



Adsorption of Cr(VI) onto Activated Carbons Prepared from Indigenous Materials

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Abstract: The adsorption of chromium(VI) on activated carbons prepared from low cost materials has been studied by batch process. The influences of various parameters like contact time, dosage, pH, pH_{Zpc} and co-ions were experimentally verified. The adsorption of Cr(VI) is maximum at strongly acidic medium (pH 3). Adsorption is explained using Langmuir and Freundlich isotherms with help of chi-square analysis. Thermodynamic parameters like ΔG^0 , ΔH^0 and ΔS^0 were calculated to understand the nature of adsorption. The surface morphology of the three activated carbons before and after metal sorption was verified using scanning electron microscope (SEM) and X-ray diffraction studies (XRD).

Keywords: Adsorption, Activated carbons, Adsorption Isotherms, Chi-square analysis, Intraparticle diffusion

Introduction

Recently, a great deal of interest in the research for the removal of heavy metals from environment has focused on the use of indigenously available materials as adsorbents¹.

Among the heavy metals chromium, cobalt, zinc, copper and iron ingestion beyond permissible quantities, causes various chronic disorders in human beings. It is well known that heavy metals can damage the nerves, liver and bones and they block functional groups of essential enzymes². The permissible limit of Cr(VI) for industrial waste water to be discharged to surface water is 0.1 mg/L. Hence it becomes imperative to remove it from waste water before discharging them into aquatic systems or onto land. Different methods such as reduction, precipitation, ion exchange, electro dialysis, solvent extraction, electrochemical precipitation and adsorption had been suggested for the removal of hexavalent chromium³. Among these adsorption is the most promising technique. The most widely used industrial adsorbent is activated carbon. However, it is an expensive material unless regeneration becomes relatively easy but is unlikely to be cost

effective. Various agricultural products and by products have been investigated to remove heavy metals from aqueous materials^{4,5}. In recent years, investigation have been carried out for the effective removal of large quantities of Cr(VI) from waste water using low cost, non conventional adsorbents which are economically viable⁶. Adsorption on activated carbon has been a popular choice in developed countries for the removal of Cr(VI) and other metal ions^{7,8}. The use of activated carbons to remove Cr(VI) from water was proposed because of their higher surface area and active functional groups leading a search for low cost adsorbents in recent years⁹. Natural materials that are available in large quantities could be potential low cost adsorbents as they represent unused resources¹⁰.

This paper narrates the investigation of Cr(VI) removal from aqueous solutions by adsorption on activated carbons prepared from *Recinius Communis* Linn (RC), *Carica Papaya* Linn (CP) and *Morinda Pubescence* (MP) with adsorption isotherms, chi-square analysis, thermodynamic parameters and intraparticle diffusion.

Experimental

The preparation of activated carbons RC, CP and MP consisted of carbonization of the respective plant materials. Each dried raw material was cut into small pieces and the carbonization was conducted in a muffle furnace at 400°C, 450°C and 500°C for RC, CP and MP respectively. The heating period was 2 hours for all materials. After carbonization, the carbon was ground using domestic mixie. The activated carbons obtained were kept in a desiccator and were characterized for the physical parameters, which are shown in Table 1.

Table 1. Characteristics of the activated carbons

S.No	Parameters	Adsorbents		
		RC	CP	MP
1	Particle size, mm	0.15	0.11	0.14
2	Density, g/cc	0.54	0.56	0.58
3	Ash content, %	2.04	1.98	2.11
4	Moisture content, %	1.64	1.34	1.50
5	Loss of ignition, %	82.0	85.1	88.3
6	Water soluble matter	0.17	0.31	0.24
7	pH of aqueous solution	7.5	7.2	7.0
8	pH, zpc	7.1	6.9	6.7
9	Iodine number, mg/g	204	236	190

Adsorption Studies

The three activated carbons shown in Table 1 were used to study adsorption of Cr(VI). Adsorption equilibrium study of Cr(VI) was carried out in 250 mL stoppered iodine flask by adding 200 mg RC, 250 mg CP, and 300 mg of MP activated carbon to 50 mL of 20 ppm chromium solution. The concentration of the samples was analyzed on UV/ Visible spectrophotometer (UV 240 Shimadzu) using 1-5 diphenyl carbazide as the complexing agent at the wavelength of 540 nm. All other water quality parameters were analyzed by using standard methods¹¹ The pH measurements were done with a pH electrode (Systronics) and pH_{ZPC} (pH of zero point charge) was determined by pH drift method¹². The surface morphology of the raw and treated activated carbons was visualized by SEM with a HITACHI-S-3000H model. XRD pattern was recorded using X¹ per PRO (model), PAN analytical (make). Computations were made using Microcal Origin, (version 6.0) software. The goodness of the fit is discussed using the regression, correlation and coefficient (R).

Results and Discussion

Effect of contact time

The optimum period for the adsorption of Cr(VI) on the sorbents can be observed by looking at the difference in time after adding the adsorbents. The effect of agitation period on the adsorption of Cr(VI) is shown in Figure 1. The adsorption of Cr(VI) increased with agitation period and attained an optimum at about 14 min for RC, 16 min for CP and 18 min for M.P.

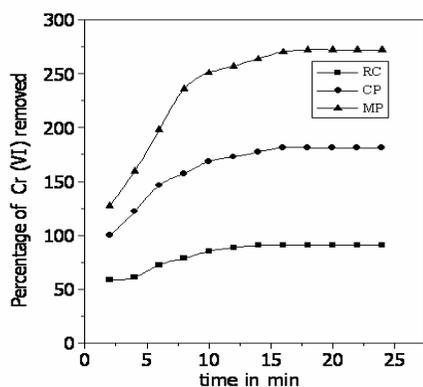


Figure 1. Effect of contact time

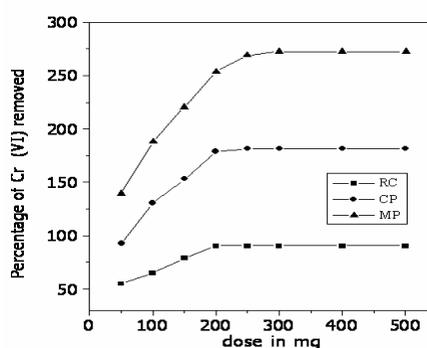


Figure 2. Effect of Dosage

Effect of dosage

The effect of adsorbent dosage is presented in Figure 2. It is evident that adsorption increases with increase in the mass of the adsorbent. This is because at higher dosage of sorbent, more adsorption sites are available due to increased surface area. This results in the removal of more metal ions and after certain dosage it attains equilibrium, beyond which no change in the adsorption occurs at higher dose of the adsorbent.

Effect of pH

Earlier studies have indicated that solution pH is an important parameter affecting adsorption of heavy metals. Cr(VI) removal was studied in the pH range of 3.0 – 7.0 for all three activated carbons and results are shown in Figure 3. It is clear from the figure that the percentage of adsorption of Cr(VI) decreases with increase in pH from 3.0 to 7.0. The maximum adsorption of Cr(VI) occurred at pH 3.0. This behaviour can be explained considering the nature of the adsorbent at different pH levels. The cell wall of activated carbons contains a large number of surface functional groups. The pH dependence of metal adsorption can largely be related to the type and ionic state of these functional groups and also on the metal chemistry in solution. Adsorption of Cr(VI) below pH 5.0 (maximum at pH 3.0) suggests that the negatively charged species (chromate/dichromate in the sample solution) bind through electrostatic attraction to positively charged functional groups on the surface of activated carbon. But at above pH 5.0, it seems that activated carbon possesses more functional groups carrying a net negative charge, which tends to repulse the anions. However, appreciable Cr(VI) removal occurs at above pH 5.0, although the rate of removal is considerably reduced. Hence, it could be said that above pH 5.0, other mechanism like physical adsorption on the surface of adsorbent could have taken an important role in the adsorption of Cr(VI). In addition, adjustment of pH is very important. The possibilities of other subsidiary substances and hydrogen bonding may affect the adsorption process and need careful analysis¹³.

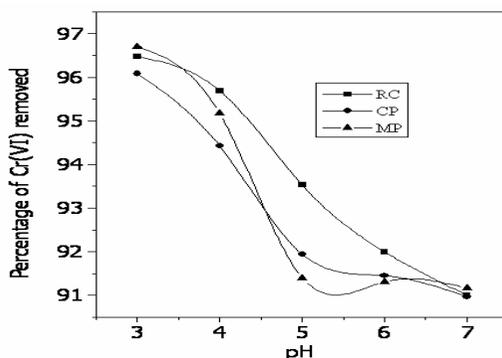


Figure 3. Effect of pH

Effect of co-ions

The influence of other co-ions such as Cl^- , HCO_3^- , SO_4^{2-} , NO_3^- , Ca^{2+} and Mg^{2+} and which are commonly present in water, on the adsorption of Cr(VI) by the activated carbons was investigated with varying initial concentrations of these ions *viz.*, 200, 400, 600, 800 and 1000 mg/L by keeping Cr(VI) concentration constant. Figure 4 gives the effect of co-ions on the adsorption of Cr(VI) by the activated carbons. In all, the presence of these co-ions did not significantly alter the Cr(VI) adsorption process by the activated carbons.

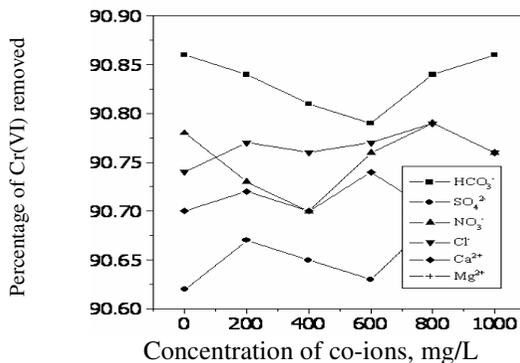


Figure 4. Effect of co-ions

Adsorption isotherms

The adsorption isotherms indicate how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose. Adsorption isotherm is basically important to describe how solutes interact with adsorbents and is critical in optimizing the use of adsorbents. Adsorption isotherm studies were carried out on two isotherm models *viz.*, Langmuir and Freundlich isotherms. Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface. The linear form of Langmuir isotherm equation is given as

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e \quad (1)$$

where C_e is the equilibrium concentration of the adsorbate (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g), Q_0 and b are Langmuir constants related to adsorption capacity and rate of adsorption. When C_e/q_e was plotted against C_e , a straight line with slope of $1/Q_0$ was obtained. The Langmuir curves pertaining to the Cr(VI) adsorption by RC is provided in Figure 5. The figures pertaining to CP and MP also behave similarly and hence are not included here. However, Table 2 provides the experimental data for all the three carbons studied. The Langmuir constants b and Q_0 were calculated from equation (2) and the values are given in Table 2. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter (R_L) which is defined by,

$$R_L = \frac{1}{1 + bC_0} \tag{2}$$

where b is the Langmuir constant and C_0 is the initial concentration (mg/L)¹⁴. The value of R_L indicates the type of the isotherm to be either favourable ($0 < R_L < 1$), unfavourable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). The value of R_L was found to be less than one in all cases reported here and this again confirmed that the Langmuir isotherm model was favourable for adsorption of Cr(VI) onto the activated carbons under the conditions used in this study.

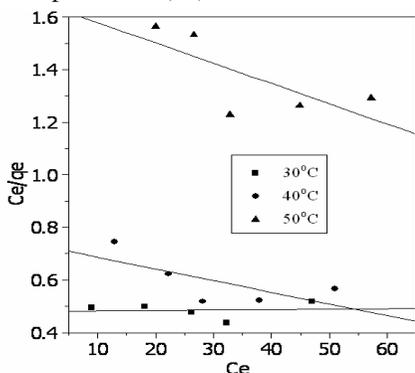


Figure 5. Langmuir plot for RC

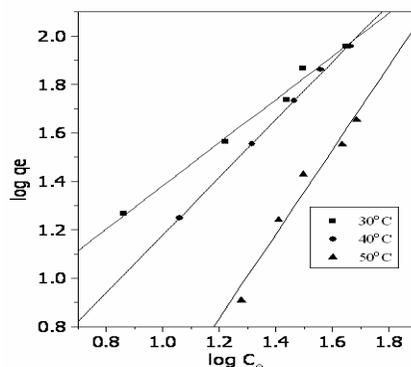


Figure 6. Freundlich plot for RC

Freundlich isotherm assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage. The well-known logarithmic form of Freundlich isotherm is given by the following equation,

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{3}$$

where C_e is the equilibrium concentration of the adsorbate (mg/L) and q_e is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g). K_f and n are Freundlich constants representing the adsorption capacity and intensity of adsorption respectively. The values of K_f and $1/n$ were obtained from the slope and intercept of the plot of $\log q_e$ versus $\log C_e$. The slope of $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero¹⁵. Freundlich constants K_f and n are listed in Table 2. The Freundlich plots for the Cr(VI) adsorption by RC is given in Figure 6.

Chi-Square analysis

To identify a suitable isotherm model for the sorption of Cr(VI) on activated carbon this analysis has been carried out. The chi-square statistics is basically the sum of the squares of the difference between the experimental data and data obtained by calculating from models,

with each squared difference divided by corresponding data obtained by calculation from the models. The equilibrium mathematic statement is

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \quad (4)$$

where $q_{e,m}$ is equilibrium capacity obtained by calculating from model (mg/g) and q_e is experimental data on the equilibrium capacity (mg/g). If data from the model are similar to the experimental data, χ^2 will be small number while if they differ χ^2 will be a bigger number. Therefore, it is necessary to also analyze the data set using chi-squared test to confirm the best fit isotherm for the sorption system. The values are given in Table 2. The lower values of χ^2 for Freundlich isotherm than those of Langmuir isotherm indicate that the former is more suitable for adsorption of Cr(VI) on the three activated carbons RC, CP and MP¹⁶

Table 2. Langmuir and Freundlich constants

Adsorbent	Langmuir constants				Freundlich constants					
	Temp K	Q ₀	b	R ²	R _L	χ ²	1/n	K _f	R ²	χ ²
RC	303	2.4284	0.0215	0.977	0.922	0.5691	0.722	2.702	0.994	0.0074
	313	2.4632	0.0235	0.988	0.715	0.2543	0.732	2.787	0.999	0.0040
	323	2.4889	0.0321	0.981	0.559	0.1964	0.843	2.957	0.980	0.0029
CP	303	2.2761	0.0115	0.971	0.826	0.4123	0.073	1.685	0.989	0.0077
	313	2.2978	0.0235	0.980	0.534	0.3478	0.308	1.588	0.994	0.0044
	323	2.3149	0.0321	0.993	0.525	0.2987	0.497	1.526	0.984	0.0037
MP	303	2.2366	0.0522	0.968	0.826	0.6591	0.856	2.706	0.995	0.0121
	313	2.2514	0.0547	0.974	0.534	0.4896	0.887	2.271	0.991	0.0058
	323	2.2865	0.0563	0.987	0.525	0.3698	0.891	2.358	0.996	0.0049

Thermodynamic treatment of the sorption process

Thermodynamic parameters of the adsorption *viz.*, standard free energy change (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0) for the reactions were calculated using the equation given below and the values are given in Table 3.

$$\Delta G^0 = -RT \ln K_0, \quad (5)$$

where the ΔG^0 is the free energy of adsorption (KJmol^{-1}), T is the temperature in Kelvin and R is the Universal gas constant ($8.314 \text{ Jmol}^{-1} \text{ K}^{-1}$). The adsorption distribution coefficient K_0 for the adsorption reaction was determined from the slope of the plot $\ln(q_e / c_e)$ against C_e at different temperature and extrapolating to zero C_e according to method suggested by Khan and Singh¹⁷. The adsorption distribution coefficient may be expressed in terms of enthalpy change (ΔH^0) and entropy change (ΔS^0) as a function of temperature,

$$\ln K_0 = \frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}, \quad (6)$$

Where ΔH^0 is the heat of sorption (KJmol^{-1}) and ΔS^0 is standard entropy change (KJmol^{-1}). The values of ΔH^0 and ΔS^0 can be obtained from the slope and intercept of the plot of $\ln K_0$ against $1/T$.¹⁸

Table 3. Thermodynamic parameters for sorption of Cr(VI) at different temperatures

Adsorbent	$\Delta G^0, \text{KJmol}^{-1}$			$\Delta H^0, \text{KJmol}^{-1}$	$\Delta S^0, \text{KJmol}^{-1}$
	303K	313K	323K		
RC	-1.966	-1.579	-1.123	+ 4.89	0.023
CP	-1.717	-1.456	-1.122	+ 5.20	0.029
MP	-1.787	-1.471	-1.071	+ 5.40	0.045

Adsorption dynamics

From a mechanistic point of view, to interpret the experimental data, production of the rate-limiting step is an important factor to be considered in the sorption process. Though kinetic and equilibrium isotherm studies help to identify the adsorption process, predicting the mechanisms is required for design purpose. For a solid - liquid sorption process, the solute transfer is usually characterized by either external mass transfer (boundary layer diffusion) or intraparticle diffusion or both.

The sorption dynamics can be described by three consecutive steps which are as follows:

- Transport of the solute from bulk solution through liquid film to the adsorbent exterior surface
- Solute diffusion into the pore of adsorbent except for a small quantity of sorption on the external surface; parallel to this intraparticle transport mechanism of the surface diffusion
- Sorption of solute on the interior surfaces of the pores and capillary spaces of the adsorbent. The last step is considered to be an equilibrium reaction of the three steps, the third step is assumed to be rapid and considered to be negligible.

The overall rate of sorption will be controlled by the slowest step, which would be either film diffusion or pore diffusion. However, the controlling step might be distributed between intraparticle and external transport mechanisms. Whatever be the case, external diffusion will be involved in the adsorption process. The adsorption of Cr(VI) on the activated carbon may be controlled due to film diffusion at earlier stages and as the adsorbent particles are loaded with chromium ions, the sorption process may be controlled due to intraparticle diffusion. But for design purposes, it is necessary to calculate the slowest step involved in the sorption process. For the adsorption process, the external mass transfer controls the adsorption process for the systems that have poor mixing, dilute concentrations of adsorbate, small particle sizes of adsorbent and higher affinity of adsorbate for adsorbent/ whereas the intraparticle diffusion will control the sorption process for a system with good mixing, large particle size of adsorbent, high concentration of adsorbate and low affinity of adsorbate for adsorbent. The most commonly used technique for identifying the mechanism involved in the adsorption process is by fitting the experimental data in an intraparticle diffusion plot. Previous studies by various researchers showed that the plot of q_t versus $t^{1/2}$ represents multi linearity which characterized the two or more steps involved in the sorption process.

According to Weber and Morris, an intraparticle diffusion coefficient is defined by the equation.

$$q_t = K_p t^{1/2}, \quad (7)$$

q_t = the amount of Cr(VI) adsorbed per unit mass of adsorbents at any time t

$t^{1/2}$ = square root of time

K_p = Intraparticle diffusion rate constant

The plots of intraparticle diffusion curves show initial curved portion followed by linear portion and a plateau. The first sharper portion is the external surface adsorption or instantaneous adsorption stage. The second portion is the gradual adsorption where the intraparticle diffusion is rate controlled. The third portion is final equilibrium stage where the intraparticle diffusion starts to slow down due to extremely low solute concentration in solutions¹⁹. The representative plot of Cr(VI) adsorption by RC is shown Figure 7.

Evidence for intraparticle diffusion (K_p)

A preliminary appraisal of the sorbent - sorbate system may provide information indicating the sorption mechanism. For instance, there are several chemical groups on the sorbent which can

undergo chemical reaction to form a chemical bond. Acid groups on the sorbent could provide ion exchange sites for metal ions and ionic dyes. Amine groups can provide a lone pair of electrons for chelation with metal ions *etc.* Relatively inert sorbent surfaces may only provide physical sites for diffusion controlled bond formation. In order to identify the exact mechanism it is necessary to carry out experiments to study several system variables namely, initial concentration, sorbent particle size, solution temperature, solution pH and agitation and analyse the data for different order kinetic reactions or for pore/solid phase diffusion mechanisms. If equilibrium is achieved within three hours, the process is usually kinetic controlled and above twenty four hours, it is diffusion controlled. Either or both kinetic and sorption processes may be rate controlling in the three to twenty four hour period. Another very general guide line is that changes in pH have a greater effect on the sorption of solutes in reaction controlled sorption processes. A more appropriate quantitative approach to distinguish between kinetic and diffusion rate control is to perform the square root of contact time analysis according to equation (7). A plot of the amount of pollutant adsorbed, q_t , against the square root of time, $t^{1/2}$, yields a straight line plot of slope k_p , a diffusional rate parameter. This straight line, passing through the origin, indicates intraparticle diffusion control²⁰. Additional confirmation of a diffusion mechanism can be obtained by analysing the effect of the system variables on K_p . The values of K_p are given in Table 4. For intraparticle diffusion controlling systems K_p should vary linearly with reciprocal particle diameter; the product of K_p times sorbent mass should vary linearly with sorbent mass.

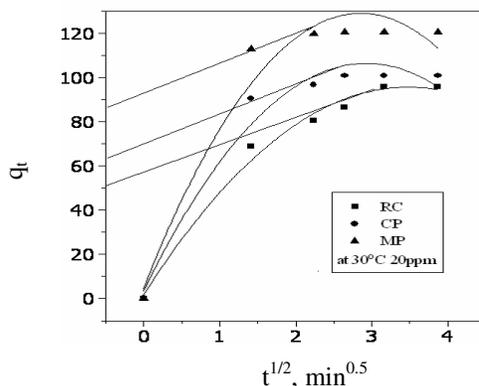


Figure 7. Intra particle diffusion for RC

Table 4. Values of K_p

Temperature (K)	Values of K_p		
	RC	CP	MP
303	6.28	4.87	5.36
313	10.76	11.08	10.72
323	18.32	18.04	15.57

Instrumental analysis

SEM images of the activated carbons before and after of Cr(VI) sorption are shown in Figures 8, 9 and 10. Comparison of these micro graphs before and after Cr(VI) sorption shows that the adsorption of Cr(VI) occurs on the surface of the activated carbon. XRD patterns of the treated adsorbents showed significant changes. The XRD data of the treated activated carbon provided evidence of decrease in the peak intensity which shows that adsorption of Cr(VI) on the surface of the adsorbent. Figures 11, 12 and 13 indicate the decrease in the peak intensity values of RC, CP and MP respectively²¹.

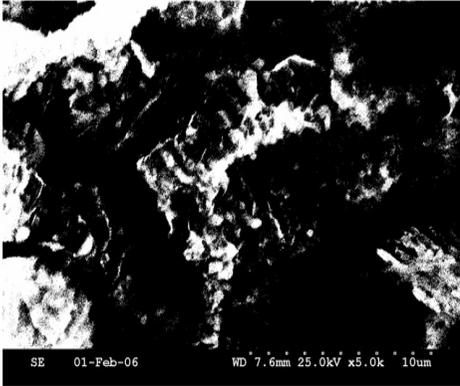


Figure 8(a). Before treatment for RC

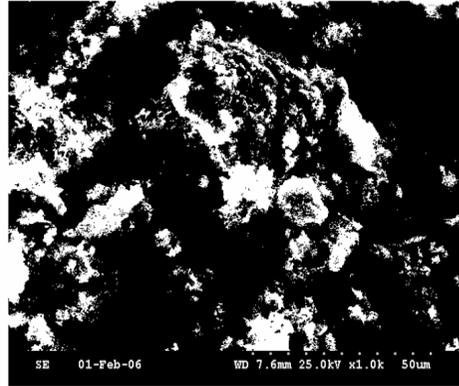


Figure 8(b). after treatment for RC

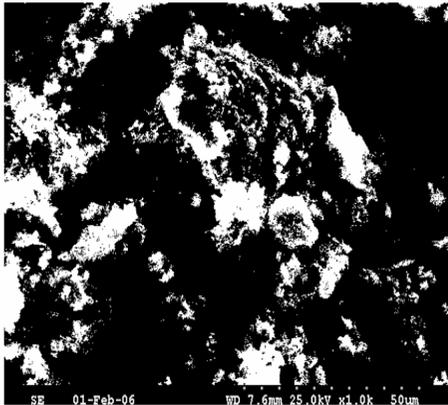


Figure 9(a). Before treatment for CP

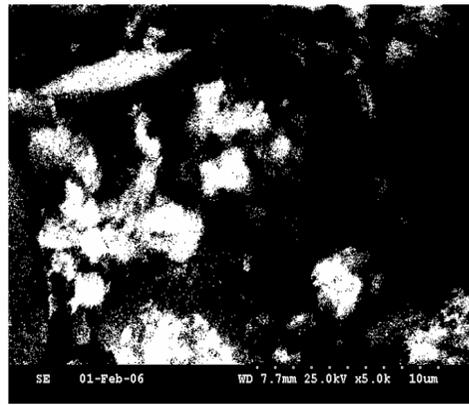


Figure 9(b). After treatment for CP

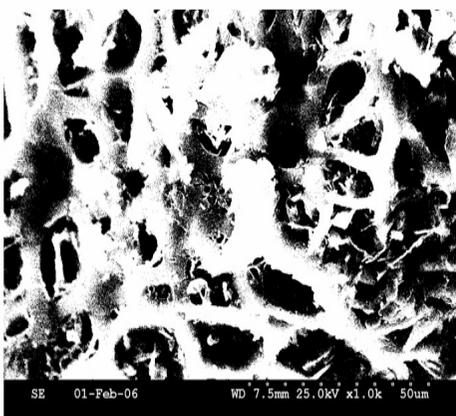


Figure 10(a). Before treatment for MP

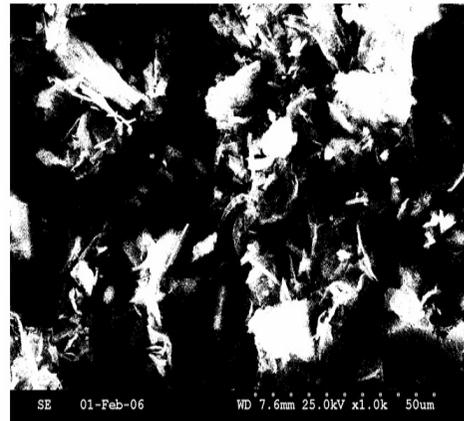


Figure 10(b). After treatment for MP

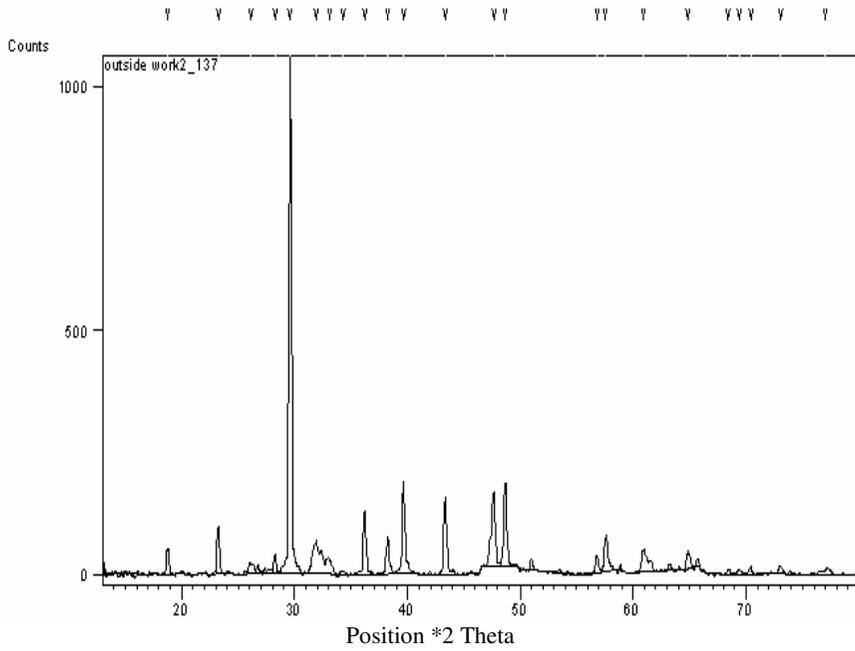


Figure 11(a). XRD before treatment for RC

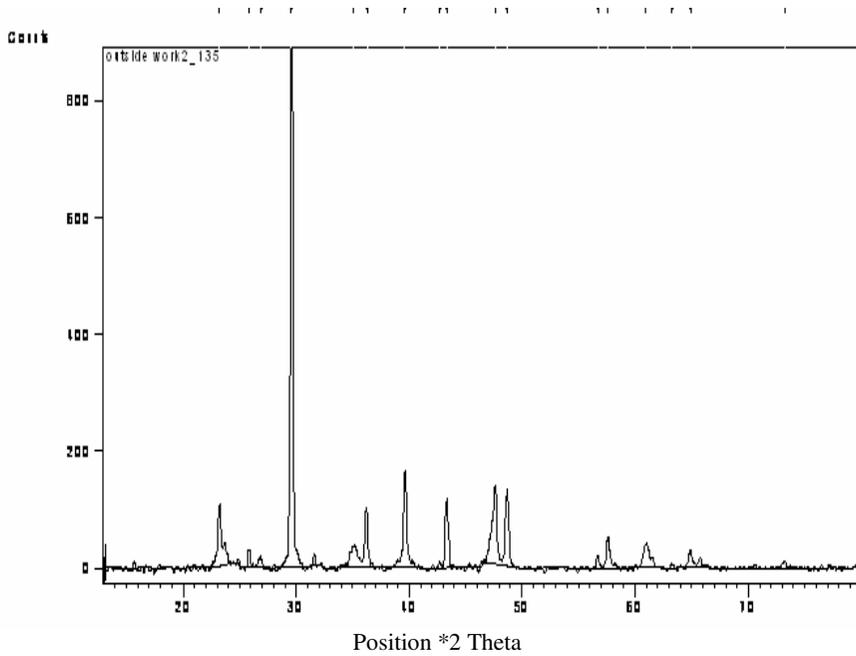


Figure 11(b). XRD after treatment for RC

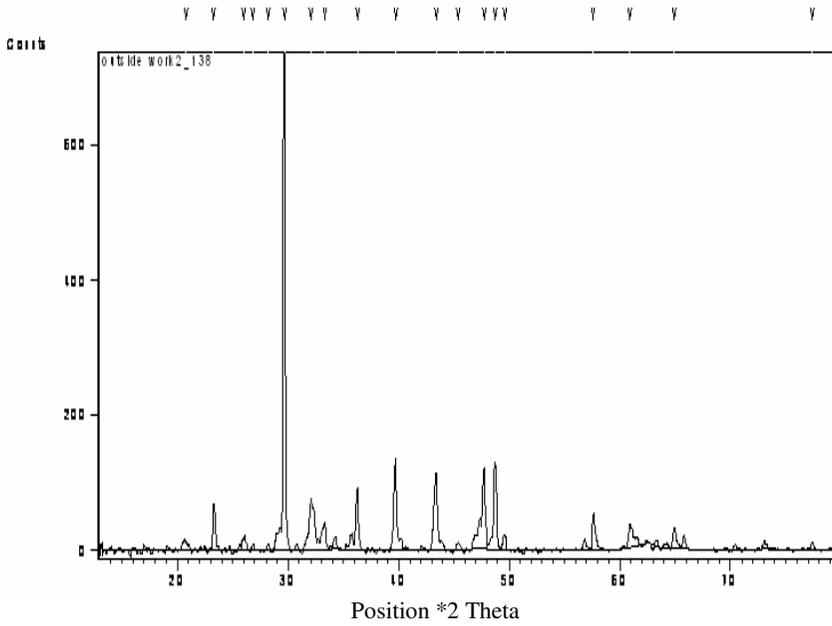


Figure 12(a) XRD before treatment for CP

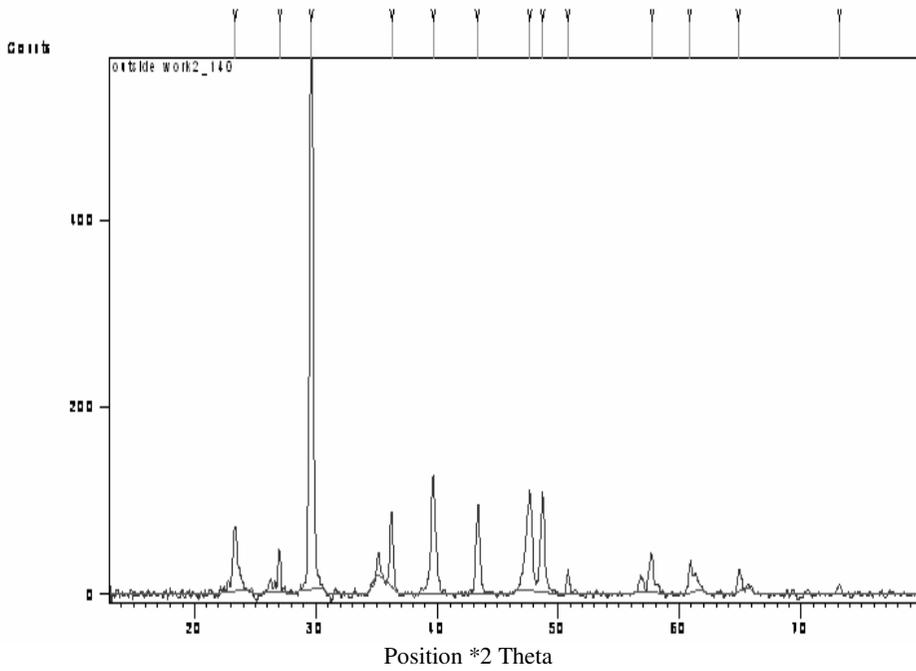


Figure 12(b). XRD after treatment for CP

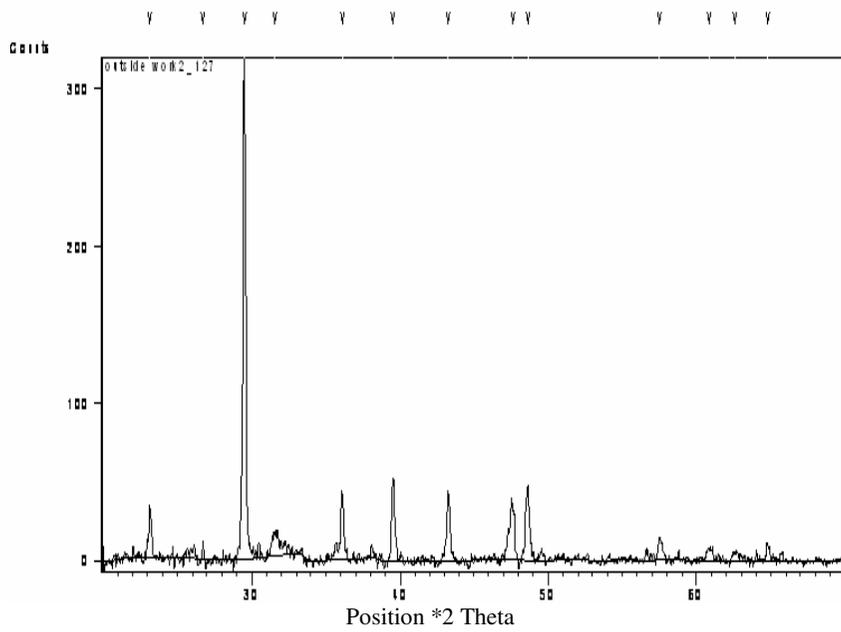


Figure 13(a). XRD before treatment for MP

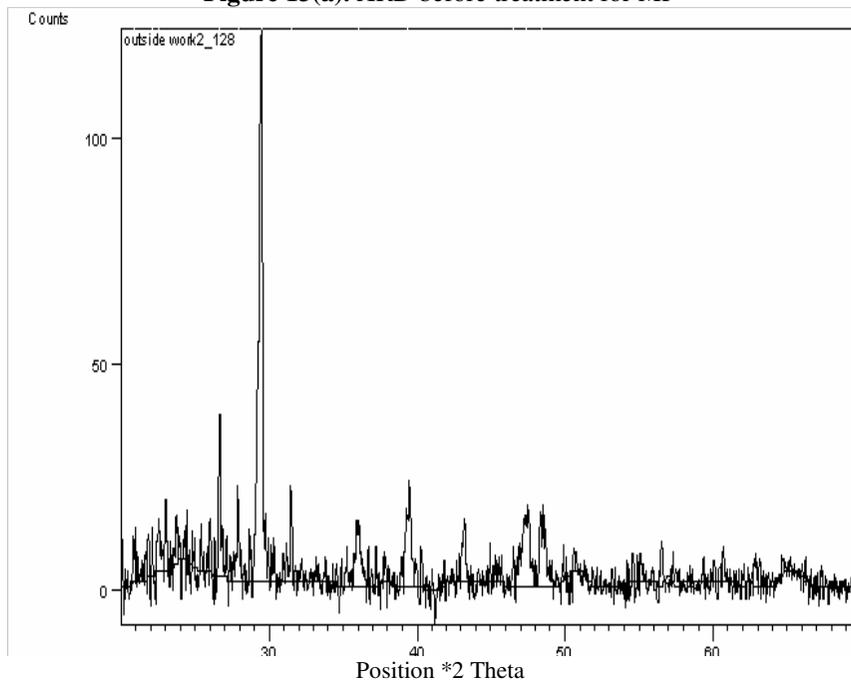


Figure 13(b). XRD after treatment for MP

Conclusion

In conclusion, the results of analysis of all the adsorbents clearly established that these activated carbons prepared from indigenous materials have good adsorption for Cr(VI). The removal percentage depended on the adsorbent dosage, contact time, co-ions, temperature and pH. The highest Cr(VI) adsorption was 96% at pH 3. The equilibrium data of adsorption are in good agreement with Freundlich isotherms model whatever the temperature or concentration. The adsorption dependence of Cr(VI) on temperature was investigated and the thermodynamic parameters ΔG^0 , ΔH^0 and ΔS^0 were calculated. The results show an endothermic heat of adsorption and negative free energy value, indicating a favored adsorption. SEM and XRD studies reveals that Cr(VI) adsorption takes place on the surface of the adsorbent.

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