Kinetics and equilibrium studies of Chromium bio-adsorption on activated carbon derived from *Cucurbita* peels

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Abstract:-- This study investigates the use of chemically activated Pumpkin (Cucurbita) peels impregnated with H_3PO_4 (APP) for toxic chromium removal from aqueous solutions. The adsorption processes were carried out through batch method at pH ranges from 2-10 and adsorbent APP dosage of 1-6 g/L. The optimum operating conditions were achieved at pH 2 and time of contact 120 min attaining the highest metal intake at 3g of the adsorbent per 1L of the aqueous solution having total chromium removal of 89%. The adsorption kinetics follows pseudo 2nd order model with a Chi square value of 0.132. Both the Freundlich and Langmuir were applied to describe the experimental data and it fitted well with both the isotherms with a correlation coefficients of 0.97 and 0.99 and a Chi square (λ^2) values of 0.001 and 0.01 respectively.

Index Terms:- Adsorption, Activated Carbon, Chromium, Cucurbita peels, Isotherms, Kinetics

I. INTRODUCTION

During the last few decades, the Industrial revolution has bloom exponentially leading to generation of quantum of industrial waste water contaminated with toxic heavy metal ions. The major pollutants causing hazards to water includes dissolved heavy metal ions like Chromium (Cr), Arsenic (As), Zinc (Zn), Mercury (Hg), Cadmium (Cd) etc.[1] and other complex compounds such as bio chemically resistant synthetic soluble dyes, Poly-nuclear hydrocarbons, Sulphur Compounds, Insecticides, Pesticides, Fertilizers etc. Only 25-30% of wastewater generated are reported treated, whereas rest are discharged polluting the groundwater and other water bodies ultimately reaching our households in highly contaminated forms. One of the most toxic heavy metal ions is hexavalent chromium. Chromium basically occurs in three forms: Cr (0) zero-valent produced by industrial process, naturally occurring Cr (III) trivalent and highly toxic Cr (VI) hexavalent. Inhalation of chromium compounds causes respiratory problems, lungs cancer, severe diarrhoea, sinus cancer and irritations of respiratory tracts [2].

Many conventional methods and techniques like sedimentation with coagulation or flocculation, ion exchange, aerobic and anaerobic treatment are also practised [3] [4]. Among these various methods employed, adsorption process is most widely used due to its versatility, eco-friendly, economic and fast, non- generation of toxic by-products or intermediates, adsorbent regeneration and superior removal of all organic and inorganic contaminants [5]. In recent years many researchers has turned their focus onto the use of bio-adsorbents like Coconut shell, rice husk, sugarcane bagasse, orange peel, apple peels etc., for Cr (VI) removal due to its easy access and availability, economical viability and eco-friendly, low carbonization temperature and short time duration [6].

The current study focuses on the removal of Chromium from aqueous solution using chemically modified Pumpkin (Cucurbita) peel (APP) as an economically viable low cost adsorbent. Pumpkin peels are rich in protein, fibres, ascorbic acids and polyphenols which contains functional groups like –COOH, -NH$_2$ and –OH which are solely responsible for chromium adsorption [7]. Alongwith the preliminary investigations like the effects of pH, concentration, amount of adsorbent and contact time, kinetic studies, thermodynamics and adsorption isotherms were also studied.

II. METHODOLOGY

A. Adsorbent preparation and analysis

Pumpkin were procured from local market, peeled, washed and were oven dried at 80°C for 12 hours. The peels were mixed with concentrated H_3PO_4 in 1:1 ratio and activated in the muffle furnace for 30 minutes at a temperature of 250°C. The activated carbon was then washed thoroughly to completely remove the acid content and oven dried again at 100°C. The dried and powdered pumpkin peel was then stored in the desiccator for further use.

B. Adsorbent characterization

Brunauer-Emmett-Teller (BET) technique was examined for measurement of specific area and the pore size distribution of

the prepared adsorbent. Surface structure of the prepared activated carbon was analysed using Scanning Electron Microscopy (SEM) (Sigma - 300) operated at 20.00 KV, magnification 500X along with Electron dispersive X-ray analysis (EDAX) (Zeiss Gemini) to assure the total chromium removal after the adsorption process [8].

C. Batch experiments

1000 ppm stock solution was prepared from $K_2Cr_2O_7$ and a series of desired solutions were prepared by diluting the stock solutions in appropriate concentrations [9]. A pre-defined amount of the adsorbent, pumpkin peel (APP) powdered activated carbon (2g) were placed into 500 mL Cr (VI) solution at various initial concentrations. The experiments were performed at optimum pH value, concentration dosage and time of contact. The desired pH of the solutions was adjusted using pH meter (PCS Testr 35). The mixtures were then shaken in an orbital shaker at 250 rpm for 180 minutes at room temperature. At the end of each adsorption batch, the adsorbent were separated by Whatman No. 47 filter paper. The residual solution for total chromium and hexavalent chromium were determined by Atomic Absorption Spectroscopy (AAS, Perkin Elmer) and UV Visible Spectrometer (Evolution 201) at a wavelength of 540nm respectively. The difference of total chromium and Cr (VI) is the reduced Cr (III) from Cr(VI). The adsorption capacity (q mg/g) is calculated as:

$$q_t = \frac{C_0 - C_t}{m} V \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1)$$

Where C_0 is the initial concentration, C_t (mg/L) is the final concentrations at time t, m (g) is the mass of the adsorbent, q_t(mg/g) is the quantity of adsorbate adsorbed at time t and V (L) is the volume of the solution.

III. RESULTS AND DISCUSSION

A. Adsorbent Characterization

APP powder used has a bulk density of 1.562 g/cc with pore volume 0.165 cc/g and pore diameter of 3.979 nm. The BET surface area of the adsorbent was observed to be 33.739 m^2/g. The SEM images of adsorbent before and after the treatment are shown in Fig. 1. The EDAX spectra of the same are also shown in Fig. 2

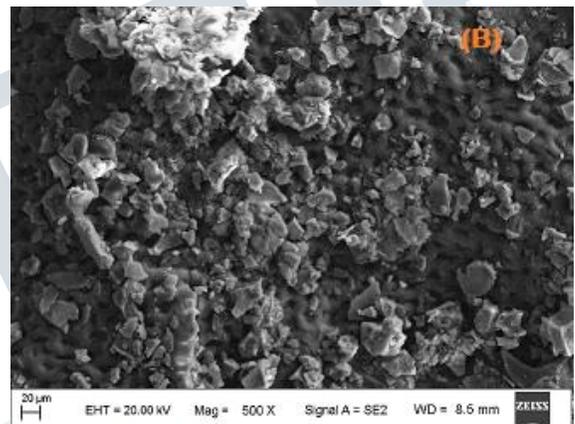**Fig.1 (a):** SEM images of APP before adsorption

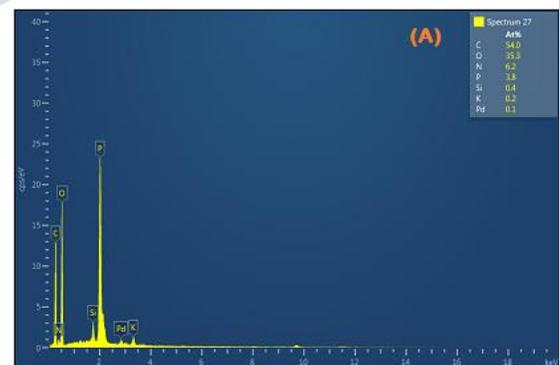**Fig.1 (b):** SEM images of APP after Chromium adsorption

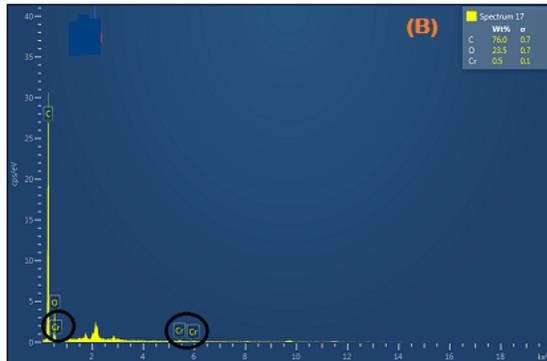**Fig.2 (a):** EDAX images of APP before adsorption.

Fig.2 (b): EDAX images of APP after adsorption

B. Effect of pH

pH of the experimentations were conducted in the range of 2–10 by keeping the other factors constant (time 120 min, agitation rate of 250 rpm, amount of adsorbent 2 g, with Cr(VI) concentration at 20 ppm) [10]. At pH of 2 and 4, the total chromium removal was observed around 89% and 82%, and further decreases from 67% - 50% at pH 8 - 10, respectively. The difference between the total chromium and Cr (VI) value gives the amount of Cr (III) reduced. It was observed that Cr (VI) is reduced to Cr (III) with a maximum of 20% at acidic pH 2. With the increase in pH reduction of chromium is decreased.
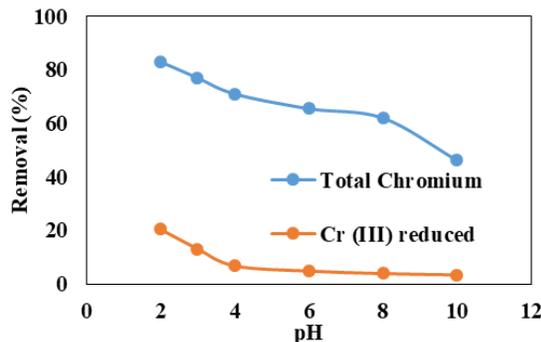

Fig.3: pH effect on total chromium and reduced Cr (III)

C. Effect of adsorbent dosage

According to the pH optimization, it was observed that acidic medium is more suitable for the adsorption of total chromium. So, at a pH of 2 with 250 rpm agitation rate and varying dosage of the concentrations (1, 2, 3, 4, 5 and 6 mg/L) for 180 minutes, optimal dose was examined, it was found that the adsorption capacity first increases rapidly attaining upto 83% removal efficiency, due to maximum availability of adsorbent sites. Thereafter, the removal percentage reaches to 89% at a concentration of 3g/L as shown in Fig. 4, but on further increasing the dose, no

significant increase in the total chromium removal was seen. Thus, optimum dose for Chromium adsorption was obtained at 3g/L.
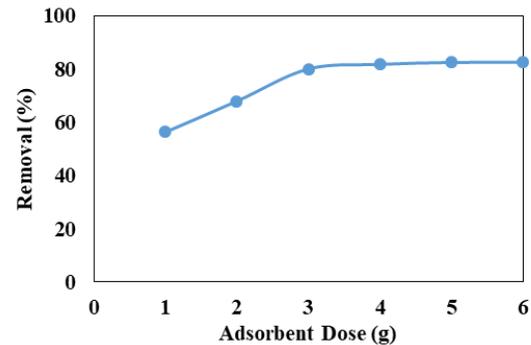

Fig.4: Dosage effect on total chromium removal

D. Effect of Contact time

Contact time affects the design and operation of the adsorption process. The removal efficiency increased on increasing the contact time as shown in Fig 5. So, on increasing the contact time from 5 to 120 minutes, at a dose of 3g/L and pH 2, the removal efficiency increases from 39% to 89%. It showed that the total chromium adsorption at 80 minutes reached equilibrium and thereafter no significant increase of ion removal was noticed.
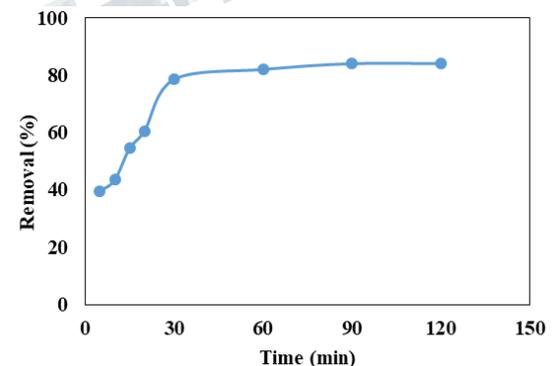

Fig.5: Effect of time on total chromium removal

E. Adsorption Kinetics

Langergan Pseudo 1st order model is represented as:

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \dots\dots\dots\dots\dots\dots\dots\dots\dots (2)$$

Where, q_e and q_t are the amounts of Chromium adsorbed at equilibrium and at time t and K_1 (min⁻¹) is the rate constant

for 1st order. On applying the initial conditions and integrating, it takes the form

$$\log(q_e - q_t) = \log q_e - \frac{K_t}{2.303} t \ldots \ldots \ldots \ldots \ldots (3)$$
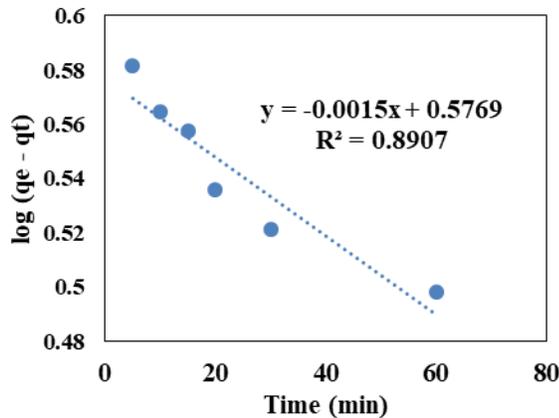

Fig.6: Pseudo 1st order kinetics plots for total chromium adsorption.

The adsorption data for 2nd order model is governed by the equation:

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \ldots \ldots \ldots \ldots \ldots \ldots \ldots (4)$$

Where, K_2 (g mg^{-1} min^{-1}) is the 2nd order rate constant.

On applying the initial conditions and integrating, it takes the form,

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \ldots \ldots \ldots \ldots \ldots \ldots \ldots (5)$$

Fig. 7 represents the pseudo 2nd order kinetics model. The experimental data implies that the adsorption kinetics suited better with the pseudo second order equation since the calculated q_e and experimental q_e are closer to each other than that of the pseudo 1st order kinetic model. Also, the correlation co-efficient R^2 for 2nd order kinetics is closer to unity (0.99) as compared to R^2 of 1st order kinetics (0.89) indicating that pseudo 2nd order kinetic model fits better than pseudo 1st order kinetic model.
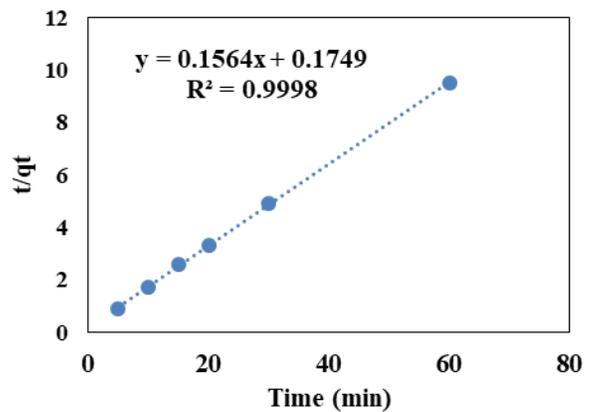

Fig. 7: Pseudo 2nd order kinetics plots for total chromium adsorption

F. Adsorption isotherms

Adsorption isotherm gives graphical representation of the amount of adsorbate adsorbed per unit mass of the adsorbent as a function of equilibrium concentration. Freundlich model is used for energetically non – uniform surface and for different adsorbent sites interaction between the adsorbed molecules [11]. The equation of Freundlich adsorption Isotherm is given by:

$$q_e = K_f C_e^{1/n} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (6)$$

Where q_e (mg/g) is the amount adsorbed at equilibrium, K_f is the Freundich constant, C_e(mg/L) is the concentration at equilibrium and n is the adsorption intensity.

And its linear form can be represented as:

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e \ldots \ldots \ldots \ldots \ldots \ldots \ldots (7)$$

Fig. 8 represents the Freundlich isotherm plot for total chromium adsorption. The slope (1/n) and intercept (K_f) of the plot between Ln q_e and Ln C_e determines the adsorption capacity of the adsorbent and was found to be 0.107 and 6.41 respectively indicating that APP has high adsorption capacity for the total chromium removal.
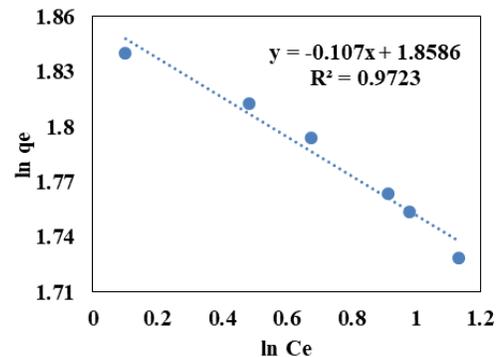

Fig. 8: Freundlich isotherm plot for total chromium adsorption.

Langmuir adsorption Isotherm model assumes that the adsorption takes place at the discrete active site and no interaction between the adsorbed molecules on the surface. One site adsorbs only one molecule and the adsorbed layer on the adsorbent is uni–molecular and energetically uniform [12].

The equation is given by:

$$q_e = \frac{q_{max}K_LC_e}{1+K_LC_e} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

Where q_e (mg/g) is the amount adsorbed at equilibrium, q_{max}(mg/g) is the maximum adsorbate adsorbed, C_e (mg/L) is the concentration of the adsorbate at equilibrium and K_L is the Langmuir constant. It can be linearized as follow:

$$\frac{C_e}{q_e} = \frac{1}{q_{max}}C_e + \frac{1}{bq_{max}} \ldots\ldots\ldots\ldots\ldots\ldots (9)$$

The equilibrium separation factor R_L describes the characteristic of the isotherm and is defined as:

$$R_L = \frac{1}{1+K_LC_o} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

Figure 9 shows linear plot between $1/q_e$ vs $1/C_e$ for adsorption of total chromium on APP over the different range of Cr (VI) concentrations. The maximum adsorption capacity was found to be 6.297 mg/g. Since the equilibrium sorption

value R_L was found to be 0.23 (<1) indicating that the APP used for total chromium removal is a favourable adsorbent. Table 2 shows the experimental regression data of Langmuir and Freundlich isotherm models and also the comparative study of different low cost bio-adsorbents with the present bio-adsorbent APP for total chromium removal.
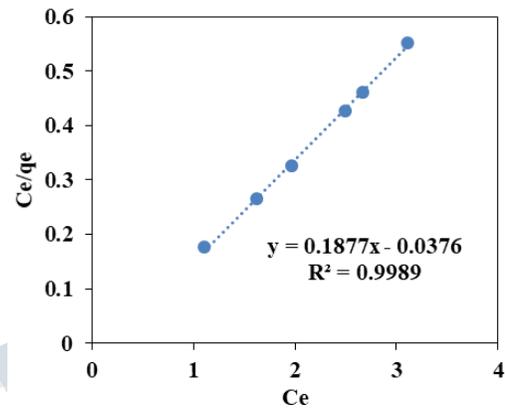

y = 0.1877x - 0.0376
R² = 0.9989

Fig. 9: (a), Langmuir isotherm plot for total chromium removal

Table I: Parameters of pseudo 1st and 2nd order kinetics models for Cr (VI) ions removal

Adsorbent	C_o (mg/L)	q_e, (expt.)	Pseudo 1st order				Pseudo 2nd order			
			K_1	R^2	q_e, (cal.)	λ^2	K_2	R^2	q_e, (cal.)	λ^2
APP	20	6.297	0.0015	0.89	4.265	11.154	0.1564	0.99	6.511	0.132

Table II. Regression data of Langmuir and Fruendlich isotherm models

Langmuir isotherm	q_{max} (mg/g)	b	R^2	λ^2
	6.297	0.163	0.99	0.01
Freundlich isotherm	K_f	1/n	R^2	λ^2
	6.41	-0.107	0.972	0.001

Table III: Comparison of various low cost bioadsorbents for total chromium removal

Bioadsorbents	q_{max} (mg/g)	pH	References
Orage peels	3.81	2.0	[12]
Rice straw	6.81	2.0	[13]
Tea leaves	4.711	2.0	[6]
Papaya peels	7.16	1.5	[14]
Oak wood char	3.031	2.0	[15]
APP	6.297	2.0	Present study

IV. CONCLUSIONS

In the current study, H_3PO_4 activated pumpkin peel (APP) was used as a bio-adsorbent for total chromium removal from aqueous solution. A substantial increase in the adsorption due to chemical modification was observed and can also bring about cost effectiveness for the treatment process. 3g/L of the adsorbent was found to be the optimum concentration at pH 2 at initial concentration of 20 mg/L. At acidic pH, maximum chromium reduction was seen (20%). The maximum total chromium ion removal was found to be 6.297 mg/g. The experimental data as shown in Table 1 clearly implies that pseudo second order model fits better as compared to pseudo !st order model with a Chi square (λ^2) value of 0.001. But the equilibrium adsorption data fitted best with both the Freundlich and Langmuir isotherms with a correlation coefficient of 0.99 and 0.89 respectively.

REFERENCES

[1] G. Wojcik, K. Wieszczycka, P. Aksamitowski, and J. Zembrzuska, "Elimination of Carcinogenic Chromium (VI) by

Reduction at Two-Phase System", Separation and Purification Technology,vol. 238, 116410, May 2020.

[2] M.W. Rahman, M.Y. Ali, I. Saha, M. Al Raihan, M. Moniruzzaman, M.J. Alam, A. Deb and M.M.R. Khan, "Date palm fiber as a potential low-cost adsorbent to uptake chromium (VI) from industrial wastewater", Desalination and Water Treatment, vol. 88, pp. 169–178, August 2017.

[3] E. Ben Khalifa, B. Rzig, R. Chakroun, H. Nouagui and B. Hamrouni, "Application of response surface methodology for chromium removal by adsorption on low-cost biosorbent", Chemometrics and Intelligent Laboratory Systems, vol. 189, pp. 18-26, April2019.

[4] Kim, M Kyung, K. S. Sundaram, G. A Iyengar, and K. Lee. "A novel chitosan functional gel included with multiwall carbon nanotube and substituted polyaniline as adsorbent for efficient removal of chromium ion", Chemical Engineering Journal, vol 267, pp. 51-64, May 2015.

[5] P. Miretzkya and A. F. Cirelli "Cr(VI) and Cr(III) removal from aqueous solution by raw and modified lignocellulosic materials: A review", Journal of Hazardous Materials, vol. 180 pp. 1–19, August 2010.

[6] A Pholosi, E. B. Naidoo and A. E. Ofomaja, "Intraparticle diffusion of Cr(VI) through biomass and magnetite coated biomass: A comparative kinetic and diffusion study", South African Journal of Chemical Engineering, vol 32, pp. 39–55, April 2020.

[7] I. Enniya, L. Rghioui and A. Jourani. "Adsorption of hexavalent chromium in aqueous solution on activated carbon prepared from apple peels", Sustainable Chemistry and Pharmacy, vol 7, pp. 9-16, March 2018.

[8] S. A. Sadeeka, N. A. Negmb, H. H. H. Hefnib, M. M. A Wahabb, "Metal adsorption by agricultural biosorbents: Adsorption isotherm,kinetic and biosorbents chemical structures", International Journal of Biological Macromolecules,vol. 81 pp. 400–409, August 2015.

[9] K.M. Sreenivas, M.B. Inarkar, S.V. Gokhale and S.S. Lele. "Re-utilization of ash gourd (Benincasa hispida) peel waste for chromium (VI) biosorption: Equilibrium and column studies", Journal of Env. Chemical Engineering, vo. 2, pp. 455-462, March 2014.

[10] L. Chandana, K. Krushnamurty, D. Suryakala and C. Subrahmanyam. "Low-cost adsorbent derived from the coconut shell for the removal of hexavalent chromium from aqueous medium", Materials Today: Proceedings 26, July 2019.

[11] I. Osasona and A. O. Adebayo and O. O. Ajayi, "Adsorptive Removal of Chromium (VI) from Aqueous Solution Using Cow Hooves" Journal of Scientific Research and Reports,vol. 2(1), pp. 288-303, January 2013.

[12] E. Pertile, T. Dvorsky , V. Vaclavik and S. Heviankova, "Use of Different Types of Biosorbents to Remove Cr (VI) from Aqueous Solution", Life 2021, vol. 11, pp. 1-22, March 2021.

[13] Ş. Parlayici and E.Pehlivan, "Comparative study of Cr (VI) removal by bio-waste adsorbents: equilibrium, kinetics, and thermodynamic", Journal of Analytical Science and Technology, vol. 10, Article number: 15, April 2019.

[14] E. Mekonnen, M. Yitbarek and T. R. Soreta, "Kinetic and Thermodynamic Studies of the Adsorption of Cr(VI) onto Some Selected Local Adsorbents", South Afican. Journal of Chemistry, vol. 68, pp. 45-52, April 2015.

[15] D. Mohan, D. Rajput, S. Singh, V.K. Steele and P.H. Pittman, "Modelling and evaluation of chromium remediation from water using low cost bio-char, a green adsorbent". Journal of Hazardous Material, vol. 188, pp. 319-333, April 2011.