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Adsorption of acid black-7 from synthetic aqueous solution onto *Cucumis sativus* peel

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ABSTRACT

The peel of Cucumis sativus L. was used as low-cost adsorbent and as an ideal alternative to the current expensive methods of removing dyes from waste water. An acid dye, Acid black-7 has been used as the adsorbate. Adsorption data were modeled using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich adsorption isotherms. The data were also fitted to kinetic models such as pseudo-first order, pseudo-second order, Intra particle and Elovich model. The adsorbent was characterized by Fourier Transform infrared spectroscope (FTIR), X-ray diffraction (XRD), scanning electron microscope (SEM) with an EDAX (energy dispersive analysis of X-ray), and zeta potential measurements will be carried out in order to find the iso electric point of the adsorbent.

Keywords: Peel of *Cucumis sativus;* Acid black - 7; Adsorption; Isotherms; Kinetics

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INTRODUCTION

Dyes are synthetic chemical compounds having complex aromatic structures which are extensively used in the textile, cosmetic, plastic, food, and pharmaceutical industries [1]. The dye-containing wastewater discharged from the industries can adversely affect the aquatic environment by impeding light penetration. Moreover, most of the dyes are toxic, carcinogenic and harmful to human health. Even at low concentration (1 mg L^{-1}), dyes could be highly noticeable, and could cause an aesthetic pollution and disturbance to the ecosystem and water sources [2]. Therefore, there is an increasing demand of efficient and economical technologies for removing dyes from water environment in the world. Many physical and chemical treatment methods including adsorption, coagulation, precipitation, filtration, electrodialysis, membrane separation and oxidation have been used for the treatment of dye-containing effluents [3], for the treatment of effluents containing dyes are available, and the most efficient one is the adsorption process, because it is simple in terms of operation and can remove the contaminant even at very low concentration. However, the choice of the adsorbent is based on economical and practical reasons agricultural waste materials are natural materials with low cost and its use as adsorbent would be very convenient for removing organic pollutants and of heavy metal ions.

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 [4]. 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[5], *Muntingia calabur*[6] , *Annona squmosa Seed*[7], *Ricinus communis* epicarp[8, 9], *Acacia nilotica*[10], coir pith[11], orange peel[12] and sunflower seed hull[13] have recently been investigated as the precursors, and are still receiving attention.

In a developing country like India where agriculture is the primary occupation, agricultural waste by-product such as *Cucumis sativus* L. fruits are abundantly available. Therefore, it would be worthwhile to develop a low-cost adsorbent from the fruit peel of *Cucumis sativus* L. In the present study, the fruit peel of *Cucumis sativus* L. is used as an adsorbent for the removal of Acid Black 7. Peel of Cucumis sativa fruit was previously investigated to adsorb

cationic dyes[14, 15]. The effects of operating parameters such as pH, intial dye concentration, adsorbent dosage, kinetics and adsorption isotherms were studied.

EXPERIMENTAL SECTION

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

The peel of *Cucumis sativus* 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 the Adsorbate solution

A stock solution of 500 mg L $^{-1}$ was prepared by dissolving the appropriate amount of Acid black-7 (obtained from S. D. Fine Chemicals, Mumbai, India) in 100 mL and completed to 1000 mL with distilled water. Different concentrations 25 and 200 mg L -1 of Acid black-7 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 Acid black-7, 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 black-7 concentration. The concentration of Acid black-7 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:

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

Where C_0 and C_e (mg L^{-1}) are the initial and equilibrium liquid phase concentration of Acid black -7, respectively, V the volume of the solution (L), and W (g) is the weight of the adsorbent used(RCS).

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 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 Acid black-7 were analyzed by the use of well-known models given by the Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich, isotherms. For the sorption isotherms, initial Acid black-7 concentration was varied whereas solution pH and amount of adsorbent were held constant. The sorption isotherms for Acid black-7 were obtained for RCS at solution pH 4.

Langmuir isotherm

The Langmuir model is based on the assumption [16] 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[17]. The monolayer capacity is represented by the expression:

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

The linear form of the above equation is represented as:

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

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[18].

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

Where K_L is the Langmuir constant and C_o is the highest initial 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:

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

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:

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

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

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

Where A is Temkin constant representing adsorbate-adsorbate interactions and b is another constant related to the heat of adsorption[19]. 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:

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

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 [20].

$$\varepsilon = RT \ln\left(1+\frac{1}{c_e}\right) \quad (9)$$

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:

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

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 < 8 kJ/mol while 8 < E < 16 kJ/mol describes chemical (ion-exchange) adsorption mechanism [21].

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 Acid black-7onto RCS was investigated for selecting optimum operating conditions for a full-scale batch process. Therefore, Pseudo-first order[22] Pseudo-second order[23, 24], Intra particle diffusion[25], Elovich [26, 27] kinetic models were applied for the adsorption of Acid black-7 on RCS 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[22]:

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

where q_e (mg g^{-1}) is the amount of dye adsorbed at equilibrium, q_t (mg g^{-1}) is the amount of Acid black-7 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[23]:

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

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 [24]. 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:

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

The effect of intra particle diffusion resistance on adsorption can be determined by use of the relationship[25]:

$$qt = K_{diff}{}^{1/2} + C \quad (14)$$

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

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

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

Characterization of the adsorbent

From SEM and EDX studies conform the presence of carbon and pores on the surface of the Raw *Cucumis sativus* and it enhance the adsorption over the pores. These are given in Fig. 1 and 1a.

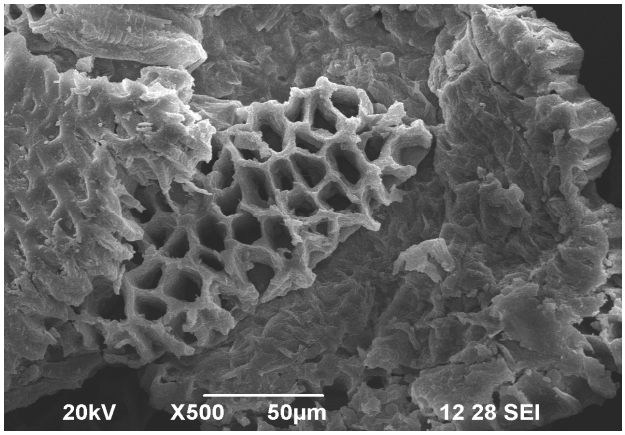

Fig: 1 SEM images of RCS

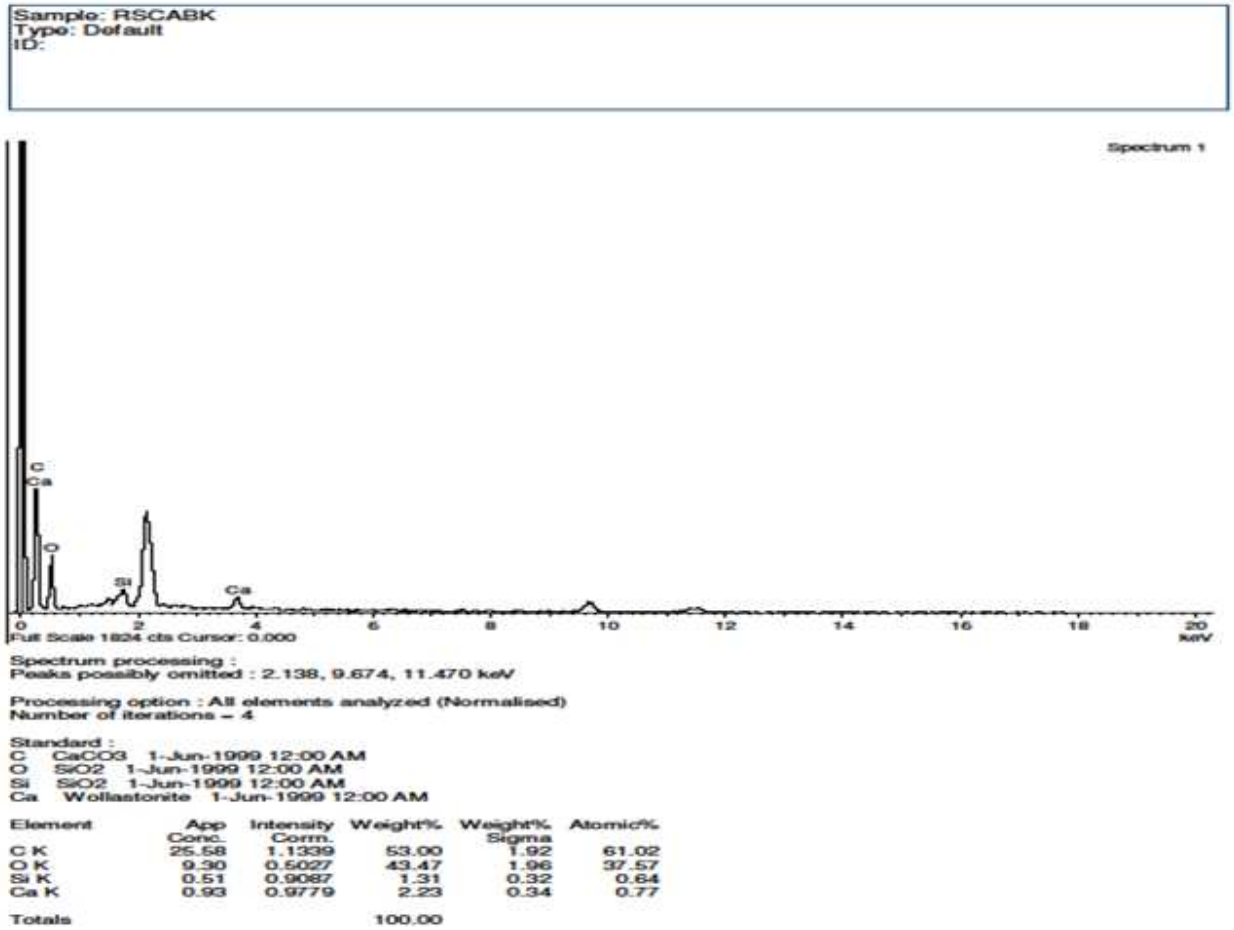

Fig: 1a EDX spectrum of RCS

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

The zeta-potentials of the RCS particles in water were measured at different pH. It was found that the RCS particles are positively charged at low pH and negatively charged at high pH. The zero point charge (pHzpc) for RCS is 6.5. It can be expected that negatively charged acid dye are likely to be adsorbed by the positively charged RCS 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 initial concentration of 100 mg/L (Fig.2). Maximum adsorption 85% occurs at acidic pH(3). The lower adsorption of Acid black-7 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[28]. As the pH of the

system increases, the number of negatively charged sites increases and the number of positively charged sites decreases. A negatively charged surface site on the adsorbent did not favor 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[29] and congo red by baggese fly ash[30].

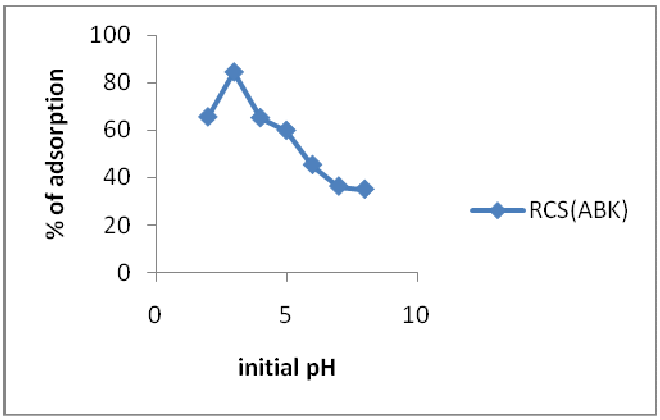

Fig: 2 Effect of initial pH on adsorption of Acid black-7 by RCS

Effect of contact time

Acid black-7 solution of initial concentration100 ppm were kept in contact with RCS from 5 to 70 min. The rate of removal was rapid for the first 55 mins; thereafter the rate of Acid black-7 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 Fig.3 .The maximum uptake of Acid black-7 by RCS at initial pH 3 was 85 % at an equilibration time of 55 min.

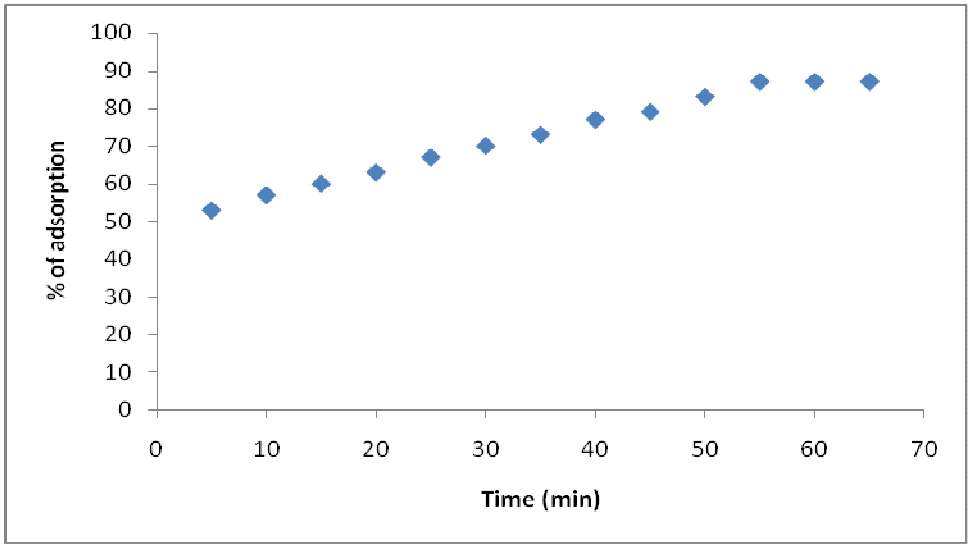

Fig: 3 Effect of contact time on adsorption of Acid black-7

Effect of adsorbent dose

Figure 4 shows that the adsorbed amount of Acid black-7 (C_o=100 mg L^{-1}) increased in adsorbent doses, due to greater adsorption sites availability. For 1 g of adsorbent, the maximum amount of Acid black-7 adsorbed on RCS at optimum pH of 3 was 85%.

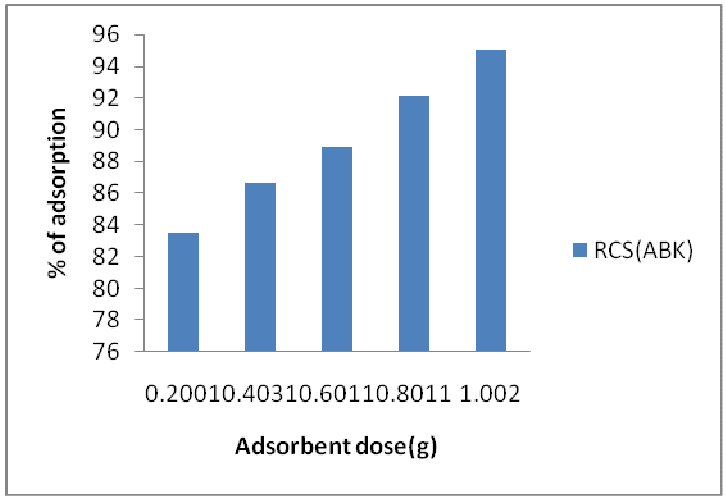

Fig:4 Effect of adsorbent dosage of Acid black-7 onto RCS

Effect of initial Acid black-7 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 Acid black-7 (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 5 shows that the percentage of adsorption efficiency of RCS 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 at a lower initial concentration of Acid black-7 was smaller than the corresponding amount when higher initial concentrations were used. However, the percentage removal of Acid black-7 was greater at lower initial concentrations and smaller at higher concentrations. The adsorption capacity for RCS was increased from 17.01 to 24.31 mg g^{-1} as the Acid black-7 concentration increased from 25 to 200 mg L^{-1}.

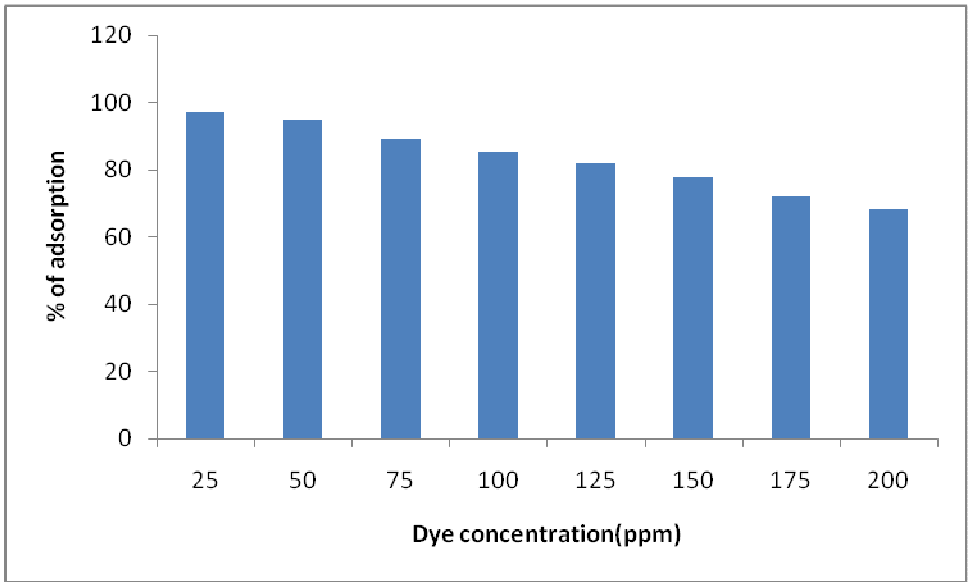

Fig: 5 Effect of initial Acid black-7 concentration on adsorption by RCS

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 Acid black- 7 on RCS 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 Table2. 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 Acid black-7 by the adsorbents used. In the intra particle diffusion model, values of q_t were found to be linearly correlated with values of $t^{1/2}$.

Table1: Comparison of the correlation coefficients of kinetic data for adsorption of Acid black-7 by RCS

Model	Experimental values	Variables	RCS
Pseudo first-order model	q_e = 21.93	k_1 (min-1) qe (mg g^{-1}) R_2	0.046 8.66 0.946
Pseudo second-order model		k_2($g^{-1}mg^{-}$ min^{-1}) qe (mg g^{-1}) h R_2	0.1078 25.00 67.37 0.983
Intra particle diffusion model	kdif (mg $^{-1}$(g min1/2)) C R_2		1.639 8.982 0.973
Elovich model	AE (mg(g^{-1}min)) BE (g mg^{-1}) R_2		3.63 41.4 0.894

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 Acid black-7 by RCS. The experimental equilibrium adsorption data were obtained by varying the concentration of Acid black-7 with fixed amounts of RCS. 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. 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 RCS (R_2 =0.995). Therefore, the equilibrium adsorption of Acid black-7 on RCS be represented appropriately by the Langmuir model in the concentration range studied.

Table 2: **Isotherm constants**

Isotherms	Constants
	RCS
Langmuir	
Qm (mg g^{-1})	17.24
K_a (L mg^{-1})	0.5087
R_2	0.995
Freundlich	
1/n	0.075
K_F (mg g^{-1})	24.94
R_2	0.868
Tempkin α (L g^{-1})	9.621
β (mg $^{-1}$)	1.576
R_2	0.898
Dubinin–Radushkevich	
Q_m mg/g	7.94
K (×10^{-5} mol^2 kJ)	0.4
E (kJ mol-1)	3
R_2	0.846

CONCLUSION

The results of present investigation shows that the peel of *cucumis sativa* have suitable adsorption capacity with regard to the removal of Acid black-7 from its aqueous solution. The adsorption is highly dependent on contact time, adsorbent dose and pH. The optimal pH for favorable adsorption of Acid black-7 is 4. Adsorption obeys the Langmuir isotherms and adsorption kinetics follows pseudo second order kinetics.

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