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Abstract
Dyes which are produced artificially or naturally in fixing colour to the fabrics cause major pollution in waterbodies. Though many eco-friendly adsorbents are used for removal of dye from wastewater, the potential use of Moringa oleifera Seed Powder (MOSP) in removal of dye has been studied in this paper. Batch experiments were conducted to determine the optimum quantity of MOSP by varying pH, dye concentration, contact time and quantity of MOSP. The adsorptive capacity of MOSP was determined by fitting the adsorption data using Langmuir and Freundlich isotherm models. The column studies were carried using the optimum value of MOSP to determine the time and volume of waste water that can be treated. From the batch studies, it was observed that 0.25 g of MOSP was found to be optimum. Also it was perceived that adsorption data were well correlated with Langmiur isotherm with coefficient of determination of 0.8207 and dye removal efficiency of more than 97%. From column studies, it was observed that steady state was reached after collection of 741 ml and 904 ml of treated water with dye concentration of 71 ppm.

Keywords: Moringa seeds; Dye removal; Isotherms; Adsorption

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Introduction
Trippur is located at a distance of 55 km east of Coimbatore in Tamilnadu from where 90% of knitted garment is exported. There are about 9000 knitting, 736 dyeing and bleaching, 300 printing units, 100 embroidery units and 200 units catering to compacting, raising and calendaring. Due to discharge of the effluent from these industries, both surface and groundwater bodies are polluted [1,2]. Dye wastewater consists of a broad spectrum of different complex chemical structures, primarily based on substituted aromatic and heterocyclic groups. The color due to disposal of dye wastewater obstructs the sunlight necessary for photosynthetic activity necessary for aquatic life [3-8] and carcinogenic effect of organic chemicals imparts toxicity to aquatic life [9,10]. The anionic dyes pose negative charge due to sulphonate group and protonated amine groups are present in cationic ions. Conventional wastewater treatment units are not efficient in removal of dye due to its stable nature to oxidizing agents and biological treatment. Though physicochemical methods such as chemical coagulation, adsorption by activated carbon, membrane filtration and ion exchange process are used for dye removal, they are not economically feasible [11-16]. Some natural plant seeds have been used for the removal of pollutants from the waste water [17, 18]. Moringa oleifera seeds are one of the cost effective bisorbents. The seeds were used to remove Orange 7 in dye wastewater and the optimum Moringa dose, dye concentration, pH and temperature were determined. Freundlich and Langmuir isotherms were used to describe the adsorption equilibrium in which Freundlich isotherm gave best correlation coefficient. The reaction mechanism was demonstrated by intraparticle diffusion kinetic model [19]. It was also observed that high removal of reactive yellow dye as pH increases and the adsorption equilibrium was explained well by Langmuir isotherm [20]. Moramudaii identified that mature Moringa seed extract is more effective than immature seed extract. It was observed that conductivity was dependent on contact time and temperature [21] has shown that Moringa seed extract in addition to alum removed dye effectively from the textile wastewater. Congo Red dye and acid dyes from wastewater was removed using natural coagulant, Chitosan [22,23]. Moringa oleifera (M.O.)
a tree growing in subtropic and tropic areas like the southern part of India, is a multi purpose plant with several applications. Among those, its ground seeds can be used as adsorbents in dye removal during textile waste water purification. This is a non-toxic biological method for water purification which, compared with common synthetic adsorbents, is more convenient in an environmental sense. In this report, experimental investigations were made to determine the efficiency of MOSP as an adsorbent in dye removal during textile waste water treatment. The first set of experiments are carried in a batch reactor to detect the influence of initial dye concentration, the variation of MOSP, the pH and the contact time. To quantify the results, Langmuir and Freundlich isotherm models were used to fit the model. In a second series of experiments, the adsorption characteristics of MOSP were evaluated on a continuous basis using column studies [24-26].

Materials and Methods

Preparation of dye stock solution

The dye waste water used in the following experiments was prepared by using black, red and yellow colour dye in the same mixing ratio adopted in the textile dyeing industry. Each dye colour solution was prepared by adding 1 g of dye powder to 100 ml distilled water. The three dye solutions are mixed in a ratio of 6% black, 1% red, 0.5% yellow and 92.5% distilled water. The concentration of the stock solution is calculated as 750 ppm, which was equivalent to 750 mg dye powder in 1000 ml of water. Using double beam UV-VIS Spectrophotometer, typical peak wavelength of the dye solution was detected as 598 nm. At this peak wavelength, the relationship between absorbance and dye concentration was obtained by varying concentrations in a range from 7.5 ppm to 75 ppm as given in Figure 1.

Batch studies

In the first set of experiments, the samples were shaken in batch reactor under equilibrium conditions. The dry MOSP of 0.5 mm is prepared through crushing the seeds. In the first experiment, a constant quantity of MOSP of 0.2 g was added to dye samples, whose concentration range varied between 43 ppm and 105 ppm. The optimum concentration (75 ppm) of dye removal was determined by observing the absorbance values. To study the influence of the amount of MOSP on the optimum dye concentration (75 ppm) obtained through batch study, different quantities of MOSP (0.05 g, 0.1 g, 0.15 g, 0.2 g, 0.25 g, 0.3 g) were added and the initial and final absorbance values were observed. The removal efficiency of dye at varying pH is determined by conducting batch studies at optimum concentration of MOSP with varying pH between 3.2 and 9.7. Finally, the quantity of MOSP required to treat the known concentration of dye was obtained by carrying out experiments with four samples at different concentrations of dy and M.O. powder. After measuring the initial absorbance and concentration, the samples were analysed for colour removal after 5, 10, 15, 30, 45 and 60 minutes to study the influence to contact time. Based on the results, the adsorption capacity of MOSP was calculated by fitting the data using Langmuir and Freundlich isotherm models.

Column studies

The continuous flow experiment was conducted in a column of a diameter of 4.75 cm, with a filter paper of pore size of 40 microns at the bottom. The column was filled with three sand layers of different particle sizes (2.33 mm, 2.33-1.18 mm and 1.18-0.06 mm), each of 6 cm height. The experiments were conducted by placing the MOSP layer on the top. In this study, the experiments were run with 3 g and 2 g of M.O. powder to study the influence of the layer thickness to the adsorption capacity. The column setup is displayed in Figure 2. Initially, the column was saturated with water until the airlock was released. After that, the dye wastewater with concentration of 85 ppm is allowed to pass continuously the column by maintaining constant flow rate. The samples were collected from different ports and bottom and analysed for colour removal.

Batch reactor studies

From the batch studies, it was observed that 0.2 gm of MOSP was able to remove 98% of dye wastewater up to concentration of 75 ppm. At higher concentrations of dye, the efficiency decreased from 98% to 88%. The amount of MOSP had strong influence on adsorption capacity as shown in Figure 3. For an initial concentration of 77 ppm, 0.25 g of MOSP was required to get an removal efficiency of 96%. The removal efficiency increased negligibly with an increasing MOSP (97.5% for 0.3 g of MOSP). When the quantity of MOSP (0.2 to 0.05 g) was less, the removal capacity decreased remarkably to 20% for 0.05 g of M.O. At least 0.25 g of MOSP was required to remove 7.7 mg of dye. There is good correlation between the results obtained.
from both experiments as given in Figures 3 and 4. In the first experiment, 0.2 g of MOSP was required to remove 7.5 mg of dye, while the MOSP requirement was slightly higher with 0.25 g for 7.7 mg of dye in the second experiment. This optimum quantity obtained from the above experiments were used for the experiments regarding pH-variation and contact time. As visible in Figure 4, the removal efficiency increased with decrease in pH. This variation is certainly at low level so that the influence of pH is negligible low. This means that pH will not be considered for the further experiments. The influence of pH has been detected as a negligible affect to the removal efficiency in this series of experiments (Figure 5). The contact time had great influence on the removal of dye removal. At different concentration of dye and different amount of MOSP, the maximal dye removal was reached after 5 minutes of contact time as given in Figure 6. It was also observed that influence of added MOSP was higher at the higher initial concentration. By adding 0.2 g of MOSP to an initial concentration of 78.8 ppm, colour removal efficiency of 86% was observed. The efficiency increased up to 95% by adding 0.25 g of M.O. powder to a 77.5 ppm concentrated solution. The influence of 0.2 g of MOSP was less at a lower concentration of 73 ppm and the influence decreased remarkably at still lower concentration. It was observed that, the adsorption capacity for every sample is satisfyingly high, varying between 89% and 99.

**Adsorption isotherm studies**

To find out the adsorption capacity of MOSP, the results obtained were fit into Langmuir and Freundlich isotherm models. The linearised form of Langmuir is given by

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{Q_m} C_e$$  \hspace{1cm} (1)

where $Q_e$ is the equilibrium respectively final concentration (mg/l), $Q_m$ and $b$ are Langmuir constants. $Q_e$ describes the adsorption capacity of MOSP under the given conditions (mg/g) and $b$ is the energy/intensity adsorption. Freundlich is described by the equation

$$\log(Q_e) = \log(K_f) + \frac{1}{n} \log(C_e)$$  \hspace{1cm} (2)

where $Q_e$ is defined as

$$Q_e = \frac{(C_e - C_0)V}{m}$$  \hspace{1cm} (3)

$K_f$ and $1/n$ are Freundlich isotherm constants. By implementing the results into the linearised Langmuir and Freundlich equations and plotting the graph as given in Figure 7. By fitting the data into the model, the adsorption capacity of MOSP was calculated to be 32.36 mg/g and $Q_e$ was observed to be 66 (mg/g). The regression coefficient and other relevant parameters are given in Table 1. From the results, it was observed that adsorption capacity of sorbent was explained well by Langmuir isotherm model than Freundlich. The coefficients of determination for Langmuir and Freundlich isotherms were 0.8207 and 0.6093 respectively. The adsorption capacity of 32.36 mg/g, obtained out of Langmuir isotherm model, is a proof for the obviously efficient dye removal of more than 97%. The parameters of Table 1 can be used to identify the saturation of MOSP at 32.36 mg/g (Figure 8). This result confirms the adsorption capacity calculated by Langmuir isotherm model and its applicability.

**MOSP experiments with column studies**

The column studies were carried out by allowing dye waste water to flow at the rate of 5 ml/min through layer of MOSP of 3 g placed above the sand layers. The concentration of dye removed...
varied between 0.08 and 2.96 ppm up to first 35 minutes with collection of 194 ml of waste water. The removal efficiency during treatment of the first 200 ml varies between 96.5% and 99.9%. With an continuous flow of wastewater, the effluent concentration increased till it reached the final concentration level of 71 ppm after 155 min. The volume of wastewater treated was 904 ml. The dye removal efficiency was observed to be 17%. When the column was run with M.O layer of 2 g, the effluent concentration remained at low level between 0.05 ppm and 4.25 ppm up to the point where saturation started. The volume of wastewater treated was 180 ml and colour removal efficiency was between 97.4% and 98.1%. After the beginning of saturation, the outcome concentration increased fast and reached steady state at 71 ppm after a passed water volume of 741 ml. The flow rate varied between 7.2 and 9.4 ml/min finally. The effluent concentration of dye was about to increate after allowing 180 ml with increase in the flow rate. The final concentration of 71 ppm was reached after 600 ml of dyed water. Similar pattern of increase in flow rate and decrease in dye removal efficiency was observed in both as given in Figure 9. It was due to the sand layers placed below the M.O layer.

**Conclusion and Future Prospects**

The seeds of *Moringa oleifera* is a good adsorbent for the removal of dye-contained waste water with its adsorption capacity of 32.36 mg/g. The adsorption capacity was explained by Langmuir isotherm. From the results of column studies, it was observed that 98% of dye removal was obtained using the optimum value of Moringa seed powder obtained from batch studies. Steady state was obtained after collection of 780 ml. The obtained results can be used as a initial impulse for further studies. M.O. seeds act as good and efficient bisorbent for dye removal in textile waste water.

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**Table 1** Langmuir and Freundlich isotherm parameters.

| Equation       | R²    | Qₑ (mg/g) | b (l/mg) |
|----------------|-------|-----------|----------|
| Langmuir       |       |           |          |
| y=0.0145x+0.0309 | 0.8207 | 32.36     | 2.13     |
| Freundlich     |       |           |          |
| y=0.0521x+1.4196 | 0.6093 | 19.19     | 26.27    |
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