Removal of Direct Dyes from Aqueous Solution Using Passion Fruit Peel as Low Cost Adsorbent

Suma Bino Thomas and Harsha Chalil

Abstract--- The present study explores the effectiveness of yellow passion fruit (Passifloraedulis) peel a surplus low value waste, in removing hazardous cationic dyes like malachite green and crystal violet and anionic dye eosin yellow from aqueous solution. The influence of contact time, adsorbent dosage and metal concentration on the removal process were investigated. Batch studies indicated that maximumsorption capacity was for Eosin yellow (94%) whereas the % removal was 75% and 70% for Malachite green and crystal violet respectively.The sorption process followed the pseudo second order rate kinetics. A good fitting of metal sorption equilibrium data is obtained with Freundlich model in all the range of metal concentrations studied. The findings showed that passion fruit peel powder can easily beenvisaged as a new, vibrant, low cost adsorbent for dye clean up operations.

Keywords--- Passion Fruit Peel, Low Cost Adsorbents, Dyes, Malachite Green, Crystal Violet, Eosin Yellow

I. INTRODUCTION

Environmental pollution due to industrial effluents is of major concern because of their toxicity and threat for human life and the environment [1]. The discharge of textile effluents to the water bodies has raised much concern because of potential health hazards associated with the entry of toxic components in to the food chains of humans and animals. Textile industry is one of the prominent polluters releasing high concentrated effluent in to the surrounding environment [2]. Dyes contain carcinogenic materials. Therefore there is a need to remove dyes before effluent is discharged in to receiving water bodies. The most popular treatment methods for textile waste water are combinations of biological treatment, chemical coagulation and activated carbon adsorption [3].

Decolorizations of dyes are important aspects of waste water treatment before discharge. It is difficult to remove the dyes from the effluent, because dyes are not easily degradable and are generally not removed from waste water by conventional waste water systems [4]. Generally biological aerobic waste water systems are not successful for decolorisation of majority of dyes. Therefore, color removal was extensively studied with physico-chemical methods as coagulation, ultra-filtration, electro-chemical adsorption and photo-oxidation. Among these methods, adsorption is a widely used for dye removal from waste waters. Granulated activated carbon (GAC) or powdered activated carbon (PAC) is commonly used for dye removal [5]. Since activated carbon is relatively expensive, the emphasis has shifted towards low cost adsorbents that can serve as viable alternative for activated carbon [6]. The high cost of activated carbon, calls for regeneration for prolonged use, which again adds to the cost of the treatment process [7]. The advantage of using low cost adsorbent is that, they can be used in a treatment process and the disposed off, without any associated costs of regeneration.The use of low-cost, locally available and eco-friendly adsorbents has been investigated as an ideal alternative to the current expensive methods of removing dyes from waste water[8].

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In the present study, removal of certain water soluble dyes namely crystal violet, malachite green and eosin yellow from aqueous solution using yellow passion fruit peel as a low cost adsorbent was investigated[9]. The effect of contact time, adsorbent dosage and concentration on adsorption, the applicability of Freundlich and Langmuir adsorption isotherms [10] and the kinetic model of adsorption were also studied [11].

II. Materials and Methods

A. Adsorbent

Yellow passion fruit peel were collected, washed with distilled water and dried in the sun. Then it was grounded and sieved to 150-500µm particle size. It was then dried in an oven to remove moisture and stored in a closed bottle for later use in adsorption studies. The adsorbent was characterized by IR spectroscopy and SEM.

B. Adsorbate

Commercial quality direct dyes(Crystal violet, Malachite green and Eosin yellow) were obtained from Nice chemicals, Kerala and Qualigens fine chemicals, Mumbai and used without any further purification. A standard solution of direct dyes was prepared in distilled water.

C. Batch Experiments

Adsorption experiments were conducted in which aliquots of dye solution with known concentrations were introduced into iodine flasks(250 cm^3) containing accurately weighed amounts of the absorbent. The bottles were shaken at room temperature using a shaker for a prescribed length of time to obtain equilibrium. The adsorbent was then removed by filtration. The equilibrium concentrations of dyes were determined by a photocolorimeter at the wavelength for maximum absorbance which are 595, 515-518, and 621 nm for crystal violet, eosin yellow and malachite green respectively. The effect of adsorbent dosage was studied with different dose of adsorbent of 150 – 500 µm average particle size.

The effect of agitation time was done by treating 0.5g of adsorbent with 50 ml samples of dyes (Crystal violet, Malachite green and Eosin yellow) of concentration 500 ppm in separate flasks at room temperature and was shaken well in an automatic shaker. The time period was varied. To study the effect of adsorbate concentration, the samples were treated with constant dose of adsorbent (0.5g) for one hour at room temperature. The concentrations of the adsorbate were varied. The isotherm studies were performed by varying initial metal concentration from 100 to 500mg/L after shaking the flask for 60min and the reaction mixture was analyzed for the residual metal concentration. Kinetics of adsorption studies were conducted by varying the contact time.

III. Results and Discussion

The passion fruit peel was characterized using IR spectroscopy and scanning electron microscopy. The IR spectrum of passion fruit peel shows peaks at 3319.21 and 2918.09 cm^{-1} which refers to (-OH) and identical alkyl group(-CH_2-) respectively. Also, the spectrum shows bands at 1736.71 and 1013.07 cm^{-1} were to be the presence of (C-O) and (-OH), respectively. The band at 3319.21cm^{-1} was attributed to the surface hydroxyl groups and chemisorbed water.

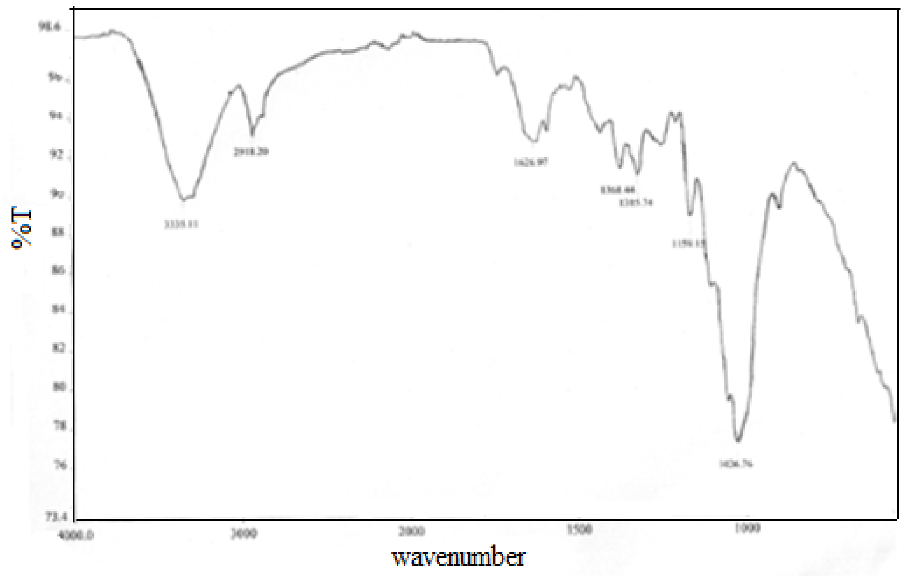

Fig. I: IR Spectrum of Passion Fruit Peel

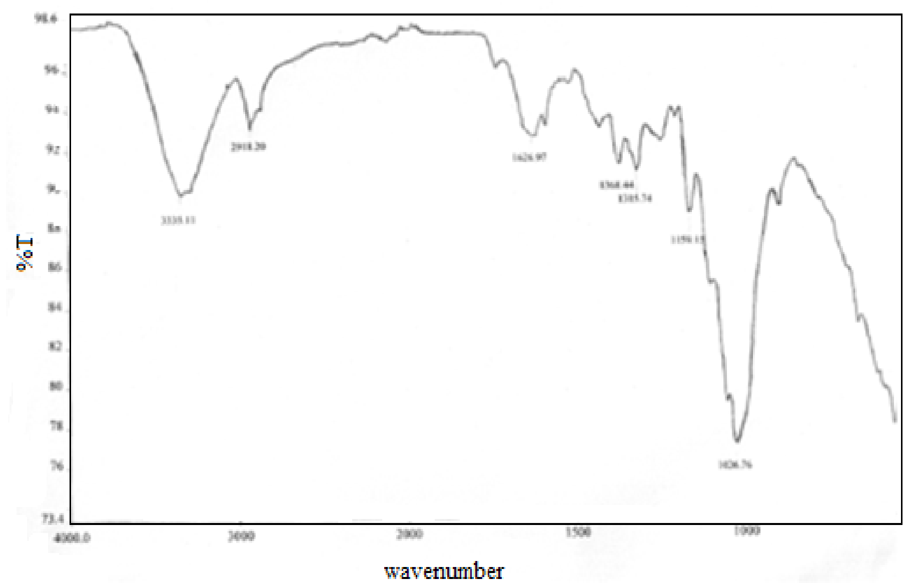

Fig. II: IR Spectrum of EY adsorbed onPF peel

An examination of the adsorbent before and after sorption reaction possibly provides information regarding the surface**.** Additional bands corresponding to the dyes appear in the region 1585-1626 cm^{-1} .It was found that the spectra of treated sorbents differ significantly from the spectrum of the ‘‘parent” (untreated) material, suggesting that the treatment procedures change the peel structure substantially.

The porous and irregular surface structure of the adsorbent can be clearly observed in SEM images shown in Figure.III. It clearly reveals the porous surface textures which endorse the adsorbent with increased surface area and high adsorption capacity. The heterogeneous pores and cavities provided a lager exposed surface area for the adsorption of dye molecules. On adsorption of the dyes, the porous structure disappears and surface becomes rough.

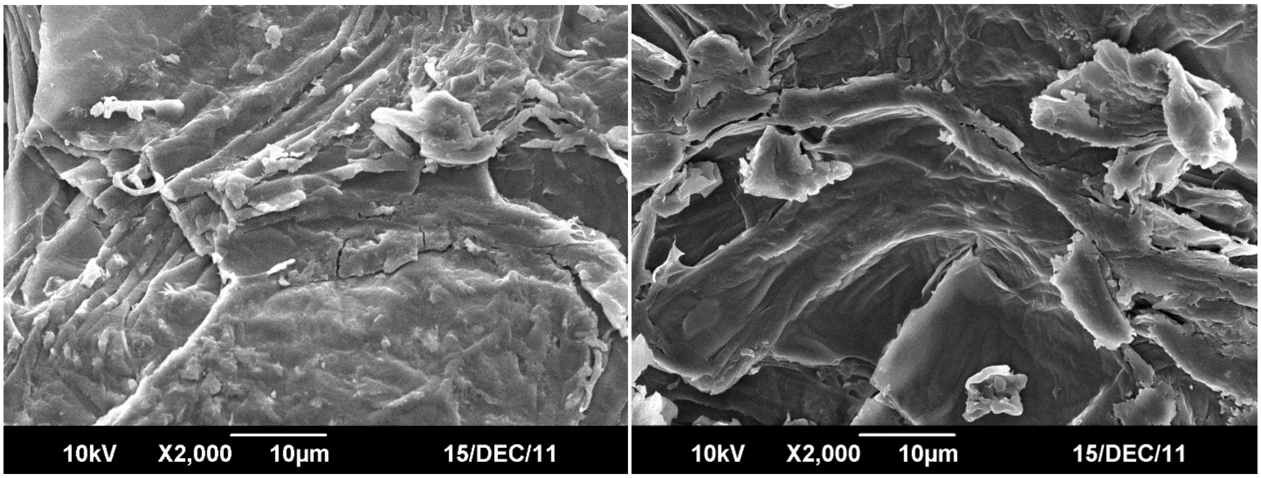

Fig. III: SEM Photograph of PF Peel Powder and Dye Adsorbed PF Peel Powder

A. *Effect of Adsobent Dosage*

The effect of adsorbent dose was investigated by varying the adsorbent dose from 50-500 mg by keeping other parameters constant.

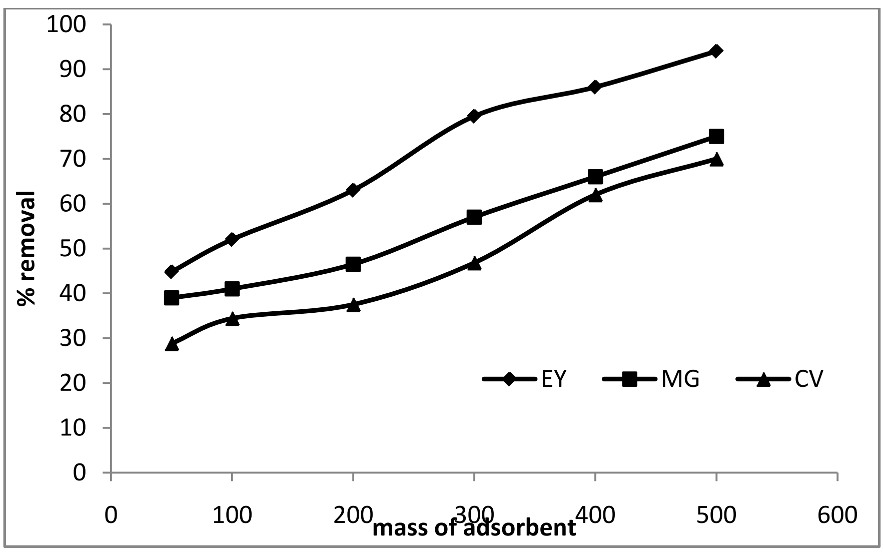

Fig. IV: Effect of Adsorbent Dose

The removal of dyes was found to be 44.5-94%, 39-75%, 28.5-70% in case of Eosin yellow, Malachite green, crystal violet (Fig IV.). The increase in removal of dyes with adsorbent dose is due to the introduction of more binding sites for adsorption. The percentage removal of Eosin yellow is higher than that of Malachite green and Crystal violet .The percentage removal of Malachite green lies between Eosin yellow and Crystal violet. The optimum adsorbent dose was found to be 400mg.

B. *Effect of Agitation Time*

The time dependent behavior of dye adsorption was examined by varying the contact time between adsorbate and adsorbent.

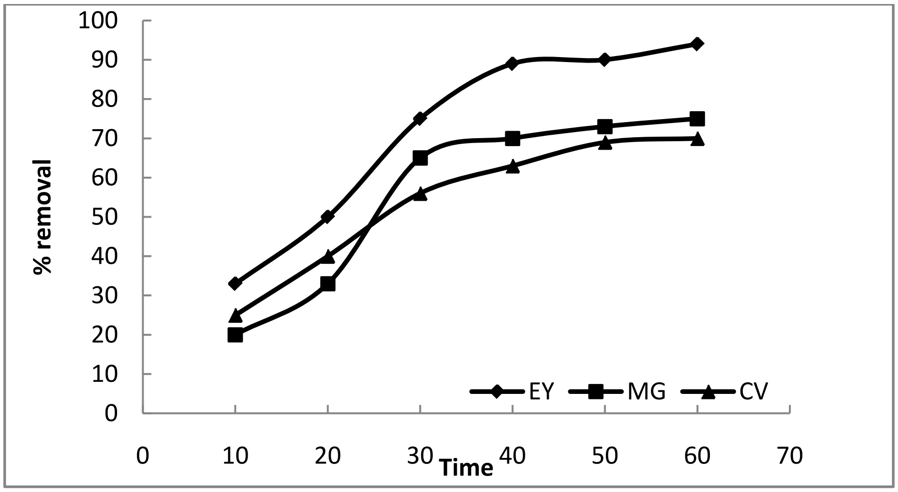

Fig. V: Effect of Time

Fig. V shows that the equilibrium between dyes and the adsorbent was attained within 40 minute. Therefore a 40 minute shaking time was found to be appropriate for maximum adsorption and was used in all subsequent experiment. The removal of direct dyes by adsorption increased with time and attained a maximum value in 40 min and there after it remained constant. The figure shows that the % removal of EY is higher than that of other two dyes (Crystal violet and malachite green).

C. Effect of Initial Concentration of Dyes

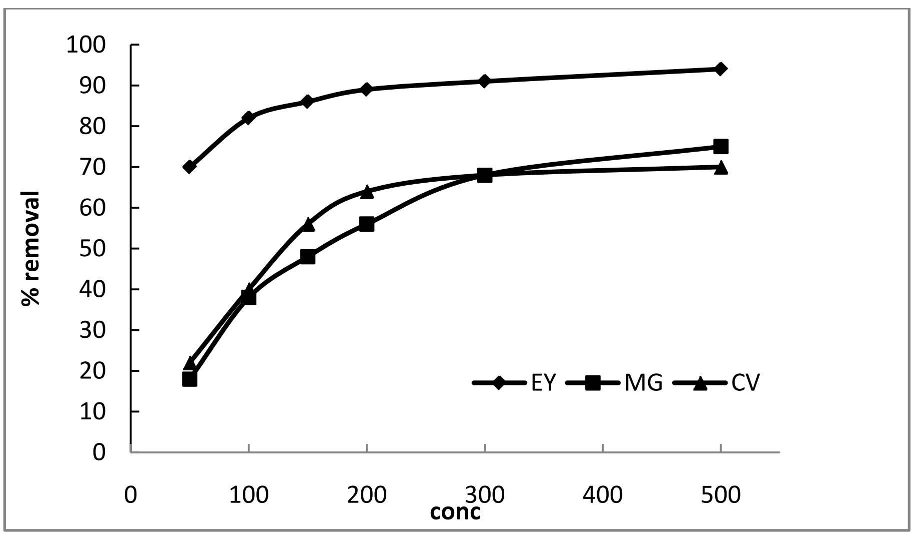

Fig.VI: Effect of Initial Concentration

The effect of concentrations of dyes has been also tested with constant dose of adsorbent at 60 min of shaking time. The removal of dyes increased from 70–94% for Eosin yellow, 18-75% for Malachite green and 22-70% for crystal violet. The plot reached a maximum value and remains constant. The adsorption attains equilibrium within the dye concentration of 300 ppm.

D. Equilibrium Study

Adsorption data are usually described by adsorption isotherms, such as Langmuir and Freundlich isotherms. These isotherms relate dye uptake per unit mass of adsorbent, q_e, to the equilibrium adsorbate concentration in the bulk fluid phase C_e.

The parameters obtained from the different isotherm models provide important information on the adsorption mechanisms and the surface properties and affinities of the adsorbent. According to the obtained data for the model parameters it is seen that Freundlich equilibrium model is favourable. Taking into consideration the values of the coefficient of correlation as criteria for goodness of fit, for most investigated systems the Freundlich equation gives a better correlation between the theoretical and experimental data for the whole concentration range when compared with Langmuir equations.

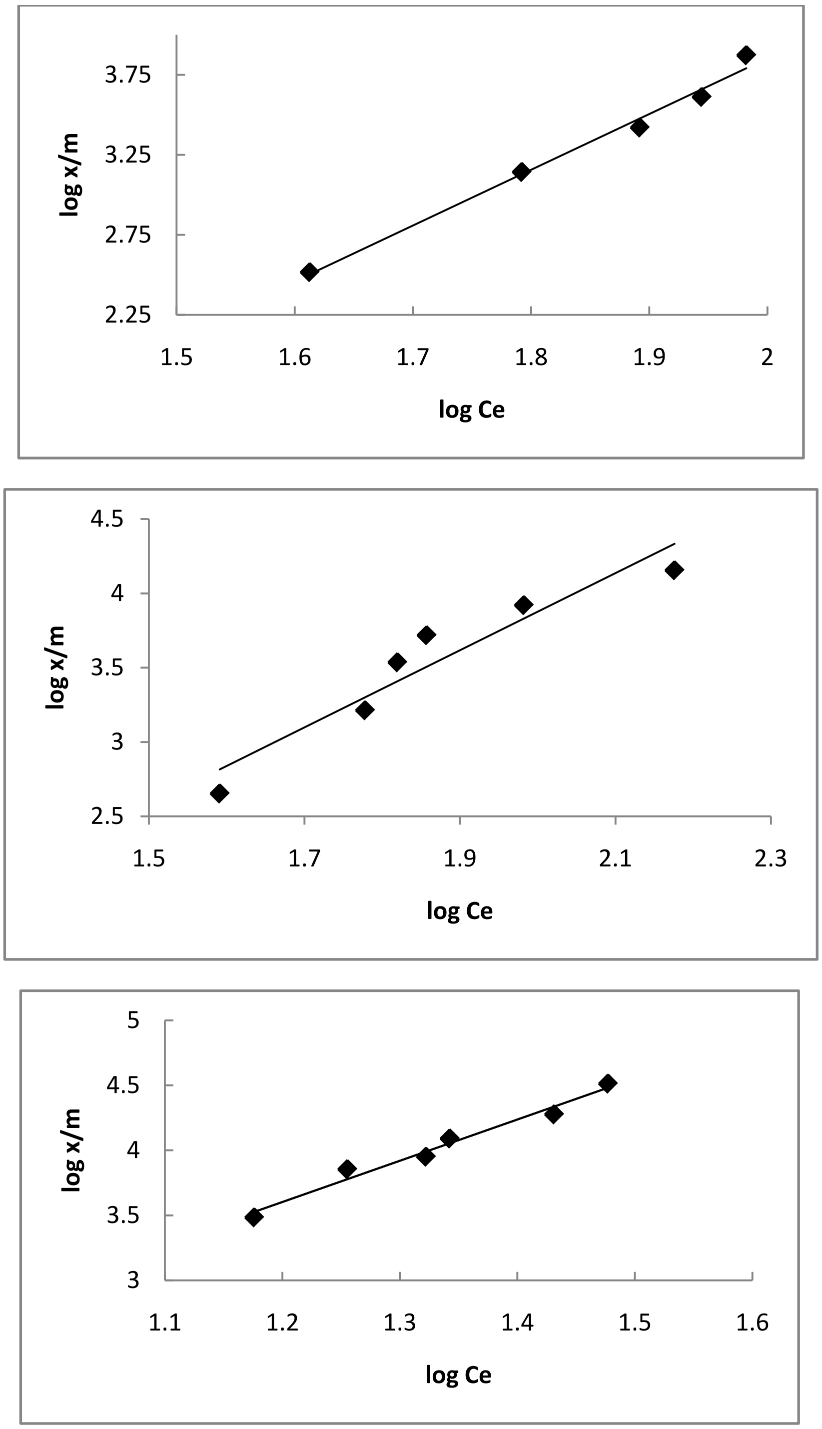

Fig. VII: a-c. Freundlich Isotherms for MG, CV and EY

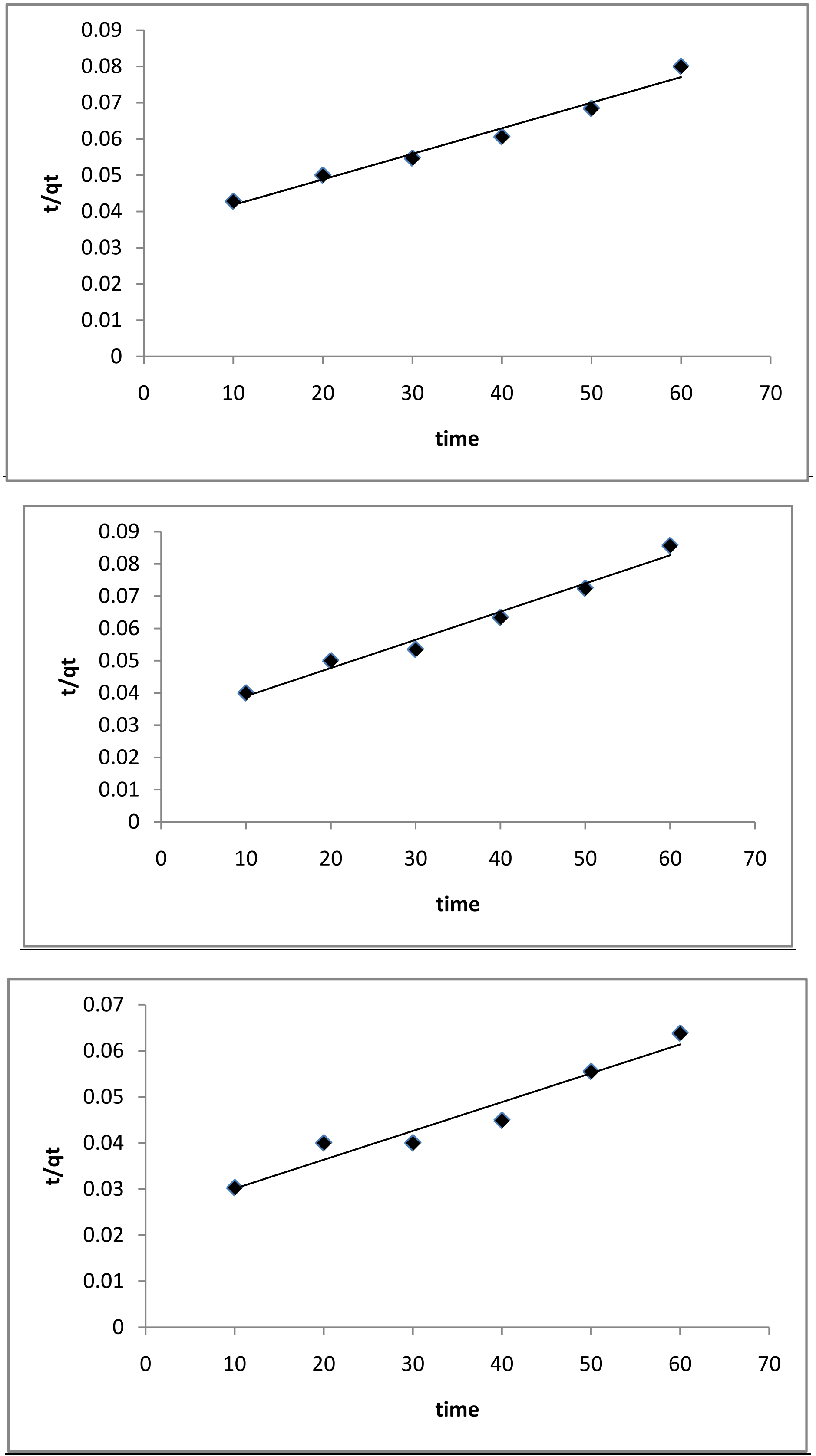

Fig. VIII: a-c. Pseudo-Second Order Kinetics of MG, CV and EY

Table 1: Kinetic Parameters for Freundlich Isotherm

Dyes	Statistical parameter constants			
	r	R^2	K	n
Malachite green	0.9942	0.9734	0.00335	0.3152
Crystal Violet	0.9522	0.9702	0.00152	0.2901
Eosin Yellow	0.9920	0.9763	0.6246	0.3175

E. Kinetic Study

In order to investigate the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, the pseudo-first-order and pseudo-second order equations are applied to model the kinetics of dye adsorption onto passion fruit peel powder. The pseudo-first-order rate equation is given as

$$\log (q_e - q_t) = \log q_e – (k_{ad}/2.303)t$$

whereq$_t$ and q_e are the amount adsorbed (mg/g) at time t, and at equilibrium respectively and k_{ad} is the rate constant of the pseudo-first-order adsorption process (min^{-1}). Straight line plots of log (q_e - q_t) against t were used to determine the rate constant, k_{ad}, and correlation coefficients, R^2, for different dye concentration. But it was seen that adsorption of dyes on passion fruit peel powder did not follow pseudo first-order kinetics compare with the correlation coefficient of pseudo second-order kinetics.

The pseudo-second-order equation is expressed as:

$$t/q_t = 1/h + (1/q_e)t$$

where $h = kq_e^2$ ($mg\ g^{-1}min^{-1}$) can be regarded as the initial adsorption rate as $t\rightarrow0$ and k is the rate constant of pseudo-second-order adsorption ($g\ mg^{-1}min^{-1}$).

Table 2: Pseudo-Second Order Parameters for Adsorption of Dyes

Dyes	Statistical parameter constants			
	r	R^2	q_e	K_{ad}
Malachite green	0.9884	0.9770	1428.57	28.82
Crystal Violet	0.9892	0.9784	1111.11	33.00
Eosin Yellow	0.9907	0.9823	1666.67	41.84

The plot t/qt versus t should give a straight line if pseudo-second-order kinetics is applicable and q_e, k and h can be determined from the slope and intercept of the plot, respectively. The plots of the linearized form of the pseudo second-order by passion fruit peel powder are shown in Fig. VIII a-c. The plot of t/q_t versus t for pseudo-second-order model yields very good straight lines (correlation coefficient, R^2> 0.97) as compared to the plot of pseudo-first order.

IV. CONCLUSION

The results of this investigation shows that passion fruit peel has a suitable adsorption capacity for the removal of malachite green, crystal violet and eosin yellow from aqueous solution. The adsorption capacity of passion fruit peel decreased in the order Eosin yellow > Malachite green > Crystal violet. About 94% removal was obtained for Eosin yellow where as the percent removal was 75% and 70% for Malachite green and crystal violet respectively.

Freundlich model gave a good fit to the experimental data. From the kinetic model analysis using coefficient of determination, the pseudo second order model was the most fitting for the description of dye transport from the bulk solution on to the surface of adsorbent.

Adsorption was an effective process for decolorisation of textile waste waters. Although activated carbon was the most effective sorbent, other low cost sorbents could be used for color removal. The final choice of the sorbent is a matter of economics. Batch studies confirm that passion fruit peel, a low cost material, can be used as a substitute for high cost adsorbents.

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