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KINETICS AND ISOTHERMS STUDIES OF THE ADSORPTION OF Cr⁶⁺, Mn²⁺ and Cd²⁺ ions ONTO CHEMICALLY MODIFIED *BOMBAX BUONOPOZENSE* CALYX

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ABSTRACT

The potential of chemically modified Bombaxbuonopozense Calyx to adsorbed Cr⁶⁺, Mn⁶⁺ and Cd⁶⁺ ions from aqueous solutions are prime intent in batch experiments. In this study, chemically modified activated carbon (AC) functionalized with H₂SO₄ (ACH) and KOH (ACK) used in batch absorption process is reported. The pseudo first, pseudo second, Natarajan and Khalaf first, Bhattacharya and Venkobachar first, elovcih and intraparticle diffusion models rate equations were tested on kinetic data and the adsorption followed the pseudo second order rate kinetics. The isotherm data were analysed for possible agreement with the Halsay model than Hurkins-Jura, Radlich-Peterson and Dubinin-Radushkevich models. Correlation coefficient (R²) values obtained isotherms range from 0.799 – 0.997. The results indicate high prospect of chemically modified Bombax buonopozense Calyx for Cr⁶⁺, Mn⁶⁺ and Cd⁶⁺ ions removal.

Keywords: *Bombaxbuonopozense Calyx, Adsorption, Kinetics Study, Isotherms Study, Ions*

INTRODUCTION

The utilization of activated carbon prepared from agricultural wastes for environmental remediation has attracted considerable attention among researchers in the field of environmental Chemistry. Agricultural wastes are considered industrially attractive for production of activated carbon (AC) due to the carbon's ability to lower the concentration of heavy metal ions in solution. These wastes represent unused resources and possess unique features such as environmental friendliness, availability and relative abundance (Farouk and Yousef, 2015). Several micro, macro and mesoporous materials have been utilized to detoxify wastewater containing known potentially toxic elements. Considering all adsorbents, activated carbon (AC) remains one of the most famous. Activated carbons are carbonaceous materials which have high internally developed porosity and large surface area of more than 500 m²/g (Siti *et al.*, 2012). They consist of irregular array of interconnected micro crystallite, each consisting of fused hexagonal ring of carbon similar in structure to graphite (Musah *et al.*, 2016).

Adsorption has now become an important phenomenon in sensing and separation of ions and molecules. Any sorbent that has high adsorptive capability and good selective ability is very important in separation through adsorption. Recently, the attention of researchers has turned to the modification of activated carbon by introducing organic functional groups that helps in modifying its surface chemical characteristics (Bagheri *et al.*, 2015). Among the various organic functional groups attached to the surface of activated carbon are amines and acidic oxygen containing groups. Carboxyl and hydroxyl groups seem to be particularly important in

the adsorption of metal ion pollutants and immobilizing bio-molecules (Atieh, 2011).

Metals and their compounds are very important and indispensable part of any nation's industrial and technological advancement and pollution derived from these metals has continued to increase as industrial activities increase. Presently, the level of heavy metals released from industrial activities into the environment has become a real threat to human and animal health (Azizi *et al.*, 2016).

These metals are not biodegradable and enter the environment via anthropogenic activities. When ingested above tolerable levels, heavy metals can cause short and long term health impact on human depending on the exposure rate. Despite the adverse health effects of heavy metals on human, exposure to these metals has continued and even on increasing scale due to poor environmental regulatory framework (Shanmugam and Arabi, 2016).

In view of this, high quality chemically modified activated carbon with acid and base were used to study the adsorption efficiency of Cr⁶⁺, Mn²⁺ and Cd²⁺ ions in stock solution by investigating the effects of contact time, adsorbent dosage (ACH and ACK), initial concentration of Cr⁶⁺, Mn²⁺ and Cd²⁺ ions in stock solution and solution pH. Also, the kinetic and adsorption isotherms were explored to establish the best fitted model with the adsorption study.

MATERIALS AND METHODS

Chemicals used in this study include Potassium dichromate, manganese chloride, cadmium nitrate, sodium hydroxide, and hydrochloric acid which were obtained from Sigma Aldrich and they were all of analytical grade with percentage purity in the range of 98-99.99%.



The effect of contact time was studied using the batch method. In the experiment, 0.2 g of the adsorbent was mixed with 20 cm³ of the solution and interacted at 200 rpm for 30, 60, 90, 120 and 150 mins. Concentration of solution was varied from 10 to 50 mg/dm³ and interacted with 20 cm³ of the solution using 0.2 g of the adsorbent. The adsorbent was separated from the solutions through filtration and the filtrates were analysed for chromium, manganese and cadmium ions using AA320N AAS. The adsorption capacity and the percentage removal of Cr⁶⁺, Mn²⁺ and Cd²⁺ ions were calculated using Eq. (1) and (2) respectively.

$$q_e = \frac{(C_o - C_e)V}{m}$$

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

Where q_e is the equilibrium adsorption capacity of the adsorbent (mg/g), C_o and C_e is the initial and equilibrium concentration of ions under consideration in solution (mg/L) respectively, m is the weight of the adsorbents (g) and V is the volume of the solution used (dm³).

Adsorption Kinetics

The kinetics of adsorption was studied using the pseudo first order, pseudo second order, Elovich and intraparticle diffusion models. The different kinetics models and equations are presented in table 1

Table 1: Adsorption kinetic models and their equations

| Kinetic model | Equation |
|-------------------------|---|
| Pseudo first order | $\log (q_e - q_t) = \log (q_e) - \frac{K_t}{2.303} t$ |
| Pseudo second order | $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$ |
| Elovich | $q_t = \frac{1}{\beta} \ln (\alpha\beta) + \frac{1}{\beta} \ln (t)$ |
| Intraparticle diffusion | $\log q_t = \log k_{id} + n \log (t)$ |

The equations take the form of equation of straight line i.e y = mx + c. For pseudo first order, the graph is a plot of log (q_e - q_t) against t; in the case of pseudo second order, it is 1/q_e versus t, while qt versus t is plotted for elovich model and log q_t versus 0.5 log (t) for intraparticle diffusion model.

Adsorption Isotherms

The different adsorption isotherm models studied are Freundlich, Langmuir, Temkin, Radlich – Peterson and Dubinin – Radushkevich. The graph of each model was plotted fitting the equation of each model into

the equation of straight line: y = mx + c, where y and x are the variable while m and c (slope and intercept) are the isotherm parameters. The various isotherm models and their equations are presented in Table 2

Table 2: Adsorption isotherm models and their equations

| Adsorption Isotherm | Equation |
|------------------------|---|
| Langmuir | $\frac{C_e}{q_e} = \frac{1}{b q_{max}} + \frac{C_e}{q_{max}}$ |
| Freundlich | $\log q_e = \log k_f + \frac{1}{n} \log C_e$ |
| Temkin | $q_e = \frac{RT}{b} \ln k_T + \frac{RT}{b} \ln C_e$ |
| Radlich – Peterson | $\ln \frac{C_e}{q_e} = g \ln C_e - \ln k_R$ |
| Dubinin - Radushkevich | $\ln q_e = \ln Q_D - B_D [RT \ln(1 + 1/C_e)]$ |

The affinity between the activated carbons and the different adsorbates were determined by fitting the adsorption values into the isotherm parameters.

RESULTS

Table 3 present results of kinetic parameters for the adsorption of Cr⁶⁺, Mn²⁺ and Cd²⁺ onto ACH and ACK. The results showed high correlation coefficient (R²) values (0.990, 0.994 and 0.997) for pseudo second

order followed by Bhattacharya and Venkobachar (0.855, 0.924 and 0.975). Values obtained for adsorption rate range from 0.007 (for Natarajan and Khalaf) to 1.022 (for pseudo second order).



Table 3: Kinetic Parameters for Adsorption of Cr⁶⁺, Mn²⁺ and Cd²⁺

| Kinetic Model | Parameter | Cr ⁶⁺ | | Mn ²⁺ | | Cd ²⁺ | |
|----------------------------------|--|------------------|-------|------------------|-------|------------------|-------|
| | | ACH | ACK | ACH | ACK | ACH | ACK |
| Pseudo first order | R ² | 0.807 | 0.606 | 0.954 | 0.841 | 0.821 | 0.790 |
| | k ₁ (min ⁻¹) | 0.029 | 0.029 | 0.039 | 0.044 | 0.032 | 0.035 |
| | q _e (exp)(mg/g) | 0.935 | 0.914 | 0.921 | 0.920 | 0.934 | 0.914 |
| | q _e (cal) (mg/g) | 0.233 | 0.219 | 0.581 | 1.064 | 0.382 | 0.229 |
| | SSE (%) | 0.314 | 0.311 | 0.151 | 0.064 | 0.247 | 0.306 |
| Pseudo second order | R ² | 0.997 | 0.990 | 0.990 | 0.997 | 0.997 | 0.994 |
| | k ₂ (mg.g ⁻¹ min ⁻¹) | 0.143 | 0.084 | 0.089 | 0.062 | 0.107 | 1.022 |
| | q _e (exp)(mg/g) | 0.935 | 0.914 | 0.921 | 0.920 | 0.934 | 0.914 |
| | q _e (cal) (mg/g) | 0.995 | 1.011 | 1.014 | 1.033 | 1.010 | 0.977 |
| | SSE (%) | 0.027 | 0.048 | 0.042 | 0.050 | 0.034 | 0.028 |
| Natarajan and Khalaf first order | R ² | 0.611 | 0.567 | 0.584 | 0.857 | 0.724 | 0.746 |
| | k (min ⁻¹) | 0.009 | 0.009 | 0.009 | 0.009 | 0.009 | 0.007 |
| Bhattacharya and Venkobachar | R ² | 0.852 | 0.865 | 0.975 | 0.924 | 0.855 | 0.674 |
| | k _B (min ⁻¹) | 0.037 | 0.039 | 0.046 | 0.053 | 0.037 | 0.018 |
| Elovich | R ² | 0.780 | 0.732 | 0.867 | 0.919 | 0.846 | 0.683 |
| | α (mg.g ⁻¹ min ⁻¹) | 3.319 | 0.346 | 0.294 | 0.269 | 1.057 | 1.415 |
| | β (mg.g ⁻¹ min ⁻¹) | 8.621 | 5.882 | 5.649 | 5.682 | 7.246 | 7.752 |

Results of Isotherm constants for the adsorption of Cr⁶⁺, Mn²⁺ and Cd²⁺ onto ACH and ACK are resented on Table 4. The highest correlation coefficient (R²) values obtained for each isotherm are 0.897, 0.998, 0.997 and 0.993 for Hurkins – Jura, Halsay, Radlich - Peterson and Dubinin - RAdushkevich respectively.

Table 4: Isotherm constants for the adsorption of Cr⁶⁺, Mn²⁺ and Cd²⁺

| Isotherm Model | Parameter | Cr ⁶⁺ | | Mn ²⁺ | | Cd ²⁺ | |
|----------------------------|---|------------------|-------|------------------|-------|------------------|-------|
| | | ACH | ACK | ACH | ACK | ACH | ACK |
| Hurkins-Jura | A _H (g ² /L) | 1.071 | 1.021 | 0.968 | 1.011 | 1.202 | 1.238 |
| | B _H (mg/L) | 1.109 | 1.144 | 1.027 | 1.085 | 1.000 | 1.060 |
| | R ² | 0.826 | 0.832 | 0.879 | 0.799 | 0.823 | 0.897 |
| | RMSE | 4.612 | 4.942 | 4.329 | 3.962 | 4.369 | 7.207 |
| | χ ² | 17.88 | 4.942 | 14.68 | 12.97 | 12.82 | 43.59 |
| Halsay | K _{HA} (mg/L) | 0.876 | 0.755 | 0.886 | 0.867 | 1.049 | 0.851 |
| | n _{HA} | 1.996 | 1.996 | 1.812 | 1.934 | 1.176 | 2.062 |
| | R ² | 0.983 | 0.982 | 0.998 | 0.974 | 0.983 | 0.975 |
| | RMSE | 0.001 | 0.057 | 0.028 | 0.039 | 0.216 | 0.070 |
| | χ ² | 0.000 | 0.003 | 0.001 | 0.001 | 0.031 | 0.004 |
| Radlich-Peterson | g | 0.498 | 0.497 | 0.446 | 0.482 | 0.135 | 0.514 |
| | K _R (L/g) | 0.931 | 0.868 | 0.934 | 0.929 | 0.997 | 1.081 |
| | R ² | 0.982 | 0.981 | 0.997 | 0.970 | 0.659 | 0.977 |
| | RMSE | 0.001 | 0.049 | 0.018 | 0.049 | 0.223 | 0.066 |
| | χ ² | 0.000 | 0.002 | 0.000 | 0.002 | 0.034 | 0.004 |
| Dubinin-Radushkevich (D-R) | B _D (mol ² /KJ ²) | 0.946 | 0.997 | 0.909 | 1.057 | 1.245 | 0.925 |
| | Q _D (mol/g) | 3.597 | 2.175 | 3.789 | 3.846 | 6.606 | 3.432 |
| | E _D (KJ/mol) | 0.727 | 0.708 | 0.742 | 0.688 | 0.634 | 0.735 |
| | R ² | 0.970 | 0.962 | 0.946 | 0.987 | 0.993 | 0.915 |
| | RMSE | 0.229 | 0.294 | 0.044 | 0.211 | 0.095 | 0.335 |
| | χ ² | 0.044 | 0.074 | 0.092 | 0.037 | 0.006 | 0.094 |

RMSE = Residual Root Mean Square Error



Discussion of Results

Adsorption Kinetics

The adsorption rate of any molecule onto a surface is important in understanding adsorption process. It is essential to apply kinetic models in describing rate of adsorption and confirming reaction mechanism.

To evaluate the kinetics for sorption of Cr^{6+} , Mn^{2+} and Cd^{2+} onto ACH and ACK, pseudo first order, pseudo second order, Natarajan and Khalaf first order, Bhattacharya and Venkobachar first order, elovich and intraparticle diffusion models were employed. A good correlation coefficient of kinetic data also helps in explaining the adsorption of ions onto adsorbent (Meera and Ganesan, 2015).

Pseudo First Order Model

The pseudo first order model is one of most widely used model in describing the removal of adsorbate from liquid phase (Farouq and Yousef, 2015).

Amount of adsorbates removed, rate constant and correlation coefficients (R^2) for pseudo first order model of adsorption of Cr^{6+} , Mn^{2+} and Cd^{2+} are presented in Table 3. The slope and intercept of plots of $\log(q_e - q_t)$ versus t were used to determine the rate constants and theoretical amount of adsorbate removed per unit mass of adsorbent ($q_{e, \text{cal}}$). Experimental q_e value ($q_{e, \text{exp}}$) obtained for the adsorption of Cr^{6+} , Mn^{2+} and Cd^{2+} ranged between 0.897 to 0.935 mg/g with ACH having the highest adsorption capacity (q_e) for Cr^{6+} . Comparing the experimental q_e value ($q_{e, \text{exp}}$) and the theoretical q_e value ($q_{e, \text{cal}}$) shows that $q_{e(\text{exp})}$ differ significantly from $q_{e(\text{cal})}$ obtained from the linear plots of $\log(q_e - q_t)$ versus t , indicating the adsorption of Cr^{6+} , Mn^{2+} and Cd^{2+} onto ACH and ACK does not follow pseudo first order model. Similar observations were reported by Rout *et al.*, (2015), Farghali *et al.*, (2013).

Rate constants (k_1) obtained were low (0.029 – 0.044 min^{-1}) and correlation coefficients (R^2) were also lower than those of pseudo second order model but the sum of square error (SSE) were significantly high (as seen in Table 3). High k_1 and R^2 with low SSE is considered an indication of good fit of a model (Musah *et al.*, 2011). The low k_1 and R^2 values with high SSE obtained further confirms that pseudo first order model did not fit experimental data, hence the process did not follow pseudo first order kinetics.

Pseudo Second Order Model

The adsorption of Cr^{6+} , Mn^{2+} and Cd^{2+} onto ACH and ACK following pseudo second order model as presented on Table 1. The plots of t/q_t versus t were used to determine pseudo second order rate (k_2) and adsorption capacity (q_e) whose values are also presented in Table 3. Pseudo second order rate constants obtained for adsorption of Cr^{6+} , Mn^{2+} and Cd^{2+} are between 0.039 $\text{mgg}^{-1}\text{min}^{-1}$ for adsorption of Mn^{2+} onto CAC to 0.143 $\text{mgg}^{-1}\text{min}^{-1}$ for removal of Cr^{6+}

by ACH. These values are higher than those obtained in pseudo first order rate constant for adsorption of same ions on same adsorbents. The higher the value of rate constant (k_2) the higher will be the adsorption of ions (Odoemelam *et al.*, 2011). The k_2 values are higher than 0.007 and 0.000869 $\text{mgg}^{-1}\text{min}^{-1}$ reported for adsorption of cadmium and strontium onto rice straw and zeolite-based activated carbons respectively (Javadian *et al.*, 2015).

Correlation coefficients (R^2) obtained ranged between 0.990 and 0.997. These values are higher than those of pseudo first order model; and high R^2 value for pseudo second order indicate the sorption process follows pseudo second order model (Musah *et al.*, 2011). Rout *et al.*, (2015) also reported pseudo second order model as best fit for describing adsorption process. Besides correlation coefficients (R^2), the applicability of pseudo second order model was verified using the sum of square error (SSE). The low SSE values (Table 3) further describe the adsorption of Cr^{6+} , Mn^{2+} and Cd^{2+} onto ACH and ACK to follow pseudo second order kinetic model.

Natarajan – Khalaf and Bhattacharya – Venkobachar first order kinetic models

Results of these models are presented on Table 3. Values of correlation coefficient (R^2) and rate constant (k) are presented in Table 3. Rate constants (k) values are between 0.009 to 0.012 min^{-1} and correlation coefficient (R^2) ranged from 0.431 to 0.857. Similarly, constants of Bhattacharya and Venkobachar first order are presented in Table 3. Correlation coefficients (R^2) for sorption of Cr^{6+} , Mn^{2+} and Cd^{2+} onto ACH and ACK are within the range of 0.777 and 0.975. These values are higher than those of Natarajan and Khalaf first order but lower R^2 values of pseudo first order and pseudo second order kinetics model for the experiments. The low R^2 values of Natarajan and Khalaf first order, and Bhattacharya and Venkobachar first order models indicate the lack of fit in describing the experimental data, hence the process did not follow these orders. Similar R^2 values were reported for the adsorption of Cd^{2+} , Cu^{2+} , Pb^{2+} and Cr^{3+} onto activated carbon from agricultural wastes (Meera and Ganesan, 2015; Musah *et al.*, 2011).

Elovich model

From Table 1, α ($\text{mgg}^{-1}\text{min}^{-1}$) is the initial adsorption rate and β ($\text{mgg}^{-1}\text{min}^{-1}$) is related to the extent of surface coverage and activated energy for sorption (Javadian *et al.*, 2015). The values of constants α and β for the adsorption of Cr^{6+} , Mn^{2+} and Cd^{2+} onto ACH and ACK were obtained from the slope and intercept of linear plots q_t versus $\ln t$ and presented in Table 3. Adsorption of Cr^{6+} onto ACH had the highest α and β values of 3.319 $\text{mgg}^{-1}\text{min}^{-1}$ and 8.621 ($\text{mgg}^{-1}\text{min}^{-1}$) respectively.



Correlation coefficients (R^2) values range between 0.683 and 0.919 and are lower than those obtained in pseudo second adsorption model of same experiment. The values are 0.9571 reported for adsorption of Cd^{2+} onto zeolite (Javadian *et al.*, 2015) but higher than 0.8595 obtained in the adsorption Cu^{2+} onto mussels shell activated carbon (Farouk and Yousef, 2015).

Adsorption Isotherms

Isotherm constants for the adsorption of Cr^{6+} , Mn^{2+} and Cd^{2+} ions onto ACH and ACK are presented in Table 4.

The interaction between adsorbates and adsorbents is usually described using adsorption isotherms; and these makes it necessary to optimize the use of adsorbent. Establishing appropriate correlation for equilibrium curve is essential in optimizing the design of an adsorption system (Pragathiswaran *et al.*, 2013). Adsorption isotherms used to analyze experimental data in this work are Hurkins-Jura, Halsay, Radlich-Peterson and Dubinin-Radushkevich.

Hurkins-Jura Adsorption Isotherm

The equation of Hurkins-Jura presented on Table 2 enables the determination of A_H and B_H (sorption equilibrium) parameters from the slopes and intercept of the plot of $1/q_e$ against C_e and their values are presented in Table 4. The isotherm equation accounts for multilayer adsorption.

The R^2 values obtained were too low and are between 0.811 for the adsorption of Mn^{2+} onto CAC to 0.799 for the adsorption of Mn^{2+} onto ACK to 0.897 for the adsorption of Cd^{2+} onto ACK. These values do not suggest a good fit of the model to the experimental data. This assertion is corroborated by the very high values of RMSE of up to 7.207 for ACK adsorption of Cd^{2+} and 43.59 obtained as the highest X^2 , and 4.942 as the lowest value. All values are greater 1.0, the maximum required for good fit and agreement between $q_{e,exp}$ and $q_{e,cal}$. Similar high values were obtained for adsorption of Zn^{2+} from aqueous solution onto pulp waste (Sampranpiboon *et al.*, 2014).

Halsay adsorption isotherm

Halsay isotherm is suitable for a multilayer sorption. The model parameters, KHA and nHA for the adsorption of Cr^{6+} , Mn^{2+} and Cd^{2+} onto ACH and ACK are presented in Table 4. The RMSE and X^2 values for the Halsay adsorption isotherm are considerably low with Cr^{6+} adsorption onto ACH having the least (0.001 for RMSE and 0.000 for X^2). These values are lower than 3.283 for RMSE and 8.660 for X^2 reported by (Sampranpiboon *et al.*, 2014). Low RMSE and X^2 values with high R^2 suggest multilayer formation on sorbent (Tichaona *et al.*, 2013) and that the model can be used to describe experimental data for the adsorption of Cr^{6+} , Mn^{2+} and Cd^{2+} ; the result also showed that multilayer was formed during sorption

Radlich-Peterson adsorption isotherm

The Radlich-Peterson adsorption isotherm is an intermediate isotherm whose parameters consist of both Langmuir and Freundlich isotherms (Shahbeig *et*

al., 2013). This isotherm gives a more realistic presentation of adsorption system which operates over a range of concentrations (Pragathiswaran *et al.*, 2013).

Radlich-Peterson adsorption isotherm constants, g and K_R were determined from the slopes and intercepts of the plot of $\ln C_e/q_e$ versus $\ln C_e$ (not shown) and their values are presented in Table 4. The values of K_R obtained ranged from 0.868 for the adsorption of Cr^{6+} onto ACK, to 1.081 for adsorption of Cd^{2+} by ACK indicating a prediction of good adsorption capacity by Radlich-Peterson model. The values are higher than 0.220 reported for the adsorption of Zn^{2+} by pulp wastes (Sampranpiboon *et al.*, 2014). A g value less than 1 ($g < 1$) indicate a favourable adsorption while g value greater than 1 ($g > 1$) suggest adsorption is not favourable (Prasat *et al.*, 2014). Values obtained were lower than 1.

The low values of X^2 suggest a good agreement between values of $q_{e,exp}$ and $q_{e,cal}$. This is corroborated by RMSE and R^2 values which also indicate a good fit between Radlich-Peterson adsorption isotherm and the experimental data.

Dubinin-Radushkevich (D-R) adsorption isotherm

The Dubinin-Radushkevich adsorption isotherm assumes the characteristics of adsorption curve to be related to the adsorbent's porosity (Sampranpiboon *et al.*, 2014). It helps determine whether the adsorption that occurred is chemisorptions or physisorption in nature (Pragathiswaran *et al.*, 2013). It also determines the apparent energy of sorption and does not assume homogeneous surface of adsorbent (Abasi *et al.*, 2011). The linear form of the model is expressed on Table 2.

B_D (mol^2/KJ^2) is related to the free energy of adsorption per mole of the adsorbate as it migrates to the surface of the adsorbent form infinite distance in solution (Itodo and Itodo, 2010) and Q_D (mol/g) is the D-R constant related to the degree of adsorption of adsorbate onto the surface of the adsorbent (Pragathiswaran *et al.*, 2013). The estimated Q_D (mol/g) values presented in Table 2 ranged from 2.175 for the adsorption of Cr^{6+} onto ACK to 6.606 for the adsorption of Cd^{2+} onto ACH. These values are higher than 0.48 reported for sorption of Cadmium using agbani clay (Dawodu *et al.*, 2012) but similar to 2.865 and 4.086 obtained for the removal of Zn^{2+} by pulp waste (Sampranpiboon *et al.*, 2014). High value of Q_D is an indication of high adsorption capacity (Dawodu *et al.*, 2012). From Q_D values in Table 4, one can infer that adsorption capacity of the adsorbents is high.

The estimated constant, B_D gives idea of the mean free energy, E_D . Values of B_D (mol^2/KJ^2) (presented in Table 4) are higher than 0.006 reported for the removal of Cd^{2+} (Dawodu *et al.*, 2012) but lower than 19.696 obtained for adsorption of Zn^{2+} (Sampranpiboon *et al.*, 2014).



E_D values less than 8 KJ/mol indicates physisorption process while values between 8 and 16 (KJ/mol) suggest the process is chemisorption (Dawodu *et al.*, 2012). Values of parameter predicting the type of sorption, E_D obtained in this research are below 1.500 KJ/mol indicating that the adsorption process is mainly physisorption, a non specific process characterised by formation of multilayer as a result of Van Der Waal's force of attraction between adsorbent and adsorbate (Itodo and Itodo, 2010) . This is corroborated by the multilayer prediction of the process by Halsey model through its low RMSE and X^2 values.

Conclusion

Chemically modified activated carbon (AC) functionalized with H_2SO_4 (ACH) and KOH (ACK) were successfully used to study the kinetics and isotherms

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