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Research Article

STUDIES ON THE REMOVAL OF MALACHITE GREEN AND METHYLENE BLUE DYES FROM AQUEOUS SOLUTIONS OF THEIR BINARY MIXTURE BY ADSORBTION OVER COMMERCIAL ACTIVATED CARBON AND TAMARIND KERNEL POWDER

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ABSTRACT

The waste water originating from textile processing industries is a complex mixture of potentially polluting substances consisting of textile dyes, heavy metals associated with dyes and the other auxiliaries used during process. Adsorption appears to offer the best prospects for over all treatment of dye stuff effluent. As Commercial Activated Carbon used as adsorbent for adsorption is very expensive, there is a need for an alternative for it. In this context, we have planned to use Tamarind Kernel Powder (TKP), a biological waste material as a low cost adsorbent[1]. Literature survey reveals that removal of various dyes using different low cost adsorbens have been carried out extensively. But a study on removal of dyes from their aqueous solution from their binary mixture is very scarce. The present work deals with combined removal of (Malachite Green & Methylene Blue) dyes from the aqueous solution of their binary mixture using the low-cost adsorbent Tamarind Kernel Powder (TKP) and Commercial Activated Carbon (CAC) and to compare the effectiveness of the adsorbent TKP with CAC in the removal of dyes. Variation of initial concentration, pH , dose, and contact time affected the adsorption process. From the results of present study, we can conclude that adsorption processes are applicable for adsorption of dyes from aqueous solution of their binary mixture. TKP can be used as low cost adsorbent as an alternative adsorbent to CAC in waste water treatment for the removal of dyes. We find that TKP has an efficiency comparable to that of CAC, expect for the optimum dose.

Keywords: Dye: MethyleneBlue, MalachiteGreen, ActivatedCarbon, Tamarind Kernel Powder.

INTRODUCTION

A large number of dye is discharged into waste stream by the textile industries. Many colour effluent are composed of non biologically oxidisable organic compounds. As a dye imparts toxicity and upsets the biological activity of water ,there is a necessity for the removal of dyes from effluents before they are mixed with water streams. These can be separated by adsorption method. Activated Carbon uses the physical adsorption process Activated carbon through adsorption also removes chemical like chlorine that combines with carbon to from chloride ions. This reactions helps not only in removing contaminants but also removes objectionable tastes and odors from drinking water. Activated carbon proves to be very effective in organic compound removal. With the increasing demands for environmental protection, activated carbon technology has quite a future. Other forms of the carbon such as fibers and microbeads are developing and colud prove to be very effective.As activated carbon is very expensive , there is a need for an alternative for it . This should be a low cost material which is available easily. Research have been carried out to find a cheaper alternative to activated carbon. In this context , we have planned to use Tamarind Kernel Powder (TKP)as a low cost adsorbent. Tamarind Kernel is a biological waste material which is easily available at a lower rate. It can be collected and powdered. Also studies on

the removal of dyes from aqueous solution of their binary mixture are very scarce. So we have carried out the studies on the removal of methylene blue and malachite green dyes from their mixture. Factors influencing adsorption include particle size distribution, nature of adsorbent and adsorbate, surface area of the adsorbent, pH, temperature, initial concentration, contact time, dose adsorbent etc. Isotherms are empirical relations which are used to product how much solute can be adsorbed by activated carbon .The most commonly used isotherm are Freundlich isotherm and Langmuir isotherm. Kinetic of adsorption is quite significant as it decides the residence time of adsorbate at solid-solution interface and helps in determining the rate of the adsorption process. This study includes adsorption rate study and intra particle diffusion study. The adsorption rate study was studied on the basis of Natarajan and Khalaf equation and Lagergren equation.

MATERIALS AND METHODS

MATERIALS

The adsorbent material used for the present work were commercial activated carbon (CAC) and Tamarind Kernel powder. Double distilled (DD) water was stored in brown bottles. The Tamarind kernel is a biological paste material which is easily available in economically. Tamarind kernels were collected, washed with water and dried over the sunlight and grinded to powder in machine. The adsorbents were activated by digesting the carbon with the required volume of 4N dilute Nitric Acid solution and heated at 80^{o} C for two hours and cooled. After cooling it was washed several times with water in order to removes soluble impurities. The adsorbents were placed in an air oven at a temperature 120^{o} C for two hours.

The adsorbate material in the present study were AR sample of dyes viz Methylene Blue (MB) and Malachite Green (MG). The other chemical reagents employed in the present work were of Analar grade sample supplied by BDH. India, Ranbaxy and SD fine chemicals India. All the reagents and solutions were prepared by using DD water. The activated adsorbents samples were stored in reagents bottles.

METHODS

In the present work , the adsorption experiments were carried out by employing the batch adsorption technique. Adsorption of methylene blue and malachite green dyes from aqueous solution of their binary mixture on Commerical Activated Carbon (CAC) , and Tamarind Kernel Powder (TKP) was studied under different experimental conditions, Initial concentration, dose by varying of adsorbent, initial pH and contact time. Optimum conditions obtained in the present studies for the maximum removal of dyes by adsorption process.

EXPERINMENTAL

General Procedure for adsorption

In the present work, the adsorption experiments were carried out by employing the batch adsorption technique. The stock solution of dyes Methylene Blue, Malachite green with known concentration (2000ppm) were prepared and stored in brown bottles. It was diluted to get different required initial concentrations of the dye and used in the adsorption experiment. The stock solution is diluted to different initial concentration 10, 20, 30 ...150ppm for methylene blue dye and 2, 4, 6 ..8ppm for malachite green dye in standard measuring flasks, by making necessary dilution with required volume of DD water. The optical density (OD) of each dye solution was measured by using UV – VIS spectrophotometer (Model –SL –150Elico) at 616nm and 668 nm (λ Max values for MB and MG dyes) respectively. A plot of optical density versus initial concentration was drawn for both the dyes. These are given in (Figures 1& 2) These plots were used as standard graphs for the estimation of dyes by interpolation technique. The values of optical density for dye solutions, before and after adsorption were obtained by using spectrophotometer at the corresponding λ max values. The corresponding dye concentration were obtained from the standard graphs by the interpolation technique.

BATCH TYPE ADSORPTION EXPERIMENTS

Stock solution of dyes (2000 ppm of MB and MG) were suitably diluted to the required initial concentration of dye with DD water. 50 ml of the dye solution of known initial concentration (C_i) was taken in 250 ml leak-proof corning reagent bottle. Required amount of adsorbent (CAC or TKP) material was exactly weighed and then transferred into each one of these bottles, with different C_i. The bottles were then placed in a mechanical shaker and shaken vigorously for a required period of contact time at room temperature (30 ± 1^{0} C).

The dye solutions were filtered through filter paper (Whatmann No.1) and the first 10 ml portion of the filtrate was rejected from each one of these bottles. The filtration was continued and the filtrates were collected

separately in clean dry conical flasks. The OD of these solutions were measured using spectrophotometer at 616 nm and 668 nm. Then, the final or equilibrium concentrations (C_e) were obtained from the standard graph (Fig.1,2) by the interpolation technique.

In all the batch adsorption experiments the extent of removal of the dye, in terms of the values of percentage removal of dye and amount adsorbed (q, in mgg-1) have been calculated using the following relationships:

Percentage removal = 100 (C_i – C_e) / C_i ------- (1)
Amount adsorbed (q) = (x/m) = (C_i – C_e)/m ---- (2)

Where C_i=initial concentration of dye (ppm) C_e = equilibrium concentration of dye (ppm) x = amount of dye adsorbed (ppm) m = mass of adsorbent (gL-1).In the batch adsorption technique the effect of several factors govern the adsorption process. The effect of various experimental parameters on adsorption of methylene blue and malachite green dyes from the aqueous solution of their binary mixture using commercial activated carbon (CAC) and tamarind kernel powder (TKP) as adsorbents was studied under different experimental condition.The various experimental parameters are initial concentration of methylene blue and malachite green dyes ,dose of adsorbent,initial pH of the solution ,and contact time.

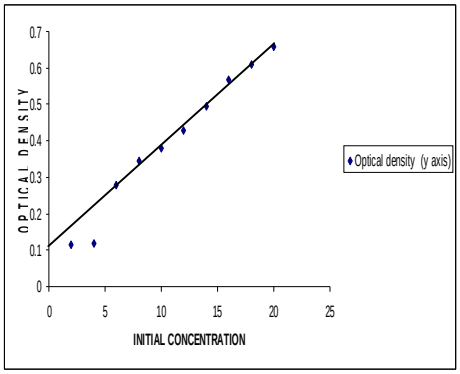

Fig.1: Standard curve for Malachite green

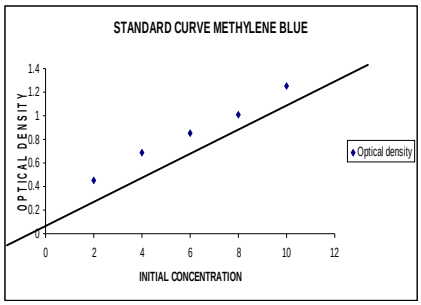

Fig.2: Standard curve for Methylene blue

RESULTS AND DISCUSSION

1. **Effect of variation of initial concentration**

The effect of initial concentration was studied by varying the initial concentration of dye keeping other factors constant.At on optimum initial concentration of dye(600 ppm for MG and MB by CAC adsorbent. 700 ppm for MB and MG by TKP adsorbent) ,the percentage removal was noted to be maximum. The experimental values of the extent of removal of dyes indicate that the rate of removal of dye decreases with the increase in the initial concentration of dye and vice versa. This is due to the fact that after the formation of mono layer at the lower initial concentration of dye over the surface of adsorbent any further formation of layer of dye species is highly hindered.The variation can be represented as in Fig 3&4

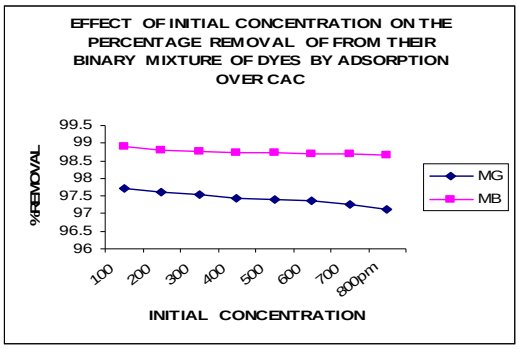

Fig.3

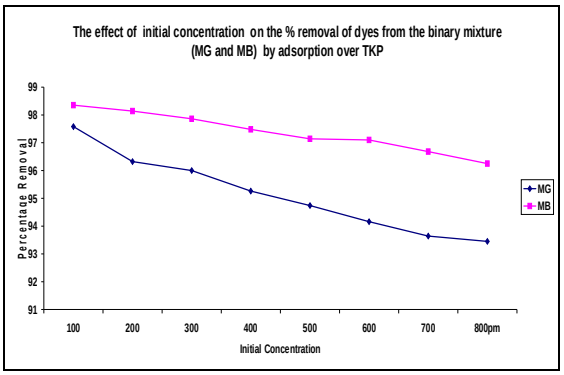

Fig. 4:

This suggest that the adsorption of dye may either block the access of dyes , to the initial pores or cause particles to aggregate and there by reducing in the availability of required number of active sites for adsorption.

2. Effect of variation of dose of adsorbent

The effect of variation of dose of adsorbent (CAC&TKP0was studied.The initial concentration of the dyes (MG&MB) and initial pH in all the bottles were kept constant and dose of adsorbent (CAC&TKP)was varied.The optimum dose of adsorbent is fixed as 5 gL^{-1} for CAC ;6gL^{-1} for TKP for the removal of mixture of dyes (MG and MB).The amount of dye adsorbed increased exponentially with the increase in the dose of adsorbent and contact time.The variation of percentage removal were found to be maximum at (MG 97.63% of CAC and 82% of TKP ;MB 99.10% of CAC and 83.42% of TKP).The variation of percentage removal against dose of adsorbent can be represented graphically represented as in Fig (5&6)

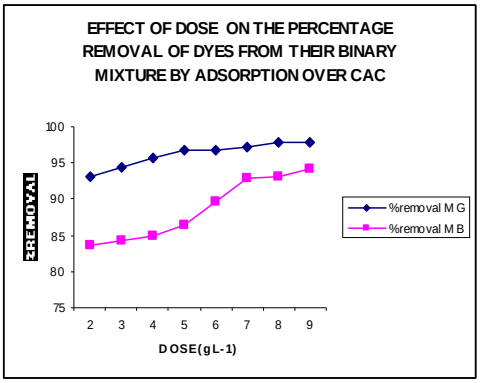

Fig. 5

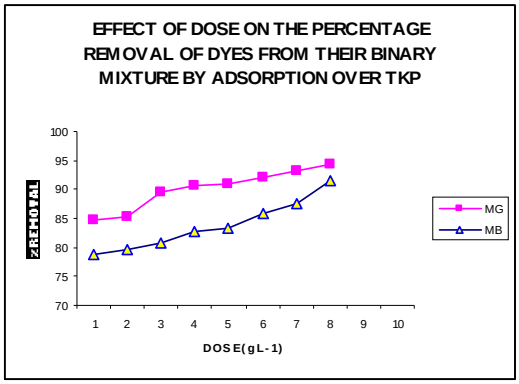

Fig. 6

3. Effect of pH variation

The effect of initial pH of dye solution was studied at different pH value (Range of pH: MG & MB = 3 – 6.8 for CAC, MG & MB = 3 – 6.8 for TKP). The percentage removal of dye decreases with the increase in initial pH for adsorption of mixture of dye MG & MB on both CAC and TKP as shown in graph (Fig.7and8). The adsorption of these dyes on CAC & TKP in found to be highly pH dependent. The effect of variation of initial pH on the percentage removal of the dyes on CAC & TKP clearly indicates that the mechanism[103] of adsorption of these two dyes are same. The increased adsorption at low P^H may be due to the basic nature of dyes.From this we fix the optimum pH for adsorption,as pH MG&MB=6.8 for CAC and MG&MB=6.8 for TKP.

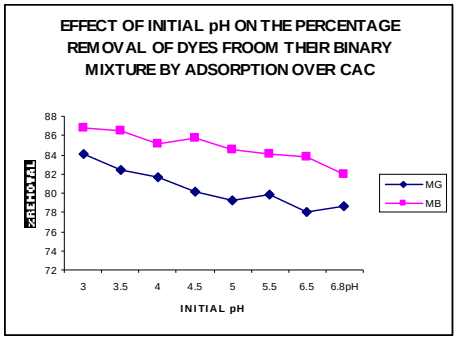

Fig.7

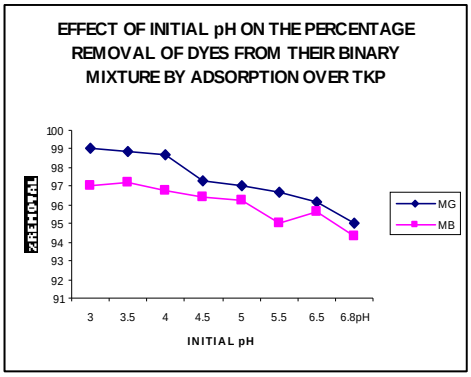

Fig.8

4. Effect of contact time

The percentage removal of dyes from mixture of MG and MB increases exponentially with the increase in contact time and reaches a maximum value. The percentage removal of binary mixture of dyes (MG and MB) at 60 min. of contact time, is 97.51 for MG and 94.86 for MG by CAC, and 96.25 for MG and 93.45 for MB by TKP respectively, This reveals that the optimum contact time is 60 min for MG & MB for both the adsorbents (CAC and TKP).The variation can be graphically rrepresented as in Fig.9&10.

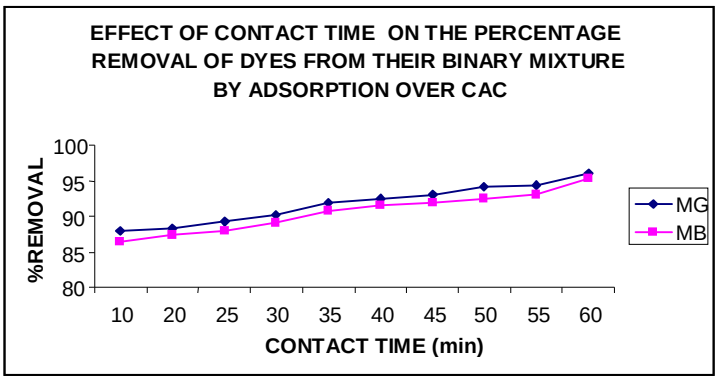

Fig. 9

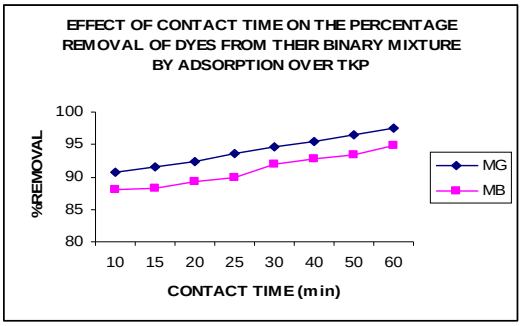

Fig. 10

5. The values of first order rate constant (K in min^{-1}) calculated using the Natarajan&Khalaf [5] and Lagergren [6] kinetic equations are tabulated in Table -1.The linear plot observed(Fig 11-14) shows that the adsorption process obeys these kinetic equation. The rate constant value is higher in TKP than in CAC. This shows that rate of adsorption is higher in TKP. This gives support for the efficiency of TKP. The rate of adsorption of dyes is in the order MB>MG for CAC and it follows the order MG>MB for TKP.

Table 20: Rate constant value

S. No.	Parameters	CAC		TKP	
		MG	MB	MG	MB
1.	Natarajan and khalaf equation 10^2K(min-1) r value	2.56 0.953	1.59 0.960	1.15 0.983	1.72 0.968
2.	Lagergren equation 10^2k(min-1) r value	2.59 0.965	1.69 0.975	2.73 0.992	2.42 0.989
3.	Intra particle diffusion modle Kp value ($mgg^{-1}min^{-1/2}$)	0.764 0.932	0.652 0.941	0.613 0.921	0.689 0.956

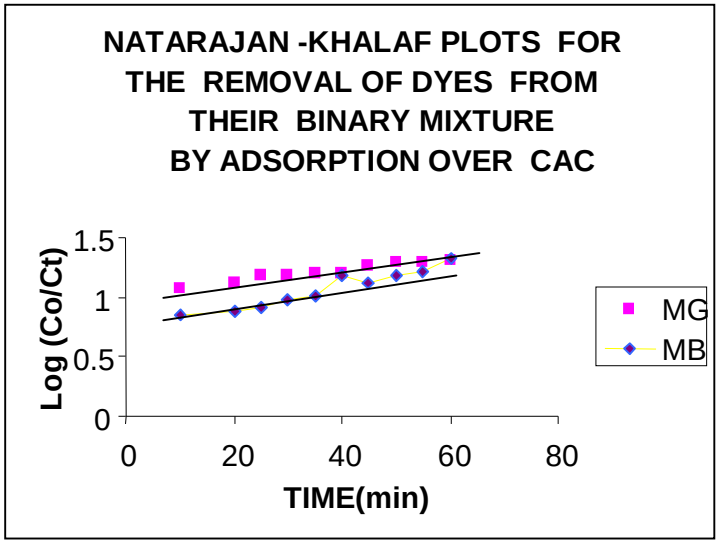
NATARAJAN -KHALAF PLOTS FOR THE REMOVAL OF DYES FROM THEIR BINARY MIXTURE BY ADSORPTION OVER CAC
Log (Co/Ct)
1.5
1
0.5
0
0
20
40
60
80
TIME(min)
MG
MB

Fig. 11

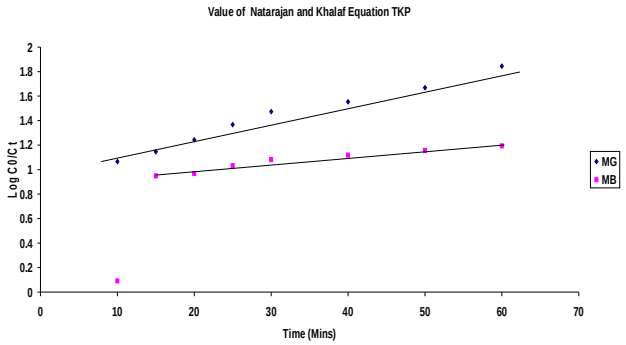
Value of Natarajan and Khalaf Equation TKP
Log C0/Ct
Time (Mins)
MG
MB

Fig. 12

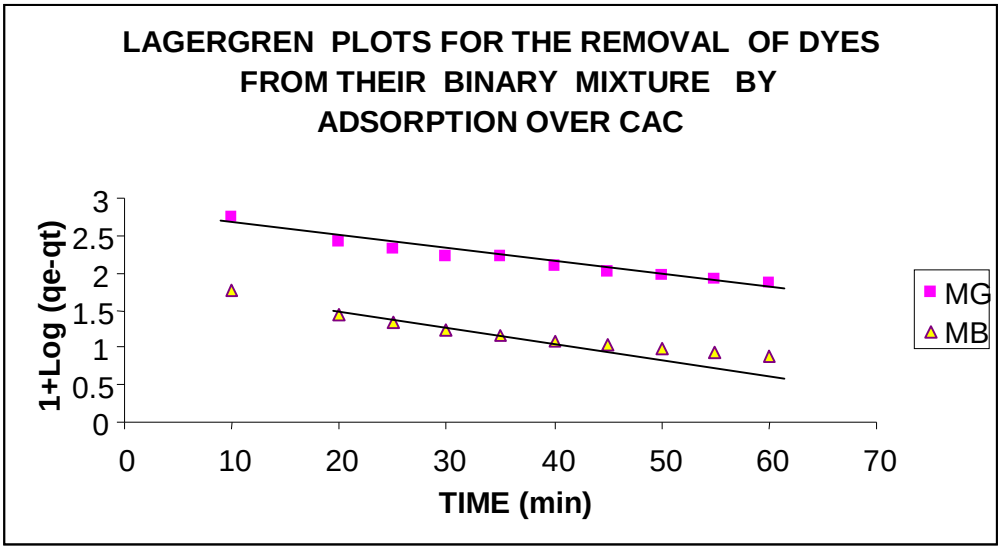
LAGERGREN PLOTS FOR THE REMOVAL OF DYES FROM THEIR BINARY MIXTURE BY ADSORPTION OVER CAC
1+Log (qe-qt)
3
2.5
2
1.5
1
0.5
0
0
10
20
30
40
50
60
70
TIME (min)
MG
MB

Fig. 13

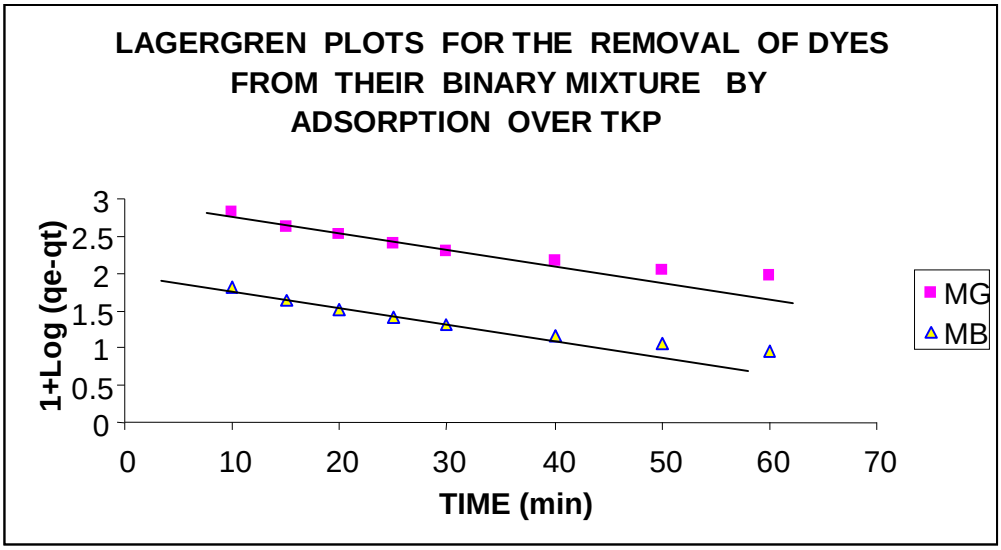

Fig. 14

6. The presence of intraparticles diffusion[7] process as the rate determining step in the adsorption process in the present adsorption system is also tested by applying the intra particle diffusion model[8,9].

The equation used for intraparticle diffusion model is

$$q_t = K_p t^{1/2} + C$$

The intraparticle diffusion plots for the removal of dyes from the binary mixture of dyes by adsorption over CAC is shown in (Fig15). Similar graphs can be obtained for the removal of dyes from their binary mixture of dyes by adsorption over TKP(Fig.16).

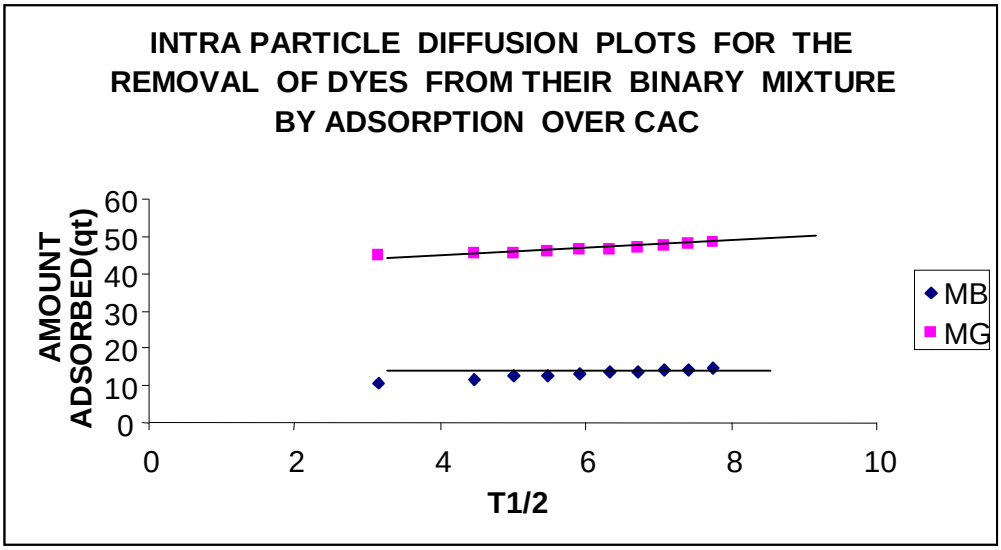

Fig. 15

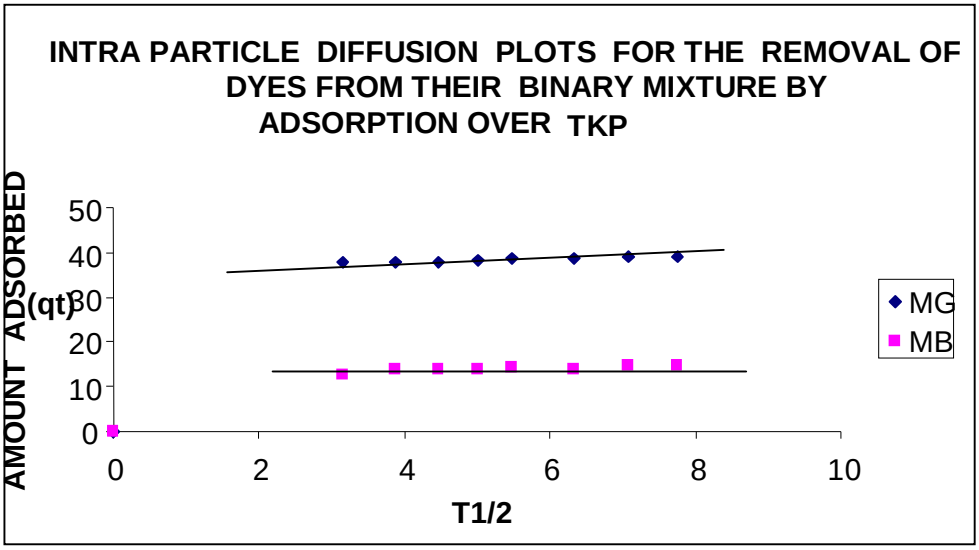

Fig. 16

CONCLUSION

From the results of the studies performed, the following conclusions can be drawn.

1) Indigenously prepared low cost adsorbent Tamarind Kernel Powder was capable of removing MB and MG from the binary mixture of their aqueous solution.
2) pH plays a significant role in the adsorption of dyes. The adsorption process is pH dependent.
3) The percentage removal of MB and MG increased with the decrease in the initial concentration of dye and pH, increase in dose of the adsorbent and contact time.
4) Adsorption data obeyed Freundlich and Langmuir adsorption isotherms.
5) The linear plots obtained for Lagergren equation and Natarajan & khalaf equation, confirmed the first order kinetics for adsorption process.
6) The Intra – particle diffusion was found to be rate determining step.
7) The optimum conditions for maximum removal was obtained and given in Table-2.

Table 2: Optimum conditions obtained in the present studies for the maximum removal of dyes by adsorption over CAC and TKP.

S.No	Mixture of dyes	Absorbent	Optimum concentration (ppm)	pH	Dose (g/L^{-1})	Contact time (min)	% removal
1	MB MG	CAC	600 600	6.8 6.8	5	60	95.23 96.12
2	MB MG	TKP	700 700	6.8 6.8	6	60	93.45 96.25

SUMMARY

The adsorption process had been widely used in water and wastewater treatment. Of all the methods like chemical oxidation, froth flotation coagulation etc. adsorption appears to offer the best prospects for overall treatment of dyestuff effluent. This accounts for the renewed interest in the use of batch-wise adsorption technique for the removal of dyes from the effluents. But the use of activated carbon as an adsorbent is limited because of its high cost. Thus more attention was focused on utilization of low cost adsorbent in the field of wastewater treatment. The studies on the simultaneous removal of the dyes from aqueous solution of their mixture by adsorption technique are scarce. So, the present work deals with combined removal of (MG and MB) dyes from the aqueous solutions of their binary mixture using low-cost adsorbent Tamarind Kernel Powder (TKP) and Commercial

Activated Carbon(CAC) and to compare the efficiency of adsorbent TKP with CAC in the removal of dyes, The mixture of methylene blue and malachite green dyes are selected for present work.

The following experimental parameters affect the adsorption process

- With the increase in the initial concentration, the percentage removal of dye on the adsorbents (CAC, TKP) decrease due to the lack of available of active sites. The maximum initial concentration of dye at which the maximum percentage removal takes place was fixed as the optimum value. This was found to be 600ppm for both methylene blue and malachite green dyes for CAC and 700ppm for both the adsorbents methylene blue and malachite green dyes for TKP.
- The amount of dye adsorbed increased exponentially with the increase in the dose of adsorbent and contact time . Thus the maximum percentage of removal of dyes were observed at optimum dose of $5gL^{-1}$ for CAC and $6gL^{-1}$ for TKP. The optimum contact time was 60 minutes for both adsorbents.
- The process of removal of dyes (MB & MG) by adsorption on CAC & TKP was found to be highly pH dependent. At lower pH the percentage removal was found to be maximum. The maximum adsorption occurred at pH 6.8 for MB & MG for adsorption over CAC and TKP respectively. This is actually the pH of the solution of mixture of dyes.
- The adsorption of dyes (MB & MG) over CAC & TKP obeyed the first order Kinetic equations proposed by Natarajan and Khalaf, Largergren and Intra particle diffusion model. All the plots obtained were found to be linear with the r value close to unity. Intra particle diffusion, can be considered as the rate determining steps.

From the results of present study, we can conclude that adsorption process are applicable for adsorption of dye from aqueous solution of their binary mixture. TKP can be used as low cost adsorbent as an alternative adsorbent to CAC in waste water treatment for the removal of dyes.

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