



## Detoxification of Chromium (VI) Ions in Aqueous Solution via Adsorption by Raw and Activated Carbon Prepared from Sugarcane Waste

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**Abstract:** The use of raw and modified agricultural waste primed from sugarcane as sorbents for the removal of Cr(VI) ions from aqueous solution were examined in a batch process. FT-IR analysis revealed that –OH, –NH, C–O and aromatic rings functional groups were involved in the sorption process. Sorption of Cr(VI) on raw and modified biomass were studied as a function of pH, contact time, initial metal concentration and temperature. Maximum experimental conditions were obtained to be initial metal concentration of 50 mg/L, temperature of 45°C, contact time of 60 minutes and pH of 2.0. The kinetics studies indicated that the sorption pattern for the sorption of Cr(VI) ions by raw sugarcane waste and acid modified sugarcane waste followed Ho's-pseudo-second-order model, while that of carbonized acid modified sugarcane waste was well fitted by Lagergren pseudo-first model. Thermodynamic parameters suggested the feasibility, spontaneity, endothermic and randomness of the sorption process. Thus, biomass from sugarcane waste can be deployed in the detoxification of Cr(VI) ions from aqueous solution.

**Keywords:** Adsorption, Chromium, Kinetics, Pollution and Thermodynamic.

## 1.0 Introduction

Chromium is one of the most common pollutants introduced into the natural water system from a range of industrial effluents such as electroplating, paints, paper, textile dyeing and metal finishing industries [1, 2]. Low-level exposure to chromium can damage the skin and cause ulceration, while long time exposure can cause liver and kidney damage, and can also damage the circulatory system. Chromium(VI) is carcinogenic to both humans and animals. Strong exposure of chromium(VI) causes cancer in the digestive tract and lungs and may cause gastric pains, severe diarrhoea, vomiting and haemorrhage [3]. The United States Environmental Protection Agency (USEPA) puts the permissible limit of chromium in wastewater to be 1.0 mg/L and that of portable water to be 0.05 mg/L [2, 4].

Several techniques have been employed for the removal of heavy metals from contaminated environment. However, most of these methods are very expensive, incomplete removal of pollutants and can also generate sludge. Thus, there is need to seek for a more credible and alternative means for the removal of toxic metals ions from contaminated environments. Biosorption has been proposed as an alternative to conventional methods for the economic removal of toxic wastes [5]. Biosorption is

the removal of pollutants by means of passive adsorption or complexation by live biomass organic waste [6]. Algae, bacteria and fungi such as yeasts have proved to be potential metal sorbent [7]. Among the sorbents that have been used in recent years for the removal of pollutants from aqueous solution include: *Trichodema* [8], *Schizophyllum commune fries*, *Ganoderma lucidum* and *Pleurotus ostreatus* [9], Walnut, hazelnut and almond shells [1], *Agaricus bisporous* [10], Palm flower [11] and *Oyster snail* and *periwinkle shells* [12].

This study explored the potential of waste sugarcane matter for the removal of Cr(VI) ions from aqueous solution. Effects of physical parameters such as initial metal concentration, contact time, temperature and solution pH on the sorption capacity was investigated in batch experiments. The kinetics and thermodynamics of adsorption process were also evaluated.

## 2.0. Materials and Method.

### 2.1. Preparation of the Biomass.

Waste sugarcane matter were obtained from papalanto in Ogun State, Nigeria and washed with fresh water. The biomass was prepared by modifying the methods of [1, 13]. The biomass was cut into smaller sizes and sundried for 21 days and was then turned into powder form and sieved in a 150

µm size to get the required size. The dried biomass was divided into two portions. One part was dissolved in 0.1M of acetic acid for 24 hours for chemical modification. The biomass was filtered and sun dried before drying in an oven. About 20 g of this acid modified biomass was thereafter carbonized at 850°C in muffle furnace for 5 hours. After burning, the yield was washed with distilled water and sundried and thereafter packed for utilization. The remaining part (unmodified biomass) was used as raw material in the sorption process.

### 2.2. Chemicals and Instruments.

All chemicals used were of analytical grade and are products of Merck, India. Standard solutions of Cr(VI) was prepared by dissolving 1 g of  $K_2Cr_2SO_4 \cdot 7H_2O$  in  $1dm^3$  of distilled water. Several concentrations of Cr(VI) ions ranging from 10 – 100 mg/L were prepared from these stock solutions. The pH of the solutions was adjusted with 0.1M HCl and NaOH solutions after the addition of the biomass.

### 2.3. Characterization of Biomass

The FT-IR spectra of the sugarcane waste before and after adsorption of Cr(VI) ions was investigated by FT-IR transmission by KBr method. The measurement was performed by adopting the method used by Olukanni [14]. The scans were done in the mid IR region of 400-4000  $cm^{-1}$  using SHIMADZU 8400S FT-IR instrument.

### 2.4. Adsorption Experiments.

The batch sorption experiments were performed on a rotatory shaker at a speed of 150 rpm in a 250mL beaker. The procedure follows the method used by Ertugay and Bayham [5].

Amount Adsorbed

$$= \frac{C_i - C_f}{m} \times V \dots\dots\dots(Eq.1)$$

Percentage Removal

$$= \frac{C_i - C_f}{C_i} \times 100 \dots\dots\dots(Eq.2)$$

Where  $C_i$  and  $C_f$  are the initial and final concentrations of Cr(VI) ions in mg/L,  $V$  is the volume in litre and  $m$  is the mass of the biomass in g.

### 3.0 Results and Discussions.

#### 3.1. FTIR Characterization of Sugarcane Waste

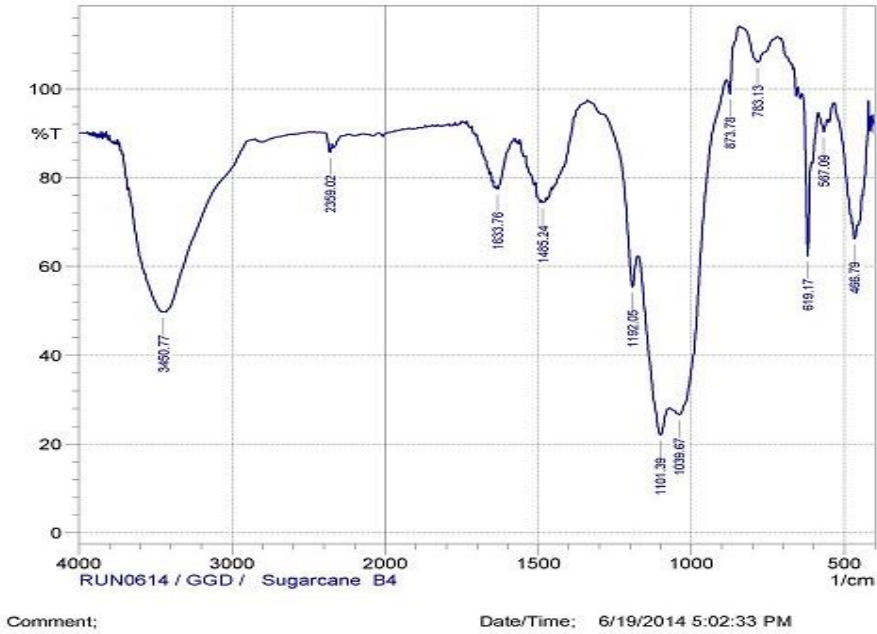


Fig. 1: FTIR spectrum of sugarcane waste before adsorption of chromium.

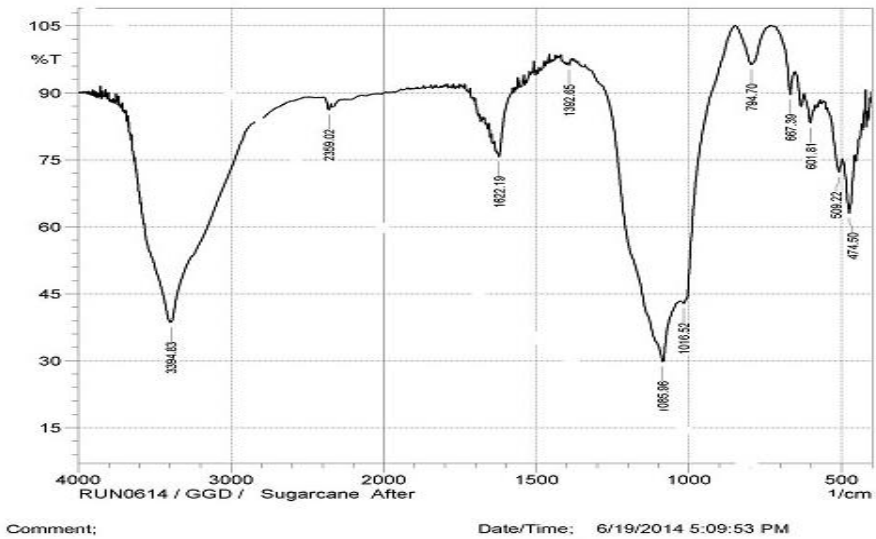


Fig. 2: FTIR spectrum of sugarcane waste after adsorption of chromium.

The FT-IR of sugarcane waste before and after adsorption displayed a number of absorption peaks (figure 1 and 2), which indicated the presence of different types of functional groups in the biosorbents. The broad and strong band ranging from 3394 to 3450  $\text{cm}^{-1}$  indicated the presence of  $-\text{OH}$  and  $-\text{NH}$  groups. The peak located at 2359  $\text{cm}^{-1}$  is a characteristic of  $\text{CH}$  stretching. The peaks between 1613 to 1622  $\text{cm}^{-1}$  can be attributed to  $\text{C}=\text{C}$  in conjugated aromatic rings. The peak located at 1192  $\text{cm}^{-1}$  which is assigned to  $\text{N-H}$  bending disappeared after chromium uptake. The absorption peaks around 1016 to 1101  $\text{cm}^{-1}$  are assigned to  $\text{C-O}$  bonds which may be due to alcohol, ether, ester or carboxylic acid.

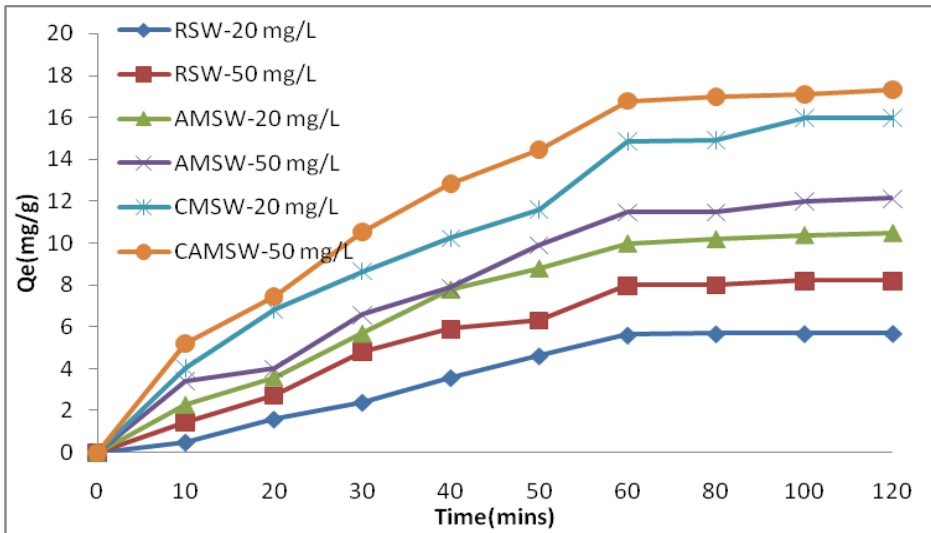
For the chromium loaded sugarcane waste, the wavenumber had shifted or subsequently lower than those before adsorption, suggesting the participation of  $-\text{OH}$ ,  $-\text{NH}$ ,  $-\text{C-O}$  and aromatic ring in the binding of chromium by sugarcane waste. The wavenumber of raw sugarcane waste at 3450, 1613, 1101, 1039, 873  $\text{cm}^{-1}$  shifted to 3394, 1622, 1085, 1016, 794  $\text{cm}^{-1}$  in the chromium loaded sugarcane waste.

### **3.2. Effect of Contact Time and Initial Metal Concentrations.**

Figure 3 shows the effect of contact time and initial metal concentrations of the sorption of  $\text{Cr(VI)}$  ions on biomasses. The results showed that the

sorption capacity of raw sugarcane waste (RSW) increases from 1.48 to 8.00  $\text{mg/g}$ , while that of the acid modified sugarcane waste (AMSW) increased from 3.44 to 12.14  $\text{mg/g}$  and when carbonized acid modified sugarcane waste (CAMSW) was used, an increase from 5.22 to 17.24  $\text{mg/g}$  was achieved on adjusting the contact time from 10 to 60 mins.

Although, the reaction was faster at the initial stage, it slows down as the reaction approaches equilibrium due to the saturation of the surface of the biosorbent. At the initial stage, there are vacant sites on the surface of the biosorbent which enhances its sorption capacity. But as the reaction progresses, the vacant sites are being filled by the sorbate and this reduces the biosorption capacity of the biosorbent. Similar results has been reported in literature [1, 15, 16]. Also, the adsorption capacity of the biomasses were found to increase with an increase in the initial concentrations of  $\text{Cr(VI)}$  ions. Maximum adsorption was attained at 50  $\text{mg/L}$ . Above this, there was no further increase in the adsorption of  $\text{Cr(VI)}$  ion by the biomass probably due to saturation of the pore sites. At lower metal concentrations, all metal ions present in the solution could interact with the binding sites of the sorbent.

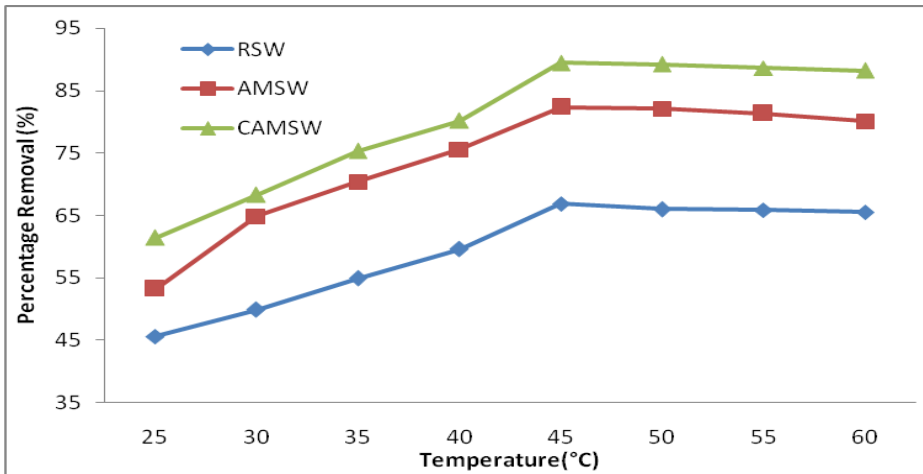


**Fig. 3:** Amount of Cr(VI) ions adsorbed against contact time at different initial metal concentration, temperature of 45°C and pH of 2.0.

### 3.3. Effect of Temperature

Figure 4 shows the effect of temperature on the adsorption capacities of raw, acid modified and carbonized sorbents prepared from sugarcane waste. The sorption capacities increased with temperature of the system. The sorption percentage of RSW increases from 45.67% to 66.88%, while that of AMSW increases from 53.20 to 82.33% when the temperature was raised from 25 to 45°C. When CAMSW was used, the percentage removal increases gradually from 61.4 to 89.4%. The increase in the sorption capacity of the biomass with the temperature may also be attributed to either an increase

in the number of active sites or surface available for sorption on the adsorbent or due to the decrease in the boundary layer thickness surrounding the sorbent, so that the mass transfer resistance of adsorbate in the boundary layer decreased. Above 45°C, there was a decrease in the adsorption capacity of the biomass suggesting the rupturing of the adsorption bands. Above 45°C, there was no further increase in the adsorption capacities of the biomasses. Thus, a temperature of 45°C was selected for subsequent experiments. Similar observations had been reported in literature [11, 17, and 18].

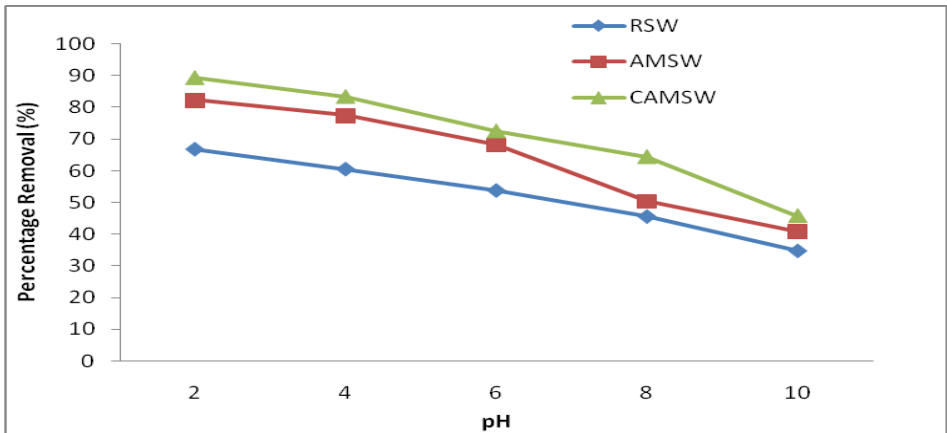


**Fig.4:** Percentage removal of Cr(VI) against temperature at a pH of 2.0, contact time of 60 mins and initial metal concentration of 50 mg/L.

### 3.4. Effect of hydrogen ion concentrations.

Figure 5 shows the effect of solution pH on the sorption capacities of raw, acid-modified and carbonized sugarcane waste for the sorption of Cr(VI) from aqueous solution. The results showed that maximum sorption capacities was achieved at a pH of 2.0. The percentage removal of Cr(VI) ions by RSW decrease linearly from 66.88 to 34.82% when the pH was raised from 2.0 to 10. Upon treatment with acid, the percentage removal also showed a

decrease from 82.33 to 40.81% and when CAMSW was used, the sorption percentage decreases from 89.41 to 45.82% when the pH was raised from 2.0 to 10. At lower pH, the functional groups on the cell walls are positively charge due to protonation and Cr(VI) ions exist in solution as anions thereby leading to electrostatic attraction between them. But as the pH increases, deprotonation of the cell walls starts, thus causing a decrease in the adsorption capacity of the biomass [1, 18].



**Fig.5:** Percentage removal of Cr(VI) ions against pH by RSW, AMSW and CAMSW at a temperature of 45°C, initial metal concentration of 50 mg/L and a contact time of 60 mins.

### 3.5. Kinetics Studies

Lagergren pseudo-first-order model and Ho's pseudo-second-order model were adopted for the kinetic studies. The linear form of the first-order equation is given as:

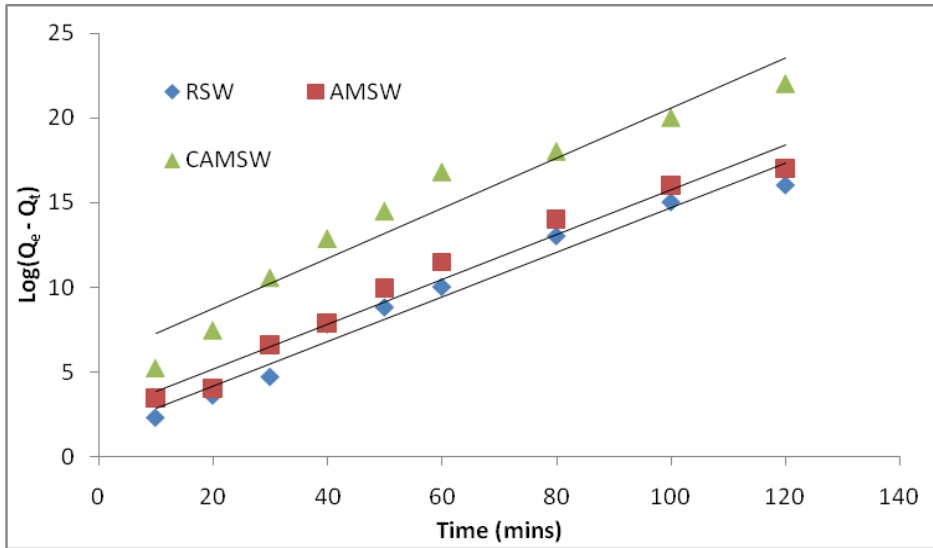
$$\log(Q_s - Q_t) = \log Q_s - k_1 t \dots\dots\dots(\text{Eq.3}),$$

while that of the second order is

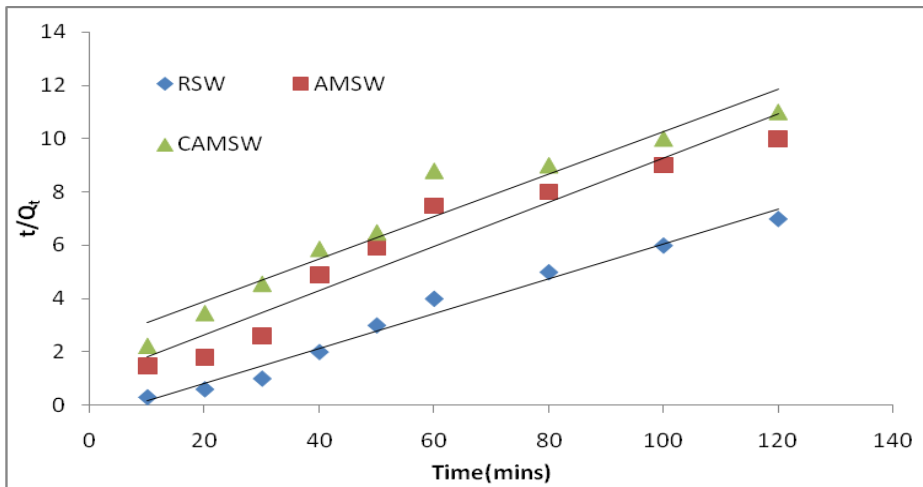
$$\text{given as: } \frac{t}{Q_t} = \frac{1}{k_2 Q_s^2} + \frac{1}{Q_s} t \dots\dots\dots(\text{Eq. 4})$$

where  $Q_e$  and  $Q_t$  are the amount of Cr(VI) ions adsorbed at equilibrium and at time  $t$  in mg/g respectively,  $k_1$  and  $k_2$  are the rate constants for a first and second-order equations respectively [2, 5, 16]. The plots of  $\log(Q_e - Q_t)$  against  $t$  and that of  $t/Q_t$  against  $t$  are shown in figures 6 and 7, while the physical parameters are presented in Table 1.





**Fig.6:** Largergren-pseudo-first-order model for the sorption of Cr(VI) ions.



**Fig.7:** Ho's-pseudo-second-order model for the sorption of Cr(VI) ions

**Table 1:** Physical parameters of the kinetic models for the sorption of Cr(VI) ions.

Biomass	$C_o$ (mg/L)	First-order model				Second-order-model		
		$Q_e$ .exp. (mg/g)	$k_1$ (mis)	$Q_e$ .cal. (mg/g)	$R^2$	$k_2$ (g/mg/mins)	$Q_e$ .exp. (mg/g)	$R^2$
<b>RSW</b>	20	5.67	0.15	0.25	0.94	0.35	4.32	0.98
<b>RSW</b>	50	8.00	0.32	1.53	0.97	0.54	9.11	0.99
<b>AMSW</b>	20	9.87	0.36	3.41	0.93	0.51	10.72	0.96
<b>AMSW</b>	50	12.14	0.53	5.38	0.95	0.72	11.30	0.95
<b>CAMSW</b>	20	14.88	0.61	13.72	0.98	0.82	7.14	0.97
<b>CAMSW</b>	50	17.24	0.74	15.42	0.99	1.24	10.72	0.95

For the sorption of Cr(VI) ions by RSW and AMSW, the high values of the correlation coefficient ( $R^2$ ) of first and second order models suggest better fitting for both sorbents. However, the values of the calculated adsorption capacities ( $Q_{ecal}$ ) of Ho's-second-order model were in agreement with the experimental adsorption capacity ( $Q_{eexp.}$ ) as against that of Lagergren pseudo-first-order model. This suggests that the sorption of Cr(VI) ions by the biomasses were governed by Ho's-second-order model. On the other hand, the kinetic data for the

sorption of Cr(VI) ions by CAMSW fitted very well with the Lagergren pseudo-first-order model due to the closeness in the values of the calculated adsorption capacities with that of experimental adsorption capacities.

**3.6. Thermodynamic Studies.**

Thermodynamic parameters such as change in free energy ( $\Delta G^\circ$ ), enthalpy changes ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) values were obtained from the plot of  $\Delta G^\circ$  against T, with a slope of  $-\Delta S^\circ$  and an intercept of  $\Delta H^\circ$  [5, 17].

**Table 2:** Physical parameters of thermodynamic for the sorption of Cr(VI) ions.

Temperature (°C)	RSW			AMSW		CAMSW	
	$\Delta G$ (kJ/mol)	$\Delta H$ (kJ/mol)	$\Delta S$ (kJ/mol)	$\Delta H$ (kJ/mol)	$\Delta S$ (kJ/mol)	$\Delta H$ (kJ/mol)	$\Delta S$ (kJ/mol)

25	-5.63	8.42		6.43		4.68	
30	-4.65	10.41	$4.7 \times 10^{-2}$	7.82	$4.1 \times 10^{-2}$	5.24	$3.5 \times 10^{-2}$
40	-2.73	13.45		9.14		7.38	
45	-1.56	15.37	$5.2 \times 10^{-2}$	11.32	$3.7 \times 10^{-2}$	9.42	$3.2 \times 10^{-2}$

The results revealed the values of the free energy change to be negative which implies that the sorption process is feasible and spontaneous; positives for enthalpy change indicate that the process is endothermic in nature. This value however increases with temperature of the system. The enthalpy change for the raw sorbent was also high which suggests the thickness of the raw biomass. Also, positive values of entropy change confirm the randomness of the system at higher temperature.

### Conclusion

This study shows the application of

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raw, chemically modified and carbonized agricultural waste prepared from sugarcane waste as an effective sorbent materials for Cr(VI) ions removal from aqueous solution as an alternative to conventional methods. The sorption capacity of the carbonized biomass was observed to be superior due to higher porous contents. Thus, the present study shows that RSW, AMSW and CAMSW are effective sorbents for the sorption of Cr(VI) ions from aqueous solutions.

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