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Adsorptive removal of Acid Red-114 dye by activated carbon prepared from Kattamanakku tree leaves (*Jatropha curcas* L)

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ABSTRACT

The aim of the present work was to investigate the feasibility of Kattamanakku tree leaf powder carbon (KTC) for Acid Red-114 (AR-114) adsorption. The adsorption of AR-114 on KTC material was studied as a function of KTC dose (0.05-1.20g). , solution pH 3-10, contact time and initial concentration (70-380 mg/l)., The influence of these parameters on the adsorption capacity was studied using the batch process. The experimental data were analyzed by the Langmuir and Freundlich isotherms. The adsorption isotherm was found to follow the Langmuir model. The monolayer adsorption capacity was found to be 450.02 mg/g. The kinetic data were fitted in the pseudo-first order and pseudo-second order models and were found to follow closely the pseudo-second order kinetic model. The results revealed that KTC adsorbent is potentially low cost adsorbent for adsorption of AR-114.

Keywords: Adsorption, Acid Red-114, isotherm, *Jatropha curcas*.

INTRODUCTION

Water pollution is one of the most undesirable environmentl problems in the world and it requires solutions. Textile industries produce a lot of wastewater, which contains a number of contaminants, including acidic or caustic dissolved solids, toxic compounds and any different dyes. Many of the organic dyes are hazardous and may affect aquatic life causing various diseases and disorders[1]. Due to their chemical structures, dyes are resistant to fading on expoure to light, wter and many chemicals and therefore, are different to be decolourized once released into the aquatic environment[2].

Various techniques have been employed for dye removal from wastewater. Currently, the princial methods of treatment involve biological, physical and/or chemical processes[2-10].

In the present study, activated carbon prepared from tree leaves was used as an adsorbent for the removal of Acid Red 114 (AR-114) dye. The materials chosen are available in large quantities as biowaste and at low cost. The aim of the present work is to explore the possibility of using these carbonaceous materials as low-cost adsorbent.

EXPERIMENTAL

The dye adsorbate and preparation of the adsorbent and the adsorbate AR-114 dye (Microscopic grade, Sigma-Aldrich, India) was used without further purification. All solutions were made in double distilled water. Mature Kattamanakku leaves (*Jatropha curcas L*), collected from a number of trees, were mixed together and washed repeatedly with water to remove dust and other impurities. The leaves were dried first at room temperature in a shade and then washed with distilled water and soaked in 98% sulphuric acid (1:2 w/v) and heated separately for 24 h at 100°C in a muffle furnace. After treatment the samples were cooled to room temperature and washed with distilled water until the filtrates ttained neutral pH. The resulting activated carbon materials (KTC) were dired in a hot air oven at 333-343 K for 30 h till the leaves could be crushed into fine powder. The powdered carbon was sieved and the 53-74 micro fractions were preserved as an adsorbent in glass bottles.

Adsorption experiments

The adsorption experiments were carried out in a batch process by using aqueous solutions of AR-114 dye. The other variable parameters were adsorbent amount, agitation time and pH of the medium. In each experiment, an accurately weighed amount of KTC was added to 50 mL of the AR-114 dye solution in a 100 mL conical flask and the mixture was agitated in a thermostatic mechanical shaker for a given length of time at a constant temperature. If necessary, the pH was adjusted by addition of a few drops of dilute HNO_3 or NaOH. The mixture was centrifuged (Remi Research Centrifuge) and AR-114 dye remaining unadsorbed (λ_{max} = 570-580nm) was determined spectrophotometrically (Hitachi 3210). Calibration curves are obtained with standard AR-114 dye solutions and the amount adsorbed was found by mass-balance procedure.

Kinetics of adsorption

The kinetics of the adsorption processes was studied by carrying out a separate set of experiments with constant temperature, KTC amount and adsorbate concentration using the pseudo first orders Lagergren equation[11]. The differential rate equation is of the form:

$$dq/dt = k_1(q_e - q_t)$$

where q_e and q_t are the amount adsorbed per unit mass of the adsorbent (in mg g^{-1}) at equilibrium and at time t, and k_1 is the pseudo first order rate constant (min^{-1}). Integrating the above equation for the boundary conditions t = 0 to t = t and $q_t = 0$ at t = 0, gives:

$$\log (q_e - q_t) = \log q_e - k_1 t/(2:303) \qquad \ldots (1)$$

A linear plot of $\log (q_e - q_t)$ vs. t verifies the first order kinetics with the slope yielding the value of the rate constant.

Intra-particle diffusion

The variation in the extent of adsorption with time at different initial dye concentrations was processed for evaluating the role of diffusion in the adsorption system. Adsorption is a multi-step process involving transport of the solute molecules from the aqueous phase to the surface of the solid particulates followed by diffusion into the interior of the pores. The intra-particle diffusion rate equation[12]:

$$q_t = k_i t^{0:5} \qquad \ldots(2)$$

where k_i is the intra-particle diffusion rate constant (mg g^{-1} $min^{-0.5}$). The k_i values were calculated from the slopes of the linear plots of q_t vs. $t^{0.5}$.

Adsorption isotherms

The well-known Freundlich isotherm, Equation (3), is widely used to describe adsorption on a surface having heterogeneous energy distribution. The Langmuir isotherm, Equation (4) on the other hand is strictly applicable to monolayer chemisorption. The experimental data are tested with respect to both these isotherms:

Freundlich isotherm:

$$q_e = K_f C_n \qquad \ldots(3)$$

Langmuir isotherm:

$$C_e/q_e = (1/K_d C_1) + (1/C_1)C_e \qquad \ldots(4)$$

where q_e is the amount of dye adsorbed at equilibrium in unit mass of DLP, C_e is the concentration of the dye in aqueous phase at equilibrium, n and K_f are Freundlich coefficients, C_1 and K_d are Langmuir coefficients. The linear Freundlich and Langmuir plots were obtained by plotting (i) $\log q_e$ vs. $\log C_e$ and (ii) C_e/q_e vs. C_e, and the adsorption coefficients were computed from the slopes and the intercepts. Another important parameter, R_L, known as the separation factor, could be obtained from the relation:

$$R_L = 1/(1 + K_d C_{ref}) \qquad ...(5)$$

where C_{ref} is any equilibrium liquid phase concentration of the solute. It has been established[12] that (i) $0 < R_L < 1$ for favourable adsorption, (ii) $R_L > 1$ for unfavourable adsorption, (iii) $R_L = 1$ for linear adsorption, and (iv) $R_L = 0$ for irreversible adsorption.

RESULTS AND DISCUSSION

Kinetics of adsorption

The kinetics of AR-114 adsorption on (KTC) was studied with respect to different amounts of the adsorbent (Fig. 1). The adsorption of dyes increased with the sorbent dosage and reached an equilibrium value after (0.7g of sorbent dosage (Fig. 1) As one was expected, the percentage of dye removal increased with increasing amount of carbon, however, the ratio of dye sorbed to carbon (mg/g) decreased with the increasing amount of carbon (Fig. 2). The interactions appeared to attain equilibrium rapidly after about 1 h of agitation. Assuming pseudo first order kinetics for the adsorption process, log (q_e-q_t) was plotted against t and the linearity of the Langmuir plots (**Fig. 2**) confirmed the same (the correlation coefficients for the plots were in the range 0.92 – 0.99). The first order rate constants evaluated from these plots were between 2.99 x10^{-3} and 5.07 x10^{-3} min^{-1} for different amounts of the adsorbent.

The AR-114 dye-KTC interactions could thus be predicted as reasonably fast. It may be noted that the pseudo first order reaction differs from a true first order reaction in two aspects: the expression $k_1(q_e-q_t)$ does not represent the number of available sites and the parameter log q_e is an adjustable parameter whose value is not equal to the intercept of the plot of log ($q_{e\ -}q_t$) vs. $t^{½}$. In the present work, the intercepts of the Langmuir plots were very close to the theoretical log q_e values, and therefore, the kinetics of AR-114 dye adsorption on KTC could be considered as almost true first order in nature. Further, the difficulty usually associated with the application of the pseudo first order model to an adsorption system arising from the uncertainty of finding reliable q_e values within a reasonable time was not applicable in the present work as the system was very close to equilibrium even after 1 h of agitation time.

A number of authors have reported pseudo first order kinetics for adsorption of dyes on various adsorbents prepared from biological sources similar to the KTC. The values of the rate constant, k_1, obtained by these workers are compared with the values obtained in the present work in Table 1 (conditions vary). It is to be noted that the first order rate constant for the interaction of AR-114 dye with KTC, k_1, in the present work were 10-100 times less when compared to the values obtained for adsorption of Methylene Blue on water hyacinth roots (4.2 x10^{-2} - 6.9x 10^{-2} min^{-1})[13], on banana peel (3.5 x10^{-1} min^{-1}) and orange peel (2.9 x10^{-1} min^{-1})[14].

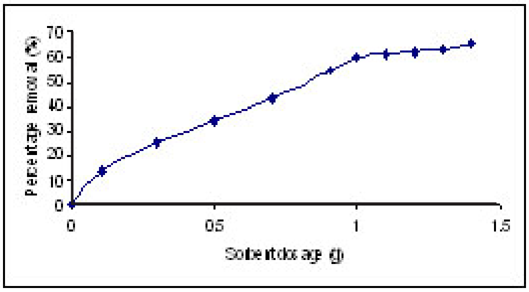

Fig.1: Effect of adsorption (%) of the dye AR-114 dye on different amounts of the adsorbent, KTC at 300 K (dye concentration 100 mg/L).

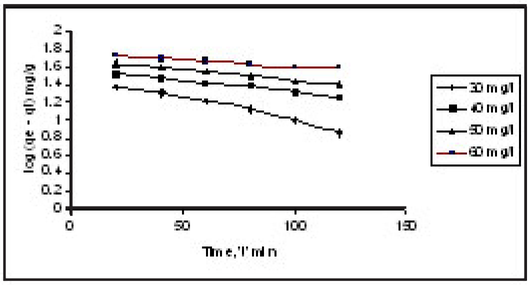

Fig. 2: Lagergren plots for adsorption of AR-114 on KTC at 300 K (dye concentration 50 mg/L).

Intra-particle diffusion

The plots of q_t vs. $t^{0.5}$ (Fig. 3) were found to be linear with regression coefficients of 0.90-0.99. The intra-particle diffusion rate constant, k_i, was in the range of (1.21-14.17) $x10^{-2}$ mg g^{-1} $min^{-0.5}$. The linearity of the plots demonstrated that intra-particle diffusion played a significant role[14] in the uptake of the dye by KTC. This also confirms that adsorption of the dye on the adsorbent was a multi-step process, involving adsorption on the external surface and diffusion into the interior. All the steps slow down as the system approaches equilibrium. If the steps are independent of one another, the plot of q_t vs. $t^{0.5}$ usually shows two or more intersecting lines depending on the exact mechanism, the first one of these lines representing surface adsorption and the second one intra-particle diffusion. The absence of such features in the plots of the present work indicated that the steps were indistinguishable from one another and that the intra-particle diffusion was a prominent process right from the beginning of dye-solid interaction. Weber and Morris[15] have proposed that if the uptake of the adsorbate varies with the square root of time, intra-particle diffusion can be taken as the rate-limiting step. Ho [16] has shown that it is essential for the q_t vs. $t^{0.5}$ plots to go through the origin if the intra-particle diffusion is the sole rate limiting step. Since this was also not the case in the present work (the q_t vs. $t^{0.5}$ plots have intercepts in the range 4.50-20.40 mg g^{-1}), it may be concluded that surface adsorption and intra-particle diffusion were concurrently operating during the AR-114 - KTC interactions.

Table 1: Pseudo first order rate constant data for adsorption of dyes on various adsorbents

Adsorbent	Dyes	k (min^{-1})	Reference
Banana pith	Acid Violet	(1.8-13.0) x 10^{-2}	[17]
Orange peel	Rhodamine B	(2.3-9.95) x 10^{-1}	[18]
Water hyacinth	Methylene Blue	(4.2-6.9) x 10^{-2}	[19]
Orange peel	Congo Red	(3.6-4.9) x 10^{-2}	[18]
Orange peel	Acid Violet 17	(3.5-6.9) x 10^{-2}	[20]
Banana peel	Methyl Orange	3.9 $x10^{-1}$	[21]
Orange peel	Methyl Orange	4.0 x 10^{-1}	[21]
Methylene Blue	2.9 $x10^{-1}$	[21]	
Rhodamine B	2.1 x 10^{-1}	[21]	
Coir pith	Congo Red	(2.1-3.9) x 10^{-1}	[22]
Neem leaf powder	Brilliant Green	7.32 $x10^{-3}$	[23]
Neem leaf powder	Methylene Blue	(2.9-5.1) x 10^{-3}	[24]

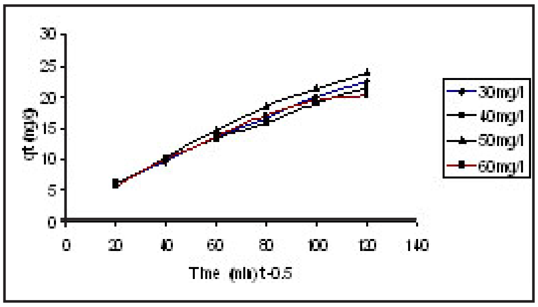

Fig.3. Plots of q_t (mg g^{-1}) vs. $t^{0.5}$ for evaluating intra-particle diffusion rate constant (AR-114 dye concentration 40 mg/L, temperature 300 K).

Effect of the amount of adsorbent and the initial concentration of the adsorbate

To investigate the effect of adsorbent mass on amount of adsorption, a series of experiments were carried out keeping the agitation time constant and varying both the amount of adsorbent and the adsorbate concentration at constant temperature. For a KTC of 50 mg/L, the amount adsorbed 3.60mg g^{-1}. The Grey BL concentration was increased from 50 to 250 mg/L (Table 2). The results as a whole indicate two distinct trends: the amount adsorbed, q_t (mg g^{-1}), increased with an increase in the dye concentration and decreased with an increase in the amount of the adsorbent. The latter trend may be due to the effect of adsorbent mass on porosity of the adsorbent suspension. In general, the trends might have been influenced by changes in a number of physical properties of the solid-liquid suspensions including their viscosity.

Table 2: Amount of AR-114 adsorbed on KTC at 300 K in mg g^{-1}

Dye conc. mg/l	Weight of carbon (mg)	Amount adsorbed (mg g^{-1} for KTC	Amount of dye Adsorbed (%)
15	50	3.10	11.30
30	100	4.20	25.55
50	150	5.32	44.38
70	200	6.27	63.72
90	250	7.01	83.20

Contact time 5h

Effect of pH

An important influencing factor for dye biosorption on agricultural by-products has been referred to pH as in most studies published in the literature. The variation of equilibrium dye uptake with initial pH is given in Fig. 4 for an initial dye concentration of 100 mg^{-1} at 300 K for a contact time of 4 h. As seen from the Fig.4, the biosorption with pH of the medium varying from 2.0 to 9.0, the adsorption of the dye oscillated between 60 and 70%. Ho et al. [17] have shown that the extent of removal of a basic dye (Basic Red 18) by activated clay decreased rapidly as pH increased from 3.0 to 5.0 and from 8.0 to 10.0. However, the adsorption remained constant within the range of pH 5.0-8.0. It was suggested that the increase in sorption depended on the properties of the adsorbent surface and the dye structure. At a lower pH, the adsorbent surface might have become negatively charged attracting more of the basic dye molecules. It is likely that positive charge develops on the surface of an adsorbent in acidic medium, resulting in a higher adsorption of anionic dyes than in a basic solution. If this is the case, the sorption of the cationic dye should decrease at a lower pH. In addition, the effect of pH may also be explained on the basis of surface hydroxylation, acid-base dissociation and surface complex formation.

The adsorption of AR-114 increases with the increase of pH of the solution. The variation in the amount of adsorbed dye with respect to pH of the medium has been shown in Fig. 4. The maximum removal was noted at pH 6.5 -7.5. With an increase of pH from 4.2 to 7.02, the uptake of AR-114 increases from 52 to 63 % which is close to the satisfactory level by KTC at a temperature 300 K.

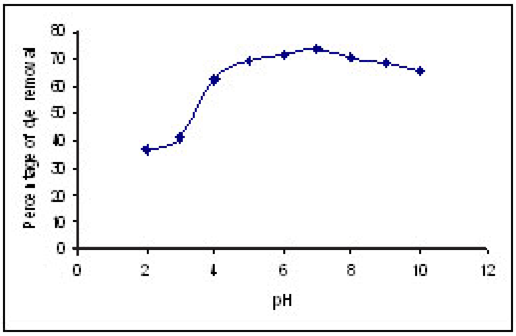

Fig. 4 Effect of pH on the removal of AR-114 by KTC (concentration 40 mg/l temperature 300 K.

Adsorption isotherms

The experimental data yielded good linear plots with both Freundlich isotherm (Fig. 5, Regression coefficient R -0.99) and Langmuir isotherm (Fig. 6, R: 0.96-0.99). The Freundlich coefficient, n, which should have values in the range of $0 < n < 1$ for favourable adsorption, remained in a narrow range of 0.51 - 0.66 for different amounts of the adsorbent. The Freundlich adsorption capacity, K_f, was in the range of 2.42-9.47 L g^{-1}.

The Langmuir monolayer adsorption capacity, C_1, was large with values between 4.26 and 11.32mg g^{-1}. The Langmuir adsorption intensity, K_d, had values of 0.186-0.729 L mg^{-1}. The dimensionless separation factor, R_L, had an average value of 0.96 in the range of 0.91-0.98 in concurrence with the suggested values for favourable adsorption. This value being very close to 1.0, the adsorption of the dye on KTC could be described as linear in nature, i.e., there was an almost linear increase in adsorption with increase in KTC amount. The isotherm constants indicated that the KTC had very good potential as an adsorbent for the dye, AR-114, and it might have similar potential for other dyes, as had already been demonstrated for Brilliant Green (Bhattacharya)[24].

The Langmuir monolayer capacity of the KTC (4.26-11.32 g kg^{-1}, may be compared with a number of adsorbents derived from biological sources like the KTC. Some of the large adsorption capacities recorded were: 160 g kg^{-1} for Atrazon Blue on Maize cob[25], 94.5 g kg^{-1} for Maxilon Red also on Maize cob[25] and 133.7 g kg^{-1} for Brilliant Green on Neem leaf powder[23].

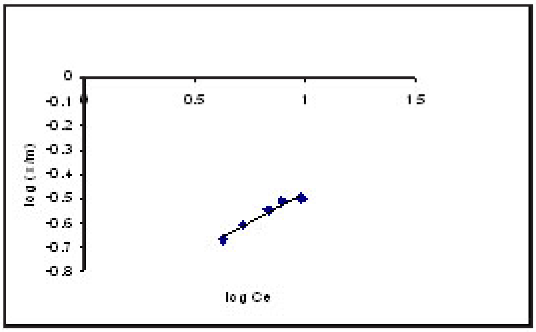

Fig.4. Freundlich isotherms for adsorption of AR-114 dye on KTC at 300 K with dye concentration of 50 mg/L and agitation time 5 h.

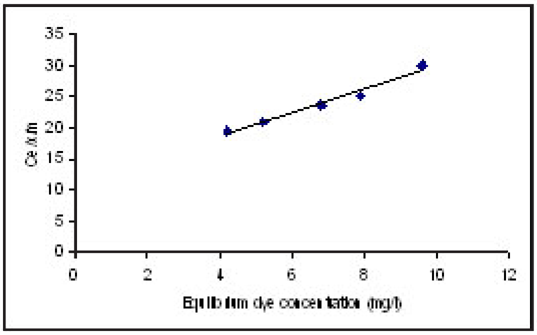

Fig.5. Langmuir isotherms for adsorption of AR-114 on KTC at 300 K with dye concentration of 50 mg/L and agitation time 5h.

The KTC thus has good potential to be used as an adsorbent for the removal of AR-114 from water.

CONCLUSION

The results of this work can be summarized as follows:

- (i) Kattamanakku leaves powder carbon is a promising adsorbent for removal of the dye AR-114 from water. A small amount (2 g/L) of the adsorbent could almost completely decolorize an aqueous solution of AR-114 (40 mg/L) if agitated for 5 h.
- (ii) The experimental data produced perfect fit with the Freundlich isotherm showing that the surface of the KTC particles was heterogeneous, non-specific and non-uniform in nature. The mechanism of the dye-KTC interactions is thus likely to be very complicated involving a wide range of sites differing in a number of aspects including energy considerations.
- (iii) The data were in good agreement with the Langmuir isotherm.
- (iv) The adsorption of the dye on KTC followed pseudo first order kinetics with the interactions largely over within the first hour.

The Kattamanakku tree regularly sheds its leaves during January-February, which become waste. These leaves can be put to good use as an adsorbent for removal of colour from industrial and other effluents. However, as with all other bio-resources, the processes are likely to be very complicated and a detailed characterization of the surface will be necessary to develop more insight into the mode of action.

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