Study on isotherm, kinetics, and thermodynamics of adsorption of crystal violet dye by calcium oxide modified fly ash

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ABSTRACT

The natural Fly ash modified with calcium oxide has been employed to eliminate the crystal violet dyestuff from the simulated solution. Herein, the effect of different physicochemical factors like primary dye concentration, sorption contact time, the quantity of the adsorbent, temperature, along with initial simulated solution pH, evaluated for illustrating the mechanism of adsorption. Furthermore, the equilibrium study was conducted, and equilibrium models like Langmuir, Freundlich, and Dubinin- Raduskevich (D-R) were fitted to obtain analytical results to endow with more insight into the process. The results acknowledged that the Langmuir model is well apt and suggests that the adsorption mechanism happens in a monolayer on the fly ash surface. Pseudo-first order, Pseudo-second order, and the intraparticle diffusion model evaluated, and the interpretation suggests the sorption method is obeying the Pseudo-second order and intraparticle diffusion model. The ascertained negative values of Gibbs free energy affirmed the unconstrained process for all symbiotic associations, and the obtained data 78.70 kJ mol⁻¹ enthalpy values manifested that exothermic mechanism was governing the reaction. The above assessment confirms the application of Calcium oxide pre-treated fly ash as a cheap adsorbent to eliminate the crystal violet dyestuff from the simulated solution.

Keywords: Adsorption, Calcium oxide, Crystal violet, Fly ash, Gibbs free energy, Isotherm, Kinetics

1. Introduction

The rapid progressive urban and industrial expansion in modern society developed a severe threat to human health, degrading the quality of water in numerous ways. The continuous increment of the pollution gave rise to an alarming stage in the present society. Although various pollutants are present, amongst them, dyes are significant key players that create unsafe situations of water pollution in the environment [1]. Dye possesses several applications in a wide span of industrial applications. Since its inception of use ubiquitously in different industries such as textile, coloring material agents, and pharmaceuticals, it's omnipresent nature. Dyes consider as the most adverse ecotoxicological material [2]. The

minute presence of the dye molecules is highly detrimental [3]. It is evident from the literature that around 10,000 different types of dyes exist commercially. The primary usage of dyes is ubiquitously present in textile, paper, plastics, leather, pharmaceutical, food industry, etc. [4-6]. The rate of production of the dyes 7×10^5 to 1×10^6 tons per year [7, 8]. It is manifest that from the literature, around 10-15% of dyes entered the natural ambience without prior treatment and posed some grave consequences to the ambience [8]. The textile industry plays a primary role in environmental pollution due to the massive discharge of wastewater containing a high concentration of dye as effluent. The presences of these chemicals are solely responsible for the destruction of the aquatic ecosystem. Not all the dye molecules incorporated for the dying process is utilized. The available dye molecules are often

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exposed to the environment causing hazardous impact. The fabric industries consume about 90% of the total dyes manufactured. For wet processing in the fabric industry, a considerable amount of water is required, and a significant amount of un-utilized dyes, acids, alkalis etc. are produced. The cost of restoration is much higher and demands suitable, sustainable technology for remediation. Total dissolved solids in the effluent wastewater should not exceed 110% i.e., above 13-14 mg L⁻¹. In Bangladesh, the total solids concentration in discharge is limited to 2100 mg L⁻¹ [9] above this permissible limit, the presence of dyes can eventually harm the aquatic life [10]. Due to the unwanted entry into a natural ambiance, the balance of the ecosystem gets disturbed and generates a high risk of causing several dreadful diseases and initiation of health hazard [11, 12]. The disorders which have been diagnosing due to this effect of these dyes are such as skin allergy, dermatitis, and cancer [13, 14]. Sometimes, due to the higher concentration of dye sunlight cannot penetrate the subsurface of the water in the natural streams, lakes, and rivers create a negative impact on the aquatic life/ phytoplankton and zooplanktons [15].

Crystal Violet (CV) a triphenylmethane dyestuff, employed in apparel and fabrics for coloring the material. In printing and paint industry used this dye [16]. CV ubiquitously used in the medical community. The CV has numerous effects that create several health disorders. [16]. The eradication or elimination of CV dyestuff from the water bodies is exceptionally vital for the betterment of society. Herein, we have attempted to eradicate CV dye from the simulated solution with the aid of modified fly ash.

It is challenging to dispose of the dye-containing effluent without proper treatment, mainly due to the inherent property of the synthetic dyes. Owing to the multifaceted molecular arrangement of the dyestuff, they are unable to degrade naturally [11, 16, 17]. There are some of the efficient and accessible technologies used presently for the removal of dyes, which include filtration technologies like ultrafiltration [18], nanofiltration [19], reverse osmosis [20]. But filtration technology exhibits certain major drawbacks like clogging of pores, membrane denaturation etc. Other than these several traditional technologies have been adopted for the eradication of the dyestuff such as photo-catalysis, Solar Photo-Fenton, biochemical degradation, etc. [6]. Lately, a technique of molecular imprinting is developed where template molecules are removed at different polymerization stages [21] the process is precise. Although, all the methods mentioned above are not fully effective and possess cons such as partial elimination, engrossment of expensive chemicals, production of hazardous substrate creates secondary issues like careful removal, massive investment, the involvement of substantial human resources, etc. Compare to traditional treatment methods of dyestuff contaminated effluents, sorption has to appear as a simple and effective process [22]. Adsorption is a technique in which a substrate coheres upon the adsorbent from its ambiance [23, 17]. This alternative method of separation in environmental engineering has gained immense importance and is now taken into consideration worldwide for its versatility [24]. Many natural materials or by-products of industries can be either used directly or after minor pre-treatment to eliminate the CV dye from the simulated solution [25, 7, 17]. Herein, this piece of the work deals with the utilization of natural fly ash and

calcium oxide modified fly ash for the elimination of cationic dye like Crystal violet used in this study. The utilization of the fly ash caters to two aspects, like removal of the dye-containing water along with the possible usage of solid waste generated in the power industry where coal used as raw material.

Fly ash is a secondary product of coal utilizing energy plants. But effective disposal of fly ash is still a significant challenge, and it is an absolute menace to the environment as a pollutant [26]. Fly ash is a pozzolanic substrate consists of SiO₂, CaO, and Al₂O₃. Fly ash has a universal application as a core substrate for sorption studies. The fly ash showed striking competencies for sorption studies regarding economic feasibility and environmental perspectives [25, 27]. Highly porous adsorbents with a significant surface area showed enhanced adsorbing capacity. Hence, fly ash has modified with calcium oxide (CaO) for the increment of its sorption capacity [28]. It is evident from the literature that hazardous gases such as SO₂, CO₂ could be entrapped with the aid of alkalinity increment of the fly ash [29]. Batch studies have performed, and the effect of the factors has evaluated. The role of primary dye concentration, sorption contact time, the quantity of the adsorbent, temperature, initial simulated solution pH, and agitation speed on CV sorption analyzed in this investigation. Further, an equilibrium study has been carried out employing Langmuir, Freundlich, and Dubinin- Raduskevich (D-R) equilibrium models [30] Furthermore, the kinetic parameters have been assessed by Pseudo-first order, Pseudo-second order and intraparticle diffusion model [31]. The activation energy (E_a) for the sorption mechanism determined by the Arrhenius equation. Additionally, thermodynamic factors such as Gibbs free energy (ΔG°), enthalpy (ΔH°), entropy (ΔS°), and Isotheric heat was determined to apply the Clausius-Clapeyron equation [32]. The entire above factors are essential for comprehending the nature of adsorption.

2. Material and Methods

2.1. Collection and Modification of Pristine Adsorbent

The natural fly ash collected from the local coal-based energy plants. Initially, after the collection of the fly ash rinsed extensively with the deionized water to eradicate the unwanted coarse particles. After rinsing, the wet fly ash sample has been dried for 24 h in a Hot Air oven at a temperature of 343 K. Further, the dried fly ash sample was subjected to exposure at 5% CaO. The sample solution was kept in an autoclave for 15 min at 10 psi. Furthermore, the suspension was purified by filtration rinsing with deionized water until the pH of the treated fly ash sample reached neutral. Additionally, after neutralization by rinsing, the modified fly ash sample was again kept for drying at 343 K for 24 h. Finally, after drying the treated fly ash was ready to use for the sorption experiments.

2.2. Simulated Dye Solutions

The procured CV employed in the experiments was ultra-pure and used with no further purification. The configuration of the CV exhibited in Fig. S1. The properties of CV employed in the study provided in Table S1. The stock solution of crystal violet

(500 mg L⁻¹) made by weighing the exact measure of the dye in the deionized water. The working solution of different concentrations was made from stock with further dilution from stock solution applying the precise volume of deionized water.

2.3. Batch Experiments

The batch study has performed in Erlenmeyer flasks (250 mL) with the cap. A primary concentration of 50 mg L⁻¹ with an adequate volume of 100 mL was used. Further, a predetermined quantity of the sorbent mixed into the dye simulated solution. The flask was stirred at a specific speed of 140 r/min for 3 h in a shaker incubator at a constant temperature 303 ± 1 K, the role of the different experimental factors, was determined such as primary pH in the range of (2-10), primary dye concentration (10-100 mg L⁻¹), sorption contact time (10-180 min), the quantity of the adsorbent (0.5-5 g L⁻¹), and temperature (303-333 K). The dye solution was collected from the Erlenmeyer flask at a particular period for further analysis of the remaining dye concentration in the solution. Furthermore, the collected sample has been subjected to centrifugation at a specific speed of 4000 r/min intended for a set time of 10 min. The residual dye concentration analysed by using the UV-VIS Spectrophotometer at 580 nm (Model SP7576–Spectrum, Shanghai, PR China) after a specific time interval. The amount of the dye adsorbed for every unit of the adsorbent (“mg” dye / “g” sorbent) was determined based on the mass balance of the dye retained within the primary solution applying Eq. (1):

$$q_e = \frac{(C_i - C_e)V}{m} \quad (1)$$

To determine the removal percentage (%) of the dye from the simulated solution was evaluated by applying the Eq. (2):

$$\text{Removal (\%)} = \frac{(C_i - C_e)}{C_i} \times 100 \quad (2)$$

Experiments have been performed in triplicate to eradicate any errors, and further, the average values have applied for the calculation of experimental data. In our study, we have performed control experiments by incorporating the adsorbent, affirmed the adsorption of the dyestuff on the internal wall of the flasks above was minuscule.

3. Theory

3.1. Equilibrium Analysis

Here in this study, equilibrium association among the sorbate concentration in liquid ambience and sorbent surface in a simulated ambience has been deciphered with Langmuir, Freundlich, and Dubinin-Raduskevich (D-R) equilibrium models. [30, 32]. The mathematical expressions of the Langmuir, Freundlich, and Dubinin-Raduskevich (D-R) equilibrium models are tabulated in Table S2. The Freundlich equilibrium model is more suitable for non-absolute sorption on the composite surface.

3.2. Adsorption Kinetics

Herein, these kinetic study models have been employed in the study, for instance, Pseudo-first order, followed by Pseudo-Second order and Intra-particle diffusion model. The model, as mentioned above, has been determined by the mathematical expression represented in Table S2.

3.3. Activation Energy and Thermodynamic Parameter

The activation energy (E_a) of the present study was determined by using the Arrhenius equation tabulated in Table S2.

The following mathematical expression can determine thermodynamic factors like Gibbs free energy change (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) of the present study as Table S2 [23].

4. Results and Discussion

4.1. Adsorbent Characterization: Scanning Electron Microscopy Analysis

The natural and modified fly ash adsorbent was characterized by Scanning Electron Microscopy (SEM) analysis for understanding the surface quality of the sorbent. The images of the SEM have captured with the help of SEM (Model S-3000N, Hitachi, Japan). Preceding to the scanning of the sorbent was layered with a fine layer of gold to provide the sample enriched with electrons or enhance the conductivity of the sample. The surface quality of the fly ash has investigated by SEM. The surface quality of the raw fly ash consists of several pores. After treatment with CaO, the pore has been broadened, and after adsorption of the dye molecules, the vacant pore has been filled with adsorbed dye molecules, which illustrated in Fig. S2.

4.2. Adsorbent Characterization: XRD Characterization

The crystalline structure of the fly ash samples was evaluated using the Rigaku X-ray diffractometer (XRD) with Cu-K α radiation, over 2 θ range 20-80°. The primary constituent in the fly ash samples is silicon-aluminous material, as confirmed by XRD spectra, Fig. 1. The major crystalline mineralogical constituents of the fly ash sample used in this study are: quartz (SiO₂), sodium aluminium silicate (Na(AlSi₂O₆)), tricalcium magnesium orthosilicate (Ca₃Al₂(SiO₄)₂),

Fig. 1. XRD Data of the fly ash samples.

magnesium silicate (Mg_2SiO_4), mullite ($\text{Al}_4\text{Si}_2\text{O}_{10}$), anhydrite and hematite (Fe_2O_3) [33]. The XRD data show that new aluminosilicates with higher peak areas are formed due to calcium oxide treatment of fly ash [34]. An increase in the crystallinity due to the alkaline chemical treatment confirms restructuring within the fly ash substrate that enhances adsorption efficiency. Along with an extensive and irregular background in the X-ray diffractogram of the fly ash data, we also observe an abundance of glassy and amorphous constituents.

4.3. Effect of Influencing Factors

4.3.1. Effect of pH of primary solution

The pH plays a substantial role in the sorption of the dye molecules. The surface charge of the molecules has been affected by the changes in the pH of the sorbate. This phenomenon might be happening due to the degree of ionization of the dyestuff [32]. For conformational stability and color, potency pH acts as a significant factor. The pH controls the competition among the hydrogen ions and the dye molecules on the active sites of the sorbent surface. In the present study, the pH range varied between 2 - 10 and elucidated in Fig. 2(a). The initial pH of the system was varied, keeping other operating experimental conditions constant at primary dye concentration: 50 mg L^{-1} , amount of adsorbent 2 g L^{-1} , temperature: 303 K , agitation speed: 140 r/min , sorption contact time 3 h . CaO modified fly ash seemed to be competent to remove the CV from the simulated solution. It was observed from the experimental data that higher removal percentage achieved with increasing pH up

to 8. Further, an increment in the pH up to 10 was not favorable in removing the dye, as mentioned earlier. Later on, pH 8 was the optimized value obtained from the experimental results.

The CV is a basic dye, present as positively charged ions in the simulated solution. At lower pH, existing of the positively charged functional group on the sorbent surface repels the positively charged dye molecules, resulting in low sorption of the dye molecules in highly acidic ambience. Contrastingly, in the basic ambience, the phenomenon above is vice-versa, resulting in adherence of the dye molecules to the sorbent surface. It is evident from the literature that increment in pH value ascribed to lowering H^+ ions on the sorbent surface, resulting in a high percentage of dye removal at higher values of the pH. In contrast, at low pH values, H^+ ions actively participate on the sorbent surface, resulting in lowering the dye removal efficiency. A similar trend observed for adsorption of CV onto sodium hydroxide modified rice husk [31].

4.3.2. Effect of amount of adsorbent

Fig. 2(b) deciphered the sorption of CV Vs. Pristine and a modified fly ash quantity of adsorbent ranges from $0.5\text{-}5 \text{ g L}^{-1}$. The initial adsorbent loading of the system was varied, keeping other operating experimental conditions constant at primary dye concentration: 50 mg L^{-1} , pH of primary solution: 8.0 , temperature: 303 K , agitation speed: 140 r/min , sorption contact time 3 h . Fig. 2(b) reveals that while raising the quantity of the adsorbent percentage of elimination too increased simultaneously. This kind of phenomenon happened might be owing to the numeral of accessible pores existing on the facade of the adsorbent. From the literature, it has suggested

Fig. 2. Effect of different factors on the adsorption of crystal violet by unmodified and calcium oxide modified fly ash (a) Effect of pH, (b) Effect of amount of adsorbent, (c) Effect of primary dye concentration, and (d) Effect of temperature.

that an increase in the amount of adsorbent might create numerous vacant active sites [31, 30]. Although, we came across the fact that the simultaneous rise in the quantity of the adsorbent will enhance the removal percentage of the CV from the simulated solution.

In contrast, increasing the percentage removal while increasing the amount of adsorbent leads to a decrease in the adsorption capacity, an inverse relationship has detected. This kind of phenomenon might be happening due to the unavailability of the pores on the facade of the adsorbent or owing to the aggregation of the filling of the active sites [31]. A significant reduction in q_e value was observed to rise in the concentration of the sorbent mass. The phenomenon might be due to a decrease in the unit mass adsorbed onto the surface of the adsorbent. Later, the highest removal percentage of the dyestuff recorded was 97.86 % at 2.0 g L^{-1} . However, there was no promising result achieved by exceeding the amount of adsorbent. This phenomenon might be due to the equilibrium achieved among dyestuff molecules adhered to the sorbent surface and the simulated solution [32]. Finally, after the evaluation of the sorption process, 2.0 g L^{-1} of the amount of sorbent was considered as an optimized mass and further employed in the analysis of other influencing factors.

4.4.3. Effect of primary dye concentration and sorption contact time

The primary dye concentration plays an essential function in the sorption investigation. The role of varying the primary concentration of CV onto the modified fly ash and natural fly ash showed in Fig. 2(c). The effect of primary dye concentration was studied, keeping other operating experimental conditions constant at the amount of adsorbent: 2 g L^{-1} , pH of primary solution: 8.0, temperature: 303 K, agitation speeds: 140 r/min, sorption contact time 3 h. It is evident from the analytical data that a higher concentration of the adsorbate solution leads to a decreasing in the percentage removal of the CV dye from the simulated solution. The justification for this kind of behaviour might be due to the lack of active sites for accommodating another dye molecule in its active site. Nevertheless, the sorption capacity at stability is positive, with an augmentation in the dye concentration. These might be an increase in a concentration gradient, which serves as enhancing the driving force to repress all mass transfer hindrances of the CV among the liquid and solid-state, notably enhancing isothermal sorption until the adsorbent saturation has gained.

The contact time between sorbent and sorbate also played an essential role in the sorption of CV. It has investigated from the obtained data that sorption of CV onto the CaO modified fly ash surface played a decisive role with increasing contact time until 120 min. The sorption reached equilibrium after 120 min. Therefore,

no significant increase observed after 120 min. Rapid adsorption that happened at the beginning step might be justified due to the presence of vacant pores upon sorbent surfaces. The reason behind the fast adsorption that occurred in the early stage might be due to the diffusion mechanism. Later on, the adsorption probably an adhered governed process might be owing to the few vacant sites.

4.3.4. Effect of temperature

Temperature plays a crucial role in the adsorption process. The rise in temperature varies the isothermal capacity of the sorbent for a specific dye. Hence, the role of temperature in the present study has investigated. Fig. 2(d) showed the role of temperature on the sorption of CV employing the CaO modified fly ash. The effect of temperature was studied, keeping other operating experimental conditions constant at primary dye concentration: 50 mg L^{-1} , amount of adsorbent: 2 g L^{-1} , pH of primary solution 8.0, agitation speed: 140 r/min, sorption contact time 3 h. It reveals from the figure that the removal percentage declined with rising in temperature up to a certain level. It observes that due to the increase in temperature, the physical bonds become weak among CV molecules and the vacant site of the sorbent. These might be a reason that leads to a shrinking in elimination percentage. The solubility of the CV dye augmented amid the rise in temperature. Subsequently, the associated forces among the solute and solvent were vigorous compared to solute and the sorbent, resulting in strenuously in solute adsorbing [32]. The ascertained progression in decreasing the percentage removal efficacy with the rise in temperature revealed that CV sorption onto CaO modified fly ash surface is an exothermic process.

4.4. Adsorption Isotherms

Equilibrium models have evaluated in the present work. The models applied in the current investigation were Langmuir, Freundlich, Dubinin-Raduskevich (D-R) to ascertain the equilibrium mechanism. The factors and correlation coefficient determined as of the graph of Langmuir (C_e/q_e Vs. C_e), Freundlich ($\log q_e$ Vs. $\log C_e$), and D-R ($\ln q_e$ Vs. ϵ^2) (not shown in the figure) enlisted in Table 1.

It is manifest from Table 1; the Langmuir equilibrium model showed well fitted with corresponding data accompanied by the highest correlation coefficients at preselected temperatures (not shown in the figure). The higher sorption capacity of modified fly ash was observed 38.57 mg g^{-1} at 303 K. The calculated value of K_L and q_m has shown a negative relation with the temperature. An increase in the temperature of the sorption study encourages the reduction of maximum sorption capacity.

Moreover, Freundlich equilibrium model reasonably fit the ob-

Table 1. Adsorption Isotherm Constants for Adsorption of Crystal Violet onto Calcium Oxide Modified Fly Ash at Preselected Temperatures

T(K)	Langmuir Isotherm Parameters			Freundlich Isotherm Parameters			D-R Isotherm Parameters			
	q _m (mg g ⁻¹)	K _L (L mg ⁻¹)	R ²	K _F (mg g ⁻¹) (L mg ⁻¹) ^{1/n}	1/n	R ²	q _m (mg g ⁻¹)	β (mmol ² J ⁻²)	E (kJ mol ⁻¹)	R ²
303	38.57	0.0301	0.999	6.342	2.502	0.977	29.98	1.98 ×109	15.14	0.934
313	36.24	0.0256	0.998	5.784	2.124	0.958	28.342	2.26 × 109	14.72	0.914
323	34.78	0.0198	0.997	5.187	1.986	0.976	24.892	2.30 × 109	14.15	0.926
333	32.12	0.0142	0.997	4.882	1.786	0.975	23.682	2.67 × 109	13.63	0.925

tained isothermal data at all preselected temperature ($R^2 > 0.97$). It is evident from the analytical data that K_F showed a negative relation to a temperature Table 1, inferred that sorption is an exothermic process. The degree of n suggests the suitability of the sorption process. The calculated value of n lies within the range of 1 and 10 (i.e., $1/n < 1$) indicates the relevance of the sorption process. In this study, the obtained results are in agreement with this theory.

To distinguish the physisorption and chemisorption on the heterogeneous surfaces, the isothermal data evaluated by the D-R model. The obtained correlation coefficient value was less compared to the Freundlich and Langmuir equilibrium models (R^2 D-R < Freundlich < Langmuir) Table 1. The constant β manifested regarding the mean free energy E (KJ mol^{-1}) of the sorption when 1 mole of the sorbate gets entered onto the solid surfaces from the absolute solution and can be determined to apply the following equation Eq. (6):

$$E = \frac{1}{\sqrt{2\beta}} \quad (6)$$

By solving the above equation, the mechanism of adsorption inferred. The sorption process proceeds to chemisorption when $E \geq 8$ to 16 KJ mol^{-1} and termed as physical sorption when $E < 8 \text{ KJ mol}^{-1}$ [23]. The sorption of CV onto CaO modified fly ash regarded as a chemisorption mechanism revealed from the value of E , i.e., $> 8 \text{ KJ mol}^{-1}$.

The experimental data obeyed the Langmuir equilibrium model, suggesting that the adhering energy of the molecule was identical to the whole surface area. Furthermore, it has revealed that the sorbed dye molecules have inert associations with each other and establishing a monolayer.

4.5. Adsorption Kinetics

For comprehending the process, kinetics involved in reactions, like Pseudo-First order, Pseudo-Second order, and Intra-particle diffusion models assessed. The data of equilibrium sorption capacity, rate constants, and nature of sorption were investigated using these three models. The rate constant k_1 for pseudo-first-order and equilibrium sorption capacity q_e evaluate the slope and intercept of the graphs of $(q_e - q_t)$ Vs. t (not shown in the figure) enlisted in Table 2 amid the R^2 (correlation coefficient). It reveals from the present study, Table 2 that the analytical data was not obeying the pseudo-first-order kinetics.

Furthermore, comprehending the kinetics of CV sorption, the pseudo-second-order kinetic model employed using Eq. (8). The rate constant k_2 for pseudo-second-order assessed from the slope and intercept of the graphs of t/q_t Vs. t at preselected temperatures

deciphered in Fig. 3. Moreover, the R^2 for the pseudo-second-order equation exhibited well agreement ($R^2 > 0.995$) compare to the pseudo-first-order correlation coefficient. It suggests from Table 2 that the pseudo-second-order kinetic model is favorable to the present study.

The rate constant k_2 showed a negative relation with the temperature affirmed that CV sorption is an exothermic process. The experimental and theoretical values of q_e were relatively closer under observed temperatures, revealing that the sorption process obeyed the pseudo-second-order kinetic model. Observations exhibited that CV sorption onto CaO modified fly ash is a chemisorption process. The initial sorption rate, h ($\text{mg g}^{-1} \text{ min}^{-1}$) determine by applying Eq. (14):

$$h = k_2 q_e^2 \quad (14)$$

Table 2 illustrated that the initial sorption rate, h was not suitable for high temperatures as its value decreased at high temperatures. The Weber-Morris model (Eq. (8)) was used to determine the intraparticle diffusion. To comprehend the diffusion Weber-Morris graph (q_t Vs. $t^{0.5}$) drawn. The curve suggests that the primary area resembles the outer surface apprehension; the next step corresponds to the reasonable perception revealing that the intraparticle diffusion was the rate hindrance step. The final step conveyed the isothermal apprehension. The obtained result narrates that the intraparticle diffusion intricate in the present study. Furthermore, it observes that apart from the process as mentioned, earlier other mechanisms might play a significant role.

4.6. Activation Energy and Thermodynamic Factors

Arrhenius equation (Eq. (10)) applied to assess the activation energy. The rate constant k_2 obtained from the pseudo-second-order Table 2. The graph has been plotted between $\ln k_2$ and $1/T$ Fig. S3. From the slope of the linear plot, E_a achieved. The obtained E_a for the adsorption was $-42.25 \text{ KJ mol}^{-1}$. It affirmed by the activation energy that the chemisorption phenomenon is the prevailing reaction. From the literature, it is manifest that two kinds of sorption are present, i.e., physisorption and chemisorption. Physisorption is weak, and its value is less than 40 KJ mol^{-1} . Chemisorption involves strong forces compare to physisorption and possesses a higher magnitude [22]. Hence, the obtained value of the activation energy reveals that the chemisorption mechanism is evolved for CV sorption on CaO modified fly ash sample surface.

Gibb's free energy (ΔG°) has been calculated by applying the Eq. (11) for modified fly ash at all preselected temperatures for the sorption of CV from the simulated solution has been provided in Table 3. The entropy (ΔS°) and enthalpy (ΔH°) values have

Table 2. Kinetic Parameters for Adsorption of Crystal Violet onto Calcium Oxide Modified Fly Ash

T(K)	q_{exp} (mg g^{-1})	Pseudo-first-order kinetic model			Pseudo-second order kinetic model			
		q_{cal} (mg g^{-1})	k_1 (min^{-1})	R^2	q_{cal} (mg g^{-1})	k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$)	H ($\text{mg g}^{-1} \text{ min}^{-1}$)	R^2
303	37.48	21.568	0.05044	0.942	38.57	0.00309	46.541	0.999
313	34.68	18.462	0.04621	0.968	35.88	0.00235	31.642	0.998
323	31.78	16.642	0.04198	0.957	32.54	0.00202	22.842	0.995
333	29.12	14.784	0.03878	0.956	29.72	0.00176	12.742	0.997

Table 3. Activation Energy and Thermodynamic Parameters for Adsorption of Crystal Violet onto Calcium Oxide Treated Fly Ash

E_a (kJ mol ⁻¹)	ΔG° (kJ mol ⁻¹)				ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)
	303K	313K	323K	333K		
-42.25	-12.24	-9.88	-7.72	-5.64	-78.70	219.0

Fig. 3. Pseudo-second order kinetic plots for adsorption of crystal violet by calcium oxide modified fly ash. (experimental conditions: primary dye concentration: 50 mg L⁻¹, amount of adsorbent: 2 g L⁻¹, agitation speed: 140 r/min, pH of primary solution: 8.0 temperature: 303K.)

been enlisted Table 3 and evaluated from the slope and intercept of the plot between Gibbs's free energy (ΔG°) and temperature (T) shown in Fig. S4. It is manifest from the literature that the negative obtained value of Gibbs's free energy (ΔG°) suggests the spontaneity of the reaction. The obtained values of Gibbs's free energy for the present study are in agreement with the literature. The increase in the value of Gibbs's free energy (ΔG°) with increasing temperature revealed that sorption proceeds smoothly at low temperatures. The present study showed the exothermic nature of the reaction affirmed by the negative obtained value of enthalpy (ΔH°). It could be assumed the character of sorption via the value of enthalpy (ΔH°). Therefore, CV adsorption by CaO modified fly ash ascribed to the chemisorption phenomena affirmed by negative values of enthalpy. The sorption process of CV on CaO modified fly ash was solely governed by the enthalpy, and it confirms by the entropy's negative value.

5. Conclusions

In the present work, CaO, modified fly ash, was considered an efficient sorbent to eradicate CV dye from the simulated solution in a batch study. The role of different parameters influencing the sorption process like primary dye concentration, sorption contact time, the amount of adsorbent, temperature, along the initial pH of the simulated solution has investigated. The comparison of the maximum adsorption capacity of CV dye by different adsorbents with the fly ash used in this study has been shown in Table S3. It is evident from the obtained experimental data that the removal percentage of the CV dye decreased with the increment of the

primary dye concentration and subsequently increased with increasing sorption contact time, and the amount of the sorbent up to a specific limit. The higher removal achieved at pH 8.0. It has manifested from the isotherm study that the experimental data obeyed the Langmuir model. The equilibrium study reveals that monolayer adsorption happening on the surface of the CaO modified fly ash sample surface. It concludes from the obtained data that with rising temperature (303-333 K) leads to a shrinking in the monolayer adsorption capacity. The higher value of sorption capacity achieved at 303 K was determined to be 38.57 mg g⁻¹. The Dubinin-Raduskevich (D-R) isotherm reveals the chemisorption nature of CV dye on CaO modified fly ash.

Additionally, the kinetic analysis also inferred the chemisorption phenomenon. The calculated experimental data affirmed that intra-particle diffusion was not the sole rate-limiting factor. Based on the Arrhenius equation, the calculation was done for the determination of the activation energy (E_a) of the sorption process. The obtained value of E_a 42.25 KJ mol⁻¹ showed that the nature of CV sorption on the CaO modified fly ash surface is chemisorption. Gibbs free energy (ΔG°), Enthalpy (ΔH°), along with Entropy (ΔS°) have assessed. The acquired thermodynamic data portrays the spontaneous and exothermic nature of the sorption. Furthermore, it suggests that CaO modified fly ash could be a cheap and promising adsorbent anticipated for the eradication of the CV dye from the simulated solution along with the industrial wastewater.

Nomenclature

C_i	Initial dye concentration (mg L ⁻¹)
h	Initial adsorption rate (mg g ⁻¹ min ⁻¹)
I	Intraparticle diffusion model constant
K_C	Distribution coefficient for biosorption
K_L	Langmuir constant (L mg ⁻¹)
k_i	Intraparticle diffusion rate constant (mg g ⁻¹ min ^{-0.5})
k_1	Pseudo-first-order rate constant (min ⁻¹)
k_2	Pseudo-second-order rate constant (g mg ⁻¹ min ⁻¹)
m	mass of biosorbent (g)
n	Freundlich adsorption isotherm constant
q_e	Equilibrium dye concentration on biosorbent (mg g ⁻¹)
q_m	Maximum biosorption capacity (mg g ⁻¹)
q_{exp}	Maximum sorption capacity experimental (mg g ⁻¹)
q_t	Amount of dye adsorbed at time t (mg g ⁻¹)
R	Universal gas constant (8.314 J mol ⁻¹ K ⁻¹)
V	The volume of the solution (L)
<i>Greek alphabets</i>	
β	D-R Isotherm constant (mmol ² J ⁻²)
ε	Polanyi potential (J mmol ⁻¹) = $RT \ln(1 + 1/C_e)$

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Author Contributions

S.C. (Senior Researcher) designed the experiments, collected the data and jointly wrote the paper. A.M. (B.Tech Student) did literature survey, revised the manuscript. S.D. (Research Engineer) did data compilation and interpretation of the experimental work. N.R.M. (Professor) reviewed the whole work and provided suggestions for the improvement of the paper. S.I. (Ph.D student) jointly discussed, analyzed, and wrote the paper. P.D. (Professor) supervised and mentored the overall work.

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