpretation of these data can help to determine the most effective adsorbent doses for heavy metal removal

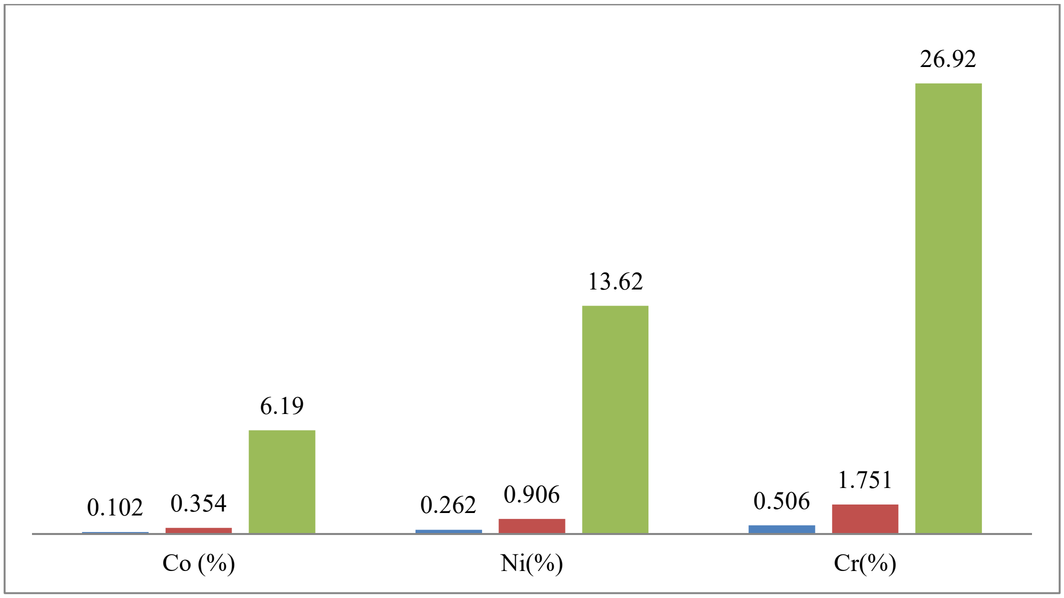
6.2.3: Effect of biomass concentration on metal removal

SNPs were applied to coffee biomass in our research at three distinct ratios: 1:2 (SNPs: Coffee), 1:5 (SNPs: Coffee), and 1:10 (SNPs: Coffee). Each of these ratios resulted in a significant reduction in the amount of heavy metal pollutants in coffee biomass. After 6 hours of shaking, the toxic heavy metal removal measurements for Co were determined to be 2.0830.15, 2.9830.01, and 33.5360.27 at the doses 1:2, 1:5, and 1:10 respectively. The removal measurements for Ni were 2.7860.60, 2.9750.42, and 4.2300.29; the removal measurements for Pb were determined to be 1.1920.15, 2.1260.10, and 3.4730.2. According to the results of the relative ratios, the 1:10 ratio was shown to be significant in efficiently reducing the amount of toxic heavy metal present in coffee biomass (Table 3). When compared to the ratio of 1:2 (SNPs: Coffee), the elimination of heavy metals by SNPs was significantly different when the ratio was 1:10 (SNPs: Coffee). This suggests that even if the amount of potatoes that are added to the coffee is doubled, the SNPs will still be able to remove the harmful heavy metals. This also suggests that the effectiveness of SNPs in eliminating toxic heavy metals from coffee is significant; even an increase in the amount of potatoes showed a rise in this efficiency. [33-37].

Table 3: Elimination of high concentrations of heavy hazardous metals

Adsorbent dose	Co (%)	Ni(%)	Pb(%)	Cr(%)
1:2 Potato	2.083 ± 0.15^{c}	2.786 ± 0.60^{b}	1.192 ± 0.15^{c}	5.003 ± 1.41^{a}
1:5 Potato	2.983 ± 0.01^{b}	2.975 ± 0.42^{b}	2.126 ± 0.10^{b}	3.346 ± 0.43^{a}
1:10 Potato	3.536 ± 0.27^{a}	4.230 ± 0.29^{a}	3.473 ± 0.26^{a}	1.418 ± 0.35^{b}
SEm.	0.102	0.262	0.104	0.506
CD	0.354	0.906	0.360	1.751
CV%	6.19	13.62	7.95	26.92

Values are mean±S.D. Treatments with same letters are not significantly different ($P<0.05$)



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For instance, in the case of "1:2 Coffee" the percentages of residual metals are as follows: Co at 2.083%, Ni at 2.786%, Pb at 1.192%, and Cr at 5.003%. Each of these values is accompanied by its standard error, providing a measure of the uncertainty associated with the measurement. The critical difference (CD) is also provided, which is used to determine if the differences between any two values are statistically significant. A higher CD suggests greater significance.

Additionally, the CV% is included, indicating the relative variability in the data compared to the mean. Higher CV% values suggest greater data variability. These results are crucial for assessing the effectiveness of the Coffee-based adsorbent in removing these heavy metals, which can have significant implications for environmental and health considerations in cases of contamination. Further analysis and interpretation of these data can help to determine the most effective adsorbent doses for toxic heavy metal removal.

6.3: DISCUSSION

The discussion section of this research aims to provide a comprehensive analysis of the results presented in Table 3 and Figure 3. These findings revolve around the effectiveness of a potato-based adsorbent in removing toxic heavy hazardous metals from coffee biomass at different adsorbent doses. The following points are discussed in detail: The study utilized three different adsorbent doses (1:2 Coffee, 1:5 Coffee, and 1:10 Coffee) and evaluated their impact on the removal of toxic heavy metals. It's evident from the data that increasing the adsorbent dose results in a progressively more effective removal of toxic heavy metals. This is a crucial observation, as it suggests that higher concentrations of the adsorbent lead to better toxic heavy metals removal. The study focused on four heavy metals, namely Co, Ni, Pb, and Cr. Each metal displayed its unique removal pattern based on the adsorbent dose. For instance, Co and Ni showed the highest removal efficiency at the 1:10 Coffee ratio, while Lead and Chromium followed similar trends. Understanding these variations is essential for tailoring remediation strategies to target specific contaminants effectively. The data presents standard errors and CD to assess the statistical significance of the results. These statistical measures indicate that differences in metal removal between various adsorbent doses are significant. This suggests that the choice of adsorbent dose can substantially impact the effectiveness of the removal process. The CV% is provided for each metal and adsorbent dose combination, indicating the relative variability of the data. Higher CV% values suggest greater data variability, which is a crucial consideration when interpreting the results. Understanding data variability helps researchers assess the reliability and consistency of their findings. The study's findings have significant implications for environmental and health considerations in cases of toxic heavy metal contamination. The ability to efficiently remove toxic heavy metals from coffee biomass, a product consumed by many, is essential for ensuring food safety and human health.

This research provides valuable insights into the potential of potato-based adsorbents for toxic heavy metal remediation. Future studies can build upon these findings, exploring different biomass-based adsorbents and their applications in diverse contexts. The results also have practical applications in environmental remediation and could lead to the development of cost-effective and environmentally friendly methods for heavy metal removal in various settings. The data presented in Table 3 and Figure 3 demonstrates the effectiveness of Coffee-based adsorbents in removing toxic heavy metals from coffee biomass. The findings underscore the importance of selecting appropriate adsorbent doses and offer insights into the variability of data. These results contribute to the broader field of environmental science and may inform strategies for addressing heavy metal contamination in food products and beyond. Further research is needed to refine and expand upon these findings to develop sustainable solutions for heavy metal remediation.

6.4: REFERENCES

[1] Gupta, N., D. K. Khan, and S. C. Santra. "An assessment of heavy metal contamination in vegetables grown in wastewater-irrigated areas of Titagarh, West Bengal, India." Bulletin of Environmental Contamination and Toxicology 80 (2008): 115-118.

[2] Raghavendra, Lingayya, and M. Venkatesha. "Water and soil quality of coffee plantations in the Western Ghats Region, Chikkamagaluru District, Karnataka, India." Current World Environment 15, no. 3 (2020): 502-514.

[3] Hamsa, N., and N. B. Prakash. "Heavy metal contamination in soils and crops irrigated with lakes of Bengaluru." Curr. Sci 119, no. 1849 (2020): 1849-1854.

[4] Hseu, Zeng-Yei, Shaw-Wei Su, Hung-Yu Lai, Horng-Yuh Guo, Ting-Chien Chen, and Zueng-Sang Chen. "Remediation techniques and heavy metal uptake by different rice varieties in metal-contaminated soils of Taiwan: New aspects for food safety regulation and sustainable agriculture." Soil Science & Plant Nutrition 56, no. 1 (2010): 31-52.

[5] Wuana, Raymond A., and Felix E. Okieimen. "Heavy metals in contaminated soils: a review of sources, chemistry, risks and best available strategies for remediation." International Scholarly Research Notices 2011 (2011).

[6] Alloway, Brian J., ed. Heavy metals in soils: trace metals and metalloids in soils and their bioavailability. Vol. 22. Springer Science & Business Media, 2012.

[7] Nriagu, Jerome O. "A history of global metal pollution." Science 272, no. 5259 (1996): 223-223.

[8] Bilal, Muhammad, Ihsanullah Ihsanullah, Mohammad Younas, and Mansoor Ul Hassan Shah. "Recent advances in applications of low-cost adsorbents for the removal of heavy

metals from water: A critical review." Separation and Purification Technology 278 (2021): 119510.

[9] Gusain, Rashi, Neeraj Kumar, and Suprakas Sinha Ray. "Recent advances in carbon nanomaterial-based adsorbents for water purification." Coordination Chemistry Reviews 405 (2020): 213111.

[10] Dlamini, Derrick S., John Michael Tesha, Gcina D. Vilakati, Bhekie B. Mamba, Ajay K. Mishra, Justice M. Thwala, and Jianxin Li. "A critical review of selected membrane-and powder-based adsorbents for water treatment: Sustainability and effectiveness." Journal of Cleaner Production 277 (2020): 123497.

[11] Saleh, Tawfik A. "Protocols for synthesis of nanomaterials, polymers, and green materials as adsorbents for water treatment technologies." Environmental Technology & Innovation 24 (2021): 101821.

[12] Crini, Grégorio. "Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment." Progress in polymer science 30, no. 1 (2005): 38-70.

[13] Sachan, Deepa, Aiyagari Ramesh, and Gopal Das. "Green synthesis of silica nanoparticles from leaf biomass and its application to remove heavy metals from synthetic wastewater: A comparative analysis." Environmental Nanotechnology, Monitoring & Management 16 (2021): 100467.

[14] Sharma, Pratibha, Jaibir Kherb, Jai Prakash, and Raj Kaushal. "A novel and facile green synthesis of SiO2 nanoparticles for removal of toxic water pollutants." Applied Nanoscience 13, no. 1 (2023): 735-747.

[15] Wang, Yu-Ying, Yu-Xue Liu, Hao-Hao Lu, Rui-Qin Yang, and Sheng-Mao Yang. "Competitive adsorption of Pb (II), Cu (II), and Zn (II) ions onto hydroxyapatite-biochar nanocomposite in aqueous solutions." Journal of Solid State Chemistry 261 (2018): 53-61.

[16] Snehal, Sikha, and Pushpa Lohani. "Silica nanoparticles: Its green synthesis and importance in agriculture." Journal of Pharmacognosy and Phytochemistry 7, no. 5 (2018): 3383-3393.

[17] Ali, Marwa, and AA-Ali Drea. "Green synthesis and characterization of antibiotic amorphous nano silicon oxide powder extracted from rice husk ash." International Journal of Current Research and Review 13, no. 24 (2021): 94-99.

[18] Alhadhrami, A., Gehad G. Mohamed, Ahmed H. Sadek, Sameh H. Ismail, A. A. Ebnalwaled, and Abdulraheem SA Almalki. "Behavior of silica nanoparticles synthesized from rice husk ash by the sol–gel method as a photocatalytic and antibacterial agent." Materials 15, no. 22 (2022): 8211.

[19] Nayak, P. P., and A. K. Datta. "Synthesis of SiO2-nanoparticles from rice husk ash and its comparison with commercial amorphous silica through material characterization." Silicon 13, no. 4 (2021): 1209-1214.

[20] Zhang, Zhiliang, Wenxiu He, Jianzhong Zheng, Guangquan Wang, and Jianbing Ji. "Rice husk ash-derived silica nanofluids: synthesis and stability study." Nanoscale research letters 11 (2016): 1-8.

[21] Yadav, Virendra Kumar, and M. H. Fulekar. "Green synthesis and characterization of amorphous silica nanoparticles from fly ash." Materials Today: Proceedings 18 (2019): 4351-4359.

[22] Sachan, Deepa, Aiyagari Ramesh, and Gopal Das. "Green synthesis of silica nanoparticles from leaf biomass and its application to remove heavy metals from synthetic wastewater: A comparative analysis." Environmental Nanotechnology, Monitoring & Management 16 (2021): 100467.

[23] Rajendran, Saravanan, A. K. Priya, P. Senthil Kumar, Tuan KA Hoang, Karthikeyan Sekar, Kar Yeen Chong, Kuan Shiong Khoo, Hui Suan Ng, and Pau Loke Show. "A critical and recent developments on adsorption technique for removal of heavy metals from wastewater-A review." Chemosphere 303 (2022): 135146.

[24] Naseem, K., Q. Imran, M. Z. Ur Rehman, M. H. Tahir, and J. Najeeb. "Adsorptive removal of heavy metals and dyes from wastewater using Azadirachta indica biomass." International Journal of Environmental Science and Technology 20, no. 5 (2023): 5799-5822.

[25] Usgodaarachchi, Leshan, Charitha Thambiliyagodage, Ramanee Wijesekera, and Martin G. Bakker. "Synthesis of mesoporous silica nanoparticles derived from rice husk and surface-controlled amine functionalization for efficient adsorption of methylene blue from aqueous solution." Current Research in Green and Sustainable Chemistry 4 (2021): 100116.

[26] Nguyen, Tan Tai. "Effective Removal of Phosphate from Waste Water Based on Silica Nanoparticles." Journal of Chemistry 2022 (2022).

[27] De la Calle, Inmaculada, Mathieu Menta, Marlène Klein, and Fabienne Séby. "Screening of TiO2 and Au nanoparticles in cosmetics and determination of elemental impurities by multiple techniques (DLS, SP-ICP-MS, ICP-MS and ICP-OES)." Talanta 171 (2017): 291-306.

[28] Punia, Pinki, Manish Kumar Bharti, Rakesh Dhar, Preeti Thakur, and Atul Thakur. "Recent advances in detection and removal of heavy metals from contaminated water." ChemBioEng Reviews 9, no. 4 (2022): 351-369.

[29] Shahid, Muhammad, Camille Dumat, Sana Khalid, Nabeel Khan Niazi, and Paula MC Antunes. "Cadmium bioavailability, uptake, toxicity and detoxification in soil-plant system." Reviews of Environmental Contamination and Toxicology Volume 241 (2017): 73-137.

[30] Åkesson, Mrs Tanja, Codex Contact Point, and Viale delle Terme di Caracalla. "Joint FAO/WHO food standards programme codex committee on contaminants in foods." WHO, Geneva (2015).

[31] Järup, Lars. "Hazards of heavy metal contamination." British medical bulletin 68, no. 1 (2003): 167-182.

[32] Joint, F. A. O., WHO Expert Committee on Food Additives, and World Health Organization. Safety evaluation of certain contaminants in food: prepared by the Seventy-second meeting of the Joint FAO/WHO Expert Committee on Food Additives (JECFA). World Health Organization, 2011.

[33] Sachan, Deepa, Aiyagari Ramesh, and Gopal Das. "Green synthesis of silica nanoparticles from leaf biomass and its application to remove heavy metals from synthetic

wastewater: A comparative analysis." Environmental Nanotechnology, Monitoring & Management 16 (2021): 100467.

[34] Wang, Weixing, Jarett C. Martin, Xiaotian Fan, Aijie Han, Zhiping Luo, and Luyi Sun. "Silica nanoparticles and frameworks from rice husk biomass." ACS applied materials & interfaces 4, no. 2 (2012): 977-981.

[35] Chen, Haoran. "Biogenic silica nanoparticles derived from rice husk biomass and their applications." (2013).

[36] Yuliasari, D. P., and S. D. Yuwono. "Removal of Ni (II), Cu (II), and Zn (II) ions from aqueous solution using Tetraselmis sp. biomass modified with silica-coated magnetite nanoparticles." Desalination and Water Treatment 80 (2017): 203-213.

[37] Mehta, S. K., and J. P. Gaur. "Use of algae for removing heavy metal ions from wastewater: progress and prospects." Critical reviews in biotechnology 25, no. 3 (2005): 113-152.