

CRYSTAL VIOLET REMOVAL FROM AQUEOUS SOLUTION USING CORN STALK BIOSORBENT

Usman Lawan Muhammad¹, Zakariyya Uba Zango², Haliru Aivada Kadir³, Armaya'u Usman⁴

^{1,2,4} Department of Chemistry, Al-Qalam University Katsina, P.M.B 2137, Katsina Nigeria

³ School of Chemical Sciences, Universiti Sains Malaysia, 11800 Pulau Penang, Malaysia

*Corresponding Author Email Address: zakariyyazango4@gmail.com

Other Authors Email Addresses: uslamad50@gmail.com, zakariyyazango4@gmail.com, hkadir2012@hotmail.com

armayau.usman@auk.edu.ng

ABSTRACT

The objective of this study was to evaluate the potential, suitability and efficiency of corn stalk (CS) for the removal of Crystal Violet (CV) dye from aqueous solution. Adsorption studies were conducted under different operational parameters such as effect of initial dye concentrations (10, 20, 30, 40 and 50 mg/L), contact time, pH and sorbent doses (0.1, 2.0, 15.0, 2.25 and 3.0g). Adsorption isotherms utilized were Langmuir and Freundlich models, while kinetics was verified using pseudo-first-order and pseudo-second-order models. The sorption processes is best described by the Langmuir isotherm and pseudo-second order kinetic model since it showed better fitting and high coefficient of determination ($R^2 > 0.98$). It was found that percentage removal of the dye increases as pH increases from acidic to basic region.

Keywords: Adsorption, Crystal violet (CV), Cornstalk (CS).

INTRODUCTION

Discharge of dye constituted effluent into natural streams and rivers poses severe problems to the aquatic life, food web and causes damage to the aesthetic nature of the environment (Annadurai *et al.*, 2002). The presence of dyes in our water bodies hinders photosynthesis in aquatic plants due to the tendency of dye to absorb and reflect sunlight entering water (Ahmad *et al.*, 2014; Bulut, 2006). The effect become severe as a result of the ability of the complex aromatic structures of the dyes to render the aquatic plant ineffective in the presence of heat, light, microbes, and even oxidizing agents and degradation of the dyes become difficult (Aksu, 2005). Hence, these pose a serious threat to human health and water quality, thereby becoming a matter of vital concern. Dyes can have acute and/or chronic effects on exposed organisms depending on the exposure time and dye concentration. Dyes can cause allergic dermatitis, skin irritation, cancer, mutation, etc. Keeping the essentiality of color removal, concerned industries are required to treat the dye-bearing effluents before dumping into the water bodies (Gonga, 2005; Mafra, 2013).

The manufacture and use of synthetic dyes for dyeing fabrics has become an industry solid. It is estimated that around 700,000 tons of dyes are produced annually around the world and about 20% is discharged as industrial wastes without previous treatment (Ghorai, 2014; El-Maghraby *et al.*, 2011). However, their use has become a matter of serious concern to environmentalists. Synthetic dyes are highly toxic substance causing negative effects on all life forms because they present groups such as sulfur, naphthol, vat dyes, nitrates, acetic acid, surfactants, chromium compounds and metals such as copper, arsenic, lead,

cadmium, mercury, nickel, cobalt and certain auxiliary chemicals (Dogan M, Abak H, 2009)-(Chamarthy, S., S. Seo and Marshall, 2001). Thus, the scientific community shoulders the responsibility of finding economically favorable methods or techniques to curb this problem.

Corn (also known as Maize or *Zea mays*) is a widely cultivated crop around the world. The by-products such as corn leaf, corn cob, corn husk, and corn stalk are often burnt without utilization in the field. The main composition of corn stalk (CS) is cellulose, hemicellulose and lignin. Thus, CS and other agricultural waste have potential to serve as a renewable agricultural waste available abundantly at little cost (Malik, Ramteke and Wate, 2007)-(Velmurugan, 2001). Crystal violet (CV) belongs to the triphenyl methane family of dyes and is widely used where fastness to light is not of great importance. It has harmful effects on living organisms on short periods of exposure. It is toxic, harmful upon inhalation or ingestion and may cause skin irritation. In extreme cases, it can lead to kidney failure, and cancer (Kumar, 2011, Miyah *et al.*, 2017). Therefore, removal of this dye from water and wastewater is of great importance.

Various low-cost natural adsorbents and agricultural waste materials have been employed for the adsorption of dyes from aqueous solutions (Ansari R, 2010, Banat and Al-Asheh, 2003). Majority of them are found to be efficient for the wastewater treatments and are environmentally friendly. The aim of the present investigations has been to evaluate the efficiency of the removal of crystal violet from aqueous solutions using corn stalk as an easily available and economically viable adsorbent. The effects of contact time, initial dye concentration, pH, and adsorbent dose on the adsorption capacity were investigated to optimize the conditions leading to maximum removal efficiency. The experimental data were evaluated using the pseudo-first-order and pseudo-second-order kinetic model.

MATERIAL AND METHOD

Raw cornstalk was obtained from Rahamawa village in Batagarawa Local Government of Katsina State, Nigeria in February 2017. Crystal violet dyes were purchased from Sigma Aldrich (USA). The sulfuric acid, hydrochloric acid and sodium hydroxide were obtained from Sinopharm Chemical Reagent Co. Ltd., China. All reagents used in this work are of analytical grade and high purity. Distilled water was used throughout the work.

Adsorbent preparation

The corn stalk collected from the farm was allowed to dry for about two months and the fiber was washed with distilled water and then dried in an oven at 80 °C overnight. Furthermore, it was

ground and screened using a set of sieves to obtain particles size in the range of 50–80 μm . The sieve fiber was stored in a desiccator until required. The stock solutions (150 mg/L) of test reagent were made by dissolving the dye in doubly distilled water. Concentration of the dye and absorbance value during the experiment was determined at maximum wavelength of 590 nm using UV-vis spectrophotometer respectively.

Adsorption experiment

In a typical experiment, 50 mL of CV aqueous solution (10 mg/L) was placed in an Erlenmeyer flask. As much as 0.1 g of the CS was added and the resulting mixture was homogenized till equilibrium is attained and filtered afterwards. In order to monitor the variation in absorbance, small portion of the mixture were withdrawn into a cuvette at different intervals of time. All the experiments were conducted at room temperature and repeated twice to ascertain accuracy of the data obtained. The removal efficiency, amount of dye adsorbed at different intervals of time, and at equilibrium were obtained from Equations (1), (2) and (3) respectively.

$$\text{CV Removal (\% R)} = \frac{C_0 - C_e}{C_0} \times 10 \quad (1)$$

$$q_t = \frac{(C_0 - C_t)V}{w} \quad (2)$$

$$q_e = \frac{(C_0 - C_e)V}{w} \quad (3)$$

Where; C_0 , C_t and C_e is initial, at time and equilibrium concentrations of the dye (mgL^{-1}), respectively, while w is the weight of the adsorbent (g) and V is the volume of dye solution (L).

Effects of initial CV concentration

The effect of initial dye concentrations on adsorption of CV onto CS was investigated in the concentration range of 10 – 50 mg/L. As much as 2.5 mg of adsorbent was utilized. Similar procedure as highlighted in section 2.1 were used but at different concentrations.

Effect of adsorbent dosage

The effect of adsorbent dosage on the removal of CV (50 mg/L) concentration was carried out using different weights of the adsorbents (0.1g, 0.15g, 0.2g, 0.25g, and 0.3g). Similar procedures for the batch adsorption study were employed.

Effect of contact time

The effect of contact time was investigated using 0.1g of the adsorbents and 50 mL of the dye solution (10 mg/L). Agitation was done for a time period range of 20 – 100 minutes. Similar procedures as in section 2.1 were employed.

Effect of pH

The effect of pH is paramount in the adsorption studies of dyes. Comparative experiments were carried out by varying the pH values of the CV. Different pH values ranging from 2 to 10 were investigated. The pH was adjusted using 0.1 M HCl and 0.1 M NaOH solutions respectively. As much as 0.15 g of adsorbent and a dye concentration of 50 mg/L were utilized for this experiment.

Adsorption isotherm and Kinetic models

Langmuir model

The Langmuir isotherm is valid for monolayer adsorption onto a surface containing a finite number of identical sites. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbates in the plane of the surface. The linear form of the Langmuir's isotherm model is given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (4)$$

Langmuir adsorption parameters can be determined by transforming the Langmuir equation, which is in linear form by the plot between C_e/q_e versus C_e (Eq.4) over the entire concentration range. Where q_e is the amount of CV adsorbed in mg/g of the adsorbent, C_e is the concentration of the dye solution at equilibrium (mg/L). Q_0 and b are Langmuir constants related to the maximum adsorption capacity (mg/g) and the adsorption energy between the Adsorbate and adsorbent (L/mg). The essential features of the Langmuir isotherm may be expressed in terms of equilibrium parameter R_L , which is a dimensionless constant referred to as separation factor or equilibrium parameter.

$$R_L = 1 / (1 + bC_0) \quad (5)$$

Where C_0 is the initial concentration and b is the constant related to the energy of adsorption (Langmuir constant). The values of R_L indicate the nature of the isotherm.

Values of R_L	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

Freundlich model

The Freundlich isotherm model is an empirical equation employed effectively to study the heterogeneity and surface energies. The most common shape of the graph of amount of dye adsorbed per unit weight of adsorbent versus the concentration in the fluid in equilibrium is these data often fit nicely the empirical equation proposed by Freundlich:

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

Where, K_F and n are, Freundlich constants; q_e is the weight adsorbed per unit weight of adsorbent; C_e = concentration of dye at equilibrium. The constant K_F is an approximate indicator of adsorption capacity ((mg/g) (L/mg) $1/n$), while $1/n$ is a function of the strength of adsorption respectively in the adsorption process. The values of K_F and n can be obtained from the plot of $\log q_e$ versus $\log C_e$ and they equal to the intercept and slope of the plot respectively.

Kinetics of adsorption

Pseudo – first order kinetic model:

This model was suggested for the adsorption of solid/liquid systems [27]. The integrated linear form of the model is as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (7)$$

Where q_e (mg/g) and q_t (mg/g) are the amounts of dye adsorbed at equilibrium and at time t and k_1 (1/min) is the equilibrium rate constant of pseudo-first order. The kinetics parameters are obtained from the plot $\log(q_e - q_t)$ against t .

Pseudo – second order kinetic model:

The adsorption mechanism over a complete range of the contact time is explained by the pseudo – second order kinetic model. The integrated linear form of the model is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (8)$$

Where k_2 (g/mg min) is the equilibrium rate constant of pseudo-second order. In this case, the kinetics parameters can be calculated from the plot t/q_t against t .

RESULTS AND DISCUSSION

Effect of contact time

The effect of adsorption contact time of Crystal Violet onto Corn stalk was investigated and results are shown in Fig. 1. From the plot, it reveals that the removal of CV onto CS cornstalk is characterized by a rapid adsorption which increases with time. The equilibrium time for the adsorption of the dye was obtained at 12 mg/g using 0.1 g/g for 80 minute. This is shown by the region in Fig. 1 where there is no noticeable change. Considering the above, 80 minutes is adopted as the equilibrium times.

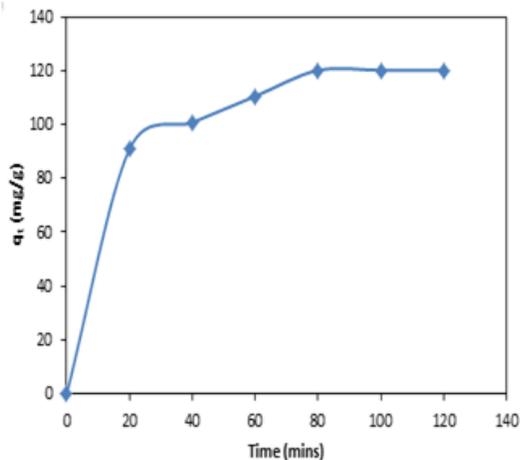


Figure 1: Effect of contact time for the adsorption of CV onto corn stalk

Effect adsorbent Dosage

The effect of adsorbent dosage on the removal of crystal violet dye is shown in Fig 2. The amount of CV adsorbed per unit weight of adsorbent on Cornstalk was found to decrease from 19.0 mg/g to 3.9 mg/g upon increase in adsorbent dosage. This trend could be as a result aggregation of particle caused by the adsorbed dye which could be obvious upon increase in adsorbent dosage thereby reducing the availability of active sites(Pathania et al., 2017 Lin et al.,2011).

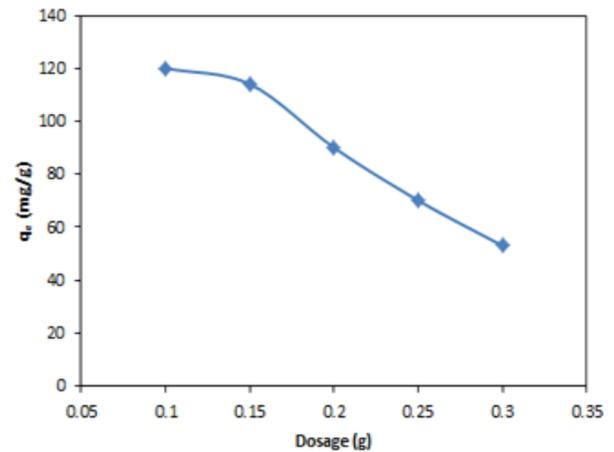


Figure 2: Effect of adsorbent dosage for the adsorption of CV onto cornstalk

Effect initial dye concentration

The effect of initial dye concentration on adsorption of CV onto CS was investigated using the concentration range 10 – 50 mg/L with equilibrium time of 120 minutes. The results are shown in Fig. 3. It is seen that the equilibrium adsorption capacity (q_e) was found to increase from 40 mg/g to 120 mg/g upon increase in initial dye concentration from 10 to 50 mg/L. On the other hand, the percentage removal was found to decrease upon increase in concentration. This is due to the scenario whereby as the concentration increased, the available sites become fewer. Thus, the percentage of dye removal was dependent upon the initial concentration(Khan, et al.,2009)

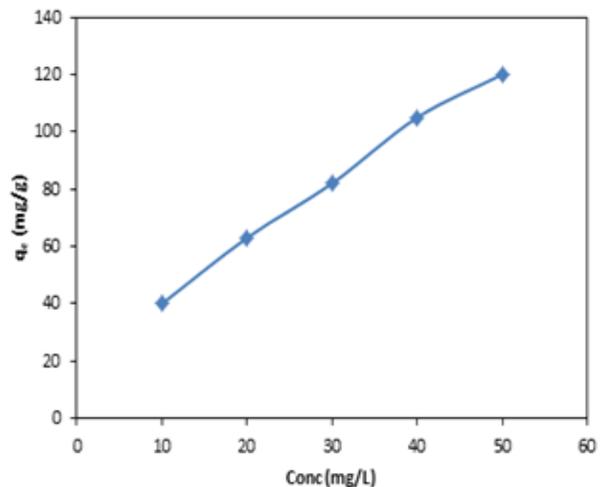


Figure 3: Effect of changing dye Concentration for the adsorption of CV onto Cornstalk.

Effect of pH

The pH is a vital factor that influences the adsorption process of a dye onto an adsorbent, particularly on the adsorption capacity and the surface charge of adsorbents. The effect of pH on the adsorption of CV was investigated from pH range of 2.0 – 10 and the result is shown in Fig 4. An observation for the increase in the % removal efficiency was recorded at higher pH values. From pH

4 to 10, the percentage removal was found to increase from 74% -82%. The lower removal of the dye at lower acidic pH may be associated with the competition that sets in between the excess concentration of H⁺ ion and the cationic part of the dye for the active site on the adsorbents (Yahya *et al.*, 2008, Namasivayam, 2002).

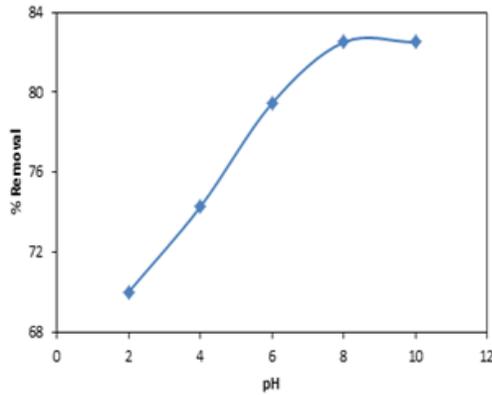


Figure 4: Effect of pH for the adsorption of CV onto corn stalk.

Adsorption isotherm:

Langmuir isotherm model

The fundamentals that facilitate better understanding about the nature of interaction between the adsorbent utilized, and the adsorbate is adsorption isotherms. Figure 5 presents the data obtained from the Langmuir isotherm, whereby the constants Q_0 and b was calculated from slope while the intercept of the plot and values obtained are tabulated in table 1. The adsorption was found to be favorable.

Freundlich isotherm

Freundlich isotherm model was employed to estimate the adsorption intensity of the adsorbates on the adsorbent surface and the results are presented in Figure 6. The Freundlich isotherms K_F represents the constant related to adsorption capacity (Lmg^{-1}) and n is the Freundlich isotherm constant related to adsorption intensity. The result of the constant values was evaluated and presented in Table 1. It show that Freundlich model fits for CV dye (R^2 0.972) adsorption process. It was also observed that the value of n was greater than 1 indicating the favorable adsorption of CV onto Cornstalk

Table 1: Adsorption isotherm models

Isotherm Models	Isotherm constants			
	Langmuir	R^2	R_L	b (l/mg)
	0.996	0.303	0.046	9.643
Freundlich	R^2	K_F (L/mg)	n	
	0.972	5.300	10.040	

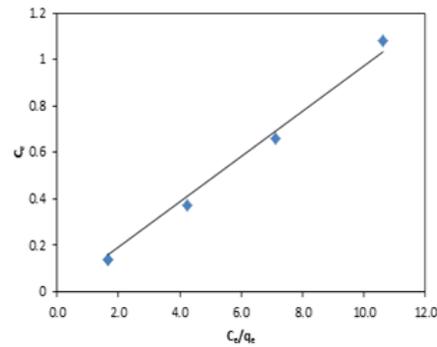


Figure 5: Langmuir isotherm model for the adsorption of CV on CS

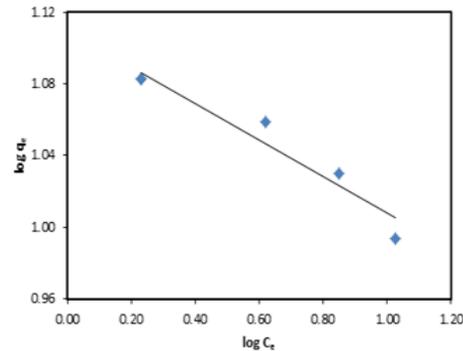


Figure 6: Freundlich isotherm model for the adsorption of CV onto CS

Adsorption kinetics

Figure 7 shows pseudo-first order plot of $\log(q_e - q_t)$ versus t from which the values of k_1 and q_e were determined from the slope and the intercept respectively, the result is presented in Table 2. The adsorption mechanism over a complete range of the contact time is explained by the pseudo – second order kinetic model. Table 2 shows that the R^2 values obtained as experimental data for pseudo second order kinetics is higher than that for the pseudo-first order kinetic model. Therefore, from the plot obtained, the adsorption was best fit by pseudo-second order kinetic model due to a high correlation coefficient determination. This is based on the assumption that the rate limiting step may be chemisorption involving valence forces through sharing or exchange of electrons between adsorbent and adsorbates(Bharathi, 2012, Bello *et al.*,2010).

Table 2: Pseudo- Kinetic first and second order Adsorption Kinetic for CV and Cornstalk

Models Isotherms	Isotherm constants		
	Pseudo- Kinetic first order	R^2	Q_e exp(mgg-1)
	0.937	12.066	0.995
Pseudo-kinetic second order	R^2	Q_e exp(mgg-1)	K_2 (min)
	0.975	12.83	0.008

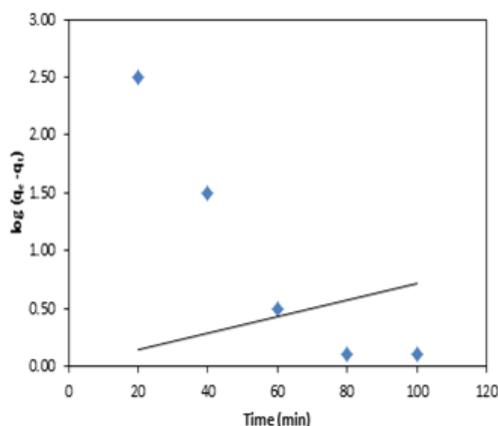


Figure 7: Pseudo-first order kinetic model for the adsorption of CV onto CS

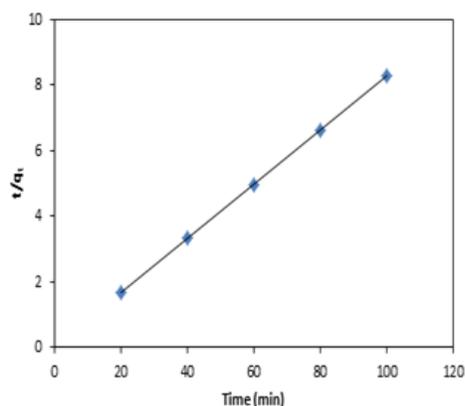


Figure 8: Pseudo-second order kinetic model for the adsorption of CV onto CS

Conclusion

In summary, the work shows the possibility of using cornstalk for the uptake of crystal violet dye. Effects of contact time, adsorbent dosage, initial Dye concentration, and pH on the % removal of the dye suggested an equilibrium adsorption time of 80 min for CS, optimum weight of 0.25g/50 cm³ of the dye and at a pH of 8. The adsorption data was well described by the Freundlich isotherm equation. The rates of sorption were found to conform to pseudo-second-order kinetics with good correlation. This study reveals that Cornstalk can be employed as a low cost adsorbent for the removal of crystal violet from aqueous solutions.

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