



REMOVAL OF MALACHITE GREEN FROM AQUEOUS SOLUTION BY ACTIVATED CARBON PREPARED FROM ALMOND SHELL

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ABSTRACT

The objective of this study is to assess the adsorption potential of activated carbon prepared from almond shell for removal of malachite green (MG) from aqueous waste. Almond shell based activated carbon was prepared chemically using ortho-phosphoric acid at 700-800°C in a modified muffle furnace. Prepared activated carbon was characterised for proximate and ultimate analysis, Iodine number, N₂-BET surface area, Fourier-Transform Infrared spectroscopy (FT-IR) and Scanning electron microscopy (SEM). FT-IR & SEM results strongly support significant spectral and chemical changes occurring due to the activation of the almond shells by phosphoric acid treatment. Batch isotherm and kinetic study experiments were conducted to determine the adsorption of the malachite green from aqueous solution with almond based activated carbon (ABAC). It is inferred from the results that ABAC is very effective and economically viable adsorbent for removal of malachite green from aqueous solution.

Key words: SEM, FT-IR, Almond shells, Adsorption, Malachite green, Kinetics, Adsorption isotherms.

INTRODUCTION

The discharge of effluents from the industries is one of the potential sources of dyes contamination and pollution¹⁻³. These industries discharge highly coloured effluents with very high Biological oxygen demand (BOD) as well as Chemical oxygen demand (COD)⁴. Malachite Green is a very popular dye and used extensively in dyeing of silk, leather, plastic & paper. The discharge of malachite green can cause serious harms to aquatic life. It can cause injuries to humans and animals by direct contact, inhalation and ingestion⁵. Various serious problems such as carcinogenesis, mutagenesis, teratogenesis, respiratory toxicity & reduced fertility in humans have been reported⁶. The removal of such dangerous pollutants to permissible limit is mandatory as per environment protection Laws. Agricultural wastes

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are the chief raw materials being studied for this purpose, for they are renewable, mostly available in huge amounts & potentially less expensive^{7,8}. Till now, adsorbents such as neem, sawdust, bentonite clay, bottom ash, orange peel, algae, rice straw, coffee bean, Kapok hull, Pandanuts, have been evaluated for the removal of dyes from aqueous solution^{6,9-13}. This study reports the use of almond shell based activated carbon (ABAC) a low cost alternative adsorbent for the removal of malachite green from aqueous solution.

EXPERIMENTAL

Materials and methods

Malachite green dye GR grade ortho-Phosphoric acid (H_3PO_4) GR grade, hydrochloric acid (HCl) GR grade, Merck India, were procured from local market. Almond shells were collected from local market as waste material.

Preparation of activated carbon

The almond shells were washed & dried in open air for 2 days then crushed to 10-12 mm size. The crushed shell mass was dried in oven at $108 \pm 2^\circ C$. For activation process, 10 g of dried raw material was impregnated with H_3PO_4 in the ratio 1:1 for 24 hrs and carbonised at $700-800^\circ$ for 1 hr. The carbonized material was then cooled to room temperature and washed with 5 N HCl thoroughly. To remove excess acid the material was washed with double distilled water. After washing the material was dried at $108 \pm 2^\circ C$ in moisture oven for about 24 hrs. This carbon was kept in a desiccator for further use. A part of Sample was pulverized and passed through 325 mesh for physico-chemical analysis.

Characterization of activated carbon

The prepared activated carbon (ABAC) was characterised for proximate, ultimate, Iodine value, N₂-BET surface area, pore volume, FT-IR and SEM, Table 1.

Table 1: Physico-chemical properties of prepared activated carbons

Carbon	M %	Ash %	V.M. %	F.C. %	C %	H %	N %	Iodine Value	N ₂ -BET surface area	Pore volume
ABAC	17.06	6.24	12.4	64.3	78.4	3.5	0.78	1093	1492.3	1.14

SEM morphology analysis

The surface morphology of ABAC is shown in Fig. 1, which shows a very clear view of the different types of pores (micro, semi micro, macro) present, which are formed

during activation process. Some white crystals are also visible in the SEM that may be due to mineral matter present in it.

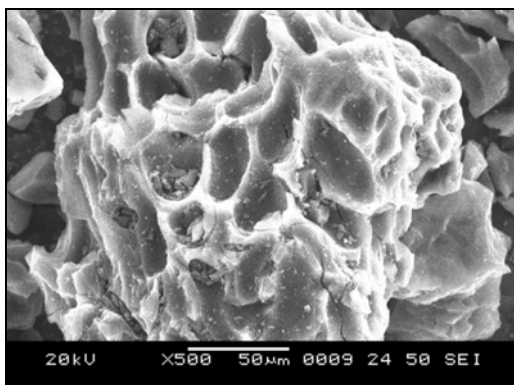


Fig. 1: SEM of ABAC

FT-IR analysis of ABAC

To resolve the functional groups and its wave numbers, spectral analysis was done for ABAC using Fourier transform infrared spectrometer (FT-IR) (Perkin-Elmer, PE-RXI) in the range of $450\text{-}4000\text{ cm}^{-1}$. The FT-IR spectrum of ABAC as shown in Fig. 2 clearly show the presence of various functional groups on ABAC. The predominant presence of free phenolic -OH , C-H stretch vibrations, C=O in the quinone configuration are found in ABAC. The asymmetric O=C=O stretch vibration of CO_2 adsorbed in pores of ABAC are also a found.

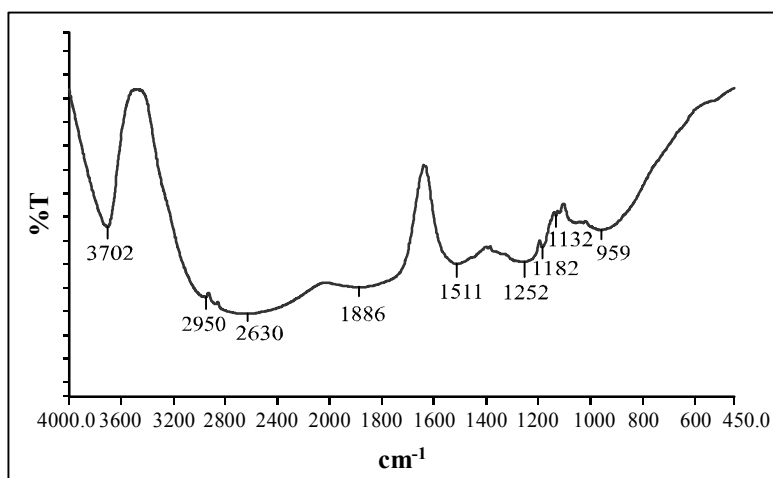


Fig. 2: FTIR of ABAC

Table 2: Physico-chemical properties of malachite green dye

Molecular formula	Molecular weight	λ_{\max} (nm)	Melting point (°C)
C ₅₂ H ₅₄ N ₄ O ₁₂	927.1	616	159°C

Estimation of malachite green

The concentration of malachite green in the supernatant solution after and before adsorption was determined using a double beam UV/VIS spectrophotometer (Lambda 35) at 616 nm. The properties of malachite green are shown in Table 2. It was found that the supernatant solution from the activated carbon did not exhibit any absorbance at this wavelength and also that the calibration curve was very reproducible and linear over the concentration range used in this work.

Method for adsorption

Adsorption studies

Adsorption experiments were performed in a set of 7 BOD bottles (250 mL) where 50 mL solution of malachite green dye with 50 mg L⁻¹ concentration was placed in each bottle. 0.0025, 0.005, 0.01, 0.015, 0.02, 0.025, 0.03 g ABAC was added to these bottles and kept in an isothermal shaker (30 ± 1°C) for 24 hr to reach equilibrium of the solid-solution mixture. The pH of the dye was found to be 6.7. After shaking the flasks for 3 days, samples were withdrawn from the conical flasks and the MG solutions were separated from the adsorbent by centrifugation at 3000 rpm. Residual dye concentrations in the supernatant solutions were estimated by measuring absorbance at 616 nm with Perkin-Elmer UV/VIS spectrophotometer.

Kinetic studies

For kinetics study a cylindrical glass vessel of 5 L capacity fitted with 8 baffles was used. 0.4 g of accurately weighted activated carbon was introduced into 2 L of dye solution of known concentration with constant stirring. The adsorbate was taken out from the vessel at regular time intervals and concentration was determined by using UV/visible spectrophotometer.

Adsorption isotherms

The amount of adsorption at equilibrium, Q_e (mg g⁻¹), was calculated by:

$$Q_e = \frac{(C_0 - C_e)V}{W} \quad \dots(1)$$

Where; C_0 and C_e (mgL^{-1}) 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 dry adsorbent used. In general, the adsorption isotherm describes how adsorbates interact with adsorbents as shown in Fig. 3 and therefore it is critical in optimizing the use of adsorbents.

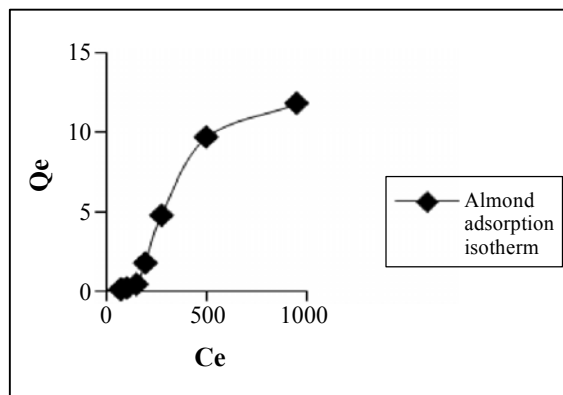


Fig. 3: Adsorption isotherm of ABAC-MG System

Fig. 3 clearly indicates favourable adsorption Isotherm for ABAC-MG system. Langmuir isotherm can be used as a model to describe the adsorption isotherm. The Langmuir equation is given as-

$$C_e/q_e = 1/(Q_0 \times b) + C_e / Q_0 \quad \dots(2)$$

Where C_e is the concentration of adsorbate solution at equilibrium (mgL^{-1}), q_e is the amounts of adsorbate adsorbed per mass of adsorbent (mg g^{-1}), b is the equilibrium constant related to the sorption energy between the adsorbate and adsorbent ($\text{dm}^3\text{mg}^{-1}$) and Q_0 is limiting amount of adsorbate that can be taken up per mass of adsorbent. The calculated Langmuir constants are given in Table 3. As shown in the Table 3, the resulting Q_0 value is 333.3 mg g^{-1} .

Table 3: Adsorption isotherm and kinetic data of ABAC-MG systems

Adsorbent	Langmuir adsorption constants		Freundlich adsorption constants		Langmuir kinetic constants	
	Q_0	b	K_f	$1/n$	K_a	K_d
Activated carbon						
ABAC	333.3	3.00	174.98	0.388	0.040	0.013

The result indicates that ABAC shows higher adsorption capacity for malachite green removal. The plot of $1/q_e$ vs $1/C_e$ in Fig. 4 for ABAC gave straight line implies that the

adsorption for adsorbent is well fitted to Langmuir adsorption model. The well-known logarithmic form of Freundlich model is given by the following equation:

$$\text{Log } q_e = \log K_F + (1/n) \log C_e \quad \dots(3)$$

Where q_e is the amount adsorbed at equilibrium (mg g^{-1}), C_e the equilibrium concentration of the adsorbate (MG) and K_F and n are Freundlich constants, n giving an indication of how favorable the adsorption process and K_F is the adsorption capacity of the adsorbent. The data, Table shows that Freundlich Isotherm model is not well fitted in the present study as shown in Fig. 5 for ABAC.

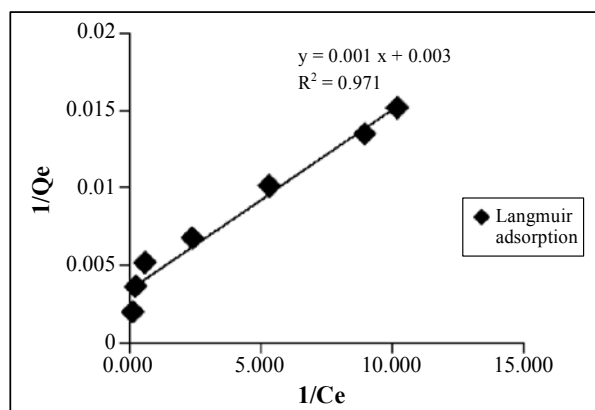


Fig.4: Langmuir adsorption of ABAC-MG System

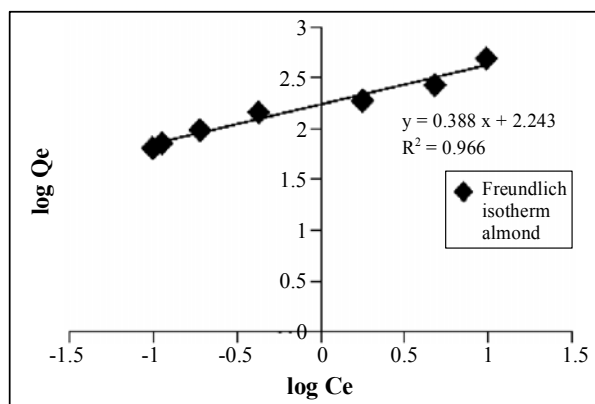


Fig. 5: Freundlich isotherm of ABAC-MG System

Adsorption kinetics

Following simplified expression based on Langmuir theory used to analyse the kinetic data.

$$\ln[(C_t - C_e)/(C_t + a)] = -k_d t + \ln[(C_0 - C_e)/(C_0 + a)] \quad \dots(4)$$

Where, $a = (C_0/k_d)$ and $K = k_a/k_d$

K is Langmuir adsorption constant, k_a adsorption rate and k_d is desorption rate constant and t is time in min. The adsorption and desorption rate constants were thus evaluated by plotting $\ln[(C_t - C_e)/(C_t + a)]$ vs t , Table 3 reports the values of adsorption constants. From the results it is evident that the rate of adsorption on ABAC is More at initial time intervals as shown in Fig. 6. The value of K_d shows that ABAC is a good adsorbent for the removal of MG from aqueous solutions. They are very well fitted with Langmuir kinetic model as shown in Fig. 7.

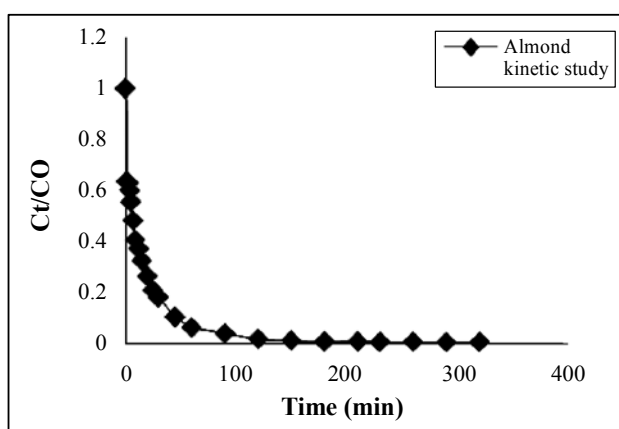


Fig. 6: Kinetic study of ABAC-MG System

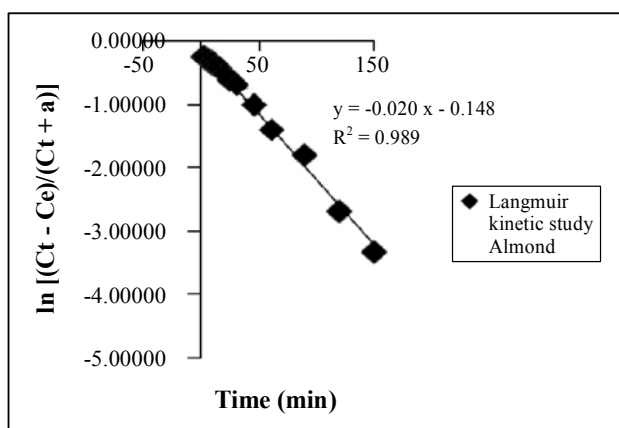


Fig. 7: Langmuir kinetic study of ABAC-MG System

CONCLUSION

In the present study, it has been concluded that;

- (i) Phosphoric acid is a suitable activating agent for the preparation of ABAC.
- (ii) Adsorption isotherms of malachite green dye on prepared ABAC are favourable.
- (iii) Prepared almond based activated carbon has potential application for the removal of malachite green from aqueous solutions.
- (iv) SEM analysis shows that ABAC has full of cavities with different pore diameter.
- (v) Adsorption capacity increases with the increase of the adsorption dose.

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