International Journal of Engineering and Advanced Technology (IJEAT)
ISSN: 2249 – 8958, Volume-9 Issue-1S4, December 2019

Biosorption of Methylene Blue Dye from Aqueous Solutions

Abhirami A. P, Anjaly Priya, Devika R., Indu G., Nidhin Sreekumar

Abstract— *Synthetic dyes, like methylene blue, in effluents of chemical industries, are reported to be toxic with alleged carcinogenic and genotoxic consequences. Biosorption is considered as a low-cost alternative to the costly removal processes. Agricultural wastes and plant biomass and are contemplated to be low-cost candidates because they can be used without or with a minimum of processing. This work was intended to test the possibility and comparative study of different low-cost natural adsorbents [Coconut husk (H), Groundnut shell (G), Cow Dung (C) and moss (M)] for the sequestration of methylene blue dye from aqueous solution. A batch process was done to study the effects of different parameters such as contact time, pH, adsorbent dosage and initial dye concentration. Adsorption equilibrium data were represented using Langmuir, Freundlich and Temkin isotherm models. 75 % of dye removal was observed with moss, hence proves to be an effective, low-cost adsorbent.*

Keywords— *dye removal, biosorption, methylene blue, Hyophila involuta*

I. INTRODUCTION

Bio-sorption processes are used to remove the toxic compound from industrial wastewater [1, 2, 3]. The dyes used to color the final products in many industries are discharged into natural water, which causes severe problems because of its toxic nature towards aquatic ecology and damages the aesthetics of nature [4]. The triple aromatic ring structure of the dyes makes it challenging to remediate by the traditional biological and physio-chemical techniques. Therefore, for the treatment of colored waters, sorption provides an attractive solution.

The most popular and widely used adsorbent is activated carbon, but it is expensive, and its regeneration is difficult. Hence, researchers are exploring low-cost materials, such as industrial and/or agricultural waste, including naturally abandoned biomass [5]. This work explores the sorption of methylene blue (MB), a cationic dye even at a very low quantity is highly undesirable and un aesthetic which is used to characterize the capacity of an adsorbent, by coconut husk, groundnut shell, cow dung and moss. We explore the possibility of moss as a novel low-cost bio sorbent. Plant biomass are considered to be low-cost bioproducts which are having good potential as bio sorbents [6]. The purpose of our work is to test the possibility and comparative study of different low-cost natural adsorbents- *Cocos nucifera* (coconut) fibre dust, *Arachis hypogaea* (groundnut) shell, Cow dung, *Hyophila involuta* (a Bryophyta).

A. Methylene Blue Dye

MB is a heterocyclic, aromatic, compound with chemical formula $C_{16}H_{18}ClN_3S$. It exists as an odorless, dark green powder at room temperature and imparts blue shade when dissolved in water [3]. Methylene blue is a cationic dye which has a complex structure (Fig. 1.).

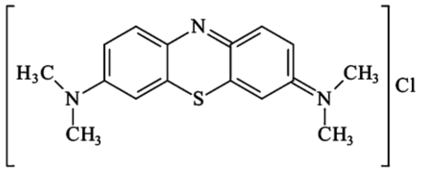

Fig. 1. Structure of Methylene Blue

Table- I. Physical and Chemical Properties of Methylene Blue

Property	*Value*
Appearance	Dark green crystals with bronze luster or crystalline powder
Odour	Odourless
Solubility	Water soluble.
Specific gravity	-
pH	-
% volatiles by volume at 21°C (70°F)	0
Boiling point	Decomposes
Melting point	100 - 110°C. (212 - 230 °F)
Vapour density (air=1)	13
Vapour pressure (mm hg)	NA.

B. Coconut Husk

Coconut husk is the most common and widely available natural biosorbent material which is being studied by many researchers. It is fibrous in nature and is obtained from the outer surface of coconut.

Revised Manuscript Received on December 15, 2019.

* Correspondence Author

Abhirami A. P., Department of Biotechnology, Sree Chitra Thirunal College of Engineering, Trivandrum, Kerala, India. Email: abhiramiap3@gmail.com

Anjaly Priya, Department of Biotechnology, Sree Chitra Thirunal College of Engineering, Trivandrum, Kerala, India. Email: vsanjalypriya@gmail.com

Devika R., Department of Biotechnology, Sree Chitra Thirunal College of Engineering, Trivandrum, Kerala, India. Email: rdevika180@gmail.com

Indu G., Department of Biotechnology, Sree Chitra Thirunal College of Engineering, Trivandrum, Kerala, India. Email: induanagha@gmail.com

Nidhin Sreekumar*, Accubits Invent, Accubits Technologies Inc. Trivandrum, Kerala India. Email: nidhins10@gmail.com

In the previously conducted experiments, the coconut husk was subjected to various treatments. Hence raw coconut husk was not yet been studied [7].

C. Groundnut Shell

Groundnut shell is a hemicellulose material which is dry in nature. It is an agriculture waste which can be easily obtained in this native [8]. Groundnut is a material which is processed and exported in large quantities; hence, its shell is readily available.

D. Moss

Hyophila involuta is a small cushion moss which grows on the wall and ground surfaces with a considerable amount of moisture content. It is greenish in appearance and has high moisture content (Fig. 2.). Upon drying, it loses its water content nearly up to 80% of its biomass weight. It is a fast-growing and quickly spreading bryophyte.

Fig. 2. *Hyophila involuta*

E. Cowdung Cake

Cow dung cake is the most abundant bio waste material, which is good manure used commonly by the farmers. They generally stored this bio waste as in the form of dry cake. The cow dung is sun dried to remove the moisture content to its minimum, like cakes. It is a by-product of animal husbandry [9].

II. MATERIALS AND METHODS

F. Preparation of Adsorbate

Methylene blue dye was purchased from Spectrum Chemicals, Edappaly, Cochin. 1 g of dye was dissolved in 1 litre of deionized water to prepare the stock solution of dye (1g/L). The dye stock solution was diluted to the required initial dye concentrations (10-50 mg/L) and was used to plot the standard curve (Fig. 3.).

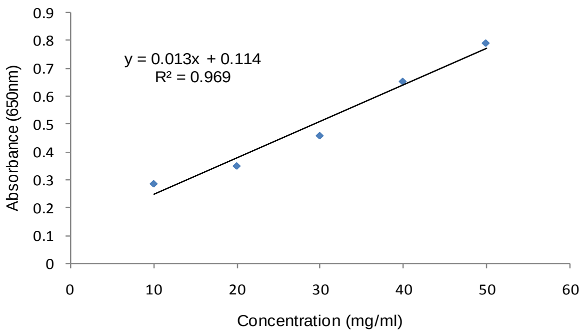

Fig. 3. Standard graph

G. Preparation of Adsorbents

Coconut husk, Groundnut shell and cow dung cake were obtained from different households. Moss was obtained from college premises [10].

Table- II. Geographical locations of various adsorbentsTable Type Styles

Sl. No.	*Material*	*Latitude*	*Longitude*
1	Coconut Husk	8°30'15.9" N	76°56'32.7" E
2	Groundnut Shell	8°35'34.5" N	76°56'59.5" E
3	Cow dung	8°43'01.2" N	76°47'49.0" E
4	Moss	8°28'10.5" N	76°58'48.9" E

The species of the moss was identified at University college Thiruvananthapuram as *Hyophila involuta.*

H. Pre-Treatment

Coconut & groundnut shell was soaked in water. Later all the four adsorbents were sun-dried for two days; the moisture content was reduced to the minimum by drying the samples in a hot air oven for 12 hrs. Then the dried samples were crushed to obtain smaller particle size [11]. Sieved the above samples to obtain the desired particle size ranging from 50 to 100 µm. Weight of the samples was measured in each step. Percentage of water removed in each step was tabulated and plotted.

I. Time Optimisation

50 ml of 20mg/ml adsorbate solution was taken in 250 ml conical flask, and 0.1g of adsorbent is added. The absorbance was measured at wavelength - λ_{max}(650 nm) at different time intervals and plotted on a graph.

J. Adsorption Process

Batch experiments were performed with 250 ml flasks. By using a mechanical shaker, 50 ml aqueous solution taken in 250 ml conical flask was shaken at 200 rpm for an equilibrium time [12].

- *Effect of adsorbent dosage:* Experiments were performed with varying adsorbent dosages (0.05-0.20g) in a 50 ml dye solution of 20 mg/l concentration. The pH was maintained at 6; room temperature was maintained and shaken till equilibrium time. The absorbance measured at 650 nm for these various concentrations. The graph was plotted using the obtained values.
- *Effect of pH:* Studies were performed over the pH range of 2.0-10.0 with 0.1g of adsorbent at room temperature in a 50 ml dye solution of concentration 20mg/l. The pH of the solution was adjusted using 0.1M H_2SO_4 and 0.1M NaOH. The graph was plotted using the obtained values.

Retrieval Number: A11381291S419/2019©BEIESP
DOI:10.35940/ijeat.A1138.1291S419

Published By:
Blue Eyes Intelligence Engineering
& Sciences Publication

- *Effect of temperature:* 0.1g of the adsorbent at a pH of 6.0 was used for studying the effect of temperature at different temperature ranges from 30-60 °C. The concentrations were measured using a UV-Visible spectrophotometer at a wavelength of 650 nm, and a graph was plotted from the obtained values.

- *Adsorption process:* Adsorption kinetic experiments are performed with 0.1g of biosorbent with 50 ml of MB in aqueous solution with varying concentrations (10-50) mg/l in 250 ml flasks, at room temperature for particular contact time. After adsorption, the sorbent and supernatant will be subjected centrifugal separation at 4000 rpm for 10 min. Samples were assessed for residual MB concentration using UV-Visible Spectrophotometer 650nm.

The dye adsorbed per gram of biosorbent (q_c) is given as:

$$q_c = V/m[C_e - C_o] \quad (1)$$

% Removal,

$$\%R = [(C_o - C_e)/C_o] * 100 \quad (2)$$

Where,

C_o : initial MB conc. (mg/l)

C_e : equilibrium MB conc. (mg/l)

V : volume of MB solution (L)

m : mass of the adsorbent (g)

III. RESULT AND DISCUSSIONS

K. Adsorbent Dosage

The adsorbent capacity for a given initial concentration of dye is dictated by the adsorbent dosage. Hence it is considered a vital parameter in adsorption studies. Cow dung, Coconut husk and Moss had functional adsorption capacity. Among them, the adsorption capacity of moss is higher compared to the other samples (Fig. 4.). Groundnut shell has the least adsorption.

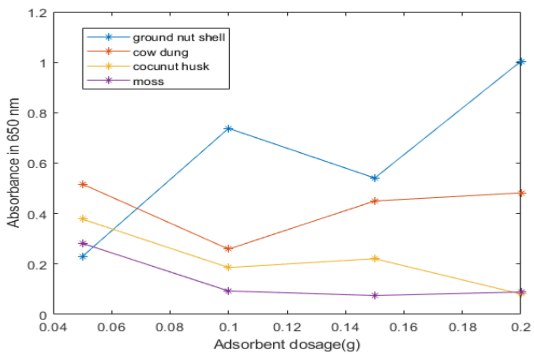

Fig. 4. Effect of adsorbent dosage

L. Effect of pH

pH is a critical factor in adsorption studies, particularly in dye adsorption. The pH controls the extend of electrostatic charges which are generated both by the ionized dye molecules and the surface charges of the biosorbent. As a result, the biosorption rate varies with the pH. Cow dung, Coconut husk and Moss are observed to have functional adsorption capacity at pH 8 (Fig. 5.). Groundnut shell has functional adsorption capacity at pH 2.

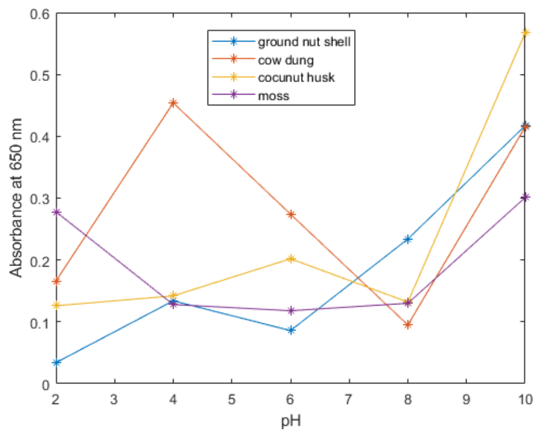

Fig. 5. Effect of pH

M. Effect of Temperature

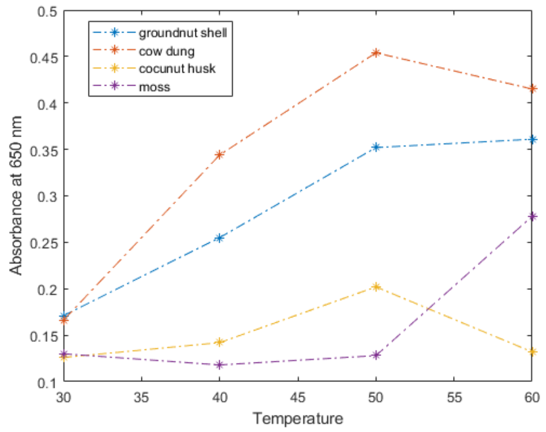

Fig. 6. Fig. Effect of temperature

Cow dung, Coconut husk and Groundnut shell were observed to have functional adsorption capacity at room temperature (30°C). Among them, Coconut husk is found to have better adsorption capacity (Fig. 6.). Moss is found to have best adsorption capacity at 30 - 50 °C.

N. Adsorption Isotherms

Adsorption isotherm explains how the adsorbate – adsorbent interaction takes place and suggests the mechanism and nature of the whole process. When equilibrium is achieved in adsorption, the isotherm models indicates the distribution of sorbate particles between the solid and liquid phase. Equilibrium data derived from the various isotherm models provide important insights on biosorption mechanisms, surface properties and affinities of the bio sorbent. Therefore, it is imperative to estimate the most matching correlation of equilibrium curves to optimize the parameters for designing a sorption system. In the present study, Temkin, Freundlich and Langmuir model were employed to explore the sorption behaviour and was observed that all the models could be used to describe the sorption behaviour.

The Langmuir isotherm equation describes monolayer adsorption owing to the presence of specific homogenous sites within the adsorbent. Since monolayer sorption is assumed, naturally adsorption becomes surface area dependent and has a finite maximum at equilibrium, where, a point of saturation is achieved after which, no further sorption occurs. The equation 3 describes the mathematical expression for Langmuir isotherm:

$$q_e = \frac{q_{max} K_L C_e}{1+K_L C_e} \quad (3)$$

The linearized mathematical expression for Langmuir isotherm used in this study is given as equation 4:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \quad (4)$$

Where, C_e is the solution concentration at equilibrium (mg/L), q_e is the amount of sorbate adsorbed per unit mass of sorbent at equilibrium (mg/g), q_{max} is the theoretical maximum adsorption capacity (mg/g), K_L is the Langmuir isotherm constant (L/mg). The values of K_L and q_{max} can be obtained plotting C_e/q_e against C_ee, where K_L will be the slope and q_{max} will be the x-intercept of the linear plot. Values of K_L increase with temperature, which corresponds to an increase in the binding forces between adsorbate and adsorbent.

The Freundlich isotherm model is an empirical equation which is applied to sorption of particles on heterogeneous surfaces with the interaction between adsorbed particles. The model works on the assumption that adsorption energy decreases exponentially as the sorptional centres in the adsorbent are completed. The Freundlich isotherm is given as:

$$q_e = K_F C_e^{1/n} \quad (5)$$

Where, the Freundlich constant, K_F, describes the sorption capacity of the sorbent ($mg1^{-1/n}$ $L^{1/n}$ g^{-1}) and n, denotes a dimensionless constant, that signifies the extent of sorption and the sorption intensity between the solute concentration and the sorbent. The linearized form of the Freundlich isotherm model is generally expressed as:

$$Log q_e = Log\, K_F + \frac{1}{n} Log\, C_e \quad (6)$$

The values of K_F and n are adopted from the plot of $log\, q_e$ versus $log\, C_e$ as intercept and slope respectively. The value of n is greater than one for the sorption of the particles at all temperatures and reduces with increase in temperature. The increase of value of K_F with temperature, corresponds an enhanced sorption at high temperatures and further confirms the endothermic nature of the sorption process.

The Temkin isotherm model addresses the sorbent - sorbate interactions. Temkin isotherm operates on the assumption that the sorption is mediated by a uniform distribution of binding energies until a maximum binding energy is attained and the heat of sorption of all the particles in the layer reduces linearly with coverage due to sorbent - sorbate interactions. The linearized form of the temkin isotherm is given as:

$$q_e = B_1 \ln K_T + B_1 \ln C_e \quad (7)$$

Where, the temkin constant, B_1, is connected to the heat of sorption. K_T is the Temkin equilibrium binding constant (L/mg). The values of K_T and B_1 obtained from plots of q_e versus $ln\, C_e$ as the intercept and slope respectively.

1) Coconut

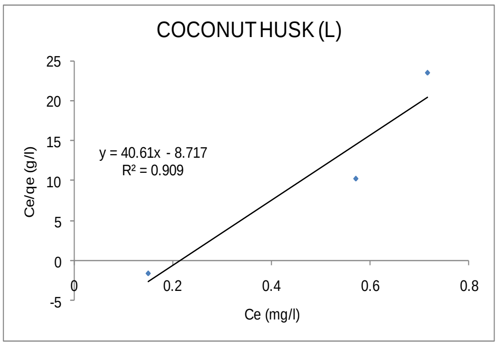

Fig. 7. Langmuir Isotherm

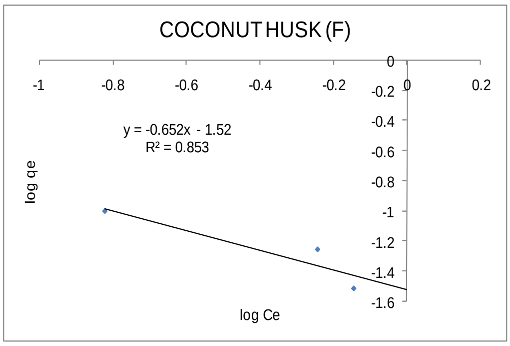

Fig. 8. Freundlich Isotherm

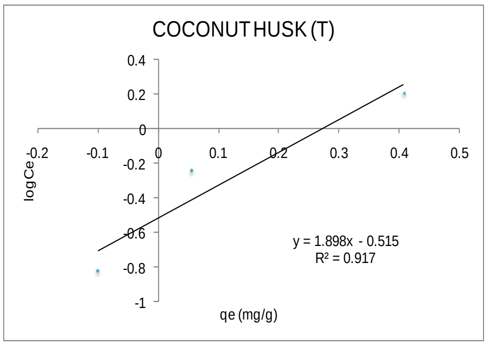

Fig. 9. Temkin Isotherm

The best fit is observed in Temkin plot. (Fig. 7-9.) From this, we can infer that the adsorption in coconut takes place due to the sorbent - sorbate interactions. Temkin isotherm is operating on the assumption that the sorption is mediated by a uniform distribution of binding energies until a maximum binding energy is attained and the heat of adsorption of all the particles in the layer reduces linearly with coverage due to sorbent - sorbate interactions.

International Journal of Engineering and Advanced Technology (IJEAT)
ISSN: 2249 – 8958, Volume-9 Issue-1S4, December 2019

2) Groundnut shell

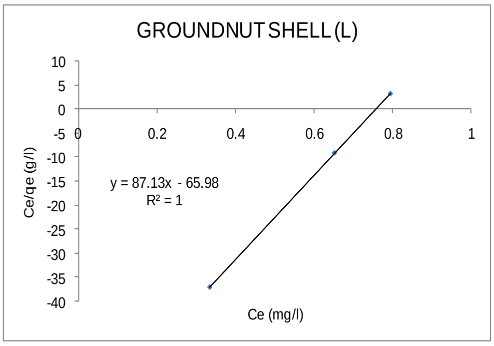

Fig. 10. Langmuir Isotherm

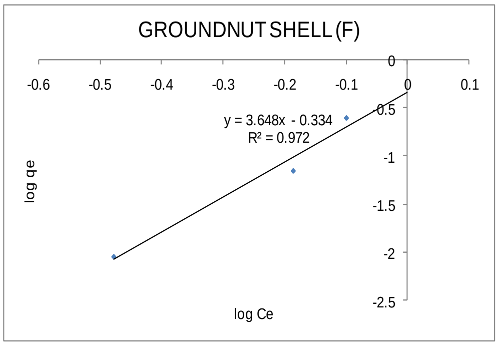

Fig. 11. Freundlich Isotherm

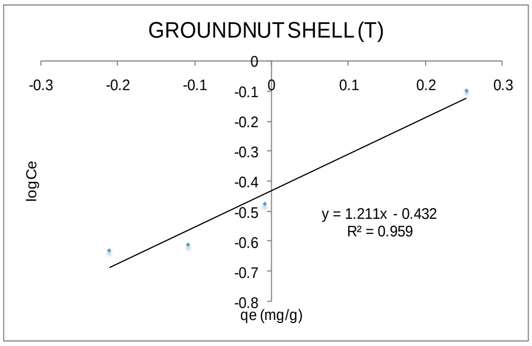

Fig. 12. Temkin Isotherm

Best fit in Langmuir isotherm. (Fig. 10-12.) From this, we can infer that the adsorption in Groundnut shell takes places due to the presence of specific takes place in a monolayer owing to the presence of specific homogenous sites within the adsorbent.

3) Moss

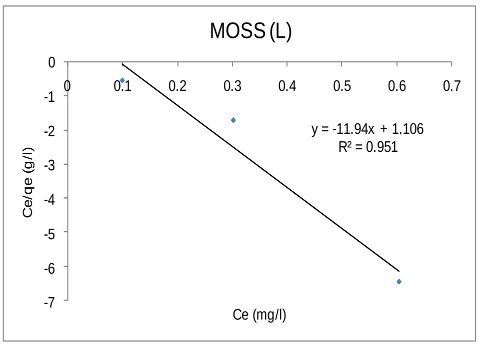

Fig. 13. Langmuir Isotherm

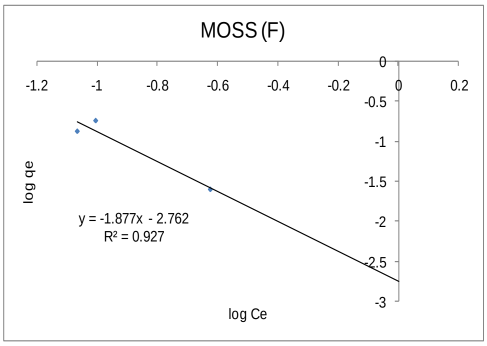

Fig. 14. Freundlich Isotherm

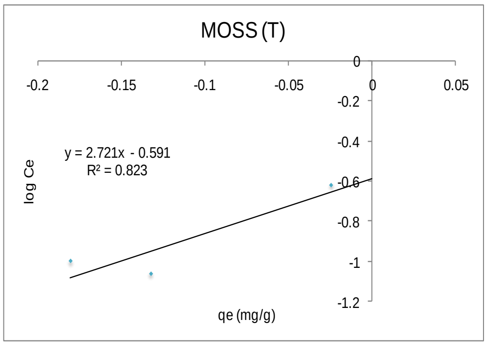

Fig. 15. Temkin Isotherm

Best fit in Langmuir isotherm. (Fig. 13-15.) From this, we can infer that the adsorption in Moss takes place in a monolayer owing to the presence of specific homogenous sites within the adsorbent. Since monolayer adsorption is assumed, naturally adsorption becomes surface area dependent and has a finite maximum at equilibrium, where, a saturation point is reached after which no further sorption occurs.

4) Cow dung cake

The best fit is observed in Temkin plot. (Fig. 16-18.) From this, we can infer that the adsorption in cow dung takes place due to the sorbent - sorbate interactions. Temkin isotherm is operating on the assumption that the sorption is mediated by the uniform distribution of binding energies until a maximum binding energy is attained and the heat of adsorption of all the particles in the layer reduces linearly with coverage due to sorbent - sorbate interactions.

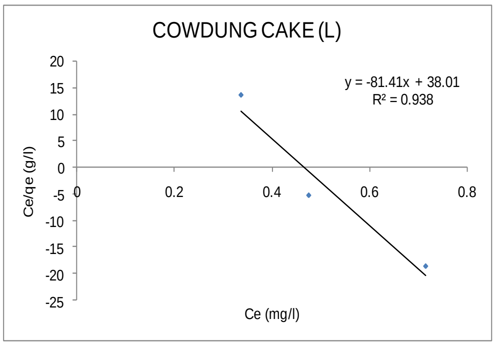

Fig. 16. Langmuir Isotherm

Retrieval Number: A11381291S419/2019©BEIESP
DOI:10.35940/ijeat.A1138.1291S419

Published By:
Blue Eyes Intelligence Engineering
& Sciences Publication

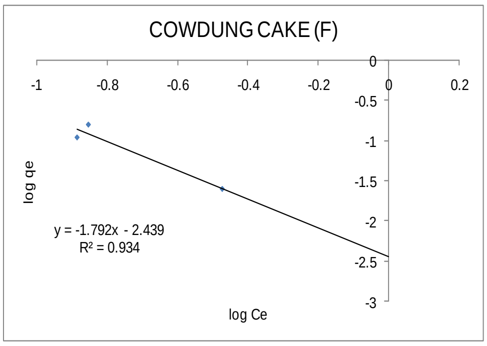

Fig. 17. Freundlich Isotherm

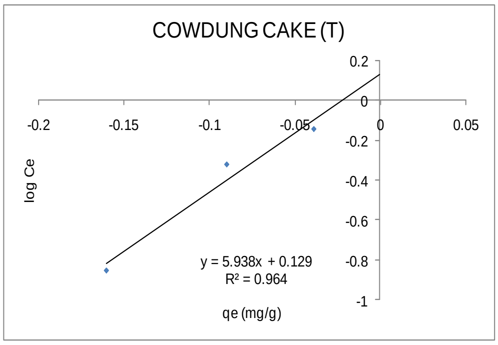

Fig. 18. Temkin Isotherm

IV. CONCLUSION

The presented work uncovers that moss is a low-cost, effective adsorbent for the removal of cationic dye, in particular Methylene Blue, from aqueous solutions. The sorbent had functional adsorption for MB and displayed significant sorption as the initial dye concentration increased. Adsorption parameters estimated from Freundlich, Langmuir and Temkin isotherms were used to explain the mechanisms of the adsorption process based on the correlation coefficient values. Coconut husk and Cow dung adsorbents are best fitted into Temkin isotherm. Groundnut shell and Moss are best fitted into Langmuir isotherm. Which says that moss supports monolayer adsorption rather than energy-dependent adsorption. By carrying out further studies in Moss, we may be able to overcome the increasing concern arisen due to the significant presence of toxic dyes such as Methylene blue in the industrial effluents. By this, we conclude that bio-sorption is a less expensive and eco-friendly method.

ACKNOWLEDGMENT

The authors thank the management and staff of Department of Biotechnology, Sree Chitra Thirunal College of Engineering, Trivandrum, Kerala, India for their support in completion of this work.

REFERENCES

1. Ferrero, Franco. "Dye removal by low cost adsorbents: Hazelnut shells in comparison with wood sawdust." Journal of Hazardous Materials 142, no. 1-2 (2007): 144-152.
2. Ramakrishna, Konduru R., and T. Viraraghavan. "Dye removal using low cost adsorbents." Water Science and Technology 36, no. 2-3 (1997): 189-196.
3. Fu, Yuzhu, and T. Viraraghavan. "Fungal decolorization of dye wastewaters: a review." Bioresource technology 79, no. 3 (2001): 251-262.
4. Tahir, Hajira, Muhammad Sultan, Nasir Akhtar, Uzma Hameed, and Tahreem Abid. "Application of natural and modified sugar cane bagasse for the removal of dye from aqueous solution." Journal of Saudi Chemical Society 20 (2016): S115-S121.
5. Gupta, V. K. "Application of low-cost adsorbents for dye removal–A review." Journal of environmental management 90, no. 8 (2009): 2313-2342.
6. Rauf, Muhammad A., I. Shehadeh, Amal Ahmed, and Ahmed Al-Zamly. "Removal of methylene blue from aqueous solution by using gypsum as a low cost adsorbent." World Academy of Science, Engineering and Technology 55 (2009): 608-613.
7. U.J. Etim, S.A. Umoren, U.M. Eduok "Coconut coir dust as a low cost adsorbent for the removal of cationic dye from aqueous solution", Journal of Saudi Chemical Society (2016)
8. Kumar, Sunil, V. Gunasekar, and V. Ponnusami. "Removal of methylene blue from aqueous effluent using fixed bed of groundnut shell powder." Journal of Chemistry 2013 (2012).
9. Rattan, V. K., Abhiti Purai, Harminder Singh, and Mahboobeh Manoochehri. "Adsorption of dyes from aqueous solution by cow dung ash." Carbon letters 9, no. 1 (2008): 1-7.
10. Li, Yanhui, Qiuju Du, Tonghao Liu, Xianjia Peng, Junjie Wang, Jiankun Sun, Yonghao Wang et al. "Comparative study of methylene blue dye adsorption onto activated carbon, graphene oxide, and carbon nanotubes." Chemical Engineering Research and Design 91, no. 2 (2013): 361-368.
11. Rafatullah, Mohd, Othman Sulaiman, Rokiah Hashim, and Anees Ahmad. "Adsorption of methylene blue on low-cost adsorbents: a review." Journal of hazardous materials 177, no. 1-3 (2010): 70-80.
12. Crini, Gregorio. "Non-conventional low-cost adsorbents for dye removal: a review." Bioresource technology 97, no. 9 (2006): 1061-1085.

V. AUTHORS PROFILE

Abhirami A. P. received her B. Tech in Biotechnology and Biochemical Engineering, Sree Chitra Thirunal College of Engineering, Trivandrum, Kerala, India. Currently pursuing Masters at Ontario College Diploma in Conestoga College, Cambridge Campus, 0730G-Food Processing Technician, Ontario, Canada.

Anjaly Priya received her B. Tech in Biotechnology and Biochemical Engineering, Sree Chitra Thirunal College of Engineering, Trivandrum, Kerala, India. Currently working as Trainee Clinical Data Management Coordinator at IQVIA.

Devika R. received her B. Tech in Biotechnology and Biochemical Engineering, Sree Chitra Thirunal College of Engineering, Trivandrum, Kerala, India. M.Tech at Visvesvarya National Institute of Technology, Chemical Engineering, Nagpur

Indu G. received her B. Tech in Biotechnology and Biochemical Engineering, Sree Chitra Thirunal College of Engineering, Trivandrum, Kerala, India.

Nidhin Sreekumar is working as Chief Research Scientist at Accubits Technologies Inc. He was working as Associate Professor in Kalasalingam Academy of Research and Education, Krishnankoil, Tamil Nadu. He received his doctoral degree from NIT Calicut in 2018.