

## **Removal of Copper and Cobalt from Textile Wastewater using Date Palm as Bioadsorbance and Implication to pH**

**Muhammad Amirul Amri Anuar<sup>1</sup>, Muhammad Daniel Sharum<sup>1</sup>, Norazreen Sharip<sup>1\*</sup>**

<sup>1</sup>Department of Science and Mathematics, Centre for Diploma Studies, Universiti Tun Hussein Onn Malaysia, Pagoh Higher Education Hub, 84600 Pagoh, Johor, MALAYSIA

\*Corresponding Author Designation

DOI: <https://doi.org/10.30880/mari.2023.04.02.027>

Received 01 October 2022; Accepted 30 November 2022; Available online 15 January 2023

**Abstract:** A lot of wastewaters has been produced by factories and has been discharged into water sources that have great potential to disrupt the health of organisms such as humans, plants, animals, and most aquatic life. Therefore, this study is important in the effort to remove heavy metals from wastewater. The wastewater was tested using Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) twice which is before and after filtration. The sample undergone ICP-OES twice to calculate the percentage of the heavy metal removal. The percentage of heavy metals removal from this experiment is too small between 2.0% to 2.4%. Even though date palm (DP) was successfully changing pH value before and after treatment of wastewater which in this case was textile wastewater evidenced by the pH meter results. ICP-OES analysis results show the type of heavy metals content on the wastewater such as Copper (Cu) and also Cobalt (Co) confirmed the removal of heavy metals by using DP as bio adsorbent was able to identify types of heavy metals content on the wastewater. In conclusion, dates are an effective natural ingredient to be used as a bio adsorbent for wastewater.

**Keywords:** Bio Adsorbent, Date Palm, Heavy Metals

### **1. Introduction**

Recently, the globalization and arise of industrial rapidly has become more serious environmental issues that are a nuisance for human beings. There are a few metals that have common characteristics such as denser approximately 5g per cubic centimeter and also are highly water soluble, well-known toxics and carcinogenic agents [1]. The following element like copper, silver, zinc, cadmium, gold, mercury, lead, chromium, iron, nickel, tin, arsenic, selenium, molybdenum, cobalt, manganese, and aluminum is considered heavy metals and concern major environmental pollution agents usually present in wastewater and industrial effluent in a certain quantity [2-4]. Various industrial sectors will produce different types of wastewaters containing heavy metals that dispose to water streams [3].

---

\*Corresponding author: [norazreen@uthm.edu.my](mailto:norazreen@uthm.edu.my)

2023 UTHM Publisher. All right reserved.

[penerbit.uthm.edu.my/periodicals/index.php/mari](http://penerbit.uthm.edu.my/periodicals/index.php/mari)

The heavy metals listed pose a dangerous threat to populations of organisms including humans as the main target species, the flora, and also fauna after receiving water bodies. They can cause serious health problems like liver cancer, organ failure, nervous system damage, or death if any organisms in the food chain absorb and accumulate in the body system [5]. The event in small quantities is highly possible to reduce the growth and development of body tissues [6]. All heavy metals generators from the various industrial sector including the manufacturing sector that by-product has become toxic to the environment such as electronic factories [7-8]. Usually, this factory will be resulting tin, lead, and nickel that are grouped as heavy metal wastes [9]. Other industrial sectors like etching, milling coating, electroplating, conversion-coating, and ionizing-cleaning and electrolysis depositions. A significant amount of heavy metals wastes including arsenic after chromate copper-arsenate wood treatment process for wood manufacturing industries.

The removal of inorganic matter carried out through research by activated carbon [10], particularly metal ions, has been significantly limited. Red mud [11] through a selective adsorption process to other materials like coal, photocatalyst beads [12], nano-particles [13], fertilizer industrial waste [14-15], biomass [16-17], activated sludge biomass, algae, etc. have created a growing and rising excitement. Industrial byproducts have the potential to be reused as catalysts such as fly ash, waste iron, iron slags [4], hydrous titanium oxide [18], [8] as well as possibly chemically modified to improve their removal performance for metal removal from wastewater.

To comply with the standards of technology-based treatment [3], methods of absorbance for treating industrial wastewater containing heavy metals often involve technologies for the reduction of heavy metals toxicity [19]. Through the process of physical-chemical treatment [20] such as adsorption of new adsorbents, their advantages and drawbacks in the application were evaluated. Without a doubt, chemical treatment methods are most applicable and the best solution rather than biosorption techniques even though bio absorption techniques are eco-friendly best solutions for toxic inorganic compounds produced from various industries which cannot be removed from biological and physical techniques.

Biosorption is another method that can use to remove heavy metals from wastewater. The sorption process is the transfer of ions from the solution phase to the solid phase, which describes a group of processes, which includes adsorption and precipitation reactions [21]. Adsorption has become one of the alternative treatment techniques [22] for wastewater. Fundamentally, when substances are bound to solid surfaces whether through a chemical or physical process [20] in addition to the process of mass transfer is termed adsorption. Various low-cost adsorbents, derived from agricultural waste, an industrial by-product, natural material, or modified biopolymers, have been recently developed and applied for the removal of heavy metals from metal-contaminated water. The removal process using activated carbon [9], [23] as the organic matter has been oriented for longer periods in water and wastewater treatment [2], [24].

## 2. Methodology

In this research, the date palm (DP) was used as the filter by combining with the concept of the bio adsorbent method. The wastewater will be undergoing Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) twice which is before and after filtration. There was undergone ICP-OES twice to calculate the percentage of the heavy metal removal by using the equation:

$$\text{Removal percentage} = \frac{co - cf}{co} \times 100 \quad \text{Eq. 1}$$

From the formula, the *co* is referring to initial concentration that is concentration before the filtration. Meanwhile, the *cf* is referring to the final concentration that is the concentration after the filtration.

### 2.1 Materials

As for the DP filter preparation, the material that was being used was DP and cheesecloth filter. The DP and cheesecloth were bought from the supermarket. The DP was used as a plate to filter the wastewater. Next is the sample of the wastewater which is textile wastewater. The textile wastewater

was gotten from the textile company. The textile wastewater then being mixed with the cobalt chloride and copper (II) sulfate.

## 2.2 Methods

As for the DP filter preparation, the material that was being used was DP and cheesecloth filter. The DP and cheesecloth were bought from the supermarket. The DP was used as a plate to filter the wastewater. Next is the sample of the wastewater which is textile wastewater. The textile wastewater was gotten from the textile company. The textile wastewater then being mixed with the cobalt chloride and copper (II) sulfate.

Based on **Figure 1**, the procedure of the experiment began with obtaining the textile wastewater from the textile company. Then, two samples of wastewater will be made by mixed the textile wastewater with copper (II) sulfate and another sample was mixed with cobalt chloride. After that, the wastewater sample had undergone a pH test using a pH meter. After the pH testing, the sample had undergone ICP-OES for the first time. When the preparation of the wastewater sample had done, the samples will be kept in a cold room before the filtration process. Hence, the DP filter was invented by using the DP and cheesecloth filter. First, take out the DP seeds, then put the DP into a blender. The DP had to blend until all the DPs had been crushed. After that, the DP was put in the cheesecloth filter and shaped the DP into a plate. The DP was then dried using an oven with the temperature set up as 85°C and the period was for 2 hours.



**Figure 1: Scheme of the process for the experiment.**

When the DP filter is fully prepared, the filtration experiment was set up by using two 500ml measuring cylinders, two filters funnel, and two filter paper. The filter funnel was placed on top of the measuring cylinder. After that, the DP filter was placed on top of the filter paper. When the experiment is fully set up, the wastewater sample was poured into the measuring cylinder slowly. The measuring cylinder that placed under the DP filter will collect all the sample. The filtration process was carried out three times. After the filtration, the sample had undergone a pH test once again to differentiate the pH value for the sample before and after filtration.

## 3. Results and Discussion

The main components of textile wastewater consist of pigment color, high pH value, and high concentration of suspended solids. These substances are usually detected, such as chlorides, nitrates, and metals like manganese, sodium, lead, copper, and cobalt. The heavy metals were detected in samples at different concentrations.

**Table 1: Initial concentration of the heavy metals in the wastewater**

Sample textile wastewater mixed copper (Before)	Mean (mg/L)	Sample textile wastewater mixed cobalt (After)	Mean (mg/L)
As 193.696	12.93	As 193.696	-168.2
Co 228.616	-0.031	Co 228.616	1351
Cu 327.393	637.7	Cu 327.393	1.406

Based on **Table 1** it was shown the concentration of the ions that are presented in the textile wastewater. The concentration of arsenic that is presented in the wastewater is low. Due to the highest concentration of copper and cobalt in textile wastewater, copper and cobalt were selected to be investigated in this research.

**Table 2: Concentration of heavy metals before and after from different solutions.**

Item	Substances	pH	Concentration	Unit	Removal Percentage	Unit
Before	Copper (Cu)	5.34	637.7	mg/L	-	-
After	Copper (Cu)	5.63	635.4	mg/L	2	%
Before	Cobalt (Co)	7.18	1351	mg/L	-	-
After	Cobalt (Co)	7.31	1319	mg/L	2.4	%

From **Eq. 1**, the percentage of the removal of heavy metals was calculated. **Table 2** show specific concentrations, pH, and removal percentage of each solution. From the result in **Table 2** obtained, most of the heavy metals contains in the wastewater are slightly acidic. It is because the textile wastewater that used were mixed with other chemical substance which is cobalt chloride and copper (II) sulfate. When they have been mixed, the acidic of the heavy metals are being neutralized by the chemical reaction. From this reaction it is provided neutral substances. Apart from that, because of the textile wastewater have been mixed together with copper (II) sulfate and cobalt chloride that is salt, so mostly the heavy metal elements are still in the form of substances not in its ion. So, there are not enough metals to be measured by using the ICP-OES. This problem can be solved if the heavy metals are being separated from their substance in the wastewater.

Apart from that, by using the DP filter, the pH of the heavy metals is reduced. Before the filtration, the copper is a bit acidic, but after the filtration, the pH is increased and nearing neutral. The reduction of the acidity is low maybe because of the DP density. If the DP density is higher, the fiber in the DP can absorb more heavy metals. In the experiment the weight of the DP for a filter is between 50g. The used of 50g DP was suitable for the size of the cheesecloth which is 15cm. The cheesecloth filter will be full if used more DP. The solution for this was by using the bigger cheesecloth filter which can fit more DP filters.

On the other hand, the percentage of heavy metals removal from this experiment is between 2.0% to 2.4%. The percentage of the heavy metal's removal is too small, it is affected by the absorption of the heavy metals. There are a few factors that affect the absorption process during the experiment. The major factor is the total ions that can be absorbed. As stated above, because mostly the ions in the wastewater are mixed and in the form of substances, there are not much of concentration ions present in the wastewater. pH value also affected the absorption process. As the reason, in the result, cobalt pH value is higher than the copper which is 7.18 meanwhile copper 5.34. The percentage of the cobalt also higher than the copper which is 0.4%. Hence, it could be proven that when the pH of the wastewater is neutral, the DP can absorb the heavy metals more than the acidic pH. The pH for both of these samples was different to determine the effect of pH on the heavy metal's absorption.

#### 4. Conclusion

DP was successfully changing pH value before and after treatment of wastewater which in this case was textile wastewater evidenced by the pH meter results. For pH of Cu changed from pH 5.34 to pH 5.63 while Co became pH 7.31 from pH 7.18. ICP-OES analysis results show the type of heavy metals

content on the wastewater such as Cu and also Co confirmed the removal of heavy metals by using DP as bioadsorbent was able to identify types of heavy metals content on the wastewater. Furthermore, the percentage of removal efficiency of the heavy metals was different between these two substances. For the first one showed that copper removal percentage was 2% from their earlier concentration of 637.9mg/L and also DP was able to remove 2.4% of Cobalt from their first concentration, 1351mg/L.

In all, the treatment of heavy metals in wastewater is of great significance from the perspective of both the ecological environment and human health. The advent of dates still does not give us a promising alternative to traditional such adsorbents as activated carbon for heavy metal removal as the heavy metal removal percentage is still at 2.0 - 2.4% and requires more in-depth study. However, the removal capabilities of these DPs are mostly investigated in stimulated water with relatively simple components. The reports of their use in practical wastewater are insufficient and are highly in need. Additionally, the risk and impacts of nanomaterials cannot be neglected when we develop them.

### Acknowledgment

The authors would like to thank the Centre for Diploma Studies, Universiti Tun Hussein Onn Malaysia for its support.

### References

- [1] R. Fried, I. Oprea, K. Fleck, and F. Rudroff, "Biogenic Colourants in The Textile Industry – a promising and sustainable alternative to synthetic dyes", *Green Chem.*, vol. 24, no. 1, pp. 13-35, 2022, <http://doi.org/10.1039/d1gc02968a>.
- [2] S. K. Gunatilake, "Methods of Removing Heavy Metals from Industrial Wastewater", *Journal of Multidisciplinary Engineering Science Studies*, vol. 1, no. 1, pp. 12–18, 2015.
- [3] M. Ariffin and S. N. M. Sulaiman, "Regulating Sewage Pollution of Malaysian Rivers and Its Challenges," *Procedia Environmental Sciences*, vol. 30, pp. 168–173, 2015, <http://doi.org/10.1016/j.proenv.2015.10.030>.
- [4] J. Yang *et al.*, "Nanomaterials for The Removal of Heavy Metals from Wastewater," *Nanomaterials*, vol. 9, no. 3. 2019, <http://doi.org/10.3390/nano9030424>.
- [5] J. Briffa, E. Sinagra, and R. Blundell, "Heavy metal pollution in the environment and their toxicological effects on humans," *Heliyon*, vol. 6, no. 9, p. e04691, 2020, <http://doi.org/10.1016/j.heliyon.2020.e04691>.
- [6] N. Singh, V. K. Gupta, A. Kumar, and B. Sharma, "Synergistic Effects of Heavy Metals and Pesticides in Living Systems", *Frontiers in Chemistry*, vol. 5. 2017, <http://doi.org/10.3389/fchem.2017.00070>.
- [7] M. S. Sankhla *et al.*, "Effect of Electronic Waste on Environmental & Human health- A Review", *IOSR J. Environ. Sci. Toxicol. Food Technol.*, vol. 10, no. 09, 2016, <http://doi.org/10.9790/2402-10090198104>.
- [8] P. JK, H. L, W. S, B. T, and M. S, "Effects of Electronic Waste on Developing Countries", *Advances in Recycling & Waste Management*, vol. 02, no. 02, 2017, <http://doi.org/10.4172/2475-7675.1000128>.
- [9] S. Z. N. Ahmad, W. N. Wan Salleh, A. F. Ismail, N. Yusof, M. Z. Mohd Yusop, and F. Aziz, "Adsorptive Removal of Heavy Metal Ions Using Graphene-Based Nanomaterials: Toxicity, Roles of Functional Groups and Mechanisms", *Chemosphere*, vol. 248. 2020, <http://doi.org/10.1016/j.chemosphere.2020.126008>.
- [10] G. Sharma *et al.*, "Activated Carbon as Superadsorbent and Sustainable Material for Diverse Applications", *Adsorption Science and Technology*, vol. 2022. 2022, <http://doi.org/10.1155/2022/4184809>.

- [11] S. Samal, "Utilization of Red Mud as A Source for Metal Ions—A Review", *Materials*, vol. 14, no. 9. 2021, <http://doi.org/10.3390/ma14092211>.
- [12] S. R. Eun, S. Mavengere, and J. S. Kim, "Preparation of Ag-TiO<sub>2</sub>/Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub>:Eu<sup>2+</sup>, Dy<sup>3+</sup> photocatalyst on phosphor beads and its photoreaction characteristics", *Catalysts*, vol. 11, no. 2, 2021, <http://doi.org/10.3390/catal11020261>.
- [13] P. Zhang, Q. Li, Y. Chen, Y. Shi, and Y. F. Ling, "Durability of Steel Fiber-Reinforced Concrete Containing SiO<sub>2</sub> Nano-Particles", *Materials (Basel)*, vol. 12, no. 13, 2019, <http://doi.org/10.3390/ma12132184>.
- [14] L. Anggria, Husnain, and T. Masunaga, "A method for Production of Pure Silica as Fertilizer from Industrial Waste Material", in *IOP Conference Series: Earth and Environmental Science*, 2021, vol. 648, no. 1, <http://doi.org/10.1088/1755-1315/648/1/012213>.
- [15] T. V. Silas, "Biosorption Kinetics of Heavy Metals from Fertilizer Industrial Waste Water Using Groundnut Husk Powder as an Adsorbent", *J. Appl. Biotechnol. Bioeng.*, vol. 2, no. 6, 2017, <http://doi.org/10.15406/jabb.2017.02.00049>.
- [16] J. Popp, S. Kovács, J. Oláh, Z. Divéki, and E. Balázs, "Bioeconomy: Biomass and Biomass-Based Energy Supply and Demand", *N. Biotechnol.*, vol. 60, 2021, <http://doi.org/10.1016/j.nbt.2020.10.004>.
- [17] Y. M. Bar-On, R. Phillips, and R. Milo, "The Biomass Distribution on Earth", *Proc. Natl. Acad. Sci. U. S. A.*, vol. 115, no. 25, 2018, <http://doi.org/10.1073/pnas.1711842115>.
- [18] S. C. Azimi, F. Shirini, and A. R. Pendashteh, "Advanced Oxidation Process as a Green Technology for Dyes Removal from Wastewater: A review", *Iran. J. Chem. Chem. Eng.*, vol. 40, no. 5, pp. 1467–1489, 2021, <http://doi.org/10.30492/ijcce.2020.43234>.
- [19] F. Ahmed *et al.*, "Development of Selenium Nanoparticle Based Agriculture Sensor for Heavy Metal Toxicity Detection", *Agric.*, vol. 10, no. 12, 2020, <http://doi.org/10.3390/agriculture10120610>.
- [20] J. Žigon, J. Kovač, and M. Petrič, "The Influence of Mechanical, Physical and Chemical Pre-Treatment Processes of Wood Surface on The Relationships of Wood with a Waterborne Opaque Coating", *Prog. Org. Coatings*, vol. 162, 2022, <http://doi.org/10.1016/j.porgcoat.2021.106574>.
- [21] E. Nakouzi and O. Steinbock, "Self-organization in Precipitation Reactions Far from The Equilibrium", *Sci. Adv.*, vol. 2, no. 8, 2016, <http://doi.org/10.1126/sciadv.1601144>.
- [22] A. F. Hasaballah, T. A. Hegazy, M. S. Ibrahim, and D. A. El-Emam, "Cement Kiln Dust as An Alternative Technique for Wastewater Treatment", *Ain Shams Eng. J.*, vol. 12, no. 4, 2021, <http://doi.org/10.1016/j.asej.2021.04.026>.
- [23] Y. Kuang, X. Zhang, and S. Zhou, "Adsorption of Methylene Blue in Water onto Activated Carbon by Surfactant Modification", *Water (Switzerland)*, vol. 12, no. 2, 2020, <http://doi.org/10.3390/w12020587>.
- [24] J. Saleem, U. Bin Shahid, M. Hijab, H. Mackey, and G. McKay, "Production and Applications of Activated Carbons as Adsorbents from Olive Stones," *Biomass Conversion and Biorefinery*, vol. 9, no. 4. 2019, <http://doi.org/10.1007/s13399-019-00473-7>.