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Adsorption Of Pharmaceuticals Compound Balsalazide In Aqueous Solutions Using Nano Talc As An Adsorbent

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Introduction:

Among the organic micro contaminants that have caught the attention of drinking water businesses and water resource authorities are pharmaceuticals, synthetic hormones, and personal care products. Pharmaceutical residues are only present in tiny levels, but dumping pharmaceuticals into neighbouring water sources without adequate treatment might have serious environmental consequences. These drugs interfere with the growth of aquatic biota and photosynthesis, as well as the solubility of gases in bodies of water. Therefore, pharmaceutical effluents must be taken out of aquatic bodies. Diverse techniques have been used to extract pharmaceutical compounds from wastewaters. Many difficult-to-remove drugs are resistant to traditional techniques of cleaning raw drinking water, such as chlorine dioxide, whereas advanced oxidation and reverse osmosis systems are extremely successful but expensive. [1, 2]. Because they are present in substantial levels in sewage treatment plant (STP) effluents and surface water, standard biological treatments appear ineffective for the majority of pharmaceuticals [3-4]. As a result, a low-cost solution with easy operation and little maintenance is needed. Novel materials with unique surface-active characteristics are being developed as a result of advances in nanotechnology [5–7], which may be useful in eliminating medicines from raw water sources.

One of the most successful and proven technologies for water and wastewater treatment is adsorption. Carbon nanotubes (CNTs) are a relatively new adsorbent that has proven to be very successful in the treatment of a wide range of trace pollutants. CNTs have been studied for the removal of organic and inorganic pollutants from water [8-10], such as Dyes [11-12], dioxins from air [13], lead [14], cadmium [15], fluoride [16], 1,2- dichlorobenzene [17], or trihalomethanes (THMs) [18], due to their large specific surface area and small, hollow, and layered structures. Researchers' comparison of carbon nanotubes to other commercial adsorbents reveals that CNTs have a lot of promise in environmental protection applications. Nano talc (single-walled carbon nanotubes) are a form of carbon nanotube that may be utilised as an adsorbent to remove hazardous contaminants. Because of its well-defined cylindrical hollow shape, wide surface area, high aspect ratios, hydrophobic wall, and easily changed surfaces, carbon nano tubes (CNTs) are emerging as possible adsorbents. The adsorptive removal of balsalazide from an aqueous solution onto single walled carbon nano tubes (NANO TALC) was investigated in this work utilising a batch adsorption approach. Anti-inflammatory medication balsalazide. The study's objectives are to: I investigate the feasibility of using Nano talc as an adsorbent for the removal of balsalazide; (ii) determine the various parameters affecting sorption, such as pH, adsorbent dose, initial concentration, contact time, and temperature; (iii) assess the utility of kinetic models and intraparticle diffusion models; and (iv) assess the applicability of linear and non-linear forms for various isotherm (i.e. Freundlich, Langmuir and Tempkin isotherms).

1. Experimental

Balsalazide (A) is chemically (E)-5-[[-4-[[(2-carboxyethyl)amino]carbonyl] phenyl]azo]-2-hydroxybenzoic acid. It is available in the form of disodium hydrate.

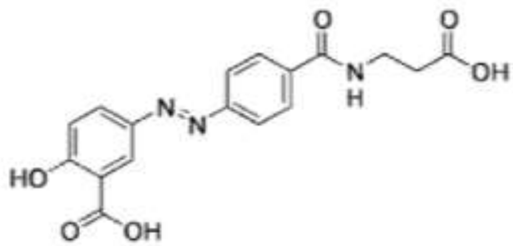

Figure 1.1: Structure of Balsalazide

1.1 Reagents And Solutions

Balsalazide was made as a stock solution by dissolving 375 mg in 100 ml of 0.5N sodium hydroxide solution. A workable solution (0.04 mg/ml) was made by diluting the stock solution in the 0.1 N NaOH Britton Robinson buffer in the pH ranges 6.5 to 12 by adding an appropriate quantity of 0.4 M NaOH solution to the stock solution of 2.14 sulphuric acid, 2.3 acetic acid, and 2.472 g boric acid. To achieve equilibrium, the solution was left overnight. All of the compounds were analytical grade, and they were employed without additional purification.

1.2 Apparatus

Adsorption was measured using a spectrophotometer (systronic spectrophotometer 166 India, throughout the wavelength range 325–900 nm) at a maximum of 456 nm with a 1.0 cm light path quartz cells. A calibration curve was prepared before to the measurement using the standard b pH measurements were carried out with a decibel DB 1011 glass electrode. During the research, a Sartorius CP224S analytical balance (Gottingen, Germany) and a Frontline FS 4 ultrasonic cleaner (Mumbai, India) were employed.

1.3 Procedure

Batch adsorption tests were carried out at temperatures of 30, 40, and 50°C. Adsorption isotherms were recorded at a fixed pH across the concentration range of 0.01 to 0.07 mg/mL of balsalazide solutions. Adsorption was tested by mixing a known amount of adsorbent with a given concentration and pH of the drug solution, then agitating the conical flask intermittently. It was agitated for 30 minutes. After reaching equilibrium, the supernatant liquid was filtered out using Whatmann filter paper No. 42, and the drug uptake was measured spectrophotometrically at a wavelength of 456 nm. The proportion of medication removed was computed using the following formula:

% Removal = (Co-Ce)/ Co) *100 (1)

Where, Co and Ce (both in mg/L) denote the original and current drug concentrations, respectively. The mass balance relationship equation was used to compute the adsorption capacity qe (mg/g) at every time:

(Co-Ce)*(V/W) = qe (2)

W is the mass of the adsorbent employed, and V is the volume of the solution (L) (g).

2. Results And Discussion

2.1 Effect of Adsorbent Dose

Because of its considerable influence on the capacity of an adsorbent at a given starting concentration of the adsorbate, adsorbent dose is an essential parameter. By adjusting the quantity of adsorbents from 0.33 to 2.66 g/L while maintaining other parameters (pH, starting concentration, and contact duration) constant, the effect of balsalazide adsorption on dosage was investigated. The increase in adsorbent (NT) dose from 0.33 to 2.66 g/L resulted in a reduction in uptake capacity, as shown in Fig. 1.2. At low doses, the adsorption capability was found to be high. The rate of adsorption decreases when the amount of adsorbent is raised to 1.66 g/L; additional increases in adsorbent doses result in a dramatic fall in balsalazide adsorption rate; the optimal amount of adsorbent dosage for all subsequent trials was 1.66 g/L. This adsorbent concentration effect might be caused by a variety of causes. The fact that adsorption sites remain unsaturated during the process is the most critical element. The non-saturation of the adsorption sites during the adsorption process is primarily responsible for the reduction in adsorption capacity with increasing adsorbent dose [19, 20]. An previous research [21] had similar results.

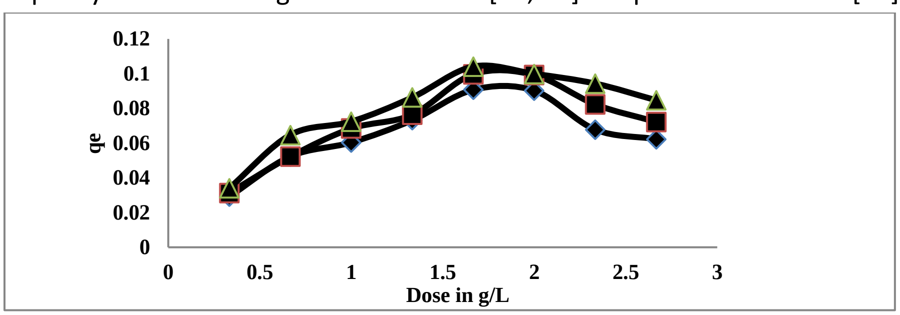

Figure 1.2: Effect of amount of adsorbent (Nano talc) for the removal of Balsalazide at 0.04 mg/mL at pH 10.5 and different temperatures.

2.2 Effect of Adsorbate Concentration

The rate-limiting step in the reaction is defined by the dependency of the adsorbate concentration on the rate of adsorption. Using various concentrations of balsalazide, the batch approach was also employed to identify the optimal medication concentration. Experiments were carried out with varied doses of balsalazide ranging from 0.01 to 0.07 mg/mL, at a fixed dosage of adsorbent (Nano talc) of 1.66 g/L, and pH 10.5. The initial drug concentration and clearance rate have a direct connection. The quantity of drug adsorbed (mg/g) increased with increased starting drug concentration and remained constant until equilibrium period, as shown in Fig. 1.3. (30 min). The concentration acts as a powerful motivator to overcome the drug's mass transfer barrier between the aqueous and solid phases [22, 23]. As a result, a larger initial drug concentration will improve the adsorption process. The NANO TALC's equilibrium sorption capacity rose as the original drug concentration increased, while the percent drug removal increased in the reverse direction (Fig. 1.3). The actual amount of drug adsorbed per unit mass of NANO TALC rose as the starting drug concentration increased, whereas the percentage clearance reduced.

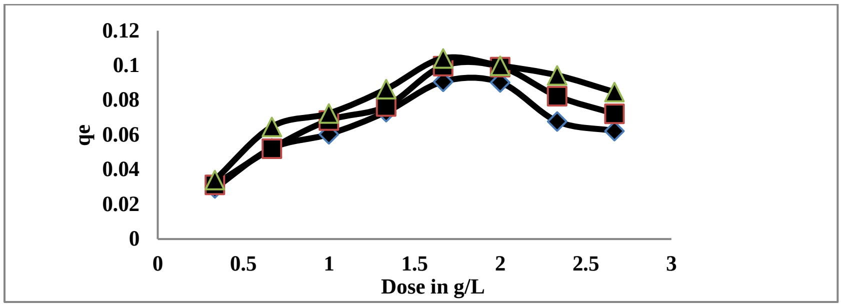

Figure 1.3: Effect of concentration of the drug for the removal of balsalazide by Nano talc at 1.66 g/L at pH 10.5 at 30° C.

2.3 Effect of Ph

Because hydrogen and hydroxyl ions are heavily adsorbed, the pH of the solution influences the adsorption of other ions. The adsorptive process is affected by pH changes due to the dissociation of functional groups on the adsorbent surface active sites. As a result, the reaction kinetics and equilibrium properties of the adsorption process change. The influence of the drug solution's starting pH on the amount of drug adsorbed was investigated by altering pH while maintaining constant process parameters (Fig. 1.4). Experiments were carried out at varied pH values ranging from 6.5 to 12 at 30°C with a fixed dosage of Nano talc of 1.66 g/L and a drug concentration of 0.04 mg/mL to determine the rate of adsorption of balsalazide (Fig. 1.4). It was discovered that the rate of adsorption increased from 6.5 to 10.5 in the neutral to alkaline range. The adsorption of balasalazide on NT tends to increase with rising pH values up to pH 10.5. When the pH rises, the drug's electrostatic attraction force with the NT surface is expected to increase. Methylene blue adsorption on wheat shells and oak sawdust [24] showed a similar pattern.

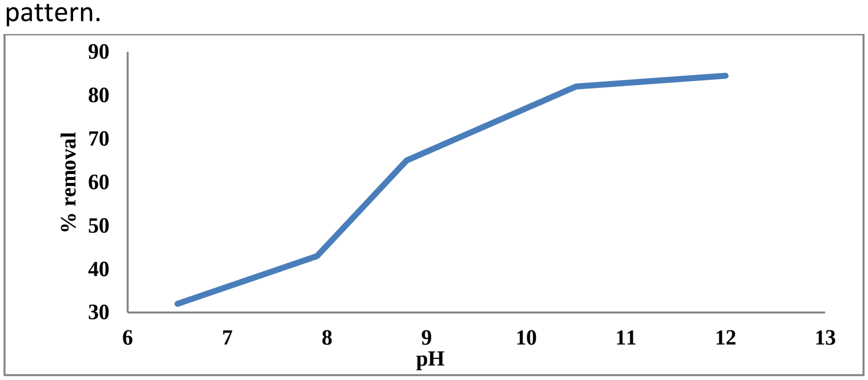

Figure 1.4: Effect of pH for the removal of Balsalazide (0.04 mg/ml) by Nano talc 0.2 g/L at pH

2.4 Effect of Contact Time

The adsorbent's ability to absorb drug molecules and the time it takes to reach equilibrium imply that this material is suitable for wastewater treatment. A contact time research was conducted to identify the equilibrium period for maximal medication absorption. At an initial drug concentration of 0.04 mg/mL on NT adsorbent, the effect of contact duration on drug adsorption was examined. As shown in Fig. 1.5, drug elimination on NT is high during the early period of contact time and subsequently becomes fast with time. Quick diffusion onto the exterior surface was followed by fast pore diffusion into the intraparticle matrix to achieve equilibrium after 30 minutes, which might be due to attractive interactions between the drug molecule and the adsorbent, such as vander waals forces and electrostatic attractions.

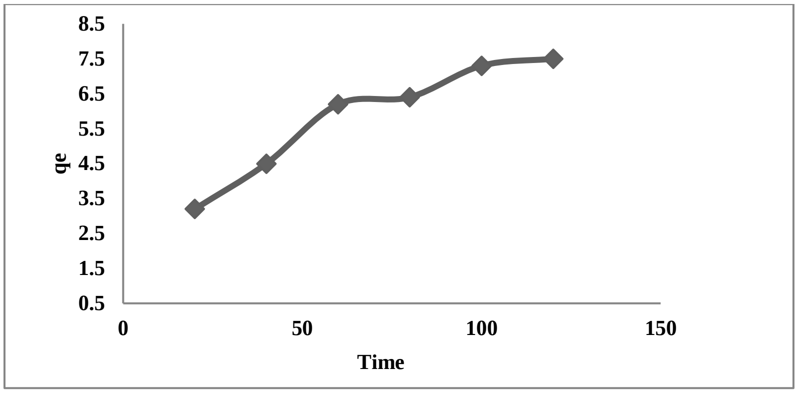

Figure 1.5: Effect of contact time for the removal of balsalazide over Nano talc at 0.2 g/L at pH 10.5 at 30^{o}C.

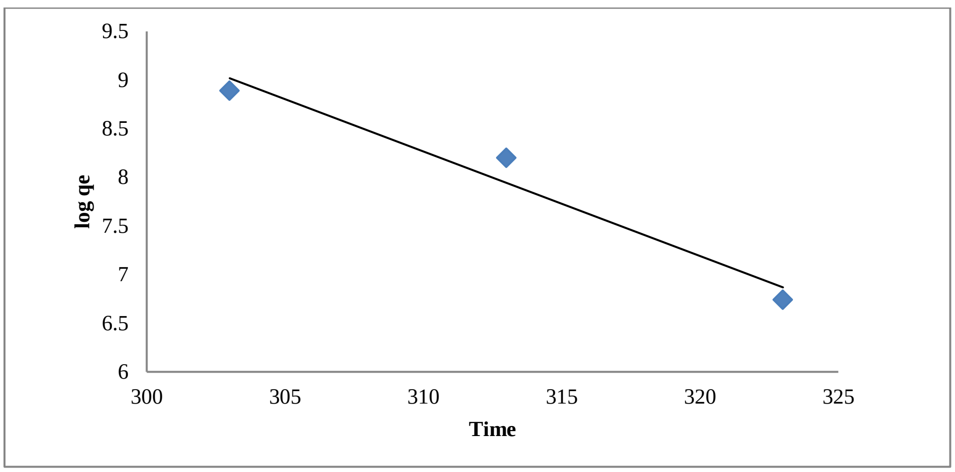

Figure 1.6: Effect of temperature for the removal of balsalazide (0.04 mg/mL) over Nano talc (1.66 /L) at pH 10.5 and different temperatures

3. Adsorption Isotherm Modeling

3.1 Langmuir Isotherm

Irving Langmuir [25] created a simple thermodynamic equilibrium model in 1916 to forecast the proportion of solid surface covered by an adsorbate as a function of its gas pressure. This was eventually extended to liquid systems, with concentrations in solution representing the equilibrium. Adsorbate and solvent molecules fight for adsorption sites on the solid's surface in this paradigm. Either a solvent molecule or an adsorbate molecule must occupy each site. The Langmuir model is the most extensively used and well-known sorption isotherm. It is founded on four theories:

The adsorbent's surface is uniform, meaning that all adsorption sites are equal. Adsorbed molecules don't interact with each other. The same process underpins all adsorption. Only a monolayer forms at maximal adsorption: adsorbate molecules do not deposit on other, previously adsorbed, adsorbate molecules, but only on the free surface of the adsorbent. The adsorption of adsorbate (Balsalazide) onto the surface of the adsorbent (Nano talc) is described by Langmuir's isotherm, which needs three assumptions:

The adsorbent's surface comes into touch with a solution containing an adsorbate that is highly attracted to it. There are a limited number of locations on the surface where the solute molecules can be adsorbed. Monolayer adsorption is characterised by the attachment of only one layer of molecules to the surface.

Langmuir isotherm (Fig. 1.7) can be expressed by the eq. (3)

$$1 / qe = 1 / Q^{\circ} + 1/bQ^{\circ}Ce) \qquad (3)$$

Where qe denotes the quantity adsorbed (mol/g) and Ce denotes the adsorbate's equilibrium concentration (mol L1). The Langmuir constants (Table-1.1) for maximum adsorption capacity and energy adsorption, respectively, are Q° and b. When you plot 1/qe versus 1/Ce, you get a straight line with a slope of 1/bQ°, indicating that balsalazide adsorption over Nano talc follows the Langmuir isotherm (Fig. 1.7)

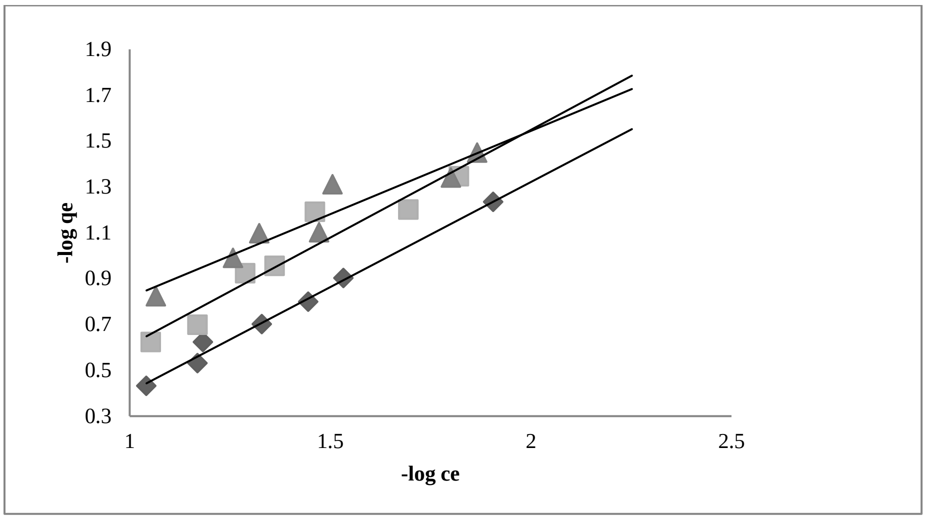

Figure 1.7: Langmuir adsorption isotherm for the adsorption of balsalazide over Nano talc

Table 1.1: Langmuir constants for balsalazide over Nano talc

Temp.(°C)	b (mol g^{-1})	Q° (L mol^{-1})	bQ°	R^2	%RSD
30 °C	10.023	0.082	128.53	0.991	1.08
40 °C	8.023	0.056	215.41	0.968	1.21
50 °C	6.235	0.043	243.16	0.964	1.35

3.2 Freundlich Isotherm

Freundlich published the first known sorption isotherm equation in 1906. It is an empirical relationship that describes the adsorption of solutes from a liquid to a solid surface and posits that many sites with various adsorption energies are involved. The Freundlich adsorption isotherm describes the connection between the quantity of balsalazide adsorbed per unit mass of adsorbent, qe, and the equilibrium concentration of balsalazide, qe.

qe = Kf Ce1/n (4)

Freundlich isotherm model [26] can be linearized in the logarithmic form (eq. 5)

log qe =log Kf +1/n log Ce (5)

Where, Kf is a system constant relating to the bonding energy. The adsorption or distribution coefficient, Kf, measures the amount of drug adsorbed onto the adsorbent for a given unit equilibrium concentration. The adsorption intensity of the drug onto the adsorbent, or surface heterogeneity, is represented by 1/n. From the plot of log (qe) vs log (Ce), the Freundlich isotherm constants Kf and 1/n may be determined (Fig.1.8) The Freundlich constants (Table-1.2) Kf (mg/g(L/g)1/n) and n are indications of adsorption capacity and intensity, respectively [27].

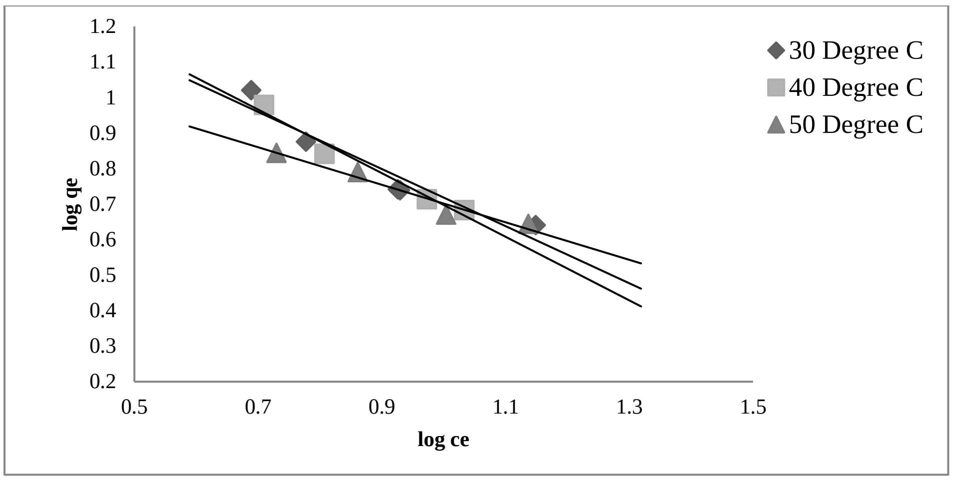

Figure 1.8: Freundlich adsorption isotherms for adsorption of the balsalazide over Nano talc

Table 1.2: Freundlich constants for the balsalazide over Nano talc

Temp. (°C)	K_f	N	R^2	%RSD#
30 °C	23.465	5.432	0.913	1.21
40 °C	25.431	7.028	0.970	1.35
50 °C	29.416	9.014	0.953	1.52

3.3 Temkin Isotherm

Heat of adsorption and the sorbent-sorbate interactions were studied by Temkin and Pyzhev. Tempkin isotherm [28] has been applied in the form given by eq. (6).

qe = RT/b In A + RT/b In Ce (6)

qe = B ln A + B ln Ce (7)

Where, B is equal to RT/b. The data on sorption may be examined using eq (7). As a result, graphing qe vs lnCe (Fig. 1.9) allows the constants (Table 1.3) A and B to be determined. R is gas constant (8.314 J/mol K), B the Tempkin constant linked to heat of sorption (J/mol), A the Tempkin isotherm constant (L/g), B the Tempkin isotherm constant, and T the absolute temperature (K).

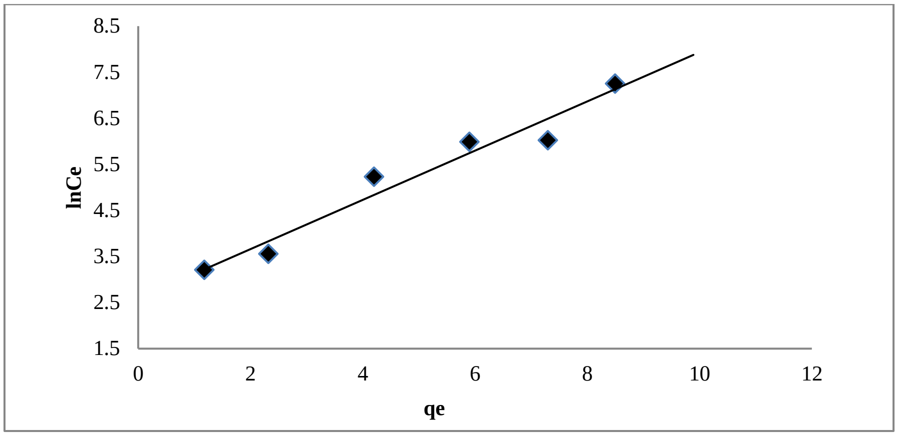

Figure 1.9: Tempkin adsorption isotherm for adsorption of the balsalazide over Nano talc

Table 1.3: Tempkin constants for the balsalazide over Nano talc

Temp.(° C)	B(J mol^{-1})	A (L g^{-1})	B	R^2
30 °C	12.468	523.146	31246	0.956

4. Thermodynamic Study

To assess the thermodynamic feasibility and spontaneous nature of the process, thermodynamic constants such as gibbs free energy change (G°), enthalpy change (H°), and entropy change (S°) were determined. The thermodynamic parameters for the adsorption of balsalazide on NT, such as the enthalpy change (H°), Gibbs free energy change (G°), and entropy change (S°), may be estimated using the following thermodynamic relations from the fluctuation of Langmuir constant with temperature (T). [29]

$\Delta G° = -RT \ln b$ (8)

$\Delta H° = -R (T2T1) / (T2 - T1) \ln (b2 / b1)$ (9)

$\Delta S° = \Delta H° - \Delta G° / T$ (10)

Where b, b1, and b2 are the equilibrium constants at various temperatures derived from the slopes of straight lines generated from Langmuir adsorption isotherms at various temperatures, R (8.314 J/mol K) is the universal gas constant, and T (K) is the absolute solution temperature Table 1.4 shows the values of the thermodynamic parameters determined using the preceding formulae. The fact that G is negative indicates that the adsorption process is endothermic. The positive value of H confirms this.

Table 1.4: Thermodynamics parameters of balsalazide over Nano talc

Δ G°($kJmol^{-1}$)	ΔH° (kJ mol^{-1})	ΔS° ($Jk^{-1}mol^{-1}$)

Adsorbent	30°C	40°C	50°C	30°C	30°C
UPR	-24.15×10^3	-27.52×10^3	-31.93×10^3	21.08×10^3	53.21

5. Adsorption Kinetics Models

Common models used to fit the kinetic sorption experiments are Lagergren's pseudo-first-order model (eq. 11) [30].

$$\log (q_e - q_t) = \log q_e - k_{ad} \times t/2.303 \qquad (11)$$

qe (mg/g) and qt (mg/g) denote the amount of drug adsorbed at equilibrium and time t, respectively. The Lagergren plot for balsalazide adsorption on NT at various temperatures, which was obtained by plotting log (qe-qt) against time, displays a straight line, showing that the adsorption process follows first order kinetics (Fig. 1.10). The rate constants for the adsorption of balsalazide on Nano talc are shown in Table 1.5.

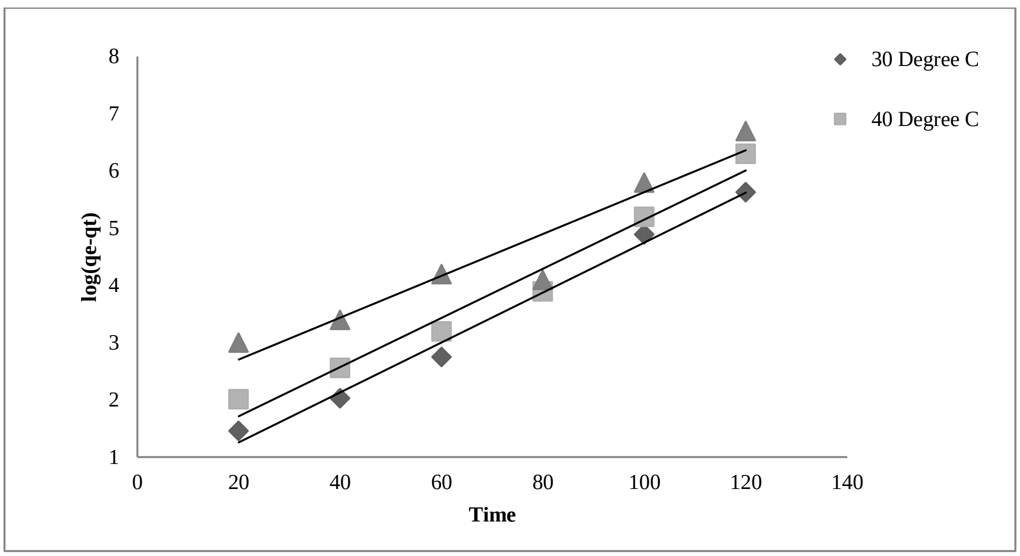

Figure 1.10: Lagergren plot for adsorption of balsalazide over Nano talc at different temperatures.

Table 1.5: Rate constant kad for balsalazide over Nano talc

Temp (°C)	k_{ad}	% RSD
30°C	0.182	0.989
40°C	0.203	0.971
50°C	0.392	0.914
# Average of three replicates measurement		

Conclusion

According to the results of the studies described in this article, balsalazide can be adsorbed effectively on single walled carbon nanotubes (Nano talc). The Langmuir and Freundlich, Tempkin, and D-R isotherms equations were used to get the characteristic parameters for each adsorption isotherm. The adsorption isotherms of Freundlich, Langmuir, and Tempkin all match equilibrium adsorption data. The process removal kinetics were explored, and rate constant values were discovered. In the adsorption process, first order kinetics with a correlation value of 0.958 is used. The negative Go values observed showed that drug adsorption was thermodynamically viable and spontaneous, but the positive Ho value indicated that the adsorption process was endothermic. The elimination of balsalazide medication by adsorption on NT is beneficial for mitigating water pollution utilising the stated adsorption approach, based on all of the findings.

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