Green Adsorption of Bismuth (III) Ions Using *Trachyspermum copticum*: Isotherm, Kinetic, and Thermodynamic Studies

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Abstract: ***The emergent demand for industrial and pharmaceutical products has contributed to increasing environmental pollution, including contamination by Bismuth (Bi(III)), a heavy metal widely used in semiconductors, metallurgy, and medicinal applications. Due to its potential toxicity and adverse effects on human health and aquatic ecosystems, the efficient removal of Bi(III) from aqueous environments is of significant concern. Among various treatment strategies, adsorption stands out as a promising, cost-effective, and environmentally sustainable method. This study explores the use of Ajwain seeds (Trachyspermum copticum) as a low-cost natural biosorbent for the removal of Bi(III) from aqueous solutions. Ajwain seeds were processed through washing, drying, and sieving, and then characterized using Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) to assess their functional groups and surface morphology. Batch adsorption experiments were performed to investigate the influence of key parameters such as contact time, initial metal ion concentration, adsorbent dosage, temperature, and agitation speed on Bi(III) removal efficiency. The results indicated a maximum removal efficiency of 98.62% under optimized conditions: 240 minutes contact time, 700 mg adsorbent dose, and 250 mg/dm³ initial Bi(III) concentration. The adsorption behavior conformed well to the Langmuir isotherm model, indicating monolayer adsorption, while kinetic data best fit the pseudo-second-order model, suggesting chemisorption as the dominant mechanism. Thermodynamic parameters confirmed the spontaneous and endothermic nature of the process. This study demonstrates the efficacy of Ajwain seeds as a green and effective biosorbent, offering a sustainable solution for the remediation of Bi(III) contaminated water.***

Keywords: Adsorption isotherms; Bismuth adsorption; Environmental remediation; Heavy metal removal; Kinetics and thermodynamics; Natural adsorbents; Water purification

1. Introduction

The increasing demand for essential goods has significantly contributed to pollution caused by various contaminants. Among these, bismuth pollution is rising due to its expanding applications. However, research on bismuth removal through adsorption remains limited (Katsumata, et al. 2003; Ossman, et al. 2013). Bismuth and its compounds are widely used in semiconductors, cosmetics, alloys, metallurgical additives, and the processing and recycling of uranium nuclear fuels (Esposito et al. 2001).. Additionally, Bi (III) salts are utilized in medical diagnostics and have been employed in the treatment of various diseases, particularly ulcers and gastritis. Due to its extensive use in pharmaceuticals, bismuth finds its way into the environment, increasing the exposure of living organisms. Moreover, bismuth compounds have been associated with several toxic effects in humans, including hepatitis and neuropathology (Agarwal and Gupta, 2015). Therefore, the effective removal of Bi (III) is crucial to mitigating its contamination and associated health risks.

Various techniques can be employed to remove heavy metals from aqueous solutions, including adsorption, ion exchange, ultrafiltration, and reverse osmosis. Among these methods, adsorption is considered a viable option both technically and economically (Bind et. al, 2018). This is especially true if the adsorbent is cost-effective and readily available, making adsorption an attractive alternative for water purification. Activated carbons are highly effective adsorbents for removing a wide range of pollutants, including organic, inorganic, and biological contaminants commonly found in industrial wastewater. In particular, activated charcoal derived from coconut shells has demonstrated remarkable efficiency in eliminating heavy metals such as Cd(II) and Pb(II), as well as cationic dyes from liquid solutions (Kumari et. al, 2023; Foroutan et. al, 2017).

In recent years, rapid population growth and increasing reliance on utilities and modern technologies have contributed to greater environmental pollution, including contamination by bismuth Bi(III). Studies have shown that Bi(III) can be successfully removed and recovered from succinate solutions using 2-octylaminopyridine (2-OAP) as an extractant in a liquid-phase reaction. This highlights the growing need for efficient and sustainable adsorption techniques to address Bi(III) contamination in aqueous environments.

In the present study, the adsorption of bismuth onto Ajwain (*Trachyspermum copticum*) seeds was investigated. Ajwain seeds are composed of essential nutrients such as proteins, moisture, fiber, iron, carotene, and niacin. Additionally, they hold significant value in Ayurvedic medicine due to their therapeutic properties. The oil extracted from Ajwain seeds is widely used in the pharmaceutical industry. Experimental studies were conducted to examine the effects of adsorption time, adsorbent dosage, and shaking speed on bismuth removal efficiency. The results indicate that Ajwain seeds possess a high adsorption capacity within a short time, making them a promising natural adsorbent for the removal of Bi(III) from aqueous solutions.

2. Material and Methods

2.1 Preparation of Adsorbent

Ajwain seeds were procured from the local market in Moradabad. Initially, the seeds were thoroughly rinsed with distilled water and then dried in an electric oven at 70 °C. The dried seeds were subsequently sieved to obtain a fine powder with a particle size range of 100–300 µm. To ensure the removal of any residual impurities, the seeds were washed multiple times with distilled water and then subjected to another drying cycle at 70 °C. The prepared Ajwain seed powder was then utilized as an adsorbent for the removal of bismuth via the adsorption process.

2.2 Preparation of Materials

A standard solution containing 1 mg/ml of Bi (III) was prepared using bismuth nitrate. This stock solution was then diluted as needed to obtain the required concentrations for experimentation.

2.3 Characterization of the Adsorbent

The adsorbent underwent comprehensive characterization using various analytical techniques. Fourier Transform Infrared Spectroscopy (FTIR) was performed using a Perkin Elmer Range 100 instrument to identify key functional groups. Scanning Electron Microscopy (SEM) imaging was conducted using a JEOL - JSM 6360 unit (Japan) to analyze the surface morphology of the adsorbent. Additionally, elemental composition analysis, including carbon, hydrogen, nitrogen, and sulfur content, was carried out using a Euro EA Essential Analyzer.

FTIR analysis revealed distinct peaks corresponding to significant functional groups, such as O-H stretching (3310.05 cm⁻¹), C-H bonds (2899.46 cm⁻¹), C=O stretching (1703.10 cm⁻¹), C=C bonds (1608.48 cm⁻¹), SO_2 (1167.01 cm⁻¹), and C-O stretching (1034.86 cm⁻¹) (Fig. 1). These peaks confirmed the presence of active adsorption sites on the surface of the adsorbent.

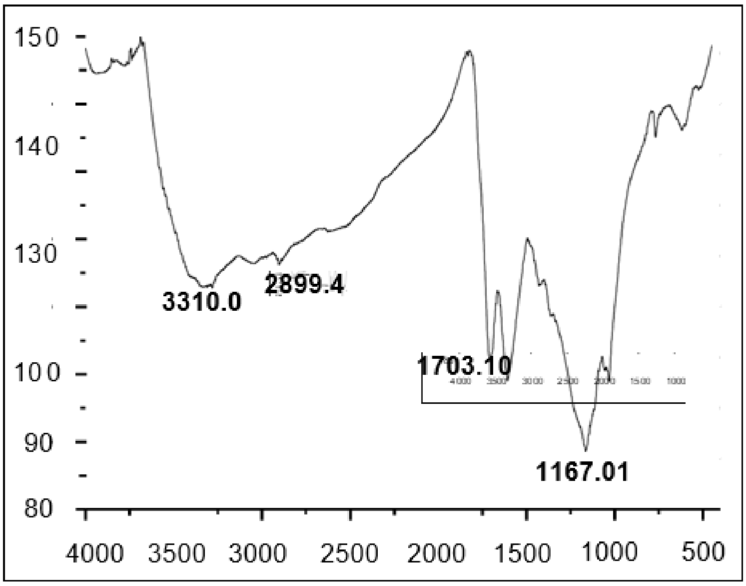

Figure 1: FTIR spectrum of Ajwain seed

Furthermore, SEM imaging (Fig. 2 and Fig. 3) revealed a highly porous surface structure, which is crucial for enhancing adsorption efficiency. The combined findings from FTIR, SEM, and elemental analysis confirmed the suitability of the Ajwain seed powder as an effective adsorbent for bismuth removal.

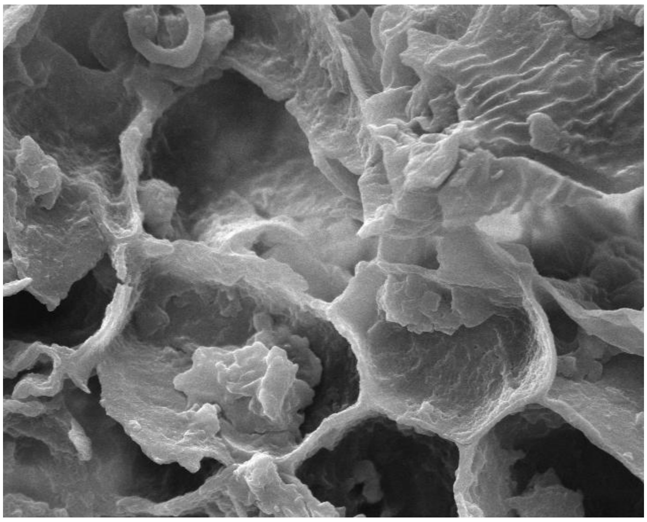

Figure 2: SEM image of native *Trachysperum Copticum*

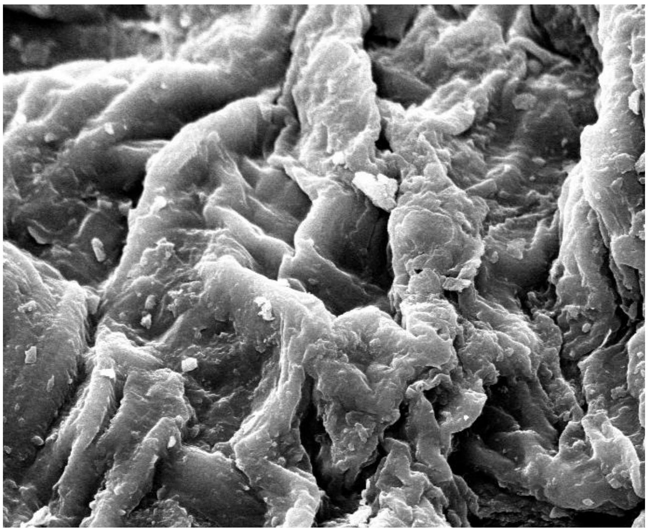

Figure 3: SEM image of *Trachysperum Copticum* after Bi(III) adsorption

2.4 Batch Adsorption Experiment

Batch adsorption experiments were conducted using an orbital shaker and Erlenmeyer flasks. The adsorption process was carried out at a constant temperature of 299 K for a predetermined duration. To prevent Bi(III) precipitation, the metal ion solution was maintained in an acidic medium with a pH of 2.0, as Bi(III) tends to precipitate at pH values above 2.5 in aqueous solutions (Shah et. al, 2018). The pH was adjusted accordingly using diluted HNO_3 or NaOH.

The prepared Bi(III) solutions were analyzed spectroscopically using xylenol orange as the chromogenic reagent (λmax = 545 nm), and the results were further validated through Nuclear Absorption Spectroscopy (Nurk et. al, 2001).. To examine the effect of initial Bi(III) concentration, experiments were conducted with Bi(III) concentrations ranging from 250 to 1000 mg/dm³, while maintaining a constant adsorbent dosage of 700 mg. Additionally, the adsorbent mass was varied from 100 to 700 mg while keeping the Bi(III) concentration fixed at 250 mg/dm³. The impact of shaking time on adsorption efficiency was assessed over a range of 15 to 300 minutes. For thermodynamic evaluation, the adsorption process was studied at different temperatures ranging from 303 to 323 K to determine its behavior under varying thermal conditions.

3. Result

It can be summarized as follows-

1) Ajwain seeds were utilized as the precursor material for the development of an efficient adsorbent. Through the adsorption process, they were transformed into a highly porous, cost-effective, and potent adsorbent, achieving a maximum Bi(III) removal efficiency of 98.62%.
2) Comprehensive characterization techniques, including Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and elemental analysis (C, H, N, S analyzers), were employed to confirm the successful formation and structural properties of the developed adsorbent.
3) The exceptional adsorption capability of Ajwain seed-based adsorbent for Bi(III) ions was demonstrated, with adsorption capacities ranging from 17.52 mg/g to 53.47 mg/g, as the initial Bi(III) concentration increased up to 1000 mg/dm³. Notably, equilibrium was attained within a short adsorption duration of 240 minutes.
4) The adsorption isotherm exhibited an L-shaped curve, indicating minimal competition between the adsorbent and adsorbate, thereby reinforcing the efficiency of the adsorption process. Several adsorption isotherm models were evaluated, including the Freundlich and Langmuir equations. However, the Langmuir model demonstrated superior correlation with the experimental data, yielding a maximum adsorption capacity of 54.35 mg/g, suggesting monolayer adsorption on a homogeneous surface.
5) A comprehensive kinetic analysis revealed that the adsorption process followed the pseudo-second-order kinetic model, as indicated by the high regression coefficient (R^2 = 0.977), confirming that chemisorption governed the Bi(III) uptake mechanism. Furthermore, thermodynamic studies, assessing enthalpy ($\Delta H°$), Gibbs free energy ($\Delta G°$), and entropy ($\Delta S°$), affirmed that the adsorption process was not only feasible and spontaneous but also endothermic, suggesting an enhanced adsorption capacity at elevated temperatures.

4. Discussions

4.1 Impact of Time on Bi(III) Adsorption

This study underscores the crucial role of time in the adsorption process of Bi(III). The adsorption efficiency was evaluated at different time intervals while maintaining constant parameters such as temperature, agitation speed, and an initial Bi(III) concentration of 250 mg/dm³ (Table 1). The results revealed that the maximum Bi(III) adsorption reached 98.62%. The rapid initial adsorption can be attributed to the abundance of active sites available on the adsorbent surface, allowing Bi(III) ions to be quickly adsorbed. However, as time progressed, repulsive forces between the adsorbed Bi(III) ions increased, leading to a gradual decline in adsorption efficiency. This observation suggests that prolonged adsorption times result in saturation of the adsorbent surface, limiting further uptake of Bi(III).

Table 1: *Effect of time on the percentage removal and amount adsorbed mg/g of adsorption of Bi(III) on Ajwain seeds (AS). Bi(III) =250 mg/g, , pH=2, agitation speed= 160 rpm, T= 299 ± 2 K*

Time min	Amount adsorbed q_t mg/g	Removal of Bi(III) %
15	7.1	38.87
30	11.35	58.20
60	12.53	64.31
90	12.89	72.25
120	14.80	77.31
150	16.17	85.00
180	17.59	92.95
210	17.95	97.75
240	18.61	98.71
270	18.61	98.71
300	18.61	98.71

Considering the influence of time on Bi(III) adsorption, it is critical to determine an optimal contact duration to maximize removal efficiency. Further research into the adsorption dynamics at different time intervals could provide deeper insights into process optimization. Based on the experimental findings, a duration of 240 minutes was selected as the optimal contact time, as a significant amount of 17.52 mg/g was adsorbed at this point and remained constant with extended durations (Fig. 4).

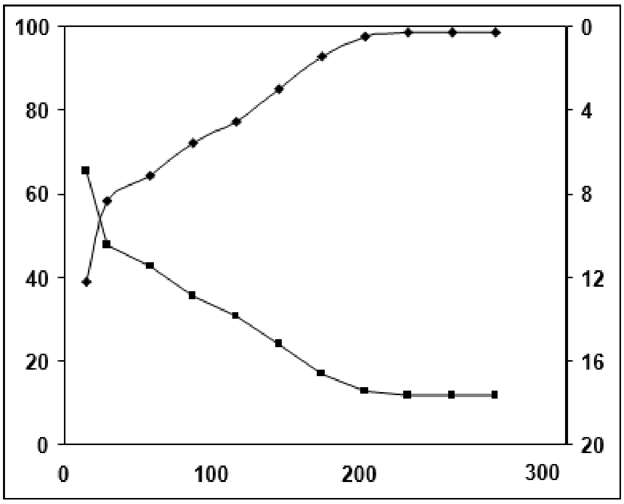

Figure 4: Plot between time and amount adsorbed, mg/g of Bi(III), on Ajwain seeds Bi(III) =250 mg/dm^3, **AS** =700 mg, agitation speed= 160 rpm, pH=2, T= 299 ± 2 K

4.2 Effect of Initial Bi(III) Concentration

The effect of initial Bi(III) concentration on adsorption efficiency was examined using Ajwain seeds as the adsorbent under controlled conditions: a fixed agitation time of 240 minutes and a Bi(III) concentration range of 250 to 1000 mg/dm³. The study demonstrated that as the Bi(III) concentration increased, the adsorbed amount also increased proportionally, from 17.52 mg/g at 250 mg/dm³ to 53.37 mg/g at 1000 mg/dm³ (Fig. 5, Table 2). This trend suggests that at higher concentrations, more Bi(III) ions were available for adsorption, leading to greater interaction with the active sites of the adsorbent.

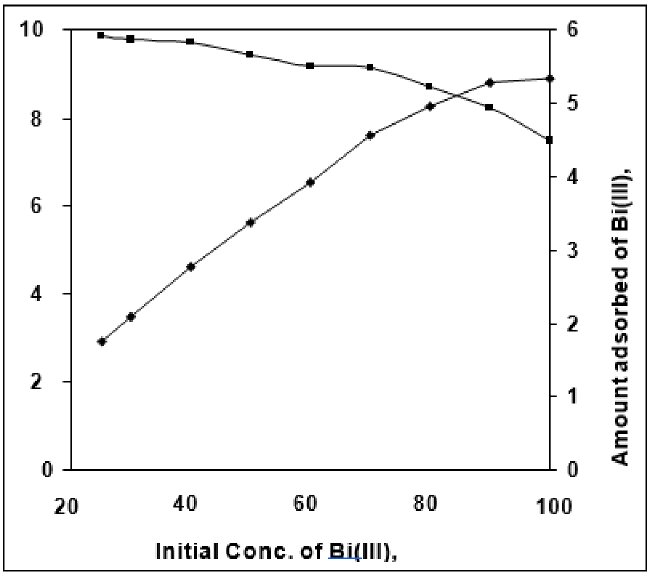

Figure 5: Plot between initial concentration of Bi(III) and amount adsorbed, mg/g removal Time= 240 min, agitation speed= 160 rpm**,** Ajwain seeds =700 mg, pH=2, T=299 ± 2

Table 2: Effect of initial concentration of Bi(III) on the percentage removal on AS.
Time= 240 min, pH=2, AS =700 mg, T= 299 ± 2 K, agitation speed= 160 rpm

Initial conc. Bi(III) mg/dm^3	Amount adsorbed, q mg/g	Removal of Bi(III), %
250	17.61	98.71
300	20.94	97.72
400	27.76	97.20
500	33.71	94.41
600	39.32	91.78
700	45.71	91.43
800	49.67	86.94
900	52.89	82.28
1000	53.46	74.85

At lower concentrations, the adsorption sites were not fully utilized, resulting in a lower quantity of Bi(III) being adsorbed per unit mass of Ajwain seeds. However, as the concentration increased, the active sites became more engaged, enhancing the overall adsorption capacity. These findings emphasize the significance of initial Bi(III) concentration in determining adsorption efficiency, reinforcing the potential of Ajwain seeds as a viable adsorbent for heavy metal removal.

4.3 Effect of Adsorbent Dosage

The impact of adsorbent dosage on Bi(III) removal was analyzed, and the findings are presented in Fig. 6 (Table 3). The results indicated that at an adsorbent dose of 700 mg of Ajwain seeds, the adsorption process reached its maximum quantitative capacity. During the experiment, a Bi(III) concentration of 250 mg/dm³ was used, with agitation for 240 minutes while maintaining all other parameters constant. At equilibrium, the highest adsorption efficiency achieved was 98.62%, corresponding to an adsorbed amount of 17.52 mg/g of Bi(III). Fig. 5 illustrates the correlation between Bi(III) removal efficiency and adsorbent dosage. As the dosage increased from 100 to 700 mg, the percentage removal of Bi(III) also increased, highlighting the effectiveness of higher Ajwain seed doses in enhancing adsorption. This is due to the increased availability of active sites at higher adsorbent concentrations, which facilitates greater interaction with Bi(III) ions. In summary, the study established that 700 mg of Ajwain seeds was the optimal dosage for achieving near-complete Bi(III) adsorption, resulting in an impressive 98.62% removal efficiency.

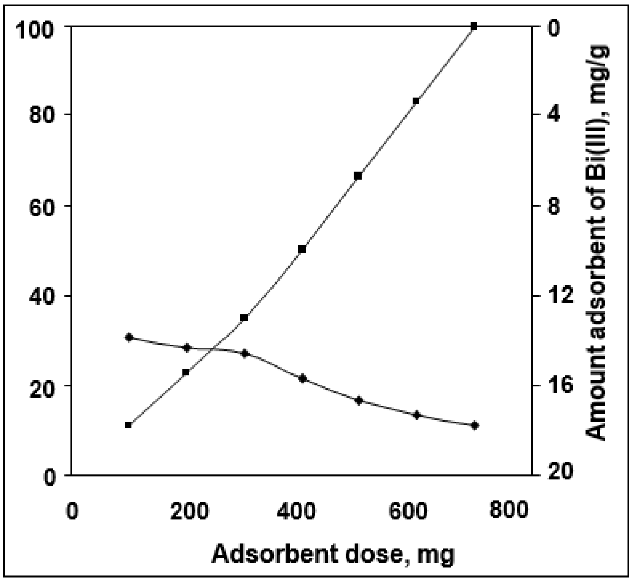

Figure 6: Effect of adsorbent dosage on removal, % and amount adsorbed, mg/g of Bi(III) on Ajwain seeds Bi(III) = 250 mg/dm^3, Time= 240 min, T= 299 ± 2 K, agitation speed= 160 rpm, pH=2

Table 3: Effect of adsorbent dosage on percentage removal of Bi(III)**.** Bi(III) = 250 mg/dm^3, T= 299 ± 2 K, pH=2, agitation speed= 160 rpm, Time= 240 min

Ajwain seeds mg	Amount adsorbed, q mg/g	Removal of Bi(III), %
100	13.85	11.08
200	14.31	22.90
300	14.56	34.96
400	15.71	50.28
500	16.68	66.51
600	17.30	83.08
650	17.55	92.33
700	17.61	98.71

4.4 Effect of Agitation Speed

The influence of agitation speed on the adsorption of Bi(III) was examined using an orbital shaker set at a controlled temperature of 299 K. The agitation speed was systematically varied from 50 to 200 rpm while maintaining a constant Bi(III) concentration of 250 mg/dm³ and ensuring all other experimental conditions remained unchanged. The results clearly demonstrated that agitation speed played a crucial role in enhancing adsorption efficiency (Fig. 7, Table 4). Higher agitation speeds significantly increased the contact between the adsorbent and the adsorbate, thereby improving the overall adsorption process. This enhancement can be attributed to the reduction in mass transfer resistance and better dispersion of Bi(III) ions in the solution, leading to more effective interaction with the active sites of the adsorbent.

Table 4: Effect of agitation speed on percentage removal of Bi(III) Bi(III)= 250 mg/g, Time= 240 min, T= 299 ± 2 K, Ajwain seeds =700 mg, pH=2

Agitation speed, rpm	Amount adsorbed, q mg/g	Removal of Bi(III), %
50	11.98	70.91
70	14.22	79.31
100	15.21	83.67
120	16.67	92.40
140	16.96	92.89
160	18.31	97.91
180	18.31	97.91
200	18.31	97.91

4.5 Adsorption Isotherm

Adsorption is commonly described through adsorption isotherms, which illustrate the relationship between the adsorbent and adsorbate at a constant temperature. As the concentration of the adsorbate increases, the number of available adsorption sites decreases, resulting in a decline in the adsorption rate

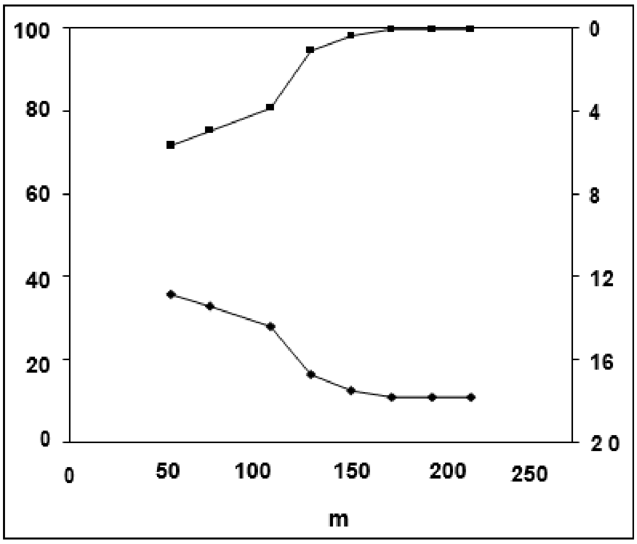

Figure 7: Effect of agitation speed on removal, % and amount adsorbed, mg/g of Bi(III) on Ajwain seeds Bi(III) = 250 mg/g, Time= 240 min, T= 299 ± 2 K, Ajwain seeds =700 mg, pH=2

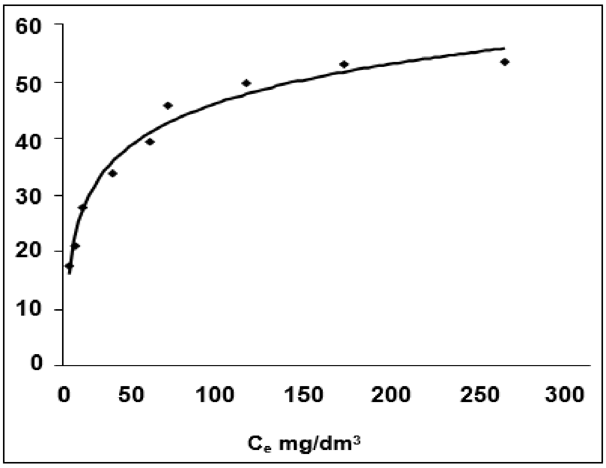

Figure 8: Adsorption isotherm for Bi(III) adsorption on **Ajwain seeds**
Time= 240 min, T= 299 ± 2 K, **Ajwain seeds** =700 mg,

agitation speed= 160 rpm, pH=2

and forming an L-shaped isotherm. This trend suggests that at low concentrations, the adsorbent exhibits a high affinity for Bi(III) ions, which gradually diminishes as the concentration increases (Acharya et. al, 2009). Various isotherm models, both empirical and theoretical, have been used to describe adsorption behavior. Figure 8 (Table 5) presents the Bi(III) adsorption isotherm on the Ajwain seed adsorbent. Additionally, further studies were conducted using the Freundlich and Langmuir isotherm models to better understand the adsorption mechanism.

Table 5: Adsorption isotherm of Bi(III) adsorption on Ajwain seeds
Time= 240 min, T= 299 ± 2 K, CSAC=700 mg, agitation speed= 160 rpm, pH=2

C_e	q
3.19	17.61
6.79	20.94
11.14	27.76
27.91	33.71
49.26	39.32
59.88	45.71
104.41	49.67
159.43	52.89
251.41	53.46

4.6 Langmuir Isotherm

The Langmuir adsorption isotherm is one of the most widely used models for describing monolayer adsorption. This model assumes that adsorption occurs at specific homogeneous sites on the adsorbent surface, with no interactions between the adsorbed molecules. It also presumes a uniform distribution of adsorption energies across the surface. The key characteristic of the Langmuir isotherm is described by the dimensionless separation factor (RL), which helps determine the favorability of the adsorption process.

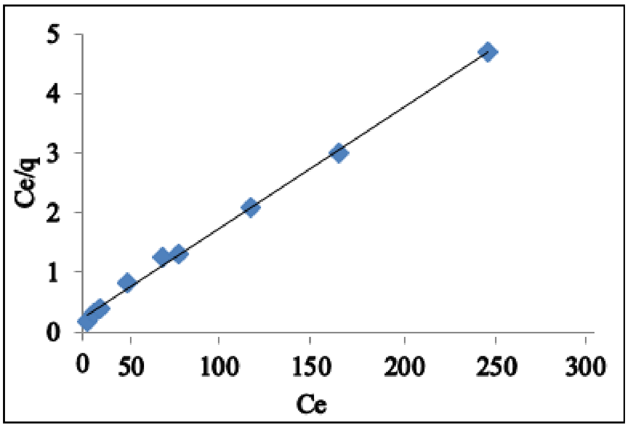

Figure 9: Langmuir isotherm for adsorption of Bi(III) on **Ajwain seeds** Time= 240 min, T= 299 ± 2 K, **Ajwain seeds** =700 mg, agitation speed= 160 rpm, pH=2

In this study, the calculated RL values ranged from 0.0304 to 0.7117, confirming that the adsorption of Bi(III) onto Ajwain seeds is favorable. Figure 9 (Table 6) illustrates the Langmuir isotherm plot, while Table 7 presents the values of qm (maximum adsorption capacity) and KL (Langmuir constant). The experimental qm value (54.35 mg/g) closely matched the computed qm value (53.47 mg/g), demonstrating the accuracy of the model. Additionally, the high correlation coefficient (R^2) indicates a strong agreement between the experimental data and the Langmuir isotherm, confirming the monolayer adsorption of Bi(III) onto the Ajwain seed surface.

Table 6: Langmuir isotherm for adsorption of Bi(III) on Ajwain seeds.
Time= 240 min, T= 299 ± 2 K, CSAC=700 mg, agitation speed= 160 rpm, pH=2

C_e	C_e/q
3.19	0.1815
6.79	0.3245
11.14	0.4014
27.91	0.8279
49.26	1.2526
59.88	1.3098
104.41	2.1018
159.43	3.0139
251.41	4.7020

Table 7: Langmuir isotherm constant for adsorption of Bi(III) on Ajwain seeds

q_m (mg/g)	K_L(1/mg)	**R^2**
54.349	0.1264	0.994

4.7 Freundlich Isotherm

The Freundlich empirical model is widely used to describe adsorption processes involving multilayer adsorption and non-ideal sorption on heterogeneous surfaces. The values of Kf and n were determined from the intercept and slope of the Freundlich isotherm plot (Fig. 10), as detailed in Tables 8 and 9. The analysis revealed that the Langmuir model provided a better fit for the experimental data. The equilibrium adsorption capacity predicted by the Freundlich isotherm was 17.52 mg/g, whereas the experimentally obtained value was 13.41 mg/g, indicating a discrepancy between theoretical and observed values.

Table 8: Freundlich adsorption isotherm for adsorption of Bi(III) on Ajwain seeds.
Time= 240 min, T= 299 ± 2 K, CSAC=700 mg, agitation speed= 160 rpm, pH=2

log C_e	log q_e
0.5051	1.2460
0.8324	1.3211
1.0472	1.4435
1.4459	1.5278
1.6925	1.5946
1.7773	1.6600
2.0187	1.6961
2.2025	1.7234
2.4003	1.7281

Table 9: Freundlich Isotherm constant for adsorption of Bi(III) on Ajwain seeds.

K_f	n	R^2
13.4	3.668	0.968

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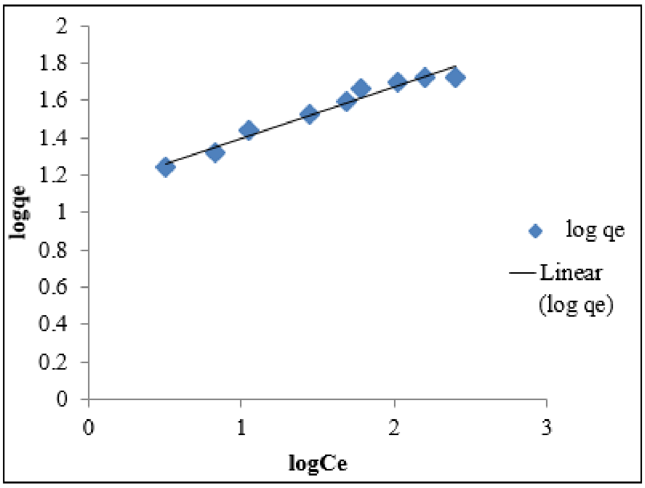

Figure 10: Freundlich isotherm for adsorption of Bi(III) on **Ajwain seeds** Time= 240 min, T= 299 ± 2 K, **Ajwain seeds** =700 mg, agitation speed= 160 rpm, pH=2

4.8 Adsorption Kinetics

The rate at which solute molecules are adsorbed plays a crucial role in controlling the overall adsorption efficiency. This rate is governed by adsorption kinetics, which describes how quickly equilibrium is reached during the adsorption process. The Lagergren equation, also known as the pseudo-first-order kinetic model, was used to analyze Bi(III) adsorption onto Ajwain seeds. A linear relationship between log (qe - qt) and time (t) was observed (Fig. 7), from which the rate constant k1 and equilibrium adsorption capacity qe were determined using the slope and intercept of the plot.

For this study, adsorption of Bi(III) was investigated using 700 mg of Ajwain seeds in a solution with an initial Bi(III) concentration of 250 mg/dm³ over a time span of 0 to 240 minutes. The pseudo-first-order model yielded a k1 value of 0.66×10^{-3} min^{-1} and a theoretical qe of 16.16 mg/g. However, the experimentally determined qe was 17.77 mg/g, indicating a poor fit between the predicted and observed values. The correlation coefficients (R^2) for the pseudo-first-order model were relatively low, suggesting that this model was not the best representation of the adsorption kinetics.

To better describe the adsorption behavior, the pseudo-second-order kinetic model was applied. The adsorption rate constant k2 ($g\ mg^{-1}\ min^{-1}$) was determined using the t/qt vs. t plot (Fig. 7), and the corresponding values are presented in Table 10. Additionally, Table 11 compares the kinetic parameters of the pseudo-first and pseudo-second-order models. The results clearly showed that the pseudo-second-order model provided a better fit for the experimental data, confirming that Bi(III) adsorption onto Ajwain seeds followed a pseudo-second-order kinetic mechanism. This suggests that the adsorption process was primarily governed by chemisorption, involving stronger interactions between Bi(III) ions and the functional groups on the Ajwain seed surface.

Table 10: Pseudo first order model for adsorption of Bi(III) on Ajwain seeds Bi(III) =250 mg/dm^3, T= 299 ± 2 K, CSAC=700 mg, agitation speed= 160 rpm, pH=2

t min	log (q_e-q_t)
0	1.2500
15	1.0349
30	0.08674
60	0.7992
90	0.6888
120	0.6627
150	0.4149
180	0.0718
210	-0.4814

Table 11: Pseudo second order model for adsorption of Bi(III) on Ajwain seeds Bi(III) =250 mg/dm^3, T= 299 ± 2 K, CSAC=700 mg, agitation speed= 160 rpm, pH=2

t	t/q_t
0	0
15	1.99
30	3.00
60	4.98
90	7.00
120	8.56
150	9.23
180	11.02
210	11.99
240	12.96

4.9 Effect of Temperature

The impact of temperature on Bi(III) adsorption onto Ajwain seeds was examined over a temperature range of 303 K to 323 K. The adsorption capacity increased with rising temperature, reaching a maximum of 59.09 mg/g at 323 K, compared to 54.90 mg/g at 303 K for an initial Bi(III) concentration of 1000 mg/dm³ at pH 2.0 (Fig. 11, Table 12). This enhancement in adsorption capacity at higher temperatures can be attributed to the increased availability of active adsorption sites on the Ajwain seed surface (Table 13).

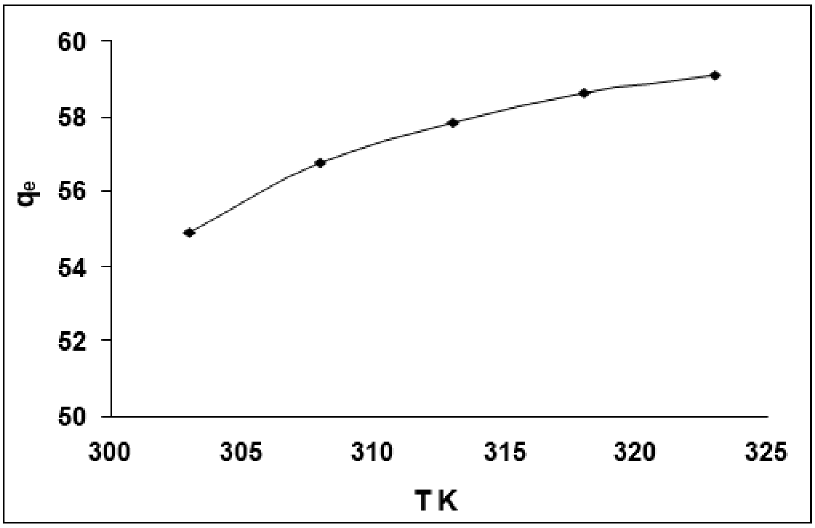

Figure 11: Effect of temperature on amount of Bi (IIII) adsorbed, mg/g on CSAC Bi(III) = 1000 mg/dm^3, time= 240 min, CSAC=700 mg, agitation speed= 160 rpm, pH=2

Table 12: Kinetic parameters values of the adsorption of Bi(III) on Ajwain seeds

Pseudo first order				Pseudo second order		
q_e exp. (mg/g)	k_1x10^{-3} (min^{-1})	q_e calc. (mg/g)	R^2	k_2 x10^{-3}	q_e calc. (mg/g)	R^2
17.61	0.65	16.16	0.868	2.158	18.61	0.977

Table 13: Values of intra particle diffusion of Bi(III) on Ajwain seeds

K_{id} (mg g^{-1}min^{-1})	R^2
0.879	0.975

To further analyze the thermodynamic aspects of the adsorption process, a Van't Hoff plot of ln Kc vs. 1/T (Fig. 9) was used to determine the entropy **(**ΔS°**)** and enthalpy (ΔH°**)** changes (Table 14). The positive value of ΔH° confirmed that the adsorption process was endothermic, meaning it required energy input to occur. Additionally, the Gibbs free energy change (ΔG°) values were negative (Table 15), indicating that the adsorption process was spontaneous and thermodynamically favorable (Table 16).

Table 14: Amount of Bi(III) adsorbed on AS at different temperature Bi(III) = 1000 mg/dm^3, Ajwain seeds =700 mg, Time= 240 min, pH=2, agitation speed = 160 rpm

T K	Amount adsorbed, q mg/g
303	55.00
308	57.01
313	58.21
318	59.01
323	59.99

Table15: Removal of Bi(III) on Ajwain seeds for Van't Hoff plot Bi(III) = 1000 mg/dm^3, AS =700 mg, agitation speed= 160 rpm, pH=2, Time= 240 min

1/T	lnK_c
0.00329	1.1231
0.00323	1.1559
0.00318	1.1750
0.00313	1.1885
0.00308	1.1966

Table 16: Study of Thermodynamic parameters on Ajwain seeds adsorption of Bi (III)

T K	ΔG° kJ/mol	ΔH° kJ/mol	ΔS° J/mol k
303	-2.829	0.347	2.278
308	-2.959		
313	-3.057		
318	-3.142		
323	-3.213		

5. Conclusions

The study highlights the potential of Ajwain (*Trachyspermum copticum*) seeds as an effective and natural adsorbent for the removal of bismuth (Bi(III)) from aqueous solutions. Given the rising concerns regarding bismuth contamination due to its extensive use in pharmaceuticals, cosmetics, and industrial applications, finding an eco-friendly and cost-effective method for its removal is crucial. The experimental findings demonstrate that Ajwain seeds possess significant adsorption capacity, making them a promising alternative to conventional adsorbents.

The research investigated various parameters influencing the adsorption efficiency, including contact time, initial Bi(III) concentration, adsorbent dosage, agitation speed, and temperature. The adsorption process was found to be rapid, reaching near equilibrium within 240 minutes, with a maximum adsorption efficiency of 98.62%. The adsorption capacity increased with rising initial Bi(III) concentrations, reaching a peak value of 53.37 mg/g at 1000 mg/dm^3. Additionally, increasing the adsorbent dosage enhanced Bi(III) removal, confirming the availability of more active binding sites.

The study also evaluated the effect of agitation speed, revealing that higher speeds facilitated improved contact between Bi(III) ions and the adsorbent surface, thus enhancing the removal efficiency. Similarly, the adsorption process was temperature-dependent, with higher temperatures favoring Bi(III) uptake, suggesting an endothermic nature of adsorption.

The adsorption data were analyzed using isotherm models, with both Langmuir and Freundlich models applied to understand the adsorption mechanism. The Langmuir isotherm provided a better fit, indicating monolayer adsorption on a homogeneous surface, with a maximum adsorption capacity of 54.35 mg/g. The Freundlich model, which accounts for multilayer adsorption on a heterogeneous surface, showed some applicability but was not as accurate in describing the experimental data. Kinetic studies revealed that the adsorption process followed a pseudo-second-order model, suggesting that chemisorption was the primary mechanism governing Bi(III) removal. Thermodynamic parameters confirmed that the adsorption was spontaneous and endothermic, indicating that higher temperatures favored the process. The negative $\Delta G°$ values confirmed the feasibility of Bi(III) removal under the studied conditions.

Overall, the study establishes Ajwain seeds as a low-cost, sustainable, and highly efficient adsorbent for bismuth removal from contaminated water. Their availability, biodegradability, and non-toxic nature make them a viable alternative to synthetic adsorbents. Further research can explore modifications or activation techniques to enhance their adsorption capacity and extend their application to other heavy metal contaminants. These findings contribute to the growing body of research on natural adsorbents, promoting environmentally friendly solutions for water purification and heavy metal remediation.

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