

# Adsorption of Crystal Violet Dye from Aqueous Solutions onto Low-Cost Untreated and NaOH Treated Almond Shell

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**ABSTRACT:** *In the present study, comparative batch adsorption of basic dye namely Crystal Violet (CV) using the almond shell as an adsorbent in untreated form and activated with sodium hydroxide was carried out in search of optimum adsorption conditions. The operation parameters investigated was contact time (10 to 80 min), initial dye concentrations (40-240 mg/L), temperature, (20-50 °C) and pH, (2-12). From the experimental results, it was found that the adsorption of crystal violet dye from aqueous solution onto both types of adsorbent (treated and untreated) was highly dependent on solutions pH, and its maximum adsorption was observed in basic medium. The adsorption equilibrium of CV was attained very rapidly after 40 min of contact time. Pseudo-first and second orders were used to examine the kinetic adsorption and found that the kinetic adsorption data were best fitted to pseudo-second order. Langmuir and Freundlich isotherm models were applied to equilibrium adsorption data, which were best fitted to Langmuir isotherm model. The thermodynamic analysis was carried out for dye-adsorbent systems. It was found that the adsorption nature of CV onto both adsorbents were endothermic. The performance of both adsorbents to adsorb CV was also compared. It was found that the adsorption capacity of almond shell activated by base was higher than untreated almond shell. Surface morphology and elemental composition of both adsorbents were examined using Scanning Electron Microscopy (SEM), and energy dispersive X-ray spectroscopy.*

**KEYWORDS:** *Crystal violet; Almond shell; SEM; EDX.*

## INTRODUCTION

Access to clean and safe drinking water is a human right; however, the availability of potable water is

a major concern in both developed and developing countries. Water treatment offers the benefit of potable

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1021-9986/2016/2/97-106

10\$/6.00

water in terms of quality (reduced level of contaminants) and quantity (availability). The world is facing formidable challenges in meeting the rising demands for safe drinking water supply due to increasing pollution of water bodies from several industrial and agricultural activities. Emerging countries emphasis on industrialization and urbanization, but in the meanwhile, they are polluting their environment especially water. Because, different industrial sectors such as: textile, leather, cosmetic, food, printing, pharmaceutical, paper etc. are using different dyes for their products colouring [1, 2]. Water discharged into the hydrosphere from these industries contains different types of dyes, which are the culprits of water contamination [3]. The presence of dyes in water causes serious environmental problems to human's health and hydrosphere due to their toxicity and carcinogenic effect. As the world is facing drastic problems due to these toxic dyes, therefore, it is necessary to remove it from industrial waste before discharging into the hydrosphere. Thus rapid and fast environmental monitoring system or device is required for complete degradation of different hazardous organic dyes in order to avoid the water pollution. In this regard, many technologies including reverse osmoses, coagulation, chemical oxidation, biological treatment, photo degradation and adsorption [4 - 6] have been applied for treatment of dye contaminated water. Among these technologies, adsorption is most attractive technique for the treatment of contaminated water, especially in the case when low cost and easily available adsorbent are used [7]. Consequently many researchers reported the feasibility of economical adsorbents for the treatment of water polluted by dyes and heavy metals. Some of the reported low cost adsorbent which treated waste water is pomegranate shell powder, rice husk, tea waste, peanut hull, saw dust, sodium aluminosilicate etc. [8 - 10].

In this study, one of the agriculture waste material (almond shell) in untreated form and treated with base were used as adsorbents for the removal of Crystal Violet (CV) dye from aqueous solutions. Furthermore, in this study the adsorption capacity of almond shell treated with base were also compared with untreated almond shell. The objective of the present work was to (i) check the adsorption capacity of low cost and easily available adsorbent for the removal of one of the carcinogenic dye from aqueous solutions; (ii) evaluate different

experimental parameters which effecting the adsorption process including solution pH, dye concentration, contact time, adsorbent amount and temperature; (iii) determine the kinetics and equilibrium isotherm models for the adsorption data; (iv) decide the thermodynamic and spontaneity feasibility of CV adsorption process using different thermodynamic parameters including entropy, enthalpy and Gibbs free energy.

## EXPERIMENTAL SECTION

### *Reagent and Solution*

Crystal violet dye was purchased from the Sigma Aldrich, and was used as such without further purification. Stock solution of 1000 ppm was prepared by dissolving 1g of crystal violet in 1000 mL of distilled water. For further study the working solutions were then prepared from the stock solution using dilution formula.

### *Preparation of Adsorbent*

Almond shells were collected from the Qissa khwani bazar Peshawar, Pakistan. The almond shells were grinded into powder form, and then sieved by sieve size of 120  $\mu\text{m}$ . The sieved almond shell were washed with distilled water for several time to remove the dust and other impurities, finally dried in oven and store in bottle for further experimental work.

### *Base treatment of adsorbent*

Cleaned and dried almond shell was taken in a round bottom flask and 100 mL of 0.1 N NaOH solutions was added to it. The almond shell and base solutions in flask were refluxed with continuous stirring and heating (80°C) for three hours. After three hours the almond shell slurry were filtered, then washed with distilled water, dried in oven and store for further work.

### *Batch adsorption program*

Adsorption of Crystal Violet (CV) dye onto untreated and base activated almond shell ((UAS, BAAS) were conducted at different adsorption parameters like: different solutions pH, contact time, adsorbent dose, initial dye concentration, temperature. For each experimental study, known volume, dye concentration, pH of the dye solutions and mass of the adsorbent were taken in 100 mL Erlenmeyer flask, and were shacked for the respective time in temperature control water bath shaker. The pH

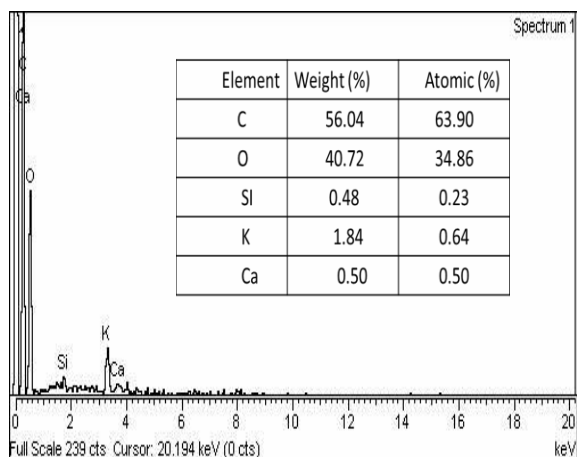


Fig.1: EDX spectra of UAS.

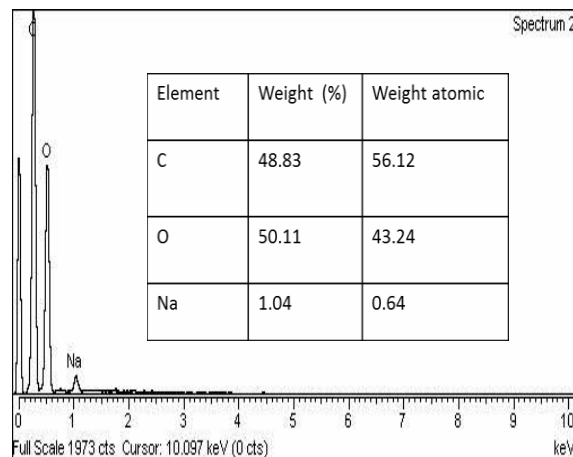


Fig. 2: EDX spectra of BAAS

of the solutions was adjusted by using dilute NaOH and HCl solutions. After the respective time, the Erlenmeyer flask was taken from the shaker and the mixture were then filter by watt man filter paper. The residual concentration of the dye in aqueous solutions was analyzed for the absorbance using Spectrophotometer. The residual concentration of the dye in aqueous solutions was calculated from the absorbance using calibration curve. The dye adsorbed per unit mass of the adsorbent (mg/g) and their percentage adsorption was calculated using equations 1 and 2.

$$q_e = \frac{(C_i - C_e)V}{W} \quad (1)$$

$$R\% = \frac{(C_i - C_e)}{C_i} \times 100 \quad (2)$$

Where  $q_e$  is the adsorption capacity of adsorbent in mg/g,  $C_i$  and  $C_e$  is the initial and equilibrium concentration of dye in aqueous solutions,  $V$  is the volume of solutions in litter and  $w$  is the mass of adsorbent in gram.

## RESULTS AND DISCUSSION

### Adsorbent Characterization

#### EDX analysis of the prepared adsorbents

Figs. 1 and 2 shows the EDX spectra of UAS and BAAS. The EDX spectra of UAS show the highest percentage of carbon and oxygen along with minute quantity of potassium, silicon and calcium. While the spectra of BAAS shows only carbon and oxygen and other elements which were present in the spectra of UAS is completely absent in the spectra of BAAS.

### Surface morphological study of the prepared adsorbents

Fig. 3a and 3b shows the SEM images of UAS and BAAS. From the Fig. 3a it can be seen that almond shell has considerable number of small pore, where appropriate condition exist for CV dye to be trapped and adsorbed to these pores. Fig. 3b shows the SEM image of BAAS, which shows that the BAAS surface have several fracture in the form of pores, cavities and drills. Because of the treatment of lignocellulosic material with sodium hydroxide can cause swelling, which lead to increase in surface area, separation of carbohydrate - lignin structural linkage and lignin structure disruption. Thus, BAAS will have more capacity to trapped and adsorbed CV dye as compare to UAS.

### Effect of pH

pH of the dye solutions is the most important factor in the adsorption study, because it controls the adsorption capacity of the adsorbent, and also the dye stability [11, 12]. At some pH the dye are more stable and very difficult to remove it from aqueous solutions. While, at some pH the dye become unstable and become easy to remove it from aqueous solutions. Due to the high role of solutions pH value in the removal of dye from aqueous solutions, so therefore, the adsorption of CV onto UAS and BAAS were carried out at different pH range from 2 to 12, and other experimental condition such as contact time (2 hours), initial dye concentration (50 mg/L), adsorbent dose (0.06 g) and temperature (25°C) were kept constant. The adsorption of CV onto UAS and BAAS are shown in Fig. 4. From the figure it can be seen

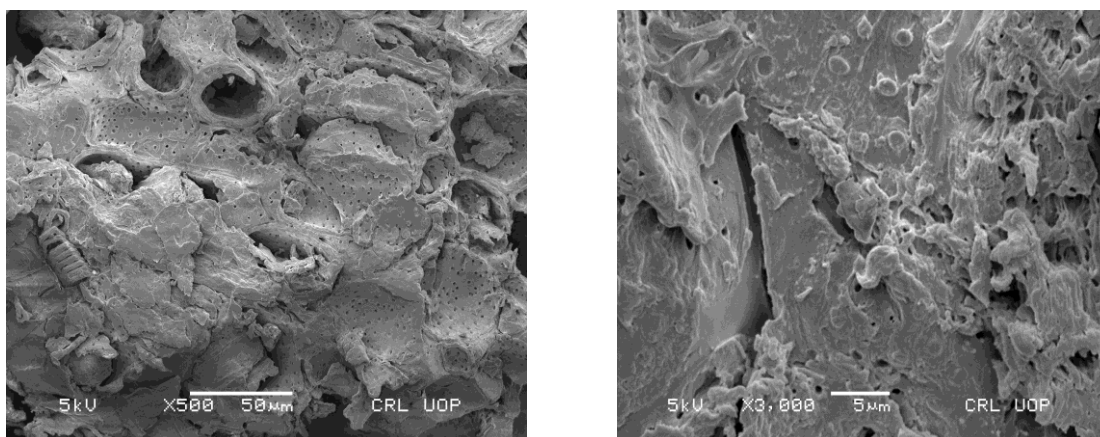


Fig. 3a) SEM image of UAS. 3b) SEM image of BAAS.

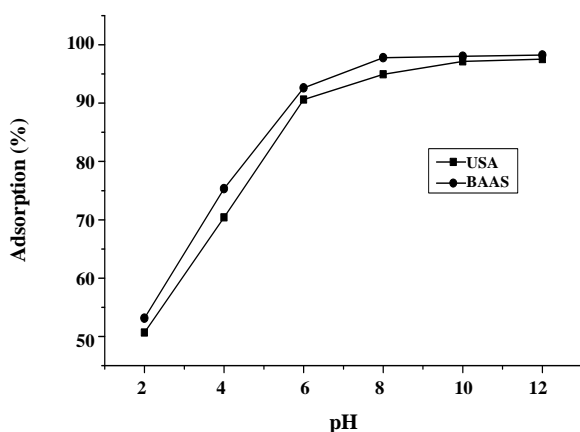


Fig. 4: Effect of pH on the CV adsorption onto UAS and BAAS.

that at pH 8 the adsorption of CV is maximum, and then after pH 8 its adsorption almost become constant, while at low pH its adsorption is minimum. From this observation it can be concluded that at low pH (acidic medium) the CV is more stable, and its stability decreases with increasing pH value of the solutions and become completely unstable at pH 8. The instability of CV at high pH value may be contributed to the structural changes occurred in the molecules of CV, and thus become easy to remove it from aqueous solutions. From this study it can be concluded that the optimum pH value for the removal of CV from aqueous solution is 8, and at higher pH value the adsorption become constant. Further study of CV adsorption was carried out at pH 8.

#### Effect of Contact time

To find the equilibrium contact time requires for the removal of CV dye from aqueous solutions; the adsorption study was carried out at different time intervals ranged from 10 to 80 minutes. Other experimental conditions like: pH 8, adsorbent dose 0.06 g, initial dye concentration 50 mg/L and temperature 25 °C were kept constant. The experimental results are given in Fig. 5. From the figure it can be seen that the adsorption of CV onto both adsorbent increases with increasing contact time up to 40 minutes and then almost become constant after the 40 minutes for both type of adsorbents. Thus the equilibrium contact time for the adsorption of CV onto both type adsorbent was 40 minutes and further experimental study was carried out at 40 minutes.

#### Kinetic study

To find a suitable mechanism for the adsorption of CV onto UAS and BAAS, kinetic study were interpreted through pseudo first and second order kinetic models in the form of equations as:

Lagergren proposed pseudo first order kinetic model [13] is given as:

$$\text{Log}(q_e - qt) = \text{Log}q_e - \frac{K_1 t}{2.303} \quad (3)$$

Where  $q_e$  and  $qt$  is the amount of dye adsorbed in mg/g at equilibrium and at respective time, and  $k_1$  is the rate constant of pseudo first order kinetic model which can be calculated from the linear plot of  $\text{Log}(q_e - qt)$  versus time.

The pseudo second order kinetic model [14] is given as:

$$\frac{t}{qt} = \frac{1}{K_2q^2} + \frac{1}{q_e}t$$

By plotting  $t/qt$  versus  $t$  give a straight line from which  $K_2$  (mg/L) and  $q_e$  (mg/g) can be calculated.

Plot of pseudo first and second order models are given in Figs. 6, 7 and their parameters are listed in Table 1. From the plot of pseudo first and second order kinetic models and their parameters comparison it can be concluded that the kinetic study followed pseudo second order kinetic better than pseudo first order kinetic; because the retrogressive value ( $R^2$ ) of pseudo second order were very close to 1 and also  $q_e$  value calculated from the plot of pseudo second order kinetic were very close to experimental  $q_e$  value as given in Table 1.

#### Effect of adsorbent dose

To optimized the adsorbent amount for the adsorption of CV from aqueous solutions, the study were carried out at different adsorbent dose range from 0.02 g to 0.1 g, other experimental condition, i.e. initial dye concentration (50 mg/L), contact time (40 min), pH (8) and temperature (25 °C) were kept constant. The percentage adsorption of CV at different adsorbent dose is given in Fig. 8, which shows that the percentage adsorption of CV onto both adsorbents increases with increasing adsorbent dose up to 0.06 g and then become constant with further increase in adsorbent dose. The increase in the percentage adsorption of the dye with increasing the adsorbent dose may be contributed to the availability of the larger adsorbent surface to the fixed amount of dye molecules. The adsorption capacity (mg/g) of both types of adsorbents was decreases with increasing the adsorbent dose which is not mention here. The decrease in the adsorption capacity of the adsorbent with increasing the adsorbent amount may be because of the aggregation of the adsorbent particles at higher adsorbent dose, due to which some active surface of the adsorbent remain unavailable for the adsorption of dye molecules [15], and thus the results is the decrease in adsorption capacity.

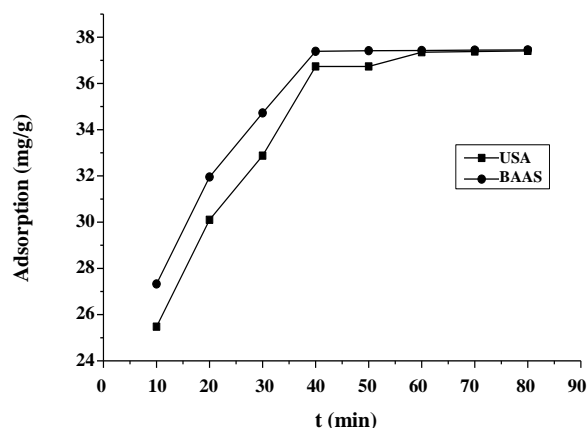


Fig. 5: Effect of contact time on the CV adsorption onto UAS and BAAS.

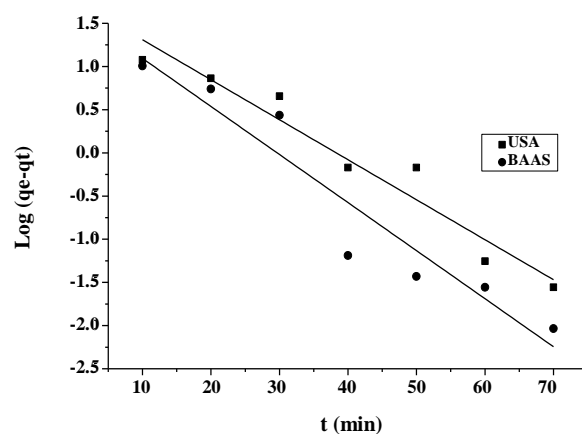


Fig. 6: Pseudo first order for the CV adsorption onto UAS and BAAS.

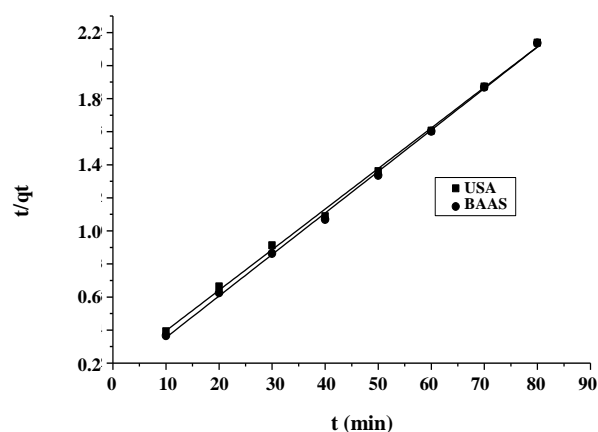


Fig. 7: Plot of pseudo second order kinetic model for the CV adsorption onto UAS and BAAS.

Table 1: Pseudo first and second kinetic models parameters.

Pseudo first order			Pseudo second order		
Qe (mg/g)	K <sub>1</sub> (min <sup>-2</sup> )	R <sup>2</sup>	Qe (mg/g)	K <sub>2</sub> (g/mg min)	R <sup>2</sup>
CV on UAS					
25.6	0.1	0.93	40.8	4×10 <sup>-3</sup>	0.99
CV on BAAS					
19.3	0.13	0.90	39.2	8.8×10 <sup>-3</sup>	0.999

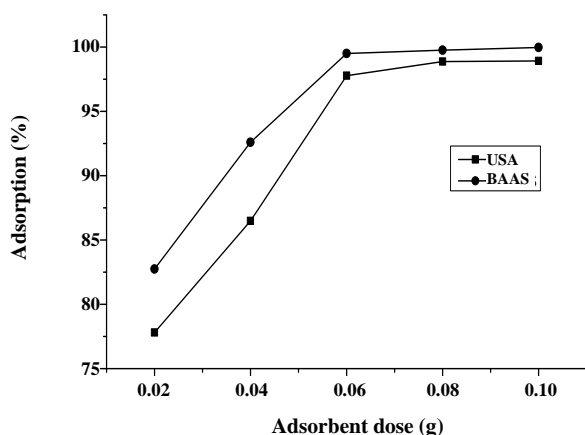


Fig. 8: Effect of adsorbent dose on the CV adsorption onto UAS and BAAS at different adsorbent dose.

#### Effect of initial dye concentration

Effluent of different industry contain different concentration of dyes, therefore it is advisable to carry out the adsorption study at different concentration of dyes. So, therefore, the adsorption of CV onto UAS and BAAS was carried out at different initial dye concentration range from 40 mg/L to 240 mg/L. Other experimental condition, i.e. contact time (40 min), adsorbent dose (0.06g), solution pH (8) and temperature (25°C) were kept constant. The percentage adsorption of CV at different concentration on to UAS and BAAS are given in Fig. 9, which shows that the percentage adsorption of CV from aqueous solution onto both adsorbents decreases with increasing the initial dye concentration. The decrease in percentage adsorption with increasing the dye concentration is due to the saturation of available active sites of the adsorbents at higher concentration of dye molecules [16]. Thus the dye molecules remain in the solutions, which lead to decrease in percentage adsorption. While the amount of dye adsorb per unit mass of the adsorbent (mg/g) was increases with

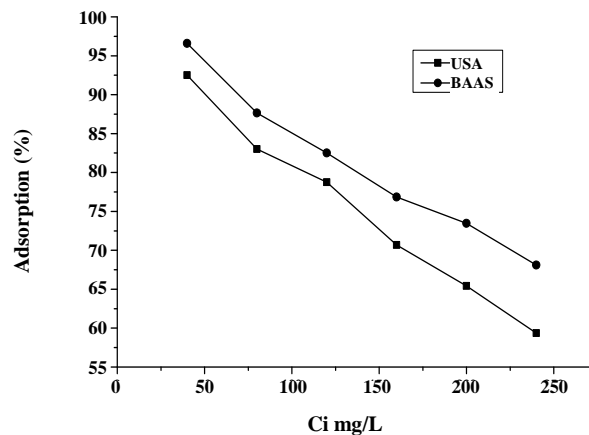


Fig. 9: Effect of initial dye concentration on the percentage adsorption of CV onto UAS and BAAS.

increasing the initial dye concentration. This increasing of dye adsorption per unit mass of the adsorbent is because of the resistance for the adsorbent to uptake the dye molecules from aqueous solutions with increasing the initial dye concentration [17].

#### Isotherm study

Langmuir and Freundlich adsorption isotherm models were used in order to interpret the isotherm data of CV onto UAS and BAAS.

The linear form Freundlich adsorption isotherm, used for heterogeneous surface [18] is given as:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

Where  $q_e$  (mg/g) is the amount of dye adsorbed at equilibrium,  $C_e$  (mg/L) is the remaining concentration of dye in solution,  $K_F$  (mg/g) (L/mg) and  $n$  is constant which can be calculated from the slope and intercepts of linear plot of  $\ln q_e$  versus  $\ln C_e$ .

Table 2: Parameters of Freundlich and Langmuir adsorption isotherm.

Freundlich isotherm			Langmuir isotherm		
$K_F$ (L/mg)	n	$R^2$	$q_{max}$ (mg/g)	$K_L$ (L/mg)	$R^2$
UAS					
20	0.32	0.931	114	0.06	0.994
BAAS					
27.3	0.22	0.988	123	0.11	0.993

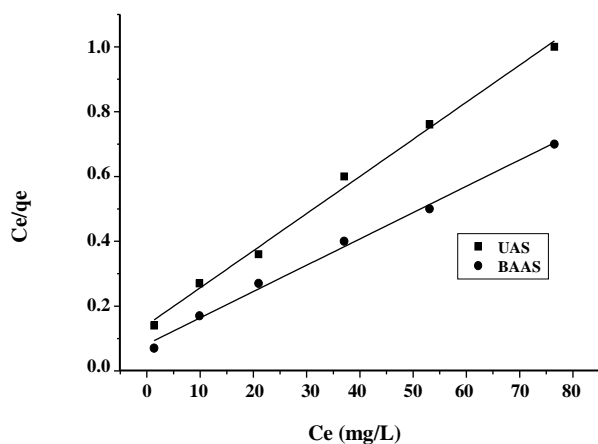


Fig. 10: Langmuir plot for the CV adsorption onto UAS and

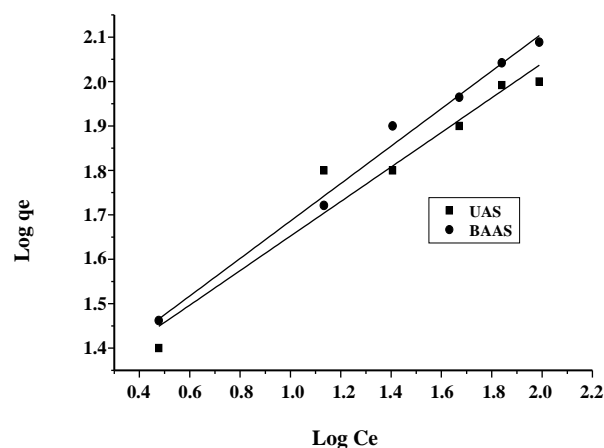


Fig. 11: Freundlich plot for the CV adsorption onto UAS and BAAS

The linear form Langmuir adsorption isotherm used for heterogeneous surface [19] is given as:

$$\frac{C_e}{q_e} = \frac{1}{Kq_{max}} + \frac{C_e}{q_{max}} \quad (6)$$

The plot of Freundlich and Langmuir adsorption isotherm are shown in Figs. 10 and 11, and their parameters are listed in Table 2. From the parameter comparison of the Langmuir and Freundlich adsorption isotherm it can be concluded that the adsorption of CV onto both forms of AS followed Langmuir adsorption isotherm, because of its close regression coefficient ( $R^2$ ) value to 1 and also the experimental  $q_e$  (mg/g) value is very close to  $q_e$  (mg/g) value calculated from the slope of Langmuir plot.

#### Effect of temperature

Temperature has a significant role in the adsorption process, because with increasing temperature the diffusion of the dye molecules to the pore of the adsorbent increases and also the solution viscosity decreases with

increasing temperature [20]. So, therefore, the adsorption of CV onto UAS and BAAS was carried out at four different temperatures, ranging from 20 °C to 60 °C. Other experimental conditions, i.e. initial dye concentration (50 mg/L), contact time (40 min), adsorbent dose (0.06 g), solution pH (8) were kept constant. The adsorption of CV (mg/g) onto UAS and BAAS are shown in Fig. 12. From the figure it can be concluded that the adsorption capacity of the adsorbent for dye increases with increasing temperature, which indicated that the adsorption process was endothermic [21].

#### Thermodynamic parameters

The thermodynamic parameters like: Entropy ( $\Delta S^\circ$ ), Enthalpy ( $\Delta H^\circ$ ) and Gibbs free energy ( $\Delta G$ ) were calculated using the following equations.

$$\Delta G^\circ = RT \ln K_D \quad (7)$$

$$\ln K_D = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (8)$$

Table 3: Thermodynamic parameters for the adsorption of CV onto UAS and BAAS.

$\Delta H^\circ$ (KJ/mole)	$\Delta S^\circ$ (KJ/mole K)	$-\Delta G^\circ$ (KJ/mole)			
		303 (K)	313 (K)	323 (K)	333 (K)
UAS					
67.7	255	76	94.6	120	153
BAAS					
71.5	275	96.5	116.2	148.7	178.1

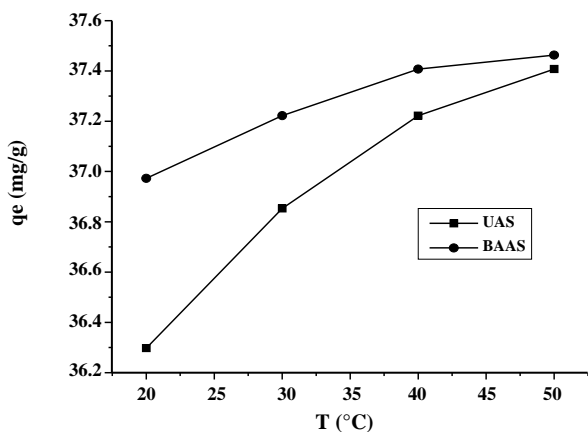


Fig. 12: Effect of temperature on the adsorption capacity of UAS and BAAS

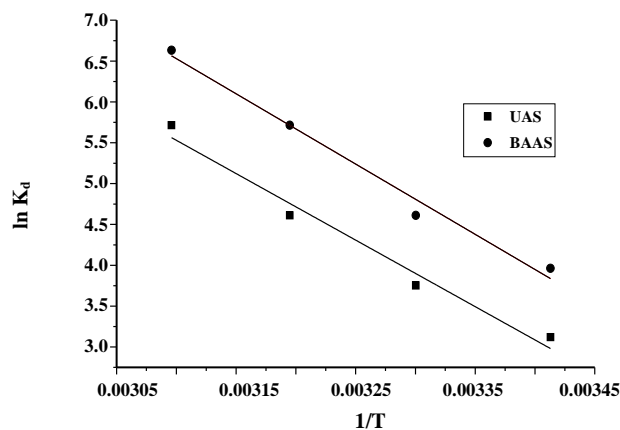


Fig. 13: The Van't Hoff plots for the adsorption of CV onto UAS and BAAS

Where  $K_D$  is the distribution coefficient,  $R$  is the ideal gas constant (8.314J/molK) and  $T$  is the absolute temperature in kelvin.  $\ln K_D$  were plotted versus  $1/T$  using Eq. (8) as given in Fig. 13. The value of Enthalpy ( $\Delta H^\circ$ ) and Entropy ( $\Delta S^\circ$ ) were calculated from the slope and intercept of the linear plot of  $\ln K_D$  versus  $1/T$ . while Gibb's free energy ( $\Delta G$ ) was calculated using Eq. (7). Enthalpy ( $\Delta H^\circ$ ), Entropy ( $\Delta S^\circ$ ) and Gibb's free energy ( $\Delta G$ ) values are given in Table 3. The positive values of Enthalpy ( $\Delta H^\circ$ ) conform that the adsorption of CV on to both adsorbent was endothermic [22], while the positive value of Entropy ( $\Delta S^\circ$ ) justified the randomly adsorption of CV onto adsorbents [22]. Gibb's free energy ( $\Delta G$ ) values for both form adsorbents are negative at all temperature, which indicated that, the adsorption process was spontaneous [23].

## CONCLUSIONS

For the adsorption process such adsorbent is required which have low cost, easily available and possess high capacity for pollutant uptake. In this study we utilized

potentially one of the agricultural byproduct (almond shell) for the removal of toxic and easily soluble dye. To enhance the adsorption capacity of almond shell, it was also treated with sodium hydroxide, which was better than the adsorption capacity of untreated form. The adsorption process was evaluated in terms of kinetics, equilibrium and thermodynamics. Kinetics adsorption was best to pseudo second order equation, while the equilibrium adsorption was fitted to monolayer Langmuir adsorption isotherm model. The effective removal of crystal violet was observed in basic medium. On the bases of all results, it can be concluded that almond shell can be used efficiently in the removal of crystal violet dye from aqueous solutions.

Received : Nov. 11, 2014 ; Accepted : Nov. 9, 2015

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