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Paper-based Heavy Metal Ion Detection in Wastewater using *Plumeria Rubra* (Kalachuchi) Latex

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An easy-to-use, portable, and cost-effective paper-based heavy metal ions detection using the latex from the kalachuchi plant was developed. Specifically, a paper strip determines heavy metal ions in wastewater using kalachuchi latex as a detecting agent. It examines the change of color in the aqueous solution containing heavy metal ions. This study also investigated the effects of the latex detecting agent in terms of the following conditions: (a) varying concentration of the solution, (b) increased pH of the solution, (c) latex dosage, and (d) recyclability. Kalachuchi latex-coated paper strips detected the heavy metals in several wastewater sample solutions. SEM micrographs were used to investigate the morphology of the latex, and EDX analysis was conducted to determine its elemental compositions. Results showed that the solutions with the lowest concentration (0.05 ppm) offer a faint color change, while those with a concentration > 0.25 ppm show considerable color change. An intense color change in solutions showed that the detection capability of the latex-coated strip increases and favors those solutions with higher pH. The latex was also tested on hybrid solutions and has also been effective in detecting the presence of heavy metal ions. Its reusability makes it more cost-efficient and practical to detect heavy metal ions in wastewaters whose concentration is as low as 0.05 ppm. Hence, this paper-based detecting agent can be used as a portable, onsite, and easy-to-use way of detecting heavy metal contamination in wastewater.

1. Introduction

Problems with heavy metal contamination are also a growing concern in developing countries such as the Philippines. Increased industrial activities and the lack of sufficient water supplies and wastewater treatments aggravate the situation, causing heavy metal contamination in streams, lakes, and seas (Joseph et al., 2019). However, the contaminated wastewater released during mining operations generally produces various kinds of mine wastes (Arif et al., 2016). And these mine tailings, slag, and wastes contain heavy metals which primarily cause pollution (Akkajit et al., 2018).

Conventional analytical equipment for heavy metal detection is extensive in size, making it difficult for the onsite analysis of samples. For the past years, paper-based analytical devices (PADs) have garnered increasing attention due to their attractive features (Lin et al., 2016). Their cost-effectiveness and ability to perform onsite and multiple analysis detection (Terra et al., 2017) are some of their prominent features. In addition, the device substrate, usually a paper sheet, is cheap and easy to handle support (Singh et al., 2018). Because of its practicality, simplicity, and availability, Plumeria-coated paper-based detection agent will be more economical to use than other existing µPADs as of today.

Many species of the genus Plumeria grew and distributed worldwide. Of these numerous species, 11 species are growing in tropical and subtropical regions of the world (Bihani, 2020). The species found in this genus include *Plumeria obtusa L.*, *Plumeria alba L*. and *Plumeria* rubra L., of which *Plumeria rubra L.* is the most abundant in the country. *Plumeria* rubra L. (syn. Plumeria acuminate (W.T. Aiton), commonly known as frangipani and locally known as kalachuchi, is grown as an ornamental tree in the Philippines (Waoo and Tarannum, 2017). From the slightest lesion, whether in the trunk, bark, leaf, or flower, the milky white juice or

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the latex of kalachuchi flows easily. This latex is considered poisonous and irritating to the skin but is also employed to treat inflammation rheumatism (Bihani, 2020).

Moreover, it has been reported that around 110 chemical substances have already been isolated and identified, including flavonoids (Bihani, 2020). However, the wide variety of biological activities of flavonoids is not limited to antioxidant properties. One application of the ability of the plant latex to coordinate metal ions is in the development of the preparative and analytical methods between the plant latex and the metal ions reactions. (Cherrak et al., 2016). Metal-chelating compounds remove the metals and can alter their redox potentials, making them inactive (Moghrovyan et al., 2019). Moreover, natural metal chelators such as flavonoids were favored against other synthetic chelators, which may present some toxicity problems (Adhikari et al., 2018). In the various medicinal and ethnical uses of Plumeria Rubra, nothing has been studied about its use to determine the presence of heavy metals in wastewater.

The study's main objective is to develop an easy-to-use, portable, and cost-effective paper-based heavy metal ions detection using the latex from the kalachuchi plant. This study was limited to developing the paper strip coated with latex from the kalachuchi plants as a paper-based ion detecting agent. Color changes were determined visually only, and the experimental procedures of the viability of the developed paper-based detecting kit were conducted locally. This study will provide an alternative paper-based detecting agent to conventional and complex analytical methods of detecting heavy metal ions in wastewater. Ultimately, this study aims to give a value upgrade of the kalachuchi latex, which is readily available and is presently has no market value.

2. Materials and Methods

2.1 Latex Collection

Healthy and non-cultivated kalachuchi trees growing in Toril Public Cemetery, located at Toril, Davao City, Philippines, were used as a source of fresh latex. Latex was collected from healthy plants by superficial incision of stem and near the youngest leaves/ends of branches allowing milky latex to drain, and then stored in sterile plastic vials containing distilled water to produce a 1:1 (v/v) mixture. The mixtures (water and latex) were gently stirred during collection to overcome the tendency of the latex to coagulate. The latex was taken to the laboratory and refrigerated at 4 ° C till needed.

2.2 Paper Sheet Fabrication

The paper sheet was fabricated by recycling white bond papers. The paper was cut into small pieces, soaked in water for 15 minutes, and put into a blender. For every 20—30 grams of shredded paper, approx. 300-500 ml of water were added. The mixture was blended until a reasonably smooth pulp was formed. The pulp was poured into a bin or pan, and then the mold was sunk into the water mixture. The mold was pulled up, making sure that the pulp covered the whole screen. A cloth or sponge was employed to press out excess water. The sheet was dried on the screen while flipping the mold over, letting the paper dry on another surface. A cloth was also pressed into the mold so the paper adheres and dries on it. Drying was either done at room temperature for 24 hours, sun-dried for 4-6 hours, or oven-dried at 40 ° C for 4-6 hours.

2.3 Paper Strip Fabrication

A cost-effective and straightforward cutting technique was used to fabricate a thin paper strip for heavy metal detection. The selective chromogenic detecting ability of the plant latex was embedded in the paper sheet to detect the heavy metal ions. In the experiment that followed, two types of paper strips were made. One was with the use of Whatman filter paper cut into rectangular paper strips. The other one was the use of the fabricated recycled paper sheet, cut into strips.

2.4 Latex Characterization

A scanning microscope (SEM, FEI Quanta 250 FEG, USA) was used to evaluate the morphology of the latex sample. To identify the elemental composition and analysis of the latex, EDX/EDS detector (Element EDAX) was employed. Moreover, the determination of the molecular composition and structure of the latex sample through its various wavelengths and infrared light absorbance was performed using Bruker's ATR accessory, specifically Platinum ATR diamond F. vacuum (Tensor II FTIR Spectrometer, USA).

2.5 Latex Extraction and Processing

Collected crude latex was taken out from the refrigerator, washed with distilled water, and then filtered. The soluble phase of the latex was filtered, and the precipitate comprising rubber was discarded. The cycle was repeated three times. The coagulated latex was then oven-dried for about 6 hours at 45ºC [Memmert 100-800], checking it every hour for its moisture content. When no significant weight change was noted, the dried latex was left to cool down and pulverized using mortar and pestle. The sample was then stored for analytical characterization.

2.6 Testing Procedure

The fabricated paper strip containing the detecting agent from kalachuchi latex was submerged in each heavy metal standard solution. Four sample solutions of the same concentration, starting from 0.05 ppm, 0.1 ppm, 0.25 ppm, 0.5 ppm, 0.75 ppm, and 1.0 ppm, represented the four standard solutions containing heavy metals (Fe, Cr, Cd, and Pb). Each test included a control (solution without paper strip) with two replicates for each concentration. A change in color of the solutions with paper strips was observed visually, and photographs were taken. The kind of color that appeared was recorded and noted. The intensity of color was observed using different concentrations of heavy metal solutions, changing the pH of the solutions, varying the number of latex dosages and solutions containing the different types of ions.

3. Results and Discussion

3.1 Characterization of the Latex

SEM micrographs of the dried and powdered samples were obtained to investigate the morphology of the plant latex (Figure 1a). The left figure shows that the latex sample presents a honeycomb structure at low magnification and a regular tetragonal shape at a higher magnification, where edges appear smooth. The EDX analysis showed spectra with peaks representing all the elements found in the latex sample, as shown in Figure 1b. Spectra were overlaid to compare the relative compositions in samples easily. This elemental analysis shows the percentage of concentration of each element present such as that of carbon (C), potassium (K), oxygen (O), aluminum, and calcium (Ca), where carbon constitutes the most significant percentage of the sample. Nowhere in the analysis can be found traces of iron, chromium, cadmium, and lead, implying that the changes in the color of the solutions containing the heavy metals are caused primarily by their reactions when in contact with the latex induced heavy metal detecting agent.

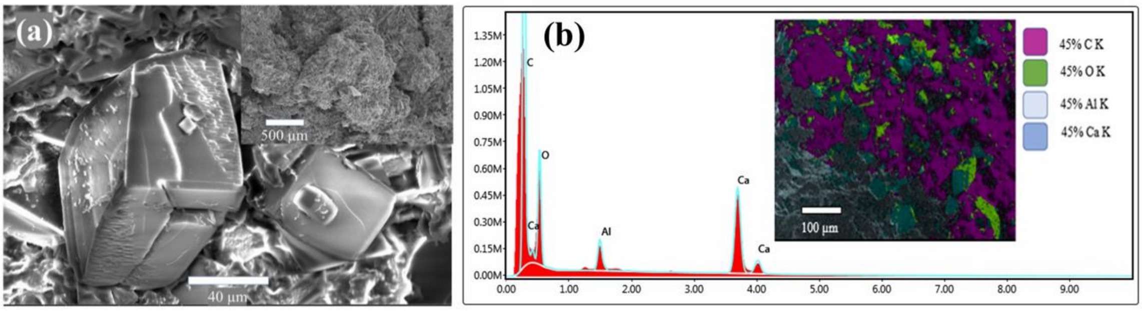

Figure 1: (a) SEM image of the dried and pulverized latex sample and (b) elemental mapping by EDX analysis

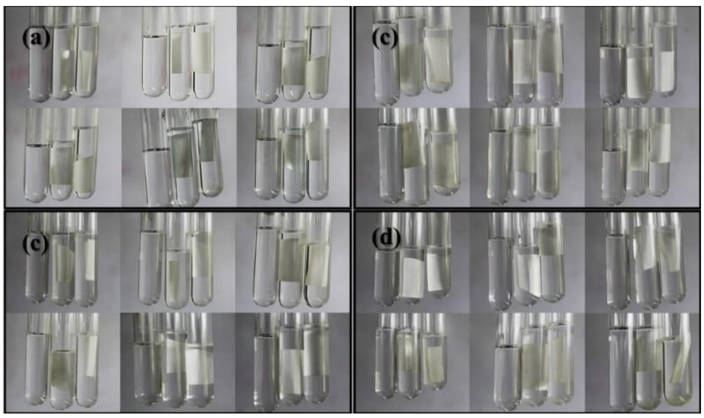

Figure 2: Three samples of each type of solution of Ferrous Ammonium Sulfate, Potassium Dichromate, Cadmium Sulfate, and Lead Nitrate were run. These solutions contain the heavy metals Fe, Cr, Cd, and Pd, respectively, with an increasing concentration of 0.05 ppm to 1.0 ppm. The left-most solution served as the control (no paper strip), while the second and the third samples contained a paper strip coated with kalachuchi latex to detect the presence of heavy metal ions present in each solution.

3.2 Effect of Concentration of Solution

Three samples of each type of solution of Ferrous Ammonium Sulfate, Potassium Dichromate, Cadmium Sulfate, and Lead Nitrate were run. These solutions contain heavy metals of Fe, Cr, Cd, and Pd, respectively, with an increasing concentration of 0.5 ppm to 1.0 ppm (Figure 2). The left-most solution served as the control where no paper strip was dipped in, while the second and the third were samples in which a paper strip coated with kalachuchi latex to detect the presence of heavy metals was immersed in each solution. From the visual observation by the naked eye, it can be observed that increasing the concentration of the different solutions showed a significant change in the color of the answers, from clear to faint yellowish. Further, the solution with the lowest concentration (0.05 ppm) offers a faint color change, while solutions with a concentration > 0.25 ppm show considerable color changes, as shown (Figure 2).

3.3 Effect of pH

The increase in pH corresponds to the increased visibility of the color changes by the naked eye in the different solutions (Figure 3). The addition of ammonia solution increases the pH and significantly affects the intensity of color change in different solutions at varying concentrations, ranging from 0.05ppm to 1.0 ppm. Hence, solutions with pH between 8-10 exhibit a significant color change than solutions with lower pH while maintaining all other conditions. There are contradicting reasons as to how the pH of the solution affects the formation of metal-flavonoid chelates (Adhikari, et al., 2018). However, this study shows that the metal-chelating effect of the latex is favored in a more alkaline solution. Hence, it is suggested that an in-depth analysis of the properties of the flavonoids present in the kalachuchi plant latex and the chemical activity of the heavy metal ions in varying pH solutions be available to get a correlation of the enhanced metal-flavonoid chelation.

Figure 3: Test tubes showing solutions of (a) Ferrous Ammonium Sulfate (b) Potassium Dichromate (c) Cadmium Sulfate (d) Lead Nitrate with increasing concentrations (0.05, 0.1, 0.25, 0.5, 0.75, 1 ppm) respectively. The pH of each solution was also increased using an ammonia-water solution. Each test included a control (solution without paper strip) and two replicates for each concentration.

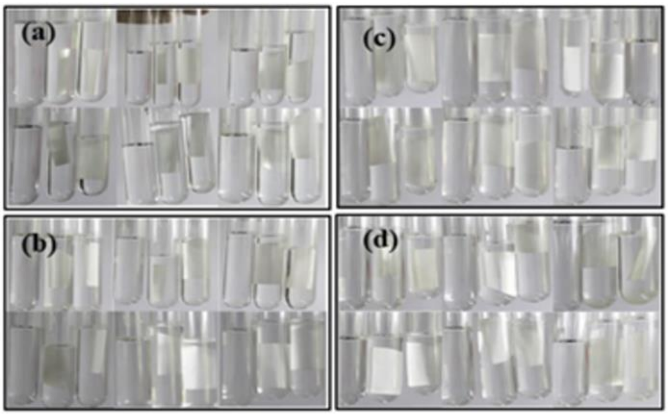

Figure 4: Test tubes showing solutions of (a) Ferrous Ammonium Sulfate (b) Potassium Dichromate (c) Cadmium Sulfate (d) Lead Nitrate with increasing concentrations (0.05, 0.1, 0.25, 0.5, 0.75, 1 ppm) respectively. Paper strips used came from a paper sheet coated with 5 ml of latex. Each test included a control (solution without paper strip) and two replicates for each concentration.

3.4 Effect of latex dosage

As the volume of latex per unit area of paper used (vol cm^{-2}) increases, the significant color change of the solution also increases. Sample trials were run by coating varied amounts of latex (3ml, 4ml, 5ml, and 7ml) on a Whatman paper (150 mm diameter). Eventually, faint color changes were observed for sample solutions with 3 ml and 4 ml latex coated paper strips. Profound color changes were observed from those solutions with 5 ml of latex-coated paper strips. However, for those solutions with 7ml latex-coated paper strips, no further significant color change was observed among those samples with 3-4 ml latex-coated paper strips. It means that a 5 ml latex is enough to instigate a color change in the solutions, thereby detecting the presence of heavy metal ions. Hence, a further increase in the latex dosage does not amplify the solution's color change, which means no further latex uptake is needed. Figure 4 shows sample solutions with 5 ml-latex coated paper strips.

3.5 Effect of Mixed Solution

The efficacy of the plant latex in detecting heavy metal ions in solutions containing a mixture of the prepared solutions (e.g., Fe, Cd, Cr, Pb) was determined by running trials to observe color changes in the mixed solution. Three test tubes contain the same mixture with the same concentration and pH. The first sample was the control, where the mixture did not include the paper-based ion detecting agent. The second and third samples have paper strips in them, and as expected, both of them manifest considerable color changes, as shown in (Figure 5). It shows that latex can detect the existence of heavy metal ions even in water samples and/or solutions containing multiple types of heavy metals.

Figure 5: Test tubes showing a mixture of solutions containing heavy metals. Three sample solutions were the first sample is the control solution, and the second and third contain paper strips with latex.

3.6 Recyclability

The reusability of the paper-based metal detecting agent was assessed by running trials to observe color changes in the solutions containing metals (Figure 6). The first sample shows the control solution without the strip. The second sample shows the solution with a previously dipped latex-containing strip and then removed afterward. Finally, the third sample contains the solution wherein the paper strip from the second solution is taken from, washed, dried, and reused. The paper strip caused the change in color for the first, second, and even subsequent solutions. Hence, the observable color change caused by the paper strip manifests its potential for long-term reusability.

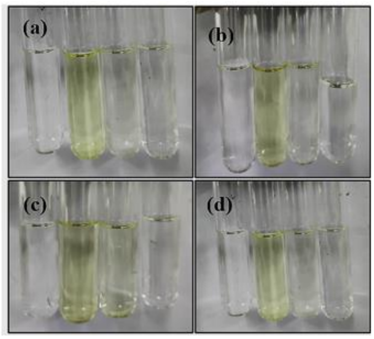

Figure 6: Test tubes showing solutions of (a) Ferrous Ammonium Sulfate, (b) Potassium Dichromate, (c) Cadmium Sulfate, (d) Lead Nitrate with the same concentration (0.5 ppm). The paper strip used was coated with 5 ml latex.

3.7 Mechanism

The natural flavonoids in kalachuchi latex give it its distinct ability to form metal complexes and act as enzyme metal ion chelators. The multiple hydroxyl groups and the carbonyl group on ring C found in natural flavonoids exhibit several active sites for metal complexation (Cherrak, et al., 2016). This ability of flavonoids to coordinate metal ions causes the formation of flavonoid-metal complexes. It is confirmed through the contact of the latex-coated paper strip with the heavy metal ions in the solutions. In addition, it caused the color changes of the solutions containing the heavy metal ions. The colorimetric change is the visual representation of the reactions between the heavy metal ions in the solutions and the plant latex present in the paper strips.

4. Conclusions

The use of kalachuchi latex as a detecting agent of heavy metal ions in wastewater offers a new and novel use of what could be a plant known commonly only for its ethical and medicinal uses. This paper-based detecting agent provides a cost-effective, portable, onsite, easy to use, and environmentally friendly way of detecting the presence of heavy metal ions in wastewater. This study determined the effects of the developed detecting agent in terms of color change under different conditions. At the varying concentration of the solution, a clear to faint yellowish color was observed. This color change also shows that the detecting agent causes a more intense color change in solutions whose pH range between 8-10. The latex dosage in the paper affect change in color of the solution. This paper strip can be recycled for prolonged use, making it more cost-efficient. However, it is suggested that a more suitable condition for drying and storing the latex-containing paper strips be considered that might increase its ability to be recycled and reused.

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References

Joseph L., Jun B.-M., Flora J. R. V., Park C. M., Yoon Y., 2019, Removal of heavy metals from water sources in the developing world using low-cost materials: A review. Chemosphere, 229, 142-159.

Arif N., Yadav V., Singh S., Kushwaha B. K., Singh S., Tripathi D. K., Chauhan D. K., 2016, Assessment of Antioxidant Potential of Plants in Response to Heavy Metals, Plant Responses to Xenobiotics, 97–125.

Lin Y., Gritsenko D., Feng S., Teh Y.C., Lu X., Xu J., 2016, Detection of heavy metal by paper-based microfluidics, Biosensors and Bioelectronics, 83, 256–266.

Terra I.A.A., Mercante L. A., Andre R. S., Correa D. S., 2017, Fluorescent and Colorimetric Electrospun Nanofibers for Heavy-Metal Sensing, Biosensors, 7(4), 61.

Singh A. T., Lantigua D., Meka A., Taing S., Pandher M., Camci-Unal G., 2018, Paper-Based Sensors: Emerging Themes and Applications, Sensors, 18 (9), 2838.

Bihani T., 2020, Plumeria rubra L.– A review on its ethnopharmacological, morphological, phytochemical, pharmacological and toxicological studies, Journal of Ethnopharmacology, 256, 113-291.

Waoo A. A., Tarannum S., 2017, Fast and Efficient DNA Extraction Method for a Plumeria Acuminata with Medicinal Potential, Scholars Journal of Research in Agriculture and Biology, 2 (2), 103-107.

Cherrak S.A., Mokhtari-Soulimane N., Berroukeche F., Bensenane B., Cherbonnel A., Merzouk H., Elbahiri, M., 2016, In Vitro Antioxidant versus Metal Ion Chelating Properties of Flavonoids: A Structure-Activity Investigation, PLoS ONE, 11(10), e0165575.

Moghrovyan A., Sahakyan N., Babayan A., Chichoyan N., Petrosyan M., Trchounian A., 2019, Essential oil and ethanol extract of oregano (Origanum vulgare L.) from Armenian flora as natural source of terpenes, flavonoids and other phytochemicals with antiradical, antioxidant, metal chelating, tyrosinase inhibitory and antibacterial activity, Current Pharmaceutical Design, 25 (6), 1809-1816.

Adhikari A., Darbar S., Chatterjee T., Das M., Polley N., Bhattacharyya M., Bhattacharyya S., Pal D., Pal S.K., 2018, Spectroscopic Studies on Dual Role of Natural Flavonoids in Detoxification of Lead Poisoning: Bench-to-Bedside Preclinical Trial, ACS Omega, 3, 5975−15987.

Akkajit, P., Jaileak, K., Suteersak, T. 2018, Assessment of heavy metals in sediment at Saphan Hin, Phuket. Chemical Engineering Journal, 63, 301-306.

Ghanbari A., Gresley A. L., Naughton D., Kuhnert N., Sirbu D., Ashraf G.H., 2019, Biological activities of Ficus carica latex for potential therapeutics in Human Papillomavirus (HPV) related cervical cancers, Scientific Reports, 9, 1013.

Cherrak S.A., Mokhtari-Soulimane N., Berrouketche F., Bensenane B., Cherbonnel A., Merzouk H., Elhabiri M., 2016, In Vitro Antioxidant versus Metal Ion Chelating Properties of Flavonoids: A Structure-Activity Investigation, PLoS One, 11(10), e0165575.