

**ADSORPTION OF INDIGO CARMINE DYE FROM AN AQUEOUS SOLUTION BY
GROUNDNUT SHELL POWDER: ISOTHERM, KINETIC AND
THERMODYNAMIC ANALYSIS IN BATCH EXPERIMENTAL PROCESS**

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Abstract

The aqueous adsorption of Indigo carmine dye onto groundnut shell powder was investigated. Contact time, initial dye concentration (20–200 mg/L), particle size (53, 75, 105, 125, and 152 m), pH (2.0–8.0), and temperature (283, 293, 303, 313, and 323 K) were all tested. The Langmuir, Freundlich, and Temkin models were used to analyze the equilibrium adsorption data of IC dye on groundnut shells. The highest adsorption capacity (q_m) was discovered to be 14.6842 mg/g. Groundnut shell powder had a reasonable ability to remove the dye. The kinetics of IC dye adsorption closely followed the pseudo-first and second-order rate expressions, demonstrating that intraparticle diffusion is important in the adsorption mechanism. Isotherms have also been used to calculate thermodynamic parameters such as free energy, enthalpy, and adsorption entropy. The fact that the enthalpy change was positive (10.9445 J/mol) indicated that the adsorption was an endothermic process. The results show that groundnut shell powder can be used as an adsorbent material for the adsorption of IC dye from aqueous solutions.

Keywords: Biosorption, Agitation time, sorbent size, pH, concentration, kinetics, and thermodynamics.

2.0 Introduction:

Wastes from textile-related firms are undeniably one of the most significant sources of water contamination and are widely acknowledged as one of the primary causes of environmental imbalance. These effluents have caused acute illnesses such as hypertension, sporadic fever, kidney damage, and cramping in aquatic creatures, which absorb them through the food chain in aquatic organisms [1, 2]. Also, the bioaccumulation of organic and inorganic toxicants is affected by the availability and permanence of toxicants in the aquatic environment, the kind of food chain, and physiological characteristics. As a result, aquatic vertebrates such as fishes and tadpoles have close contact with the aquatic ecosystem via their gills, which are the major organs for respiration, acid-base balance, and ionic and osmoregulation, rendering them

vulnerable to aquatic contaminants. If pollution levels get too high, the function of these organs may induce homeostatic problems, resulting in poor overall life performance of aquatic animals owing to the breakdown of various physiological systems [3, 4]. Pollutants in the water environment have an inhibitory effect on aquatic biota and have a specific impact on the rate of photosynthesis for green biome species. Although synthetic dyes are non-degradable in nature, they are broken down anaerobically in sediment, where hazardous amines are frequently generated [3, 4, 5]. Karthikeyan et al. investigated the impact of textile effluents on *Mastacembelus armatus*, a proteinous edible freshwater fish, by comparing the ionic regulation of some selected tissues (liver, kidney, and muscles) before and after exposure to Acid Blue 92 (C.I. No. 13390) (exposed to sublethal concentrations of Acid Blue 92 for 35 days) [6]. When compared to the variations of the other ions, the magnesium ion concentration increased just marginally. The cationic concentrations of the test subjects revealed that the influence of textile effluents harms the ionic regulations. Soni et al. conducted comparative toxicological research on textile dye wastewater concerning the treatment/nontreatment of freshwater fish (*Gambusia affinis*) [7]. The study found a significant reduction in RBC mortality and cytotoxic effects, as well as a decrease in their numbers and % alterations in their form (poikilocytosis) and variation in their size. As a result, Selvaraj et al. conducted a study to investigate the toxicological and histological effects of textile dyeing industry effluents on teleost fish (*Poecilia reticulata*) [8]. There is a critical need to develop treatment techniques capable of eliminating pollutants from textile waste. Various approaches are used, each with advantages and disadvantages. Their decision is based on effluent characteristics, available technology, and economic considerations. This section describes the use of physical and chemical techniques in the treatment of textile effluents for environmental safety.

2.0 Experimental Procedure

The current study is a batch experiment on the biosorption of IC dye from aqueous solutions onto Groundnut shells waste powder biosorbent.

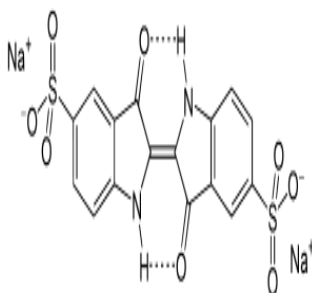
2.1 Structure and properties:

Indigo carmine, also known as 5,5'-indigodisulfonic acid sodium salt, is an organic salt derived from indigo by aromatic sulfonation, which makes the chemical water-soluble. It is safe to use as a food coloring. Its E number is E132. It also serves as a pH indicator. Indigo carmine solutions are commonly used in obstetric surgery to identify amniotic fluid leakage. Intravenous injection of indigo carmine is frequently used in urologic surgery to highlight sections of the urinary system. Indigo Carmine is among the most widely used textile dyeing

agents for the dyeing of polyester fibers and denim. It's an atypical recalcitrant dye and is toxic to human health.



a) Chemical bottle



b) Chemical Structure



c) Sample of Indigo carmine

Fig. 2.1 Indigo Carmine dye

Table – 2.1 properties of dye

Properties	
Chemical formula	$C_{16}H_8N_2Na_2O_8S_2$
IUPAC name	Disodium [2(2') <i>E</i>]-3,3'-dioxo-1,1',3,3'-tetrahydro[2,2'-biindolylidene]-5,5'-disulfonate
Appearance	purple solid
Density	4 g/cm ³
Molar mass	466.36 g/mol
Solubility	10 g/L (25 °C (77 °F))
Wave Length(nm)	289 nm.

2.2 Preparation of the biosorbents

Rajam, Mandal in Srikakulam, Andhra Pradesh, India, was where the Groundnut shells were gathered. The gathered Groundnut shell waste was washed many times with distilled water until the dirt particles were cleaned. Following a thorough washing with distilled water, the biosorbents were sun-dried until crisp, chopped into little pieces, powdered, and sieved. Without any further pretreatments, 53, 75, 105, 125, and 152 μm size powders were utilized as biosorbents in the current investigation.



Fig. 2.2 Biosorbent**2.3 Preparation of IC stock solutions:**

Indigo Carmine dye powder was used to create stock solutions. All of the necessary solutions are made with double distilled water. To make 1000 mg/L IC stock solution, dissolve 1.0 g of IC in 1.0 L of distilled water. Dilutions of this stock solution are used to create samples with varying amounts of IC. Proper dilutions are used to create a 10 mg/L IC solution. In a 1000 ml volumetric flask, 10 ml of 1000 mg/L IC stock solution is taken and brought up to the mark with distilled water. Dye solutions with concentrations of 20 mg/L, 50 mg/L, 100 mg/L, 150 mg/L, and 200 mg/L were produced. The pH of the solution is adjusted by adding the appropriate quantities of 0.1 N HCl and 0.1 N NaOH.

2.4 Dye Adsorption Experiments in Batch

The amount of dye decolorized and the percentage of dye removal were calculated using the equation Dye Removal percent = $(C_o - C_e)/C_o \times 100$.

$$\text{Dye uptake } q_e = (C_o - C_e) V/W$$

Where q_e denotes the amount of dye decolorized at equilibrium, C_o (mg/L) is the initial IC concentration, and C_e (mg/L) is the IC equilibrium concentration. V (L) denotes the volume of the IC solution, and W (g) denotes the weight of the powder.

2.5 Equilibrium Studies

This was done in a batch process by adding a pre-weighed amount of Groundnut shell powder to a known volume of an aqueous solution for a predetermined time interval. The procedures used to assess various parameters such as agitation time, pH, initial concentration of Indigo Carmine in aqueous solution, dosage, and temperature.

2.6 Ultraviolet-Visible Spectroscopy

Various molecules, according to this technique, hold brilliant or clear light. When the light of explicit repeat is passed through the models, the degree of transport light radiation is concluded. As part of the recurrence, this spectrophotometer examination records the force of ingestion (A) or optical thickness ($O.D$). Absorbance is related to the engaging species' way length, L , and concentration, c .

3.0 Results and Discussion

Experimental data are generated in a batch mode of operation to study the effect of various parameters for the removal of IC dye from the aqueous solution using Groundnut shells powder as biosorbent. The effect of various parameters was studied on the biosorption of IC

dye. Various experimental runs are conducted in the present study. In any adsorption study, one of the most important parameters is required to understand the behavior of the adsorption process in the adsorption isotherm. The shape of an isotherm not only provides information about the dye molecules' association with adsorption but also simulates the likely mode for adsorbing dye molecules. The most common method for obtaining an adsorption isotherm is to measure the concentration of the dye solution before and after the adsorption experiments. Several studies have been conducted to determine dye uptake. Experiment data are generated in batch mode to investigate the effect of various parameters on the removal of IC dye from an aqueous solution using Groundnut shell powder as a biosorbent.

3.1 Influence of agitation time

The following discussions are about the effects of various parameters on the biosorption of IC dye by groundnut shell powder. The experiment is carried out over a period ranging from 5 to 180 minutes. The agitation time is plotted against the percent biosorption in Fig. 3.1 and it is found to increase up to 60 minutes. The maximum 67 % biosorption is achieved after 40 minutes of agitation and becomes constant after 60 minutes, indicating the achievement of equilibrium (67 %) [9, 10].

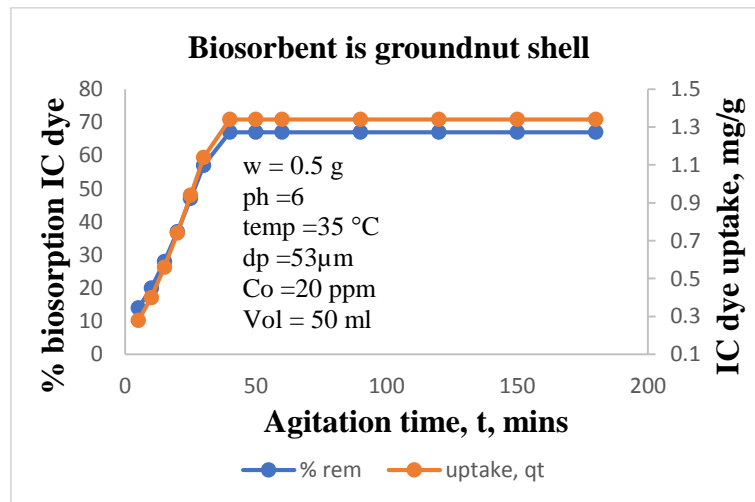


Fig. 3.1. Effect of Agitation time on % biosorption of IC dye

3.2 Influence of biosorbent size:

Figure 3.2 depicts the relationship between particle size and the percentage of IC dye biosorption by groundnut shell powder. The biosorbent size is increased from 53 to 152 μm, while its percentage is reduced from 67 to 47 percent. As the surface area of the biosorbent increases, an additional number of active sites on the biosorbent become available to the biosorbate, and the particle size decreases [11, 12].

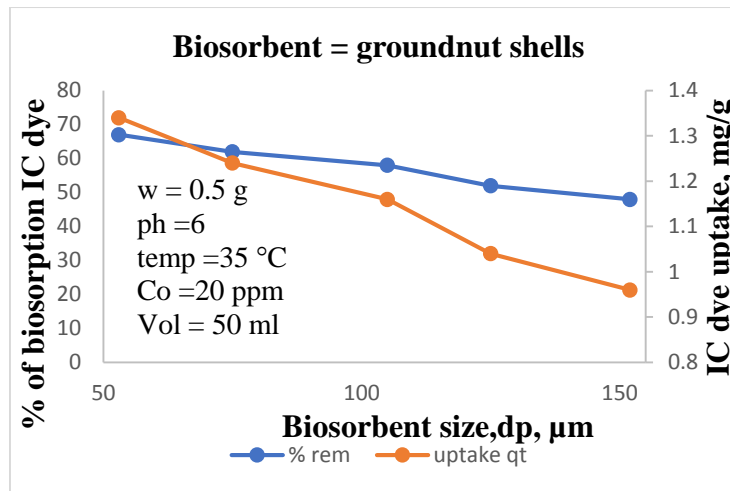


Fig. 3.2 Effect of size on % biosorption of IC dye

3.3 Influence of pH:

Figure 3.3 depicts the effect of aqueous solution pH on the percentage biosorption of IC dye by groundnut shell powder. As the pH rises from 2 to 5, the percent biosorption rises from 61.50 percent to 78 percent, while the pH falls from 6 to 8 and the percent biosorption falls from 72 to 62 percent. The electrostatic interaction of biosorbent and biosorbate is the driving force for dye biosorption. The greater the interaction, the greater the biosorption of dye. The IC dye from groundnut shell powder interacts with H⁺ ions bound to the biosorbent to form part of the surface functional group [13, 14].

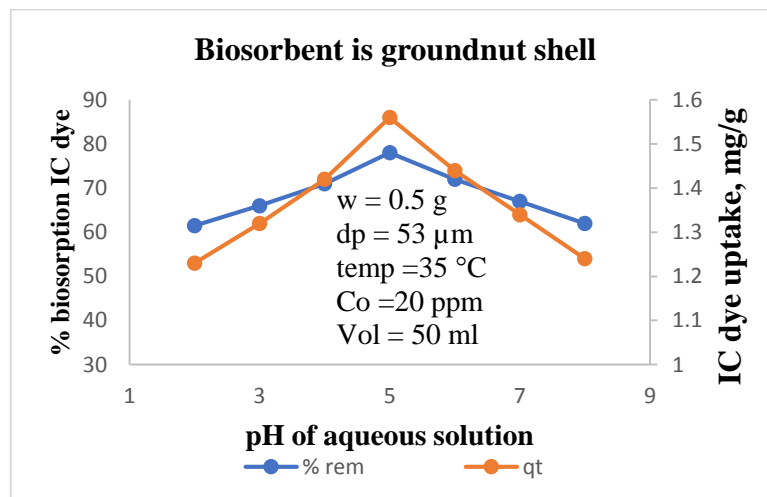


Fig. 3.3 Effect of pH on % biosorption of IC dye

3.4 Influence of initial concentration of IC dye by groundnut shells powder

The graph below depicts the relationship between the initial concentration of IC dye by groundnut shell powder and the percent biosorption of IC dye by groundnut shell powder, which decreases from 78 percent to 52 percent as the initial concentration of IC dye by groundnut shells powder increases from 20 to 200 mg/L. The increase in the amount of

biosorbate can be attributed to the continuous number of freely active sites on the biosorbent, as shown in fig 3.4 [15, 16].

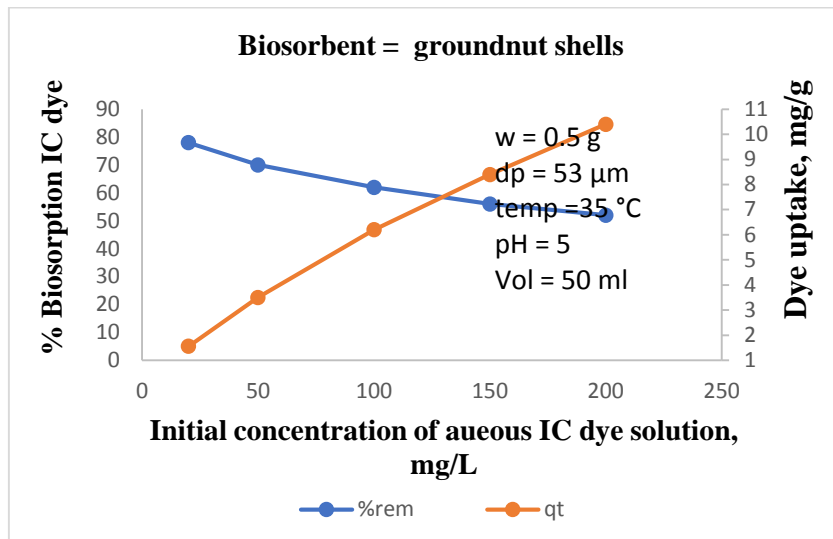


Fig. 3.4 Effect of initial concentration on % biosorption of IC dye

3.5 The Influence of Biosorbent Dosage:

Figure 3.5 depicts the biosorbent dosage and the percent biosorption of IC dye by groundnut shell powder. As the percentage of biosorption increases, so does the dosage of biosorbent. The percent biosorption increases from 78 to 90 percent for a biosorbent size of 53 μm as the dosage increases from 0.5 to 4 gm/L. For dye removal the number of available sites where this behavior is obvious increases with the amount of biosorbent [17, 18].

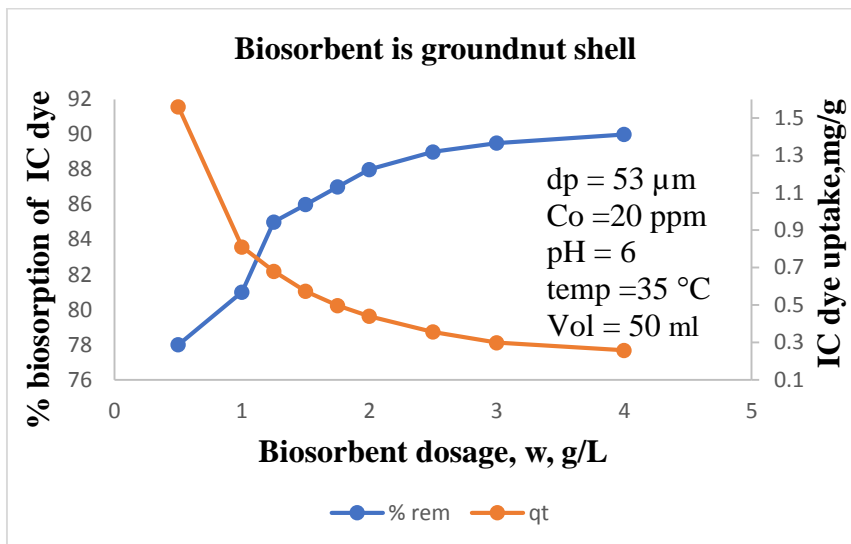


Fig. 3.5 Effect of dosage on % biosorption of IC dye

3.6 Influence of temperature

Especially in the context of the equilibrium dye uptake, the effect of temperature on IC dye biosorption is critical. The effect of temperature changes on IC dye uptake by groundnut

powder dye is shown in fig 3.6. This system is an exothermic process, indicating that the biosorption of dyes and its capacity increased as temperature increased. The temperature varied from 283 to 323 K during the experiment. At higher temperatures, the formation of new active sites may be attributed to the increased penetration of reactive dyes inside micropores. At higher temperatures, the formation of more than one molecular layer on the surface of groundnut shell powder is achieved in the case of IC dye by groundnut shell powder [19, 20].

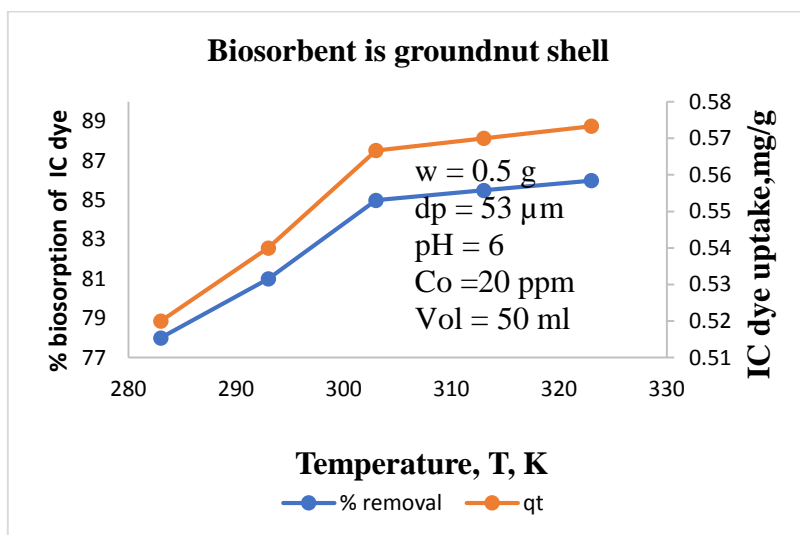


Fig. 3.6 Effect of temperature on % biosorption of IC dye

3.7 Isotherms

3.7.1 Langmuir Isotherm:

For the existing data, the Langmuir isotherm depicted in fig. 3.7, yielded the equation:

$$C_e/q_t = 0.0681C_e + 3.0754, R^2 = 0.9707 \quad \text{----- (3.1)}$$

The correlation coefficient value of 0.9978 indicates that the IC dye is strongly bound to the biosorbent.

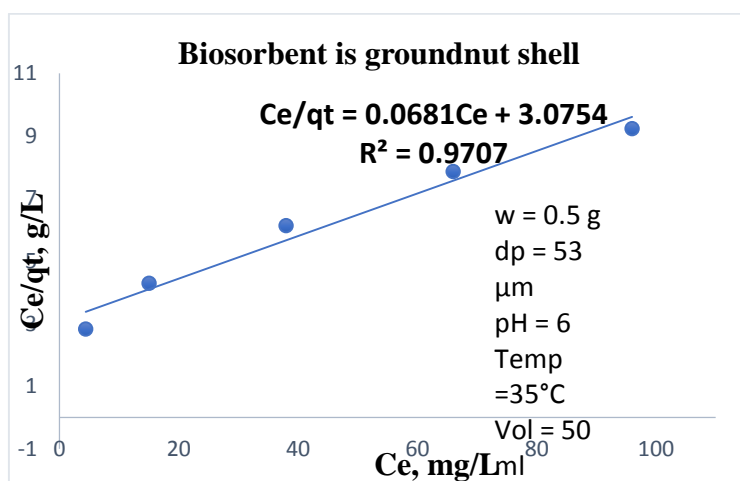


Fig. 3.7. Langmuir isotherm for biosorption of IC dye

3.7.2 Freundlich Isotherm:

The equation follows from Fig. 3.8, which is drawn between $\ln C_e$ and $\ln q_e$:

$$\ln q_e = 0.6153 \ln C_e - 0.4421, R^2 = 0.9988 \text{-----(3.2)}$$

The correlation coefficient of the equation is 0.9988. The 'n' value of 0.705 satisfies the condition of $0 < n < 1$, indicating that biosorption is favorable.

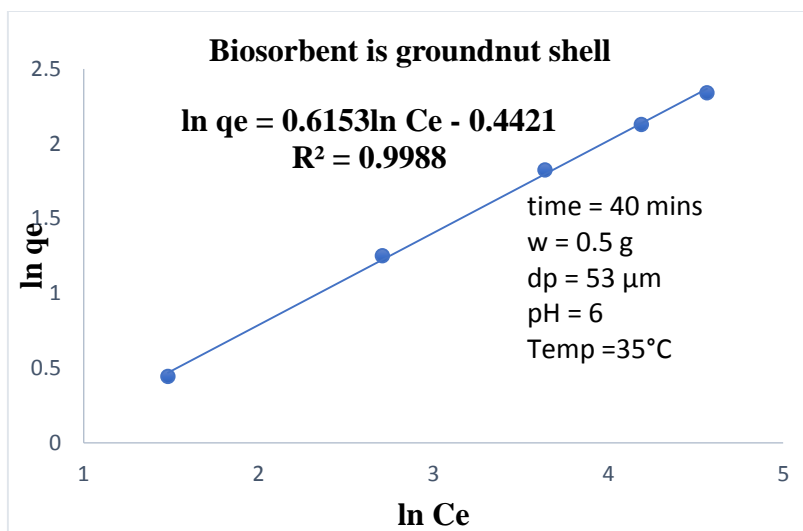


Fig. 3.8 Freundlich isotherm for biosorption of IC dye

3.7.3 Temkin Isotherm:

The existing data are analyzed using the linear form. Figure 3.9 depicts a linear plot of the Temkin isotherm. The obtained equation for IC dye biosorption is:

$$q_t = 2.8116 \ln C_e - 3.3119, R^2 = 0.9525 \text{-----(3.3)}$$

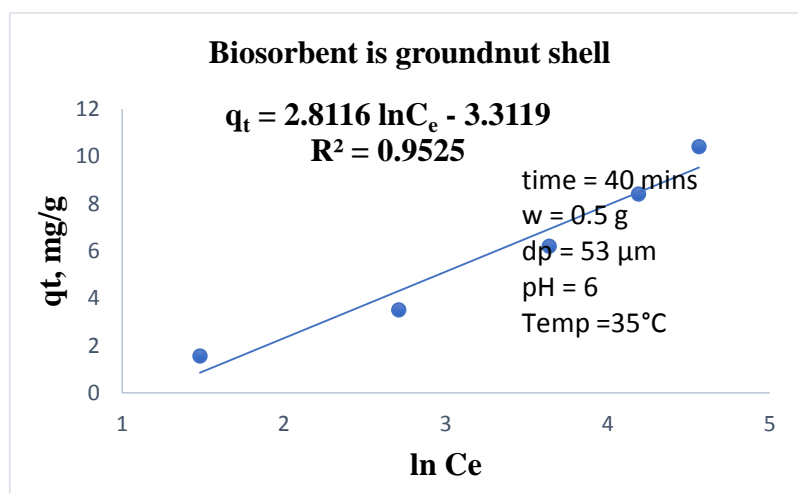


Fig. 3.9 Temkin isotherm for biosorption of IC dye

With a coefficient of correlation is 0.9525. Table-3.1 lists the isotherm constants for the three isotherms. The equilibrium data are well explained by the Langmuir (0.9707), Freundlich (0.9988), and Temkin (0.9525) isotherms [21, 22].

Table – 3.1 Isotherm constants (linear method)

Langmuir isotherm	Freundlich isotherm	Temkin isotherm
$q_m = 14.68429 \text{ mg/g}$	$K_f = 0.642685 \text{ mg/g}$	$AT = 0.3079 \text{ L/mg}$
$K_L = 0.022143$	$n = 0.7050$	$bT = 895.98$
$R^2 = 0.9707$	$R^2 = 0.9988$	$R^2 = 0.9525$

3.8 Kinetics Investigation:

3.8.1 Lagergren first-order rate equation

The experimental data are subjected to tests for the Lagergren first-order rate equation and the pseudo-second-order rate equation. Figure 3.10 depicts a Lagergren plot of $\log(q_e - q_t)$ vs agitation time (t). Rate constant values for first and second-order rate equations are summarised in Table-3.2 [23, 24]. It should be noted that the lagergren first-order rate equation explained the biosorption interactions very well, as evidenced by the high correlation coefficient.

$$\log(q_e - q_t) = - 0.0012 t + 1.0743, R^2 = 0.9994 \quad \text{-----}(3.4)$$

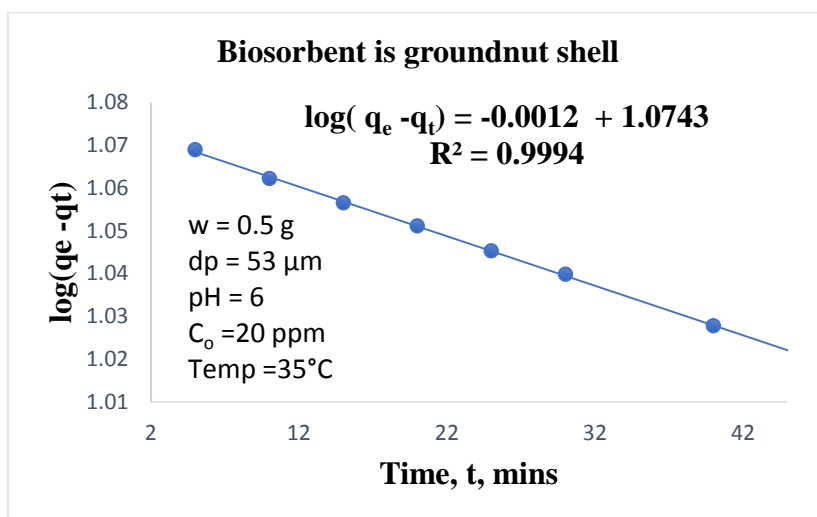


Fig. 3.10 first-order kinetics for % biosorption of IC dye

3.8.2 pseudo-second-order rate equation

Figure 3.11 depicts a pseudo-second-order kinetics plot of 't' vs 't/qt' for IC dye biosorption. The obtained linear regression equation for the pseudo-second-order reaction is shown below.

$$t/qt = 0.3322 t + 18.451, R^2 = 0.8754 \quad \text{-----}(3.5)$$

According to table- 3.2, first-order kinetics fit well for the present investigation.

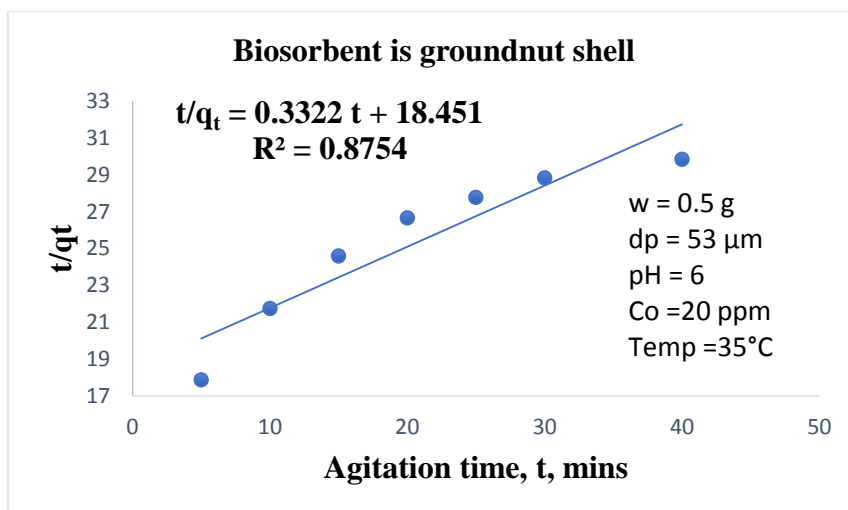


Fig. 3.11 Pseudo Second-order Kinetics for biosorption of IC dye

Table – 3.2 Equations and rate constants

Order	Equation	Rate constant	R ²
Lagergren first order	$\log(q_e - q_t) = - 0.0012 t + 1.0743$	0.0638 min^{-1}	0.9994
Pseudo Second order	$t/q_t = 0.3322 t + 18.451$	$0.0036 \text{ g}/(\text{mg}\cdot\text{min})$	0.8754

The table above shows the Lagergren first order and pseudo-second-order kinetics of rate equations and rate constants.

3.9 Thermodynamic Investigation :

A series of thermodynamic parameters are determined: change in Gibbs free energy (ΔG), change in enthalpy (ΔH), and change in entropy (ΔS). The ΔG value of $- 6435.2 \text{ J/mole}$ indicates that IC dye biosorption by groundnut shell powder could occur spontaneously. Temperature increases have aided biosorption and increased the equilibrium biosorption capacity. Positive ΔH of 10.9445 J/mole indicates that biosorption is endothermic, whereas positive $\Delta S = 21.2743 \text{ J/mole}\cdot\text{K}$ indicates that groundnut powder has an affinity for IC dye [25, 26].

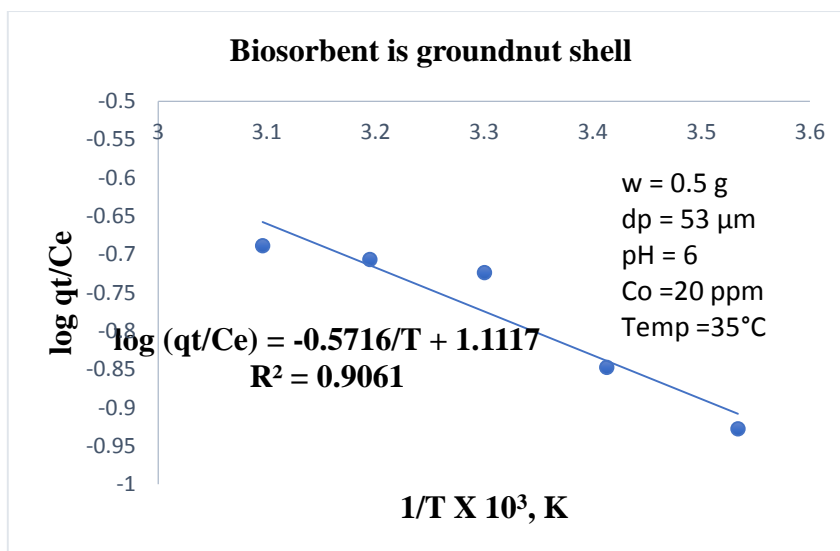


Fig. 3.12 Vant Hoff's plot for biosorption

4.0 CONCLUSIONS

The IC dye biosorption equilibrium agitation time is 40 minutes. With an increase in pH from 2 (61.50 percent) to 5, the percentage of IC dye biosorption from the aqueous solution increases significantly (78.0 percent). The percent biosorption decreases from 72.0 to 62 percent as the pH rises from 6 to 8. 1.25 g or 25 g/L (0.680 mg/g) is the best dosage for biosorption. At 303 K, the maximum uptake capacity of 14.6842 mg/g is achieved. According to the kinetic studies, the decolorization of IC dye is described by both Lagergren first-order ($R^2 = 0.9994$) and pseudo second-order ($R^2 = 0.8754$) kinetics. The experimental data is accurately represented by the Langmuir ($R^2 = 0.9707$), Freundlich ($R^2 = 0.0.9988$), and Temkin ($R^2 = 0.9525$) isotherms. The thermodynamic data show that the % biosorption of IC dye is increased with an increase in temperature. The investigation also reveals the endothermic nature of biosorption as ΔH is positive (10.94451), irreversible nature of biosorption as ΔS is positive (21.27439) and spontaneity of biosorption as indicated by negative ΔG ($\Delta G = -6435.20$ J/mole).

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