

REMOVAL OF DYES FROM INDUSTRIAL WASTE WATER BY GHERKIN LEAF POWDER

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ABSTRACT

The present work, the leaves of Gherkin (*Cucumis Sativus*) treated with sulphuric acid and formaldehyde were used as an adsorbent for the removal of acid blue, acid red and malachite green from aqueous solution. The adsorption characteristics of all the three acid dyes on activated Gherkin leaf powder (GLP) were evaluated as a function of pH, adsorbent dose, initial concentration of adsorbate, temperature. The effective adsorption was found to be in pH range 3.4 to 7.1, adsorbent dose 0.5g to 0.8g, initial concentration (1×10^{-5} to 5×10^{-5} M) and Temperature range (308 to 318 K). The results reveal that maximum adsorption of all three acid dyes onto GLP is within the range of 59.80% to 71.0%. The adsorption data fitted well into Freundlich and Langmuir adsorption models. The results show that Gherkin leaf powder holds a great potential in removal of acid dyes from industrial wastewater.

Keywords: Acid Dyes, Gherkin leaf powder, Freundlich isotherm, Langmuir isotherm.

INTRODUCTION

Dyes are highly colored polymers and low biodegradable in nature. Dye being one of the important recalcitrant, persist for long distances in flowing water, retards photosynthetic activity, inhibit the growth of aquatic biota by blocking out the sunlight and utilizing dissolved oxygen and also decrease the recreation value of stream. Synthetic dyes have been increasingly used in the textile, paper, rubber, plastic, cosmetics, and pharmaceutical and food industries because of their ease of use, inexpensive cost of synthesis, stability and variety of color compared with natural dyes. Today there are more than 10,000 dyes available commercially most of which are difficult to biodegrade due their complex aromatic molecular structure and synthetic origin. The extensive use of dyes often poses pollution problems in the form colored wastewater discharge into environmental waterbodies which interferes with transmission of sunlight into streams, therefore, reduces photosynthetic activity. In addition, some dyes or their metabolites are either toxic or mutagenic and carcinogenic adverse effect of dyes on environment and human such as skin, lung and other respiratory disorders are also reported. Conventional physico-chemical and biological treatment methods are ineffective for the removal of dyes due to the large degree of organics present in these molecules, hence there was a need for other effective methods. Adsorption techniques for wastewater treatment have become more popular in recent years owing to their efficiency in the removal of pollutants. Activated carbon is the most widely used adsorbent but commercially available activated carbons are very expensive, consequently, many investigators have studied feasibility of using low cost substances such as rice husk, orange peel walnut shell charcoals, rice bran, *Euphoria antiquorum* L Wood, Jute and Sunnhemp, Teak leaves. The main objective of the work is to investigate the adsorption properties of Gherkin leaf powder for the removal of acid dyes i.e. acid blue, acid red and malachite green. The study includes adsorption as a function of time, adsorbent dose and concentration of dye solution, pH of the solution and temperature of the system. The isotherm studies were fitted for Freundlich and Langmuir adsorption isotherm.

MATERIALS AND METHODS

Adsorbent: The adsorbent used in the present investigation were leaves of Gherkin plants collected from Kanchipuram District of Tamil Nadu State (India). The leaves of Gherkin were dried in shadow avoiding direct sunlight on them. The dried plant leaves were grinded into powder and were boiled in distilled water to remove the suspended dust for one hour and filtered. The residue left was treated with formaldehyde and finally with very dilute solution of sulphuric acid, stirred for 60 minutes vigorously using mechanical stirrer at room temperature, it was filtered and washed with distilled water repeatedly to remove free acid. After chemical treatment residue were dried first in air and finally in oven at 100°C for 10 hours and powdered using electric grinder. The homogeneous powder was then passed through mesh for desired particle size (9.6 - 41.5 micron). The adsorbent once prepared were used throughout the experimental work. The particle size selected for these experiments were on the basis of their settlement at the bottom of the system, so that the portion of the solution could be taken out conveniently from the supernatant liquid.

Preparation of Adsorbate Solution: Acid blue, acid red and malachite green were the acid dyes selected for the present investigation. The chemicals used were of Analar grade and used without further purifications. The solutions were prepared in doubly distilled water.

Batch Adsorption Experiments: Each batch adsorption study was carried out by contacting activated Gherkin leaf powder (GLP) with acid dyes. i. e. acid blue, acid red and malachite green under different conditions for 60 minutes in a glass tube. Stock solutions (1.0×10^{-3} M) were prepared by dissolving weighed quantities of dyes in double

distilled water. The concentration of dye solution were determined from calibration curve spectrophotometrically at their respective wavelength, i.e. acid blue ($\lambda_{\text{max}} = 664\text{nm}$), acid red ($\lambda_{\text{max}} = 548$) and for malachite green ($\lambda_{\text{max}} = 616\text{nm}$).

RESULTS AND DISCUSSION

Effect of pH: The initial pH value of the solution can significantly influence the adsorption of dyes. In the present study the effect of pH on the amount of dye removal was analyzed over the pH range from 3.4 to 7.1 and is presented in graphical form as given in figure 1. The adsorption at lower pH may be attributed to the increase in the concentration of hydrogen ion in dye solution which neutralizes hydroxyl group in the vicinity of adsorbent surface and facilitates the diffusion of dye molecule towards the surface of adsorbent. Similar diminishing adsorption was also reported by Bahadur et.al, at higher pH which may be due to the availability of large number of OH⁻ (hydroxyl ions) and consequently the diffusion barrier is increased which results in poor adsorption. Our findings are in good agreement with Prasad et.al. The study restricted at higher pH level upto 7.1 which may be attributed to the adsorbent which is a plant material and consists of various organic acid components and may lead to the aqua complex formation and thus retards dye adsorption onto the surface of GLP. Our findings are supported by Mohan et.al.

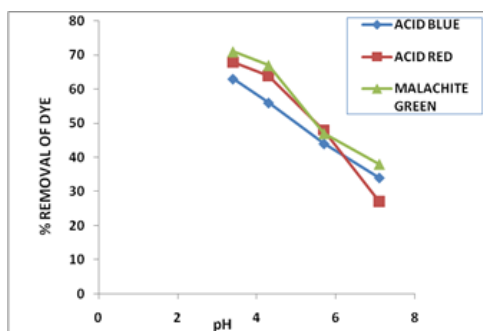


Figure 1. Effect of pH on removal of dyes

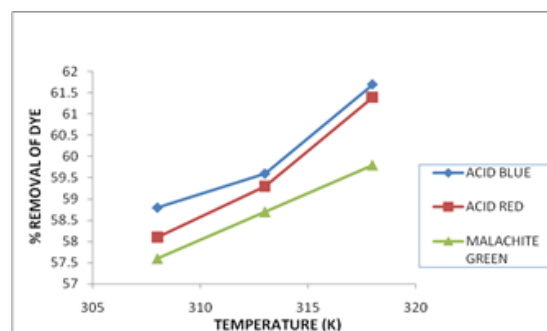


Figure 2. Effect of temperature on removal of dyes

Effect of Temperature: The data of dye adsorption onto GLP at different temperature indicates a change in the dye removal efficiency. This effect is shown in Figure 2. The increase in the equilibrium adsorption capacity of acid dyes indicates that a high temperature favors dye removal. Indeed by increasing the temperature of the reaction from 308K to 318K, The percentage removal of all three acid dyes average increased range was from 56.7% to 61.8%. Consequently it is clear that adsorption equilibrium is a thermo-dependent process. This effect may be due to the fact that at higher temperature, an increase in the movement of the solute occurs. Similar findings are also reported by other researchers.

Effect of adsorbent dose: Effect of adsorbent dose play a important role in standardizing the adsorption process with amount of adsorbate solution and the adsorbent. In our present investigation with increase in the amount of GLP adsorbent i.e. from 0.5g to 0.8g the removal efficiency of all three acid dyes increase rapidly (figure-3) which may be attributed to the greater availability of the exchangeable sites or surface areas at higher concentration of the adsorbent. Our findings are in good support with Hussein et al..

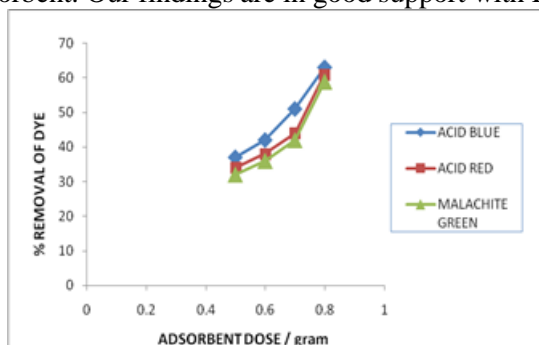


Figure 3. Effect of adsorbent dose on removal of dyes

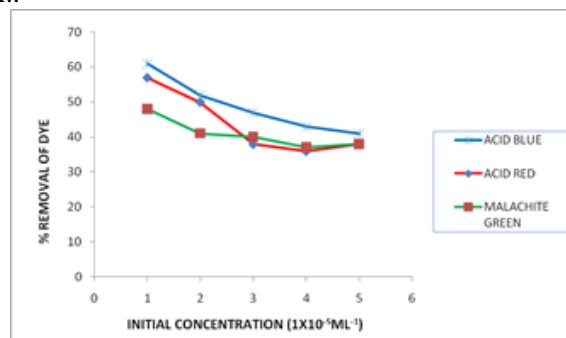


Figure 4. Effect of initial concentration on removal of dyes

Effect of Initial Concentration: The adsorption of all three acid dyes onto the surface of GLP were rapid initially, slow down later on and finally reached towards equilibrium (figure-4) indicating saturated adsorption as also reported by McKay et al.. The increased adsorption of the acid dyes onto the GLP may be attributed to increase in surface activity and due to micelle formation or the aggregation of dye molecule in the concentration range studied. Similar results have been also reported by several researchers.

Adsorption Isotherms: The adsorption isotherm data were fitted to the classical Freundlich and Langmuir isotherm equations. The linearized forms of isotherm equations used are Freundlich equation:

$$\log Q_e = \log K + \frac{1}{n} \log C_e \dots\dots\dots 1$$

Where Q_e is the equilibrium dye uptake Capacity and C_e the residual dye concentration at equilibrium. The constant K is a measure of adsorption capacity and $1/n$ is the intensity of adsorption. A plot of $\log Q_e$ versus $\log C_e$ gives a straight line of slope $1/n$ and intercepts $\log K$ and the values are enlisted in Table 1.

Table.1.Freundlich adsorption constants for acid blue, acid red, malachite green using GLP as adsorbent at 25°C

Acid Dyes	Acid Blue	Acid Red	Malachite Green
K	0.1684	0.7464	0.1698
N	1.0204	1.4535	1.0148
R ²	0.9422	0.9626	0.9539

The Correlation coefficient (R^2) for acid blue, acid red and malachite green found to be 0.9422, 0.9626 and 0.9539 respectively.

Langmuir equation,

$$\frac{1}{Q_e} = \frac{1}{Q_{\max}} + \frac{b}{C_e} \dots\dots\dots 2$$

Where Q_{\max} represent the maximum specific dye uptake C_e , the residual dye concentration at equilibrium and b the ratio of adsorption / desorption rates related to energy of adsorption. The capacities of GLP for binding with all three acid dyes were determined by plotting C_e/Q_e against C_e using Langmuir equation. The plot of the Specific sorption C_e/Q_e against equilibrium concentration C_e gave the linear isotherm parameters Q_{\max} and b are enlisted in Table 2. The correlation (R^2) for acid blue, acid red and malachite green found to be 0.9242, 0.9316 and 0.9518 respectively. The adsorption equilibrium data fitted well for both Freundlich and Langmuir isotherms.

Table 2: Langmuir adsorption constant for acid blue, acid red, malachite green using GLP as adsorbent at 25°C

Acid Dyes	Acid Blue	Acid Red	Malachite Green
Q_{\max}	1.0456	1.0232	1.0228
b	0.0124	0.0136	0.0142
R^2	0.9242	0.9316	0.9518

CONCLUSION

It has been proved that activated Gherkin leaf powder is an excellent adsorbent for removal of acid dyes from aqueous solution, under certain physiochemical conditions. The result indicates the potentially practical value of GLP as adsorbent. The calculated dimensionless equilibrium parameter R_L found to be in the range between 0 and 1 is indicative of favorable adsorption onto the surface of GLP. Adsorption of acid dyes onto GLP was first order kinetic process with low activation energy which is an indicative of rapid adsorption process.

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