

Optimising The Parameters For The Congo Red Dye Decontamination In Aqueous Solutions By Polyvinylpalmitate Adsorbents

S Rathika*, P S Raghavan**

Department of Chemistry, Madras Christian College, Chennai -600059, India.

ABSTRACT

Polyvinylpalmitates were prepared by condensing polyvinyl alcohol with palmitic acid in different ratios and their efficiency tested as adsorbents for the removal of the congo red dye from aqueous solution. The effect of various parameters like pH, contact time and initial concentration of the dye, etc., on the amount of adsorption has been studied. The adsorption is most effective at pH 4 and equilibrium was found to reach at about 120 minutes. The rate of adsorption conformed to second order kinetics and obeyed Langmuir adsorption isotherm. Chemisorption is suggested to be the mechanism driving this adsorption.

* Currently member in the faculty, Department of Chemistry, Sri Sairam Institute of Technology,

Sai Leo Nagar, West Tambaram, Chennai – 600044, India.

** Author for correspondence

1. Introduction

The effluents from industries like leather, paper, plastics, textile, printing and dyeing are loaded with different types of dyes and pollute the surface and ground water systems. There may be a chance for the transfer of dyes into drinking water and it can also cause various diseases including allergy, skin irritation, cancer and eye irritation [1]. Hence we have to protect our environment from dye pollution. Many methods like reverse osmosis, sedimentation, coagulation, oxidation, precipitation, electro dialysis are adopted for treating effluents and their relative merits have been discussed [2] by the

removal of dyes and pigments but the cost is relatively high. In most of the cases, the low cost adsorbents like clay [3], wood powder [4], fly ash [5], sugar-extracted spent rice biomass [6], red mud [7], natural zeolite [8] have also shown to be effective. Different types of bentonites are also used as adsorbents because of their availability and low cost [9,10]. Zhengyongzhang [11] reported that the vinyl acetate had a high adsorption capacity used for treatment of methylene blue enriched waste water. Elifilmazozmen [12] reported that cyclodextrin and starch based polymers can be used as a sorbent for the removal of anionic azo dyes through physisorption. The efficient biosorption performance of penicillium YW 01 for the removal of acid black 172 metal-complex dye (AB) and congo red was studied by yuyi yang et al [13]. The adsorbent N,O-carboxymethyl-chitosan has been found [14] suitable for the removal of congo red from dye waste water and that sugar extracted spent rice biomass has been recommended [15] to remove methylene blue from the solution. Besides, the adsorption of congo red has also been shown to be effective with adsorbents like ball-milled sugarcane bagasse [16], magnetic cellulose/Fe₃O₄/activated carbon composite [17], calcium chloride modified bentonite [18] and cattail root [19].

The present study deals with adsorption of congo red from its aqueous solution by polyvinyl esters. The effect of factors such as contact time, initial dye concentration, pH, adsorption kinetics and isotherm are discussed in detail.

2. Materials and Methods

2.1 Materials.

Congo red (E-merck), polyvinyl alcohol (E-merck), palmitic acid (E-merck), sulphuric acid (4N), sodium hydroxide (sd fine chemicals), and HCl (qualigens), all of AR grade and double distilled water, have been used in this work.

2.1.1 Methods

(a) Preparation of adsorbents

Polyvinyl esters which have been used as adsorbents were prepared by esterification of polyvinyl alcohol and palmitic acid. Known quantities in the ratio of 1:1 (PVP1), 10:1 (PVP2), 20:1 (PVP3), 1:10 (PVP4), 1:20 (PVP5) of polyvinyl alcohol and palmitic acid respectively were mixed with 5mL of 4N sulphuric acid and 95mL of water and then it is refluxed for 8 hr at room temperature. The resultant solid substance was taken out from the reaction vessel and then it was purified with ether by ether extraction. The dried sample was used as adsorbent.

2.1.2. Adsorption experiment

The quantity of adsorption of the dye has been measured as follows. A known amount of the aqueous solution of the dye was made to be in contact with the adsorbent for a specific time interval to attain equilibrium and then the absorbance of the supernatant liquid was measured at 497nm. The amount of dye adsorbed could be calculated using the calibration curve and noting down the difference in concentration of the dye

before and after adsorption. In a typical experiment, a predetermined quantity of congo red solution (20 mg/L, pH=4) was added to different amount, say 20,40,60mg of the polyvinyl ester was taken in a 100mL beaker. The contents were stirred continuously for about 2h at room temperature. The loaded adsorbent was then separated by centrifugation and washed gently with distilled water. Afterwards, the congo red concentration of the supernatant liquid was measured at 497 nm using spectrophotometer. Calibration curves were drawn for absorbance and concentration of standard dye solution. The amount of dye adsorbed on the polyvinyl esters were evaluated using the well known relationship,

$q_t = (C_i - C_t)V/m$, where q_t = Amount of dye adsorbed onto the adsorbent at any time, t (mg/g);

C_i = initial dye concentration; C_t = concentration of dye solution at any time (mg/L);

V = volume of dye solution; m = mass of adsorbent (mg);

3. Results and discussion

3.1 Characterization of adsorbent

3.1.1. TGA Analysis of polyvinyl palmitate

The thermal stability of polyvinyl palmitates prepared through esterification were analyzed and the TGA curves of the polyvinyl palmitate were recorded from 0°C to 1000°C.

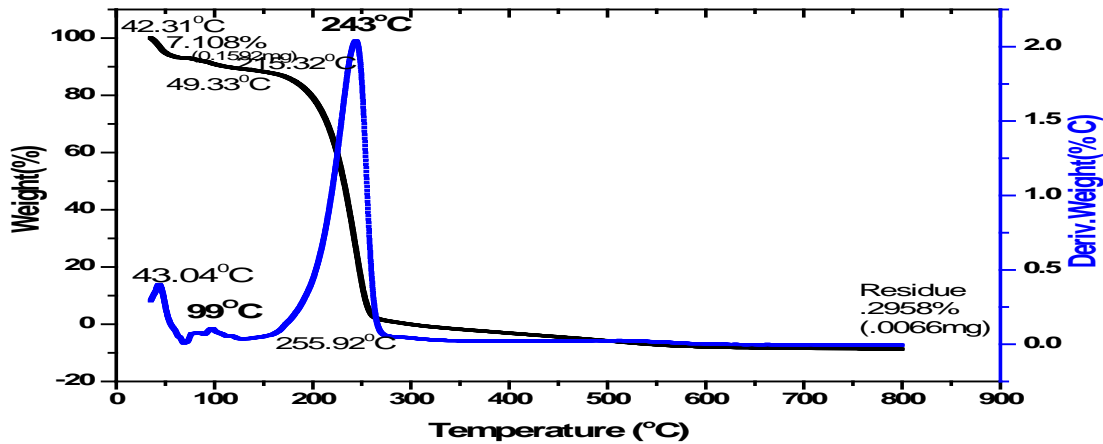


Figure 1. TGA curve for PVP 1

The thermogram of PVP1 is given in fig.1. From this figure it could be seen that an enhanced thermal stability is observed upto 244⁰C accounting to 2.039% weight loss . A prominent weight loss was observed from 98.75⁰C-244.80⁰C due to excessive burn of PVP constituent. Similar thermograms have been observed for the other PVP adsorbents also and their salient parameters are listed below.

In PVP2, an enhanced thermal stability is observed upto 526.67⁰C which accounts for 0.8048% weight loss. A prominent weight loss was observed from 39.84⁰C which accounts for 0 .3036% weight loss. During the second (230.06⁰C), third(361.68⁰C) and fourth at(464.46⁰C) 0.2543%, 0 .1138% and 0.1986% weight loss were found.

In PVP 3, two steps of transitions were found corresponding to 0.4610% weight loss (210⁰C)and 0.5917% weight loss (449⁰C) respectively.

In PVP 4, three step transition were found. At 136.39⁰C, 0.07%, at 368⁰C, 0.2988% and at 440.53⁰C, 0.6068% weight losses were found.

In PVP5 , two transitions corresponding to 0.7989% weight loss (339⁰C) and 0.5867% weight losses (434⁰C) were found.

The differential plots of these weight loss patterns of corresponding materials show no significant weight loss below 100⁰C . For these samples the weight loss starts at a higher temperature , which suggests that these samples are thermally stable, at the temperature at which they are used as adsorbents.

Comparing the TGA curves for all the five samples it was observed that above 450⁰C less decomposition is observed for PVP4; hence this material possesses good thermal stability. Besides the initial weight loss was also low when compared to other samples.

In PVP5 the initial weight loss is low but above 361⁰C thiscontinuous weight loss was progressive. Hence from the observations it is clear that the material PVP4 is good and hence it is chosen for further studies.

3.1.3 IR characterization for polyvinyl ester

The FTIR spectrum of the PVP 1 is shown in fig.2 . The intense broad band at 3367 cm^{-1} is due to stretching vibration of free-OH group. The appearance of intense peak between $1180\text{-}1290\text{ cm}^{-1}$ is for the -C-O-C- stretching vibrations characteristic of esters, which confirms the ester

formation. The peaks at 2847 cm^{-1} and 2910 cm^{-1} are due to symmetric and asymmetric stretching vibrations of -CH_2 groups. The corresponding bending vibrations are at 145 cm^{-1} and 1375 cm^{-1} . The stretching vibrations of the carboxyl function of ester occurred at 1695 cm^{-1} . Similar spectral data have been found for other adsorbents also.

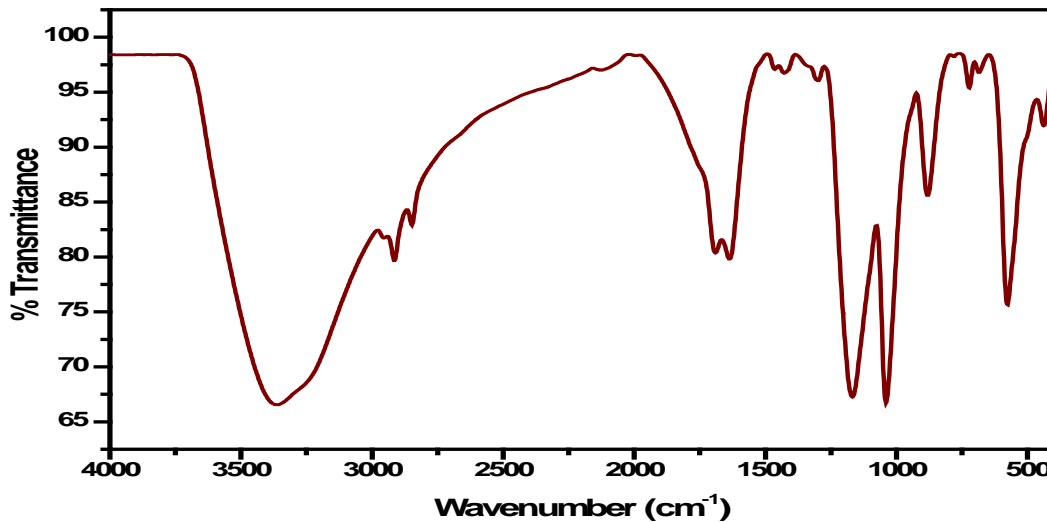


Figure 2. FTIR spectra for PVP 1

3.1.4 SEM image

The adsorbents were characterized by recording the SEM image of the adsorbents. The images were also recorded for all the adsorbents after the dye adsorption. As an example, the SEM image of sample PVP (1) is shown in fig.3. It displays amorphous morphology with aggregates of smaller pores. This morphology facilitates the adsorption of simple

organic molecules. The SEM image of this sample recorded after adsorption of the dye (fig.4.) displayed sponge like morphology with the size of the pores enlarged. Each sponge has appeared to have agglomeration of several tiny sponges. Distribution of sponge-like enlarged throughout the surface pores was also evident point to the strong adsorption of the dye.

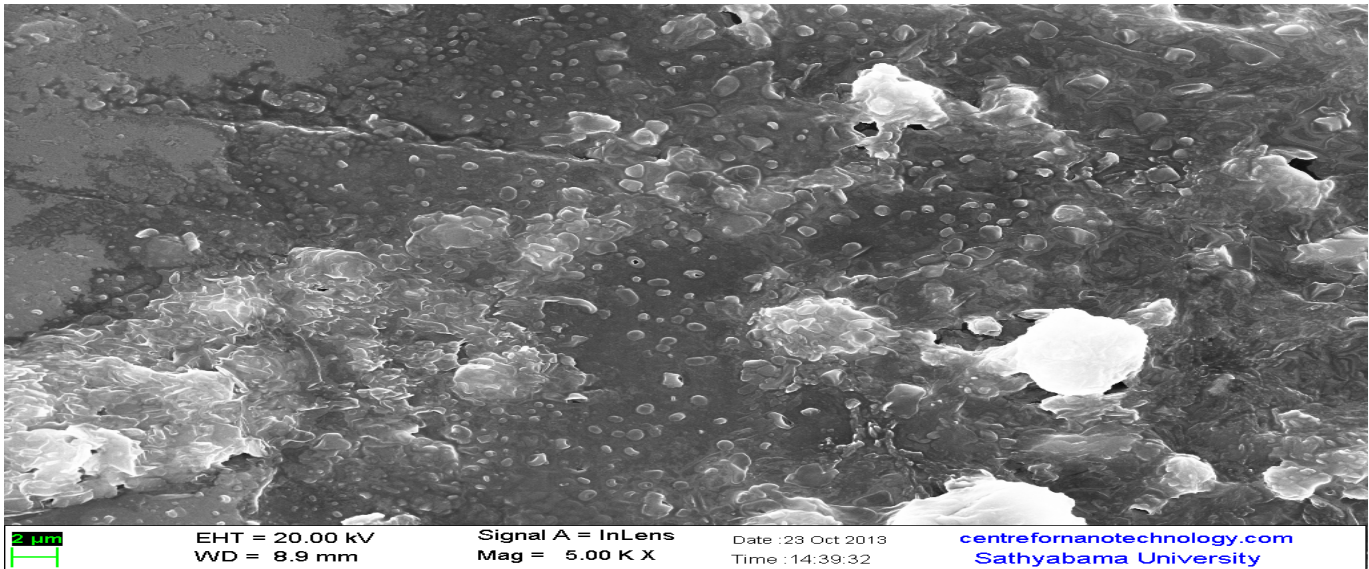


Figure 3. SEM image of PVP 1

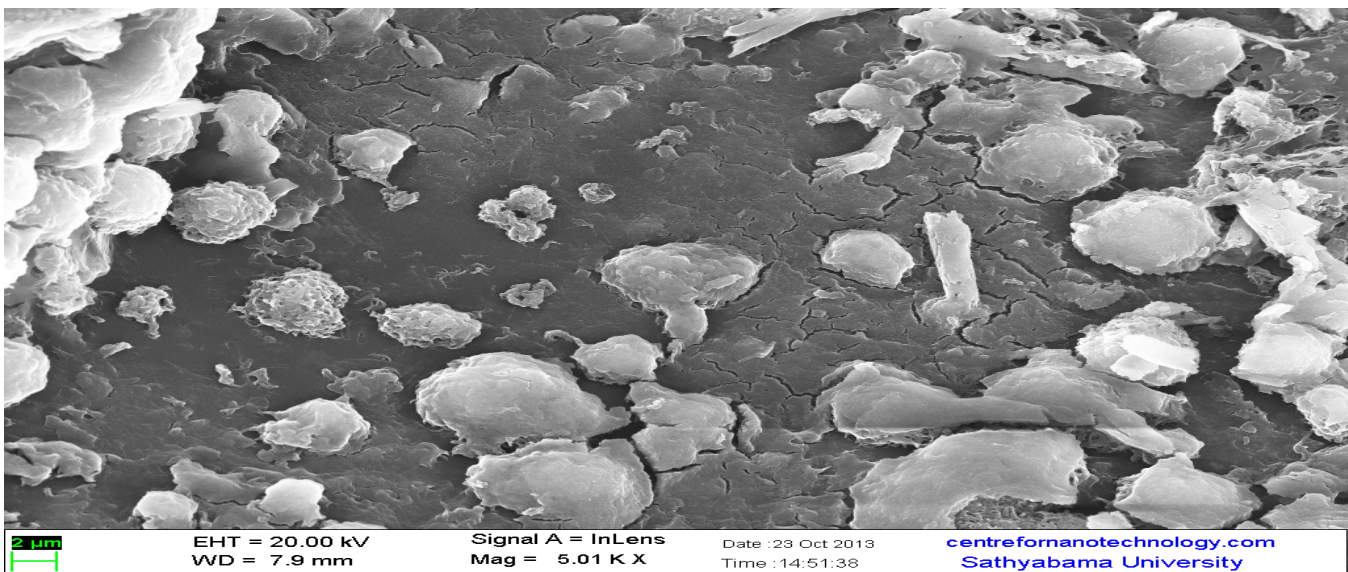


Figure 4. SEM image of PVP 1 after adsorption

3.2 Effect of pH

The uptake of congo red as a function of pH was examined over a pH range of 2-10. An aqueous congo red solution (20mg/L), adjusted to the required pH range of 2-10 with appropriate buffer solution was allowed to stand on 2g of the adsorbent for 2h. Then the absorbance of the supernatant dye solution was measured at 497nm.

From the difference in absorbance values measured before and after adsorption, the quantity of the dye adsorbed (q) was calculated as $q_t = (C_i - C_v)/C_i$ and these values are given in table.1. The quantity of adsorption (q) Vs pH profile (fig.5.) is sigmoidal with its maximum at pH=4. It is interesting to note here that an enhanced adsorption of congo red dye has been reported [20] to be at pH 4, on carbon nano tubes impregnated with chitosan derivatives.

Table :1 The quantity of adsorption (q) of congored by PVP’s at different pH.

pH	PVP (1)	PVP (2)	PVP (3)	PVP (4)	PVP (5)
2	2.2	2	1.9	2.1	2.3
3	3.9	3.1	2.3	2.4	3.1
4	6.5	5.9	6	6.8	6.7
6	5.5	5	5.8	5.9	5.8
8	4.2	4	4	3.9	3.7
10	3.4	2.1	3.9	2.1	2.4

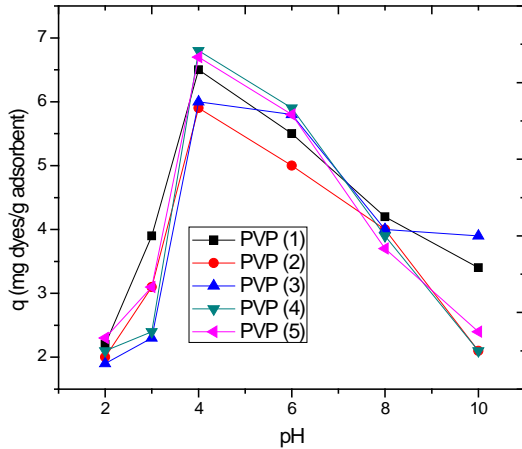


Figure 5. pH dependence of CR adsorbed by PVP 1

3.3 Effect of contact time

The amount of dye adsorbed onto each of the adsorbents (PVP’s) has been measured at different intervals of contact time at pH = 4 and the data are represented in fig.6-10. For all the adsorbents, the quantity of dye adsorbed increased with contact time and reached saturation between 90 and 120 minutes. The profiles are also simple and continuous indicating a monolayer coverage on the adsorbent surface. It is also seen that the higher the initial concentration of the dye, the faster the saturation is reached. However, the reduced quantity of adsorption at higher concentration of adsorbate, more obvious with PVP1 and PVP5 suggests the existence of an equilibrium between the adsorbed and the free dye.

3.4. Adsorption kinetics

The kinetics of adsorption was followed by measuring the absorbance of the dye at 497nm at

different time intervals. Batch mode adsorption studies were carried out using three different initial concentrations of 20, 40 and 60mg/L at pH 4 and at 30⁰C. The samples were removed at different time intervals and centrifuged for 5 minutes. The data fitted very well into the second order kinetic model with R²= 0.99 (fig 11-15) expressed as,

$t/q_t = 1/K_2q_e^2 + t/q_e$ where q_e and k_2 are the adsorbed quantity of dye at equilibrium and the equilibrium constant respectively. The derived values for K_2 and q_e for these systems are collected in table 2. The equilibrium constant increases with increase in quantity of adsorbent. However, the quantity of adsorbate adsorbed at equilibrium (q_e) ranges from 44 to 68% with a general trend exhibiting decrease with increasing amount of adsorbents.

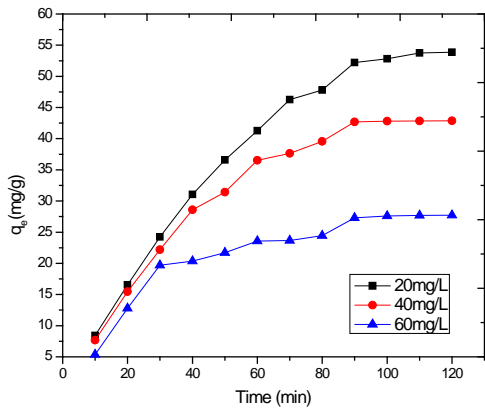


Figure 6. Effect of [dye] on adsorption time for CR at pH = 4 for PVP 1.

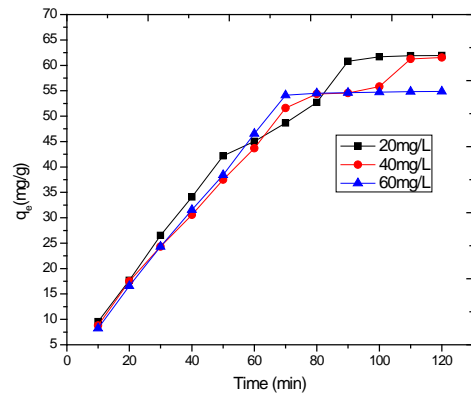


Figure 7. Effect of initial [dye] on adsorption time for CR at pH = 4 for PVP 2

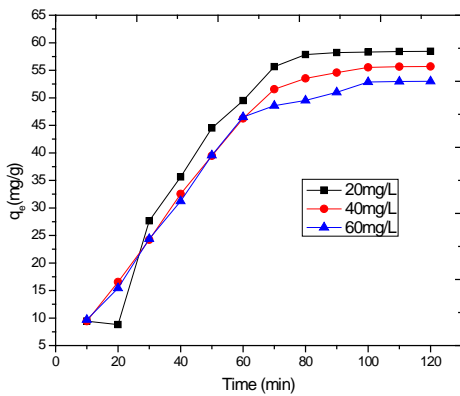


Figure 8. Effect of initial [dye] on adsorption time for CR at pH = 4 for PVP 3.

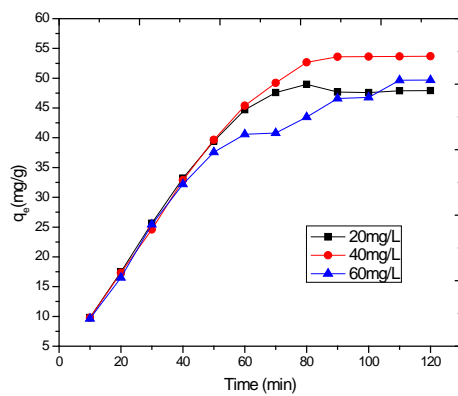


Figure 9. Effect of initial [dye] on adsorption time for CR at pH = 4 for PVP 4.

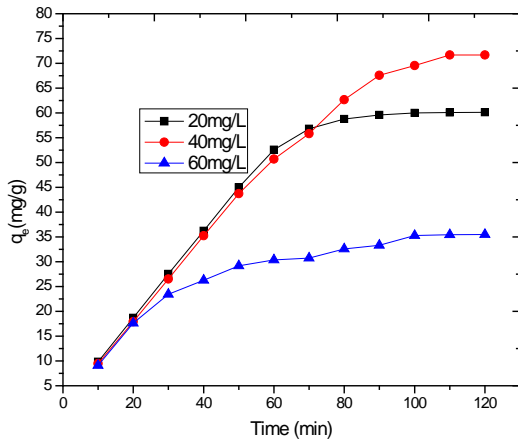


Figure 10. Effect of initial [dye] on adsorption time for CR at pH = 4 for PVP 5

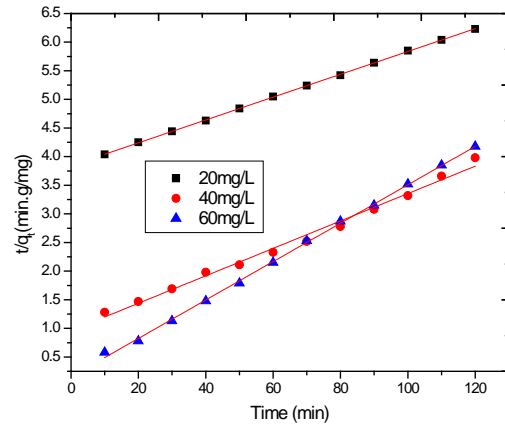


Figure 11. The second order plot for adsorption of CR at pH=4 for PVP (1)

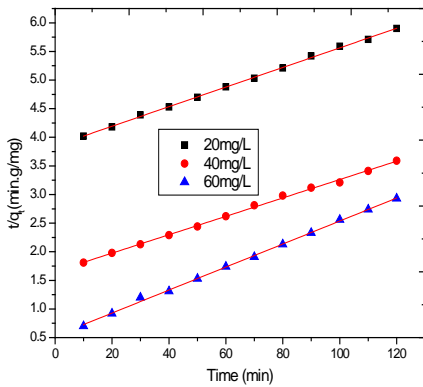


Figure 12. The second order plot for adsorption of CR at pH=4 for PVP (2)

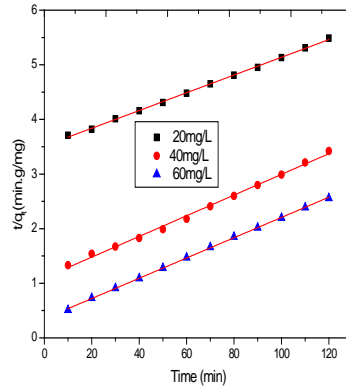


Figure 13. The second order plot for adsorption of CR at pH=4 for PVP (3)

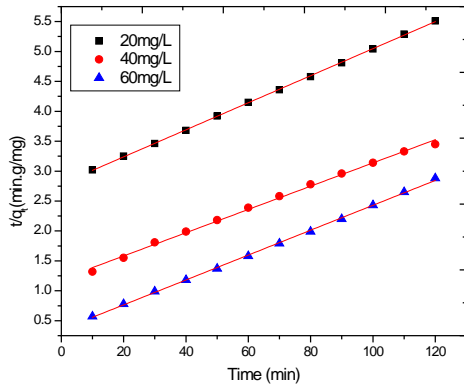


Figure 14. Thesecond order plot for adsorption of CR at pH=4 for PVP (4)

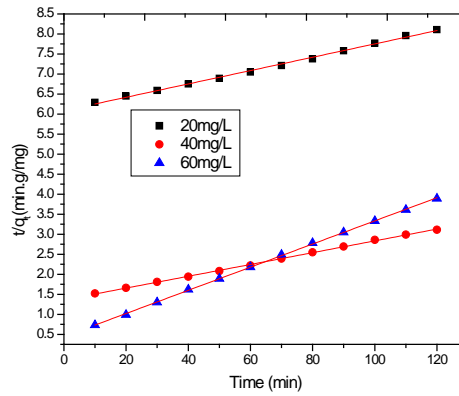


Figure 15. The second order plot for adsorption of CR at pH=4 for PVP (5)

Table : 2 K_2 and q_e values for different PVP's

Adsorbent	K_2			q_e		
	20 mg/L	40 mg/L	60 mg/L	20 mg/L	40 mg/L	60 mg/L
PVP (1)	0.0001	0.00059	0.0073	50.12	41.73	29.81
PVP (2)	0.000075	0.00015	0.00076	58.47	49.75	62.22
PVP (3)	0.000075	0.00072	0.00098	61.57	54.05	52.79
PVP (4)	0.00018	0.00016	0.00124	44.24	41.44	40.07
PVP (5)	0.000045	0.00015	0.00188	67.88	60.02	34.79

3.5. Intra particle diffusion model

The kinetic data of the adsorption process can be analysed by fitting the data to various models [21]. The intraparticle diffusion model is the one that fits the data in the present work. According to this model, adsorption of the dye from aqueous solution by polyvinyl palmitate would consist of three consecutive steps.

- (i) transport of the adsorbate from bulk solution to the outer surface of the

adsorbent molecule, known as external or film diffusion.

- (ii) internal diffusion i.e the transport of adsorbate from the particle surface into interior sites.
- (iii) the adsorption of the the solute molecules from the active site into interior surface of the pores.

The overall rate of the adsorption process will be controlled by the slowest, i.e. the rate- limiting step. The nature of the rate-limiting step in the adsorption

system can be determined by the properties of the adsorbate and adsorbent.

Since the particles are vigorously agitated during the adsorption period, it is probably reasonable to assume that mass transfer from the bulk liquid to the particle external surface does not limit the rate. One might postulate that the rate-limiting step may be either film or intraparticle diffusion. As they act in series, the slower of the two will be the rate determining step. According to this model, the

quantity adsorption is proportional to the square root of the time.

$$q_t = k_p t^{1/2} \quad \text{or} \quad \log q_t = \log k_p + 0.5 \log t$$

where k_p is the intraparticle diffusion rate constant.

The adsorption rates for intraparticle diffusion, under different conditions were calculated from the slopes of the linear portions of the respective plots (figures 16 – 20). The linear portions are the result of intraparticle diffusion effects.

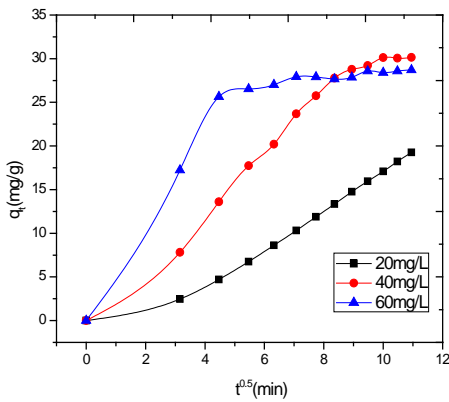


Figure 16. Concentration of dye adsorbed Vs time for PVP1

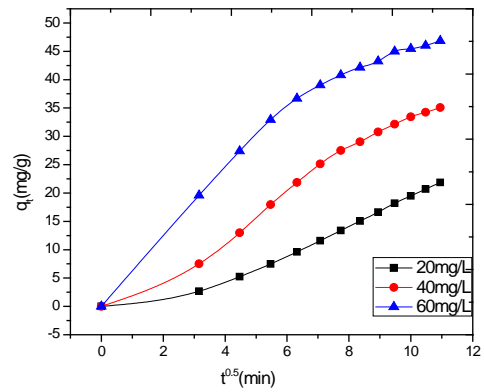


Figure 17. Concentration of dye adsorbed vs Time for PVP2

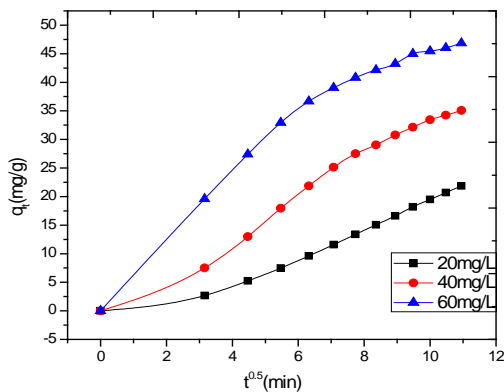


Figure 18. Concentration of dye adsorbed Vs time for PVP3

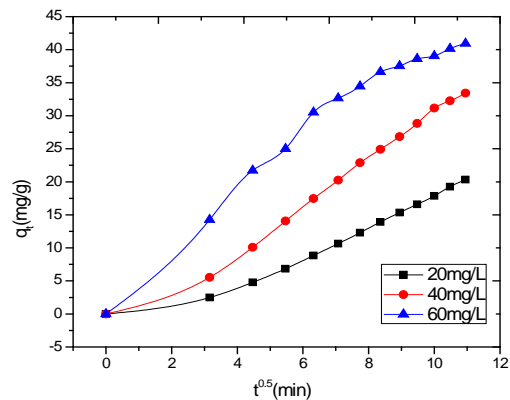


Figure 19. Concentration of dye adsorbed Vs time for PVP4

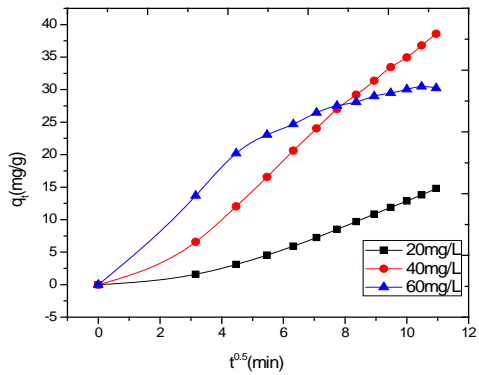


Figure 11. Concentration of dye adsorbed Vs time profile for PVP5

3.6. Adsorption isotherm

Langmuir adsorption isotherm

The Langmuir adsorption isotherm is based on the assumption that the monolayer adsorption onto a surface contains a finite number of adsorption sites, of uniform energies of adsorption, with no mutual interaction between the adsorbed molecules. The study of Langmuir isotherms is essential in assessing the adsorption efficiency of the adsorbent. This study is also useful in optimizing the operating conditions for effective adsorption. In this respect, the Langmuir isotherm is important, though the restrictions and the limitations of this model have been well-recognized.

The Langmuir isotherm is given as $C_e/Q_e = C_e/Q_0 + 1/Q_0b$, Where,

C_e is the concentration of congo red (mg/L), Q_e is the amount of dye remove at equilibrium (mg/g), Q_0 is the monolayer capacity of the adsorbent(mg/g), and b is the Langmuir adsorption constant(L/mg).

Thus a plot of C_e/Q_e Vs C_e should yield a straight line having a slope of $1/Q_0$ and an intercept $1/Q_0b$.

The experimental data were treated in accordance with this model and it was observed that the relationship between C_e/Q_e and C_e was linear (fig. 21-25), indicating that the adsorption behaviour followed Langmuir adsorption isotherm. The Q_0 and b values are given for all the adsorbents in Table.3. The correlation co-efficient was found to be 0.99.

Table :3 Langmuir constants for polyvinyl palmitate adsorbents

Adsorbent	Q_0 (mg/g)			b (L/mg)		
	20 mg/L	40 mg/L	60 mg/L	20 mg/L	40 mg/L	60 mg/L
PVP (1)	62.50	52.63	31.25	0.112	0.0900	0.0100
PVP (2)	71.42	70.42	62.52	0.1609	0.1468	0.1044
PVP (3)	62.50	61.50	56.50	0.333	0.1739	0.1524
PVP (4)	57.80	52.35	51.28	0.2963	0.2447	0.1889

PVP (5)	82.64	62.50	36.90	0.5353	0.2145	0.1687
---------	-------	-------	-------	--------	--------	--------

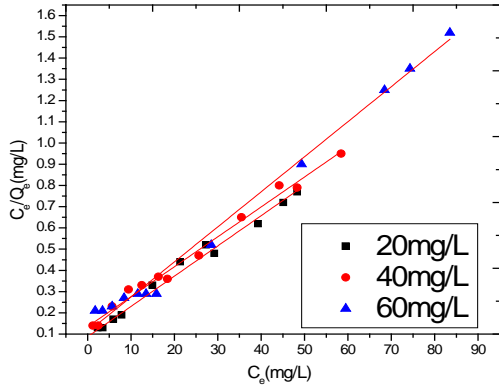


Figure 21 .Langmuir plot for adsorption of CR by PVP1

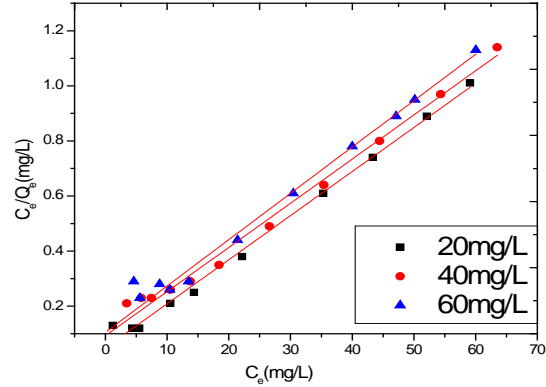


Figure 22. Langmuir plot for adsorption of CR by PVP2

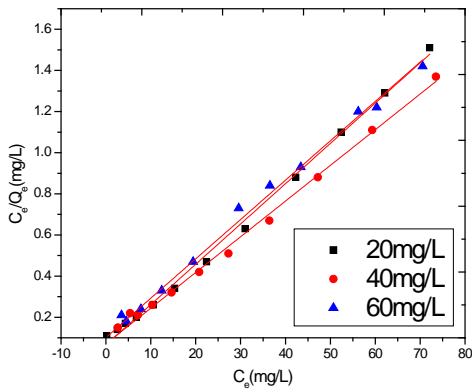


Figure 23.Langmuir plot for adsorption of CR for PVP3

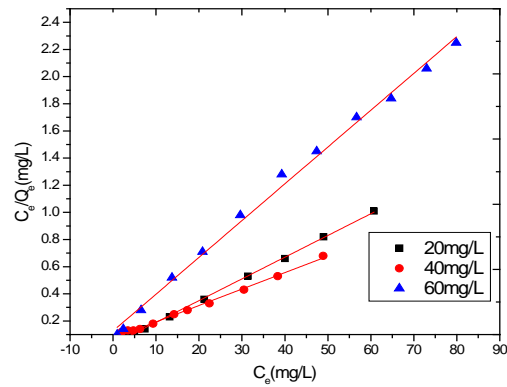


Figure24. Langmuir plot for adsorption of CR for PVP4

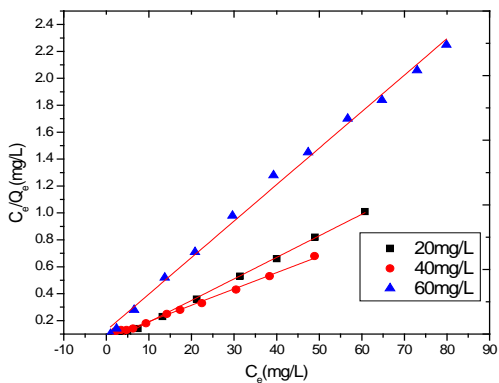


Figure 25. Langmuir plot for adsorption of Congo red for PVP5

3.8. Desorption of CR

It is used to elucidate the mechanism of adsorption [21]. If the desorption is done with water it is concluded that attachment of dye on the adsorbent is by very weak bonds. If the desorption is done with strong acids and bases from which it is assumed that the process is done by ion exchange. If the desorption is done with acids like CH₃COOH it is assumed that adsorption is chemisorption. Adsorbent loaded with the dye was stirred with 20mL of various alkalies, HCl(0.1M) and acetic acid (V/V) for 30 minutes, sequentially. From which it is seen that a very low desorption occurs for various

alkalies. It is concluded that chemisorptions might have taken place between active sites of adsorbent and functional groups of CR. Among HCl and acetic acid most of the desorption occurred with acetic acid which confirms that adsorption of CR on the adsorbent follows significantly the chemisorption mechanism.

$$\text{Desorption(\%)} = \frac{\text{Amount of CR desorbed(mg)}}{\text{Amount of CR adsorbed by the adsorbent(mg)}} \times 100$$

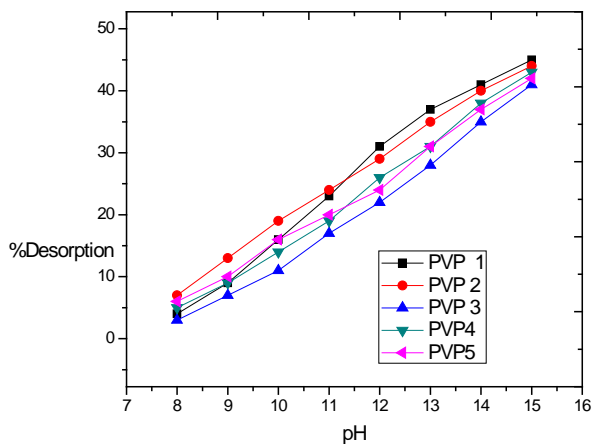


Figure 26. Effect of pH on colour removal for PVP adsorbents at different pHs

CONCLUSION

Polyvinylpalmitate esters can be used as adsorbents for an anionic dye (CR). The following conclusions were made. A treatment time of 120 min was sufficient to attain the equilibrium value. A Langmuir type of adsorption was observed. pH was the most important parameter, and pH 4.0 was

found to be the optimum value in this process. It was recognized that polyvinyl palmitate esters could be used as adsorbents for CR dye from an aqueous medium.

REFERENCES

1 .C.Namasivayam, N.Muniasamy, K.Gayatri, M. Rani, and K.Ranganathan, Bioresource technology 57(1996)37.

2. M.Dogan and M.Alkan, *Chemosphere* 50 (2003)517
3. P.Nigam,G.Armour,I.M.Banat,D.Singh and R.Marchant, *Bioresource technology* 72(2000)219
4. Y.S.Ho and G.Mckay, *Chem..Eng .J.* 70(1998)115
5. Muhammedsaifurrehman, Gookkim and Jong in Han, *carbohydrate polymers*,90(3), 15(2012), 1314.
6. C.Namasivayam, and D.J.S.E.Arasi, *Chemosphere*,34(2) (1997),.401.
7. S.B.Wangand E.Ariyanto, *J.colloid interface*,314(1)(2007),pp.25-31.
8. Qian Li, Qin-yanyue, Yuan su, Bao-Yu gao and Hong-jian sun, *Chemical Eng. J.* 158(3),(2010), 489.
9. B.Zohra,K.Aicha,S.Fatima, and B. *Chem..Eng.J.* 136(2008) 295
- 10 .E.Eren and B.Afsin, *Dyes and pigments*,72(2)(2007),PP.228-232.
- 11 .Zhengyongzhang, Zebiaozhang and Y.Fernandez, *Applied surface science*,256,(2010),2569
12. Elifyilmazozman, Mehmet Sezgin, Aydanyilmaz, and Mustafa yilmaz, *Bioresource technology*,99(3), (2008), 526.
13. Yuyiyang,Guanwang, and Bingwang, *Bio resource Technology*,102(2) (2011),828.
- 14 .Li wang and Aiqinwang, *Bio resource technology*,99(5),(2008), 1403.
15. MuhammedSaifurRahman, II gook kim,Jong in han, *carbohydrate polymers*,90(3), 15 oct2012, 1314
- 16 .Zhanyingzhang, Lalehvashmoghadam, IanM.oHara, Williamo.s.Doherty, *Chemical engineering journal*, 178 (15)(2011),122.
- 17.H.Y.zhu,Y.Q.Fu,R.Jiang, J.H. Jiang, L.Xiab, G.M. Zeng,S.L. Zhao, Y.Wang *Chemical engineering journal*,173(2), 15 (2011), 494.
18. S.P. Nandi, P.L. Walker Jr,*Fuel* Vol.50(4) oct 1971,pages 345-366.
- 19.Zhenhuhu,huichen, FengJi, Shoujan Yuan, *Journal of hazardous materials*, Vol.173,Issues 1-3, (2010) 292.
20. Bhatnagar, A and Sillanpaa, M (2009), *Adv. Colloid interface sci.*, 152: 26-38 .
21. Arslan, M.; Yigitoglu, M.; wiley Periodicals, inc. *J Appl. Polym. Sci* 107: 2846-2853, 2008.