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Abstract:

The adsorption behaviour of Crystal Violet from aqueous solution onto biosorbent prepared from Water hyacinth under various experimental conditions were investigated, to evaluate the adsorption capacity. The initial dye concentrations of 50 ppm, 60 ppm and 70 ppm with the contact time of 30 minutes and pH 6.5 were investigated in batch mode. Langmuir and Flory-Huggins isotherms were used to analyze the equilibrium adsorption data. The equilibrium adsorption capacity q_{\max} computed from Langmuir equation is 12.216 mg/g. The Flory-Huggins isotherm gives the degree of surface coverage characteristics of the adsorbate on the adsorbent. The value of 'n' indicates that the adsorbate molecules adhered to the surface of the adsorbent. Finally, the value of separation factor was analyzed to validate the adsorption process. The separation factor shows that the adsorption process is favourable in nature.

Key Words: Water hyacinth, Crystal Violet, Biosorbent & Isotherm

1. Introduction:

Textile industry has been listed as one of the six key industrial sectors for priority prevention and control of chemical pollutants [1]. It is estimated that around 700,000 tons of dyes are produced annually around the world [2]. Of this estimated amount of dye, about 20% is unloaded from the industrial wastes without previous treatment. Effluents discharged from dyeing industries are highly colored and can be toxic to aquatic life in the receiving waters [3,4]. This causes enormous atmospheric change and it has increased severe environmental problems which is called as environmental pollution. Color is the first contaminant to be recognized in waste water [5]. It's not only aesthetically displeasing but also hinder light penetration and may in consequence disturb biological process in water – bodies. In addition, the expanded uses of dyes have shown that some of them and their reaction products such as aromatic amines are highly carcinogenic which make the removal of dyes before disposal of the wastewater is necessary. Most of the dyes are stable to photo degradation, bio-degradation and oxidizing agents. The high concentration of chemicals and coloring agents in the effluents can adversely affect the ecosystem, causing ecological degradation when discharged without proper treatment [6]. Adsorption using different adsorbents is superior to the other separation techniques because of its efficacy, economy, ability to separate a wide range of chemical compounds, and simple procedure. The present investigation deals with the removal of CV dye by biosorbent using the aquatic weed, water hyacinth. The effect of pH, temperature and the other chemical parameters are also evaluated. Finally, the adsorption isotherms are developed.

2. Materials and Methodology:

Adsorbent Preparation: The Water hyacinth (Eichhornia Crassipes) was collected from the local Ukkadam lake, Coimbatore. Various parts of the WH (such as leaves, petioles and roots) were separated and washed with tap water. In this study, we are taking only the leaves of water hyacinth. It was well chopped and kept in muffle furnace at 60°C for 48 hours. It was then dried as and blended with the help of blender. Finally, it was sieved for 15 minutes through 45µm sieve and stored in the bottle for future use. Commercial carbon is also being used as an adsorbent.

Adsorbate Preparation: Crystal violet (Molecular formula: C25H30N3Cl, M.W.: 407.979, C.I. no. 42555, CAS: 548-62-9, mp=205°C) was purchased from Merck India private Ltd., Mumbai and used without purification. Stock solution of dye was prepared by dissolving 1gm of dye in 1000ml of double distilled water to give the concentration of 1000mg/L. The stock solutions were diluted with known initial concentrations say 20, 40, 60 and 80 and 100mg/L in accurate proportions.

Adsorption Experiment: Adsorption experiments were carried out in a temperature controlled mechanical shaker at a constant speed of 125rpm using 250mL conical flasks containing different dosages of the adsorbents with 200mL of dye solution at room temperature. All the experiments are carried out at a constant pH of 6.5 and contact time of 30 minutes. After agitating the flasks for predetermined time intervals, samples were withdrawn from the flasks and the adsorbents were separated from the solution by filtration. The absorbance of the supernatant solution was estimated to determine the residual dye concentration, measured at $\lambda_{\max} = 590$ nm spectrophotometrically using spectrophotometer. The amount of adsorbate adsorbed at equilibrium condition, q_e (mg/g) was calculated using the following equation:

$$q_e = (C_0 - C_e) \times V/W \quad (1)$$

Where, C_0 and C_e are the initial and equilibrium adsorbate concentrations (mg/ L) respectively, V is the volume of solution (L) and W is the mass of adsorbent (g). The dye removal percentage can be calculated as follows:

$$\% Q = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

Where, C_0 and C_e (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. Adsorption data obtained from the effect of initial concentration and contact time were employed in testing the applicability of isotherm.



3. Results and Discussions:

Effect on Various Factors Affecting Adsorption: In order to investigate the various factors affecting adsorption, a series of adsorption experiments was carried out with different adsorbent dosages at initial concentrations of 50mg/l, 60mg/l and 70mg/l respectively, without changing the volume of dye solution (200ml) with constant speed of 125rpm for 30 minutes. Similarly the pH (6.5) and temperature (35⁰C) was kept constant. The results follow the expected pattern, in which the percentage sorption increased with increased adsorbent dosage (fig.- 1). The increase in adsorbent dosage is due to the increase in surface area

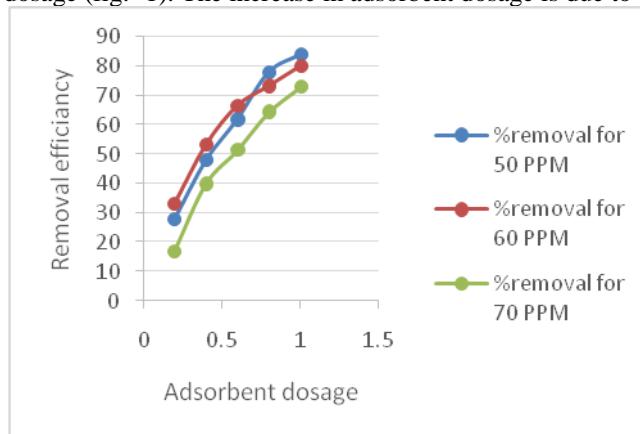


Figure 1: Graphical representation of removal efficiencies for water hyacinth.

The formation of monolayer of crystal violet ions on the outer surface of the adsorbent was observed, since the curves are single, smooth and continuous as shown in Fig.1 [7]. (Mohammad Jerahim, 2012).

Adsorption Isotherms: Adsorption isotherm parameters obtained from the different models provide important information on the surface properties of the adsorbent and its affinity to the adsorbate. Several isotherm equations have been developed.

Langmuir Isotherm: Langmuir isotherm quantitatively describes the formation of monolayer adsorbate on the outer surface of the adsorbent further which no adsorption takes place. Thereby, the Langmuir represents the equilibrium distribution of metal ions between the solid and liquid phases. 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 adsorbate in the plane of the surface. Based upon these assumptions, Langmuir represented the following equation:

$$q_{\max} = \frac{(c_e + (1/k_L))}{(c_e/q_e)} \quad (3)$$

Where:

C_e = the equilibrium concentration of adsorbate (mg/L⁻¹)

q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g)

q_{\max} = Maximum adsorption capacity (mg/g)

K_L = Langmuir isotherm constant (L/mg)

The essential characteristic of Langmuir isotherm can be expressed in terms of dimensionless separation factor of equilibrium parameters RL. It can be defined by,

$$RL = \frac{1}{1+bC_0} \quad (4)$$

Where, C_0 is the initial dye concentration (mg/L) and b is the Langmuir constant (L/mg). The RL values indicate the type of isotherm as follows,

RL>1 Unfavorable; RL=1 Linear; 0< RL<1 Favorable;

RL=1 Irreversible

LANGMUIR ISOTHERM GRAPH

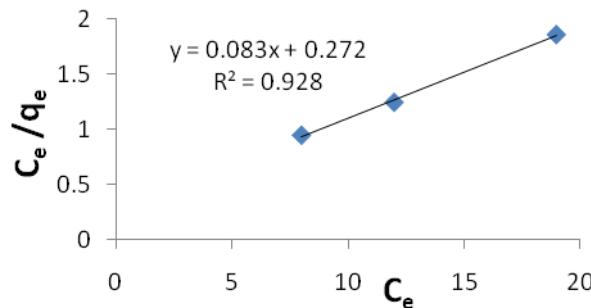


Figure 2: Graph of Langmuir Isotherm

It is observed that the Langmuir isotherm fits well for the adsorption process from R^2 value. The values of separation factor of equilibrium parameter falls between 0 and 1 indicating the favourable biosorption process.

Flory Huggins Isotherm: The Flory–Huggins solution theory is a mathematical model of the thermodynamics of polymer solutions which takes account of the great dissimilarity in molecular sizes in adapting the usual expression for the entropy of mixing. The result is an equation for the Gibbs free energy change for mixing a polymer with a solvent. Although it makes simplifying assumptions, it generates useful results for interpreting experiments.

$$\log \left(\frac{\theta}{C_e} \right) = \log K_c + n \log (1-\theta) \quad (5)$$

Where,

θ = degree of surface coverage.

n = number of metal ions occupying sorption site.

K_c = Equilibrium amount of dye adsorbed by the adsorbent.

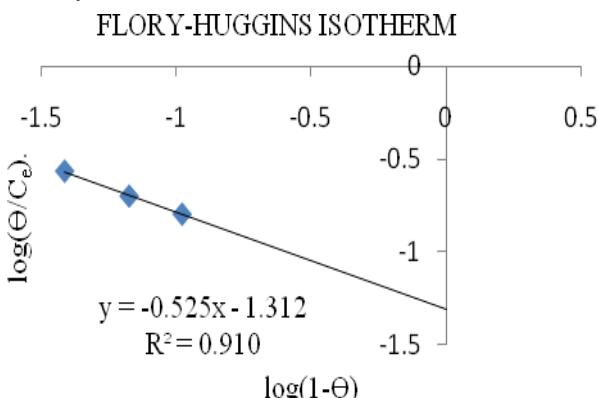


Figure 3: Graph of Flory-Huggins Isotherm

K_c values and R^2 values were found to be within the limit. Also, it is observed that there is a slight decrease in the adsorption energy takes place with the increase in surface coverage. This clearly indicates that the Flory-Huggins isotherm fits well with the experimental data.

4. Conclusion:

The removal of CV from aqueous solution has been investigated under different experimental conditions in batch mode. The following conclusions have been drawn from the study,

- ✓ The removal of Crystal Violet dye shows that water hyacinth could be used as good biosorbent.
- ✓ The increase in biosorbent dosage results in maximum removal efficiency.
- ✓ The removal percentage decreases with increase in initial concentration of dye solution for water hyacinth.
- ✓ The maximum adsorption capacity q_{max} was recorded as 12.21mg/g.
- ✓ The separation factor R_L lies between $0 < R_L < 1$, it represents a favourable condition for adsorption process.
- ✓ The high correlation existing between the parameters in Flory-Huggins isotherm represents that equilibrium amount of dye adsorbed by the adsorbents is good.

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