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Research Article

Cranberry Stem as an Efficient Adsorbent and Eco-Friendly for Removal of Toxic Dyes from Industrial Wastewater, Physico Studies

Shameran Jamal Salih[*1] and Baref Zahir Rashid[2]

[1]*Department of Chemistry, Faculty of Science and Health, Koya University, University Park, Danielle Mitterrand Boulevard, Koya KOY45, Kurdistan Region of F.R. Iraq*
[2]*Technical Institute, Department of Pharmacy, Wrme St. , Mardin 327 , Alley 76, Sulemaniyah, Kurdistan Region of F.R. Iraq*

Abstract

The adsorption of Congo red (CR) from aqueous solution using treated ground cranberry stem by varying the parameters such as contact time, dye concentration, adsorbent dose, pH and temperature was investigated. Adsorption isotherms of CR onto CS were analyzed by Langmuir and Freundlich. It was observed that the optimum CR adsorption onto ground CS occurred at contact time of 30 minutes, the adsorbent dosage of 8 g, initial concentration of 50 mg/L and pH 2. In addition, the particle size of ground CS has no significant effect on the adsorption of CR. Adsorption isotherms studied through the use of graphical methods revealed that the adsorption of CR onto cranberry stem follows both Langmuir and Freundlich models, with the maximum adsorption capacity was 95.25mg g^{-1}. The ground cranberry stem investigated in this study thus exhibited as a high potential adsorbent for the removal of CR from aqueous solution.

Keywords: Cranberry stem; Lagergren equation; Congo red; Equilibrium; Isotherm; Wastewater treatment.

1. Introduction

Nowadays, one of the key environmental problems facing humanity is the increasing worldwide contamination of fresh water systems with thousands of industrial chemical compounds [1]. Out of all contaminants contained in industrial sewage, dyes are the most undesired ones, as human eyes can easily recognize them. Furthermore, dyes can significantly affect photosynthetic activity in aquatic systems. In addition, some dyes degrade into compounds that have toxic, mutagenic or carcinogenic influences on living organisms [2]. Various techniques have been employed for removal of dyes from wastewaters. These methods include adsorption [3], flocculation [4], oxidation [5], and electrolysis[6]. Compared with other techniques, adsorption is not only efficient but also economical for elimination of dye stuffs [3].

Dyes have long been used in dyeing, paper and pulp, textiles, plastics, leather, cosmetics and food industries. Color stuff discharged from these industries poses certain hazards and environmental problems. These colored compounds are not only aesthetically displeasing but also inhibiting sunlight penetration into the stream and affecting aquatic ecosystem. Dyes usually have complex aromatic molecular structures which make them more stable and difficult to biodegrade. Furthermore, many dyes are toxic to some microorganisms and may cause direct destruction or inhibition of their catalytic capabilities. Textile industry use dyes and pigments to color their product. There are more than 100,000 commercially available dyes with over 7×105 tons of dyestuff are produced annually. Many types of dye are used in textile industries such as direct, reactive, acid and basic dyes. Most of these dyes represent acute problems to the ecological system as they considered toxic and have carcinogenic properties, which make the water inhibitory to aquatic life. Due to their chemical structure, dyes

* Correspondence Info
Shameran Jamal Salih,
Department of Chemistry,
Faculty of Science and Health,
Koya University, University Park,
Danielle Mitterrand Boulevard,
Koya KOY45, Kurdistan Region of F.R. Iraq
E-mail: shameran.jamal@koyauniversity.org

possess a high potential to resist fading on exposure to light and water [10]. The main sources of wastewater generated by the textile industry originate from the washing and bleaching of natural fibers and from the dyeing and finishing steps. Given the great variety of fibers, dyes and process aids, these processes generate wastewater of great chemical complexity and diversity, which are not adequately treated in conventional wastewater treatment Plant.

1.1 Adsorption Process

The outcome of an atomic or molecular collision that results in the retention of the molecule on the surface is called adsorption. The atom or molecule being adsorbed on the surface is usually described asthe adsorbate the adsorbing surface is usually termed the adsorbent or substrate. There are two types of interactions that can occur in adsorption process [2].

i) Physical adsorption or physisorption, which involves the balancing of a week attractive force e.g., Van der waals force. Physisorption is non-specific and any atom or molecule can adsorb on any surface under appropriate experimental condition(s) (i.e. temperature and pressure). Large amount of physisorption are favored when the surface is at low temperature.

ii) Chemical adsorption or chemisorption, which involves the formation of one or more chemical bonds between the adsorbed molecule and the surface. The bonds formed may be ionic or covalent, or mixture of the two. Chemisorption differs markedly from physisorption in that there is usually a high degree of specificity in the interaction of different adsorbate with different substrate.

1.2 Characteristics of Good Adsorbent

A good adsorbent has the following characteristics:

i) Capacity or loading

Adsorption capacity is the most important characteristics of an adsorbent. Simply stated it is the amount of adsorbate taken up by the adsorbent, per unit mass (or volume) of the adsorbent. It depends on the fluid phase concentration, the temperature and other conditions; especially the initial condition of the adsorbent [15].

ii) Selectivity

Selectivity is related to the capacity. It is the ratio of the capacity of one component to that of another at a given fluid concentration [15].

1.3 Importance of Low Cost Adsorbents

Adsorption onto costly adsorbent e.g. onto commercially activated carbon has emerged as one of the most efficient and highly accepted method in eliminating dyes and other hazardous pollutants from water. However, in a developing country like ours it is not commercially viable so the current emphasis is on exploring the possibilities of use of suitable low cost and locally available alternative adsorbents, which are efficient and cost effective and have the entire characteristic mentioned earlier. In this regard industrial solid waste such as power plant fly ash, saw dust, agricultural waste (like rice husk ash, saw dust, sugarcane bagasse pith, activated carbon prepared from rubber wood, silk and cotton hull, used tea leaves, bamboo dust, coconut shell, and straw etc.), coconut coir pith, orange peel etc. Other carbonaceous adsorbents prepared from clay minerals, solid, algae, wood etc. has proven their efficiency as good low cost adsorbent [4,15,18,24].

1.4 Statement of the Problem

In the present study, locally available cranberry stem (CS) used to remove color contributed by commonly applied industrial dye Congo Red (CR) from the aqueous solution i.e. simulated or synthetic wastewater.

2. Experimental

2.1 Materials and Instruments

2.1.1 Adsorbent

Cranberry stem was obtained from Koya; Kurdistan inside university campus, the stem was used as a biomass. The biomass obtained was washed several times using distilled water to get rid of impurities like dirt and sand, then was dried in an oven at 60°C for 24 hours. It was cut into smaller sizes and grounded into smaller particles using house mill then sieved using 500 μm sieve. Surface modification was done by weighing 25gm of ground Cranberry stem into a beaker and adding 100 ml, 3M of 85% ortho-phosphoric acid with constant stirring at 80°C for 3 hours. It was further dried at 105°C for 10 hours. The CS was obtained cooled, and washed again several times until pH becomes around 6. Dried and kept in desiccator for later use.

2.1.2 Adsorbate

The Congo red dye was first synthesized in 1883 by Paul Bottiger who was working then for the Friedrich Bayer Company in Elberfeld, Germany. Synthetic dyes as Congo red (CR) are difficult to biodegrade due to their complex aromatic structures, which provide them physico-chemical, thermal and optical stability. It is a secondary diazo dye. $\lambda max = 497nm$

Figure 2.2: Serial dilution of Congo red dye

Molecular formula	:	$C_{32}H_{22}N_6Na_2O_6S_2$
Molar mass	:	696.665
IUPAC name	:	disodium 4-amino-3-[4-[4-(1-amino-4-sulfonato-naphthalen-2-yl)diazenylphenyl]phenyl]diazenyl-naphthalene-1-sulfonate

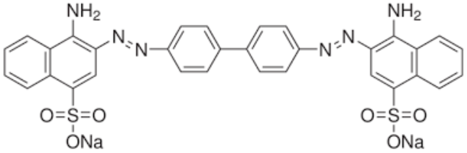

Figure 2.3: Chemical formula of Congo red

3. Instruments

Table 3.1: List of Instruments used during the whole experiment their make and function

Instruments	Make	Function
Sensitive weight balance	HTCE 3000g 0.01g	To measure weight
PH meter	pH/Ion 510	Measurement of pH
Spectrophotometer(UV/Vis)	Aglient Technology Cary UV-Vis spectrophotometer	Absorbance
Incubator shaker	GFL 3031	To shake the samples in dye solution
Oven	Desert Chamber Pro	To dry samples

3.1 Methods

Adsorption Studies

1. Effect of contact time

150 ml of dye solution with dye concentration (50 mg/L) is to be prepared in a conical flask with adsorbent concentration (0.5g/150ml) and kept inside the shaker. Dye concentration to be estimated spectrophotometrically at the wavelength corresponding to maximum absorbance, λmax, using a spectrophotometer. The samples to be withdrawn from the incubator shaker at predetermined time intervals and the dye solution should be separated from the adsorbent by the help of a micropipette. The absorbance of solution is then measured. The dye concentration is to be measured after 5, 10, 20, 30, 60, 90, 120 min until equilibrium reaches. A graph is to be plotted with q_e vs time. The q_e is expressed as

$$q_e = \frac{c_\circ - c_e}{X} \quad (1)$$

Where q_e: Amount of dye adsorbed per unit mass of adsorbent (mg/g)

C_o: Initial dye concentration (mg/l)

C_e: Final dye concentration (mg/l)

X: Dose of adsorbent (g/l)

The amounts of adsorbed dye at equilibrium and dye removal efficiency were calculated from the mass balance equation 1 and equation 2, respectively, as follows:

$$q_e = \frac{V}{M}\left(C_\circ - C_e\right) \qquad (2)$$

$$R\ \% = \frac{C_\circ - C_t}{C\circ} \times 100 \qquad (3)$$

Where: C_t and $C_\circ$ are the concentration of dye at any time and initial concentrations of dye (mg/l), respectively; q_e is the equilibrium dye concentration on adsorbent (mg/g); V is the volume of dye solution (L); M is the mass of adsorbent (g) and R is the removal percentage.

2. Effect of initial pH

150ml of dye solution was prepared in a conical flask with dye conc. 50 mg/L and adsorbent conc.(1g/150ml) and initial pH of the conical flask is to be measured. The pH of the dye solutions was adjusted with dilute HCl (0.1N) or NaOH (0.1N) solution by using a pH meter. 150 ml of dye solution was prepared and the pH of solution is changed from 2 to 10.The flasks were put inside the incubator shaker (150 rpm fixed throughout the study) maintained at 25^{o}C and the final concentration of dye was measured using UV spectrophotometer and the calibration plot of the dye after 2 hours. A graph is to be plotted with q_e vs. initial pH.

3. Effect of adsorbent dose

150ml of dye solution was prepared in different conical flasks with dye conc.(50 mg/L) and adsorbent concentration 0.5, 1, 2, 5, 8 g/150ml. The final dye concentration readings were taken after putting the 5 flasks inside the shaker for 2 hours. A plot of q_e vs. adsorbent dose is taken.

4. Effect of temperature:

150 ml of dye solution was prepared in conical flask with dye concentration 50mg/L and adsorbent dose (1g/L) and put inside the incubator shaker. The temperature was maintained at 20°C. The final dye concentration readings were taken at 5, 10, 20, 30, 60,120 min. The same procedure was followed for temperatures 30°C and 40°C. A plot of qe vs. time at different temperatures is obtained.

4. Result and Discussion

4.1 Calibration plot for CR

For the CR dye five different concentrations were prepared by correct serial dilution from the stock solution (1000 mg/L) and absorbance were measured for each dye concentration using the Carry UV-VIS Spectrophotometer. A plot of absorbance (abs) against concentration (mg/L) for the results obtained and the calibration graph is depicted as follows;

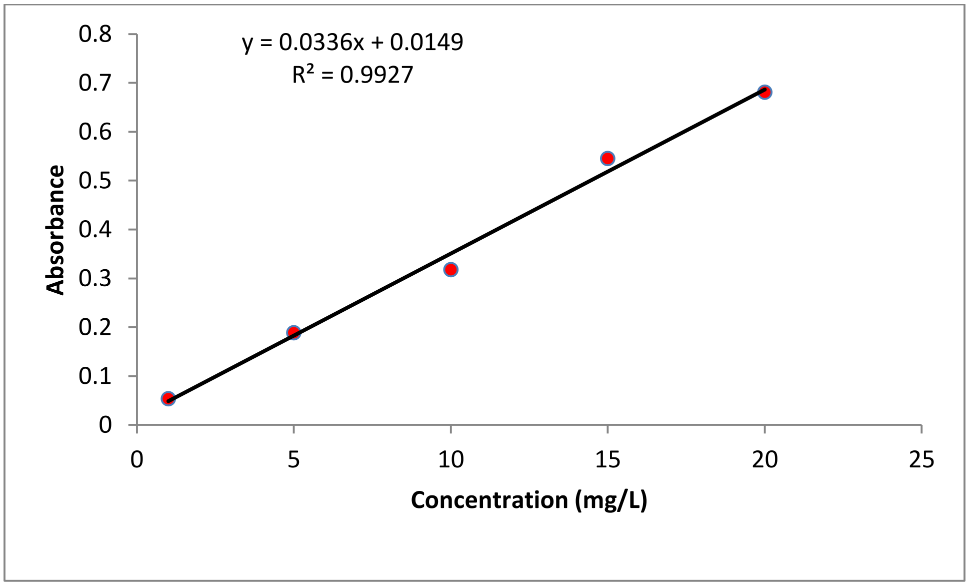

Figure 4.1: Calibration curve of cong red dye

4.2 Adsorption Studies

4.2.1 Effect of Contact time

The effect of contact time can be seen from Fig.4.2.1 for the CR dye. It is clear that the extent of adsorption is rapid in the initial stages and becomes slow in later stages till saturation is allowed.

The final dye concentration did not vary significantly after 2 hours from the start of adsorption process. This shows that equilibrium can be assumed to be achieved after 2 hours (120 min). It is basically due to saturation of the active site which do not allow further adsorption to take place.

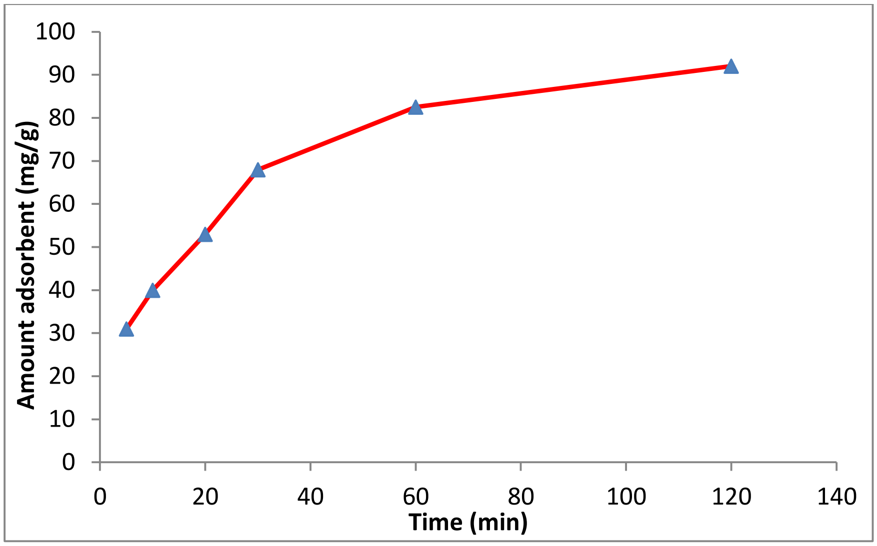

Figure 4.2.1: Effect of contact time

4.2.2 Effect of initial pH

Effect of pH on the removal of CR is shown in Figure 4.2.2 For 20 mg/L dye concentration the percent removal decreased from 95% to 37%, when the pH was increased from 2 to 8 and then the percent removal remained almost the same up to pH 10. The possible mechanisms of adsorption of CR onto CS may be considered as electrostatic interaction between the protonated surface of grounded CS and dye. The decrease of CR removal may be related to the formation of negative surface charges of CS at higher pH. Our study previously shows that the zero point of charge (pH_{PZC}) of ground CS was at pH= 8.8. At pH < pH_{PZC}, the surface becomes positively charged, and favors uptake of dye due to increased electrostatic force of attraction. At the solution having pH > pH_{PZC}, the adsorbent surface becomes negatively charge and does not favors the adsorption of dye anions due to the electrostatic repulsion. The results show that the dye removal decrease with increasing initial pH of the dye solution and maximum removal occurs at pH 2 [3, 8, 17, 22].

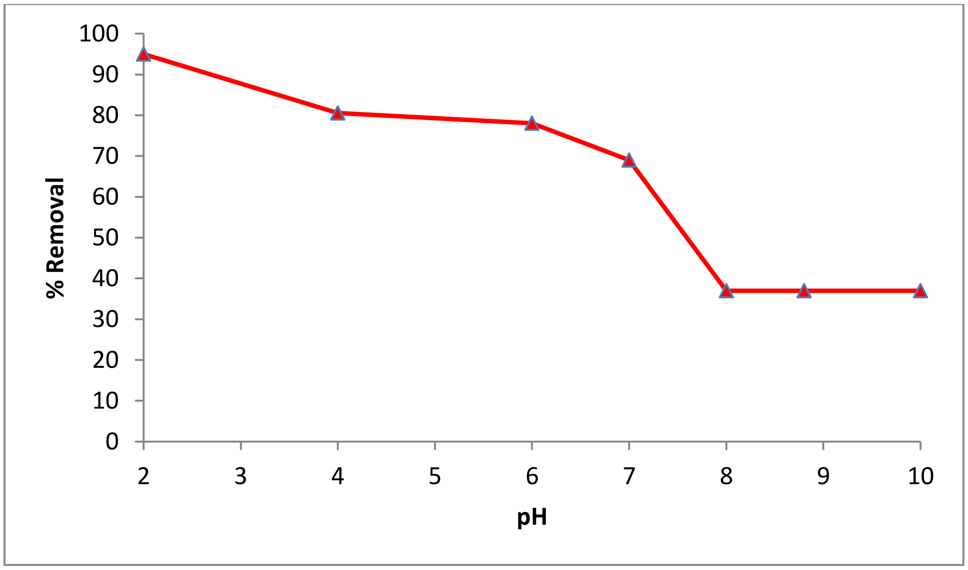

Figure 4.2.2: Effect of pH solution on CR removal

4.2.3 Effect of adsorbent dose

Figure 4.2.3 shows the removal of CR by ground CS at different adsorbent doses (0.5-8g) for the dye concentrations of 50 mg/L at pH 2. Increase in adsorbent dosage increased the percent removal of dye, which is due to the increase in absorbent surface area of the adsorbent.

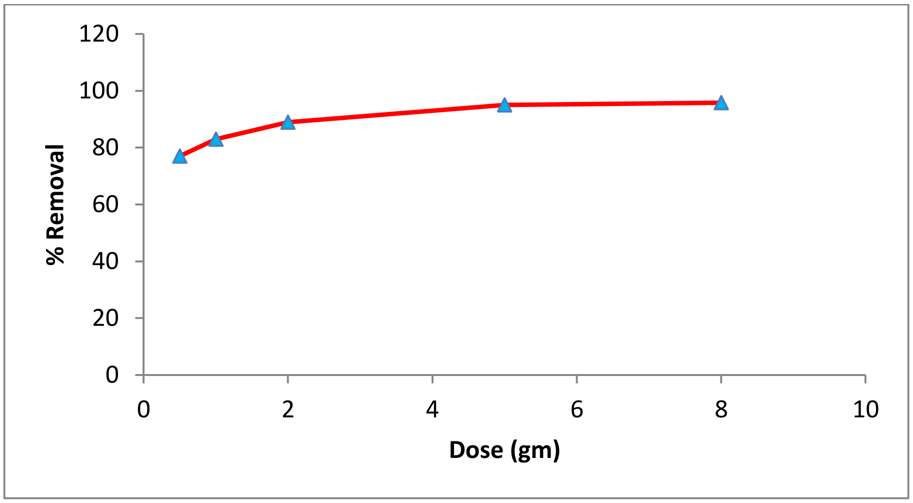

Figure 4.2.3: Effect of adsorbent dose on adsorption process

4.2.4 Effect of particle size of powdered eggshells on sorption process

Determination of the effect of particle size on adsorption was conducted using samples of three different average particle sizes: 50, 100 and 150 μm at pH 2 and temperature of 25^{0}C for 90 minutes. The result is shown at Figure 4.2.4. As seen from Figure 4.2.4, variation of the particle size of CS statistically has no significant effect on the removal of CR compounds as indicated by 86 - 91%.

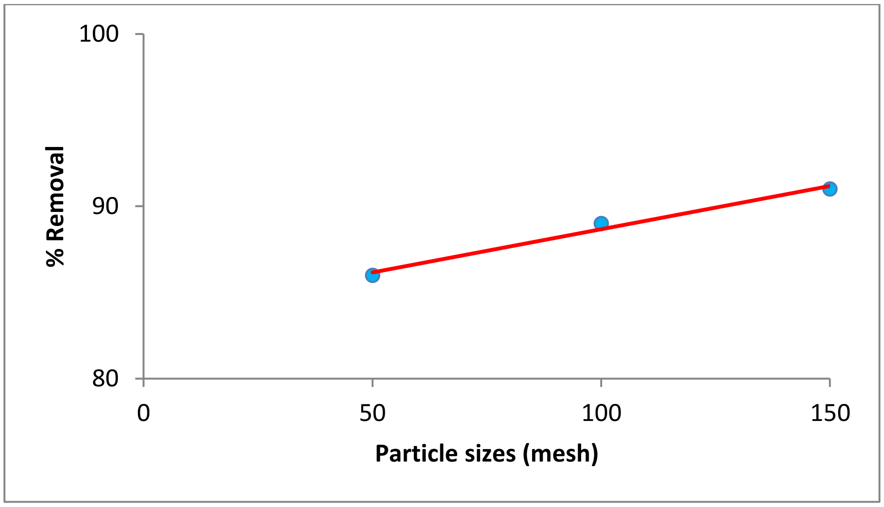

Figure 4.2.4: Effect of particle size on dye removal

4.2.5 Effect of temperature

The effect of temperature on adsorption of dye solution with initial concentration of 50mg/ L at pH= solution pH at temperatures 20, 30 and 40°C on has been determined. The result of time rate studies for the adsorption of the Congo red at different temperature has been shown in the figure below.

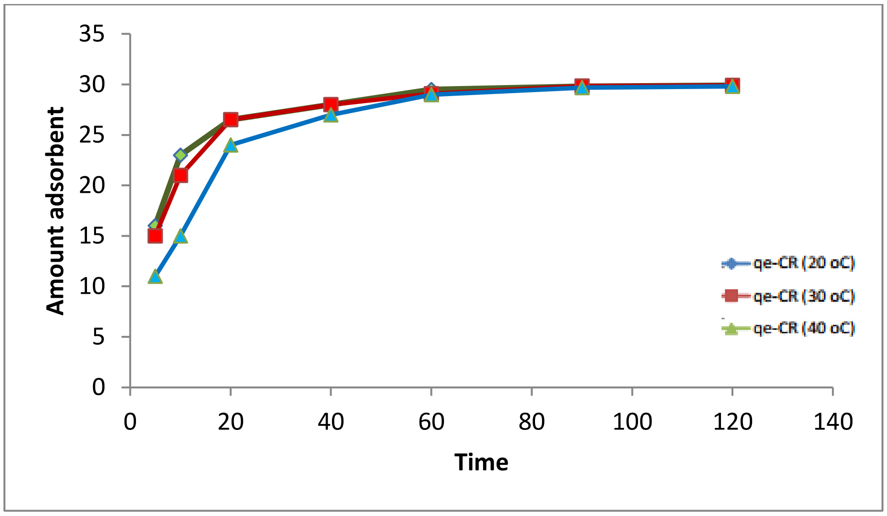

Figure 4.2.5: Effect of various temperatures on adsorption process

Results indicate that the adsorption capacity of ground CS for the CR dye increased with temperature. This may be a result of increase in the mobility of the large dye ion with temperature. An increasing number of molecules may also acquire sufficient energy to undergo an interaction with active sites at the surface [15,16].

4.3 Adsorption kinetics

Two kinetic models, pseudo-first-order and pseudo-second-order model were applied to investigate the reaction pathways and potential rate limiting steps of the adsorption of CR onto grounded cranberry stem. The pseudo-first-order rate constant, k1 and the equilibrium adsorption capacity, q_e at different temperatures were determined from the slope and intercept of the plots of log (q_e-q_t) versus t and are listed in Table 4.1 with the correlation coefficient (R^2). From the kinetic data in Table 4.1, a large difference between theoretical and experimental equilibrium adsorption capacity, q_e, is observed at all temperatures, indicating a poor fit of the pseudo first-order equation to the experimental data. The pseudo-second-order model constants were determined from the slope and intercept of the plot of t/q_t versus t [9-11].

Table 4.1: Kinetics parameters for adsorption of CR onto grounded CS at different temperatures

Temp	**$q_e$exp (mg g^{-1})**	**Pseudo-first-order kinetic model**			**Pseudo-second-order kinetic model**			
		$q_e$cal (mg g^{-1})	K1 min^{-1}	R2	$q_e$cal (mgg^{-1})	K2	h (mg g-1 min-1)	R2
303	0.203	0.014	0.052	0.723	0.212	4.685	0.211	0.999
313	0.198	0.013	0.014	0.722	0.21	1.047	0.045	0.995
323	0.185	0.012	0.014	0.722	0.19	0.844	0.03	0.994
333	0.174	0.011	0.013	0.721	0.18	0.796	0.026	0.987

The plot of t/q_t against t at different temperatures is shown in Figure 4.3.1. Contrary to the pseudo-first-order equation, the fitting of the kinetic data in the pseudo-second-order equation showed excellent linearity with high correlation coefficient (R^2> 0.999) over the temperature range of 303-333 K. It is also observed from Table 4.1 that rate constant, k_2 decreased as the temperature increased indicating exothermic nature of adsorption of CR onto CS grounded. Furthermore, the calculated q_e values were found to be quite close to the experimental q_e values at all temperatures studied. So, it was inferred that the adsorption of CR onto cranberry stem followed pseudo second-order kinetics. This finding suggests that the rate-limiting step of the adsorption system may be chemisorption. The initial adsorption rate, h (mgg^{-1}min^{-1}), decreased with increase in temperature (Table 4.1) suggesting that adsorption of CR onto cranberry stem was not favorable at higher temperatures.

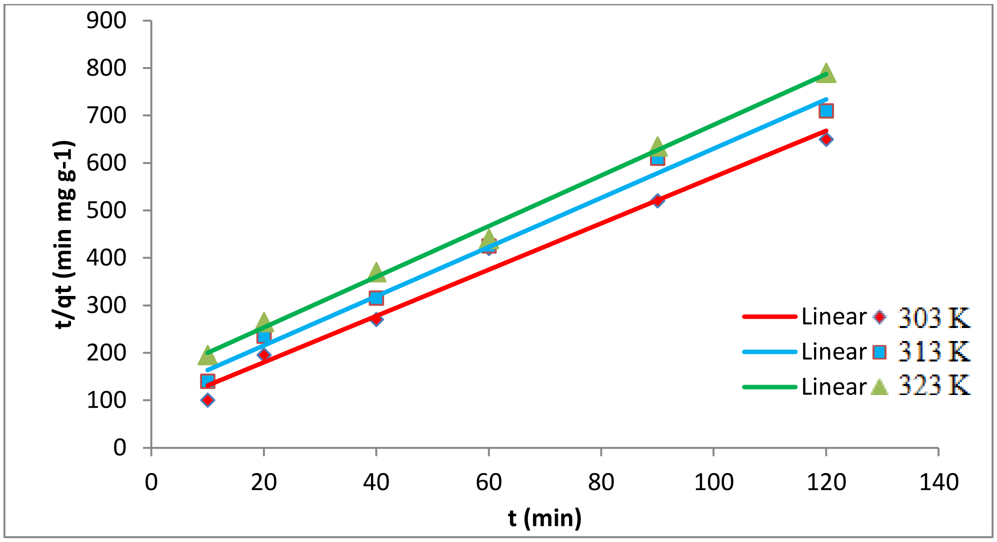

Figure 4.3: Pseudo-second-order kinetic plots for adsorption of CR onto ground CS at different temperatures

4.4 Isotherm equations

The Freundlich and Langmuir models were used to describe the equilibrium between the adsorbate and the adsorbent which can be represented respectively as follows [21].

$$\log q_e = \log K + \frac{1}{n}\log C_e \qquad (4)$$

K and n are constants that depict the adsorption capacity and intensity, respectively.

The Freundlich isotherm was also applied for the adsorption of CR onto CS by using the equation below:

$$q_e = K_F C_e \frac{1}{n} \qquad (5)$$

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \qquad (6)$$

where Ce is the equilibrium concentration (mg/L), q_e is the amount of adsorbate adsorbed per unit mass of absorbent (mg/g), K_F and n is Freundlich constants.

Langmuir Model		Freundlich Model	
q_m(mg/g)	95.25	q_m	90.3
R^2	0.990	R^2	0.988
b(L/mg)	0.236	1/n	5.29

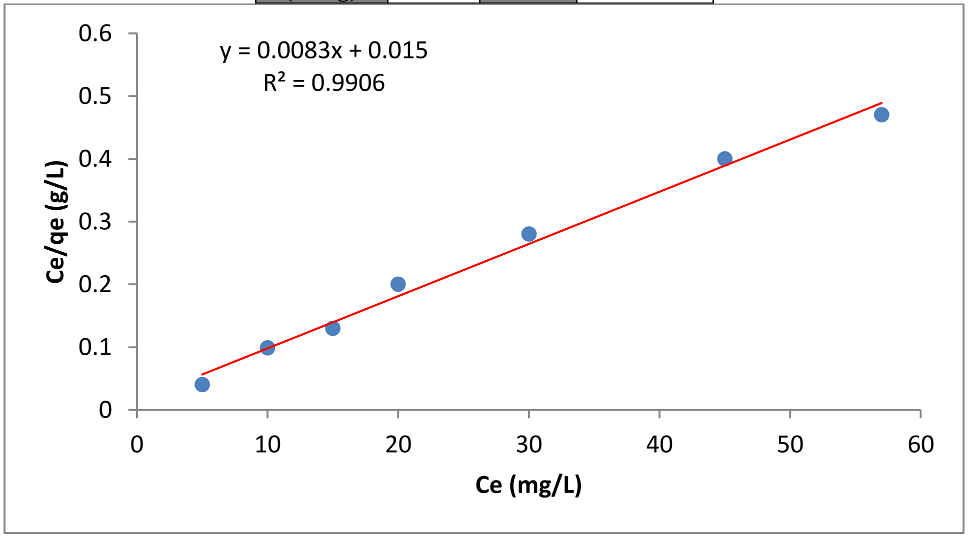

Figure 4.4.1: Langmuir plot

Figure 4.4.1 shows Langmuir isotherm fittings for CS adsorbent. The maximum monolayer adsorption capacity of CS and constant related to the adsorption system.

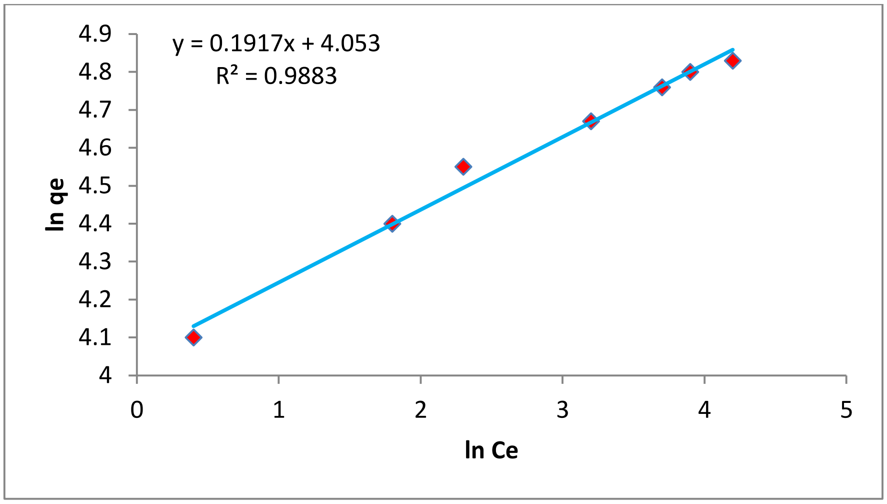

Figure 4.4.2: Freundlich plot

Figure 4.4.2 showed the Freundlich isotherm fittings for CS adsorbent, with a linear correlation coefficientR^2 of 0.9808. Freundlich constants, i.e., rate of adsorption, n, and adsorption capacity, K_F, are calculated from this plot.

4.5 Thermodynamic studies

The Gibbs free energy (ΔG°) for adsorption of CR onto CS at all temperatures was obtained from equation 7 and presented in Table 4.2. The values of ΔH° and ΔS° were determined from the slope and intercept of the plot of ΔG° versus T (Figure 4.4) and are also listed in Table 4.2. The negative value of ΔG° at all temperatures indicates the feasibility of the process and the spontaneous nature of the adsorbate onto adsorbent.

Increase in value of ΔG° with increase in temperature suggests that higher temperature makes the adsorption unfavorable. The negative value of ΔH° implies that the adsorption phenomenon is exothermic and obtained entropy ΔS° (-0.162 J $mol^{-1}K^{-1}$).

$$\log K_e = \frac{\Delta S^\circ}{2.303R} + \frac{-\Delta H^\circ}{2.303RT} \qquad (7)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \qquad (8)$$

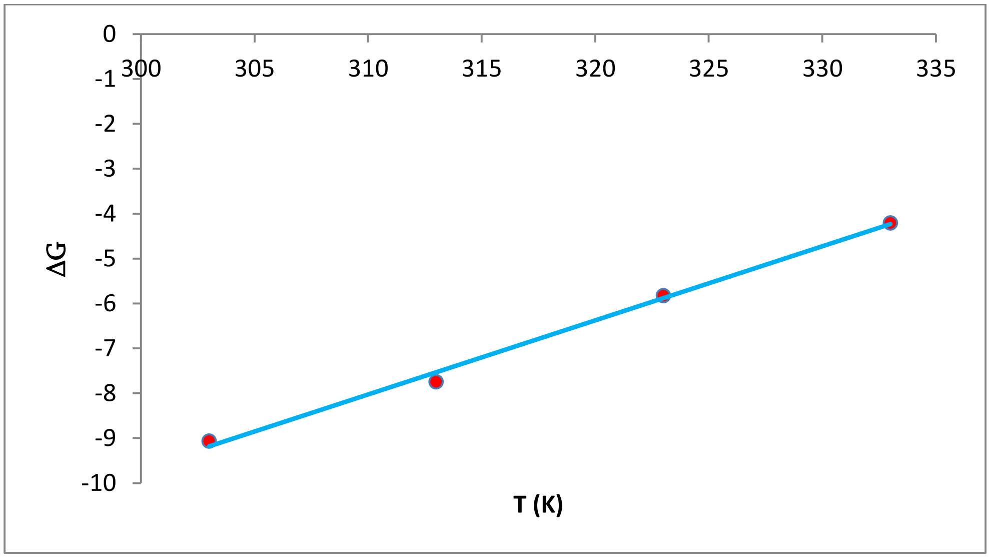

Figure 4.5: Plot of Gibb's free energy change versus temperature for adsorption of CR onto CS adsorbent.

Table 4.3: Thermodynamic parameters for adsorption of CR onto grounded CS

ΔG° (KJ mol^{-1})				ΔH° (KJ mol^{-1})	ΔS° (J mol^{-1})
303 K	313 K	323 K	333 K	-58.149	-0.162
-9.063	-7.7443	-5.823	-4.203		

5. Conclusion

This study shows the potential of cranberry stem application for the CR removal from wastewater. The results revealed that during the adsorption was taking place on the active surfaces cranberry stem particles. The Langmuir and Freundlich constants have been determined. The percentage removal of CR from synthetic and actual wastewater was 96% and 75% respectively. The beauty of the cranberry stem application for CR removal from wastewater is that it is ecologically sound and environmental desirable treatment technique. The adsorption process was obeyed both isotherm models. The obtained results indicated that the pseudo-second order kinetic fits the experimental data suitably, the adsorption process was found to be feasible, spontaneous and exothermic in nature as described by the thermodynamic properties of the process.

On the bases of this study, cranberry stem may also be effective in removing other harmful species, such as heavy metal ions.

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Abbreviations

CS: Cranberry stem; CR: Congo red dye; Ce: Equilibrium CR concentration, ppm (mg L^{-1}); C_o: Initial MB concentration, ppm (mg L^{-1}); C_t :CR concentration at time t, ppm (mg L^{-1}); ΔG°: Gibbs free energy change (kJ mole^{-1}); ΔH° : Enthalpy change (kJ mole^{-1}); ΔS°: Entropy change (J mole-1K^{-1}); K_1: Pseudo-first-order rate constant (min^{-1}); K_2: Pseudo-second-order rate constant (mg g-1min^{-1}); K_F: Freundlich adsorption constant (mg g^{-1}); M: Mass of adsorbent per unit volume (g L^{-1}); m: Amount of adsorbent added (g); n: Freundlich constant; b: Langmuir constant; q: Amount of adsorbate per gram of adsorbent (mg g^{-1}); q_e : Amount of adsorbate per gram at equilibrium(mg g^{-1}); q_t : Amount of adsorbate per gram of adsorbent at any time, t; q_m: Equilibrium adsorption capacity using model; R^2: Linear correlation coefficient; t: Time (min); T: Temperature (K); V: Volume of the solution (ml); λmax: Maximum wavelength (nm)