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Batch and continuous adsorption of crystal violet and congo red by raw coconut fiber

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In this study, raw coconut fiber (*Cocosnucifera*) was employed as an adsorbent for elimination of cationic dye and anionic dye viz. crystal violet (CV) and congo red (CR) respectively. Batch adsorption experiments were performed at identical conditions to understand the impact of parameters viz. initial concentration (6 to 100 mg/L), adsorbent dosage (0.05 to 3.5 g), contact time (10 to 150 min), pH (3 to 11) over adsorption. Experimental results revealed that the maximum CV removal of 99% was obtained at pH 11 and CR removal of 82% at pH 3. The equilibrium data was best denoted by Langmuir isotherm demonstrating monolayer deposition with maximum adsorption capacity of 32.8 mg/g for CV and 27.6 mg/g for CR at 50°C. The kinetic study results shows that the adsorption of CV and CR is well described by pseudo-second order model by R^2 value (>0.99). Degree of crystallinity and functional groups of the adsorbent were analyzed using XRD and FTIR respectively. The results suggest that raw coconut fiber showed strong adsorption for cationic dye than anionic dye. Continuous adsorption study was additionally performed in order to check the feasibility of the adsorbent if employed practically.

Keywords: Raw coconut fiber, crystal violet, congo red, column study.

Introduction

Dyes are water soluble or water dispersible organic compound. Synthetic dyes are utilized in various industries, for example, food processing, plastics, cosmetics, textile, biomedicines, paper and pulp, ceramics, paints etc. Textile industries are the major consumer of synthetic dyes. Synthetic dyes are said to have biologically resistive nature having complex chemical structure which are not easy to break[1]. Even 1 ppm concentration of synthetic dyes in water bodies is not fit for the environment and human consumption[2]. Occurrence of dyes in water bodies hinders the photosynthesis action of aquatic biota. On inhalation, dyes can give rise to various health problems such as nausea, diarrhea, vomiting and gastritis. Thus, it is necessary to eliminate the dyes from the effluent stream before their final disposal.

There are distinct methods used for treatment of effluents coming out of different industries but only few are found effective namely adsorption and photochemical degradation. However, adsorption has gained interest because of low energy and maintenance cost, simplicity and reliability, limited amount of supervision and maintenance is needed and is highly efficient.

Though there are lots of literatures available for the removal of dye using adsorption, comparative study in the removal of anionic and cationic dye using adsorption is not comprehensively studied yet. The purpose of this study is to estimate the removal efficiency of the two dyes which differs in nuclear structure using raw coconut fiber (RCF) as adsorbent.

Materials and methods

Coconut husk obtained locally was washed many times in order to remove all dust particles and other impurities. After regular wash coconut fiber was obtained. Coconut fiber was oven dried at 60°C for 3 h to remove moisture content and then stored in air tight container prior to use. It is abbreviated as RCF.

Stock solution has been prepared by dissolving precisely weighed dye (crystal violet (CV) and congo red (CR)) in distilled water. Investigational solutions with distilled water were then obtained through successive dilutions.

Results and discussion

The SEM image as shown in Fig. 1 exposes that the RCF is having porous and non-uniform structure which shows that

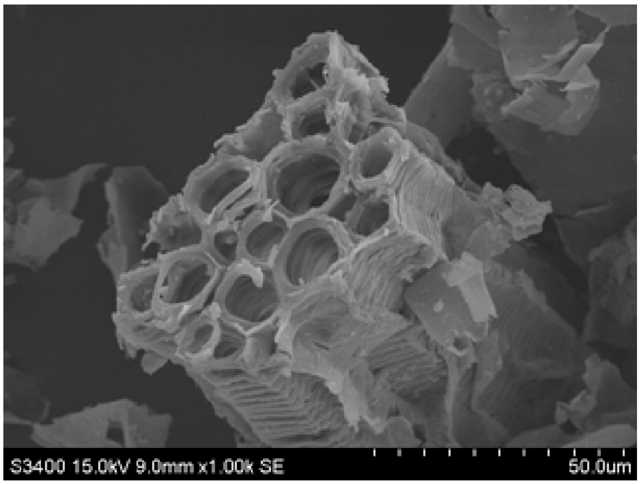

Fig. 1. SEM micrograph of RCF.

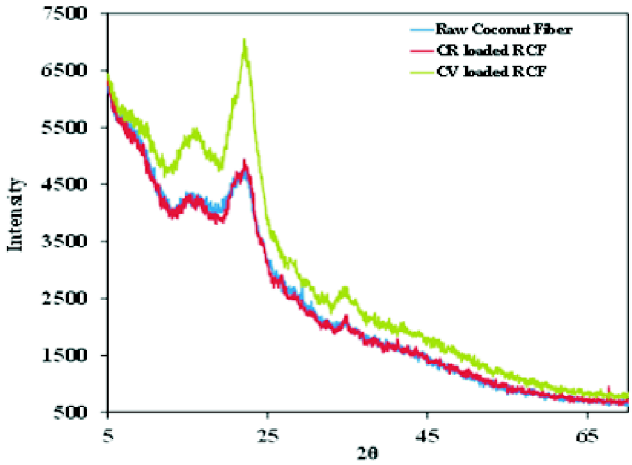

Fig. 3. XRD analysis of RCF and dye loaded RCF.

the RCF showing possibility to use as adsorbent for adsorption.

Several functional groups are depicted from FTIR study as shown in Fig. 2: hydroxyl stretching (3420 cm^{-1}), C-H group stretching (3024 cm^{-1}), axial deformation of C-H (2923 cm^{-1}), C-O-C in cellulose chain (1196 cm^{-1}), C-OH stretching vibration (1057 cm^{-1}). From XRD analysis shown in Fig. 3 two characteristic diffractions at around 16° and 22° were observed. At 22° higher crystallinity degree was observed for CV loaded RCF which suggest that crystallinity increase after CV adsorption over adsorbent whereas there is no significant deviation between the peak of RCF and CR loaded RCF.

To conduct this study solutions of different concentration (6, 12, 25, 50, 100 mg/L) was prepared for CR and CV. 50 ml of each concentration is taken in 100 ml plastic conical flask then adsorbent dosage of 0.1 g was supplemented to each flask. The flask was retained in orbital shaker at temperature 30°C, stirring speed 120 rpm for an hour. As shown in Fig. 4 that with the surge in the concentration, the percentage removal of dyes drops for both the dyes i.e. the highest percentage of removal at the lowest concentration (6 mg/L) was achieved.

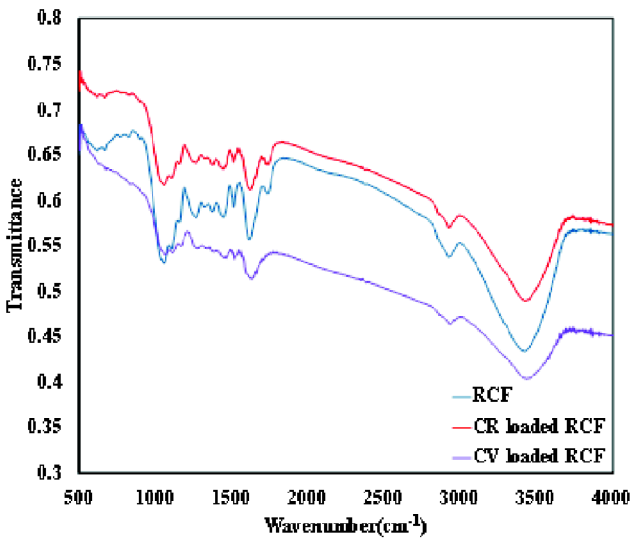

Fig. 2. FTIR spectra of RCF and dye loaded RCF at range of 500–4000 cm^{-1}.

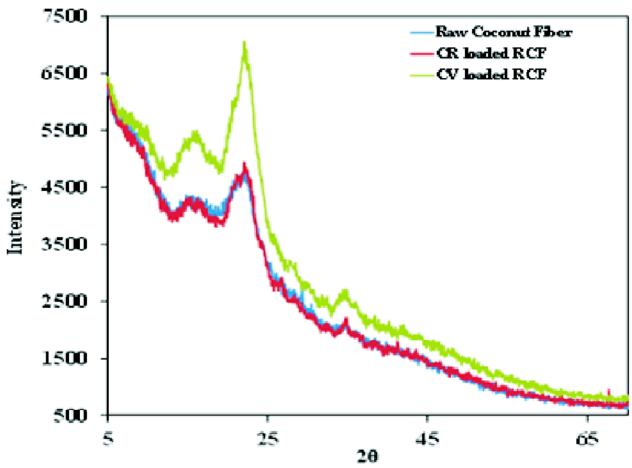

Fig. 4. Influence of concentration of CR and CV on RCF.

In order to understand the influence of adsorbent dosage, the experiment was executed for different dose of adsorbent varying from 0.05 to 0.35 g with initial dye concentration as 6 mg/L. The fraction of dye removal surges with increased dosage of adsorbents due to availability of more number of adsorption sites[3,4] as can be seen in Fig. 5.

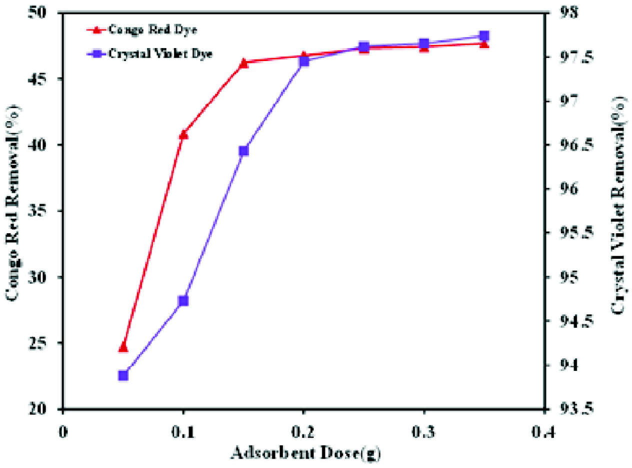

Fig. 5. Influence of adsorbent dosage.

The impact of contact time on removal of CR and CV experiment was carried out with initial dye concentration as 6 mg/L, adsorbent dosage as 0.15 g as illustrated in Fig. 6. The highest percentage removal for CV was achieved in 90 min and for CR it was achieved at 110 min. It was observed that there was slower rate of adsorption after certain period of time which may be due saturation of the adsorbent surface as sites get occupied with the adsorbate molecule with time[5].

pH affects adsorption process by influence of the surface charge on the adsorbent. Fig. 7 shows the effect of pH on the removal of CR and CV. Experiments with initial concentration of dye as 6 mg/L, adsorbent dosage as 0.15 g were carried out. It was found that the highest percentage removal for CR was at pH 3 and for CV at pH 11. At pH < 6 the surface of the adsorbent is charged positively by protonation, while at pH > 6 the surface becomes negative by deprotonation in the presence of a large number of hydroxyl ions[6].

Adsorption isotherm study was performed to comprehend the extent of adsorption and the relationship between adsorbate and adsorbent. In this isotherm study, experiments was done by adjusting the initial dye concentration = 6 to 100 mg/L, adsorbent dosage = 0.15 g, agitation time = 120 min, agitation speed = 120 rpm, pH (CV) = 11, pH (CR) = 3 for the temperature range of 35 to 50°C. The validation of any isotherm process is done according to regression correlation coefficient, R^2 value. The isotherm models used to check adsorption study were Freundlich, Temkin and Langmuir isotherm. Amongst these Langmuir isotherm model was considered perfect fit for CV and CR adsorption study with regression coefficient (R^2) values (≥ 0.99). Langmuir adsorption parameters were found by using the linearized form of Langmuir equation[7].

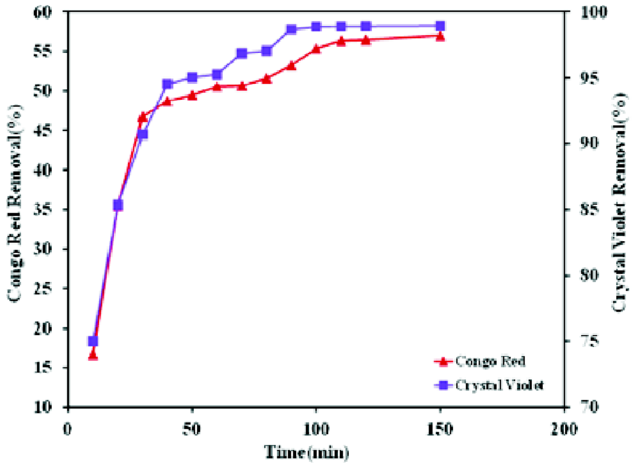

Fig. 6. Influence of contact time.

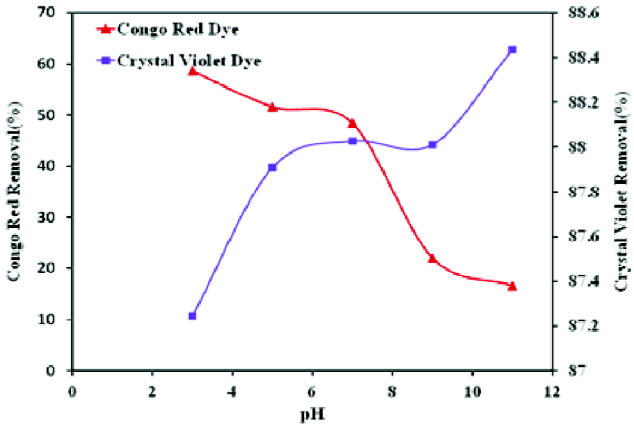

Fig. 7. Influence of pH on CR and CV on RCF.

The values thus obtained are given in Table 1. The vital characteristic of Langmuir model is separation factor (R_L) which is given in eq. (1). R_L is used to access the adsorption behavior of the adsorbate on to adsorbent. R_L>1 is unfavorable, 0 < R_L < 1 is favorable and irreversible, R_L = 1 is linear.

$$R_L = \frac{1}{1 + K_L C_0} \quad (1)$$

where, C_0 is the initial concentration of dye (mg/L), K_L is the Langmuir constant (L/mg). R_L value was found to be less than 1 and greater than zero (0 < R_L < 1) for CV which denotes that the adsorption is favorable and irreversible.

Table 1. Langmuir isotherm parameters for RCF loaded CV and RCF loaded CR

Dyes	T (°C)	R^2	q_{max} (mg/L)	K_L (L/mg)
CV	35	0.997	166.67	0.0221
	40	0.996	43.478	0.0878
	45	0.998	125	0.0523
	50	0.991	25.641	0.2868
CR	35	0.991	10.309	0.0212
	40	0.997	32.258	0.0133
	45	0.993	19.231	0.0446
	50	0.997	50	0.0247

Analysis of the kinetic model was done to identify the order of the reaction and rate constant. Kinetic analysis was performed by adjusting contact time and all other parameters were kept constant. The adsorption obeys pseudo-second order model[7] and second order rate constant values are given in Table 2.

As given in Table 3 for CR ΔG is found to be positive which shows that the adsorption process for CR is non-spontaneous. ΔH is found to be positive which confirms adsorption to be endothermic. ΔS show the randomness during adsorption at the solid-solution interface whereas for CV ΔG is found to be negative which shows feasibility of the adsorption process. Also, adsorption process for CV is spontaneous. ΔH is found to be positive which ratifies that the adsorption is endothermic. ΔS illustrate the randomness at the solid-solution boundary during adsorption process.

Table 2. Pseudo-second order data for RCF loaded CV and RCF loaded CR

	C_i (mg/L)	$q_{e,exp}$ (mg/L)	K_2 (g/mg/min)	$q_{e,cal}$ (mg/L)	R^2
CV	100	33.3	0.005	33.33	0.99
	50	16.6	0.041	16.66	0.99
	25	8.21	0.092	8.26	0.99
	12	3.99	0.207	3.96	1
	6	1.99	0.42	1.98	1
CR	100	27.6	0.014927	4.67	0.99
	50	13.65	0.014927	4.67	0.99
	25	6.78	0.01366	5.05	0.99
	12	3.22	0.055684	2.32	0.99
	6	1.58	0.149781	1.14	0.99

A fixed bed column made of acrylic with 30 cm height and 3 cm diameter was used for carrying out the continuous adsorption study at lab scale. The efficiency of RCF based column for the removal of CV and CR was checked through breakthrough curve which is plotted in between the ratio of outlet concentration to the inlet concentration and time (C_t/C_i vs t).

Table 3. Thermodynamic parameters of RCF loaded CV and RCF loaded CR

Dyes	ΔH	ΔS	ΔG (kJ/mol)			
	(kJ/mol)	(kJ/mol K)	308 K	313 K	318 K	323 K
CV	190.916	0.638	–2.66	–3.621	–5.015	–6.832
CR	38.122	0.11	1.751	1.544	1.323	1.023

Impact of bed height of RCF on dyes adsorption is shown in Fig. 8 and Fig. 9. The 2 g, 3 g, 4 g of weighed RCF is used for packing of column, where rise in the weight of the adsorbent corresponds to rise in height of bed also. It was found that the rise in bed height caused increase in the exhaustion time of adsorbent which may be due to increase in the adsorbent dosage which provides more binding sites thus increases the residence time of the solution.

Flow rate effect was analyzed by changing the flow rate (2 ml/min, 4 ml/min, 6 ml/min) shown in Fig. 10 and Fig. 11. The solution having initial concentration as 25 mg/L is pumped from the top of the column using peristaltic pump and bed weight as 2 g is used for packing and the set-up was ran at

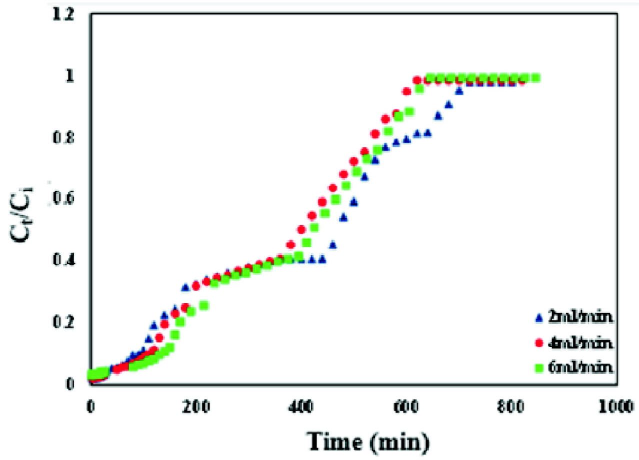

Fig. 8. Breakthrough curve for CR adsorption on RCF for different feed flow rate.

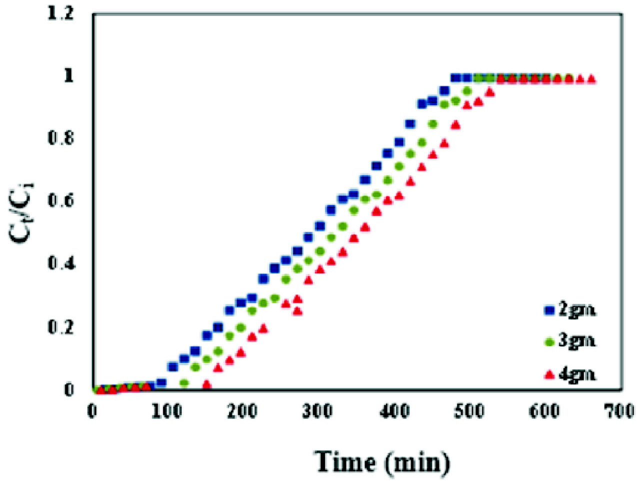

Fig. 10. Breakthrough curve for CV adsorption on RCF for different bed height.

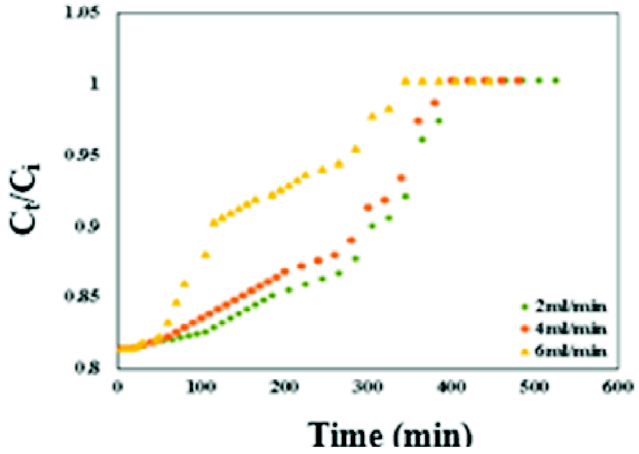

Fig. 9. Breakthrough curve for CV adsorption on RCF for different feed flow rate.

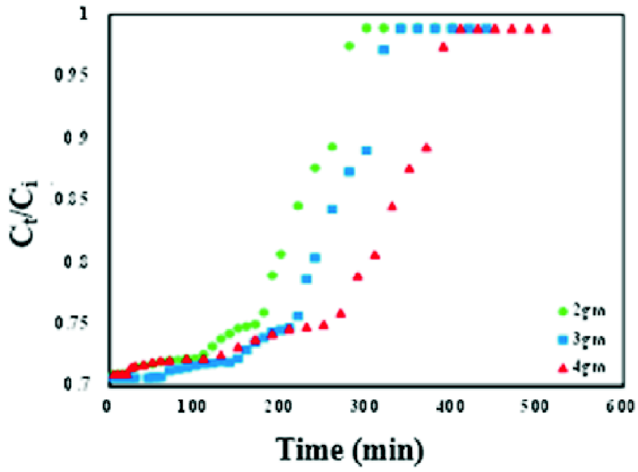

Fig. 11. Breakthrough curve for CR adsorption on RCF for different bed height.

room temperature. The exhaustion time of bed decreased significantly with the increase in the flow which can be due to the fact that increase in the flow rate results in higher Reynolds number which prolongs the mass transfer zone which marks shorter breakthrough time. Rise in the feed flow rate provides less residence time which doesn't provide sufficient time for the adsorbate-adsorbent interaction thus lower feed rate should be preferred.

Conclusion

RCF is prepared with minimum processing which makes it less expensive than other commercially used adsorbents. While conducting adsorption experiment for CV and CR and it was found that RCF shows higher removal efficiency for CV rather than CR. To check the feasibility of the RCF industrially, continuous adsorption study was done using different parameters such as bed height, feed flow rate.

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