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Removal of Methylene Blue from aqueous solution by activated carbon of *Vigna mungo L* and *Paspalum scrobiculatum*: Equilibrium, kinetics and thermodynamic studies

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The adsorption capacity of the activated carbons of the agricultural waste materials of *Vigna mungo L* (Black gram husk - ACBGH) and *Paspalum scrobiculatum* **(**Varagu millet Husk - ACVMH) have been explored for the removal of Methylene Blue (MB) from water and was proved to be an efficient adsorbent. The morphology and chemical structure of the adsorbents have been investigated by using Fourier Transform Infrared spectroscopy (FTIR), Scanning Electron Microscopy (SEM) and Brunauer Emmett Teller (BET). Adsorption studies are conducted on a batch process, to study the effects of contact time, initial concentration, temperature and *p*H. Equilibrium data has been analysed using Langmuir, Freundlich and Dubinin-Radushkevich isotherm models and the monolayer adsorption capacity of the adsorbents are calculated. Kinetic data has been studied using pseudo-first and pseudo-second order kinetic models. The data fits well with the Langmuir model, with a maximum adsorption capacity of 198.40 mg g^{-1} and 166.30 mg g^{-1} for ACBGH and ACVMH respectively. The pseudo-second-order kinetics is found to be the best for the adsorption of MB by the adsorbents with good correlation. Thermodynamic studies show that the adsorption is spontaneous, endothermic and entropy controlled. The desorption studies suggest that chemisorptions may be the major mode of adsorption.

Keywords: Activated carbon, Adsorption, Isotherms, Kinetics, Methylene blue, Thermodynamics

A considerable amount of waste water is generated from industries such as dyestuffs, textile, paper and plastics. There are more than 100,000 commercially available dyes and more than 7×10^5 metric tons of dyes are produced worldwide annually[1]. Colour is the first contaminant to be recognized in water and has to be removed from waste water before discharging it into water bodies. Colour impedes light penetration, retards photosynthetic activity, inhibits the growth of biota and also has a tendency to chelate metal ions which results in micro toxicity to fish and other organisms[2]. It is estimated that about 2% of dyes that are produced are discharged directly in aqueous effluent during the manufacturing process and during the textile coloration process almost 10% of the dye loss occurs[3].

Many of the dyes are toxic and when fed into the water bodies, pose a serious hazard to aquatic living organisms. Among the various dyes used, methylene blue (MB) is the most commonly used substance for dyeing the natural fibers as cotton or silk. It can cause eye burns by direct contact and nausea, vomiting, profuse sweating, mental confusion and methemoglobinemia by ingestion[1]. Therefore the treatment of effluent containing such dyes is of interest due to its harmful impact on receiving waters.

For several decades, various methods have been evolved in wastewater treatment such as electrochemical treatment methods, oxidation and ozonation[4]. However, the adsorption process has been proved as the most effective and reliable method for the dye removal. The major advantage of adsorption treatment for the control of water pollution is less investment in terms of initial development cost, simple design, easy operations, free from generation of toxic substances and easy and safe recovery of the adsorbent as well as adsorbate materials[5]. In the process of adsorption, a solid adsorbent is employed in order to attract the dye component and finally lead to its removal from the water by the formation of physical and chemical bonds. Many low- cost adsorbents have been used for this purpose such as banana peels[6], rice straw[7], papaya seeds[8], orange peels[9], saw dust[10], wheat shells, and brans[11], but there is still a need for adsorbents which are cheap, easily available, and efficient.

Activated carbon has been found to be an effective adsorbent having high surface area and high adsorption capacity[12]. In order to increase the adsorption capacity of the adsorbent, researchers have followed different activation methods and they usually used the Langmuir isotherm to indicate the effectiveness of the activation process. Activation methods involve physical activation such as carbonization of material and chemical activation such as using chemical activating agents. Many cheap, easily available agricultural and/or plant-based materials such as silk cotton hull, coconut tree sawdust, sago industry waste, banana pith, maize cob[13], rattan sawdust[14], jute fiber[15], pistachio shells[16], palm kernel shell[17], date pits[18], rice bran[19], coir pith[20], rice husk[21], mango seed kernel powder[22], rubber wood sawdust[23], plum kernels[24], rosewood sawdust[25], straw[26], coconut coir dust[27], palm fiber[28], pine cone[29], walnut shell, almond shell, hazelnut shell, apricot stones[30], coconut shells, groundnut shell, bamboo dust[31], deoiled soya[32], and wheat husk[33] have been used as a source of the production of activated carbon for the removal of textile dye effluents. Adsorption by activated carbon is an important way to clean up effluents and waste water, where it used to polish the influent before it is discharged into the environment[34].

Black Gram belongs to the family *Leguminoseae* bearing the botanical name as *Vigna mungo L*. It is one of the important pulse crops in India. It is reported that Black gram is originated in India and is the largest producer and consumer in the world. It is a rich protein food which contains about 26 percent protein, almost three times that of cereals. Black gram supplies a major share of protein requirement of vegetarian population of the country. Black gram originated in India, where it has been in cultivation from ancient times and is one of the most highly priced pulses of India and Pakistan. The coastal Andhra region in Andhra Pradesh is famous for black gram after paddy. The Guntur District ranks first in Andhra Pradesh for the production of black gram. Black gram has also been introduced to other tropical areas mainly by Indian immigrants.

Paspalum scrobiculatum, kodo millet, also known as cow grass, rice grass, ditch millet, Native Paspalum or Indian Crown Grass originates in tropical Africa and has been domesticated in India 3000 years ago. Kodo millet is an annual grain that is grown not only in India, but also in the Philippines, Indonesia, Vietnam, Thailand, and West Africa where it originates. It is grown as a minor crop in most of these areas, with the exception of the Deccan plateau in India where it is grown as a major food source. It is a very hardy crop that is drought tolerant and can survive on marginal soils where other crops may not survive, and can supply 450-900 kg of grain per hectare.

Experimental Section

Adsorbate

Methylene blue (CI 52015) is a heterocyclic aromatic compound with the molecular formula $C_{16}H_{18}N_3SCl$ and IUPAC name as 3, 7-bis (dimethylamino)-phenothiazin-5-ium chloride. The solution is prepared in doubly distilled water. All the test solutions were prepared by diluting the stock solution with double distilled water. Figure 1 gives the chemical structure of MB.

Preparation of adsorbents

Black gram husk and Millet Husk collected from the mills in Chennai, after removal of the pulses, were washed several times with water to remove any adhering substances and dried at room temperature. These were powdered by grinding in a mechanical blender and sieved. All the above collected materials were impregnated with orthophosphoric acid at 450°C for 1 h in a muffle furnace. The carbonized materials were washed with water until neutral *p*H was obtained. It was dried at 110°C overnight and ground into powder. The activated carbon serves as the adsorbents namely ACBGH and ACVMH for Black gram husk and Millet Husk respectively.

Adsorption experiment

Adsorption studies were carried out by the batch technique to obtain the rate and equilibrium data. The experiment to observe the effect of important parameter like *p*H, adsorbent dose, contact time and temperature on the adsorptive removal of MB was conducted at 305±1 K. For each experimental run, 50 mL of MB solution of known concentration and a known amount of the adsorbent were taken in a

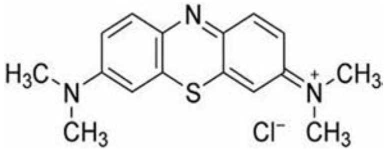

Fig. 1 — Chemical structure of Methylene Blue

100 mL stoppered conical flask. This mixture was agitated in a temperature-controlled shaker and samples were centrifuged for 10 min for the suspended particles to settle down. After centrifugation clear supernatant samples were obtained and their residual dye concentration was analyzed for absorbance at 663 nm by using a UV visible spectrophotometer.

Kinetic study of MB on various adsorbents

Experiments to determine the adsorption equilibrium time on various activated carbons for MB were performed for a time interval ranging from 5 to 120 min. A known weight of the adsorbents were placed in 100 mL stoppered conical flask containing 50 mL of the dye solution at known concentrations (1.2×10^{-3} M, 1.4×10^{-3} M, 1.8×10^{-3} M) under constant Shaking. The experiments were made without *p*H correction. The adsorbents were separated from dye solution by centrifugation. The supernatant was collected and the absorbance was measured using a UV-visible Spectrophotometer (Elico) at an absorbance wavelength of 663. The dye concentration was calculated from a calibration curve of absorbance versus dye concentration. The adsorption amount at time t, qt (mg/g), was calculated by:

$$\text{Amount Adsorbed } (q_t) = (C_O - C_t) \times \frac{V}{m} \qquad \ldots (1)$$

where C_0 and C_t (mol/L) are the concentrations of the dye solution initially and at time t respectively. V (L) is the volume of dye solution and m (g) is the mass of the adsorbent used.

Results and Discussion

Characterisation of the ACBGH and ACVMH

FTIR analysis of ACBGH and ACVMH

The bands around 3606 and 3780 cm^{-1} were observed for the black gram husk and millet husk samples, which was attributed to the O-H stretching vibration of the hydroxyl functional groups of alcohols and phenols. The peaks at 1590 and 1594 cm^{-1} in ACBGH and ACVMH correspond to stretching vibration of COO−. The bands at 2921.50 and 2850.80 cm^{-1} in black gram husk and millet husk samples, indicate the presence of an aliphatic C-H stretching also specifically the methylene group sp^3 stretching. The bands around 1164 and 1169.96 cm^{-1} in black gram and millet husk have been assigned to C-O stretching in acids, alcohols, phenols, ethers and/or ester groups. It is the stretching frequencies of the phenolic and lactonic groups.

Scanning Electron Microscope images

Scanning electron microscopy (SEM) has been a primary tool for characterizing the surface morphology and fundamental physical properties of the adsorbent. SEM of the adsorbent material was taken for ACBGH and ACVMH. The SEM picture of the adsorbents samples show very distinguished dark spots which can be taken as a sign for effective adsorption of dye molecules in the cavities and pores of this adsorbent. The external surfaces for the carbon are full of cavities and quite irregular as a result of activation. From (Figs 2a and 2b) it is clear that there is a good possibility for dyes to be trapped and adsorbed into these pores. The results showed that the major constituent was carbon (45.60%, 40.41%), along with some amount of hydrogen (2.15%, 1.76%) and nitrogen (1.94%, 0.75%).

X-Ray diffraction analysis

The X-ray diffraction pattern of the prepared activated carbons exhibited two peaks at 2θ = 25.58, 26.45 and 41.48, 42.69 for black gram and millet husk respectively, which are attributed to (002) plane and

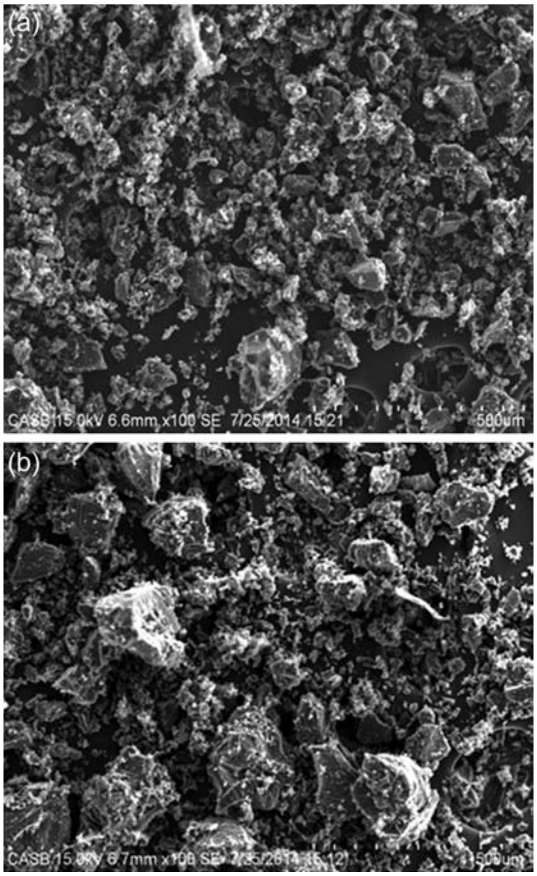

Fig. 2 — (a) SEM image of ACBGH; (b) — SEM image of ACVMH

(101) plane respectively (Fig. 3) and which are similar to that of graphite[35]. The crystallite size of ACBGH and ACVMH along L_c or L_a were determined by Scherrer equation and found to be 2.96 nm and 2.974 nm for L_c respectively. The interlayer spacing (d_{002}) was calculated using Bragg's Equation[36]. Typically, in a crystalline carbonaceous structure, such as graphite, the interlayer distance between two adjacent carbon sheets is 0.335 nm. In this study, the peaks at 2θ = 25.58, 26.45 corresponds to an interlayer distance of 0.348 nm and 0.335 nm respectively for ACBGH and ACVMH, which is quite near to that of pure graphitic carbon[37].

Raman spectroscopy

The graphitic nature of the adsorbents is further confirmed through Raman spectrum. The activated carbons exhibited two distinct peaks at about 1326 cm^{-1},1327 cm^{-1} (D- band) and 1598 cm^{-1}, 1594 cm^{-1} (G-band) respectively for ACBGH and ACVMH. The D-band is often referred to the "disorder" band, which results from the imperfection or loss of hexagonal symmetry of the graphite structure. The G-band is related to the vibration of sp^2 bonded carbon atoms in a two-dimensional hexagonal lattice, which often relates to the formation of ordered graphite layers. It is known that the relative intensity ratio between the D and G bands (I_D/I_G) reflects the degree of graphitization. Accordingly, the low I_D/I_G value indicates a high degree of graphitization[38]. The I_D/I_G value of ACBGH and ACVMH are 0.8297, 0.8324 respectively, suggesting that the activated carbons has highly graphitic characteristic with high degree of graphite ordering. The above mentioned bands and the value of I_D/I_G confirm the presence of graphitic carbon in the adsorbents.

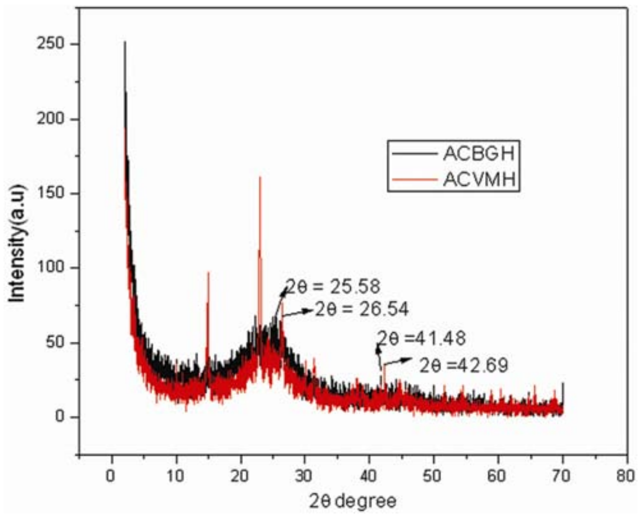

Fig. 3 — XRD pattern of ACBGH AND ACVMH

BET analysis

Pore characteristic of the activated carbon was determined byN_2 adsorption. The nitrogen adsorption/desorption isotherms of the activated carbon were plotted. The activated carbons possessed type IV of IUPAC isotherm as defined by Union of Pure and Applied Chemistry (IUPAC) classification with H1 hysteresis. Due to the presence of hysteresis, the surface has mesoporous nature. According to IUPAC, the adsorbent pores are classified into three groups: micropores (size < 2 nm), mesopores (2 – 50 nm), and macropores (> 50 nm). Further the micropores were divided into ultramicropores (< 0.7 nm) and supermicropores (0.7 to 2 nm).The t-plot method was used to calculate the micropore volume and external surface area. Total pore volume was determined at $P/P_0 = 0.99$ for both the adsorbents. The pore characteristics of the activated carbons are given in Table 1. The average pore diameter of ACBGH and ACVMH was found to be 4.17 nm and 6.75 nm (Table 1) which further confirms the presence of mesopores. The mesopore volume and micropore volume was found to be around 96.4% , 97.95% and 3.6%, 2.1% respectively of the total pore volume determined indicating that the adsorbents are mesoporous in nature.

Chemical characterization of ACBGH and ACVMH by Boehm titrations

The Boehm titration method was used to determine the oxygen containing functional groups present over the surface of the activated carbon. 0.5g of the activated carbon (ACBGH) was kept in contact with 50 mL each of $NaHCO_3$ (0.05N), Na_2CO_3 (0.05N) and NaOH (0.05N) for evaluating acid groups and 0.05N HCl for evaluating basic groups respectively at room temperature for 24 h. Subsequently the aqueous solutions were back titrated with HCl (0.05N) for acidic groups and NaOH (0.05N) for basic groups. The acidic sites were calculated considering that NaOH neutralizes carboxylic, lactones and phenolic groups, Na_2CO_3 neutralizes carboxylic and lactone groups and $NaHCO_3$ neutralizes carboxylic groups only. The difference in the titration value of Na_2CO_3 and $NaHCO_3$ was due to lactone and the difference in the titration value of NaOH and Na_2CO_3 was assumed to be phenol. Basic sites were determined by titration

Table 1 — S_{BET} and pore structure of ACBGH and ACVMH

Adsorbent	S_{BET}	S_{ext}	S_{ext}/S_{BET}	S_{mic}	S_{mic}/S_{BET}	V_{tot}	V_{mic}	V_{meso}	D_p
	(m^2/g)	(m^2/g)	(%)	(m^2/g)	(%)	(cm^3/g)	(cm^3/g)	(cm^3/g)	(nm)
ACBGH	480.10	431.99	89.79	48.10	10.01	0.500	0.018	0.482	4.17
ACVMH	397.33	359.03	90.36	38.30	9.63	0.671	0.014	0.657	6.75

with HCl. The most common oxygen groups on the surface are carboxylic (0.52 meq/g) and (0.4 meq/g), phenolic (0.48 meq/g) and (0.161 meq/g), lactonic (0.12 meq/g) and (0.05 meq/g) respectively for ACBGH and ACVMH.

Zero point charge of the adsorbents

The point of zero charge of ACBGH and ACVMH was determined by solid addition method. In this method 0.1 M KCl solution was taken in ten bottles maintained with *p*H in the range of 1-10 and 0.14 g of ACBGH and 0.20g of ACVMH was added to each bottle. These solutions were shaken for 24 h at room temperature and the final *p*H was measured. The difference between the initial and final *p*H was measured and the point where $\Delta p\text{H} = 0$ was taken as the point of zero charge. At $p\text{H} < p\text{H}_{zpc}$, the surface has a net positive charge and at $p\text{H} > p\text{H}_{zpc}$, it is negative. The $p\text{H}_{zpc}$ of ACBGH was found to be 2.0 and that of ACVMH was 2.1. The previous study of adsorption of Methylene blue onto sunflower oil cake activated carbon has found that the zero point of charge ($p\text{H}_{zpc}$) for the activated carbon lies between *p*H 2.5 and 5.5 (Ref. 39).

Effect of the amount of adsorbents

The study of the effect of amount of the adsorbents was carried out to observe the minimum possible amount, which shows maximum adsorption. Effect of the amount of adsorbents was carried out by selecting an adsorbent range of 0.04-0.32 g for black gram husk and Varagu millet husk with a dye concentration of 1.8×10^{-3} M concentration. A graphical representation indicates that an increase in the amount of the adsorbent leads to an increase in the removal of the dye for both the system. The greater percentage adsorption at high adsorbent dosage is due to availability of more active sites of the adsorbents for the adsorption. An amount of 0.14 g and 0.20 g was chosen as optimum amount for ACBGH and ACVMH respectively for the batch study of the adsorption process.

Effect of concentration at varying temperatures

Adsorption experiments for the dye MB were carried out by varying the concentration from 0.4×10^{-3} to 2.6×10^{-3} M with an adsorbent dosage of 0.14 g and 0.20 g of ACBGH and ACVMH respectively at 305 K, 315 K and 325 K. The experimental results show that an increase in the concentration led to an increase in the amount of the dye adsorbed. It is observed that the amount adsorbed increases from1.422×10^{4} mol/g to 7.2011×10^{4} mol/g for black gram husk and from 0.9972×10^{4} mol/g to 5.7342×10^{4} mol/g for Varagu millet husk. For further studies, an optimum concentration of 1.8×10^{-3} M of the dye solution was considered. For both adsorbents the amount adsorbed increased with increase in concentration of the dye due to greater degree of interaction between the adsorbate and the adsorbent materials.

Effect of *p*H

As the *p*H affects the adsorption it is necessary to determine the adsorption behavior of the dye. The study of *p*H was carried out at predetermined experimental conditions taking initial dye concentration as 1.8×10^{-3} M. Solutions of NaOH and HCl were employed to adjust the *p*H of the test solutions. A *p*H range of 2 to 12 was selected for the adsorption of MB on ACBGH and ACVMH. Increase in the adsorption occurred, in the case of both adsorbent materials with the increase in *p*H from 2 to 12 and this is due to neutralization of the negative charge at the surface of the adsorbents by the positively charged dye molecule. An increased diffusion process facilitates dye attachment at the active sites of the adsorbents. The results reveal that with increase in *p*H from 2.0 to 12.0, the adsorption increases for both the adsorbents. Greater percentage adsorption is due to the electrostatic attraction between the negatively charged sites of the adsorbents and the positively charged dye molecules. This can be explained by considering the $p\text{H}_{zpc}$ of the adsorbents. The pH_{zpc} of ACBGH and ACVMH was found to be 1.9 and 2.0 respectively. As *p*H of the system decreased below the $p\text{H}_{zpc}$ of the adsorbents, the number of negatively charged adsorbent sites decreased and the positively charged surface sites increased, which did not favour the adsorption of cationic dyes due to electrostatic repulsion. At higher *p*H, negatively charged adsorbent sites increased, which enhances the adsorption of positively charged dye cations through electrostatic forces of attraction[40].

Effect of contact time

Contact time plays a vital role in the adsorption studies as it suggests that necessary required time of contact for deriving maximum adsorption of the dye at the adsorbent surface. The amount of the dye adsorbed at definite intervals of time ranging from 5 to 120 min was monitored for a fixed amount of adsorbents (0.14 g of ACBGH and 0.2 g of ACVMH) at a particular concentration. Experiments were carried out using a definite amount in a time interval ranging from 5 to 120 min for various concentrations of the dye solution as 1.2×10^{-3} M, 1.4×10^{-3} M and 1.8×10^{-3} M which indicates that with the increase in time the adsorption rate of the dye over both adsorbents increases and almost 120 min of time was required to bring complete saturation of the active sites of both adsorbents.

Adsorption isotherm

The equilibrium process between adsorbent and adsorbate are best explained by sorption isotherms. The present investigation deals with the applicability of Langmuir, Freundlich and D–R adsorption isothermal models to the experimental data. The thermodynamic parameters were calculated from the effect of temperature on the MB adsorption on the various activated carbons by using the Langmuir adsorption isotherms at different temperatures of 305K, 315K and 325K.

Freundlich isotherm

The Freundlich isotherm is a result of the assumption that the adsorption occurs on a heterogeneous surface and non-uniform distribution of the heat of adsorption over the adsorbent surface takes place. The Freundlich model was applied to calculate the adsorption data of MB, as per the given relation:

$$\mathrm{Log}\ (qe) = \log (K_f) + \frac{1}{n}\log(C_e) \qquad \text{... (2)}$$

K_f (mol/g) and n are the Freundlich constants, indicating adsorption capacity and adsorption intensity respectively. The graphical presentations for the Freundlich isotherm for the two adsorbents along with their R^2 values are given in Figs 4a and 4b.

Langmuir isotherm

The Langmuir isotherm proposes that the coverage of adsorbate molecules on a solid surface occurs in a monolayer. It is assumed that once the adsorbent site is covered with the dye molecules no further adsorption occurs at that site. It also suggests that all the adsorption sites are of equivalent energy. Langmuir equation is stated as

$$\frac{C_e}{q_e} = \frac{1}{Q_m K_L} + \frac{1}{Q_m} C_e \qquad \text{... (3)}$$

where, q_e (mol/g) and C_e (mol/L) are the amount of dye adsorbed per unit weight of adsorbent and the concentration of the dye solution at equilibrium respectively. The constant Q_m(mol/g) is the adsorption capacity and K_L (L/mol) is the Langmuir equilibrium constant. Figures 5a and 5b show plots obtained for $1/q_e$ against $1/C_e$, at each temperature with the help of which Langmuir constants can be calculated (Table 2).

On comparing the regression coefficients obtained for Freundlich and Langmuir it can be predicted that

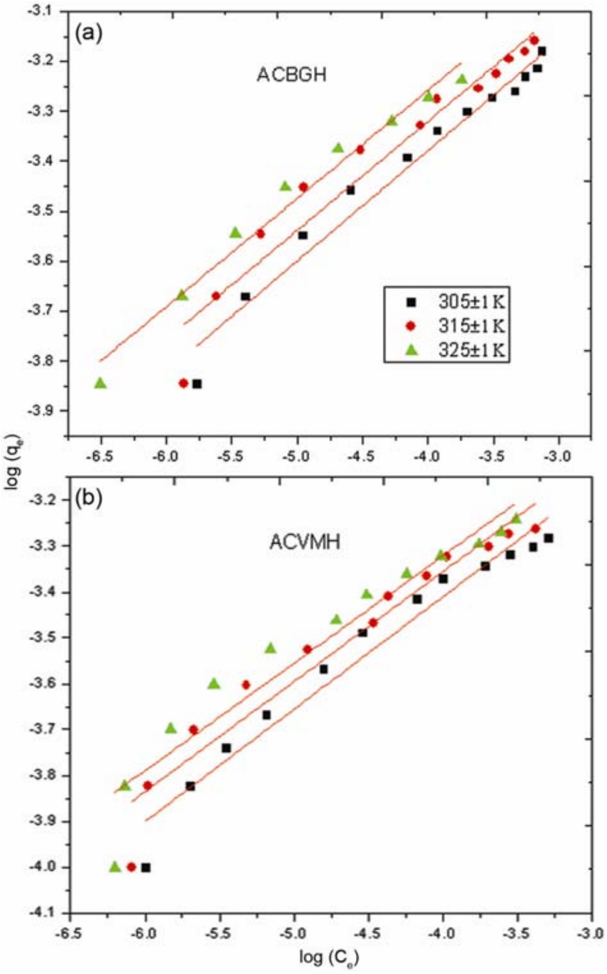

Fig. 4 — (a) Freundlich Isotherm of ACBGH; (b) Freundlich Isotherm of ACVMH

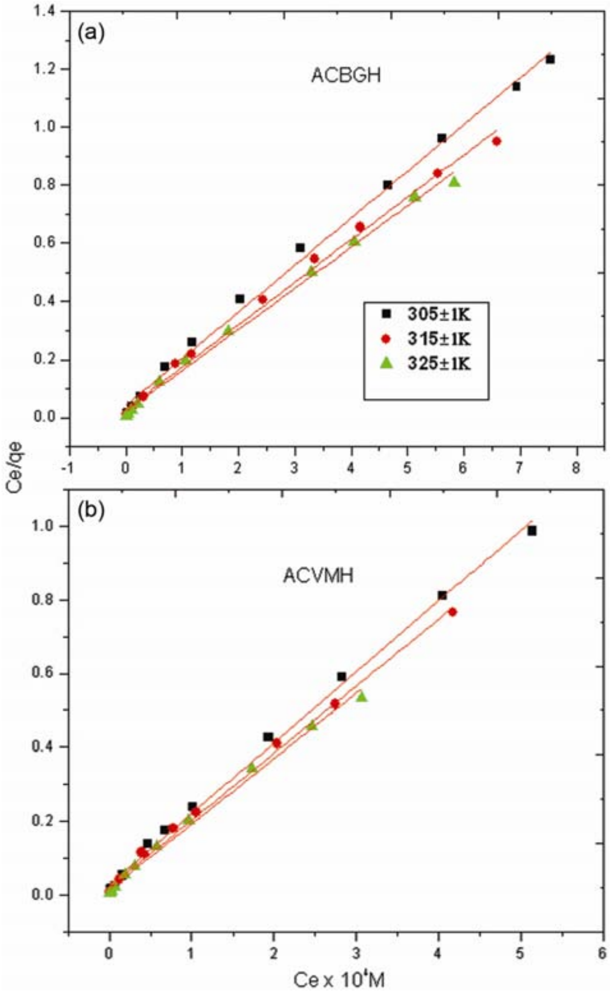

Fig. 5 — (a) Langmuir Isotherm plot of ACBGH; (b) Langmuir Isotherm plot of ACVMH

the Langmuir isotherm is more favoured by the adsorption process. The data presented above show that Langmuir adsorption isotherm graphs are better fit than Freundlich adsorption isotherms. The adsorption capacities of black gram husk and millet husk were found to be 198.40 and 166.29 mg/g respectively. The favourability of the adsorption process was also determined by calculating a dimensionless separation constant R_L by using the Equation.

$$R_L = \frac{1}{1+K_L C_O} \quad \text{... (4)}$$

where C_0 is the initial dye concentration (mol/L) and K_L (L/mol) is Langmuir equilibrium constant. The value of R_L indicates the type of adsorption isotherm to be unfavorable (R_L >1), linear (R_L = 1), favourable (0 < R_L < 1) or irreversible (R_L = 0).

Dubinin-Radushkevich (D-R) adsorption isotherm

Radushkevich adsorption isotherm was used to describe the adsorption on both homogeneous and heterogeneous surfaces. It is used to distinguish the adsorption taking place by physical or chemical processes. The linear form of the isotherm can be expressed as follows

$$\text{In}\,(qe) = \text{In}\,(Qm) - K\varepsilon^2 \quad \text{... (5)}$$

where K is constant related to the adsorption constant (mol^2/kJ^2), and ε is the Polanyi potential that can be calculated from the Equation.

$$\varepsilon = RT\ \text{In}\left(1+\frac{1}{C_e}\right) \quad \text{... (6)}$$

where R is the Universal gas constant (8.314 J $mol^{-1}K^{-1}$), T is the temperature (K) and C_e is the concentration at equilibrium. Figures 6a and 6b show the plot of ln (q_e) vs ε^2 of the experimental data for the adsorption of MB onto ACBGH and ACVMH. The slope gives K and from the intercept the adsorption capacity Q_m can be calculated.

The mean energy of sorption, *E* (kJ/mol), is calculated by the following equation.

$$E = \frac{1}{\sqrt{(2K)}} \quad \text{... (7)}$$

The mean sorption energy (E) calculated from D-R isotherm provides important information about the physical and chemical nature of the adsorption process. The mean energy of adsorption (E) in the range 15.35 to 18.16 kJ/mol for MB indicates the involvement of chemisorption in the process.

The graphs obtained in Langmuir plots further help in the determination of thermodynamic parameters. The thermodynamic parameters such as Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated using the following relations. The thermodynamic parameters are calculated by using the well known Equations.

$$\Delta G^O = -\,RT\ \text{IN}K_L \quad \text{... (8)}$$

$$\Delta H^O = -\frac{R\dfrac{T_2\,T_1}{T_2\ -T_1}\,\text{In}\,K_{L_2}}{K_{L_1}} \quad \text{... (9)}$$

$$\Delta S^O = \frac{\Delta H^O - \Delta G^O}{T} \quad \text{... (10)}$$

The negative values of ΔG^0 (-26.72 to -29.84 kJ/mol) and (-28.23 to -31.47 kJ/mol) confirm the

Table 2 — Adsorption isotherm parameters for the adsorption of MB onto ACBGH and ACVMH

	Temperature					
	305±1K	315±1K	325±1K	305±1K	315±1K	325±1K
		ACBGH			ACVMH	
Langmuir isotherm						
Q_m(mol/g)	6.203×10^{-4}	6.848×10^{-4}	7.074×10^{-4}	5.199×10^{-4}	5.506×10^{-4}	5.642×10^{-4}
K_L(l/mol)	3.781×10^{-4}	4.954×10^{-4}	6.254×10^{-4}	6.847×10^{-4}	8.414×10^{-4}	11.470×10^{-4}
R^2	0.99	0.99	0.99	0.99	0.99	0.99
R_L	0.062	0.048	0.038	0.035	0.028	0.021
Freundlich isotherm						
K_f(mol/g)	3.201×10^{-3}	3.573×10^{-3}	4.061×10^{-3}	3.725×10^{-3}	4.032×10^{-3}	4.146×10^{-3}
1/n	0.220	0.218	0.216	0.245	0.240	0.2345
n	4.525	4.582	4.618	4.075	4.163	4.263
R^2	0.96	0.93	0.97	0.95	0.93	0.92
Dubinin – Radushkevich isotherm						
Q_m (mol/g)	1.116×10^{-3}	1.232×10^{-3}	1.251×10^{-3}	1.061×10^{-3}	1.142×10^{-3}	1.186×10^{-3}
K (mol^2/KJ^2)	1.721×10^{-9}	1.558×10^{-9}	1.384×10^{-9}	1.763×10^{-9}	1.607×10^{-9}	1.448×10^{-9}
E (kJ/mol)	17.04	17.91	19.00	16.83	17.63	18.57
R^2	0.98	0.96	0.96	0.95	0.95	0.94

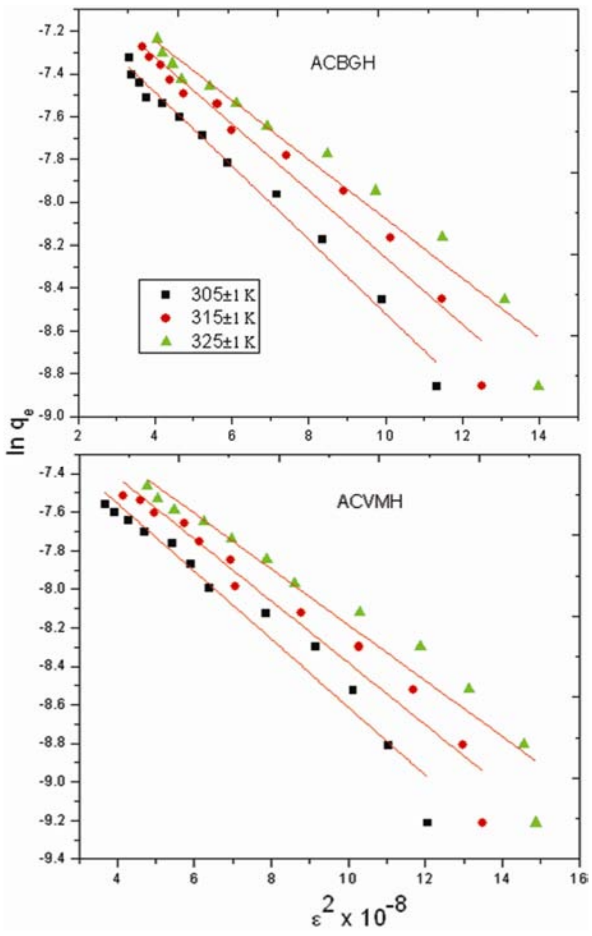

Fig. 6 — (a) D-R isotherm plot of ACBGH; (b) D-R isotherm plot of ACVMH

feasibility and spontaneous nature of the adsorption process. The calculated ΔH^0 (19.82 kJ/mol and 26.36 kJ/mol) and ΔS^0 (152.63 J/molK and179.01 J/molK) are calculated and given respectively for ACBGH and ACVMH. The feasibility of the adsorption process is proved from the negative values of free energy. The positive nature of the enthalpy change and the entropy change confirms the endothermic nature of the process and affinity of the adsorbent towards adsorbate, respectively. The positive ΔS^0 value reflects that the adsorption mechanism is an entropy controlled process.

Rate constant study

Lagergrens first-order kinetics

In order to determine the order of the ongoing adsorption process and also to evaluate the specific rate constants, Lagergrens first-order rate Equation was employed for both systems.

$$\text{Log}\,(q_e - q_t) = \log q_e - \frac{k_t}{2}.303\,t \qquad \ldots (11)$$

where q_e and q_t (mol/g) are the amounts adsorbed at equilibrium and at a time t and k_1 is the rate constant of the pseudo first order adsorption and presented in Figs 7a and 7b

Pseudo-second-order kinetics

A second-order rate equation was also applied to ACBGH-MB and ACVMH–MB systems. The second-order rate expression is represented as

$$\frac{t}{q_t}=\frac{1}{k_2 q_e^2}+\frac{1}{q_e}t \qquad \text{... (12)}$$

k_2 is the rate constant of the pseudo second order adsorption (g $mol^{-1}min^{-1}$).

The values of the various parameters (q_e, k_1 and k_2) were calculated by using the intercept and the slope obtained from the plots and tabulated in Table 3. Figures 8a and 8b shows the plot of second order (t/q_t vs t) kinetic model.

The R^2 values obtained for second-order kinetics are equal to unity, which is greater than that of first-order kinetics at all temperatures. This suggests that the second-order kinetic model is a perfect fit for the ACBGH-MB and ACVMH–MB systems.

Desorption studies

The percentage of desorption by water, HCl and NaOH are 2.87% and 0.98% respectively. When acetic acid, ethanol and acetone were used, it led to desorption of 43.8%, 45.53% and 54.29% respectively. The maximum desorption occurred with acetone as the desorbing medium. The maximum desorption occurred with acetone. This further confirms that the process of adsorption is mainly chemical adsorption.

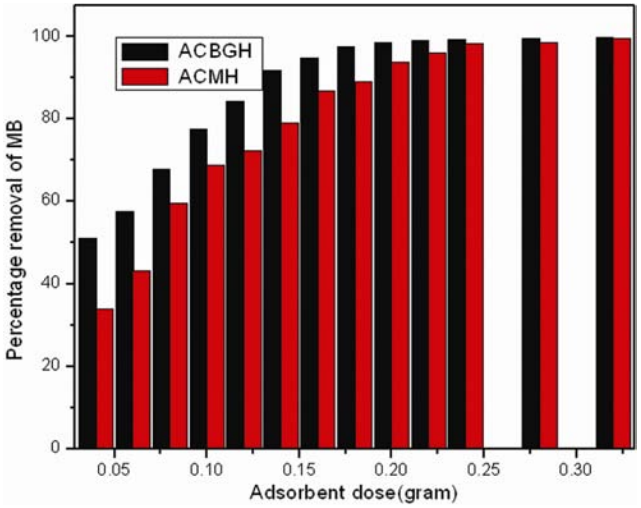

Fig. 7 — Effect of adsorbent dose on the aolsorption of MB onto ACBGH and ACVMH

Testing of real effluent

To evaluate the efficiency of the prepared adsorbents towards the removal of the dyes, the real effluent collected from a textile industry was used. The adsorption of the dyes were performed with

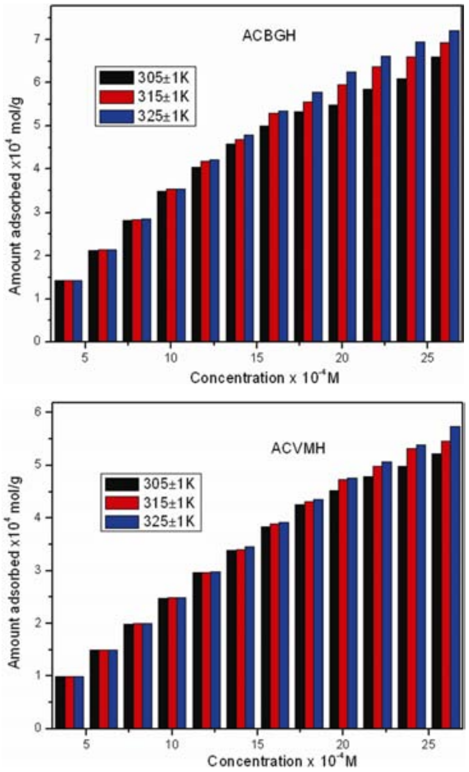

Fig. 8a — (a) Effect of concentration on the adsorption of MB onto ACBGH at different temperature; (b) Effect of concentration on the adsorption of MB onto ACMVH at different temperature

Table 3 — Adsorption kinetic parameters for the adsorption of MB by ACBGH and ACVMH

	Pseudo-first order				Pseudo-second order		
				ACBGH			
Adsorbate conc	q_e(exp) (mol/g)	k_1 (1/min)	q_e(calc) (mol/g)	R^2	k_2 (g/mol min)	q_e(calc) (mol/g)	R^2
1.2×10^{-3}	4.035×10^{-4}	0.017	1.485×10^{-4}	0.985	0.474×10^3	4.165×10^{-4}	0.999
1.4×10^{-3}	4.595×10^{-4}	0.030	1.954×10^{-4}	0.995	0.313×10^3	4.789×10^{-4}	0.999
1.8×10^{-3}	5.317×10^{-4}	0.032	2.002×10^{-4}	0.987	0.250×10^3	5.313×10^{-4}	0.999
				ACVMH			
1.2×10^{-3}	2.971×10^{-4}	0.037	0.529×10^{-4}	0.916	1.699×10^3	3.016×10^{-4}	0.999
1.4×10^{-3}	3.387×10^{-4}	0.042	0.937×10^{-4}	0.992	1.050×10^3	3.470×10^{-4}	0.999
1.8×10^{-3}	4.217×10^{-4}	0.047	1.868×10^{-4}	0.839	0.543×10^3	4.301×10^{-4}	0.999

Table 4 — Physical and chemical examinations of the real effluent

Physical examination			
	Thirupur effluent	ACBGH	ACVMH
Turbidity, NT units	36	16.9	15.2
Total dissolved solids, mg/L	7170	5299	4914
Electrical conductivity, Micro mho/cm	10243	7570	7020
Chemical examination			
*p*H	8.22	6.966	8.3
Total alkalinity	1840	456	408
Total hardness	3200	476	508
Calcium as Ca mg/L	760	133	126
Magnesium as Mg, mg/L	312	30	22
Sodium as Na, mg/L	900	1405	1270
Potassium as K, mg/L	160	45	35
Iron as Fe, mg/L	0.82	0.70	0.63
Manganese as Mn, mg/L	0	0	0
COD- mg/L	6060	281	277
BOD- mg/L	1800	100	90

50mL of the real effluent, with 0.4 g and 0.5 g of ACBGH and ACVMH respectively and allowed for shaking for 120 min. The solution after filtration was subjected to physical and chemical examinations and the results are tabulated (Table 4).

Conclusion

The results have prove that the adsorbent materials can be effectively employed for the removal of the dye Methylene blue form the waste waters and these materials are easily and abundantly available. The value of the adsorption capacity reveals that the activated carbons prepared are efficient. The amount of dye removed increase with increasing adsorbent dose, temperature and decreased with increase in concentration. The isotherm study indicates that adsorption data can be adequately modelled by the Langmuir. The adsorption kinetic process was described by a pseudo-second-order rate expression. The positive nature of the enthalpy change and the entropy change confirms the endothermic nature of the process and affinity of the adsorbent towards adsorbate, respectively. The positive ΔS^0 value reflects that the adsorption mechanism is an entropy controlled process. Removal of dyes from the industrial effluent also proved the efficiency of the adsorbents.

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