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Research Paper

Adsorption of Acid violet-17 from Synthetic aqueous Solution on Two kinds of *Cucumis sativus* L. Peel adsorbent

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Abstract: *The use of low-cost and eco-friendly adsorbents has been investigated as an ideal alternative to the current expensive methods of removing dyes from waste water. The peel of Cucumis sativus L. was collected from the locale and converted into low cost adsorbents. An acid dye, Acid violet 17 has been used as the adsorbate. Adsorption data were modeled using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich adsorption isotherms.*

Keywords: Raw peel of *Cucumis sativus* and Zinc chloride activated peel of *Cucumis sativus*, Acid violet 17, Adsorption, Isotherms, Kinetics.

Introduction

Dyeing technology is synonymous to man's existence and the usage of dye products is inevitable[1]. Acid dyes are used by several industries, such as textile, paper, printing and plastics to colour their products[2]. The major challenge with dyeing process is how dyes are indiscriminately released into the environment causing pollution to man and his environment due to their slow biodegradability [3,4]. There are several treatment technologies like photo degradation[5], biodegradation[6], coagulation flocculation[7], and electro chemical oxidation[8] available for the treatment of coloured waste water. Among the numerous techniques of colour removal, adsorption[9] is considered to be one of the more efficient and less expensive methods. The removal efficiency of dyes via adsorption mainly depends on the choice of the adsorbents employed. Commercial activated carbon is used mostly for adsorption processes but its expensive nature has equally motivated researchers to find substitutes[10].

In recent years, there has been growing interest in finding inexpensive and effective alternatives to low cost adsorbents such as rice husk and saw dust[11], *Muntingia calabura*[12], *Annona squmosa Seed*[13], *Ricinus communis* epicarp[14,15], *Acacia nilotica*[16], coir pith[17] orange peel[18] and sunflower seed hull[19] have recently been investigated as the precursors, and are still receiving attention. Two methods are used for preparation of AC, physical and chemical activation. During physical activation, the raw material is first carbonized at high temperature then activated by CO_2 or steam under pressure to increase the porosity and surface area of the AC. In chemical activation the carbon yield is higher and the temperature used is lower than in physical activation. The behavior of the reagents during chemical activation has different effects on the final product. $ZnCl_2$ is widely used as activating reagent, because it results in high surface areas and high yield [20,21]. When $ZnCl_2$ is used the activated carbon obtained has larger surface area and greater micro pore structure [22,23]. To prepare activated carbon, conventional heating is usually adopted, the energy being produced by use of an electrical furnace. Recently, microwave heating has been used in the production of activated carbon because it enables rapid and uniform heating [23].

In a developing country like India where agriculture is the primary occupation, agricultural waste by-product such as *Cucumis sat*ivus L. fruits are abundantly available. Therefore, it would be worthwhile to develop a low-cost adsorbent from the fruit peel of *Cucumis sa*tivus L. In the present study, the fruit peel of *Cucumis sa*tivus L. is used as an adsorbent for the colour removal of Acid Violet 17. Peel of *Cucumis sativa* fruit was previously investigated to adsorb cationic dyes [24, 25]. The effects of operating parameters such as pH, intial dye concentration, adsorbent dosage, kinetics and adsorption isotherms were studied.

Material and Methods

Preparation of the peel of *Cucumis sativus L.* fruit (RCS)

The peel of *Cucumis sa*tivus L. fruit was obtained from local vendors, Eachnari railway Gate, Coimbatore District (Tamil Nadu). Then the material was washed with distilled water and dried at 110±2 ^{0}C it was air-dried and powdered in a grinder. The dry biomass was crushed into granules, sieved to different particle sizes, and then preserved in desiccators for use.

Preparation of activated carbon from zinc chloride-treated peel of *Cucumis sativus L.* fruit (ZnCS)

The dried and powdered fruit peel of *Cucumis sa*tivus L. (6 g) were mixed with 30 mL $ZnCl_2$. The slurry was kept at room temperature for 24 h to ensure access of the $ZnCl_2$ to the peel of the *Cucumis sa*tivus L. fruit. After mixing, the slurry was placed in a MW heating apparatus (MW71E, Samsung). After exposure to the microwave heating power of 100W for 8min the carbonized samples were washed with 0.5 M HCl, hot water, and cold distilled water until the pH of the washing solution reached 6-7, filtered, and finally dried at 110 ºC.

Preparation of the Adsorbate solution

A stock solution of 500 mg L^{-1} was prepared by dissolving the appropriate amount of AcidViolet-17 (obtained from SD Fine Chemicals, Mumbai, India) in 100 mL and completed to 1000 mL with distilled water. Different concentrations 25 and 200 mg L^{-1} of AcidViolet-17 were prepared from the stock solution. All the chemicals used throughout this study were of analytical-grade reagents. Double-distilled water was used for preparing all of the solutions and reagents. The initial pH is adjusted with 0.1 M HCl or 0.1 M NaOH.

Batch adsorption experiments

To study the effect of parameters like pH, adsorbent dosage and initial concentration for the colour removal of AcidViolet-17, batch experiments were carried out in a rotary shaker at 150 rpm using 250 mL shaking flasks at room temperature (27±2 ^{0}C) for 100 min. The adsorption isotherm experiment was carried out by agitating 50 mL of the dye solution of various concentrations. After agitation, the dye solutions were separated from the adsorbent and analyzed for the residual Acid Violet-17 concentration. The concentration of AcidViolet-17 in solution was measured by using Digital photocolorimeter and the wavelength used is 540 nm. The effect of pH on dye removal was studied over a pH range of 2-10. The pH of the dye solution was adjusted by the addition of dilute HCl or NaOH (0.1M) solutions. The amount of dye adsorbed at equilibrium, qe (mg g^{-1}) was calculated using the following relationships:

$$q_e = (C_0 - C_e)\ V/W \qquad (1)$$

Where C_0 and C_e (mg L^{-1}) are the initial and equilibrium liquid phase concentration of AcidViolet-17, respectively, V the volume of the solution (L), and W (g) is the weight of the adsorbent used(RCS or ZnCS).

Adsorption isotherms

The adsorption isotherm is extremely important information indicating how adsorbate molecules are distributed between the liquid and solid phases when the adsorption process reaches equilibrium. Knowledge of when the system is at equilibrium is of importance for determining the maximum sorption capacity of RCS and ZnCS for the dye in solution. Equilibrium data are basic requirements for design of adsorption systems and adsorption models, which are used for the mathematical description of the adsorption equilibrium of the dye. The results obtained for adsorption of AcidViolet-17 were analyzed by use of well-known models given by the Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich, isotherms. For the sorption isotherms, initial AcidViolet-17 concentration was varied whereas solution pH and amount of adsorbent were held constant. The sorption isotherms for AcidViolet-17 were obtained for RCS at solution pH 4 and ZnCS at pH 3.

Langmuir isotherm

The Langmuir model is based on the assumption[26] that adsorption takes place at specific homogenous sites within the adsorbent and once a dye molecule occupies a site, no further adsorption takes place at that site. Theoretically, the sorbent has a finite capacity to adsorb the sorbate. Therefore, a saturation value is reached beyond which no further sorption tales place[27]. The monolayer capacity is represented by the expression:

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \qquad (2)$$

The linear form of the above equation is represented as:

$$\frac{C_e}{q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \qquad (3)$$

Where C_e is the concentration of the dye solution (mg L^{-1}) at equilibrium q_e the amount of dye adsorbed per unit weight of adsorbent (mg g^{-1}) and K_L is the constant related to the free energy of adsorption (L mg^{-1}). Q_m is the maximum adsorption capacity. The values of Q_m and K_L were calculated from the slope and intercept of the linear plot.

An essential characteristic of Langmuir isotherm can be expressed in terms of a dimensionless constant called equilibrium parameter[28].

$$R_L = \frac{1}{1+K_L} C_o \qquad (4)$$

Where K_L is the Langmuir constant and C_o is the highest intial dye concentration (mg L^{-1}). The value of R_L indicates the type of isotherm to be favourable ($0 < R_L < 1$), linear ($R_L=1$), unfavourable ($R_l > 1$) or irreversible $R_L=0$.

Freundlich isotherm

Freundlich isotherm is an empirical equation employed to describe heterogenous systems. The freundlich equation is commonly given by:

$$q_e = K_F C_e^{1/n} \qquad (5)$$

Where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg g^{-1}), C_e the equilibrium concentration of solute in the bulk solution (mg L^{-1}), K_F the Freundlich constant indicative of the relative adsorption capacity of the adsorbent (mg g^{-1}) and 1/n is the heterogeneity factor. A linear form of the Freundlich expression can be obtained by taking logarithms of the non-linear form:

$$log q_e = log K_F + \frac{1}{n} log C_e \qquad (6)$$

A plot of log q_e versus log C_e enables the constant K_F and exponent 1/n to be determined from the intercept and slope of the line, respectively.

Temkin isotherm

Temkin isotherm is expressed as

$$q_e = B ln A + B ln C_e \qquad (7)$$

Where A is Temkin constant representing adsorbate-adsorbate interactions and b is another constant related to the heat of adsorption[29]. The Temkin isotherm takes into account adsorbing species-adsorbent interactions. Isotherm constants A and B can be determined from plot q_e against ln C_e.

Dubinin-Radushkevich (D-R) isotherm. The Dubinin-Radushkevich model is used to estimate the characteristic porosity and the apparent free energy of adsorption. It helps to determine the nature of adsorption processes whether physical or chemical. The D-R sorption is more general than the Langmuir isotherm, as its derivation is not based on ideal assumption such as equipotent of the sorption sites, absence of steric hindrances between sorbed and incoming particles and surface homogeneity on microscopic level.

The non-linear presentation of the D-R isotherm equation is as follows:

$$q_e = q_m \exp(-\beta \varepsilon^2) \qquad (8)$$

Where q_e is the amount of dye molecules adsorbed on per unit weight of adsorbent (mol l^{-1}), q_m is the maximum adsorption capacity mol g^{-1}, β is the activity coefficient related to adsorption mean free energy mol $^2J^{-2}$, and ε is the Polanyi potential given by:

$$\varepsilon = RT \ln(1+\frac{1}{C_e}) \qquad (9)$$

A plot of q_e against ε^2 gave non-linear graphs (figure not shown). The adsorption mean free energy, E (kJ mol $^{-1}$) is given as:

$$E = \frac{1}{(2\beta)^{0.5}} \qquad (10)$$

The mean free energy (E) of adsorption specifies the adsorption mechanism whether it's physical or chemical. Physical adsorption process occurs if the value of E<8kJ/mol while 8<E<16kJ/mol describes chemical (ion-exchange) adsorption mechanism [30].

Batch kinetic studies

Several models were used to examine the rate-controlling of the adsorption process such as chemical reaction, diffusion control and mass transfer. Since the kinetic parameters are helpful for the prediction of adsorption rate and give important information for designing and modeling the adsorption processes. The kinetics of the adsorption of AcidViolet-17onto RCS and ZnCS was investigated for selecting optimum operating conditions for a full-scale batch process. Therefore, Pseudo-first order[31] Pseudo-second order [32,33], Intra particle diffusion[34], Elovich[34,35] kinetic models were applied for the adsorption of AcidViolet-17 on RCS, ZnCS, and the conformity between experimental data and the model-predicted values was expressed by the correlation coefficients($R^{2,}$, the values close or equal to1).

The Lagergren pseudo-first-order rate expression is given by the equation[26]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (11)$$

where q_e (mg g $^{-1}$) is the amount of dye adsorbed at equilibrium, q_t (mg g^{-1}) is the amount of Acid violet-17 adsorbed at time t, and k_1 (min^{-1}) is the rate constant of the Pseudo-first-order adsorption model.

The pseudo-second-order model is given by the equation[27]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (12)$$

where k_2 (g mg^{-1} min^{-1}) is the rate constant of the pseudo-second order kinetic model. In the pseudo-second-order model chemical sorption is the rate-limiting step[28]. In reactions involving chemisorptions of adsorbate on to a solid surface without desorption of products, adsorption rate decreases with time because of increased surface coverage.

The second –order rate constants were used to calculate the initial sorption rate, given by the following equation:

$$h=k^2qe^2 \qquad (13)$$

The effect of intra particle diffusion resistance on adsorption can be determined by use of the relationship[29]:

$$qt = K_{diff}{}^{½} + C \qquad (14)$$

where k_{diff} is the intra particle diffusion rate constant (mg g^{-1} min$^{-1/2}$). If the intra particle diffusion model is obeyed, the values of qt were found to be linearly correlated with the values of $t^{1/2}$ and the rate constant k_{diff} directly evaluated from the slope of the regression line (Table 2). The value of intercept C (Table2) provides information about the thickness of the boundary layer, the resistance to the external mass transfer increase as the intercept increase.

The Elovich equation is another rate equation based on the adsorption capacity generally expressed as

$$dqt/dt = B_E \exp(-A_E q_t) \qquad (15)$$

where B_E is the initial adsorption rate(mg g^{-1} min^{-1})and A_E is the desorption constant(g mg^{-1}) during any experiment.

Results and Discussion

Effect of pH on adsorption, desorption, and possibility of recycling

The zeta-potentials of the RCS and ZnCS particles in water were measured at different pH. It was found that the RCS and ZnCS particles are positively charged at low pH and negatively charged at high pH. The zero point charge (pHzpc) for RCS is 6.5, when pH is 4 and pHzpc for ZnCS is 7.2, when pH is 3. It can be expected that negatively charged acid dye are likely to be adsorbed by the positively charged RCS and ZnCS at a pH < pHzpc.

The effect of pH on the adsorption of dye by various adsorbents was studied by varying the pH of the dye solution from 2.0 to 9 for an intial concentration of 100mg/L (Figure 1). Maximum adsorption occurs at at acidic pH (pH for RCS is 4 and for ZnCs is 3). The lower adsorption of AcidViolet-17 an anionic dye, at alkaline pH is because of the presence of excess OH^- ions competing with dye anions for the adsorption sites. At lower pH, a significantly high electrostatic attraction exists between the positively charged surfaces of the adsorbent and negatively charged anionic dye[32].

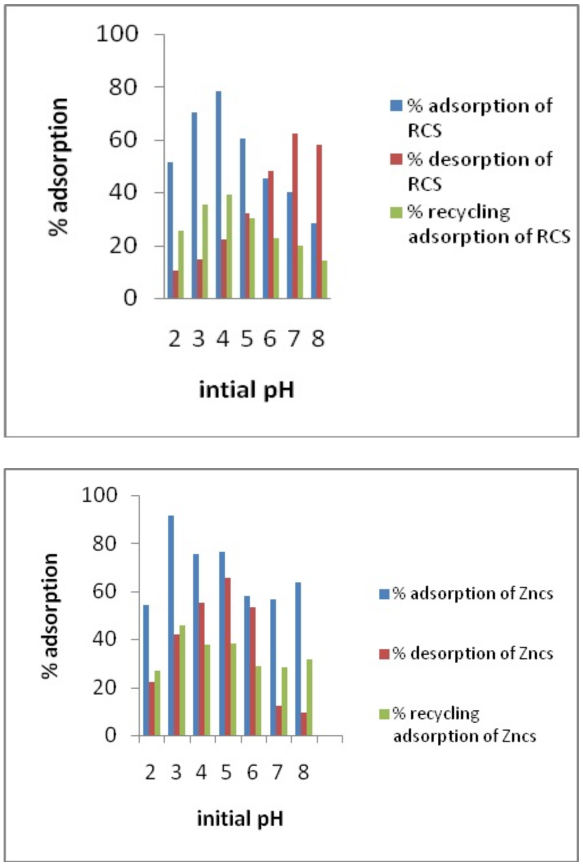

Figure: 1 Effect of initial pH on adsorption of AcidViolet-17 by RCS and ZnCS

As the pH of the system increases, the number of of negatively charged sites increases and the number of positively charged sites decreases. A negatively charged surface site on the adsorbent did not favour the adsorption of the anionic dye due to electrostatic repulsion. A similar result was observed for the adsorption of acid red 14 by soya meal hull [33] and congo red by baggese fly ash[34].

Desorption studies helps to elucidate the mechanism of the adsorption and recovery of the adsorbate and adsorbent. The regeneration of the adsorbent may make the treatment process economical. The percent desorption increases with increase in pH of the aqueous medium (Figure 1). This is just opposite to pH effect, indicating that ion exchange is probably then major mode of adsorption process.

Effect of contact time

Aqueous Acid Violet-17 solutions of initial concentration100 ppm were kept in contact with RCS and ZnCS from 5 to 70 min. The rate of removal was rapid for the first 35 min for both the adsorbents, thereafter the rate of AcidViolet-17 removal reaches equilibrium. During the initial stage of adsorption, a large numbers of vacant surface sites are available for adsorption. After a lapse of sometime, the remaining vacant surface sites are difficult to occupy, because of repulsive forces between adsorbate molecules on the solid surface. This is shown in Figure 2 .The maximum uptake of AcidViolet-17 by RCS at initial pH 4 was 78.2 % and the maximum uptake of AcidViolet-17 by ZnCS at initial pH 3 was 91.2 %, both after an equilibration time of 40-55 min.

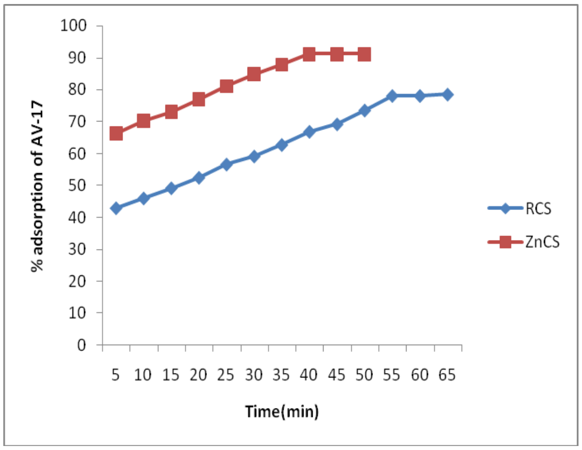

Figure: 2 Effect of contact time on adsorption of Acid Violet-17 (Co=100 mg L^{-1}) onto RCS (initial pH:4) and ZnCs(initial pH:3)

Effect of adsorbent dose

Figure 3 shows that the adsorbed amount of Acid Violet-17 (C_o=100 mg L^{-1}) increased in adsorbent doses, due to greater adsorption sites availability. For 1 g of adsorbent, the maximumamount of Acid Violet-17 adsorbed on RCS at optimum pH of 4 was 92.07% and on ZnCS at optimum pH was 99.03%.

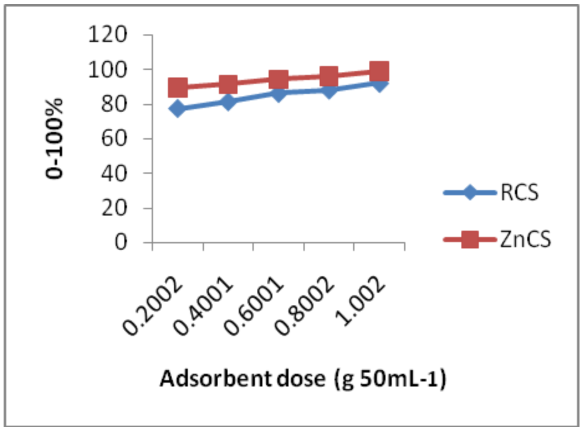

Figure 3: Effect of adsorbent dosage of AcidViolet-17 adsorption (C_o=100mg L^{-1}) onto RCS(initial pH:4) and ZnCS (initial pH:3)

Effect of initial AcidViolet-17 concentration on adsorption

The initial dye concentration is an important driving force, hence, a higher initial concentration of dye will increase the sorption rate. The experiments were carried out at fixed adsorbent dose (0.2 g/50 mL) in the test solution at room temperature (27±2 ^{0}C), with pH (4, 3) and at different initial concentrations of AcidViolet-17 (25,50,75,100,125,150,175 and 200 mgL^{-1}) for different time intervals (10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 min) .

Figure 4 shows that the percentage of adsorption efficiency of RCS and ZnCS decreased with the increase of initial dye concentration in the solution. It is evident from the figure that the amount adsorbed on the solid phase RCS and ZnCs at a lower initial concentration of Acid Violet-17 was smaller than the corresponding amount when higher initial concentrations were used. However, the percentage removal of Acid Violet-17 was greater at lower initial concentrations and smaller at higher concentrations. The adsorption capacity for RCS was increased from 10.67 to 19.62 mg g^{-1} and for ZnCS was 16.51 to 22.78 mg g^{-1} as the Acid Violet-17 concentration increased from 25 to 200 mg L^{-1}.

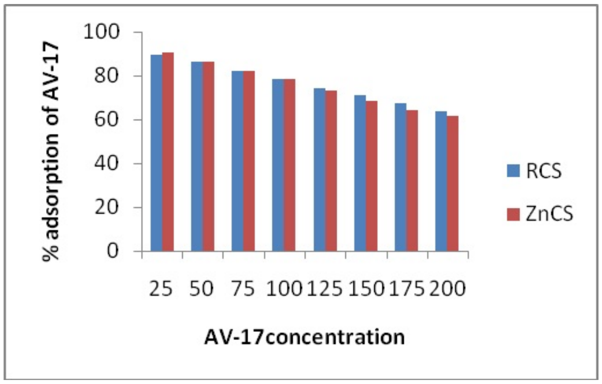

Figure 4: Effect of initial AcidViolet-17 concentration on adsorption process by RCS and ZnCS

Adsorption kinetic models

The results of two models tested showed that both pseudo-second and pseudo-first-order models described well the adsorption process but, pseudo-second-order model gave the best adsorption of AcidViolet-17 on ZnCS as can be seen from the small value of the model's rate adsorption constant when compared with the adsorption constant values for first order. Similarly, the calculated adsorption capacity values for second-order model were equally closer to the experimental adsorption capacity values than those of the pseudo-first-order adsorption capacity. The values are presented in the Table 2. Also, the correlation coefficients are also closer to unity for pseudo-second order kinetics than that for the pseudo –first order kinetics. This suggests that the sorption system can be well represented by the pseudo-second-order model for the adsorption of AcidViolet-17 by the adsorbents used. In the intra particle diffusion model, values of q_t were found to be linearly correlated with values of $t^{1/2}$.

The k_{dif} values were calculated by use of correlation analysis. k_{dif} = 1.728, R_2 = 0.922 for RCS and k_{dif} = 1.452, R_2 = 0.978 for ZnCS. The R_2 values were closer to unity forZnCS than for RCS, indicating the application of this model is a better fit for ZnCS than for RCS. When the Elovich equation was used, the linear coefficient for RCS was found to be 0.883 whereas it was 0.939 for ZnCS. The Elovich constant AE was 0.262 mg g^{-1} min for RCS and 0.3252 mg g^{-1} min for ZnCS. These values were also better for ZnCS than for RCS, which proves the suitability of the Elovich equation for ZnCS.

Table1: Comparison of the correlation coefficients of kinetic data for adsorption of AcidViolet-17 by RCS and ZnCS

Model	Experimental values	Variables	RCS	ZnCS
Pseudo first-order model	qe=23.52	k_1 (min-1) qe (mg g^{-1}) R_2	0.069 19.62 0.772	0.191 22.78 0.757
Pseudo second-order model	qe=26.05	k_2(g^{-1}mg^{-} min^{-1}) qe (mg g^{-1}) h R_2	0.083 22.72 43.10 0.967	0.223 25 66.05 0.994
Intra particle diffusion model	kdif (mg $^{-1}$(g min1/2)) C R_2		1.728 5.836 0.922	1.452 12.99 0.978
Elovich model	AE (mg(g^{-1}min)) BE (g mg^{-1}) R_2		0.262 7.872 0.883	0.325 33.45 0.939

Adsorption isotherm

To optimize the design of an adsorption system, it is important to establish the most appropriate isotherm model. Different isotherm equations (Langmuir, Freundlich, Tempkin, Dubinin–Radushkevich) were used to describe the mono-component equilibrium characteristics of adsorption of AcidViolet-17 by RCS and ZnCS. The experimental equilibrium adsorption data were obtained by varying the concentration of AcidViolet-17 with fixed amounts of RCS and ZnCS.

The adsorption data obtained by fitting the different isotherm models with the experimental data are listed in Table 1, with the linear regression coefficients, R_2.RCS and ZnCS have a homogeneous surface for adsorption of AcidViolet-17. The Langmuir isotherm equation is therefore expected to best represent the equilibrium adsorption data.

The R_2 values for the Langmuir model are closer to unity than those for the other isotherm models for both RCS (R_2 =0.975) and ZnCS (R_2 = 0.996). Therefore, the equilibrium adsorption of AcidViolet-17 on RCS and ZnCS can be represented appropriately by the Langmuir model in the concentration range studied.

Table 2: Isotherm constants

Isotherms	Constants	
	RCS	**ZnCS**
Langmuir		
Qm (mg g^{-1})	15.87	18.86
K_a (L mg^{-1})	0.351	0.841
R_2	0.975	0.996
Freundlich		
1/n	0.101	0.056
K_F (mg g^{-1})	25.76	24.49
R_2	0.919	0.839
Tempkin		
α (L g^{-1})	15.69	18.96
β (mg $^{-1}$)	1.940	1.220
R_2	0.941	0.863
Dubinin–Radushkevich		
Q_m mg/g	7.277	4.924
K ($\times 10^{-5}$ mol^2 kJ)	0.05	3
E (kJ mol-1)	3	0.13
R_2	0.296	0.393

Conclusion

The results of present investigation show that the peel of raw *cucumis sativa* and $ZnCl_2$ activated *cucumis sativa* have suitable adsorption capacity with regard to the removal of Acid violet-17 from its aqueous solution. $ZnCl_2$ activated *cucumis sativa* carbon has better adsorption capacity than the raw *cucumis sativa*. The adsorption is highly dependent on contact time, adsorbent dose and pH. The optimal pH for favorable adsorption of Acid violet-17 is 3. Adsorption obeys the Langmuir isotherms and adsorption kinetics follows pseudo second order kinetics.

Reference

1. Rauf M. A., Ashraf S.S., Fundamental principles and application of heterogenous photocatalytic degradation of dyes in solution, *Chem. Eng. J.*, **15**, 10-18 **(2009)**

2. Ramakrishna K.R., Viraraghavan T., Dye removal using low cost adsorbents, *Water Sci. Technol.*, **36**, 189-196 **(1997)**

3. Shen C., Wen Y., Kang X., Liu W., H_2O_2- induced surface modification, a facile, effective and environmentally friendly on conditions for pretreatment of chitosan for dyes removal, *Chem. Eng. J.*, **166,**474-482 **(2011)**

4. Baskaraslingam P., Pulikesi M., Ramamurthi V., Sivanesan S., Modified hectorites and adsorption studies of a reactive dye-technical note, *Appl. Clay Sci.*, **37**, 207-214**(2007)**

5. Vautier M., Guillard C., Herrmann J.M., Phtocatalytic degradation of dyes in water: case study of Indigo and indigo carmine, *J. Catal.*, **201**, 46-59 **(2001)**

6. Walker G.M., Weatherley L.R., Biodegradation and biosorption of acid anthraquinone dye, *Environ. Pollut.*, **108**, 219-223 **(2000)**

7. Allegrea C., Maisseub M., Charbita F., Moulina P., Coagulation-flocculation-decantation of dye house effluents: concentrated effluents, *Journal of Hazardous Materials*, **B116**, 57-64 **(2004)**

8. Vlyssides A.G., Loizidou M., Karlis P.K., Zorpas A.A., Papioannou D., Electrochemical oxidation of a textile dye waste water using a Pt/Ti electrode, *Journal of Hazardous Materials*, **B70**, 41-52 **(1999)**

9. Garg V.K., Gupta R., Yadav A.B., Kumar R., Dye removal from aqueous solution by adsorption on treated sawdust, *Bioresour. Technol.*, **89**, 121-124 **(2003)**

10. Won S.W., Kim H., Choi S., Chung B., Kim K., Yun Y., Performance kinetics and equilibrium in biosorption of anionic dye Reactive Black 5 by the waste Biomass of *Corynebacterium glutamicum* as a low cost biosorbent, *Chem. Eng. J.*, **121**, 37-43 **(2006)**

11. Malik P.K., Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of Acid Yellow 36, *Dyes and Pigments*, **56**, 239-249 **(2003)**

12. Santhi T., Manonmani S. and Ravi S., Uptake of Cationic Dyes from Aqueous Solution by Biosorption onto Granular *Muntingia calabura*, *E-Journal of Chemistry*, **6 (3),** 737-742 **(2009)**

13. Santhi T. and Manonmani S., Uptake of Cationic Dyes from Aqueous Solution by Biosorption Using Granulized *Annona squmosa* Seed, *E-Journal of Chemistry*, **6(4),** 1260-1266 **(2009)**

14. Santhi T., Manonmani S., Smitha T., Removal of malachite green from aqueous solution by activated carbon prepared from the epicarp of Ricinus communis by adsorption, *Journal of Hazardous Materials*, **179**, 178–186 **(2010)**

15. Makeswari M. and Santhi T., Use of *Ricinus communis* leaves as a lowcost adsorbent for removal of Cu(II) ions from aqueous solution, *Res. Chem Intermed* DOI 10.1007/s11164-013-1029-z.

16. Ashly Leena Prasad, Thirumalisamy Santhi, Adsorption of hazardous cationic dyes from aqueous solution onto *Acacia nilotica* leaves as an ecofriendly adsorbent, *Sustain. Environ. Res.*, **22(2)**, 113-122 **(2012)**

17. Han.R.P., Zou.W.H., Cheng S.J., Wang Y.F. and Shi.J., Biosorption of methylene blue from aqueous solution by fallen phoenix tree's leaves, *Journal of Hazardous Materials*, **141**, 156–162 **(2007)**

18. Khaled Azza, Ahmed El Nemr, Amany El-Sikaily, Ola Abdelwahab, Treatment of artificial textile dye effluent containing Direct Yellow12 by orange peel carbon, *Desalination* , **238**, 210-232 **(2009)**

19. Thinakaran N., Baskaralingam P., Pulikesi M., Panneerselvam P., Sivanesan S., Removal of Acid Violet 17 from aqueous solutions by adsorption onto activated carbon prepared from sunflower seed hull, *Journal of Hazardous Materials*, **151**, 316–322 **(2008)**

20. Almansa C., Molina-Sabio M., Rodruguez-Reinso F., Adsorption of methane into $ZnCl_2$-activatedcarbon derived discs, *J. Microporous Mesoporous Mater.*, **76**, 185–191 **(2004)**

21. Li W., Li-bo Zh., Jin-hui P., Ning L., Xue-yun Zh., Preparation of high surface area activated carbonsfrom tobacco stems with K_2CO_3 activation using microwave radiation, *J. Ind. Crops Prod.,* **27**, 341–347 **(2008)**

22. Williams P.T., Reed A.R., Development of activated carbon pore structure via physical and chemical activation of biomass fibre waste, *Biomass Bioenergy,* **30(2)**, 144–152 **(2006)**

23. Molina-Sabio M., Rodriguez-Reinoso F., Role of chemical activation in the development of carbon porosity, *Colloids Surf.*, **A 41(1–3)**, 15–25 **(2004)**

24. Smitha T., Santhi T., Manonmani S., Equilibrium and kinetics study of adsorption of Crystal violet onto the peel of of *Cucumis sativa* fruit from aqueous solution, *E-journal of Chemistry,* **9 (3)**, 1091-1101, **(2012)**

25. Santhi T., Manonmani S., Smitha T., Sugirtha D. and Mahalakshmi K., Uptake of cationic dyes from aqueous solution by bioadsorption onto Granular *Cucumis sativa*, *Journal of applied sciences in environmental sanitation*, **4(1)**, 29-35 **(2009)**

26. Langmuir I., The adsorption of gases on plane surfaces of glass, mica and platinum, *J. Am. Chem. Soc.*,**40 (9)**, 1361-1403 **(1918)**

27. Wang Y.C., Szeto Y.S., Cheung W.H., McKay G., Equilibrium studies for acid dye adsorption onto chitosan, *Langmuir*, **19**, 7888-7894 **(2003)**

28. Freundlich H.M.F., Uber die adsorption in lasungen, *Z. Phys. Chem.*, **57**, 385–470 **(1906)**

29. Tan I.A.W., Hameed B.H., Ahmad A.L., Equilibrium and kinetic studies on basic dye adsorption by oil palm fibre activated carbon, *Chem. Eng. J.*, 127, 111–119 **(2007)**

30. Dubinin M.M., Zaverina E.D., Radushkevich L.V., Sorption and structure of activated carbons, I. Adsorption of organic vapours, Zh. Fiz. Khim. **21**, 1351–1362 **(1947)**

31. Polanyi M., Theories of the adsorption of gases, A general survey and some additional remarks, *Trans. Faraday Soc.*, **28**, 316–332 **(1932)**

32. Ho Y.S., Citation review of Lagergren kinetic rate equation on adsorption reaction, *Scientometrics,* **59**, 171–177 **(2004)**

33. Ho Y.S., McKay G., Kinetic models for the sorption of dye from aqueous solution by wood, *J. Environ. Sci. Health Part B*, **76**, 183–191 **(1998)**

34. Wang X.S., Sun C., Removal of copper (II) ions from aqueous solutions usin Na-mordenite. Sep., *Sci. Technol.,* **42**, 1215–1230 **(2007)**

35. Gundogan R., Acemioglu B., Alma M.H., Copper (II) adsorption from aqueous solution by herbaceous peat, *J. Colloid Interface Sci.,* **269**, 303–309 **(2004)**

36. Lagergren S., About the theory of so-called adsorption of soluble substances, K. Sven. Vetenskapsakad Handl., **24**, 1–39 **(1898)**

37. Elovich S.J., Schulman J.H. (Ed.), Proceedings of the Second International Congress on Surface Activity, vol **11** (Academic Press, Inc., New York, 1959), 253, **(1959)**

38. Kadirvelu K., Karthika C., Vennilamani N., Pattabi S., Activated carbon from industrial solid waste as an adsorbent for the removal of Rhodamine-B from aqueous solution: Kinetic and equilibrium studies, *Chemosphere*, **60**,1009-1017 **(2005)**

39. Arami N.Y., Limaee Mahmoodi N.M., Tabrizi N.S., Equilibrium and kinetics for the adsorption of direct dyes from aqueous solution by soymeal hull, *Journal of Hazardous Materials B*, **135**, 171-179 **(2006)**

40. Mall D., Srivastava V.C., Agarwal N.K., Mishra I.M., Removal of Congo red from aqueous solution by bagasse fly ash and activated carbon: kinetic study and equilibrium isotherm analysis, *Chemosphere,* **61**, 492-501 **(2005)**