Experimental Study of Adsorption Efficiency of Methylene Blue Dye by Using Banana Leaf Biochar as an Adsorbent

Umesh Kumar1*, Bhalchandra Vibhute 2, Sachin Parikh 3

1 Environmental Engineering, School of technology, RK University, Rajkot -360020, Gujarat, India and Amity University, Patna-801503, Bihar, India
2 Associate professor, Agricultural Engineering, School of Engineering, RK University, Rajkot-360020, Gujarat, India
3 Professors, L.D. Collage of Engineering, Ahmedabad, Gujarat.

Abstract. Removal of dye from wastewater has been a matter of concern, both as health point of view and in aesthetic sense. Colour removal from dye wastewater has been given much attention, not only because of its toxicity and water problem, but also mainly due to its visibility problem. There have been various promising techniques for the removal of dye from effluent. However, the adsorption effectiveness for dye removal from waste water has made it an ideal alternative to other expensive treatment methods. Agricultural wastes are inexpensive, biodegradable. Agricultural wastes are excellent sources for the production of adsorbent, which can be used as alternate, low cost treatment systems for the dye generated during the textile processing. Biochar was prepared by activating banana waste and used as an effective biosorbent to remove methylene blue (MB) dye from aqueous solution. Batch adsorption experiments are carried out using banana leaves as adsorbent. The adsorption study was performed by varying the adsorption parameter such as pH, adsorbent dose, contact time, temperature, agitation speed, and adsorbent particle size.

Keywords: Dye, agricultural waste, Adsorption, percentage removal of dye.

Introduction
In the world, there are various types of pollution which interfere with whole earth's world. Water pollution is the main concern about our sustainable life. The different types of hazards pollution activities in the environment have producing due to industrial and agricultural. The most of the pollutants in wastewater which is released from textile and other industries contains organic dyes. Among 7x10²¹ and approximately 10,000 different types of dyes and pigments produced worldwide annually, during the dyeing process about 1-15% of the dye is lost in effluents as estimated. [1]. Dye plays a crucial role in increasing water pollution. Effluent wastewaters coming from various industries such as dye manufacturing, textile, printing, plastic, leather, and pharmaceuticals contains dye [2]. Contamination of water with dyes even in small amounts is undesirable because dyes can impede light penetration and if discharged directly into surface water cause toxicity and result in threat to aquatic life [3]. Textile effluents contain different dyes such as methylene blue (MB), red-blue 19, congo red, brilliant green. Malachite green, reactive blue 19, reactive red 141, violet B, etc., Among all dyes, MB dye is used in a large scale from the different industries. MB is a cationic dye which is extensively used in the dyeing industry. MB is a toxic dye and causes several health risks in humans exposure, such as nausea, vomiting, eye injury, and methemoglobinemia [4]. Various methods including aerobic and anaerobic microbial degradation, coagulation, chemical oxidation, precipitation, filtration, membrane separation, electrochemical treatment, filtration, flotation, hydrogen peroxide catalysis, ozonation, reverse osmosis, and biological techniques can be employed to remove various pollutant form the textile industry wastewater.[5]
Several different methods were reported in the literature for the removal of pollution from effluents shown in table-1. The technology can be divided into three categories: Physical, chemical, biological.

| Process                        | Technology                      | Advantages                                                                 | Disadvantage                                                                                                                                 |
|--------------------------------|--------------------------------|-----------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------|
| Conventional Treatment processes | Coagulation, Flocculation       | Simple process, economically cheaper                                         | Large sludge production, problematic in handling and disposal                                                                         |
|                                 | Adsorption on activated carbon  | The most effective adsorbent, great capacity, a high-quality treated effluent is produced | Ineffective against disperse and vat dyes, the expensive regeneration results in loss of the adsorbent, non-destructive process       |
| Established Recovery processes  | Membrane separations            | Removes dye of all types, high-quality treated effluent is produced         | High pressures, economically expensive, incapable of treating large volumes, concentrated sludge production                           |
|                                 | Ion-exchange                    | No loss of sorbent on Regeneration                                          | Economic unfeasible, Not effective for all dyes                                                                                           |
|                                 | Oxidation                       | Quick and efficient process                                                 | High energy cost, chemicals required                                                                                                       |
| Emerging Removal processes      | Advanced oxidation process      | No sludge production, little or no consumption of chemicals, efficiency for recalcitrant dyes | Economically unfeasible, formation of by-products, technical constraints                                                                |
|                                 | Selective                       | Economically viable, regeneration is not necessary, high selectivity        | Requires chemical modification, non-destructive process                                                                                   |
|                                 | Bio adsorbents                  | Low operating expense, good efficiency and selectivity,                     | Slow method, performance depends on some external factors (pH and salts)                                                                 |
|                                 | Biomass                         |                                                                             |                                                                                                                                              |

The mentioned methods are valid only when there is a low concentration of organic compounds present in wastewater from the textile industry. The adsorption process provides an feasible alternative to the above procedures because it is inexpensive and easiness to control the various pollutants in the water and wastewater [6]. Adsorption process with help of activated carbon and prepared from different raw material represents the very effective adsorbent. Activated carbon have an important characteristic such as high surface areas, high adsorption, and porous structure capacity has shown a high potential in dye substances removal. Mainly researcher tried to find noval and cheap adsorbents, thus, a lot of research have been conducted to promote the usage of low-cost adsorbents [7].
In current year, adsorption of contaminants by biochar has encroachingly has come into the limelight as eco-friendly alternative and a mitigation strategy to climate change. Biochar contains as a carbon-rich, stable, and porous material, and it is developed from the thermal decomposition of biomass under the pyrolysis process and heated at a relatively low temperature (<700°C) [8]. Biochar has a lot of critical intrinsic features such as high porosity, high alkalinity, and high oxygen-containing functional groups, high adsorption capacity, high specific surface area, and hydrophobic characteristics [9]. Fig. 1 shows outline the basic methods of utilizing the agricultural by-products for the dye adsorption.

![Fig. 1 Schematic representation of dye adsorption by agricultural waste products](image)

The study aimed to investigate the performance of banana leaves biochar for removal of methylene blue (MB) dye from the aqueous solution. Hence, we used alkaline-treated banana leaves biochar (ATBLB) as an inexpensive and locally available material for the adsorbents preparation. In this study, we investigated the contact time, amount of adsorbent, the temperature, parameters affecting the performance of adsorption including pH of the solution and the initial dye concentration.

2. MATERIALS AND METHODS

2.1. Chemicals

Methylene blue (MB) dye powder was purchased from Merck Chemicals Ltd., Germany. MB empirical formula C₁₆H₁₈ClN₃S·3H₂O; and molecular weight 373.9 g/mol was used as the adsorbate. The chemical structure of MB, as shown in Fig.2. MB has a highest visible absorbance at the wavelength of 661 nm. The MB stock solution (1,000 mg/L) was prepared by dissolve MB in distilled water. 1gm of powder was dissolved in 1000 ml of distilled water to prepare 1000 ppm stock solution and maintain the pH of the stock solution was adjusted at natural pH.

![Fig. 2. Chemical structure of methylene blue](image)
2.2 Preparation of banana leaves as adsorbent
Banana leaves used as raw materials was collected from the local garden of Rajkot, Gujarat. Leaves cut into tiny pieces was washed with distilled water to remove dust particles and was kept into the water for 2-3 minutes. After putting those into hot air oven for drying. Dried leaves were powdered by the domestic mixture. It was sieved at 425 microns and thus, powder of banana leaves adsorbent was prepared. It is a natural adsorbent, without using any chemical for the preparation of powdered form.

Fig: 3. Standard curve of methylene blue dye

2.3 Preparation of ATBLB
Banana leaves biochar ware ready in slow pyrolysis process within a muffle furnace at temperatures 450–600 °C, and it was deep into 1 M NaOH solution for 1 hour. Here, NaOH was used to increase the number of active surfaces and prevent the elution of tannin compounds. The sample was repeatedly washed with distilled water for the elimination of NaoH. After drying of the sample at 105 °C for 48 hour, it was trampled and passed through a range of sieves at 425 microns [10]. The sample was dried out an oven at 82–87 °C for 2 hour after sieving and stored in air tight bags for further use.

Fig: 4. preparation of Banana leaves biochar as Adsorbent.

2. 4 Batch adsorption studies of banana leaf
100 ppm of stock solution was taken in a 200 mL beaker, and 0 gm of banana leaves adsorbent was added. The sample was shaken on a rotatory shaker at 150 rpm at room temperature for 10 min. Similarly, few more samples are prepared in a beaker and adding 0 gm of adsorbent and exposed to varying agitation times like in minute 10, 20, 30 and 40. These samples are filtered separately in a Whatman filter paper the filtrate solution is analyzed in UV-visible spectrophotometer at 661 nm to obtain final concentration. The same experimental procedure was also repeated for different dose in (gram)of 0.2, 0.4, 0.6, 0.8, and 1.0 gram of adsorbent for various agitation times like 10 min, 20 min, 30 min, and 40 min. The graphs are plotted between the agitation time and % removal of MB dye to a determine the optimum agitation time for different dosage of the adsorbent.
Methylene blue adsorbed per unit adsorbent (mg Methylene blue per gram adsorbent) was calculated in pursuance of mass balance on the Methylene blue absorption by the Equation 1.

\[ y = 0.0116x + 0.0034 \]

\[ R^2 = 0.9942 \]
\[ q_e = \frac{(C_i - C_f)V}{m} \quad (1) \]

Where \( C_i \) was the initial Methylene blue concentration (mg/L), \( C_f \) was the equilibrium Methylene blue concentration in solution (mg/L), \( V \) was the volume of the solution (L) and \( m \) was the mass of the adsorbent in gram.

The percentage adsorption of Methylene blue was calculated by the equation 2.

\[ \text{Adsorption} \% = \frac{(C_i - C_f) \times 100}{C_i} \quad (2) \]

3. RESULTS

3.1 Adsorbent characterization

![Fig. 5. FTIR spectra of banana leave Raw](image)

![Fig. 6. FTIR spectra of banana leaves activated](image)

The FTIR spectra were characterized of adsorbent at a range between 400–4,000 cm\(^{-1}\). The FTIR spectra displayed in Fig. 5 & Fig. 6. The absorption peaks representing by various functional groups. The band at 3,500 cm\(^{-1}\) corresponds to hydroxyl (\(-\text{OH}\)) stretching, even as the peak at 3000 cm\(^{-1}\) is recognized as the aliphatic C–H stretching. The band at around 1100 cm\(^{-1}\), which shows a peak very strong, it may have happened due to some shaking of inorganic ingredients [10]. An assessment between the FTIR spectra of the banana leaf raw and banana leaf activated was changed in absorption frequencies at 3,000, and 3,500 cm\(^{-1}\), due to existing in the surface of the adsorbent. It proves that the stated functional groups impact the MB adsorption on the banana leaf in experiment.

3.2 Effect of banana leaf adsorbent dosage

The percentage removal of methylene blue was increased as the adsorbent dosage is increased from 0-1 g. The percentage removal of dye is drawn against different dosages in Figure 7 maximum percentage removal of methylene blue dye is obtained 65% at 0.4gm dosage of adsorbent in 100 ppm.
of an aqueous solution. Thus with the increasing the adsorbent dosage from 0-1 gm the % removal of MB dye is also increasing and also affects the time interval.

![Graph: % removal vs dose](image)

**Fig. 7** Removal of MB dye and adsorbent dosage (gm/l) with time (minute)

### 3.2.1 EFFECT OF TIME

The percentage removal of methylene blue was increased as the agitation time is increased from 10-40 min. The percentage removal of dye is drawn against different time. The maximum percentage removal of methylene blue dye is obtained 65% at 40min. thus with the increasing the agitation time from 10-40min the % removal of MB dye is also increasing.

![Graph: % removal vs time](image)

**Fig.: 8** Removal of MB dye and time (minute)) with adsorbent dosage (gm/l)

### 3.3 Effect of ATBLB adsorbent dosage

The (%) removal of methylene blue was increased as the adsorbent dosage is increased from 0-1 g. The (%) removal of dye was drawn against different dosages in Figure 9. The maximum percentage removal of methylene blue dye was obtained 87.51 % at 0.8 gram dosage of adsorbent in 100 ppm of aqueous solution at 50 minute. Thus with the increasing the adsorbent dosage from 0-1 g the % removal of MB dye is also increasing and also affects the time interval.
3.3.1 EFFECT OF TIME
The (%) removal of methylene blue was increased as the agitation time was increased from 10-60 min. The % removal of dye was drawn against different time in Figure 10. The maximum % removal of methylene blue dye was obtained 87.51 % at 50 min. Thus with the increasing the agitation time from 10-60 minute the % removal of MB dye was also increasing.

4. CONCLUSIONS
This project work will help in designing low-cost adsorption columns for the removal of industrial effluent or other adsorption processes which help to maintain health hazardous, water pollution, ecosystem and sustainable development and also help to find out % removal of MB dye by using different adsorbent like banana leaves. By varying different parameters like pH, contact time, adsorbent dosage, etc., We can get maximum % removal by using batch adsorption process in biochar methods. We find out the maximum % of dye removal by using leaves adsorbent is 87.51 % at time 50 min and dosage 0.8 g and by using stem is 83.60 % at time 50 min and 1 g dosages. It can help in designing low cost adsorption columns for the removal of industrial effluent or other adsorption
processes which help to maintain health hazards, water pollution, ecosystem and sustainable development, implementation of cleaner production, effect the economic factor of textile industry, low cost and easily available in natural ecosystem. Finally, we conclude that biochar process gives good result as compared to natural methods.

Acknowledgment
The Authors would like to thanks RK University, Rajkot for providing facilities to undertake this research works.

REFERENCES
[1] H. Zollinger, Color Chemistry: Synthesis, Properties and Applications of Organic Dyes and Pigments, VCH, New York, NY, 1991
[2] Monika Kharub, use of various technologies, methods and adsorbents for the removal of dye, Journal of Environmental Research And Development Vol. 6 No. 3A, Jan-March 2012
[3] Chandra T. C., Mirna M. M, Sudaryanto Y., and Ismadji S. Adsorption of Basic Dye onto Activated Carbon Prepared from Durian Shell: Studies of Adsorption Equilibrium and Kinetics. Chem. Eng. J., 127,121–129, 2007
[4] Al-Anber, Z. A., Al-Anber, M. A., Matouq, M., Al-Ayed, O., & Omari, N. M. Defatted Jojoba for the removal of methylene blue from aqueous solution: Ther-modynamic and kinetic studies. Desalination, 276, 169–174. 2011
[5] Ibrahim M. Banat, a Poonam Nigam, h Datel Singh " & Roger Marchant, Microbial decolorization of textile dye containing effluents:- a review, Bioresource Technology 58, 217-227, 1996.
[6] Ho, Y. S., and McKay, G, “A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents”, Trans. chem. 76, pp 332-340.1998
[7] M. Ghaedi, H. Hossainian, M. Montazerrozohori, A. Shokrollahi, F. Shojaipour, M. Soylak, M.K. Purkait, A novel acorn based adsorbent for the removal of brilliant green, Desalination 281 (2011) 226–233
[8] J. Tang, W. Zhu, R. Kookana, A. Katayama, Characteristics of biochar and its application in remediation of contaminated soil, J. Biosci. Bioeng. 116 (2013) 653–659.
[9] Y. Wang, L. Wang, G. Fang, H.M.S.K. Herath, Y. Wang, L. Cang, Z. Xie, D. Zhou, Enhanced PCBs sorption on biochars as affected by environmental factors: Humic acid and metal cations, Environ. Pollut. 172 (2013) 86–93.
[10] M.K. Hossain, V. Strezo, K.Y. Chan, A. Ziolkowski, P.F. Nelson, Influence of pyrolysis temperature on production and nutrient properties of wastewater sludge biochar, J. Environ. Manage. 92 (2011) 223–228.
[11] Natarajan, B., Obaidat, M.S., Sadoun, B., Manoharan, R., Ramachandran, S. and Velusamy, N., 2020. New Clustering-Based Semantic Service Selection and User Preferential Model. IEEE Systems Journal. DOI: 10.1109/JSYST.2020.3025407.
[12] Nataraj, S.K., Al-Turjman, F., Adom, A.H., Sitharthan, R., Rajesh, M. and Kumar, R., 2020. Intelligent Robotic Chair with Thought Control and Communication Aid Using Higher Order Spectra Band Features. IEEE Sensors Journal, DOI: 10.1109/JSEN.2020.3020971.
[13] Babu, R.G., Obaidat, M.S., Amudha, V., Manoharan, R. and Sitharthan, R., 2020. Comparative analysis of distributive linear and non-linear optimised spectrum sensing clustering techniques in cognitive radio network systems. IET Networks, DOI: 10.1049/iet-net.2020.0122.
[14] Sitharthan, R., Yuvaraj, S., Padmanabhan, S., Holm-Nielsen, J.B., Sujith, M., Rajesh, M., Prabaharan, N. and Vengatesan, K., 2021. Piezoelectric energy harvester converting wind aerodynamic energy into electrical energy for microelectronic application. IET Renewable Power Generation, DOI: 10.1049/rpg.2.12119.
[15] Sitharthan, R., Sujatha Krishnamoorthy, Padmanaban Sanjeevikumar, Jens Bo Holm-Nielsen, R. Raja Singh, and M. Rajesh. "Torque ripple minimization of PMSM using an adaptive Elman
neural network-controlled feedback linearization-based direct torque control strategy." International Transactions on Electrical Energy Systems 31, no. 1 (2021): e12685. DOI: 10.1002/2050-7038.12685.