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# STUDY OF ISOTHERM MODELS FOR THE ADSORPTION OF Cr (VI) ION FROM AQUEOUS SOLUTION ONTO *Bombax buonopozense* CALYX ACTIVATED CARBON

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## ABSTRACT

This study investigates the application of activated carbon prepared from *Bombax buonopozense* calyx as an adsorbent for heavy metal removal from aqueous solution. Batch adsorption experiments were conducted to investigate and evaluate the performance of *Bombax buonopozense* calyx activated carbon in the adsorption of Cr (VI) from aqueous solution at pH 6.0 and for a period of 60 minutes. The optimum adsorption of Cr (VI) occurred at 10 mg/L. The equilibrium sorption data were analyzed using Freundlich, Langmuir, Temkin, and Jovanovich isotherm models. The Langmuir and Freundlich models were found to adequately describe the adsorption of Cr (VI) onto *Bombax buonopozense* calyx activated carbon.

**Keywords:** Adsorption, Isotherm, Freundlich, Langmuir, Temkin, Jovanovich, *Bombax buonopozense*

## INTRODUCTION

Heavy metals can remain for decades when released into the environment and can be harmful to human health upon ingested above tolerable levels (Pragathiswaran *et al.*, 2013). Despite the adverse effects of heavy metals on human health, exposure to these metals has continued to increase (Musah *et al.*,2016). One of such metals is chromium, which exists as Cr (III) and Cr (VI). Cr (III) exists as natural form found in rocks, animals, plants, volcanic dust and gases. Activities that increase the concentration of Cr (III) in the environment include leather, steel and textile manufacturing. Known Industrial sources of Cr (VI) include chromate pigments in dyes, inks, paints and plastics, particles released during smelting of ferrochromium ore, fumes from the welding of stainless alloys, addition of chromates as anti-corrosive agents in paints, chromate plating by depositing chromium metal onto the surface of materials using solution of chromic acid (Pragathiswaran *et al.*, 2013).

Chromium (VI) is a known human toxin;breathing high levels of Cr (VI) can cause irritation to the lining of the nose, nose ulcer, runny nose and breathing problems, such as asthma and cough. Skin contact can cause skin irritation and allergic reactions consisting of severe redness and swelling of the skin. Long term exposure to Cr (VI) can cause damage to liver, kidney circulatory and nerve tissues (Musah *et al.*, 2011).

**Adsorption Isotherm**

Adsorption isotherm is an important requirement in designing an adsorption system. The capacity of the isotherm is fundamental, and plays an important role in the determination of maximum capacity of adsorption. It indicates how efficient an activated carbon will adsorb and allows an estimation of the validity of activated carbon's application. It also represents the amount of adsorbate bound on the surface of adsorbent as a function of the material present in the solution. Isotherms studied in this study include Freundlich, Langmuir and Temkin.

**Freundlich adsorption isotherm**

The Freundlich isotherm is used to quantify the equilibrium relationship between the amount of adsorbate adsorbed per unit weight of the carbon and the adsorbate concentration remaining in the solution (Sampranpiboon *et al.*, 2014). Freundlich isotherm is expressed as:

$$q_e = K_f C^{1/n} \quad (1)$$

n is a constant related to adsorption efficiency and energy of adsorption, $K_f$ is a constant measuring adsorption capacity, $q_e$ (mg/g) is amount of adsorbate adsorbed per unit weight of carbon and $C$ is equilibrium concentration of the adsorbate in solution

The Freundlich equation is basically empirical but is often useful as means for data description. This is because of the adequacy of the equation to describe non-linear adsorption in a narrow range of adsorbate concentration, its mathematical simplicity which allows it to be used easily, and its ability to describe adsorption process on surface adsorption sites that are energetically heterogeneous (Sampranpiboon *et al*, 2014). Freundlich equation can be used in linear form by the taking logarithm of both sides of the equation

$$\log q_e = \log K_f + \frac{1}{n} \log C \quad (2)$$

Where:

n is a constant related to efficiency of sorption and sorption energy.

$K_f$ is a constant measuring adsorption capacity

$q_e$ is the amount of adsorbate removed per unit weight of carbon

$C$ is the equilibrium concentration of the adsorbate in solution (Mohamed *et al*., 2016),

A plot of log $q_e$ versus log $C$ gives a straight line with the slope $1/n$ and the intercept log $K_f$. The $K_f$ value increases with the total adsorption capacity of the adsorbent to bind the adsorbate (Shahbeig *et al.*, 2013)

**Langmuir adsorption isotherm**

In his model, Irving Langmuir considers the surface of adsorbent to possess active interaction sites that allow adsorption to occur. He assumed that (Meera and Ganesan, 2015; Shahbeig *et al.*, 2013):

i. On the surface of each adsorbent are fixed adsorption sites and a fraction these sites could be occupied by adsorbate molecules at a given temperature and pressure
ii. Uptake of adsorbate occur on homogeneous surface and it is by monolayer
iii. Each adsorption site on the adsorbent surface can accommodate one entry
iv. Heat of adsorption for each site is the same and independent of the fraction of sites adsorbate molecule occupy.
v. No interaction exists between adsorbate molecules occupying different adsorption sites.

From the assumptions above, Langmuir isotherm is valid for only monomolecular adsorption and is expressed as:

$$q_e = \frac{bCeQ^o}{1 + bCe} \quad (3)$$

$q_e$ (mg/g) is amount of adsorbate adsorbed per unit weight of carbon, $Q^o$ is a constant relating to monolayer adsorption capacity, *b* is a constant which measure the surface energy of the adsorption process and *Ce* is equilibrium concentration of the adsorbate in solution

The linear form of Langmuir equations are:

$$\frac{Ce}{q_e} = \frac{1}{bQ^o} + \frac{Ce}{Q^o} \quad (4)$$

$$\frac{1}{q_e} = \frac{1}{Q^o} + \left[\frac{1}{bQ^o}\right]\left[\frac{1}{Ce}\right] \quad (5)$$

A plot of $1/q_e$ versus $1/C$ gives a straight line with slope $1/ bQ^o$ and intercept of $1/ Q^o$

The Langmuir isotherm model can be used to describe equilibrium conditions for adsorption and to provide parameters ($Q^o$ and *b*) with which to quantitatively compare adsorption behaviour in different adsorbate-adsorbent system (Abasi *et al.*, 2011).

**Temkin adsorption isotherm**

Temkin adsorption isotherm assumes that the heat of adsorption would decrease linearly with sorption coverage due to adsorbent/adsorbate interactions (Sampranpiboon *et al*, 2014). Temkin isotherm equation can be expressed as:

$$qe = \frac{RT}{bT}\ln(\mathrm{KtCe})\, C \quad (6)$$

Equation 2.19 can be presented in the linear form as:

$$\mathrm{qe} = \frac{RT}{b}\ln \mathrm{Kt} + \frac{RT}{b}\ln \mathrm{Ce} \quad (7)$$

Kt ($dm^3/g$) is equilibrium binding energy which correspond to maximum binding energy, $b_T$ (J/mol) is a constant related to heat of adsorption. R is the ideal gas constant (0.08206 L.atm/K.mol) and T is the absolute temperature (Pragathiswaran *et al.*, 2013).

**Analysis of Error**

Isotherm adsorption parameter has usually been determined using linear regression and results gives good fit to experimental data with $R^2$ based on the linear form of isotherm equations. But this does not represent the errors in the curves of the isotherm; the evaluation of the fit of the adsorption isotherm equation to experimental data requires the use of different error functions to determine the model parameters, residual root mean square error (RMSE) and chi-square test could be used (Sampranpiboon *et al.*, 2014). The Residual root mean square error is expressed as:

$$\text{RMSE} = \sqrt{\frac{1}{n-2}\sum_{n=1}^{n} (q_{e,exp} - q_{e,cal})^2}. \quad (8)$$

Where the subscripts 'exp' and 'cal' are the experimental and calculated values of qe and n represent the number of observations in the experiment. The smaller the residual mean square error (RMSE) value the better the curve fitting of the isotherm (Meera and Genasan., 2015).

Thechi-squaretest isgivenas:

$$x^2 = \frac{(qe,exp - qe,cal)^2}{qe,exp} \quad (9)$$

If data from the model calculation iscloseto the experimental data,$\chi^2$ will be a small number. The $\chi^2$ value can be used to measure how well the model fits.

## MATERIALS AND METHODS

The batch adsorption method was used for the interaction of aqueous solution with adsorbent. About 0.2 g of activated carbon was interacted with $20cm^3$ of aqueous solutions. This was allowed to shake for 60 minutes at 250 rpm. The experiment was performed at different concentrations of the solution (10, 20, 30, 40 and 50mg/L) after which each mixture was filtered separately using Whatman filter paper (No.42) and filtrate collected into sample bottles (Shama *et al*, 2010). Concentrations of heavy metal ions in the solution were determined before and after interactions with activated carbon using Atomic Absorption Spectrophotometer and the removal efficiency (%) was calculated as (Okewale *et al.*, 2013):

$$RE(\%) = \frac{(C_o - C_f) \times 100}{C_o} \quad (10)$$

$Co$(mg/dm$^3$)is concentration of heavy metal ion before interaction with activated carbon and $C_f$is concentration of heavy metal ion after interaction with activated carbon

Adsorption capacity at time t ($q_t$) was calculated using the formula:

$$q_t = \frac{(C_o - C_t)\, v}{m} \quad (11)$$

$v$ (dm$^3$)is volume of aqueous solution used for interaction and $m$ (g) is mass of adsorbent used

## RESULTS AND DISCUSSION

### *Freundlich Adsorption Isotherm*

Freundlich constants $K_F$ and $1/n_F$ related to adsorption capacity and adsorption intensity were calculated from the slope and intercept of the linear plot of log $q_e$ vs log $C_e$ as shown in figure 1 and model parameters are presented in Table 1 for the sorption of Cr (VI). The magnitude of $K_F$ (dm$^3$/g) for the sorption of Cr (VI) onto *Bombax buonopozense* Calyx activated carbon showed high capacity (0.931) for sorption of Cr (VI) with $K_F$ value of 0.931.

**Table 1: Isotherm Constants for the Adsorption of $Cr^{6+}$ onto *Bombax buonopozense* Activated Carbon**

| Isotherm Model | Parameter | Cr (VI) HAC | Isotherm Model | Parameter | Cr (VI) HAC |
|---|---|---|---|---|---|
| Freundlich | $K_F$ (L/g) | 0.931 | Temkin | $K_T$ (L/g) | 2.197 |
| | $1/n_F$ | 0.501 | | $b_T$ (J/mol) | 0.962 |
| | $R^2$ | 0.982 | | $R^2$ | 0.977 |
| | RMSE | 0.002 | | RMSE | 0.135 |
| | $\chi^2$ | 0.00004 | | $\chi^2$ | 0.015 |
| Langmuir | $q_m$ (mg/g) | 4.444 | Jovanovich | $K_J$ (L/g) | 0.086 |
| | $K_L$ (g/mg) | 0.214 | | $q_{max}$ (mg/g) | 1.121 |
| | $R^2$ | 0.975 | | $R^2$ | 0.831 |
| | RMSE | 0.117 | | RMSE | 0.297 |
| | $\chi^2$ | 0.011 | | $\chi^2$ | 0.074 |

RMSE = Residual Root Mean Square Error

The magnitude $K_F$ obtained is higher than the 0.578, 0.80 and 0.751 reported for the sorption of Zn (II) onto pulp waste at 30$^oC$, 40$^oC$ and 50$^oC$ (Pragathiswaran, *et al.*, 2013) indicating high adsorption capacity of the activated carbon, as high $K_F$ value indicate an easy uptake of adsorbate from solution (Patil *et al.*, 2010).

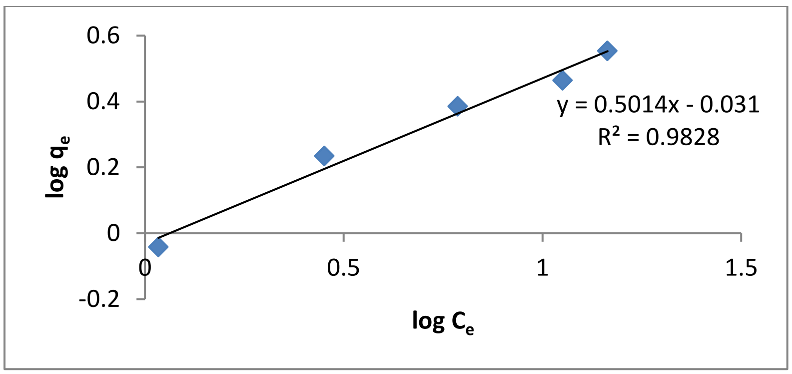


Figure 1: Freundlich Isotherm for Adsorption $Cr^{6+}$ onto *Bombax buonopozense* activated carbon

If $1/n_F$ value is less than one ($1/n_F < 1$), the adsorption process is considered favourable (Farouq and Yousef, 2015). $1/n_F$ values obtained was 0.501 indicating favourable adsorption of Cr (VI) by the adsorbent. $R^2$ value of 0.982 was obtained and is higher than the $R^2$ valuefor Langmuir isotherm suggesting that Freundlich isotherm better fit the experimental data. $R^2$ which is value is based on linear equation, does not represent errors in the isotherm curves (Sapranpiboon *et al*, 2014). To further evaluate the fit of the Freundlich isotherm model to experimental data taking into account the isotherm curve, the residual mean square error (RMSE) was calculated using equation 10. The 0.002 value of RMSE obtained suggest that Freundlich isotherm showed good fit to experimental data when Cr (VI) is adsorbed. To determine the closeness of $q_{e,\ exp}$ to $q_{e,cal}$, equation 11 was employed. The result (0.0004) showed higher degree of closeness of $qe_{,\ exp}$ to $q_{e,cal}$. The lower the values of RMSE and $X^2$ obtained the better the fit (Meera and Genasan, 2015). These results indicate favourable adsorption and easy uptake of Cr (VI) ions from the solution.

***Langmuir Adsorption Isotherm***

Langmuir adsorption isotherm is based on the assumption that uptake of adsorbate occurs on a homogeneous surface and is by monolayer (Farouk and Yousef, 2015). The model is used to predict the performance of adsorbent. The parameter $K_L$ indicates adsorption affinity and $q_m$ represent maximum adsorption capacity (i.e monolayer saturation) decreases with increasing temperature (Sapranpiboon *et al*, 2014). Langmuir adsorption isotherm constants, $K_L$ and $q_m$ were obtained from slope and intercept in figure 2 and the values are presented in Table 1. $K_L$

values of Cr (VI) adsorption is 0.214 and is indicative of high adsorption affinity of adsorbent to adsorbate than 0.15 reported for Cr (VI) ion adsorption onto Aloevera adsorbent (Pragathiswaran *et al.*, 2013).

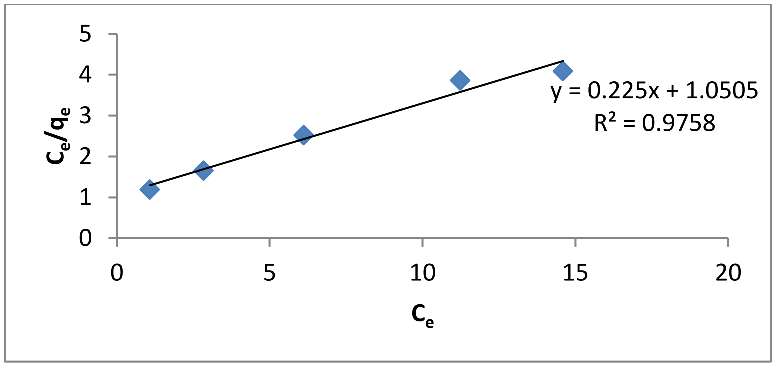


Figure 2: Langmuir Isotherm for Adsorption $Cr^{6+}$ onto *Bombax buonopozense* activated carbon
RMSE and $X^2$ values (0.117 and 0.011) obtained for Langmuir isotherm are higher than Freundlich adsorption isotherm suggesting Freundlich adsorption isotherm gives a better fit than Langmuir isotherm. This is also corroborated by the low $R^2$ value of the Langmuir isotherm. The monolayer saturation capacity, $q_m$ was 4.444; this value is higher than 0.15 for Cr (VI) adsorption but lower than 27.119 reported for Cu (II) adsorption (Farouk and Yousef, 2015; Pragathiswaran *et al.*, 2013).

Langmuir adsorption isotherm is also expressed using the equilibrium parameter, $R_L$ a dimensionless constant separation factor (Prasath *et al.*, 2014):

$$RL = \frac{1}{1+bCo} \quad (12)$$

Where, $C_o$ (mg/dm$^3$) is the highest initial concentration and b (dm$^3$/mg) is the Langmuir constant. The parameter, $R_L$ indicates the nature of the isotherm shape and is interpreted in Table 2:

**Table 2: Langmuir Isotherm Constant Parameter**

| $R_L$ Value | Type of Isotherm |
|---|---|
| $R_L > 1$ | Unfavourable |
| $R_L = 1$ | Linear |
| $R_L = 0$ | Irreversible |
| $0 < R_L < 1$ | Favourable |

Source: Shokoohi *et al*, 2009:

The $R_L$ value 0.315 was obtained for the sorption of Cr (VI) and is also presented in Table 1. The value is within the range of $0 < R_L < 1$ for favourable adsorption and is lower than the 0.9377 reported for the adsorption of Cr (VI) ion on aloevera adsorbent (Pragathiswaran *et al.*, 2013) but slightly higher than 0.303 and 0.2008 obtained for adsorption of Cd (II) and Ni (II) onto Embolica bark and *Thespesia populnea* bark activated carbons (Meera and Ganesan, 2015; Prabakaran and Arivoli, 2012).

***Temkin Adsorption Isotherm***

Temkin adsorption parameters, $K_T$ and $b_T$ were obtained from the slope and intercept of the plot of $q_e$ versus ln $C_e$ (Figure 3). The isotherm assume that adsorption process is characterized by uniform distribution of binding energies and heat of sorption of molecules in the layer and this energy decreases linearly with surface coverage; the isotherm also assumes chemisorption of adsorbate onto the adsorbent (Tichaona *et al.*, 2013). Positive value (0.962) was obtained for $b_T$ adsorption of Cr (VI) indicating the process is endothermic. This value is higher than 0.30 reported for the adsorption of Cu (II) by *Vigna subterranean* but lower than 12.560 obtained for removal of Cr (VI) onto Aloevera activated carbon (Tichaona *et al.*, 2013; Pragathiswaran *et al.*, 2013). The $R^2$ value (0.977) obtained for shows that Temkin isotherm fits the data.

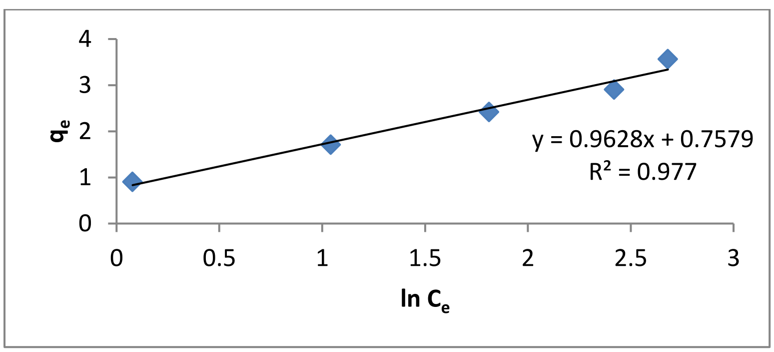


Figure 3: Temkin Isotherm for Adsorption $Cr^{6+}$ onto *Bombax buonopozense* activated carbon

The RMSE value (0.135) is lower than 0.245 and 0.173 reported for adsorption of Zn (II) by pulp waste (Sampranpiboon, *et al.*, 2014). $X^2$ value of 0.015 is an indication of good agreement between experimental and calculated $q_e$ values.

**Jovanovich Adsorption Isotherm**

This model corresponds to approximation for monolayer adsorption without literal interactions. The model is similar to the Langmuir adsorption isotherm except that allowance is made in Jovanovich adsorption isotherm for surface vibrations of adsorbed species (Farouk and Yousef, 2015). The linear form of the isotherm is expressed as:

$$\ln qe = \ln q_{max} - KjCe \quad (13)$$

$q_{max}$ is the maximum uptake of adsorbate

Parameters of the Jovanovich adsorption isotherm are presented in figure 4 and Table 1.
The $q_{max}$ recorded for the adsorption of Cr (VI) is 1.121 and is lower than the 4.444 obtained Langmuir adsorption isotherm but higher than the 1.115 reported for adsorption of Cu (II) onto pulp waste (Sampranpiboon, *et al.*, 2014).. Even though $q_{max}$ for Jovanovich is similar to Langmuir isotherm, it does not describe the sorption process as well as Langmuir adsorption isotherm

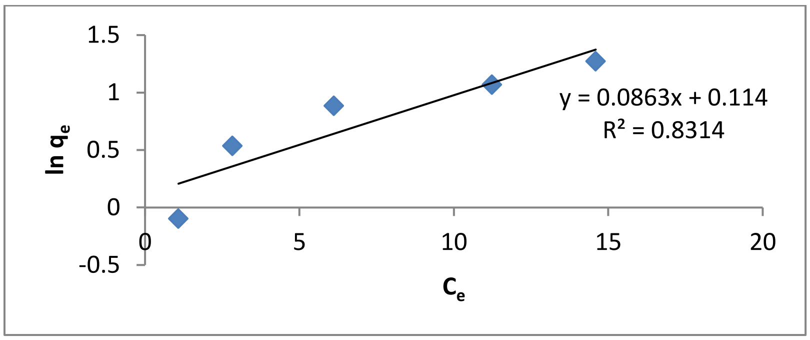


Figure 4: Jovanovic Isotherm for Adsorption $Cr^{6+}$ onto *Bombax buonopozense* calyx activated carbon
RMSE values of 0.297 was obtained for the removal of Cr (VI) and is lower than 4.444 obtained for Langmuir isotherm but slightly higher than the 1.115 reported for adsorption of Cu (II) onto pulp waste (Sampranpiboon, *et al*, 2014). $R^2$ value for Jovanovich adsorption isotherm (0.831) is also lower than $R^2$ for Langmuir Isotherm (0.975) in the same research, and also lower than 0.9212 reported for adsorption of Cu (II) by Farouk and Yousef (2015). $X^2$ values of Jovanovich adsorption isotherm are higher those of Langmuir isotherm indicating less agreement between experimental $q_e$ and calculated $q_e$.

## CONCLUSION

Activated carbon prepared from *Bombax buonopozense* calyx was used as adsorbent for the removal of Cr (VI) ions from aqueous solutions. Adsorption was influenced by initial concentration of the solutions at equilibrium time of 60 minutes. Results revealed that *Bombax buonopozense* calyx activated carbon could be used as adsorbent for the removal of Cr (VI) ions from wastewater and the process followed Feundlich and Langmuir models.


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