Chelonian Conservation And Biology

Vol. 18 No. 2 (2023) | https://www.acgpublishing.com/ | ISSN - 1071-8443

DOI: doi.org/10.18011/2023.11(4).256-276

ADSORPTION OF TARTRAZINE ON POLYANILINE-WATER HYACINTH COMPOSITE

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Abstract

The study focused on the adsorptive elimination of Tartrazine from water based solutions using a Polyaniline-Water Hyacinth nanocomposite. The influence of contact time dye concentration at the start, pH, and dosage of adsorbent on the percentage elimination of Tartrazine dye was examined. Enhance in pH and dosage of adsorbent, along with a reduction in first dye concentration, resulted in higher E102 dye removal. The Polyaniline-Water Hyacinth nanocomposite was prepared and characterized using EDX, XRD, SEM and BET techniques. XRD analysis validated the polycrystalline nature of the prepared Polyaniline-Water Hyacinth nanocomposite. Equilibrium data was collected at different temp (25°C, 45°C, 55°C and 35°C,) and examined utilizing Temkin, Isotherms of Langmuir, Dubinin-Radushkevich and Freundlich. Kinetic data was also examined utilizing second order of pseudo, first order of pseudo, Diffusion of intra particles, and Elovich models. The diffusion of intra particle model revealed a linear connection (R2 = 0.92showing that pore diffusion is a limiting phase in the entire adsorption process. The adsorption process was further investigated at different temp (25°C, 45°C 35°C, and 55°C) to obtain thermodynamic factors for the adsorption system..

Keywords: Adsorption, Tartrazine, Polyaniline-Water Hyacinth (PANI-WH), Nanocomposite.

1. Introduction

The contamination of natural water bodies and industrial effluents by synthetic organic dyes has become a critical environmental issue. The presence of synthetic organic dyes in industrial effluents and natural water bodies is an environmental concern due to their adverse effects on both ecosystems and human health [1]. Tartrazine, a widely used synthetic azo dye, is recognized for its vivid yellow color, making it a popular choice in the food, pharmaceutical, and textile industries. However, this popularity comes at a price: the release of Tartrazine into the environment poses serious challenges. The dye's water solubility, chemical stability, and resistance to conventional treatment processes make it difficult to remove from aqueous systems, leading to

potential pollution concerns. Tartrazine is an anionic azo dye with the molecular formula $C_{16}H_9N_4Na_3O_9S_2$. It is sometimes referred to as E102, FD&C Yellow 5, and Acid Yellow 23. The daily intake for tartrazine is 7.5 mg/Kg of body weight, and the maximum amounts permitted in nonalcoholic and alcoholic beverages are 200 mg/L and 100 mg/L, respectively [2]. It is the most prevalent yellow-orange pigment that is widely utilized in food, clothing, and medicine. Recent research, however, has indicated that tartrazine may have adverse health consequences in people, including migraine, allergy, lupus, asthma, and hyperactivity in children. Overdosing on it can lead to carcinogenicity, reproductive toxicity, neurobehavioral poisoning, and changes in hepatic and renal parameters. In response to these concerns, researchers have been exploring innovative and sustainable methods for the removal of Tartrazine from water. One promising approach is adsorption, a widely recognized and environmentally friendly technique that involves the binding of dye molecules to a solid substrate, typically referred to as an adsorbent. Over the years, various adsorbents, including activated carbons, clay minerals, and metal oxides, have been investigated for their efficiency in removing Tartrazine from aqueous solutions. Nevertheless, there is still room for the development of novel and more sustainable adsorbents [3].

This research aims to address this gap by exploring the adsorption of Tartrazine onto a novel composite material consisting of Polyaniline and Water Hyacinth. This composite material presents a unique combination of organic polymer and natural plant-based material. Polyaniline, a conducting polymer, possesses favorable adsorption characteristics and electrical conductivity, making it an interesting candidate for adsorption studies. Water Hyacinth, on the other hand, is a rapidly growing aquatic plant known for its high biomass production and biodegradable nature. The combined use of Polyaniline and Water Hyacinth in a composite material aims to harness their individual strengths and create an efficient and sustainable adsorbent for Tartrazine removal.

The motivation for this research is driven by several factors including the removal of synthetic dyes like Tartrazine from water bodies is essential to mitigate potential environmental contamination and protect aquatic ecosystems. The use of a natural, renewable, and biodegradable material such as Water Hyacinth in combination with Polyaniline aligns with the principles of sustainability and green chemistry [4]. The composite material offers a unique and potentially more effective approach to dye removal, addressing current limitations of existing adsorbents. The primary objectives of current research are to investigate the adsorption capacity and efficiency of the Polyaniline-Water Hyacinth composite for Tartrazine removal from aqueous solutions, the adsorption mechanisms involved in the interaction between Tartrazine and the composite material, the adsorption process by exploring the influence of various parameters, such as pH, temperature, initial dye concentration, and contact time and evaluate the reusability and stability of the composite material for practical applications.

2. Materials and Reagents

2.1. Preparation and Synthesis of Polyaniline-Water Hyacinth Composite

2.1.1. Polyaniline Synthesis

The synthesis of Polyaniline was carried out following the chemical oxidative polymerization method. Aniline monomer (Sigma-Aldrich, purity ≥ 99%) was used without further purification. Ammonium persulfate (APS) served as the oxidizing agent, and hydrochloric acid (HCl) was used as the dopant. The synthesis was conducted as per established protocols with modifications for the desired properties [4].

2.1.2. Water Hyacinth Preparation

Water Hyacinth plants were harvested from [Location]. The plants were carefully washed to remove any contaminants and debris, followed by air-drying to a constant weight. Dried Water Hyacinth plants were then ground into fine particles using a mechanical grinder to ensure a uniform size distribution. The resulting Water Hyacinth particles were sieved to obtain the desired particle size fraction [5].

2.1.3. Composite Synthesis

The Polyaniline-Water Hyacinth composite was prepared by intimately mixing the synthesized Polyaniline and the prepared Water Hyacinth particles in a specific weight ratio, considering the optimal properties for adsorption. The mixture was homogenized using a mechanical mixer to ensure a uniform distribution of Polyaniline within the Water Hyacinth matrix. The composite material was then dried at [Temperature]°C for [Time] hours to remove moisture and solvent residues. The dried composite material was subsequently crushed into a fine powder to create the final adsorbent material [6].

2.1.4. Adsorbate preparation

A stock solutions of Tartrazine (E102) dyes were synthesized by dissolve 1g of them in 1 L of distilled water to obtain a solution of 1000 mg/L. All studies were carried out by diluting the initial solution with purified water to achieve the desired concentration [8].

2.2. Characterization of the Composite Material

2.2.1. Surface Area and Pore Size Analysis

The specific surface area and pore size distribution of the Polyaniline-Water Hyacinth nano composite were determined using Brunauer-Emmett-Teller (BET) analysis. Nitrogen gas adsorption-desorption isotherms were obtained using a surface area analyzer. The data were used to calculate the specific surface area and pore size distribution [9].

2.2.2. Structural Analysis

2.2.2.1. Fourier-Transform Infrared (FTIR) Spectroscopy: FTIR analysis was performed to examine the functional groups and chemical bonding within the Polyaniline-Water Hyacinth

composite. The composite was ground into a fine powder, mixed with KBr, and pressed into pellets for analysis [10].

2.2.2.2. X-ray Diffraction (XRD): XRD analysis was conducted to investigate the crystallinity and structural properties of the composite. The composite material was ground into a fine powder and analyzed using a diffractometer [10].

2.2.2.3. Scanning Electron Microscopy (SEM): SEM imaging was employed to observe the surface morphology and microstructure of the Polyaniline-Water Hyacinth composite. The samples were sputter-coated with a conductive layer and imaged at various magnifications [10].

2.2.3. Elemental Analysis (EDX)

Energy-dispersive X-ray spectroscopy (EDX) was employed to assess the elemental composition of the Polyaniline-Water Hyacinth composite. EDX analysis was performed concurrently with SEM to provide complementary information about the elemental distribution [11].

2.3. Isotherm Studies

The Freundlich, Langmuir, Temkin, and Dubinin-Radushkevich (D-R) models were used to describe the adsorption mechanism. Additionally, the D-R model was used to improve the adsorption equilibria between the adsorbed dye and the remaining dye in the solution. The isotherms describe the distribution of adsorbate molecules in the solid and liquid phases. Equilibrium tests were conducted using an initial dye concentration range of 10-50 mg/L for tartrazine, together with a known quantity of the adsorbent Polyaniline-Water Hyacinth nanocomposite (0.05-0.3 g) for tartrazine. The experiment involved employing a shaker thermostat set to a temperature of 25 degrees Celsius to agitate the flasks at a frequency of 140 rotations per minute. The ideal pH range (1-12) for both dyes can be maintained by increasing the concentration of sodium hydroxide (0.1 mol/L) or hydrochloric acid (0.1 mol/L) in the solution, respectively. Adsorption isotherms were employed to analyze the equilibrium adsorption behavior of Tartrazine onto the Polyaniline-Water Hyacinth composite. Equilibrium studies were conducted by contacting the composite material with Tartrazine solutions of varying initial concentrations under controlled conditions [12].

2.3.1. Langmuir Isotherm: The Langmuir isotherm model was used to describe the monolayer adsorption of Tartrazine onto the composite material. The linear form of the Langmuir equation was used to determine the maximum adsorption capacity and the Langmuir adsorption equilibrium constant.

2.3.2. Freundlich Isotherm: The Freundlich isotherm model was employed to describe the heterogeneous adsorption behavior of Tartrazine on the composite. The Freundlich equation was linearized to estimate the Freundlich constants.

2.3.3. Temkin Isotherm: The Temkin isotherm model was applied to describe the interaction between Tartrazine molecules and the composite material. The linear form of the Temkin equation was used to determine the Temkin constants.

2.3.4. Dubinin-Radushkevich (D-R) Isotherm: The D-R isotherm model was used to ascertain the adsorption mechanism and energy distribution of Tartrazine on the composite material. The D-R equation was employed to estimate the mean free energy of adsorption.

2.4. Adsorption Parameters

The goal of this research was to examine the adsorbing activity of the Polyaniline-Water Hyacinth nano composite by conducting adsorption experiments on Tartrazine from water based solution. The study looked at the effects of contact time, quantity of adsorbent, starting dye concentration, and pH on the process of adsorption. In all experimental trials, the starting concentration of tartrazine ranged from 10 to 50 mg/L. A predetermined quantity of PANI-WH nanocomposite adsorbent, namely 0.05 to 0.3 g for tartrazine, was added to a set of Erlenmeyer flasks, each with a volume of 100 mL. The flasks were affixed to a shaker thermostat and agitated at a rotational speed of 140 revolutions per minute (rpm) at a temperature of 25°C. The pH of the solution was controlled at the required level for both dyes, ranging from 2 to 12, by the addition of either sodium hydroxide (0.1 M) and hydrochloric acid (0.1 M). At regular intervals, a flask was recovered and the nanocomposite particles were methodically extracted from the solution using filtering using glass filter paper. The amount of dye adsorbed on the PANI-WH nanocomposite was determined by measuring the absorbance of the leftover dye in the filtrate at the maximum wavelengths of 427 nm for tartrazine [11]. The following equations were used to calculate the percentage of dye removal and the amounts of dye adsorbed at time t (qt) and at equilibrium (qe). The average particle size (D) of the selected samples can be determined using the Scherrer equation provided below.

Removal % =

$$= \frac{Co-Ct \times 100}{Co}$$

$$Qt = \frac{(Co-Ct)\ V}{M}$$

$$Qe = \frac{(Co-Ce)\ V}{M}$$

where “Co” is the starting concentration, Ct is the concentration over time, and Ce is the amount at the dyes' equilibrium. “V”, (L) is the volume of the working solution, and “M” is the mass (g) of the composite

2.4.1. Effect of pH

The pH of the Tartrazine solution was adjusted to various levels (1-12) using appropriate acid (0.1 M HCl) and base (0.1M NaOH) solutions. The effect of pH on the adsorption capacity and

efficiency was investigated by equilibrating the composite material with Tartrazine solutions at different pH values [9].

2.4.2. Initial Adsorbate Concentration

A series of Tartrazine solutions with varying initial concentrations (10 to 50 mg/L) were prepared to investigate the effect of the initial concentration on adsorption. The composite material was contacted with these solutions under constant conditions [8].

2.4.3. Adsorbent Dosage

Different quantities of the Polyaniline-Water Hyacinth composite material (0.05 to 0.3 g) were added to Tartrazine solutions of fixed initial concentration to explore the influence of adsorbent dosage on adsorption efficiency.

2.4.4. Contact Time

The influence of contact time on the adsorption process was studied by allowing the composite material to equilibrate with Tartrazine solutions for various time intervals (10-80min).

2.5. Adsorption kinetics

The study of the rate at which adsorption occurs (Adsorption kinetics). Kinetic experiments pertaining to adsorption are commonly conducted in order to ascertain the duration required for the adsorbate to reach its maximal adsorbing capacity on the adsorbent. The phenomenon can alternatively be characterized as the rate at which the solute is removed, which dictates the duration of the sorbate's presence at the solid-solution interface. Kinetic experiments are conducted in a batch setting, wherein a range of parameters are varied. These factors include temperatures, agitation speeds, particle size, pH values, as well as different types of sorbent and sorbate materials. Linear regression is utilized to determine the optimal equation that best fits kinetic rate data, including models such as first order of pseudo, second order of pseudo, Elovich, and diffusion kinetics [11]. The utilization of pseudo second order and pseudo first order kinetic models is highly appropriate for investigating the kinetics of adsorption. The liquid/solid adsorption process can be broken down into three distinct steps. The first step involves the transfer of mass through the outermost border layer of liquid that surrounds the particle, also known as outside diffusion or film diffusion. The 2nd step involves the adsorptive and desorptive of molecules between the active sites on the solid surface and the adsorbate, following the principles of the mass action. The third step involves the diffusion of adsorbate molecules towards an adsorption site, which can occur via a pore diffusion process within the liquid-filled pores or by means of a solid surface diffusion process, known as intra-particle diffusion. The kinetic adsorption process is often governed by either intra-particle diffusion or liquid film diffusion, while the mass action mechanism, associated with rapid physical adsorption, is deemed insignificant. The study investigated the kinetic

parameters of E102 dye adsorption onto a PANI-WH material, with an adsorbent dose of 0.3 and an initial dye concentration of 20 mg/L.

3. Results and Discussion

3.1. Characterization of Polyaniline-Water Hyacinth Nanocomposite

We use different techniques such as SEM, EDX, XRD and BET.

3.1.1. Field Emission Scanning Electron Microscope Analysis

Structural study of the Polyaniline-Water Hyacinth nanocomposite was done by FESEM. This was recorded using ZEISS Gemini SEM Germany Instrument. The fibrous nature of polyaniline, with an average length of about 800nm, indicates that the material possesses favorable characteristics as a nanofiber and holds potential for further use in many applications. The statement suggests that the composite material exhibits a significant degree of microporosity, which in turn enhances the interfacial area between the liquid and solid phases. This increased interfacial area facilitates the insertion and extraction of ions, hence promoting a high reaction rate [36]. The images presented in Figure depict the SEM observations of Polyaniline-Water Hyacinth nanocomposite at varying levels of magnification.

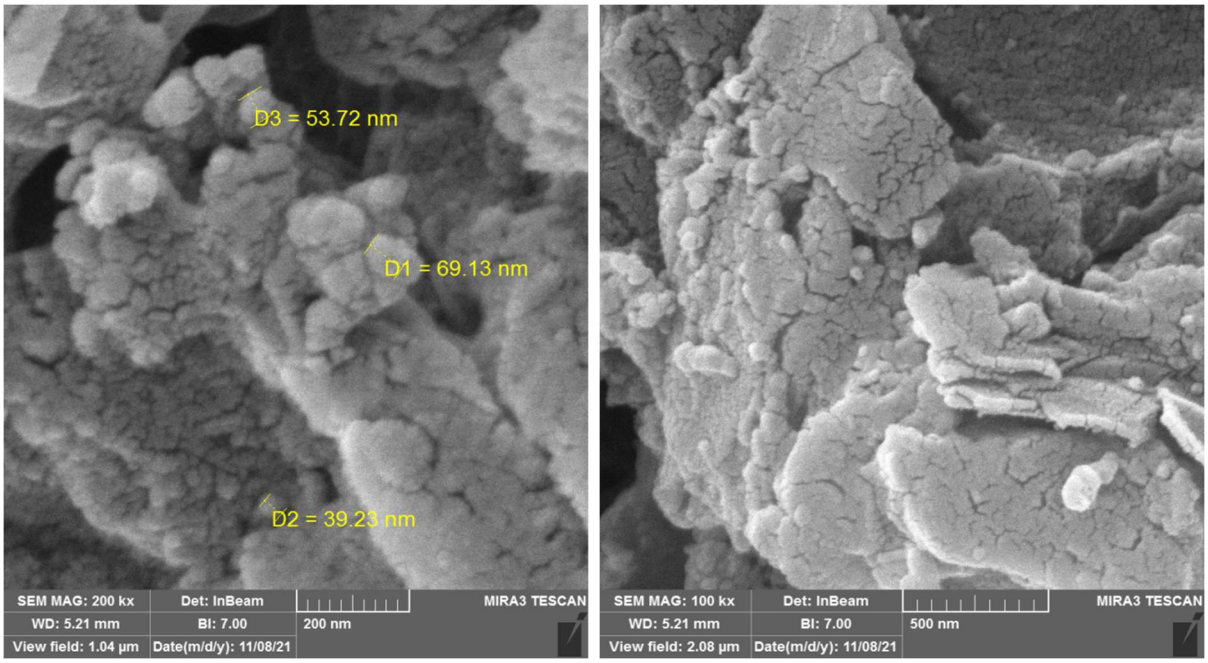


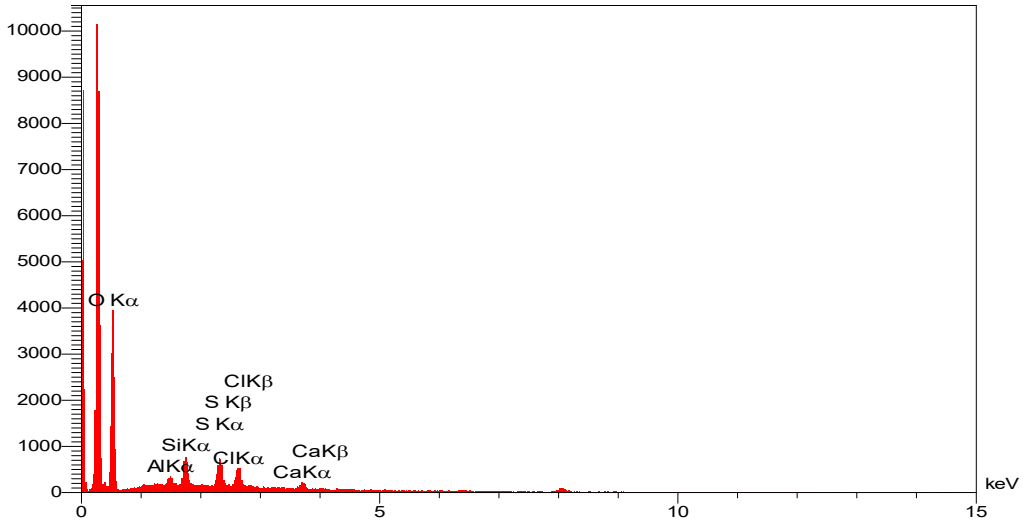
Figure 1: SEM images of Polyaniline-Water Hyacinth nanocomposite at different magnifications

3.1.2. Energy Dispersive X-ray Analysis

The elemental composition of Polyaniline-Water Hyacinth nanocomposite material was determined by EDX and their results are Element and W% is C- 51.57, O-38.13, Al- 1.28, Si- 2.76,

S- 2.74, Cl- 2.38, Ca - 1.14. In the EDX spectra of PANI/PC peaks appeared in the region of 0-5 Kev which correspond to the binding energies of O, N, C, Cl and S respectively.

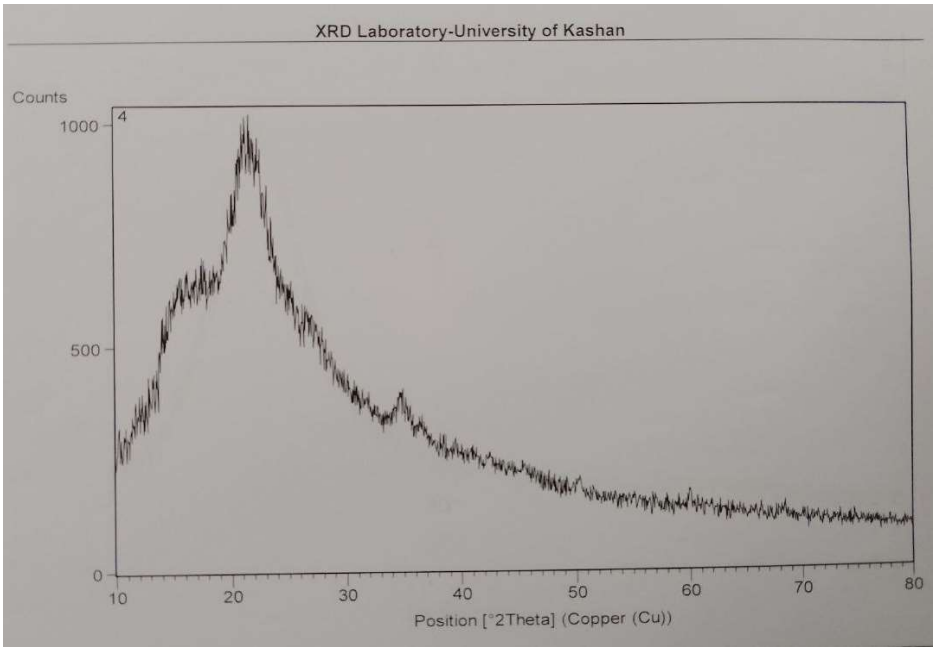
Figure 2: Energy-dispersive-X-ray analysis of PANI-WH.



3.1.3. X-Ray Diffraction (XRD) Analysis

Because of the presence of benzenoid and quinonoid groups in the polyaniline-polycardonate nanoparticle, the polymer is semi-crystalline in form. The XRD analysis of a Polyaniline-Water Hyacinth nanocomposite is depicted in Fig 3.

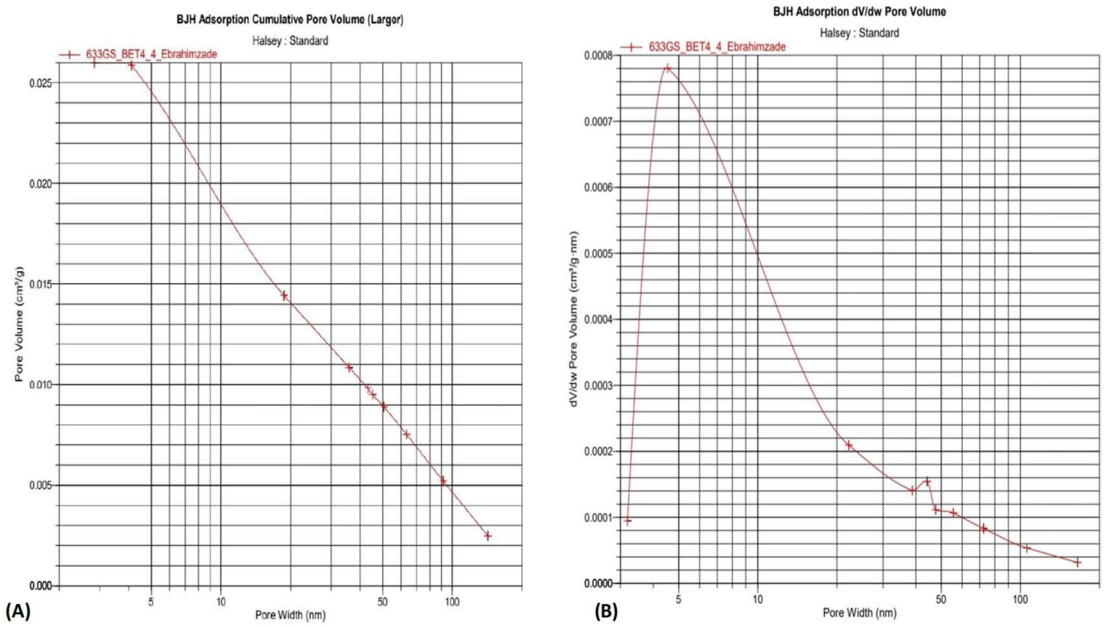
Figure 3: represents pattern of XRD related to PANI-WH



3.1.4. Brunauer-Emmet-Teller analysis (BET) Analysis

We use BJH isotherm to calculate the volume of pores using adsorption-desorption nitrogen at 77 K and relative pressure .The specific surface area according BET isotherm is 1.7 m^2/g and pore size is 43.83 and 48.122 nm using adsorption-desorption nitrogen at 77 Kand relative pressure up to saturation 0.99.

Figure 4: Pore size distribution curve of PANI – WH. (A) Adsorption (B) Desorption



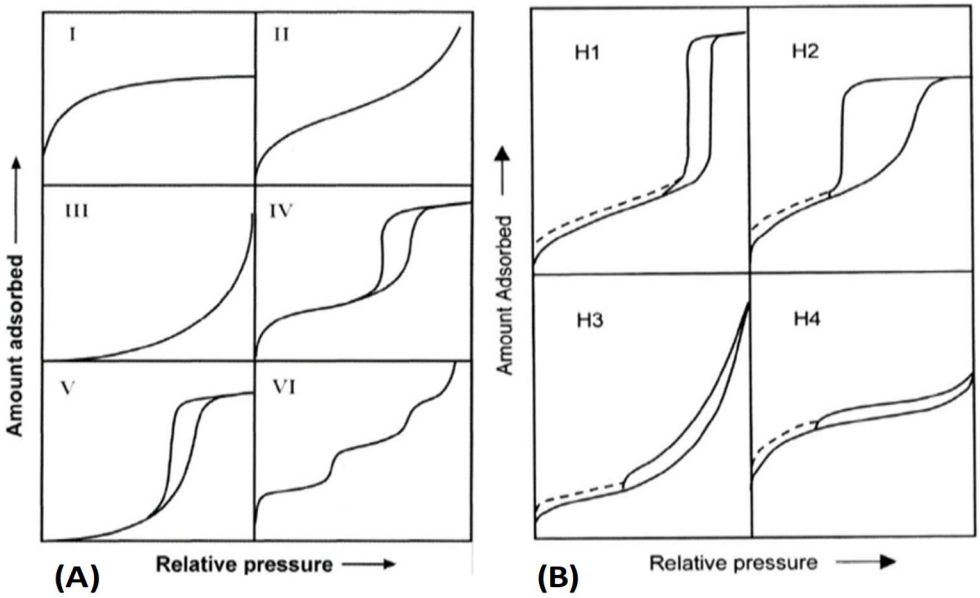


Figure 5: IUPAC report (A) Classification of adsorption isotherms (B) classification hysteresis loops

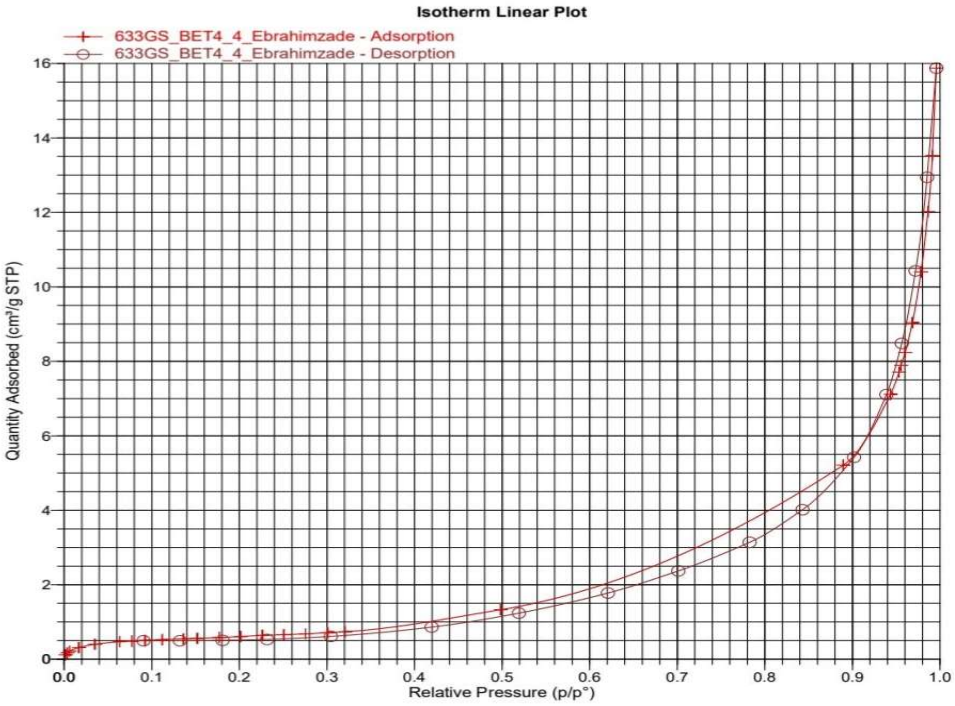


Figure 6: represents Nitrogen adsorption-desorption isotherm for PANI-WH

3.2. Batch Adsorption Studies

3.2.1. Effect of Contact Time

Outcome of contact time on adsorption of tartrazine(E102) by polyaniline-water hyacinth nano composite were studied at 25℃ , pH 7 ,adsorbent dosage 0.3g ,initial E102 dye concentration 20 mg/L and agitation speed 140 rpm. It can be clearly seen from % removal values in table 3.2 that by cumulative the contact time from 10 min to 80 minutes the %adsorption of E102 dye on polyaniline-water hyacinth nano composite increases 24.0% to 78.75%.

Table 1: Effect of contact time on adsorption of tartarzine by polyaniline-water hyacinth nano composite

Time (min)	Tartrazine dye removal %
10	24.0
20	44.4
30	65.7
40	68.0
50	70.0
60	72.8
70	75.0
80	77.0

90	78.75

3.2.2. Effect of pH

The determination of the pH of the dye solution is a crucial factor in the process of eliminating dyes from aqueous solutions. The adsorptive intake of Tartrazine molecules can be significantly influenced by the pH, as it has an impact on the surface voltages of the adsorbent. Effect of pH on adsorption of E102 by polyaniline-water hyacinth nano composite were studied at 25℃,adsorbent dosage 0.3 g, initial E102 concentration 20 mg/L and agitation speed 140 rpm. It can be clearly seen from fig. 3.12 % removal graph that by increasing the pH from 1 to 12 the %adsorption of E102 dye on polyaniline-water hyacinth nano composite decreases 88.75% to 16.95%.

Table 2: Effect of pH on adsorption of E102 by polyaniline-water hyacinth nano composite.

pH	E102 dye removal %
1	88.75
2	89
3	88.8
4	88.76
5	88.6
6	88.54
7	72.58
8	44.5
9	32.6
10	29.2
11	24.3
12	22.3
13	16.95

3.2.3. Effect of Adsorbent Dosage

Effect of adsorbent dosage on adsorption of E102 by polyaniline-water hyacinth nano composite were studied at 25℃, pH 2,initial E102 dye concentration 20 mg/L and agitation speed 140 rpm .It can be clearly seen from figure 3.14% removal graph that by increasing the adsorbent dosage from 0.1 to 0.4g the %adsorption of E102 dye on PANI-PAN nanocomposite increases from 62.6% to 89.5%. Figure: Effect of adsorbent dosage on adsorption of E102 by polyaniline-water hyacinth nano composite

Table 3: Effect of adsorbent dosage on adsorption of E102 on polyaniline-water hyacinth nano composite

Adsorbent dosage (g/100 ML)	E102 dye removal %
0.1	62.6
0.2	73.6
0.3	89.2
0.4	89.5

3.2.4. Effect of Initial Concentration

Effect of initial E102 dye concentrations on adsorption of E102 by polyaniline-water hyacinth nano composite were studied at 25, pH 2, adsorbent dosage 0.3g, agitation speed 140 rpm for 90 minutes. It can be clearly seen from fig. 3.16% removal graph that by increasing the adsorbent dosage from 10 to 50mg/L the %adsorption of E102 dye on polyaniline-water hyacinth nano composite decreases from 96.7% to 48.46%.

Table 4: Effect of initial E102 dye concentration on adsorption of E102 by polyaniline-water hyacinth nano composite

E102 Conc.	E102 dye removal %
10	96.7
20	91.25
30	69.0
40	56.25
50	48.46

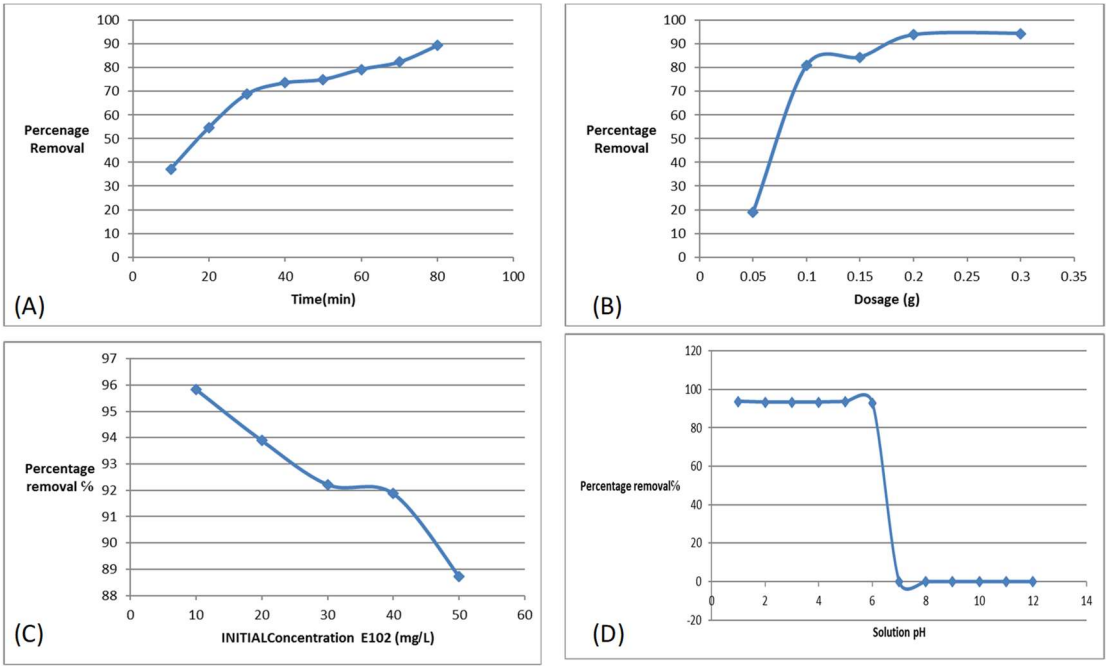


Figure 6: Effect of contact time on tartrazine (20 mg/L 100 ml) adsorption onto PANI-WH (0.1 g) at 298 K, pH 7, rpm 140 (B) Effect of polyaniline- water hyacinth dosage on tartrazine dye removal. (C) Effect of initial concentration on adsorption of tartrazine onto PANI – WH (0.2 g) nanocomposite (D) Effect PH on the adsorption E102 onto polyaniline-water hyacinth nano composite.

3.3. Adsorption Isotherms Studies

Adsorption isotherms characterize the equilibrium distribution and interaction of dye molecules within the adsorbent [15]. They establish connections between the adsorption capacity and the remaining concentration of the adsorbate under constant temperature conditions. In this study, the equilibrium data was analyzed using four different isotherm models: Langmuir, Freundlich, Dubinin–Radushkevich (D–R), and Temkin isotherms.

3.3.1. Langmuir model

The concept of Langmuir is based on the premise that the absorption area is uniform, with all sites being equal, resulting in monolayer adsorption with little interactions between dye molecules. Based on these assumptions, the Langmuir isotherm was developed, can be expressed as follows:

$$Qe = \frac{qoK_LCe}{1+K_LCe}$$

Where qe (mg/g)-dye adsorb at equilibrium, qo (mg/g)-adsorption capacity, Ce-sorbate amount at equilibriumqe(mg/L), and KL - Langmuir constant are all present. Figures illustrate the Langmuir isotherm graphs for E102 dye.

3.3.2. Freundlich adsorption

The Freundlich adsorption model is widely utilized for dye sorption and assumes a heterogeneous surface of the adsorbent, allowing for multilayer adsorption. It can be represented as follows:

$$Qe = K_FCe^{1/n}$$

Where K_F- Fruendlich constant ($mg^{1-1/n}L^{1/n}g^{-1}$) the parameter "n" is an empirical value associated with adsorption intensity, while the bonding energy is another relevant factor. Figure illustrate the Freundlich isotherm graphs for E102 dye [16].

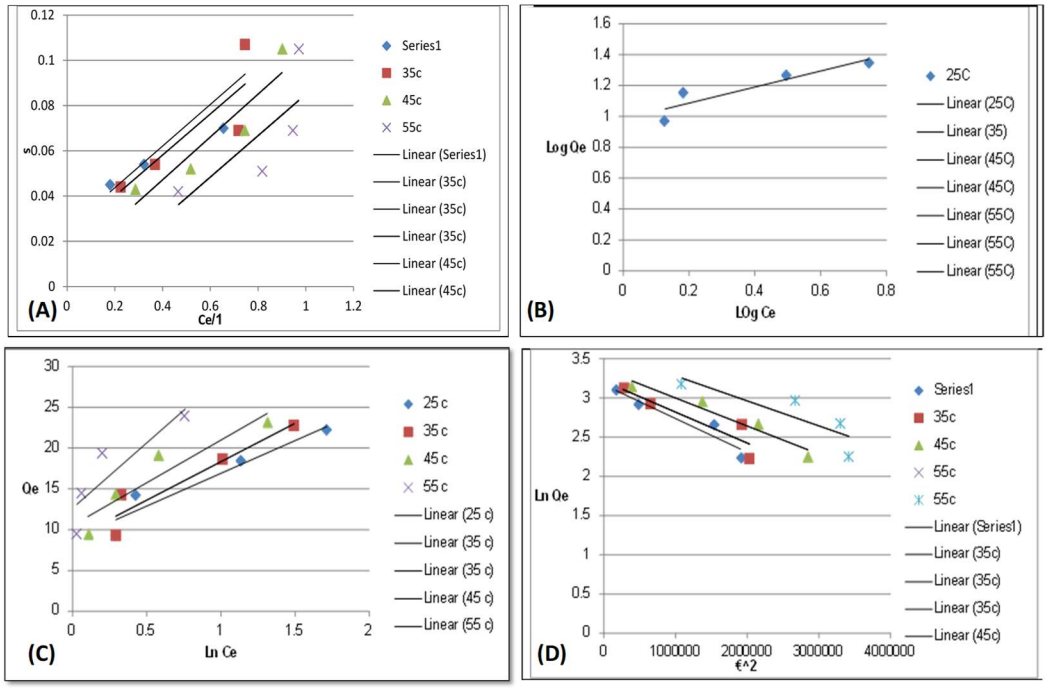


Figure 7: (A) Langmuir isotherm for adsorption of E102 on polyaniline incorporating hyacinth water (B) Freundlich isotherm for adsorption of E102 on polyaniline incorporating hyacinth water (C) Tempkin isotherm for adsorption of E102 on polyanaline incorporating hyacinth water (D) D-R isotherm for adsorption of E102 on polyaniline incorporating hyacinth water

3.3.3. Temkin model

The investigation of adsorption equilibria also involved the study of the Temkin model. Unlike the previous two models, the Temkin model considers the influence of indirect connections between the molecules that adsorb and adsorbate, which are associated with the adsorption free energy [17]. This relationship can be show as follows:

$$qe = R_T \ln (K_T Ce)/b_T$$

Where KT is the equilibrium binding constant proportional to the maximal binding energy (l/mg) and bT is the Temkin isotherm constant proportional to the heat of adsorption (g kJ mg-1 mol-1).Figure shows Temkin isotherm graph for both E102 dye.

3.3.4. Dubinin–Radushkevich (D–R)

The D-R isotherm is used to distinguish between chemical and physical adsorption processes. Originally derived for sub-critical vapor adsorption on Surfaces that are energetically variable in microporous solids, it has become a commonly employed equation to describe the adsorption techniques equilibria of organic matter within porous materials [18]. The representation of the D-R isotherm is as follows:

qe = qsexp(-Bϵ)

whereby "qs" is the potential capacity for saturating (mg/g), "B" denotes the D-R constant (kJ2/mol2), and is the capacity Polanyi the stable Є and B are calculated utilizing:

Є=RTln[1+1/Ce]
E = 1/^2B

Table 5: Comparison of the coefficients and isotherm parameters for adsorption of E102(20-50 mg/L) onto composite of polyaniline-hyacinth water.

Isotherm Model	Isotherm Parameter		Temperature		
		25°C	35°C	45°C	55°C
Langmuir	Q_m(mg/g)	39 .526	45.662	45.455	92 539
	K_L(L/mg)	0.275	0.242	0.233	0.118
	R_L	0.5	0.5	0.5	0.5
	R^2	0.8141	0.7225	0.8616	0.82
Freundlich	K_f	9.6	9.835	10.774	12.388
	n	1.928	1.658	1.535	1.056
	R^2	0.84	0.7728	0.79	0.65
Tempkin	A_T	3.038	2.568	2.742	2.208
	B_T	8.0148	9.4399	10.447	15.97
	b_T	309.125	271.265	253.073	170.757
	R^2	0.9162	0.8918	0.88	0.7643
D-R	Qm(mg/g)	24.682	24.886	28.68	36.522
	$K_{D-R} \times 10^{-7\ mol}2^{\ J}$--2	4	4	4	3
	E(KJ/mol)	1.12	1.12	1.12	1.29
	R^2	0.9076	0.8255	0.9368	0.85

3.4. Adsorption Kinetics Studies

The study of adsorption kinetics plays a crucial role in the process design as it governs how quickly the adsorbent captures substances. Moreover, by conducting kinetic studies, we can explore the procedure that governs the absorption onto the polyaniline-hyacinth water material and identify the step that limits the rate [19]. To analyze the experimental data, three kinetic models were utilized: the pseudo-first order model, the pseudo-second order model, and the intraparticle diffusion model based on the Elovich equation.

3.4.1. Pseudo-First Order

Based on solid capacity the pseudo first order equation, is given below:

log (qe - qt) = log qe - k_1/2:303 t

where the equilibrium adsorption capacity (mg/g) is represented by "qe", and the adsorption capacity at time "t" (mg/g) is denoted by "qt", and $k_1$is the pseudo-first order rate constant (min^{-1})[37]. Figure 3.26: Pseudo First order for adsorption of E102 on polyaniline-hyacinth water nanocomposite can be seen.

3.4.2. Pseudo-Second Order

The pseudo-second order model is represented by as:

$t/qt = 1/ k_2qe^2 + 1/qe\ t$

where k_2 is the rate constant of pseudo-second order adsorption (g/ mg min)[37]. Pseudo second kinetics for adsorption of E102 on polyaniline-hyacinth water nanocomposite can be seen in figure.

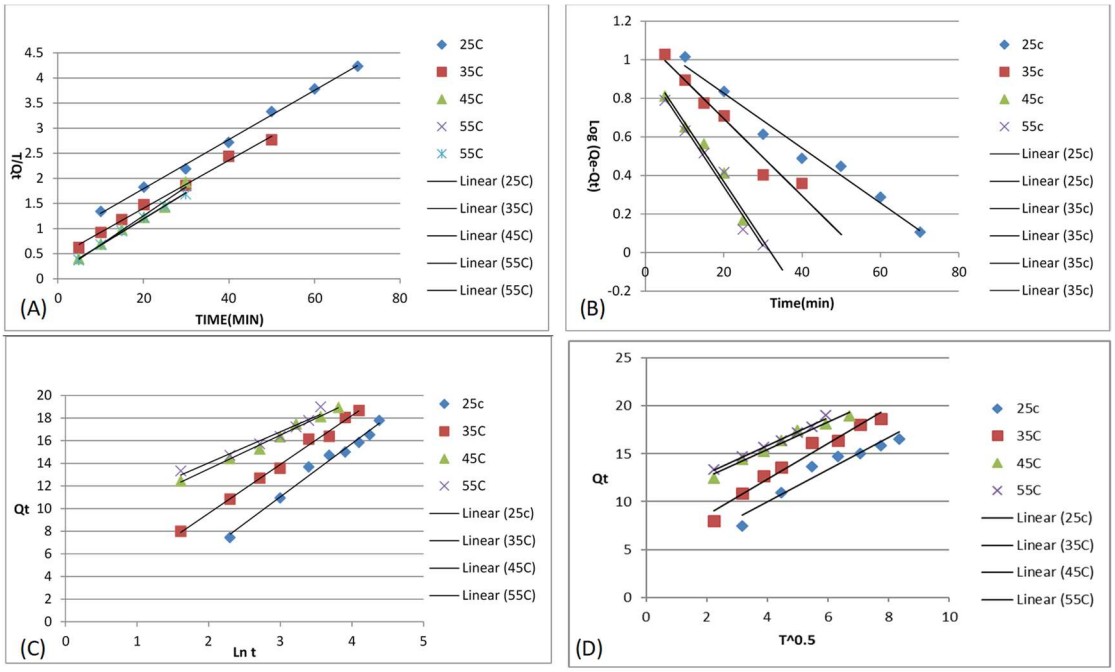


Figure 8: Pseudo second order kinetics for adsorption E102 on polyaniline incorporating hyacinth water (B) First Pseudo order for adsorption of E102 on polyaniline incorporating hyacinth water (C) Elovich model for adsorption of E102 onto polyaniline-water hyacinth nano composite (D) intraparticle Diffusion model plot for adsorption of E102 on polyaniline loaded on hyacinth water [17].

3.4.3. Intraparticle Diffusion Model

The transport of the solute from bulk of the solution into the adsorbent pores via an intraparticle process called rate limiting step which is describe through intraparticle diffusion model.

This formula is given as: $qt = k_{ip}t^{0:5} + Ci$

The rate uniform of intraparticle dispersion. (mg/g $min^{1/2}$) is denoted by "$k_{ip}t$"and the boundary layer thickness is denoted by "Ci".Intraparticle Diffusion for adsorption of E102 on polyaniline-water hyacinth nano composite can be seen in figure.

3.4.4. Elovich kinetic model

Second-order kinetics was described by Elovich kinetic model, when the adsorbent's surface remain inherently variable. The Elovich formula in linear shape is determined as:

$$Qt = 1/\beta \text{ In } (\alpha\beta) + 1/\beta \text{ In } (t)$$

where "Qt" is the total quantity of dye adsorbed at time "t" (mg/g), "" represents the first 599 absorption rate (mg/min), where "" denotes the extent of surface covering and 600 activation energy (g/mg), and "t" is the contact duration (minutes) [11]. Elovich kinetic for adsorption of E102 onto polyaniline-water hyacinth nano composite can be seen in figure.

Table 6: Kinetic parameters of E102 adsorption onto polyaniline-hyacinth water (adsorbent dose 0.1g and initial E102 dye concentration 20 mg/L)

Kinetic Model	Parameter	25°C	35 °C	45 °C	55°C
Pseudo first-order	$K_1(min^{-1})$	0.0327	0.0463	0.0704	0.0709
	$Qm(mgg^{-1})$ (exp)	17.845	18.667	18.944	19
	$Qm(mgg^{-1})$ (calc)	12.945	12.47	9.56	9.07
	R^2	0.9771	0.9605	0.9723	0.9737
Pseudo-second-order	$K_2(g\ mg\text{-}^1min^{-1})$	0.00295	0.00513	0.0573	0.0185
	$Qm(mgg^{-1})$ calc	20.408	20.877	13.158	19.157
	R^2	0.99	0.9944	0.9838	0.9972
Elovich	$B(gmg^{-1})$	0.21216	0.23177	0.33453	0.36475
	α (mg g^{-1} min^{-1})	9.0995	21.6025	37.2152	62.2892
	R^2	0.9832	0.99	0.9916	0.99
Intraparticle diffusion	K diff (mg g^{-1} $min^{-0.5}$)	1.6731	1.8744	1.4421	1.4592
	B_L(mg/g)	3.2698	4.8354	9.6952	10.032
	R^2	0.93	0.9669	0.97	0.99

3.5. Thermodynamic Studies

To ascertain the spontaneous occurrence of any adsorption process, it is crucial to consider both energy and entropy factors in the thermodynamic factors. These values serve as practical indicators for the feasibility of the process. The investigation of the amount of dye adsorbed at equilibrium at various temperatures (25°C, 35°C, 45°C, and 55°C) has been conducted to derive the thermodynamic parameters for the adsorption system. The relationship between the pseudo-second-order rate constant of dye adsorption and temperature is expressed using an Arrhenius-type relationship:

$$\ln k_2 = \ln A - Ea/RT$$

Ea is Arrhenius activation energy of adsorption, along with the Arrhenius factor (A), and the gas constant (R), which has a value of 8.314 J mol−1 K−1, play crucial roles in the relationship. The temperature at which the adsorption process is operated is represented as T. Plotting the natural logarithm of k_2 against 1/T (shown in Fig.) results in a linear graph with a slope of -Ea/R. The magnitude of the activation energy provides insights into the predominant type of adsorption, either chemical or physical. Physi sorption is typically characterized by low activation energies ranging from 5 to 40 kJ mol−1, while chemisorption is associated with higher activation energies in the range of 40 to 800 kJ mol−1. Other important thermodynamic factors, such as the variation in free energy (ΔG◦), entropy (ΔS◦) and enthalpy (ΔH◦) can be find using the following equations [12].

$$K_C = C_A/C_S$$

$$\Delta G^\circ = -RT \ln KC$$

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

where "K_C" is the equilibrium constant; "C_A", the quantity of dye adsorbed on the adsorbent of the elucidation at equilibrium "(mol dm^{-3})"; "C_S", the equilibrium concentration of the dye in the solution (mol dm^{-3}).

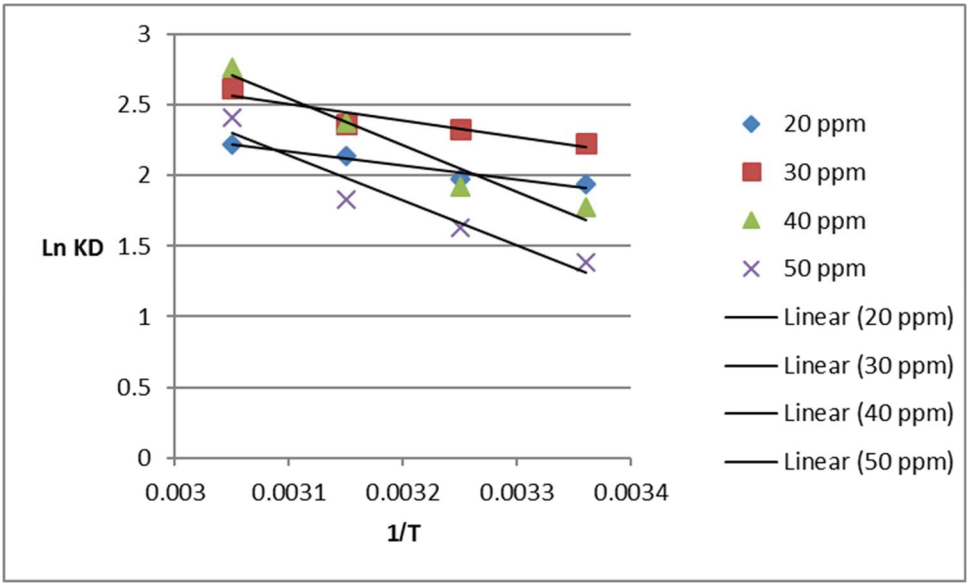


Figure 9: Plot of Vant-Hoff equation for adsorption of E102 onto polyaniline incorporating hyacinth water (0.2g) PH 7.

Table 7: Thermodynamic parameters for adsorption of E102 dye onto polyaniline –hyacinth water Nano composite (0.2g).

E102.Con mg/L	H^o KJ/mol	S^o J/mol K	G^o KJ/mol				
			25°C	35°C	45°C	55°C	R^2
20	8.0955	43.15	-4.7632	-5.626	-5.627	--6.057	0.9338
30	9.6359	50.706	-5.4745	-5.982	-6.489	-6.996	0.88
40	27.4445	106.262	-4.222	-5.284	-6.347	-7.409	0.9542
50	26.3969	99.652	-3.2994	-4.296	-5.293	-6.289	0.9258

Conclusion

polyaniline –hyacinth water nanocomposite was prepared and then describes by using different characterization technique include XRD, EDX, SEM and BET techniques. FTIR results recognized the major functional groups found in polyaniline –hyacinth water nano composite while on the other side XRD confirmed the polycrystalline nature of the prepared polyaniline –hyacinth water nano composite. According to BET research, the particular surface area is 1.7 m^2/g and pore size is 43.83 and 48.122 nm using adsorption-desorption nitrogen at 77 K. At different temperature (25,35,45,55) ºC the data best fitted with the Langmuir ,Freundlich and Tempkin and least fitted with Dubinin–Radushkevich (D–R) isotherm as can be seen from R^2 values for both dyes.The kinetic results were fitted well with the first order of pseudo, pseudosecond order, intraparticle diffusion and Elovich model. Optimum pH 6 for E102 are concluded in batch adsorption studies. The polyaniline –hyacinth water nano composite has a high aptitude for Tartrazine dye removal from the water.

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