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Removal of methylene blue dye from wastewater using low cost activated carbon prepared from *Delonix regia*

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Abstract

Dyes are one of the pollutants and due to their toxicity, carcinogenesis and irreversible the environment and humans. The efficient removal of various dyes from the waste waters of textile industries is an important and challenging task. In the present study, activated carbon (AC) have been prepared from *Delonix regia* seeds by chemical activation with H_2SO_4 and it is attempted to validate the applicability of a new adsorbent for the removal of a cationic dye Methylene blue from the effluent wastewaters. Batch experiments were done to investigate the contact time, effect of pH, effect of adsorbent, initial dye concentration and Langmuir isotherm models were used to describe the interaction between the adsorbate and adsorbent. As the dose increased, removal efficiency increased with statistical significance ($P<0.05$). The experimental sorption equilibrium followed by Langmuir ($R^2=0.9991$) and the RL value was 0.4975 which means Langmuir isotherm is favorable for this treatment. The adsorption behavior of *Delonix regia* has been investigated to understand the physicochemical behaviour of water like pH, electrical conductivity, salinity, temperature, color, TDS and TSS before and after adsorption. The result found was 5.13 ± 0.0137, 900.00 ± 0.11µs/cm , 0.40, 27.13± 2.82 °C, blue, 442.66±0.316 mg/L and 850 mg/L before Adsorption and 6.83 ± 0.27, 362 ± 0.96 µs/cm, 1.87 ± 3.25, 26.63 ± 0.57 °C, Colorless, 458.2 mg/L and 540 mg/L after adsorption. This showed that *Delonix regia* seed are suitable candidates for use as biosorbents in the removal of dyes from aqueous solutions.

Key words: Adsorption, Methylene Blue, *Delonix regia*, Physico-chemical Properties, Langmuir Adsorption Isotherms

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1. Introduction

1.1. Background of the Study

Water is a basic source of life, energy and thus is essential element to all living things on earth. In purest form water is colorless, odorless and tasteless in nature. But several industries such as textile, paper and plastics use dyes to colour their materials, as a result these dyes are invariably released as waste water into the water bodies [1]. During the processing of dye manufacturing and dye application, up to 15% of the used dyestuff are released into the process water so the effluents from these industries are highly coloured [2]. Dyes, once released into water bodies not only produce toxic amines by the reductive cleavage of azo linkages which causes severe effects on human beings through damaging the vital organs such as the brain, liver, kidneys and reproductive systems but also prevent photosynthetic activity in aquatic life by reducing light penetration [3, 4]. Wastewater from domestic and industries contain contaminants that are harmful for the environment as well as our health, therefore it should be treated before discharging it out [5, 6].

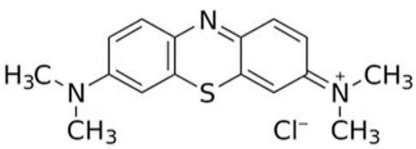
Several physical and chemical treatment methods including coagulation, adsorption, filtration and precipitation have been used for the removal of the dye from industrial wastewater [7]. Among all treatment techniques, adsorption has been shown to be superior to the other techniques because of its simplicity of design, low cost and high efficiency [8]. Adsorption is a widely used as an effective physical method for elimination or lowering the concentration of wide range of dissolved pollutants (organic and inorganic) in an effluent [9]. Activated carbon has been proven effective for dye removal but it is expensive. Therefore, there is a growing interest in using low cost, easily available materials for the adsorption of dye colours. A low cost adsorbent is defined as one which is abundant in nature, or is a by-product or waste material from another industry [10].

Activated carbons prepared from *Delonix regia* tree

(Dire Dawa tree) have the highest degree micro-porosity volume. Activated carbons have the largest surface area. Activated carbon is generally recognized as an effective adsorbent due to its large surface area, high porosity and high adsorption capacity [8]. The *Delonix regia* flower used as natural color, as an acid base indicator while its dried form used for preparation of activated carbon and the leaves are used as antimicrobial, anti-malaria and antioxidant [11,12]. *Delonix regia* pods have been utilized for the preparation of activated carbon. This could be attempted for the removal of metals and dyes from the effluent water [13,14]. Activated carbon prepared from *Delonix regia* seed can be used as an adsorbent for the removal of Mercury (II) [13], Lead, Nickel [15] and Methylene blue [14,16] from aqueous solution.

Figure 1: Leaf and seed of *Delonix regia*

Methylene blue has Molecular formula $C_{16}H_{18}N_3SCl$ and IUPAC name 3,7-bis (Dimethyl amino)-phenothiazin-5-ium chloride with Molar weight (g/mol) = 319.85 and λ_{max} = 665nm. Methylene blue is a compound consisting of dark green crystals or crystalline powder, having a bronze-like luster. Solutions in water or alcohol have a deep blue color. Methylene blue is used as a bacteriologic stain [12]. To overcome this situation the present study gave reports on how to remove methylene blue from waste water by using low-cost activated carbon prepared from *Delonix regia*.



Scheme 1: Structure of Methylene blue dye

2. Materials and Methods

2.1. Chemicals and Apparatus Chemicals

Hydrochloric acid (HCl), Sulphuric Acid (H_2SO_4), sodium hydroxide (NaOH), catalyst (Cu), $ZnCl_2$, H_3PO_4, Na_2CO_3or K_2CO_3, distilled water and aluminum sulphate ($Al_2(SO_4).14H_2O$ Methylene Blue ($C_{16}H_{18}N_3SCl$).

Apparatus

UV-spectrophotometer, Oven, Mechanical Shaker, Sieve, Reagent bottle, pestle, Mortar, PH meter, Aluminum foil, test tube, burets, Digital balance, stirrer, thermometer, hot plate, water bath, Mechanical grinder, Furnace.

2.2. Preparation of Adsorbate

Methylene blue is a basic dye with heterocyclic aromatic chemical nature. The molecular formula is $C_{16}H_{18}N_3SCl$ (3,7-bis (dimethylamino)-phenazathionium chloride) with absorption maxima at 665 nm. The dye stock solution 1000 ppm was prepared by dissolving 1g dye in 1000 ml distilled water. The experimental solutions were obtained by diluting the dye stock solution to the desired initial concentrations [11].

2.3. Preparation of Activated Carbon

Delonix regia seed pods were collected from Arba Minch University Institute of Technology Science. Then seeds were removed from the pods, sorted, seeds were cleaned manually to remove unwanted matter. Latter it was washed with distilled water and dried on oven at 650 °C for 24 hour and grinded in to fine powder and sieved through 600 microns. The 600-micron particle was dipped in H_2SO_4 for 5 hour. The material then soaked in 5% sodium bicarbonate solution to remove any residual acid then washed with distilled water, dried and used for study.

2.4. Method Applied for Adsorption

A stock solution of Methylene blue dye with a concentration of 1000 ppm was prepared. Batch adsorption experiments were conducted by shaking a series of eight bottles containing 50 ml dye solution with different adsorbent dosage such as 0.2, 0.4, 0.6, 0.8, 1 and 1.2 g and poured into each of the bottles, and the bottles were tightly fixed in the mechanical shaker. Then shaking proceeded for different contact times, to establish equilibrium [11]. Percentage of methylene blue dye removed is determined by applying the equation below [7].

$$\% \text{ Removal} = \frac{C_0 - C_e}{C_0} \times 100$$

Where:

- Co- Initial concentration (mg/L)
- Ce-Concentration at equilibrium time t (mg/L)

Or the amount of adsorbed substance is expressed by:

$$q_e = \frac{C_0 - C_e}{w} \times V$$

Where:

- w = weight of adsorbent in gram
- V = volume of solution in liter
- qe = amount of adsorbed substance in mg/g

2.5. Physico-chemical Parameters Before and After Adsorption

pH determination, conductivity, TDS, TSS, of both before and after adsorption was done for methylene blue [5]. Ash content, moisture content was determined for activated carbon prepared. The temperature, pH, electrical conductivity (EC), salinity and total dissolved solid (TDS) of the waste water before and after adsorption were measured using HACH HQ40d multifunctional portable meter [17].

2.6. Effect of adsorbent dosage

50ml of dye solution were taken in six conical flask with dye conc. (100 mg/L) and adsorbent concentration 0.2, 0.4, 0.6, 0.8, 1, 1.2 g. were added in 50 ml of dye solution. The final dye concentration readings were taken.

2.7. Effect of variation of pH

Low cost adsorbent powders are used to remove the Methylene blue dye; the effect of variation of pH at acidic, neutral and alkaline solution i.e. at pH 1, 3, 5, 7, 9 and 11 was checked using 0.1N HCl or NaOH solutions to change the pH [3].

2.8. Effect of contact time

50 ml of dye solution added to each bottle with adsorbent concentration (100 mg/L) and kept inside the shaker. Dye concentration was spectrophotometrically estimated at the wavelength corresponding to maximum absorbance λ_{max}, using a spectrophotometer. The samples withdrawn from the bottle shaker at predetermined time intervals. The absorbance of solution measured while dye concentrations were determined after 20, 40, 60, 80, 100 and 120 minutes until the equilibrium is reached [11].

2.9. Effect of Methylene blue Concentration

For the determination of concentration effect on Methylene blue dye six samples of different concentration of Methylene blue dye (10 mg/L, 20 mg/ L, 30 mg/L, 40 mg/L, 50mg/L and 60 mg/L) was prepared by the diluting of stock solution. Next, maximum wavelength of Methylene blue dye and the absorbance value for each sample were taken using UV-Visible Spectrophotometer and calibration curve constructed. Concentration of a sample can be found directly from the calibration curve using its absorbance value λ_{max} = 665nm [11].

3. Results and Discussions

3.1. Calibration of Methylene Blue

For the calibration of Methylene blue dye, six samples of different concentration of Methylene blue dye (10 mg/L, 20 mg/ L, 30 mg/L, 40 mg/L, 50 mg/L and 60 mg/L) was prepared from the dilution of the stock solution. Next, maximum wavelength of Methylene blue dye and the absorbance value for each sample were taken using UV-Visible Spectrophotometer and the calibration curves were constructed. The concentration of a Methylene blue was determined directly from the calibration curve using its absorbance value λ_{max} = 665nm as follows.

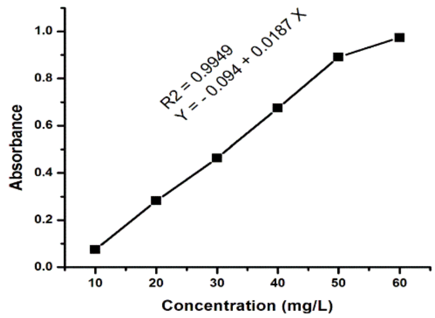


Figure 2: Calibration Curve of standard solution

3.2. Effect of Adsorbent Dosage

50ml of dye solution was taken in different bottles with dye concentration (100 mg/L) and adsorbent concentration 0.2, 0.4, 0.6, 0.8, 1, 1.2 g were added in 50 ml of dye solution. The final dye Absorbance readings taken as following then percentage of methylene blue removal calculated from absorbance value.

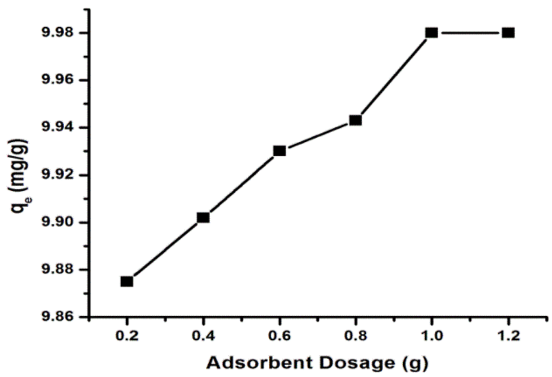


Figure 3: Effect of adsorbent dose on the adsorption of *Delonix regia* (Co = 100 mg/L)

The effect of various adsorbents dosages on the adsorption are tested with various amounts of adsorbents with the masses range between 0.2 and 1.2 g. These tests were carried out at room temperature, at neutral pH the samples were constantly stirred for 100 minutes. The concentration of the remaining solution was observed with UV Visible spectrophotometer. These studies reveal that the adsorption is maximum at 1g of adsorbent dosage.

3.3. Effect of Contact Time

50 ml of dye solution added to each bottle with adsorbent concentration (100 mg/L) and kept inside the shaker. Dye concentration was spectrophotometrically estimated at the wavelength corresponding to maximum absorbance, λ_{max}, using a spectrophotometer. The samples withdrawn from the bottle shaker at predetermined time intervals. The absorbance of solution measured while dye concentration was determined after 20, 40, 60, 80, 100 and 120 minute percentage of methylene blue removal calculated.

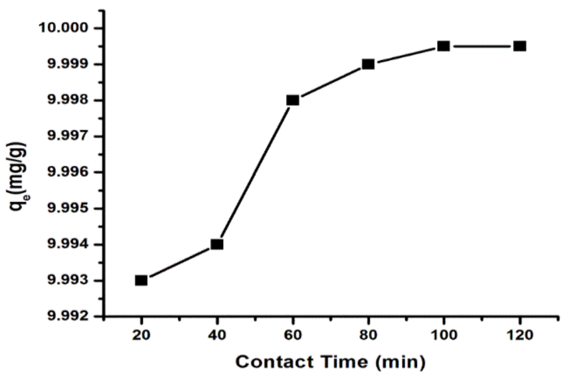


Figure 4: Effect of contact time on the adsorption of methylene blue on *Delonix regia* (C_0 = 100 mg/L, weight of Adsorbent = 1 g)

Effect of contact time on the removal of methylene blue described in figure 4, that shows the concentration of methylene blue adsorbed on *Delonix regia* as a function of time at controlled initial pH. The rate of adsorption rapidly increases in the initial stage of the adsorption process and gradually increases later after 20 minutes until end of the run. Thus the results reveal that the adsorption takes place slower rate at initial on the surface of adsorbent. Further the experimental results indicate that the particle has a principal influence on the rate of methylene blue uptake. The maximum adsorption of *Delonix regia* occurs at contact time of 100 minute.

3.4. Effect of variation of pH

Low cost adsorbent powders are used to remove the Methylene blue dye; the effect of variation of pH at acidic, neutral and alkaline solution i.e. at pH 1, 3, 5, 7, 9 and 11 using HCl or NaOH solutions to change the pH. The effects of pH on methylene blue adsorption by the adsorbents are tested in acidic and in basic range sand then percentage of methylene blue removal calculated.

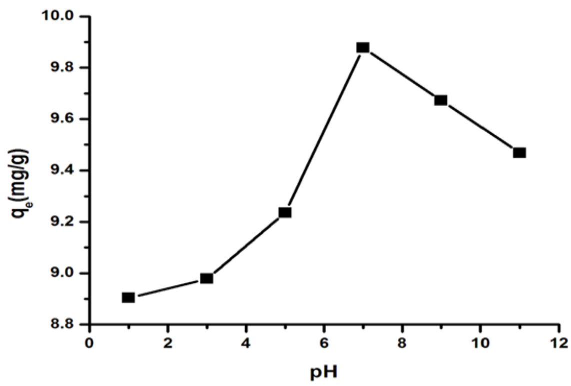


Figure 5: Effect of pH on the methylene blue on *Delonix regia* (C_0 - 100mg/L and weight of adsorbent is 1g)

The efficiency of sorption is dependent on the pH of the solution because variation in pH leads to the variation in degree of ionization and the surface properties of the sorbent. In view of this, experiments were performed over a pH range 1.0-11.0. The dye removal is affected by the solution pH and the effect has been shown in (Figure 5). It is observed that the adsorption capacity increases when pH increases up to 7 and then after decreases. The maximum adsorption of *Delonix regia* occurs at pH 7. This shows that in the aqueous medium the functional groups on the surface are protonated in neutral medium causing more electrostatic interactions between the protonated adsorbent and the cationic dye.

3.5. Effect of Concentration

To determine effect of concentration difference on methylene blue six solution of methylene blue dye with different concentration was prepared as 10ppm, 20ppm, 30ppm, 40ppm, 50ppm and 60ppm from 100mg/L stock solution and the same (pH value, adsorbent dosage, contact time) recorded on each conical flask in order to know only effect of concentration difference on Methylene blue dye removal which is at 1g. Adsorbent weight and pH = 7 for 100 min shaking time. Percentage of methylene blue removal calculated.

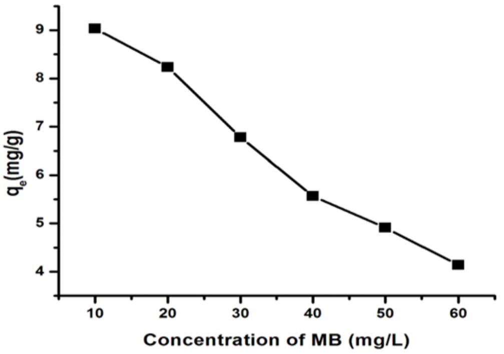


Figure 6: Amount of adsorbed substance vs. Concentration of methylene blue

The study on initial dye concentration was studied by varying the dye concentration from 10 to 60 mg/L leads to a decrease in the percentage of the methylene blue dye removal. The rapid adsorption takes place in the first 20 min and the adsorption rate decreased gradually and the adsorption reached equilibrium at an optimum contact time (100 min). This is because at low adsorbate/adsorbent ratio, the number of sorption sites in the adsorbent material decreases with increase of adsorption at beginning and the adsorption sites are saturated and results a decrease in the adsorption. At high initial concentration, the gradient between the solution sample and the particles enhances dye diffusion through the adsorbent during the adsorption.

3.6. Langmuir Adsorption isotherm

Langmuir isotherm model assumes the uniform energies of adsorption on to the surface and no transmigration of adsorbate in the plane of the surface. Langmuir sorption is a model based on the physical hypothesis that there are no interaction between adsorbed molecules and the adsorption energy over the entire coverage surface. Also there is no transmigration of the adsorbent in the plane of the surface of the adsorbent [18]. On the other hand in the Langmuir model, it is assumed that inter molecular forces decrease rapidly with distance and this leads to the prediction that the coverage of *Delonix regia* was a particular site of the adsorbent is occupied by an adsorbate molecule, no further adsorption takes place at the site. The linear form of Langmuir isotherm equation is:

$$\frac{C_e}{q_e} = \frac{1}{k_1 k_2} + \frac{C_e}{k_2}$$

Where:

- Ce is the equilibrium concentration of the adsorbate (mg/L)
- qe is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g)
- k_1 and k_2 is the Langmuir constants to adsorption capacity and rate of adsorption respectively

When, Ce/qe was plotted against Ce, a straight line with slope of $1/k_2$ was obtained and the correlation coefficient of Langmuir isotherm R^2 is 0.9991

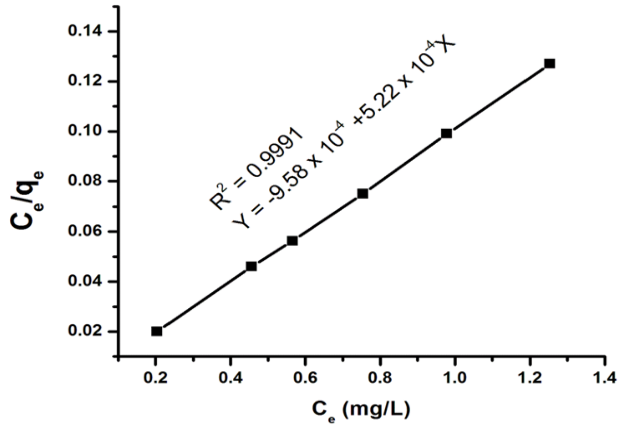


Figure 7: Langmuir isotherm for methylene blue sorption on *Delonix regia*

Langmuir separation factor can be determined as:

$$R_L = \frac{1}{1 + (1 + K_L \times C_0)}$$

Where:

- C_0 is initial concentration
- K_L is Langmuir Constant which is (0.065)
- R_L is relative adsorption nature

$$R_L = \frac{1}{1 + (1 + 0.065 \times 0.2)} = 0.4975$$

Which indicates that Langmuir isotherm is favorable

3.7. Physico-Chemical Properties Comparison

The average results of physicochemical parameters for waste water samples before and after adsorption are presented in table 1. The pH of water samples ranged between 5.13 - 6.83 before and after adsorption. The pH of water samples is slightly acidic before adsorption and became almost neutral after adsorption. EC values were in the range of 900 µs/cm before adsorption to 362 µs/cm after adsorption. High EC values indicating the presence of high amount of dissolved inorganic substances in ionized form. Total dissolved solids (TDS) and total suspended solids (TSS) values were well within the permissible limits respectively. Generally, the electrical conductivity, total suspended solid decrease after adsorption indicates decrease of ions from methylene blue dye with removed (adsorbed) color. Ash content (%) of *Delonix regia* seed was found 91.6.

Table1. Physico-chemical properties of water before and after adsorption

No	Properties	Mean value with RSD			
		Before Adsorption	After Adsorption	WHO Standards	Ref
1	TDS(mg/L)	442.66±0.316	458.2	500	19
2	Salinity (ppm)	0.40	1.87 ± 3.25	-----	19
3	Electrical Conductivity$\mu s/cm$	900.00 ± 0.11	362 ± 0.96	300	19
4	pH Value	5.133 ± 0.0137	6.83 ± 0.27	6.5 – 8.5	19
5	Colour	blue	Colourless	colourless	19
6	Temperature (°C)	27.13 ± 2.82	26.63 ± 0.57	30	19
7	TSS (mg/L)	850	540	500	19

5. Conclusion

The Experimental results of this study shows good removal efficiency of Methylene blue from synthetic solution by using activated carbon derived from *Delonix regia* seed pods. The effect of different parameters such as pH, adsorbent dose, contact time and dye concentration was studied. The data and results from the experiment reveal that removal of Methylene blue increases with increase in contact time and attain equilibrium at particular time, the result of experiment on optimization of dosage of adsorbent reveals that, increase in amount of dosage added, increases the removal of Methylene blue from the solution. The adsorption of Methylene blue is mainly pH dependent. The removal efficiency of adsorbent increases with increasing pH value upto optimum value. It has been observed that maximum adsorption takes place in slight neutral medium.

Generally, results showed that *Delonix regia* seed adsorbent can be effectively used as an adsorbent for the removal of dye from wastewater. Langmuir model is the best model fitted to equilibrium data in this study to describe methylene blue and *Delonix regia* seed adsorption system. The physico-chemical parameter of water like pH, electrical conductivity, salinity, TDS, TSS, temperature and color of water before and after adsorption were also studied. The electrical conductivity, total suspended solid decrease after adsorption indicates decrease of ions from methylene blue dye with removed (adsorbed) color.

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