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Adsorption of acid dyes from aqueous solution onto the surface of acid activated kammoni leaf powder: A case study

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ABSTRACT

*The plant powder of Kammoni (*L. Solanum nigrum*) were activated with sulphuric acid and used as low cost easily available and renewable biological adsorbent for the removal of acid dyes (acid blue, acid red and malachite green) from aqueous solution. Batch experiments were carried out for adsorption kinetics and isotherms. Operating variable studied were pH, temperature, adsorbent dose, initial concentration of adsorbate. Adsorption capacity seems to be enhanced by increasing temperature, adsorbent dose and for pH. Maximum dye adsorption was found to be in acidic range. Kammoni leaf powder (KLP) treated with Sulphuric acid (H_2SO_4) solution increased the adsorption efficiency upto 80 percent. Equilibrium data represented by the Freundlich Langmuir isotherm model for all adsorption systems. Beside these the thermodynamic study has showed that the acid dye adsorption onto the surface of acid activated Kammoni leaf powder (KLP) was physical adsorption and the process was spontaneous and exothermic.*

Keywords: Kammoni, Acid dyes, Adsorption isotherms, Freundlich isotherms.

INTRODUCTION

Synthetic dyes have been increasingly used in the textile, paper, rubber, plastic, cosmetic, pharmaceutical and food industries because of their ease of use, inexpensive cost of synthesis, stability and variety of color compared with natural dyes[1-3]. Today there are more than 10,000 dyes available commercially. Most of which are difficult to biodegrade due to their complex aromatic molecular structure and synthetic origin. The extensive use of dyes often poses pollution problems in the form of colored wastewater discharge into environmental water bodies,

which interferes with transmission of sunlight into streams therefore reduces photosynthetic activity[4]. In addition, some dyes or their metabolites are either toxic or mutagenic and carcinogenic. A lot of case throughout the world is reported about the role of dyes in connection with variety of skin, lung and other respiratory disorders[5]. Use of variety of dyes and chemicals in the dyeing processes causes considerable variation in the wastewater characteristics like pH, color and chemical oxygen demand (COD). The presence of these heat and light stable complex dye molecule in wastewater made the conventional methods of sewage treatment, such as primary and secondary treatment systems unsuitable. The adsorption process provides an attractive alternative treatment, especially if the adsorbent is inexpensive and readily available. Granular activated carbon is the most popular adsorbent and has been used with great success[6] but is expensive. Consequently, many investigators have studied the feasibility of using low cost substances, such as plum kernels[7], rice husk[8], peat[9], banana pith[10], orange peel[11], Eichhornia ash[12], saw dust[13], wall nut shells charcoal[14] etc. as adsorbents for the removal of dyes from wastewater. Critical review of low cost adsorbents for waste and wastewater treatment has been represented by pollard *et. al.* [15], Mall *et. al.*[16] and Bailey *et. al.*[17].

The purpose of the present work was to investigate the possibility of plant material (Kammoni) which is locally available, free of cost all over India as an adsorbent for the removal of acid dyes from aqueous solution. The acid dyes selected as an adsorbate were acid blue, acid red and malachite green. The effects of various operating parameters on adsorption such as pH, initial concentration, adsorbent dosage, temperature and dye concentration were studied.

EXPERIMENTAL SECTION

Adsorbent

The adsorbent used in the present investigation were leaves of Kammoni Plants collected from Ahmednagar District of Maharashtra State (India). The leaves of Kammoni 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 30 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 was dried first in air and finally in oven at 90-100⁰C for 8-10 hours and powdered using electric grinder. The homogeneous powder was then passed through mesh for desired particle size (9.8 - 41.8 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.

FT - IR Spectrum of Kammoni Leaf Powder (KLP)

The surface chemistry of KLP was determined by the type, quantity and bonding of oxygen containing functional groups such as hydroxyl, carbonyl, carboxyl, nitro groups[18-19].

The FT - IR spectrum of KLP adsorbent can be summarized from the bands observed as:

- (1) Medium based overlapping bands at 3310.21cm⁻¹ may be attributed to -OH group stretching present in secondary alcohol of KLP.
- (2) The bands at 2917.77cm⁻¹ indicates C-H stretching assigned to secondary asymmetric carbon.
- (3) The bands at 1730.8 cm⁻¹ indicates C=O stretching in α - β unsaturated Ketones.

(4) The bands range of 668.21cm^{-1} ascribed to N-H deformation (out of plane band) in primary, secondary amines of KLP.

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. A distilled water prepared by using first metal distillation unit and then all quick fit glass assembly in permanganic condition, wherever necessary the prepared solutions were standardized as per literature[20].

Batch Adsorption Experiments

Each batch adsorption study was carried out by contacting acid activated Kammoni leaf powder (KLP) with acid dyes. i.e. acid blue, acid red and malachite green under different conditions for 60 minutes in a glass tube. Stock solutions ($1.0 \times 10^{-3}\text{M}$) were prepared by dissolving weighed quantities of dyes in double distilled water. The concentration of dye solution were determined from calibration curve spectrophotometrically (Shimatzu-1211) 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 Temperature

The data of dye adsorption onto KLP at different temperature indicates a change in the dye removal efficiency. This effect is shown in Figure 1. 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 308.15 K to 318.15 K, The percentage removal of all three acid dyes average increased range was from 67 % to 77 %. 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[21-22].

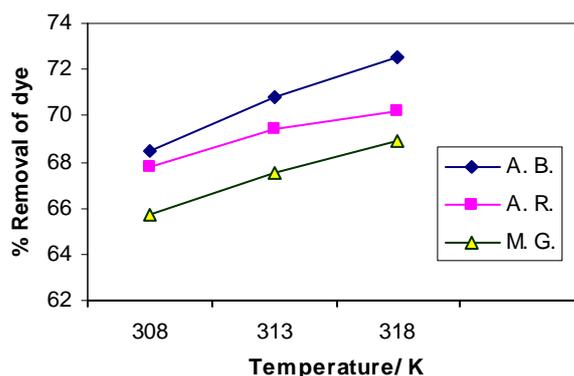


Figure 1. Effect of temperature on removal of dyes

Effect of pH solution

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 3.5 to 7.2 and is presented in graphical form as given in figure 2. 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[23], 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[24]. The study restricted at higher pH level upto 7.2 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 KLP. Our findings are supported by Mohan et.al.[25].

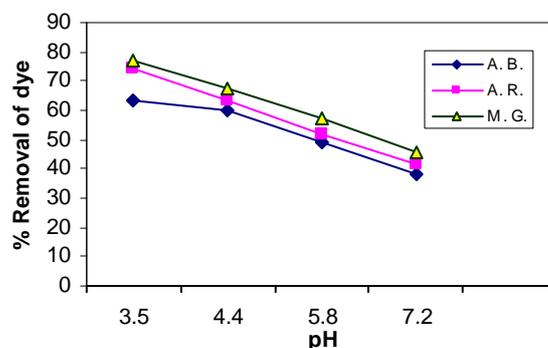


Figure 2. Effect of pH on removal of dyes

Effect of adsorbent dose

Effect of adsorbent dose plays an important role in standardizing the adsorption process with quantification of adsorbate solution and the adsorbent. In our present investigation with increase in the amount of KLP adsorbent i.e. from 0.5gms to 0.8gms 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.[26].

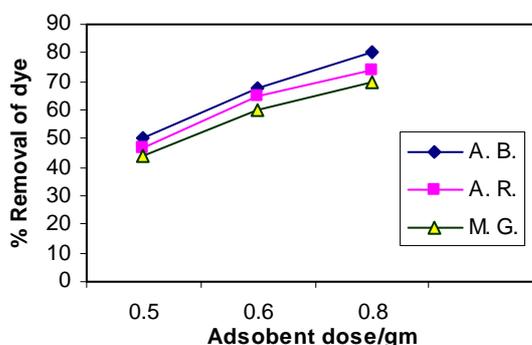


Figure 3. Effect of adsorbent dose on removal of dyes

Effect of Initial Concentration

The adsorption of all three acid dyes onto the surface of KLP were rapid initially, slow down later on and finally reached towards equilibrium (figure-4) indicating saturated adsorption as also reported by McKay et.al.[27-28]. The increased adsorption of the acid dyes onto the KLP 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 [29].

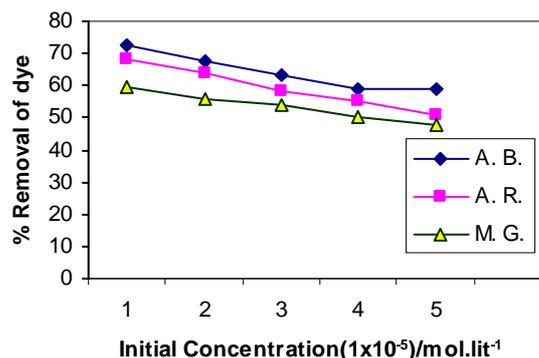


Figure 4. Effect of initial concentration on removal of dyes

Adsorption Kinetics

Kinetics of adsorption describes the solute uptake rate which in turn governs residence time or adsorption reaction. It is one of the important characteristics in defining the efficiency of adsorption[30]. A simple analysis of adsorption is the pseudo-first order rate expression of the Lagergren equation [31-32]. The kinetic data reveals that adsorption follows the first order reaction kinetics. From the pH study it can be concluded that in acidic media the dye removal percentage is maximum. Our findings are in good agreement with Mumin *et al.*[33]. The decrease in adsorption rate may be explained on the basis of aqua complex formation and subsequent acid-base dissociation at solid-solution interface [34]. The increase in adsorbent dose from 0.5gm to 0.8gm the rate constant increases i.e. the removal efficiency of dye increases. The available adsorption site increase which furnishes more adsorption and, therefore rate constant (K_1) also increases. Similar finding were also reported by other workers³⁵. The rate constant K_1 at different temperature were applied to estimate the activation energy of the adsorption of dyes onto KLP by Arrhenius equation,

$$\ln k = \ln A - E_a/RT$$

Where E_a , R and A refers to Arrhenius activation energy, the gas constant and Arrhenius factor respectively. The slope of the plot K_1 versus $1/T$ were found to be 8594.960J, 8279.97J and 8503.63J respectively for acid blue, acid red and malachite green. The minimum value of 8279.97J was for acid red – KLP system which is an indicative of higher adsorption and which may be attributed to lesser energy barrier.

Adsorption Isotherm

The adsorption isotherm is a graphical representation of amount of substance adsorbed against the residual concentration of the adsorbate in the solution[36]. The adsorption data for a wide range of adsorbate concentration and adsorbent doses were analyzed using Langmuir and Freundlich isotherm in order to find the adsorption capacity of KLP adsorbate.

Freundlich Theory: Freundlich theory suggested that the ratios of the amount of solute adsorbed onto a given mass of adsorbent to the concentration of the solute in the solutions are not constant at different concentration of solution [37]. The Freundlich isotherm was verified by using least square fit and regression analysis and computer programming in EXCEL. The value of regression coefficient r^2 found to be very close to one which indicates the good correlation exists between $\log x/m$ and $\log C$. The Langmuir model [38] represents monolayer adsorption on a set of distinct localized adsorption sites having the same adsorption energies no interaction between adsorbed molecules. The essential characteristic of Langmuir isotherm is expressed in terms of dimensionless constant separation factor or equilibrium factor R_L , which is indicative of the nature of the isotherm and is enlisted below as:

R_L Value	Types of Isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R = 0$	Irreversible

The adsorption of all three acid dyes are favorable onto the surface of KLP as R_L value in the present study falls in the type $0 < R_L < 1$ and the range found to be 0.009 to 0.010 and is in good agreement with the findings of Lodha et. al.[39].

Thermodynamic Parameters

Thermodynamic parameters such as free energy (ΔG°) enthalpy (ΔH°) and entropy (ΔS°) of adsorption were calculated from the binding constant K^1 which is obtained from Langmuir equation using following relations:

$$G^\circ = -RT \ln K \quad 1$$

$$\ln K = -\Delta H^\circ / RT + \text{constant} \quad 2$$

The ΔH° values were calculated from the slopes of linear variation of $\ln K$ vs $1/T$; furthermore, the values of ΔS° were calculated using the relation $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. The negative value of ΔG° indicates high affinity of dye to the surface of KLP, also negative value of ΔH° indicates exothermic process and the randomness of adsorption phenomena can be explained on the basis of entropy (ΔS°) which is also negative (**Table 1**). The values demonstrate a spontaneous and favourable adsorption process and are in good agreement with Saleem et. al.[40].

Table 1. Thermodynamic Parameters at different temperature

Adsorbate	Temperature /K	$-\Delta G$ /KJ	$-\Delta H$ /KJ	$-\Delta S$ / J.
Acid Blue	308	3.138	14.334	57.205
	313	3.472		
	318	3.265		
Acid Red	308	3.599	6.640	33.166
	313	3.127		
	318	3.103		
Malachite Green	308	3.240	8.635	38.718
	313	3.415		
	318	3.291		

CONCLUSION

The adsorption mechanism of dyes onto the surface of KLP adsorbent and the calculated ΔG° (free energy) found to be below -15KJ which is indicative of physical adsorption. The calculated dimensionless equilibrium parameter R_L found to be in the range between 0 to 1 is indicative of favorable adsorption onto the surface of KLP. Adsorption of acid dyes onto KLP was first order kinetic process with low activation energy which is an indicative of rapid adsorption process.

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