Research Article

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Synthesis and Application of Eco-Friendly Adsorbent for Treatment of Congo Red and $KMnO_4$ Dye Aqueous Solution

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ABSTRACT

The use of natural resources as environmentally acceptable adsorbents for wastewater treatment was investigated in two research. The first concentrated on using bamboo leaves as an inexpensive adsorbent to remove the dye $KMnO_4$. Bamboo leaves were carefully synthesised, spectrophotometrically analysed, and showed different adsorption capabilities according to unit adsorbent concentration. The second study used a systematic synthesis procedure and spectrophotometric characterization to remove Congo red dye from mango leaves. The Mangifera indica adsorbent demonstrated a noteworthy 88.27% adsorption peak at a dye concentration of 50 mg/L. Both programmes emphasised the potential of renewable resources and focused on low-cost, environmentally friendly methods to address the problem of water contamination. The research emphasised the adaptability and effectiveness of natural adsorbents, underscoring the significance of sustainable approaches in the treatment of wastewater. These findings contribute significantly to developing green solutions, showcasing the feasibility of utilizing bamboo and mango leaves in addressing diverse dye contaminants. Further optimization and mechanistic understanding are crucial for enhancing the efficiency of these eco-friendly adsorbents, paving the way for environmentally conscious water treatment practices.

Keywords: Adsorbent; $KMnO_4$ dye; Congo red dye; Environment.

1. INTRODUCTION

Water pollution remains a strategic concern that requires attention. Water is the source of human life on Earth. In actuality, there is a decreasing amount of clean water that is readily available to people. Ninety percent of the water is salt water in the ocean, with only one percent accessible to living creatures directly. The remaining two percent is fresh water from melted glaciers at the north and south poles (Setiadi *et al.* 2003). It is crucial to make sure the water that is readily available is pure and devoid of any impurities. Unfortunately, as human and industrial activity increase, there is a strong chance that the availability of clean water will decrease due to waste disposal and environmental degradation. The practice of using dyes as the primary colouring agent in large-scale industries including paper, printing, tanning, and textiles has resulted in a significant amount of waste (Bello *et al.* 2014; Aswin Sriram *et al.* 2020; Hassan *et al.* 2018). Large industries are the ones who employ synthetic dyes the most due to their affordability, longevity, and wide colour range. Despite these benefits, synthetic dye use poses a risk to the environment if it is discharged as pollution. According to certain research, up to 15% of the dyes used in the colouring process will be wasted (Wang *et al.* 2008). According to some research, industrial sectors consume hundreds of thousands of tonnes of dyes annually, which means that dye waste might potentially reach tens to hundreds of thousands of tonnes annually. Due to their mutagenic and genotoxic properties, dye waste products have been shown in a number of academic articles to potentially be harmful to human health (Lellis *et al.* 2019). When dye concentrations are high, they can prevent sunlight from entering aquatic systems, which can interfere with biological processes in living beings (Alhogbi *et al.* 2021). Furthermore, the amount of BOD and COD in the waterways can also rise due to the presence of dyes. Large amounts of the dyes are difficult for the environment to spontaneously breakdown unless outside assistance is provided (Rahman *et al.* 2012).

One of the most popular techniques for managing garbage is adsorption. It has been shown to be successful in lowering toxins such dyes, organic pollutants, and heavy metals. Adsorption technology has advanced in the modern era due to the utilization of organic/biomass waste, such as agricultural waste and forest products including rice husks, wood powder, tree bark, and foliage. Certain interactions occur between pollutant molecules and biomass, also known as biosorbent, during the adsorption process. The process is frequently referred to as biosorption. Utilising biomass-based biosorbents to reduce pollutants has various benefits, including low-cost raw materials and preparations, ease of use, regeneration potential, selectivity for certain heavy metals, and environmental safety (Nadeem *et al.* 2015). Mango trees (*Mangifera Indica L.*) are a seasonal fruit tree that grows in nearly every climate. The tree has thick, shaded leaves. Its fruit started to be traded across continents. Mango trees are commonly found in front of yards as shade trees and fruit trees in many parts of Indonesia. Mango trees are still frequently seen to be somewhat shaded, even in urban settings. Every day, mango trees create litter that is mostly made up of leaves. Ecologically, mango leaf litter is worthless. Mango leaves can be used as biosorbents without interfering with the use of other materials. Disodium 4-amino-3-[4-[4-(1-amino-4-sulfonato-naphthalen-2-yl) diazenylphenyl] phenyl] diazenyl-naphthalene-1-sulfonate is the IUPAC designation for Congo red, an anionic azo dye. Fig. 1 shows the Congo red's molecular structure.

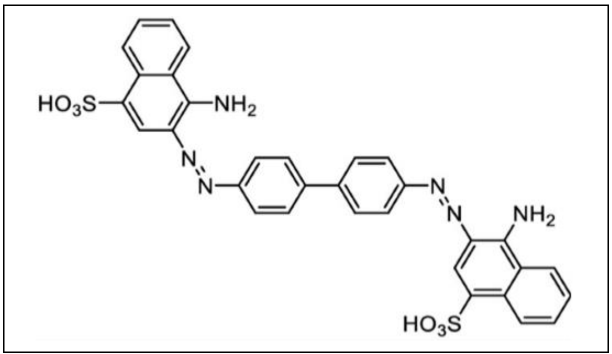

Fig. 1: Molecular structure of Congo red

2. EXPERIMENTAL PROCEDURE / MATERIALS AND METHOD

2.1 Preparation of Adsorbent

1. Leaves of Bambusa vulgaris and Mangifera indica were collected and washed thoroughly with clean water to remove any dirt or impurities.
2. They were dried in a well-ventilated area, away from direct sunlight, until they were completely dry. This took several days, due to the humidity and temperature.
3. Once the leaves were dried, they were ground into a fine powder using a grinder. It's important to grind the leaves into a fine powder to increase their surface area and maximize their adsorption capacity. After that, the powder was washed with distilled water until the filtrate had no colour. Furthermore, the powder was oven-dried at 55 °C for a full 24 hours.
4. To achieve a uniform size, the dried leaf was ground and sieved using an 80-mesh screen.
5. The paste was cleansed with distilled water until the filtrate had a neutral pH and was colourless when it had dried again. After that, the powders were stored in an airtight container in a dry, cool place until they were needed.

Figures 2 and 3, respectively, show the preparation method for the bio-adsorbents made from Bambusa Vulgaris and Mangifera Indica.

Fig. 2: Preparation of Bambusa Vulgaris bio adsorbent

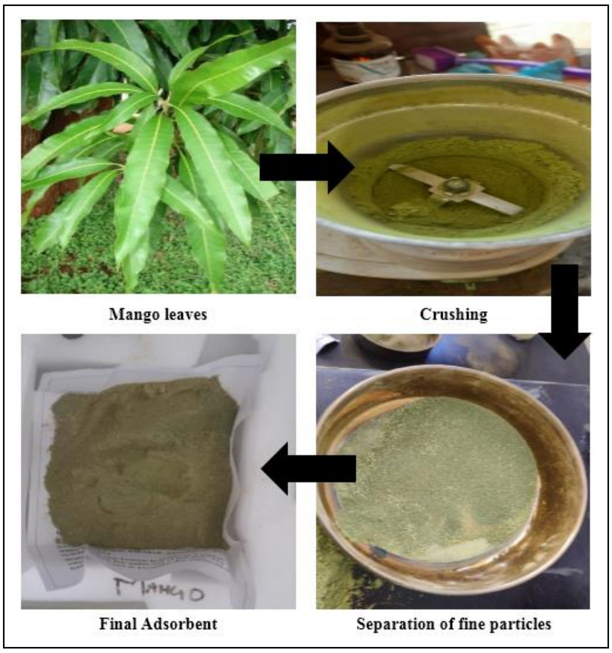

Fig. 3: Preparation of Mangifera Indica bio adsorbent

2.2 Preparation of Dye Solutions

The following steps were taken in order to prepare a 100 ppm (parts per million) solution of Congo red dye and $KMnO_4$ dye:

1. Using a digital scale, precise measurements of 0.1 g of Congo red dye and $KMnO_4$ dye powder were made.
2. Each of the measured dye powders was then separately dissolved in one litre of distilled water. Facilitating the dissolution process, a magnetic stirrer was employed.
3. Upon achieving complete dissolution of the dye powders, the resulting solutions were carefully transferred to clean, dry containers and thoroughly mixed.
4. A spectrophotometer or colorimeter was used to detect absorbance at a specific wavelength, usually 500 nm, in order to determine the concentration of the dye solutions. The concentration was adjusted by adding water or dye, as necessary, to achieve a final concentration of 100 ppm.
5. The prepared dye solutions were stored in clean, dry containers, safeguarded from direct sunlight or heat.

Additionally,

- Solutions of varying concentrations (80 ppm, 60 ppm, 40 ppm, 20 ppm) were derived from a 100 ppm stock solution.
- In each of these solutions, 0.1 g of adsorbent was added, catering to the respective dyes.
- The solutions were then placed in an incubator shaker, where they underwent agitation for 5 hours at a speed of 120 rpm.

The preparation of the $KMnO_4$ dye and Congo red dye stock solution, as well as the addition of an appropriate quantity of adsorbent in various concentrations, are depicted in Fig. 4 and 5, respectively.

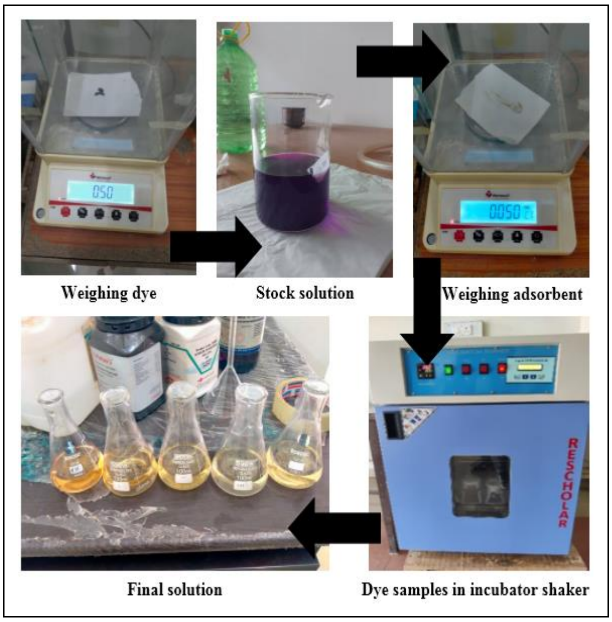

Fig. 4: Preparation of $KMnO_4$ dye stock solution and adding suitable amount of adsorbent in different concentration

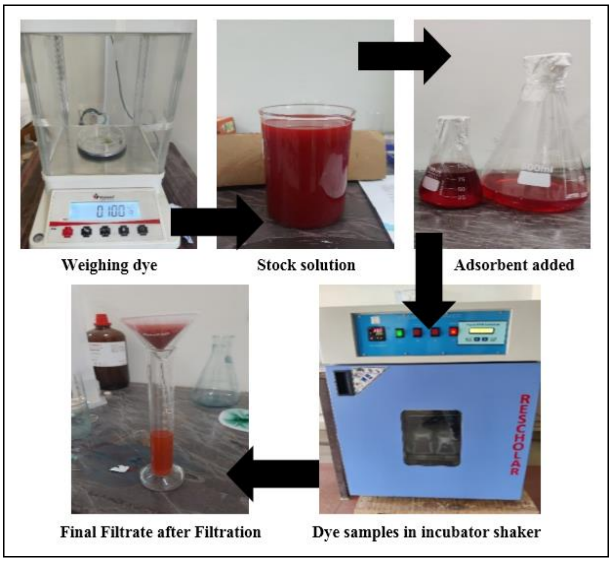

Fig. 5: Preparation of Congo red dye stock solution and adding suitable amount of adsorbent in different concentration

2.3 Incubator Shaker

The incubator shaker combines two essential parts, an incubator and a shaker, which each have different but complementary functions. This device allows samples or culture material to be stirred while also creating a controlled environment that supports growth or reaction activities. The incubator module makes sure that the environmental factors that are necessary for ideal circumstances are carefully controlled. This includes maintaining temperature, humidity, and other relevant parameters like pH and gas composition precisely. A complex range of processes, such as heating elements, cooling systems, humidity control modules, and gas regulation systems, are required to achieve this precision. Temperature regulation is kept between 4°C and 60°C, depending on the particular needs of the application. On the other hand, the shaker section evenly distributes nutrients, gases, and other essential elements throughout samples or culture media by applying controlled agitation. To meet the needs of a given application, a variety of agitation methods, including orbital, reciprocating, and linear shaking, can be used. The speed and amplitude of the shaking can be adjusted. Combining the functions of an incubator and shaker creates a carefully regulated, turbulent environment that is ideal for specific development or reaction processes. An indispensable tool for ensuring precision and uniformity in investigations, the incubator shaker finds extensive use in chemical engineering as well as in microbiology, cell culture, molecular biology, and biochemistry studies.

2.4 UV-vis Double Beam Spectrophotometer

A scientific tool used to detect light absorption in the visible and ultraviolet portions of the electromagnetic spectrum is the UV-vis double beam spectro-photometer. It functions according to the principle that some light is absorbed and some light is transmitted through a sample when it passes through it. Two light beams are used by the apparatus, one of which goes through the sample and the other through a reference solution. The amount of light absorption by the sample can be ascertained by comparing the two beams. One of the main parts is a dual light source that produces visible and ultraviolet light, respectively, utilising tungsten and deuterium lamps. The sample holder firmly places the sample so that light can pass through it, and the monochromator separates a particular wavelength to pass through it. Both the reference solution and the sample's transmitted light intensity are measured by the detector. By examining the difference in light intensity between the sample and reference solution, the data processor determines absorbance. The outcomes are then presented for in-depth examination in printed matter or on a screen. In many scientific areas, the UV-vis double beam spectrophotometer is an essential tool for analytical procedures.

3. RESULT AND DISCUSSION

3.1 Mangifera Indica

The straight line found at low concentrations in the context of Beer-Lambert law, which correlates a substance's absorbance to its concentration in a solution, is the outcome of the linear relationship between absorbance and concentration. In accordance with the Beer-Lambert rule, there exists a direct correlation between the path length (l) of the sample and the concentration (C) of the absorbing species with the absorbance (A) = ϵlC. The absorbance corresponding to various concentrations of Congo red dye solutions are illustrated in Table 1.

Table 1. Data for standard calibration of Congo red dye solution

Concentration	Absorbance	Concentration	Absorbance
1	0.102	10	0.641
2	0.167	15	0.914
3	0.232	20	1.211
5	0.317	25	1.42

Because the concentration term (C) is very small at low concentrations, the relationship between absorbance and concentration is linear. This linear relationship is evident in the Beer-Lambert plot, where absorbance is plotted against concentration. Factors including solute-solute interactions, solvent effects, and non-linear absorption behavior at high concentrations can cause deviations from linearity as concentration increases. However, at low concentrations where these factors are minimal, the Beer-Lambert plot typically yields a straight line. The calibration graph illustrating the relationship between absorbance and dye concentration for Congo red dye solutions is presented in Fig. 6.

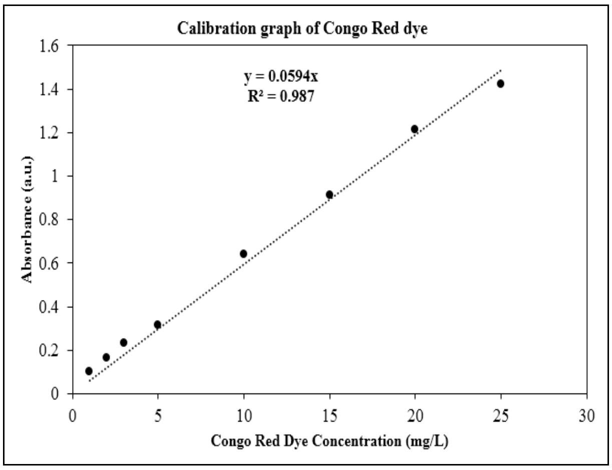

Fig 6: Calibration graph of Congo red dye

Table 2. Calculation of final concentration and rejection (%)

Treated dye solution	Absorbance	Final Concentration	Rejection (%)
20	0.151	2.54	87.29
40	0.311	5.24	86.91
60	0.474	7.98	86.70
80	0.642	10.81	86.49
100	0.852	14.31	85.66

3.2 Equations Used

The equation of the linear curve obtained from the calibration graph is given by

$$y = mx \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where, y is the absorbance, m is the slope, x is the concentration of the $KMnO_4$ dye (in ppm).

With the help of this equation concentration of the dye solution can be calculated if absorbance value is known (Mall *et al.* 2005)

$$Concentration\ of\ dye\ solution = \frac{(absorbance\ of\ dye\ solution)}{(slope\ of\ standard\ solution)} \quad \ldots 2$$

Further, the percentage of dye removed is calculated using the relation (Murugan *et al.* 2010):

$$\%\ dye\ removal = \left[\frac{C_0 - C_t}{C_0}\right] 100\% \quad \ldots\ldots\ldots 3$$

Where, C_0 is the initial concentration, C_t is the concentration at any absorbance value.

The degree to which a piece of data matches a calibration curve is indicated by the coefficient of determination, or R^2 value. The subsequent calculations concerning the final concentration and rejection percentage of the treated dye solution are delineated in Table 2 and the Effect of concentration of unit Adsorbent is illustrated in Fig. 7.

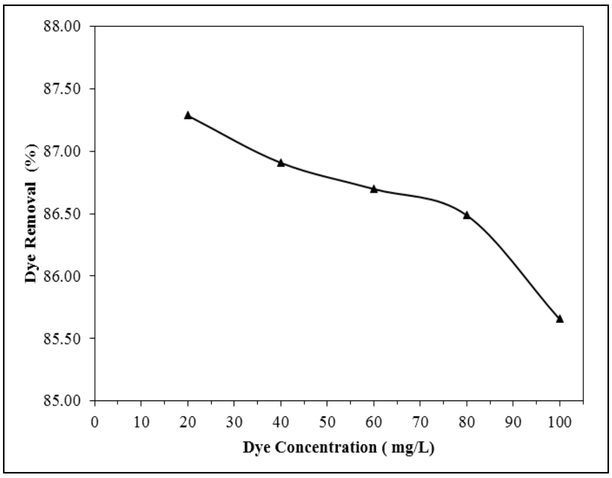

Fig. 7: Effect of concentration of unit adsorbent

There are more dye molecules accessible to adsorb onto the surface of the adsorbent as the concentration of the dye in the solution rises. The number of dye molecules that can be adsorbed per unit mass of the adsorbent is limited, though. Additional increases in dye concentration do not provide a proportionate rise in adsorption once the adsorbent's adsorption sites are saturated. A lower rejection rate could arise from this.

The adsorption process on a fixed amount of adsorbent material is modified when the concentration of the chemical being adsorbed in a solution is changed. The term "effect of concentration on a unit adsorbent" describes this.

3.3 Effect of Contact Time on Dye Adsorption

The adsorption process is mostly influenced by contact time. The adsorbent can be used to treat contaminated water if there is a sufficient contact time. The range of this parameter was 5 to 180 minutes. Fig. 8 displays the findings about the ability of mango leaves to eliminate CR dye. According to the specified operating parameters, as illustrated in Fig. 8, the examined adsorbent's adsorption capacity grew rapidly within the first 30 minutes of contact time. There are many accessible sites, which causes the first adsorption stage to proceed quickly. After 60 minutes, equilibrium was reached.

3.4 Effect of temperature on adsorption of Congo red dye

The study examined the impact of temperature on the adsorption of Congo red dye at an initial concentration of 30 mg/L on an adsorbent dosage of 1 g/L mango leaves. The results of the trials, which are shown in Fig. 9, were obtained at 293 K, 303 K, and 323 K. As seen in Fig. 9, adsorption capacity is positively impacted by temperature; that is, as temperature rises from 293 to 323 K, its value increases.

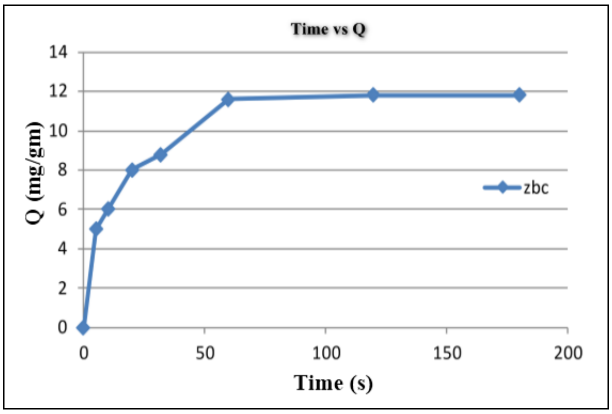

Fig. 8 Effect of Contact time on Dye Adsorption

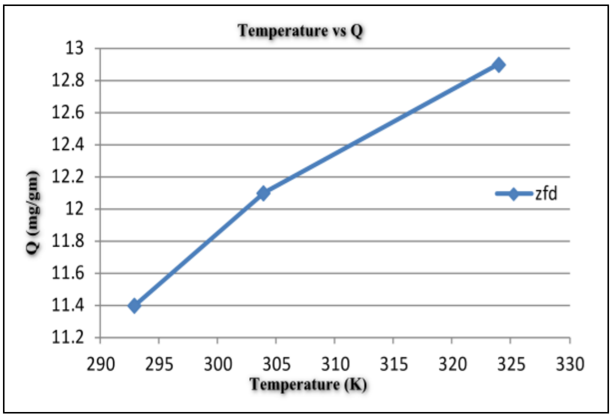

Fig. 9 Temperature's impact on Congo red dye absorption

The investigation into the synthesis and application of an eco-friendly adsorbent for the treatment of Congo-red dye aqueous solution yielded substantive outcomes. The eco-friendly adsorbent (Mangifera indica) exhibited remarkable efficacy, removing approximately 86.61% of Congo red dye from aqueous solutions. This noteworthy removal rate underscores the potential of the synthesized adsorbent to address water pollution concerns linked to dye contaminants. The calibration graph in the study played a pivotal role in establishing a quantitative correlation between dye concentration and the adsorption process. This graph served as a crucial tool, facilitating the precise determination of the final dye concentration and calculation of the rejection percentage, thereby enhancing the assessment of adsorption efficiency. Additionally, a minor decreasing trend was seen in the analysis of the unit adsorbent concentration on dye removal percentage. This provides useful information on the adsorption capacity at different concentrations and provides guidance for optimising adsorption settings. Furthermore, a dynamic tendency was found in the analysis of the impact of contact duration on dye adsorption, which first increased with longer contact times before stabilising. For practical applications, this temporal awareness is essential since it helps determine optimum contact durations in real-life scenarios.

3.4.1 Bambusa Vulgaris

The absorbance corresponding to various concentrations of $KMnO_4$ dye solutions are illustrated in Table 3.

Table 3. Data for standard calibration of $KMnO_4$ dye solution

Concentration	Absorbance	Concentration	Absorbance
1	0.138	10	1.371
2	0.274	15	2.055
3	0.415	20	2.745
5	0.685		

The calibration graph illustrating the relationship between absorbance and dye concentration for $KMnO_4$ dye solutions is presented in Fig. 10.

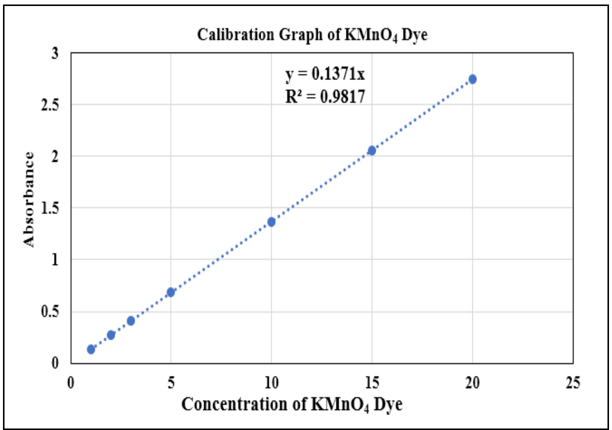

Fig. 10: Calibration graph of $KMnO_4$ dye

The subsequent calculations concerning the final concentration and rejection percentage of the treated $KMnO_4$ dye solution are delineated in Table 4.

Table 4: Calculation of final concentration and rejection (%)

Treated dye solution	Absorbance	Final Concentration	Rejection (%)
20	0.267	1.947	90.26
40	0.583	4.252	89.37
60	0.824	6.010	88.98
80	1.120	8.169	87.78
100	1.313	9.576	86.47

3.5 Effect of concentration of unit adsorbent

Adsorption process insights are obtained by examining the impact of adsorbate concentration on a unit mass of adsorbent, like bamboo leaves. When more molecules come into touch with the adsorbent surface, adsorption typically speeds up as the concentration of adsorbate rises. Even at higher concentrations, saturation eventually happens, at which point the adsorbent surface is unable to adsorb any more molecules. This equilibrium adsorption is governed by rates of adsorption and desorption, which may shift towards higher adsorption until saturation is reached. This relationship is shown by the widely used Langmuir isotherm model, which helps to explain how adsorption varies with concentration. In the end, this research helps to optimize the circumstances in order to maximize adsorption efficiency. The impact of the concentration of the unit adsorbent is depicted in the graph illustrating dye removal (%) versus dye concentration (mg/L) in Fig. 11.

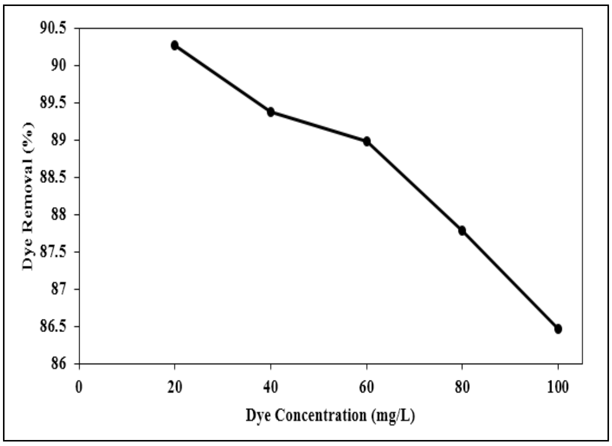

Fig. 11: Effect of concentration of unit Adsorbent

3.6 Effect of contact time on dye adsorption

Fig. 12 illustrates how contact time affects $KMnO_4$ adsorption using bamboo leaves. The graph indicates that the adsorption capacity increased in the early stages of contact time, from 16.03 mg/g to 38.84 mg/g; the optimal contact duration was found to be 50 min. This rise in adsorption capacity may have been caused by the unoccupied adsorbing space on bamboo leaves. Beyond 50 minutes, there is no discernible difference in the dye adsorption capability. The saturation of the bamboo leaf surface prevents $KMnO_4$ molecules from readily entering the adsorbent's deeper pores. Repulsion between solutes in solid and aqueous phases developed over time as a result of the massive amount of adsorption that occurred during the initial period (Sulyman et al., 2014). Similar results were also reported for the removal of $KMnO_4$ using dead leaves of Posidonia Oceanica (Cengiz and Cavas, 2010). The graphical representation illustrating the influence of contact time on dye adsorption is presented in Fig. 12.

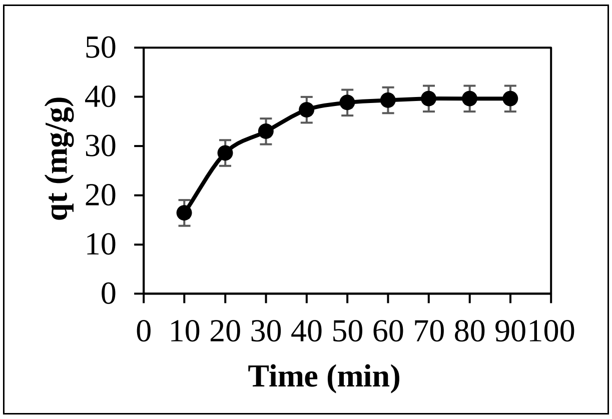

Fig. 12: Contact time's impact on dye adsorption

3.7 Effect of initial pH

As in the majority of investigations published in the literature, pH has been identified as a significant influencing factor for dye biosorption on agricultural by-products. Researchers looked at how starting pH affected dye adsorption percentages across a pH range of 2 to 10. For the dye $KMnO_4$, as seen in Figure 13, the dye clearance ratio was at its lowest at pH 2. When the starting pH was raised from pH 2 to pH 7, the ratio of dye absorbed increased. However, after pH 8, the dye removal ratios did not change significantly ($P > 0.05$). According to the findings in Figure 13, 64.25% of the coloring matter in the pH range of 7-8 is adsorbed by the pH biomass. Thus, during the entire investigation, a pH of 7 is regarded as ideal. The graph presented in Figure 13 delineates the correlation between the percentage of dye adsorbed and pH, elucidating the influence of initial pH on the adsorption of $KMnO_4$ by bamboo leaves. This investigation's experimental settings include a temperature of 300 K, a sorbent dose of 1 g/L, a dye concentration of 100 mg/L, a particle size of 400 µm, and a contact time of 5 hours.

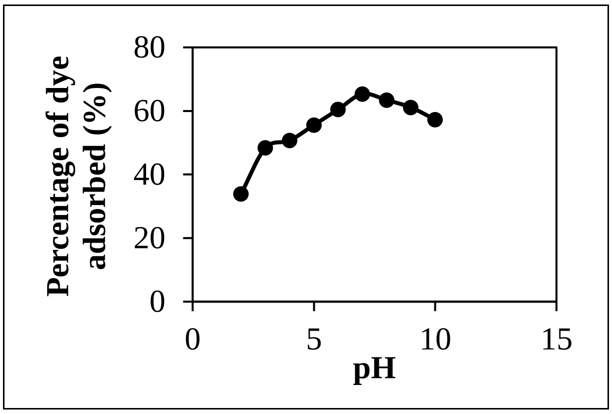

Fig. 13: The impact of initial pH on $KMnO_4$ adsorption by bamboo leaves (100 mg/L dye concentration; 1 g/L sorbent dosage; 400 µ particle size; 5 hours of contact duration; 300 K temperature).

4. CONCLUSION

In conclusion, Mangifera indica and Bambusa vulgaris exhibit significant promise as environmentally sustainable and economically viable adsorbents for the effective removal of dyes from wastewater. Mangifera indica leaves exhibit notable adsorption capacity and favorable behavior, particularly concerning Congo red dye, whereas Bambusa vulgaris proves effective in removing $KMnO_4$ dye. The inherent advantages of their natural abundance, cost-effectiveness, and minimal environmental impact position these botanical materials as promising alternatives to conventional adsorbents. Nonetheless, further investigations are imperative to optimize adsorption conditions and elucidate the underlying mechanisms. In summary, these research findings underscore the substantial contributions of both Mangifera indica and Bambusa vulgaris to sustainable water treatment, presenting innovative solutions for the mitigation of diverse contaminants and advocating for environmental stewardship across various industrial and environmental contexts.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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