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Optimization, Statistical and Adsorption Analysis of Cr(VI) using Corn Industry Sludge: Kinetic and Isotherm Studies

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Abstract

A novel, cost-effective activated carbon was prepared from local corn industry waste sludge to treat chromium (VI) ions from an aqueous solution. Adsorption is one of the promising techniques for treating chromium. The adsorption efficiency depends on temperature, pH, metal ion concentrations, contact time, and adsorbent dose. Activation increase the adsorbent sites on the surface of the adsorbent, and SEM micrographs indicate the adsorption sites before and after adsorption. IR spectrum of FT-IR spectrophotometer was used for analysis Investigation of equilibrium adsorption isotherm data reveals suitability of corn industry waste for treating chromium (VI) ions. The adsorption isotherm and kinetics of chromium (VI) adsorption indicate agreement of the experimental data to Freundlich isotherm and pseudo-second-order model and chemisorption as the reason for Cr(VI) removal. The corn industry waste is thermally activated by heating in a controlled atmosphere at 500° C. Kinetic data studies elucidated that adsorption tracks a pseudo-second-order kinetic model. The maximum

adsorption capacity and adsorption efficiency of chromium (VI) were found to be 6.80 mg/g at were pH of 4 with a contact time of 150 min and 91.43% using 1.5 g of adsorbent. The outcomes of corn industry sludge as the advantage of low-cost material and an effective adsorbent for Cr (VI) removal. The statistical analysis of adsorption was studied through response surface methodology (RSM). The experimental and theoretical values for percentage adsorption of Cr were observed as 92.91% and 91.43%, respectively. The experimental results closely agree with the central composite design.

Keywords: Adsorption, Freundlich isotherm, Langmuir isotherm, Optimization, Efficiency, Central Composite Design (CCD).

1. Introduction

Eliminating toxic materials from effluents has gained the wide attention of researchers and scientists around the globe [1]. Heavy metals such as zinc, vanadium, silver, platinum, nickel, lead, copper, chromium, and cadmium are generated during electroplating, leather tanning etching and magnetic tape manufacturing processes [2, 3]. Chromium compounds are considered superlative from these inorganic hazardous water toxic water pollutants. The agency for disease registry and toxic substances of the United States rates Cr hierarchical on number 17 in the priority list of dangerous substances. Cr is found naturally in two forms, Cr(VI) and Cr(III) and is found in plants, rocks, and soils. Cr(VI) is a potent poison, whereas Cr(III) is to be a vital trace nutrient for humans [4]. Cr(VI) is carcinogenic and mutagenic and known to cause lung cancer and gastric, liver, and kidney impairment [5]. The toxicity of Cr (VI) and its effect on the environment have invoked interest in techniques such as electrochemical precipitation, electrolyzing, chemical precipitation, reverse osmosis, adsorption, ion exchange, reduction, solvent extraction and evaporation. Cr is highly reactive, and removal techniques' primary shortcomings are partial removal and residual sludge generation [6, [7, 8]. Thus removal of Cr(VI) from the effluents becomes necessary due to the strict environmental regulations and also to prevent the adverse impact of Cr(VI) on public health and the environment [9, 10]. Researchers have reported treating of Cr(VI) from effluents by preparing raw/modified/activated adsorbents from various carbonaceous sources [27], such as seed pods of *Ocimum americanum* [11], (Muthukumaran V. et al. 2009), coconut shell [12] (Gilbert Chan et al. 2005), rice husk [13] (Xiaoguang Meng et al. 2008), olive oil industry waste [14] (Emine M. et al. 2007), peanut shell (Rahmat Ali et al. 2012) [15], fertilizer industry waste [16] (Arshi Rastogi et al. 2010), pteropus crassipes root (Rajkishore Patel et al. 2013)

[17], Quorn waste [18] (C. Karthika et al. 2005), sawdust [19], groundnut husk [20], neem leaves [21], walnut shell [22] (AA. Ghoreyshi et al. 2015), sago waste [23], agro waste [24], coffee husk [25], and wheat bran [26]. Prior studies (Mondal NK. et al. 2019; Nayek P. 2019) emphasized using locally available adsorbents like sawdust, spent activated clay, magnolia leaf, rice husk carbon, floating macrophytes, fly ash, and rice bran for Cr(VI) removal. Organic wastes from corn industry sludge have revealed a boundless potential for treating Cr(VI). Based on the literature cited above, the present research is formulated to use corn industry sludge to remove Cr(VI) at a laboratory scale in a batch setup and study the effects of adsorbent dose, initial concentration, temperature, contact time and pH.

2. Materials and Methods

2.1 Preparation of CISAC (Corn Industry Sludge Activated Carbon)

The corn (Poaceae) industry sludge was collected from the treatment plant to provide us with valuable raw material near Belagavi, India's factory. The main activity of the factory is to produce dextrose, corn flour, fructose, starch and gluten from maize. The leftover was dried for 30 days before use.

2.2 Analysis of Activated sample

Acid treatment and heat treatment were the methods used to activate the sample. The results obtained were compared with the unprocessed (raw) sample in Table 1. The table signifies that the heat treatment sample (S1) has the highest yield compared to others. Thus, the recommended path for further studies. But it can also be observed that the Acid-treated samples (S2, S3 and S4) showed equivalent results. Therefore, it was preferred as the activation method.

Table 1. Analysis of different activated samples.

Entry	Sample	Absorbance	% Removal
1	Acid Treatment –H ₂ SO ₄ (S2)	0.0096	93.2
2	Acid Treatment -HNO ₃ (S3)	0.0058	91.9
3	Acid Treatment-HCl(S4)	0.0174	89.7
4	Heat Treatment (S1)	0.0040	93.6

2.3 Stock Solution Preparation

The chemicals employed for the investigation of analytical component grade and spent without purification. Current work uses potassium dichromate as a standard solution for the experiment. The experimental solutions of different concentrations of metals are prepared by diluting the stock solution. Using a pH meter, pH was accustomed accordingly. The concentrations of solution before and after adsorption of respective metal ions were examined via UV–Visible spectrophotometer.

2.4 Characterization of the Adsorbent

Batch adsorption tests were conducted in an incubated shaker. Sludge obtained from the corn industry and activated sludge trials were examined to find an alteration in surface morphology after acid activation by scanning electron microscope (SEM). The surface morphology of corn sludge-activated carbon was studied using SEM-JEOL JSM IT-500LA instrument at different magnifications. The BET pore size and surface area dispersals of organized adsorbent before and after Cr (VI) is examined.

3. Results and Discussion

3.1 Characterization of adsorbent

The adsorbent used is activated carbons owing to their degree of surface, elevated surface area, adsorption capacity and microporous structure. About imperative physicochemical features of CISAC are specified in Table 2. The CISAC samples were determined through a typical test process for moisture in AC [29]. The adsorptive power of water gratified carbon has no consequence; it mitigates C, which is essential for using the additional weight of carbon in the treatment procedure. The lower volatile and ash content are ascribed to sophisticated fixed carbon and minor inorganic matter. The elevated static carbon rate in the adsorbent improves stability and productivity [30].

Table 2. Physiochemical characteristics of CISAC.

Entry	Constraint	Value
1	Ash content (%)	22.01
2	Volatile matter (%)	4.74
3	pH	7
4	Moisture content (%)	8.89

5	Fixed carbon (%)	74.23
6	Particle size (μm)	146

3.1.1 FTIR Spectroscopy

To categorize superficial functional groups, FTIR spectroscopy is a vital tool to subsidize suggestively by surface complexation to enhance the adsorption efficiency of activated carbon. FTIR spectrum of adsorbent formerly and subsequently adsorption (Figure 1) is recorded. The weak absorption peak detected at 840, and 611 cm^{-1} is ascribed to the aliphatic alkane of the elongated chain band. The solid band 1169 cm^{-1} region for alcoholic C–O stretching. The peak detected near 1439 cm^{-1} was credited to CH_3 bending, and the peak corresponding to 1569 cm^{-1} was for CH_2 bending. Peak located 2931 cm^{-1} for C–H aliphatic methyl asymmetric stretching. A broad peak of 3392 cm^{-1} corresponds to the -OH group extending the vibration.

The FTIR spectrum of CISAC adsorption of Cr(VI) before and later is shown in Figure 1. It illustrates subsequent adsorption of Cr (VI) on CISAC is a minor shift in frequency sections that were preoccupied, and this reflection designated the contribution of Cr (VI) adsorption of CISAC.

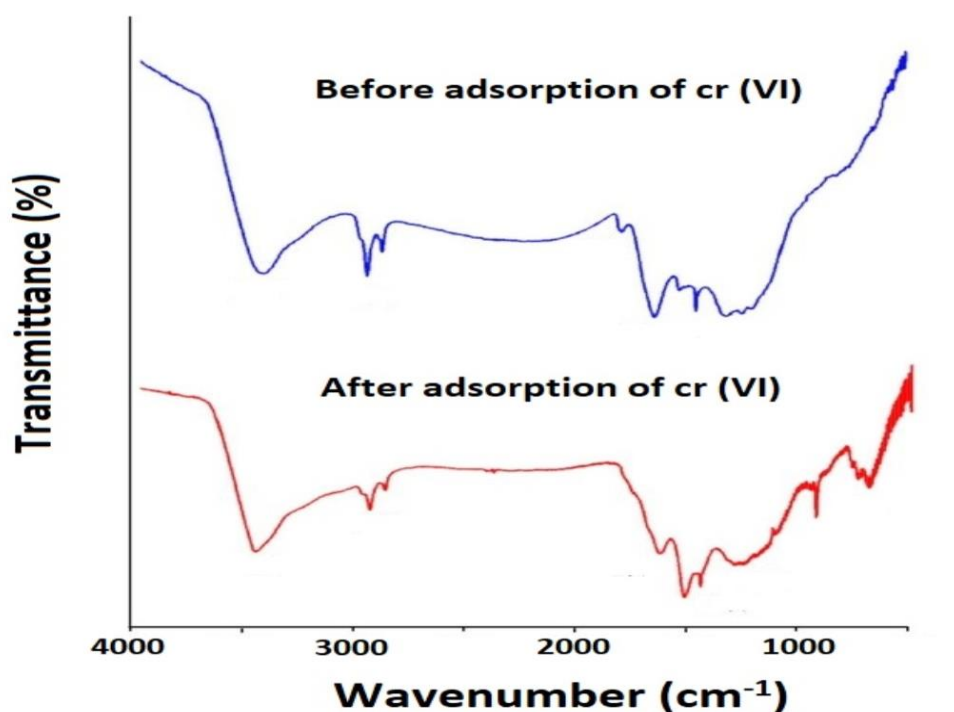


Figure 1. FTIR spectra of CISAC for adsorption of Cr (VI).

3.1.2 Scanning Electron Microscope Studies

Figure 2 demonstrates an SEM image of sludge obtained from the industry. The resulting micrographs show that sludge presents an unordered structure with heterogeneous distribution of particles. Characterization of thermally treated and SEM examined raw corn sludge. The thermally treated and raw sludge samples unevenly filled with flake-like particles have similar surface morphology. Sludge obtained from the corn industry and activated sludge trials were studied to recognize surface morphology changes after acid activation. The resulting micrographs show that sludge presents an unordered structure with heterogeneous distribution of particles. After heat treatment, the pore and surface of activated sludge were coated with a layer of impurities, causing a smaller pore size and smoother texture, as shown in Figure 2. The surface morphology exposed that activated sludge obtained to be porous and irregular and thus would enable adsorption of metal ions on diverse parts of materials. Similar results were also observed by Krishna and Padma (2013) [31], Thai Anh Nguyen, and Ruey-Shin Juang (2014) [32]. As shown in Figure 2 (a) and (b), the SEM images discovered irregular and porous morphology. Activated and raw sewage sludge seems as grey and black colour particles. The main chemical composition of sludge consists of mass % of carbon; after activation, mass % of carbon is decreased. After activation, trace elements are noticed. Aluminium, Silica, Iron and Calcium.

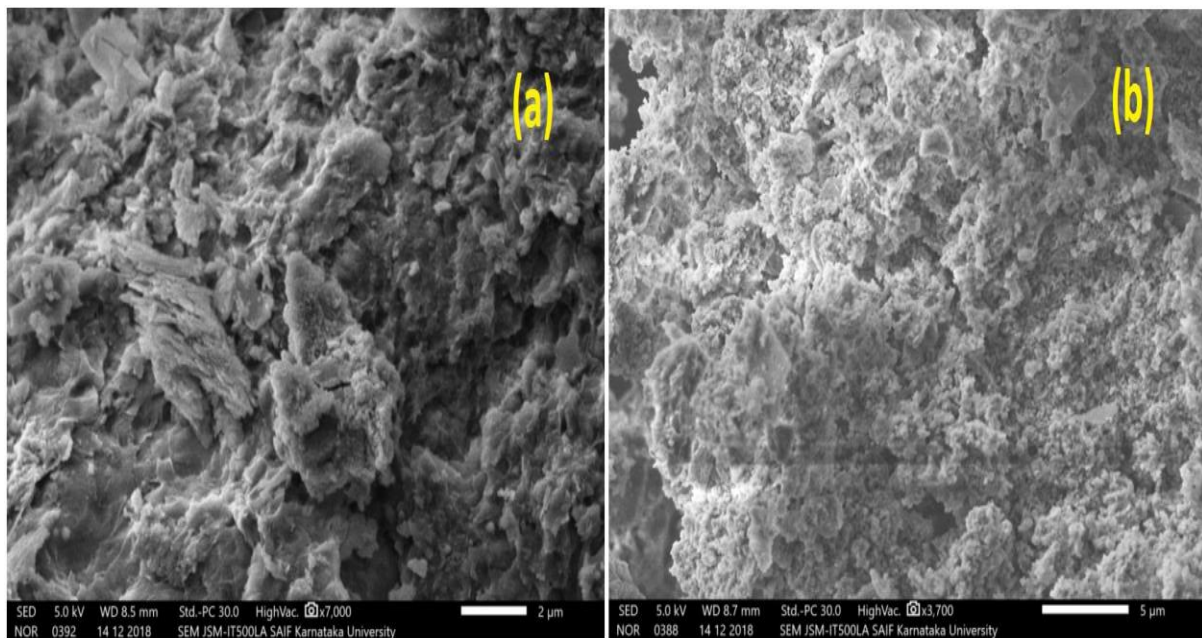


Figure 2. (a) SEM image of raw sludge showing different pores size and shape. (b) SEM image of activated sludge.

3.1.3 BET Analysis

BET study was supported to determine the pore volume and surface area of raw sludge and the activated sludge using BET Apparatus Model No. SMART SORB 92/93. The following results were recorded as shown in Table 3. It illustrates that the surface area of the activated sample is more than the raw sample. This is due to the increase in pore size due to the activation. The same results were observed for the increase in pore volume for the activated sample. An increase in its adsorption efficiency can be attributed due to chemical activation action that can adapt BET and the aperture volume of the adsorbent. Z. Liguó et al. 2015 [33] reported an increase in pore size of the adsorbent occurred after heat treatment modification.

Table 3. Physiochemical characteristics of CISAC.

Sample	Raw Sludge (Dried)	Activated Sludge
Pore Volume	0.0070 cc/g	0.0123 cc/g
Pore size	8.96 nm	9.92 nm
Surface Area	1.207 m ² g ⁻¹	2.410 m ² g ⁻¹

3. Adsorption Study

The stock solution of 1000 mg/L is made by liquifying 2.835g of K₂Cr₂O₇ in one liter of distilled water. Several concentrations of the solution are attained by diluting 1000 mg/l of standard solution. To achieve desired concentrations of Cr (VI) for batch study solution was diluted using distilled water. The absorbance is measured using a Hitachi U-2900 uv-visible spectrophotometer at 540 nm. The spectrophotometer was first calibrated via various concentrations of Cr (VI) solution (2 to 16 ppm). The withdrawn samples from shake flasks were centrifugated at 8,000 rpm for 0.5 h at room temperature to eliminate suspended biomass, 1,5-diphenyl carbazide (DPC) reagent in an acid solution of Cr (VI) ion was determined. A straight line calibration curve is drawn to determine the percentage removal of adsorbent, corresponding to the following equation 1 [34].

$$\% R = \frac{C_o - C_e}{C_o} \times 100 \quad \dots(1)$$

Where C_o is the primary concentration, R is Cr (VI) adsorbed, and C_e is the equilibrium concentration (mg/L). The prepared CISAC adsorption capacity was evaluated using equation 2 [35].

$$q_t = \frac{C_o V_o - C_t V_t}{m} \quad \dots(2)$$

Using 0.14 g of sample with 100ml of metal ion solution by diverse conditions for adsorption analysis was carried out. The adsorption studies were achieved at 300K using a constant water bath to regulate the impact of contact time, pH and initial metal ion concentration on adsorption.

3.1 Impact of pH on adsorption

The influence of pH for metal adsorption was incorporated by keeping a pH extent of 1 to 8. The process operated is analogous to what was previously described in the literature [36]. Using UV visible spectrophotometer, the filtrate is examined for residual metal ions of the aqueous solution. It may be realized that the utmost of Cr(VI) adsorption (92.98%) arises at the lowest pH (Figure 3), and the outcome is testified by several researchers [37], originating that Cr (VI) removal is better in acidic pH. The favourable low pH is perhaps ascribed to the nullification of negative charges on the surface by excess H^+ ions, thus simplifying dissemination of $HCrO_4^-$ (hydrogen chromate ions) and succeeding adsorption. Aladdin et al. 2011 [38] reported the foremost and ionic ($HCrO_4^-$) form of chromium (VI) with a pH range of 2-4. The author found that favourably better adsorption on the surface of the carbon. Under acidic conditions, $HCrO_4^-$ species are utmost effortlessly switched with OH^- ions at dynamic exteriors of the adsorbent. The negative charges outcomes since oxygenated functional clusters of elementary nature, for example, hydroxyl or lactones groups, are substantially adsorbed at superficial pores.

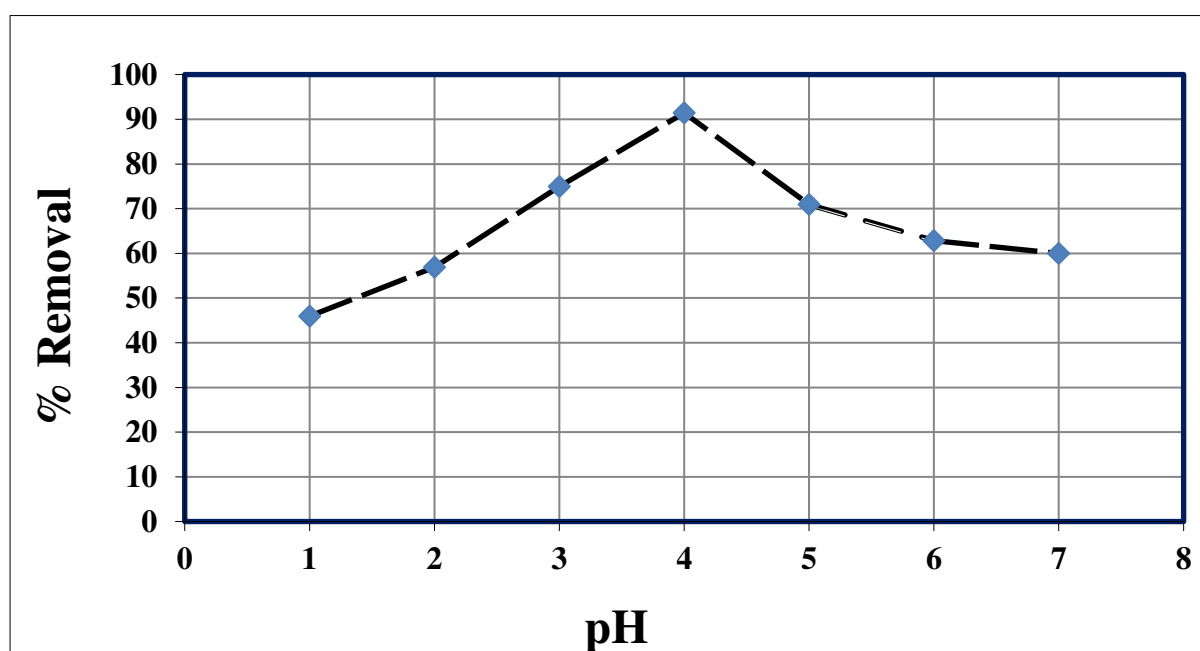


Figure 3. Impact of pH on Cr (VI) adsorption.

Considering that optimal pH was detected at 4 and by increasing the pH value, a sweeping reduction in adsorption percentage was perceived. Owing to fading of electrostatic strength of attraction amid conversely charged adsorbent and adsorbate eventually leads to a decrease in adsorption capacity [39-40].

3.2 Impact of adsorbent dosage

Figure 4 illustrates the outcome of dosage on adsorption of Cr (VI) on CISAC. The graph indicates per cent adsorption rises (29.12 to 91.43%) with growth in dosage of CISAC (0.25 to 2.0 g) and higher than 1.5 g adsorbent quantities persisted nearly constant. Owing to superior readiness of adsorption spots of adsorbent and thus creating easier for Cr (VI) [41,42]. Meanwhile, the extent of metal ion remained constant, as an increase in the quantity of adsorbent exceeding an amount that can entirely adsorb Cr(VI) obligated no superficial impact on the supplementary rise in adsorption and as the dosage is increased, adsorption capacity declines from 9.32 to 6.80 for Cr (VI)

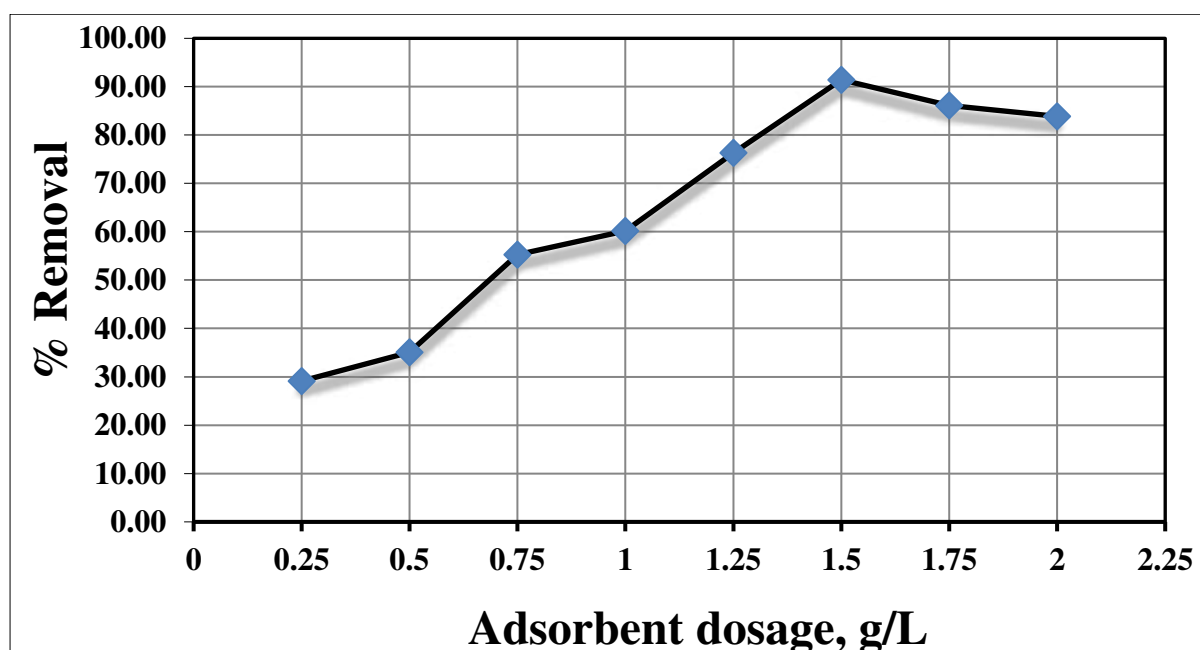


Figure 4. The outcome of adsorbent dosage for adsorption of Cr (VI).

The Cr (VI) removal efficiency increased from 29.12 to 91.43% as the adsorbent dosage increased from 0.25 to 1.5 g/l. At the same time, adsorption capacity declined from 6.80–1.51 mg g⁻¹ when adsorbent increased from 0.25-2.0 g/l owing to increased adsorption sites and larger surface area at an elevated concentration. Adsorption capacity decreases since sites endure unsaturated through adsorption. However, the number of available sites increased by

an increase in CISAC and caused in the progress of exclusion efficiency [43] (Choi K et al. 2014).

3.3 Impact of contact time (CT)

Contact time is another factor in the batch adsorption method, and the impact of CT on Cr adsorption efficiency is presented in Figure 5. At the concentration of 100 ppm and various time intervals (20–160 min), activated carbon adsorptions of metal ions have been experimented. The optimal time for adsorption of Cr (VI) by industry sludge was determined by agitating 1.5 g of adsorbent and 100 mL solutions of 50 mg/l Cr(VI) ion. The adsorption rate primarily increased quickly, and removal efficiency reached within 60 min for the initial concentration. The uptake of metal ions occurs through initial rapid uptake supported by successive sluggish uptake. The adsorption seemed to progress rapidly once the number of offered sites was higher than the number of metal species adsorbed. The initial reaction is due to the high number of unoccupied areas, hence the increased concentration gradient among adsorbate in solution and adsorbent. 93.27 % of adsorption in 10 mg/l of solution occurs 30 min after the adsorption percentage remains undeviating. During the initial stage, many vacant spots are available for adsorption, which are very difficult to find, owing to a significant time interval and repulsive forces of solute on bulk and solid phases [44].

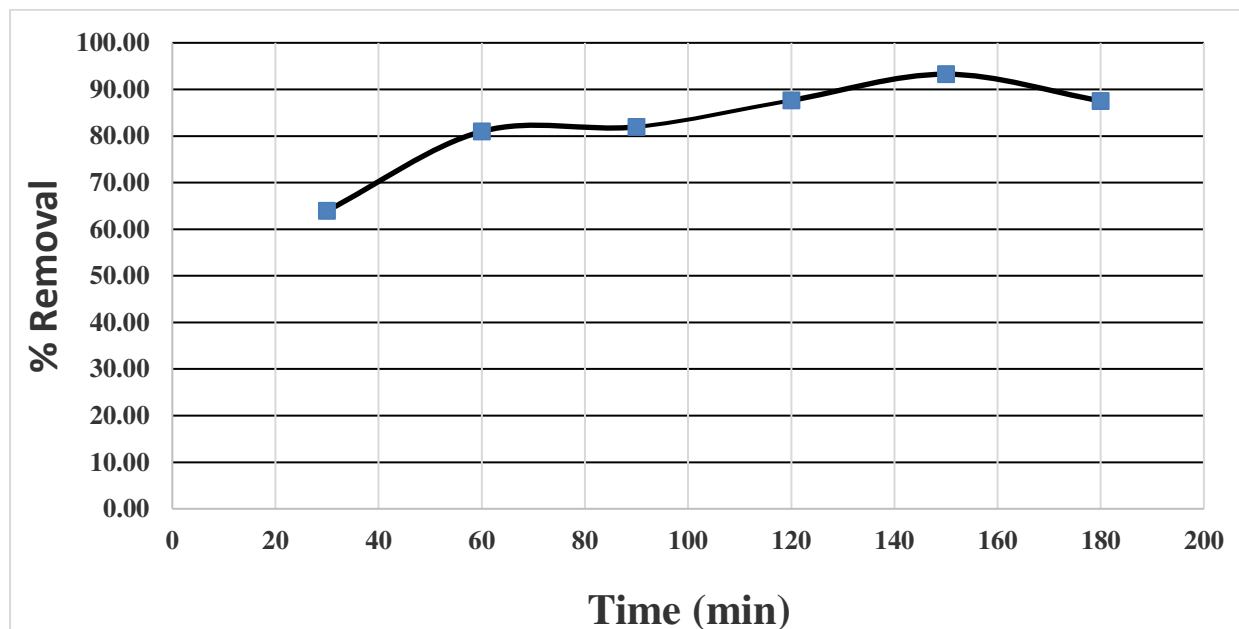


Figure 5. Impact of CT for adsorption of Cr(VI).

3.4 Impact of initial metal concentration

The adsorption studies of Cr (VI) are carried out at concentrations ranging from 2 to 16 (mg/L), which are shown in Figure 6, consisting of initial concentrations versus percentage removal of Cr (VI), keeping optimum CT and pH. The efficiency of Cr (VI) increased from 0 to 92.43 %, with an enlarged initial concentration from 0 to 16 mg/L, but it was found that equilibrium reached 10 mg/L and decreased to 16 mg/L. The capacity of adsorption increases from 18.92 to 52.71 mg/g as the initial metal ion concentration upsurges.

The number of collisions between adsorbents and metal ions increases the driving force [45]. Adsorption of Cr(VI) occurred slowly at lower concentrations and grew in concentration, offering competition on the CISAC surface; thus experimental isotherm acquired the mass balance equation of adsorption capacity of the adsorbent on adsorbate in a system using solution volume for the experiment [47].

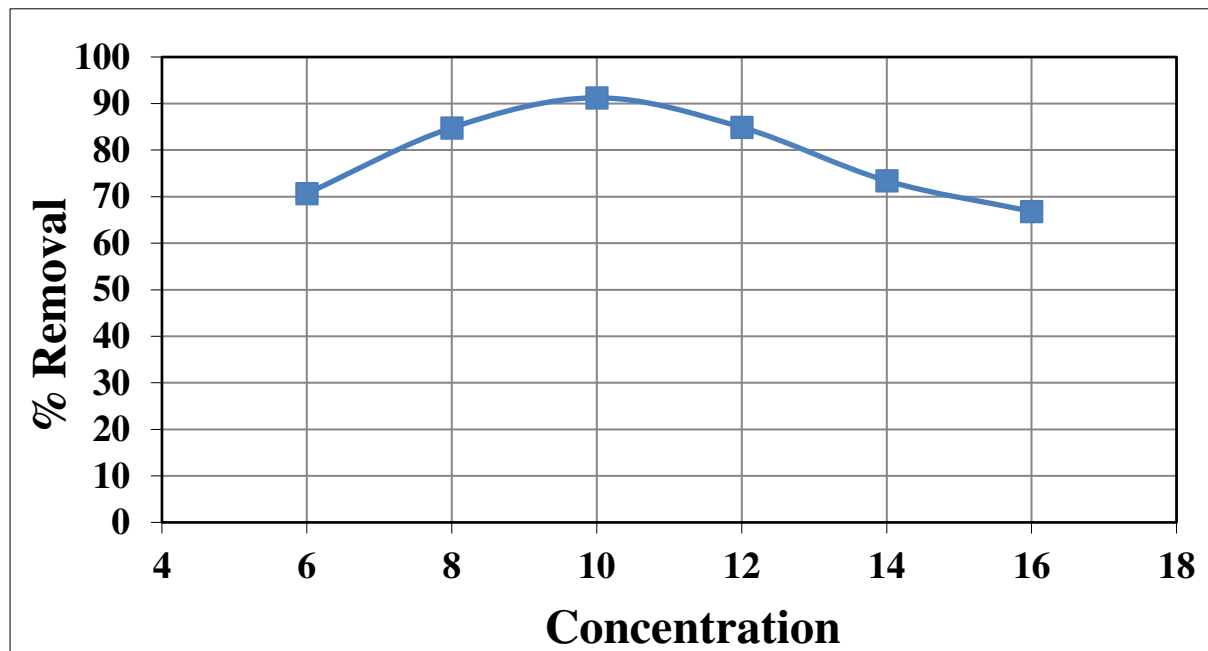


Figure 6. Impact of initial metal ion concentration on Cr (VI).

3.5 Impact of temperature on adsorption

Whilst fixing other parameters constant in a thermostatic shaker machine, the impact of temperature was investigated at temperatures ranging from 15 to 85 °C. Figure 7 shows adsorption of Cr(VI) ion improved speedily with an initial improvement in temperature and subsequently weakened with an added upsurge. Experiments were achieved at diverse temperatures (15, 25, 35, 45, 55 and 65 °C) at optimum CT and pH. The experimental result showed that the adsorption percentage increased to 92.67 % for Cr(VI) with the upsurge in

temperature to 55 °C. The maximum adsorption capacity and removal efficiency were found to be 6.80 mg/g and 92.43%, respectively, representing the method to be endothermic [48-49].

The effect of the adsorption process is distinctive for a chemical reaction or bond being intricate [50-51]. Alao et al 2014 reported similar results in the adsorption of Zn (II) ions on Carica papaya root with the mobility of ionic diffusion and enhancement of adsorption capacity due to temperature [52].

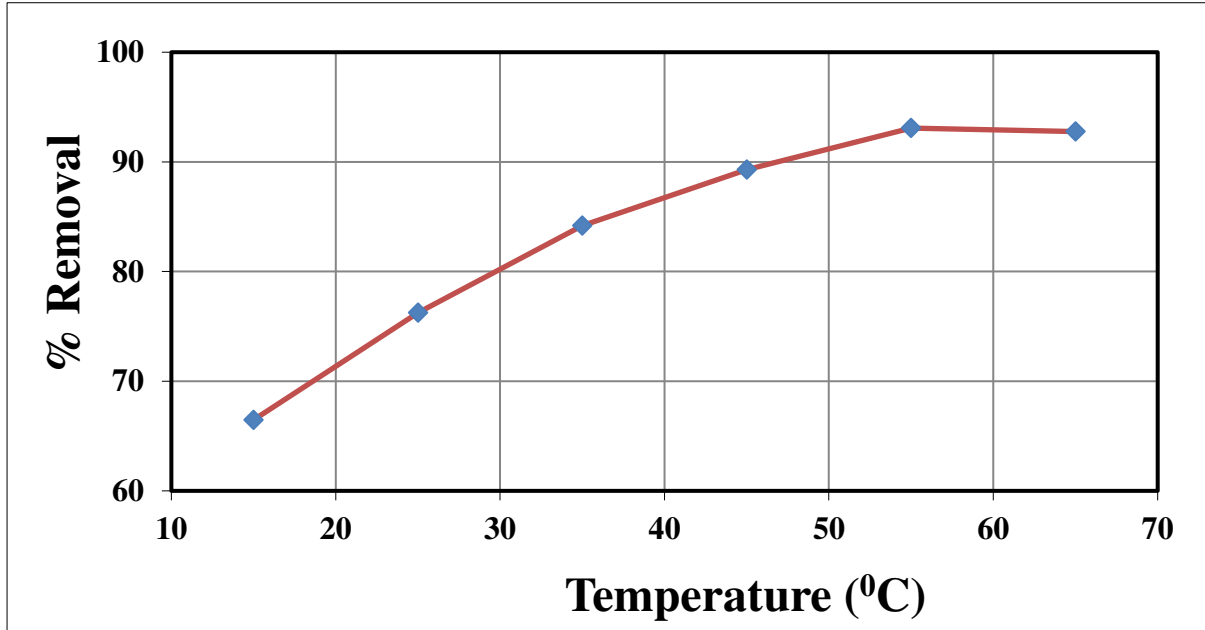


Figure 7. Impact of temperature for adsorption of Cr (VI).

4. Isotherm studies

Isotherms describe the adsorption process. Langmuir and Freundlich's isotherms are the common isotherms. The Langmuir isotherm arises at consistent sites and forms a monolayer that forms a linear equation given by equation 3 [54].

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad \dots (3)$$

Where q_e mg.g⁻¹ is the equilibrium concentration of Cr(VI) and C_e (mg L⁻¹) is the equilibrium concentration in the liquid phase. The slope of the linear plot C_e/q_e Vs C_e gives constant values related to adsorption energy (b_L) and adsorption capacity (q_m). The Langmuir equation in terms of dimensionless factor, R_L is given by equation 4.

$$R_L = \frac{1}{1 + b_L C_o} \quad \dots (4)$$

C_0 is the initial Cr(VI) concentration (mg L^{-1}), and R_L is the separation factor. The relationship of equilibrium liquid and solid phase capacity of heterogeneous surface based on multilayer adsorption property is given by Freundlich isotherm. K_L is related to the energy of adsorption by the Arrhenius equation. The assumption that adsorption sites are distributed exponentially concerning heat of adsorption and linear Freundlich isotherm is calculated by equation 5.

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad \dots (5)$$

Where q_e is the equilibrium amount adsorbed, $1/n$ is the heterogeneity factor related to intensity, and K_f is the Freundlich constant. The slope and intercept of $\log q_e$ against $\log C_e$ give K_f and $1/n$ values. Nevertheless, the current investigation endeavoured to diverse isotherm parameters at 300K, and R^2 is determined by fitting experimental equilibrium data for Cr (VI) of the CISAC system using two isotherms, which are elucidated in Table 4. The graphs show adsorption of Cr (VI) on CISAC fits well with Langmuir isotherm.

The results demonstrated adsorption of Cr (VI) on CISAC fits well with Langmuir isotherm. The physical adsorption and heterogeneous distribution of active sites on the CISAC surface make Langmuir isotherm a good fit for experimental adsorption data. The correlation coefficient for Langmuir isotherms was 0.9989. If the value of n is equal to unity, adsorption is linear. [56]. Current work showed that n at equilibrium is more than unity, signifying favourable adsorption. Likewise, the dimensionless factor R_L value is between 0 to 1, which proposes good adsorption among Cr (VI) and CISAC.

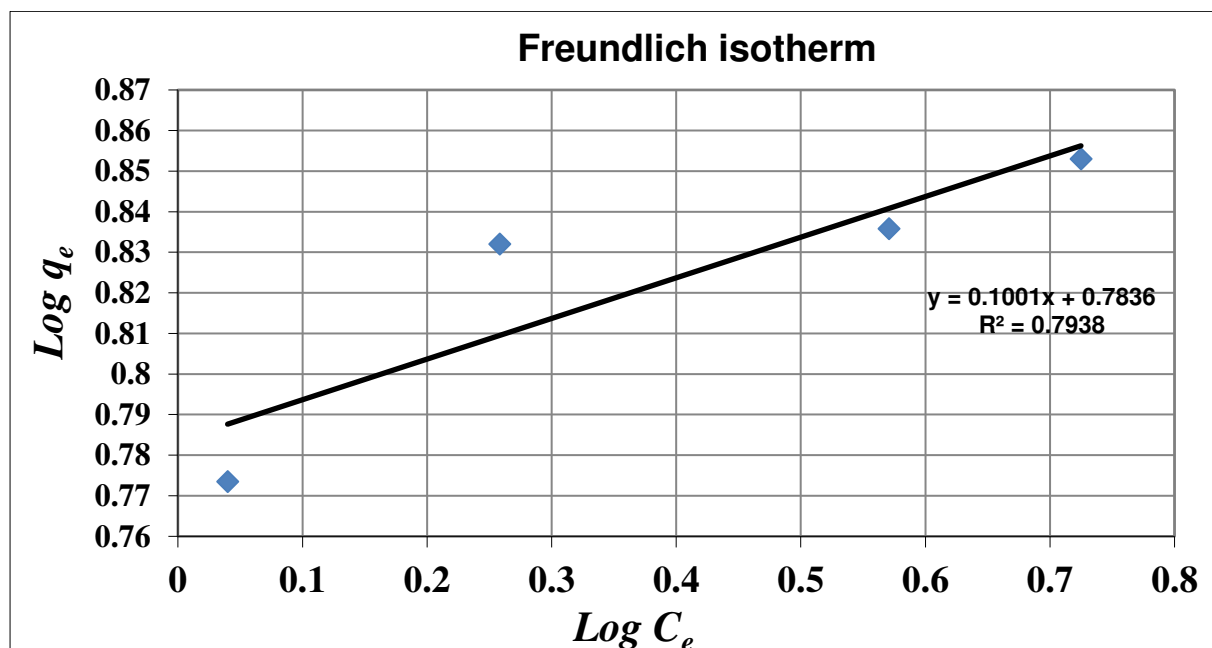


Figure 8. Freundlich isotherm model for the Cr (VI) adsorption onto CISAC.

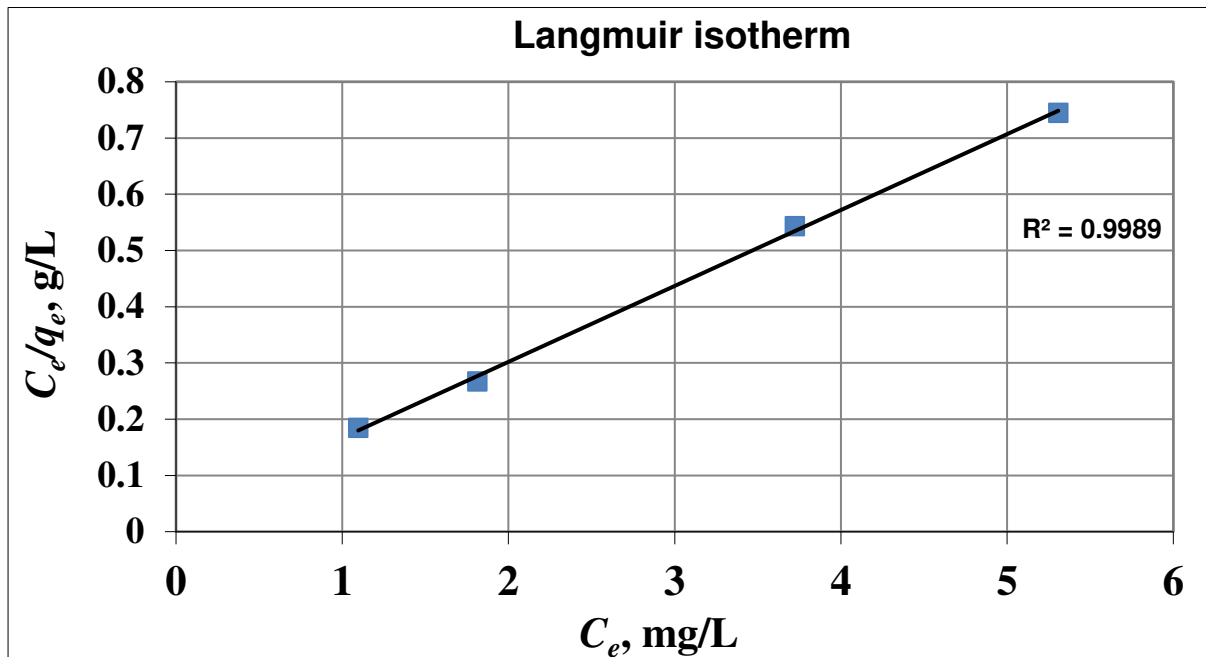


Figure 9. Langmuir isotherm for Cr (VI) adsorption onto CISAC.

Table 4. Outcomes of isotherms for adsorption of Cr (VI) by CISAC at 300K.

Adsorption isotherm	Values
Langmuir isotherm	
b_L (L/mg)	4.2269
q_m (mg/g)	7.4075
R^2	0.9989
Freundlich Isotherm	
$1/n$	0.1001
K_f	6.0764
R^2	0.7938
R_L (mg/L)	0.0231

Figure 8 indicates Langmuir isotherm fits the adsorption of Cr (VI) onto CISAC inferred from correlation coefficient (R^2) of 0.9989, which interprets metal ions from solution were adsorbed on a homogeneous specific monolayer (Kumar and Sivanesan 2017) [57]. From Table 4, the R^2 value lies between 0 and 1, which makes the adsorption process promising under studied conditions.

5. Adsorption Kinetic Studies

Equilibrium adsorption isotherm data are essential to appropriately operate an adsorption system and investigate the capacity of CISAC for the adsorption of Cr(VI). The pseudo-first and pseudo-second-order kinetics parameters helped the analysis of experimental data. The pseudo-first-order equation is related as per equation 6 [58].

$$\log(q_e - q_t) = \log q_e \frac{k_1 \times t}{2.303} \quad \dots(6)$$

Where q_t and q_e are the amounts adsorbed (mg/g) at any time, t , equilibrium and k_1 (min^{-1}) are the first-order rates constant. By plotting the graph (Figure 10) of $\log(q_e - q_t)$ Vs t , the value of k_1 is calculated from the slope and hypothetical q_e seemingly gained by intercepts. Pseudo-second order equation specified by equation 7 [59].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \dots(7)$$

where k_2 is the rate constant of the second-order rate constant. The plots of t/q_t Vs t determine $1/k_2 q_e^2$ as intercept and $1/q_e$ as slope.

Figure 11 shows a linear plot of pseudo-second order, and the correlation coefficient R^2 of pseudo-first-order kinetics was 0.8531. The correlation coefficient, R^2 , for second-order kinetics was equal to unity, indicating closer agreement than pseudo-first-order kinetics of Cr (VI) onto CISAC (Table 5). Likewise, calculated q_e (mg/g) obtained from pseudo-second-order kinetics were in reasonable settlement with the experimental value. Hence, a rate-limiting step may be chemisorptions concerning valance forces through sharing and exchanging electrons under study is more appropriately designated by pseudo-second kinetics [60]

Table 5. Adsorption kinetic model rate constants for Cr(VI) removal.

$Q_{e, \text{exp}}$ (mg/g)	Pseudo-first-order			Pseudo-second-order		
	$Q_{e \text{ cal}}$ (mg/g)	K_1 (min^{-1})	R^2	$Q_{e \text{ cal}}$ (mg/g)	K_2 (min^{-1})	R^2
5.935	4.4221	0.0086	0.8531	6.804	0.00313	0.9842

Figures 10 and 11 show sections of experimental facts at the diverse initial concentration of pseudo-first-order and second-order, respectively. The kinetics prediction depends on matching experimental results with Pseudo-second-order kinetics of Cr (VI) onto CISAC and is found to be superior in comparison with Pseudo-first-order.

It seemed investigation is more properly distinct by pseudo-second-order kinetics grounded on a supposition that rate preventive step may be chemisorption relating to forces through

allotment and conversation of electrons. The adsorption capacity of various adsorbents for the adsorption of Cr (VI) is shown in Table 6.

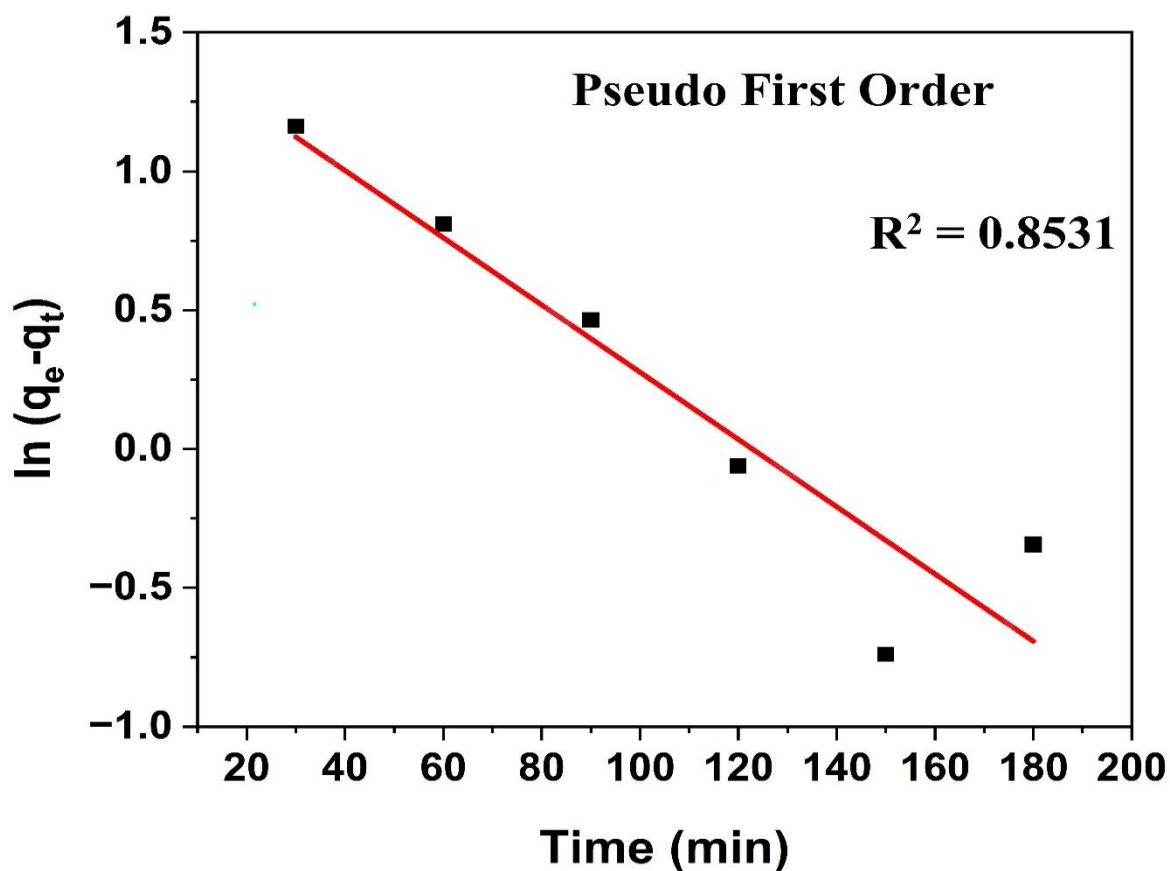


Figure 10. First-order-kinetic for Cr (VI) adsorption by CISAC.

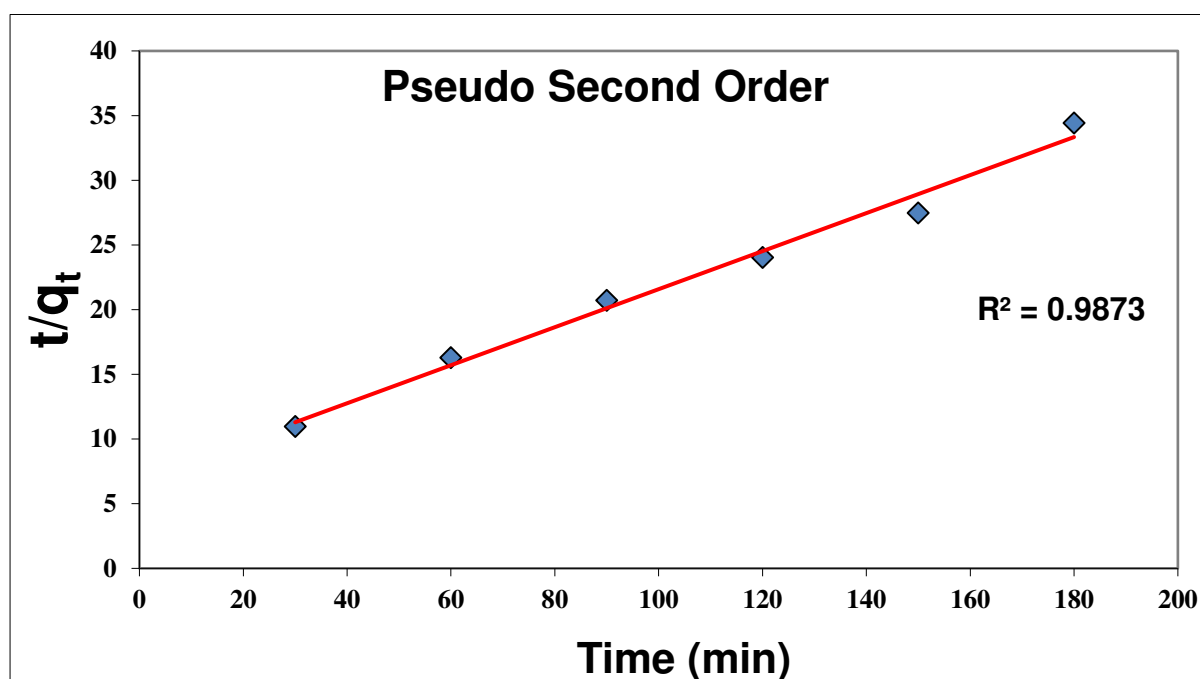


Figure 11. Second-order-kinetic for Cr (VI) adsorption by CISAC.

Table 6. The adsorption capacity of Cr (VI) with other adsorbents.

Adsorbent	Adsorbent capacity (mg/g)	Reference
Musa lacatan (Banana waste)	10.2	61
Palm shell	12.8	62
Wood apple shell	13.7	63
Rice husk	13.1	64
Mango kernel activated with H ₃ PO ₄	7.81	65
Rice straw	3.15	66
Fly ash (Bagasse)	4.31	67
Red mud	4.38	68
Corn industry sludge	6.80	Present work

6. Optimization Using Response Surface Methodology (RSM)

Numerous researchers use many tools to understand the correlation among select variables and to optimize process variables [69]. The objective of the current work is to deliver statistical evidence correlated to mathematical modelling of the process by the design of experiments (DOE) with the help of multiple regression, and statistical analysis is called RSM Response surface methodology (RSM) [70]. Using coded equations, the relative impact of factors by comparing parameter coefficients and fully crossed design experiment which consists of two or more factors each of them with discrete possible levels. The experimental units will be taken on all parameters of possible combinations of levels across all parameters. Such an experiment permits the researcher to study the influence of each variable on the response and understand the interactions of each variable on the response. In layman's terms, this method takes in consideration the factors (input variables) given and concocts certain combinations to produce the individual result (response variables). The most uncomplicated factorial study contains 2 variables, also called levels. The total number of combinations possible is 2×2 i.e., 4. For 3 it would be 8, and so on. If the number is difficult to comprehend, then a certain number of logically infeasible experiments are omitted. In the present investigation, the input variables are pH, CT and dosage of the sample during the response variable in the percentage of removal of Cr(VI) from the aqueous solution. To study the parameters to achieve a reasonable percentage of chromium adsorption within the range, the following investigations were carried out.

The three parameters (pH of the solution, CT and adsorbent dosage) have been identified as potential parameters which are represented in Table 7.

Table 7. Experimental series and levels of the selected parameters.

parameters	Range and Level				
	-1.68	-1	0	1	+1.68
pH	2	4	6	8	12
Contact time	20	140	90	40	160
Adsorbent dosage	0.2	0.5	0	1	2

6.1 The 3-level design

The three-level design consists of three factors, which can be expressed as equation (8) and will carry a total of 33 experiments. [71]

$$Y_{ijk} = \mu + A_i + B_j + AB_{ij} + C_k + AC_{ik} + BC_{jk} + ABC_{ijk} + \epsilon_{ijk} \quad \dots(8)$$

Each case is comprised of a minor factor rather than a continuous variable. In such a case, significant impacts have 2 degrees of freedom. The two-factor interaction is ($2 \times 2 = 4$) with four degrees of freedom, and k interaction is 2^k . The model contains 26 degrees of freedom. If there is no replication, one should assume there will be no three-factor interactions and will have 8 degrees of freedom for the error calculation. In the current work, we are considering 27 experiments for process optimization. By cautious DOE, the aim is to enhance the percentage removal of Cr(IV) dependent on pH, contact time and adsorbent dosage [72].

The above experiments are the indicators to measure the errors using experimental results. Based on the experimental results, the noise can be calculated, representing continuous physical phenomena (Giunta et al., 1996) [73]. The RSM is used in the present investigation to reduce the cost of experimental time and analysis and their linked statistical noise.

6.2 Central Composite Design (CCD)

CCD uses RSM for edifice a second order (quadratic) for response variable deprived of requiring to use wide-ranging three-level factorial experimentation [74]. The design consists of following

- ❖ A factorial (perhaps fractional) design considers the factors comprising two levels.
- ❖ A set of **centre points**, experiment values of individual factors are the centre of values used in the factorial design. This point is replicated to progress the precision of the experiment
- ❖ A set of **axial points**, experiments are similar to centre points excluding one parameter, that consider below and above the median of the two-level factorial, and

In figure12, the design involves 1 central point, 2N axial point and 2N factorial points.

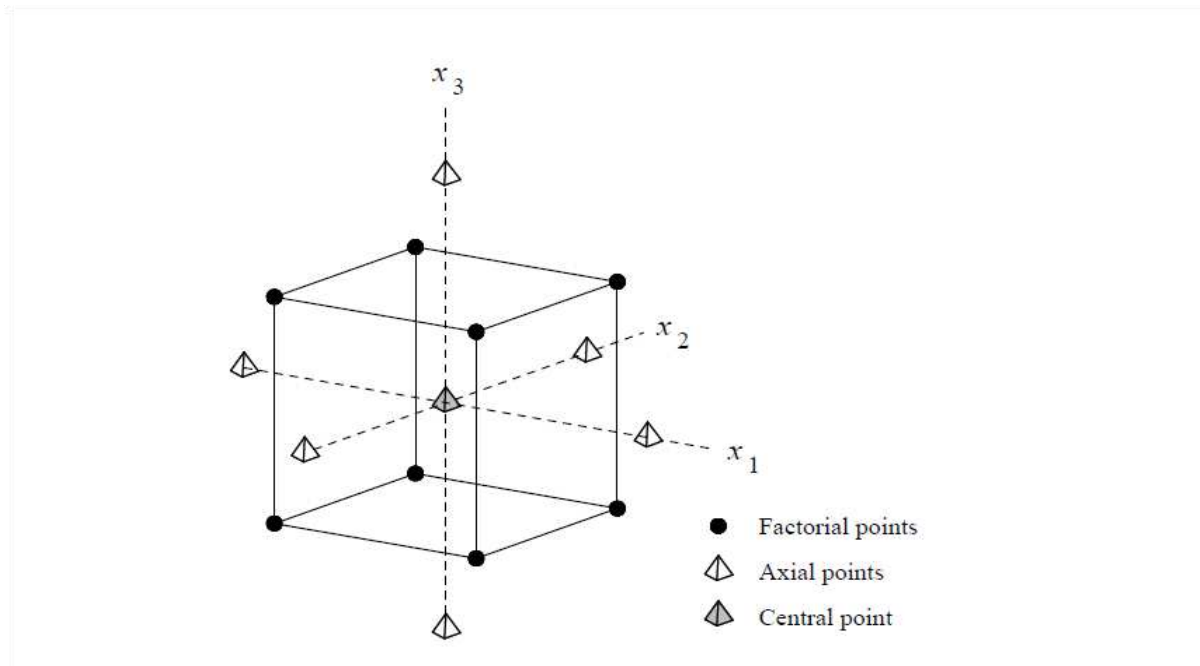


Figure 12. Reduced factorial design plot for 3 factors.

CCD offers another to $3N$ designs in building a second-order model since the number of experiments is condensed as related to a full factorial design [75]. **R-Squared** is another critical term when discussing the system. R^2 is the proportion of response variable distinction that is elucidated by its association with one or more forecaster variables. Typically, the higher R^2 , the better the model fits with the data. R^2 is also known as the coefficient of determination.

6.3 Optimization of various parameters using Minitab-14 software

The optimization of factors for the initial Cr concentration, pH, and activated sludge dosage for the removal efficiency of Cr batch trials are conducted using CCD with the three factors at five levels [76]. The choice of levels represented in the form of coded and uncoded forms aimed

at different parameters is shown in Table 7. The response is the percentage removal of Cr at equilibrium. Twenty batch runs were planned, and experimental trials were carried out as per the CCD conditions shown in Table 8.

Table 8. CCD matrix coded and real values along with experimental values for % adsorption of Cr (VI).

Entry	pH	Contact Time	Adsorbent dosage	% Removal Experimental	% Removal Predicted
1	6.00000	140.000	0.50000	59.23	60.2027
2	3.50000	90.000	0.15910	50.26	51.1284
3	3.50000	90.000	1.00000	78.96	80.7326
4	1.00000	40.000	1.50000	39.56	38.9818
5	3.50000	90.000	1.84090	77.26	75.8337
6	3.50000	90.000	1.00000	81.26	80.7326
7	-0.70448	90.000	1.00000	43.56	46.0400
8	3.50000	90.000	1.00000	82.57	80.7326
9	3.50000	174.090	1.00000	82.36	81.6222
10	7.70448	90.000	1.00000	70.26	67.2221
11	6.00000	40.000	0.50000	51.69	52.4669
12	6.00000	40.000	1.50000	60.23	61.7817
13	3.50000	90.000	1.00000	80.26	80.7326
14	3.50000	90.000	1.00000	81.26	80.7326
15	6.00000	140.000	1.50000	86.59	88.7176
16	1.00000	140.000	1.50000	78.26	77.8776
17	3.50000	5.910	1.00000	42.23	42.4099
18	1.00000	40.000	0.50000	39.85	38.1169
19	3.50000	90.000	1.00000	79.99	80.7326
20	1.00000	140.000	0.50000	58.97	57.8128

6.4 Factorial design

As per the CCD matrix, twenty trials (Table 8) were designed to understand the effects of parameters on the removal of Cr by adsorption. The three principal variables pH (X1), dosage (X2), CT (X3) were varied at 5 levels (−2, −1.68, 0, +1.68, +2). The lower and higher levels

were designated as "-" and "+", respectively. Cr removal percentages obtained from the experiments at the end of 120 min (equilibrium time) for each experiment are shown in Table 8. A multiple regression model in the uncoded form was generated using the regression coefficients in equation 9. The analysis of coefficients indicates the relative significance of terms on percentage adsorption [77]. The coefficient of X1 is +ve (pH), indicating that % removal of Cr increases with pH, X2 (dosage) is -ve, indicating as dosage increases, the percentage removal of Cr decreases, and the +ve coefficient of X3 (initial concentration) indicates that % removal increases with an increase in dosage. The ANOVA interaction term $p < 0.05$ indicates the high significance and appropriateness of the model. The model's coefficient of determination ($R^2 = 0.938$) was high, displaying a good fit for the statistical model. Predicted values of percentage removal are shown in Table 8 and indicate agreement with experimental values. Process optimization was performed with "Response optimizer" tool of MINITAB 14 [78]. The optimum values pH= 4.0 contact time = 150mins, dosage = 1.5 g/l were found. The ANOVA result also supports that the interaction of initial Cr (VI) concentration and CT significantly affects removal efficiency with a p-value of less than 0.001 (Table 9). Consequently, the interaction between initial Cr(VI) concentration and CT substantially affects the removal efficiency of CISAC.

$$\% \text{ Adsorption} = 25.3378 + (-13.2395)*X_1 + 62.3595*X_2 + (-0.0147)*X_3 + (-0.9165)*X_1^2 + (-13.3912)*X_2^2 + (-0.0006)*X_3^2 + (-4.1955)*X_1*X_2 + 0.012*X_2*X_3 - 0.0175*X_1*X_3 \dots (9)$$

Table 9. Analysis of variance for percentage adsorption.

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	5285.74	587.30	147.19	0.000
Linear	3	3134.42	1044.81	261.85	0.000
pH	1	541.61	541.61	135.74	0.000
CT	1	1856.06	1856.06	465.17	0.000
D	1	736.76	736.76	184.65	0.000
Square	3	1859.77	619.92	155.37	0.000
pH*pH	1	1046.42	1046.42	262.25	0.000
CT*CT	1	631.05	631.05	158.15	0.000
D*D	1	536.13	536.13	134.36	0.000
2-Way Interaction	3	291.54	97.18	24.36	0.000
pH*CT	1	71.52	71.52	19.92	0.002

pH*D	1	35.70	35.70	8.95	0.014
CT*D	1	184.32	184.32	46.19	0.000
Error	10	39.90	3.99		
Lack-of-Fit	5	32.05	6.41		
Pure Error	5	7.85	1.57		
Total	19	5325.64			

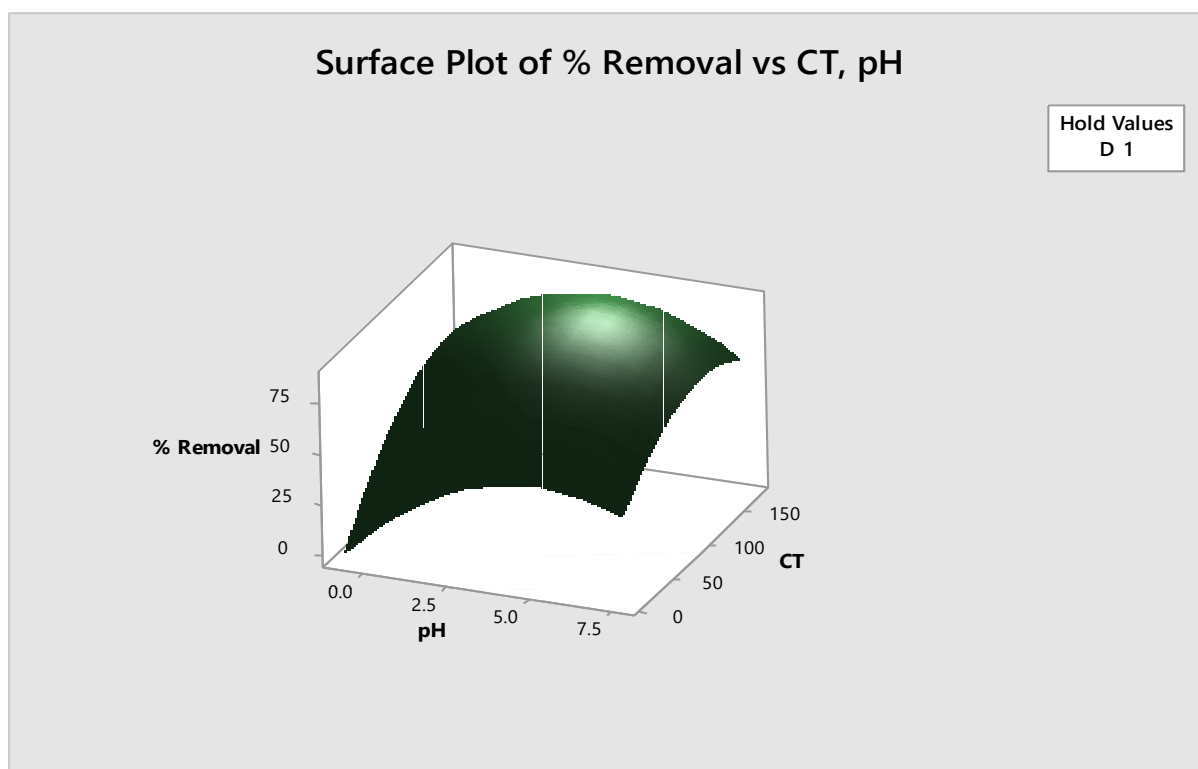


Figure 13. Surface plot of % Removal Vs CT, pH.

Figure 13 shows 3D pH and CT on adsorption of Cr (VI) at a constant dosage (1.5 g/l). The adsorption percentage increases with decreasing pH and lower concentration levels. The percentage adsorption declines with advanced concentration and through higher pH. The 3D RSM for the combined effect of CT of Cr and dosage on adsorption of Cr at constant pH of 4.

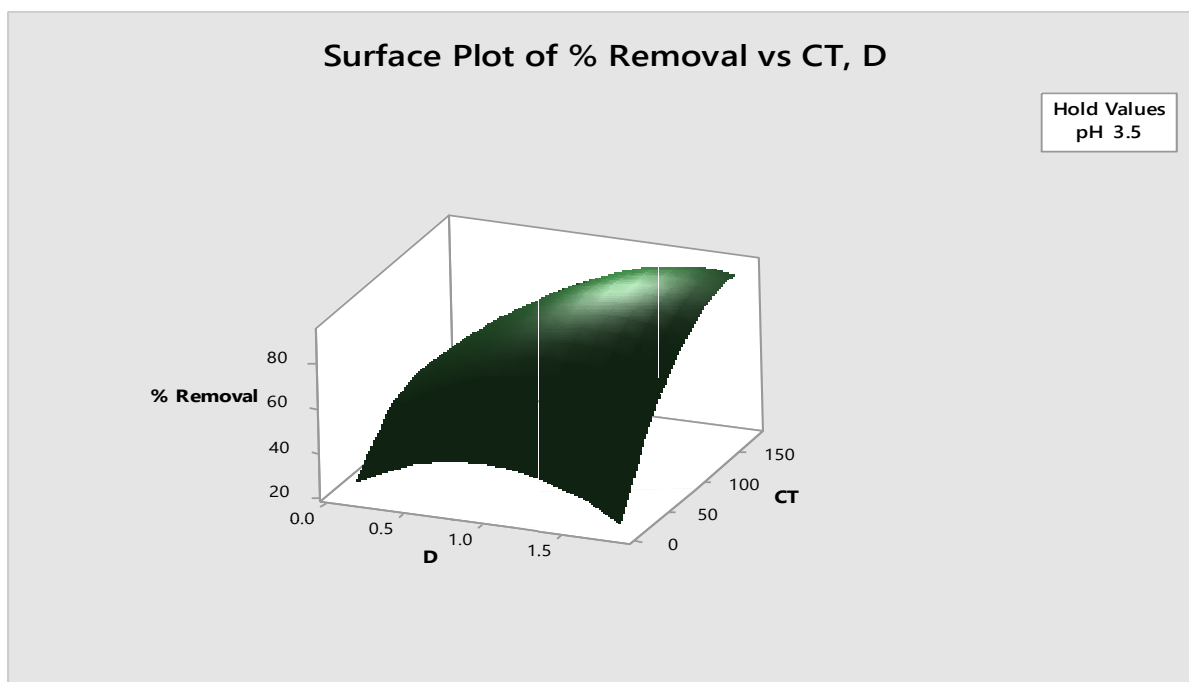


Figure 14. Surface Plot of % removal Vs CT, Dosage.

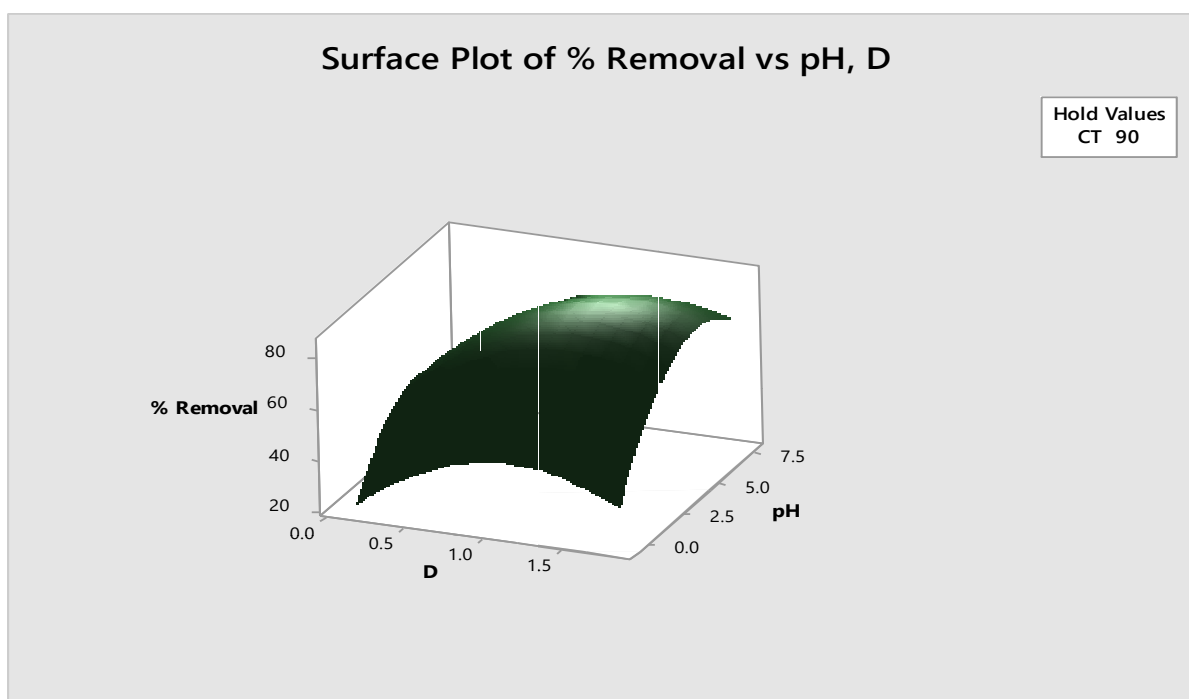


Figure 15. Surface plot of % Removal Vs pH, dosage.

The effect of pH and dosage on adsorption on the removal of Cr with CT (150 mins) is shown in Figure 14. Percentage adsorption increases first with pH and then drops with an increase in pH, and the adsorption rate increases with adsorbent dosage. The optimized adsorbent dosage was found to be with a pH of 4. Hence, dosage and pH interaction are negligible (Figure 15). The optimizer diagram of pH, CT and dosage is shown in Figure 16.

Table 10. Optimization results (Global Solution).

Entry	Parameter	Optimized values
1	pH	4.2220
2	Contact Time	152.0055
3	Dosage, g/l	1.5691

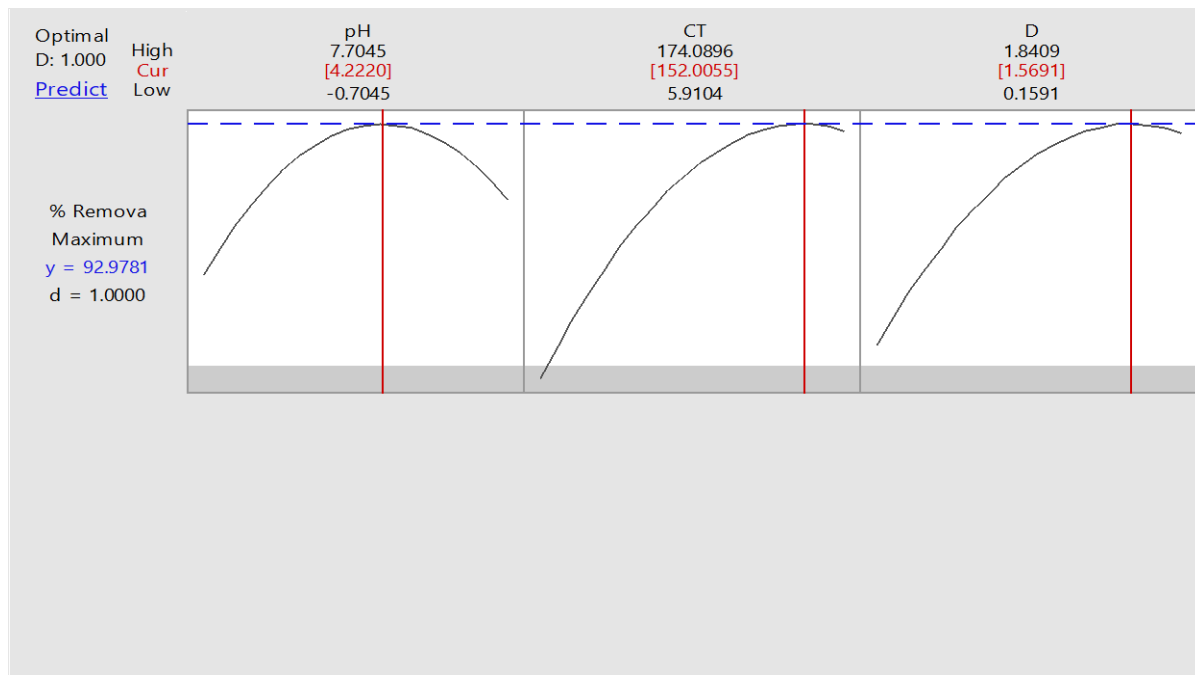


Figure 16. Optimizer diagram.

7. Conclusion

Activated carbon from corn industry sludge was prepared and characterized. Experimental results disclosed excessive porosity and the occurrence of functional groups convenient in adsorption. The pseudo-second-order and Langmuir isotherm described the adsorption of Cr (VI) ions onto CISAC. Critical parameters such as solution pH, CT, and initial metal ion concentration can affect batch adsorption experiments. Experimental results of current work suggested that adsorption of Cr (VI) on CISAC is a physical adsorption method achieving equilibrium within 20 min for Langmuir isotherm. The pseudo-second-order kinetic model was a better fit for the adsorption of Cr (VI) by CISAC. The outcomes of fitting processes were verified by evaluating using correlation coefficients (R^2). With solution pH 4, an equilibrium time of 150 min with the adsorbent dosage of 0.14 g per 100 ml was found to be the optimum condition for adsorption of maximum Cr (VI) uptake of 6.80 mg/g. The CISAC adsorbent

yielded an adsorption capacity of 6.80 mg/g due to its mesoporous structure, its high BET surface area and the presence of functional groups acting as a chelating agent to adsorb heavy metal ions through different approaches. Thus, CISAC can be used as an efficient, low-cost adsorbent to remove Cr(VI) ions, even in small quantities. To support the optimization of factors such as initial Cr concentration, pH and activated sludge dosage for efficient removal of Cr, batch trials were considered per CCD through three factors at five levels. This result is substantiated by ANOVA, which showed that interaction of CT and initial Cr (VI) concentration substantially impacted removal competence.

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Declarations

Conflict of Interest

All the authors declare that they do not have any conflict of interest

Data Availability

The data that supports the findings of this study enclosed in the manuscript and more data are available from the corresponding author upon reasonable request.

Ethics approval

All the authors declares that the present research work does not involve any human and/or animals

Consent to participate

All the authors declare that the present study does not involve any human objects or organs or tissues in any form.

Authors Contributions

Shankamma S. Kerur contributed to the preparation of the batch study of the experiments, Manjunath S. Hanagadakar was involved in the characterization of the samples, Ratnamala Sholapurmath contributed in the sample characterization and partly by preparation of the manuscript. Santosh S. Nandi was involved in the preparation of the manuscript, and Sateesh N. Hosamane contributed to Statistical Analysis and Optimization study.

Consent for publication

All the authors declare that the data deposited with the manuscript can be published freely online and will be used for educational publications intended for professionals.

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