

Green Method for Amputation of Hazardous Anionic Dye from Waste Water over Silica

C. Kannan and K. Muthu Raja

Manonmaniam Sundaranar University, Tirunelveli-12, Tamilnadu, India

Sathiya

Periyar University, Salem-11, Tamilnadu, India

E-mail: chellapandiankannan@gmail.com

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Abstract: The present paper is aimed to investigate and develop economically cheap physical method for colour removal from wastewater using silica as adsorbent. Silica was successfully utilized for removing a water-soluble anionic dye, Indigo carmine (IC) from wastewater, which will hazardous to the environment. The batch adsorption method was employed for the removal of Indigo Carmine over silica and the influence of various factors such as Contact time, Dye concentration (100-500mg/L), Temperature (303K – 333K) and adsorbent dosage (0.5g – 2.5g) were studied. Adsorption isotherm of Indigo Carmine onto the Silica was determined at room temperature. Equilibrium data were fitted to the Langmuir and Freundlich isotherm models. The adsorption data are applied pseudo-second order kinetics and it found that the pseudo-second order kinetic model is the appropriate model.

Keywords: Adsorption, Indigo Carmine, Silica, Dye removal, Isotherm

1. Introduction

Environmental Pollution (due to hazardous dyes) control is the main concern of society today. 15% of the total production of dyes is lost as dye effluent during dye production and dyeing process¹. These dye molecules are common water pollutants and a very small amount in water is highly visible and can be toxic to aquatic life². In order to solve this environmental problem, physical and chemical processes have been investigated, such as coagulation, flocculation, biosorption, photodecomposition and ultrafiltration³⁻⁶. Among these techniques of dye removal, adsorption process is a procedure of choice for the removal of organic compounds from wastewater⁷. Particularly Indigo Carmine (IC), an anionic dye, could produce serious environmental problems. Various researchers have utilized

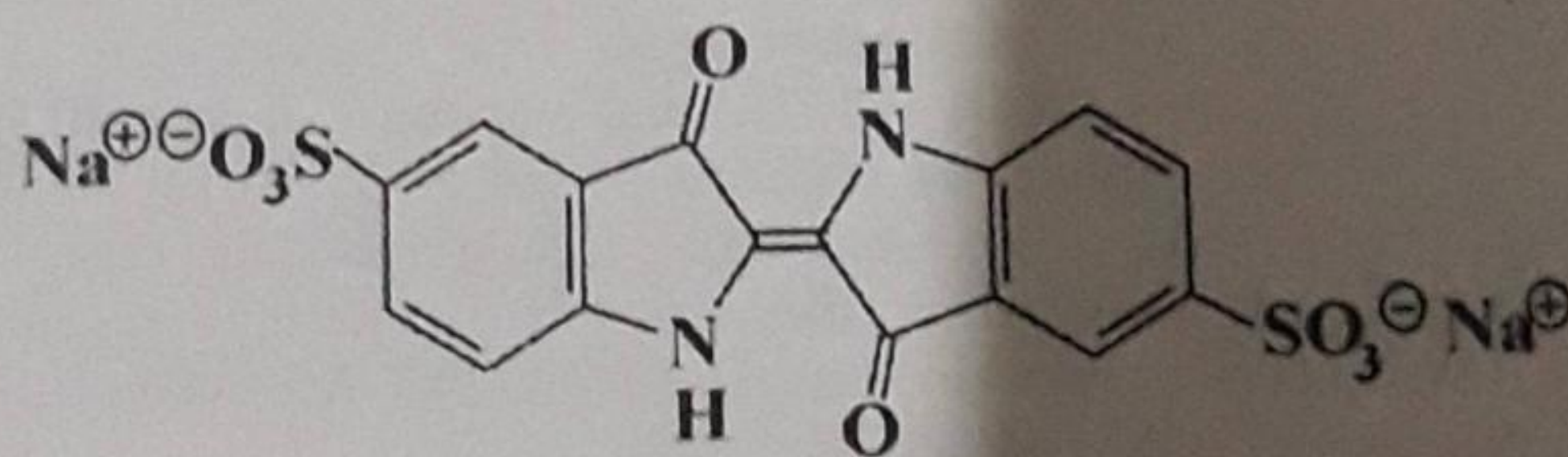
adsorption technique for the removal of toxic IC from wastewater by using various adsorbents like Amino functionalized acrylamide-maleic acid hydrogels⁸, bottom ash, deoiled-soya⁹, Fe-zeolitic tuff¹⁰, Brazil nut shells¹¹, cross-linked chitosan¹², banana pith¹³⁻¹⁴, coir pith¹⁵⁻¹⁶, bagasse pith¹⁷, corn cob¹⁸, sawdust¹⁹, and apple pomace²⁰.

Based on the literature, there are no reports for the removal of IC on Silica by adsorption technique. Hence, this study investigate the removal of IC from aqueous solution by adsorption technique using silica as an adsorbent. Both the kinetics and isotherms of the adsorption of IC are investigated.

2. Materials and Methods

The adsorbent, commercially available silica purchased from Loba chemie is used to remove the hazardous anionic dye. The adsorbate, IC (C.I. 73015, chemical formula: $C_{16}H_8N_2O_8S_2Na_2$, M.W: 466.35; anionic dye) is supplied by Loba Chemie.

The structure of IC is illustrated in Scheme 1.



Scheme 1. Structure of Indigo Carmine dye

2.1. Preparation of stock solution

Stock solution (1000 mg/l) of dye is prepared by dissolving in double-distilled water. Experimental solutions of the desired concentrations are then obtained by successive dilutions with distilled water.

A double beam UV/ VIS spectrophotometer (PerkinElmer, Lambda 25) is used to determine the concentration of dye samples. The silica is characterised by FT-IR spectrum. The FT-IR of the silica is recorded on Jasco FT-IR model Spectrophotometer.

2.2. Adsorption Experiment

Before the adsorption experiment, the adsorbent is activated by heating

in an electric Bunsen at 500°C for 6 hours to remove the physically adsorbed species present on the surface of silica²¹. The silica is added with 50ml of IC dye solution. The solution is agitated (Kemi agitator) at 160 rpm and at the end of the experiment, the solutions concentrations are measured spectrophotometrically. The effect of contact time is studied upto adsorption equilibrium. The adsorption process of IC on silica is studied in the concentration range of 100 – 500 mg/L. The temperature effects of adsorption of IC on silica are studied in the range of $30 - 60^{\circ}\text{C}$. The silica dosage effect is studied in the range of 500 – 2500mg.

3. Results and Discussion

3.1. Characterization of adsorbent

The FT-IR spectrum of silica is shown in the Figure 1. The Si-O-Si asymmetric stretching is observed at 1085 cm^{-1} due to presence of tetrahedral framework of silica and corresponding symmetric stretching is observed at 800 cm^{-1} . The Si-O-Si bending mode is positioned at 466 cm^{-1} . The broad peak at 3443 cm^{-1} is due to uncondensed OH groups and water molecules present in silica²².

This FT-IR spectrum confirmed the tetrahedral framework of SiO_2 .

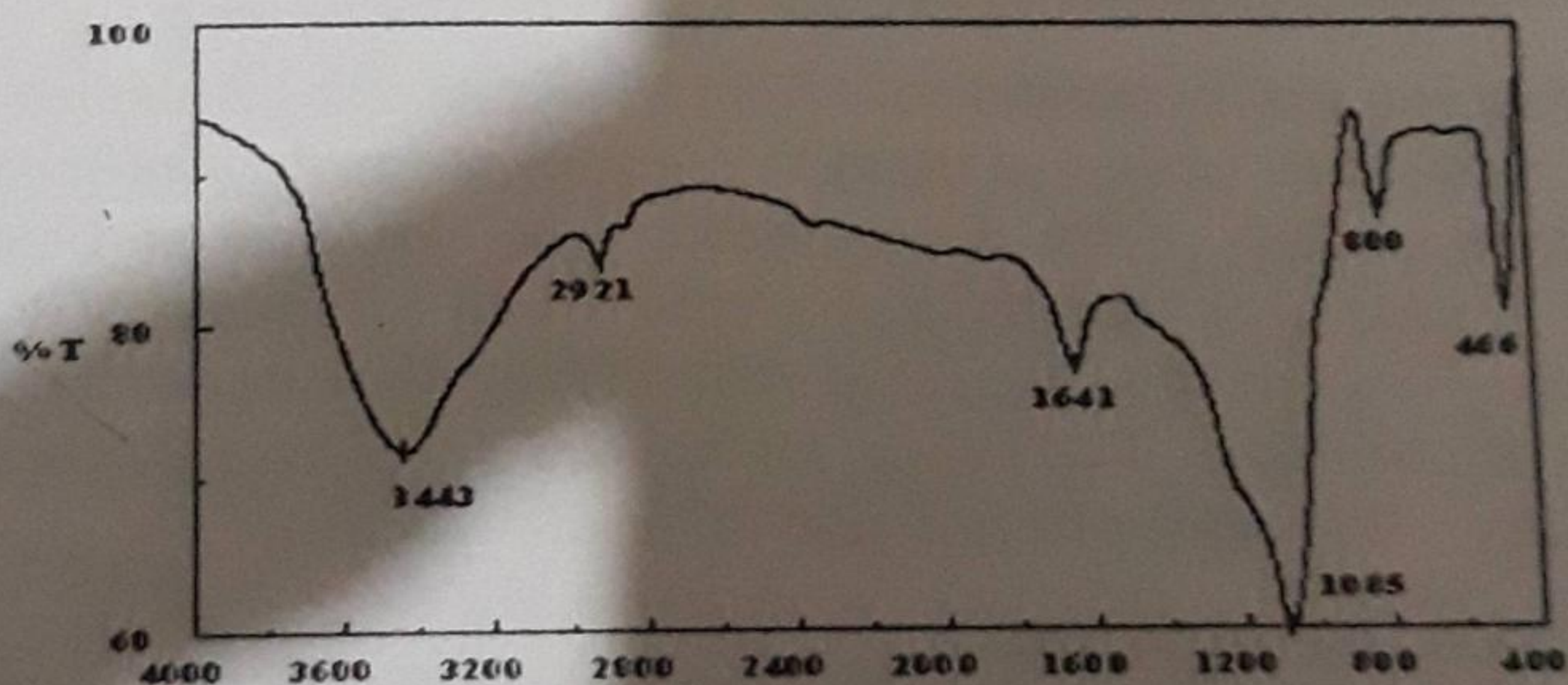


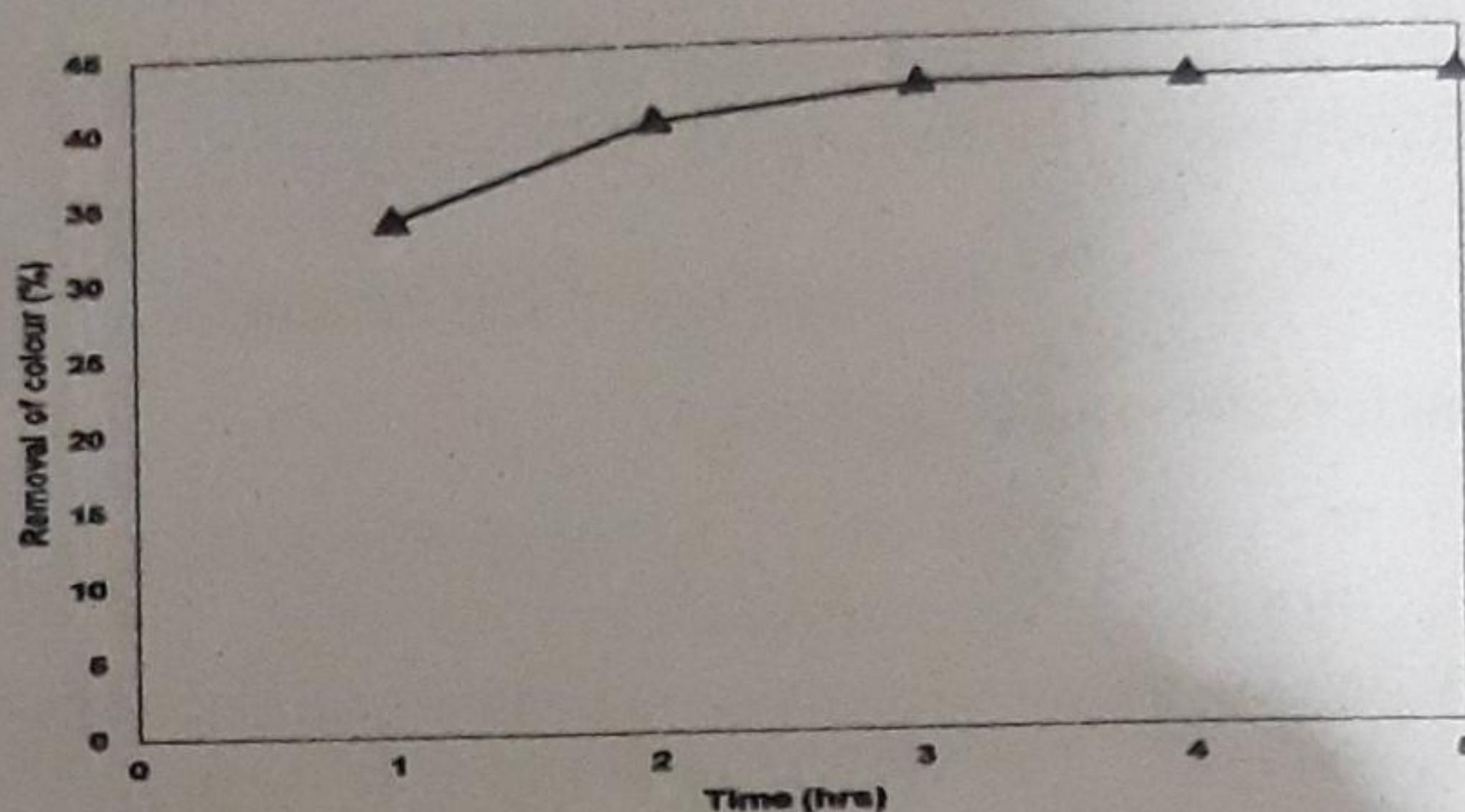
Fig.1. FT-IR spectra of Silica

3.2. Adsorption studies

The effect of adsorption of IC on silica at different parameters such as contact time, concentration, temperature and adsorbent dosage are optimized for maximum adsorption.

3.2.1. Effect of contact time

The effect of contact time is carried out at room temperature for the adsorption of IC on silica is shown in the Figure 2. The maximum adsorption equilibrium is observed at 2 hrs on silica and further increased of contact time not much increased the adsorption.



Temperature- 30°C; Concentration – 100 ppm, Silica dosage-500mg

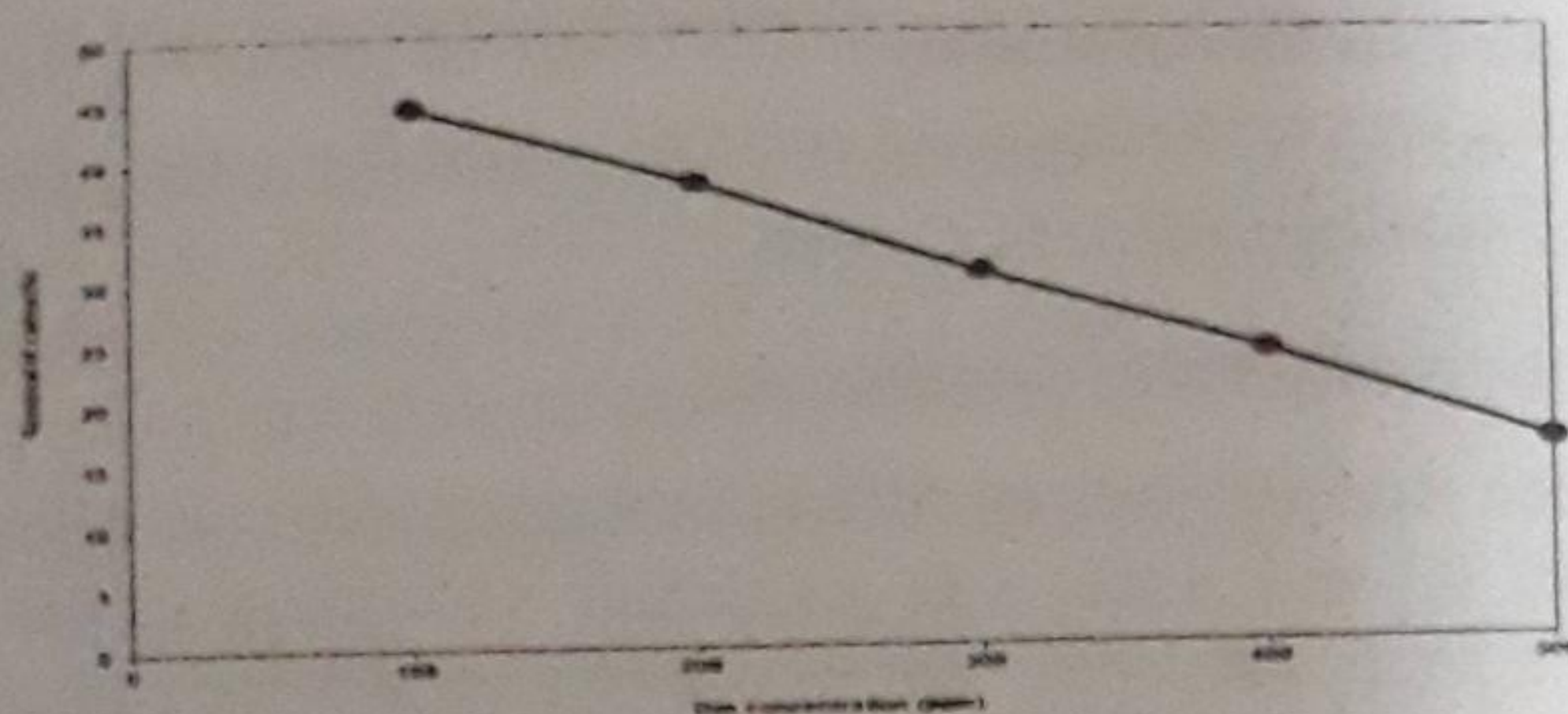
Fig. 2 Effect of contact time for the adsorption of IC on silica

3.2.2. Effect of concentration of dye

The effect of concentration of IC adsorption on silica is studied between the concentration ranges 100ppm - 500ppm at room temperature. The absorption capacity of the dye is found to be maximum at 100ppm and further increased of concentration decreased the adsorption of IC on the adsorbent. The uptake is decreased with increases of concentration may be due to the saturation of adsorbent surface and active sites. Hence, the dye adsorption is decreased with increases of concentration.

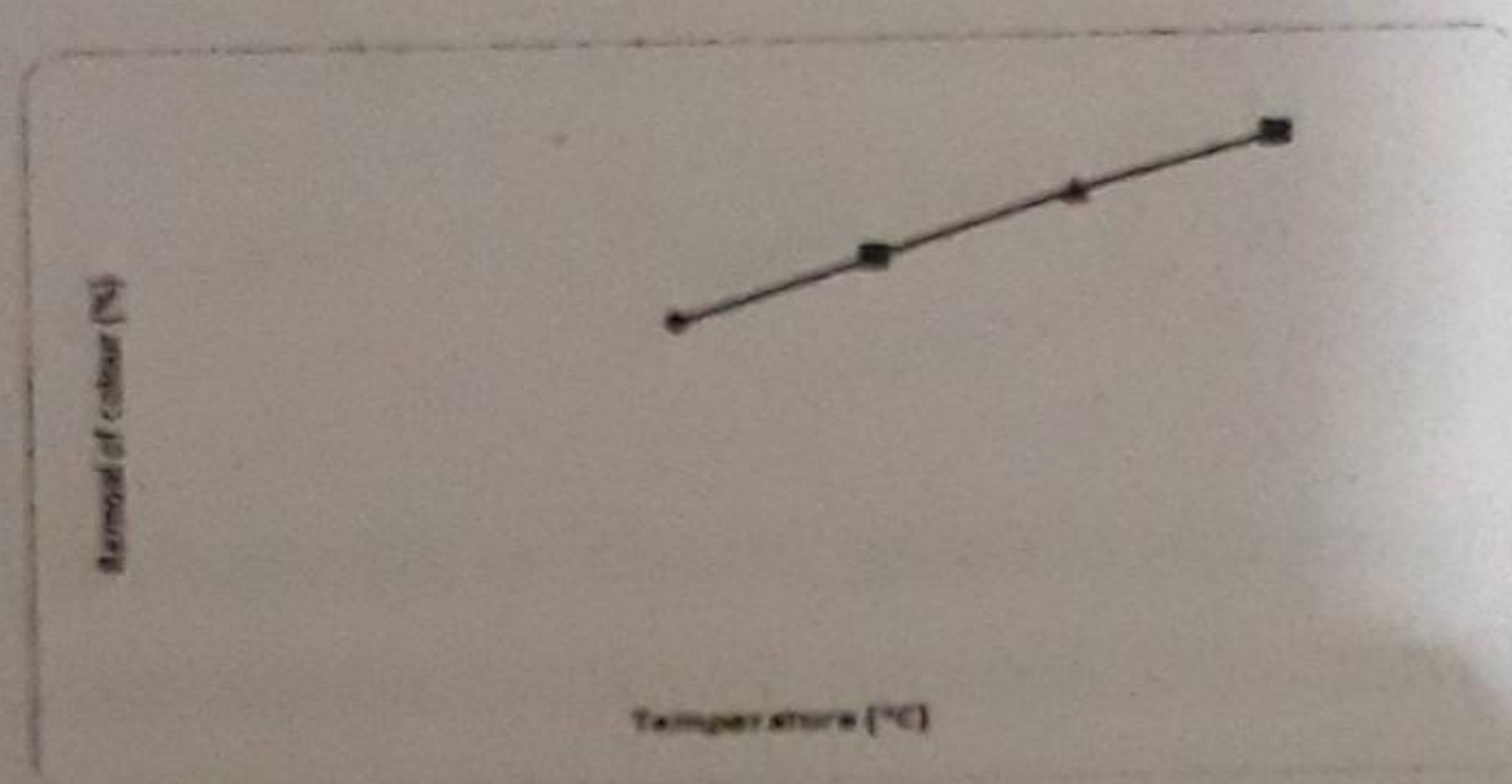
3.2.3. Effect of temperature

The effect of temperature for the removal of IC on silica is studied in the range of 30 to 60°C (Figure 4). In Silica, the adsorption increased with increased of temperature. This may due to increase of interaction between adsorbate and adsorbent ²³.



Temperature- 30°C, Dosage -500mg, Contact time -2 hrs

Fig. 3. Concentration effect of IC adsorption on silica

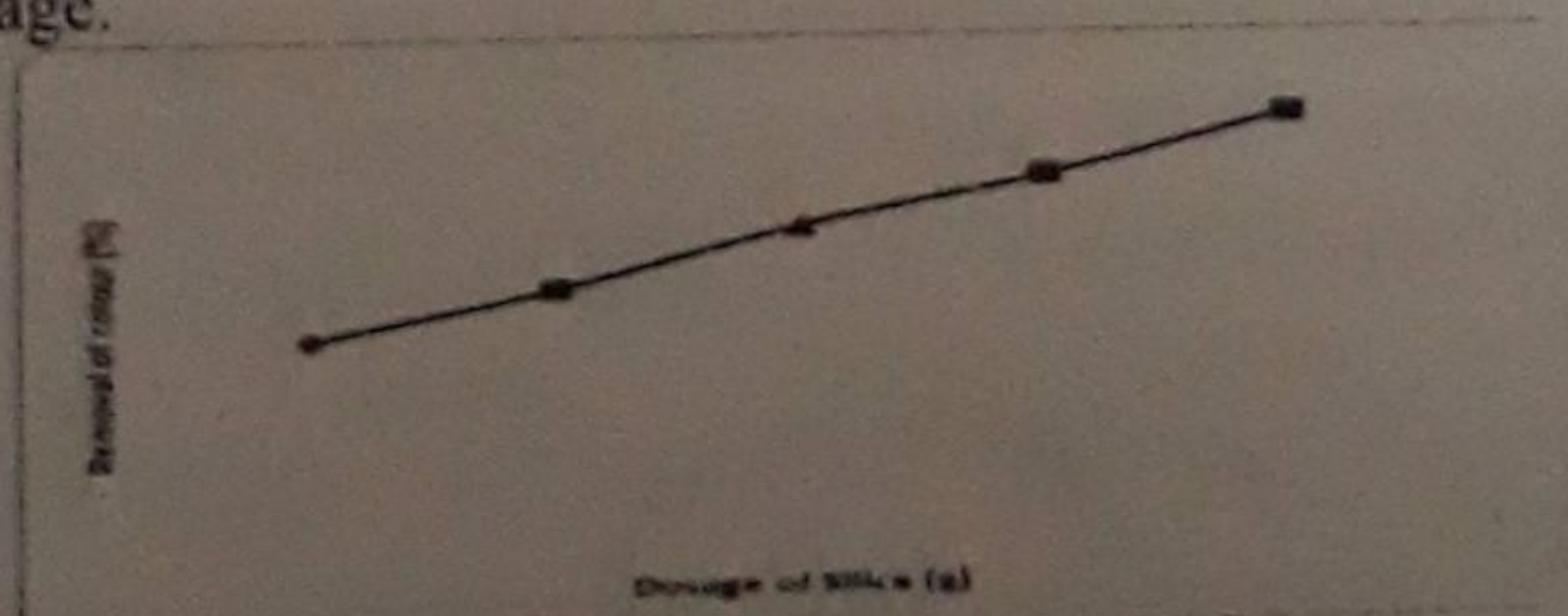


Concentration - 500ppm, Dosage-500mg, Contact time -2 hrs

Fig. 4. Temperature effect of IC adsorption on silica

3.2.4. Effect of adsorbent dosage

The effect of adsorbent dosage (500-2500mg) on adsorption of IC is studied (Figure 5). The percentage removal of the IC is found to be increased with increase of adsorbent dosage. Since the increased of dosage increased the surface area and active sites. Hence, adsorption increased with increased of silica dosage.



Temperature- 30°C, Concentration - 500ppm, Contact time - 2 hrs

Fig. 5. Adsorbent dosage effect for IC adsorption on silica

3.3. Adsorption isotherm studies

The distribution of IC between the adsorbent and solution is determined by Langmuir and Freundlich isotherms.

3.3.1. Langmuir adsorption isotherm

Adsorption isotherm data at different concentrations are measured for the adsorption of IC and fitted with Langmuir adsorption isotherm equation (Fig. 6). This study has been carried out as a model for understanding the monolayer adsorption of IC on silica.

The Langmuir equation is represented as

$$(3.1) \quad \frac{C_e}{Q_e} = \frac{1}{Q_{\max} K_L} + \frac{C_e}{Q_{\max}}$$

where

Q_e is the equilibrium concentration of dyes on the adsorbent (mg g^{-1})

C_e is the equilibrium concentration of dyes in solution (mg L^{-1})

$Q_{\max}$ is the monolayer capacity of Adsorbents and K_L is the Langmuir adsorption constant

The Langmuir constant K_L is a measure of the affinity between adsorbate and adsorbent and $1/K_L$ value gives half maximum adsorption. Plots of C_e/Q_e Vs C_e is a straight line with slope $1/Q_{\max}$ and intercept $1/Q_{\max} K_L$.

The R^2 value for the adsorption of IC on silica is given in the Table-1. The R^2 value is very close to 1, indicated that the adsorption follows the Langmuir adsorption isotherm.

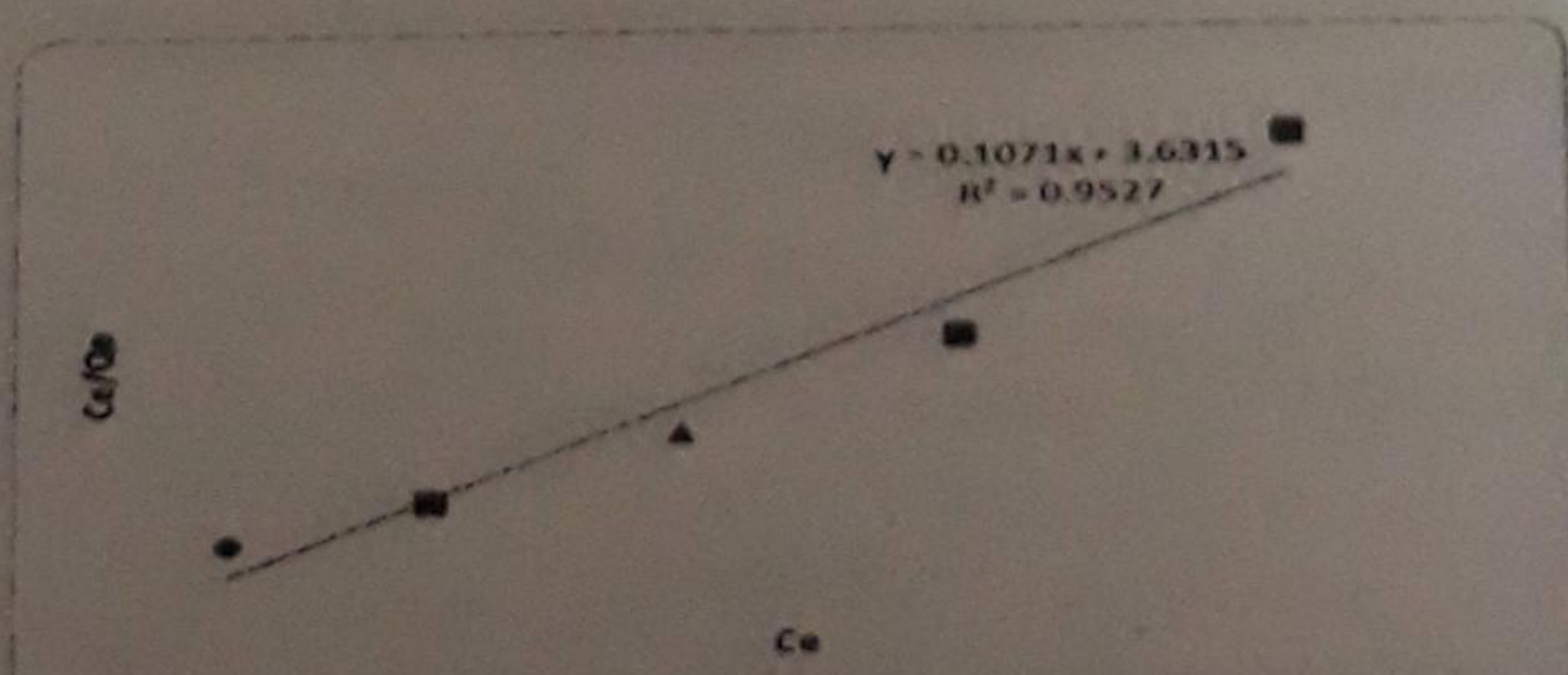


Fig. 6. Langmuir adsorption isotherm for the adsorption of IC on silica

3.3.2. Freundlich adsorption isotherm

The adsorption studies are carried out at various concentrations for the adsorption of IC and the adsorption values are applied to the Freundlich equation to verify the adsorption isotherms (Table 1). This study has been carried out as a model for understanding the multilayer adsorption of IC dye.

The Freundlich equation is represented as

$$(3.2) \quad \ln Q_e = \ln K_F + (1/n) \ln C_e,$$

where K_F and $1/n$ are the Freundlich constants indicate the adsorption capacity and adsorption intensity respectively.

The plot of $\ln Q_e$ Vs $\ln C_e$ gave a straight line (Fig. 7) with the intercept K_F and the slope $1/n$.

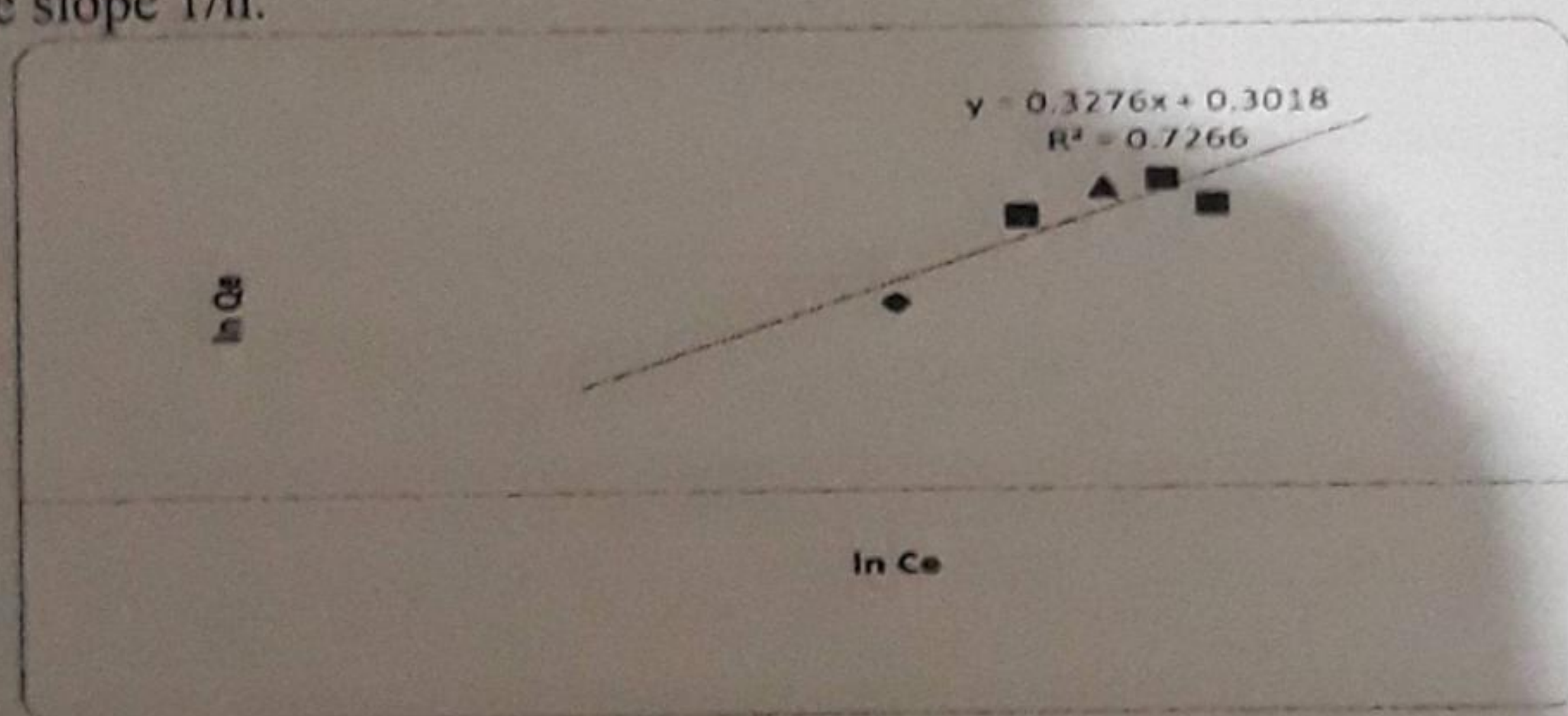


Fig., 7. Freundlich adsorption isotherm for adsorption of IC on silica

The Freundlich constant, n should have values lying in the range of 1 to 10 for classification as favorable adsorption²⁴. A smaller value of $(1/n)$ indicates a stronger bond between adsorbate and adsorbent²⁵. In this study the value of $1/n$ (<1) obtained from the linear plot of $\ln Q_e$ vs $\ln C_e$ indicate that a stronger bond present in between IC and Silica and also the positive ' n ' value (3.0) indicates the process is classified as favourable adsorption.

Table 1. Langmuir and Freundlich adsorption isotherm parameters

S.No	Langmuir isotherm parameters		Freundlich isotherm Parameters	
1.	Q_{max}	9.35	$1/n$	0.327
2.	K_L	0.029	K_F	1.35
3.	R^2	0.952	R^2	0.726

3.4. Adsorption kinetics

The adsorption kinetics of IC on silica is studied as a model study for find out the rate constant of the adsorption. The adsorption of dye is studied at regular time interval at room temperature. The experimental values are introduced in the pseudo second order kinetics equation for calculating rate constant. The equation is

$$(3.3) \quad t/Q_t = 1/kQ_e^2 + 1/Q_e t,$$

where, k is the rate constant, Q_e and Q_t are the amount of dye adsorbed per unit mass of the adsorbent at equilibrium and t is time. The plot of t/Q_t Vs t gives straight lines. Linear plots of the t/Q_t Vs t is given in the Figure 8 for dye adsorption on silica. The linear regression coefficients higher than 0.99 (Table 2) indicated that the adsorption of IC on silica is fitted with the pseudo-second order kinetics.

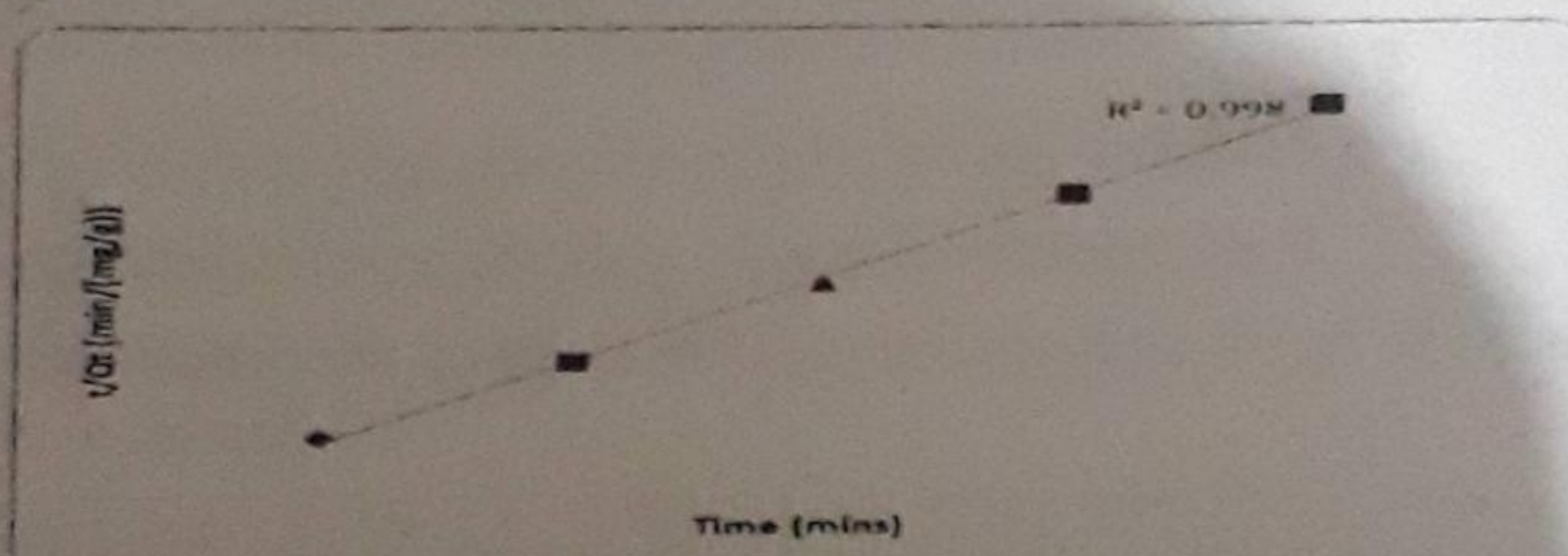


Fig. 8. Psuedo- second order model for the adsorption of IC on silica

Table 2. Kinetics parameters for the adsorption of IC on Silica

$T = 303 \text{ K}, \quad C_0 = 100 \text{ mg/L}$

S.No	Kinetic parameters	Values
1.	K	0.0147
2.	Q_e	4.46
3.	R^2	0.998

Adsorption thermodynamics

The thermodynamic parameters, namely free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) have an important role to determine spontaneity and heat change for the adsorption process. The thermodynamic parameters are calculated using the following relations.

$$(3.4) \quad K_D = \frac{q_e}{C_e},$$

$$(3.5) \quad \Delta G^\circ = -RT \ln K_D,$$

where

K_D is the distribution coefficient of the adsorbate, q_e and C_e are the equilibrium concentration of IC on silica (mg g⁻¹) and in the solution (mg L⁻¹), respectively. R is the universal gas constant (8.314 J/mol K) and T is the temperature (K). ΔH° and ΔS° parameters can be calculated from the slope and intercept of the plot $-\ln K_D$ vs. $1/T$, respectively (Figure 13). From Equation (19), ΔG° is calculated using the equation (3.5) for different temperatures. Results are summarized in Table 3.

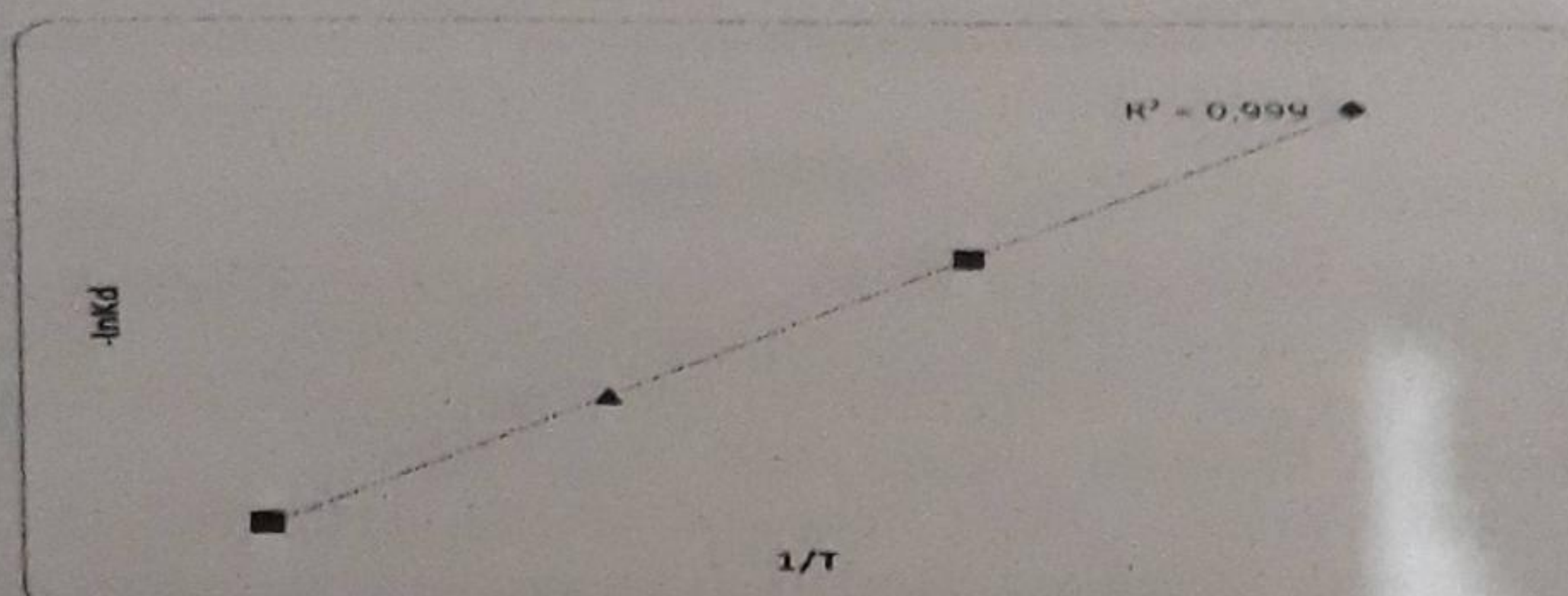


Fig. 9. Plot of $-\ln K_D$ vs. $1/T$ for estimation of thermodynamic parameters

Table 3. Thermodynamic parameters for the adsorption of IC on silica

S.No	Thermodynamic parameters	Values
1.	H° (KJ/mol)	13.210
2.	S° (J/mol K)	12.530
3.	G° (KJ/mol)	
	T=303 K	9.420
	T=313 K	9.286
	T=323 K	9.160
	T=333 K	9.040

ΔG° values at the temperatures of 303, 313, 323 and 333 K are positive. These indicate that the adsorption process is a non-spontaneous process. The positive ΔH° value confirms that the adsorption process is endothermic for IC on Silica. Moreover, the positive value of ΔS° indicates that the degrees of freedom increased at the solid-liquid interface during the adsorption of IC on Silica.

5. Conclusion

This study investigates that the silica is an adsorbent for the removal of IC from aqueous solution. Higher percentage of IC removal by silica is possible provided that the initial concentration of the dye solution is low (100 mg/L). The equilibrium between the adsorbate in the solution and on the adsorbent surface is practically achieved in 2 hrs. Adsorption kinetics is found to follow pseudo second-order rate expression. Equilibrium adsorption data for IC on silica are well represented by the Langmuir and Freundlich isotherm models. Adsorption of IC on silica is favorably influenced by an increase in the temperature of the operation. The adsorption capacities of silica for IC dye were obtained as 9.6, 11, 12.4 and 13.8 mg/g at 293, 303, 313 and 323 K, respectively. This study concludes that from the positive ΔG° value, adsorption of IC on environmentally stable adsorbent silica is non-spontaneous and has less adsorptive property.

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