

KINETICS AND ISOTHERM STUDIES ON CATIONIC DYE (SAFRANIN O) ONTO TREATED FRUIT WASTE

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Abstract: The kinetic studies on the removal of Safranin O by adsorption onto Phosphorous (V) oxy chloride treated fruit waste has been studied in this work. The parameters studied are agitation time, initial dye concentration, adsorbent dose, pH and temperature. The kinetic data were fitted to the pseudo second order, Elovich models. The equilibrium data are fitted to the Langmuir and Freundlich isotherm equations. The adsorption of dye increased with increase in temperature from 302K to 322K indicated the process endothermic and spontaneous. Desorption studies show that adsorption of dye on fruit waste is chemisorption.

Keywords: Adsorption Isotherm, Basic Red 2(Safranin O), Kinetics, Treated Fruit waste.

1. INTRODUCTION

Coloured waters are objectionable on aesthetic grounds for drinking and other agricultural purposes. Wastewater from dyeing industries are released into near by land or rivers without any treatment because the conventional treatment methods are not cost effective in the Indian content. Adsorption is one of the most effective method and activated carbon is the preferred adsorbent widely used. Recognising the economic drawback of dyes, commercial activated carbon[1] many investigators have been studied the feasibility of using inexpensive alternative materials which include almond shells, pinebark, woolwaste, orange peel, lemon peel, jack fruit peel, etc., as carbonaceous precursors for the removal of dyes from wastewater[2].

2. EXPERIMENTAL METHODS

Materials

Waste fruit residues obtained from juice processing industry after the removal of impurities (washed with dil. HCl, distilled water and dried) is mixed with Phosphorous (V) Oxy Chloride in 1:3 ratio boiling with stirring on a water bath for half an hour, cooled, washed with water to remove excess Phosphorous (V) Oxy Chloride and finally dried at 383K for 12 hours in a hot air oven were used as biosorbent for the removal of basic dye. They were ground and sieved to particle size 0.200mm – 0.300mm. The reagents were used were all of analytical grade (AR). All pH measurements were made on Elico pH Meter and colorimetric estimations were carried out on UV-Visible Spectrophotometer(JASCO V750).

A stock solution of dye was prepared using doubly distilled water. Various dye solutions with different initial concentration were prepared by diluting the stock solution. The adsorbate used in this study is Safranin O.

Methods

Characterisation of the adsorbent

Physico chemical characteristics of the prepared adsorbent were studied as per the standard testing methods[3]. The results are reported in Table -1. Infrared Spectroscopy provides information on the chemical structure of the adsorbent. The surface morphology of adsorbents were visualized via Scanning Electron Microscopy(Fig.1).

Batch adsorption experiments

Entire batch mode experiments were carried out by taking 50mL of the dye solution and known amount of the adsorbent in conical flask. The flasks were then agitated at 120rpm for pre-determined time intervals using mechanical shaker at 302K. The adsorbent and adsorbate were separated by centrifugation. Studies on the effects of agitation time, pH, initial concentration of dye solution, adsorbent dose and temperature were carried out by using known amounts of adsorbent.

TABLE 1: Physico chemical characteristics of the adsorbent

Sl. No	Parameter	Value
1	Bulk density g/ml	0.91
2	Specific gravity	0.28
3	Porosity %	69.23
4	Moisture %	9.72
5	Ash %	2.98
6	Volatile matter %	10.00
7	Solubility in water %	0.45
8	Solubility in 0.25M HCl %	2.00
9	pH _{zpc}	5.00
10	Conductivity mS/cm	0.33
11	Decolourising power mg/g	32.56
12	Iodine number mg/g	659.0
13	Surface area m ² /g	310
14	Functional groups	
	Carboxyl group meq/g	0.244
	Phenolic group meq/g	0.310
	Lactonic group meq/g	0.097
15	Yield %	44
16	Particle size	0.200mm-0.300mm

3. RESULTS AND DISCUSSION

Effect of Agitation time and Initial concentration on adsorbate

The results of variation of adsorption of Safranin O with contact time are shown in Fig. 1. The results revealed that, percent adsorption decreased with increase in initial dye concentration, but the actual amount of dye adsorbed per unit mass of the adsorbent increased with increase in dye concentration showing due to that the adsorption is highly dependent on initial concentration of dye [4].

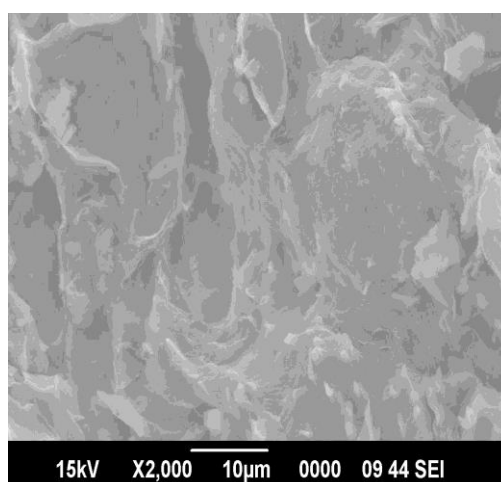


Fig. 1: SEM Photograph of the adsorbent

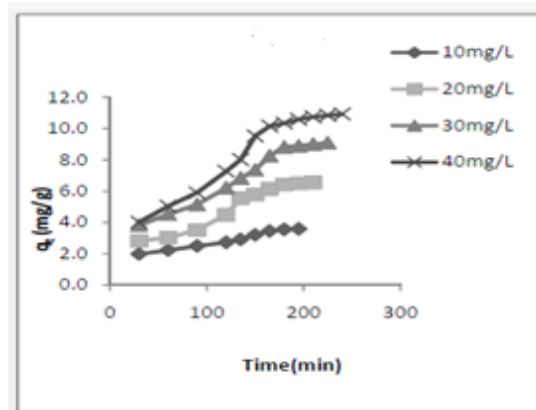


Fig. 2: Effect of agitation time

Effect of Adsorbent Dose

Adsorbent dosage is an important parameter as this factor determines the capacity of an adsorbent for a given initial concentration of the adsorbate. The effect of adsorbent dosage on basic dye removal was studied by keeping all other experimental conditions constant. The results showed that as the adsorbent concentration increased, the amount adsorbed per unit mass of the adsorbent decreased considerably [5] (Fig.3).

Effect of pH

Effect of pH on adsorption of Safranin O was investigated. The results are shown in Fig.4 indicate that the percent removal increased with increase in pH [6].

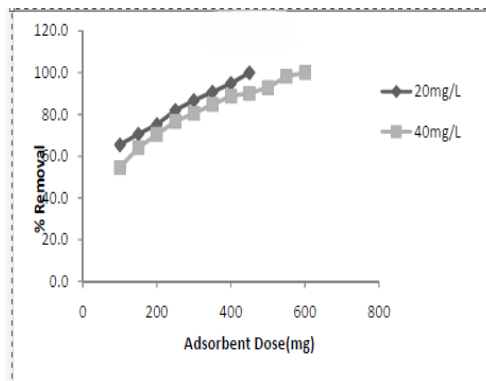


Fig. 3: Effect of Adsorbent Dose

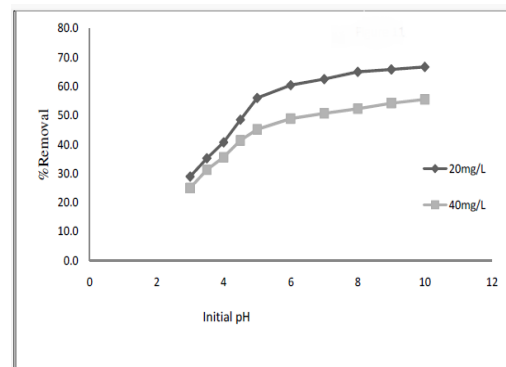


Fig. 4: Effect of pH

Effect of Temperature

Temperature has important effects on the adsorption process. As the temperature increases, the rate of diffusion of adsorbate molecules across the external boundary layer and internal pores of adsorbent particles increases [7].

Adsorption Isotherm

Several mathematical models have been applied for describing equilibrium studies for the removal of pollutants by adsorption on a solid surface. Out of several isotherm equations, the Freundlich and Langmuir isotherm equations have been used most frequently.

Langmuir Isotherm

The Langmuir Isotherm assumes that uptake of dye ions occurs on a homogeneous surface by monolayer adsorption. The Langmuir equation is,

$$C_e/q_e = 1/Q_0b + C_e/Q_0$$

Where

The plot of C_e/q_e Vs C_e for the dye used was linear (Fig.5). The fact that the Langmuir isotherm fits the experimental data very well may indicate a homogeneous distribution of active sites on the adsorbent surface [8].

Freundlich Isotherm

The Freundlich isotherm is an empirical equation used to describe heterogeneous systems and can be expressed as:

$$\log q_e = \log K + 1/n \log C_e$$

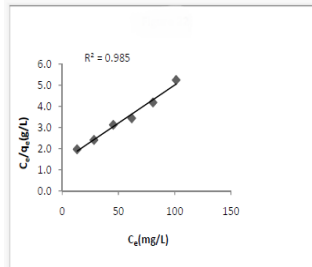


Fig. 5: Langmuir Isotherm

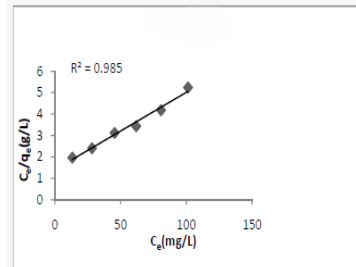


Fig. 6: Freundlich Isotherm

The plot of $\log q_e$ Vs $\log C_e$ gave a straight line showing the adsorption of Safranin O follows Freundlich isotherm [9].

Kinetics of Adsorption

Many kinetic models have been proposed to elucidate the mechanism of solute adsorption. These kinetic models are useful for the design and optimization of effluent treatment process. In order to investigate the mechanism of Safranin O dye adsorption by the adsorbent, the two kinetic models were considered.

Pseudo First Order Kinetic Model

The integrated linear form of pseudo first order kinetic model proposed by Lagergren is,

$$\log(q_e - q) - \log q_e = -k_1 t / 2.303 \dots\dots\dots (1)$$

Where

q_e and q (both in mg/g) are the amounts of dye adsorbed at equilibrium and at time t , respectively, and k_1 is the adsorption rate constant. The plots of $\log(q_e - q)$ versus time t at different temperatures and at different initial concentrations of dye. In this study the experimental data does not fit well with the pseudo first order order equation (1) for the whole range of contact time. The results indicate that the reaction does not follow pseudo first order kinetics.

Pseudo Second Order Kinetics

The adsorption may also be described by pseudo second order kinetic model [10]. The linearised form of the pseudo second order model is,

$$t/q_t = 1/k_2 q_e^2 + t/q_e$$

k_2 – rate constant of second order adsorption (g/mg/min)

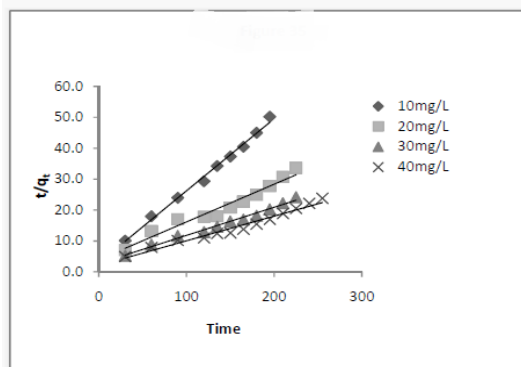


Fig. 7: Pseudo Second Order Kinetics

From the results(Fig.7) it can be suggested that pseudo second order kinetics describes the adsorption of Safranin O by fruit waste much better than pseudo second order kinetic model.

Elovich equation:

The Elovich equation is mainly applicable for chemisorption kinetics. The equation is often valid for systems in which the adsorbing surface is heterogeneous. The Elovich model is generally expressed as

$$dq_t/dt = a \exp(-bq_t)$$

a, b are constants

a – initial adsorption rate(mg/g/min)

b – extent of surface coverage and activation energy for adsorption (g/mg)

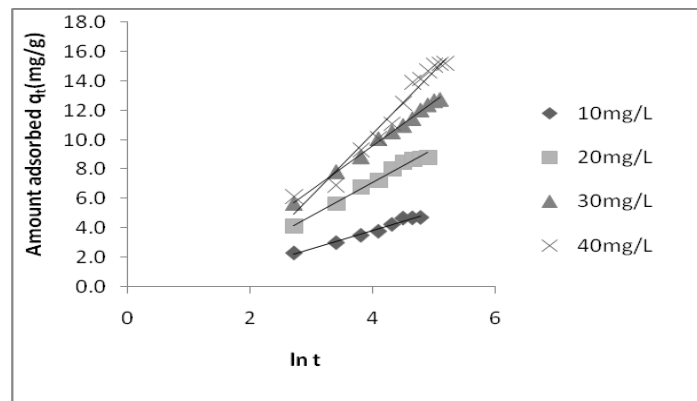


Fig.8 Elovich Model

The plot of q_t versus $\ln t$ gives a linear trace with good correlation coefficient(Fig.8). The results show that adsorption follows pseudo second order kinetics[11] and Elovich kinetic model very well[12].

Thermodynamic Studies

Thermodynamic parameters like ΔH° , ΔS° and ΔG° were evaluated at different temperatures using Van'tHoffs equation¹⁰ (Table-2).

$$\ln K_c = \Delta S^\circ / R - \Delta H^\circ / RT$$

where

K_c is the Langmuir equilibrium constant.

ΔH° and ΔS° are the standard enthalpy and entropy changes of adsorption respectively and these values are calculated from slope and intercept of the linear plot of $\ln K_c$ vs $1/T$. The free energy of this adsorption is calculated using the following expression.

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

The values of K_c increased with increase in temperature indicates the endothermic nature of removal process. The negative standard free energy of adsorption confirms that the adsorption is favourable and spontaneous in nature.

TABLE-2 Effect of Temperature

Dye	- ΔG° K J / mol			K_c			ΔS° J / K / mol	ΔH° KJ / mol
	302 K	312 K	322 K	302 K	312 K	322 K		
Safranin O	11.89	12.25	12.61	0.676	0.757	0.854	38.14	14.26

Desorption studies

Desorption studies with organic acid revealed that the regeneration of adsorbent was not satisfactory, which indicates the chemisorptive nature of adsorption.

4. CONCLUSION

In this work Phosphorous (V) oxy chloride treated fruit waste has been used successfully as an adsorbent for the removal of Safranin O dye from aqueous solution. Adsorption was influenced by various parameters such as initial dye concentration, adsorbent dose, initial pH and temperature. The maximum adsorption of the dye Safranin O occurred at pH value of 6.1. Removal efficiency increased with decreasing the dye concentration, increasing adsorbent dose and increasing the temperature. The Langmuir and Freundlich adsorption isotherm models were used for the description of the adsorption equilibrium of dye onto fruit waste. The data were in good agreement with Langmuir isotherm and Freundlich isotherm. It was shown that the adsorption of basic dye (Safranin O) best fitted with Pseudo second order kinetic model than pseudo first order kinetic model and also supported by Elovich model. The thermodynamic study reveals that the adsorption process is spontaneous in nature, endothermic and increased randomness at the solid solution interface of the dye and adsorbent. Desorption studies reveal that the regeneration of adsorbent was not satisfactory, which shows the chemisorptive nature of adsorption.

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