Research Article

Jackfruit leaf as an adsorbent of malachite green: recovery and reuse of the dye

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Abstract
Dry leaf powder of jackfruit (*Actocarpus heterophyllus*) was utilized for the removal of an industrial dye malachite green from the aqueous solution by the batch adsorption method. The parameters which effect on adsorption such as adsorption dose, contact time between adsorbent and the dye in solution, and pH of the solution were studied and standardized. The scanning electron microscope (SEM) photography of the jackfruit leaf powder (JLP) indicated that it had a large number of pores, spaces and empty sites. The SEM photography of used JLP shows that the dye is confidently attached on the JLP. Fourier-transform infrared spectroscopy analysis of the adsorbent confirmed the presence of different functional groups like –OH, –NH and C=O on its surface, which can be correlated with the fine adherence of the dye on the surface of the adsorbent. Moreover, the shifting of the functional group on the surface of adsorbed adsorbents indicates the affinity of the dye towards the adsorbent. The Freundlich isotherm model with the correlation coefficient (r^2) value of 0.9880 is considered as a suitable absorption model for adsorption of dye. The pH of the aqueous solution was reduced from pH 7 to pH 5. This helped the recovery of the 80% of the attached dye. The present work concludes that jackfruit leaf powder can be used as an efficient adsorbent to remove malachite green from aqueous medium and the adsorbed dye can also be recovered for reuse from the surface of the adsorbent.

Keywords Malachite green · Batch adsorption · Jackfruit · Recovery of dye

1 Introduction

Industrial discharge water contains a large variety of inorganic and organic compounds. Their quality and quantity depends on the type of industry where it is produced. The presence of compounds is the reflection of raw materials being used for production and the chemicals utilized for processing of finished products of that industry [2]. The industrial effluents if added to the natural water bodies either untreated or inadequately treated cause water pollution. Some industries like textile, plastic, leather, pulp and paper and tannery have been consumed a massive amount of different dyes for their production, and therefore, these industries generate huge amount of coloured effluent [18]. When these effluents approach to the natural water bodies, they affect aquatic life, soil micro-flora and fauna of that vicinity and also cause toxicological and aesthetical problems. It is estimated that production of one kilogram of the finished product in textile industry generates on an average of the 150 L wastewater [10]. Synthetic dyes are frequently used in industries due to low cost and more efficient as compared with natural dyes [16, 25]. Certain synthetic dyes are either non-biodegradable or stay for a longer period in the environment cause pollution. Thus, it is highly necessary to remove the dyes present in industrial effluents to beat water pollution. Physical methods like adsorption, electro-coagulation, ultra-filtration, ion exchange, etc., have been adopted for the removal of dyes from industrial waste water, but it is observed that each process has their own pitfalls [3]. Activated carbon can be used as an adsorbent for the removal of dyes from aquatic solution, but limitation is high production cost [9].

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Many reports are available today on the use of plant parts as low-cost adsorbents for the removal of the dye from aqueous medium [12, 14, 28], but leaf powder is found to be quite suitable due to their availability and reproducibility. Plant leaf as an adsorbent for the removal of the basic dye has been reported by some workers [5, 7, 22], but reports on recovery of the dye after use are scanty.

Malachite green (MG) has a three-benzene-ring-structured compound (Fig. 1) of molecular formula $C_{23}H_{25}ClN_2$ and molecular weight 364.917 g/mol. It is used in industries like silk, leather, food, health, textile and paper industries as dye [1]. The compound is also used in aquaculture to control parasites due to its antiprotozoal and antifungal properties [26]. Malachite green of high concentration or low concentration with longer exposure causes toxicity to mammals such as the internal organs damage, mutagenesis, carcinogenic effect and developmental abnormalities [23]. The jackfruit (*Actocarpus heterophyllus*) is also known as jack tree, which belongs to family Moraceae, native to South-West India [19]. The leaf of jackfruit is simple, entire, green colour, adaxial side is dark green and shiny, but the abaxial side is lighter green colour, elliptical–obovate in shape and measure about 20 cm long [6]. In the present investigation, an effort has been made to find out the efficiency of jackfruit leaf powder as an adsorbent to remove malachite green from the aqueous solution.

2 Materials and methods

2.1 Preparation of the adsorbent

Jackfruit plant growing nearby GIET University was used for the preparation of the adsorbent. The plant was authenticated at the Floristic Laboratory, Botany Department, Berhampur University, Berhampur. The matured and healthy leaves were collected and then washed thoroughly in running tap water. They were dried in an oven at 80 °C for 48 h. The dried leaves were powdered by a domestic mixer and sieved in a 1-mm pore to get homogenous powder. The leaf powder was again washed thoroughly with distilled water to remove pigments and tannins present within it. The jackfruit leaf powder (JLP) is stored in an air-tight container which is used as adsorbent for future use.

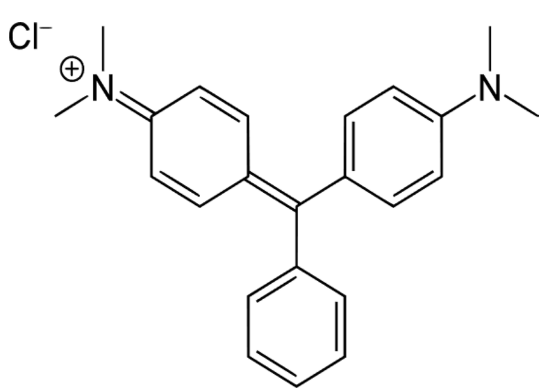

Fig. 1 Structure of malachite green

2.2 Preparation of the dye solution

Malachite green (MG) AR grade was obtained from HI Media Pvt. Ltd., Mumbai. One gram malachite green is added to 1 L double distilled water to prepare the stock solution. Later on, different working solutions were prepared from stock solution with distilled water.

2.3 Designing of the experiment

Batch adsorption method was followed to evaluate the adsorption of malachite green by the adsorbent. Adsorption of the dye was measured by UV–Vis spectrophotometer (model 119) at 616.5 nm (λmax = 616.5 nm). The experiment was designed in an Erlenmeyer flash (capacity of 250 mL volume) with 100 mL of the working quantity. The experimental flasks were kept in slow agitation (150 rpm) during the study. The parameters such as adsorbent dose, contact time and pH of the solution were standardized. Different doses of jackfruit leaf powder in a range of 0.1–1.0 g/100 mL were added to the aqueous dye solution in separate flasks, and the adsorption of dye in each flask was recorded. The standardization of contact time for adsorption of the dye was established. The optimum dose adsorbent was added to the standard aqueous dye solution, and adsorption of the dye was recorded in a range of 20–200 min. The adsorption of dye in the flask was determined with the help of UV–Vis spectrophotometer with respect to its absorption maxima. Similarly, to find out the effect of pH on the adsorption of the dye, the aqueous solution was maintained from pH 2 to pH 10 in different containers. The optimum doses of adsorbent were added to the containers. The adsorption efficiency of the adsorbent was calculated by

$$\text{The percentage of removal of dye} = \frac{C_i - C_f}{C_i} \times 100$$

$$\text{The adsorption efficiency of leaf powder} = \frac{(C_i - C_f)V}{M}$$

where C_i and C_f are the initial and the final concentration of dye, respectively, V = volume of the solution (mL), and M = mass of the adsorbent (g).

To recovery of the attached dye on the surface of the adsorbent, the pH of the solution was altered from pH 7 to pH 5 with 1 NH_2SO_4 and the amount of dye detached from the adsorbents was recorded carefully following the same procedure as mentioned earlier.

2.4 The characterization of the adsorbent

As adsorption is a surface phenomenon, the ultra-morphological structure of the adsorbents and the presence of any group on the surface of the adsorbent were analysed. The jackfruit leaf powder was observed under the scanning electron microscope (SEM) at different magnifications, and the photograph was taken. Similarly, to identify the existence of functional groups on the surface, the adsorbent was experiential with Fourier transmission infrared spectroscopy (FTIR) in a spectrum range from 400 to 4000 wavelength cm^{-1}.

3 Results and discussion

Jackfruit leaf powder was used as an adsorbent for the removal of the dye. The prepared leaf powder was washed thoroughly with distilled water to remove the pigments/tannins present in the adsorbent. Now the adsorbent has hard tissues of the plant like xylem, phloem, sclerenchyma, etc. (Fig. 2).

3.1 Adsorbent dose standardization

Different doses of JLP were prepared in a range of 0.1–1.0 g and added to the dye solution of 100 mg/L in separate containers, and the amount of dye adsorbed in each one was recorded. The adsorption of the dye increased up to 0.5 g/L and then found to constant (Fig. 3). Thus, the optimum dose of the prepared adsorbent to remove the dye is 0.5 g/L. At this circumstance, the total dye present in the solution is absorbed by all the available spaces on the adsorbents. Therefore, the adsorption value remained constant even though more adsorbents were added to the solution.

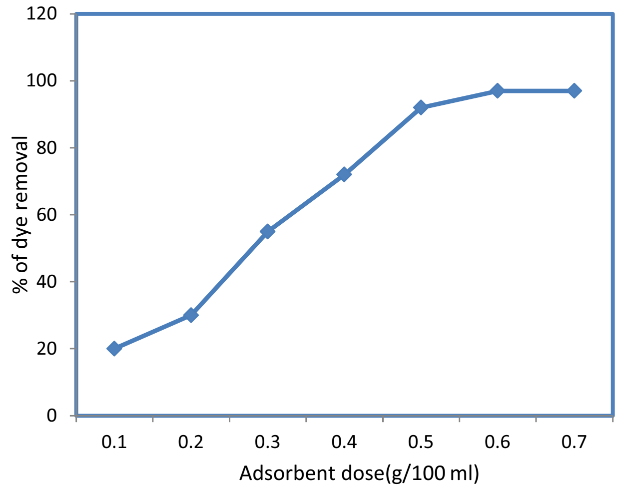

Fig. 3 Adsorption of malachite green onto the different doses of jackfruit leaf powder (JLP)

3.2 Standardization of contact time

The optimum dose (0.5 g/L) of adsorbent was added to a standard dye solution and was kept for a period up to 200 min. The adsorption of the dye at an interval of every 20 min was recorded (Fig. 4). The optimum contact time of the prepared adsorbent for the removal of malachite green in aqueous medium was recorded at 150 min of incubation.

3.3 Standardization of pH

The adsorption of the dye onto the JLP was recorded the maximum at pH 8 (Fig. 5). Therefore, low adsorption was

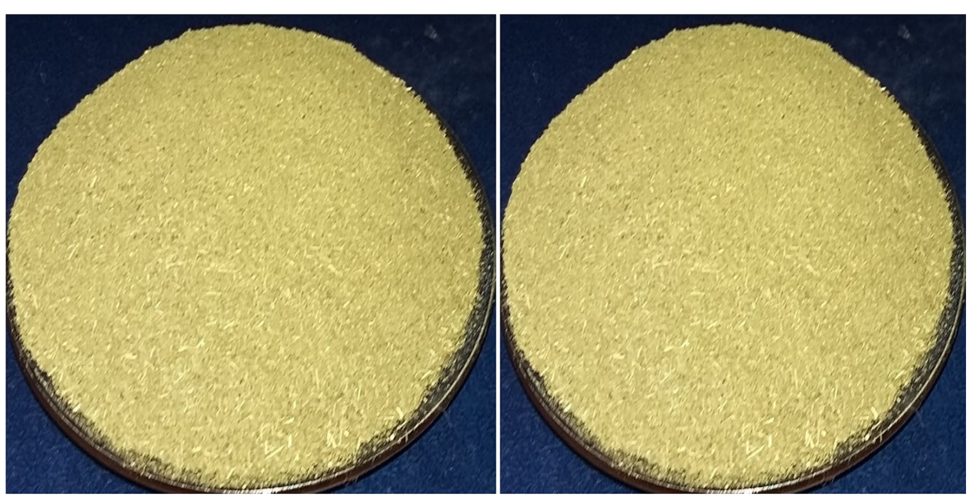

Fig. 2 Jackfruit leaf powder (JLF) as an adsorbent for the removal of the dye

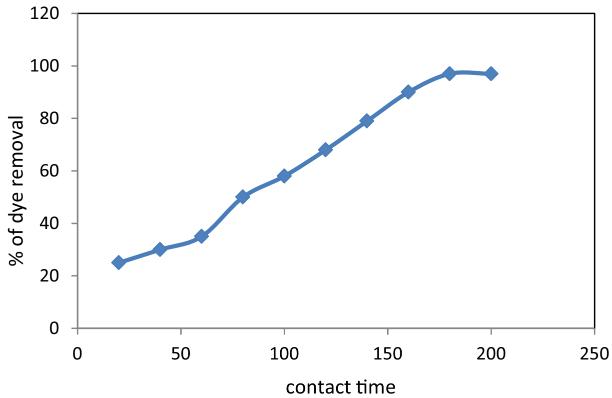

Fig. 4 Effect of contact time on the adsorption of malachite green onto jackfruit leaf powder (JLP)

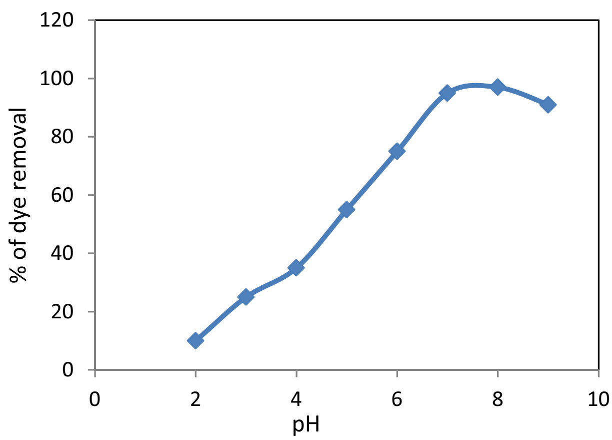

Fig. 5 Effect of pH on the adsorption of malachite green onto jackfruit leaf powder (JLP)

observed in acidic surroundings. In acidic medium, the dye might be competing H^+ ion there in the solution so that less adsorption was found. Alternatively, in the alkaline environment no such ions were found; therefore, the situation facilitates the adsorption of the dye. Earlier investigators also reported that alkaline ambiance favours adsorption of malachite green in tea leaf [11], pine apple leaf [8] and maize leaf [15].

3.4 Surface characterization of the adsorbent

The adsorbent was prepared from leaves of jackfruit. The leaves were dried and made into powdered. The powder was sieved to maintain the homogenous size of ≤ 1 mm. Then, it was washed with distilled water for several times to remove the pigments and metabolites present in it. Now they are constituted of plant hard tissue only. The dried hard plant tissues are good adsorbents [30]. The prepared adsorbent has more surface area due to smaller in size. Therefore, both the composition and size of the adsorbent together facilitate the adsorption of the dye.

The surface structure of the adsorbent was viewed under scanning electron microscopy (SEM). The SEM photograph clearly indicates that the surface of the adsorbent is rough and the presence of many concave sites (Fig. 6). This typical surface structure of the adsorbent encourages the attachment of the dye on the surface. The SEM photograph of the utilized adsorbent showed that the entire surface of the adsorbent was fully occupied by the dye. The dye was finely adhered to the surface of the adsorbent. To establish the attachment of the dye on the surface of the adsorbent, FTIR analysis was made. The FTIR analysis of both raw and adsorbed JLP is represented (Fig. 7). The raw one showed peaks at 2921.4, 2851.5, 2318.5, 2316.5, 1730.1, 1613.9, 1049.7 and 450.1 wavelengths cm^{-1}. Similarly, the adsorbed JLP had peaks like 2911.8, 2851.3, 2201.9, 2186.8, 2162.9, 1736.8, 1365.1, 1216.8, 1051.9 and 113.1 wavelengths cm^{-1}. The peaks can be correlated with the presence of functional groups like –C=O, –CHO, –OH and $–NH_2$ on the adsorbent [17]. The shifting of the absorption wavelength indicates the stretching of the functional group on the surface of the adsorbent due to adsorption of the dye.

3.5 Adsorption isotherm

To design an appropriate adsorption system, it is quite necessary to set up a proposed existing adsorption isotherm model with the experimental value. The adsorption values have been analysed with three popular isotherm models such as the Langmuir model, the Freundlich model and the BET model. The correlation coefficient (r^2) value of the model was determined from the plotted graph, and the value close to one is considered as the most fitting model for designing of the adsorption system.

3.6 The Langmuir isotherm model

The isotherm model explains that the adsorbent contains a large number of equivalent sites where the species are attached on it either by physical or by chemical sorption [21]. Langmuir postulated that the adsorbate variety has affinity to the surface of the adsorbent at an isothermal condition. The isotherm has many assumptions, one of them is adsorbent surface containing the adsorbing sites in a flat plane, and there is no interaction between adsorbate and adsorbent site. The equation can be represented as

$$\frac{C_e}{Q_e} = \frac{1}{K_l . Q_m} + \frac{C_e}{C_e}$$

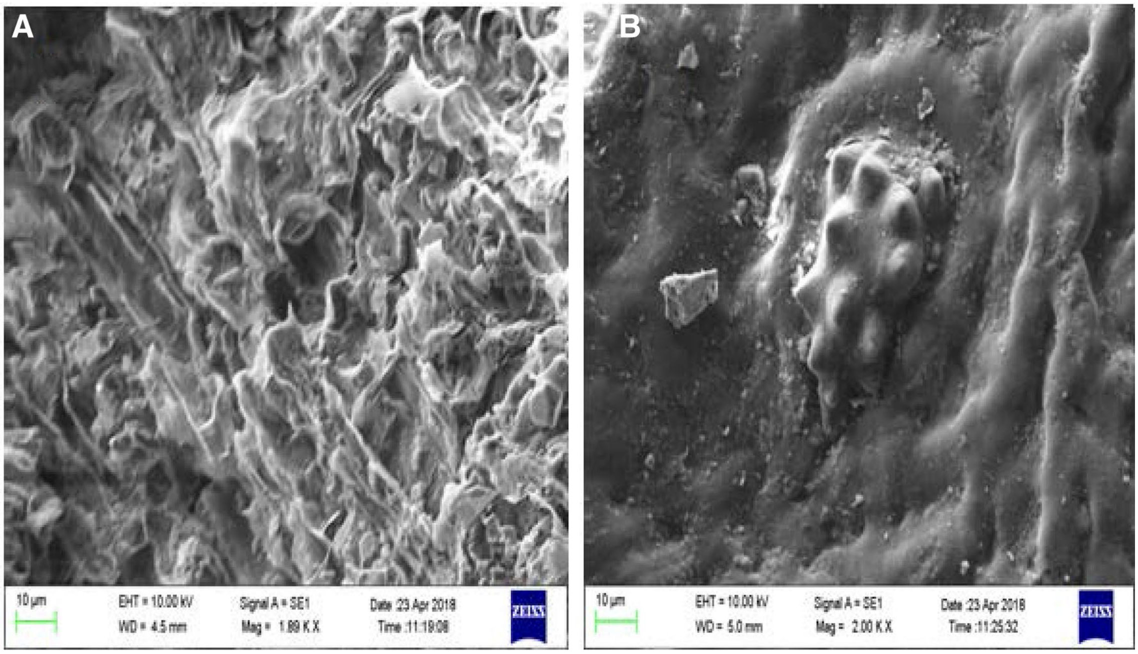

Fig. 6 SEM photograph of jackfruit leaf powder (JLP). **a** Raw JLP and **b** adsorbed with malachite green

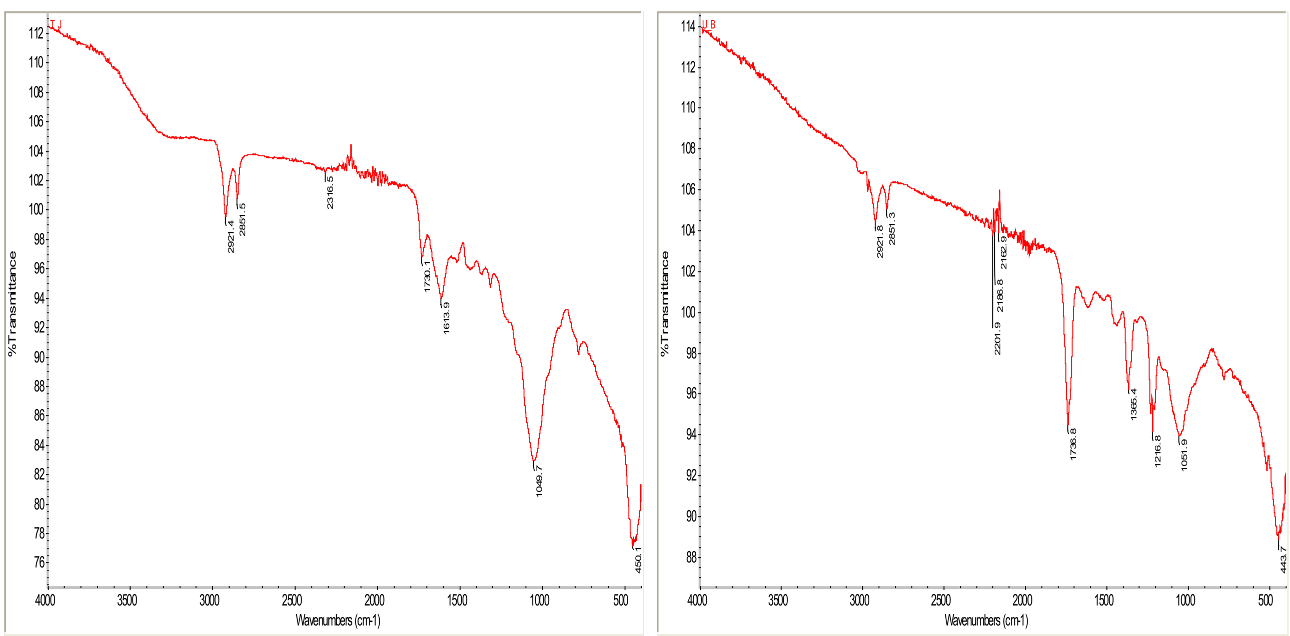

Fig. 7 FTIR spectrum of jackfruit leaf powder (JLP). **a** Raw JLP and **b** adsorbed JLP

where C_e is the equilibrium concentration of the ion in solution (mg/g), Q_e is the ion adsorbed per unit weight of adsorbent (mg/g), Q_m is the adsorption capacity in monolayer and K_l is the equilibrium constant. The correlation coefficient (r^2) value of the adsorption is calculated from the graph for malachite green and found to be 0.9015 (Fig. 8).

3.7 The Freundlich isotherm model

Freundlich adsorption isotherm indicates the relation between the concentrations of a solute and the surface of an adsorbent in the liquid medium. It is the isothermal variation of adsorption quantity at the unit mass of solid adsorbent. It assumes that the adsorption process takes

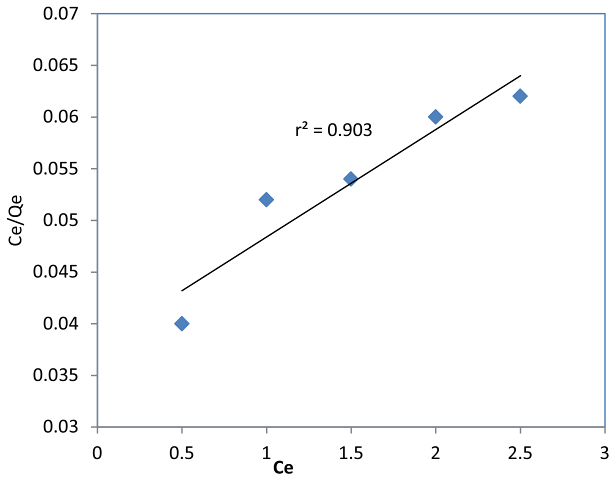

Fig. 8 Langmuir isotherm plot of malachite green on adsorption onto jackfruit leaf powder (JLP)

place on the heterogeneous surface, and the adsorption capacity is related to the concentration of dye. The Freundlich isotherm model is used where the actual quantity of the solute in the solution is not known, which can be represented as [13]

$$l_n v_e = l_n k_f + \frac{1}{n} l_n c_e$$

where v_e is the ion adsorbed on the surface, k_f is the relative adsorption capacity of the adsorbent (mg/g) which is a constant and n is an empirical parameter which indicates the intensity of adsorption. The correlation coefficient value (r^2) marked from the plot is 0.9880 (Fig. 9).

3.8 The BET isotherm model

Brunauer–Emmett–Teller (BET) isotherm explains the physical adsorption of adsorbent molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of materials. The model explains the physical adsorption of gas molecules on a solid surface [24]. The model is applicable to systems of multilayer adsorption, and the adsorbing molecules do not chemically react with the material surface. It is represented by

$$\frac{q_e}{c_e} = \frac{c \cdot x}{(1 - x)(1 - x + c \cdot x)}$$

where q_e is the adsorbed quantity, c_e is the concentration of monolayer adsorbed quantity, c the is constant and x is p/po, the equilibrium and the saturation pressure of adsorbents.

The adsorption values are plotted in the graph, and the correlation coefficient value (r^2) is found to be 0.8895 (Fig. 10).

Out of the studied three isotherm models with respect to adsorption of malachite green on the adsorbent, the maximum correlation coefficient value ($r^2 = 0.9880$) is found at the Freundlich isotherm model. Therefore, Freundlich isotherm model is the best suitable model for adsorption of malachite green on the jackfruit leaf powder.

Earlier investigators reported that plant parts can be exploited for the removal of malachite green from the aqueous solution. Teak leaf powder [20], rice husk activated carbon [29], marine algae *Caulerpa racemosa* var, *cylindracea* [31] and wood apple shell [27] can be used for the removal of malachite green from the solution of 95, 94.91, 95.02 and 98.87%, respectively.

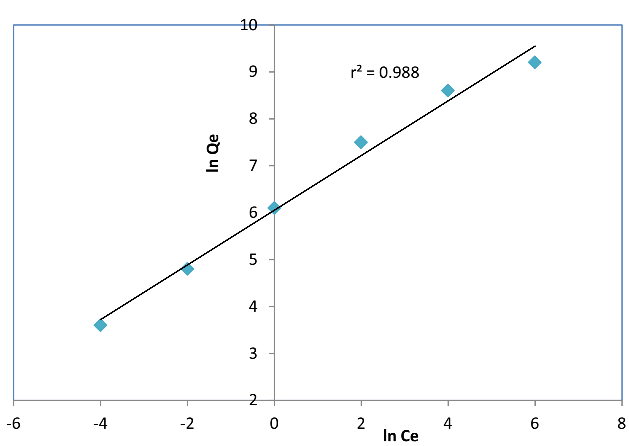

Fig. 9 Freundlich isotherm model of malachite green on adsorption onto jackfruit leaf powder (JLP)

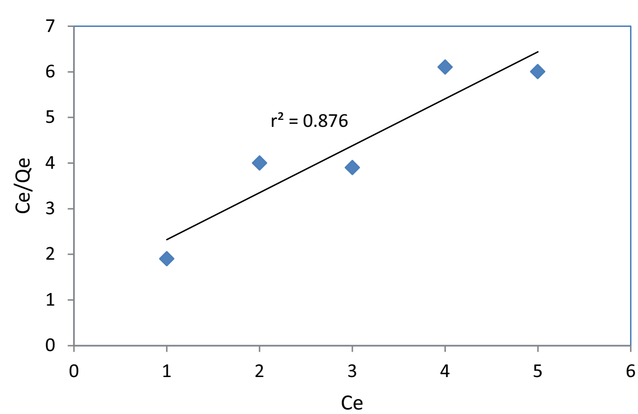

Fig. 10 BET isotherm model of malachite green on adsorption onto jackfruit leaf powder (JLP)

The dye used in the investigation is malachite green. It is popularly known as benzaldehyde green or aniline green. The dye is commonly used in silk, textile and leather industry for colouring the products. The structure and nature of malachite green are described earlier. Chemically, it is an acidic nature, but due to the presence of chromophores, it serves as the basic dye [4]. The structure of the compound indicates that it has both the tertiary amino group and quaternary N^+ group. These groups may have affinity towards the functional groups present in the adsorbent. The FTIR analysis of the adsorbent revealed that the prepared adsorbent is an organic compound constituents functional groups like –C=O, –CHO, $-NH_2$, etc. Thus, the dye had firmly attached to the surface of the adsorbent.

The maximum removal efficiency of the adsorbent was found to be 97.8%. To recovery of the adsorbed dye from the surface of the JLP, the aqueous medium was slowly turned to an acidic environment (pH 5) using 1 NH_2SO_4. It was observed that about 80% of the attached dye was detached from the adsorbent.

4 Conclusion

Jackfruit tree is a medium-sized tree famous for its delicious fruit. The leaf of the plant is thick and oval shaped. The JLP was tested as an adsorbent to remove a basic dye, malachite green, from the aqueous solution. Malachite green is used in different industries for colouring the product. The JLP has maximum 97.8% removal efficiency of malachite green. The parameters that effect on adsorption such as adsorbent dose, contact time and pH of the aqueous solution for maximum adsorption were standardized. The adsorption dose was 0.4 g/L for maximum removal of the dye. Similarly, the contact time and pH of the solution were identified as 150 min and pH 8, respectively. The Freundlich isotherm model with correlation coefficient (r^2) value 0.9880 was found suitable to design an adsorption model. Therefore, the present investigation can be concluded that JLP can suitably be used for the removal of malachite green from the aqueous solution. Moreover, due to low cost and easily available naturally at garden and forest, the technique is cost-effective as compared to the other removal processes.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no competing interests.

References

1. Ahmad MA, Alrozi R (2011) Removal of malachite green dye from the aqueous solution using rambutan peel-based activated carbon: equilibrium, kinetic and thermodynamic studies. Chem Eng J 171:510–516
2. Ahmad R, Kumar R (2010) Adsorption studies of hazardous malachite green onto treated ginger waste. J Environ Manag 91:1032–1038
3. Ahmad A, Rafatullah M, Sulaiman O, Ibrahim MH, Hashim R (2009) Scavenging behaviour of meranti sawdust in the removal of methylene blue from aqueous solution. J Hazard Mater 170(1):357–365
4. Arivolis S, Hema M, Martin P, Prasath D (2009) Adsorption of malachite green onto carbon prepared from *Borassus* bark. Arab J Sci Eng 34(2):31–43
5. Balarak D, Jaafari J, Hssani G, Madavi Y, Tyagi I, Agrawal S, Gupta VK (2015) The use of low-cost adsorbent (Canola residues) for the adsorption of methylene blue from aqueous solution: isotherm, kinetic and thermodynamic studies. Colloids Interface Sci Commun 7:16–19
6. Begum R, Aziz MG, Uddin MB, Yusof YA (2014) Characterization of jackfruit (*Artocarpus Heterophyllus*) waste pectin as Influenced by various extraction conditions. Agric Agric Sci Proc 2:244–251
7. Bhattacharyya KG, Sharma A (2005) Kinetics and thermodynamics of methylene blue adsorption on neem (*Azadirachta indica*) leaf powder. Pigments 65(1):51–59
8. Das P, Datta S (2016) Continuous biosorption of malachite green by *Ananus comosus* (pine apple) leaf powder in a fixed bed reactor: experimental, breakthrough time and mathematical modeling. Desalin Water Treat 57:25842–25847
9. Do M, Abak H, Alkan M (2009) Adsorption of methylene blue onto hazelnut shell: kinetics, mechanism and activation parameters. J Hazard Mater 164:172–181
10. Dural MU, Cavas L, Papageorgiou SK, Katsaros FK (2011) Methylene blue adsorption on activated carbon prepared from *Posidonia oceanica* (L.) dead leaves: kinetics and equilibrium studies. Chem Eng J 168:77–85
11. Hameed BH (2009) Removal of cationic dye from aqueous solution using jackfruit peel as non-conventional low-cost adsorbent. J Hazard Mater 162:344–350
12. Hameed BH (2009) Spent tea leaves: a new non-conventional and low cost adsorbent for removal of basic dye from aqueous solutions. J Hazard Mater 161:753–759
13. Hameed BH (2011) Grass waste: a novel sorbent for the removal of basic dye from aqueous solution. Desalination 265:159–168
14. Hameed BH, El-Khaiary MI (2008) Kinetics and equilibrium studies of malachite green adsorption on rice straw-derived char. J Hazard Mater 153:701–708
15. Jalil AA, Triwahyono S, Yaakob MR, Azmi ZZA, Sapawe N, Kamarudin NHN, Setiabudi HD, Jaafar NF, Sidik SM, Adam SH, Hameed BH (2012) Utilization of bivalve shell-treated *Zea mays* L. (maize) husk leaf as a low-cost biosorbent for enhanced adsorption of malachite green. Bioresour Technol 120:218–224
16. Kadirvelu K, Kavipriya M, Karthika C, Radhika M, Vennilamani N, Pattabhi S (2003) Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metals ions from aqueous solutions. Bioresour Technol 87(1):129–132
17. Kumar KV, Sivanesan S (2007) Isotherms of Malachite green onto rubber wood (*Hevea brasiliensis*) saw dust: comparison of linear and non linear method. Dyes Pigments 72(1):124–129
18. Lata H, Garg VK, Gupta RK (2007) Removal of a basic dye from aqueous solution by adsorption using *Parthenium hysterophorus*: an agricultural waste. Dyes Pigments 74:653–658

19. Madruga MS, Albuquerque FSD, Silva IR, Amaral DS, Magnani M, Queiroga VN (2014) Chemical, morphological and functional properties of Brazilian jackfruit (*Artocarpus heterophyllus*) seed starch. Food Chem 143:440–445
20. Mishra Y, Sowmya V, Shanthakumar S (2015) Adsorption studies of basic dyes onto teak (*Tectona grandis*) leaf powder. J Urban Env Eng 9:102–108
21. Mittal A (2006) Adsorption kinetics of removal of a toxic dye, malachite green from waste water by using hen feather. J Hazard Mater 133:196–202
22. Mohammad P, Ahmad RK (2015) Adsorption of methylene blue onto *Platanus orientalis* leaf powder: kinetic, equilibrium and thermodynamic studies. J Ind Eng Chem 21:1014–1019
23. Nebbia C, Girolami F, Carletti M, Gasco L, Zoccarato I, Giuliano AA (2017) *In vitro* interactions of malachite green and leucomalachite green with hepatic drug-metabolizing enzyme systems in the rainbow trout (*Onchorhyncus mykiss*). Toxicol Lett 280:41–47. https://doi.org/10.1016/j.toxlet.2017.07.900
24. Nethaji S, Sivasamy A, Thennarasu G, Saravanan S (2010) Adsorption of malachite green dye onto activated carbon derived from *Borassus aethiopum* flower biomass. J Hazard Mater 181:271–280
25. Rajeshwari S, Subburam V (2002) Activated *Parthenium* carbon as an adsorbent for the removal of dyes and heavy metal ions from aqueous solution. Bioresour Technol 85(2):205–206
26. Saha M, Bandyopadhyay PK (2017) Phytochemical screening for identification of bioactive compound and antiprotozoan activity of fresh garlic bulb over trichodinid ciliates affecting ornamental goldfish. Aquaculture 473:181–190
27. Sartape AS, Mandhare AM, Jadhav VV, Raut PD, Anuse MA, Kolekar SS (2013) Removal of malachite green dye from aqueous solution with adsorption technique using *Limonia acidissima* (wood apple) shell as low cost adsorbent. Arab J Chem 10:S3229–S3238
28. Sartape AS, Mandhare AM, Jadhav VV, Raut PD, Anuse MA, Kolekar SS (2017) Removal of malachite green dye from aqueous solution with adsorption technique using *Limonia acidissima* (wood apple) shell as low cost adsorbent. Arab J Chem 10(2):3229–3238
29. Sharma YC, Singh B, Uma (2009) Access fast removal of malachite green by adsorption on rice husk activated carbon. Open Environ Pollut Toxic 1:74–78
30. Tsai WT, Chen HR (2010) Removal of malachite green from aqueous solution using low cost chlorella-based biomass. J Hazard Mater 175:844–849
31. Zehera B, Yoldas S, Levent C (2009) Removal of malachite green by using an invasive marine alga *Caulerpa racemosa* var, *cylindracea*. J Hazard Mater 161:1454–1460