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Biosorptive removal of Congo red on to Caulpera Sp. from aqueous solution: Kinetic and isothermal investigations

G Arvind[2], M Venkata Tharun[2], K Parveen Kumar Reddy[2], P Kishore Kumar Reddy[2], S Sumithra[1*]
[1] Department of Environmental Science. Yogi Vemana University, Kadapa, Andhra Pradesh, India
[2] Department of Civil Engineering, K. S. R. M. College of Engineering, Kadapa, Andhra Pradesh, India

Abstract
Caulerpa species were used to study the removal of toxic dye from aqueous solution. Experiment were carried out in batch mode and an influencing parameters such as adsorbent dosage, contact time, solution pH and desorption were described. The adsorption capacity was found to be 55. 56 mg/L and better fit with Langmuir isotherm. The adsorbent were characterized via SEM, FTIR and XRD techniques. The experimental data were applied to first and second order kinetics. pH study were performed ranging from 3 – 11. Higher adsorption capacity pointed towards usage of the unwanted material as an efficient adsorbent for the removal of congo red.

Keywords: Caulerpa species, Langmuir, Isotherm, Second order kinetics, Congo red

Introduction

The dying industries effluent has many environmental issues that include high chemical oxygen demand (COD), suspended solids, toxic compounds etc. (Alam *et al*. 2015) [1]. The major issue of paramount concern to dyes industry is that, due to their complex chemical structure, many dyes are toxic and bio - recalcitrant and the problem is further aggravated from the presence of aromatic rings in their structure (Sasmal *et al*. 2017; Miandad *et al*. 2018) [14, 7]. Dyes have been classified according to their chemical structures, that influence their characteristics and are divided as both anionic and cationic dyes (Chiu et. al 2019) [3].

Congo red dye (CR) is a non biodegradable anionic dye used widely in printing, silk, textile and wool industries and due to its high solubility and stability, while it is also used in histology, is the standard agent for the diagnosis of amyloidosis and act as a pH indicator (Ziane *et al*. 2018; Sasmal *et al*. 2017) [16, 14]. Congo red, an ago dye that metabolises to benzidine which poses great risk to human health and aquatic ecosystems, even at low concentrations, such as inhibition of plant growth, kidney disease and carcinogenicity (Na Hu *et al*. 2023) [9]. Congo red is amongst main culprits of skin and eye irritation, vomiting, diarrhoea, gastrointestinal irritation, blood clotting, somnolence and breathing problems (Rasilingwani *et al*. 2024; Semwal *et al*. 2023) [12, 15].

Congo red is difficult to degrade under natural conditions because of its stable and complex aromatic molecular structure. A small quantity of dye (1.0 mg/L) in water is detectable and objectionable (Rehman *et al*. 2018) [13]. However dyes remain in the environment for a long period and have negative effects on the flora and fauna. Therefore there is an urgent need for the removal Congo red dye from aqueous solutions. The removal of Congo red dye from wastewater has been adopted by a variety of techniques such as membrane separation, coagulation, ultrafiltration, reverse osmosis, ion -exchange and adsorption (Mishra *et al*. 2021) [8]. Adsorption as a fast rising to the forefront of treatment techniques for handling dye contaminated aqueous effluent.
In this study Caulerpa species was utilized for treating wastewater containing Congo red. Isotherm analysis was performed for 3 models and 2 kinetic studies were examined for better fit. Characteization of the adsorbent was done to determine the surface and functional groups that are possibly involved in adsorption of Congo red to the adsorbent.

Methodology

Preparation of adsorbent: The Caulerpa species was obtained from the marine environment. This species was cut into smaller sizes, and then it was dried using hot air oven, and crushed using a crusher or grinder to obtain a uniform powder form. The powder was then sieved for uniform particle size of 60 um.

Caulerpa Species **Caulerpa Species Powder**

Preparation of Dye solutions

Accurately 1000 mg of the congo red dye was separately weighed and made up to 1000 ml in a standard measuring flask to obtain a dye solution of 1000 ppm. These were kept as stock solutions. The absorbance was measured by using Lab India UV-Vis spectrophotometer, and the maximum absorbance of the dye was found to be 497 nm for the used dye congo red.

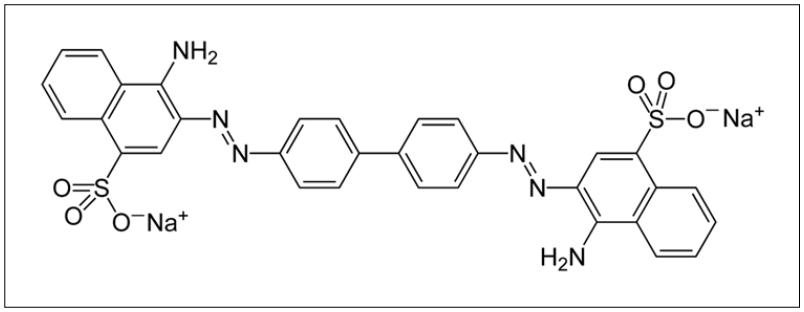

Fig 1: Structure of Congo Red

Results and discussion

Characteristics of the adsorbent:

The morphological features of the biosorbent surface were analysed by SEM, XRD and FTIR. Figure 2 depicts after adsorption with congo red, the surface appearance changes to become smoother and acquire flaky patches. The Fourier transform infrared spectroscopy of Caulerpa species are given in Fig. 3 indicating the presence of functional groups and bands onto the adsorbent. The existences of the C-N length of the aliphatic amines were confirmed by the peak at 1034 cm^{-1} which are shifted to1032 after congo red treatment. Figure 4 show the X- ray diffraction spectrum of the adsorbent. The intensity of the adsorbent started at 20 degrees. A broad peak was observed at 32 degrees in the adsorbent and the peak was disappeared after treatment with dye solution.

Before Adsorption

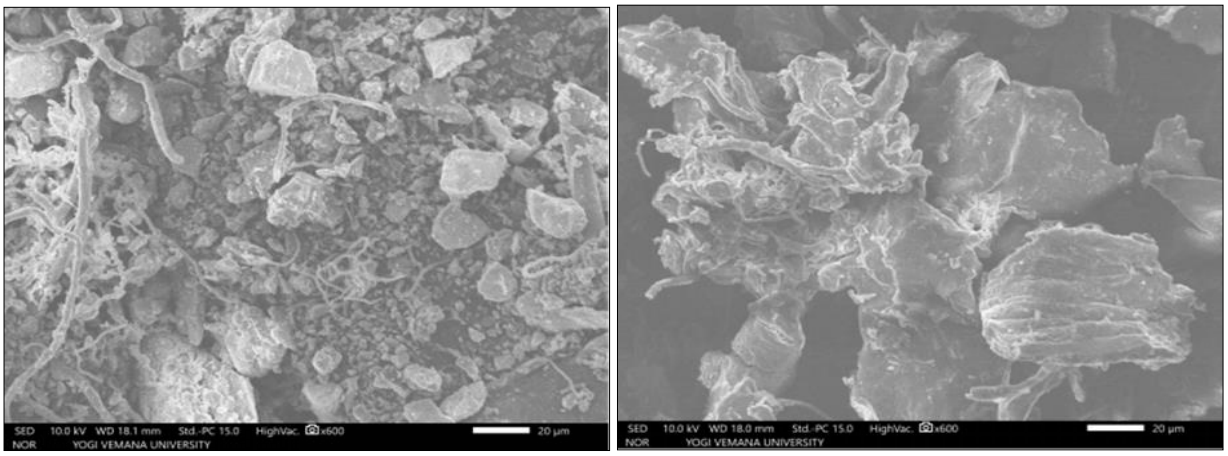

Fig 2: SEM photographs

After adsorption

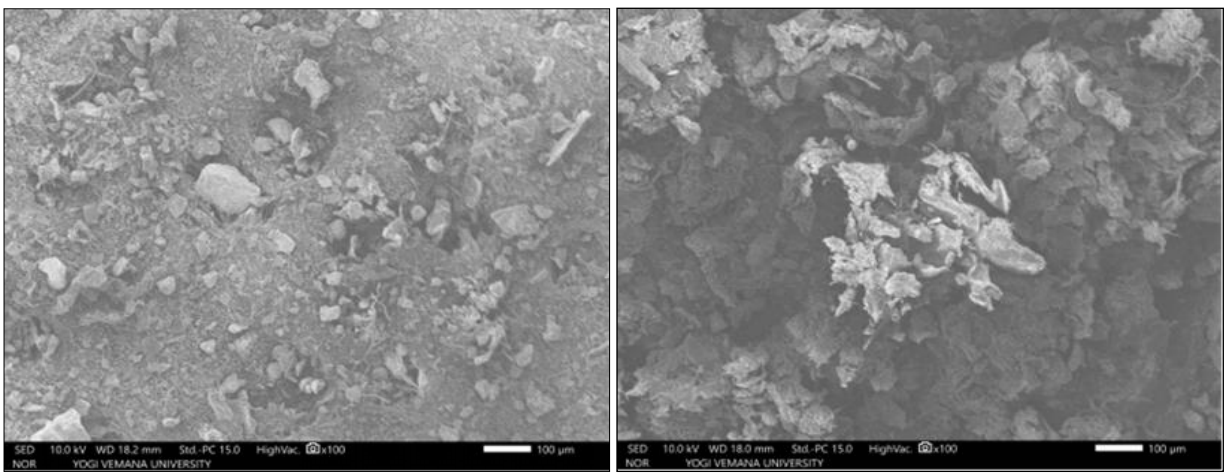

Fig 3: Exhibits the diffraction patterns of both materials

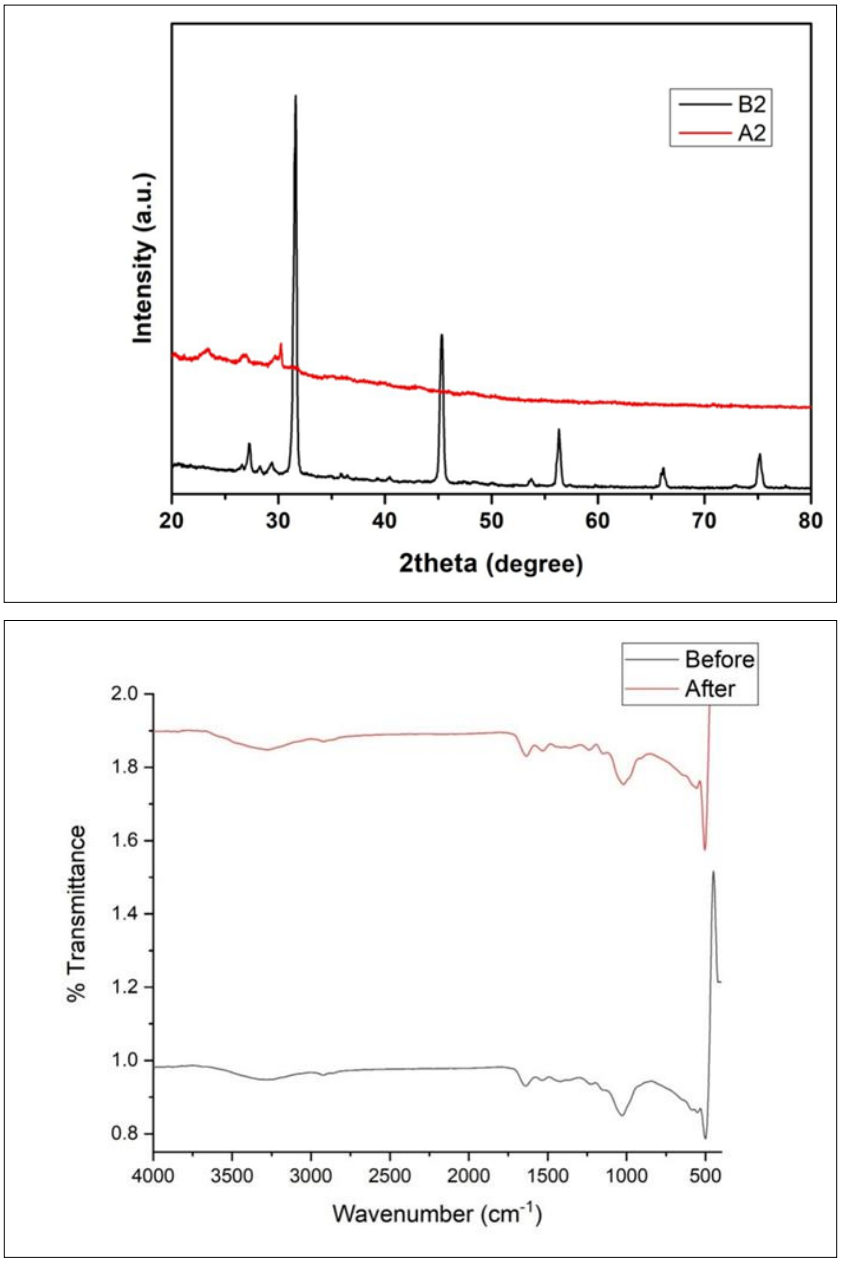

Fig 4: FTIR Spectra of before and after congo red by Caulerpa species.

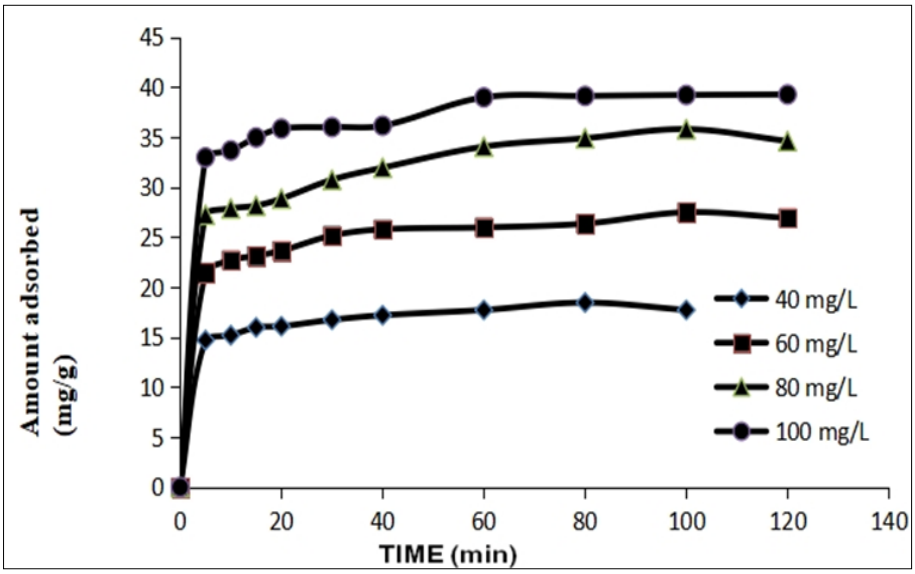

Fig 5: Influence of contact time on congo red adsorption studies.

Batch adsorption process

The effect of the various parameters such as dosage, agitation time, pH and desorption were studied.

The increase in concentration has a biggest impact on the removal of congo red. The equilibrium time increased with the increase in the initial concentration of congo red (Fig. 5). The equilibrium uptake of congo red (q_e) was 17.714 mg/g at 32°C for an initial concentration of 40 mg/L.

Adsorption Kinetics

The adsorption kinetic tests were carried out for different time intervals by using the dye concentrations of 40, 60, 80 and 100 mg/L. The uptake of congo red onto Caulerpa species was determined by fitting the experimental data to the two different kinetic models such as first order and second order kinetics. The coefficients and linear expressions of the above said kinetic models are reported in Table 1 and the adsorption of congo red by Caulerpa species obeyed second order kinetics with an R^2 value of 0.999 for 40 and 100 mg/L. As well as the q_e values estimated by the second order kinetics were closely similar to that of the experimental data. Kinetics study for the adsorption process is important as it provides theoretical information on possible mechanisms for the application of adsorbents on an industrial scale. Similar studies were recorded in the adsorption of congo red onto black cardamom activated carbon (Ahmad Aftab *et al*. 2023) [2], onto Ag –Cu- CeO_2 nanocomposites (Semwal *et al*. 2023) [15].

Table 1: Comparing the first order and second order model for adsorption of Congo Red.

Initial conc. (mg/L)	q_e (exp) (mg/g)	First order kinetics			Second order kinetics		
		k_1 (1/min)	q_e (cal) (mg/g)	R^2	k_2 (g/mg/min)	q_e (cal) (mg/g)	R^2
40	17.714	0.048	3.981	0.987	0.037	17.857	0.999
60	25.965	0.088	9.204	0.936	0.019	27.027	0.998
80	34.876	0.039	11.561	0.942	0.009	35.714	0.996
100	38.96	0.018	5.662	0.873	0.027	38.462	0.999

Adsorption Isotherm

Adsorption isotherms for the experimental data were analyzed by employing the Langmuir, Freundlich, and D – R isotherm models and are depicted in the fig 6. Langmuir isotherm considers a monolayer adsorption at homogenous surfaces of the adsorbent; on the other hand Freundlich isotherm is suitable to heterogeneous surfaces for adsorption and involves multilayer adsorption.

D – R isotherm is primarily applied to calculating the free energy on adsorbent surface.

Among the three studied isotherms the coefficients of determination (R^2 = 0.953) obtained for the adsorption of congo red showed better agreement with the Langmuir isotherm. The adsorption capacity was found to be 55.56 mg/g (Table 2). The adsorption capacity of congo red onto activated teak leaf powder is 33.33 mg/g (Gedam *et al*. 2019) [5] onto Litchi seed are 20.49 mg/g (Edokpayi and Makete 2021) [4] onto Solanum tuberosum peels and Pisum sativam peels are 6.9 and 16.6 mg/g (Rehman *et al*. 2018) [13] and onto fly ash are 22.12 mg/g (Harja *et al*. 2022) [6] respectively.

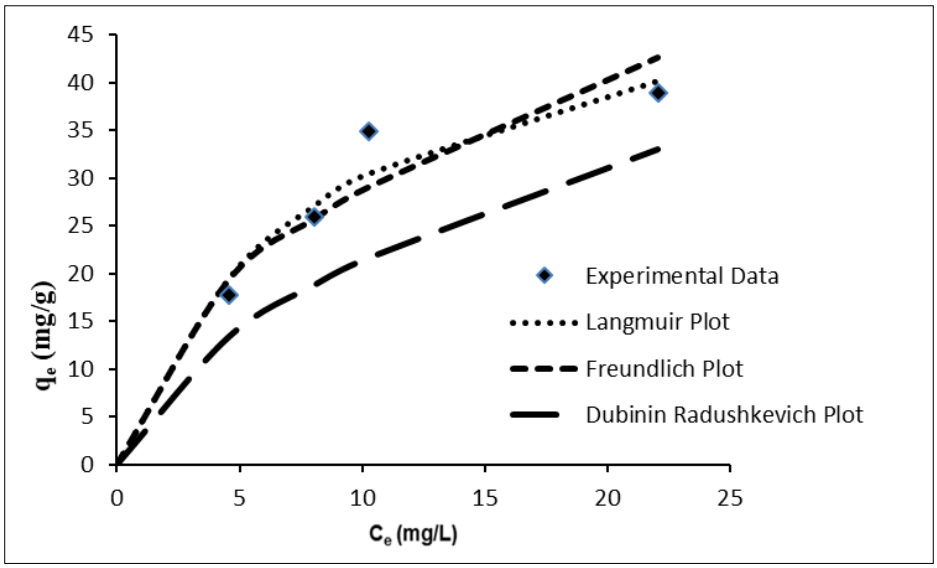

Fig 6: Adsorption isotherms of Congo Red

Table 2: Isotherm constant for the adsorption of Congo Red.

Langmuir Isotherm			Freundlich Isotherm		
Q_0 (mg/g)	b (L/mg)		k_f ($mg^{1-1/n}\ L^{1/n}\ g^{-1}$)	n	R^2
55.56	0.118	0.175	9.036	1.996	0.863
		0.124			
		0.096			
		0.078			

Influence of Adsorbent dosage

The amount of adsorbent dosage varied from 20 – 300 mg and the removal efficiency increased from 33.19 % to 93.06 % for 60 mg/L. As the adsorbent used is increased there is increase in the removal of congo red which can be explained that a greater quantity of adsorbent creates more surface area to bind the congo red molecules. Similar results were investigated for the congo red removal by egg shell membrane (Parvin *et al*. 2019) [10].

Influence of pH

The solution of the congo red dye changes its colour from dark blue to red at acidic and alkaline pH. The effect of pH on congo red dye removal was studied at pH 3 -11 as depicted in fig 7. Figure 7 showed that the amount of dye adsorbed was decreased from 87.39 to 50.1 for 60 mg/L. This was mainly attributed due to the pH_{ZPC} of the adsorbent which were reported to be 7.4. This signifies that the charge facilities electrostatic attraction between the negatively charged anionic congo red dye and positive charge of the adsorbent surface. This is in accord to the findings of removal of congo red by fish bone powder (Parvin *et al.* 2021) [11].

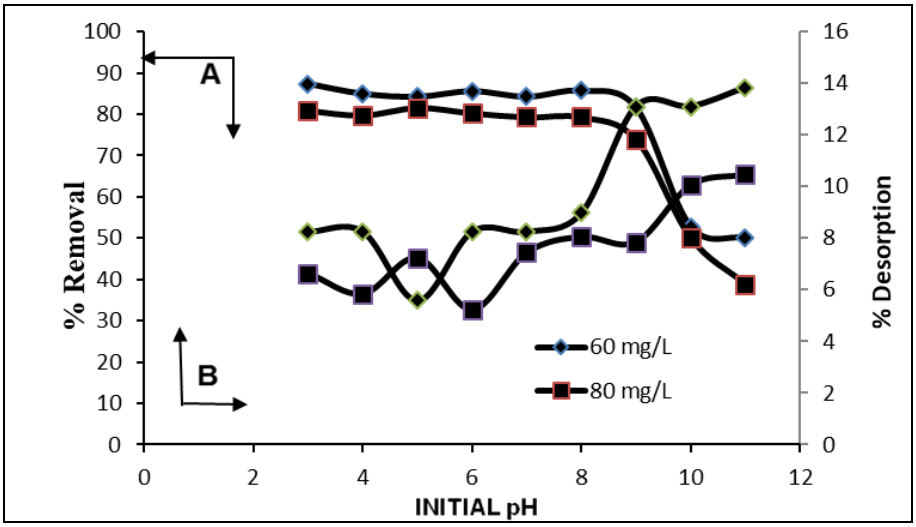

Fig 7: Impact of pH on adsorption and desorption of Congo Red

Study of desorption and regeneration

Desorption of the adsorbent is one of the factor in evaluating the adsorption process viability in terms of both economical and practical use. During the process the dye molecules are liberated from the surface of the adsorbent. The desorption percentage was found to increase from 8.25 to 13.83 % for 60 mg/L. The regeneration study of the Caulerpa species adsorbent decides the cost and process efficiency.

Conclusion

The percent removal of congo red exponentially increases with increase in dose of the adsorbent. The SEM photograph assigned fully covered pores in the after adsorption of congo red dye molecule that supported the adsorption process. It was investigated that Langmuir isotherm model fitted well for the adsorption of congo red and the kinetic study disclose that the adsorption studies obeyed the pseudo – second order kinetics. The maximum percentage removal of congo red was observed at pH 6.25. With the present study we can say that Caulerpa Species have an ability to treat the dye from aqueous solution.

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