Methylene blue removes from the waste water by *Babylonia Spirata* shells bio-adsorbent

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Abstract- **In this paper represent the preparation and evaluation of *Babylonia Spirata* shells powder for removal of methylene blue from textile industrial waste water. The adsorbent was prepared by simple hydrothermal method. The adsorbent powder has enhanced mechanical properties, highly chemical stability and large specific surface area due to the powder was attracted researchers' interest as a type of bio-adsorbent and suggestion an attractive option for the removal of organic and inorganic contaminates from water. In this paper shown that, the preparation of *Babylonia Spirata* shells and evaluate the adsorption aptitude for effect of adsorbent dose, effect of concentration of adsorbent, effect of contact time, effect of pH, effect of surfactant the removal of methylene blue as a model compound for basic dyes.**

Index Terms- **Adsorbent, Babylinia shells, methylene blue, waste water**

I. INTRODUCTION[

The coloration process, a large percentage of the dye does not bind to the fabric and is lost to the wastewater stream. Approximately 10-15% dyes are released into the environment during dyeing process making the effluent highly coloured and aesthetically unpleasant [1-5]. Although, removal of colour from wastewater is often viewed as more important than the removal of the soluble colourless organic substances. Methylene blue (MB) is the most commonly used substance for dyeing cotton, wood and silk.[6-9] Furthermore presence of dyes in water causes several harmful effects such as increased heart rate, nausea, vomiting, shock, cyanosis, jaundice, and tissue necrosis in humans. A considerable amount of work has also been reported in the literature regarding the adsorption of methylene blue on various adsorbent surfaces such as, activated carbon rice husk, peanut hull, glass fibers, Indian rosewood sawdust neem leaf powder. Even though very few works have been completed on the marine source as adsorbent. Physico-chemical processes (chemical precipitation coagulation-flocculation, and ionic exchange) can be used to separate dissolved, emulsified and solid-separating compounds from water environment.[10-13]

However, these methods are not widely used due to their high cost and economic disadvantage. Chemical and electrochemical oxidations, coagulation are generally not feasible on large scale industries. The major advantages of an adsorption system for water pollution are less investment in terms of initial cost, simple design, easy operation, less energy intensiveness, non-toxic, and superior removal of organic waste constituents as compared with the conventional biological treatment processes [14-17]. The most common adsorbent materials are alumina, silica, metal hydroxides and activated carbon adsorbent used for the removal of organic impurities from waste water [18-20]. In this way, this paper focused on the Babylonia Spirata sea shells used as adsorbent for the removal of the methyl blue from the industrial waste water.

2. EXPERIMENTS

2.1Materials and Equipments

Materials used in the manufacture of the sample in this study were cuttlefish bone, ethanol, ammonium dihydrogen phosphate ($NH_4H_2PO_4$) and methanol. The equipment used for the manufacture of the sample were, electric oven, magnetic stirrer, autoclave, pH meter and furnace.

3. EXPERIMENTAL WORK

3.1 Preparation of adsorbate stock solution and working solution

All working solutions of the desired concentrations were prepared by diluting the stock solution with distilled water. The stock solution was prepared by dissolving 1gm of methylene blue in 1000 ml of distilled water to get a concentration of 1000 mg/L. All working solution of the desired concentration was prepared by diluting the stock solution with distilled water.

3.2 Preparation of adsorbent

Shells were collected by hand picking from fish landing centres from Besent nagar beach and identified by the Zoologist of R.V. GOVT Arts College Chengalpattu and a specimen was kept in their laboratory. After the collection, the marine bio waste is placed in properly labelled plastic bags subsequently were separated based on size, shape, colour etc.

The collected material was allowed to dry in sunshade for a week and after that it was crushed and powdered and then screened for homogenizing. The homogenized powder is used as adsorbent in our study.

3.3 Photoelectric colorimeter

The essential parts of a single beam instrument are a source of light with a cancave reflector, an adjustable diaphragm, a coloured class filtered for monochromatising light, cuvette for holding the absorbing solution, a single photocell to receive the radiation and, a directly connected galvanometer. The current output of the cell is directly proportional to the radiant power falling upon it at a given wave length.

In order to determine the absorbance of a solution, cuvette is filled up with pure solvent. Then the diaphragm is adjusted so that the meter reads full scale (100 percent). Now the solvent is replaced by solution without disturbing the diaphragm. Then, the meter will read the percent transmittance from which the absorbance of the solution can be evaluated.

3.4 Adsorption equilibrium experiment

The batch adsorption experiment was carried out the to determine the equilibrium time. 100 ml of sample solution was added to one gram of adsorbent and allowed to agitate in a shaker at 200 rpm and 27^{o}C. After 10 minutes of agitation, the content of the flask was filtered and from the filtrate 10 ml was taken in a cuvette and its OD at 660 nm was recorded. The remaining 90 ml of the sample was again added to one gram and the procedure was repeated. This step was continued until same OD was obtained. The values are recorded in Table 1. The concurrency of OD shows the time required for the attainment of equilibrium.

To study the various factors influencing the adsorption process, the following experiments were carried out and the readings are tabulated.

3.4.1 Effect of adsorbent dose

The effective removal of dye from the sample solution may vary with respect to the amount of the adsorbent used. To study this, 50ml of sample solution was added to 4 flasks which contains 5, 10, 15, and 20 g of adsorbent in the ratio 1:10 respectively. The optical density data at different adsorbent concentrations are tabulated in Table 2.

3.4.2 Effect of concentration of adsorbent

To study the effect of concentration on adsorption the experiment was carried out at difference concentrations of adsorbent and the optical density measurements are tabulated in Table 3.

3.4.3 Effect of contact time

Adsorption is a surface phenomena, and the quantity of adsorbate adsorbed on the adsorbent depends on the contact time. To evaluate the effect of contact time on adsorption, 10g of adsorbent and 50ml of sample were studied at various contact times. The optical density data at different contact time are presented in Table 4.

3.4.4 Effect of pH

The pH of the solution plays an important role in the whole adsorption process, particularly on the adsorption capacity. To study the effect of pH, 50ml of solution at different pH were studied at fixed adsorbent dosage and a contact time of 40 minutes. The optical density data at different pH are tabulated in Table 5.

3.4.5 Effect of surfactant

Presence of surfactant may interfere the adsorption process. Therefore study on adsorption in presence of surfactant was carried out. Sodium dodecyl sulfonate was used as surfactant. The change in optical density in the presence of surfactant for the adsorption process at various concentration of surfactant was found out and listed in Table 6.

4. RESULTS AND DISCUSSION

4.1 Adsorption equilibrium experiments

The batch adsorption experiments were conducted in 250 ml conical flask containing adsorbent and 50 ml of 50 mg/L methylene blue solution at a pH of 7. The flasks were agitated in a shaker at 200 rpm and 27°C until the equilibrium is reached. After decantation and filtration, the equilibrium concentrations of dye in the solution were measured at 660 nm using colorimeter. The agitation was contain are 20, 30, 40, 50, 60 minutes. Each time after decantation and filtration OD was found out.

The constant at 50 min and 60 min shows the attainment of equilibrium, shown in the Table 1.

Table – 1 Adsorption equilibrium experiments

S.NO	Time(min)	Optical density
1	10	0.25
2	20	0.36
3	30	0.45
4	40	0.50
5	50	0.52
6	60	0.52

4.2 Effect of adsorbent dose

In order to study the effect of adsorbent mass on the adsorption of methylene blue, a series of adsorption experiments was carried out with different adsorbent dosages at initial dye concentration of 1g. shown in the Table 2. Figure 1 shows the effect of adsorbent dose on the removal of methylene blue, along with the increase of adsorbent dosage from 1 - 4g, percentage of dye adsorption increased from 20.8 - 98.91%. Above 1 - 4g of adsorbent dose, the adsorption equilibrium of dyes were reached and the removal ratios of dyes maintenance almost invariable. The increase in adsorption may be due to the availability of more adsorbent sites as well as greater availability of specific surfaces of the adsorbents. However, no significant changes in removal efficiency were observed beyond 1 g/ 50 ml adsorbent dose. It is due to conglomeration of adsorbent particles, there is no increase in effective surface area of adsorbent.

OD Before Adsorption (Dye only A_0): 1.12
Concentration of adsorbate : 50 ml
Time: 60 min

Table – 2 Effect of adsorbent dose on adsorption

S. No	Concentration of adsorbate (ml)	OD After Adsorption	% Dye removal= $\frac{A_0 - A_1}{A_0} \times 100$
1	10	0.33	70.53
2	20	0.68	39.28
3	30	0.96	14.28
4	40	1.02	8.92

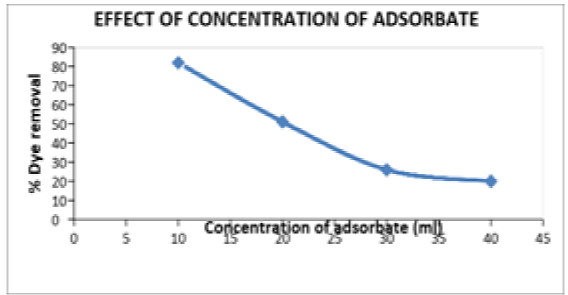

Fig – 1 Effect of adsorbent dose on adsorption

The Fig.1 shows that when the concentration of adsorbent increases the % of dye removal decreases. From this it is clear that the adsorption of methylene blue on Babylonia Spirata is effective only at low concentration.

4.3 Effect of concentration of adsorbate

Exactly one gram adsorbent was weighed and adsorbate of various volume is added to it and allowed to be shaken for 60 minutes in orbital shaker with 200 rpm the optical density of the adsorbate at 660 nm after one hour was observed and recorded in the following Table 3. The percentage removal of methylene blue was calculated using the following equation similar experiment were conducted with different weight of adsorbent.

Table. 3 Effect of concentration of adsorbent on adsorption

S.No	Weight of Adsorbent (gm)	Optical Density	% Dye removal= $\frac{A_0 - A_1}{A_0} \times 100$
1	1	1.45	29.46
2	2	1.35	20.53
3	3	1.29	15.17
4	4	1.15	2.67

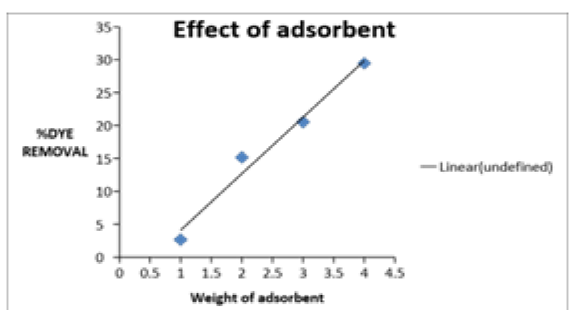

Fig. 2 Effect of concentration of adsorbate on adsorption

The Fig. 2 reveals that the concentration of adsorbate increases adsorption of dye removal on Babylonia Spirata decreases.

4.4 Effect of contact time

Exactly one gram of adsorbent was weighed and 50 ml of adsorbate was added to it and allowed to be shaken for 60 minutes in orbital shaker with 200 rpm .The optical density of the adsorbate at 660 nm after different contact time was observed and recorded in Table 4. The dye removal increased with the increase of contact time initially, and there is no much change was observed after the equilibrium was reached as shown in Fig 3. The change in the rate of adsorption might be due to fact that initially all the adsorbent sites would have been vacant and solute concentration gradient is very high. Later, the lower adsorption rate is due to a decrease in number of vacant sites of adsorbent and dye concentrations.

Table – 4 Effect of contact time on adsorption

S. No	Contact time (minutes)	Optical density	% Dye removal= $\frac{A_0 - A_1}{A_0} \times 100$
1	30	0.52	53.57
2	60	0.30	73.21
3	90	0.25	77.67
4	120	0.915	86.60

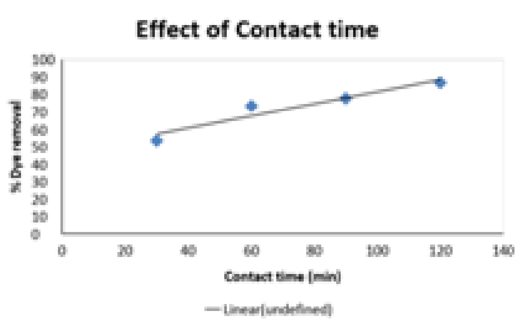

Fig. 3 Effect of contact time on adsorption

The Fig.3 shows that the percentage of dye removal increases with increases in contact time and this confirms that the rate of adsorption process is very low at the beginning

4.5 Effect of pH

Exactly one gram of adsorbent was weighed and 50ml of adsorbate added to it and, various volume of HCl are allowed to be shaken for 30 minutes in orbital shaker with 200 rpm.

The optical density of the adsorbate at 660 nm after one hour was observed and recorded in Table.5

Table.5 effect of pH on adsorption

S.NO	Volume of HCl (ml)	PH	Optical Density	% Dye removal $= \frac{A_0 - A_1}{A_0} \times 100$
1	0.5	0.301	0.85	24.10
2	0.1	1.00	0.72	35.71
3	0.05	1.301	0.35	68.75
4	0.01	2.00	1.05	6.25
5	0.001	3.00	1.08	3.571

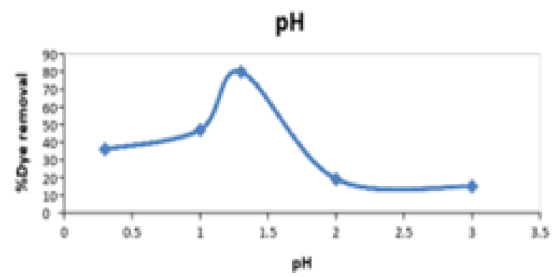

Fig-4 Effect of pH on adsorption

The above graph shows that at low pH, the % of dye removal is very low. At particular pH, the % of dye removal is maximum and this shows that adsorption is effective at pH more than 0.5. As shown in Fig.4 a consistent increase in adsorption capacity was noticed as the pH increased from 0.3 – 1.3, whereas in the range 1.5 – 3.0, the adsorption amount was only slightly affected by pH. As pH of the system increased, the number of negatively charged adsorbent sites decreased and the number of positively charged surface sites increased, which did not favour the adsorption of positively charged dye cations due to electrostatic repulsion. In addition, lower adsorption of methylene blue at acidic pH might be due to the presence of excess H+ ions competing with dye cations for the available adsorption sites.

4.6 Effect of surfactants

Exactly one gram of adsorbent was weighted; 50 ml of adsorbate and various volumes surfactant sodium dodecyl sulphate (SDS) are added to it and allowed to be shaken for 60 minutes in orbital shaker with 200 rpm. The optical density of the adsorbate at 660 nm after one hour was observed and recorded in Table 6

Table.6 Effect of surfactants on adsorption

S.NO	Surfactant (ml)	Optical density	% Dye removal= $\frac{A_0 - A_1}{A_0} \times 100$
1	10	0.95	15.17
2	20	0.40	64.28
3	30	0.35	69.64
4	40	0.21	81.25

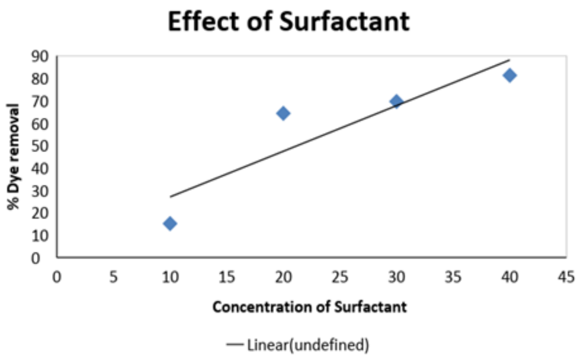

Fig.5 Effect of surfactants on adsorption

The Fig.5 and Table 6 shows that the % of dye removal increases with the increase of concentration of surfactant sodium dodecyl sulfate (SDS). This may be attributed due to tendency of surfactant to increase surface tension between the dye layer and the solid layer of adsorbent. From this it is clear that increase of surfactant increases the efficiency of adsorption.

5. CONCLUSION

Methylene blue is a common dye which is used in number of dye industries in the modern world. The dye present in industrial effluent enters in to the surface water, ground water and also sewage water. Higher concentration in water can alter the aesthetic quality of water. Hence its presence in aquatic environment must be affected regularly. The dye removal process can be utilized well in any water treatment process. Based on the obtained results conclude that, The efficiency of the adsorption is excellent. The handling of materials is very easy and harmless. The adsorption on the adsorbent used is effective at high concentration of adsorbate. The percentage of adsorption increases with increases in contact time and increases with less pH in the range of 3-4. The efficiency of adsorption increases with increases of concentration of surfactant sodium dodecyl sulfate.

However the above work we draw the conclusion that the experimental conditions are very simple and operational cost is low. The proposed technology is economically feasible and eco-friendly in nature. The adsorption in aqueous solution is 95% with the effective dose of 2g of adsorbent. This process can be effectively used for the removal of dye from industrial waste water.

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