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Microwave Assisted Chemical Activation of Papaya Leaf Stem Activated Carbon for the Removal of Dyes from Aqueous Solution

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Abstract

The preparation of papaya leaf stem activated carbon by microwave induced chemical activation with $Zncl_2$ for the adsorptive treatment of Malachite Green and Reactive Orange dyes from aqueous solution. The effect of important parameters viz initial concentration, contacttime, adsorbent dose, temperature and pH have been studied. The equilibrium behavior of PAR was investigated by performing batch adsorption experiments using Malachite Green and Reactive Orange as adsorbate. Langmuir and Freundlich equations were used to model the adsorption equilibrium data, and pseudo-first order and pseudo-second order models were used to correlate the kinetic data. From this we suggest papaya leaf stem activated carbon done better activity for Malachite Green than Reactive Blue.

Keywords: *Malachite Green; Microwave radiation; Papaya leaf stem; Reactive Orange 30.*

1. INTRODUCTION

Dyes are extensively employed in various industries like textiles, leather, paper, plastic and cosmetics. The textile industry ranks first in usage of varieties of natural and synthetic dyes to color the fabrics Malachite Green (MG), which is classified as a basic dye is widely used in the silk, wool, cotton, leather and paper industries for coloring purposes Despite its extensive use, dyes consists of toxic properties which are known to cause carcinogenesis, mutagenesis, teratogenesis and respiratory toxicity (Robinson *et al.* 2001) However adsorption is known to be the most efficient method especially if the adsorbent is inexpensive and exhibits high adsorption capacity suitable for removing the dyes from wastewater. Activated carbons as adsorbent were investigated especially from agricultural wastes which are inexpensive, abundantly available and renewable materials. From the literature, bamboo, oil palm empty fruit bunch, date stone, orange peel, rubber seed coat, coconut coir, banana peel, and partheniumwere used to prepare activated carbons (Kadhirvel, *et al.* 2001). The conventional thermal process may take several hours or even up to a week to reach the desired level of activation. This slow thermal process increases the expense associated with the process (Foo *et al*. 2013). In the microwave method, microwave irradiation interacts directly with the particles inside the pressed compact material and changes electromagnetic energy into heat transfer inside the dielectric materials (Menendez *et al.* 2010).

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Thus, in the present work, an attempt has been made to prepare low-cost adsorbent from papaya leaf stemplant by micro wave induced chemical adsorption method. papaya leaf stemhas no use from the land and is thus inexpensive and readily available and may causes disposal problem in environment pollution. Thus, conversion of papaya leaf stemserves as low cost adsorbent purpose.

2. MATERIALS & METHODS

2.1 Preparation of activated carbon

The papaya leaf stemwere collected from the local areas and it washed with water and dried in sunlight for a weak. Dried papaya leaf stemwere cut into small pieces of 5mm.from this 6 g of papaya leaf stem material was mixed with 30 ml of $ZnCl_2$ (30% w/v) solution. Microwave heating was applied for 10 min. The resultant activated carbon was washed with distilled water repeatedly until the filtrate reached to neutral pH. Finally it was dried into a hot oven at 80 $^{\circ}$C over night after that it was powdered and screened to less than 1-2 mm.

2.2 Equilibrium adsorption studies

The batch adsorption experiments were carried out by agitating 30 mg of PAAC with 50 mL dye solution of desired concentrations in a set of 250 mL Erlenmeyer flasks .The dye concentration in the supernatant was determined using a double beam UV–V is spectrophotometer. Each experiment was duplicated under identical conditions. Dye uptake at equilibrium, qe (mg/g), was calculated by:

$$qe =(Co\text{-}Ce)V/W$$

where Co and Ce (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. V (L) is the volume of the solution, and W (g) is the mass of adsorbent used. The effect of pH on dye removal was examined by varying the pH from 3 to 11, with initial dye concentration of 50 mg/L, PAAC dosage of 40 mg/50 mL and adsorption temperature of 30 °C. The initial pH of the dye solution was adjusted by addition of 0.10 M solution of HCl or NaOH. The equilibrium data were simulated using the Freundlich, Langmuir isotherm models.

2.3 Sorption isotherms

The isotherm study was carried out with various initial dye concentrations and three different temperatures at neutral pH with fixed equilibrium adsorbent concentration. Adsorption isotherms are used for understanding the mechanism and quantifying the distribution of the adsorbate between the liquid phase and solid adsorbent phase at equilibrium during the adsorption process. The langmuir, freundlich and isotherm models are most commonly used in sorption studies.

2.3.1 Langmuir isotherm

It is originally derived for the solid–gas interface; the general kinetic features of the Langmuir model (Eq. 1) are equally applicable for any interface.

$$q_e = \frac{q_{max} b C_e}{1 + b C_e} \qquad (1)$$

Where q_e is the amount of adsorbate adsorbed at equilibrium per unit weight of adsorbent (mg/g), C_e is the equilibrium solute concentration (mg/L), q_{max} and b are Langmuir constants which are related to saturated monolayer adsorption (mg/g) and binding energy or affinity parameter of the sorption system, respectively.The corresponding linear form of the equation is

$$\frac{1}{q_e} = \frac{1}{bq_{max}C_e} + \frac{1}{q_{max}} \qquad (2)$$

This empirical model assumes uniform surface having equivalent adsorption sites with no lateral interactions between the adsorbed species. Thus, Langmuir model refers to homogeneous sorption, where each molecule has equal sorption activation energy with no trans migration of the adsorbate in the plane of the surface (Thakur *et al.* 2007).

2.3.2 Freundlich isotherm

Like the Langmuir model, the Freundlich model (Eq. 3) also has an empirical origin, but is extremely useful for experimentally determining the adsorption capacity (K_F).

$$q_e = k_f C_e^{1/n} \qquad (3)$$

Where *n* is constant representing adsorption intensity and is always greater than unity.

The corresponding linear form of the equation is

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \qquad (4)$$

The Freundlich equation is a special case for heterogeneous surface energies in which the binding energy term *b*, in the Langmuir equation, varies as a function of the surface coverage q_e, essentially due to variations in heats of adsorption . This model agrees quite well with the Langmuir model at moderate concentrations (Rodriguez-Reinoso *et al.* 1992).

3. RESULT & DISCUSSION

3.1 Adsorbent characteristics:

In the present work activated carbons were prepared from papaya leaf stemby different methods. Out of the activated carbon one superior quality carbon was selected for the adsorption studies of two classes of dyes namely (Malachite Green) and Reactive dye (Reactive Orange 30). The prepared activated carbon was characterisied by FTIR, XRD, SEM analysis.

3.1.1 X-Ray diffraction studies

X-Ray diffraction pattern of the sample show sharp peaks, thereby indicated the amorphous nature of the product. It gives the major peak which could be nano and crystalline substance in the activated carbon (Fig.1a). In the raw material sample, a sharp peak appearing at 2θ = 31.786° which can be attributed to the presence of nano particles and derived activated carbons are amorphous nature (Khattria *et al.* 2009).

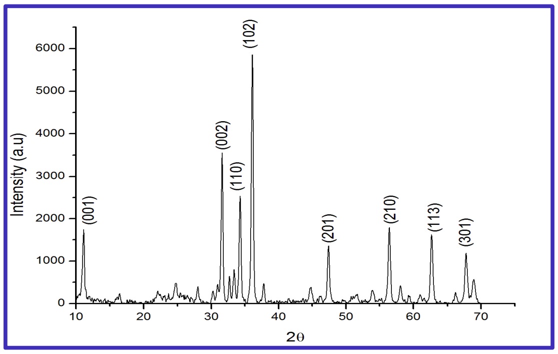

Fig.1a: XRD of PAAC

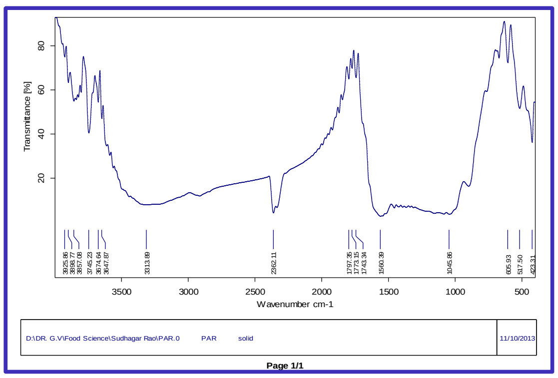

Fig. 1b: FTIR of PAAC

3.1.2 Structural Analysis –FTIR studies

A FTIR study can provide useful qualitative information about the surface functionality. The FTIR spectra of PAAC are used to determine the frequency changes in the functional groups in the adsorbent. The FTIR spectra of the adsorbent have been measured within the range of 500–4000 cm^{-1} and shown in fig.1b. An adsorption peak around 3600 cm^{-1} to 3900 cm^{-1} representing bonded hydroxyl groups is present in PAAC. An absorption peak around 1797-1750 cm^{-1} represents the C=O group. An adsorption peak around 1000-650 cm^{-1} represents the =C-H group, 568-C–H derivatives, 500 and 850, Aromatic substitution by aliphatic groups (Daifullah *et al*. 2003).

3.1.3 SEM Analysis

The SEM technique was used to observe the surface physical morphology of the prepared waste material. Fig.2a presents the micrographs of extracted papaya leaf stem. The material presents a surface morphology in the form of particles, possibly with a low specific surface area. However, after activation, the compact structure of the sample turned to be crispy and porous. For the papaya leaf stem prepared under the optimum conditions its surface is smooth and different from the flavor like surface of the raw material of papaya leaf stem. All of the pores observed by SEM are macro pores. Hence, that surface will be suitable for the adsorption of the dye molecules and hence suitable for the environmental applications (Muthanna *et al.* 2012).

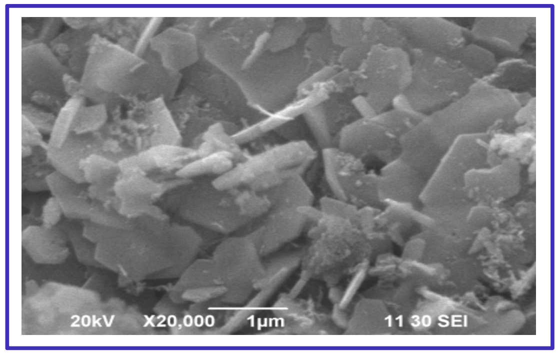

Fig.2a: SEM image of PAAC

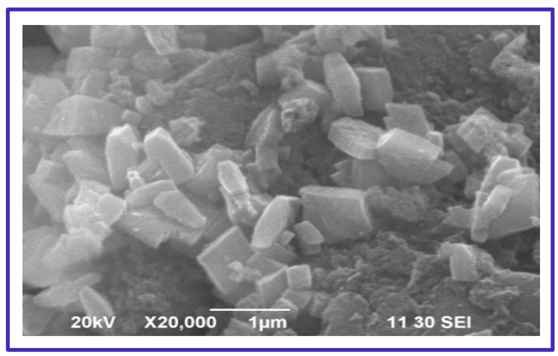

Fig.2b: SEM image of PAAC with MG

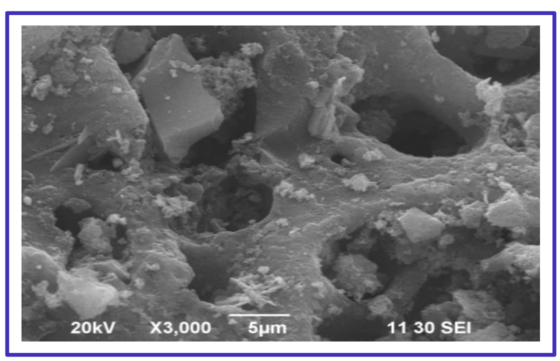

Fig.2c: SEM image of PAAC with RO 30

3.2 Effect of contact time and dosage

The contact time between adsorbate and adsorbent is the most important parameter that affects the performance of adsorption processes. The effect of contact time on the performance of papaya leaf stem adsorbing MG and RO 30 was investigated. The initial dye concentrations for all test solutions were 50,100,150 and 200 ppm shows removal efficiency of the dye as a function of rotating times ranging between 5 and 200 min for MG and RO 30 (fig. 3). Hence, the optimum dosage of papaya leaf stem in MG and RO 30 for removing MG and RO 30 dye was found to be 0.4 g and 0.5 g respectively. From the results adsorption efficiency of papaya leaf stem is higher for MG than that for RO 30 (Arivoli *et al.* 2008).

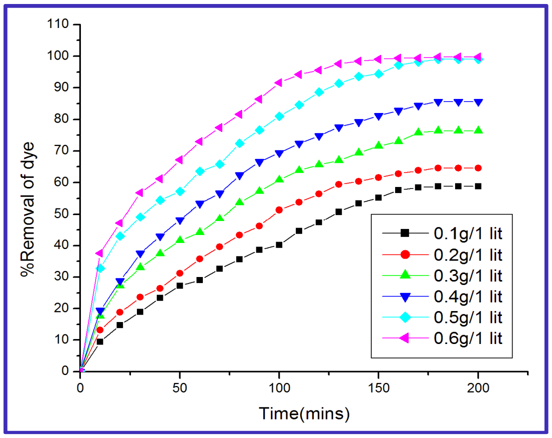

Fig. 3: Effect of concentration of the removal of MG

(a) RO 30 (b) by various dosage of PAAC

3.3 Adsorption kinetics

3.3.1 Pseudo first order kinetic

To investigate the mechanism of adsorption, the pseudo first order and pseudo second order kinetics were studied. The pseudo first order constant ranges between 0.057 and 0.064 min^{-1} at various concentrations. The correlation coefficient (q_e) for the pseudo-first-order model changed in the range of 0.8892 and 0.8890 for adsorption of MB and RO30, respectively. The calculated q_e values obtained from pseudo first order model are not in good agreement with the experimental q_e values at various concentrations. The correlation co-efficient (r^2) at various concentration and various temperature are relatively low for the pseudo first order kinetic model. Similar results were observed for the removal of Acid Violet 17 onto orange peel (Kamari *et al*. 2009).

3.3.2 Pseudo second order kinetic

The data for the adsorption of PAAC were applied to pseudo second order kinetic model at various concentration and temperatures.The correlation coefficient for the pseudo-second-order model changed in the range of 0.964 and 0.951 for adsorption of MG and RO30, respectively. The correlation coefficients (r^2) for the pseudo second order model, have the highest values (> 0.95) suggesting the dye adsorption process is predominant by the pseudo second order adsorption kinetic model **(**Baek *et al*. 2010).

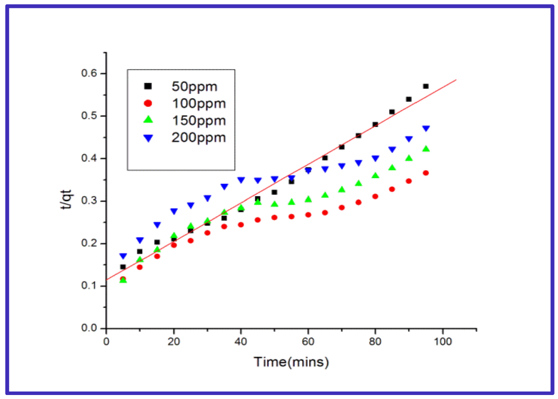

Fig. 4a: Pseudo second order rate constant for MG

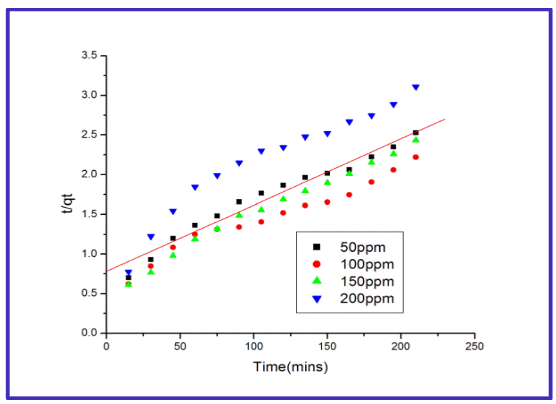

Fig. 4b: Pseudo second order rate constant for RO 30

3.4 Adsorption isotherm:

Adsorption properties and equilibrium parameters, commonly known as adsorption isotherms, describe how the adsorbate interact with adsorbent, and comprehensive understanding of the nature of interaction.from this data (table1.) PAAC fit for Langmuir isotherm Model (Vadivelan *et al.* 2005).

Table 1. Isotherm data

Temperature 40 °C (313 k)					
Langmuir Model			**Freundlich model**		
	MG DYE	RO 30 DYE		MG DYE	RO 30 DYE
Q^o (mg/g)	352	163	1/n	0.866	0.627
R_L	0.439	0.417	K_f ($mg^{11/n}L^{1/n}/g$)	1.278	1.869
r^2	0.939	0.913	r^2	0.434	0.576

4. CONCLUSION

The results showed that papaya leaf stem plant is a potential raw precursor for preparation of high quality activated carbon. Integration of microwave heating has promoted porosity development in a short heating period. The adsorption behavior could be favorably described by Langmuir isotherm model, while the adsorption kinetic was well fitted to the pseudo-second-order model. . From the above conclusion papaya leaf stemact as a good adsorbent for removal of MG and RO 30 dyes.

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