







Research Article

Biosorption of Malachite Green from Aqueous Phase by Tamarind Fruit Shells Using FBR

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The aim of this research is to remove malachite green (MG) from a created water environment utilising tamarind fruit shell (TFS) and a fixed-bed reactor (FBR) technology at room temperature. Biosorption is the finest method for dye removal among the several approaches available. It produces excellent results and may be used to remove a wide range of colouring components. It is used to weigh different options for firm things. The option which balances other ones on various counts is the finest one. Various studies have found that eating malachite green-contaminated fish poses a major health risk to people. From the FBR studies, the effect of various factors such as flow rate, initial sorbate concentration, biosorbent size, and bed depth on breakthrough of MG is assessed. The study was carried out to fix the flow rates. This is done by varying the biosorbent size with constant bed depth of 30 cm. The trend in flow rate variation appears to be similar for 0.33 and 0.6 mm sizes, whereas for 0.13 mm size, it is slightly different. The head loss and swelling of TFS particles are insignificant, during the fixed-bed studies. It is estimated that 30.9 T of crude TFS is required to get 8300 kg of 0.6 mm size of TFS. The service time obtained from design was more than the experimental breakthrough time, and calculated bed efficiency was >90%. The biosorption of MG by TFS can be well explained by the BDST approach. Acid regenerants such as 0.5 N H₂SO₄ and 0.5 N HCl can satisfactorily regenerate the spent TFS in the FBR system, with 0.5 N HCl being a better one.

1. Introduction

Industries such as textiles, paper, carpet, and printing use dyes and pigments. The use of dyes necessitates a large amount of water and generates a significant amount of effluent. Because most dyes are resilient to light and oxidizing

chemicals, removing colour from dye-bearing wastewaters is difficult [1]. Because of its unappealing appearance, even a trace amount of colouring material makes it unfit for drinking and other pleasurable reasons. The removal of toxic dyes such as malachite green is must because of its effects on human and environment [2]. Chemical coagulation,

biological reduction, photocatalytic fermentation, ozone treatment, membrane filtering, and electrolysis are all standard techniques for removing colour from colourants [3, 4]. These approaches fail to meet the desired limitations because refractory organic molecules are resistant to aerobic digestion and are also stable to light, heat, and oxidizing agents. Fixed-bed adsorption studies using various adsorbates are reviewed, and it is observed to be an effective one [5, 6]. The novel of this study is to effectively remove the malachite green by tamarind fruit shells in the fixed-bed reactor and to investigate the breakthrough analysis, design fixed-bed with scale-up, and regeneration aspects. Among the numerous techniques of dye removal, biosorption is the best method which can give good results, and it can be used to remove different types of colouring materials [7]. The major advantages of biosorption over conventional treatment methods include low cost, good efficiency, minimization of chemical and or biological sludge, regeneration of biosorbents, and possibility of solute recovery. Biosorption is the ability of biological materials to accumulate solute from wastewater through metabolically mediated or physico-chemical pathways of uptake [8]. Various adsorbents are used in this adsorption process. The efficiency directly depends on the effectiveness of the adsorbents chosen for removal. The adsorption capacities and removal efficiencies of different types of adsorbents are compiled, and results were obtained [9]. Removal of malachite green is also obtained using algae. Low-cost materials such as rice husk are also used in the dye removal. The efficiency of tamarind fruit shell as an adsorbent is high in removal of dyes [10]. The tamarind fruits shells increase its effectiveness in dyes removal after proper machining with respect to the desired size. Adsorption of methylene blue is done by tamarind fruit shells [11]. Nowadays nanomaterials play a major role in the treatment process. Nanoparticles derived from iron oxides were also used in the adsorption technique [12–14]. The low-cost adsorbents which include the charcoal show higher efficiency in the removal of dyes [15]. The removal of malachite green using activated carbon as an adsorbent is also studied [16]. But the effectiveness can be increased by replacing any other abundantly available low-cost adsorbent. So, TFS is used in this study to determine its efficiency in removal of malachite green under varying factors such as flow rate, sorbate concentration, and biosorbent size.

2. Materials and Methods

2.1. Tamarind Fruit Shells. The tamarind tree is a slow-growing, lengthy, enormous tree that may grow to a height of 80 or even 100 feet (24–30 metres) under optimal circumstances, with a width of 40 feet (12 metres) and a base diameter of 25 feet (7.5 m). Being a tropical tree, it widely grows in several countries such as India, Spain, Portugal, Dutch, Germany, Italy, Philippines, Malaysia, Thailand, Vietnam, and other countries [17, 18]. The sticky, stringy dark brown flesh, that surrounds 4–6 seeds, has a delightful tart taste, and the tamarind pods or shells are generally 100–150 mm long. Figure 1 shows the sample of the tamarind fruit shells. The tamarind tree yields the fruit



FIGURE 1: Tamarind fruit shells.

seasonally, during January. The shells are converted to activated carbon.

2.2. Malachite Green. Malachite green is a synthetic dye used to colour silk, wool, jute, leather, cotton, and paper along with tannin. Humans who consume fish polluted with malachite green face a considerable health risk, according to the recent study. Because it is hazardous to human cells and functions as a carcinogen or mutagen, the substance is categorized under class II health hazard [19, 20]. As per literature, a safe limit of 0.11 mg/l is fixed based on experiments conducted on rats. This study focuses on the assessment of the effect of various factors such as flow rate, initial sorbate concentration, biosorbent size, and bed depth on breakthrough of MG. Generation of theoretical breakthrough curve and comparison with experimental breakthrough curve were also done. MG analysis was carried out using the UV-vis spectrophotometer at a wavelength of 620 nm. Concentrations of MG were assessed using a calibration curve [21].

2.3. Fixed-Bed Column. The most frequent method of interacting wastewater with a bed is to employ a fixed-bed column. A single fixed-bed column, in series, or in parallel, can be used. The water to be treated is injected at the top and extracted at the bottom of the column. Although upflow fixed-bed reactors have been employed, downflow beds are more typically used to reduce the risk of particle material accumulating in the bed's bottom [22]. The bed's performance may be harmed by inconsistencies in pH, concentration, bed depth, and flow velocity. The experimental setup of the fixed-bed reactor is shown in Figure 2.

3. Results and Discussion

3.1. Breakthrough Analysis. The breakthrough curve is a plot of fractional sorbate concentration at any time t , with respect to C_0 . This breakthrough analysis is an essential part of operation and design of columns. The breakpoint indicates the termination of the FBR process and also dictates the point at which regeneration of the bed is required. The appearance of breakpoint depends on several factors such as flow rate, sorbent size, sorbate concentration, bed depth, pH, temperature, nature of isotherm, and others [23].



FIGURE 2: Fixed-bed setup.

3.2. *Preliminary Study.* The study was carried out to fix the flow rates. This was done by varying the biosorbent size with constant bed depth of 30 cm. The trend in flow rate variation appears to be similar for 0.33 and 0.6 mm sizes, whereas for 0.13 mm size, it is slightly different.

3.3. *Effect of Flow Rate Analysis.* Range of parameters considered for the breakthrough study are biosorbent sizes, 0.13 mm, 0.33 mm, and 0.6 mm (geometric mean), bed depths, 10 cm, 20 cm, and 30 cm, influent biosorbate concentrations, 50 mg/l, 30 mg/l, and 10 mg/l, and flow rates, 100 ml/min, 80 ml/min, 50 ml/min, and 15 ml/min, as shown in Figure 3. The kinetic equations widely applied to this type of statistics include the two sites model and the linear portion mode; the enzyme retains two distinct binding sites, which are responsible for the “early phase” and “later phase” metabolisms, respectively [24].

3.4. *Effect of Initial Sorbate Concentration.* Figure 4 shows the effect of initial concentration of malachite green on bed performance, the variation of biosorptive capacity with service time, and initial concentration is well explained with the EBT model [25]. Furthermore, a relationship was developed between initial concentration of MG and biosorptive capacity of malachite green shown in (1) and (2).

Actual uptake, mg/g, is given as

$$q = CoVp / 1000M \int \left(1 - \frac{C}{Co}\right) dN. \quad (1)$$

Efficiency of bed, %, is given as

$$E = \left(\frac{qM1000}{CoVpN}\right) * 100. \quad (2)$$

3.5. *Effect of Biosorbent Size.* From Figure 5, the biosorbent size in FBR operation not only affects the bed porosity but

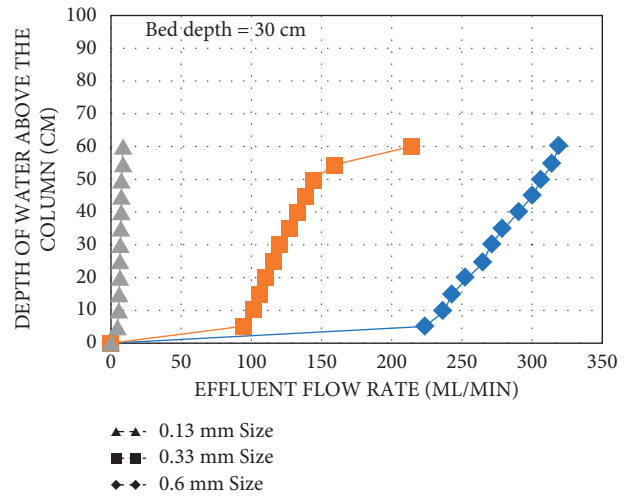


FIGURE 3: Effect of flow rate analysis.

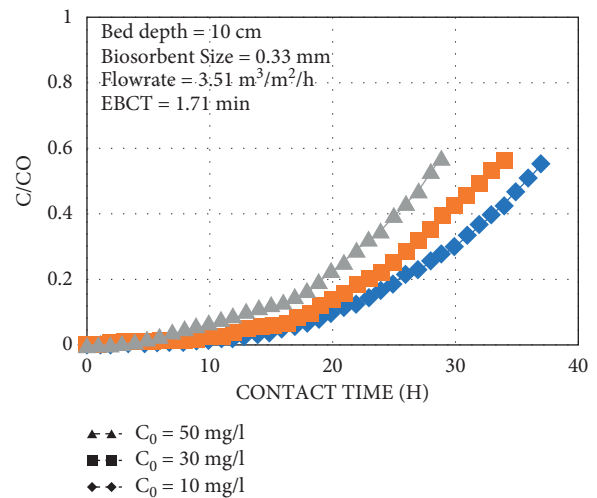


FIGURE 4: Effect of initial sorbate concentration.

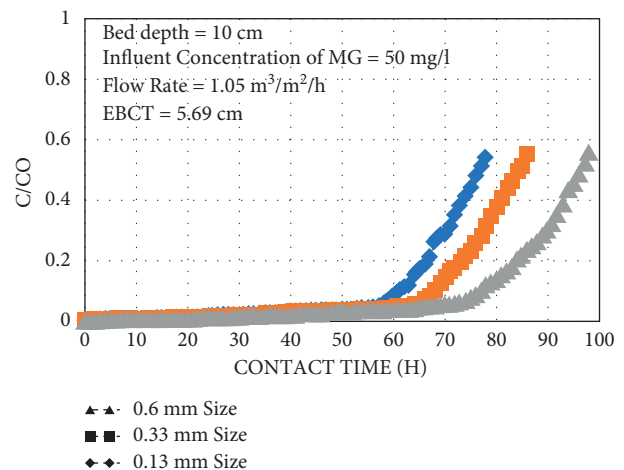


FIGURE 5: Effect of biosorbent size.

TABLE 1: Effect of initial sorbate concentration.

Initial MG concentration (mg/l)	Breakthrough time (h)	Pore volumes (N)	Ideal uptake (mg/g)	Actual uptake (mg/g)	Efficiency of bed (%)
10	20	701.5	8.24	0.62	7.49
30	10	350.7	12.36	0.26	2.09
50	4.8	168.4	9.89	0.18	1.83

TABLE 2: Effect of biosorbent size.

Biosorbent size (mm)	Actual mass of biosorbent used (g)	Breakthrough time (h)	Pore volumes (N)	Ideal uptake (mg/g)	Actual uptake (mg/g)	Efficiency of bed (%)
0.60	77.83	28	294.6	16.18	0.265	1.64
0.33	72.79	34	357.7	21.02	0.371	1.76
0.13	66.96	48	505.1	32.25	0.564	1.74

TABLE 3: Effect of flow rate.

Flow rate (ml/min)	Breakthrough time (h)	Pore volumes (N)	Ideal uptake (mg/g)	Actual uptake (mg/g)	Efficiency of bed (%)
100	3	210.4	12.36	0.123	0.99
80	3.6	202.0	11.86	0.185	1.55
50	4.8	168.4	9.89	0.181	1.83
15	34	351.7	21.02	0.371	1.76

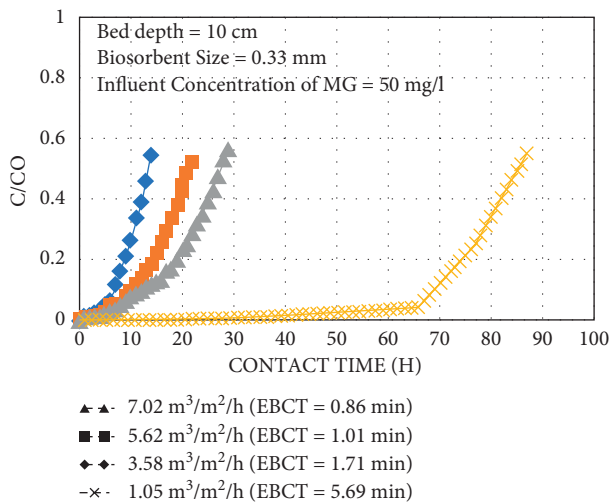


FIGURE 6: Effect of flow rate.

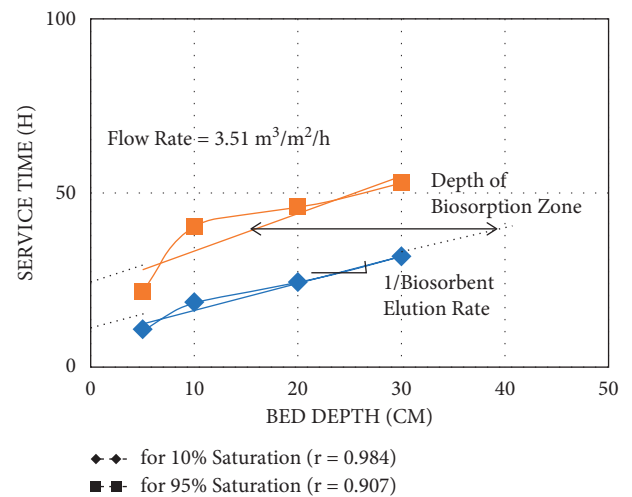


FIGURE 7: Bed depth service time.

also greatly influences the flow rate; it can be seen that the service time (at 1.7% saturation level) is increased with decrease in the geometric mean particle size.

From Table 1, it is noted that the efficiency of the biosorption decreases with increases in initial concentration of MG, and also from Table 2, it is clearly seen that the efficiency increases with decrease in the size of the TFS. From Table 3, the efficiency increases with decrease in the flow rate. The sorption starts with a simple single element solution to understand the kinetics, diffusion behaviour, sorption mechanism (physisorption, electrostatic, or chemical), and type (single layer and multilayer) and also optimize the parameters such as initial ion concentration and pH [26].

3.6. Effect of Flow Rate. Based on the results of Figure 6, a plot of service time high mass-exchange main impetus yields a bigger rate of progress in bed limit regarding administration time of the beds. Table 3 provides the idle, actual, and efficiency uptake of MG to tamarind fruit shells.

3.7. BDST Approach. The BDST approach is carried out for modeling and design purposes of FBR. In order to carry out this approach, three fixed-bed studies are required. Then, the BDST curve is plotted to find the sorption zone. This can be confirmed relating interfaces energies of the sorbate-sorbent vs. sorbate-sorbate (low sorbate, sorbent energies will lead to type II, while high ones (or nanopores) would lead to type I),

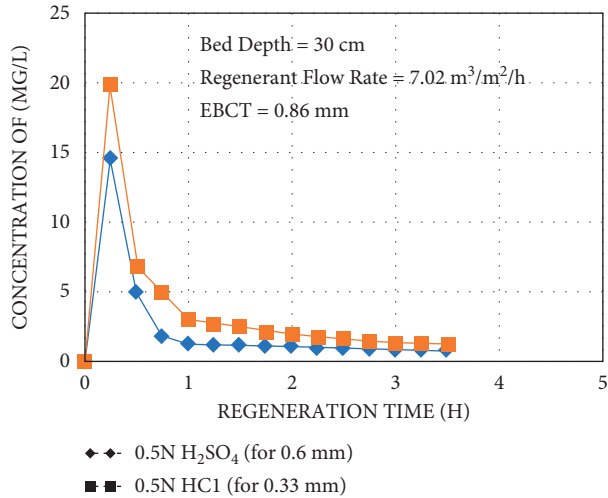


FIGURE 8: Regeneration time vs. concentration removal.

TABLE 4: Regeneration and recovery efficiency.

Regenerant used	Recovery of MG in the FBR system (%)	
	At 1 h	At 3.5 h
0.5 N H ₂ SO ₄	16.2	22.5
0.5 N HCl	25.7	37.18

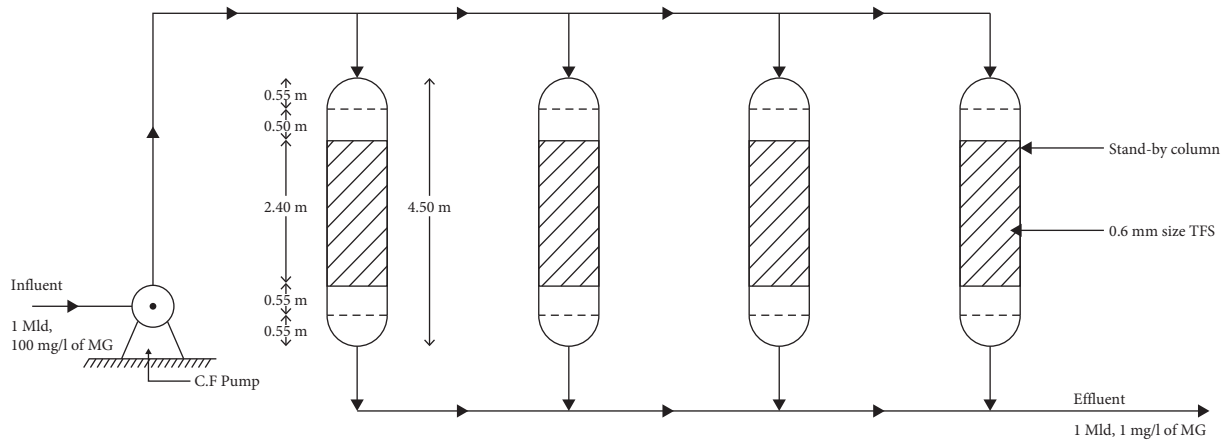


FIGURE 9: Scale-up set up.

as shown in Figure 7. Also, by *R* square equation, based upon the studies, various design parameters such as biosorption velocity, sorbate use, sorption loading rate, and bed efficiencies are calculated.

The values of N_0 grew as the C_t/C_0 ratio increased, while K_a decreased. The BDST model parameters can be used to scale up the process for different flow rates without having to undertake any more experiments. Figure 8 shows the h-D lines at C/C_0 values of 0.2, 0.4, and 0.6, respectively. Table 3 provides the BDST constants that are connected to the slopes and intercepts of the lines. In Table 3, the relative parameter uncertainties are also listed. The calculated bed efficiency was >90%, and the service time obtained from design was longer than the experimental breakthrough time [27, 28].

3.8. Regeneration. Regeneration of the bed is carried out using 0.5 N H₂SO₄ and 0.5 N HCl. This is done to regenerate the spent TFS bed. It was found that the regeneration rate was faster in 0.5 N HCl medium and is given in Table 4. Analytical chemical methods are for determining reaction mechanisms in soils and sediments. Desorption of the columns can be done using EDTA. After exhausting the column, drain off the remaining aqueous solution [29].

3.9. Scale-Up. In order to design a FBR for industrial scale, as shown in Figure 9, hydraulic and process-based design approach is carried out. As per the design, four columns each of height 4.5 m is essential to meet the proposed requirement

of 1 MLD influent flow, influent MG concentration of 100 mg/l, desired effluent MG concentration of 1 mg/l, and a TFS size of 0.6 mm. It is estimated that 30.9 T of crude TFS is required to get 8300 kg of 0.6 mm size of TFS [30].

4. Conclusions

The TFS is an efficient biosorbent in removing MG from the aqueous phase. The TFS is highly suitable in FBR systems, in all size ranges. The uptake of MG by TFS in the FBR system is about 4-5 times higher than the uptake in the CMBR system. In all fixed-bed studies, the pattern of the breakthrough curves is significantly different with respect to a typical S-shaped curve. The ideal capacities of TFS are far higher than the actual capacities, in all the studies. The biosorption of MG by TFS can be well explained by the BDST approach. The head loss and swelling of TFS particles are insignificant, during the fixed-bed studies. Substantial deviation between the experimental and theoretical breakthrough curves can occur in biosorption of MG by TFS. Acid regenerants such as 0.5 N H₂SO₄ and 0.5 N HCl can satisfactorily regenerate the spent TFS in the FBR system, with 0.5 N HCl being a better one. Process-based scale-up is better than the hydraulic-based scale-up.

Data Availability

The data used to support the results of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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