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Adsorptive batch and column studies of Congo Red onto gulmohar leaf powder

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RESEARCH ARTICLE

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ABSTRACT

The present manuscript describes the adsorptive batch and column treatment of synthetic Congo Red dye onto naturally prepared adsorbents *viz.* gulmohar leaf powder and activated gulmohar leaf powder using sulfuric acid. The surface characterizations of naturally prepared adsorbents were performed by various sophisticated analytical techniques. Effect of various process parameters like adsorbent dosage, temperature, initial concentration, and pH for batch study; and flow rate and bed height for column study are explored. All batch adsorption data are analyzed using Freundlich and Langmuir adsorption isotherm model. The Thomas, Yoon-Nelson, Adams and Bohart, and Bed Depth Service Time model are applied to predict the breakthrough curves and to determine the characteristic parameters of the column useful for process design. Activated gulmohar leaf powder is more feasible adsorbent compared to normal gulmohar leaf powder. Maximum adsorption capacity related to Adams and Bohart model; and Langmuir isotherm was found to be 919.4 mg/L; and 434.7 mg/g, respectively, for activated gulmohar leaf powder.

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1. Introduction

Disposal from dyeing industry, poses one of the major problem, because such effluents contain a number of contaminants including acid or base, dissolved solids, toxic compounds, and color. Out of these, color is the first contaminant to be recognized because it is visible to the human eye. Removal of many dyes by conventional waste treatment methods is difficult since these are stable to light and oxidizing agents and are resistant to aerobic digestion [1]. Most dyes are usually have synthetic origins and complex aromatic molecular structures and designed to be resistant to environmental conditions like light, effects of pH and microbial attack. Some dyes are found to be toxic, mutagenic and carcinogenic. Dyes released by the industries can get into the water bodies and eventually contaminate the water supply system. Consumption of dye-polluted water can cause allergy reactions, dermatitis, skin irritation, cancer and mutation both in babies and grown-ups. In addition, this problem can impact several vital activities such as fisheries, livestock and agriculture since the polluted water is no longer suitable for their particular use [2].

Adsorption is an efficient and economically feasible process for separation and purification. It plays an important role in a number of natural and industrial systems. The performance of any adsorption-based process greatly depends on the effectiveness of its design and operating conditions [3]. Batch experiments are used to obtain equilibrium sorption isotherms and to evaluate the sorption capacity of sorbents for given metals present in fluid phases. But, adsorption in columns appears to have a distinct advantage over a batch-type operation. This is due to the fact that in batch type operation the adsorbent effectiveness for removing solute from solution decreases as the adsorption proceeds, whereas in column operation the adsorbent is continuously in contact with a fresh solution and, consequently, the concentration in the solution in contact with a given layer of adsorbent in the column is relatively constant. However, the optimum operating capacity and contact time must be determined to decide upon the best column dimensions and the number of units needed for continuous treatment [4].

One of the most used processes for treatment of wastewater and synthetic wastewater (dye solution) has been adsorption by activated carbon, an efficient solution. However, this treatment needs a high investment and operating costs, due to the high price of the activated carbon and to the high wastewater flow rate always involved, and these costs can be greatly increased when there are no carbon regeneration units locally. Research has recently been directed towards alternative adsorbents, namely low-cost naturally prepared adsorbents, including natural and waste materials like coir pith, passion fruit and mandarin peels, rice, Tendu (*Diospyros*

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Table 1. Experimental detail for adsorption study of CR onto a-GUL and GUL.

Effect of system	Adsorption dose (g/L)	Temperature (K)	Initial concentration (ppm)	pH
Effect of Adsorption dose	2, 4, 8, 10 and 12	300	60	7
Effect of temperature	5	310, 320, 330, 340, 350, 360 and 370	60	7
Effect of Initial concentration	5	300	30, 45, 60, 75, 90 and 105	7
Effect of pH	5	300	60	1, 3, 5, 7, 9 and 11

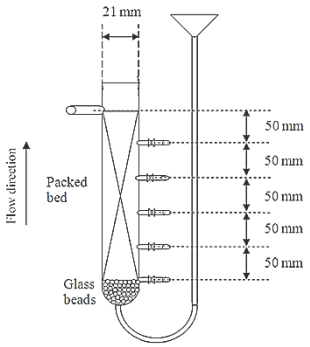


Figure 1. Schematic diagram of fixed bed column used in adsorption study of CR onto GUL and a-GUL.

melanoxylon) leaves, orange peel, banana peel, wood sawdust, sunflower (*Helianthus annuus L.*), seed hull, and invasive marine alga *Caulerpa racemosa var. cylindracea*, and *Caulerpa lentillifera,* husk, palm kernel, tendu leaves, silkworm pupa, dead leaves of *Posidonia oceanic* Mango (*Mangifera Indica*) Leaves [5-11]. Also, some acids were utilized for activation of adsorbent [12,13].

The aim of study is to prepare naturally prepared adsorbents i.e. gulmohar leaf powder (GUL) and activated gulmohar leaf powder (a-GUL) using sulfuric acid and analyze by sophisticated instruments. The adsorptive batch and continuous conditions using a laboratory scale fixed bed column treatment for Congo Red (CR) removal using GUL and a-GUL were performed.

2. Experimental

2.1. Adsorbent and adsorbate

The gulmohar (*Delonix regia*; Family: *Leguminosae*) tree are easily available in Indian region. The mature gulmohar leaves used in the present investigation are collected from the available trees near Navyug Science College, Gujarat, India. They are washed thrice with water to remove dust and water soluble impurities and are dried until the leaves become crisp. The dried leaves are powdered and further washed with distilled water till the washings are free of color and turbidity. Then the gulmohar leaf powder is dried and preserved in glass bottles for use as an adsorbent. For activated GUL, it was stirred with 0.1 N sulfuric acid for 30 min. Thereafter, it washed with de-ionized water to remove untreated acid dried in an oven at 60±2 °C. Previously gulmohar and its derivatives was utilized as adsorbent for removal of various contaminations from its aqueous solution by investigators [14,15]. To analyze feasibility of normal GUL and a-GUL (GULs) for adsorption technique, the surface properties were performed by Fourier Transform Infrared (FT-IR) Spectrophotometry (Shimadzu, Japan, Model: 8400S), Particle size distribution (Sympatic, Germany, Model: Helos-BF), Scanning Electron Microscopy (SEM) (Philips, The Netherlands, Model: XL-30 ESEM), Surface area (Micromeritics, ASAP 2010), Pore Volume, Pore Diameter and Porosity analysis (Mercury Porosimeter, Thermo Quest, Pascal-140). The details including structure of synthetic textile azo dye CR, obtained from Sigma Aldrich, India was mentioned [16]. Colored industrial effluent contains many varieties of synthetic dyes including azo dyes and their residues which are mostly toxic and mutagenic, and even carcinogenic in nature [17]. The purposes of selection of these dyes are due to their extended regional use in the textile industry [18]. The concentration of CR in each aqueous solution was measured on an UV-Visible spectrophotometer (ELICO SL 164 Double Beam UV-VIS Spectrophotometer) at λ_{max} = 500 nm.

2.2. Experimental design

For batch treatment, experiments were carried out by preparing CR solution and maintaining process parameters as shown Table 1. Briefly, 20 mL of the aqueous solution containing required amount of dye was treated with adsorbent in a 250 mL conical flask by shaking at 200 rpm and 60 min of time duration on orbital shaker at requisite temperature and pH. The sample was allowed to settle down and then it was filtered through a Whatman filter paper No 1.

Continuous adsorption of CR was studied using a fixed bed glass column with internal diameter of 2 cm and five sampling points at 5 cm intervals without channeling. At the bottom of the packing 2 cm high layer of glass beads were used to ensure uniform inlet flow to the column. CR solution was introduced into the column in bottom to top mode using a peristaltic pump at desired flow rate. The schematic diagram of fixed bed column used in adsorption study was shown in Figure 1. Briefly, the experiment was carried out by passing through CR (initial concentration: 60 ppm) into column (packed with 23.50 and 21.87 g of GLP and a-GLP, respectively) with controlled flow-rate and neutral pH. Effect of different flow rate (5, 10, 15 and 20 mL/min) and bed-height (5, 10, 15 and 20 cm) were studied. The pH of system was maintained by 1.0 N HCl or 1.0 N NaOH during batch and column experiment. All other chemicals used were of analytical reagent grade.

2.3. Adsorption isotherm for batch treatment

Freundlich adsorption equation most widely used mathematical description of adsorption in aqueous an system, which is shown in Equation (1).

$$\frac{x}{m} = K_f C_{eq}^{1/n} \text{ or } \log x/m = \log K_f + 1/n \log C_{eq} \quad (1)$$

where, x is the amount of the solute adsorbed, m is the weight of the adsorbent, C_{eq} is the solute equilibrium concentration and K and $1/n$ are constant characteristics of the system, which are determined from the graph of log x/m *vs*. Log $C_{eq.}$ Also, Langmuir adsorption is useful for predicting adsorption capacities and also interpreting into mass transfer relationship. The isotherm can be written as follows:

$$\frac{1}{q_e}=\frac{1}{q_{max}\,bC_e}+\frac{1}{q_{max}} \tag{2}$$

where, q_e is the equilibrium adsorption capacity (mg/g), C_e is the equilibrium concentration (mg/L), q_{max} represents the maximum amount adsorbed on per unit weight of adsorbent to form a complete monolayer on the surface(mg/g), b is the Langmuir constant that directly relates to the adsorption affinity (L/mg). Langmuir parameters, q_{max} and b are calculated from the slop and intercept of the linear plots of $1/q_e$ *vs* $1/C_e$ [19].

2.4. Column adsorption models

The Thomas, Yoon-Nelson, Bed Depth Service Time (BDST) and Adams and Bohart Model were used to analyze the behavior of adsorbent-adsorbate system in this column study.

The Thomas solution is one of the most general and widely used methods in column performance theory. The expression by Thomas for an adsorption column is given as follows.

$$\frac{C_t}{C_0}=\frac{1}{1+\exp\left(\frac{k_{Th}q_0x}{v}+k_{Th}C_0t\right)} \tag{3}$$

where k_{Th} (mL/min.mg) is the Thomas rate constant; q_0 is the equilibrium uptake capacity (mg/g); x is the mass of adsorbent packed in the column (g); V is the flow rate (mL/min); and C_0 and C_t are the concentrations (mg/L) of metal ion in the influent and in the effluent at any time t, respectively (min). Here, t = V_{eff}/V, where V_{eff} is the effluent volume (mL). k_{Th} is Thomas rate constant and qo maximum dye adsorption capacity of the adsorbent (mg/g), which is calculated from plot of $\ln[(C_t/C_o) - 1]$ *vs*. t [20].

The linear form of Yoon-Nelson model is

$$\ln\left(\frac{C}{C_0-C}\right)=k_{YN}\,t-\tau\,k_{YN} \tag{4}$$

where k_{YN} is Yoon-Nelson constant, τ is time required for 50 % adsorbate breakthrough and t is a sampling time. A plot of $\ln(C/(C_o - C))$ *vs*. t gives straight-line curve with a slope of k_{YN} and intercept of $-\tau\,k_{YN}$. Base of τ, the adsorption capacity, k_{oYN} was find out using

$$k_{oYN}=\frac{q_{total}}{X}=\frac{C_oQ\tau}{1000X} \tag{5}$$

So, adsorption capacity (k_{oYN}) is calculates from inlet dye concentration (C_o), flow rate (Q), 50% breakthrough time derived from Yoon-Nelson equation (τ) and weight of adsorbent (X) [21].

The Bed Depth Service Time model relates the service time of a fixed-bed with the height of adsorbent in the bed, hence with its quantity, because quantity is directly proportional to the bed height. The measurement of sorbent quantity is more precise than the determination of the respective volume, especially for the case of granules. Therefore, sorbent quantity is being preferably used, instead of the bed height. The linear form of BDST model [4] is

$$t=\frac{N_0Z}{C_0F}-\frac{1}{k_aC_0}\ln\left(\frac{C_0}{C_t}-1\right) \tag{6}$$

where t is the service time (min), N_o the adsorption capacity (mg/L), F is the superficial liquid velocity (cm/min), Z the height of column (cm) and k_a the rate constant of adsorption (L/min·mg), at time t. A plot of t *vs* bed depth, Z, should yield a straight line where N_o and k_a, the adsorption capacity and rate constant, respectively, can be evaluated. Application of the BDST model requires specification of the breakthrough time, which was selected arbitrarily in this work as the time corresponding to C/C_o = 0.1 to 0.6.

Bohart and Adams established the fundamental equations that describe the relationship between C/C_o and time in an open system for the adsorption of CR on GULs. In spite of the fact that the original studies of Adams-Bohart were performed with the gas-charcoal adsorption system, its overall approach can be applied successfully in quantitative description of other systems. The model proposed assumes that the adsorption rate is proportional to both the residual capacity of the GULs and the concentration of the sorbing species. Assuming certain conditions, the linear form of this model [22] is

$$\ln\frac{C}{C_o}=k_{AB}C_o\,t-k_{AB}\,N_o\left(\frac{Z}{U_o}\right) \tag{7}$$

where, U_o is the linear flow rate calculated by dividing the flow rate by the column cross-sectional area (cm/min), Z is the bed depth (cm) of the column, and N_o (mg/l) is the adsorption capacity coefficient saturation concentration and k_{AB} is the kinetic constant (L/mg min), which are calculated from plot of $\ln(C/C_o)$ *vs*. time, t.

3. Results and discussion

3.1. Surface characteristics of GULs

Figure 2 shows the FT-IR spectra of GUL and activated GUL, in which various functional groups such as amino (1250-1200 cm^{-1}), hydroxyl (3700-3200 cm^{-1}) and carbonyl groups (1775-1700 cm^{-1}) were presented. These groups are generally used as adsorbents for removal of various contaminations and dye from water and wastewater stretching having large adsorption capacities of 80 to 90% [23,24]. Further, Gong *et al*. [25], Liu *et al*. [26] and Ahmad *et al*. [27] have reported that hydroxyl group, -COOH/-COO- and ether group, respectively, is important functional group in the adsorption phenomena. Peak at 1030 cm^{-1} represents the carbonyl group, which is also help in adsorption process [28]. The scanning electron microscopic images of GUL and a-GUL were mentioned in Figure 3, which reveals that surface of GUL and a-GUL was porous and used as an adsorbent.

Table 2 mentioned the particle size, porosity, pore volume, pore diameter and BET surface area analysis of GUL and a-GUL. This shows that H_2SO_4 was effective in creating well-developed pores on the surface of GUL with large surface area and porous structure.

3.2. Batch study

3.2.1. Effect of adsorbent dose and temperature

The effect of different amount of adsorbent and temperature on adsorption of CR can be inferred from Figure 4.

Table 2. Surface characterization of GUL and a-GUL.

Name of adsorbent	GUL	a-GUL
Surface Area (m^2/g)	437	524
Particle Size (mesh)	124	157
Porosity (%)	28	35
Pore Volume (cm^3/g)	0.057	0.087
Ave. Pore Diameter (nm)	8.5	10.8

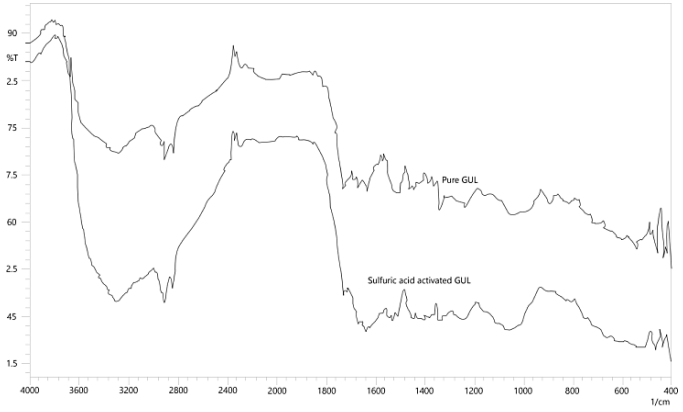
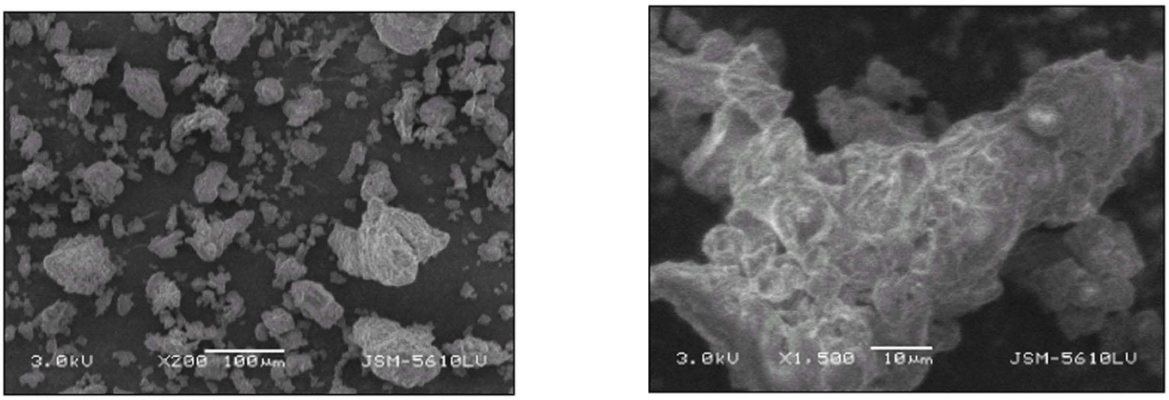


Figure 2. FT-IR Spectra of GUL and a-GUL.



(**a**) (**b**)

Figure 3. SEM images of (a) GUL and (b) a-GUL.

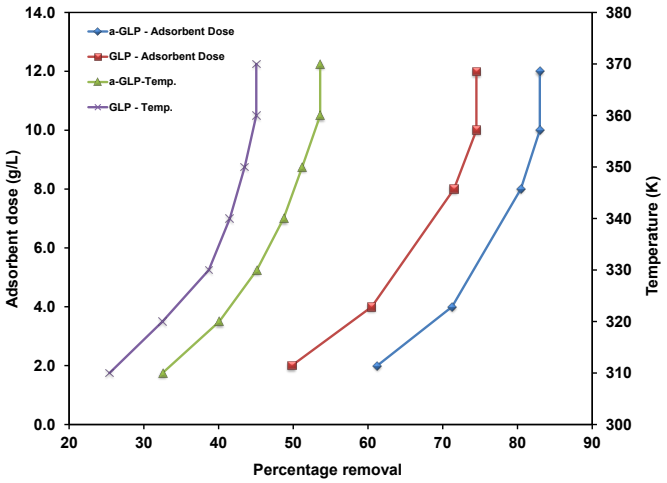


Figure 4. Effect of adsorption dose and temperature for adsorption of CR onto GUL ad a-GUL.

Table 3. Freundlich and Langmuir parameters for adsorption of CR onto a-GUL and GUL.

Equilibrium isotherm	Equilibrium parameters	Adsorbent	
		GUL	a-GUL
Freundlich isotherm	K_F (mg/g)	237.4	447.5
	n	2.3419	3.1565
	r^2	0.9634	0.9485
Langmuir isotherm	Q_{max} (mg/g)	285.7	434.7
	K_L (L/mg)	0.4000	0.3477
	r^2	0.9818	0.9825

Table 4. Adsorption of Congo Red using various adsorbent.

Sr. No.	Adsorbent	Maximum adsorption capacity related to Langmuir model, Q_{max} (mg/g)	Reference
1	Cranberry stem	95.2	[32]
2	Ackee apple (*Blighia sapida*) seed	161.89	[33]
3	Spent mushroom	147.1	[34]
4	Open burnt clay	22.86	[35]
5	Surfactants	378.7	[36]
6	Magnetic charcoal	265.0	[37]
7	Lignocellulosic waste	134.4	[38]
8	Powdered egg shell	96.0	[39]

As the amount of adsorbents increases up to 10 g/L, the percentage removal of dye from solution increases. The increase in adsorption with increase in adsorbent may be attributed due to the reason of increased adsorbent surface and availability of more adsorption sites. The reason behind the phenomenon may be speculated to be due to the interference between binding sites at higher concentrations or insufficiency of dye in solution with respect to available binding sites [29]. The highest percentage removal was found to be 82.9 and 74.5 using a-GUL and GUL at dosage of 10 g/L at temperature of 300 K and dye initial concentration of 60 ppm. Also, Figure 4 indicate that dye uptake increases with temperature up to 360 K. This may be explained on the basis of the fact that increase in temperature enhances the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particles as a result of the reduced viscosity of the solution [30]. Further, it is observed that percentage removal of a-GUL is higher than that of GUL in both cases.

3.2.2. Effect of initial concentration and pH

Figure 5 show the variation of initial concentration of CR and pH at constant adsorbent dose (5 g/L) and temperature (300 K). From Figure 5, it is observed that as the initial concentration of dye increases from 30 to 105 ppm, biosorption capacity of adsorbent increases, and the removal percentage increases from 63.6 and 56.1% for a-GUL and GUL, respectively. This sorption characteristic inferred that surface saturation is dependent on the initial dye concentration. As the dye concentration increases, adsorption capacity also increases because it provides a driving force to overcome the mass transfer resistances of dyes between the aqueous and solid phase. At higher dye concentration, the dye ions are adsorbed more than at low dye concentration, as more binding sites of the biosorbent are free for interaction at low dye concentration and due to the rise in the mass transfer from the concentration gradient [31].

As evident from Figure 5, with increase in pH of the solution the amount adsorbed increases till pH = 7.0 but with further increase in the pH, percentage adsorption drops in case of both adsorbents. The increase in the extent of adsorption with increase in pH value is due to the neutralization of the charges at the surface of the adsorbents. It can be safely assumed that by increasing the pH of the solution preference of the negative centers (SO^{-3}) of the dye for the active sites of the adsorbents increases, which in turn facilitates the adsorption process. However, beyond pH = 7.5 with increase in alkaline conditions protonation of the dye is reduced, and electrostatic repulsion between OH-adsorbed on the adsorbent and ionized dye molecule retards the extent of diffusion and adsorption thereby [16]. Since maximum adsorption is obtained at pH = 7.0, all further studies were carried out at pH = 7.5.

3.2.3. Adsorption isotherm

The isotherm data has linearized using the Freundlich and Langmuir equation and shown in Table 3, in maximum adsorption capacities (Q_{max}) of linear equation Langmuir isotherm were found to be 434.7 and 285.7 mg/g for a-GUL and GUL, respectively. Further, Langmuir isotherm was found to be linear over the entire concentration range studies, with good linear correlation coefficients (r^2 = 0.9818 and 0.9825) for GUL and a-GUL, respectively, confirming monolayer and heterogeneous surface of adsorbents. Numerous approaches have been found on the literature regarding adsorption of CR and their Q_{max} values were depicted into Table 4.

3.3. Column study

3.3.1. Effect of flow-rate

The effect of flow-rate for adsorption of CR onto GUL and a-GUL bed at different flow rates of 5, 10, 15, and 20 mL/min at influent concentration 60 ppm and bed height of 15 cm is shown in Figure 6, which indicated that breakthrough times and the exhausting times for the flow rates of 5-20 mL/min were increasing from 210 to 585 min and 75 to 405 min, respectively for GUL and 180 to 555 min and 60 to 255 min for a-GUL, respectively. It clearly indicates breakthrough occurred faster with higher flow rate of 20 mL/min. And breakthrough curve of the lower flow-rate of 5 mL/min tended to be more gradual, meaning that the column was difficult to be completely exhausted. This is attributed to the fact that low contact time between the adsorbate and adsorbent reduces the adsorption efficiency in the GULs bed. In addition, at higher flow-rates, the movement of adsorption zone along the bed is faster reducing the time for adsorption of dye on the GULs bed [40].

3.3.2. Effect of bed-height

The column adsorption experiment was carried out at heights of 5, 10, 15, and 20 cm using initial CR concentration of 60 ppm and of flow rate 15 mL/min. The breakthrough time increased with the increase in bed-height (Figure 7), which indicated that the breakthrough and the exhausting times for

Table 5. Thomas, Yoon-Nelson and Adams and Bohart parameters for adsorption of CR onto a-GUL.

Flow-rate (mL/min)	Bed-height (cm)	Thomas			Yoon-Nelson				Adams and Bohart		
		k_{TH} (mL/mg. min)	q_o (mg/g)	r^2	k_{YN} (1/min)	τ (min)	k_{oYN} (mg/g)	r^2	$K_{AB}\times10^5$ (g/mg. min)	N_o (mg/L)	r^2
5	15	0.2322	12.16	0.9909	0.0139	238.2	5.41	0.9909	40.8	621.5	0.8908
10	15	0.2398	11.33	0.9736	0.0144	296.1	9.29	0.9736	45.3	520.2	0.9147
15	15	0.2917	9.29	0.9402	0.0175	363.9	11.34	0.9402	61.6	397.0	0.9100
20	15	0.3423	5.41	0.9493	0.0205	424.1	12.16	0.9493	65.3	219.4	0.8844
15	5	0.3863	13.72	0.9827	0.0232	468.8	55.15	0.9827	72.2	604.6	0.9457
15	10	0.3299	15.16	0.9864	0.0198	386.5	45.47	0.9884	68.2	730.1	0.9478
15	15	0.3071	20.02	0.9760	0.0184	340.3	40.04	0.9760	62.9	826.2	0.9389
15	20	0.2984	31.64	0.9919	0.0179	298.9	35.17	0.9919	51.5	919.4	0.9046

Table 6. Thomas, Yoon-Nelson and Adams and Bohart parameters for adsorption of CR onto GUL.

Flow-rate (mL/min)	Bed-height (cm)	Thomas			Yoon-Nelson				Adams and Bohart		
		k_{TH} (mL/mg. min)	q_o (mg/g)	r^2	k_{YN} (1/min)	τ (min)	k_{oYN} (mg/g)	r^2	$K_{AB}\times10^5$ (g/mg. min)	N_o (mg/L)	r^2
5	15	0.2938	9.89	0.9630	0.0176	399.5	30.69	0.9630	50.3	450.6	0.9221
10	15	0.3574	8.88	0.9691	0.0214	323.7	27.55	0.9666	53.4	392.3	0.9293
15	15	0.3298	8.26	0.9769	0.0198	240.5	25.63	0.9763	60.1	366.9	0.9153
20	15	0.4208	5.48	0.9790	0.0252	150.6	17.00	0.9790	66.2	216.3	0.9508
15	5	0.4327	11.36	0.9737	0.0260	166.9	11.36	0.9737	80.5	621.9	0.9120
15	10	0.3656	12.36	0.9720	0.0219	243.7	12.36	0.9720	58.8	640.8	0.9041
15	15	0.3336	14.62	0.9749	0.0200	308.9	14.62	0.9566	61.2	698.0	0.9369
15	20	0.3002	20.03	0.9412	0.0180	397.6	20.03	0.9412	51.5	886.7	0.9785

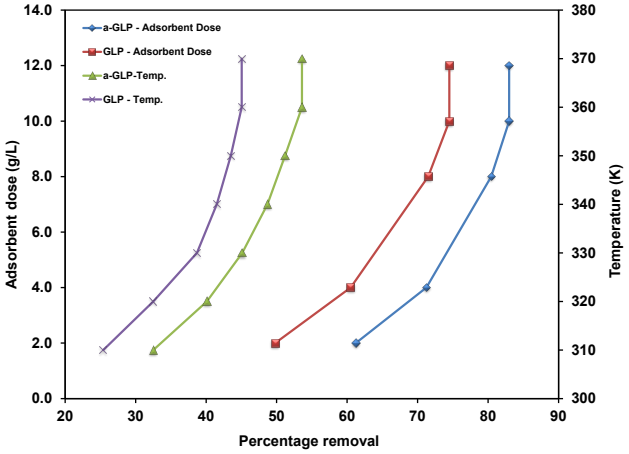


Figure 5. Influence of initial concentration and pH for adsorption of CR onto GUL ad a-GUL.

different bed height of 5, 10, 15, and 20 cm were deceased as 75, 135, 255 and 345 min and 405, 480, 525 and 585 min, respectively for GUL and also, 30, 75, 150 and 240 min and 285, 405, 485 and 540 min respectively for a-GUL. The throughput volume of dye solution was increased with the increase in bed height due to the increase in surface area of adsorbent which provided more binding site for the adsorption more number of sorption sites [40].

3.3.3. Column adsorption model

Thomas parameters like Rate Constant, K_{TH} (mL/mg min) and Adsorption Capacity, q_o (mg/g), Yoon Nelson parameters [Rate Constant, K_{YN} (1/min), 50 % Breakthrough Time, $t_{1/2}$ (min) and Adsorption Capacity, Q_{oYN} (mg/g)] and Adam Bohart parameters [Rate Constant, K_{AB} (L/mg.min) and Adsorption Capacity, N_o (mg/L)] and also, correlation coefficient for adsorption CR at different flow-rate (5, 10, 15 and 20 mL/min) and different bed height (5, 10, 15 and 20 cm) onto a-GUL and GUL were calculated and mentioned in Table 5 and 6, respectively. From these tables, it revealed that value of K_{TH}, K_{YN} and K_{AB} increases, but q_o, $t_{1/2}$, Q_{oYN} and N_o decreases, when flow rate increases (5 to 20 ml/min). Further, it is observed that as the bed height increases (5 to 20 cm), the value of K_{TH}, K_{YN}, Q_{oYN} and K_{AB} decreases, but q_o, $t_{1/2}$ and N_o increases. The maximum adsorption capacity related to Adams and Bohart model was found to be 919.4 and 886.7 mg/L for a-GUL and GUL respectively at flow rate of 15 mL/min and bed height of 20 cm.

Various scientists had tried to adsorb Congo Red by column studies and their maximum adsorption capacities related to 2.15, 3.41, 2.21 and 3.08 using tea waste [42], saw mill waste [43], rice husk [44] and surfactants [45], respectively.

The BDST parameters [Rate Constant, k (mL/mg min) and Adsorption Capacity, N_o (mg/g)] were mentioned in Table 7, in which value of constant, k was decrease and N_o was increase with increasing ratio of C/C_o. The adsorption capacity related to BDST was found to be 105.30 to 116.10 mg/g at C/C_o of 0.2 to 0.6 respectively using C/C_o = 0.6 using for GUL and also, 127.44 to 144.18 mg/g at C/C_o of 0.2 to 0.6 respectively using C/C_o = 0.6 using for a-GUL.

4. Conclusion

The feasibility of naturally prepared adsorbents, GUL and a-GUL was studied by various analytical techniques and adsorptive batch and column treatment, in which a-GUL was preferable than GUL.

Table 7. BDST parameters for adsorption of CR onto GUL and a-GUL.

Adsorbent	C/C_o	k_a (mL/mg. min)	N_o (mg/L)	r^2
GUL	0.2	0.1711	105.30	0.9982
	0.3	0.0836	111.78	0.9981
	0.4	0.0370	113.40	0.9873
	0.5	0.0000	113.40	0.9841
	0.6	-0.0273	116.10	0.9973
a-GUL	0.2	0.7453	127.44	0.9972
	0.3	0.2973	135.90	0.9841
	0.4	0.0819	138.60	0.9873
	0.5	0.0000	141.30	0.9981
	0.6	-0.0606	144.18	0.9982

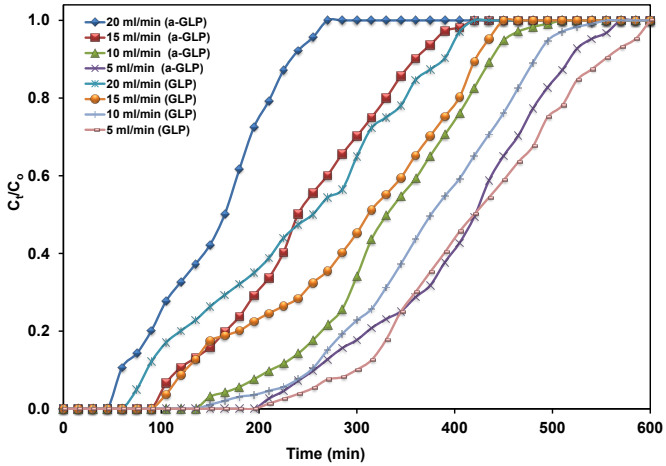


Figure 6. Breakthrough curve of the effect of flow rate on CR adsorption onto GUL and a-GUL column.

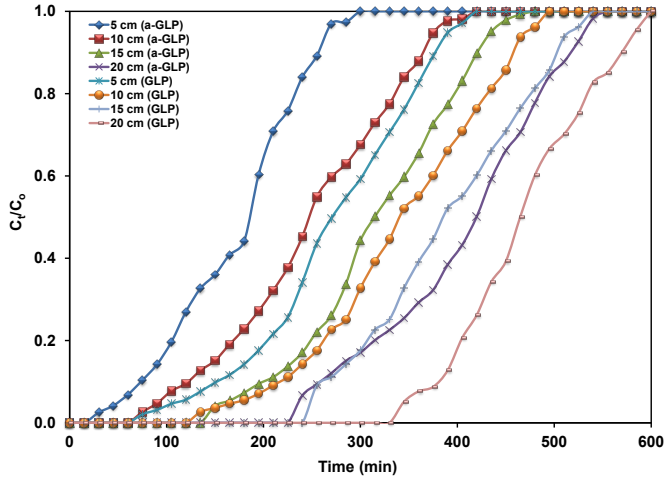


Figure 7. Breakthrough curve of the effect of bed-height on CR adsorption onto GUL and a-GUL column.

The highest percentage removal of CR was found to be 82.9 and 74.5 using a-GUL and GUL at dosage of 10 g/L at temperature of 300 K and dye initial concentration of 60 ppm. Maximum adsorption capacities, Q_{max} of Langmuir isotherm were found to be 434.7 and 285.7 mg/g for a-GUL and GUL, respectively. Langmuir isotherm was found to be more fitted than Freundlich isotherm confirming monolayer and heterogeneous surface of adsorbents. All the column data were analyzed by Thomas, Yoon and Nelson, BDST and Adam and Bohart model, in which maximum adsorption capacity related to Adams and Bohart model was found to be 919.4 and 886.7 mg/L for a-GUL and GUL respectively at flow rate of 15 mL/min and bed height of 20 cm. So, batch treatment is more preferable than column studies in this case.

Disclosure statement

Conflict of interests: The authors declare that they have no conflict of interest.
Author contributions: All authors contributed equally to this work.
Ethical approval: All ethical guidelines have been adhered.
Sample availability: Samples of the compounds are available from the author.

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References

[1]. Gupta, V. K.; Srivastava, S. K.; Mohan, D. *Ind. Eng. Chem. Res.* **1997**, *36,* 2207-2218.
[2]. Patel, H.; Vashi, R. T. *E-J. Chem.* **2010**, *7,* 975-984.
[3]. Liang, H.; Gao, H.; Kong, Q.; Chen, Z. *J. Chem. Eng. Data* **2007**, *52*, 695-698.
[4]. El Qada, E. N.; Allen, S. J.; Walker, G. M. *Ind. Eng. Chem. Res.* **2006**, *45*, 6044-6049.
[5]. Nagda, G. K.; Ghole, V. S. *Int. J. Environ. Res.* **2008**, *2*, 385-390.
[6]. Cengiz, S.; Cavas, L. *Mar. Biotechnol.* **2010**, *12*, 728-736.
[7]. Mugugan, T.; Ganapathi, A.; Valliappan, R. *E-J. Chem.* **2010**, *7,* 669-676.
[8]. Mittal, A.; Mittal, J.; Malviya, A.; Kaur, D.; Gupta V. K. *J. Colloid Interface Sci.* **2009**, *337*, 345-354.
[9]. Mittal, A.; Kaur, D.; Malviya, A.; Mittal, J.; Gupta V. K. *J. Colloid Interface Sci.* **2010**, *342*, 518-527.
[10]. Gupta, V. K.; Ali, I. , Saleh, T. A. , Nayak, A. , Agarwal, S. *RSC Advances* **2012**, *2*, 6380-6388.
[11]. Saha, P.; Chowdhury S.; Gupta S.; Kumar, I.; Kumar, R. *Clean-Soil Air Water* **2010**, *38*, 437-445.
[12]. Bhattacharyya, K. G.; Gupta, S. S. *Chem. Eng. J.* **2008**, *136*, 1-13.
[13]. Rozic, L.; Novakovic, T.; Petrovic, S.; Vukovic Z.; Cupic, Z. *Chem. Ind. Chem. Eng. Q.* **2008**, *14*, 227-229.
[14]. Patil, A. K.; Shrivastava, V. S. *Arch. Appl. Sci. Res.* **2010**, *2,* 404-413.
[15]. Ponnusami, V.; Aravindhan, R.; Karthik Raj, N.; Ramadoss, G.; Srivastava, S. N. *J. Environ. Prot. Sci.* **2009**, *3,* 1-10.
[16]. Mittal, J.; Malviya, A.; Gupta, V. K. *J. Colloid. Interface. Sci.* **2009**, *340*, 16-26.
[17]. Banat, I. M.; Nigam, P.; Singh, D.; Marchant, R. Bioresour. Technol. **1996,** *58*, 217-227.
[18]. Reid, T. M. , Morton, K. C. , Wang, C. Y. , King C. M. , *Mutat Res.* **1983**, *117*, 105-112
[19]. Prahas, D.; Kartika, Y.; Indraswami, N.; Ismadji, S. *J. Environ. Prot. Sci.* **2008**, *2*, 1-10.
[20]. Patel, H. , Vashi, R. T. , *Can. J. Chem. Eng.* **2012**, *90*, 180-185.
[21]. Priya, P. G.; Basha C. A.; Ramamurthi, V. *Clean Soil, Air, Water* **2011**, *39*, 88–94.
[22]. Maiti, A.; DasGupta, S.; Basu, J. K.; De, S. *Ind. Eng. Chem. Res.* **2008**, *47*, 1620-1629.
[23]. Amran, M. B.; Zulfikar, M. A. *Int. J. Environ. Studies* **2010**, *67,* 911-921.
[24]. Sankar, M.; Sekaran, G.; Sadulla, S.; Ramasami, T. *J. Chem. Technol. Biotechnol.* **1999**, *74*, 337-344.
[25]. Gong, R.; Ding, Y.; Li, M.; Yang, C.; Liu, H.; Sun, Y. *Dyes. Pigm.* **2005**, *64*, 187-192.
[26]. Liu, Y.; Wang, W.; Wang, A. *Clean Soil Air Water* **2010**, *38*, 670-677.
[27]. Ahmad, R.; Mondal, P. K. *Sep. Sci. Technol.* **2009**, *44*, 1638-1655.
[28]. Patel, H.; Vashi, R. T. Feasibility of Naturally Prepared Adsorbent, Elsevier BV, 2015
[29]. Saha, P.; Datta S.; Sanyal, S. J. Environ. Eng. **2010**, 136, 1409–1417.
[30]. Patil, S.; Deshmukh, V.; Renukdas, S.; Patel, N. *Int. J. Environ. Sci.* **2011**, *1*, 404-413.
[31]. Saha, P.; Datta, S. *Desalin. Water Treat.* **2009**, *12*, 219-228.
[32]. Salih, S. J.; Rashid, B. Z. *Int. J. Pharm. Chem.* **2015**, *5*, 207-217.
[33]. Bello, O. S.; Auta, M.; Ayodele O. B. *Chem. Ecol.* **2013,** *29*, 58-71
[34]. Tian, X.; Li, C.; Yang, H.; Ye, Z.; Hu, H. Desalin. Water Treat. **2011**, *27*, 319-326
[35]. Mumi, M. A.; Khan, M. M. R.; Akhter, K. F.; Uddin, M. *J. Int. J. Environ. Sci. Tech.* **2007**, *4*, 525-532.
[36]. Chatterjee, S.; Lee, D. S.; Lee, M. W.; Woo, S. H. *Bioresour. Technol.* **2009**, *100*, 3862-3868.
[37]. Safaric, I.; Nymburska K.; Safarickova, M. *J. Chem. Tech. Biotechnol.* **1997**, *69*, 1-4.
[38]. Paska, O.; Lanos, R.; Pacurariu C.; Bradeanu A. *Wat. Sci. Technol.* **2014**, *69(6)*, 1234-1240.
[39]. Zulfikar, M. A.; Setiyanto, H. *Adsorption* **2013**, *5*, 1532-1540.
[40]. Sekhula, M. M.; Okonkwo, J. O.; Zvinowanda, C. M.; Agyei, N. N.; Chaudhary, A. J. *J. Chem. Eng. Process Technol.* **2012**, *3*, 1-5.
[41]. Pahari, P. K.; Sharma, M. M. *Ind. Eng. Chem. Res.* **1991**, *30,* 1880-1886.
[42]. Foroughi-Dahr, M.; Esmaieli, M.; Abolghasemi, H.; Shojamoradi, A.; Pouya, E. S. *Desalin. Water Treat.* **2015**, *57*, 8437-8446.
[43]. Khan, T. A.; Sharma, S.; Khan, E. A.; Mukhlif, A. A. *Toxicol. Environ. Chem.* **2014**, *96*, 555-568.
[44]. Han, R.; Ding, D.; Xu, Y.; Zou, W.; Wang, Y.; Li, Y.; Zou, L. *Bioresour. Technol.* **2008,** *99*, 2938-2946
[45]. El-Messaoudi, N.; El Khomri, M.; Dbik, A.; Bentahar, S.; Lacherai, A.; Bakiz, B. *J. Environ. Chem. Eng.* **2016**, *4*, 3848-3855.