

Adsorptive Removal of Vat Yellow 4 on Activated *Mucuna pruriens* (Velvet bean) Seed Shells Carbon

ABSTRACT

Aim: To study the removal of vat yellow 4 from wastewater on activated carbon produced from *Mucuna pruriens* seed shells (MPS).

Methodology: The seed sample was activated using two methods and carbonized at 500°C for 2 hours to produce two different adsorbents. The physicochemical properties of the adsorbents were determined. Their structural elucidation were established using Fourier transform infrared (FTIR), X-ray Fluorescence (XRF), X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) spectral techniques. The effect of process variables such as particle size, adsorbent dose, pH, dye concentration and solution temperature on the process of adsorption were studied using batch operation. Three isotherm and four kinetic models were used to study the adsorption process. The linear regression method of analysis was used to model the experimental data. The adequacy of the models was tested using the correlation coefficient (R^2). The thermodynamic parameters, changes in standard free energy (ΔG^0), entropy (ΔS^0) and enthalpy (ΔH^0) were also evaluated.

Results: The results showed that adsorption is influenced by particle size, adsorbent dose, contact time, initial pH of solution, solution temperature and dye concentration. Maximum adsorption capacity for vat yellow 4 on the adsorbents was observed at pH of 2. The equilibrium data fitted well to the Langmuir, Freundlich and Temkin models. The Langmuir isotherm was found to have the best fit to the experimental data suggesting monolayer adsorption on a homogeneous surface. The pseudo second-order kinetic model was found to best describe the experimental data and the adsorption process was controlled by film diffusion. The adsorption process has been found to be feasible, spontaneous and endothermic in nature. The spontaneity of the process increased with increase in the solution temperature.

Conclusion: This study has shown that *Mucuna pruriens* seed shells, an agro waste, can be used for the removal of vat yellow 4 from wastewater. The phosphoric acid treated adsorbent performed better than the sodium chloride treated adsorbent.

Keywords: Adsorption, Isotherm, Kinetics, *Mucuna pruriens* Seed Shells, Thermodynamics, Vat Yellow 4, Wastewater

1. INTRODUCTION

The discharge of dye containing effluents has been generating a lot of environmental concerns in the world today [1]. The total consumption of dyes by textile industry worldwide is more than 10^7 kg/year [2]. There are more than 10,000 commercially available dyes with over 7×10^5 tonnes of dyestuff produced annually across the world [2]. Vat yellow 4 (golden yellow GK, dibenzochrysenedione, dibenzpyrenequinone, 3,4:8,9-dibenzopyrene-5,10-dione) (anionic dye) is a yellow synthetic anthraquinone vat dye. Vat dyes cause environmental concerns when released in industrial wastewaters due to their carcinogenic effects on humans [3]. Vat dyes are insoluble in water and incapable of dyeing fibers directly [4]. Anionic dyes carry a net negative charge due to the presence of sulphonate groups, while cationic dyes carry a net positive charge due to the presence of protonated amine or sulfur containing groups in aqueous solution [5]. Many techniques have been used for the treatment of coloured wastewaters but application of adsorption has been shown to follow a simple design, ease of operation and also guarantees relatively high efficiency [6].

The most widely used adsorbent is activated carbon because it has a high capacity for colour removal but its use is limited because of high cost [7]. The production of activated carbon from agricultural by-products has potential economic and environmental impacts. It converts unwanted, low – value agricultural waste to useful, high-value adsorbents. Agro wastes are less expensive and locally available in large quantities. Agro wastes are better than other adsorbents because the agricultural wastes are usually used without or with a minimum of processing and thus reduce production costs by using a cheap raw material and eliminating energy costs associated with thermal treatment [8].

Mucuna pruriens is a tropical legume known as velvet bean or cowitch and by other common names, found in Africa, India and the Caribbean. The plant is an annual, climbing shrub with long vines that can reach over 15 m in length. The endocarp of *Mucuna pruriens* is non toxic. Many studies have been done using different agro wastes on the removal of synthetic dyes [9]-[12].

The objectives of this research is to (1) produce activated carbon from *Mucuna pruriens* seed shells, locally available adsorbent which has not been found to be in good use in Nigeria; (2) determine the properties of the adsorbent; (3) investigate its removal efficiency in simulated wastewater containing vat yellow 4 dye; (4) establish the adsorption isotherms of process; (5) determine the kinetic model that best correlates the kinetic data; (6) evaluate the thermodynamic parameters of the adsorption process.

2. MATERIAL AND METHODS

2.1. Preparation of the Activated Carbon

Mucuna pruriens seed shells (MPS) were obtained from *Mucuna pruriens* seed processing, main market, Enugu, Nigeria and washed thoroughly with de-ionized water to remove dirt, dried in the oven at 105°C for 24 h. The MPS was ground, sieved to the desired particle size. One portion of the sample was soaked in 60% phosphoric acid (H_3PO_4) acid and the other in sodium chloride (NaCl) for 24 h at room temperature and carbonized at 500°C for 2 h. The carbonized samples were washed with de-ionized water until a pH of 7, filtered and dried in the oven at 105°C for 8 h. The dried samples were allowed to cool to room temperature, sieved to different particle sizes and stored in air tight container for avoid change in its characteristics.

2.2. Characterization of the Carbon

The physicochemical properties of the activated *Mucuna pruriens* seed shells carbon; phosphoric acid treated activated carbon (PAMC) and sodium chloride treated activated carbon (SAMC) were determined using methods described by [13]. The Fourier transform infrared (FTIR) and X-ray Fluorescence (XRF) were used to ascertain the chemical groups and oxides present in the adsorbents respectively. X-ray diffraction (XRD) was used to determine their diffractive pattern. Scanning Electron Microscopy (SEM) was used to determine the surface morphology of MPS, PAMC and SAMC.

2.3. Batch Adsorption Studies

The vat yellow 4 (VY4) was of analytical grade and was used without further purification. 0.1g of VY4 (Fig. 1) was dissolved in 1000 ml of distilled water to get a dye solution of 100 mg/l. De-ionized water was used to prepare all solutions. VY4 (chemical formula = $C_{24}H_{12}O_2$ and formula weight = 332.35 g/mol) with 99.99% purity was obtained from LOBA Chemie PVT LTD., India. Dye adsorption experiments were performed adding a determined dose of adsorbent to 100 mg/l of dye solution (10 mg/l). The variables studied were particle size, solution pH, adsorbent dose, solution temperature, dye concentration and contact time. After desire time of treatment, the dye solution was centrifuged and the concentration of the residue was determined using the UV–vis spectrophotometer (Model UV 752) at maximum absorption, λ_{max} of 419 nm.

The equilibrium adsorption studies, experiments were carried out in a batch process at 303, 313, and 323 K using different initial dye concentrations of 100, 200, 300, 400 and 500 mg/l. The contents were shaken thoroughly using a stirrer rotating at 120 rpm for 60 min. The amount of dye adsorbed per unit mass of adsorbent was determined as follows [14]:

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

Where q_e is the equilibrium adsorption capacity per gram dry weight of the adsorbent, mg/g; C_0 is the initial concentration of dye in the solution (mg/l); C_e is the final or equilibrium concentration of dye in the solution (mg/l); V is the volume of the solution (l); and W is the dry weight of adsorbent (g).

The percentage dye removal was calculated as follows [11]:

$$\text{Percentage adsorbed} = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

Batch kinetic studies were carried out at different solution temperatures of 303, 313 and 323 K and contact times of 10, 20, 30, 45, 60, 90, 120 and 150 min, concentration of 100 mg/l and agitation speed of 120 rpm. The sorption capacity at a given time t , q_t (mg/g) was obtained using equation (3) as follows [15]:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (3)$$

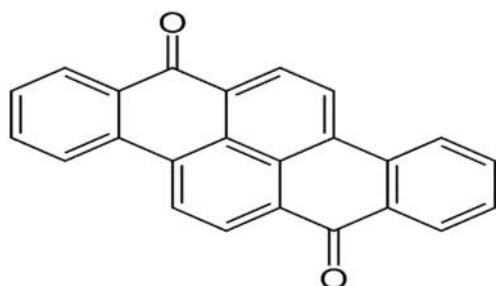


Fig. 1. Structure of vat yellow 4

3. RESULTS AND DISCUSSION

3.1. Characteristics of the Produced Carbon

3.1.1. Physicochemical Properties of the Carbon

The physicochemical properties of PAMC and SAMC are presented in table 1. The adsorbents were found to have a high percentage fixed carbon, surface area and iodine number. The iodine number and bulk density recommended as minimum by the AWWA (American Water Works Association) for activated carbon to be used in the removal of low molecular weight compound is 500 mg/g and 0.25 gm/ml respectively [16]. The pH value is near neutral which will be helpful for the treatment of all cases of dye wastewater and the carbons can also be used for drinking water purification [17]. PAMC and SAMC were found to have low ash content (5.38 and 5.62 % respectively). If the ash content is high, it will interfere with the pore structure development and hence adsorption will be less [16].

Table 1. Physicochemical properties of the carbon PAMC and SMAC

Property	Value	
	PAMC	SAMC
Ash content (%)	5.38	5.62
Bulk density (g/cm ²)	0.45	0.45

Fixed carbon (%)	80.37	80.20
Iodine number (mg/g)	724.61	821.22
Moisture content (%)	7.0	5.0
pH	7.3	7.1
Surface area (m ² /g)	847.43	838.65
Volatile matter (%)	14.25	14.18

3.1.2. Fourier Transforms Infrared Spectroscopy (FTIR) Study of the Carbon

FTIR was used for the identification of the functional groups and chemical structural elucidation of PAMC and SAMC. Adsorption in the IR region takes place because of rotational and vibrational movements of the molecules present in the functional groups [18]. The infrared transmittance was plotted against the wavelength (cm⁻¹). The FTIR spectrum of PAMC and SAMC are shown in fig. 1 and 2 respectively. The FTIR analysis of PAMC indicates the presence of C – Br stretch band of alkyl halides (564.20 cm⁻¹), C – N stretch of aliphatic amines (1115.86 cm⁻¹), and -C ≡ C- stretch of alkynes (2272.22 cm⁻¹). The O – H stretch of alcohols (3464.27, 3635.94, 3748.78 and 3852.94 cm⁻¹) and N – O asymmetric stretch of nitro compounds (1542.14cm⁻¹) which are very strong and broad band were also indicated in the activated carbon. SAMC indicates the presence of C – Br stretch band of alkyl halides (598.92 cm⁻¹), C – Cl stretch of alkyl halides (749.37 cm⁻¹), C – N stretch of aliphatic amines (1045.45cm⁻¹), and -C ≡ C- stretch of alkynes (2264.51 cm⁻¹). The O – H stretch of alcohols (3653.30, 3751.67, and 3867.40 cm⁻¹) and N – O asymmetric stretch of nitro compounds (1540.21cm⁻¹) which are very strong and broad band were also indicated in the activated carbon. The hydroxyl group is the most dominant amongst the other frequencies in PAMC. The O-H stretches in alcohols detected in the carbons are very strong and broad band which are important adsorption sites for VY4. The effect of the hydroxyl group is more experienced because of the hydrogen bonding with other hydroxyl bonds since they do not exist in isolation forming a stable structure [19].

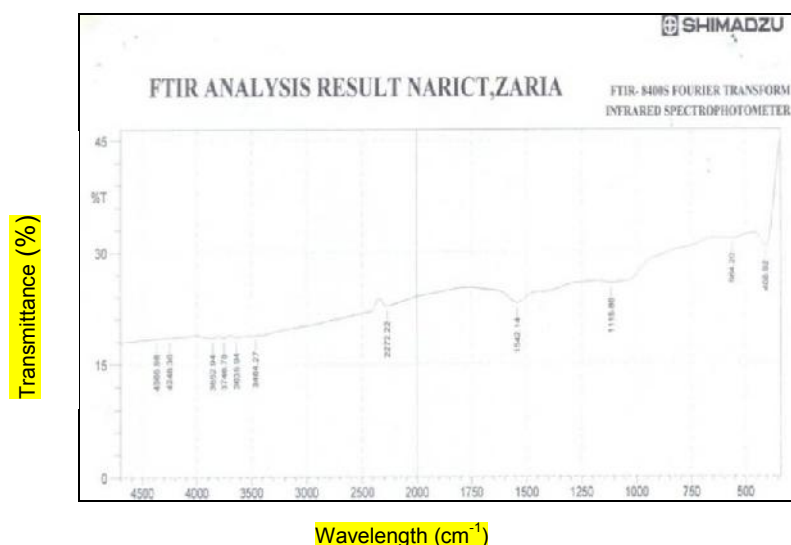


Fig. 2(a). FTIR spectrum on PAMC

Transmittance (%)

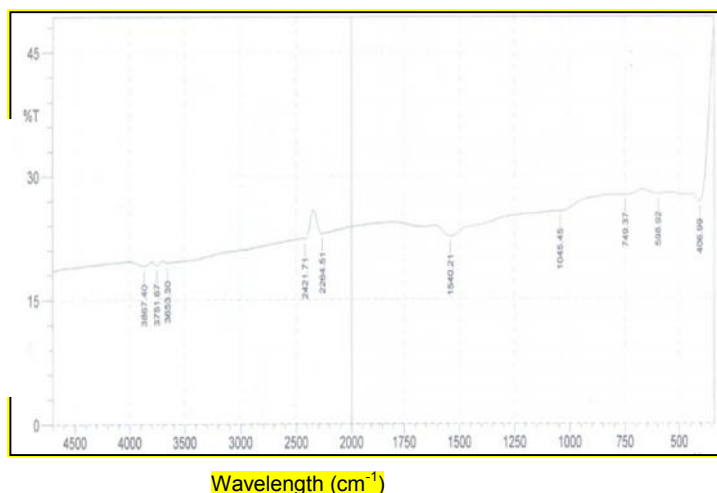


Fig. 2(b). FTIR spectrum on SAMC

3.1.3. X-ray Fluorescence (XRF) Spectrometry Analysis of the Carbon

XRF was used to determine the oxides present in PAMC and SAMC. The oxides present in the adsorbents may be attributed to adsorption study are shown in table 2. The oxides of calcium and potassium are the major constituents of the adsorbents which indicate that they can be a source of obtaining these elements.

Table 2. XRF results of the carbon (AMC)

Chemical constituent	Composition (%)	
	PAMC	SAMC
CaO	44.9	57.6
K ₂ O	22.1	20.4
P ₂ O ₅	10.4	8.37
Fe ₂ O ₃	11.5	5.14
TiO ₂	1.80	0.75
MnO	1.30	1.80
BaO	0.82	0.72
ZnO	0.57	1.10
CuO	0.27	0.38
Re ₂ O ₇	0.16	0.20
NiO	0.08	0.08

3.1.4. X-ray Diffraction (XRD) Spectrometry Analysis of the Carbon

XRD was used to determine the diffraction pattern and inter planar spacing of PAMC and SAMC. XRD pattern of the adsorbents were obtained on a powder X-ray diffractometer (Stchmabzu model 6000) with CuK α radiation having a scanning speed of 8.000 deg/min and tested at 40.0 kV and 30 mA. The patterns were recorded over a 2-theta (2θ) range of 2.0000 – 60.0000 deg. The XRD spectrum of the adsorbents showed broad peaks (fig. 3a and 3b), which indicates the presence of high content of amorphous form of carbon and fewer amounts of crystalline materials in the carbons. Their interplanar spacing, d calculated for the three strongest peaks in PMAC and SMAC were 9.0445, 4.76731 and 4.45514(Å); and 3.70739, 2.17612, 4.25500(Å) respectively.

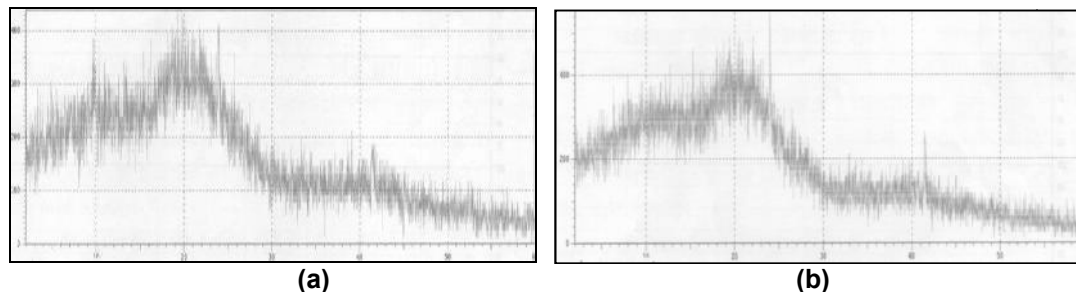


Fig. 3. XRD profile of (a) PAMC, (b) SAMC

3.1.5. Scanning Electron Microscopy (SEM) of the Carbon

SEM was used to determine the surface morphology of MPS, PAMC and SAMC. SEM images (figures 4 and 5) showed that phosphoric acid, H_3PO_4 treatment increased the porosity of MPS than sodium chloride, NaCl. The SEM of PAMC and SAMC (fig. 5) seems to be threadlike with, some breakage in nature and dotted illuminations.

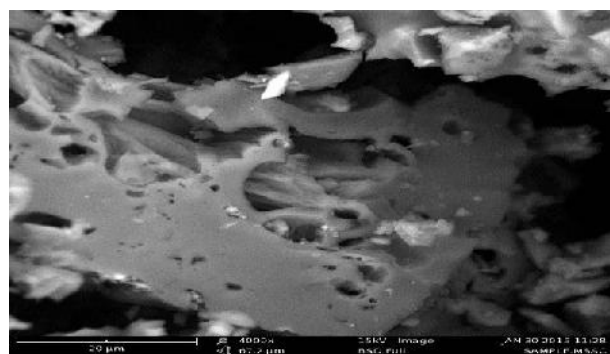


Fig. 4. SEM image on MPS

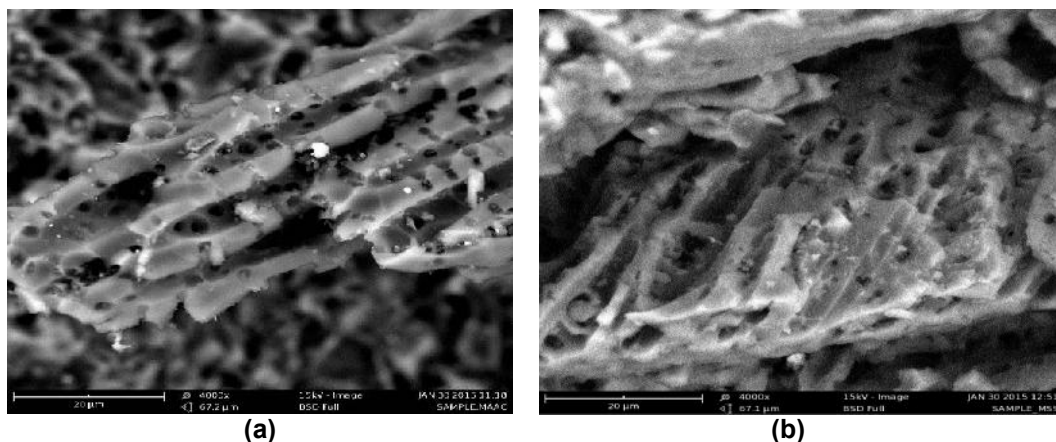


Fig. 5. SEM image on (a) PAMC, (b) SAMC

3.2. Effect of Process Variables on Adsorption Process

3.2.1. Effect of Particle Size

The study was carried out with different particle sizes of the adsorbents (PAMC and SAMC) of 0.30, 0.60, 0.85, 1.00 and 1.50 μm using adsorbent dose of 1g agitated for 1 h at 120 rpm and 303 K. Fig. 6 shows the effect of particle size on the adsorption of VY4 from aqueous solutions. The percentage removal of the dyes decreased with increase in particle size of the activated carbon. This may be attributed to the fact that smaller particles yield large surface areas [20].

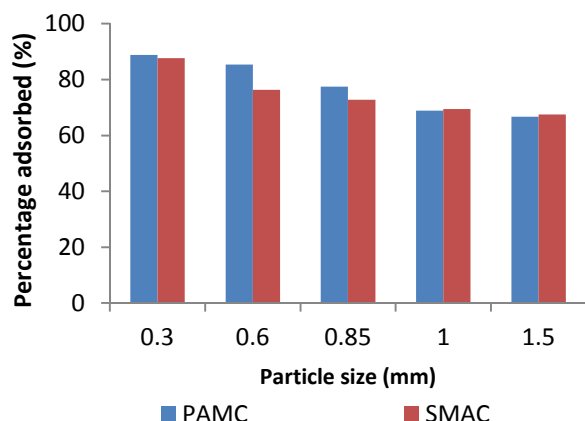


Fig. 6. Effect of particle size on VY4 adsorbed on PAMC and SAMC

3.2.2. Effect of Initial pH of Solution

The effect of pH on adsorption of dye was studied at pH range of 2–10 with 1g dose of adsorbent at 303 K. The pH was adjusted using 0.10 M HCl or 0.10 M NaOH aqueous solutions. The pH of the solution was determined using the potable pH meter. The result shows that the removal of VY4 is highly dependent on pH (Fig. 7). Higher uptakes obtained at lower pH of 2 on both adsorbents may be due to the electrostatic attractions between negatively charged functional groups located on the anionic dye and positively charged adsorbent surface [21]. Maximum removal efficiency was also achieved for anionic dyes at pH of 2 [1, 11].

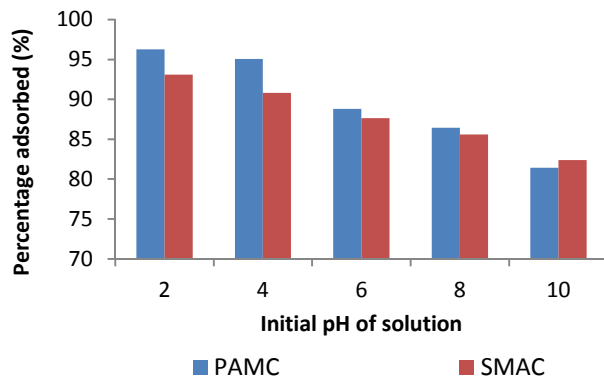


Fig. 7. Effect of solution pH on VY4 adsorbed on PAMC and SAMC

3.2.3. Effect of Adsorbent Dose

The effect of adsorbent dose was investigated between 0.2-2.0g at fixed temperature of 303K for 60 min (Fig. 8). The adsorption percentage increased as dosage of PAMC and SAMC were increased until saturation point was reached. This may be as a result of increase in the number of active sites [16], which nearly becomes constant as the dosage was increased further. Similar observations were reported in the literature by [22].

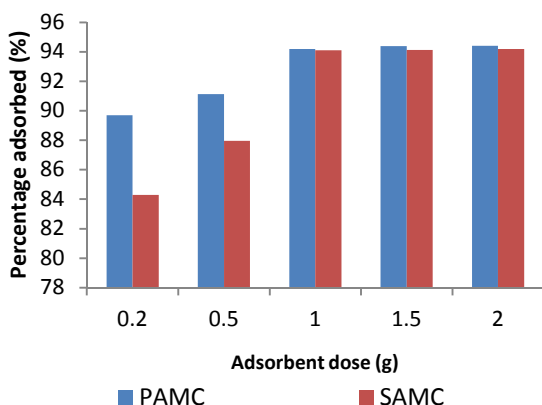


Fig. 8. Effect of adsorbent dose on VY4 adsorbed on PAMC and SAMC

3.2.4. Effect of Solution Temperature and Adsorbate Concentration

The influence of the dye concentration was investigated in the range of 100 – 500 mg/l at different temperatures at 303, 313 and 323 K as shown in fig. 9. The percentage removal of the dye decreased as the dye concentration was increased but the actual amount of dye adsorbed per unit mass of the adsorbent increased with increase in dye concentration showing that the adsorption is highly dependent on initial concentration of dye [23]. The percentage adsorbed slightly increased with increasing solution temperature from 303 to 323 K which indicates the endothermic nature of the process [10]. The increase in the adsorption capacity with temperature may be due to the increase in the mobility of the dye molecule with increase in their kinetic [10].

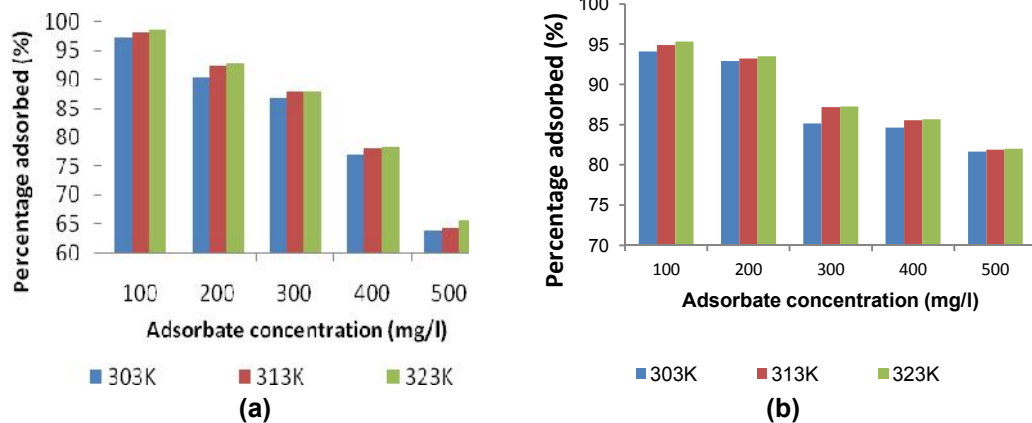


Fig. 9. Effect of concentration on VY4 adsorbed on (a) PAMC, (b) SAMC

3.2.5. Effect of Contact Time

Fig. 10 shows that the adsorption percentage increased with increasing the contact time from 10 -150 min. The rate of removal of the adsorbate is higher in the beginning due to the large surface area of the adsorbents available for the adsorption of dye ions and after a certain period, only a very low increase in the dye removal was observed because there are few active sites on the surface of adsorbents [24].

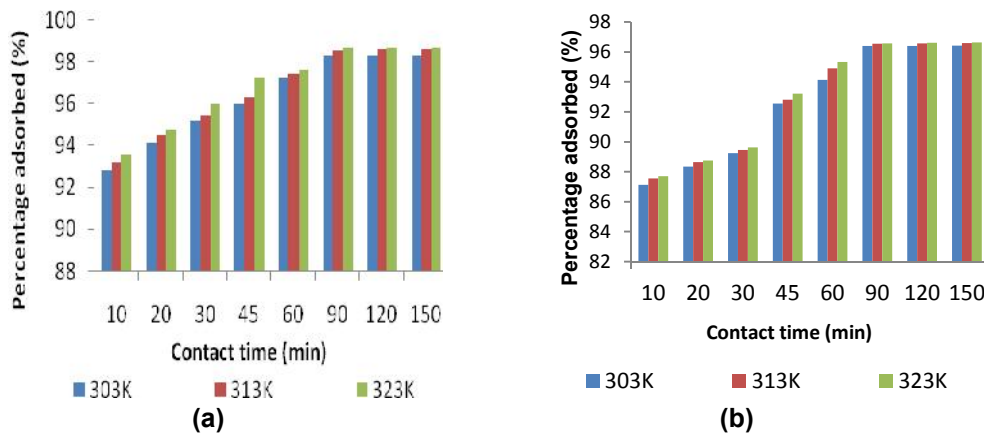


Fig. 10. Effect of contact time on VY4 adsorbed on (a) PAMC, (b) SAMC

3.3. Adsorption Isotherm

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state [25]. Different isotherms have been developed to describe equilibrium relationships. In the present study, Langmuir, Freundlich and Temkin were used to describe the equilibrium data.

3.3.1. Langmuir Isotherm

Langmuir isotherm assumes a monolayer coverage and uniform activity distribution on the adsorbent surface [26]. The linear form of Langmuir model [27]:

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

where C_e is the equilibrium concentration of dye (mg/l) and q_e is the amount of the dye adsorbed (mg) per unit of activated carbon (g). Q_m and K_L are the Langmuir constants related to the adsorption capacity (mg/g) and the equilibrium constant (l/mg) respectively. The separation factor (R_L) is used to predict whether an adsorption process is favourable or unfavourable. Langmuir isotherm is then classified using a dimensionless constant separation factor (R_L), which can be defined as [28]:

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

where K_L is a Langmuir constant. R_L value implies the adsorption to be unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$), or irreversible ($R_L = 0$). The plot of C_e/q_e against C_e is shown in fig. 11. The correlation coefficients (R^2) showed that the adsorption conformed to the Langmuir model since they are close to unity. The Langmuir adsorption isotherm was found to have the best fit to the experimental data, suggesting monolayer adsorption on a homogeneous surface [29]. The separation factors, R_L were found to be less than one indicating favourable adsorption (table 3).

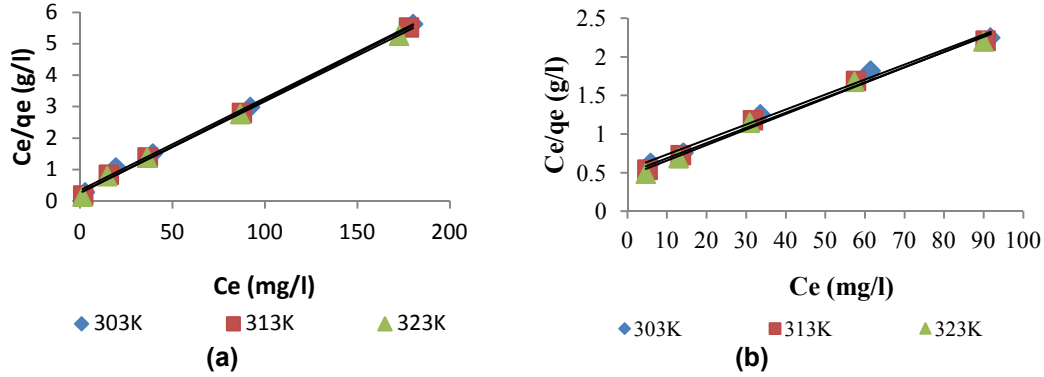


Fig. 11. Langmuir isotherm for the adsorption of VY4 on (a) PAMC, (b) SAMC

3.3.2. Freundlich Isotherm

Freundlich isotherm can be expressed as [20, 30]:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (6)$$

This equation can be linearized as:

$$\log q_e = \frac{1}{n} \log C_e + \log K_F \quad (7)$$

The respective Freundlich constants, n and k_f (table 3) were calculated from the slopes and intercepts of the linear plots (Fig. 12) of $\log q_e$ versus $\log C_e$. The values of k_f (measure of adsorption) increased with increasing temperature. The R^2 values obtained in table 4 portray that the adsorption of VY4 on the AMC conformed to the Freundlich isotherm generally.

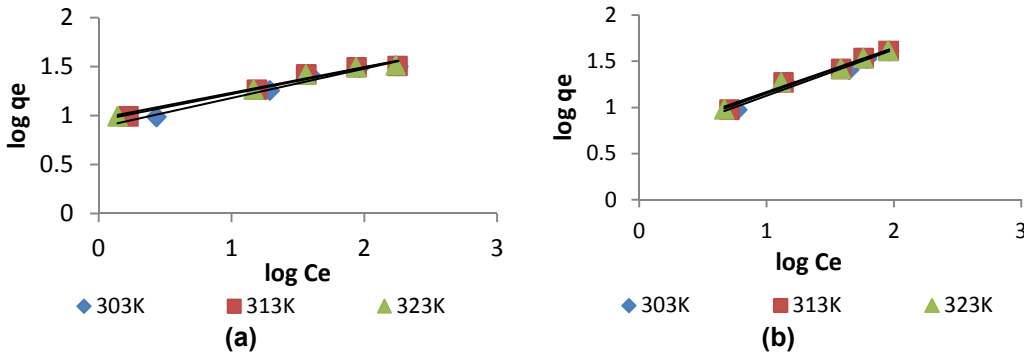


Fig. 12. Freundlich isotherm for the adsorption of VY4 on (a) PAMC, (b) SAMC

3.3.3. Temkin Isotherm

The Temkin isotherm has commonly been applied in the following form [31]:

$$q_e = \frac{RT}{b_T} \ln (A C_e) \quad (8)$$

The linear form of this isotherm can be given by

$$q_e = \frac{RT}{b_T} \ln A + \frac{RT}{b_T} \ln C_e \quad (9)$$

q_e is the amount adsorbed at equilibrium in mg/g; k_1 is the Temkin isotherm energy constant. The constants b_T which is related to the heat of adsorption and A which is the equilibrium binding constant corresponding to the maximum binding energy were determined from the plot of q_e versus $\ln C_e$ (Fig. 13). The constants are presented in table 3. The higher values of b_T indicate that the interaction between VY4

and the adsorbents were strong. The values of A increased with increase in temperature for VY4 adsorption. The correlation coefficients, R^2 value obtained indicate that the isotherm model fitted well to the equilibrium adsorption experimental data.

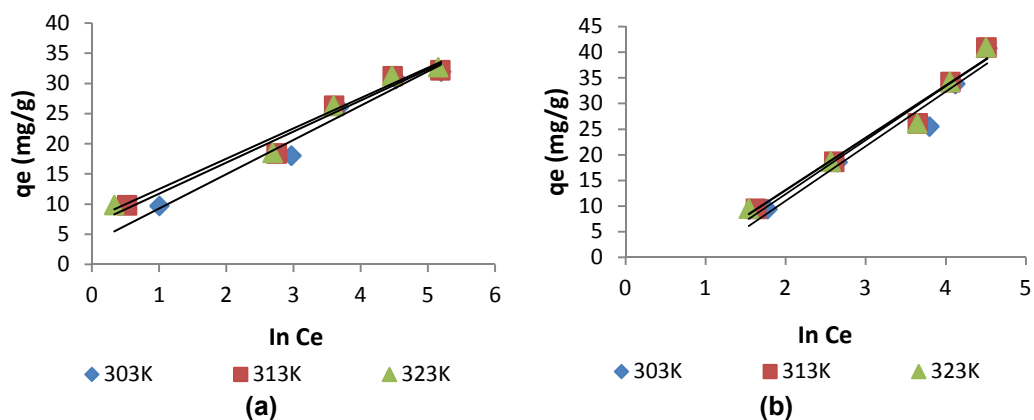


Fig. 13. Temkin isotherm for the adsorption of VY4 on (a) PAMC, (b) SAMC

Table 3. Calculated isotherm parameters for VY4 adsorption on PAMC and SAMC

Isotherm model	Temperature (K)					
	PAMC			SAMC		
	303	313	323	303	313	323
Langmuir						
Q_m (mg/g)	34.483	34.480	34.480	52.63	52.63	50.00
K_L (L/mg)	0.0861	0.1142	0.1151	0.0352	0.0390	0.0442
R_L	0.1041	0.0805	0.0799	0.2212	0.2044	0.1843
R^2	0.997	0.997	0.997	0.989	0.992	0.990
Freundlich						
N	3.3333	3.7175	3.8168	1.9960	2.0367	2.1008
K_f (L/g)	7.5336	8.8920	9.311	4.1976	4.5604	4.8865
R^2	0.962	0.969	0.978	0.989	0.981	0.978
Temkin						
b_T (J/mg)	442.73	505.69	534.09	236.98	247.84	263.79
A	1.8764	3.6135	4.4136	0.3827	0.4377	0.4901
R^2	0.965	0.969	0.973	0.949	0.969	0.966

3.4. Adsorption Kinetics

The kinetics of adsorption was studied in order to know the mechanism of the adsorption process. The following kinetic models were used.

3.4.1. Pseudo First-Order Kinetic Model

The pseudo-first-order Lagergren equation is given by [31]:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (10)$$

Where q_t and q_e (mg/g) are the amounts adsorbed at time t and equilibrium respectively and k_1 (min^{-1}) is the pseudo-first-order rate constant for the adsorption process. On integration under the boundary conditions of $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, gives a linear expression. The integrated linear form of equation (10) can be expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (11)$$

k_1 and q_e were determined from the slope and intercept of the plot $\log(q_e - q_t)$ versus t (Fig. 14). The pseudo first order rate constants calculated from the plots are given in table 5. The values of the correlation coefficients (R^2) indicate that the removal of VY4 on AMC generally follow the pseudo first – order kinetic model.

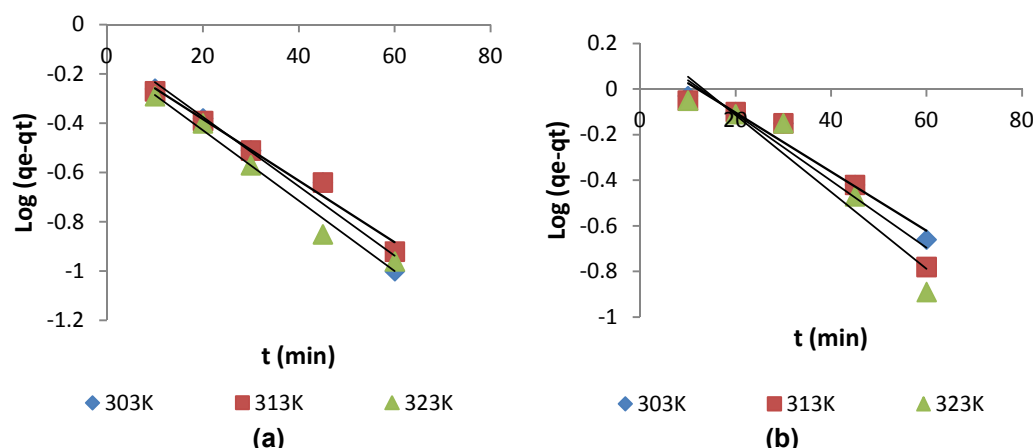


Fig. 14. Pseudo-first order kinetic plot on VY4 adsorption on (a) PAMC, (b) SAMC

3.4.2. Pseudo Second-Order Kinetic Model

The pseudo second – order adsorption kinetic rate equation is expressed in the form [30]:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (12)$$

Where, k_2 is the rate constant of pseudo second order adsorption (g/mg/min). For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of equation (12) becomes:

$$\frac{t}{q_t} = \frac{1}{k_2} + \frac{1}{q_e} t \quad (13)$$

The values of k_2 and q_e were calculated from the plots of t/q_t versus t as shown in fig. 15. The respective constant values are given in table 4. The R^2 values which are close to unity shows that the adsorption of VY4 on AMC is best described by the pseudo second-order mechanism. This suggests that the rate-limiting step is a chemical adsorption [32].

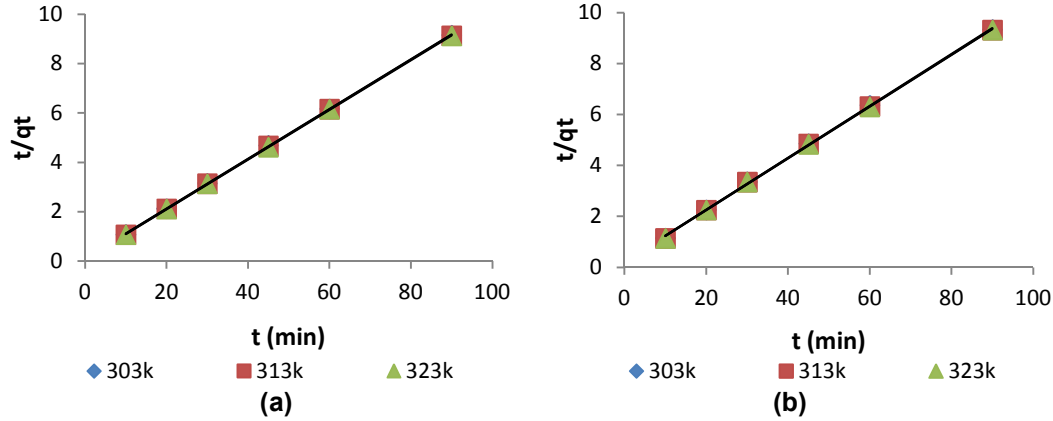


Fig. 15. Pseudo-second order kinetic plot on VY4 adsorption on (a) PAMC, (b) SAMC

3.4.3. Intraparticle Diffusion Kinetic Model

The intraparticle diffusion plot is the commonly used technique for identifying the mechanism involved in the adsorption mechanism. According to the theory proposed by Weber and Morris, the intraparticle diffusion model equation is given by [11, 33]:

$$q_t = k_{pi} t^{0.5} + C_i \quad (14)$$

where k_{pi} ($\text{mg/g/min}^{0.5}$), the rate parameter of stage i , is obtained from the slope of the straight line of q_t versus $t^{0.5}$ (Fig. 16) and C_i is the intercept of the plot that gives an idea about the thickness of the boundary layer. The values of intercept C_i (table 4) provide information about the thickness of the boundary layer. The C_i increased with increasing the solution temperature. Bayramoglu et al. [26] stated that if the regression of q_t versus $t^{0.5}$ is linear and passes through the origin, then intraparticle diffusion is the sole rate-limiting step. The linear plots did not pass through the origin which indicates that the intraparticle diffusion is involved in the adsorption of VY4 by AMC but it is not the only rate controlling step. Other mechanisms such as complexation or ion-exchange could also control this adsorption [33].

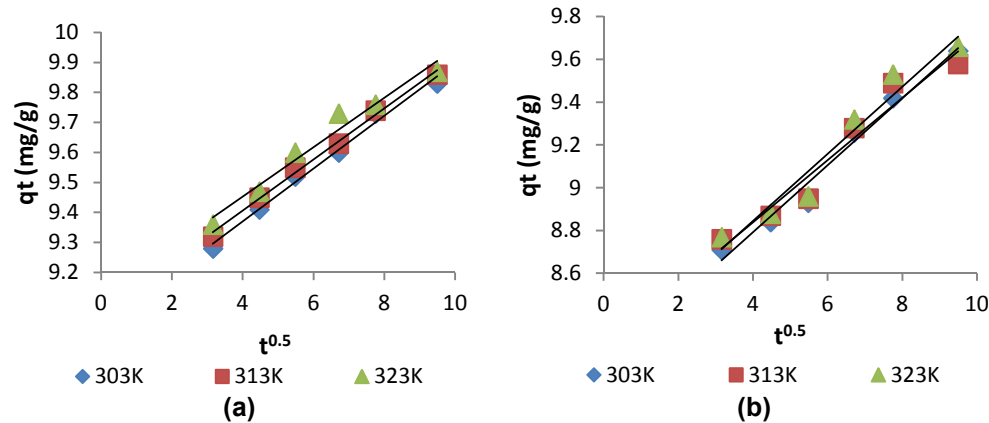


Fig. 16. Intraparticle diffusion plot on VY4 adsorption on (a) PAMC, (b) SAMC

3.4.4. Bhattacharya – Venkobachor Kinetic Model

Bhattacharya and Venkobachar equation is given by [34]:

$$\log(1 - U_{(t)}) = \frac{k_2}{2.303} t \quad (15)$$

Where C_i and C_t = concentration of dye at time zero and time t , respectively (mg/l).

q_e and q_t = amount of dye adsorbed at equilibrium time and time t , respectively (mg/g).

$$U_{(t)} = \frac{C_i - C_t}{C_i - C_e} \quad (16)$$

Where C_e = equilibrium dye concentration (mg/l) and k_1 = first order adsorption rate constant (min^{-1}). The linear plots of $\ln(1 - U_t)$ versus t (fig. 16) were used to obtain the constant, K_B at different temperatures (table 5). The values of correlation coefficient, R^2 showed that data obtained from the adsorption of VY4 on AMC conformed to the Bhattacharya - Venkobachor kinetic model.

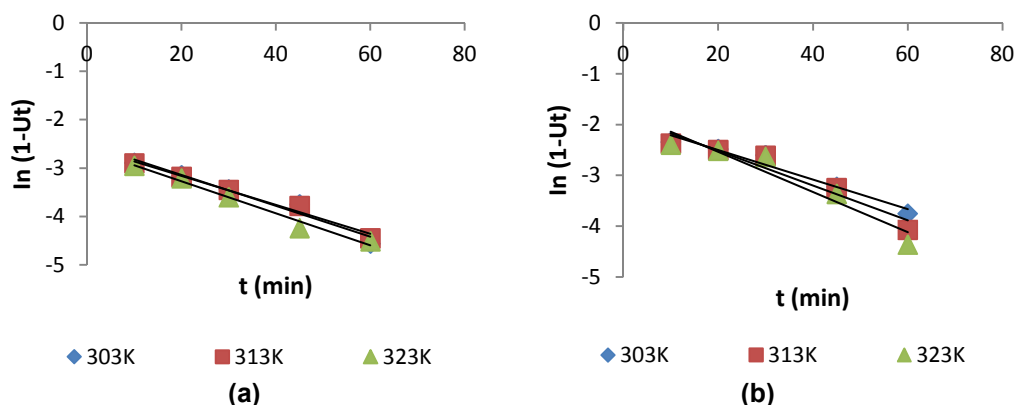


Fig. 17. Bhattacharya-Venokobachor kinetic plot on VY4 adsorption on (a) PAMC, (b) SAMC

Table 4. Calculated kinetic parameters obtained for the adsorption of VY4 on AMC

Kinetic model	Temperature (K)					
	PAMC			SAMC		
	303	313	323	303	313	323
Pseudo first-order						
k_1 (min^{-1})	0.0322	0.0276	0.0322	0.0276	0.0322	0.0368
q_e (mg/g)	0.8072	0.7345	0.7194	1.4256	1.5276	1.6672
R^2	0.962	0.981	0.980	0.958	0.921	0.912
Pseudo second-order						
k_2 (g/mg/min)	0.0909	0.0952	0.1064	0.0455	0.0470	0.0474
q_e (mg/g)	10.000	10.000	10.000	9.9010	9.9010	9.9010
R^2	0.999	0.999	0.999	0.999	0.999	0.999
Intra particle diffusion						
k_{pi} ($\text{mg g}^{-1} \text{min}^{-0.5}$)	0.088	0.085	0.082	0.156	0.145	0.157
C_i	9.017	9.065	9.122	8.164	8.255	8.217
R^2	0.989	0.994	0.968	0.976	0.947	0.952

Bhattacharya-Venkobachor						
$K_B \text{ (min}^{-1}\text{)}$	0.031	0.029	0.033	0.029	0.034	0.039
R^2	0.963	0.981	0.982	0.956	0.925	0.911

3.5. Adsorption Thermodynamics

Three thermodynamic parameters standard free energy (ΔG^0), standard enthalpy (ΔH^0) and standard entropy (ΔS^0) were used to characterize the adsorption process. The values of ΔH^0 and ΔS^0 can be evaluated from the following equation [28]:

$$\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (17)$$

where R (8.314 J/mol K) is the universal gas constant, T (K) is the absolute solution temperature and K_L (L/mg) is the Langmuir isotherm constant. ΔG^0 can then be calculated using the relation below [27, 35]:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (18)$$

The calculated thermodynamic parameters at three different temperatures of 303, 313 and 323 K are presented in table 5. The negative values of ΔG^0 confirm the adsorption process is feasible and the spontaneous in nature [35]. As temperature was increased, its feasibility and spontaneity increased. The change in adsorption enthalpy for physical adsorption is in the range of -20 to -40 kJ/mol, but chemisorptions are between -40 and -80 kJ/mol [26]. The values of ΔH^0 and ΔS^0 were calculated from the plots of $\ln K_L$ versus $1/T$ (Vant Hoff's plot). The positive value of enthalpy, ΔH^0 suggests that the adsorption process is endothermic in nature and the positive value of ΔS^0 shows the increased randomness at the solid/liquid interface [37]. The enthalpy change value 12.396 and 9.395 kJ/mol indicates that the uptake of VY4 on PAMC and SMAC respectively are physical adsorption.

Table 5. Thermodynamic parameters for the adsorption of VY4 on PAMC and SMAC

Adsorbent	Temperature (K)	ΔG^0 (kJ /mol)	ΔH^0 (kJ /mol)	ΔS^0 (J/K /mol)
PAMC	303	-6.303	12.396	20.843
	313	-6.511		
	323	-6.720		
SAMC	303	-0.943	9.395	3.143
	313	-0.974		
	323	-1.006		

4. CONCLUSION

The present study has established that *Mucuna pruriens* (Velvet bean) seed shells, locally sourced; less expensive and abundantly available bio-adsorbents in South-east, Nigeria can be used for the removal of vat yellow 4 (VY4) from wastewater. The results showed that adsorption is influenced by particle size, adsorbent dose, contact time, initial pH of solution, solution temperature and dye concentration. The equilibrium data fitted well to the Langmuir, Freundlich and Temkin models. The Langmuir adsorption isotherm was found to have the best fit to the experimental data obtained for vat yellow 4 removal, suggesting monolayer adsorption on a homogeneous surface. The mechanism of adsorption was best described by the pseudo second-order mechanism. The intra-particle diffusion played a role in the adsorption. The negative value of free energy indicates the spontaneity of the adsorption process. The

adsorption process was also found to be endothermic in nature. The feasibility and spontaneity of the process increased with increase in the solution temperature. The phosphoric acid treated adsorbent performed better than the sodium chloride treated adsorbent.

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