

Use of activated *Chromolaena odorata* biomass for the removal of crystal violet from aqueous solution: Kinetic, Equilibrium and Thermodynamic study

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Abstract

In the present study, biomass from the *Chromolaena odorata* plant's stem was activated using sulfuric acid to absorb crystal violet (CV) dye. The adsorption operation of CV dye was studied considering the effect of variables like pH, initial dye concentration, time, adsorbent dosage, and temperature. The pseudo-second-order equation best fitted the kinetic study, and thermodynamic parameters calculated were activation energy (9.56 kJ/mol), change in Gibbs energy (81.43 to 96.7 kJ/mol), enthalpy change (6.89 kJ/mol), and entropy change [-254.4 J/ (mol K)]. Response surface methodology (RSM) estimated at pH (4.902), adsorbent dosage (8.33 g/L), dye concentration (82.30 ppm), temperature (300.13 K) dye removal of 97.53% is possible. FTIR, SEM, XRD, BJH, and BET confirmed adsorption operation. The adsorbent can be reused for 5 cycles effectively. Langmuir isotherm best fitted the adsorption operation was used for designing a theoretical single-stage batch adsorber for large-scale operation.

1 Introduction

Mauveine was the first synthetic dye invented in 1856; since various synthetic dyes were created, the use and development of other synthetic dyes in textile industries have continuously increased. Synthetic dye meets nearly 65–70% of the dyeing industry's needs. They possess a large variant of color available at a relatively low price than natural dye and could colorize the target molecules easily with greater stability (Zhang et al. 2016b). Around 700,000 metric tons of pigments and dye are produced from over 10,000 types of dyes each year (Sahu & Patel 2016). Dyes are primarily organic and toxic. Dye pollutants from industry find their way to natural water bodies that pose a severe threat to both humans and the environment (Zhao et al. 2017). The dye-rich wastewater hinders the growth of aquatic life by reflecting and absorbing the sunlight needed for photosynthesis needed by the underwater plant; thus, the presence of underwater flora and fauna is affected. This raises the serious issue of treating the dye effluent before discharging into the water source (Amri et al. 2018, Intarasuwan et al. 2017).

Water is a important component as all the living organism on earth needs water for their daily vital activities. With the growth of population and urbanization, the need for water gets intensified. However, the various man-made activity allows the pollutants like dye molecules making their way into natural water bodies, rendering the water dangerous for consumption. The polluted water bodies deeply affect the health of humans and many other living organisms consuming it. Thus, it becomes essential to treat water in a large quantity, with the fast and straightforward process to make it safe for consumption of not only humans but also to the other living organism living amongst us (Ali 2012, Bolisetty et al. 2019, Zhang et al. 2016a).

Crystal violet (CV) is a synthetic dye of triarylmethane dyes commonly employed in the textile and paper industry. The CV dye is mutagenic, teratogenic, and suspected carcinogen biohazards dye with a long half-life period, which, when dumped in the environment, will remain active for a longer time. In humans, a small dosage (less than 1 ppm) of CV dye dosage causes serious health problems like kidney failure, respiratory disorder, etc. Various physical and chemical process is present for removing CV dye before they are discharged in water bodies like membrane filtration, photocatalytic reaction, ion exchange, chemical precipitation, solvent extraction, electrochemical treatment (Kalpana et al. 2020, Michael Rahul Soosai et al. 2021, Michael Rahul Soosai 2020, Samuel P N Karl J et al. 2020, Thangam et al. 2021). Adsorption is the best-suited method for the removal of CV dye as compared to other water treatment methods. It is easy to operate, has low operation & installation costs, yields high efficiency, and most importantly, does not produce any secondary pollutant (Puri & Sumana 2018, Wang et al. 2018)

Biomass for the adsorption operation in the present study was derived from a local invasive plant, *Chromolaena odorata*, commonly referred to as Siam Weed. Originally native to South America *C. odorata* has spread to various

parts of India. One of the peculiar growth characteristics associated with the *C. odorata* species of plant is that it grows up to 2.5 m tall in open space. It has a woody base but soft stem, which enables it to grow as a creeper (Dahunsi et al. 2018) over other vegetation where it can reach a maximum height of 10 m, around 80,000 to 90,000 seeds are produced per plant, which can attach to cloth, fur, and machinery, which help in long-distance disposal, the plant can regenerate from roots and also in the favorable condition it can grow 3 cm per day. Moreover, the plant's leaf has anti-microbial properties and is used for healing wounds (Anyanwu et al. 2017, Dahunsi et al. 2018).

In the present work, the stem of *C. odorata*, an invasive plant that disrupts local vegetation, was used for CV dye adsorption operation. As per our understanding and knowledge, the biomass of *C. odorata* is not employed so far for the adsorption operation. First, the adsorption study was conducted using one variable at a time approach, followed by a statistical approach like response surface methodology (RSM) for finding the optimum condition of variables to maximize dye removal % with further studies on reusability of the adsorbent. Moreover, a single-stage batch adsorber was designed to study the possibility of a large-scale dye removal operation.

2 Materials And Methods

2.1 Materials

Crystal Violet, Sodium hydroxide, Sulfuric acid, hydrochloric acid were purchased from Himedia Laboratories, India. The stem of the invasive plant *Chromolaena odorata* was collected from Alanchi (8.1965°N, 77.2355°E) in the Kanyakumari District of Tamil Nadu, India.

2.2 Adsorbent Preparation

The stem of *Chromolaena odorata* was dried in sunlight to reduce its moisture content, followed by grinding and sieving to a particle size of approximately 75 to 100 μm . After grinding 50 gm of the sample for adsorption activation, it was mixed with 500 mL 0.1 N H_2SO_4 and stirred for 18 h. The material thus obtained was drenched in 0.1 N NaHCO_3 solution to remove traces of acid further; it was dried using an oven for 6 h at 353 K (Jain & Gogate 2017).

2.3 Adsorption batch Study

The adsorption of CV dye by the acid-activated stem of *Chromolaena odorata* (AASCO) was conducted in a series of experiments using a 250 mL Erlenmeyer flask holding 100 ml of dye solution. The dye solution of desired concentration was prepared using a stock solution of 500 ppm CV dye solution by further diluting it. A known quantity of AASCO was added to the CV dye Solution. The mixture thus obtained was placed at a constant temperature in an orbital Incubator shaker (Promega, PIPL-LSI) at 120 rpm for 3 h. Effect of variables like pH (2 to 10), AASCO adsorbent dosage (5 g/L to 30 g/L), CV dye concentration (25 to 200 ppm), time (0 to 180 min), and temperature (293 to 353 K) on adsorption operation was studied. After the adsorption operation, the samples were filtered with Whatman Number 1 Filter paper, and the filtrate thus obtained was analyzed using a UV-Vis Spectrophotometer (UV1700, Shimadzu) to determine the residual concentration of CV dye at a maximum absorption wavelength ($\lambda_{\text{max}} = 590\text{nm}$). All the experiments were done in triplicates, and the average value was used for further analysis (Sellaoui et al. 2021).

Dye removal % and biosorption capacity (mg/g) are calculated (Santos et al. 2013) using:

$$DyeRemoval\% = \frac{(C_o - C_t)}{C_o} \times 100 \quad (1)$$

$$BiosorptionCapacity(mg/g) = \frac{(C_o - C_t) V}{M} \quad (2)$$

where C_o is the concentration of CV dye initially present in aqueous solution (mg/L), C_t is the CV dye concentration at time t (mg/L), M is the mass of the biomass (g), and V is the volume of the solution (L).

2.4 Kinetic and Isotherm Study

The kinetic mechanism involved in the adsorption operation of CV dye with AASCO adsorbent was studied using one intraparticle diffusion otherwise known as Weber and Morris kinetic model. Three kinetic models like Pseudo-first-order kinetic equation, Pseudo-second-order kinetic equation, Elovich model were also used. Langmuir isotherm, Freundlich isotherm, Tempkin isotherm, and Dubinin - Raduskevich isotherm were the four isotherm models used to interpret the study adsorption data. The kinetic model which best fitted the adsorption operation was used with Arrhenius and Eyring equation to calculate thermodynamic parameters like activation energy, change in Gibbs free energy, change in enthalpy, and change in entropy. The isotherm which best fitted the adsorption data was used in designing a single-stage batch adsorber.

2.5 Characterization Study

The microstructure properties of *C. odorata* biomass, AASCO & CV dye adsorbed on AASCO were studied using Scanning electron microscope (SEM) image and X-ray diffraction (XRD). In the range 400–4000 cm^{-1} , the Fourier Transform Infrared Spectra (FTIR, IR Tracer – 100 Shimadzu) is used to determine the functional group in the samples. Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods were used to determine the Surface area and pore size distribution.

2.6 Response Surface Methodology (RSM) Statistical approach methodology

For the design of the statistical experiment, a central composite rotatable design (CCRD) was employed to optimize the influence of pH, Adsorbent dosage, Dye concentration, and temperature on dye removal % in the present work. The CCRD is a three-part experimental design process. The two-level factorial portion, which chooses a resolution V design and estimates two-factor interaction and linear terms, is the first part of the CCRD experimental design. At the center point portion, the number of Replications is the second point of the design. It is denoted by n_c and calculated as,

$$n_c = 4\sqrt{n_f + 1} - 2k \quad (3)$$

where, n_f is the total number of runs carried out in a factorial portion of design and

k is the number of factors for the factorial portion of the design.

The information about the existence of curvature is provided by the centre point in the system.

The third part is the use of an axial portion, also known as star point. The star point contributes to quadratic term estimation. In CCRD, the axial distance is given by,

$$\alpha = (n_f)^{1/4} \quad (4)$$

Thus, a total of 30 (16 + 6 + 8) experimental runs were needed to find optimum conditions for a better dye removal percentage. For all the variables, values at the center were coded as zero. Tables 1 & 2 show the selected variable range and experimental design used, respectively. For the experimental data, a non-linear polynomial second-order equation was fitted:

$$Y = \beta_o + \sum_{i=1}^n \beta_i X_i + \sum_{i=1}^n \beta_{ii} X_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^n \beta_{ij} X_i X_j + \epsilon \quad (5)$$

where Y is the response, which is dye removal %, β_o is intercept term of the model, β_i is the effect of the linear term, β_{ii} is the effect of square term, β_{ij} is the effect of the interaction term, while X_i & X_j are the levels of independent variables, ϵ denotes the random error. For finding optimum conditions for the variables needed to find the better dye removal % equation, no. 5 is used. For optimizing multiple responses, Derringer's desirability function methodology is used. In this method, response Y_i is converted into d_i (individual desirability function). The desirability function ranges from the value of 0 (completely undesirable) to 1 (ideal response value) (Ganesh Moorthy I & Baskar R 2013). The equation for the overall desirability function is written as:

$$D = \left(\prod_{i=1}^n d_i \right)^{\frac{1}{n}} \quad (6)$$

where, D denotes the overall desirability, d_i denotes individual desirability and n represents the number of responses. The criteria for determining the individual desirability is given as,

$$d = \begin{cases} 0, & y < L \\ \left(\frac{y-L}{U-L} \right)^r, & L \leq y \leq U \\ 1, & y > U \end{cases} \quad (7)$$

where r represents the weight factor, L shows lower response, and U denotes higher response.

2.7 Desorption and reusability study

After the adsorption experiments, Whatman No. 1 Filter paper was used to collect and filter the sample. The adsorbed CV dye on the AASCO was desorbed in an alkaline medium over a pH range of 7 to 12. The desorption experiment was performed to find out the optimum pH at which desorption took place. The volume used in the desorption experiment was the same as used in the adsorption experiment. The reusability of the AASCO for the adsorption of CV dye was tested by the adsorption-desorption cycle for the same adsorbent to find the number of times the adsorbent could be reused.

3 Results And Discussion

3.1 Adsorption Characterization study

The spectrum of *C. odorata* biomass obtained from FTIR is revealed in Fig. 1(a), broadband at 3500 to 3000 cm^{-1} indicating – OH bond stretching, also a small peak at 1750 cm^{-1} attributing – CH_2 and – COOH bond stretching is witnessed. A distinctive peak near 1150 cm^{-1} displays the presence of – COOH in *C. odorata* biomass associated with aldehydes, ketones, carboxylic acid, and amides. The presence of carbonyl and hydroxyl functional groups in *C. odorata* makes it hydrophilic. Thus *C. odorata* can bind pollutants in water (Zwane et al. 2019). The FTIR spectra of sulfuric acid-activated biomass of *C. odorata* shows the formation of a new peak at 1109 cm^{-1} displaying $\text{C}=\text{S}$ bond stretching near the originally present – COOH bond. Similarly, two new peaks are seen at 2837 cm^{-1} & 2974 cm^{-1} , indicating the formation of the carboxylic acid group near the alkane and alcohol group present in *C. odorata*. Thus, the activation of *C. odorata* biomass with sulfuric acid was confirmed. The characteristic AASCO adsorbent loaded with CV dye shows three peaks 1056.99 cm^{-1} indicating $\text{S}=\text{O}$ bond, 1595.13 cm^{-1} representing cyclic alkaline, and 2360 cm^{-1} showing $=\text{NH}^+$ – Bond; all the new peaks emerging for CV dye adsorbed on AASCO molecule are very close to the peaks formed after the activation of *C. odorata*. This presence of peak point indicates that on activation of *C. odorata* new peak emerges with a function similar to the one derived from sulfuric acid. Further, the FTIR analysis of CV adsorbed biomass shows the formation of a new peak indicating adsorbed CV dyes formed near the active sites. Therefore, active sites undoubtedly being the one which was formed during the activation process, where the adsorption of CV dye molecules takes place.

One of the significant factors contributing to the adsorption of AASCO molecules is its porous structure. The porosity of the AASCO adsorbent was determined by the N_2 adsorption-desorption experiment, as displayed in Fig. 1 (b). The surface area as per the BET method was 40.132 m^2/g . Using the BJH method [Fig. 1 (b): insert]] the pore volume was calculated as 0.081 cm^3/g , with 3.628 nm as an average pore diameter for AASCO adsorbent molecules. Thus, the AASCO adsorbent can be stated as a mesoporous material.

SEM analysis was used for the physical morphology study of the surface of the biomass. The SEM image of *C. odorata* biomass, AASCO & CV dye adsorbed on AASCO are displayed in Fig. 2 (a-c). From the SEM image, it is clear that on acid activation of *C. odorata* biomass, the cavity of the biomass has increased. Therefore, after the adsorption study, the dye molecules were attached to the activated surface of the biomass.

The XRD spectrum is indicated in Fig. 2 (d-f), which shows a well-defined and intense peak at 2θ (degree of 21.956), indicating the presence of crystalline and well-defined structures present in *C. odorata* biomass. Furthermore, the intensity of the well-defined peak does not reduce after the biomass is activated with acid Fig. 2 (e) or after the adsorption operation. Therefore, Fig. 2 (f) indicates that the adsorption of CV dye on AASCO will probably take place on the upper part of the crystalline surface.

3.2 Effect of the variable pH on adsorption operation

The pH of the aqueous solution greatly influences the adsorption operation. The pH of the solution in which adsorption operation takes place affects the charges present on the functional group at the active site of the adsorbent surface (Jantawatchai et al. 2017, Kalita et al. 2017). The adsorption efficiency of AASCO over CV dye was investigated over a range from pH 2 to 10. The cationic dye CV at an acidic pH of 5, as outlined in Fig. 3 (a), with a maximum dye removal efficiency of 94.25% by AASCO and an adsorption capacity of 18.85 mg/g. Further experiments were carried out for solution at pH 5. It was evident that at pH 5, maximum protonation and deprotonation occur. A similar observation was also noticed for removing brilliant green by the oxidized peel of cactus fruit at a pH of 3 (Kumar & Barakat 2013) and with a pH of 1 for removal of Reactive Red 120 using *Chara contraria* biomass (Çelekli et al. 2012).

3.3 Effect of the variable adsorbent dosage on adsorption operation

The AASCO adsorbent dosage was varied from 5 g/L to 30 g/L to observe the CV dye removal operation. Figure 3 (b) indicates that an increase in AASCO adsorbent dosage over the range from 5 to 10 g/L CV dye was rapidly removed from 89.88–94.82%. Still, with further addition of adsorbent AASCO dosage from 15 to 30 g/L, the CV dye removal was a steady operation with a maximum of 96.38% removal was observed. The biosorption capacity reduced from 17.98 mg/g to 3.21 mg/g as the AASCO adsorbent dosage was increased from 5 g/L to 30 g/L.

The increase in active sites available in AASCO adsorbent helped in rapid CV dye removal percentage with an initial increase in adsorbent dosage. However, a further rise in AASCO dosage caused the diffusion path length to get longer, which resulted in an almost constant removal rate of CV dye (Cao et al. 2014). Thus, the optimum adsorbent dosage was considered 15 g/L, which was used as an adsorbent dosage for further experiments. A similar observation was noticed in jujube seed used for removing Congo red with an adsorbent dosage of 6 g/L (Reddy et al. 2012), removal of yellow 194, red 357, black 210 dyes using the waste of chromium tanned leather (Piccin et al. 2012).

3.4 Effect of the variables time and initial dye concentration on adsorption operation

The concentration of initial CV dye was varied over a range of 25 ppm to 200 ppm for a time period of 180 min as samples were examined every 10 min for removal of dye in percentage. At 40 min, it was observed that rapid reduction of CV dye in the solution takes place, after which the dye concentration in the aqueous sample solution almost remained constant. As the initial dye concentration increased, a decrease in dye removal % was observed. For

25 ppm initial dye concentration, 97.37% of dye was removed, whereas only 94.62% of dye was removed with 200 ppm initial dye concentration as visible in Fig. 3 (c).

The concentration of CV dye in an aqueous solution plays an important role in adsorption operation. Most adsorption happens during the initial period; CV dye gets adsorbed onto the vacant active site of AASCO, reaching equilibrium during this period. As time progresses, the saturation of the vacant site reduces the adsorption rate. The CV dye adsorption occurs both at the exterior surface of AASCO and at the pores. At a low initial CV dye concentration, most of the adsorption operation occurs at the outer surface. In contrast, at a higher concentration of CV dye, adsorption due to slow diffusion at the pore site occurs (Pařka et al. 2014). A similar observation was obtained in the removal of Malachite green by rice husk. 90% of dye was removed for 30 ppm dye concentration in the first 45 min after which the removal % did not differ much (Ramaraju et al. 2014). For removal of amido black 10B by jackfruit leaf powder also showed that much of the decolorization occurs at lower concentrations and during the early stage of adsorption (Ojha & Bulasara 2015).

3.5 Effect of the variable Temperature on adsorption operation

Over a temperature range of 293 to 353 K, adsorption of CV dye on AASCO adsorbent was investigated. An increase in adsorption was observed from 93.78% at 293 K to 96.7% removed at 353K, as shown in Fig. 3 (d). An increase in CV dye removal during the adsorption operation on AASCO surface is attributed to three main reasons. The first reason being a gradual decrease in boundary layer thickness for adsorption with an increase in temperature, the second reason being an increase in active site at the surface of AASCO adsorbent as temperature increases, and the last one being that of the improved ability of functional group at the surface of AASCO adsorbent to link with CV dye as temperature increases. Such observation was similar to adsorption of textile dye waste increased by 42–68% using alkali-activated Sunflower as the temperature was increased from 293 to 333 K (Oguntimein 2015). Jujube seed used for the removal of Congo red dye from 79.68–99.82% as the temperature was increased from 303 to 333 K (Reddy et al. 2012).

3.6 Kinetic study

The complex phenomenon of CV adsorption on the surface of AASCO can be described in four steps. The first step involves the movement of CV dye molecules to the surface of AASCO adsorbent from the bulk aqueous solution; the next step is the diffusion at the film surrounding the outer layer of AASCO adsorbent surface by CV dye molecules. In the third step, the CV dye ions migrate within the internal pores of AASCO adsorbent. Finally, an interaction force of attraction occurs between the active site present at the external surface of AASCO adsorbent molecules and CV dye molecules.

Like Weber Morris's intra-particle kinetic equation, the diffusion model provides information about the mechanism involved in adsorption operation like diffusion on the surface, external diffusion or film, pore diffusion or pore surface adsorption, or the amalgamation of more than one step.

The intra-particle diffusion like Webber Morris model [Fig. 4 (d)] in its linear model is given as:

$$q_t = K_{id}t^{0.5} + C \quad (8)$$

where K_{id} represents the rate constant of the intra-particle diffusion ($\text{mg/g min}^{-0.5}$), C represents the intercept. In adsorption of the CV dye onto AASCO adsorbent, the rate constant of intra-particle diffusion was attained to be in the range of 1.54 to 11.9 ($\text{mg/g min}^{-0.5}$) for the concentration of initial CV dye from 25 ppm to 200 ppm. Thus, it was evident that the diffusion at the boundary layer increase with an increase in the concentration of CV dye.

The kinetic mechanism studies help determine the efficiency of CV dye removal operation and the possibility of large-scale adsorption operation using AASCO adsorbent.

Pseudo-first-order model (Sinha et al., 2018) in its linear form [Fig. 4 (a)] is given as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (9)$$

where k_1 (L/min) is the rate constant of Pseudo-first-order equation;

q_e represents the adsorption capacity at equilibrium;

q_t represents the adsorption capacity after time t (min)

The Pseudo-second-order model in its linear form [Fig. 4 (b)] is given as:

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

where k_2 (g/g min) are the rate constant of Pseudo-second-order equation;

The linear equation for the Elovich model [Fig. 4 (c)] is

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (11)$$

where α represents the initial sorption rate (mg/g min);

β represents desorption constant (mg/g);

The kinetic model is plotted on the graph as per their linear equation as shown in Fig. 4 [(a) -(d)] and their intercept and slope are used to derive the value of the parameter as represented in Table 3.

The highest value of the coefficient of Regression R^2 (0.999) is for Pseudo-second-order kinetic equation; thus, it best fits the CV dye adsorption by AASCO adsorbent data. Moreover, the adsorption capacity at equilibrium (q_e) obtained using Pseudo-second-order is nearly equivalent to adsorption capacity at equilibrium (q_e) obtained experimentally (Banerjee et al. 2015).

3.7 Isotherm model

The isotherm provides an empirical relationship between the dye molecules present in an aqueous state and the amount of adsorbed CV dye on the surface of AASCO. Such empirical relation and data are important to optimize mathematical modeling for designing large-scale adsorption operations.

The Langmuir isotherm assumes that a single layer of adsorbate is formed at many fixed sites at the adsorbent molecules during the adsorption operation. Heat of adsorption is independent of the adsorbate coverage and between the adsorbate molecules no interaction occurs. If a vacant site of the adsorbent molecule is occupied by an adsorbate molecule, equilibrium is attained, and no more adsorbate will occupy the site.

The linear equation used in the study of Langmuir isotherm model Fig. 5 (a) are:

$$\left[\frac{1}{q_e} = \left(\frac{1}{Q_m} K_L \right) \frac{1}{C_e} + \frac{1}{Q_m} \right] \quad (12)$$

where $q_e \rightarrow$ Biosorption capacity (mg/g)

$Q_m \rightarrow$ Langmuir constant associated with biosorption constant

$K_L \rightarrow$ Langmuir constant correlated with the rate of biosorption

$C_e \rightarrow$ The equilibrium concentration of CV dye molecules (mg/L)

The energy of adsorption involved in CV dye molecule adsorption at the external surface of AASCO molecules is 40 L/mg; the value thus suggests that there is a good attraction between adsorbent and adsorbate. The Hall Separation factor R_L determines the sustainability of the biosorption process. The value of R_L has varied significance, it states if the isotherm is favorable (if $0 < R_L < 1$), linear (if $R_L = 1$), unfavorable (if $R_L > 1$) or reversible (if $R_L = 0$) (Paşka et al. 2014).

$$\left[R_L = \frac{1}{(1 + K_L C_o)} \right] \quad (13)$$

where, C_o is the highest initial dye concentration.

The adsorption operation of CV dye molecules on the AASCO surface, R_L value was found to be 25×10^{-5} , thus implying the adsorption operation was favorable. With an R^2 value of 0.996, Langmuir isotherm best fitted the adsorption data.

Freundlich isotherm Fig. 5 (b) is generally considered for reversible and non-ideal adsorption operation, with the interaction between adsorbed molecules on the heterogeneous surface of adsorbent (Sivarajasekar et al. 2019).

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (14)$$

where, $k_f \rightarrow$ Freundlich constant showing bioadsorption capacity

$1/n \rightarrow$ Biosorption intensity (L/g)

The biosorption intensity for adsorption of CV dye molecules on the surface of AASCO lies in the range ($0 < 1/n < 1$) the Freundlich constant was obtained to be 4.95 (L/mg)^{1/n}, and the obtained biosorption intensity was 0.74 L/g. Thus the process can be described as a favorable adsorption operation, but with an R² value that falls behind the Langmuir isotherm, therefore it is not considered the isotherm best fit for the adsorption operation.

The Temkin isotherm Fig. 5 (c) assumes energy to be distributed equally during the adsorption operation, and the heat of adsorption decreases linearly during the adsorption operation.

$$q_e = B_1 \ln A + B_1 \ln C_e \quad (15)$$

where, $A \rightarrow$ Constant for equilibrium binding at the maximum binding energy (L/mg)

$B_1 \rightarrow$ Temkin constant for adsorption heat

Temkin isotherm was initially developed for adsorption of hydrogen on the platinum electrode in an acidic medium. For the adsorption of CV dye by AASCO 1.93 (L/mg), the value of the constant A was obtained, and the Temkin constant for adsorption heat was attained as -19.33 mg/g.

Dubinin –Radushkevich isotherm Fig. 5 (d) model in its linear form can be written as,

$$\ln q_e = \ln q_{mD} - \beta \left[RT \left(1 + \frac{1}{C_e} \right) \right]^2 \quad (16)$$

where, $q_{mD} \rightarrow$ The Dubinin-Radushkevich monolayer adsorption capacity

$\beta \rightarrow$ Adsorption energy

$R \rightarrow$ Ideal gas constant

$T \rightarrow$ Temperature (K)

The mean free energy calculated in the isotherm is:

$$E = \sqrt{1/2\beta} \quad (17)$$

Dubinin –Radushkevich isotherm Fig. 5 (d) model is temperature-dependent and was developed for adsorption of subcritical vapor on the porous surface of solid. The adsorption mechanism depicted by the isotherm implies that the adsorption mechanism occurs with Gaussian energy distribution (Jan et al. 2021). The mean free energy for adsorption of CV dye on the surface of AASCO was 0.3922 kJ/mol, which implies that the adsorption operation was very spontaneous. Thus, this model cannot be used to describe the adsorption operation as it has the least value of R^2 . The error analysis (Kalpana et al. 2020) statics used in the study was:

$\text{Chi - square error statics} = x^2 = \sum \frac{(q_{e_{\text{calcu}}} - q_{e_{\text{exp}}})^2}{q_{e_{\text{calcu}}}} \quad (18)$
$\text{Root mean square error} = \sqrt{\frac{1}{n-2} \sum (q_{e_{\text{calcu}}} - q_{e_{\text{exp}}})^2} \quad (19)$

Table 4 represents the parameter's value obtained from the slope of the plots and its intercept from the graph, drawn using the linear equations of the various isotherm. From the value of R^2 close to unity and error analysis, it was evident that the best-fitted model for the adsorption operation of CV on the surface of AASCO is the Langmuir isotherm model.

3.8 Thermodynamic property

The best fit adsorption kinetics equation Pseudo-second-order is substituted in Arrhenius equation to yield the activation energy (E_a), the equation thus obtained is given below,

$\ln k = \ln A - \left(E_A / RT \right) \quad (20)$
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where, A is Arrhenius constant ($1 / \text{min}$), R denotes universal gas constant [$8.314 \text{ J}/(\text{mol K})$], and k represents Pseudo-second-order constant (g/g min).

The activation energy for the adsorption operation of CV dye using AASCO was 9.5611 kJ/mol. The value of activation energy lies between 5 and 40 kJ/mol. Thus, the adsorption operation is reversible and physical with low energy consumption. On the other hand, if the activation energy value lies within 40 to 800 kJ/mol, the process will be chemical sorption in nature, irreversible and high energy-consuming (Çelekli et al. 2012).

Arranging Eyring equation in its linear form the value of change in total enthalpy (ΔH) and change in total entropy (ΔS) can be calculated [Fig. 6 (a & b)]. The equation thus becomes,

$\ln \frac{kh_p}{k_B T} = \left(\frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \right) \quad (21)$

Where h_p represents the Plank constant (6.6261×10^{-34} J), and k_B denotes Boltzmann constant (1.3807×10^{-23} J/K). Change in enthalpy ΔH was calculated as 6.897 kJ/mol. The adsorption operation is endothermic as the value of ΔH is positive. The value of change in entropy ΔS was negative [-254.4 J/ (mol K)] which means that the adsorbent structure internally remains the same during adsorption operation.

The change in total Gibbs free energy (ΔG) of activation was calculated using the equation.

$$\Delta G = \Delta H - T\Delta S \quad (22)$$

As the value of change in total Gibbs free energy is positive, it suggests that the adsorption of CV dye by AASCO adsorbent requires energy for the process of converting reagent into products (Sivarajasekar et al. 2017). The ΔG values at different temperatures are presented in Table 5.

3.9 Single-stage batch adsorber design

The best-fit isotherm for the adsorption operation was found to be the Langmuir isotherm model. Using this model, a batch adsorber of the single-stage is designed. The adsorber aims to reduce the concentration of CV dye molecule from C_0 (mg/L) at the initial time ($t = 0$) to a concentration of CV dye C_1 (mg/L) at time t . Adsorbent AASCO has a biosorption load q_0 (mg/g) at initial time ($t = 0$) to q_t (mg/g) at time t . The concentration of CV dye at equilibrium in the solution and the biosorption capacity at the equilibrium of AASCO adsorbent is represented by C_e (mg/L) & q_e (mg/g) respectively. Further, M represents the mass of adsorbent (gm), at time t , the material balance across the batch adsorber of single-stage is given as:

$$V(C_0 - C_1) = M(q_1 - q_0) \quad (23)$$

Assuming that at time ($t = 0$) no adsorption takes place

$$V(C_0 - C_1) = Mq_1 \quad (24)$$

At equilibrium, employing the CV dye concentration and AASCO adsorbent biosorption capacity at equilibrium in the above equation using the Langmuir equation, the above equation becomes

$$V(C_0 - C_e) = Mq_e \quad (25)$$

using the Langmuir equation, the above equation becomes

$$M = \frac{V(C_0 - C_e)}{\bar{q}_e} = \frac{V(C_0 - C_e)(1 + K_L C_e)}{\bar{q}_m K_L C_e} \quad (26)$$

Equation no. 14 was used in designing a batch adsorber of single-stage. The solution to equation no. 29 yields stationary points, stage for 90% (from the table representing the amount 96% of the dye is removed at lab scale experiment, hence assuming 90% of dye can be removed in a large-scale operation) reduction in initial CV dye concentration. The mass of AASCO adsorbent required for 1 liter to 5 liters of effluent entering the single-stage batch adsorber at the various initial concentrations of dye from 1000 to 10,000 ppm is shown in Fig. 6 (c). For example, suppose 1 L of CV dye enters at 4000 ppm. In that case, the data from the above design recommend that for reducing the initial dye concentration to 400 ppm, about 25.2 gm of AASCO of adsorbent was needed. Thus, from the graph, it is quite evident that for removing a large quantity of dye (10,000 ppm) from a large volume of effluent (5 L), only a relatively small amount of adsorbent (283.5 g) are needed.

3.10 Response Surface Methodology

The experiments were designed using CCRD for obtaining better dye removal % and a non-linear polynomial equation was obtained by fitting the actual value of independent variables data. The equation is:

$$\begin{aligned} Y = & (-515.5815 - 57.1525X_1 + 51.5712X_2 - 4.1360X_3 + 4.7636X_4 \\ & - 0.3545X_1X_2 + 0.1468X_1X_3 + 0.2288X_1X_4 + 0.0889X_2X_3 \\ & - 0.1666X_2X_4 + 0.0104X_3X_4 - 2.0870X_1^2 - 0.3831X_2^2 - 0.0026X_3^2 \\ & - 0.0090X_4^2) \end{aligned} \quad (27)$$

From the table representing the analysis of variance (ANOVA) Table 6 F-value and probability p-value was used to determine the significance of individual, interactive and quadratic term. The model can be supposed to be significant as it has 69.71 as the Model F-value. The model adequacy was determined by determination coefficient (R^2), adjusted R^2 , predicted R^2 , and predicted error sum of square (PRESS). With a value of 0.9849 for R^2 , it is clear that the model could explain 98.49% of the total variation. The value of the predicted R^2 is 0.9136, and the adjusted R^2 of 0.9707 is quite in reasonable agreement with each other. The three-dimensional (3D) response surface graphs is shown in Fig. 7. The interaction among the variables is shown in this graph, which is plotted based on the model equations. These graphs were plotted by taking two variables on the x and y axes and the response on the z axes, while the value of another variable was taken at its center. A strong interaction among the independent variables is visible in this plot. To obtain a maximum response, stationary points were determined to attain the optimum value of the independent variables. The stationary point was estimated by equating the first derivative of response to zero (Ganesh Moorthy I & Baskar R 2013).

$$y = \beta_0 + x'b + x'Bx \quad (28)$$

where

$$x = \begin{bmatrix} x_1 \\ x_2 \\ \vdots \\ x_k \end{bmatrix} \quad b = \begin{bmatrix} \beta_1 \\ \beta_2 \\ \vdots \\ \beta_k \end{bmatrix} \quad \text{and } B = \begin{bmatrix} & & & \beta_{1k}/2 \\ \beta_{11} & \beta_{12}/2 & \cdots & \beta_{1k}/2 \\ \text{sym.} & \beta_{22} & \ddots & \vdots \\ & & & \beta_{kk} \end{bmatrix}$$

in which b is a regression coefficient of the first-order vector (k x 1), B is a symmetric matrix (k x k) with a pure quadratic coefficient (β_{ij}) diagonal.

For finding the stationary points, the equation is equated as

$$\frac{\partial y}{\partial x} = b + 2Bx = 0 \quad (29)$$

The solution to equation no. 29 yields stationary points,

$$x_s = -\frac{1}{2}B^{-1}b \quad (30)$$

At the stationary point, the predicted response is given by equating equation no. 28 and 30

$$y_s = \beta_o + \frac{1}{2}x_s'bs \quad (30)$$

Adopting this procedure, for our equation no. 27 system we get,

$$x = \begin{bmatrix} x_1 \\ x_2 \\ x_3 \\ x_4 \end{bmatrix} \quad b = \begin{bmatrix} -57.1525 \\ 51.5713 \\ -4.1361 \\ 4.7636 \end{bmatrix} \quad \text{And } B = \begin{bmatrix} -2.0870 & -0.1772 & 0.0734 & 0.1144 \\ -0.1772 & -0.3832 & 0.0448 & -0.0831 \\ 0.0734 & 0.0448 & -0.00265 & 0.0521 \\ 0.1144 & -0.0831 & 0.0521 & -0.0090 \end{bmatrix}$$

the estimated stationary points was obtained by solving equation no. 9 by using the above values and the values of x_1 (pH) = 4.95, x_2 (adsorbent dosage) = 6.48 g/L, x_3 (dye concentration) = 68.68 ppm and x_4 (temperature) = 306 K. The maximum response (dye removal %) was found to be 96.67% at the stationary points.

3.11 Desorption study

The adsorption study was performed at a pH of 5; hence desorption study was performed at neutral to increase in alkaline condition (pH 7 to 12). It was observed that at higher alkaline condition (pH 11–12) maximum desorption of

CV dye adsorbed on the surface of AASCO occurs (95.12–97.35%) as shown in Fig. 6 (d). A similar trend was observed in the desorption of textile effluent dye adsorbed on the surface of chitosan (Kyzas et al. 2011).

To investigate the reuse of the adsorbent, desorption experiments were performed. It was found that the AASCO adsorbent could be reused for over 5 cycles with significant CV dye removal %, as presented in Fig. 6 (d: insert). The gradual decrease of CV dye removal % by AASCO can be attributed to reasons like degradation of the functional group over time in adsorbent material as it is subjected to salinity conditions at extreme pH or saturation of active sites by dye molecules (Maeda et al. 2019).

Conclusion

The present adsorption study has shown the feasibility of CV dye adsorption on the AASCO adsorbent. The batch adsorption experiment data was used in the study of adsorption kinetics and isotherm. AASCO with an adsorption capacity of 19.35 mg/g removed 96.78% of CV dye for an initial dye concentration of 100 ppm at 353 K, indicating excellent adsorption efficiency for CV dye removal, thus indicating the potential of activated adsorbent to remove the maximum quantity of dye molecules. Eyring and Arrhenius's equation was modified by the kinetic model equation Pseudo-second-order best fitted for the adsorption operation to yield thermodynamic parameters. The adsorption operation of CV dye molecules on the external surface of AASCO is a physical adsorption operation, as it has an activation energy of 9.561 kJ/mol. Change in Gibbs energy lies in the range 81.43 to 96.7 kJ/mol implies that energy is required for adsorption operation. Change in entropy – 254.4 J/ (mol K) indicates that the internal structure of AASCO adsorbent remains intact, and change in enthalpy 6.897 kJ/mol value suggests that the adsorption operation is endothermic. The adsorption-desorption reusability study indicated that the AASCO adsorbent could be reused for 5 cycles with higher CV dye removal efficiency. This study primarily suggests that the adsorption operation of CV dye molecules by AASCO adsorbent is a thermodynamically feasible process. A scale-up of the adsorption operation was theoretically investigated by designing a single-stage adsorber. Langmuir isotherm model was used, as it best fits the adsorption model. The design clearly showed that a relatively less quantity of adsorbent is required for treating a large quantity of CV dye molecules in an aqueous solution. These results thus indicate that the adsorbent used in the study AASCO is suitable potential adsorbent biomass that can be used to remove CV dye molecules in an aqueous solution.

Declarations

Author contribution

“All authors contributed to the study conception and design. Material preparation, data collection and analysis were performed by Michael Rahul Soosai, Innasi Muthu Ganesh Moorthy, Perumal Varalakshmi, Asad Syed, Abdallah Mohamed Elgorban, Sean Patrick Rigby, Sivrajasekar Natesan, Sathaiah Gunaseelan, Yonas Camy Joshya, Rajoo Baskar, Rajaram Shyam Kumar, and Sankar Karthikumar. The first draft of the manuscript was written by Michael Rahul Soosai and Innasi Muthu Ganesh Moorthy and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.”

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Data availability

"The datasets used and analysed during the current study are available from the corresponding author on reasonable request."

Ethics approval and consent to participate

"Not applicable."

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Tables

Table 1

RSM experimental design variables and their levels

Notation	Variables	Levels				
		- α	- 1	0	+ 1	+ α
X_1	pH	4	4.5	5	5.5	6
X_2	Adsorbent dosage (g/L)	5	6.25	7.5	8.75	10
X_3	Dye Concentration (ppm)	50	62.5	75	87.5	100
X_4	Temperature (K)	293	298	303	308	313

Table 2

Experimental design using RSM

Run Number	Coded Variables				Dye Removal %		Residual Value
	X ₁	X ₂	X ₃	X ₄	Experimental	Predicted	
1	-1	-1	-1	-1	97.19	97.14	0.05
2	1	-1	-1	-1	94.17	94.27	-0.11
3	-1	1	-1	-1	97.38	97.47	-0.09
4	1	1	-1	-1	93.88	93.71	0.17
5	-1	-1	1	-1	91.96	91.76	0.20
6	1	-1	1	-1	92.88	92.56	0.32
7	-1	1	1	-1	97.36	97.65	-0.29
8	1	1	1	-1	97.34	97.56	-0.22
9	-1	-1	-1	1	96.56	96.42	0.14
10	1	-1	-1	1	95.98	95.84	0.14
11	-1	1	-1	1	92.11	92.58	-0.47
12	1	1	-1	1	90.84	91.11	-0.27
13	-1	-1	1	1	93.32	93.64	-0.32
14	1	-1	1	1	96.74	96.73	0.01
15	-1	1	1	1	95.39	95.36	0.03
16	1	1	1	1	97.36	97.56	-0.20
17	-2	0	0	0	95.36	95.09	0.27
18	2	0	0	0	94.39	94.42	-0.04
19	0	-2	0	0	93.54	93.87	-0.33
20	0	2	0	0	95.59	95.03	0.56
21	0	0	-2	0	94.76	94.66	0.11
22	0	0	2	0	95.84	95.72	0.12
23	0	0	0	-2	96.18	96.31	-0.13
24	0	0	0	2	95.94	95.58	0.36
25	0	0	0	0	96.88	96.85	0.04
26	0	0	0	0	96.73	96.85	-0.12
27	0	0	0	0	96.89	96.85	0.05
28	0	0	0	0	96.88	96.85	0.03
29	0	0	0	0	96.83	96.85	-0.02
30	0	0	0	0	96.86	96.85	0.02

Table 3

Adsorption study kinetic parameter

	25 ppm	50 ppm	100 ppm	200 ppm
Pseudo-first-order kinetic model				
R^2	0.900 ± 0.06	0.906 ± 0.07	0.867 ± 0.10	0.845 ± 0.12
K_1 (L/min)	0.028 ± 0.01	0.026 ± 0.01	0.026 ± 0.01	0.027 ± 0.01
q_e (mg/g)	0.062 ± 0.11	0.130 ± 0.09	0.218 ± 0.07	0.481 ± 0.10
Pseudo-second-order kinetic model				
R^2	0.999 ± 0.001	0.999 ± 0.001	0.999 ± 0.001	0.999 ± 0.001
k_2 (g/g min) $\times 10^{-3}$	0.614 ± 0.004	0.310 ± 0.002	0.156 ± 0.001	0.079 ± 0.002
q_e (mg/g)	1.628 ± 0.06	3.225 ± 0.08	6.410 ± 0.06	12.65 ± 0.07
Elovich kinetic model				
R^2	0.720 ± 0.04	0.750 ± 0.05	0.699 ± 0.07	0.720 ± 0.05
$A \times 10^{16}$	134 ± 5.3	82.0 ± 9.1	73.6 ± 7.8	53.8 ± 6.2
B	32.25 ± 1.2	16.67 ± 1.3	7.518 ± 1.4	3.533 ± 1.1
Weber Morris intra particular diffusion kinetic model				
R^2	0.551 ± 0.12	0.583 ± 0.10	0.523 ± 0.09	0.51 ± 0.08
k_{id} (mg/g min ^{0.5})	1.54 ± 0.19	3.05 ± 0.14	6.04 ± 0.13	11.9 ± 0.15
C	0.007 ± 0.01	0.014 ± 0.01	0.03 ± 0.01	0.064 ± 0.01
q (mg/g) (exp)	1.623 ± 0.21	3.215 ± 0.25	6.379 ± 0.58	12.617 ± 0.96

Table 4

Isotherm parameters

Isotherm model	Parameter	Values of Isotherm Parameter		Chi-square error statics (x^2)		Root mean square error		R^2
		Linear Equation	Non-Linear Equation	Linear Equation	Non-Linear Equation	Linear Equation	Non-Linear Equation	
Langmuir	q_m (mg/g)	142.85 ± 31.45	98.47 ± 5.62	20.77 ± 2.25	29.98 ± 3.19	12.46 ± 1.21	26.84 ± 2.12	0.996 ± 0.02
	K_L (L/mg)	40 ± 9.86	24.21 ± 2.34					
Freundlich	K_F (L/mg) ($1/n$)	4.95 ± 1	3.5 ± 2.3	198.21 ± 17.3	219.48 ± 3.03	40.13 ± 2.97	30.3 ± 2.57	0.966 ± 0.07
	n (g/L)	1.35 ± 0.11	1.1 ± 0.4					
Temppkin	B_1 (mg/g)	19.33 ± 1.56	16.31 ± 3.4	87.19 ± 14.33	46.84 ± 2.4	20.33 ± 2.07	29.7 ± 3.19	0.987 ± 0.06
	A (L/mg)	1.93 ± 0.43	0.65 ± 0.22					
Dubin-Raduskevick	q_{mD} (mg/g)	482.99 ± 8.46	351.14 ± 20.5	421.5 ± 29.2	290.2 ± 28.4	98.11 ± 10.3	39.18 ± 2.84	0.947 ± 0.04
	β	3.25 ± 0.99	4.96 ± 0.51					

Table 5

Evaluation of thermodynamic property at various temperature

Temperature (K)	ΔG (kJ/mol)	ΔH (kJ/(mol))	ΔS J/(mol K)
293	81.43 ± 0.34	6.897 ± 0.05	-254.4 ± 7.84
313	86.52 ± 0.39		
333	91.61 ± 0.42		
353	96.70 ± 0.40		

Table 6

Analysis of Variance for percentage removal of dye.

Source	Sum of Squares	Degree of Freedom	Mean Square	F-Value	Probability -Value
Model	97.11	14.00	6.94	69.71	< 0.0001
X ₁	0.67	1.00	0.67	6.75	0.0202
X ₂	2.03	1.00	2.03	20.36	0.0004
X ₃	1.70	1.00	1.70	17.13	0.0009
X ₄	0.79	1.00	0.79	7.96	0.0129
X ₁ X ₂	0.79	1.00	0.79	7.90	0.0132
X ₁ X ₃	13.47	1.00	13.47	135.42	< 0.0001
X ₁ X ₄	5.24	1.00	5.24	52.62	< 0.0001
X ₂ X ₃	30.91	1.00	30.91	310.67	< 0.0001
X ₂ X ₄	17.35	1.00	17.35	174.40	< 0.0001
X ₃ X ₄	6.77	1.00	6.77	68.03	< 0.0001
X ₁ ²	7.47	1.00	7.47	75.04	< 0.0001
X ₂ ²	9.83	1.00	9.83	98.82	< 0.0001
X ₃ ²	4.70	1.00	4.70	47.24	< 0.0001
X ₄ ²	1.40	1.00	1.40	14.06	0.0019
Residual	1.49	15.00	0.10		
Lack of Fit	1.47	10.00	0.15	38.86	0.0004
Pure Error	0.02	5.00	0.00		
Cor Total	98.61	29.00			

Figures

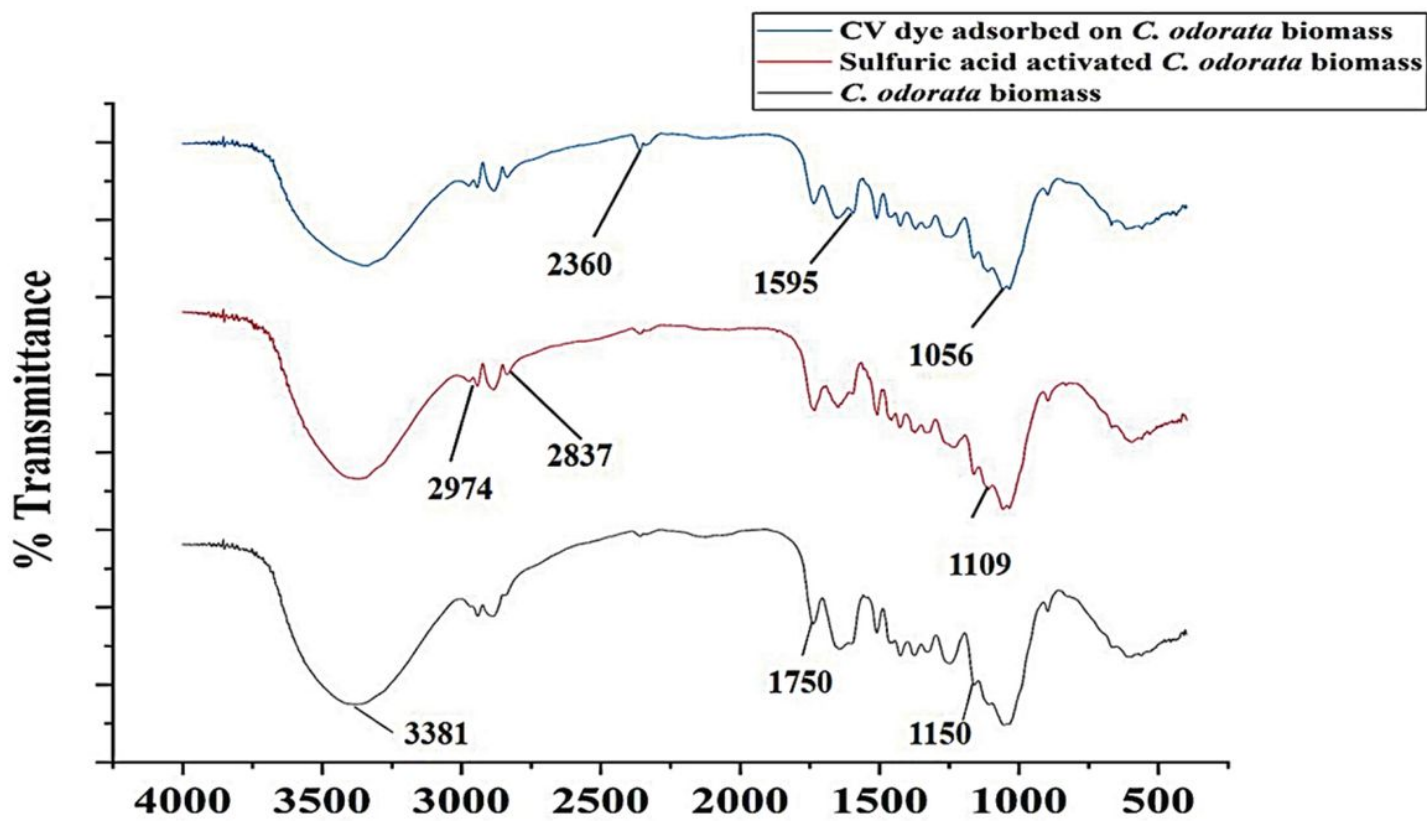


Figure 1

FTIR image of *C. odorata* biomass, Sulfuric acid activated *C. odorata* biomass and CV dye adsorbed on *C. odorata* biomass.

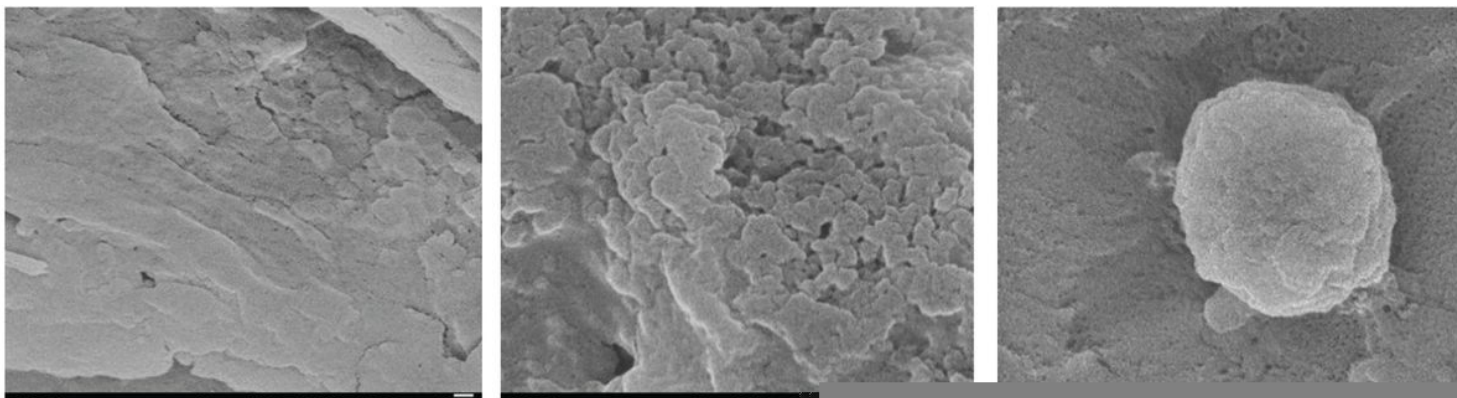


Figure 2

SEMs of (a) *C. odorata* biomass, (b) AASCO (c) CV dye adsorbed on AASCO and XRD spectrum of (a) *C. odorata* biomass, (b) AASCO (c) CV dye adsorbed on AASCO

Figure 3

(a) Adsorption-desorption isotherms of the AASCO using N₂, (b) Sorption isotherm by the Barrett–Joyner– Halenda (BJH) approach using N₂ to obtain pore size distribution.

Figure 4

Adsorption studies (a) Effect of increase in pH (b) Effect of increase in adsorption dosage (c) Effect of increase in initial dye concentration with time (d) Effect of increase in temperature

Figure 5

(a) Pseudo-first-order kinetic study for adsorption @ 313 K, (b) Pseudo-second-order kinetic study for adsorption @ 313 K, (c) Elovich model kinetic study for adsorption @ 313 K (d) Weber and Morris kinetic study for adsorption @ 313 K

Figure 6

(a) Langmuir isotherm study @ 313 k (b) Freundlich isotherm study @ 313 k (c) Tempkin isotherm study @ 313 k (d) Dubinin - Raduskevich isotherm study @ 313 k

Figure 7

Thermodynamic parameter determination (a) plot to determine activation Energy (b) plot drawn using Eyring equation

Figure 8

Design of Single stage batch adsorber

Figure 9

3D RSM plot showing the interaction effect of various selected variables on dye removal %. (a) temperature vs. dye concentration (b) temperature vs. adsorbent dosage (c) initial dye concentration vs. adsorbent dosage (d) temperature vs. pH (e) dye concentration vs. pH (f) adsorbent dosage vs. pH. In all the panels two factors were kept at its center level, and two factor on x and y axes were varied

Figure 10

(a) Effect of pH on desorption of dye (b) Adsorption-Desorption cycle for AASCO adsorbent