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Solochrome Black-T Removal From Aqueous Solution Using Activated Carbon Prepared From Bottle Guard Peel

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Abstract
In the present investigation, activated carbon prepared by chemical activation method from bottle guard peel has been used for the removal of solochrome Black-T dye from aqueous solution. Batch adsorption studies were conducted to study the effect of contact time, adsorbent dosage and initial dye concentration on the adsorption. Data analysis was done by different adsorption isotherms such as Langmuir and Freundlich and the results showed Langmuir isotherm as a suitable model to define the adsorption behaviour. Kinetic study was carried out using pseudo - first order, pseudo-second order models and intraparticle diffusion rate and the pseudo-first order model described the solochrome black-T adsorption process with a well-fitting (R^2 = 0.9962).
Keywords: *solochrome black-T, Bottle guard peel, Adsorption, Kinetics, Isotherms*

1. INTRODUCTION

With time the usage of synthetic dyes increasing for various purposes due to ease of availability, accessibility, durability and cheap in cost. Approximately 0.7 million tons of dyes are produced and used annually for various industrial purposes[5]. To name few industrial applications of synthetic dyes such as textile, leather, food, paint and pigment manufacturing, among all these industries, textile industry accounts for around 75% of global industries. Though various treatment technologies available in various countries for wastewater treatment, still the industries often dispose partially treated waste water into the environment. Dye pollution contributes around 10-15% of total water pollution in the universe. To specifically name textile firms stands high in generating wastewater containing dye pollutants. To account roughly 20% of the dyes such as methylene blue, solochrome black-T, eosin yellow, congo red, and indigo blue dyes are utilized by textile firms annually[9]. Even a very low concentration of these dyes are dangerous and affects aquatic life as well as food web[2]. Further the dyes hinders the penetration of sunlight to the lower layers of water bodies, thus affecting the photosynthetic efficiency of the plant species and there by also affects the plant dependent aquatic organisms, and also harm humans because of carcinogenic, mutagenic and teratogenic properties as well as respiratory toxicity [8]. Hence to protect the aquatic ecosystem and the environment it is necessary to remove the coloring material from the effluents before their discharge. Solochrome black-T(SBT) is an azo dye that turns red when it forms a complex with calcium, magnesium or other metal ions.

Many treatment methods are available for the removal of pollutants from the wastewater such as biological and physicochemical treatment methods. Though the biological treatment methods are cost effective and are helpful in removing biological oxygen demand, chemical oxygen demand and suspended materials but not that efficient in removing coloured materials or dyes[5]. To overcome the ineffectiveness of biological treatment methods for the dye removal, physicochemical treatment techniques are developed such as coagulation, membrane, microextraction[10], flocculation, ion exchange, adsorption and many others[11]. However the dyes are not completely removed by these methods because of the stability of the dyes[6].

Among the pysicochemical methods, Adsorption is considered as simple, efficient and economical for dye removal[19]. Adsorption is a surface phenomenon involves the adsorbate attaching itself to the surface of the adsorbent. Among several adsorbents used, activated carbon has been found to be superior because of its ability in adsorbing a wide range of different types of adsorbates efficiently [7]. However, commercially available activated carbons are still considered expensive. This has led to the study of relatively inexpensive and abundant materials which can serve as cheap adsorbents and at the same time endowed with reasonable adsorption capacity [1]. In this method variety of materials, either natural or synthetic, can be used as adsorbents[20]. However, carbon and its compounds are widely used adsorbents for purification of various water sources, as these have a vast network of internal pores with high surface. So these are considered as universal adsorbents [21].

This study explores the use of bottle guard peel, an abundant kitchen waste, for activated carbon production via chemical activation using $ZnCl_2$ as an activating agent. Bottle guard peel is easily available in Indian kitchens, not much explored, potential, and low-cost. The prepared activated carbon was characterized by FTIR and used in batch studies to assess its adsorption performance for solochrome black-T or Eriochrome black T dye under varied operating parameters, including contact time, adsorbent dosage, and initial dye concentration were examined. Kinetics data were fitted to pseudo-first order, pseudo-second order models, and intraparticle diffusion rate and also the isotherm data fitted to Langmuir and Freundlich models.

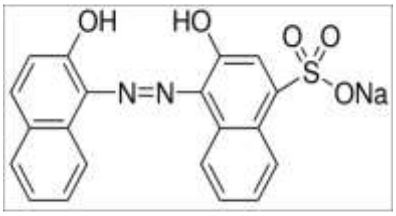

Fig 1.1: Chemical structure of Solochrome Black-T or eriochrome black -T [3]

2. MATERIALS AND METHODS

2.1. Materials

Bottle Guard peel was obtained from home. The Zinc Chloride ($ZnCl_2$), Hydrochloric Acid (HCL), Distilled Water, and solochrome black - T dye were purchased from local vendor.

2.2. Methods

2.2.1. Preparation of activated carbon from bottle guard peel (adsorbent)

Fresh bottle gourd peels were collected, thoroughly washed to remove dirt and sun-dried for 15-20 days. The dried peels were ground into powder and sieved using 120-mesh size to obtain uniform particle size.The powder was soaked in 1.23 M $ZnCl_2$ solution and kept for 24 hours for impregnation. The impregnated sample was placed in a muffle furnace at 600°C for 2 hours to activate the carbon.The carbonized powder was washed thrice with 0.5N HCl and then rinsed with distilled water and then normal water to remove residual chemicals.The washed sample was dried in an oven at 100°C for 24 hours and stored in airtight container for further studies.

2.2.2. Preparation of Solochrome black-T dye stock solution (Adsorbate)

A stock solution of 1000 ppm of solochrome black - T dye was prepared by dissolving 1 g of the dye in a 1L distilled water. Standard solutions of solochrome black-T dye with concentrations of 100 ppm, 120 ppm, 140 ppm, 160 ppm and 10 ppm were then prepared by serially diluting the stock solution.

2.2.3. Batch adsorption studies

Batch studies were conducted by mixing a measured quantity of adsorbent with 20 ml of dye solution. The samples were placed on a magnetic stirrer at 150 rpm at a constant temperature. The samples were withdrawn from the shaker at specified time intervals and filtered using Whatman No. 1 filter paper. The filtrates were analyzed using a spectrophotometer to determine the absorbance and final concentration of the dye. The effects of contact time (20-150 minutes), adsorbent dosage (0.02 - 0.1 g), and initial dye concentration of 10,100,120,140 and 160 ppm on the adsorption process were investigated.

$$q_e = \frac{(C_o - C_e)V}{m} \qquad (1)$$

where C_o is the initial concentration of adsorbate (mg/L), C_e is the final concentration of adsorbate (mg/L), 'm' is the mass of the adsorbent in gram (g) and 'v' is the volume of the adsorbate in liters (L). The adsorption efficiency can be expressed as percentage adsorption of dye solution as;

% removal (R)= $\frac{C_o - C_e}{C_o} \times 100$ (2)

Where 'C_o' is the initial adsorbate concentration (mg/L) and 'C_e' is the final adsorbate concentration (mg/L).

3. RESULTS AND DISCUSSION

3.1. Characterization of the Adsorbent

The Fourier Transform Infrared (FTIR) spectrum gives the information about the functional groups present on the surface of the adsorbent [24]. Fig. 3.1. depicts the FT-IR spectrum of bottle guard peel activated carbon(BGPAC), each peak in the spectrum corresponds to different functional group[12]. The absorption band near 3277 cm^{-1} can be attributed to O-H, 1747 cm^{-1} to C=O bending streching, 1680 to C=C streching, 1541 to C=O streching, and 1008 to C-O streching.

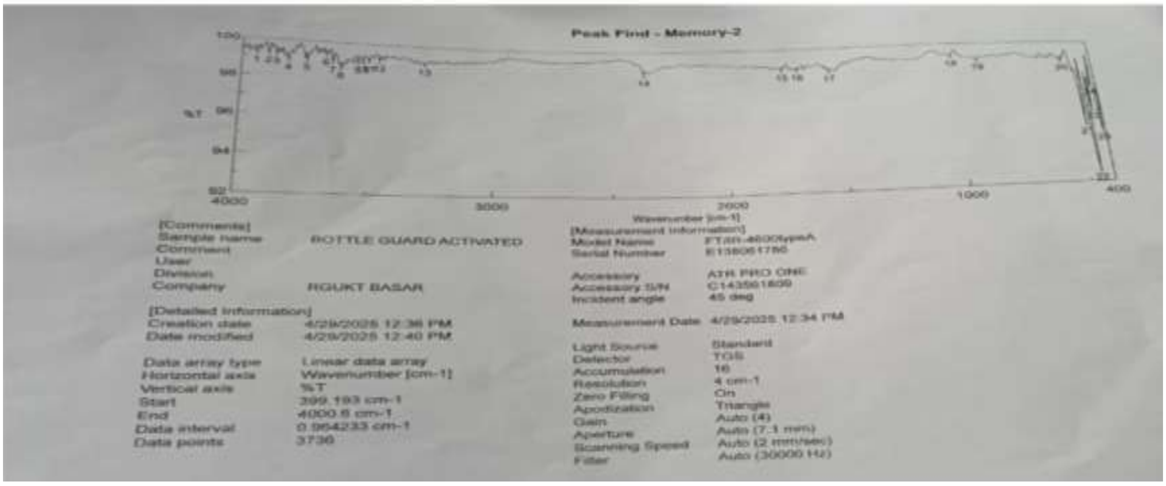

Fig. 3.1. FTIR Spectra of prepared activated carbon

3.2. Effect of contact time

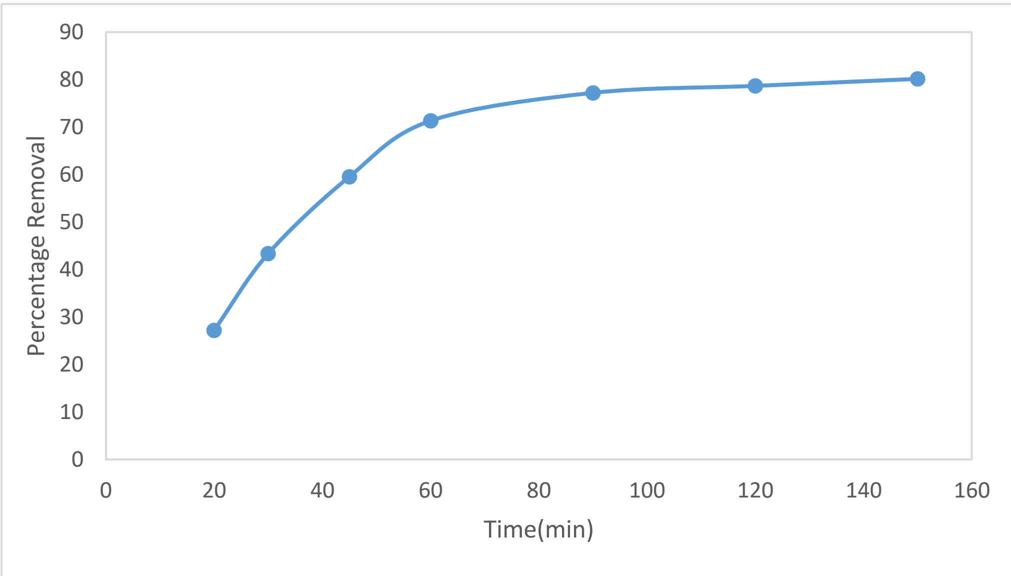

Fig. 3. 2. Effect of contact time

Effect of contact time on adsorption process helps in the determination of adsorption efficiency and equilibrium time. The above Fig.3.2 represents percent removal against contact time of the adsorption of dye on to BGPAC shows that as the time of contact between adsorbent and dye increases , the percentage removal of dye also increases. At initial stages percentage removal and hence dye uptake is high compared to the end of the process. This is because initially the concentration difference(driving force) is maximum but it decreases with time, same was observed in previous work [12]. Further increase in contact time did not result in any significant adsorption and maximum adsorption was achieved at 60 minutes. The initial rapid removal of the dye and the establishment of equilibrium within a short time signifies the efficiency of the adsorbent for wastewater treatment [13].

3.3. *Effect of Adsorbent Dosage*

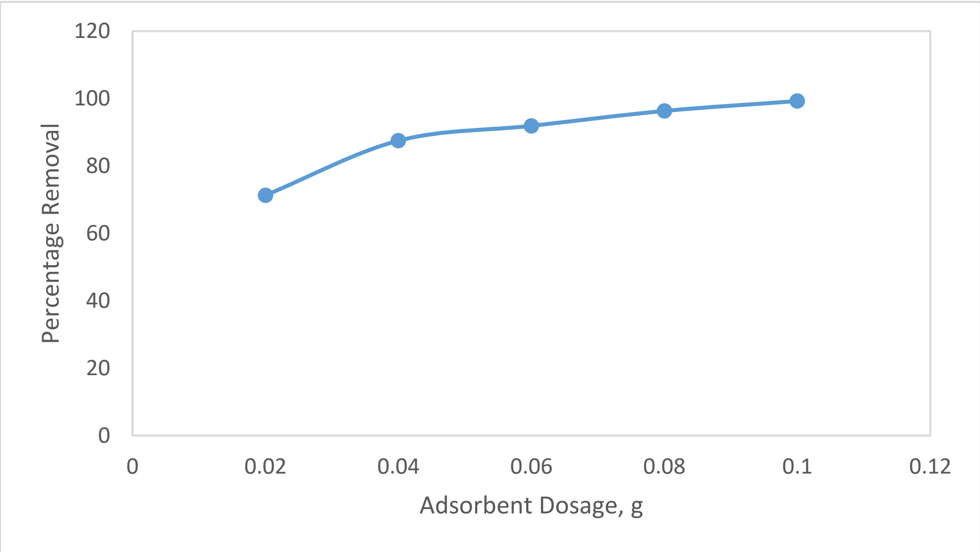

Fig. 3.3. Effect of adsorbent dose on percentage removal of solochrome black-T dye

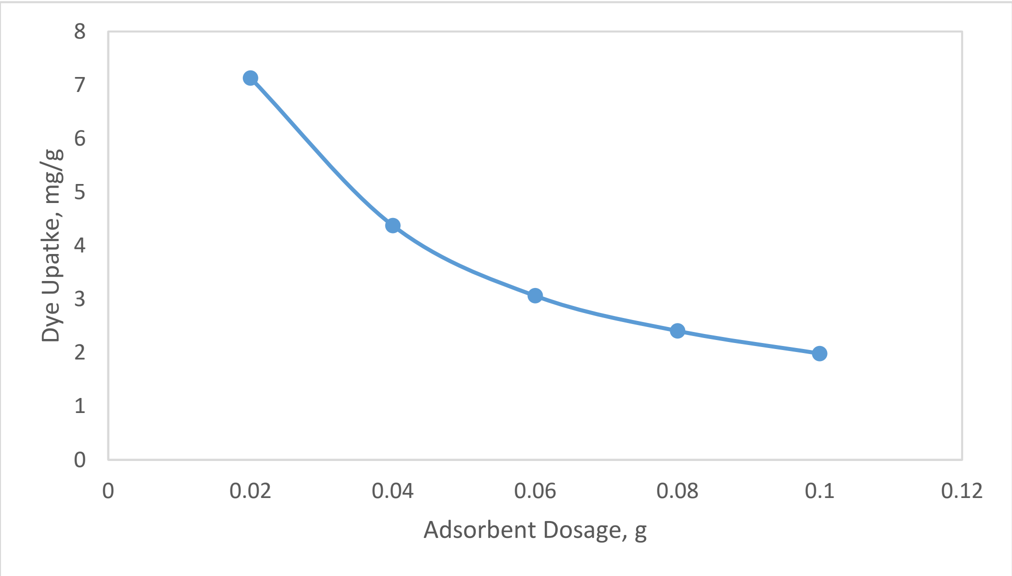

Fig. 3.4. Effect of adsorbent dose on the dye uptake onto the AC

The effect of adsorbent dosage on the adsorption of Solochrome Black - T dye was studied between dose range 0.02 - 0.1 g as shown in Fig.3.3. It was observed that the adsorption of the dye increased with increasing adsorbent dosage as expected. This is principally due to increase in surface area of the adsorbent, which consequently increases the number of adsorption sites. The amount of dye adsorbed, however, decreased as the dosage increases as shown in Fig.3.4 which could be attributed to the overlapping or aggregation of the active sites as the dosage increases which makes the sites inaccessible for the dye, same was observed in previous studies[12].

3.4. Effect of Initial Dye Concentration

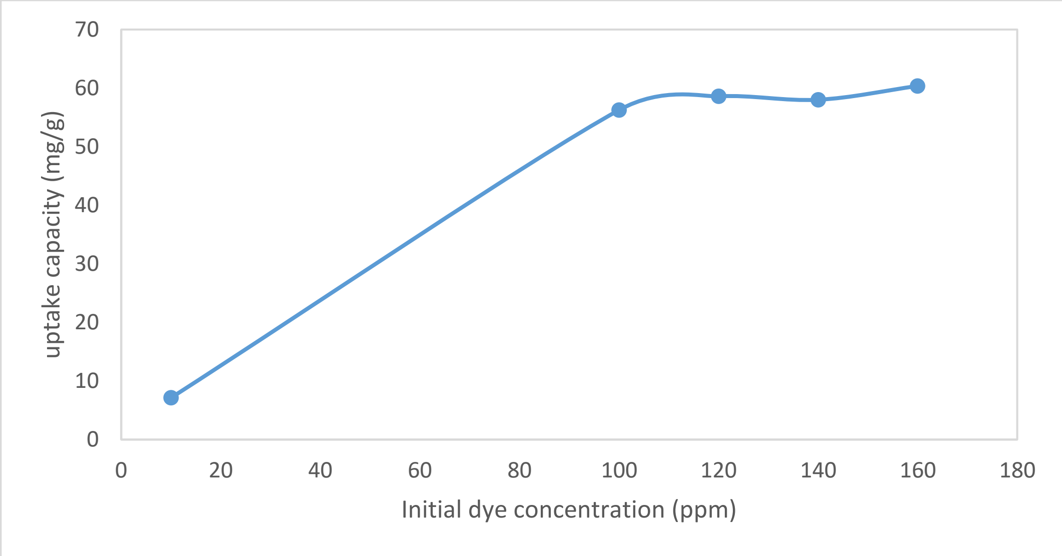

Fig.3.5. Effect of initial dye concentration on the dye uptake onto the AC

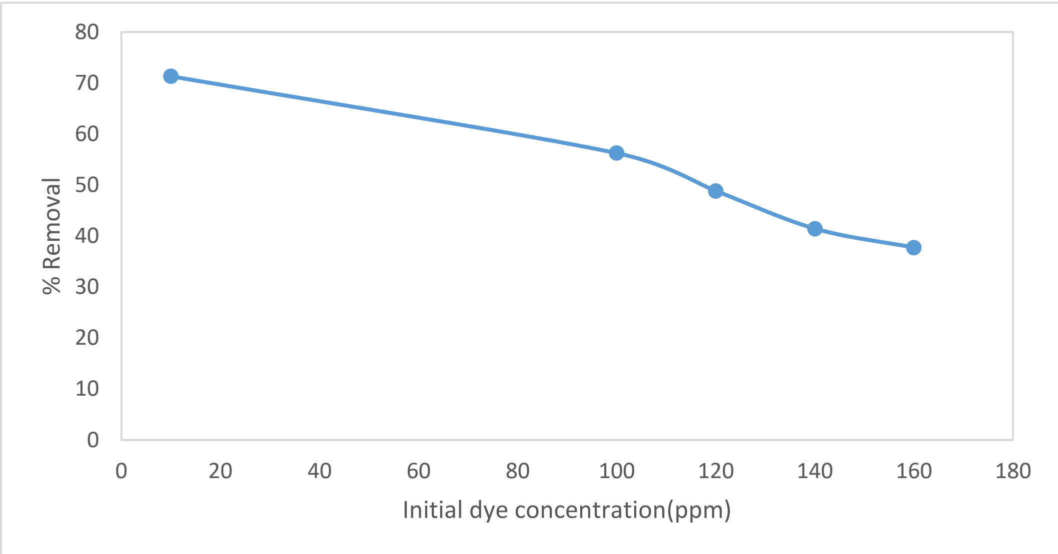

Fig.3.6. Effect of initial dye concentration on the percentage removal of dye

The above fig.3.5 represents the effect of initial dye concentration on the adsorption process. It was observed that adsorption capacity of the dye increases with an increase in initial dye concentration which implies that adsorption process depends on initial dye concentration. A higher concentration of dye provides a higher driving force for dye molecules to approach adsorption sites more rapidly [14]. The rate of diffusion of dye molecules at lower initial dye concentration is slow, hence few dye molecules reach adsorption sites.

3.5. Adsorption Kinetics

Kinetic studies are important to know the uptake rate of solute, to investigate this experimental data was analysed firstly using pseudo first order model using the equation given below

$$\log(q_e - q) = \log q_e - \left({}^{K_1 t}/_{2.303}\right) \qquad (3)$$

where q is the amount of dye adsorbed (mg/g) at time t (min), qe is the amount of dye adsorbed at equilibrium (mg/g), and K_1 is the equilibrium rate constant of pseudo-first order adsorption. K_1 and q_e were obtained from the plot of $\log(q_e - q)$ against t. The R^2 obtained was high (0.9962) and the experimental and the calculated q_e values are close .

After the pseudo first order analysis the pseudo second order model was analysed using the below equation.

$$t/q = 1/K_2 q_e^2 + t/q_e \quad (4)$$

where K_2 is the pseudo-second order rate constant.
The data was further analysed using the intraparticle diffusion rate eqauion expressed below, to inquire the step that governs the overall rate of removal.

$$q = K_d t^{1/2} + C \quad (5)$$

where K_d (mg/g $min^{1/2)}$ is the intraparticle diffusion rate constant and C is the intercept.

Table. 3.1. Kinetic parameters

Kinetic Model	Parameter	Value
Pseudo-first order	Experimental q_e (mg/g)	7.13
	q_e (mg/g)	13.17
	$K_1(min^{-1})$	0.053
	R^2	0.9962
Pseudo- second order	q_e (mg/g)	33.22
	K_2 (g/mg min)	0.00014
	R^2	0.7012
Intraparticle diffusion rate	K_d (mg/g $min^{1/2}$)	1.3428
	R^2	0.9946

Table. 3.1. represents the kinetic parameters of Pseudo- first order, Pseudo-second order and intrapartcile diffusion rate. The correlation coefficient (R^2 = 0.9962) shows an almost perfect fit of the data to Pseudo - first order model and the calculated q_e (13.17) is close to the experimental value (7.13).Considering the correlation coefficient value and the closeness of experimental and calculated values of q_e the adsorption of solo-chrome black-T dye onto the BGPAC can best described by the pseudo -first order model. It indicates uniformly distributed monolayer coverage of the dye on the adsorbent BGPAC surface[25]. The high value of R^2 (0.9946) for intraparticle diffusion rate indicates that there was indeed intraparticle diffusion, but it is not the rate controlling step since the intercept C is not equal to zero [16]. Presence of the intercept shows that boundary layer diffusion occurs in the initial stages of the adsorption [17].

3.6. Adsorption Isotherms

The purpose of adsorption isotherm studies were to understand the interaction between the dye molecules and the activated carbon at equilibrium. This will give an indication of the practicability of using the activated carbon for removal of the solochrome black - T dye from wastewater. To come up with the most suitable equilibrium curve that can be used for design of adsorption system, the data was analysed using two different isotherm models namely Langmuir and Freundlich. The isotherm parameters of the two models are calculated using Equations represented as below (6) to (7).

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (6)$$

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad (7)$$

where C_e= any liquid phase concentration of the dye in equilibrium with the adsorbent,
q_e = equilibrium adsorption capacity of the adsorbent, q_m = monolayer capacity, q_e = theoretical monolayer saturation capacity of adsorbent (mg/g), K_L = Langmuir adsorption constant, K_F = Freundlich constant for relative adsorption capacity of adsorbent [18].

Table. 3. 2. Isotherm coefficients for the Solochrome black T dye adsorption

Isotherm Model	Parameter	Value
Langmuir	q_m (mg/g)	80
	K_L (L/mg)	0.0397
	R^2	0.9809
Freundlich	K_F (mg/g)(mg/L)$^{1/n}$	3.845
	n	1.554
	R^2	0.9701

Table. 3.2 represents the isotherm coefficients of two different isotherm model such as Langmuir, and Freundlich. The R^2 value for Langmuir isotherm is greater than that of Freundlich isotherm, which demonstrates monolayer adsorption on the homogeneous surface of bottle guard peel activated carbon [25].

Table. 3. 3. Maximum adsorption capacities of solochrome black -T from aqeuous media using various Adsorbents.

Adsorbents	q_m(mg/g)	References
Bottle guard peel activated carbon	80	This study
$NiFe_2O_4$ Nanoparticles	47	[27]
Eucalyptus bark	52.37	[24]
Activated carbon prepared from rice hulls	160.36	[25]
B-Cyclodextrins/Polyurethane Foam Material	20.17	[26]

4. CONCLUSIONS

Bottle guard peel activated carbon was prepared by impregnation of $Zncl_2$ through chemical activation. The functional groups on the adsorbent are known by FTIR. The percentage removal was observed to increase with increase in adsorbent dosage and contact time but the dye uptake decreases with increase in adsorbent dosage due to the overlapping or aggregation of the active sites. The adsorption process was investigated by employing pseudo-first order, pseudo-second order and intraparticle diffusion rate models. The kinetic studies shows that the adsorption kinetics was more accurately described by pseudo first -order model. The equilibrium isotherm data were in best agreement with Langmuir isotherm model, demonstrating the monolayer adsorption process. This study has shown the potential of bottle guard peel activated carbon as an low cost adsorbent for the removal of colour from solo-chrome black T dye solutions.

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