ADSORPTION OF A DYE (CRYSTAL VIOLET) ON AN ACID MODIFIED NON-CONVENTIONAL ADSORBENT

Oguanobi Nonso Collins¹, Onu Chijioke Elijah², Onukwuli Okechukwu D.¹

¹ Department of Chemical Engineering
Nnamdi Azikiwe University, P.M.B. 5025 Awka, Anambra State Nigeria
E-mail: oguanobinonso@gmail.com

² Department of Chemical Engineering
Chukwuemeka Odumegwu Ojukwu University, P.M.B 01, Uli, Anambra State Nigeria

ABSTRACT

This research is aimed at removal of crystal violet (CV⁺) dye from synthetic wastewater by an adsorption technique in the course of a batch process carried out with modified clay adsorbents from Awka. Acid activation is used as a modification method. The effect of the contact time, the initial concentration, pH, the temperature, the particle size, and the adsorbent dosage is followed. The raw and modified clays are characterized by scanning electron microscopy (SEM) and Fourier transform infrared (FTIR) analysis. The performance evaluation of the adsorbent is further evaluated at 323K using the linear and non-linear equilibrium models of Freundlich, Langmuir, Temkin and Dubinin-Radushkevich (D-R) adsorption isotherms and the kinetic models of a pseudo-first and a pseudo-second-order, as well as that of Elovich. The thermodynamic parameters ΔG, ΔH, ΔS and the activation energy Eₐ are evaluated. The system is optimized using RSM.

The modification applied results in an increase of the surface area and thus in an increase of CV⁺ adsorption in the batch system studies. The SEM images obtained show a clear difference in the samples morphology. It is found that the dye adsorption increases with the adsorbent particle size decrease and the increase of the initial dye concentration, the contact time, the temperature and the adsorbent dosage. Dubinin-Radushkevich isotherm provides the best description of the adsorption data, while the pseudo-second order model is the best one among those used for kinetic data treatment. The thermodynamic results indicate that a physical endothermic adsorption proceeds spontaneously under the conditions studied. The optimum point determined refers to pH of 6, temperature of 45°C, a concentration of 300 mg L⁻¹ and contact time of 66.2 min.

The results of this research verify that modified Awka clay is a good alternative non-conventional cost efficient adsorbent which can be used for dye removal from industrial effluents.

Keywords: adsorption, dye, thermodynamics, kinetics, isotherms.

INTRODUCTION

Concerns about environmental protection have increased over the years from a global view point. The exponentially growing population in the past decades changes the productivity and the consumption habits. The affluent life-style, the resource use and the continuing development of the industrial technologies is accompanied by rapid generation of municipal and industrial solid wastes [1].

Water pollution represents a great challenge. Activated carbon is a common adsorbent used to remove hazardous contaminants from wastewater [2]. Dyes are coloured compounds suitable for colouring textiles, wool, leather, paper and fibres. Natural dyes such as indigo have been in use for over 5000 years. Synthetic dyes have replaced natural dyes because of their low cost and vast range of new colours [3]. Today, more
than 10,000 dyes of different chemical structures are commercially available [4]. Effluents of textile, paper and pulp, paint, printing, cosmetic industries contain significant amounts of these dyes and must be treated to bring down their concentration to a permissible limit prior to their discharge into the water bodies as required by the environmental regulation act [5]. The dyes high solubility in water results in their wide dissemination into the environment, thus making them detrimental to crops, aquatic life and human health [6,7]. It is worth noting that most of these pollutants cannot be removed by the conventional wastewater purification systems [7]. The latter usually apply adsorption, precipitation, coagulation, flocculation, ion-exchange, reverse osmosis, sedimentation, electrochemical operation, and biological treatment [8]. However, all of these methods except adsorption suffer from one or other limitations and none of them provides the complete removal of color from wastewater [9]. Hence, adsorption is regarded superior to other methods [10]. Furthermore, adsorption is preferred as an effective technique due to its low cost and high treatment efficiency [11].

Adsorption is a major industrial separation technique used for effluent media purification. It is a mass transfer operation through which a solid material can selectively remove dissolved components from an aqueous solution by attracting the solute to its surface. Therefore, it involves interphase accumulation of concentrated substances. This separation technique finds wide application for dye removal from aqueous media. Specifically, adsorption finds application in textile, leather, dyeing, cosmetics, plastics, food and paper industries where water recovery is very essential. To achieve and sustain efficient recovery of the desired water quality, a careful selection of adsorbent is of paramount importance [7]. Activated carbon is a conventional adsorbent. It has a large surface area, a controllable pore structure, thermo-stability, and low acid/base reactivity. It is currently receiving great attention owing to its superior and efficient ability in air pollution control [12], solvent recovery [13]. But adsorption by activated carbon has some restrictions referring to activated carbon regeneration after exhaustion and adsorption efficiency loss [14]. Due to these restrictions, quest for non-conventional cost effective adsorbents is reviewed. Some examples amongst others include banana stalks [15], groundnut hulls [16], oil palm ash [17], oil palm fruit fibres [18], rice husks [19], periwinkle shells [20], palm kernel shells [21], coconut shells [22], cassava peels [23], papaya seeds [24]. Very recently, Metal organic frameworks (MOFs) are recently used in dye adsorption [25].

However, clay is singled out to be more effective and efficient adsorbent in dye removal among all non-conventional adsorbents due to its abundant availability, large surface area and high adsorption capacity. Clay can be in the form of granules or a powder [26]. Its adsorbing capacity increases through activation [27]. The latter can be acid, alkaline and thermal one. Acid activation is proved as the most effective [28].

This work is aimed at evaluating the effect of acid activation on the adsorptive properties of Awka clays on removal of dyes from an aqueous solution. It develops the best equilibrium model fitting the experimental data using non-linear forms of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms.

**EXPERIMENTAL**

**Materials and methods**

Milk colored clay material from Okpuno village in Awka South Local Government Area of Anambra state, Nigeria was used as the primary raw material. All chemicals/reagents employed were of an analytical grade. They were products of Bridge Head Market Onitsha, Anambra State, Nigeria. All solutions were prepared with distilled water.

**Acid activation of the clay sample**

The clay material was sun dried. Then it was ground using a laboratory mortar and pestle and sieved to a particle size of 75µm. The sample was mixed with HCl in w/v ratio of 1:5 (160 g of the clay sample was mixed with 800 ml of the prepared acid) in a flask. The resulting suspension was left to soak for 24 h. The resulting slurry was poured into a Buchner funnel to separate the acid and the clay. The clay residue was washed several times with distilled water until a neutral reaction was obtained (pH indicator was used). The clay slurry was
then dried in an oven at a temperature of 80°C for 4 h. The dried sample was crushed, sieved again and stored.

**Characterization**

The functional group of the activated and raw sample was determined using Fourier transform infrared (FTIR) spectroscopy. The latter was carried out using Shimadzu S8400 spectrophotometer using the conventional KBr disc method. The surface morphology of the adsorbent was determined using scanning electron microscopy. The analysis was carried out using Joel scanning electron microscope model JSM 6400 with coated gold film layers approximately 20 Å - 25 Å thick.

**Batch Adsorption Studies**

Batch experiments were conducted to investigate the effect of the adsorbent particle size, the adsorbent dose, the initial adsorbate concentration, the adsorption time, pH and the temperature on the adsorption studied. The CV+ sample was prepared by dissolving a known quantity in distilled water. It was used as a stock solution and diluted to the required initial concentration range (from 100 mg L⁻¹ to 500 mg L⁻¹). 100ml of CV+ solution of a known concentration (C₀) was mixed in a 250ml beaker with a required amount of the adsorbent and was shaken for different time duration. The solution pH was adjusted by using either 0.1N HCL or 0.1N NaOH. The solution was then filtered using a filter paper. UV-visible spectrophotometer was employed to determine the remaining concentrations of CV+ in the filtrate.

**Equilibrium Studies**

The equilibrium studies were carried out using the Langmuir, Freundlich, Temkim and Dubinin-Redushkevich isotherms.

The adsorbed amount at equilibrium, qₑ (mg g⁻¹), was calculated using the equation:

\[
q_e = \frac{(C_o - C_e) V}{W}
\]

where \(C_o\) and \(C_e\) (mg L⁻¹) were the initial and equilibrium liquid-phase concentrations of the dye, respectively, \(V\) (l) was the volume of the solution, while \(W\) (g) was the mass of the dry sorbent used.

The dye removal percentage was calculated on the ground of the expression:

\[
\text{Percentage removal} = \left( \frac{C_o - C_e}{C_o} \right) \times 100
\]

**Kinetic Studies**

The procedure of the kinetic experiments was basically identical to that of the equilibrium study. Aqueous samples were taken at definite time intervals and the dye concentration was measured.

The adsorbed amount at time t, \(q_t\) (mg g⁻¹) was calculated using the relation:

\[
q_t = \frac{(C_o - C_t) V}{W}
\]

**Isotherm models**

The adsorption isotherm provides the description of the interaction between the adsorbate and adsorbent of any system. The parameters obtained from the different models are used to identify the surface properties and the adsorbent affinity and hence to suggest the mechanism of the process studied. Four adsorption isotherms were employed in this study – that of Langmuir [29], of Freundlich [30], of Temkim [31], and of Dubinin-Redushkevich. The corresponding non-linearized forms are presented by Eqs. 4-7:

\[
q_e = \frac{Q_m K_L C_e}{1 + K_L C_e}; \quad R_L = \frac{1}{1 + K_L C_e}
\]

\[
q_e = K_F C_e^{1/n_F}
\]

\[
q_e = \frac{R T}{b_T} \ln (K_T C_e)
\]

\[
q_e = Q_m \exp \left(-b_{DR} \left[ RT \ln \left(1 + \frac{1}{C_e}\right) \right]^2\right)
\]

where \(Q_m\) (mg g⁻¹) and \(K_L\) (L mg⁻¹) are the Langmuir constants related to the adsorption capacity and energy of adsorption, respectively; \(C_e\) (mg L⁻¹) and \(q_e\) (mg g⁻¹) are the equilibrium concentration and the amount of the dye adsorbed at equilibrium, respectively; \(K_F\) and \(n_F\) are the Freundlich constants characterizing the adsorption capacity and adsorption intensity, respectively; B and \(K_T\) are the Temkin isotherm constants, R is the gas constant (8.314 J mol⁻¹K⁻¹), while T is the absolute temperature (K).
Kinetic Models

The study of the adsorption kinetics is very important aiming to understand the adsorption dynamics in relation to time. The most common models used to fit the kinetic sorption experiments are those of the pseudo first and pseudo second order. They were used in this study together with the Elovich model. The corresponding forms are described by Eqs. 8-11;

\[ q_e = q_0[1 - \exp(-K_1t)] \]  
\[ q_t = \frac{K_2q^2_e}{1+K_2q_e t} \]  
\[ q_t = \frac{1}{\beta} \ln(1+\alpha\beta t) \]  
\[ q_e = K_{id}\sqrt{t} \]

Where \( q_e \) (mg g\(^{-1}\)) and \( q_t \) (mg g\(^{-1}\)) are the adsorbate amount at equilibrium and at time \( t \), respectively; \( K_1 \) (min\(^{-1}\)) and \( K_2 \) (g mg\(^{-1}\) min\(^{-1}\)) are the pseudo first order and pseudo second order adsorption rate constants, respectively; \( k_{id} \) (mg g\(^{-1}\) min\(^{-1/2}\)) is the rate parameter of stage i. It is obtained from the slope of the straight line of \( q_t \) versus \( t^{1/2} \).

Adsorption Thermodynamics

The thermodynamic parameters characterizing the process studied are evaluated using the following equations:

\[ \Delta G^o = -RT \ln K_c \]  
\[ K_c = \frac{c_s}{c_e} \]  
\[ \ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \]

where \( \Delta G^o \), \( \Delta H \), \( \Delta S \) are the standard free energy change, the standard enthalpy change and the standard entropy change, respectively; \( K_c \) is the equilibrium constant; \( C_s \) is the equilibrium concentration of CV\(^+\) in solution (mg L\(^{-1}\)); \( R \) is the ideal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), while \( T \) is the adsorption temperature (K).

Activation energy

The activation energy can be calculated using the Arrhenius equation whose linear form is given by:

\[ \ln K = \ln A - \frac{E_a}{RT} \]  

There \( A \) is the frequency factor (min\(^{-1}\)), \( E_a \) is the activation energy (kJ mol\(^{-1}\)), while \( T \) is the absolute temperature (K).

RESULTS AND DISCUSSION

Characterization Results

FTIR analysis

The FTIR spectrum of AC is shown in Figs. 1(a), 1(b), and 1(c). They refer to raw clay (RAC), HCL activated (HAC), ACV\(^+\) on HAC (following CV\(^+\) adsorption), respectively. It is evident that some peaks are shifted or disappear, while some new peaks are detected. The changes observed in the spectrum are connected with possible involvement of some functional groups on the adsorbent surface. The presence of polar groups there is likely to provide considerable cation exchange capacity of the adsorbent. The wave number range of 3697.67 cm\(^{-1}\) - 3620.60 cm\(^{-1}\) indicate the presence of amide and alcohol (N-H/O-H stretching), that of 3420.19 cm\(^{-1}\) - 3422.23 cm\(^{-1}\) is attributed to the presence of alcohol (O-H stretching), that of 1635.80 cm\(^{-1}\) - 1636.82 cm\(^{-1}\) indicates the presence of alkene (C=C stretching), that of 1031.63 cm\(^{-1}\) - 912.10 cm\(^{-1}\) shows the presence of alkyl halides (strong C-O stretching), that of 796.36 cm\(^{-1}\) - 694.46 cm\(^{-1}\) refers to the presence of alkyl halides (strong C-Cl stretching), that of 536.64 cm\(^{-1}\) - 534.40 cm\(^{-1}\) indicates the presence of alkyl halides (C-Br stretch), while that of 467.47 cm\(^{-1}\) - 425.08 cm\(^{-1}\) the is attributed to the presence of alkyl halides (C-I stretching). These functional groups play an important role in the course of the adsorption due to their properties. The oxygen-containing functional groups can provide numerous adsorption sites and thus increase the adsorption capacity in respect to the dye molecules. The presence of nitrogen groups on the adsorbent surface of adsorbent provides the removal of dyes and organic pollutants.

SEM micrographs

Figs. 2(a), 2(b) and 2(c) present the SEM micrographs of AC sample in its raw state, that following the activation applied and the corresponding CV\(^+\) adsorption, correspondingly. It is clear from Figs. 2(a) and 2(b) that
Particle size effect

The particle size effect is studied in case of particle size ranging from 75 µm to 850 µm. The results obtained are shown in Fig. 3. It is seen that the percentage removal decreases with particle size increase. This is so because the smaller particles provide a larger surface area. Furthermore, the breaking of the larger particles tends to open tiny cracks and channels leading to greater accessibility and hence better diffusion. Similar results are reported in ref. [32].

Adsorbent dosage effect

The dosage effect is studied in case of its variation from 0.1 g to 0.5 g. The results obtained show that, as the adsorbed amount increases with the dosage increase as illustrated in Fig. 4. This is due to the increase of the surface area [33]. It is also observed that the amount
adsorbed per unit mass of the adsorbent decreases with the adsorbent dosage increase. This effect is explained with the presence of adsorption sites left unoccupied. Similar results are reported in ref. [32].

Concentration and contact time effect

The initial concentration effect is in case of its variation from 100 mg L⁻¹ to 500 mg L⁻¹. The contact time varies from 2 min to 150 min. The results obtained are presented in Fig. 4. It is evident that the amount of CV⁺ adsorbed per unit mass increases with the initial ion concentration increase. This is so because the ratio of the initial number of dye molecules and the available surface area is low at lower concentrations [33]. The further increase of the adsorbate initial concentration results in increase of the adsorbed amount as the active sites on the adsorbent surface stays unchanged. This is so because the initial dye concentration provides the driving force to overcome the resistance to the mass transfer of the dye from the bulk of the solution to the solid surface of the adsorbent. Similar results are reported in ref. [32]. Besides, the adsorbed amount increases with the contact time increase at all initial concentrations studied. The results presented show that CV⁺ adsorption is a three-step process including: (i) a rapid initial adsorption; (ii) a period of slower uptake; (iii) a period of no significant
uptake. The first step is attributed to the instantaneous occupation of the most readily available active sites on the adsorbent surface (bulk diffusion). The second step referring to additional adsorption is attributed to the diffusion of the adsorbate from the surface film to the micro-pores present (pore and intra-particle diffusion) stimulating further CV⁺ molecules transfer from the liquid phase to the clay surface. The last stage is an equilibrium one [34]. Similar behavior is observed in case of Congo red dye adsorption on raw pine and an acid treated pine cone powder [35].

**pH effect**

The effect of solution pH is important when the adsorbing molecules are capable of ionizing [36]. The percentage of CV⁺ dye adsorption is studied and illustrated in Fig. 6. CV⁺ is a cationic dye. The adsorption capacity and the corresponding rate constant of cationic dyes tend to increase with initial solution pH increase as the number of OH⁻ ions accumulated on the adsorbent surface increases. The effect of pH is studied in the course of its variation between 2 and 10. This is illustrated in Fig. 6. It is seen that the maximum removal efficiency is achieved around pH of 6. The number of the positively charged ions on the clay surface increases at pH < 6 and hence the dye cations adsorption is not favored because of the electrostatic repulsion present. Besides, the presence of excess H⁺ ions competing with the dyes cations for the clay adsorption sites may also decrease CV⁺ adsorption [37]. The decrease of the dye percentage removal in an alkaline medium may be due to the adsorbent surface hydrolysis creating positively charged sites [38]. Similar results are reported for the adsorption of MB on yellow passion fruit peel [39] and that of a basic dye using acid treated kenaf fiber char [40].

![Fig. 6. Effect of pH on adsorption of CV⁺.](image)

**Temperature effect**

The study of the temperature effect on the adsorption process is important as it indicates whether the change is exothermic or endothermic one [41]. The temperature values are ranged in the present investigation from 303K to 323K. The results obtained are shown in Fig. 7. It is seen that the amount of CV⁺ adsorbed on activated clay increases with temperature increase which is valid for an endothermic process [42]. The effect reported refers to the increase of the dye molecules mobility and that of the active sites number with temperature increase [41, 42]. It is so because an increasing number of molecules can obtain the energy required for the interaction with the surface active sites. Furthermore, the temperature increase can bring about a swelling effect within the internal structure of the clay which in turn can enable the further penetration of the large dye molecules.

**Equilibrium modeling**

The adsorption isotherm describes the relationship between the mass of adsorbate per unit weight of adsorbent and the equilibrium bulk concentration of the adsorbate [43]. The results obtained in the present investigation are analyzed using the non-linear forms of the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms. They are presented by Eqs. 4-7, while the corresponding plots are shown in Fig. 8.

![Fig. 7. Effect of temperature on HAC CV⁺ adsorption.](image)

![Fig. 8. Non-linear isotherm plot for adsorption CV⁺ on HAC (A plot of qₑ against Cₑ).](image)
The Langmuir isotherm assumes that the adsorption occurs at the homogeneous adsorbent surface, which is saturated when the dye molecules occupy all available active sites. The values of the constants $K_L$ and $q_m$ of the non-linear model are estimated using the Excel software. In 2007 Ramesh et al. [45] reported that the Freundlich isotherm constant $n_f$ can be used to identify the favorability of the adsorption process. When the value of $n_f$ is within the range of $1 < n_f < 10$, the adsorption is favorable. If not, it is unfavorable. The constant $K_f$ measures the adsorption capacity. The Freundlich constants values are listed in Table 1. It is seen that lie $n_f$ values are within the range of $1 < n_f < 10$ verifying a favorable uptake of CV$^{+}$ dye.

The Freundlich isotherm is applied to an adsorption on a homogenous surface whose binding sites are not equivalent. The values of the constants $K_F$ and $n_F$ of the non-linear model are estimated using the Excel software. In 2007 Ramesh et al. [45] reported that the Freundlich isotherm constant $n_f$ can be used to identify the favorability of the adsorption process. When the value of $n_f$ is within the range of $1 < n_f < 10$, the adsorption is favorable. If not, it is unfavorable. The constant $K_f$ measures the adsorption capacity. The Freundlich constants values are listed in Table 1. It is seen that lie $n_f$ values are within the range of $1 < n_f < 10$ verifying a favorable uptake of CV$^{+}$ dye.

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The Temkin isotherm provides information on the heat of the adsorption (weather the adsorption process is endothermic or exothermic) and the adsorbate-adsorbent interaction. It is assumed that the energy of the molecule adsorption decreases linearly with coverage increase. The constants $K_T$ and $b_T$ of the non-linear model are evaluated using the Excel software and the values obtained are listed in Table 1. The positive value of $b_T$ indicates that the adsorption reaction is endothermic [46].

The Dubinin-Radushkevich (D-R) isotherm predicts the adsorption effect, i.e. weather the process of adsorption is a physical or a chemical nature. This is done on the ground of the value of mean free energy [47]. The values of $K_{DR}$ and $B$ constants are determined using the Excel software and are listed in Table 1. $K_{DR}$ is related to the mean free energy of adsorption through Eq.17 [47].

$$E = \frac{1}{\sqrt[2]{K_{DR}}}$$  \hspace{1cm} (17)

The adsorption process is considered of a physical nature when the value of $E$ is less than 8 KJmol$^{-1}$, while the value of $E$ for a chemical adsorption process is within the range of 8 kJ mol$^{-1}$–16 kJ mol$^{-1}$[47-49]. The value of $E$ as seen from Table1 is within the range of 0 kJ mol$^{-1}$–8 kJ mol$^{-1}$. It verifies that the adsorption process of CV$^{+}$ dye is a physical one.

To define the model that better fitted the experimental values in adsorption study, The correlation coefficient ($R^2$) and the normalized standard deviation ($\Delta q_e$) are used to identify which adsorption isotherm provides the best description of the process studied. The reason for

| Table 1. Calculated isotherm parameters for the adsorption of CV$^{+}$ on HAC Temperature 323K. |
|---------------------------------|-----------------|-----------------|
| **Linear**                     | **Non-linear**  |
| Langmuir                       |                 |
| $q_m$                          | 79.3651         | 69.2606         |
| $K_L$                          | 0.2505          | 3.6068          |
| $R^2$                          | 0.9779          | 0.98628         |
| $R_L$                          | 0.00792         | 0.00055         |
| $\Delta q_e$%                  | 4.68517         |                 |
| Freundlich                     |                 |
| $n_f$                          | 8.95255         | 1.38            |
| $K_F$                          | 43.4887         | 3.01615         |
| $R^2$                          | 0.9759          | 0.9144          |
| $\Delta q_e$%                  | 11.7029         |                 |
| Temkin                         |                 |
| $B$                            | 534.709         | 255.374         |
| $K_T$                          | 40160           | 35.6813         |
| $R^2$                          | 0.8968          | 0.99344         |
| $\Delta q_e$%                  | 3.24075         |                 |
| Dubinin-Radushkevich           |                 |
| $K_{DR}$                       | 59.6563         | 75.6664         |
| $B$                            | 4.00E-09        | 9.91E-06        |
| $E$                            | 0.09155         | 0.22457         |
| $R^2$                          | 0.7928          | 0.99999         |
| $\Delta q_e$%                  | 1.70114         |                 |

The Langmuir isotherm assumes that the adsorption occurs at the homogeneous adsorbent surface, which is saturated when the dye molecules occupy all available active sites. The values of the constants $K_L$ and $q_m$ are estimated using the Excel software. The essential feature of the Langmuir isotherm can be expressed by $R_L$, a dimensionless constant, which can be treated as a separation factor or an equilibrium parameter. $R_L$ is calculated using the equation considered in ref. [44]. Its value indicates whether the adsorption is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The values of the Langmuir constants and $R_L$ are listed in Table 1. It is seen that CV$^{+}$ dye uptake is favorable.
not using $R^2$ in testing the best fit of a non-linear model is because SS Regression + SS Error do not equal SS Total in the non-linear regression. This completely invalidates $R^2$ for non-linear models. It is true that some software packages calculate $R^2$ for non-linear regression. However, academic studies have shown that this approach is invalid. Using $R^2$ to evaluate non-linear models will generally lead you astray [50]. The best fit of $R^2$ in a linear model is when its value is close to unity, while that of $\% \Delta q_e$ in a non-linear model is the smallest.

Table 1 shows that the Langmuir model yields the highest value of the correlation coefficient ($R^2$) of 0.9779 compared to that of Freundlich, Temkin and D-R linear models. The D-R model yields the lowest value of the normalized standard deviation of 1.701141 compared to those of the Langmuir, Freundlich and Temkin non-linear models. The deviation in the fit model (from Langmuir to D-R) may be as a result of a linearization error. In 2008 El-Khaiari [51] suggested that the linearized equation apparently generated a real problem and an error arising from the complexities and the complications connected with the simultaneous transformation of the data leading to violation of the isotherms theories. In 2009 Hong et al. [52] pointed out that substantial constriction related to the linearized isotherm expressions, which produce a vast amount of different outcome, implicitly alter the error structure, violate the error variance and normality assumptions of standard least squares leading thus to adsorption data bias. In 2007 Mane et al. [53] concluded that the linearization isotherm model was inappropriate in predicting the fit for a particular set of conditions due to an error arises during the linearization. In 1984 Harter [54] concluded that the non-linear models yielded a more precise and accurate estimation.

**Kinetics modeling**

The pseudo-first and pseudo-second-order, Elovich and intra-particle kinetic models are used to fit the experimental data referring to the adsorption kinetics of $CV^+$ on HAC. The pseudo-first and pseudo-second-order kinetic models assume that the adsorption is a pseudo-chemical reaction. The Elovich model is preferred [55] in case the adsorption proceeds through chemisorption. The details referring to non-linear forms are described by Eqs. 8-11, while the corresponding graphs are presented in Fig. 9.

From pseudo-first-order values of $K_1$ and $q_e$ are estimated using the Excel software. They are listed in Table 2. It is evident that $q_e$ values do not agree with the experimental one, while that of $\% \Delta q_e$ is higher than that of the pseudo-second order model. Hence, the pseudo-first order model does not fit well.

The pseudo-second-order model is also used. The value of $K_2$ and $q_e$ are estimated using the Excel software. The values of $K_2$, $R^2$ and $q_e$ are listed in Table 2. It is seen that $R^2$ value is higher than that of the pseudo first order and the Elovich model. Besides, the calculated $q_e$ value is in agreement with the experimental one. The non-linear parameter ($\% \Delta q_e$) value obtained is smaller than that of the pseudo-first-order and the Elovich model. This indicates that the adsorption kinetics is better described by the pseudo-second-order model.

The Elovich model is also applied. Its parameter $\beta$ refers to the desorption constant [56, 57]. The values
of β and α for the non-linear model are estimated using the Excel software. They are listed in Table 2. It is seen that R² value is smaller than that of the pseudo-second-order, while % ∆qe value is higher than those of the pseudo-first and the pseudo-second-order. Hence, it can be concluded that the Elovich model does not fit well. The smaller value of β is also indicative of the almost irreversible adsorption of CV⁺ on HAC.

**Thermodynamic Study**

The variation of dye removal efficiency with the temperature increase can be explained on the ground of the values of the thermodynamic parameters ∆G°, ∆H° and ∆S° [58] estimated using Eqs. (12 - 14). The plot of ln Kc versus T⁻¹ referring to CV⁺ adsorption is presented in Fig.10. The values of the slope and the intercept obtained by a curve-fitting program are used to calculate ∆H and ∆S. The values of ∆G, ∆H and ∆S are shown in Table 4. The negative value of ∆G indicates that the adsorption is a spontaneous one, the positive value of ∆H shows that it is endothermic, while the positive value of ∆S suggests increased randomness at the solid/solution interface during CV⁺ adsorption on HAC as it corresponds to an increase of the degree of freedom of the adsorbed species [40]. Thus, it can be concluded that CV⁺ adsorption is favored. Similar phenomenon is observed in case of removal of Congo red from an aqueous medium using jujuba seeds [59].

**Activation energy**

The magnitude of the activation energy yields information on whether the adsorption is mainly physical or chemical. The Arrhenius equation is applied (Eq. 16) to evaluate

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>T(K)</th>
<th>∆G(KJ/MOL)</th>
<th>∆S(J/mol K)</th>
<th>∆H(KJ/mol)</th>
<th>Ea (KJ/mol)</th>
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<td>1180.67</td>
<td>-358042</td>
<td>33.7839</td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>-2837</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Calculated kinetic parameters for the adsorption of CV⁺ on HAC.

<table>
<thead>
<tr>
<th>Source</th>
<th>Std. Dev.</th>
<th>R-Squared</th>
<th>Adjusted R-Squared</th>
<th>Predicted R-Squared</th>
<th>PRESS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear</td>
<td>3.76</td>
<td>0.4774</td>
<td>0.3938</td>
<td>0.2913</td>
<td>478.71</td>
</tr>
<tr>
<td>2FI</td>
<td>4.07</td>
<td>0.5345</td>
<td>0.2896</td>
<td>-0.3131</td>
<td>886.94</td>
</tr>
<tr>
<td>Quadratic</td>
<td>0.76</td>
<td>0.9873</td>
<td>0.9755</td>
<td>0.9351</td>
<td>43.84</td>
</tr>
<tr>
<td>Cubic</td>
<td>0.31</td>
<td>0.9990</td>
<td>0.9957</td>
<td>0.8793</td>
<td>81.50</td>
</tr>
</tbody>
</table>

Table 3. Thermodynamics parameters for the adsorption of CV⁺ on HAC.

Table 4. Model Summary Statistics for CV⁺ adsorption on HAC.
the activation energy of adsorption. Fig. 11 shows the corresponding plot, while Table 3 present the values determined. It is seen that \( E_a \) is less than 40 KJ mol\(^{-1}\). This indicates that CV\(^+\) adsorption on HAC is in fact a physisorption process.

In 2007 Wu [60] suggested that the physisorption process normally had activation energy ranging from 5 KJ mol\(^{-1}\) to 40 KJ mol\(^{-1}\), while that of the chemisorption one was higher (40 KJ mol\(^{-1}\)– 800 KJ mol\(^{-1}\)). In 2005 Al-Ghouti et al. [61] accepted that the low activation energy values (< 42 KJ mol\(^{-1}\)) indicated diffusion control processes, while the higher activation energy values (> 42 KJ mol\(^{-1}\)) referred to chemically controlled one. Moreover, the lower values of \( E_a \) (\( E_a < 40 \text{ KJ mol}^{-1} \)) indicate that CV\(^+\) physical adsorption is in fact the rate-controlling step. A similar phenomenon was observed in case of adsorption of a basic dye on an acid treated kenaf fiber char [40].

### OPTIMIZATION USING RESPONSE SURFACE METHODOLOGY

#### ANOVA Analysis of CV\(^+\) Removal

A design expert trial version is used to analyze the results obtained in this investigation. The summarized \( P \)-value and model statistics are shown in Table 4.

A quadratic model is suggested on the ground of the CCD module of high adjusted and predicted R-squared values of 0.9755 and 0.9351, respectively. The cubic model is aliased because CCD does not contain enough runs to support it. The analysis of the variance (ANOVA) carried out confirms the adequacy of the quadratic model. The ANOVA results are given in Table 5.

All terms whose \( P \)-values are less than 0.05 are considered significant [62]. Therefore, A, B, C, D, BC, BD, \( A^2 \), \( B^2 \) and \( C^2 \) are significant terms. The empirical

---

**Table 5. ANOVA analysis for CV\(^+\) adsorption on HAC.**

<table>
<thead>
<tr>
<th>Sum of Source</th>
<th>Mean Squares</th>
<th>df</th>
<th>Square</th>
<th>F Value</th>
<th>Prob &gt; F</th>
<th>p-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>666.91</td>
<td>14</td>
<td>47.64</td>
<td>83.44</td>
<td>&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>A-pH</td>
<td>10.47</td>
<td>1</td>
<td>10.47</td>
<td>18.33</td>
<td>&lt; 0.0007</td>
<td></td>
</tr>
<tr>
<td>B-Temperature</td>
<td>92.60</td>
<td>1</td>
<td>92.60</td>
<td>162.19</td>
<td>&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>C-Concentration</td>
<td>132.46</td>
<td>1</td>
<td>132.46</td>
<td>232.02</td>
<td>&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>D-Time</td>
<td>86.94</td>
<td>1</td>
<td>86.94</td>
<td>152.29</td>
<td>&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>AB</td>
<td>8.556E-003</td>
<td>1</td>
<td>8.556E-003</td>
<td>0.015</td>
<td>0.9042</td>
<td></td>
</tr>
<tr>
<td>AC</td>
<td>2.20</td>
<td>1</td>
<td>2.20</td>
<td>3.85</td>
<td>0.0686</td>
<td></td>
</tr>
<tr>
<td>AD</td>
<td>0.70</td>
<td>1</td>
<td>0.70</td>
<td>1.23</td>
<td>0.2851</td>
<td></td>
</tr>
<tr>
<td>BC23.84</td>
<td>1</td>
<td>23.84</td>
<td>41.76</td>
<td>&lt; 0.0001</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BD</td>
<td>9.29</td>
<td>1</td>
<td>9.29</td>
<td>16.27</td>
<td>0.0011</td>
<td></td>
</tr>
<tr>
<td>CD</td>
<td>2.57</td>
<td>1</td>
<td>2.57</td>
<td>4.50</td>
<td>0.0510</td>
<td></td>
</tr>
<tr>
<td>A2</td>
<td>33.92</td>
<td>1</td>
<td>33.92</td>
<td>59.41</td>
<td>&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>B2</td>
<td>121.04</td>
<td>1</td>
<td>121.04</td>
<td>212.02</td>
<td>&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>C2</td>
<td>24.31</td>
<td>1</td>
<td>24.31</td>
<td>42.57</td>
<td>&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>D2</td>
<td>1.50</td>
<td>1</td>
<td>1.50</td>
<td>2.63</td>
<td>0.1255</td>
<td></td>
</tr>
<tr>
<td>Residual</td>
<td>8.56</td>
<td>15</td>
<td>0.57</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lack of Fit</td>
<td>8.56</td>
<td>10</td>
<td>0.86</td>
<td>15111.80</td>
<td>&lt; 0.0001</td>
<td></td>
</tr>
<tr>
<td>Pure Error</td>
<td>2.833E-004</td>
<td>5</td>
<td>5.667E-005</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor Total</td>
<td>675.48</td>
<td>29</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The relationship between the response and the independent variables of the coded units is presented on the basis of the experimental results as follows:

\[ Y_{\text{HAC}} = 98.60 - 0.72A + 2.15B - 2.57C + 2.08D + 1.22BC - 0.76BD - 1.91A^2 - 3.60B^2 - 1.61C^2 \]

ANOVA indicates that the equation and the actual relationship between the response and the significant variables described by it are accurate. The significance of the coefficient term is determined by the values of F and P. The model F-value of 83.44 implies that it is significant. The P-values are used as a tool to check the significance of each of the coefficients. The significance of the coefficient considered increases with F value increase and P value decrease [63]. In addition, a probability p < 0.0001 also validates the model significance.

The predicted \( R^2 \) of 0.9351 is in reasonable agreement with the adjusted \( R^2 \) of 0.9755. The adequacy precision measures the signal to noise ratio. It is reported that a ratio greater than 4 is desirable. The ratio of 34.029 suggests an adequate signal [64]. Hence this model can be used to navigate the design space. The fitness of the model equation is validated using the coefficient of regression, \( R^2 \). The high \( R^2 \) value of 0.9873 implies that 98.73% of the response variability can be explained by the model.

![Fig. 11. Activation energy plot for the adsorption of CV^+](image1)

![Fig. 12. Plot of the experimental and predicted response](image2)

![Fig. 13. 3D surface plot for CV^+ adsorption on HAC showing combined effects of pH and temperature](image3)

![Fig. 14. 3D surface plot for CV^+ adsorption on HAC showing combined effects of temperature and concentration](image4)

![Fig. 15. 3D surface plot for CV^+ adsorption on HAC showing combined effects of temperature and time](image5)
PLOT OF THE EXPERIMENTAL AND THE PREDICTED RESPONSE
The data is analyzed to examine the correlation between the actual and the predicted values of the response. As given in Fig. 12, the data points are well distributed close to a straight line of $R^2$ of 0.9873. This suggests an excellent relationship between the actual and the predicted values of the response, and appropriate underlying assumptions of the analysis presented above. The results also indicate that the selected quadratic model is adequate in assuming the response variables of the actual data.

RESPONSE SURFACE MEASUREMENTS
3D surface plots are drawn to follow the effect of any two independent variables on the removal of CV⁺. The nature of the response surface curves of Figs.13-15 reveals the interaction between the variables. The elliptic nature of the contour in the graphs indicates that there is a relative significance between every two variables.

CONCLUSIONS
The present study establishes the fact that HAC may be used as an adsorbent for the removal of a dye from an aqueous solution. The adsorption of CV⁺ on HAC is found to be dependent on the solution pH, the initial dye concentration, the temperature, the adsorbent dosage, the contact time and the adsorbent particle size. The equilibrium adsorption data is best described by Dubinin-Radushkevich isotherm model. The maximum adsorption capacity ($q_m$) value amounts to 69.26 mg g⁻¹. The thermodynamic values determined show that a physical endothermic adsorption proceeds spontaneously under the conditions studied. The adsorption kinetics is best described by a pseudo-second order kinetic model. The results of the present investigation indicate that HAC has the potential to be used in removal of dyes from aqueous solutions.

NOMENCLATURE
q Adsorption capacity, mg g⁻¹.
$q_e$ Adsorption capacity at equilibrium, mg g⁻¹.
$q_t$ Adsorption capacity at time, mg g⁻¹.
$C_e$ Equilibrium concentration of dye in solution, mg L⁻¹.

Kₗ Langmuir constant, L mg⁻¹.
Rₛ Dimensional separation factor
K₇ Freundlich constant, L g⁻¹.
n Freundlich constant
D Effective diffusion coefficient, m²s⁻¹.
R Universal gas constant, J mol⁻¹ K
T Temperature, °C, K
K₉ Temkin constant, L g⁻¹.
$q_d$ Dubinin-Radushkevich constant, mg g⁻¹.
β Constant related to sorption energy, mol²
E Mean free energy, KJ mol⁻¹.
Cₒ Initial concentration, mg L⁻¹.
$q_s$ Equilibrium concentration of dye on adsorbent, mg L⁻¹.
Kₑ Equilibrium constant
Cᵣ Concentration at time t, mg L⁻¹.
K₁ Pseudo first order kinetic constant
τ Time, min
K₂ Pseudo second-order kinetic constant
a Elovich constants
Kₜ Intra-particle diffusion rate constant, mg g⁻¹ min⁻¹²
ΔG Free energy change, KJ mol⁻¹.
ΔH Free enthalpy change, KJ mol⁻¹.
ΔS Free entropy change, J mol⁻¹ K
Eₐ Activation energy, KJ mol⁻¹.
$q_{max}$ Maximum adsorption capacity
M Total mass of the adsorbent, g
W Weight of adsorbent
$Δq_s$ Normalized standard deviation
HCl Hydrochloric acid
HAC Hydrochloric acid Awka activated clay
CV⁺ Crystal violet

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