Bio-remediation of Effluents: Developing a Bio-adsorbent Medium to Treat Water Heavy Metal and Textile Dye Pollutants Based on the Combined Adsorption by Neem and Other Biosorbents

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With the expansion of textile industries and their extensive use of chemicals, industrial wastewater contaminated with heavy metals and textile dyes is finding its way into our usable water sources more frequently than ever. The high cost of current treatment procedures, as well as the environmental concerns associated, puts our drinkable water at risk of contamination. Agricultural byproducts, or biosorbents, can function as bio-adsorbents to remove dissolved substances from wastewater through adsorption. These materials are abundant and organic but are usually underutilized due to their generated sludge and lack of extensive efficiency. The purpose of our research is to develop a contact adsorbent medium by processing and combining five well-known biosorbents: neem (*Azadirachta indica*) leaf and bark, peanut (*Arachis hypogaea*) husk, coffee (*Coffea arabica*) ground, watermelon (*Citrullus lanatus*) rind, and banana (*Musa sapientum*) peels. By combining their treatment capacities, we were able to treat copper-contaminated water. We found that a paper-shaped medium can efficiently remove a significant portion of dissolved material while minimizing sludge, thus creating potential for replacing our existing non-sustainable treatment materials with an organic alternative derived from agricultural wastes.

Introduction

The influx of heavy metal substances into the environment has been increasing at a concerning rate over the past few centuries, with the majority of the freshwater bodies near cities and human habitats passing the safe levels set by WHO (Panchamoorthy et al., 2024; World Health Organization, 2017). Almost a third of the world's population still lacks clean and safe drinking water, one major cause of which is heavy metal pollution. In Bangladesh, an estimated 70 million people who consume groundwater are exposed to unsafe levels of arsenic (World Health Organization, 2017). In addition to heavy metals, production of over a million tons of dyes and pigments takes place annually worldwide. The effluents from dyeing industries are contaminated with highly colored compounds (e.g., azo dyes such as malachite green, aniline yellow, and methylene blue) and have a high chemical and biological oxygen demand (COD and BOD) (Garg et. al., 2004). If allowed into usable water bodies, they can harm aquatic ecosystems and human beings alike due to their carcinogenic, allergenic, and toxic effects.

The use of adsorbent organic materials in treating effluents is a well-studied phenomenon, with many works of research focused on a particular pair of adsorbent and adsorbates. In Garg et al., rosewood sawdust pretreated with sulfuric acid is used to treat methylene blue, a common blue dye in textile industries (2004). Sawdust is a very common byproduct of the timber industry, so their approach also fulfilled the conditions of low cost and sustainability. Khattri et al. take on a similar approach using neem sawdust and targeting malachite green dye (2009). While some of these studies focus on very specific topics, studies such as the one done by Farias et al. look at the overall porous adsorption capacity of a specific biosorbent, namely banana peel powder (2023). Most of the existing literature on organic bio-adsorbents focuses on the specific adsorption capacities of a given biosorbent, which, due to the physical and chemical properties of that specific biosorbent, act primarily well on a particular dye or heavy metal component. By combining these individual biosorbents in a manner that preserves their individual adsorbent properties, it is possible to create a more versatile effluent-treating medium.

In this project, we combined a range of organic materials—neem leaf powder (NLP) and sawdust, peanut shell powder (PSP), banana peel powder (BPP), coffee grounds (CG), and watermelon rind (WMR)—to remove heavy metals and common textile dyes through adsorption. Adsorption is the physicochemical process in which molecules from an aqueous solution (adsorbates) adhere to the adsorbent surface. The primary ingredient, Neem, contains high levels of flavonoids and tannins, which assist in the effective removal of heavy metals from water (Khattri et al., 2009). PSP has a structural formation consisting mainly of cellulose networks, making it quite effective in the removal of turbidity (Nkansah et al., 2019). BPP is known for decontaminating wastewater, mainly in the removal of textile dyes, heavy metals, and even crude oil (Farias et. al., 2023). Another common waste material, CG, has a lignocellulosic composition of 51.5% cellulose and 40.6% hemicellulose, which makes it an efficient bio-adsorbent (Mukti & Hidayat, 2019). WMR is composed of carbonaceous materials (e.g., cellulose, pectin, etc.), making it a suitable adsorption agent for metals and dyes (Bhattacharjee et al., 2020). The primary causes of physical adsorption are the Van der Waals and electrostatic forces between the adsorbate molecules and the adsorbent surface. Using a paper-like structure maximizes the surface area while keeping the composition to a minimum. It also creates a reinforced structure that can work without breaking down into suspension as soon as it encounters water, which, along with an extra biopolymer layer covering the paper, significantly minimizes sludge.

Each of the discussed bioadsorbents can work as effective removal agents for pollutants, and in this paper, their individual remedial potencies were combined into a paper-shaped contact adsorption medium to create an efficient solution for wastewater remediation that performs on the same level as existing adsorbent mediums, with over a 50% reduction in treatment costs and reduced environmental concerns. Furthermore, the adsorption capacity of this medium was analyzed in the theoretical framework of adsorption isotherms, which is an empirical model of an equilibrium function between adsorbent concentration and the amount of adsorption at a given temperature. By fitting our limited data points on these empirical models, we can predict the behavior of the adsorption mechanism. The Langmuir isotherm is one such model that well describes adsorption in a solid/liquid interface, an interface similar to our case, and the bio-adsorbent paper indeed is found to fit well to this model.

Methods

In designing the paper to acquire maximum adsorption with minimum dissociation, we chose a simplistic design where the bio-adsorbent paper has two individual layers—one adsorbent layer and one protecting layer (Fig. 1). The outer layer is made of a biopolymer that creates a thin separation between the bio-adsorbent paper and the solution. As adsorption does not require chemical interaction, the dye molecules and metal ions attracted by the bioadsorbent layer accumulate on the polymer, and the inner layer stays intact and reusable. We do expect the paper to degrade and will eventually need to be replaced, but because of the polymer layer, this will be substantially delayed.

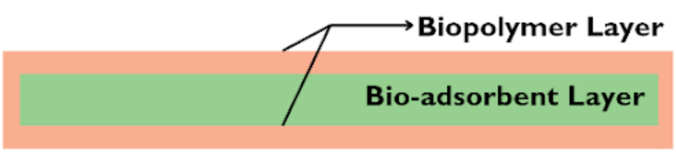

Figure 1. Schematic diagram of the bioadsorbent paper. The inner layer is composed of a mixture of plant byproducts from *Azadirachta indica*, *Arachis hypogaea*, *Coffea arabica*, *Musa sapientum*, and *Citrallus lanatus*. The outer layer is a biopolymer made from agar and glycerin.

Material Processing and Papermaking

The initial part of our project was preparing the bioadsorbent paper, for which we had to first process the materials. For Neem, we washed the leaves with distilled water and dried them, first leaving them outside for two days and then in an oven at 100°C for an hour. After that, we blended the leaves and strained the powder until we were left with fine-grained NLP (Nkansah et al., 2019). For neem sawdust, PSP, BPP, and WMR, we carried out similar processes of drying, blending, and straining. For CG, we only had to dry them to use for our purposes. For the papermaking step, we mixed the processed materials in the desired ratio by mass (Table 1) and blended them together with some water to make a pulp. In deciding on the effective ratio, the two factors we considered were how available the biosorbents were locally (year-round agricultural products compared to seasonal products) and the structural integrity. For example, WMR is not only a seasonal agricultural waste but also more prone to liquefying the pulp too much to have the proper density to become a paper-like structure. We added okra extract as a binding agent to keep the paper from breaking down, courtesy of its effective glue-like property. We ran the mixture through a tub of water and into a paper mold. After letting it dry for a day, we carefully separated the sheet of bio-adsorbent paper. For the outer layer, we mixed agar and water to work as a substitute for starch and then processed it with glycerin to create a polythene resembling a biopolymer.

Biosorbent	Neem	PSP	BPP	Coffee ground	WMR
%[a]	40	20	20	10	10

Table 1. Percent by mass composition of biosorbents in the bio-adsorbent paper.

Preparation of the Removal Rate Test Apparatus

Our efficiency testing was done in two steps: NLP/Neem sawdust testing and bioadsorbent paper testing. For testing, we used a controlled molarity solution of the heavy metal salt copper (II) sulfate ($CuSO_4.5H_2O$). In the first test, using a weight balance with an accuracy of a thousandth of a gram, we measured 2.00g of $CuSO_4$ salt and made five beakers of 150mL solution, giving the total volume of 150mL × 5 = 750mL. Given that the molar mass of $CuSO_4.5H_2O$ is 249.5, the molarity, M, of our solution was,

$$M = \frac{2\ \text{g}}{2.495\ \text{g}/\text{mol}} \times 0.750\ \text{L} = 0.011\ \text{M} \quad (1)$$

Beaker 1 was kept as the reference beaker; in beaker 2 and 3, we weighed and added 1.800g of NLP; in beaker 4 and 5, we added 1.200g of Neem sawdust. We added 1 mL of dilute hydrochloric acid (HCl) to work as a pH activator (Kalam et al., 2021). After leaving the beakers for two hours, we filtered out the precipitated substance using a filter paper for further analysis. For testing the bio-adsorbent paper, we used an isomolar solution of copper sulfate, adding 50 cm^2 (5 cm x 10 cm) pieces of the paper, weighing on average 2.460 g.

Removal Rate Testing

The primary and crudest method of our testing was to observe the change in the solution's color. Using copper (II) sulfate for testing has an advantage due to its blue hue, whose strength is approximately proportional to Cu^{2+} concentration. The next test was weight comparison; comparing the final precipitate (or paper) weight with the pre-adsorption weight gives an estimate of the removal rates. The differences were precisely measurable as we used a high-concentration solution. Even though real-life wastewater will likely have much lower levels of copper concentration, having a high molarity helps to reduce the uncertainty in our tests while preserving the relative removal capacities. To measure the removal capacity for lower concentrations, a more sophisticated testing apparatus is required (see discussions). In each of the beakers, there were 0.4g of $CuSO_4.5H_2O$. Therefore the weight of Cu^{2+}, w_{Cu}, was,

$$w_{Cu} = \frac{0.4\ \text{g} \times 63.5\ \text{g}/\text{mol}}{249.5\ \text{g}/\text{mol}} = 0.102\ \text{g} \quad (2)$$

We then calculated Cu^{2+} removal using the following equation, where w_i is the initial mass and w_f is the final mass,

$$Cu^{2+}\ \text{removal} = \frac{w_f - w_i}{w_{Cu}} \times 100\% \tag{3}$$

Lastly, we did an ion test with potassium ferrocyanide ($K_4[Fe(CN)_6]$), which reacts with Cu^{2+} to produce copper (II) hexacyanoferrate ($Cu_2[Fe(CN)_6]$), a reddish brown precipitate.

$$CuSO_4 + K_4[Fe(CN)_6] \rightarrow Cu_2[Fe(CN)_6] + K_2SO_4 \tag{4}$$

We took 4 mL of solution from the beakers into a batch of test tubes and added 1 mL of $K_4[Fe(CN)_6]$. The level of precipitation gives an effective estimate of metal ion removal.

Ion Identification Test

There was a significant visual difference in $Cu_2[Fe(CN)_6]$ precipitation in the two test tubes (Fig. 2b), as well as in reaction rate. In the treated solution, the reaction took place rapidly, but in the reference solution, it took a much longer time, indicating a notable difference in Cu^{2+} concentration.

Weight Comparison Test

For this test, we first carry out the test for unprocessed (not processed into the bio-adsorption paper) neem sawdust, which is the largest constituent element of our bio-adsorbent paper and can give us a reference to measure the efficacy of giving the biosorbent a paper-like structure.

NLP/Sawdust Testing: After measuring the weights for beakers 2-5, we used equation (3) to calculate the removal rates. Table 2 shows the results.

Adsorbent	Initial Weight (g)	Final Weight (g)	Cu^{2+} Removal (%)	Average Removal Rate (%)
NLP	1.800	1.863	61.7	64.2
NLP	1.800	1.868	66.7	
Sawdust	1.200	1.274	72.5	71.6
Sawdust	1.200	1.272	70.6	

Table 2. Measured removal rates for neem leaf powder (NLP) and neem sawdust..

Bioadsorbent Paper Testing: We weighed the paper before and after adsorbent uptake, and conducted three tests for a statistically significant result. The removal rates in each test and the average rates are presented in Table 3. In both cases, the reference beakers (beaker 1) were used to make sure there are no implicit factors other than the bio-adsorbent contributing to the heavy metal removal, and indeed, no precipitations were observed in the reference beakers.

Labels	Paper Area (cm^2)	Initial Weight (g)	Final Weight (g)	Cu^{2+} Removal (%)	Average Removal Rate (%)
Pap-1	50	2.443	2.520	75.5	76.5
Pap-2	50	2.426	2.510	82.4	
Pap-3	50	2.514	2.587	71.6	

Table 3. Measured removal rate for bio-adsorbent paper.

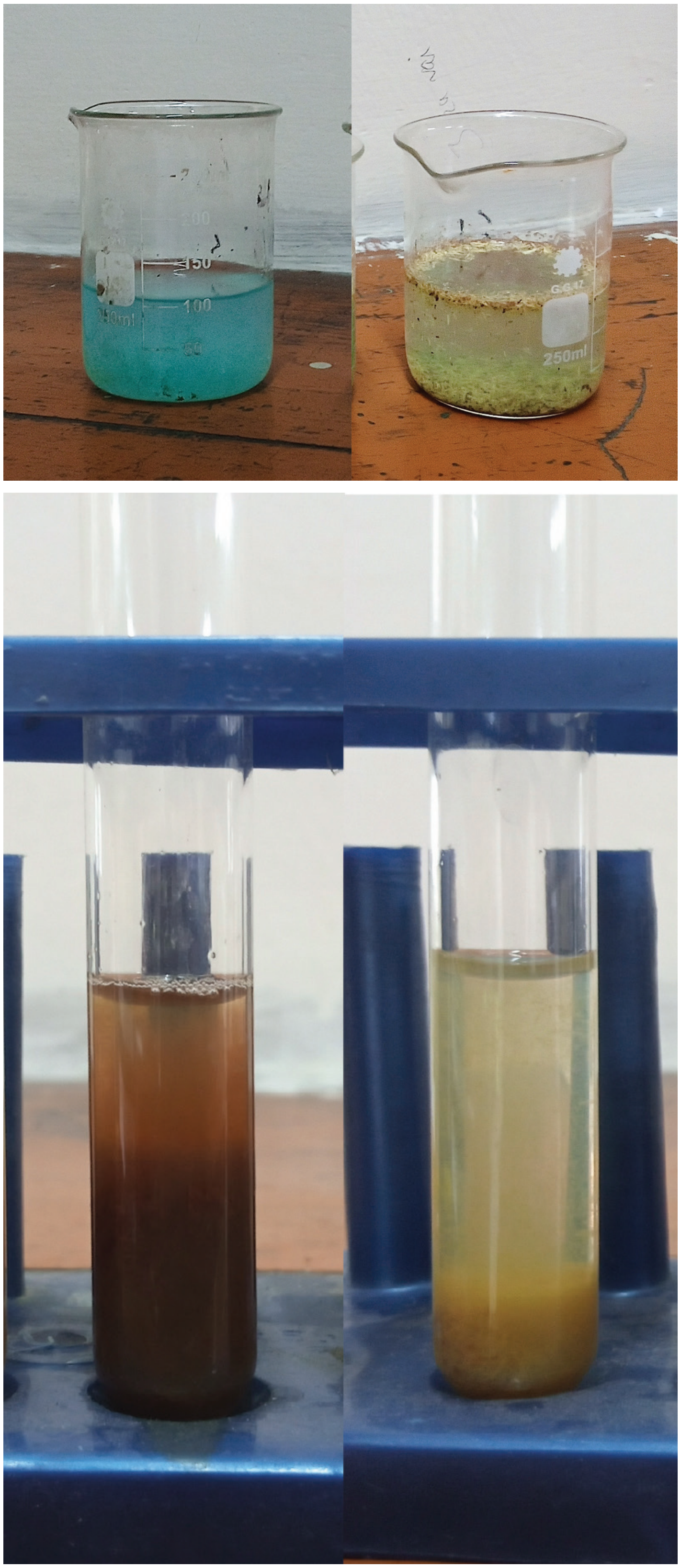

Figure 2. (a) Visual results from the color test. (b) Visual results from the ion test. In both images, the left and right parts contain reference and treated solutions, respectively.

Finally, we repeated the test for a continuous set of removal rates with time, to fit a graph for the adsorption mechanism under constant temperature. Paper sizes of 50 cm^2 and 40 cm^2 were used for two different graphs. Using the data points, we fitted the best fit curves, which are shown in Fig. 3. The isotherms showed a similar trend to Langmuir isotherms, which was reasonable given the monolayer and homogeneous surface of the bioadsorbent paper

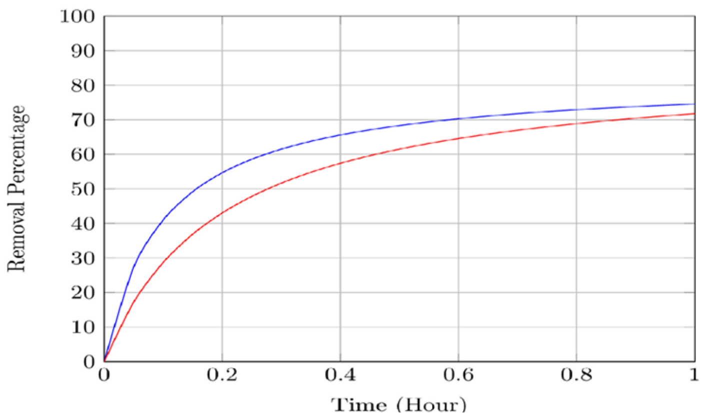

Figure 3. Adsorption mechanism isotherms for 40 cm^2 (red) and 50 cm^2 (blue) sized pieces of the bioadsorbent paper.

(Kalam et al., 2021).

Discussion

The main objective of our project was to develop an adsorbent medium by combining a wide range of biosorbents capable of water remediation. Our bioremediation technique has shown the ability to remove heavy metals from water at around 80% efficiency without creating any substantial sludge. Although not explicitly tested, we expect this adsorption medium to work well in removing textile dyes as well, given the ionic constitution of the majority of dyes (McCord & Roza, 2018). Our experiments showed higher removal rates in slightly acidic solutions, and NLP and sawdust have been found to work best in the pH range of 4 to 6 (Kalam et al., 2021). The reason we focused more on an acidic apparatus is due to the basic nature of dissolved metallic ions, as well as the fact that most textile dyes tend to be basic. Carrying out the experiments in a neutral or basic solution instead, while it may lower the adsorption capacity, will give us more information on how removal rates and pH values may be connected. A number of past studies also look at this correlation, including Garg et al. (2004) and Febriana et al. (2009), and although their pH ranges do not necessarily always overlap, they find better removal rates in an acidic environment. More acidic is not necessarily better, as the extra protons (H+) present in the solution start to compete with Cu2+ ions for the active sites. Temperature is another factor; as adsorption is an exothermic process ($\Delta H < 0$), the removal rates should slightly increase with increasing temperature (Kalam et al., 2021). Surface properties such as surface area, polarity, and pore size distribution can also influence adsorption rates. Designing to maximize these properties should facilitate the removal capacity. In our work, we have used a high-molarity test solution for a higher level of accuracy. Real-life contaminated water usually has a much lower concentration of contaminants, in the mg/L levels, compared to the g/L levels tested in this paper, and methods such as atomic absorption spectrometry (AAS) can further validate our results.

Unlike chemical treatment methods, the discussed biosorbents do not introduce harmful chemicals into our waters, making them safe for drinking and irrigation. These biosorbents can be produced locally almost everywhere in the world, reducing the overall cost and the environmental impact associated with transportation. As these materials are mostly discarded as agricultural waste, utilizing them helps waste management and promotes recycling. Moreover, the process is similar to industrial papermaking and can be mass-produced with minimum effort. The usability of our bioadsorbent paper is versatile, on both the industrial and personal scale. Regular-sized strips could be used to treat water to remove the bulk of the heavy metals and textile dyes from water in the event of flooding or an industrial spill. For industries such as textiles, this paper can be incorporated in the tertiary stage of the conventional effluent treatment process.

In this paper, we have discussed the design, constituents, and implementation of an adsorption medium made entirely from organic biosorbents. This can provide a pragmatic solution to the high expense of industrial wastewater treatment, due to which many middle- to small-scale industries fail to treat their effluents. Using our bioadsorbent paper can reduce environmental harm and waterbody degradation, as well as providing a cost-effective solution for industries to treat their effluents and help create a sustainable future.

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