Adsorbents made from pine bark for the removal of dye from aqueous solution

Deven Singh[1], Dr. Ray Singh Meena[2]

M.Tech Student[1], National Institute of Technology, Hamirpur, Himachal Pradesh
Assistant Professor[2], National Institute of Technology, Hamirpur, Himachal Pradesh
E-mail 21mce405@nith.ac.in

Abstract—*According to the results of the current study, pine bark activated carbon has the potential to be used as an adsorbent to remove crystal violet dye from aqueous solutions. Before being activated with potassium hydroxide, raw pine bark is pyrolyzed at 700 degrees Celsius. The addition of the oxidizing agent has resulted in a rise in the adsorbent's surface area, which was measured to be 340 (m^2/g) using the BET method. The effects of contact time, concentration, temperature, pH, and dosage were studied in experiments. The initial solution pH was found to affect the amount of dye uptake, and the maximum amount of adsorption was found at pH 4. In 3 hours, equilibrium was reached. The Langmuir and Freundlich adsorption models are used to organize the analysis of experimental results. The Langmuir isotherm model's effect states that the maximum amount of adsorption capacity is produced at a temperature of 55 °C.*

Introduction

Fish and other aquatic life are often killed by the wide range of organic compounds and toxic substances found in industrial wastewater. Dyes are used to add colour in numerous manufacturing processes, including those for dyestuffs, textiles, papers, and plastics. Therefore, they produce a great deal of coloured wastewater. Color is used as a primary identifier for contaminants in wastewater systems [1]. Small amounts of dyes in water (less than 1 ppm for some dyes) are easily detectable and undesirable [2]. Since soluble colourless organic substances typically make up the largest portion of the biochemical oxygen demand, the removal of colour from wastewaters is frequently more crucial than the removal of these substances (BOD) [3]. Due to their high organic loading, toxicity, and colour contamination, as well as the fact that they reduce light penetration and photosynthesis, which has an impact on aquatic life, Significant environmental issues are caused when these effluents are released directly into waterways. Additionally, the majority of dyes are either poisonous or mutagenic and cancerous [4]. To lessen their environmental impact, scientists have developed a variety of strategies for filtering out synthetic dyes from water and wastewater. Electrochemical coagulation and other physicochemical techniques like adsorption have recently gained in popularity [2]. Over the past decade, adsorption techniques have come to the forefront as a viable option for the elimination of these contaminants. because it is flexible and easy to use. It's a straightforward method that can measure kinetic and equilibrium states without the need for complex apparatus [5]. It has been discovered that adsorption onto activated carbon is superior to other wastewater treatment techniques in terms of its ability to effectively adsorb a wide range of adsorbates and its ease of design, among several chemical and physical methods. However, activated carbons that are sold commercially are still regarded as expensive [6]. which prompted the development of inexpensive activated carbon or the search for cheap adsorbents [7]. Because it is inexpensive and widely accessible, pine bark activated carbon may be a better option for the treatment of wastewater containing crystal violet dye [2]. Pine bark is rich in several natural compounds with adsorption properties; these include 45% lignin, 25% Cellulose and 15% hemicellulose. In addition to reducing waste from the forestry industry, using pine lark as an absorbent is a cost-effective and renewable alternative to synthetic adsorbents.

A triarylmethane, crystal violet is also known as gentian violet, methyl violet 10B, and methyl violet. In histology, it serves as a standard stain and in the Gram staining method to categorize bacteria. The chemical formula is $C_{25}H_{30}N_3Cl$ and the molecular weight is 407.98 gm. mol^{-1}.[8]. Absorption is most effective between 589 and 594 nm. It is used as a bacteriostatic agent because it is the main ingredient in Gram's stain. The dye is used as a topical antiseptic on the skin of both humans and animals. It is widely used as a purple dye for textiles like cotton and silk, and in other media like paint and printing ink [9]. Therefore, the purpose of this research is to look into the efficacy of adsorbents made from pine bark in removing crystal violet dye from water. The study's goals include characterizing adsorbents made from pine bark, improving the adsorption process, and gauging its effectiveness and efficiency. This research has the potential to lead to a more cost effective and eco-friendly approach to treating wastewater by removing dyes using adsorbents made from pine bark.

Materials and methods

Adsorbate

Adsorption of crystal violet using the adsorbent, Crystal violet dye stock solution with a concentration of 1000 ppm was produced by combining the required quantity of dye powder with the required quantity of purified water in the appropriate proportions [10]. After that, the stock solution was diluted with distilled water to make the working solutions at the appropriate concentrations. Before being used, each of the compounds was first [11]. acquired as a chemical of research-grade quality and then purchased without undergoing any further purification.
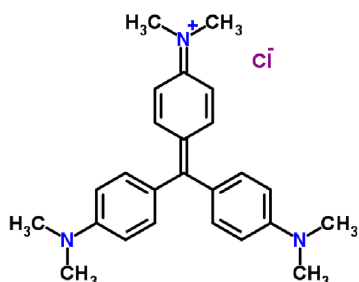

Figure 2.1 Chemical Structure of crystal violet

Preparation of adsorbent from pine bark

Collecting and washing, pyrolysis, chemical activation and purification are the four steps that are typically involved in the process of preparing activated carbon from pine bark. The following is an outline of the procedure:

Collecting and washing

Pine barks were collected from the NIT Hamirpur campus in Himachal Pradesh to make activated carbon, which was then applied. The raw pine bark was first reduced in size with a pestle and mortar, then it was rinsed twice to three times with distilled water. The sample is cleaned, then placed in an oven for 24 hours to get rid of any moisture that may have remained.

Pyrolysis

Pine bark is used to create an adsorbent in a muffle furnace. A 250 g specimen of dried pine bark is used, and it is pyrolyzed for one hour at 700°C temperature with a 5°C/min heating rate. In order to be used in subsequent experiments, the product is cooled to room temperature in a desiccator, then washed and crushed to a size range of 450-700 μm [12].

Chemical activation

Oxidizing chemicals are used to alter the surface of biochar, which, as a result, results in an increase in multiplication of functional groups on the surface of the biochar. In this research KOH is being used for chemical activation. 10% KOH is used in the solid-liquid ratio of 1:4 for chemical activation for the time of 2h [13]. Then the sample of biochar is washed 2 to 3 times before drying in an oven.

Purification

After being washed in distilled water to remove any remaining potassium hydroxide, the activated pine bark is dried in a hot air oven for six hours at 105°C.

Characterization of pine bark activated adsorbent

Surface area

The specific surface area of an adsorbent is a key factor in determining how well it will perform throughout the adsorption process. In this study, the BET method is used to calculate surface area. Its specific surface area is 340 m^2/g for the activated adsorbent made from pine bark.

Calibration curve

A calibration curve for crystal violet is created by using a spectrophotometer to measure the absorbance values of a number of standard solutions of crystal violet at the appropriate wavelength. This allows for the creation of a crystal violet calibration curve. The calibration curve is obtained by comparing the readings of absorbance to the concentrations of crystal violet that correspond to those readings.
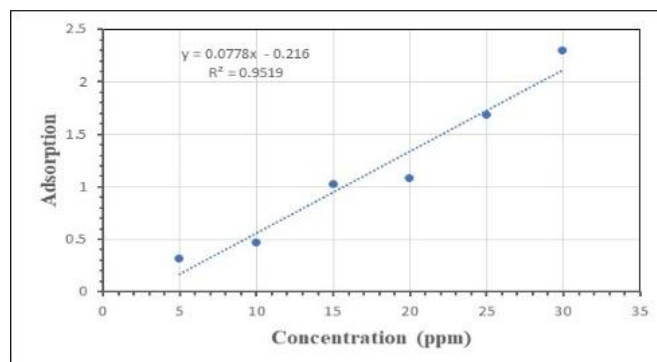

Fig. 1. Calibration curve of crystal violet

Adsorption studies

The batch method was utilized in order to analyze the kinetics and equilibrium of the adsorption process. At a pH of 8, isometries of adsorption were determined using a series of 250 mL conical flasks containing 100 mL of dye solution each. The flasks were sequentially arranged. The concentrations that were present at the beginning of the experiment ranged from 25ppm to 100ppm. To achieve equilibrium, flasks were placed in an orbital shaking incubator and agitated for 180 minutes at 150 revolutions per minute. This experiment utilized temperatures of 25, 35, 45, and 55 degrees Celsius throughout its entirety. Each of the dye solutions was activated by the addition of 1 gm of bulk modified biochar. This was done to accelerate the coloring process. It is possible to eliminate the need for biochar in the dye solution if the solution is initially filtered through filter

paper. In order to determine the final concentration, a UV/VIS spectrophotometer with a 590 nm wavelength is utilized. Using the below-provided formula, one can determine the percentage of dye that has been extracted from a mixture.

$$: \% \text{ Removal} = \frac{(C_o - C_t)}{C_o} \times 100 \ldots\ldots\ldots\ldots (1)$$

Where C_0 and C_t (mg/L) represent the dye concentration at starting time and final time at t, respectively.

The procedures followed to carry out the kinetic trials and the equilibrium tests were extremely like one another. All of batch studies were conducted with the temperature set at 25°C and the dye concentration varied from 25 ppm all the way up to 100 ppm. The following equation was utilized to determine the amount of adsorption that occurred at time t, which was expressed as a mg/g ratio.:

$$Q_t = \frac{(C_o - C_t)V}{W}$$

……………………….(2)

Results and discussion

Effect of contact time

The percentage adsorption increases with contact time, suggesting that adsorption is time dependent. Adsorption increases the concentration of the adsorbate at the solid-liquid interface by accumulating it on the adsorbent's surface. The initial low percentage adsorption may be due to poor mixing of the adsorbate and absorbent or low adsorbate concentration in the solution. The number of active adsorption sites grows as the contact time increases because the adsorbate has more time to diffuse into the pores. Adsorption percentages rise as a result.

As contact time increases, the percentage adsorption may plateau or achieve equilibrium. The equilibrium point occurs when the adsorbent has reached its maximum capacity and all potential adsorption sites on its surface are occupied by the adsorbate. The maximum Adsorption capacity is found as 82% after the removal for 3h.
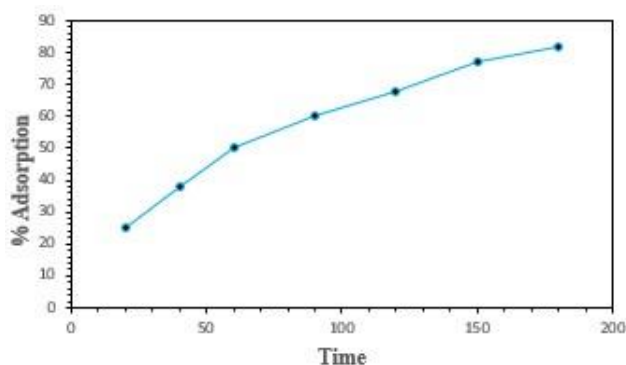
Fig.2. Effect of contact time

Effect of initial dye concentration

Even at low initial dye concentrations, the adsorbent is able to remove a large percentage of the dye molecules because it has plenty of active adsorption sites available. Increases in both initial dye concentration and the number of dye molecules in solution increase competition for active adsorption sites on the adsorbent surface. Saturation of the active site reduces the efficiency with which dye is eliminated. The efficiency of the removal process is concentration-dependent, as the percentage of removal decreases with increasing dye concentration.
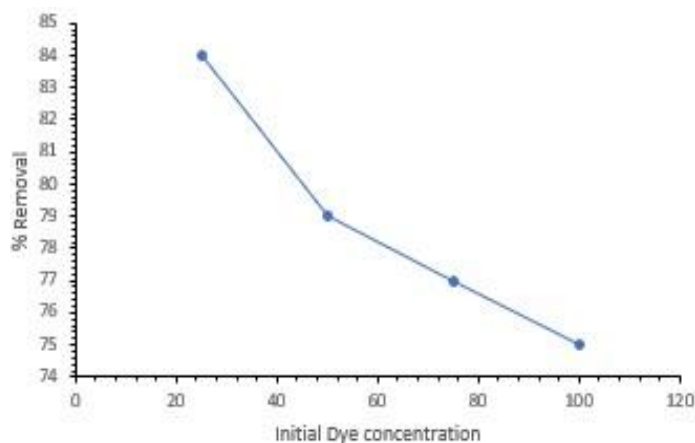
Fig.3. Effect of initial dye concentration

Effect of pH on dye removal

The surface charge of the dye molecules and the adsorbent surface are both affected by the pH of the solution. With a rise in pH, more of the color is neutralized. This is because the surface charge of the adsorbent material gets more negative as the pH of the solution rises, making it more attractive to the positively charged cationic dye molecules. Dye molecules may be more likely to be adsorbed onto an adsorbent surface, and the solubility of the dye may decrease at higher pH values. Keep in mind that a pH of 8 is ideal for crystal violet dye adsorption.
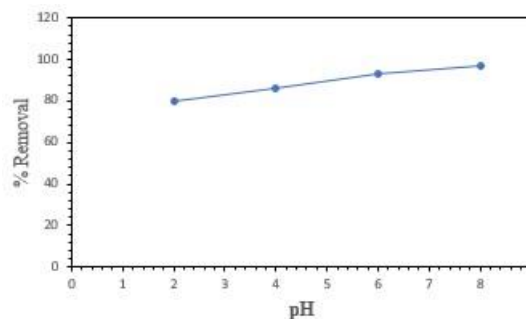
Fig.4. Effect of pH

Effect of adsorbent dosage

The effectiveness of the adsorption process is significantly impacted by the adsorbent dosage. Maximal dye adsorption can only be achieved by using the optimum amount of adsorbent. As adsorbent concentrations rise, a higher proportion of the dye is taken up. As the dosage is increased, more adsorption sites become available, indicating that the adsorbent has a strong affinity for the dye molecules. However, the enhanced adsorption capability is not as noticeable at higher dosages as it is at lower levels. The maximum removal is found to be 86% at the adsorption dosage of 1gm.
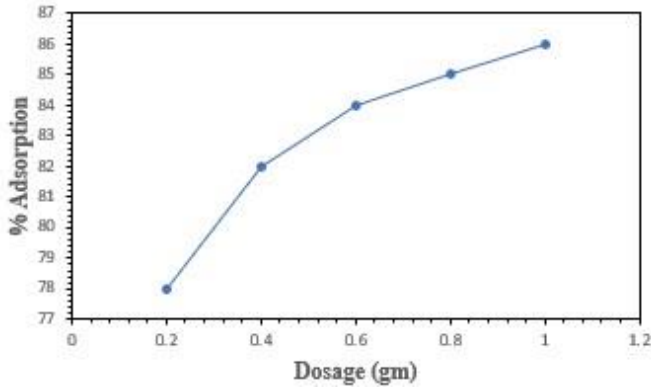

Fig.5. Effect of adsorbent dosage

Effect of temperature

As depicted in Figure 6, it was discovered that the temperature influences the adsorption of crystal violet over a wide range of dye concentrations, from 25 to 100 ppm. Other experimental conditions included a pH of 8, a contact time of 180 minutes, an adsorbent concentration of 1 g/l, and a stirring speed of 150 revolutions per minute. As the temperature rose from 25 to 55 degrees Celsius, the amount of color eliminated increased proportionally. The rate at which molecules of the adsorbate diffuse between the internal pores and external boundary layer of the adsorbent particle is accelerated by an increase in temperature, In contrast, when dealing with highly concentrated suspensions, the solution's viscosity will decrease. Moreover, if the temperature is altered as a result, the equilibrium capacity of the absorbent for a given adsorbate will shift in a different direction. At a temperature of 55 degrees Celsius, the maximum dye removal percentages for dye concentrations of 25, 50, 75, and 100 ppm are 85, 87, 90, and 92 percent, respectively.
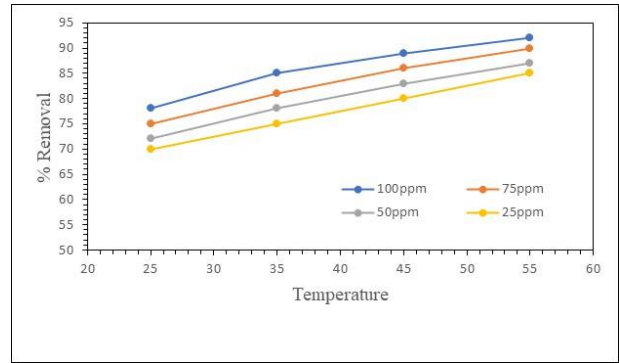

Fig.6. Effect of temperature

Adsorption isotherms

For the purpose of determining adsorption equilibrium, the Langmuir model is utilised, as shown in the figure. The Langmuir isotherm model postulates a monolayer adsorption in which the molecules that are adsorbed do not interact laterally with one another [14].

The Langmuir Isotherm linear form equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad \ldots\ldots\ldots\ldots(3)$$

Where q_e is the absorbed dye concentration in mg/g of adsorbent. When the dye solution has reached equilibrium, the concentration (in ppm) is represented by the symbol C_e. The maximum adsorption capacity, denoted by the constant Q_o (mg/g), and the adsorption rate, denoted by the constant b (mg/L), are both defined by the Langmuir constants. As can be seen in Figure 7, Crystal violet adsorption onto activated carbon results in a straight line with a slope of $1/Q_o$ and an intercept of $1/Q_o b$. Its slope is $1/Q_o$, and its intercept is $1/Q_o b$. The slope of this line is $1/Q_o$ and the value at the line's b-intercept is $1/Q_o b$. The fundamental features of the Langmuir isotherm can be illustrated using the dimensionless equilibrium parameter R_L. Because R_L is a scalar, this is the case. Here is a detailed description of the parameter's parameters:

$$R_L = \frac{1}{1 + bC_o} \ldots\ldots\ldots\ldots\ldots(4)$$

where C represents the highest dye concentration in ppm and b represents the Langmuir constant. The isotherm's type is determined by the value of R_L. It can be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 \, R_L \, 1$), or irreversible ($R_L = 0$).
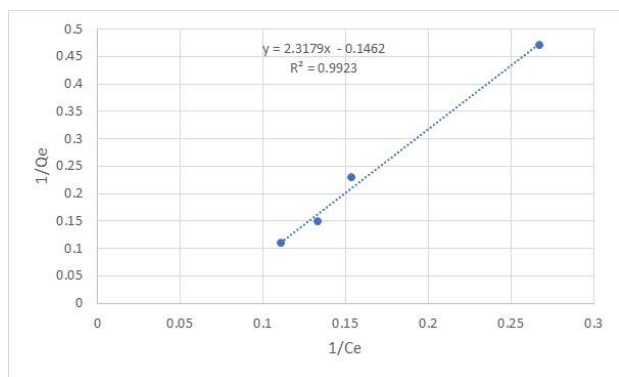
Fig.7. Langmuir adsorption isotherm

The logarithmic notation an expression for the Freundlich equation is:

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

where Freundlich constants K_F(mg/g) (L/mg)$^{1/n}$ and $1/n$ represent the adsorbent's capacity and adsorption strength, respectively. As the slope $1/n$ approaches zero, the surface becomes more heterogeneous, serving as a measure of the adsorption intensity [15].

The linearized forms of both equations were compared for their correlation coefficients (R^2), and it was found that the Langmuir model better represents the experimental data on equilibrium adsorption. The data was analysed using both models, leading to this result.
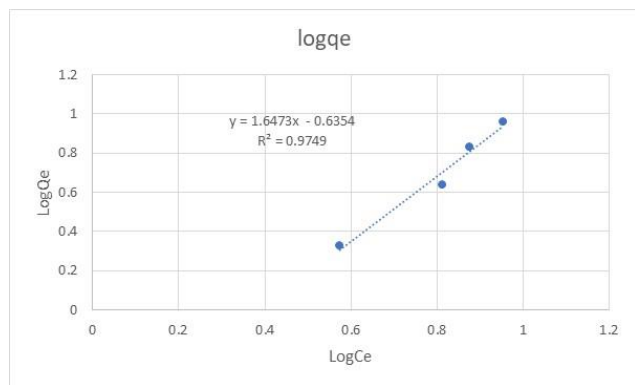

Fig.8. Freundlich adsorption isotherm

Conclusion

The concentration of the dye, the dosage of the adsorbent, the pH of the solution, and the temperature at which the adsorption takes place all play a role in the removal of crystal violet, as shown by studies on the adsorption of crystal violet from an aqueous solution upon activated adsorbent prepared from pine bark. The amount of dye absorbed by the absorbent was found to grow in response to three variables: solution temperature, contact time, and adsorbent concentration. However, the amount of dye removed decreased as the starting dye concentration increased. Experiments proved this to be true. When the pH was raised to 8, more dye was absorbed. When the equilibrium data was fitted to both the Langmuir and Freundlich isotherms, it was discovered that the Langmuir isotherm model best characterized the data. The efforts have paid off, as crystal violet can now be extracted from wastewater using an activated adsorbent made from pine bark.

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