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Adsorption Dynamics and Mechanistic Insights into Chloride Removal from Distillery Effluent Using Sawdust Adsorbent

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ABSTRACT

The present study investigates the potential of sawdust as an inexpensive and eco-friendly adsorbent for the reduction of chloride from distillery effluent. Batch adsorption experiments were conducted to estimate the effects of contact time, adsorbent dosage, initial chloride concentration, and temperature on chloride removal efficiency. The surface characteristics and functional groups of sawdust were examined using Fourier transform infrared spectroscopy (FTIR), Scanning Electron Micrograph (SEM) and X-ray diffraction (XRD) analysis, confirming the involvement of surface functional groups and the amorphous nature of the adsorbent in the adsorption process. Equilibrium data were analyzed using Langmuir and Freundlich isotherm models, where the Langmuir model showed an excellent fit with a correlation coefficient (R^2) of 0.996 and a maximum monolayer adsorption capacity (qmax) of 49.72 mg/g, indicating monolayer adsorption on a homogeneous surface. The Freundlich model also showed reasonable agreement (R^2 =0.9138), suggesting surface heterogeneity. Kinetic studies revealed that the adsorption process followed pseudo-first-order kinetics with a higher correlation coefficient (R^2 = 0.988) compared to the pseudo-second-order model. Thermodynamic parameters showed negative values of Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°), indicating that the adsorption process is spontaneous, exothermic, and accompanied by decreased randomness at the solid–solution interface. Overall, the results reveal that sawdust is an efficient and sustainable adsorbent for chloride removal from distillery wastewater.

Keywords Distillery waste water, Sawdust, Batch adsorption, Adsorption isotherm, Adsorption kinetics, Thermodynamics.

INTRODUCTION

Rapid industrialization in India has increased the industrial wastewater which is discharged into nearby natural water bodies without proper treatment and disturbs the ecological balance of the aquatic environment causing aquatic environmental pollution. The

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per capita renewable water resources are dwindling due to the synergistic pressures of population growth, industrial development, and the pursuit of improved health and social welfare (Nizam *et al*. 2025). The surging global demand for ethanol as a biofuel, chemical feedstock, and potable alcohol has driven rapid growth in the distillery industry, leading to the large-scale generation of distillery industry effluent. It is a highly complex, dark-colored, and organically rich effluent with extreme biochemical oxygen demand (BOD) and chemical oxygen demand (COD), Chloride, Sulfate along with endocrine disruptors, recalcitrant organics, melanoidins, phenolics, and heavy metals. The untreated discharge of such effluents causes severe aquatic toxicity, soil degradation, and significant health risks to humans and other organisms (Chandel *et al.* 2026). The major color contributing pollutants present in Distillery wastewater are melanoidins, an amino-carbonyl polymer, produced during the processing of sugarcane juice in sugar industries and molasses in distillery waste water. Chloride contamination is a formidable challenge to environmental sustainability and public welfare worldwide. With origins spanning industrial discharge, agricultural runoff practices, elevated chloride levels present a pervasive threat (Dhumal and Sadgir 2024).The discharge and improper treatment of wastewater containing high chloride concentrations can result in various issues affecting human production and the environment. Among biological, physicochemical, and thermal treatment options, adsorption is a highly effective treatment technique for distillery wastewater because it can efficiently eliminate numerous contaminants, including high amounts of organic pollutants. To mitigate these impacts, various treatment techniques have been employed, including oxidation, membrane processes, electrocoagulation, aerobic and anaerobic treatments, fungal remediation, and adsorption.

Distillery wastewater also causes soil pollution and acidification in the cases of inappropriate land discharge. It is reported to inhibit seed germination, reduce soil alkalinity, cause soil manganese deficiency and damage agricultural crops (Ammari *et al* 2025). Current research on lignin-based adsorbents for organic pollutant removal remains relatively limited. Lignin modification typically encompasses chemical and physical approaches, with chemical modification being the most widely used method to enhance lignin's adsorption capacity. Sawdust mainly contains cellulose (45–50%), lignin (23–30%), hemicellulose (20–30%), and various extractive substances such as acids, soluble sugars, resins, waxes, and oil (5–15%). Thus, sawdust is a lignocellulosic material, freely accessible and abundant (up to 24.15 million m3 per year worldwide), can be utilized as a good precursor for alternative activated carbon (Chikri *et al.*2020).

MATERIALS AND METHODS

Preparation of adsorbent

The sawdust used as the adsorbent was collected from a local source and initially sieved to obtain a uniform particle size. To eliminate surface dust, soluble matter, and other adhering impurities, the material was washed repeatedly with double-distilled water and subsequently oven-dried at 105 °C for 6 h. Chemical activation of the dried sawdust was carried out by soaking it in a 0.1 N NaOH solution for 24 h. Following activation, the material was thoroughly rinsed with double-distilled water until the washings attained neutral pH, ensuring the complete removal of excess alkali. The activated sawdust was then dried overnight at 105 °C and stored in an sealed container to avoid moisture absorption and maintain its stability before use in adsorption experiments.

Investigation of batch parameters

Batch adsorption studies were carried out to estimate and optimize the major operational factors influencing adsorption efficiency, namely initial contaminant concentration, adsorbent dose, contact time, and temperature. All experiments were conducted using 100 mL of wastewater. The effect of initial contaminant concentration was examined by changing it from 250 to 1000 mg/L. To determine the optimal adsorbent dose, different amounts of sawdust ranging from 5 to 25 g were employed. Contact time experiments were performed at the optimized adsorbent dosage over time intervals of 30-180 min to establish the equilibrium time. The influence of temperature on the adsorption process was assessed by conducting experiments at 298, 303, and 308 K. These systematic investigations facilitated the determination of opti-

mal operating conditions for maximum adsorption performance.

Adsorption experiments

Batch equilibrium experiments were carried out in 250 mL flasks containing 100 mL of effluent with initial contaminant concentrations in the range of 250-1000 mg/L. Based on the optimized conditions, a constant adsorbent dose of 10 g of activated sawdust was added to each flask. The flasks were agitated on a rotary shaker at 180 rpm and maintained at 30 °C for 3 h to ensure the attainment of adsorption equilibrium. Upon completion of the adsorption process, the samples were filtered to separate the spent adsorbent and avoid interference during analysis. The contaminant concentrations in the filtrates were measured before and after equilibrium to evaluate the adsorption capacity and removal efficiency.

The removal rate (% Removal) and adsorption capacity at equilibrium (qe mg/g) were calculated using the following formula:

$$\text{Removal}\,(\%) = \text{Co-Ce/Co*100} \quad (1)$$

$$\text{Adsorption capacity} = \text{Co} - \text{Ce} * \frac{V}{M} \quad (2)$$

where Co and Ce (mg/l) are the concentrations at initial and equilibrium, respectively. V is the volume of the solution and M is the mass of dry adsorbent used (g) (Misran *et al.* 2025).

Adsorption isotherm models

Langmuir isotherm

$$\frac{ce}{qe} = \frac{1}{KLqm} + \frac{ce}{qm} \quad (3)$$

In the equation, q_e = the amount of substance adsorbed per unit mass of adsorbent, maximum capacity (mg/g), KL = Langmuir constant depending on the adsorption energy (L/mg), and Ce= the concentration of the substance remaining in the solution after adsorption (mg/L) (Edet and Ifelebuegu 2020).

Freundlich isotherm

$$\text{In}\,(Qe) = \text{lnKf} + \frac{1}{nf} * \text{lnCe} \quad (4)$$

where 'qe' indicates the capacity of equilibrium adsorption (mg/g), Kf denotes the constant for the Freundlich model (L/g), 'Ce' represents the final concentration at the equilibrium level (mg/L), and 'n' denotes exponent of the Freundlich adsorption model.

Kinetic models

Pseudo-first-order and pseudo-second-order models.

$$\ln\,(q_e - q_t) = \text{lnqe} - K_1 t \quad (5)$$

$$\frac{1}{qt} = \frac{1}{K_2\, q_2^2} + \frac{1}{qe} \quad (6)$$

Where q_e (mg/g) and q_t(mg/g) correspond to the adsorbed amounts at equilibrium and time t (min), respectively. K_1 denotes the rate first-order rate constant (min^{-1}) and K_2 represents the second-order rate first-order rate constant (g/mg (min^{-1}). (Ammari *et al.* 2025).

Thermodynamic studies

The values of the standard thermodynamic parameters such as: free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°)were determined from the effect of temperature on the adsorption, using the Van't Hoff equation.

$$\Delta G° = RT \ln KD \quad (7)$$
$$\Delta G° = T(\Delta S°) + \Delta H° \quad (8)$$

The value uses of enthalpy and entropy was calculated from the intercept and slope of the plotted curve of temperature vs. change in the standard free energy of Eq. (7) , as well as ΔG°, which can be calculated from Eq. 8. (Dar and kurella 2025).

RESULTS AND DISCUSSION

Factors influencing batch parameters

The effect of operational parameters on chloride

removal using sawdust was systematically evaluated by varying adsorbent dosage, contact time, initial concentration, and temperature. The removal efficiency increased with adsorbent dosage from 5 to 10 g, reaching a maximum of about 90.51%, due to the increased accessibility of active adsorption sites; however, further increases in dosage up to 25 g did not significantly enhance removal, indicating site overlap and aggregation effects. Adsorption efficiency improved with contact time from 30 to 180 min, achieving a maximum removal of approximately 91.04% at 180 min, after which equilibrium was attained. The highest chloride removal efficiency (90.18%) was observed at the lowest initial concentration of 250 mg/L, while a decline in percentage removal occurred at higher concentrations (500-1000 mg/L) owing to saturation of available adsorption sites. Temperature studies showed that maximum removal (90.48%) occurred at 298 K, with a slight decrease at higher temperatures (303-308 K), confirming the exothermic nature of the adsorption process. Overall, the optimal conditions for chloride removal were identified as 10 g adsorbent dosage, 180 min contact time, 250 mg/L initial concentration, and 298 K temperature.

Adsorption isotherms studies

The equilibrium adsorption data for chloride removal from distillery effluent were assessed using the Langmuir and Freundlich isotherm models to explain the adsorption mechanism and surface features of the adsorbent. The Langmuir isotherm (Fig. 1) exhibited an excellent fit to the experimental data, with a high

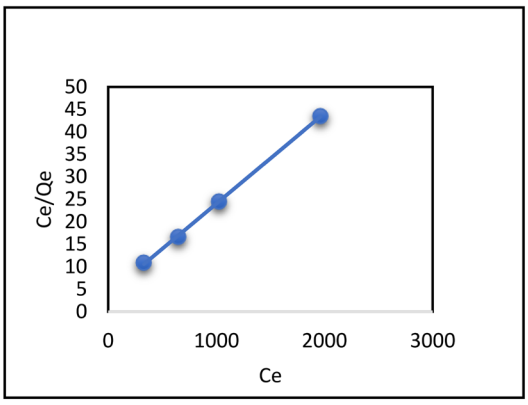


Fig. 1. Langmuir isotherm.

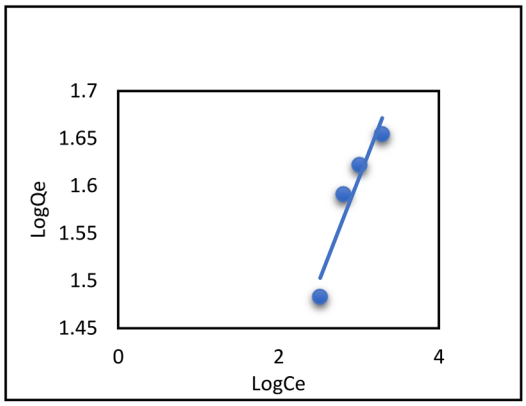


Fig. 2. Freundlich isotherm.

coefficient of determination ($R^2 = 0.996$), indicating that chloride adsorption occurred predominantly as monolayer coverage on a homogeneous adsorbent surface with finite and identical active sites (Imam and Hamza 2025).

The maximum monolayer adsorption capacity (q) obtained from the Langmuir model was 49.72 mg g^{-1}, demonstrating the strong affinity and high uptake potential of the adsorbent for chloride ions (Asadi *et al.* 2023). The Langmuir constant (K) was found to be 0.00513 L mg^{-1}, reflecting favorable adsorption interactions between chloride ions and the adsorbent surface.

The Freundlich isotherm model (Fig. 2) was applied to evaluate the adsorption behavior of chloride ions from distillery effluent on the adsorbent surface, particularly to assess surface heterogeneity and multilayer adsorption characteristics (Oukhemamou *et al.* 2026). The Freundlich model showed a reasonably good correlation with the experimental data, with a coefficient of determination ($R^2 = 0.9138$), indicating

Table 1. Langmuir and Freundlich isotherm parameters.

Isotherm	Parameter	Value	Unit
Langmuir	Q_m	49.72	mg/g
	K_L	0.0051	L/mg
	R_2	0.999	-
Freundlich	1/n	0.2180	-
	K_F	0.9534	L/mg
	R^2	0.9138	-

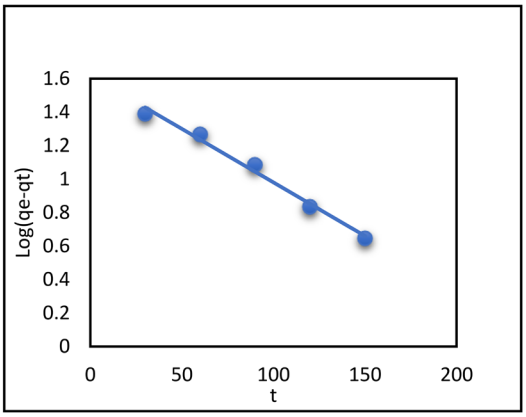


Fig. 3. Pseudo first order.

that adsorption occurred on a heterogeneous surface with varying energy sites. The Freundlich adsorption constant (K) (Table 1) was determined to be 0.953 mg g^{-1} (L mg^{-1}), representing the relative adsorption capacity of the adsorbent for chloride ions (Petrovič *et al.* 2026).

The intensity of adsorption, expressed by the Freundlich constant n, was found to be 0.2180, suggesting a strong interaction between chloride ions and the adsorbent surface and indicating a highly favorable adsorption process at lower concentrations (Donat and Esen 2026).

However, when compared with the Langmuir model, the Freundlich model exhibited a lower goodness of fit, confirming that monolayer adsorption on homogeneous sites is the predominant mechanism for chloride removal in the present study.

Adsorption kinetics insights

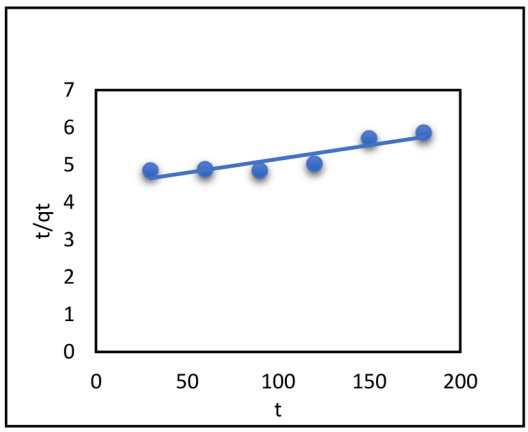
For the kinetic study, the experimental data were analyzed using the pseudo-first-order kinetic model (Fig. 3) to describe the adsorption behavior of the adsorbent. The linear plot of log (qe-qt) versus time showed an excellent fit with a high correlation coefficient (R^2 = 0.988), indicating that the adsorption process closely follows pseudo-first-order kinetics (Bayuo *et al.* 2020).

The calculated rate constant (k_1) (Table 2) was found to be 0.0063 min^{-1}, suggesting a moderate rate of adsorption under the studied conditions (Shefa *et al.* 2025). The theoretical equilibrium adsorption capacity (qe,cal) obtained from the model was 5.04 mg g^{-1}, which is in reasonable agreement with the experimental qe value, further confirming the applicability of the model (Abin *et al*. 2022).

Table 2. Pseudo first order and second order kinetics parameters.

Models	Parameters	Value	Unit
PFO	Q_e	5.0469	mg/g
	K_1	0.0063	min^{-1}
	R^2	0.988	-
PSO	Q_e	136.054	mg/g
	K_2	4184	mg/g.min^{-1}
	R^2	0.792	

The good agreement between experimental and calculated values, along with the high R^2, implies that the adsorption process is predominantly governed by physical adsorption and that the rate of occupation of adsorption sites is proportional to the number of unoccupied sites (Aningo *et al.* 2025). These results demonstrate that the pseudo-first-order model is fit for describing the adsorption kinetics. The pseudo-second-order kinetic model (Fig. 4) was also applied to estimate the adsorption kinetics of chloride removal by the adsorbent. The linear plot of (t/qt) versus time exhibited a comparatively lower correlation coefficient (R^2 = 0.79), indicating a weaker fit of the experimental data to the pseudo-second-order model. (Sevim *et al.* 2025). This suggests that the chloride



Fig, 4. Pseudo second order.

Table 3. Thermodynamic parameters.

Temp K	ΔG° KJ/mol	ΔS° J/mol.K	ΔH° KJ/mol
298	-5.5		
		-286.63	-90.0
303	-3.4		
308	-2.7		

adsorption process is not predominantly controlled by chemisorption involving valence forces or electron sharing between the adsorbent and adsorbate (Khandamov *et al.* 2025).

Thermodynamic studies

Thermodynamic parameters (Table 3) were evaluated to understand the feasibility and nature of the chloride adsorption process. The values of enthalpy change (ΔH°) and entropy change (ΔS°) were determined from the slope and intercept of the Van't Hoff plot (Alotaibi *et al.* 2025). The calculated ΔH° value was -90.78 kJ mol^{-1}, indicating that the adsorption process is exothermic in nature (Meena *et al.* 2025).

This negative enthalpy change suggests that lower temperatures favor chloride removal, which is consistent with the observed decrease in adsorption efficiency at higher temperatures (Susilawati *et al.* 2025). The negative entropy change (ΔS° = -286.64 J mol^{-1} K^{-1}) reflects a decrease in randomness at the solid-solution interface during adsorption, implying an increased orderliness as chloride ions are adsorbed onto the adsorbent surface (Girish 2025).

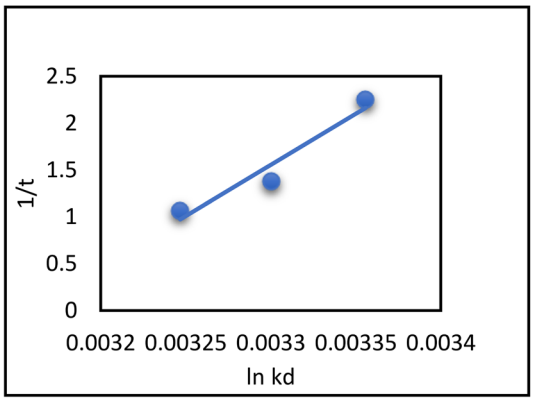


Fig 5. Thermodynamic plot.

The Gibbs free energy change (ΔG°) values were calculated at different temperatures (298, 303, and 308 K). The negative ΔG° values of -5.58, -3.47, and -2.73 kJ mol^{-1} at 298, 303, and 308 K, respectively, confirm that the adsorption of chloride onto the adsorbent is spontaneous under the studied conditions (Pasa *et al.* 2025). The magnitude of ΔG° became less negative with increasing temperature, indicating that the spontaneity of the process decreases at higher temperatures, further supporting the exothermic nature of adsorption (Khan *et al* 2025). Thermodynamic plot is shown in Fig.5.

CONCLUSION

The present investigation clearly establishes the potential of sawdust as an efficient, low-cost, and environmentally sustainable adsorbent for the removal of chloride ions from distillery wastewater. Equilibrium studies revealed that the adsorption data fitted the Langmuir isotherm model exceptionally well, with a high correlation coefficient ($R^2 = 0.998$), indicating monolayer adsorption on a homogeneous surface with finite identical sites. The maximum adsorption capacity (qmax) of 49.72 mg/g further confirms the strong adsorption potential of sawdust. Kinetic modelling showed that the adsorption process followed pseudo-first-order kinetics, suggesting that physical adsorption mechanisms, such as van der Waals forces and electrostatic attraction, dominate the rate-controlling steps. Thermodynamic parameters provided additional confirmation of the feasibility of the adsorption process. The negative values of Gibbs free energy change (ΔG°) at all studied temperatures indicated the spontaneous nature of chloride adsorption. The negative enthalpy change (ΔH°) confirmed that the process is exothermic, while the negative entropy change (ΔS°) suggested decreased randomness at the solid–solution interface during adsorption.

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