Equilibrium and Thermodynamic Studies of Chromium ions removal using *Lagenaria siceraria* as a novel bio – adsorbent

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Abstract: - **A novel bio – adsorbent Lagenaria siceraria, chemically activated was prepared for the removal of chromium ions from aqueous solutions. Structure, morphology and pore size distributions were studied using SEM, EDAX and BET. The adsorption kinetics (Intra – particle diffusion, pseudo 1st order and 2nd order) and isotherms (Langmuir and Freundlich models) were used to analyse the adsorption capacities of chromium ions on the adsorbent surfaces at optimum pH, dose and contact time of 3, 4 g/L and 120 min respectively. The studied experimental data confirms that pseudo 2nd order kinetics fits best with a correlation coefficient (R^2) of 0.99 but agrees well with both the Langmuir and Freundlich isotherms with correlation coefficients (R^2) of 0.96 and 0.94 respectively. The maximum adsorption capacity attained was 6.325 mg/g with a maximum percentage removal of 86%.**

Keywords: Bio – adsorbent, Chromium ions, Kinetics, Isotherms, Thermodynamics

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I. INTRODUCTION

Chromium is a naturally occurring element found mainly in rocks, animals and plants. It exist in combination with other elements to form various compounds. They mainly exist in the forms, Cr (III) and Cr (VI). Chromium is mostly released into the water bodies as industrial effluents such as, electroplating, leather tanning, textile products and other chromium based products. Inhalation and ingestion of chromium affects the respiratory tracts, irritation and ulcer, breathing problems and blood anaemia [1]. The International Agency for Research on Cancer (IARC) has confirmed that Cr (VI) compounds are carcinogenic to humans. The Environmental Pollution Act (EPA) and Food and Drug Administration (FDA) has established a maximum level of 0.1 mg/L for total chromium in drinking water and 0.5 mg/L for wastewater discharge[2].

Many techniques have been adopted for the removal of this carcinogenic chromium from wastewater to protect against water contamination. Some of them are coagulation flocculation, chemical precipitation, ion exchange, membrane separation and bio adsorption [2]. Among these bio adsorption method is mainly employed for chromium removal due to its efficient and economical technique, easy handling, low maintenance, flexibility in design and operation and production of high quality treated effluent. Bio adsorption rate is affected by the pH of wastewater, initial concentration of the adsorbent and temperature of adsorption [3]. So, investigations are done to understand the mechanism of the bio adsorption process using a bio adsorbent.

In the past decades, the use of low cost and easily available adsorbents such as chitin, apples remaining, sawdust, clay, zeolite, waste tea, agricultural waste, coconut shell etc. were studied for the removal of toxic chromium ions. So, an attempt has been made using Bottle gourd for the chromium ions removal. Bottle gourd (Lagenaria siceraria) belongs to Cucurbitaceae family. It is found mainly in the tropical regions and is available almost all throughout the year. They are rich in proteins (37.1%), carbohydrate (12.5%) and crude fibres (4.29%) [1]. Due to the availability of these, in the present study, an attempt is made using Bottle gourd peel after activation, for the removal of toxic Chromium ions.

II. MATERIALS AND METHODS

A. Adsorbent and adsorbate preparation

Bottle gourd were procured from local market. The peels were taken off, washed and sundried. The dried peels were crushed, sieved and treated with phosphoric acid (H_3PO_4). The chemically treated powder was activated and carbonized in the muffle furnace for 30 min at 150^0C. By carbonization, the non – carbon elements (H2 and O2) were removed in the gaseous forms and the remainings were grouped into organized elementary crystallites [6]. The prepared activated Bottle gourd (ABG) were stored in the desiccator for further use.

All chemical reagents used were of analytical grade. A standard stock solution of 1000 ppm was prepared by dissolving 1.414 mg $K_2Cr_2O_7$ in 100 mL distilled water. Working standard concentrations varying from 1 – 10 ppm were prepared from the stock solution.

B. Batch Experiment

The batch experiments were conducted with 250 mL aqueous solution of standard chromium solution in 500 mL Tarson beaker and pH of the solution were adjusted with 0.1N H_2SO_4 or 0.1N NaOH using PCS Testr 35. The Tarson beakers were set onto the Jar test apparatus (PB – 600, USA) and agitated at a uniform speed of 250 rpm by adding the appropriate amounts of adsorbents. The beakers were unloaded at an interval of different time and the chromium solution concentration are determined from the calibration curve [7]. At the end of each adsorption batch, the adsorbent were separated by using Whatman No. 47 filter paper. And the residual chromium solution were determined by UV Visible spectrophotometer (Evolution 201) at a wavelength of 540 nm and Atomic Absorption Spectroscopy (AAS Perkin Elmer, USA).

The amount of chromium adsorbed on the adsorbent ABG and the percentage of removal were calculated by:

$$q_t = \frac{C_o - C_t}{m} V \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$\% \, Removal = \frac{C_o - C_t}{C_o} X 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where, C_o is the initial concentration (mg/L), C_t is the final concentration (mg/L), m is the mass of the adsorbent (g) and V is the volume of the solution (L).

III. Results and discussions

A. Adsorbent Characterization

Scanning Electron Microscopy (SEM) at an acceleration voltage of 20 kV with a thickness of 20 μm was use to get the image of the adsorbent, the textures and pores. Fig. 1(a) demonstrates a porous morphology with multiple hollow pores on the adsorbent sites. After the adsorption, the sites was found to be highly swollen in heterogeneous manner. The energy dispersive X – ray analysis (EDAX) was utilized to identify the elementary compositions. It focuses on different areas and the corresponding peaks are shown in Fig. 2 and 3. The detailed spectra values measured in atomic and weight % are in Table 1 and 2. The Brunauer-Emmett-Teller (BET) was also used to calculate the surface area and the average pore diameter of the used adsorbent. It was found that the ABG has a surface area of 38.63 m^2/g with pore diameter of 10.61nm and pore volume of 0.335 cc/g.
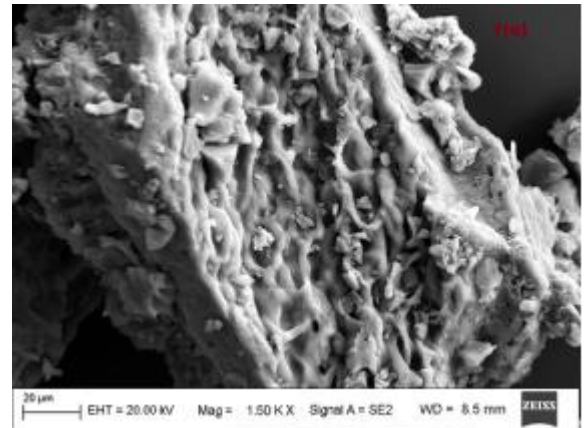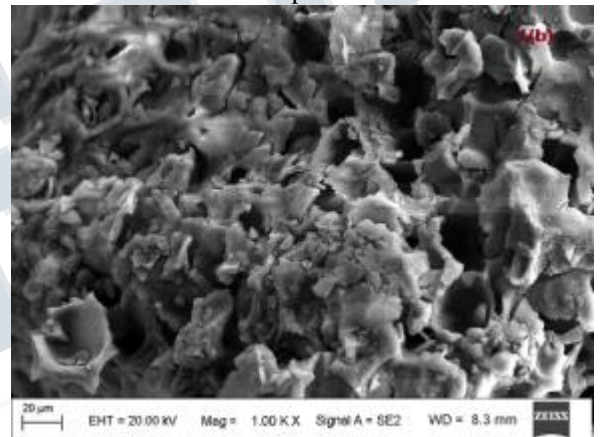

Fig. 1(a): SEM image of ABG before chromium adsorption

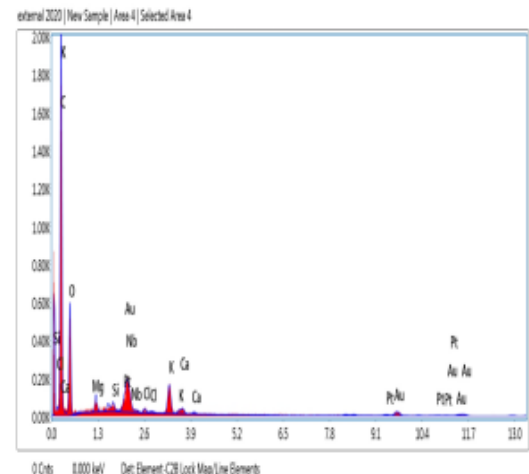**Fig. 1(b):** SEM image of ABG after chromium adsorption
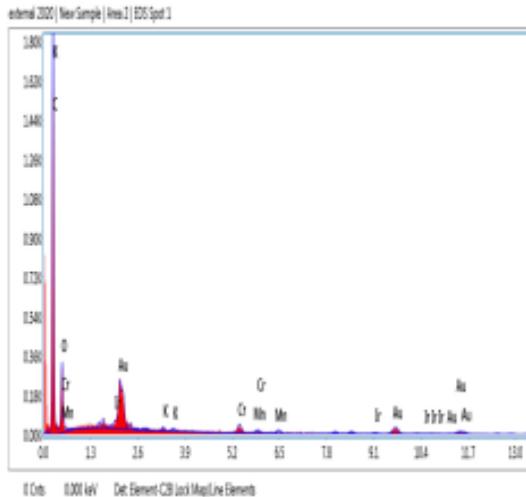

Fig. 2: EDAX image of ABG before chromium adsorption

Fig. 3: EDAX image of ABG after chromium adsorption

Table 1: Elemental composition of ABG adsorbent before adsorption			
Element	**Weight %**	**Atomic %**	**Error %**
C	49.23	68.29	7.41
O	25.56	26.61	11.77
Mg	1.25	0.86	12.10
Si	0.57	0.34	16.64
Cl	0.42	0.20	34.02
K	4.03	1.72	7.58
Ca	0.86	0.36	25.15
Pt	3.53	0.30	44.42
Au	13.59	1.15	21.79

Table 2: Elemental composition of ABG adsorbent after adsorption			
Element	**Weight %**	**Atomic %**	**Error %**
C	54.44	78.89	7.11
O	16.16	17.58	14.03
K	0.53	0.24	41.40
Cr	2.35	0.79	15.60
Mn	0.66	0.21	26.34
Ir	2.81	0.25	45.44
Au	23.05	2.04	19.06

B. Effect of pH

The pH of the solution were varied from 2 – 10 keeping other parameters constant. It can be seen from the graph that at pH 3, the maximum removal is attained. Fig. 5 shows the influence of pH on the adsorption of chromium. The adsorption capacity of chromium at basic pH was decreased because of the protonation of OH and COOH groups onto the surface of the adsorbent. So, the electrostatic interaction between the adsorbent and chromium ions weakened. This can also be explained by the zeta potential value. The pH at point of zero charge was located around 2 as shown in Fig. 4, indicating a positive surface charge below pH of 2, and negative surface charge above pH of 2 which attracts cation. So, pH of 3 was chosen as the optimal pH for the subsequent experiment with a removal percentage of 86%.
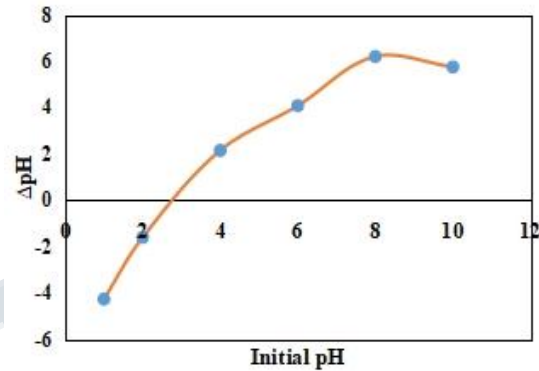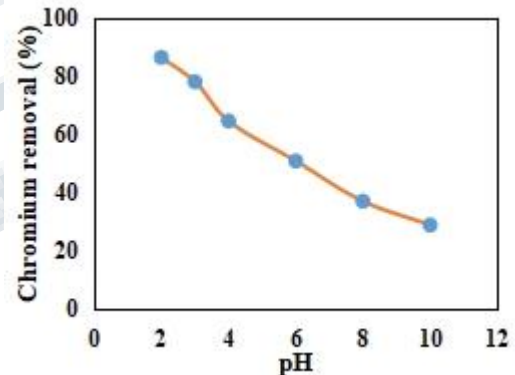

Fig.4: Zeta potential of ABG adsorbent

FFig.5: Effect of pH on adsorption behaviour of Chromium ions onto ABG

C. Effect of adsorbent dosage

The effect of adsorbent dosage on the removal of chromium ions was studied by adjusting the pH at 3. Fig. shows the effect of adsorbent dosage on the removal of chromium ions. The adsorption efficiency increases with the increase in dosage due to the availability of number of active sites and functional groups. The removal percentage increases from 32% to 84% from 1 – 4 g/L but on increases the dosage no further increase in the removal was observed. Thus, dosage of 4 g/L was chosen as the optimal dosage for adsorbing chromium ions.
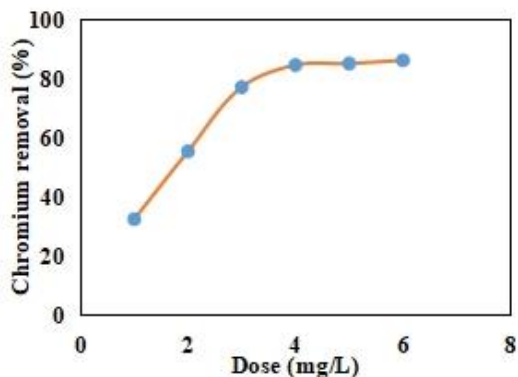
Fig.6: Effect of adsorbent dosage of ABG

D. Effect of contact time

The rate of adsorption is an important parameter to understand the kinetics of adsorption [4]. Fig. 7 shows the effect of contact time on the adsorption of chromium ions. As seen, the chromium ions were rapidly absorbed by ABG right after 5 min of contact time and about 77% of chromium ions were removed in 30 min time. But the rate of adsorption capacity slows down on increasing the time of contact. The maximum removal percentage of 84% was attained at 120 min. This shows that the adsorption process accelerates at the initial stage due to more active sites and diffusion and later decreases probably due to back distribution of the adsorbed species.
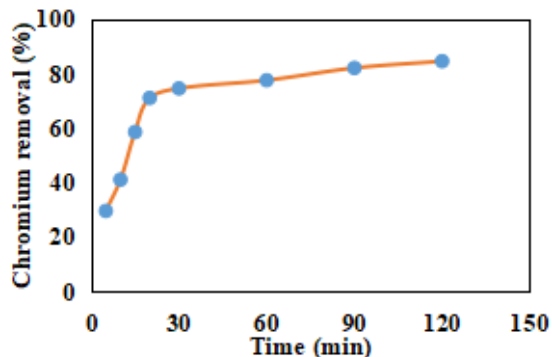

Fig.7: Effect of time on ABG adsorbent

E. Adsorption kinetics

The adsorption kinetics of chromium ions with ABG was studied using intra - particle diffusion, pseudo 1st order and 2nd order kinetics.

$$q_t = K_{IPD}t^{1/2} + C \dots\dots\dots\dots\dots\dots\dots\dots\dots. (3)$$

$$\log(q_e - q_t) = logq_e - \frac{K_1 t}{2.303} \dots\dots\dots\dots\dots\dots.. (4)$$

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

Where, q_t (mg/g) is the adsorption at time t (min), q_e

(mg/g) is the adsorption capacity at equilibrium, K_{IPD}, K_1 and K_2 are the kinetic rate constants of intra particle diffusion, 1st order and 2nd order kinetics respectively.

The parameters of intra particle diffusion, pseudo 1st order and 2nd order kinetics are depicted in Figs. 8, 9, 10 and Table 3. The table indicates that the chromium ions adsorption on ABG adsorbent fits best with the pseudo 2nd order model with a correlation coefficient of 0.99 and a chi square value of 0.015.
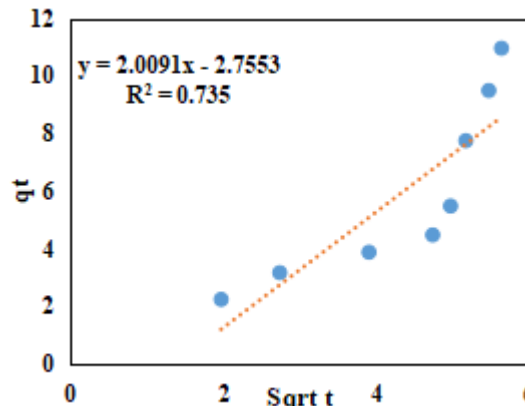

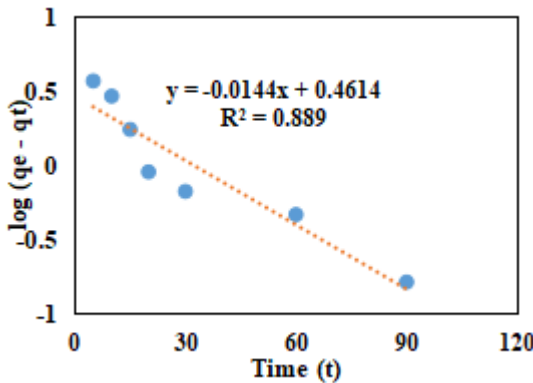**Fig.8:** Intra particle diffusion model for chromium ions adsorption onto ABG

Fig.9: Pseudo 1st order model for chromium ions adsorption onto ABG
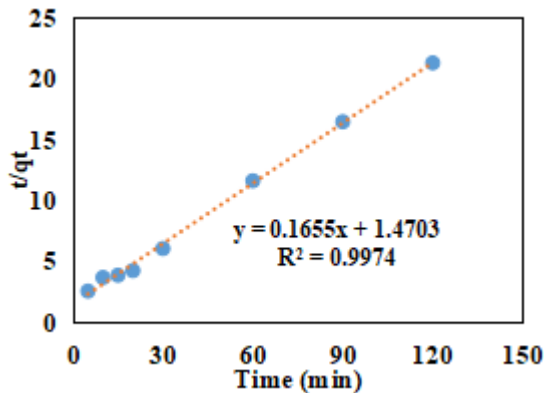
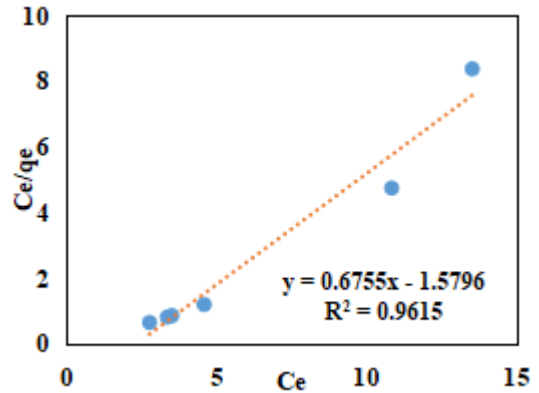**Fig.10:** Pseudo 2nd order model for chromium ions adsorption onto ABG

Table 3: Parameters for different kinetic models

Intra -particle diffusion	K_{IPD}	C	R^2	$\square^2$
	1.2842	-0.641	0.735	0.421
Pseudo first order	K_1	R^2	q_e (cal)	$\square^2$
	5.46	0.89	6.132	1.256
Pseudo second order	K_2	R^2	q_e (cal)	$\square^2$
	3.58	0.99	6.856	0.015

F. Adsorption Isotherms

The adsorption isotherms describes the effect of concentrations of the solutions on adsorption capacities of chromium ions and the interactions of the adsorbates on the adsorbents [5]. The adsorbent ABG is equilibrated with chromium ions at different concentrations with pH of 3, dosage 4 g/L and 120 min of contact time. Finally the equilibrium concentrations were evaluated.

The two adsorption isotherm model, Langmuir and Freundlich were used to describe the adsorption of chromium ions on ABG adsorbent.

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots (6)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \dots \dots \dots \dots \dots \dots \dots \dots \dots (7)$$

Where, q_m and K_L are maximum adsorption capacity and Langmuir constant respectively. K_F and n are the Freundich adsorption capacity and heterogeneity factor respectively.
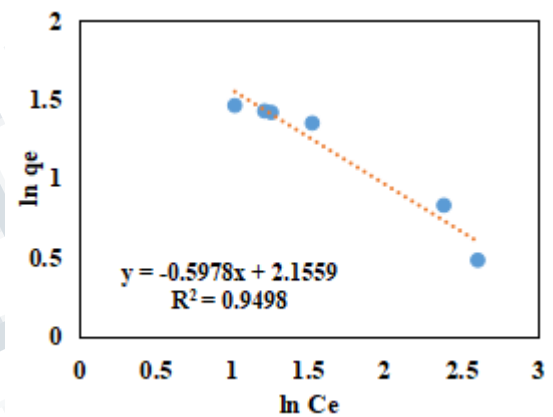

Fig.11: Langmuir isotherm model for chromium ions adsorption onto ABG

Fig.12: Freundlich isotherm model for chromium ions adsorption onto ABG

Table 4: Parameters for different isotherm models

Langmuir Isotherm	K_L (L/mg)	q_m (mg/g)	R^2
	1.473	6.325	0.96
Freundlich Isotherm	K_F (mg/g)	n	R^2
	8.153	-0.49	0.94

The adsorption isotherm plots of the measured data along with the parameters are presented in the Table 4 and Figs. 11 and 12.

On comparing the correlation coefficient values of both the models, it can be concluded that both the models fit well probably due to their ability to interact with the hydroxyl and carbonyl acid groups on the surface through the formation of both homogenous and heterogeneous surface of the ABG adsorbent attaining a maximum adsorption capacity of 6.325 mg/g.

G. Adsorption thermodynamics

The effects of temperature on the adsorption capacity of chromium solution was investigated at different temperatures (298, 303, 313 and 323K) at pH of 3 and contact time of 120

min. the thermodynamic parameters for chromium ions adsorption on ABG adsorbent was estimated using the equations:

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \dots \dots \dots \dots \dots \dots \dots \dots \dots (8)$$

$$\Delta G = -RTlnK \dots \dots \dots \dots \dots \dots \dots \dots \dots (9)$$

$$K = \frac{q_e}{C_e} \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots (10)$$

Where, R is the universal gas constant (8.314 J mol), T is the temperature (K), K is the thermodynamic equilibrium constant.

The enthalpy (ΔH) and entropy (ΔS) were calculated from the slope and intercept of the plot of ln K vs 1/T as shown in Fig. 13, and the thermodynamic parameters are given in Table 5.
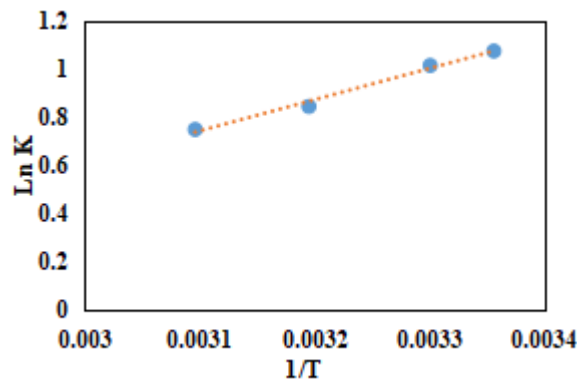

Fig.13: Thermodynamic parameter plot for chromium ions adsorption onto ABG

Table 5: Thermodynamic parameters of Chromium ions on ABG adsorbent

T (K)	ΔG (KJ/mol)	ΔS	ΔH	R^2
298	-2.6			0
303	-2.55	27.16	10.75	.99
313	-2.19			
323	-2.01			

The negative values of ΔG and ΔH indicates that the adsorption reaction was exothermic and that the adsorption of chromium ions on ABG adsorbent was spontaneous all throughout the process.

IV. CONCLUSION

A novel bio – adsorbent, ABG was used for the removal of chromium ions from aqueous solution. The maximum adsorption capacity of the chromium ions was found to be 6.325 mg/g at a contact time of 120 min. The adsorption kinetics fitted best with the pseudo 2nd order model with a R^2 value of 0.99 and $\square^2$ value of 0.015. And the isotherm

models fits with both the Langmuir and Freundlich Isotherms models with R^2 values of 0.96 and 0.94 respectively indicating that the adsorbent surface is both homogenous and heterogeneous. From the thermodynamic study, it can be concluded that the adsorption process is exothermic and a spontaneous process.

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