Novelty Journals

ISSN 2394-7349

International Journal of Novel Research in Engineering and Science
Vol. 4, Issue 1, pp: (1-16), Month: March 2017 - August 2017, Available at: www.noveltyjournals.com

Equilibrium, Kinetic and Themodynamics Adsorption Study of Cationic Dye from Aqueous Solution onto Modified Awka Clay

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Abstract: **Biosorption potentials of acid (HCl) modified Awka clay for the removal of cationic dye (Crystal violet) from aqueous solution was investigated. The raw and modified clays were characterized by scanning electron microscope (SEM) and Fourier transform infrared (FTIR) analysis. The modification caused an increase in surface area and as a result increases the adsorption of CV^+ in batch system studies. The effect of contact time, initial concentration, pH, temperature, particle size, adsorbent dosage was studied. It was observed that dye adsorption increases with decrease in adsorbent particle size, increase in: initial dye concentration, contact time, temperature and dosage. Optimum dye removal was observed at pH 4. Adsorption equilibrium was determined at 323k and the experimental data obtained were fitted with Linear and non-linear models of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) isotherms. Adsorption kinetic was determined at 323k and the experimental data obtained were fitted using linear and non-linear models of the pseudo-first-order, pseudo-second-order, Elovich and Intra-particle diffusion kinetic. By considering the experimental results of equilibrium and kinetic adsorption models applied in this study, it can be concluded that equilibrium data were best fitted to Langmuir isotherm using linear model and D-R isotherm using non-linear model while the pseudo second order kinetic fitted best in adsorption kinetic of both models. The results of this research indicate that modified Awka clay is a good activated carbon alternative non-conventional and naturally abundant adsorbent to rely on for dye removal from aqueous solution.**

Keywords: **Biosorption potentials of acid (HCl), Dubinin-Radushkevich (D-R).**

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1. INTRODUCTION

Pollution and its control has been a major global issue which requires ongoing evaluation and revision of pollution resource policy at all level. The most concerned environmental pollution is air pollution, water pollution and solid waste. Air pollution usually comes from open burning especially the forest and vehicles combustion, water pollution comes from the industrial effluent, surface run-off and domestic sewage while solid waste are materials that arises from various human activities and which is normally discarded as useless or unwanted (Rao, 1991). Among the three mentioned environmental pollution, this research centered its focus on water pollution and its control.

Water pollution is the contamination of water bodies or the alteration in physical, chemical and biological characteristics of water which may course harmful effect on humans and aquatic life. This form of environmental degradation occurs when pollutants are directly or indirectly discharged into water bodies without adequate treatment to remove harmful compounds. Water pollutants includes: industrial effluents, surface run-off, domestic sewage, oil and other wastes.

An industrial effluent is any wastewater generated from industrial activity. High degree of industrialization world wild has resulted in environmental problem (Selvaraj et al., 2013). Greater environmental awareness in both the public and regulatory spheres in recent years has necessitated greater treatment of industrial effluent (Abdel-Ghani, et al., 2007).

Industrial effluent contains large amount of dissolved dyestuffs and other product such as dispersing agents, dye bath carrier, salts, emulsifiers, leveling agents and heavy metals (Noroozi et al., 2007). Dye wastewater arises as a direct result of the production of dye and also as a consequence of its use in textile, paper, rubber, plastic, leather, cosmetic, pharmaceutical and food industries (Emrah et al; 2007). Unproductive ways to reduce dye in wastewater may bring long-term risks to the ecosystem and humans (Nurdan and Okan, 2013). The disposal of dye wastewater without proper treatment is a big challenge as it causes harm to the aquatic environment such as reducing light penetration and photosynthesis (Montano et al, 2008). The removal of color from aquatic system caused by the presence of synthetic dyes is extremely important from the environmental view point because most of these dyes are toxic, mutagenic and carcinogenic. Some of the dyes present in wastewater even decompose into carcinogenic aromatic amines under anaerobic conditions and cause serious health problems to human beings as well as other animals (Chen et al, 2003). Due to the complex molecular structure, dyes are usually very difficult to be biodegraded, and are too hard to eliminate them under natural aquatic environment (Kar et al, 2009). Many dyes and their by-products break down into products which are toxic for living organisms (Sarioglu and Atay, 2006).

The dyes have low biodegradability. Conventional biological wastewater treatment processes are not efficient in treating dye present in wastewater (Mondal, 2008). Therefore dye wastewater is usually treated by physical and chemical methods, such as sonochemical degradation (Abbasi and Asl 2008), electrochemical degradation (Fan et al; 2008), coagulation and flocculation (Zonoozi et al, 2009), activated carbon adsorption (Tan et al, 2008), Oxidation and zonation (Malik and Saha 2003). However, all of these methods except adsorption suffer from one or other limitations and none of them were successful in completely removing of color from wastewater (Lorenc-Grabowska and Gryglewiez 2007).

Adsorption is preferred as an effective technique due to its low cost and high treatment efficiency (Qadeer 2007). In adsorption process activated carbon is a conventional adsorbent but adsorption by activated carbon has some restrictions such as the activated carbon, the need for regeneration after exhausting and the loss of adsorption efficiency after regeneration (Srivastave et al, 2007). Due to these restrictions, quest for non-conventional cost effective adsorbents has been reviewed. Many non-conventional cost effective adsorbent such as peanut hull (Gong et al, 2005), Jute stick powder (Panda et al, 2009), Wheat bran and rice bran (Xue and Jing 2009), Alternatherabettzichiana plant powder (Patil and Shrivastave 2010) Jackfruit peel (Hameed 2009) spent brewery grains (Jaikuma et al, 2009), Chitosan based composite hydro gels (Perju and Dragan 2010), etc. have been all used to remove color/dye from wastewater.

However among all non-conventional used adsorbent, clay is singled to be more effective and efficient adsorbent, clay is singled to be more effective and efficient adsorbent in dye removal due to its abundant availability, large surface area and high adsorption capacity. Clay can be n granules or in powdered form (Djebbar et al, 2012). It has been proved that the adsorbing capacity of clay increases by activating the clay (Ehssa and Yehia 2012). Different type of clay activation includes acid activation, alkali activation and thermal activation. But acid activation has been proved as most effective of clay activation (Igbokwe et al, 2011).

This work is aimed at evaluating the effect of acid activation on the adsorptive properties of Awka clays on removal of dyes from aqueous solution and also aimed to develop the best equilibrium model to fit the experimental date of the adsorption of CV+ on HAC using linear and non-linear forms of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms.

2. 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 used were analytical grade, bought from Bridge Head Market Onitsha, Anambra State Nigeria. All solutions were prepared with distilled water.

2.1 Acid activation of clay sample:

The clay material was prepared for activation by sun drying. The dried clay sample was then reduced to small seize by grinding with a laboratory mortar and pestle and sieved to a particle size of 75µm. The sieved clay sample was mixed in a flask with HCL acid in w/v ratio of 1:5 (160g of the clay sample was mixed with 800ml of the prepared acid). The resulting suspension was allowed to soak for 24 hours. At the end of the duration, the resulting slurry was poured into a Buchner funnel to separate the acid and the clay. The clay residue was washed severally with distilled water until a neutral point was obtained with pH indicator. The clay slurry was then dried in an oven at a temperature of 80°C for 4 hours, the dried sample obtained after activation were crushed and sieved again to different particle size and stored.

2.2 Characterization:

The functional group of the activated and raw sample was determined using Fourier transform infrared (FTIR). This FTIR analysis was carried out using Shimadzu S8400 spectrophotometer, with samples prepared by conventional KBr disc method. The surface morphologies of the adsorbent were determined using Scanning Electron Microscope SEM. The SEM analysis was carried out using Joel scanning electron microscope model JSM 6400 with coated gold film of layers approximately 20-25A thick.

2.3 Batch adsorption studies:

Batch experiments were conducted to investigate the parametric effects of adsorbent particle size, adsorbent dose, initial adsorbate concentration, adsorption time, pH and temperature for CV+ adsorption on the modified clay. CV+ sample were prepared by dissolving a known quantity in distilled water and used as a stock solution and diluted to the required initial concentration (range: 100 to 500mg/l). 100ml of CV+ solution of known concentration (C_o) was taken in a 250ml beaker with a required amount of adsorbent and was shacked for different time duration in a shaker at different pH and temperature. The pH of the solution was adjusted by using either 0.1N HCL or NaOH. The solution was then filter through a filter paper after a specific time duration. UV- visible spectrophotometer was employed to determine the remaining concentrations of CV+ in the filtrate.

2.4 Equilibrium studies:

Equilibrium adsorption experiment was carried out by adding a fixed amount of sorbent into a number of 250ml glass beakers containing a definite volume of different initial concentrations of dye solution of the same pH level. The beakers containing the solute were placed on magnetic stirrers regulated at the fixed temperature level for a period of 2hrs to ensure equilibrium was reached. The remaining or equilibrium concentration of dye is determined using UV-visible spectrophotometer.

The amount of adsorption at equilibrium, q_e (mg/g), was calculated by

$$qe = \frac{(C_o - C_e)V}{W} \qquad (1)$$

Where C_o and C_e(mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. V(L) is the volume of the solution and W(g) is the mass of dry sorbent used.

The dye removal percentage can be calculated as follows.

$$\text{Percentage removal} = \frac{(C_o - C_e)}{C_o} \times 100 \qquad (2)$$

2.5 Kinetic studies:

The procedures of kinetic experiments were basically identical to those of equilibrium study. In kinetic study, aqueous sample were taken at preset time intervals and concentrations of dye were similarly measured.

The amount of sorption at time t, qt(mg/g) was calculated by

$$qt = \frac{(C_o - C_t)V}{W} \qquad (3)$$

2.6 Theory of adsorption isotherm and kinetics:

Isotherm models:

The application of adsorption isotherm is very useful to describe the interaction between the adsorbate and adsorbent of any system. The parameters obtained from the different models provide useful information on the adsorption mechanisms, surface properties and adsorbent affinity. In this study four models were employed. The Langmuir (Langmuir, 1916), the

Freundlich (Freundlich 1906), the Temkin (Temkin 1940), and the Dubinin-Redushkevich. There linearized and non-linearized forms are listed below. All the numbers attached (a) are the non-linear forms.

i. $$\frac{C_e}{q_e} = \frac{1}{k_L\, q_m} + \frac{1}{q_m}C_e \qquad (4)$$

ii. $$q_e = \frac{Q_m K_L C_e}{1+K_L C_e};\ R_L = \frac{1}{1+K_L C_o}(4a)$$

iii. $$Inq_e = \ln k_f + \frac{1}{n}\ln C_e\ (5)$$

iv. $$q_e = K_F {C_e}^{1/n_F} \qquad (5a)$$

v. $$q_e = \frac{RT}{b}\ln k_T + \frac{RT}{b}\ln C_e\ (6)$$

vi. $$q_e = \frac{RT}{b_T}\ln(K_T C_e) \qquad (6a)$$

vii. $$\ln q_e = \ln q_D - B_D\left[RT\ln\left(1+\frac{1}{C_e}\right)\right]^2\ (7)$$

viii. $$q_e = Q_m \exp\left(-b_{DR}\left[RT\,ln\left(1+\frac{1}{C_e}\right)\right]^2\right) \qquad (7a)$$

Where q_m (mg/g) and K_L (l/mg) are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. C_e (mg/L) and q_e (mg/g) are the equilibrium concentration and the amount of dye adsorbed at equilibrium, respectively. K_f and n are the Freundlich constants which are indicator of adsorption capacity and adsorption intensity, respectively. B and KT are Temkin isotherm constant, R is gas constant (8.314J/mol k). T is absolute temperature (k)

2.7 Kinetic model:

The application of adsorption kinetics is of very important to understand the adsorption dynamics in relation to time. The most common models used to fit the kinetic sorption experiment are pseudo first order and pseudo second order model. In this study both of them were used together with Elovich and intraparticle diffusion model. There linearized and non-linearized forms are listed below. All the numbers attached (a) are the non-linear forms.

i. $$\ln q_e - q_t = \ln q_e - k_1 t \qquad (8)$$

ii. $$q_e = q_e[1 - exp(K_1 t)] \qquad (8a)$$

iii. $$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \qquad (9)$$

iv. $$q_e = \frac{K_2 q_e^2 t}{1+K_2 q_e t} \qquad (9a)$$

v. $$q_t = \frac{1}{\beta}\ln\left(\frac{\alpha}{\beta}\right) \times \frac{1}{\beta}\ln t \qquad (10)$$

vi. $$q_e = \frac{1}{\beta}\ln(1+\alpha\beta t) \qquad (10a)$$

vii. $$q_t = k_{id}t^{0.5} + c \qquad (11)$$

viii. $$q_e = K_{id}\sqrt{t} \qquad (11a)$$

Where q_e (mg/g) and q_t (mg/g) are the amount adsorbate adsorbed at equilibrium and at time t, respectively. K_1 (min^{-1}) and K2 ($gmg^{-1}min$) are the pseudo first order and pseudo second order adsorption rate constants, respectively. k_{id} ($mgg^{-1}min^{1/2}$), the rate parameter of stage i, and it is obtained from the slope of the straight line of q_t versus $t^{1/2}$.

2.8 Adsorption thermodynamics:

Thermodynamics is studied to observe the process involved in the adsorption. Thermodynamic parameters are calculated using the following equations

$$\Delta G^o = -RT\ \text{In}Kc \qquad (12)$$

$$\text{Where } Kc = \frac{Cs}{Ce} \qquad (13)$$

$$\text{In } Kc = \left(\frac{\Delta S}{R}\right) - \left(\frac{\Delta H}{RT}\right) \qquad (14)$$

Where ΔG^o, ΔH, ΔS are standard free energy change, standard enthalpy change and standard enthropy change, respectively. Kc is the equilibrium constant, Cs is the equilibrium concentration of CR in solution (mg L^{-1}), R is the ideal gas constant (8.314) mol^{-1} K^{-1}) and T is the adsorption temperature on Kelvin scale.

2.9 Determination of Point zero charge (pH_{pzc}) of HAC:

The zero surface charge characteristics of the clays were determined using the solid additional method (Hameed 2010, Ponnusami 2008). 40ml of 0.1M KNO_3 solution was transferred to a series of 100mL beakers. The initial pH values of the solutions were roughly adjusted between 2 and 14 by adding either 0.1N HCl or NaOH and were measured by using pH meter. The total volume of the solution in each beaker was exactly adjusted to 25mL by adding KNO_3 solution of the same strength. The initial pH of the solutions was then accurately noted. 0.05g of clay was added to each beaker. The suspensions were then kept shaking for 24h and allowed to equilibrate for 0.5h. The final pH values of the supernatant liquid were noted. The difference between the initial and final pH values ΔpH was plotted against the initial pH. The point of intersection of the resulting curve with abscissa at which pH 0, gave the pH_{pzc}.

3. RESULTS AND DISCUSSION

3.1 Characterization result:

FTIR analysis:

The FTIR spectrum of AC is shown in Fig. 1a, b. for HCl activated (HAC), and after CV^+ adsorption (ACV^+) on HAC, respectively. The figure shows that some peaks are shifted or disappeared and some new peaks are also detected. The changes observed in the spectrum indicate the possible involvement of those functional groups on the surface of the AC in the adsorption process. FTIR date of AC adsorbent is shown in Table 1.

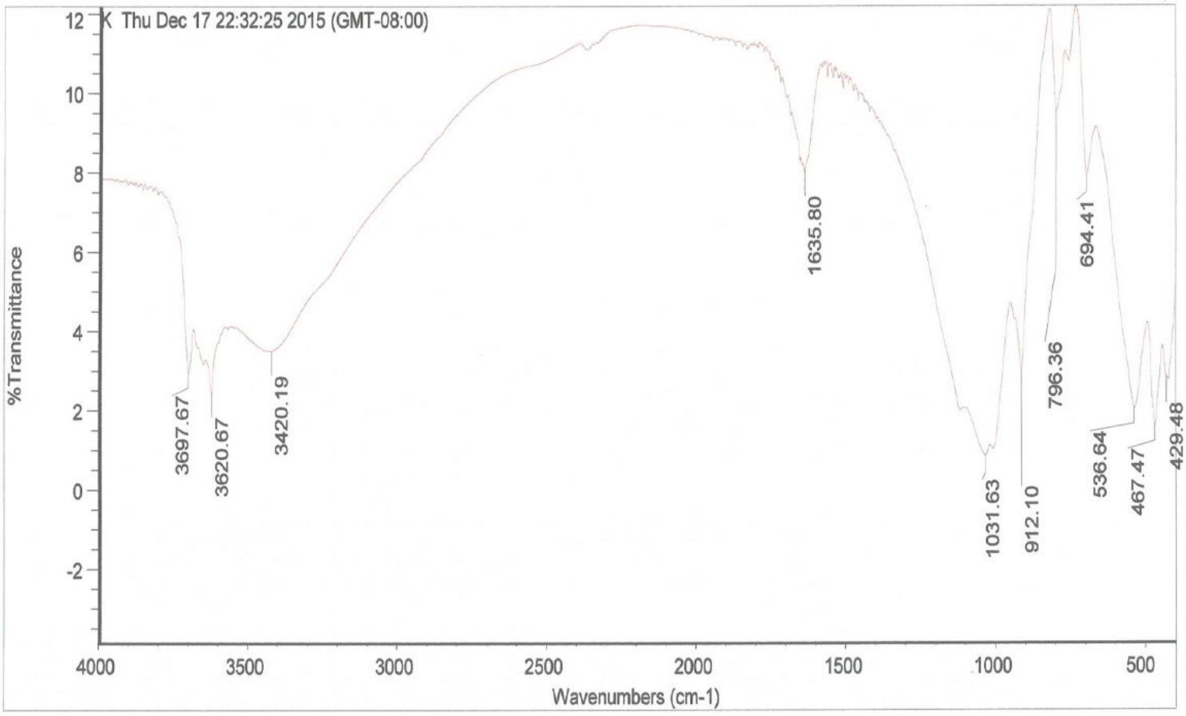

Fig. 1a. FTIR of HCL activated Awka clay (HAC)

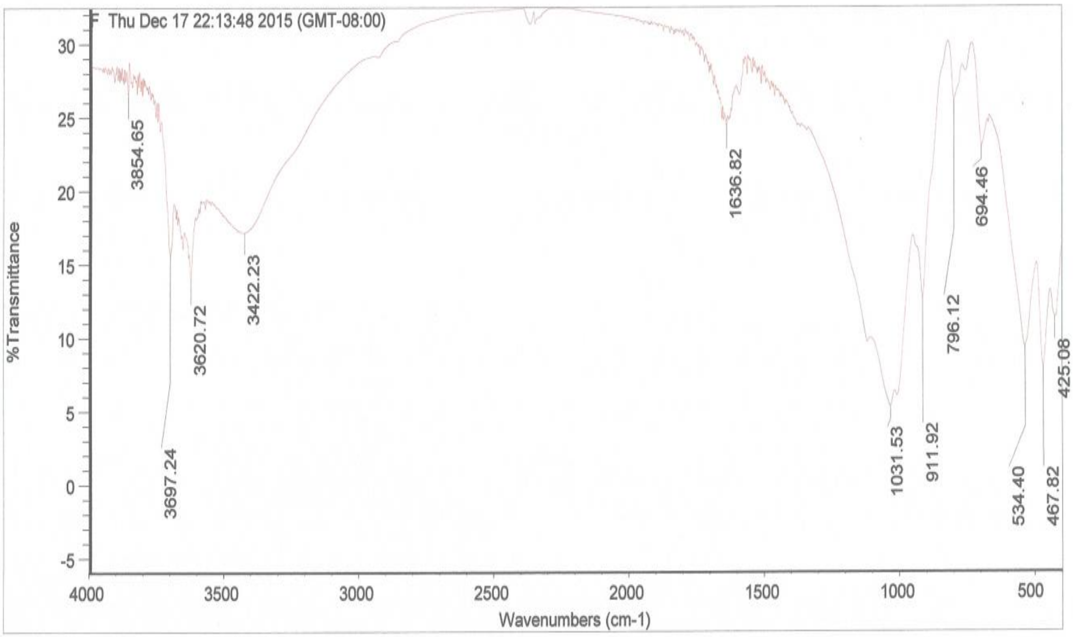

Fig. 1b. FTIR of after CV$^+$ adsorption on HAC

Fig. 1 FTIR of raw, activated, and after CV$^+$ adsorption on AC

SEM micrographs:

Fig. 2. Shows the SEM micrograph of AC sample at activated state and after CV$^+$ adsorption on HAC, they are indicated with subscript 2a, 2b, respectively in Fig.2. It is clear from Fig. 2a that HAC has considerable number of heterogeneous layer of pores, which shows that there is a good possibility for CV$^+$ to be adsorbed on HAC sample. The surface of Fig 2b, however clearly shows that the surface of HAC is covered with CV$^+$ molecules.

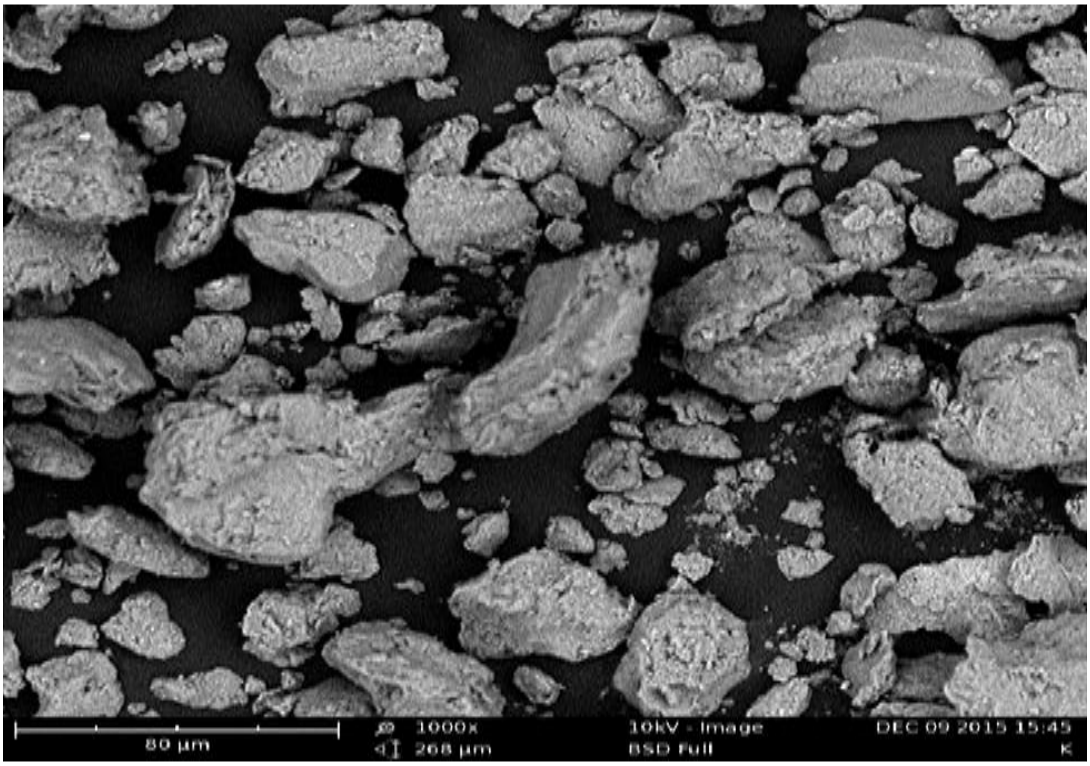

Fig.2a scanning electron microscopic photograph of HAC

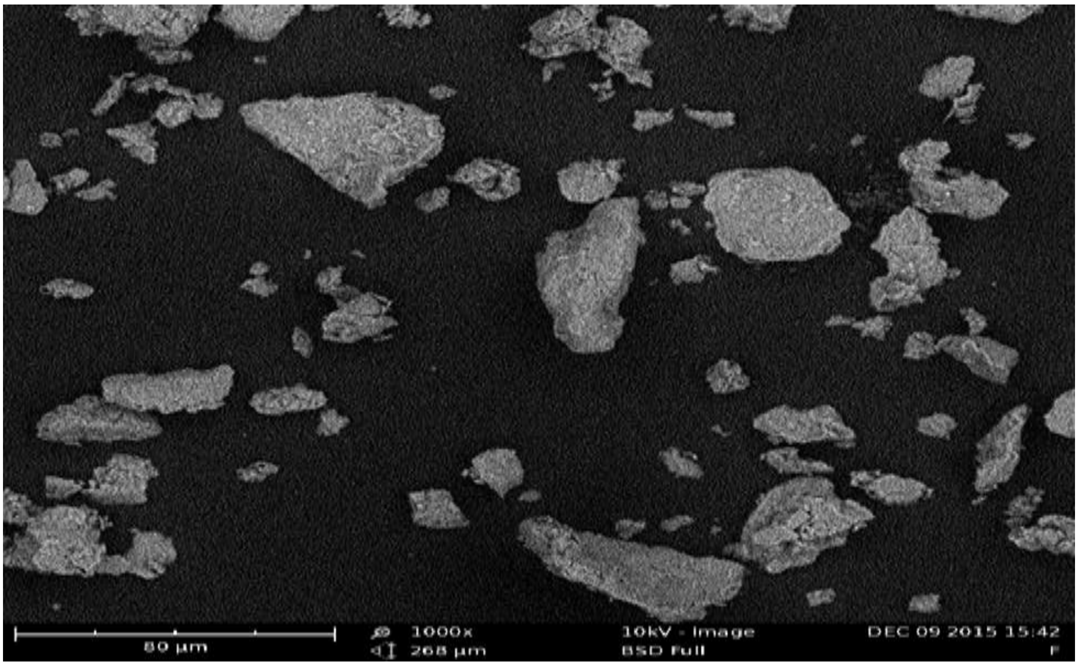

Fig.2b scanning electron microscopic photograph of HAC after CV$^+$ adsorption

Fig.2 scanning electron microscopic

3.2 Effect of particle size:

The effect of particle size was studied with particle sizes ranging from 75µm to 850µm and the results are shown in Fig. 3; below. It can be seen that the percentage removal decreases with increase in particle size. This is because smaller particles tend yield larger surface area. Furthermore, the breaking of larger particles tend to open tiny cracks and channels on the particle surface of the material resulting in more accessibility to better diffusion, owing to the smaller particle size.

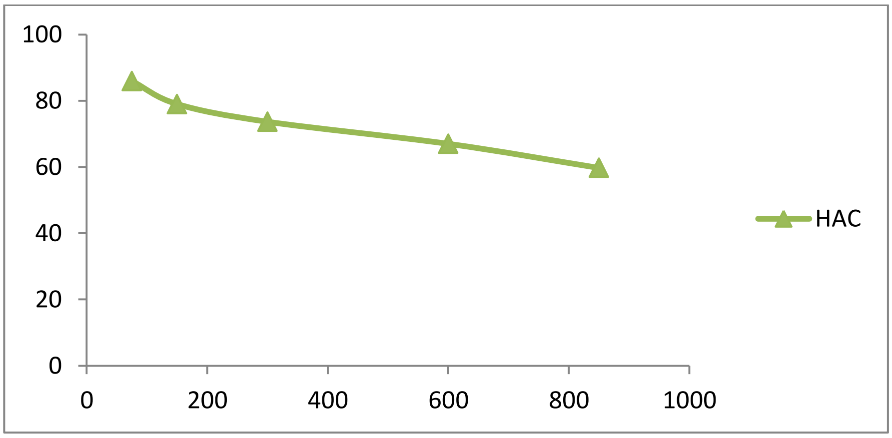

Fig.3. Effect of particle size on CV$^+$ adsorption. (A plot of %adsorb against particle size)

3.3 Effect of adsorbent dosage:

The effect of dosage was studied for adsorbent dosages for the range of 0.1 to 0.5. The results showed that, as the adsorbent dosage increased, the percentage of adsorption also increased as can be seen from Fig. 4. The increase in the percentage removal of dyes with the increase in adsorbent dosage is due to the increased surface area with more active functional groups which also gives rise to more availability of more adsorption sites (Arivoli et al, 2009)

It was also observed that the amount adsorbed per unit mass of the adsorbent decreased as the adsorbent dosage increased. This decrease in unit adsorption with increasing adsorbent amount is mainly due to adsorption sites remaining unsaturated during the adsorption reaction (Bulut and Aydin, 2006).

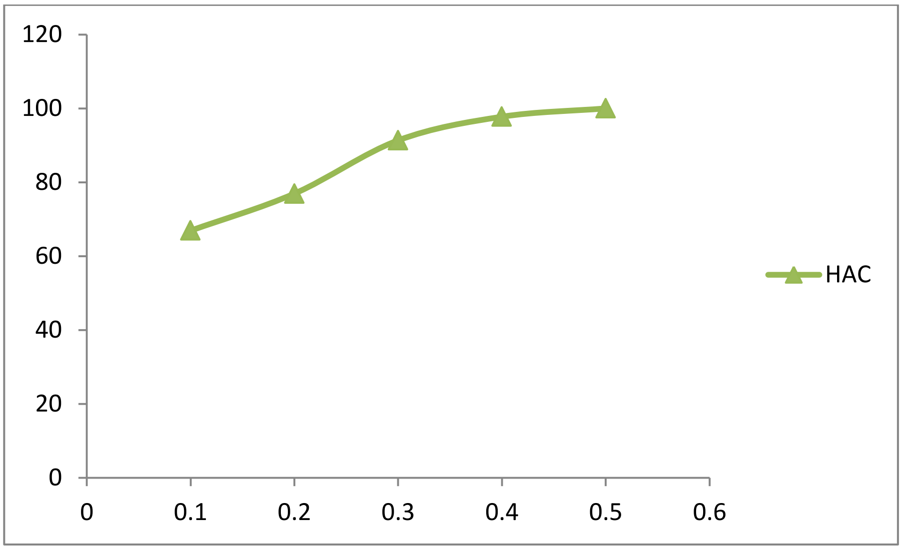

Fig.4. Effect of dosage on adsorption of CV$^+$ (A plot of % adsorb against dosage)

3.4 Effect of concentration and contact time:

The effect of initial concentration was studied for the initial concentration ranging from 100 to 400 mg/l and contact time from 2 to 150 mins and the results were presented in Fig. 4. The results showed that while the amount of CV+ adsorbed per unit mass increased with increase in initial ion concentration, the adsorption percentage decreased. This is because at lower concentration, the ratio of the initial number of the dye molecules to the available surface area is low (Arivoli et al, 2009). Because for fixed concentrations of active sites remain the same, the number of substrates ions accommodated in the interlayer space increased so that the removed ones is decreased. This may be due to the fact that with increase in initial concentration of the dye, more dye molecules are also adsorbed on the surface of the clay. Moreover the result showed that the amount of adsorption i.e mg of adsorbate per g of adsorbent increases with increasing contact time at all initial concentrations till equilibrium is attained. This is so because the initial dye concentration provides the driving force to overcome the resistance to the mass transfer of dye between the aqueous and the solid face. Furthermore the result also showed that adsorption of CV+ follows three-step processes, (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 utilization of the most readily available active site on the adsorbent surface (bulk diffusion). Second step, exhibiting additional adsorption is attributed to the diffusion of the adsorbate from the surface film into the micro-pores of the adsorbent (pore diffusion and intra-particle diffusion) stimulating further movement of CV+ molecules from the liquid phase onto adsorbent clay surface. The last stage is an equilibrium stage (Mohammad et al., 2010).

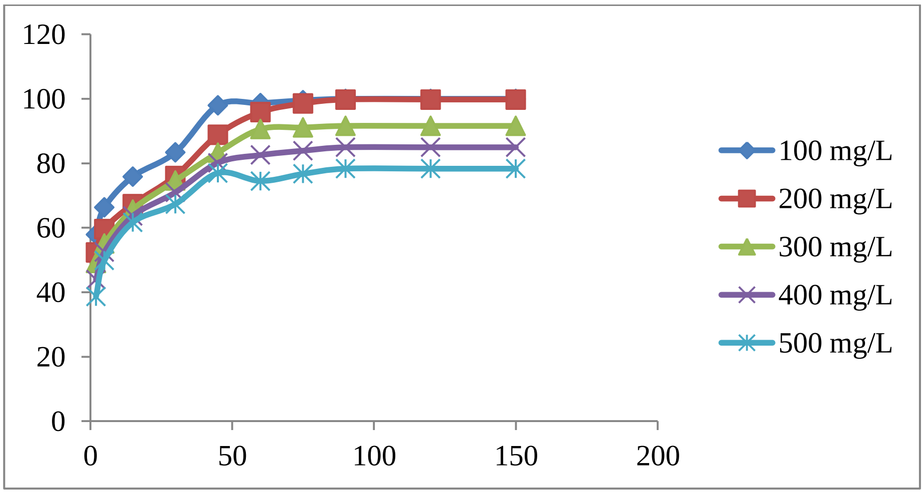

Fig. 5. Effect of concentration & contact time on HAC CV$^+$ adsorption.(A plot of %adsorb against time)

3.5 Effect of pH:

The effect of solution pH is important when the adsorbing molecules are capable of ionizing in response to pH (Hamad et al, 2010). The percentage of adsorption of CV^+ dye was studied and reported in Fig.6.

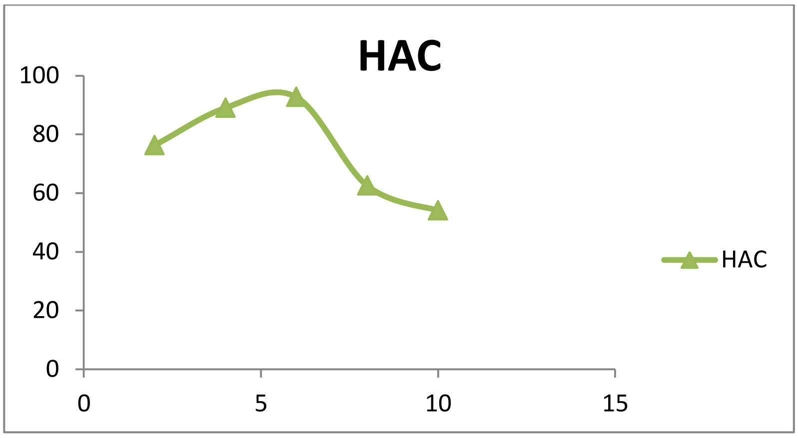

Fig.6. Effect of pH on adsorption of CV^+ (A plot of % adsorb against pH)

CV^+ is a cationic dye. Generally, for cationic dyes, the adsorption capacity and rate constant have the tendency to increase as initial pH of the solution increases. When solution pH increases, high OH^- ions accumulate on the adsorbent surface (Ahmad and Kumar, 2010). The effect of pH is studied between 2 and 10. PH values as shown in fig 6 above. As reported in figure, the maximum removal efficiency is achieved around pH6. At lower pH < 6, the number of positively charged on the surface site of the clays increases, which does not favor the adsorption of dye cations due to electrostatic repulsion. Besides, the presence of excess H^+ ions competing with dyes cations for the adsorption sites on clay may also decrease the adsorption of CV^+ (Langmuir 1918). The decrease of dye percentage removal at alkaline medium may be due to the hydrolysis of adsorbent surfaces, which create positively charged sites (Hamdaoui 2006).

3.6 Effect of temperature:

Temperature is an indicator for the adsorption nature whether it is an exothermic or endothermic process. Temperature values ranging from 303K to 323K were used to study the effect of temperature on the adsorption process in this research. The results of the effect of temperature are shown in Fig.7; the result shows that amount of CV^+ adsorption on activated clay increased with increasing temperature of the solution, which indicates that the process was endothermic (Mahmoodi et al., 2011,). This may be due to increasing the mobility of dye molecules and an increase in the number of active sites for the adsorption with increasing temperature (Mahmoodi et al., 2011). An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface. Further, increasing temperature may produce swelling effect within the internal structure of the clay enabling large dye molecule to penetrate further.

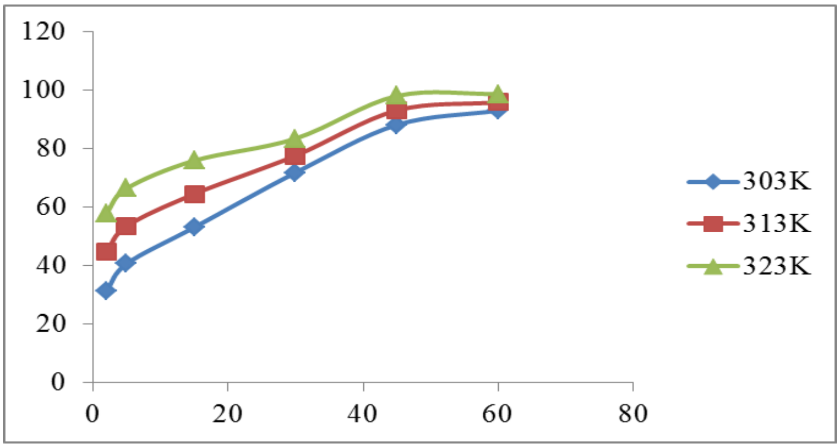

Fig.7. Effect of temperature on HAC CV^+ adsorption.(A plot of %adsorb against time)

3.7 Equilibrium modeling:

The equilibrium adsorption is represents the relationship between the mass of adsorbate adsorbed per unit weight of adsorbent and the liquid-phase equilibrium concentration of the adsorbate (Lata et al, 2007). The equilibrium results were analysis using linear and non-linear forms of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm. The details of their linear and non-linear form are shown in Eqs. 4-7.

The Langmuir isotherm assume that the adsorption occurs at homogeneous sites at adsorbent surface, and saturation take place when the dye molecules fill the sites where no more adsorption can occur at that site. The constant K_L and q_m values for linear model can be evaluated from the intercept and slope of the linear plot of experimental data of C_e/q_e versus C_e (Fig 8a) While that of non-linear model are evaluated using Excel software. The essential feature of the Langmuir isotherm can be expressed by means of R_L, a dimensionless constant referred to as separation factor or equilibrium parameter. R_L is calculated using equation according to previous study by Hall et al (1966) and the value of R_L indicates whether the adsorption isotherm is unfavorable ($R_L>1$), Linear ($R_L =1$), favorable ($0<R_L<1$), or irreversible ($R_L=0$). The Langmuir constants and R_L values for both linear and non-linear model are listed in Table 2. The values of R_L as can see from the table for both model confirmed that there was favorable uptake of CV^+ dye.

The Freundlich isotherm can be used for adsorption on a homogenous surface energy system where the binding sites are not equivalent. The constant K_F and n_F values for linear model can be evaluated from the intercept and slope of the linear plot of experimental data of $\ln q_e$ versus $\ln C_e$ While that of non-linear model are evaluated using Excel software. Atia et al. (2008) reported that the Freundlich isotherm constant n_f can be used to explore the favorability of adsorption process. When the value of n_f is within $1<n_f<10$, it is favorable adsorption. If not, it is unfavorable adsorption. The constant K_f measures the adsorption capacity. The Freundlich constants values for both linear and non-linear model are listed in Table 2. The n_f values as can see from the Table 2 for both models lie within the range of $1<n_f<10$ and thereby confirmed that there was favorable uptake of CV^+ dye.

The Temkin isotherm studied the heat of adsorption (weather the adsorption process is endothermic or exothermic) and the adsorbate-adsorbent interaction on the adsorption isotherms. They assumed that because of the adsorbate- adsorbent interactions, the energy of the molecule adsorption will decrease linearly with coverage. The constants K_T and b for linear model can be evaluated from the intercept and slope of the linear plot of experimental data of q_e versus $\ln C_e$ While that of non-linear model are evaluated using Excel software. The Temkin constants values for both linear and non-linear model are listed in Table 2.

The Dubinin-Radushkevich (D-R) isotherm predicts the adsorption effect. The constants K_{DR} and B for linear model can be evaluated from the intercept and slope of the linear plot of experimental data of $\ln q_e$ versus ε^2, While that of non-linear model are determined using Excel software. The D-R constants values for both linear and non-linear model are listed in Table 2.

To define the model that better fitted the experimental values in adsorption study, correlation coefficient (R^2) was used in linear model while non-linear error parameter ($\%\Delta q_e$) was used in non-linear model. The best fit of R^2 is when its value is close to unity while that of $\%\Delta q_e$ is the smallest value of it.

From Table 1, the Langmuir model yielded the highest value of correlation coefficient (R^2) compared to that of Freundlich, Temkin and D-R using linear model. While D-R model yield the lowest value of normalized standard deviation and highest value of correlation coefficient R^2 compared to that of Langmuir, Freundlich and Temkin using non-linear model. The deviation in fit model (from Langmuir to D-R) may be as a result of linearization error. (El-Khaiary, 2008).

TABLE 1

Calculated isotherm Parameters for the Adsorption of CV^+ on HAC

	Temperature 323k	
	Linear	Non-linear
langmuir		
q_m	79.3651	69.26056
K_L	0.2505	3.606797
R^2	0.9779	0.986281
R_L	0.007921	0.000554
$\Delta q_e\%$		4.685168
Freundlich		
n_f	8.95255	1.38
K_f	43.4887	3.016153
R^2	0.9759	0.914402
$\Delta q_e\%$		11.70288
Temkin		
b	534.709	255.3743
K_T	40160	35.68134
R^2	0.8968	0.993436
$\Delta q_e\%$		3.240753
Dubinin-Radushkevich		
K_{DR}	59.6563	75.66643
β	4.00E-09	**9.91E-06**
E	0.09155	0.224572
R^2	0.7928	0.999988
$\Delta q_e\%$		1.701141

3.8 Kinetic modeling:

For evaluating the adsorption kinetics of CV^+ onto HAC, the pseudo-first-order, pseudo-second-order, Elovich and intra-particle kinetic models were used to fit the experimental data. The pseudo-first-order and pseudo-second-order kinetic models assume that adsorption is a pseudo-chemical reaction. When the adsorption processes occur through chemisorption, the Elovich model is most use (Dotto and pinto, 2011). The details of their linear and non-linear form are shown in Eqs. 8-11.

From pseudo-first-order, the values of K_1 and q_e were obtained from the slope and intercept respectively of plots of log (q_e-qt) versus t, while that of non-linear model are evaluated using Excel software. The values, K_1 and q_e for both linear and non-linear model are listed in Table 3. From the table, it is clearly seen that the calculated q_e values did not agree with experimental q_e values, and $\%\Delta q_e$ value is higher than that of pseudo-second order thus the pseudo-first order model did not fit well.

The pseudo-second-order model also used to study the adsorption kinetics. The value of K_2 and q_e can be determined experimentally from the slope and intercept of the linear plot of t/qt versus t (9b), while that of non-linear model are evaluated using Excel software. The values, K_2, R^2 and q_e for both linear and non-linear model are listed in Table 3. From the table, it can be seen that the R^2 obtain from the linear plot of pseudo second order is higher to compare that of pseudo first order and Elovich model, and the calculated q_e value is in agreement with the experimental q_e values. The non-linear parameter (%Δq_e) value obtained is smaller to that of pseudo-first-order and Elovich model. This indicates that the adsorption kinetics is better represented by pseudo-second-order using both models.

The Elovich model also used to study the adsorption kinetics. For the Elovich model, parameter β is the desorption constant (Malash and El-Khaiary, 2010). The value of β and α can be determined experimentally from the slope and intercept of the linear plot of q_t versus lnt, while that of non-linear model are evaluated using Excel software. The values, α, R^2 and β for both linear and non-linear model are listed in Table 2. From the table, it is clear that the R^2 value is smaller to that of pseudo-second-order and the %Δqe value is higher than that of pseudo-second-order and pseudo-first order model thus Elovich model did not fit well. The smaller values of β as can see from the table also indicate that the adsorption of CV+ onto HAC is almost irreversible.

The intraparticle diffusion model was proposed to identify the adsorption mechanism and to predict the rate controlling step. This model usually includes three steps. The first step is the external surface adsorption or boundary layer diffusion. The second step is the gradual stage of adsorption which is the intraparticle diffusion. If the plot is linear and passes through the origin, then the intraparticle diffusion is the rate-controlling step. The third step is is the final equilibrium stage in which the intraparticle diffusion starts to the slow down due to the extremely low dye concentration left in the solution (Cheung et al; 2007).

TABLE 2

le.3 Calculated kinetic Parameters for the Adsorption of CV^+ on HAC						
		Temperature 323k				
			Linear		Non-linear	
q_e exp (mg/g)			19.99982		19.99982	
Pseudo first order						
R^2			0.8493		0.999329	
K_1(min-1)			0.0399		0.218038	
q_e cal(mg/g)			3.710995		19.99982	
Δqe%					0.814153	
Pseudo second order						
R^2			0.9982		0.999832	
K_2(min-1)			0.013278		0.019749	
q_e cal(mg/g)			20.70393		19.58657	
Δq_e%					0.406809	
Elovich						
R^2			0.9578		0.989722	
β(g/mg)			0.434443		1.045745	
α(mg/gmin)			29.09929		498807.6	
Δqe%					3.186039	
Intra-particle diffusion						
R^2			0.8935		0.99999	
K_d(mg/gmin$^{1/2}$)			0.9431		5.937574	
δ			11.403			
Δq_e%					40.76887	

3.10 Point zero charge (pH_{pzc}):

Point of zero charge for a given mineral surface is the pH at which that surface has a net neutral charge. Point of zero charge plot of HAC is reported on Fig.8

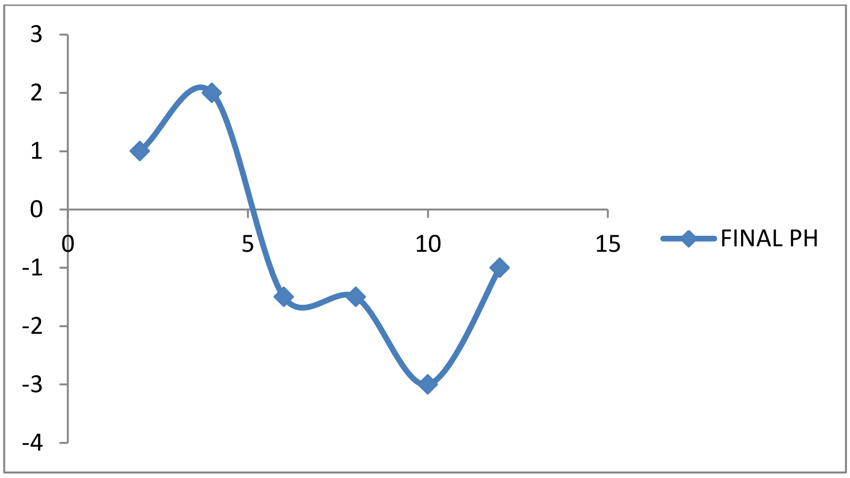

Fig.8. Point of zero charge of CV^+ adsorption on HAC (A plot of ΔpH against pH_i)

From fig.8, it is observed that the surface charge of HAC around pH 5.5 for CV^+ is zero. This indicates that, the pH_{pzc} of HAC is 5.5 for CV+ adsorption. The effect of pH on the biosorption efficiency of CV+ was shown in fig.4, and CV+ uptake is higher around pH of 4. Similar result was reported by the adsorption of reactive orange 16 on non-activated Brazilian-pine fruit shell (Calvete et al., 2010).

4. CONCLUSIONS

The present study establishes the fact that HAC may be used as an adsorbent for the removal of dye from aqueous solution. The adsorption of CV^+ onto HAC was found to be dependent of the pH solution, initial dye concentration, temperature, adsorbent dosage, contact time and adsorbent particle size. The equilibrium adsorption data was best represented by Langmuir isotherm using linear model while Dubinin-Radushkevich isotherm best represented the equilibrium adsorption using non-linear model. The maximum adsorption capacity (q_m) value obtain from linear model is 79.37mg/g while that of non-linear is 69.26mg/g. The adsorption kinetic is best described by pseudo second order kinetic in both models. The results of the present investigation indicate that HAC has the potential for the use in removing of dyes from aqueous solutions.

NOMENCLATURE:

q	Adsorption capacity, mg/g.	C_t	Concentration at time t, mg/l
q_e	Adsorption capacity at equilibruim, mg/g.	K_1	Pseudo first order kinetic constant
q_t	Adsorption capacity at time, mg/g.	t	Time, min
C_e	Equilibruim concentration of dye in solution, mg/l	K_2	Pseudo second-order kinetic constant
K_L	Langmuir constants, l/mg.	A	Elovich constants
R_L	Dimensional separation factor	K_d	Intra-particle diffusion rate constant, mg/gmin$^{1/2}$
K_f	Freundlich constants, l/g	ΔG	Free energy change, KJ/mol
n	Freundlich constants	ΔH	Free enthalpy change, KJ/mol
D	Effective diffusion coefficient, m^2/s	ΔS	Free entropy change, J/mol K
R	Universal gas constants, J/mol K	E_a	Activation energy, KJ/mol
T	Temperature, ^oC, K	q_{max}	Maximum adsorption capacity
K_T	Temkpin constant, l/g	M	Total mass of the adsorbent, g
q_D	Dubinin-Radushkevich constant, mg/g	W	Weight of adsorbent
β	Constant related to sorption energy, mol^2	Δq_e	Non-linear error parameter
E	Mean free energy, KJ/mol	HCl	Hydrochloric acid
C_o	Initial concentration, mg/l	HAC	Hydrochloric acid Awka activated clay
C_s	Equilibrium concentration of dye on adsorbent, mg/l	CV^+	Crystal violet
Kc	Equilibrium constant		

REFERENCES

[1] Abbasi, M. N; Asl, R; (2008) Sonochernical degradation of Basic Blue 41 dye assisted by nanoTIO$_2$ and H$_2$O$_2$, J. Hazard. Mater. 153. 942-947.

[2] Abdel-Ghani N.T., Hefry M., and El-chaghaby G. A. F; (2007) “Removal of head from aqueous solution using low cost abundantly available adsorbents” environmental science and technology, vol.4, no.1, pp.67-73,

[3] Ahmad, R; and Kumar, R; (2010) Adsorption studies of hazardous malachite green onto untreated ginger waste. J.Environ. Manage.,91(4), 1032-1038.

[4] Arivoli, S.; Hema, M.; and Martin, P. D. (2009). Adsorption of malachite green onto carbon prepared from Borassus bark. The Arabian Jol. for Sci. and Eng. 34(2A), 31-43.

[5] Atia, A. A.; Donia, A. M.; Yousif, A. M. (2008).Removal of some hazardous heavy metals from aqueous solution using magnetic chelating resin with iminodiacetate functionality. Separation and Purification Technology. Vol 61(3), 348-357

[6] Bulut, Y. and Aydim, H. (2006). A kinetic, thermodynamic study of methylene blue adsorption on wheat shells. Journal Desalination

[7] Calvete, T; Lima, E. C; Cardoso, N. F; Vaghetti, J. C. P; Dias, S. L. P; Pavan, F. A; (2010) Application of carbon adsorbents prepared from the Brazilian pine-fruit-shell for the removal of reactive orange from aqueous solution: kinetic, equilibrium and thermodynamic studies J.Environ. Manage, 91. 1695- 1706

[8] Chen, K. C; Wu, J. Y; Yang, W. B; Hwang, S. C. J. (2003) Evaluation of effective diffusion coefficient and intrinsic kinetic parameters on azo dye biodegradation using PV-immobilized cell beads, Biotechnol. Bioeng. 83. 821-832.

[9] Cheung, W. H., Szeto, Y. S.; Mckay, G. (2007).Intraparticle diffusion processes during acid dye adsorption onto chitosan. Bioresour.Technol. 98, 2897-2904.

[10] Djebbar M., Djafri F., and Bouchekara D.A. (2012) Adsorption of phenol on natural clay. apply water Sci2, 77-86.

[11] Dotto, G. L; Pinto, L. A. A; (2011) Adsorption of food dye acid blue 9 and food yellow 3 onto chitosan: stirring rate effect in kinetics and mechanism. J. Hazard. Mater. 187, 164-170.

[12] Ehissan N, and Yahia E. (2012) Adsorption of phenol from aqueous solution by local Egyptian Bentonite. Journal of American Science 8(8), 1-9.

[13] El-Khaiary, M. I. (2008) Least-squares regression of adsorption equilibrium data: comparing the options, J. Hazard. Mater. 158, 73-87.

[14] Fan, L; Zhou, Y; Yang, W; Chen, G; Yang, F; (2008) Electrochemical degradation of aque-oussolution of Amaranth azodye on ACF under potentiostatic model, Dyes Pigments 76. 440-446

[15] Freundlich, H. M. F. (1906) Over the adsorption in solution. J. Phys. Chem. 57 , 385-470.

[16] Gong, R. M; Ding, Y; Li, M; Yang, C; l.iu, H. J; Sun, Y. Z; (2005) Utilization of powdered peanut hull as biosorbent for removal of anionic dyes from aqueous solution. Dye Pigments 64.187 192

[17] Hall, K. R.; Eagleton, L. C.; Acrivos, A.; Vermeulen, T. (1966) Pore and solid-diffusion kinetics in fixed-bed adsorption under constant pattern conditions.Ind.Eng. Chem. Fundam. 5, 212-223.

[18] Hamdaoui, O; (2006) Batch study of liquid phase adsorption of methylene blue using cedar sawdust and crushed brick, J. Hazard.Mater. 135, 264-273.

[19] Hameed, B. H; EI-Khaiary, M. I; (2008) Sorption kinetics and isotherm studies of a cationic dye using agricultural waste: broad bean peels, J. Hazard. Mater. 154. 639-648.

[20] Hameed, B. H; (2009) Removal of cationic dye from aqueous solution using jackfruit peel as non-conventional low-cost adsorbent. J. Hazard Metcr. 162. 344-350.

[21] Hameed, B. H; (2010) Evaluation of papaya seed as a novel non-conventional low cost adsorbent for removal of methylene blue. J. Hazard. Mater 162.939-994.

[22] Igbokwe, P. K., Olebunne, F. L. and Nwakaudu, M. S. (2011) Effect of activation parameters on conversion in clay-catalysed esterification of acetic acid. International Journal of Basic & Applied Sciences 11(5), 1-8.

[23] Jaikumar, V; Shathish Kumar, K; GnanaPrakash, D; (2009) Biosorption of acid dyes using spent brewery grains: characterization and modeling. Int. J. Appl Sci. Eng.7. 115-125.

[24] Kar, A; Smith, Y. R; Subramanian, V; (2009) Improved photo catalytic degradation of textile dye using titanium dioxide nanotubes formed over titanium wires, Environ. Sci. echno! 43. 3260-3265.

[25] Langmuir, I. (1916). The constitution and fundamental properties of solid and liquids. J. AM. Chem. Soc. 38 (11) 2221-2295.

[26] Langmuir, L; (1918).The adsorption of gases on plane surfaces of glass, mica, and plantinum, J. Am chem. Soc. 40. 1361- 1403

[27] Lata, H., Garg, V. K.; Gupta, R. K. (2007) Removal of basic dye from aqueous solution by adsorption using Partheniumhysterophorus: an agricultural waste, Dye pigments 74, 653-658.

[28] Lorenc-Grabowska, E.; Gryglewicz, G. (2007). Adsorption characteristics of congo red on coal-based mesoporous activated carbon. Dyes and pigments. 74, 34-40.

[29] Mahmoodi, M; Hayati, M. B; Arami, M; Lan, C; (2011) Adsorption of textile dyes on pine cone from colored wastewater: kinetics, equilibrium and thermodynamics studies. Desalination 268, 117-125.

[30] Malash, G. F.; El-Khaiary, M. I.; (2010) Methylene blue adsorption by the waste of Abu-Tartour phosphate rock. J. Colloid Interface Sci. 348, 537-545.

[31] Malik, P. K; Saha, S. K; (2003) Oxidation of direct dyes with hydrogen peroxide using ferrous ion as catalyst, Sep. Purif. Technol. 31.241-250.

[32] Mohammad, M; Maitra, S; Ahmad, N; Bustam, A; Sen, T. K; Dutta, B. K; (2010) Metal ion removal from aqueous solution using physic seed hull. J. Hazard. Mater. 179, 363-372.

[33] Mondal, S; (2008) Methods of dye removal from dye house effluent-an overview. Environ. Eng. Sci. 25. 383- 396 .

[34] Montano, J. G; Torrades, F; Perez Estrada, L. A; Oller, I; Malato, S; Maldonado, M. L; Peral, J. (2008) Degradation pathways of the commercial reactive azo dye Procion Red H-E7B under solar-assisted photo-Fenton reaction, Environ. Sci. Technol. 42 666-6670.

[35] Noroozi, B; Soria, G.A; Bahrami, . I, H; Arami, M; (2007) Equilibrium and kinetic adsorption study of Ionic dye by a natural adsorbent-Silkworm pupa, j. Hazard. Mater. B1391. 161- 174 .

[36] Nurdan, G. T; and Okan, O; (2013) “study of montmorillonite clay for removal of copper (11) by Adsorption” the scientific world journal volume 2013.

[37] Panda, G. C; Das, S. K; Cuha, A. K; (2009) Jute stick powder as a potential biomass for the removal or Congo red and rhodamine B from their aqueous solution.J.Hazard.Mater.164.374-379

[38] Patil, A. K;Shrivastava, V. S; (2010) Alternantherabeuzictuana plant powder as low cost adsorbent for removal of Congo red from aqueous solution. Int. J.Chem Tech Res 2.842-850.

[39] Perju, M. M; Dragan, E. S; (2010) Rernoval of azo dyes from aqueous solution using chirosan based composite hydrogels, Ion Exchange Let t . 3. 7-11.

[40] Qadeer, R; (2007) Adsorption behaviuor of ruthenium ions on activated charcoal from nirtic acid medium, colloids surf. 293, 217-223.

[41] Rao, C. S. (1991). Environmental Pollution Control Engineering.Revised second edition.

[42] Sarioglu, M; Atay, U.A; (2006).Removal of methylene blue by using biosolid, Global NESTj. 8. 113-120.

[43] Selvaraj, K; Maronmani, B; and Pattabhi S.,(2013) “Removal of hexavalent chrominum using distillery sludge” Bioresource technology vol. 89, no.2, pp.207-211,

[44] Srivastava, V. C; Mall, I. D; Mishra, M; (2007) Adsorption thermodynamics and isosteric heat of adsorption of toxic metal ion onto bagasse fly ash (BFA) and rice husk ash (RHA), Chem. Eng. J.(132, 267-278.

[45] Tan, L. A. W; Ahmad, A. L; Hameed, B. H; (2008) Adsorption of basic dye on high-surface area activated carbon prepared from coconut husk: equilibrium, kinetic and thermodynamic studies, J. Hazard. Mater. 154. 337-346. "

[46] Temkin, M. J.; Pyzhev, V. (1940) Recent modifications to Langmuir isotherms. ActaPhysiochim. URSS 12, 217-222.

[47] Vimonses, V., Lei, S., Jin,BO, Chow, C. W. K., Saint, C. (2009) Kinetic study and equilibrium isotherm analysis of congo red adsorption by clay materials. Chem. Eng. J. 148, 354-364.

[48] Xue S. W; Jing P. C; (2009) Biosorption of Congo red from aqueous solution using wheat bran and rice bran: batch studies, Sep. Sci. Technol. 44 1452-1466.

[49] Zonoozi, M. H; Moghaddam, M. R.A; Ararni, M; (2009) Coagulation/Flocculation of dye containing solutions using polyalurniniurnchloride and alum, Water Sci. Technol.59. 1343-1351