Adsorptive Studies for the Removal of Crystal Violet Dye from Aqueous Solution by using Cicca acida L. Stem - Activated Carbon

SHARMILA RAMASAMY¹, ANBARASU KALIYAPERUMAL¹* and THAMILARASU POMMANAICKAR²

¹Department of Chemistry, Arignar Anna Government Arts College, Musiri, Affiliated to Bharathidasan University, Tiruchirappalli – 620 024, Tamilnadu, India.
²Department of Chemistry, Arignar Anna Government Arts College, Namakkal – 637 002, Tamilnadu, India.

Abstract
Textile industries discharge wastewater containing various dyes including Crystal Violet dye. These dyes are very harmful for human beings, animals and plants. Therefore, the attempt is made for adsorption framework on elimination of crystal violet dye by using Cicca acida L. stem-activated carbon from aqueous solution carried out under various experimental methods and optimization conditions. Adsorption data modeled with Freundlich, Langmuir and Tempkin adsorption isotherms. Thermodynamic factors like as ∆H°, ∆S° and ∆G° were calculated, which indicated that the adsorption was spontaneous and endothermic nature. Based on kinetic study, pseudo-second order kinetic model was fit compared to the pseudo-first order kinetic model. The adsorbent has been characterized by SEM before and after adsorption of crystal violet dye solution.

Introduction
Various developed productions comparable dyes, plastics, textiles and paper productions using dyes in direction to colour produces too ingest considerable progression of water. As a consequence it types a significant quantity of coloured wastewater. It devises improved concerning the long period of poisonous outcome of water covering these liquefied contaminants. Dyes holding wastewater is frequently unconfined straight into the adjoining stagnant ponds, drains and river. Such wastewater discarding to environment, to polluting water bodies, the water eco-system and biodiversity of water atmosphere.¹ Existence of lesser quantity of colorants (less than 1ppm) is extremely noticeable; objectionable
besides essentials to be separate earlier the wastewater can be liquidated into the atmosphere. It is challenging to confiscate the colorants from the industrialized waste, since colorants are not simply degradable. Exploration towards period includes several approaches to eliminate dyes remained systematically considered such as coagulation, adsorption, photo-oxidation, nano-filtration, ultra-filtration, flocculation, adsorption on triggered carbon, etc. But the system remains precise costly. Consequence, different environmental-friendly proficiency has developed an essential for the colour production. Amongst these systems, adsorption is a broadly used for colorant elimination from fabric wastewater\textsuperscript{4} Ground triggered carbon or pulverised triggered carbon is normally recycled for colorant deletion.\textsuperscript{5,6} Hence, the usage of some low price adsorbents devises has been considered as several studies. They must be considered as probability of consuming low price ingredients such as waste orange peel,\textsuperscript{7} lemon peel,\textsuperscript{8} banana pith, bentonite clay, powdered activated sludge, neem leaf powder, perlite; bamboo dust, duck weed, algae, straw, sewage sludge, etc.

Adsorbents are commonly recycled for its Environmental-friendly behaviour, availability in environment besides are very considerable charge effective. It can be remain recycled an effectual besides charge effective bio-adsorbent for removing colorants from industrialized effluents.\textsuperscript{9} In addition, unrefined sawdust is substitute an adsorbent for plenty environment, non-poisonousness and biodegradability.\textsuperscript{10} Mostly, maximum generally recycled adsorbent for colorant removal activated carbon, since of its high surface zone besides ability for proficiently adsorbing wide variety of different kind’s adsorbates.\textsuperscript{11} However, usage remains partial as high price and renewal price stands equally very high. Hence, usage in behaviour of wastewater might remain sparingly not feasible. An essential to learning the absorptive features of little cost adsorbents,\textsuperscript{12} Usage of non-conventional adsorbents, mainly stand for certainly renewed, change activated carbon in elimination of colorant from wastewater has mentioned.

Total adsorbent may subsidise near the sustainability of the atmosphere and offer encouraging profits for the feasible resolution in imminent. Plenty of besides little rate of agrarian derivatives and hopeless houseplant supplies marks them righteous precursor for grounding of activated carbon. Activated carbon previously equipped from agrarian surplus and spare houseplant supplies like peanut hull,\textsuperscript{13} rice husk,\textsuperscript{14} orange waste,\textsuperscript{15} cashew nutshells,\textsuperscript{16} tobacco stem ash,\textsuperscript{17} coffee husks,\textsuperscript{18} saw dust,\textsuperscript{19} palm kernel coat,\textsuperscript{20} eucalyptus bark,\textsuperscript{21} corncob,\textsuperscript{22} pine saw dust,\textsuperscript{23} modified mango seed,\textsuperscript{24} babool wood,\textsuperscript{25} etc. The rate of activated carbon armed from remaining provisions is insignificant related to the profitable activated carbon. Amongst several industries that donate colored effluent, textile, dye manufacturing, paper and pulp, tanneries are the most.\textsuperscript{26}

Based on the above literature review, the carbonized Cicca acida L. stem activated carbon (CASAC) is cheap and low cost material obtained from the local area and used to study adsorption of Crystal Violet dye (CVD) from aqueous solutions.

Materials and Methods

Materials
The Crystal Violet dye (E-Merck) aqueous solution was used as adsorbate and Cicca acida L. stem activated carbon was used as adsorbent. Entirely, the chemicals were recycled for these revisions are commercially obtainable Anala R grade (E-Merck and SD-fine, India).

Methods
Activated carbon was prepared from Cicca acida L. stem activated carbon and this uncooked solid was acquired from a resident vendor. The solid material was washed with hot distilled water to eliminate the earthy matter, cut into lesser sizes and dehydrated up. The activated carbon was organized the exceeding materials soaked through Concentrated H$_2$SO$_4$. For soaked, a share of 0.5:1 of acid volume and weight of the material occupied. Afterward, the burnt solid material cleaned some times in distilled H$_2$O until, pH of washing befits impartial. Then solid material was dehydrated and carbonized at 350°C expending muffle furnace (Techno). Lastly, it ground and sieved the activated carbon used for further studies.

A standard aqueous solution of the adsorbate comprising 1000 mg/L of dye solution arranged through dissolving well-known quantity of Crystal Violet Dye (CVD) in twice purified H$_2$O. Doubly purified liquid was recycled during the experimentations. The
adsorption experimentations remained accepted in consignment symmetry process. 100 mg of adsorbent taken in the iodine flask and added 100 ml of known concentration of CVD solution and mixture was agitated with different time intervals in hotness regulator water-bath shaker (Techno). The solutions centrifuged at systematic intermissions besides remaining concentration of CVD solution existing in filtrate at every time was determined by using Spectrophotometer (Systronics 169 model) at 592 nm. The experiments were continual by three dissimilar temperatures viz., 303, 313 and 323K for confiscation of CVD solution. The adsorption study was characterized by using Fourier Transform Infrared Spectroscopic (FTIR) and Scanning Electron Microscopic (SEM) Study.

Results and Discussion

Effect of Adsorbent Dosage, pH and Agitation Time

These experiments remained completed by expending from 50 mg to 200 mg of adsorbent, 100 ml of 20 mg/L of CVD solution and agitation of various time intervals. Results indicated the optimum dosage was static as 100 mg owed to the measure of dye uptake was high; the optimal pH was static as 8 owing towards extreme confiscation of CVD solution and pHzpc value is 5.74. All the experiments conducted at optimal agitation time of 50 min.

Effect of Initial Concentration and Temperature

Table 3.1 showing that, the quantity of CVD adsorbed (qe) rises with the removal percentage falls while increasing the initial concentration of CVD, because of relatively greater driving force for mass transfer. At greater concentrations of dye solution, dye removal decreased, due to reduced obtain ability of active sites on surface of CASAC as such as mass transfer resistances between aqueous solution and solid phase.

The removal of CVD percentage increases from 30°C to 50°C, the process of adsorption probably endothermic nature. These results showed that, avoidance tendency of CVD from solid phase to bulk phase, due to electrostatic interaction between active sites of adsorbent and adsorbate species.

| Initial Conc. of CVD(C₀), mg/L | Equilibrium Conc. of CVD (Cₑ), mg/L | CVD adsorbed quantity at equilibrium (qₑ), mg/g | Removal of CVD (%) |
|--------------------------------|-----------------------------------|-----------------------------------------------|--------------------|
|                               | 30°C | 40°C | 50°C | 30°C | 40°C | 50°C | 30°C | 40°C | 50°C |
| 20                             | 4.136 | 2.500 | 1.046 | 15.86 | 17.50 | 18.95 | 79.32 | 87.50 | 94.77 |
| 40                             | 10.046 | 7.864 | 3.773 | 29.95 | 32.14 | 36.23 | 74.89 | 80.34 | 90.57 |
| 60                             | 18.318 | 15.636 | 9.227 | 41.68 | 44.36 | 50.77 | 69.47 | 73.94 | 84.62 |
| 80                             | 28.091 | 23.773 | 15.818 | 51.91 | 56.23 | 64.18 | 64.89 | 70.28 | 80.23 |
| 100                            | 39.364 | 36.136 | 27.546 | 60.64 | 63.86 | 72.45 | 60.64 | 63.86 | 72.45 |

Adsorption Isotherms

The results of adsorption are generally defined and modelled based on adsorption isotherms. It refers to quantity of colorant adsorbed per unit weight of adsorbent to symmetry concentration of bulk phase. The linear form of Langmuir model\textsuperscript{29} and Freundlich equation\textsuperscript{30} is used to study the adsorption isotherm.

The monolayer adsorption capacity (Qₒ) values decreases with temperature, signifying that adsorption is favoured at lower temperature. It can be recognized that dyes diffuse into adsorbent at slower rate with temperature increases. The energy of adsorption (bₒ) values suggests the affinities of binding sites with dyes are favourable. The values of adsorption capacity (kₒ) increased with temperature from 30°C to 50°C. This shown adsorption is preferred at higher concentration. The adsorption intensity (n) values slightly changes when temperature increases. The values of n were found to be 2. The values of all n are > 1, indicating favourable adsorption. Tempkin isotherm revealed the equilibrium binding constant readings and heat
of adsorption readings are shown to lowest binding energy and lowest heat of adsorption by adsorption of CVD. The adsorption equilibrium data was presented in figure 3.1, figure 3.2. and table 3.2.

Table 3.2: Results for Adsorption Isotherm Models

| Temp. (ºC) | Langmuir Isotherm | Freundlich Isotherm | Tempkin Isotherm |
|------------|-------------------|---------------------|------------------|
|            | Correlation       | Constants           | Correlation      | Constants           | Correlation | Constants |
|            | Coefficient       | (mg/g)              | Coefficient      | (L/mg)              | Coefficient | (kJ mol⁻¹) |
| r²         | Q₀                 | bL                  | r²               | kᵢ                 | n           | r²        |
| 30         | 0.998             | 90.909              | 0.995            | 7.161              | 1.684       | 0.995     |
|            | 0.049             |                     |                  | 13.865             |             | 45.462    |
| 40         | 0.993             | 82.645              | 0.998            | 11.361             | 2.026       | 0.989     |
|            | 0.088             |                     |                  | 14.965             |             | 40.378    |
| 50         | 0.997             | 84.034              | 0.994            | 19.611             | 2.404       | 0.995     |
|            | 0.212             |                     |                  | 16.353             |             | 38.289    |

Fig. 3.1: Langmuir Adsorption Plot  
Fig. 3.2: Freundlich Adsorption Plot

Table 3.3: Thermodynamic Parameters

| C₀ (mg/L) | K₀            | ΔG°(kJ mol⁻¹) | ΔH°(kJ mol⁻¹) | ΔS°(J K⁻¹ mol⁻¹) |
|-----------|---------------|---------------|---------------|------------------|
| 20        | 3.84          | -3.39         | 63.02         | 218.58           |
| 40        | 0.98          | -2.75         | 47.32         | 164.53           |
| 60        | 2.28          | -2.07         | 35.72         | 124.13           |
| 80        | 1.85          | -1.55         | 31.87         | 109.83           |
| 100       | 1.54          | -1.09         | 21.65         | 74.66            |

Thermodynamic Parameters

The equilibrium constants, standard ΔG, ΔH and ΔS changes were shown in table 3.3. Based on above parameters, the endothermic process of adsorption showed by rises in K₀ with increasing temperature. The results showed the standard free energy values increase with increasing initial CVD concentration. The standard ΔG values negative, adsorption process is spontaneous. The ΔH change observed from 21.65 to 63.02 kJ mol⁻¹ for adsorption of CVD on CASAC. The standard enthalpy values are positive, suggested adsorption method is endothermic nature. Standard entropy values for the adsorption method are positive which was the
range from 74.66 to 218.58 JK\(^{-1}\) mol\(^{-1}\) for adsorption of CVD. It suggested that high degree of randomness at solid-solution interface by adsorption of CVD on CASAC. The activation energy of the adsorption of CVD on CASAC was found to be 9.2549 kJ/mol/K.

### Table 3.4: Pseudo-first and Pseudo-second order kinetic models

| \(C_0\) (mg/L) | \(q_s^{(exp)}\) (mg/g) | \(q_s^{(cal)}\) (mg/g) | \(k_1\) (min\(^{-1}\)) | \(r^2\) | \(P\) | \(q_s^{(cal)}\) (mg/g) | \(k_2\) (g mg\(^{-1}\) min\(^{-1}\)) | \(r^2\) | \(P\) |
|----------------|------------------------|------------------------|-----------------|------|-----|------------------------|-----------------|------|-----|
| 20             | 15.864                 | 1.478                  | 0.048           | 0.971| 90.681| 16.077                 | 0.069           | 0.999| 1.328|
| 40             | 29.955                 | 5.329                  | 0.071           | 0.987| 82.207| 30.487                 | 0.029           | 0.999| 1.749|
| 60             | 41.682                 | 3.377                  | 0.021           | 0.974| 91.896| 42.553                 | 0.015           | 0.999| 2.047|
| 80             | 51.909                 | 7.490                  | 0.049           | 0.897| 85.571| 53.191                 | 0.012           | 0.999| 2.411|
| 100            | 60.636                 | 8.124                  | 0.032           | 0.935| 86.601| 62.112                 | 0.008           | 0.999| 2.375|

**Fig. 3.3: Pseudo-second order kinetic plot**

**Adsorption Kinetics**

To study Lagergren pseudo-first order and pseudo-second order adsorption kinetic models were used by adsorption data. The outcomes presented table 3.4 and figure 3.3. The correlation coefficient \((r^2)\) of kinetics of pseudo-second order found to be 0.999. From the values of correlation coefficient and less percentage of deviation, this was showed that the pseudo-second order kinetic plot fit superior to the pseudo-first order kinetic plot.

**Scanning Electron Microscopic Studies**

The SEM photographs of CASAC before and after adsorption of CVD are showed in the figures 3.4 and 3.5. It was evidently stated that presence of porous structure of adsorbent before adsorption. It has caves and holes type of openings on surface which might absolutely raise the surface area. After adsorption of CVD, SEM photographs are obviously shown the surfaces of CASAC are covered by CVD. This has clearly indicated that adsorbent structure was changed by adsorption of CVD.
Fourier Transform Infrared Spectroscopic (FTIR) Studies

The CASAC spectrum of before adsorption (figure not shown) at 3412 cm⁻¹ specified the existence of –OH groups of activated carbon. The aromatic –CH stretching group at 2920 cm⁻¹ specified the existence of –CO stretching group of aldehydes. The peak at 1591 cm⁻¹ specified the N-H bending of primary amines and -C-C stretching of aromatic groups. The region at 1380 cm⁻¹ specified –CH stretching of alkanes group. The region at 1118 cm⁻¹ indicated C-N stretching of aliphatic amines. After adsorption, there is a small shift in wave number of the peaks and some of the peaks are shown in FTIR spectrum. It showed that these active groups are responsible for participation of adsorption of CVD on CASAC.

Conclusion

The Cicca acida L. stem-activated carbon (CASAC) is locally available, environmental friendly and low cost material. It was used as prospective adsorbent for removal of Crystal Violet Dye in aqueous solution. The optimum adsorbent dosage is 100 mg, optimum pH is 8, and optimum contact time is 50 min used for removal of CVD. The Freundlich, Langmuir and Tempkin adsorption isotherm models described the adsorption behaviour of CVD on CASAC. The pseudo-second order kinetic model more fit related to pseudo-first order kinetic model. The percentage removal of CVD was raised with increase in the temperature from 30 to 50°C. The adsorption of CVD was confirmed by using before and after SEM studies. The future perspectives and challenges are to be done the recovery of spent activated carbon and adsorbate.

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Conflict of Interest

The authors do not have any conflict of interest.

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