



Adsorption of Methylene Blue from Aqueous Solution onto *Polyalthia longifolia* Seeds - a Low-cost Adsorbent

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Received: 18.10.2018 Accepted: 12.12.2018 Published: 30-06-2019

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ABSTRACT

The preparation of activated carbon from *Polyalthia longifolia* seeds by various chemical methods have shown excellent improvement in the surface characteristics. Surface morphology also plays a significant role in the adsorption properties along with surface functional groups. The morphology of the resulting samples was reviewed by Scanning electron microscopy and the surface functional groups were investigated by Infrared spectroscopy techniques; physico-chemical characteristics such as bulk density, moisture content, ash content, matter soluble in water, soluble in acid, pH, iodine number, conductivity, porosity, yield percentage and surface area have been investigated to assess the suitability of carbon as adsorbent. Results of the examination have indicated that the activated carbon prepared using *Polyalthia longifolia* by H₂O infuse process followed by activation at 110 °C, yielded activated carbon with the highest surface area and more developed micro-, meso-, macro-porosity. The prepared Activated carbon can be used to remove methylene blue dye.

Keywords: *Polyalthia longifolia*; Activated carbon; Methylene blue; Carbonization; SEM; XRD; IR.

1. INTRODUCTION

Water, being used for drinking, domestic, agricultural and industrial purposes, is essential for our day-to-day life activities. Contamination of the water bodies from cosmetics, pharmaceutical and food industries pose serious environmental problems due to the persistent and recalcitrant nature of the dyes. In addition, some dyes are either toxic or mutagenic and carcinogenic (Chen *et al.* 2003). The traditional methods for treating dyes containing wastewaters are coagulation and flocculation, oxidation or ozonation, membrane separation and activated carbon adsorption. These methods are costly and cannot be used effectively to treat the wide range of dye waste-waters when compared with adsorption processes. An attempt has been made in the present work to remove methylene blue dye by an adsorption process. Adsorption is an important method in the separation and purification process. The objective of this study is to prepare activated carbon from *Polyalthia longifolia* (PAL) seeds by chemical activation with potassium hydroxide. The large availability of this material around the author's locale attracted them to make use of it as a potential adsorbent for the removal of aqueous organic dyes with varying process factors including initial dye concentration, contact time, initial pH, adsorbent dose and temperature.

2. EXPERIMENTAL TECHNIQUES

2.1 Adsorbent Preparation

Polyalthia longifolia seeds used in the study were collected from the local fields. The collected seeds were extensively washed with tap water to remove soil and dust, sprayed with distilled water, then dried and charred with the required quantity of water for 3 weeks. Then the resultant carbon was washed with an excess quantity of distilled water and dried at 110 °C for 1 h, and stored in an airtight container for further studies. Finally, it was ground, screened through a mesh sieve and collected (Namasivayam and Kavitha, 2002).

2.2 Preparation of Adsorbate

The dye (methylene blue) in commercial purity was used without further purification. The dye stock solutions were prepared by dissolving 1 g of accurately weighed dye in distilled water to the concentration of 1000 mg/L. The experimental solutions were obtained by diluting the dye stock solutions in accurate proportions to different initial concentrations (Arami *et al.* 2005).

3. SEM ANALYSIS

Scanning Electron Microscopy (SEM) has been a primary tool for characterizing the surface morphology

and fundamental physical properties of adsorbents' surface. It is useful for determining the particle size, porosity and appropriate size distribution of the adsorbent. SEM images of raw PAL is shown in Fig 1. Obviously, PAL has sizeable number of pores with a good possibility for dyes to be trapped and adsorbed into these pores. The very prominent dark spores in the SEM images can be taken as a sign of effective adsorption of dyes molecules in the cavities and pores of this adsorbent.

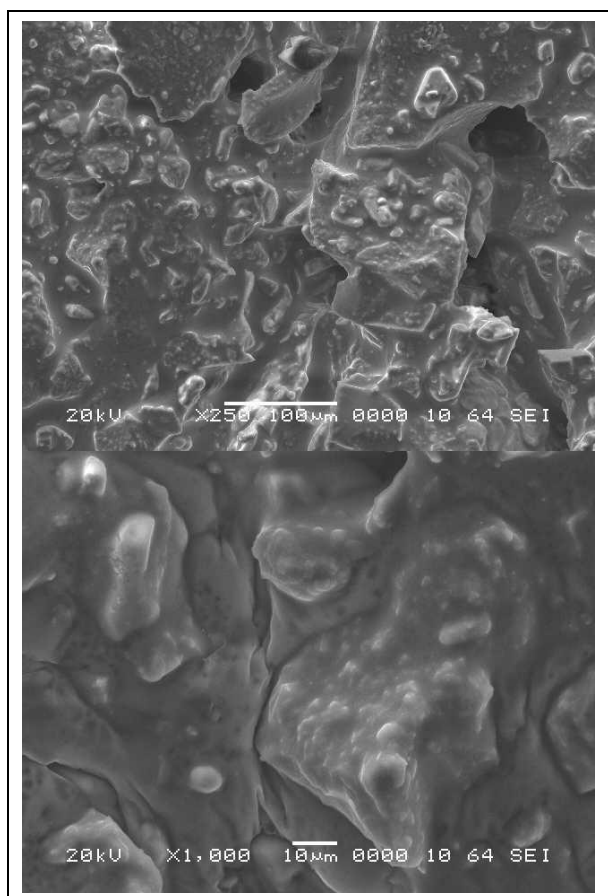


Fig. 1: SEM image of activated carbon from *Polyalthia longifolia* seeds

4. ISOTHERM MODELS

Sorption isotherms define the equilibrium relationship between sorbent and sorbate; in other words, how the sorbed nano-level molecules interact with sorbents when the sorption process approaches an equilibrium state can be narrated by sorption isotherms (Tsai *et al.* 2003). Sorption isotherms are characterized by certain constants whose values express the surface properties and affinity of the sorbent and can also be used to find the sorptive capacity of a mass (Han *et al.* 2007). Different isotherm models are available; three of them were selected for study: Langmuir, Freundlich and Tempkin models, due to their simplicity and reliability (Langmuir, 1916).

4.1 Effect of Agitation Time and Initial Dye Concentration

The initial concentration of methylene blue dye solution was varied from 5, 10, 15 and 20 mg/L and batch experiments were carried out with 100 mg of the adsorbent at 30 °C and at pH 7.0. A decreased percentage removal of methylene blue from 20% to 90% was observed with 100 mg of the adsorbent for the agitation time of 50 minutes (Fig. 2). In order to establish equilibration time for maximum uptake and to know the kinetics of the adsorption process, the adsorption of methylene blue on adsorbent was studied as a function of contact time. It was found that the time of equilibrium as well as the time required to achieve a definite fraction of equilibrium adsorption were dependent on initial concentration.

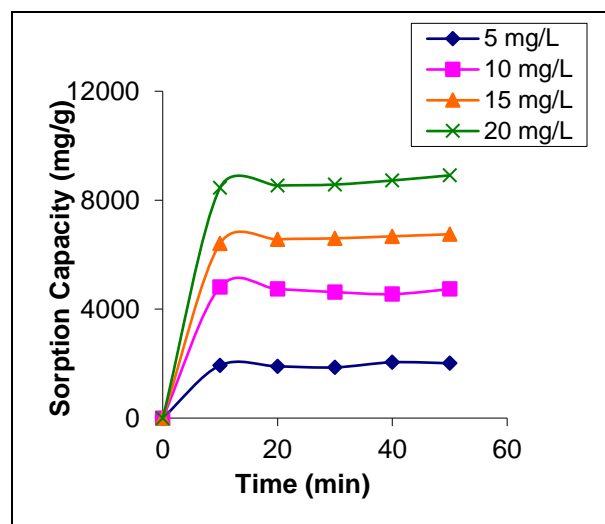


Fig. 2: Effect of agitation time and initial dye concentration.

4.2 Langmuir Adsorption Isotherm

Adsorption isotherm obtained by fixing adsorbent dosage as 100 mg for 120 minutes of agitation time is shown in Fig. 3. The adsorption capacity Q^0 values were found to be comparable with commercial activated carbon. The values of R_L obtained in this study indicated the applicability of Langmuir adsorption isotherm. The calculated value R^2 confirmed the applicability of Langmuir adsorption isotherm (Langmuir, 1918; Langmuir, 1917).

4.3 Freundlich Adsorption Isotherm

Freundlich plot for the adsorption of methylene blue onto PALS activated carbon is shown in Fig. 4. The applicability of Freundlich isotherms to the sorption of the dye implied that both monolayer adsorption and heterogeneous conditions existed under the experimental

conditions used. Several researchers have reported similar results in their studies.

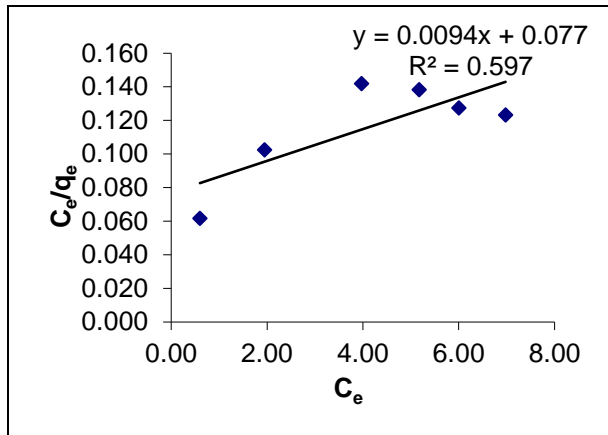


Fig. 3: Langmuir adsorption isotherm

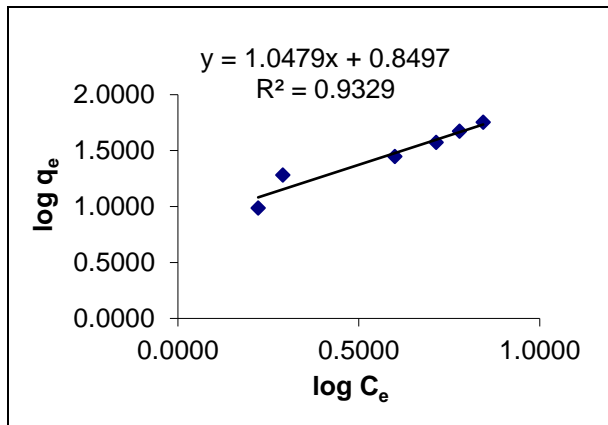


Fig. 4: Freundlich adsorption isotherm

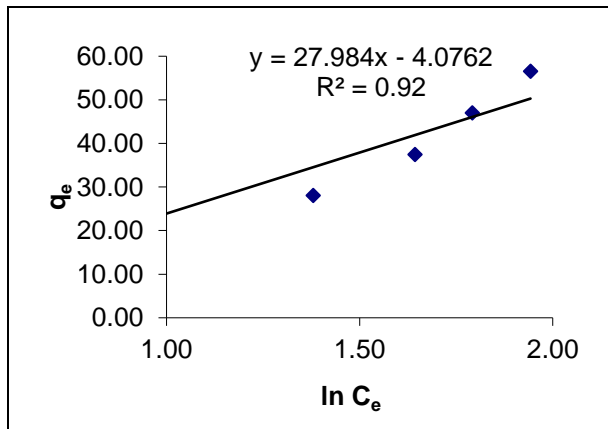


Fig. 5: Temkin adsorption isotherm

4.4 Temkin Adsorption Isotherm

The linear form of the Temkin isotherm can be expressed as,

$$q_e = B \ln A + B \ln(C_e)$$

where, C_e - concentration of the dye at equilibrium (mg/L), q_e - amount of dye adsorbed at equilibrium (mg/g), and a plot of q_e vs. $\ln(C_e)$ was used to determine the constants A and B.

4.5 Dubinin-Radushkevich Isotherm (D-R)

The D-R isotherm equation is more general than Langmuir isotherm because it does not assume a homogeneous surface or constant sorption potential. It was applied to distinguish between the physical and chemical adsorption of dyes.

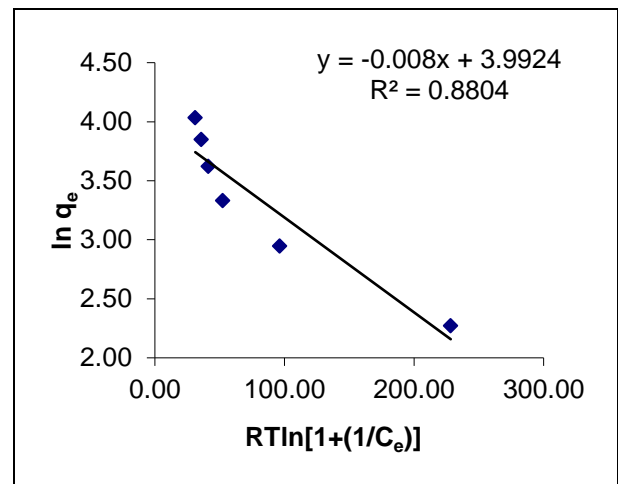


Fig. 6: Dubinin-Radushkevich isotherm

5. pH AND CONDUCTIVITY

1 g of carbon in 200 ml of distilled water was equilibrated by agitating at 165 rpm for 1 h and filtered using Whatman filter paper. The supernatant solution was analyzed for pH and conductivity using pH meter and conductivity meter, respectively.

$$\text{pH carbon} = 2.69$$

6. MOISTURE CONTENT

1 g of carbon was placed in a china dish and heated in an oven at 110 °C for 1 h. After heating, the china dish was cooled in a desiccator and then weighed. Heating, cooling and weighing were repeated at 30-minute intervals until the difference between the two consecutive weighing was less than 1 mg; the loss in weight gives the moisture content.

$$\text{Moisture content (\%)} \text{ by mass} = \frac{M-X}{M} \times 100$$

where,

M - mass of the material taken for test (g) and X - mass of the material after drying (g).

Moisture content carbon = 42.8944%

7. ASH CONTENT

About 1 g of carbon was weighed accurately in a silica crucible and placed in an electric furnace at 180 °C for about 1 h. The crucible was removed from the electric furnace. After heating, the crucible was cooled in a desiccator and then weighed. The process of heating and cooling was repeated until the difference between two consecutive weighing was less than 1 mg.

$$\text{Ash (on dry basis) \% by mass} = \frac{M_1}{M_2 - X} \times 100$$

where,

M_1 - mass of the ash (g)

M_2 - mass of the material taken for test (g) and

X - percent moisture content present in the material taken for test.

Ash content carbon = 36.860%

8. MATTER SOLUBLE IN WATER

5 g of carbon material of known moisture content was weighed accurately and transferred to a 1-litre beaker. About 300 ml of distilled water was added and heated to boiling with continuous stirring. Stirring was continued for 5 min after the flame was removed. The material was then allowed to settle. The supernatant was filtered with a crucible fitted with an asbestos mat. The procedure was repeated thrice with the residue in the beaker using 300 ml of water each time; the combined liquid was concentrated to less than 100 ml over a water bath, cooled and made up to 100 ml mark in a volumetric flask. Exactly 50 ml of the concentrate was transferred to China dish and evaporated to almost dryness on boiling water bath and finally dried in an electric oven, maintained at 100 ± 5 °C, then cooled in a desiccator and weighed. The procedure of drying and weighing was repeated at 30-minute intervals until the difference between the two consecutive weighing was less than 5 g.

$$\text{Matter soluble in water (\%)} = \frac{M_1}{M_2 - X} \times 100$$

M_1 - mass of the residue (g)

M_2 - mass of the material taken for test (g) and

X - percent of moisture present in the material.

Carbon = 1.4183%

9. MATTER SOLUBLE IN ACID

5 g of carbon material of known moisture content was weighed accurately and transferred to an 1-litre beaker. About 300 ml of 0.25 N HCl was added and

heated to boiling with continuous stirring. The stirring was continued for 5 minutes, after the flame was removed. The material was then allowed to settle, and the supernatant was filtered using a rough crucible fitted with an asbestos mat. The procedure was repeated thrice with the residue in the beaker using 300 ml of acid each time. The combined liquid was concentrated to less than 100 ml over a water bath, cooled and made up to 100 ml mark in a volumetric flask. Exactly 50 ml of the concentrate was transferred to China dish and evaporated to almost dryness on boiling water bath and finally dried in an electric oven, maintained at 100 ± 5 °C, then cooled in a desiccator and weighed. The procedure of drying and weighing was repeated at 30-minute intervals, until the difference between the two consecutive weighing was less than 5 g.

$$\text{Acid soluble Matter (\%)} = \frac{A}{M - X} \times 100$$

A - mass of the residue (g)

M - mass of the material taken for test (g) and

X - percent of moisture present in the material.

Carbon = 9.6219%

10. CONCLUSION

The present study has shown that *Polyalthia longifolia* (PALS) activated carbon modified with H₂O can be used as an effective adsorbent for the removal of methylene blue dye from aqueous solution. The characterization studies were carried out: SEM has shown highly porous nature; XRD has revealed a high degree of graphitization. The maximum adsorption capacity was obtained (90%) by using carbaceous *Polyalthia longifolia* seeds at pH 6 with an adsorbent dose of 100 mg for an agitation time of 50 minutes. PALS obeys the adsorption isotherms like Freundlich, Langmuir, Temkin and D-R, indicating that the dye adsorption on PALS was an endothermic chemical reaction.

Based on the present study, PALS was found to be an eco-friendly adsorbent for dye removal from colored textile waste-water.

FUNDING

This research received no specific grant from any funding agency in the public, commercial, or not-for-profit sectors.

CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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