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# EQUILIBRIUM AND KINETICS STUDY OF CRYSTAL VIOLET DYE REMOVAL BY USING LOW COST WATER HYACINTH ROOT POWDER

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## ABSTRACT

**Adsorption of crystal violet (CV) dye on water hyacinth root powder (WHRP) has been investigated as a function of solution pH, adsorbent dose, initial concentration and treatment time in batch reactor. A low cost natural adsorbent WHRP was used for the removal of CV. The optimized parameters were found to be pH: 7, adsorbent dose: 10 g/L, initial concentration: 20 mg/L, and treatment time: 160 min. At these optimum conditions 90% removal of CV was observed. The maximum adsorption capacity of CV was found to be 8.40 mg/g. Freundlich isotherm suitably fitted to equilibrium data. Adsorption kinetic facts are satisfactorily represented by the pseudo-second order kinetic model. The results of experimental study showed that WHRP an outstanding adsorbent for the removal of CV from wastewater.**

**KEY WORD :** Adsorption, Crystal violet, Water hyacinth root powder, Isotherm, Kinetics

## INTRODUCTION

Wastewater of dyeing industries are the major source of water and soil pollution due to the presence of dyes. The dye (color) is the first pollutant to be renowned in wastewater by naked eyes (Banat *et al*., 1996). The presence of very little amounts of dyes in water is extremely observant and undesirable (Robinson *et al*., 2001). Worldwide more than $7x10^5$ tonnes of dyestuff created per annum (Wang *et al*., 2008). From dye manufacturing operations approximately 2% of a produced dyes discharge in effluent, while fabric and related industries discharged nearly 10% of dyestuff in the effluent (Wang *et al*., 2008).The release of dyes by industries into water streams is highly adverse and causes severe environmental harms. It contains a range of organic compounds and lethal substances which are hazardous and harmful to aquatic organisms.

The colored effluent in the receiving water streams reduces the light diffusion through the water's surface and therefore, reduces photosynthetic action (Weisburger, 2002). The Crystal Violet (CV) dye is a cationic artificial dye which transmits violet color when dissolve in aqueous solution. This dye is used widely in the fabric industries for dying wool, cotton, nylon, silk etc. It also used in production of printing inks and biological stain (Adak *et al*., 2005; Ayed *et al*., 2009). The CV is lethal and may be immersed through the skin, causing impotence and also injurious to living being by inhalation and intake. In severe cases it can lead to kidney faillure, harsh eye annoyance leading to everlasting blindness and cancer (Senthilkumaar *et al*., 2006). Thus, it's gaining the attention of researchers for the elimination of CV from industrial effluents due to its main environmental concerns.

For the dealing of colored effluent a range of traditional treatment technologies, namely biological, physical and chemical methods are available, but it frequently treated with either by physical or chemical processes. Conventional biological method is not very effective due to

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structure complexity and low biodegradability of synthetic dyes. Moreover, these processes are very costly and sometimes produce toxic byproducts so it cannot be effectively used for the treatment of wide range of dyes. Adsorption process can treat high flow wastewater with superior ultimate excellence and without injurious matter making (Wong *et al.*, 2004) thus provides an attractive substitute for the dealing of colored effluent. Activated carbon is an effective adsorbent for the treatment of colored effluent but its large scale application is limited due to higher prices and renewal trouble.

In current scenario researchers pay a lot of attention in exploring the potential of inexpensive adsorbents for dyes elimination. Numerous materials similar to green peas shell (Dandge *et al*., 2016), date palm fiber (Alshabanat *et al*., 2013), potato peels (Lairini *et al.*, 2017), agricultural wastes (Mahmoud *et al.*, 2012), Subabul Seed Pods (Patil and Shrivastava, 2012), acacia nilotica Leaves (Prasad and Santhi, 2012), banana pith (Namasivayam *et al*., 1998), grass waste (Hameed, 2009), tea waste (Uddin *et al.*, 2009), sesame hull (Feng *et al*., 2011), rice husk (Chakraborty *et al.,* 2011) and lanatus rind (Bharathi and Ramesh, 2012) are widely used for dye elimination. Water hyacinth is available in the local stream Kshipra can be used a natural adsorbent for CV removal. In the present study adsorption potential of water hyacinth root powder (WHRP) has been tested for the elimination of CV dye from synthetic wastewater.

The aims of present research are (i) to study the performance of WHRP for the removal of CV dye (ii) to study the effect of process parameters such as pH, adsorbent dose, treatment time, initial concentration (iii) to nd out the kinetic constants (iv) to determine the applicability of isotherm model.

## MATERIALS AND METHODS

### Adsorbent Preparation

A fast growing, noxious weed water hyacinth was acquired from local stream Kshipra of Ujjain. The water hyacinth plant roots were cut from the stem and washed thoroughly first with tap water then many times with distilled water. Washed roots were cut into pieces and then dried overnight in oven at 50 $^{o}$C. After drying the roots, it finely grounded, sieved for further use or stored in air tied container.

### Adsorbate and Chemicals

For experimentation work stock solution of 1 gm/L of CV ($C_{25}H_{30}N_3Cl$, molar mass 408 g/mol, C.I. No. =42555, $\lambda_{max}$ = 590 nm) was prepared and diluted as per experimental requirement. Solution pH was attuned by using 0.1 M NaOH and 0.1 M HCl. All used chemicals are of analytical grade.

### Batch Adsorption Experimentation

Batch adsorption experiments were performed at room temperature to examine the adsorption parameters by adding a fixed amount of WHRP to 100 mL CV dye solution. The suspension of WHRP and CV was shaken at room temperature for 20 to 200 minutes with a constant speed of 60 rpm in orbit shaker. The CV concentration was analyzed using a UV spectrophotometer (Systronics, 2105) at wave length of 590 nm. The adsorption capacity of WHRP was calculated by using Eq. (1).

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

Where, $q_e$ represents the adsorption capacity of WHRP adsorbent (mg/g), $C_e$ and $C_i$ is the equilibrium and initial concentrations of CV (mg/L), respectively, W represents the adsorbent mass (gm), V in liters represents the volume of solution. The % removal of CV was computed from Eq. (2).

$$\% \text{ removal} = \frac{(C_i - C_o)x100}{C_o} \quad .. (2)$$

## RESULTS AND DISCUSSION

### Effect of pH

Solution pH plays an important role for adsorption process. Batch experiments were performed in the pH range of 2.0 to 10.0, while all others parameters were kept constant to get the optimum pH for adsorption process. Fig. 1 shows that the adsorption of CV was minimum 37.3% at pH 2.0 and increased up to 90% at pH 7.0 and then remained almost

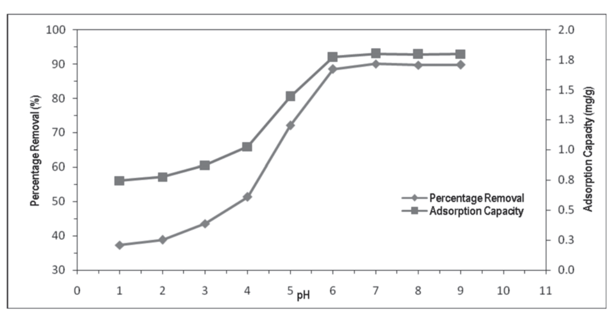


**Fig. 1.** Effect of pH on Adsorption of CV (initial concentration: 20 mg/L, treatment time: 160 min., adsorbent dose: 10 g/L)

constant over the pH range of 7.0-10.0. At acidic pH lower adsorption of CV was occurred due to the repulsion of $H^+$ ions and the dye cation for the positive adsorption sites. As the pH increase to neutral and above negatively charged sites increases thus the maximum removal of CV found due to electrostatic attraction. Alshabanat *et al.* (2013) reported similar trends of pH for CV adsorption onto date palm fiber.

### Effect of Adsorbent Dose

The effect of adsorbent dose on removal of CV is illustrate in Fig 2. It is revealed from Fig. 2 that the percent removal of dye increases from 53.2% to 90% by increasing the dose of the WHRP from 1 g to 10 g, respectively. As the dose increases at fix concentration of CV more surface area as well as active site were available for adsorption thus removal increases. The equilibrium was achieved at 10 g adsorbent dose as no increase in percentage removal was observed on additional of the adsorbent dose.

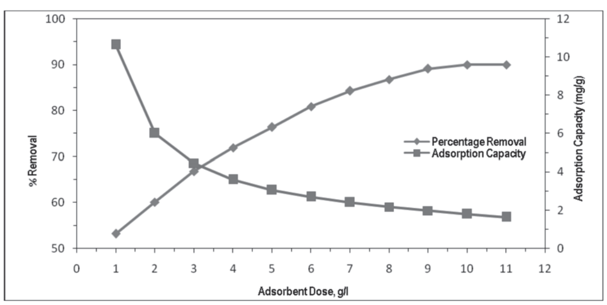


**Fig. 2.** Effect of Adsorbent dose on removal of CV (pH: 7, initial concentration: 20 mg/L, treatment time: 160 min.)

### Effect of Treatment Time

Fig. 3 illustrates the effect of treatment time on adsorption of CV on WHRP. For 20 mg/L initial concentration nearly 76% of total dye uptake achieved in first 20 minutes and then increases gradually to 90 % at 160 min and finally attained equilibrium value. In the start of adsorption, more active site was available at fix concentration hence high removal (76%) achieved. As the time passes free site of adsorbent and concentration driving force both reduces which result in less removal. For further experiment an equilibrium time of 160 minutes was selected as the optimum time.

### Effect of Initial Concentration

The experimental result of adsorption of CV by WHRP at various initial concentrations 20, 40, 60, 80, and 100 mg/L for fixed dose 1 mg/100 mL of adsorbent at pH 7.0 is shown in Fig. 4. It is found that with the increase in initial CV concentration, the CV removal decreases, while the adsorption capacity increases and became maximum at 100 mg/L. Maximum percentage removal (90%) achieved at 20 mg/L initial concentration. At lower CV concentration, the number of WHRP adsorbent surface active sites is sufficiently high and accommodates abundant of CV ions. An increase in the CV concentration causes a reduction in the proportion of surface active sites of WHRP to CV ions, and thus an insufficient accommodation of CV ions results in the decreasing % CV removal efficiency. When initial concentration of CV increases percent adsorption decreases, whereas the quantity of CV adsorbed per unit mass of WHRP increased. The equilibrium adsorption ability is augmented from 1.8 to 6.7 mg/g as the CV concentration increased from 20 to 100 mg/L. Furthermore, a driving force is provided by initial CV concentration to overcome all mass transfer resistances between the adsorbent and adsorption medium which consequences in higher adsorption capacities at higher initial CV concentration.

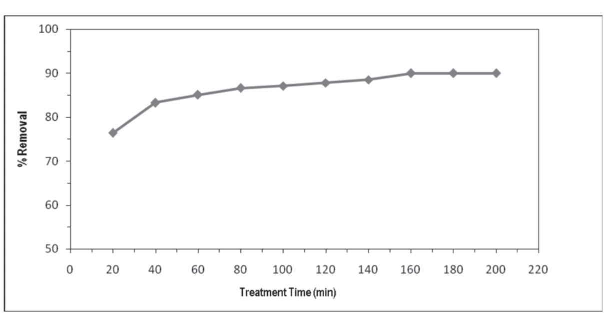


**Fig. 3.** Effect of treatment time on removal of CV (pH: 7, initial concentration: 20 mg/L, adsorbent dose: 10 g/L)

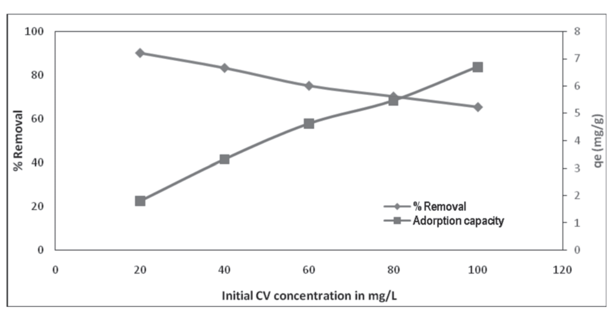


**Fig. 4.** Effect of initial CV concentration on removal of CV (pH: 7, adsorbent dose: 10 g/L, treatment time: 160 min.)

### Adsorption Isotherm Model Studies

Adsorption isotherm indicates the circulation of adsorbate molecules among solid and liquid phase while system is in equilibrium. For the design purpose adsorption model with isotherm data are essential.

Langmuir isotherm model (Langmuir, 1916) is largely implemented to monolayer adsorption on uniform and vigorously standardized surfaces. The Freundlich isotherm model (Freundlich, 1906) is extensively in use to conclude the adsorption amount of absorbent surfaces with non-uniform energy division. The mathematical equations of Langmuir and Freundlich isotherm models are articulated by equation no. 3 & 4, respectively:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \quad .. (3)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad .. (4)$$

Where, $q_{max}$ (mg/g) is the maximum amount of dye adsorbed at equilibrium, $K_L$ is the Langmuir isotherm constant, $K_f$ is the Freundlich isotherm constant, n is a heterogeneity factor.

Graph between $C_e/q_e$ Vs $C_e$, $\log q_e$ Vs $\log C_e$ were plotted. The Langmuir isotherm model and Freundlich isotherm model of CV on WHRP are shown in Fig. 5 and Fig. 6, respectively. The values of $q_{max}$, $K_L$, $K_f$, n were calculated by use of the slopes and intercepts of the graphs (Fig. 5 and, 6) and shown in Table 1.

For Langmuir model, CV adsorption onto WHRP monolayer maximum adsorption capacity is found to be 8.40 mg/g. The value for Langmuir constant is found to be 0.1059 for CV at $R^2$ of 0.983. Hall *et al.* (1966) narrated a dimensionless equilibrium parameter to be precise separation factor ($R_L$), in order to disclose the vital feature of the Langmuir isotherm involving $R_L$ with Langmuir constant band the initial concentration of the adsorbate solution, $C_o$ i.e. $R_L = 1/(1+bC_o)$. The $R_L$ is found to be 0.3205 thus $R_L$ falls in between zero and one, which signifies highly favorable adsorption and applicability of the Langmuir isotherm also.

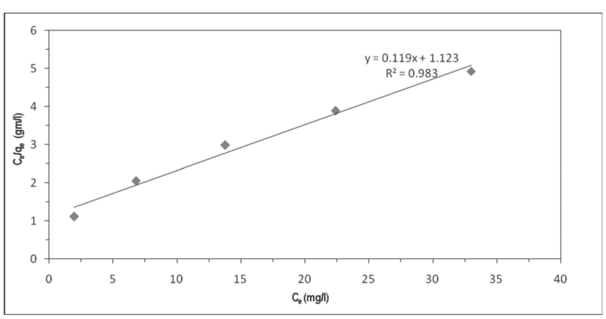


**Fig. 5.** Langmuir Isotherm for Adsorption of CV onto WHRP

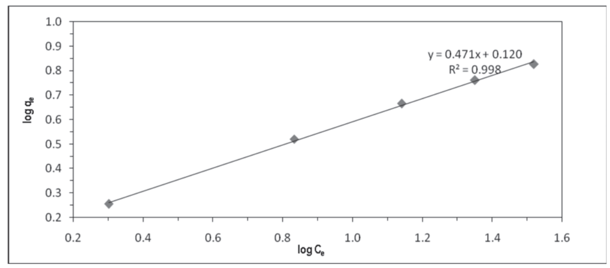


**Fig. 6.** Freundlich Isotherm for Adsorption of CV onto WHRP

Fig. 6. Shows the logarithmic graph of the Freundlich isotherm for the CV. The adsorption activities of the dyes undertaken could be described well by Freundlich isotherm model with high values of correlation coefficient ($R^2$: 0.998). When n>1 indicates a favorable adsorption condition (Treybal, 1998). According to Kadirvelu and Namasivayam (2000), the value of n between 1 and 10 represents a beneficial adsorption process. Heterogeneity factor 1/n is related to the intensity of adsorption. In this study 1/n is found to be 0.471, which is observed to be less than 1 and describes a favorable nature of adsorption onto WHRP. Based on the $R^2$ value, Freundlich isotherm suitable represents the equilibrium data of CV adsorption process.

### Adsorption Kinetics Models Fitting

For adsorption study both rate and time are essential to understand the adsorption kinetic and interaction of CV on WHRP. Hence, two kinetic models pseudo-first-order (PFO) and pseudo-second-order (PSO) were used to designate the kinetic data of CV adsorbed onto WHRP. These

**Table 1**. Langmuir isotherm model and Freundlich isotherm model constants for adsorption of CV onto WHRP.

| Langmuir | | | Freundlich | | |
|---|---|---|---|---|---|
| $q_{max}$ | $K_L$ | $R^2$ | $K_f$ | n | $R^2$ |
| 8.40 | 0.1059 | 0.983 | 1.318 | 2.121 | 0.998 |

**Table 2.** Adsorption rate constant and coefficient of correlation associated with the pseudo first and pseudo- second-order kinetic model.

| | $C_o$(mg/L) | $q_e$ (mg/g) | $q_{cal}$ (mg/g) | k | $R^2$ |
|---|---|---|---|---|---|
| Pseudo $I^{st}$ order kinetic model | 20 | 01.80 | 0.299 | 0.016 | 0.963 |
| Pseudo $II^{nd}$ order kinetic model | 20 | 01.80 | 01.84 | 0.118 | 0.999 |

numerical equations for pseudo-first and pseudo-second-order kinetics models were articulated by equation 5 & 6, respectively:

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad .. (5)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad .. (6)$$

Where, $q_e$ (mg/g) and $q_t$ (mg/g) are adsorption capacity at equilibrium and time t, respectively. Whereas $k_1$ ($min^{-1}$) and $k_2$ (g $mg^{-1}min^{-1}$) are the rate constant of PFO and PSO, respectively.

Table 2 represents the kinetic parameters for CV adsorption on WHRP. From Table 2, it is evident that the pseudo-second-order model gives better t to the experimental data for CV adsorption on WHRP with $R^2$ values of 0.999. Therefore, it may be concluded that CV adsorption on WHRP follows a chemisorption/ion exchange mechanism.

## CONCLUSION

The study showed the effectiveness of water hyacinth root powder (WHRP) for removing crystal violet (CV) dye from wastewater using adsorption techniques. WHRP natural adsorbent is found outstanding adsorbent for removal of CV. The kinetic study data fitted well with pseudo-second-order kinetics model rather than pseudo-first-order kinetics model. Adsorption isotherm data is well fitted in Freundlich isotherm. The obtained adsorbent shows a high removal (90%) of CV in most natural optimum conditions. Moreover, the natural WHRP adsorbent provides an economical and feasible method for a removal of CV. In addition to that, results obtained from the experimental research would be useful in the design of a CV treatment process for practical application.

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