Plant waste used as a solution for removing dye pollution

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Abstract- Bio sorption is a promising and an economical technology for removal of dyes from waste water. Previous researches have shown that many biosorbents present in the nature have great capacity for removal of dyes. Methylene Blue, a carcinogenic dye, is released as an effluent during the dyeing and rinsing processes of textile industries. In the present study, bio sorption experiments were carried out under various conditions, such as different contact times, pH, initial concentrations, and average particle size of the bio sorbent, rpm, and temperature. About 0.1 g of sawdust was found to be effective in removing 98% of Methylene Blue at a concentration of 20 mg/l from 30 ml of its aqueous dye solution in 90 min. The optimum pH was found to be 7.0. Hence, bio sorption is an effective and a promising ecofriendly technique to minimize the environmental abuse.

Keywords: Bio sorption, Methylene Blue, Waste water, Sawdust, Eco sustainable method.

I. INTRODUCTION

Dyes are highly colored polymers with low biodegradable nature [1]. Dyes and pigments are widely used in textiles, paper, plastics, leather, food and cosmetic industries to color products [2]. Organic dyes are an integral part of many industrial effluents and demand an appropriate method to dispose them off. Most commercial dyes are chemically stable and are difficult to eliminate from waste water. It is reported that the volumes of discharge of these waste water reaches 14.13×10^8 tons per year [3].

The release of colored waste water from these industries presents an eco-toxic hazard and introduces the potential danger of bioaccumulation. Bioaccumulation is the accumulation of substances, or any chemicals into an organism. It may enhance the persistence of industrial chemicals in the ecosystem as a whole, since they can be fixed in the tissues of organisms [4]. This may occur when an organism absorbs a substance at a rate faster than that at which the substance is lost by catabolism and excretion. This process may eventually affect man through the food chain. Various techniques like precipitation, ion exchange, chemical oxidation and adsorption have been used for the removal of toxic pollutants from waste water. The discharge of dyes in the environment is worrying for both, toxicological and aesthetical reasons.

Dyes are extensively used in leather, paper, textile industries and few have a role in clinical labs also. The removal of dyes and other chemicals in an economic way remains an important problem, although a number of systems have been developed with adsorption techniques. Adsorption was found to be better than other techniques due to various advantages like low cost, simple instruments, easy methods of operation. Activated carbon is very widely used as an adsorbent in the removal of dyes and chemicals but it is often difficult to match the financial scenario of developing countries; hence, identifying new adsorbents like clay fly ash [5], tobacco dust [6], agriculture waste, fruit waste (peels etc) had been an essential target for these countries. A number of studies in the last years focused on the adsorption of some dyes (acid, basic, reactive, and metal complex) on sawdust [7-9] of various plants like beech [10], rubber wood, pine and cedar. Leaf powders of various plants like pineapple [11], neem, and plum, husks of rice and wheat, garlic peel [12] were also used.

Bio sorption is a physiochemical process that occurs naturally and allows the passive concentration of contaminants into its cells. It is a metabolically passive process, which does not require any energy inputs. The efficiency of a sorbent to remove contaminants is dependent on kinetic equilibrium and the composition of the cellular surface of the sorbent. Contaminants are adsorbed onto the cellular structure. Though using biomass in environmental cleanup has been in practice for a while, scientists and engineers are hoping this phenomenon will provide an economical alternative for removing toxic heavy metals from industrial waste water and aid in environmental reclamation. In recent years, bio sorption has been strongly recommended as an economically viable sustainable technology for the treatment of waste water streams. The importance and usefulness of bio sorption in waste water treatment is well established [13].

II. MATERIALS AND METHODS

A. Adsorbate:

Methylene Blue (MB)

Methylene blue is also called ***Methylthionine chloride, Methylthioninium.***

It is a dark-green crystalline compound forming a blue aqueous solution, used as a mild antiseptic and a biological stain. It is also used as a medication, mainly to treat methemoglobinemia.

Formula: $C_{16}H_{18}ClN_3S$

Molar mass: 319.85 g/mol

Trade name: Urelene blue, Provayblue, Proveblue, other

Figure 1: (a) Methylene Blue powder, (b) chemical structure of Methylene Blue [14].

Effects:

- Causes eye injury in both, humans and animals.
- Ingestion through the mouth produces a burning sensation and may cause nausea.
- On inhalation, it can give rise to:
- Short periods of rapid or difficult breathing,
- vomiting,
- profuse sweating,
- diarrhea,
- gastritis,
- mental confusion and,
- Methemoglobinemia.

Thus, the elimination of MB from industrial effluents has become one of the major environmental concerns. A range of conventional treatment methods like biological treatment, adsorption, chemical oxidation, coagulation, and reverse osmosis have been used extensively for dye removal. However, most of the above methods suffer from one or more limitations and none of them are successful in completely eliminating the dye from waste water.

A. Sawdust

It is one of the non-conventional adsorbents that is easily available, free of cost, easy to handle, does not require any processing and available in different mesh sizes.

Figure 2: Saw dust of various mesh sizes.

2.1 Preparation of anionic dye solutions:

De-ionized water was used throughout for preparation of solutions. A stock solution (1000 mg/l) of Methylene blue (MB) was prepared in de-ionized water. The working solutions were obtained by diluting the dye stock solution to the required concentrations. pH of the solutions was adjusted using 0.1M Sodium hydroxide or Hydrochloric acid. The concentration of MB in the experimental solution was determined from the calibration curve prepared by measuring absorbance of different predetermined concentrations of MB solutions at k-max 497 nm using a spectrophotometer.

2.2 Bio sorbent collection and preparation:

Sawdust was collected from local saw mill and it was extensively washed with double distilled water to remove impurities. It was then dried for 5 h at 100 °C and cooled for 24 h. This sawdust was then sieved at different sizes and then stored in plastic bags for bio sorption studies.

2.3 Experimental parameters:

Batch bio sorption equilibrium experiments were carried out in 250 ml stoppered conical flasks at a constant agitation speed at room temperature. The concentrations of dye solutions before and after sorption were determined using UV spectrophotometer by monitoring the absorbance for the dye used.

2.3.1 Contact time:

Contact time studies are helpful in understanding the amount of dye adsorbed at various time intervals. Studies were carried out by agitating the adsorbent with 30 ml aqueous solution of the dye at room temperature (37°C) in 250 ml conical flasks at different time intervals, ranging from 10 min to 150 min. The suspensions were agitated for time intervals greater than the equilibrium time. After the agitation time, the adsorbent and the adsorbate were separated by filtration and the supernatant was estimated for the dye spectrophotometrically.

2.3.2 pH:

The effect of pH on the equilibrium uptake of the dye [15] was investigated using 30 ml of dye solution with 20 mg/l concentration, which may be changed after the standardization after the initial experimental runs. The initial pH values were adjusted with 0.1 M HCl or 0.1 M NaOH to attain a pH ranging from pH 3.0 to pH 8.0. The suspensions were agitated for time intervals greater than the equilibrium time. After the agitation time, the adsorbent and adsorbate were separated by filtration and the supernatant was estimated for the dye spectrophotometrically.

2.3.3 Initial concentration:

Studies were carried out by agitating the adsorbent with 30 ml aqueous solution of dyes at different concentrations (10 to 20 mg/1) at desired pH (which would be identified in the earlier parameter) and at room temperature (37 ^{o}C) in 250 ml conical flasks for same amount of time. After the agitation time, the adsorbent and adsorbate were separated by filtration and the supernatant was estimated for the dye spectrophotometrically.

2.3.4 Particle size:

The effect of the adsorbent size on the equilibrium uptake [16] of 30 ml of 20 mg/l concentration of dye was investigated by agitating it with different sizes of adsorbent (22, 52, 85, 120, 170, 200 μm size) maintaining the above parameters for a time greater than their equilibrium time. The suspensions were agitated for time interval greater than the equilibrium time. After the agitation time, the adsorbent and adsorbate were separated by filtration and the supernatant was estimated for the dye spectrophotometrically.

2.3.5 Temperature:

Studies were carried out by agitating the adsorbent with 30 ml aqueous solution of the dye at different temperatures (25, 35, 45, 55 & 65 ^{o}C) by adding a reweighted amount of adsorbate and maintaining the above parameters for a time greater than their equilibrium time. After the agitation time, the adsorbent and adsorbate were separated by filtration and the supernatant was estimated for the dye spectrophotometrically.

2.3.6 Agitation:

Studies were carried out by shaking the adsorbent with 30 ml aqueous solution of dye at various speeds (50 to 250 rpm) by maintaining the above parameters for a time greater than their equilibrium time. After agitation time, the adsorbent and adsorbate were separated by filtration and the supernatant was estimated spectrophotometrically.

III. RESULTS AND DISCUSSION

Based on literature survey, the experimental parameters and their range were selected.

Table:1 List of experimental parameters and their ranges.

Parameters	Minimum	Maximum
Time, min	60	110
Initial concentration, mg/l	10	60
pH	3	8
Biosorbent particle size, μm	22	200
Temperature, ˚C	25	65
Agitation, rpm	50	250

Dye used (Adsorbate) : Methylene blue
Substrate used (biosorbant) : Sawdust
Method used : Batch adsorption
Initial dye concentration : 20 mg/l
Amount of biosorbant used : 0.1 g
Vol. of working solution : 30 ml
Keeping the above aspects constant, the experiments were carried out to optimize various parameters.

3.1 Effect of contact time

It was found that the adsorption increases with an increase in the contact time and attains equilibrium after some time. 94% adsorption has been observed at an agitation period of 90 min.

Table 2: Effect of time on % adsorption of dye.

S.no	Time (mins)	Final concentration (mg/l)	% adsorption
1	60	5.6	72
2	70	3.6	82
3	80	1.6	92
4	90	1.2	94
5	100	1.6	92
6	110	1.6	92

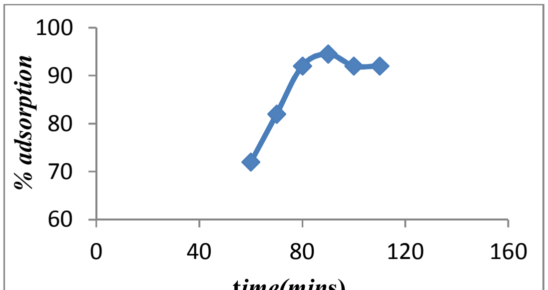

Fig:3 Effect of time on % adsorption of dye

3.2 Effect of dye concentration

Adsorption was greatly influenced by the concentration of the solution, as the adsorptive reactions are directly proportional to the concentration of the solute. A concentration range of 20 - 60 mg/l are taken in separate 100 ml experimental flasks and added with fixed amounts of the adsorbents. It was found that with the increase in concentration of the dye, adsorption decreased. The maximum adsorption of 95% was observed at 20 mg/l.

Table 3: Effect of dye concentration on % adsorption of dye.

S.no	Concentration (ppm)	Final concentration (mg/l)	% adsorption
1	10	1.2	88
2	20	1.0	95
3	30	2.4	92
4	40	2.8	93
5	50	4.5	91
6	60	6.0	90

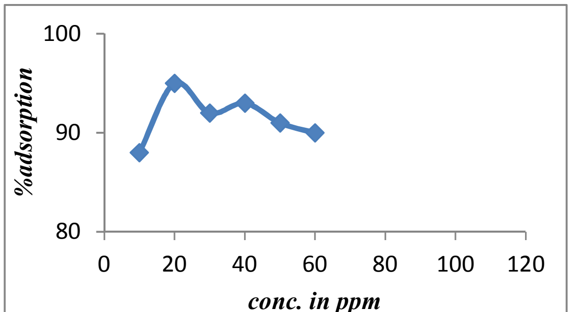

Fig:4 Effect of concentration on % adsorption of dye

3.3 Effect of initial pH

To investigate the effect of pH on the adsorption of MB, the pH range 3.0 - 8.0 was chosen. The effect of pH on equilibrium capacities of Methylene Blue biosorption was studied with initial Methylene Blue concentration of 20 mg/l. The pH of the test solutions was adjusted by using 0.1 M HCl and NaOH solutions. Adsorption decreases with increase in pH of the solution. Fig. 5 shows the effect of pH change in the range 3.0 to 9.0 on the adsorption of Methylene Blue to sawdust. Maximum elimination of Methylene Blue was observed at pH 7.0. The extent of dye adsorption on sawdust was low at basic pH. This may be due to the existing of dye molecule as cation at acidic pH and therefore, adsorption of Methylene Blue on the sawdust is much higher at acidic pH. As the pH of the system increases, the number of negatively charged sites increases and the number of positively charged sites decreases. The negatively charged surface site on the adsorbent does not favour the adsorption of dye anions due to the electrostatic repulsion. 96% of Methylene blue was eliminated at pH 7.0.

Table 4: Effect of pH on % adsorption of dye.

S.no	pH	Final conc (mg/l)	% adsorption
1	3.0	7	65
2	4.0	5	83
3	5.0	3	89
4	6.0	1.6	92
5	7.0	0.8	96
6	8.0	1.2	94

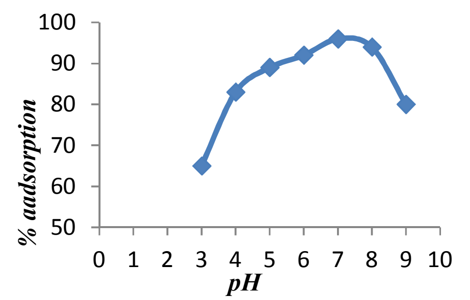

Fig: 5 Effect of pH on %adsorption

3.4 Effect of particle sizes

The dye uptake was also observed with different particle sizes, 22, 52, 85, 12, 170 and 200 µm. It was observed that by increasing the particle size, the surface area for adsorption increases. Maximum adsorption of 96.5% was observed at 170 µm.

Table 5: Effect of particle sizes on % adsorption of dye.

S.no	Particle size (µm)	Final conc. (mg/l)	% adsorption
1	22	1.6	92
2	52	1.4	93
3	85	1.2	94
4	120	1.0	95
5	170	0.7	96.5
6	200	1.6	92

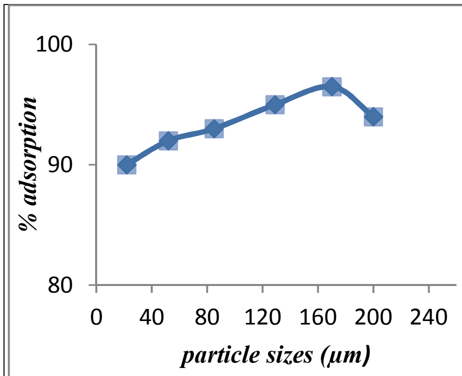

Fig:6 Effect of particle size on %adsorption of dye

3.5 Effect of temperature

The effect of temperature on the adsorption capacity was observed, by the batch experiments carried out at four different temperatures (35, 45, 55 and 65 °C) using 0.1 g of sawdust per 30 ml of the solution. It has been observed that with increase in temperature, adsorption capacity increases upto 35 °C and thereafter decreases as shown in Fig.7 Maximum adsorption of 97.5% was observed at 35 °C.

Table 6: Effect of temperature on % adsorption of dye.

S.no	Temperature (°C)	Final conc. (mg/l)	% adsorption
1	25	1.4	93
2	35	0.5	97.5
3	45	0.8	96
4	55	1.2	94
5	65	1.6	92

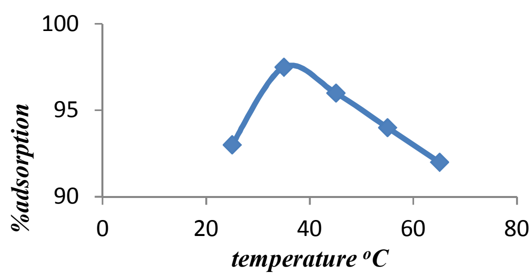

Fig:7 Effect of temperature on %adsorption of dye

3.6 Effect of agitation speed

In order to establish the effect of agitation speed on the biosorption of Methylene Blue on sawdust, batch studies at different agitation speeds were conducted in the range of 50 - 200 rpm. The maximum adsorption of 98% was observed at 200 rpm.

Table 7: Effect of agitation on % adsorption of dye.

S.no	Agitation	Final conc. (mg/l)	% adsorption
1	50	1.8	91
2	100	1	95
3	150	0.6	97
4	200	0.4	98
5	250	0.8	9

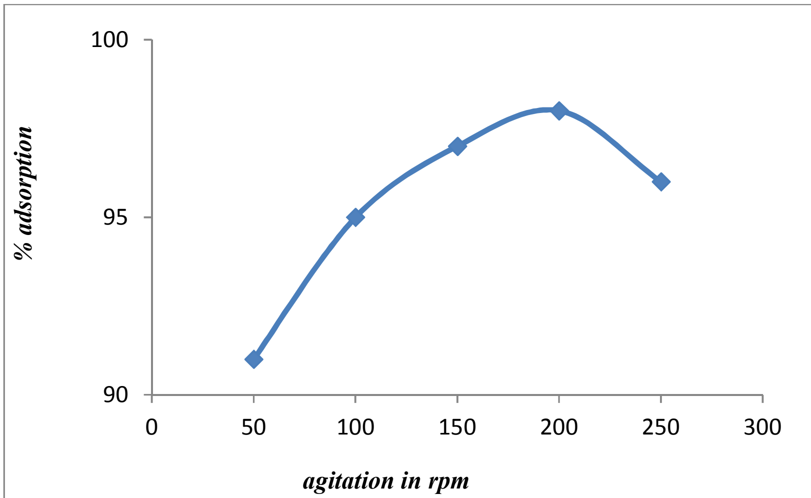

Fig:8 Effect of agitation speed on % adsorption of dye

IV.CONCLUSION

Experimental data were obtained for removal of Methylene Blue dye ions using sawdust as bio sorbent. Based on the results and subsequent analysis, the following conclusions were made:

1. The dye removal performance is strongly affected by parameters such as initial concentration, pH, and average particle size of the biosorbent, agitation speed and temperature.
2. The effective time of contact for better dye removal performance is 90 min.
3. The plot of pH versus % dye removal shows that significant biosorption takes place at pH 7.0.
4. The % dye removal increases with increase in the agitation speed upto 150 rpm further increase in the agitation decreases the % of dye removal.
5. The % dye removal increases with increase in the particle size of the biosorbent.
6. The % dye removal decreases with increase in the temperature.

Result of the present work indicates that sawdust can be used as an adsorbent for the efficient removal of Methylene Blue dye from waste water. The treated waste water can thus be used for irrigation purposes, washing of vehicles, etc. Maximum removal at 98% of dye was achieved at the pH 7.0 and temperature 35 ^oC. Since sawdust is easily and cheaply available, its application for dye removal could be expected to be a practical solution.

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