Kinetic, Isotherm and Adsorption of 2-Chlorophenol using Corn Industry Sludge Derived Activated Carbon Synthesized by a Novel Activation Method: Optimization and Statistical Studies in Aqueous Solutions

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Abstract

2-Chlorophenol (2-CP) is non-biodegradable and has a gradual and non-infinite toxicity to the environment, bio-adsorption technology employing agricultural waste material including corn industry waste material has become a modern dream. The waste was chemically treated, activated, characterized, and used for the adsorption of 2-Chlorophenol.Batch adsorption tests were carried out under a variety of parameters, comprising contact time, concentration of initial 2-CP, adsorbent dose, and pH of solution, to see how these affected the solid support's retention capacity. To investigate the adsorption behaviour, the Freundlich and Langmuir isotherm models are used. The Langmuir model fit the equilibrium information rather well. At 20°C, corn sludge had an extreme monolayer adsorption potential of 7.407±1.234 mg g^{-1}. Lastly, the kinetic studies revealed that the adsorption mechanism was pseudo 2nd-order. Finally, corn industry sludge demonstrated that it can extract 2-CP from aqueous solutions. The corn industry sludge shows advantage of low-cost material an effective adsorbent for removal of2-Chlorophenol.The response surface methodology tool was used to study the statistical analysis of adsorption. The both theoretical and experimental values for percentage adsorption of 2-CPresulted with 95.97% and 96.05% correspondingly. It is evident that experimental values of % adsorption are in close settlement with those values expected by Central Composite Design.

Keywords: Central Composite Design (CCD), Adsorption,Optimization,Freundlich isotherm, Langmuir isotherm, 2-Chlorophenol.

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1. Introduction

Over the past decades, the removal of toxic materials from wastewater and water has been a fundamental attention of many researchers and scientists around the globe [1]. Because of its enormous controllable pore conformation, porous surface area, and low acid/base reactivity, high thermo-labile, activated carbon had to be the utmost broadly applied adsorbent for the elimination of water contaminants. ACs have been produced from a variety of wastes, including coconut shells [2], fruit stones [3], fertiliser unwanted [4], walnut shell [5], bagassess [6], coir pith [7], sewage [8], cornand industrial wastes [9]. Biologically, the adsorption approach employing agricultural waste products is an effective and cost-effective strategy for removing heavy metals, since it offers several benefits, including low cost, high efficiency, minimal waste, and the ability to recycle it [10]. The interaction between inactive and non-living biological matter and metal ions in aqueous solution to adsorb and gather phenols by adsorption, ion exchange, surface complexity, and deposition is the principle of adsorption technology (Bayan and Jaafar, 2020) [11]. Due to the low cost of agricultural waste products, their application as bio-absorbents in the elimination of phenols from drinking water or contaminated water had turn into commonplace. Different agriculture waste products have been investigated for their ability to act as bio-absorbents, with Corn waste products being one of the most promising (Muthusamy and Murugan, 2016; Eskandarian et al., 2014) [12,13]. The major goal of this research is to figure out how to remove 2-chlorophenol from aqueous solution. Chlorophenols are found in wastewaters from a variety of industrial operations and should be eliminated because of their high harmfulness.

Phenols and their compounds are widely used compounds in everyday life, with significant levels found in contaminated water (Prashantha kumar et al., 2018) [14]. Chlorophenols (CPs) are an example of a class of organic pollutants [15]. Mono-chlorophenols (2, 3, 4-chlorophenols), di-chlorophenols (DCPs), tri-chlorophenols (TCPs), tetra-chlophenols (TeCPs), and penta-chlorophenols (PCPs) were a set of organochlorides of phenol comprising single or more covalently attached chlorine atoms (Fan et al., 2015) [16]. Chlorophenols have a negative impact on the nervous and respiratory systems of humans, posing substantial health risks. They are stable in nature, had a strong odour, are weakly digestible, and were potentially dangerous and carcinogenic [17].Because of their adamant character, dumping them into the hydrosphere is a substantial cause of contamination. Sonochemical degradation [18], photo-fenton degradation electrochemical deterioration [19-20], membrane filtration [21], reverse osmosis [22] and flocculation/coagulation [23]. It has a 99.9% effectiveness in removing both soluble and insoluble organic contaminants, with the use of activated carbon the greatest significant and frequently utilised adsorbent (Garba et al., 2019) [24].

Chlorophenols were found in industrial wastewaters from a variety of petrochemical and chemical processes that produce polymeric resins, insecticides, dyes, medicines, wood preservation, cellulose pulp, and chemicals. Chlorophenols and similar chemicals, which were included to the list of importance and dangerous contaminants, are present in the wastewaters produced from these activities [25]. Because they were extremely poisonous, recalcitrant, and bio accumulating types, their destiny in the biosphere is of major concern. 2-Chlorophenol (2-CP) is chosen as the study's target pollutant because it is produced not only from the sources indicated above, but also from the degradation of chlorinated aromatic compounds and pesticides, as well as during chlorination of contaminated water [26]. The result showed 2-CP can be removed from the aqueous solution more efficiently than precipitation, ion exchange, membrane filtration, physical adsorption, chemical oxidation/reduction, and bio removal method [27]. In this paper, we convert corn sludge to useful bioadsorbent for eliminating the 2-CP from aqueous solution and reusability of the bioadsorbent was evaluated. The result showed the most effective and promising method which

is eco-friendly,low-cost, and more efficient adsorbent.

2. Materials and Method

2.1Preparation and Analysis of Activated sample

All the chemicals, reagents and solvents are procured from Sigma-Aldrich and Spectro-chem without purification. An analytical grade 2-chlorophenol (C_6H_5ClO) has been used to make the stock solution (1.0 g L^{-1}). By diluting stock solution to the necessary concentrations, experimental solutions of varying beginning concentrations (C_0) were created. The adsorbent was made in the following manner: Corns were first washed in distilled H_2O and dried at room temperature on the spotless table. Corn parts which were employed as adsorbent are broken and samples were filtered with 60 mesh sizes using an electrical device. A sample was taken and air dried (105°C) prior to getting treated for 48 hours in a 3.0 M H_2SO_4 solution at a mass ratio of 1:1 with magnetic agitation. The additional solutions were then drained, and the resultants dense were dried by air at 105°C for another 48 hours. Thereafter, 15 g of chemically stimulated substance were pyrolyzed in a muffle furnace at a specific temperature of 650°C for 1 hour at a rate of 10°C/minutes. The substances were pyrolyzed, then eroded with 3 M HCl and hot dis.H_2O to a specific pH, then dried at 105°C for 24 hours to a consistent weight. Then, the adsorbent was crushed to a small particles and size of 0.125 mm and sieved. 2.3 mm.Figure 1 shows the sludge samples activated by different method.

Figure 1. Sludge samples activated by different method.

For the activation of the sample acid and heating treatment methods are employed and the obtained results are compared with unprocessed (raw) sample as shown in the Table 1. The heat-treated sample (S1) signifies the percentage removal of 94.7 % whereas sample with acid (S2) observed higher percentage removal.Consequently, it was preferred as the activation method. Batch adsorption study was conducted in incubated shaker. The surface morphology of corn sludge was studied by JOEL's (Japan) JSM 6390 to examine the filler dispersion and surface morphology. The BET pore size and surface area were examined by Horiba SA-9600 instrument.

Table 1. Different activated adsorbent samples.

Entry	Sample	Absorbance	% Removal
1	Heat Treatment (S1)	0.0040	94.7
2	Acid Treatment (S2)	0.0096	96.3

2.3 Batch adsorption studies

A batch experiment was utilised to investigate the sensitivity of corn waste

products to adsorbed 2-chlorophenol, considering numerous factors to establish the ideal adsorption conditions, like contact time (min), pH, temperature(°C), and mixing speed (rpm). In a conical flask, 50 mg of adsorbate was combined with 15 ml of 2-chlorophenol, and the mixture was agitated at 50-200 rpm and 15-55°C. The pH should be between 5.5 and 9.5, with a contact time of 0 to 90 minutes. Using the Atomic Adsorption spectrophotometer (AA7000- Shimadzu), solutions of sample was taken at intervals and filtered mixtures using Whitman filter paper No. 40 to fix the residual from the Pb (II) ions (Mohammadi et al., 2017). Using the Mathematical equation 1 and equation 2, the Pb (II) fraction of ions removed was calculated, and the total number of Pb (II) ions adsorbed (mg/g) were determined (Onwordi et al., 2019) [28]

$$Q_e = \frac{V(C_p - C_f)}{n} \quad (1)$$

$$R\% = \frac{C_p - C_t}{C_p} \times 100 \quad (2)$$

Where,Q_e - Per unit weight of adsorbent, the amount of MB that has been absorbed (mg g^{-1}),

C_p and C_f (mg L^{-1}) - MB's initial and equilibrium conditions, respectively, V (L) - Volume of the solution, m (g) –Adsorbent for Dry mass.

2.4 Desorption/reuse procedure

Five adsorption-desorption cycles were used to test the reusability of the activated maize. The adsorption studies were carried out for five consecutive cycles with an initial concentration of 550 mg/L phenol and PCP in 120 minutes under ideal conditions. The used adsorbent was magnetically recovered and mixed in methanol, NaOH, and NaCl for three hours to regenerate the spent activated corn for the next adsorption cycle. The adsorbent was then filtered and dried overnight before being used again. The adsorbents' stability was also assessed by determining the concentration of dissolved iron in the aqueous phase.0.10 g of activated corn loaded with 2-CP was agitated at 200 rpm for 24 hours with 5 ml of desorbent solutions at 25±1°Cfor desorption tests. The desorption potential was then calculated. The activated corn was then washed three times with DI water, dried for four hours at 100°C, and reused for the next adsorption-desorption cycle (Equation 3).

$$\%\ \text{Desorption} = \left(\frac{\text{Amount of 2CP Desorbed}}{\text{Amount of 2CP adsorbed}}\right) \ldots (3)$$

3. Adsorption Study

The stock solutionis prepared by dissolving desired quantity of $K_2Cr_2O_7$in distilled water and different concentrations of solution isprepared by dilution of standard solution. To attain desired concentrations of 2-CP for batch study solution was diluted by means ofdistilled water.The absorbance was measured using prepared solution UV-Visible spectrophotometer [LAMBDA 1050]. After 10 min, absorbance of purple coloured was evaluated at wavelength of 570 nm. Spectrophotometer was first calibrated via various concentrations of 2-CP solution (2 to 16 ppm). The solitary samples flasks were centrifugated at 10,000 rpm for 15 min at room temperature to eliminate suspended biomass, 1,5-diphenyl carbazide (DPC) reagent in acid solution as complexing agentthe concentration of 2-CP ion was determined. To determine the percentage removal of adsorbent, straight line calibarion curve is drawnand corresponding to following equation 4 [29].

$$\%\ \mathrm{R} = \frac{\mathrm{C_o} - \mathrm{C_e}}{\mathrm{C_o}} \times 100 \quad \ldots(4)$$

Where C_O is primary concentration, C_e is equlibrium concentrations (mg/L) and R is 2-CP adsorbed.The prepared activated carbon adsorption capacity was calcluted by usingsucceeding equation 5.

$$\mathrm{q_t} = \frac{\mathrm{C_o V_o} - \mathrm{C_t V_t}}{\mathrm{m}} \quad \ldots(5)$$

The analysis was carried out using sample with 100 ml of metal ion solution by diverse conditions of adsorption by constant water bath to regulate impact of pH, initial metal ion concentration and contact time on adsorption.

3.1Impact of pH on Adsorption

Table 2 shows the findings of a study on the effect of pH on the adsorption of 2-CP atoms by corn. The results revealed that raising the solutions a pH augmented the adsorption of 2-CP atoms for both studied materials. The highest percentages of adsorption were found in the pH ranges of 6.5 and 8.5-9.5 (67.18 %, 96.51 and 72.85 % respectively) (Figure 2 (a)). The pH of the adsorbed surface, as well as its surface charges and capacity to ionise in aqueous solutions, is regarded one of the great significant factors in the adsorption method (Alghamdi et al., 2019) [30]. The low adsorption in acidic pH less than 4 could be explained as follows: in the acidic medium, protons and metal ions compete for effective sites on the adsorbed surface. As the pH raises, the competition for proton-free effective sites decreases, allowing the sites to become free and ready to interact with positively charged metal atoms (Alghamdi et al., 2019) [31]. The findings of this study are compatible with those of (Bayan and Jaafar, 2020) and other studies reported in the book chapter of, as well as with those of (Bayan and Jaafar, 2020) [32].

Table 2. The adsorption of 2-CP at different pH value

pH	Weight capacity of adsorption mg g^{-1} (q_e)	Adsorption percentage (%)
5.5	0.453	60.09
6.5	0.502	67.18
7.5	0.178	23.94
8.5	0.645	96.51
9.5	0.548	72.85

The influence of pH on metal adsorption was incorporated by keeping pH extent of 4 to 10.The process operated is analogous to those previouslydescribed in the literature. Using UV–Visible spectrophotometer filtrate is examined for residual metal ion and pH of aqueous solution is evidently a vital factor operated in adsorption.

3.2Impact of adsorbent dosage

Figure 2 (b) depicts the impact of bio adsorbents on the proportion of 2-CP elimination and exact uptake over time. The efficacy of 2-CP removal rose considerably as the bioadsorbent dosages were raised, owing to the increased number of accessible adsorption sites in the bioadsorbent(Eskandarian et al., 2014) [33].The graph indicates percent adsorption rises(52.48 to 95.96%) with growth in dosage ofCISAC (0.25 to 2.0 g) and higher than 1.5 g adsorbent quantities persisted nearly constant. Owning to superior readiness of adsorption spots of adsorbent and thus creating easier for 2-CP [34]. An upsurge in quantity of adsorbent exceeding a quantity that can entirely adsorb 2-CPobligated no superficial effect on supplementary rise in adsorption and as dosage is increased, adsorption capacity declines from9.12 to 5.35 for 2-CP.

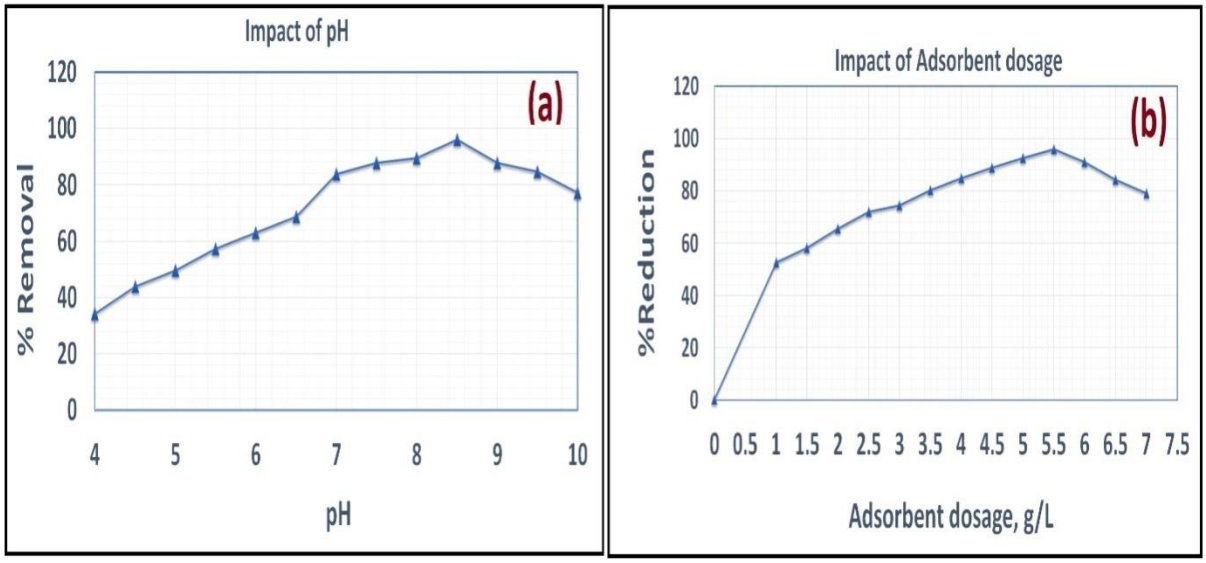

Figure 2 (a) Impact of pH on 2-CP adsorption and (b) Outcome of adsorbent measure for adsorption of 2-CP using 20ppm.

3.3Impact of Contact time (CT)

In the adsorption treating wastewater, the contact period among the adsorbate and the adsorbent is critical. The values obtained (Figure 3 (a)) reveal that the 2-CP may be eliminated quickly, with 80% of maximal adsorption occurring in a small period (in the first 45 minutes).At various time intervals (300–700min) using activated carbon adsorptions of metal ions were tested keeping concentration of 100 ppm. To regulateideal time for adsorption of 2-CPvia industry sludge, 2-CP ion and adsorption rate primarily increased quickly and removal efficiency reached within550 min for initial concentration. The adsorption seemed to progressrapidlyonce number of offered sites are higher than quantity of metal species to be adsorbed.The uptake of metal ion takes place through initial rapid uptake supported by successive sluggish uptake. 96.05 % of adsorption in 10 mg/l of solution occurs at 550 min after adsorption percentage and vacant spots are existing for adsorption during initial stage and after a time interval vacant surface sites are very hard to get engaged owning to repulsive forces of solute on solid and bulk phases.

3.4 Impact of initial metal concentration

At diverge initial 2-CP ion concentrations ranging from 100 to 800 mg/L, adsorption studies of 2-CP were carried out. With increased 2-CP concentration, the adsorption capacities of 2-CP into bioadsorbent steadily improve (Figure3 (b)). At a primary concentration of 500 mg L^{-1}, 2-CP had high adsorption capabilities of 96.05 %. The eradication effectiveness for 2-CP significantly increased before declining, which might be explained by the fact that at reduced beginning concentrations, it had more vacant active sites available for adsorption, and following saturated sites are difficult to catch the 2-CP (Eskandarian et al., 2014) [35].Figure 5 shows the graph of initial concentration vs % removal of 2-CP keeping optimum CT and solution pH. The driving force between solid and aqueous phase increased the number of collisions between metal ion and adsorbent. Thus, to acquire experimental adsorption isotherms, adsorption capacity of adsorbent which is gained from mass balance equation on adsorbate in a system with solution volume is often used.

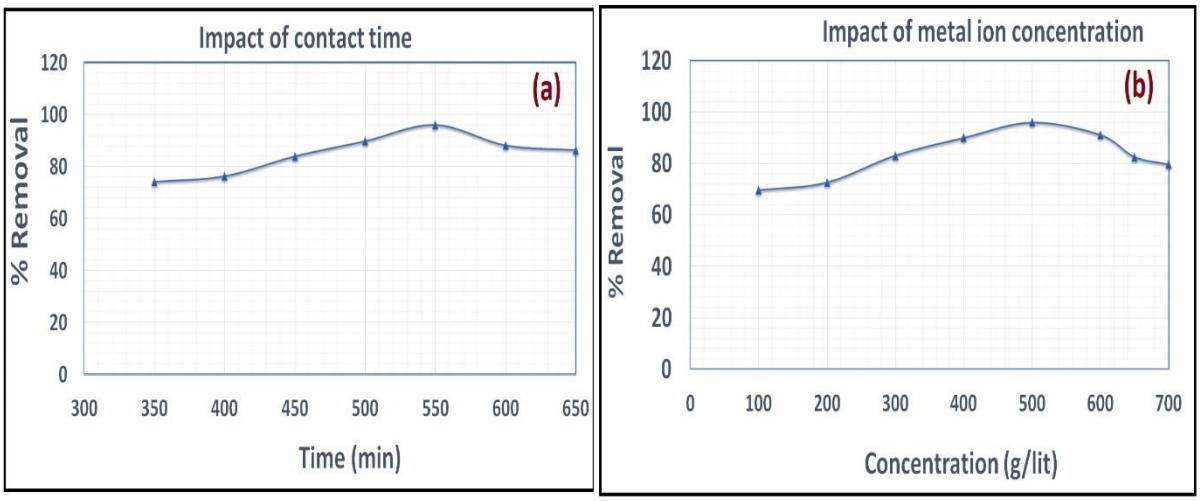

Figure 3 (a) Impact of CT for adsorption of 2-CP and (b) Impact of initial metal ion concentration on 2-CP.

3.5 Impact of temperature on adsorption

In a thermostatic shaker machine effect of temperature was implemented at five unlike temperatures extending from 15 to 85 °C. Figure 4shows adsorption of 2-CP ion improved rapidly with an initial improved in temperature and later weakened with anaddedupsurge. This effect of adsorption process is distinctive of a chemical reaction or bond being intricate. Similar results were observedon adsorption of Zn (II) ions on carica papaya root powder Alao et al. 2014 [36]. They reported enhancement of adsorption capacity when temperature is enlarged owning to mobility of ionic species and improved diffusion. Table 3 illustrates the findings of a study on the effect of temperature on the adsorption of 2-CP by Corn over a temperature range of 10 to 50°C. In the case of Corn, the results showed that increasing the temperature reduced 2-CP absorption, with the adsorption % and the temperature range ranging (10-50°C). Because adsorption is an exothermic process, adsorbent particles tend to separate from the adsorbent surface as the temperature rises (Fadhil and Eisa, 2019) [37]. The current findings are consistent with Bayan and Raghad's findings (2020).

Table 3: The adsorption of 2-CP at different temperature value

Temperature	**Weight capacity of adsorption mg g^{-1} (q_e)**	**Adsorption percentage (%)**
10	0.040	5.36
20	0.018	2.51
30	0.040	5.36
40	0.070	9.5
50	0.112	14.95

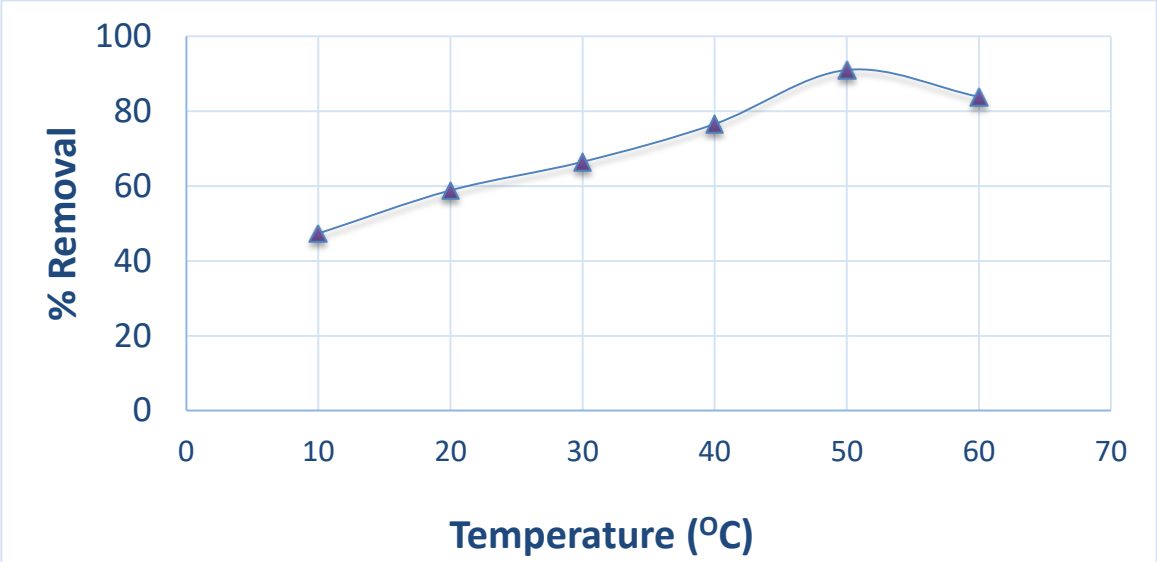

Figure 4. Impact of temperature for adsorption of 2-CP.

4.Isotherm studies

Amongst the different isotherm studies, Freundlich and Langmuir isotherms are most suitable for the adsorption of 2-CP. Freundlich isotherm gives the relationship of equilibrium liquid and solid phase capacity based on multilayer adsorption properties comprising of heterogeneous surface. Based on the assumption that adsorption sites are distributed exponentially with respect to heat of adsorption [38]. The linear form of Freundlich isotherm is calculated using equation 6.

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \quad \ldots(6)$$

Where q_e is amount adsorbed at equilibrium, C_e is equilibrium concentration, 1/n is heterogeneity factor which is correlated to intensity and K_f is Freundlich constant. The value of 1/n and K_f is obtained from intercept and slope of log q_e against log C_e. The Langmuir isotherm forecast adsorption at consistent sites and forms a monolayer due to which adsorbate gets attached to a site and no more adsorption happens (Figure 5 (a)). The Langmuir isotherm (i.e., Linear equation) is

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad \ldots(7)$$

where C_e (mg/L) is equilibrium concentration in liquid phase and q_e(mg/g) is equilibrium concentration of 2-CP in adsorbed phase. The linear plot of C_e/q_eVs C_e gives the slope with straight line, intercept of $1/q_{max}$ $b_L$and slope of $1/q_{max}$ is obtained [39]. The constants are interrelated to adsorption capacity (q_m) and energy of adsorption (b_L) which can be expressed in terms of a dimensionless factor, $R_L$is given as

$$R_L = \frac{1}{1+b_L C_O} \quad \ldots(8)$$

Where C_0 is initial 2-CP ion concentration (mg/L) and R_L is separation factor. The current investigation endeavoured to two isotherm parameters at 20 ^{0}C and correlation coefficient $R^2$is calculated by experimental equilibrium data for 2-CP ion of CISAC, which are interpreted in Table 4. The adsorption of 2-CP on CISAC fits well to Langmuir isotherm since physical adsorption along with a heterogeneous distribution of active sites on CISAC surface makes Langmuir isotherms is a good fit to detected correlation coefficients for Langmuir isotherms were 0.997. Current work showed value of n at equilibrium is more than unity, signifying favourable adsorption. Likewise, dimensionless factor R_L value is between 0 to 1 which propose a favourable adsorption among 2-CP and CISAC.

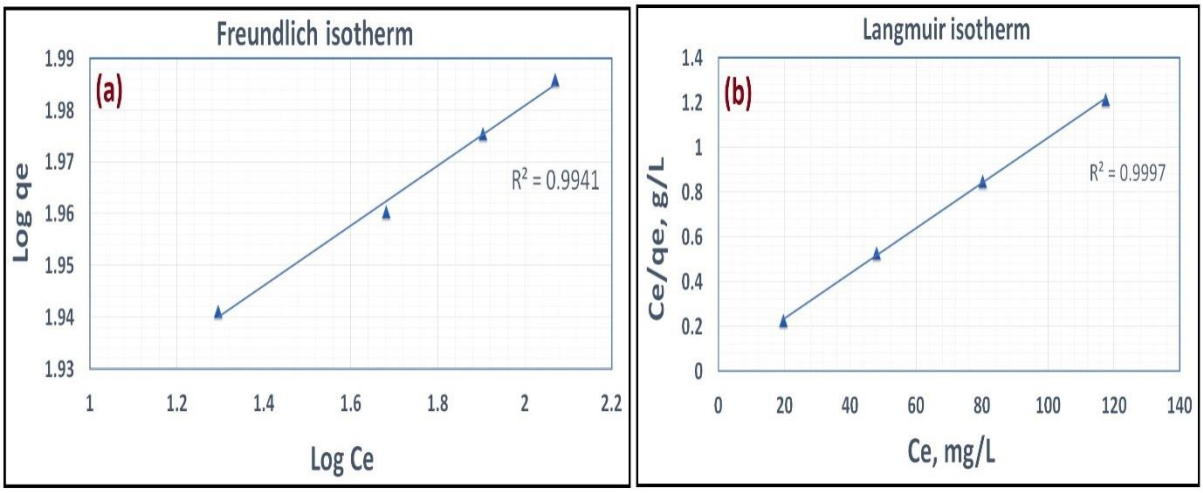

Figure 5. (a) Freundlich isotherm model for the 2-CP adsorption onto CISAC and (b) Langmuir isotherm for 2-CP adsorption onto CISAC.

Table 4. Outcomes of isotherms for adsorption of 2-CP by CISAC at 293 K.

Adsorption isotherm	**Values**
Langmuir isotherm	
b_L(L/mg)	0.2924
q_m (mg/g)	7.4075
R^2	0.9997
Freundlich Isotherm	
1/n	0.0535
K_f	74.469
R^2	0.9941
R_L (mg/L)	0.0057

Figure 5 (b),indicates Langmuir isothermfits adsorption of 2-CP on toCISAC from aqueous solution as reported by high correlation coefficient (R^2) of 0.997. From Table4, the R^2 value lies between 0 and 1 which makes adsorption process to be promising under studied conditions.

5. Adsorption Kinetic Studies

To assess kinetic parameters, pseudo-first and pseudo-second order kinetic were applied to analyze experimental data of CISAC for adsorption of 2-CP. Second-order kinetic for all concentrations was approximately equal to unity representing most suitable. Likewise, calculated q_e(mg/g) obtained from pseudo-second order kinetics were in good settlement with experimental value. Hence, rate limiting step may be chemisorptions concerning valances forces through sharing and exchange of electrons under study is more appropriately designated by pseudo-second kinetics [40].The pseudo-firstorder equation statedusing equation 9.

$$\log(q_e - q_t) = \log q_e \frac{k_1 \times t}{2.303} \quad \ldots (9)$$

Where $q_t$and q_e is amount adsorbed (mg/g) at any time t and at equilibrium and k_1 (min^{-1}) is first-order rate constant. Byplotting graph (Figure 6 (a)) oflog (q_e-q_t) Vs t,value of k_1 calculated from slope and hypothetical $q_e$seemingly gainedby intercepts. Pseudo-secondorder equation apparently specified by equation 10 [41].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \ldots (10)$$

Where k_2 is rate constant of second-order rate constant. The plots of t/q_tVs t determine $1/k_2q_e^2$ as intercept and $1/q_t$ as slope. Figure 6 (b)shows linear plot of pseudo-secondorder and correlation coefficient R^2, of pseudofirstorder kinetics was 6.804 but calculated q_e (mg/g) value obtained from firstorder kinetics does not match with experimental (mg/g) data (Table 5). Consequently, pseudo-first order kinetic does not fit to envisage adsorption kinetic of 2-CP onto CISAC.Whereas, correlation coefficient, R^2, for

Table 5. Adsorption kinetic model rate constants for 2-CP removal.

$Q_{e,\,exp}$	Pseudo-first-order			Pseudo-second-order		
(mg/g)	$Q_{e\,cal}$ (mg/g)	K_1 (min^{-1})	R^2	$Q_{e\,cal}$ (mg/g)	K_2 (min^{-1})	R^2
5.935	4.4221	0.0086	0.9882	6.804	0.00313	0.9972

Figure 6 (a) and (b) show section of experimental facts at diverse initial concentration of pseudo-first order and second-order respectively. Pseudo-first order kinetics did not approve thriving by experimental (mg/g) values (Table 5). Accordingly, we resolved suitable to use pseudo-first order kinetic to predict adsorption kinetics of 2-CP. The study is more properly distinct by pseudo-second order kinetics grounded on supposition that rate preventive step may be chemisorption relating to forces through allotment and conversation of electrons.

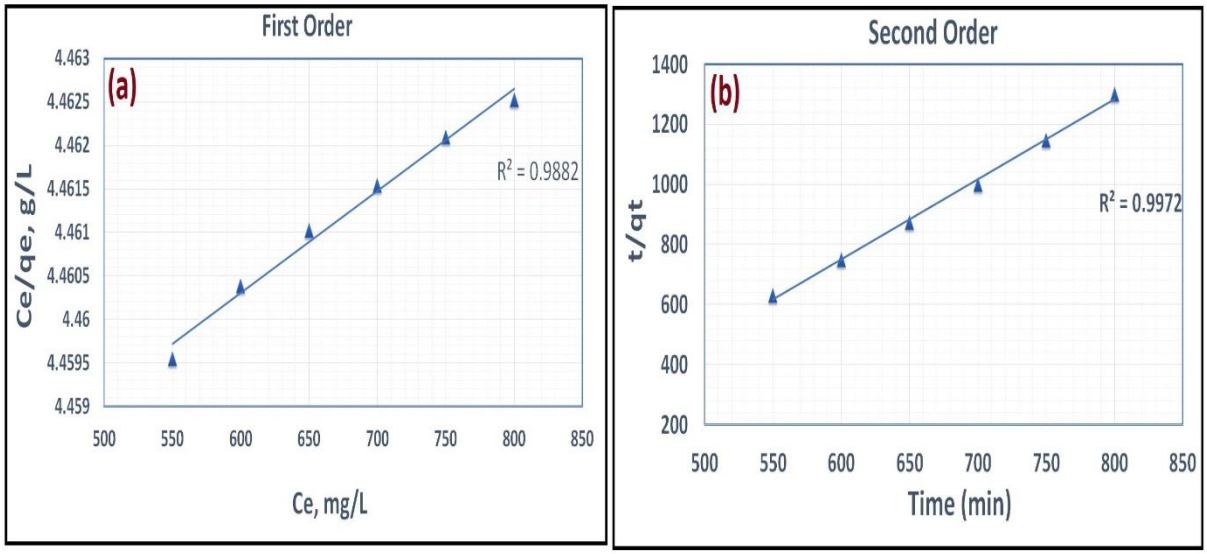

Figure 6.(a) First-order-kinetic for 2-CP adsorption by CISAC and (b) Second-order-kinetic for 2-CP adsorption by CISAC.

Optimization Using Response Surface Methodology (RSM)

To understand the correlation between variables and optimize the process the current work is to deliver statistical evidence correlates to mathematical modelling of the process by the design of experiments (DOE) with usage of statistical analysis and multiple regression is called response surface methodology [42]. The relative impact of factors by comparing coded equations parameter coefficients and fully crossed design experiment which consists of two or more factors each of them with discrete possible levels. The researcher studied the influence of each variables considering all experimental unit parameters of levels across all levels of combinations which influence the response and interactions of each of the variable. The layman's term, the factors of input variables factors with certain combinations to produce the respective results. The simplest factorial study contains 2 levels, also called variables. 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 discarded. In the present work, the input levels are CT, pH and dosage of sample while, the response variable in the percentage of removal of 2-CP from the aqueous solution [43]. The chlorophenol adsorption is achieved by reasonable percentage within the range of the following investigation 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 6.

Table 6. Experimental series and levels of the independent parameters.

Independent parameters	**Range and Level**				
	-1.68	**-1**	**0**	**1**	**+1.68**
pH	5.5	6.25	7	7.75	8.5
Contact time	350	325	400	475	550
Adsorbent dosage	2.5	3.12	3.75	4.37	5

6.1 The 3-level design

Thethree-level design consists of three factors, which can be expressed as equation 11 and will be carrying total of 33 experiments.

$$Yijk=\mu+Ai+Bj+ABij+Ck+ACik+BCjk+ABCijk+\epsilon ijk\ldots (11)$$

Where each cause is comprised as a minor factor than as a continual variable. In such a case, major impacts have 2 degrees of freedom. The interaction of two-factor is (2×2 = 4) with four degrees of freedom and k interaction is 2k. The model contains 26 degrees of freedom. If there is no replication then, 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 the process optimization.By cautious DOE, the aim is to enhance a percentage removal of chlorophenol that is dependent on pH, contact time and adsorbent dosage.

The above experiments are the indication to measure the errors using experimental results. Based on the experimental results the noise can be calculated which is the representation of continuous physical phenomena. 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 [44]. The design consists of following

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

In Figure 7, the design involves 1 central point, 2N axial point and 2N factorial points.

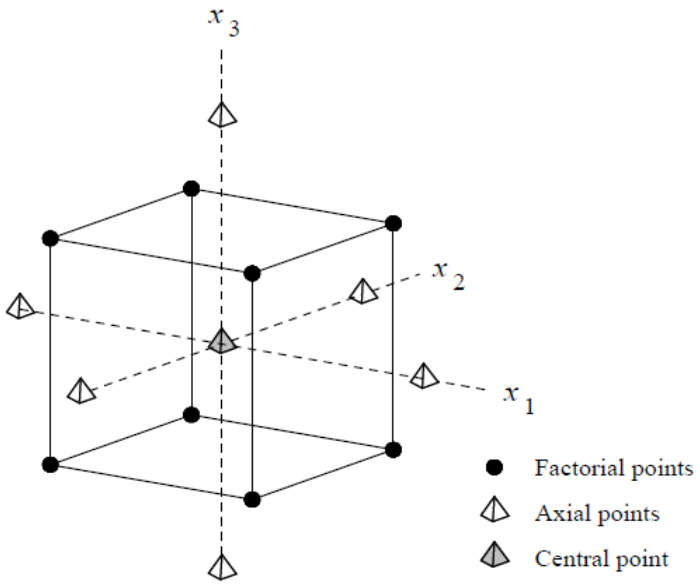

Figure7. Reduced factorial design plot for 3 factors

CCD offers an alternative to 3N designs in construction ofsecond-order model since, number of experiments is reduced as related to afull factorial design R^2 is percentage of response variable variation that is elucidated by its relationship with one or more predictor variables. Typically, higher R^2, better the model fits with data. R^2 is also known as coefficient of determination.

6.3 Optimization of various parameters using Minitab-14 software

To support in optimization of factors such as initial chlorophenol concentration, pH and activated sludge dosage for efficient removal of chlorophenol, batch trials were considered as per CCD through three factors at five levels.The range of levelsin uncoded and coded form for different parameters.The response in this study is percentage adsorption of 2-CP at equilibrium. Twenty sets of batch adsorption experiments were supported as per CCD under conditions shown in Table 7.

Table 7.CCD matrix coded and real values along with experimental values for % adsorption of Chlorophenol.

Expt.	pH	CT	Dosage	% Removal (Actual)	% Removal (Predicted)
1	7.00000	281.82	3.75000	54.26	55.4031
2	7.00000	450.000	3.75000	48.26	47.7955
3	5.50000	550.000	2.50000	57.26	55.9645
4	5.50000	350.000	2.50000	47.26	46.2680
5	8.50000	350.000	5.00000	80.65	80.2263
6	7.00000	450.000	3.75000	50.28	47.7955
7	5.50000	550.000	5.00000	61.28	60.3879
8	7.00000	450.000	1.64776	48.98	50.3869
9	4.47731	450.000	3.75000	46.85	48.5502
10	5.50000	350.000	5.00000	45.69	44.6163
11	7.00000	618.1790	3.75000	67.53	68.8181
12	7.00000	450.000	3.75000	46.84	47.7955

13	7.00000	450.000	3.75000	47.56	47.7955
14	7.00000	450.000	3.75000	86.99	84.7955
15	8.50000	550.000	5.00000	95.21	96.4829
16	7.00000	450.000	5.85224	63.84	64.8643
17	8.50000	350.000	2.50000	68.26	67.4330
18	9.52269	450.000	3.75000	87.56	88.2910
19	7.00000	450.000	3.75000	47.26	47.7955
20	8.50000	550.000	2.50000	68.26	67.6146

6.4 Factorial design

The CCD matrix with twenty sets of trials (Table 8) designed to conduct the study of diverse effects of parameters influencing adsorption process as an individual and on interaction with each other, to optimize method of RSM [45].Multiple regression model relating the factors in uncoded form to the response were developed with the regression coefficients. The matrix of three variables pH (X1), dosage (X2), CT (X3)was varied at five levels (-1.68, -1, 0, +1, +1.68). The lower level was designated as "–" and higher level of variable was designated as "+". 2-CPremoval percentage obtained from the experiments at the end of 550 min (equilibrium time)for each experiment are shown in Table 8.The MRA model developed in terms of uncoded factors is shown in the Equation12.The coefficient of X1 (pH) are positive signifying that increase in this parameter percentage removal of 2-CP increases first and then decreases. The X2 (dosage) is negative term indicating that with increase in parameters, the increased percentage of chlorophenol removal. The positive coefficients of X3 (initial concentration) indicate % removalincreases with increase in dosage.ANOVA exhibited interaction terms are highly significant ($P < 0.05$) and the model is well appropriate. The coefficient of determination (R^2= 0.997) for model was high, displaying good fit of statistical model. Predicted values of percentage removal for all 20 experiments are shown in Table 8and found to settle well with experimental values.Process optimization was carried out based on data using "Response optimizer" tool of MINITAB 14. The optimum values pH= 8.5 contact time = 550 mins, dosage = 5.5 g/l were found.This result is also supportedby ANOVA result showed that interactionof initial 2-CP concentration and CT has significant effect on removal efficiency with pvalue of less than 0.001 (Table 9). Consequently, interactionbetween initial 2-CP concentration and CT have a substantial effect on removal efficiency of CISAC.

$$\% \text{ Adsorption} = 114.409 - 9.33105*x_1 - 18.8354*x_2 + 175.922*x_3 + 0.550656*x_1*x_2 + 4.96767*x_1*x_3 - 3.61552*x_2*x_3 \text{---------- (12)}$$

Table 8. Analysis of variance for percentage adsorption.

Source	DF	Adj. SS	Adj. MS	F-Value	F-Value
Model	9	3666.51	407.39	168.82	0.000
Linear	3	2376.66	792.22	328.29	0.000
pH	1	1906.42	1906.42	790.01	0.000
CT	1	217.23	217.23	90.02	0.000
D	1	253.01	253.01	104.84	0.000
Square	3	1121.80	373.93	154.96	0.000

pH*pH	1	766.31	766.31	317.56	0.000
CT*CT	1	369.15	369.15	152.97	0.000
D*D	1	174.07	174.07	72.13	0.000
2-Way Interaction	3	168.05	56.02	23.21	0.000
pH*CT	1	45.27	45.27	18.76	0.001
pH*D	1	104.33	104.33	43.23	0.000
CT*D	1	18.45	18.45	7.65	0.020
Error	10	24.13	2.41		
Lack-of-Fit	5	15.87	3.17	1.92	0.246
Pure Error	5	8.26	1.65		
Total	19	3690.64			

Figure 8 (a) shows 3D response surface to explain combined effect of pH and CT on adsorption of chlorophenol at constant dosage (5.5 g/l). The percentage of adsorption is more at lower pH and lower concentration values. But percentage adsorption decreases with higher concentration and through higher pH.The 3D response surface for combined effect of CT of chlorophenol and dosage on adsorption of Chlorophenol at constant pH of 8.5.

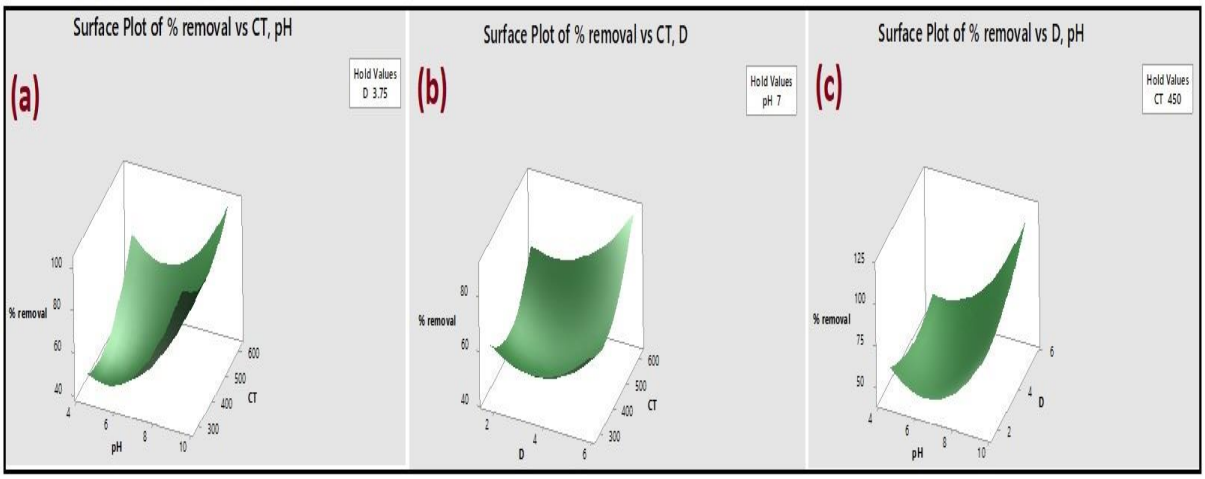

Figure 8. (a) Surface plot of % Removal Vs CT,pH, (b) Surface Plot of %removal Vs CT, Dosage and (c) Surface plot of %Removal Vs pH,dosage.

Table 9. Optimization results (Global Solution)

Entry	Parameter	Optimized values
1	pH	8.5393
2	Contact Time	551.0914
3	Dosage, g/l	5.50

The effect of pH and dosage on adsorption of chlorophenol at CT (550 mins) is shown in Figure 8 (b). Percentage adsorption increases first with pH and then drops with an increase in pH. The rate of

adsorption is increasing with an adsorbent dosage. The optimized adsorbent dosage was found to be with the pH of 8.5. Hence, dosage and pH interaction are negligible (Figure 8 (c)). The optimizer diagram of pH, CT and dosage is shown in Figure 9.

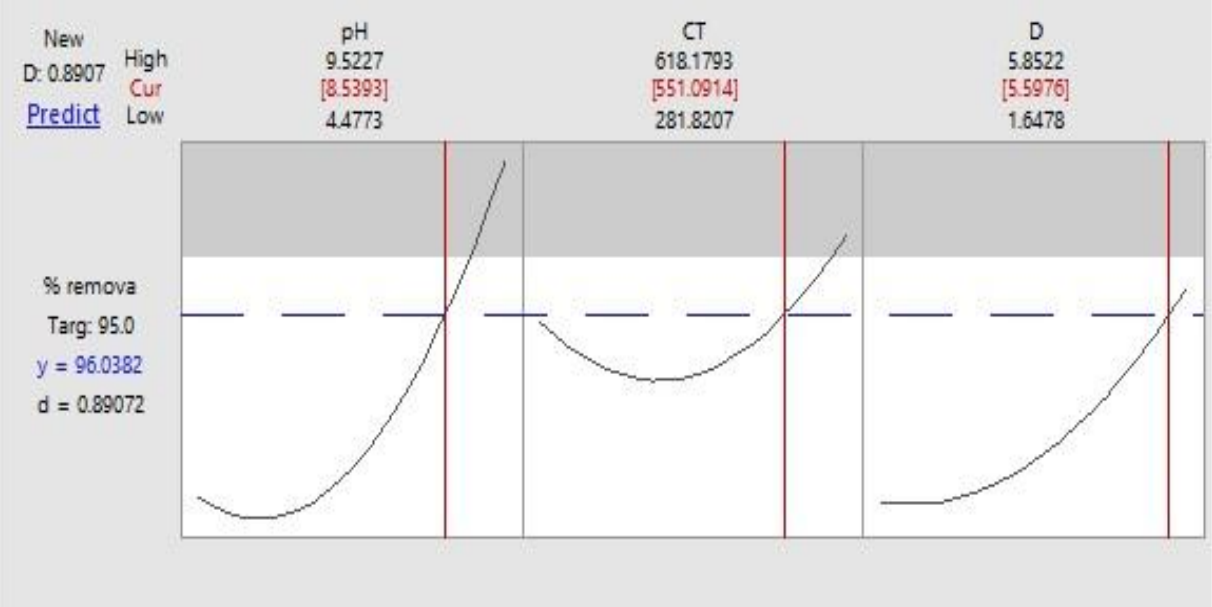

Figure 9. Optimizer diagram

7. Conclusion

Corn industry sludge derived activated carbon was prepared, characterized and the experimental results indicate excessive porosity in activated carbon with presence of functional groups convenient in adsorption. The adsorption of 2-CP ions using CISAC was well described by the Langmuir isotherm and 2nd order kinetics. Experimental work suggested that 2-CP adsorption of CISAC is physical adsorption achieving equilibrium at 20 ^{0}C for Langmuir isotherm. Batch adsorption experiments were carried out by various parameters such as contact time, solution pH, adsorbent dosage, and initial metal ion concentration. The outcome of fitting processes for 2nd order kinetics were verified by assessing the correlation coefficients (R^2) with solution pH 8.5, equilibrium time of 550 min, adsorbent dosage of 5.5 g/l was found to be optimum conditions for adsorption of maximum 2-CP uptake capacity of 6.80 mg g^{-1} due to its mesoporous structure, high surface area and presence of functional groups acting as chelating agent to adsorb heavy metal ions through different approaches. Consequently, CISAC adsorbent can be used as an efficient low cost for the removal of 2-CP ions along with support in optimization of factors such as initial chlorophenol concentration, pH and activated sludge dosage for efficient removal of 2-CP batch study were considered as per CCD through three factors at five levels. The obtained result isfavouredby ANOVA which showed that interactionof initial chlorophenol concentration and contact time has a substantialoutcome on removal competence.

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Declarations

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Conflict of interests

All the authors declare that they do not have any competing interest.

Availability of data

All data generated or analysed during this study are included in this published article.

Further data can be obtained by corresponding author on request.

Authors Contributions

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

Nomenclature

CISAC : Corn Industry Sludge Activated Carbon
2-CP : 2-Chlorophenol
AC : Activated Carbon
CCD : Central Composite Design
CT : Contact time
q_e : Equilibrium concentration
C_e : Equilibrium concentration in the liquid phase
b_L : Adsorption energy
q_m : Adsorption capacity
D : Dosage
RSM : Response Surface Methodology

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