



Removal of Acid Blue 113 dyes from aqueous solution by activated carbon of Varagu millet husk: Equilibrium, Kinetics and Thermodynamic Studies.

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Abstract: Activated carbon was prepared from Varagu millet husk (ACVMH). The Characterizations of prepared activated carbon (ACVMH) was determined using SEM, XRD, BET and FTIR analysis. The surface area was found to be 397.33m²/g. Experiments were carried out to evaluate the batch adsorption isotherms and kinetics of Acid blue (AB113) on ACVMH at different temperatures. Experimental equilibrium data were analyzed by the Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models. The results show that the best fit was achieved with the Langmuir isotherm equation with a maximum adsorption capacity of 231.92mg/g. Pseudo-first order and pseudo-second order models were used to analyze the kinetic data. The adsorption kinetic data were well described by the pseudo-second order model. The calculated thermodynamic parameters, namely ΔG^0 , ΔH^0 , and ΔS^0 showed that adsorption of AB113 onto activated carbon of Black gram husk was spontaneous and endothermic under examined conditions.

Keywords: Activated carbon; Adsorption; Isotherm; Kinetics; Thermodynamics.

1. Introduction

The disposal of textile waste water is currently a major problem from a global viewpoint. Textile industries produce a lot of wastewater, which contains several contaminants, including acidic or caustic dissolved solids, toxic compounds, and dye [1]. The discharge of effluents from these industries contain large amount of dyes, not only damage the aesthetic nature of receiving water bodies, but also may be toxic to aquatic life [2]. In order to remove dyes from aqueous solutions many chemical or biological treatments have been used either individually or together. Various methods of dye/colour removal, including aerobic and anaerobic microbial degradation, coagulation, chemical oxidation, membrane separation, electrochemical treatment, filtration, flocculation, softening, hydrogen peroxide catalysis and reverse osmosis have been proposed from time to time have been developed over the years to remove these toxic dyes from wastewater. Among the methods developed, one of the best ways to remove toxic dyes is by adsorption using suitable adsorbents, such as granulated or powdered activated carbon.

However, due to the high cost in the production of good quality activated carbon, attention is being turned to the use of low-cost biosorbents as viable alternative [3]. A number of non-conventional, low-cost agricultural materials are used as adsorbents for removal of pollutants from wastewater. Some of them are lentil straw, tamarind fruit shell, macuaba palm cake, tannery solid waste, cattail root, jute stick powder, peanut hull, soya meal hull, papaya seed, spent brewery grains, maize cob, straw, coir pith, sesame hull, jackfruit peel, hazelnut shells, de-oiled soya, hen feathers, guava leaf powder pumpkin seed hull etc [4].

Varagu millet (*Paspalum scrobiculatum*), also known as cow grass, rice grass, ditch millet, Native Paspalum or Indian Crown Grass originates in tropical Africa, and it is estimated to have been cultivated in India 3000 years ago. Varagu millet is an annual grain that is grown in India, the Philippines, Indonesia, Vietnam, Thailand, and in 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.

In this study **Acid blue 113** (AB113) dye was taken which is widely used in wool dyeing to obtain a deep shade of navy blue colour. These dyes have affinity for the fibre substrates and better fastness of colour could be achieved. When the effluent containing these dyes is released into the environment it can cause long term effect adverse effects on aquatic organisms.

The aim and scope of the present study is to ascertain adsorption capacity and removal efficiency Acid Blue 113 dye from aqueous solution on the adsorbent namely ACVMH by the batch adsorption method.

2. Materials and methods.

2.1. Preparation of the adsorbent:

STEP	PROCESS
01	Varagu millet husk
02	Pre-treatment: Washing, drying, grinding, sieving
03	Chemical activation of Varagu millet husk with Orthophosphoric acid in the ratio of 5:1 (g H ₃ PO ₄ /g Varagu millet husk)
04	Heated in muffle furnace at 450°C for 1hr.
05	Washed with double distilled water.
06	Dried overnight at 110°C
07	Cooled to room temperature and powdered
08	Activated carbon of Varagu millet husk— Adsorbent (ACVMH)

2.2. Adsorbate

Acid blue 113 is an anionic dye with a synonym of Sodium 8-phenylamino-5-(4-(3-sulphonatophenylazo)-1-naphthylazo) naphthalene sulphonate. The stock solution of the dye was prepared in double distilled water. All the test solutions were prepared by diluting the stock solution with double distilled water.

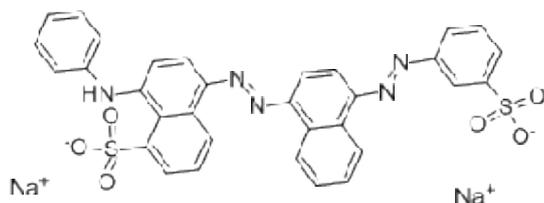


Fig.1. Chemical structure of AB113

2.3 Adsorption studies

Batch experiments were carried out in order to evaluate the effects of amount of adsorbent, contact time, initial dye concentration and solution pH. In the adsorption experiments 50 ml of different concentrations of AB113 dye solution was taken in each of 100 ml volumetric flasks with fixed amount of adsorbent in each flask. The flasks were then mechanically agitated in water bath shaker at a constant temperature until the equilibrium was reached. These solutions were centrifuged and the absorbance of the supernatant solution obtained was determined with a UV-Visible spectrophotometer at the maximum wavelength. The percentage removal was calculated by the following equation [5].

$$\text{Percentage removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C_0 and C_e are the initial and equilibrium liquid-phase concentrations of AB113 (mol /l) respectively. The amount of dye adsorbed at equilibrium (q_e) was calculated from the mass balance equation as follows [6].

$$\text{Amount Adsorbed}(q_e) = (C_0 - C_e) \times \frac{V}{m} \quad (2)$$

where q_e is the amount of adsorbed dye at equilibrium (mol/g), C_0 and C_e are the initial and equilibrium liquid-phase concentrations of AB113 (mol /L) respectively, V is the volume of the dye solution (L) and m is the mass of adsorbent added (g).

2.4 Adsorption Kinetic study

The kinetics of dye adsorption is an important characteristic for understanding the efficiency of adsorption and the feasibility of using an adsorbent for wastewater treatment. Hence, the kinetics of removal of the dye has been followed as a function of dye concentration and time. For examination of the kinetic and the equilibrium data, a series of 50 ml sample of AB113 of known concentrations (1.2×10^{-3} M, 1.4×10^{-3} M and 1.8×10^{-3} M) were taken in an airtight 100 ml volumetric flask containing 0.2g of the adsorbent. The entire set of flasks with the mixture were mechanically agitated in a water bath shaker. The solution from the flasks were taken at different predetermined intervals of time and centrifuged. The supernatant solution was quantified spectrophotometrically. The amount of dye adsorbed (q_t) at time t was calculated from the equation as follows.

$$\text{Amount Adsorbed}(q_t) = (C_0 - C_t) \times \frac{V}{m} \quad (3)$$

Where q_t is the amount of adsorbed dye (mol/g); C_0 and C_t are the concentrations of AB113 (mol /l) at initial and at time t (min) respectively; V is the volume of the dye solution (L) and m is the mass of adsorbent added (g).

3. Results and discussion.

3.1 Characterisation of ACVMH

3.1.1 FTIR analysis of ACVMH.

The band around 3780 cm^{-1} were observed for millet husk sample (Fig.2), which was attributed to the O-H stretching vibration of the hydroxyl functional groups of alcohols and phenols[7]. The peak at 1594 cm^{-1} in ACVMH corresponds to stretching vibration of COO^- . The bands at 2850.80 cm^{-1} in millet husk sample, indicates the presence of an aliphatic C-H stretching also specifically the Methylene group sp^3 stretching. The bands around 1169.96 cm^{-1} in millet husk has 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.

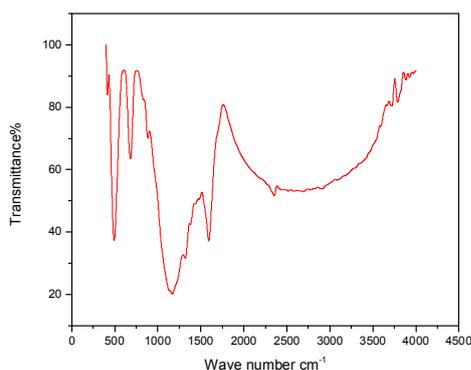


Fig.2 FTIR spectrum of ACVMH

3.1.2. 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, ACVMH was taken. The SEM picture of the adsorbent sample shows 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 Fig. 3 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 40.41% along with some amount of hydrogen 1.76% and nitrogen 0.75%.

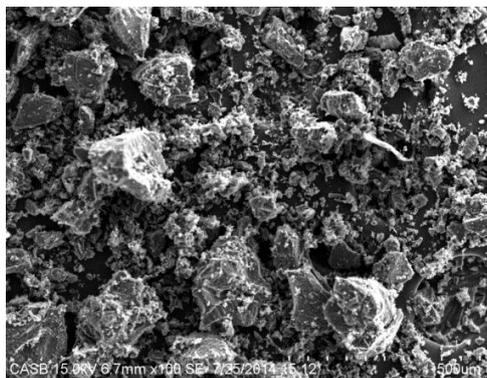


Fig.3.SEM image of ACVMH

3.1.3. X-Ray Diffraction analysis.

The X-ray diffraction pattern of the prepared activated carbons exhibited two peaks at $2\theta = 26.45$ and 42.69 for millet husk, which are attributed to (002) plane and (101) plane respectively (Fig.4) and which are similar to that of graphite. The crystallite size of ACVMH along L_c or L_a were determined by Scherer equation and found to be 2.974 nm for L_c . The interlayer spacing (d_{002}) was calculated using Bragg's equation [8]. 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 $2\theta = 25.58$, corresponds to an interlayer distance of 0.335nm for ACVMH, which is quite near to that of pure graphitic carbon.

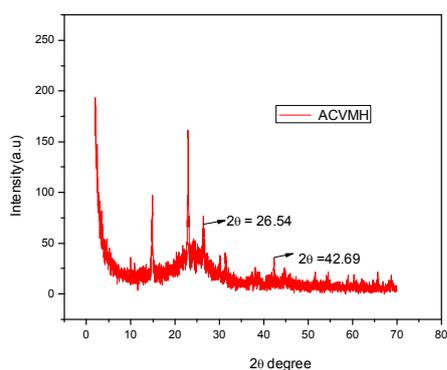


Fig.4. XRD pattern of ACVMH

3.1.4. Raman Spectroscopy.

The graphitic nature of the adsorbents is further confirmed through Raman spectrum. The activated carbons exhibited two distinct peaks at about 1327 cm^{-1} (D- band) and 1594 cm^{-1} (G-band) respectively for ACVMH (Fig.5). 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 [9]. Accordingly, the low I_D/I_G value indicates a high degree of graphitization. The I_D/I_G value of ACVMH is 0.8324, 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.

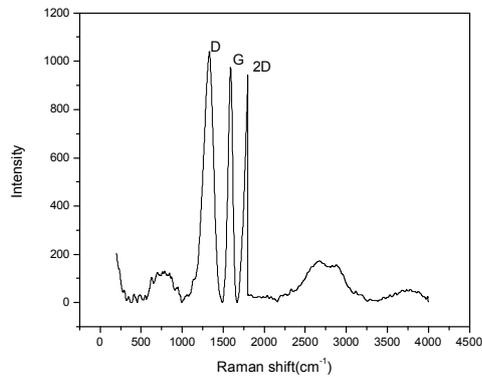


Fig.5 Raman Spectrum of ACVMH

3.1.5. BET analysis

Pore characteristic of the activated carbon was determined by N_2 adsorption. The nitrogen adsorption /desorption isotherms of the activated carbon is illustrated in Fig.6. 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 IUPAC the adsorbent pores are classified into three groups: micropores (size < 2 nm), mesopores (2–50 nm), and macropores (>50 nm) [10]. Further the micropores were divided into ultramicropores (< 0.7nm) and supermicropores (0.7 to 2nm). 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 the adsorbent. The average pore diameter of ACVMH was found to be 6.75nm (Table1) which further confirms the presence of mesopores. The mesopore volume and micropore volume was found to be around 97.95% and 2.1% respectively of the total pore volume determined indicating that the ACVMH is mesoporous in nature.

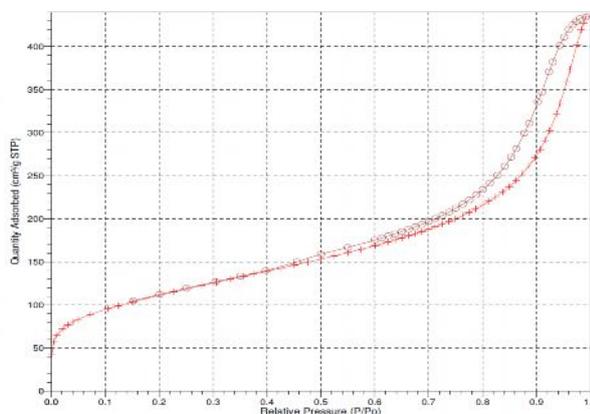


Fig.6 Nitrogen adsorption – desorption isotherm of ACVMH sample obtained at 77K.

Table 1: S_{BET} and pore structure of ACVMH

Adsorbent	S_{BET} (m^2/g)	S_{ext} (m^2/g)	$S_{\text{ext}}/S_{\text{BET}}$ (%)	S_{mic} (m^2/g)	$S_{\text{mic}}/S_{\text{BET}}$ (%)	V_{tot} (cm^3/g)	V_{mic} (cm^3/g)	V_{meso} (cm^3/g)	D_p (nm)
ACVMH	397.33	359.03	90.36	38.30	9.63	0.671	0.014	0.657	6.75

3.1.6. Chemical Characterization of and ACVMH by Boehm Titrations.

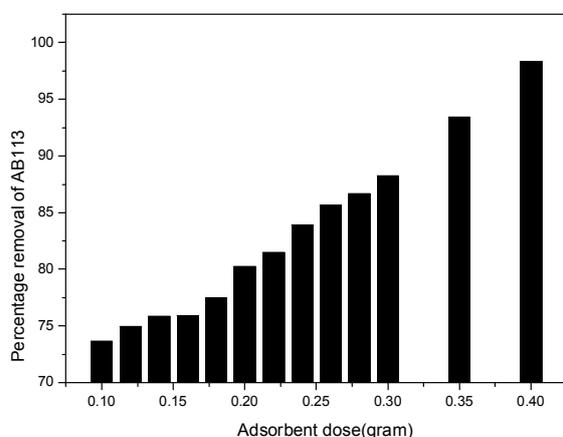
The Boehm titration method was used to determine the oxygen containing functional groups present over the surface of the activated carbon. 0.5g of the activated carbon () was kept in contact with 50ml each of NaHCO_3 (0.05N), Na_2CO_3 (0.05N) and NaOH (0.05N) for evaluating acid groups and 0.05N HCl for evaluating basic groups respectively at room temperature for 24h. 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 with HCl. The most common oxygen groups on the surface are carboxylic (0.4meq/g), phenolic (0.161 meq/g), and lactonic (0.05meq/g) for ACVMH.

3.1.7. Zero point charge of the adsorbents.

The point of zero charge of ACVMH was determined by solid addition method. In this method 0.1M KCl solution was taken in ten bottles maintained with pH in the range of 1-10 and 0.20g of ACVMH was added to each bottles. These solutions were shaken for 24h at room temperature and the final pH was measured. The difference between the initial and final pH was measured and the point where $\Delta\text{pH} = 0$ was taken as the point of zero charge. At $\text{pH} < \text{pH}_{\text{zpc}}$, the surface has a net positive charge and at $\text{pH} > \text{pH}_{\text{zpc}}$, it is negative. The pH_{zpc} of ACVMH was found to be 2.1.

3.2 Effect of adsorbent dose

Adsorbent dosage is an important parameter for the adsorption process because this determines the capacity of an adsorbent for a given initial concentration of the adsorbate at particular temperature. The effect of adsorbent dose was studied by maintaining the dye concentration at $1.8 \times 10^{-3}\text{M}$, solution pH and the contact time was 120min. The adsorption of dyes increased with adsorbent dosage and reached a constant after a particular dosage. Fig.7 Increase in the adsorption with adsorbent dosage could be attributed to increased adsorbent surface area of mesoporous and the availability of more adsorption sites for further adsorption [11].

**Fig.7. Effect of adsorbent dose for the adsorption AB113 onto ACVMH.**

3.3 Effect of contact time

The contact time is one of the important parameters for economical wastewater treatment application. Effect of contact time for the removal of the dyes was carried out at different concentrations namely 1.2×10^{-3} , 1.4×10^{-3} and 1.8×10^{-3} M with 0.2g of ACVMH, The adsorption of dyes increased with increase in agitation time. It is observed from Fig.8 that the adsorption of the dye increases as the time increases. The percentage removal curves were continuous and distinct but leading to saturation after a certain time, suggesting possible monolayer coverage of dyes onto the surface of the activated carbon of Varagu millet husk [12]. The optimum contact time was found to be 120min for AB113 dye on ACVMH.

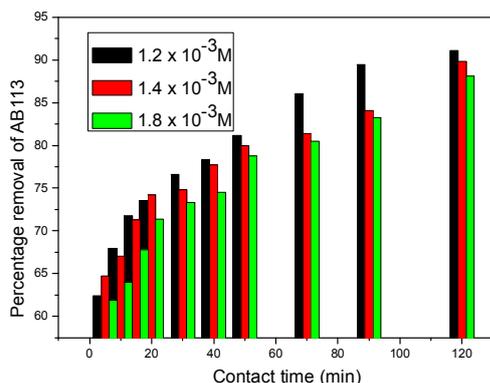


Fig.8 Effect of contact time for the adsorption of AB113 onto ACVMH.

3.4 Effect of concentration at different temperatures

The removal of dyes was studied at different temperatures of 305, 315, and 325 ± 1 K with constant adsorbent dose of 0.2g of ACVMH and at different concentrations of dyes. The percentage of adsorption of AB113 increased with increase in temperature (Fig.9). This may be due to the increasing mobility of the dye molecules and enlarging in the pore sizes of ACVMH for the adsorption process. The positive effect of temperature on the adsorption of dyes revealed that the adsorption process should be endothermic or chemisorption in nature.

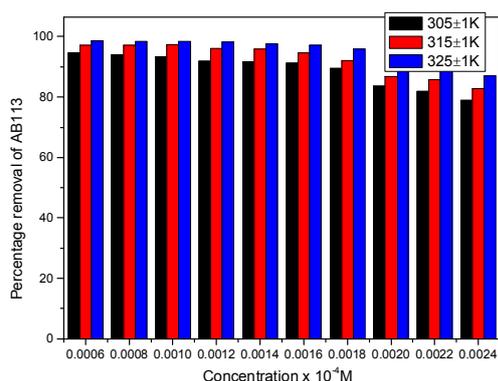


Fig.9 Effect of concentration at different temperatures.

3.5 Adsorption Isotherm

Isotherms were used to describe the adsorption progress and to investigate the adsorption mechanism. The variation of the adsorbate concentration with the same mass of the adsorbent was used to describe the adsorption mechanism at constant temperature. Langmuir, Freundlich and Dubinin Radushkevich (D-R) adsorption isotherms were applied for the adsorption of AB113 over the surface of ACVMH.

3.5.1 Langmuir adsorption isotherm:

The Langmuir adsorption isotherm is valid for monolayer coverage of the adsorption onto the surface with a finite number of adsorption sites and it is assumed that the adsorption takes place on homogeneous surface. It is used to determine of the adsorption capacity of the adsorbent. The linear form of the Langmuir adsorption equation is [13].

$$\frac{C_e}{q_e} = \frac{1}{Q_m K_L} + \frac{1}{Q_m} C_e \quad (4)$$

Where q_e (mol/g) and C_e (mol/L) are the amount of dye adsorbed per unit Mass 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. The feasibility of Langmuir adsorption isotherm was tested by using dimensionless constant called separation factor R_L or equilibrium parameter which is defined by the following equation [14].

$$R_L = \frac{1}{1 + K_L C_0} \quad (5)$$

where C_0 is the initial RB 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 either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

3.5.2 Freundlich adsorption isotherm:

The Freundlich adsorption isotherm assumes that the adsorption takes place on heterogeneous surface as well as multilayer sorption. The Freundlich adsorption isotherm equation can be expressed as [15].

$$\log(q_e) = \log(K_f) + \frac{1}{n} \log(C_e) \quad (6)$$

where q_e (mol/g) is the amount of dye adsorbed at equilibrium and C_e (mol/L) is the equilibrium dye concentration in solution. K_f (mol/g) and n (dimensionless) are constants for a given adsorbate and adsorbent at a particular temperature. The values of K_f and $1/n$ can be obtained from the intercept and the slope of the plot of $\log(q_e)$ versus $\log(C_e)$.

3.5.3 Dubinin-Radushkevich adsorption isotherm:

Dubinin– 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.

where K (mol^2/KJ^2) is constant related to the adsorption constant, and ϵ is the Polanyi potential that can be calculated from the equation: where T is the temperature in K and R is the universal gas constant (8.314 J/mol/K). The constant K (Slope of $\ln(q_e)$ versus ϵ^2) gives the mean free energy of sorption, E (kJ/mol) and is calculated by the following equation [16].

$$\epsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (8)$$

Adsorption equilibrium isotherms were expressed by relating the amount of adsorbate uptake per gram of adsorbent, q_e (mol/g), to the equilibrium solution concentration, C_e (mol/L), at a fixed temperature. Fig.10 shows the plot obtained for $1/q_e$ against $1/C_e$, at each temperature with the help of which Langmuir constants can be calculated.

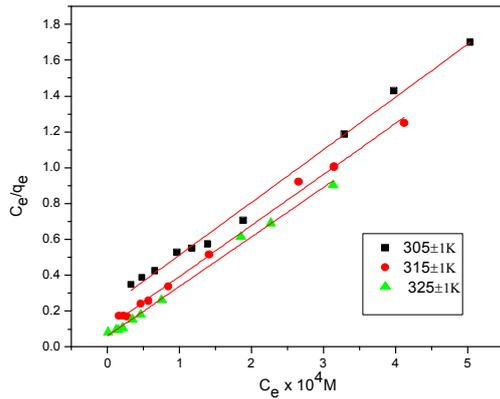


Fig.10 Langmuir Isotherm plot of ACVMH

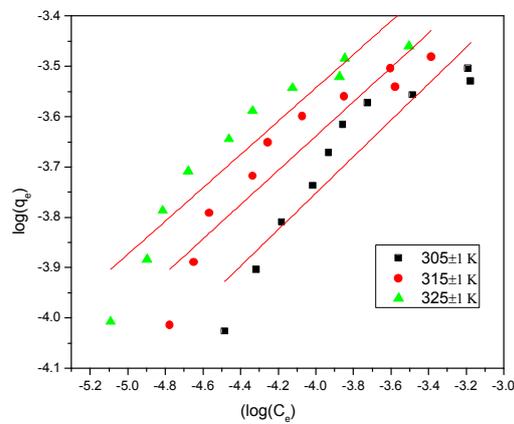


Fig.11 Freundlich Isotherm of ACVMH

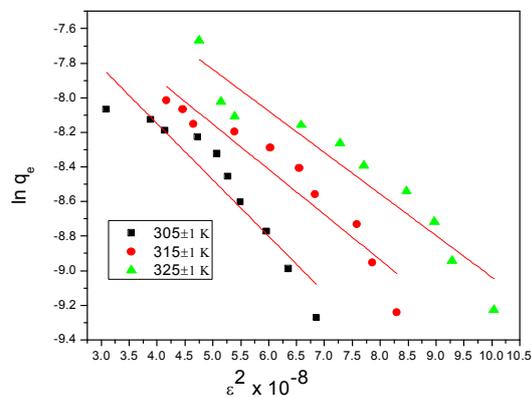


Fig.12 D-R isotherm plot of ACVMH

The Langmuir adsorption constants Q_m , K_L and R_L with correlation coefficients are listed in Table 2. The R_L values were found to be in the range of 0.035 to 0.021, indicating that the adsorption was favourable. The maximum adsorbent capacity was found to be 231.92mg/g. The adsorption equilibrium data were also verified by using the linear form of the Freundlich adsorption isotherm. Fig. 11 shows the plots of $\log(q_e)$ versus $\log(C_e)$ for the adsorption of AB113 onto ACVMH at 305±1K, 315±1K and 325±1K. The Freundlich constants K_L and n are presented in Table 2. The values of n were found to be in the range of 1-10 indicating the adsorption was favourable. Further seen from Table 2, the values of Q_m , K_f and K_L increased with temperature indicating that the adsorption process was endothermic in nature. Dubinin- Radushkevich adsorption isotherm was employed for the adsorption equilibrium experimental data. The plot of $\ln(q_e)$ versus ε^2 gives a straight line (Fig12).

Table 2: Adsorption isotherm parameters for the adsorption of AB113 onto ACVMH.

Temperature			
Langmuir isotherm			
$Q_m(\text{mol/g})$	5.199×10^{-4}	5.506×10^{-4}	5.642×10^{-4}
$K_L(\text{l/mol})$	6.847×10^{-4}	8.414×10^{-4}	11.470×10^{-4}
R^2	0.99	0.99	0.99
R_L	0.035	0.028	0.021
Freundlich isotherm			
$K_f(\text{mol/g})$	3.725×10^{-3}	4.032×10^{-3}	4.146×10^{-3}
$1/n$	0.245	0.240	0.2345
n	4.075	4.163	4.263
R^2	0.95	0.93	0.92
Dubinin – Radushkevich isotherm			
$Q_m(\text{mol/g})$	1.061×10^{-3}	1.142×10^{-3}	1.186×10^{-3}
$K(\text{mol}^2/\text{KJ}^2)$	1.763×10^{-9}	1.607×10^{-9}	1.448×10^{-9}
$E(\text{kJ/mol})$	16.83	17.63	18.57
R^2	0.95	0.95	0.94

The value of E is useful for determining the adsorption mechanism. If the value of $E < 8$ kJ/mol then the adsorption could take place by physical forces. If E is in the range of 8-16 kJ/mol, adsorption occurs by ion exchange mechanism, while E is greater than 16 kJ/mol indicates chemisorption could be taking place in the adsorption process. The value of E is found to be greater than 16 kJ/mol, indicating that the chemisorption process for the adsorption of AB113 onto ACVMH.

3.6 Adsorption kinetics

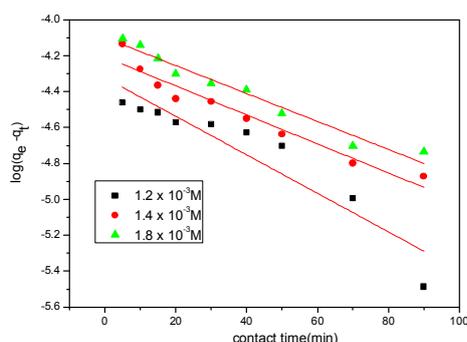
Adsorption kinetics is very essential in determining the efficiency of adsorption process. The Lagergrens pseudo first order equation and pseudo second order equation and were applied for the adsorption of AB113 onto ACVMH.

3.6.1 Pseudo first order kinetics:

In order to study the adsorption kinetics, pseudo first order pseudo second order models and intra-particle diffusion were applied to the experimental data. The pseudo first order rate equation is given as [17].

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (10)$$

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. Fig.13 shows the plot of second order (t/q_t vs t) kinetic model. If the calculated q_e value is equal to the experimental q_e then the adsorption is following the pseudo first order kinetics.

**Fig.13. Pseudo first order of ACVMH**

3.6.2 Pseudo second order kinetics:

Then pseudo second order chemisorption kinetic rate equation is expressed as follows [18]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{11}$$

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

If the pseudo second order kinetic equation is applicable, then the plot of t/q_t versus t should give a straight line, from which q_e and k_2 can be obtained from the slope and intercepts of the plot (Fig.14) The values of R^2 are closer to unity in pseudo second order (0.999) than that of the pseudo first order. The values of q_e calculated from pseudo second order are in good agreement with q_e experimental values (Table3) and this indicates that the AB113 adsorption system obeys the pseudo second order kinetic model.

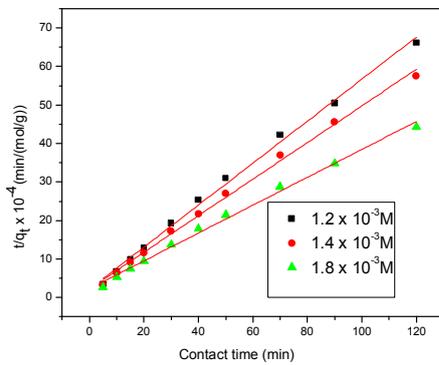


Fig.14 Pseudo second order of ACMVH

Table 3: Adsorption kinetic parameters for the adsorption of AB113 by ACBGH and ACVMH

Adsorbate conc	Pseudo-first-order				Pseudo-second order		
	$q_e(\text{exp})$ (mol/g)	k_1 (1/min)	$q_e(\text{calc})$ (mol/g)	R^2	k_2 (g/mol min)	$q_e(\text{calc})$ (mol/g)	R^2
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

3.7 Thermodynamic parameters:

The thermodynamic parameters such as standard Gibb’s free energy change (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were determined by using the following relationships [19].

$$\Delta G^0 = -RT \ln K_L \tag{13}$$

The enthalpy ΔH^0 and entropy ΔS^0 values were estimated from the following equations [20].

$$\Delta H^0 = -R \frac{T_2 T_1}{T_2 - T_1} \ln \frac{K_{L2}}{K_{L1}} \tag{14}$$

where K_L , K_{L1} and K_{L2} are the Langmuir constants at different temperatures, R is the universal gas constant (8.314 J/mol/K) and T is the Kelvin temperature [21].

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \quad (15)$$

The negative values of ΔG^0 in the temperature range of 305–325 K, indicate that the process is of spontaneous in nature. The positive values of ΔH^0 and ΔS^0 (Table.4) indicate that the adsorption process is of endothermic in nature and the adsorption mechanism is an entropy controlled process respectively. Even though the positive values of ΔH^0 indicate the endothermic process, the process becomes spontaneous having negative value of ΔG^0 because of the positive value of ΔS^0 .

Table.4 Thermodynamic parameters of ACVMH on AB113.

T (K)	Thermodynamic parameters		
	ΔG^0 (KJ/mol)	ΔH^0 (KJ/mol)	ΔS^0 (KJ/mol/K)
305	-24.099	46.369	231.04
315	-26.643		
325	-28.961		

4.0 Conclusion

Removal of Acid blue 113 dyes from aqueous solution by adsorption with ACVMH has been experimentally determined. The percentage of colour removal increased with increasing adsorbent dose and contact time for the adsorbent. Optimum contact time to reach equilibrium was found to be 120min. The kinetic and isotherm studies revealed that the experimental data well described by the pseudo second order model and Langmuir isotherm. The adsorption capacity of ACVMH with Acid blue 113 dyes was found to be 231.92mg/g. The positive value of ΔH^0 indicates that the adsorption of AB113 over ACVMH is an endothermic process. The negative value of ΔG^0 indicates the spontaneous nature of the adsorption process and is entropy driven process. The results of present investigation show that ACVMH could be utilized as low cost and natural adsorbent for the removal of AB113 and it can be used as an alternative to more costly materials.

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