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Available Low Cost Agro-Waste as an Efficient Medium to Eliminate Heavy Metal Contamination using Sustainable Approach Achieving Zero Residue Level

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ABSTRACT

Although bismuth is a low toxic metal compared to other heavy metals, but its continuous accumulation in living tissues is considered a serious issue for health and environment. The present investigation aims to test the adsorption technique for removing bismuth ions from polluted aqueous medium via pomegranate peels as low-cost medium in an adsorption unit of batch-type at various operating parameters. The obtained results showed that pomegranate peels have a remarkable efficiency in to recover Bi^{+3} ions from polluted water, reaching approximately 75% at 38 ppm initial bismuth concentration, agitation speed of 350 rpm, 2.4 h contact time, acidity function of 7.5 g dose of pomegranate peel, and 20 °C temperature. Isothermal and kinetic studies indicated that the Langmuir and pseudo-second order models are the closest to describing the adsorption. Furthermore, the adsorption was spontaneous, physical, and of low entropy according to thermodynamic, while the adsorption capacity was 2.26 mg/g. In order to dispose of the residual waste in an environmentally safe manner, it was investigated to convert them into a rodenticide. The pomegranate peels loaded with bismuth ions showed a clear and effective effect against laboratory rats of Sprague Dawley type, and the lethal half dose (LD_{50}) calculated was very close to what was mentioned in the literature.

Keywords: adsorption, batch unit, bismuth, pomegranate peels, ZRL.

INTRODUCTION

Environmental problems vary between natural and human. Examples of natural problems include volcanoes, earthquakes and floods, which occur naturally and often have a specific impact on a specific area. Human problems, however, have the greatest impact and the widest reach. Since the existence of humans on planet Earth, human-caused problems have developed, the most important of which is the ongoing problem of pollution. Heavy metals are among the most important pollutants released by human industrial, agricultural, military and recreational activities (Hameed and Abbas, 2024). The accumulation problem of the various heavy metals is one of the major environmental issues that countries are paying increasing attention at the present time, not due to its mischievous impacts on the people health and the milieu and its deformation of the urban face, but also for its public and frugal impacts, and each of these sides has a high cost that states incur in expenditures that they could have saved, or losses that they could have avoided (Hashem et al., 2021). With population increase, the altitude in the requirements of living, the speedy industrial and technical grew up, the quantities of wastewater resulting from various human activities have diversified and increased, and consequently the number of heavy metals thrown into the environment has increased (Khaleel et al., 2022). The process of getting rid of them has become one of the most outstanding issues facing societies and human combination due to the serious of this waste on the environment, the natural resources and to health and safety of human (Abbas and Abbas, 2013a). Accordingly, the development of an integrated management system for wastewater and its contents of heavy metals has become one of the most important matters of waste management strategies to find a special orientation towards the removal and disposal of heavy metals in an appropriate manner (Ali et al., 2020a). Simultaneously, advancing technical and economic approaches by leveraging contemporary technical methods and modern trends in this field, while also ensuring the execution of diverse operations and the engagement in various activities essential for human life (Al-Hermizy et al., 2022). To remedy the solutions polluted by heavy metals, there are different manner including ultra-filtration, reverse osmosis, nano-membrane filtration, coagulation-flocculation, ion exchange, chemical precipitation, flotation, oxidation, advanced oxidation process (AOP), catalytic ozonation, evaporation, biological methods, and adsorption (Abbas et al., 2020). The adsorption technique is among the most important methods used in water treatment, especially in the last four decades (Abbas and Abbas, 2013b). The advantages of this technique compared to other methods and techniques, this method is considered efficient at low concentrations of polluting substances in general and heavy metals in particular, and does not require any initial preparations and does not consume high energy and has a low operating cost, especially if a substance with a high surface area such as activated carbon is used (Alalwan et al., 2021). However, like all other methods, it has drawbacks and limitations, some of which are the high price of the adsorbent material (activated carbon), its decreasing capacity and efficiency over time, and 10–15% of its mass waste by every regeneration process, in addition to the accumulation of toxic residues that require disposal in a safe manner (Maddodi et al., 2020). These obstacles prompted researchers to search and find new materials available, with suitable efficiency, non-toxic and non-valuable (Alwan et al., 2021). The researcher found what they want in the various agricultural and industrial wastes that achieve these specifications, as they can be used directly or can be converted into activated carbon (Abbas and Abbas 2013c). On the one hand, these wastes - which represent one of the types of solid waste - must be disposed of because they represent a source of environmental pollution and are available throughout the year in different types (Abbas and Alalwan, 2019). On the other hand, these wastes possess specifications, advantages and components that can be utilized and exploited in the treatment of environmental pollution, among these specifications is the valuable surface area (Alhamd et al., 2024a). Although it has a low surface area compared to activated carbon, it has an appropriate efficiency due to the possibility of using it in sufficient quantity and replacing it without a significant cost (Rajaa et al., 2023). These materials include rice husks (Alalwan et al., 2018), banana peels (Abdullah et al., 2023), lemon peels (Alalwan et al., 2020), watermelon rinds (Abbas and Nussrat, 2020), alumina (Shadhan et al., 2024), egg shell (Abbas and Ibrahim, 2020), sunflower seed husk (Abdulkareem et al., 2023), tea leaves (Al-Ali et al., 2023), algae (Abbas et al., 2019a), orange peels (Hasan et al., 2021), hyacinth leaves (Ali and Abbas, 2020), aluminum foil residues (Ghulam et al., 2020), tree leaves (Ali et al., 2024), mandarin peels (Alhamd et al., 2024b) and others. These materials have been used to remove harm pollutants not only from polluted water, but also from crude oil (Ali et al., 2021) and soil (Abbas et al., 2019b). But the problem of residuals after ending the adsorption process represented the greatest burden for researchers, because it is often toxic and cannot be disposed of by throwing it into water, soil or burning (Abbas and Abbas, 2014). Among the ideas to treat this negative side is the application of zero residue level concept's, which consider these materials as a raw materials that can be used in beneficial, economic and environmentally friendly ways (Ibrahim et al., 2021). The residual waste are used as a concrete additive (Abbas et al., 2022a) or to produce a benefit substances, like bioethanol (Hamdi et al., 2024) and acetone (Abbas et al., 2022b) or used as a catalyst (Abbas et al., 2021). Another methods are using these residues as soil fertilizer (Abbas, 2015), a raw material for the preparation of nanoparticles (Alminshid et al., 2021), or use as a pesticide due its toxic effect (Ali et al., 2018). The current research aims to achieve the zero residual level principle through two steps, the first step was investigated the removal of one of the low toxic metals, i.e. bismuth (Bi), from simulated polluted water by adsorption technique using pomegranate peels as an available, low cost and non-valuable adsorption media under different operating conditions. While the last step, included the study of using of the residues as a rodenticide, through tested on rats of the type albino rats of the scientific name *Rattus norvegicus domestica*, and calculating the half-lethal dose (LD_{50}) and comparing it with that is mentioned in the literature to reach the concept of zero residue level (ZRL).

METHODOLOGY

Pomegranate peels adsorbent

The mature pomegranate peels of scientific name *Punica granatum* utilized in this study were obtained from household employment. After collection, the peels were rinsed with excess tap water many times, then rinsed by of 1.0 μS/cm double-distilled water to remove any impurities and dust that might be still stuck on them. The clean peels were subjected for natural drying using sunlight for continuous two days. After that, the peels were soaking in distilled water and boiled for suitable period to get rid the tanner and colour from them. After drying, the treated peels were then dried, kept in the fridge using amber glass jars.

Stock solution

Avoiding to any additional pollutants or materials that could affect the precision of the results, the adsorption experiments were carried out by preparing previously prepared simulated solutions with the required concentrations, by preparing a stock solution of 1000 ppm of bismuth (III) concentration. Bismuth nitrate salt of a chemical formula $Bi(NO_3)_3 \cdot H_2O$ (supplied by Indian company Omkar specialty chemicals Ltd. Co.) was used as a source of bismuth (III), where the needed amount of nitrite salt was dissolved in 1 L of double distilled water supplied from distillation apparatus of a type (GFL Double Distiller, 2014). The dissolving process was conducted by a magnetic mixer of type (Fisher Scientific, IKA™ C-MAG MS 7) for 30 minutes at room temperature. The concentration of prepared stock solution was 1000 ppm, i.e., every 1 cm^3 of the stock solution contains 0.001 g of trivalent bismuth ions.

Calibration curve

The stock solution and the solutions of adsorption-treated were tested by the atomic absorption spectrophotometer with the assistant of the calibration curve graphed previously prepared for this goal. In order to determine the value of the percentage removal and the efficiency of the adsorbent material, the calibration curve was prepared. Using the precision plot, the important variable, the concentration of bismuth ions remaining in the solutions treated by pomegranate peel can be revealing. Thus, the calculating of the adsorption capacity is performed accurately. The calibration curve was prepared by the method described by (Ali et al., 2020b) through examining several known concentrations of bismuth solution at a wavelength of 222.8 nm, and then by recording the level of atomic absorbance, the correction curve was drawn. Each concentration was rechecked at least triplicate to reduce the percentage error and record the most accurate results. Figure 1 shows the calibration curve prepared and used to determine the concentrations of bismuth ions in this study.

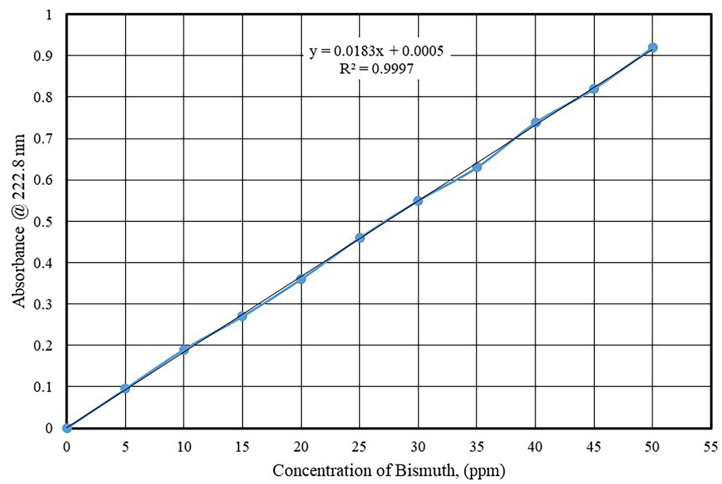

Figure 1. Calibration curve of bismuth using AAS device at λ_{max} = 222.8 nm

Adsorption unit

The batch adsorption unit is one of the simplest and best types of adsorption units, as it is of suitable size and can be carried from one place to another without reconstructed of the parts, does not consume high energy, does not require preliminary preparations and does not require additional equipment in addition to its low operational cost compared to the continuous adsorption unit. Through it, useful and accurate results can be obtained by using small and limited volumes of contaminated solutions to study the adsorption phenomenon, in contrast to the continuous system that requires large and continuous quantities of contaminated solutions. The process of preparing the required samples was done by determining the concentration of bismuth studied and adjusting the value of the pH function of the solution using 0.1 M solutions of hydrochloric acid (HCl) and sodium hydroxide (NaOH) before adding the specified dose of pomegranate peels. Adsorption experiments were carried out using 100 ml Erlenmeyer flask with screw cap (Witeg Labortechnik GmbH) completely covered with aluminum foil to ensure there isn't any effect of the light on the content of flaks. The flasks were put in a Benchtop Orbital Digital Water Bath Shaker ThermoFisher SHKE7000 MaxQ 7000, after that, the agitation speed and temperature are adjusted, and the unit starts to work continuously until reached the specified time. After that, the samples are extracted and the adsorbent is carefully separated from them using filter paper and a vacuum filtration kit with vacuum pump (Southern Labware, FG53405L). Finally, the samples are analyzed using AAS device and calibration curve to know the concentration of bismuth ions remaining in the solution. According to the AAS measurements, the calculation of adsorption efficiency and capacity can be achieved via Equations 1 and 2, respectively.

$$\%R = \frac{C_\circ - C_f}{C_\circ} \quad (1)$$

$$q = \frac{V}{m}(C_\circ - C_f) \quad (2)$$

where: $C_\circ$ and C_f – initial and final concentrations of Bi^{+3} ions in the solution, ppm; V – volume of solution, l; m – mass of adsorbent media (pomegranate peel) used in each experiment; and $\%R$ – percentage removal of Bi^{+3} ions from contaminated solution during adsorption experiment.

The Equations 1 and 2 permit for the quantitative estimate of the adsorption performance, as long as enough data on the efficiency of pomegranate peels in recovering bismuth ions from aqueous solution.

RESULTS AND DISCUSSION

Acidic function effect

The acidic function effect on the removal efficiency of the Bi^{+3} from the polluted solutions was studied within a range 1–10, keeping other variables constant. Figure 2 shows the relation between two factors. It is noticed from Figure 2 that the relationship is direct between the percentage of removal and the value of the pH, as the efficiency increases with increasing pH and vice versa. This result can be explained by the fact that the surface

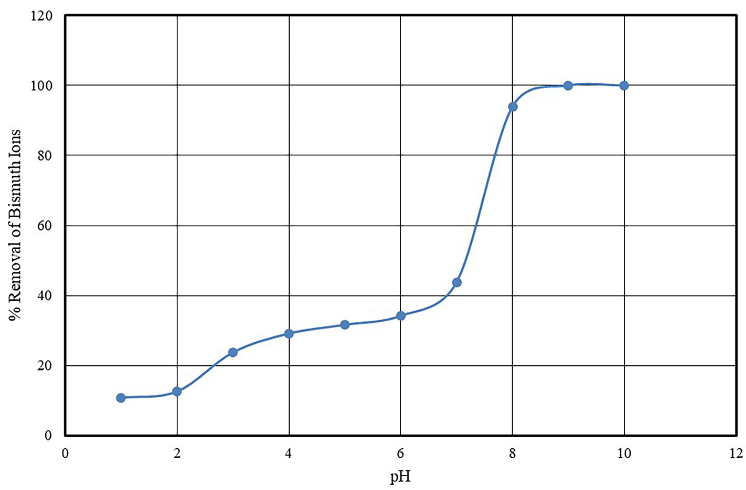

Figure 2. Effect of pH of bismuth (III) ions on the percentage removal

of the adsorbent material (pomegranate peels) will be protonated i.e. charged with positive ions (protons) at the value of the low pH function, because the concentration of hydrogen ions will be higher than the concentration of hydroxide ions, which leads to create of a state of competition between the positive bismuth (III) ions and hydrogen ions to occupy the active sites on the surface of the adsorption media. As a result, bismuth ions remain in the solution, and the percentage of removal decreases due to that competition. With increasing the value of pH, the number of positive ions (protons) begins to decrease, which leads to a decrease in competition between them and the bismuth (III) ions, so the chance of the pollutant ions reaching the active sites on the surface of the pomegranate peels decreases, their number in the solution increases and the removal efficiency increases. It is noted that the removal efficiency increases sharply after pH = 7, which attributed to precipitation process not to adsorption technique. Thus, the optimum pH of adsorption is 7, not any higher value. This result agrees with (Hameed and Abbas, 2024).

Impact of agitating speed

Figure 3 shows the effect of agitation speed on the efficiency of removing bismuth (III) ions from contaminated solutions while the remaining variables kept constants at optimum values. The effect of agitation speed was investigated within a range between 100–450 rpm, where the obtained results showed that the direct relationship between removal efficiency and agitation speed before 350 rpm and after that the efficiency remains constant and is not affected by increasing agitation speed. The agitation speed is considered as one of the vital factors affecting the adsorption process in batch systems, as it affects the mass transfer rate of the adsorbate (i.e. Bi^{+3}) ions from the solution to the surface of the adsorbent (i.e. pomegranate peels). Increasing the agitation speed may lead to accelerate the arrival of bismuth ions to the surface of the adsorption, or the high agitation speed may lead to destruction the film layer formed on the surface of the pomegranate peels, facilitating the access of the pollutant to the adsorption surface as a result of the diminished resistance. By reaching the optimum agitation speed, the substance will be in a state of saturation, and then it will not be able to absorb any additional amount of bismuth ions, or the rate of lost ions will be equal to the rate of adsorbed ions on the surface. This result is consistent with the findings of (Hasan et al., 2021) in their study on the removal of Sb^{+5} using orange peels.

Initial concentration effect

Within a range between 1–50 ppm, the effect of the initial concentration of bismuth ions on the efficiency of removal from contaminated aqueous solutions was studied, and the other operational variables set at the optimum value, and this is illustrated by Figure 4. The practical values for studying this variable gave an intuitive result as the relationship was inversely between concentration and percentage of removal, and this is similar to the results of (Alhamd et al., 2024a). Concentration is defined as the ratio of the mass of pollutant measured by milligrams to the volume of solution measured by litters. From

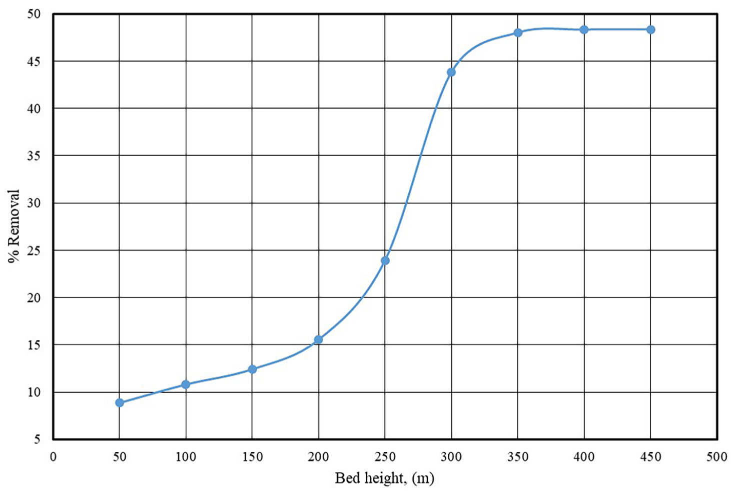

Figure 3. Effect of agitation speed on the percentage removal of bismuth (III) ions

this definition, it becomes clear that an increase in concentration means an increase in the mass of the pollutant substance with a constant volume, meaning that the adsorbent media will deal with increasing quantities of up to 100 times of bismuth ions. Since the mass of the adsorbent material is constant, so its surface area will be constant per unit mass, which means that the active sites will also be constant, as will the functional groups. Since these limited sites have a constant ability to adsorb a specific number of bismuth ions, the adsorption efficiency will decrease with the increasing the initial concentration value, and as a result, the percentage of adsorption will decrease.

Behaviour of adsorbent dose

The results of the study of this variable with the percentage of bismuth removal using pomegranate peels are represented in Figure 5 by holding the remaining variables at the optimal values. From the observation of the above figure, it becomes clear that the relationship between the two variables is direct, as the small amount of a substance corresponds to small adsorption efficiency and vice versa. As previously shown in the explanation of the effect of the initial concentration, the adsorbent material (pomegranate peel) has a specific surface area per unit mass, i.e. the greater amount of adsorbent material, means greater

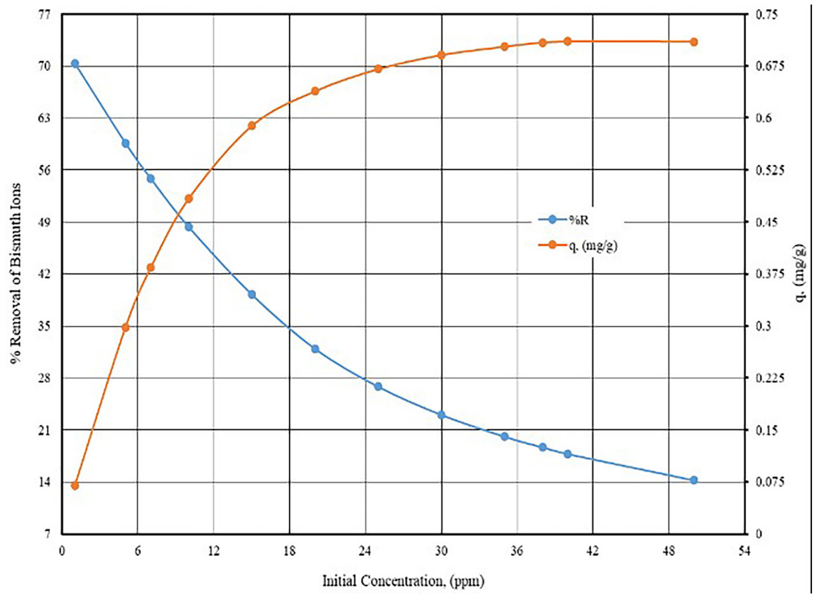

Figure 4. Effect of initial concentration on bismuth ions removal

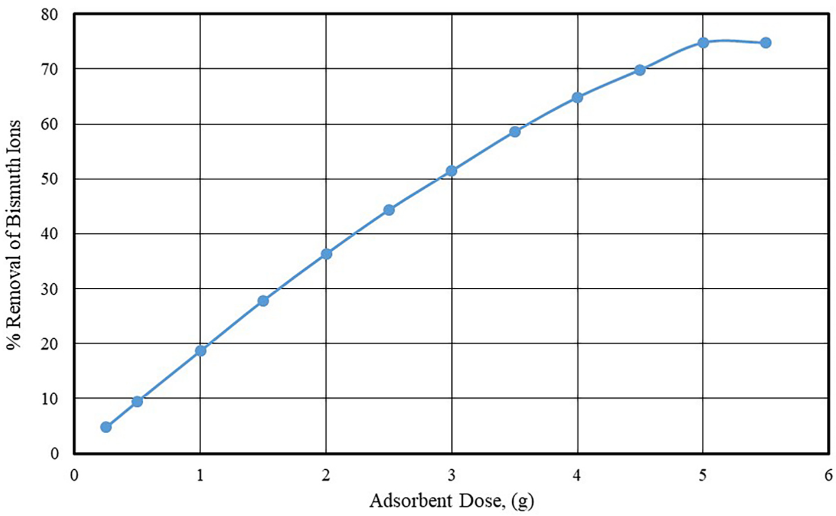

Figure 5. Effect of adsorbent dose on the percentage removal of bismuth (III) ions

surface area, and this leads to an increase in the active sites and functional groups. Thus, the ability of the substance to adsorb a greater number of bismuth ions will increase, and then their number in the solution will decrease and the removal efficiency will increase too. This result is matched with the findings of most previous researchers, including (Alalwan et al., 2021).

Contact time effect

As shown by the practical results obtained from conducting time set experiments, the increased contact time between bismuth (III) ions and the adsorbent material leads to increased removal efficiency and this is explained by the Figure 6.

The increase in contact time means an increase in the required time that the ions can be spent in contact with the adsorbent material at the constant agitation speed. This means increasing the chance of ions reaching the active sites and attaching to the functional groups. Consequently, the number of adsorbed ions increases, and the number of free bismuth ions in the solution decreases, thus increasing the adsorption efficiency. It is also noted that the removal efficiency remains constant after 144 minutes despite the increase in contact time. The reason for this is due to the occurrence of saturation state in the adsorbent particles (pomegranate peels), which means that a greater number of bismuth ions cannot be absorbed under the current conditions and therefore the percentage of removal will remain unchanged no matter how long the contact time increases. This result is agreed with (Al-Hermizy et al., 2022).

Temperature effect

The effect of temperature on the percentage removal of bismuth was studied, exhibitionist an outstanding descending in removal ability from 74.79% to 59.25% when the temperature escalating from 20 to 50 °C as illustrated in Figure 7. There are several factors that contribute to this observed decrease in removal efficiency with increasing temperature. The first factor is weakened interactions between the adsorbent material and bismuth ions. As higher temperatures can disrupt the physical adsorption process by causing weaker interactions between the adsorbent material and the bismuth ions.

As the temperature rises, the increased thermal energy can weaken the attractive forces between the active sites of adsorbent media and the bismuth ions, resulting in a reduced adsorption capacity and hence a lower percentage of bismuth ions being removed. Other factor is desorption of adsorbate. The elevated temperatures can also enhance desorption of previously adsorbed bismuth ions from the surface of the adsorbent material. As the temperature increases, the molecules' kinetic energy increases, leading to greater movement and desorption from the active sites. Consequently, the removal efficiency decreases as a result of a higher proportion of bismuth ions being released back into the solution. Furthermore, higher temperatures may accelerate certain chemical reactions that could potentially interfere with the adsorption process. For example, the presence of reactive species or the occurrence of competing reactions in the solution may be encouraged at elevated temperatures,

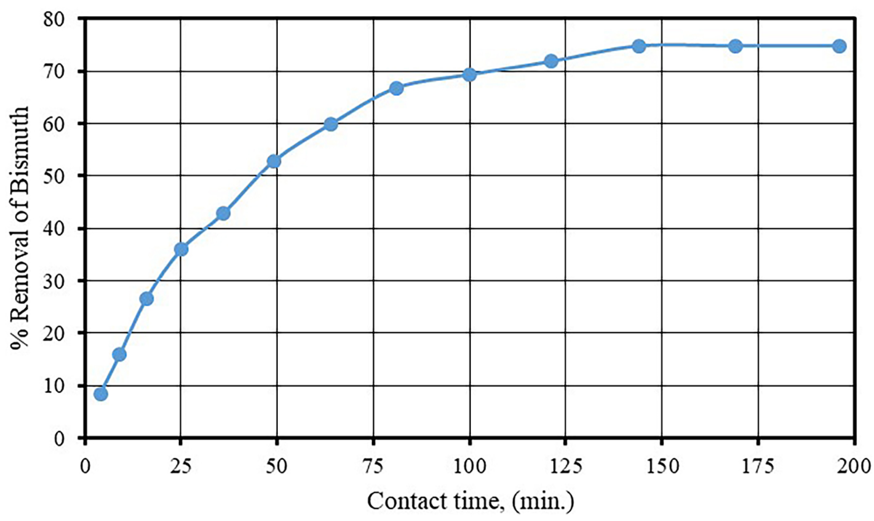

Figure 6. Effect of contact time on the percentage removal of bismuth (III) ions

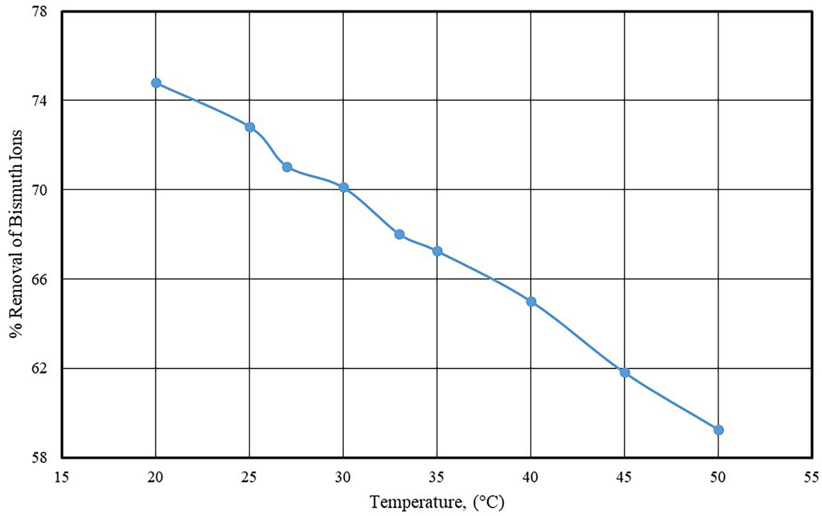

Figure 7. Effect of temperature on the percentage removal of bismuth (III) ions

hindering the effective adsorption of bismuth ions onto the adsorbent material. This interference can further contribute to the reduction in removal efficiency observed with increasing temperature (Abdullah et al., 2023).

BEHAVIOUR OF ADSORPTION

Isothermal study

Isothermal study embraces exploring the demeanour of the adsorption process when the temperature of the system is remaining constant. Langmuir, Freundlich, and Temkin adsorption isotherm models are considered famous models used to describe adsorption characteristics and equilibrium relevance's between the two sides of adsorption process, (i.e., adsorbate and adsorbent) (Shadhan et al., 2024). The algebraic formulas which dub the various mathematical equations of the isothermal models used in this study are listed in Table 1. These models assist know and estimate the behaviour of adsorption in different scientific and industrial implementations. Following detailed scrutiny, explained through Figures 8–10 and Table 2, it was ascertained that the Langmuir model displayed the optimal precision. The correlation coefficient (R^2) value resulted from the Langmuir model was 0.9936, signalizing a strong match between the prophesy values and the real data from experimental part. On the other hand, the other isothermal formulas (i.e., Temkin and Freundlich models) exhibited R^2 values of 0.9893 and 0.9836, respectively (Abbas et al., 2019 b). This result refers that these models may not sufficiently represent the adsorption behaviour investigated in contrast to the Langmuir model. The main assumptions of Langmuir model is the adsorption happens on a regular surface where every adsorption position possess an equal alliance for the adsorbate. It also supposes that when the adsorption site is occupied, no more adsorption

Table 1. Details of the isotherm models used in the current study

Model	General form	Linear form	Slop	Intercept	Augmented parameter
Langmuir	$q_e = \frac{q_{max} \cdot K_L C_e}{1 + K_L C_e}$	$\frac{1}{q_e} = \frac{1}{q_{max} K_L} \frac{1}{C_e} + \frac{1}{q_{max}}$	$\frac{1}{q_{max} K_L}$	$\frac{1}{q_{max}}$	$R_L = \frac{1}{1 + K_L C_e}$
Freundlich	$q_e = K_F C_e^{\frac{1}{n}}$	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	$\frac{1}{n}$	$\ln K_F$	–
Temkin	$q_e = \frac{RT}{b} \ln K_T C_e$	$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e$	$\frac{RT}{b}$	$\frac{RT}{b} \ln K_T$	–

Note: C_e – adsorbed concentration at the equilibrium (mg/l), q_e – capacity of the adsorption at the equilibrium (mg/g), q_{max} – maximum adsorption capacity (mg/g), R_L – separation factor, (dimensionless), K_L – Langmuir constant, expressed the binding sites (l/mg), K_F – Freundlich constant, [(mg/g)·(l/mg)$^{1/n}$], n – intensity of adsorption (–), R – universal gas constant (8.3144 J/mol.K), T – absolute temperature (K), b – Temkin isotherm constant related to adsorption heat (J/mol), and K_T – Temkin isotherm equilibrium binding constant (L/g).

Table 2. The values of constants of isotherm models

Model	Constant			
Langmuir	R^2	q_{max}	K_F	R_L
	0.9959	0.4015	4.0565	0.0064
Freundlich	R^2	K_F	n	
	0.9824	0.1912	5.5127	
Timkin	R^2	b	K_T	
	0.9885	40.6231	13.6386	

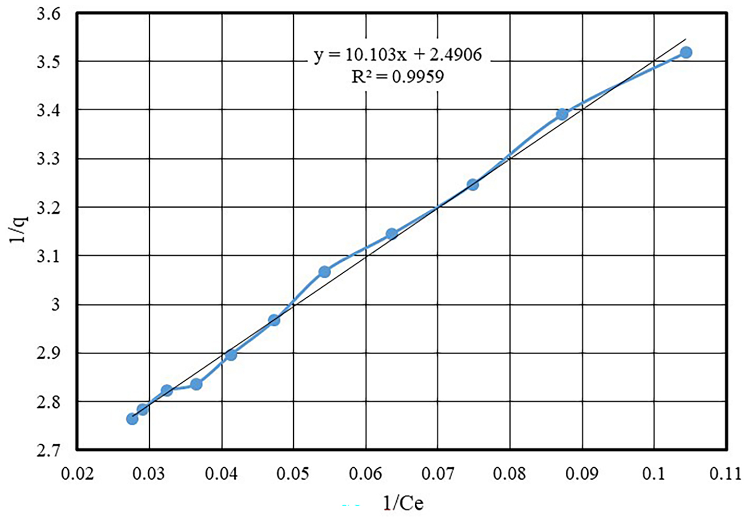

Figure 8. Langmuir isotherm model

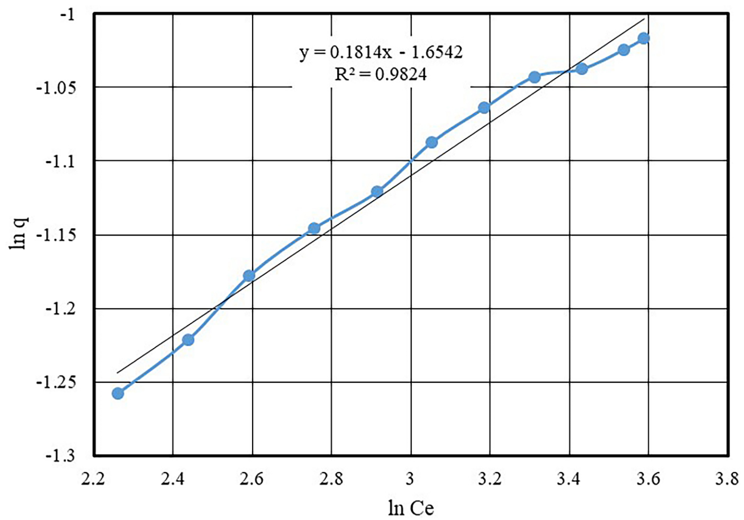

Figure 9. Freundlich isotherm model

can take place at that adsorption position. These hypothesizes make the Langmuir model predominately appropriate for characterizing the conduct of monolayer adsorption on a surface. Its high accuracy implies that it can effectively predict and explain the adsorption behaviour of the system under investigation (Ibrahim et al., 2021).

Kinetic study

Kinetic studies in adsorption processes aim to understand the rate at which adsorbate molecules are taken up by an adsorbent material. Several models are commonly used to describe these processes, including pseudo first order, pseudo

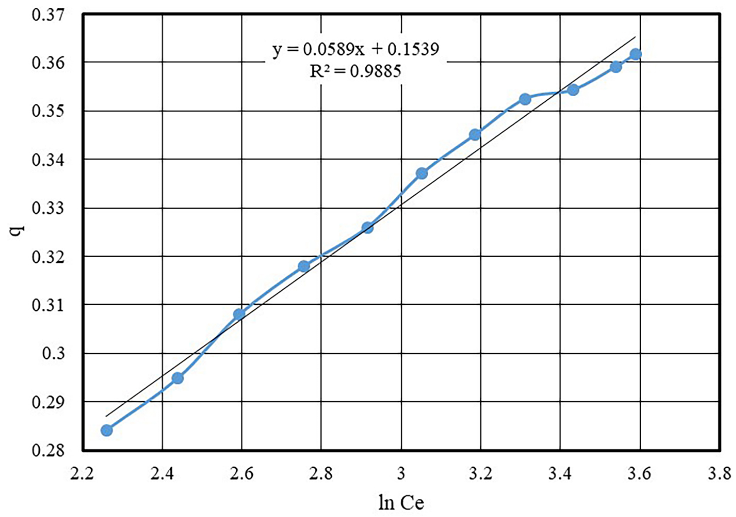

Figure 10. Temkin isotherm model

second order, Elovich, and intra-particle diffusion models. These models provide mathematical equations that describe the relationship between the amount of material adsorbed and time taken, allowing for a better understanding and prediction of the adsorption kinetics.

Table 3 explains the models used to describe the kinetic study in the current research. The results of the kinetic study are represented by Figures 11–12 and Table 4 indicate that the pseudo second order model yielded the best fit to the experimental data comparing the other aforementioned models (Shadhan et al., 2024). The correlation coefficient (R^2) for this model was found to be 0.9972, which suggests a very strong agreement between the predicted values and the actual experimental observations (Alhamd et al., 2024b). The pseudo second order model assumes that adsorption takes place through chemical reactions on the surface of the adsorbent, and that the rate of adsorption is proportional to the square of the number of unoccupied sites on the surface. The rate of reaction is the determining factor for the rate of adsorption, not diffusion into the adsorbent or in solution. It also assumes that there is sufficient time for equilibrium between adsorption on the surface and dissociation from the surface to be reached. All of the above assumptions occur at constant temperature and on homogeneous sites. The strong agreement between the predicted and experimental values supports the suitability of the pseudo first order model for this particular adsorption system. On the other hand, the intra-particle diffusion, pseudo second order, and Elovich models exhibited lower correlation coefficients of 0.9638, 0.8882, and 0.9805, respectively (Fig. 13, Fig.14). These lower correlation coefficients suggest that these models were relatively less effective at capturing the kinetics of bismuth metal ions adsorption onto pomegranate peels.

Table 3. Details of the kinetic models used in the current study

Kinetic model	Differential form	Linear form	Slop	Intercept
Pseudo first order	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	$\ln(q_e - q_t) = \ln q_e - k_1 t$	$-k_1$	$\ln q_e$
Pseudo second order	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t$	$\frac{1}{q_e}$	$\frac{1}{k_2 {q_e}^2}$
Elovich model	$\frac{dq_t}{dt} = \alpha e^{-\beta q_t}$	$q_t = \frac{1}{\beta} \ln t + \frac{1}{\beta} \ln \alpha\beta$	$\frac{1}{\beta}$	$\frac{1}{\beta} \ln \alpha\beta$
Intra-particle diffusion	–	$q_t = k_P t^{0.5} + I$	k_P	I

Note: q_t – adsorbate adsorbed onto adsorbent at time t (mg·g), q_e – capacity of the adsorption at the equilibrium (mg/g), t – time (min), k_1 – first order rate constant (min^{-1}), k_2 – second order rate constants (g·mg^{-1}·min^{-1}), α – rate of the initial adsorption (mg·g·min), β – constant of desorption (dimensionless), k_p – rate constant mg·g·min$^{0.5}$, and I – constant.

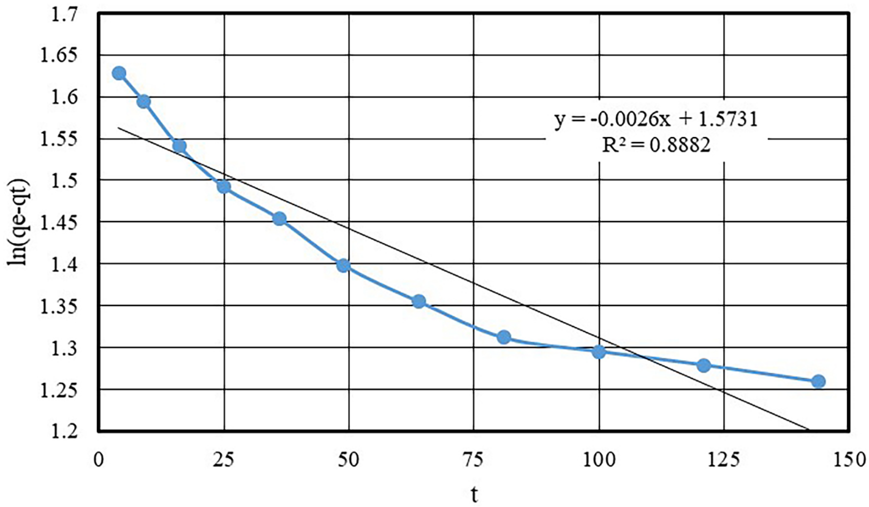

Figure 11. Pseudo-First-Order Kinetic Model

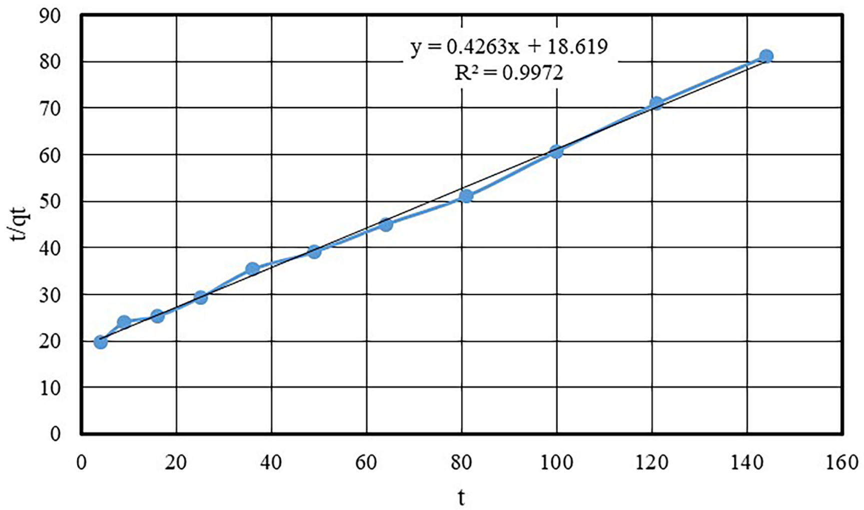

Figure 12. Pseudo-Second-Order Kinetic Model

Table 4. Values of constants of kinetic models

Model	Constants		
Pseudo-first-order	k_1	q_e	R^2
	0.0026	4.8216	0.8882
Pseudo-second-order	k_2	q_e	R^2
	9.7602×10^{-3}	2.3458	0.9972
Elovich	α	β	R^2
	0.3579	2.0738	0.9805
Intra-particle diffusion	k_p	I	R^2
	0.1645	0.0177	0.9638

Thermodynamic study

Thermodynamic studies in adsorption processes focus on understanding the energy changes that occur during the adsorption process. This includes examining the effects of temperature on the adsorption behaviour. The functions used to describe the thermodynamic of adsorption system are Enthalpy (H), Entropy (S), and Gibbs free energy (G). The

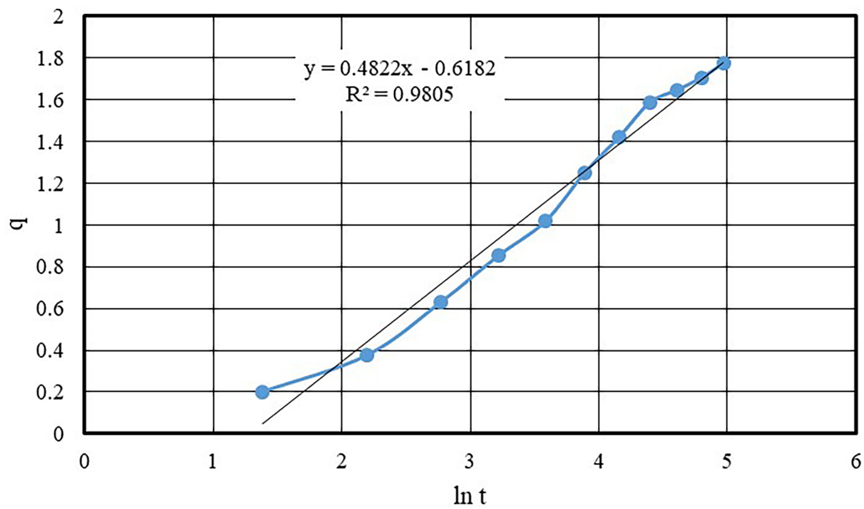

Figure 13. Elovich kinetic model

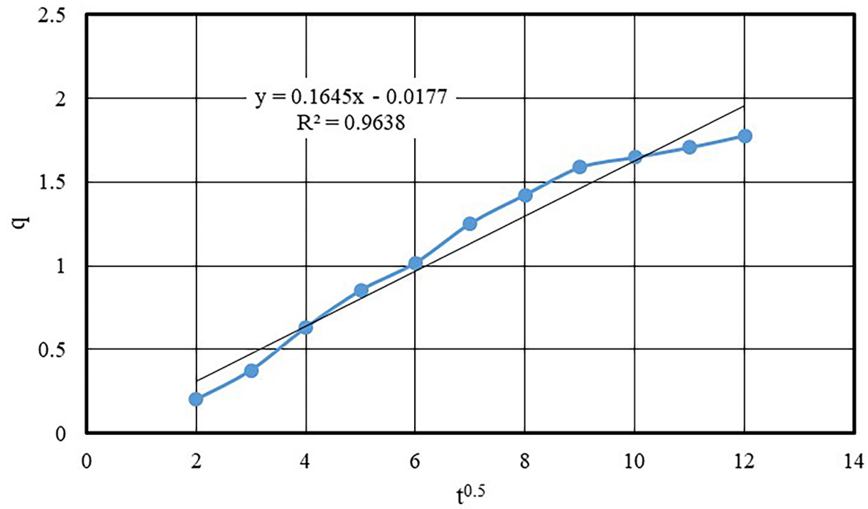

Figure 14. Intra-Particle Diffusion Kinetic Model

relationship between these thermodynamic functions is given by the Equation:

$$\Delta G = \Delta H - T\Delta S \quad (3)$$

where: ΔG the change of Gibbs free energy, ΔH the change in enthalpy, T the temperature in Kelvin, and ΔS the change in entropy. Determining these thermodynamic functions for any adsorption process provides insights into the physical and chemical nature of the process (Shadhan et al., 2024).

Also, it helps to optimize the efficiency of the adsorbent material by understanding the mechanism of adsorption, estimating the heat exchange, evaluating the spontaneity of the process, and characterizing the disorder level. From Table 5 and Figure 15, it can be seen that the adsorption is of chemical type, spontaneous, exothermic and of decreased entropy, according to the value of enthalpy and the sign of ΔG, ΔH, and ΔS, respectively.

Table 5. The values of thermodynamic properties constants

T, °C	Δ*H* (kJ/mol)	Δ*S* (J/mol·K)	Δ*G* (kJ/mol)
20	-18.8322	-2.2466	-19.4908
25			-19.5021
27			-19.5066
30			-19.5133
33			-19.5200
35			-19.5245
40			-19.5358
45			-19.5470
50			-19.5582

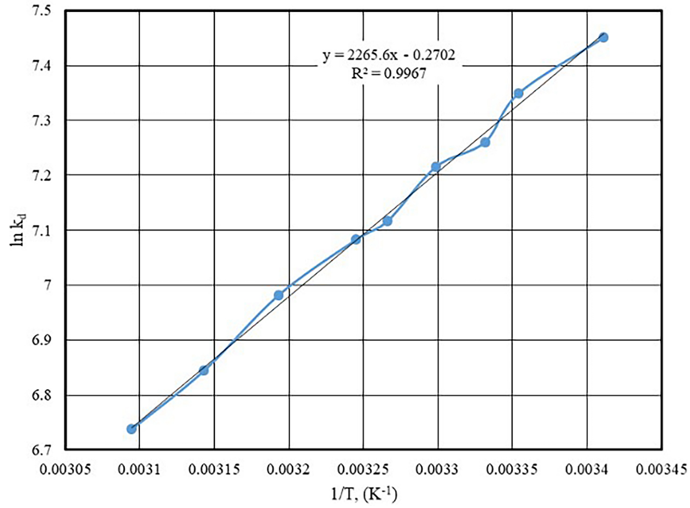

Figure 15. Thermodynamic behaviour of bismuth (III) adsorption using pomegranate peels

Table 6. Effectiveness of Bi^{+3}- loaded adsorption remnant as a rodenticide

Group	Type of provender	Calculated LD_{50}, (mg/kg)		Standard LD_{50} (mg/kg)
		Male	Female	
Control (CG)	Ordinary	No-deaths	No-deaths	–
1	Ordinary provender + pomegranate peels	No-deaths	No-deaths	–
2	Ordinary provender + Bi^{3+} - pomegranate peels	3805.61	3306.89	< 2.000 (Sano et al., 2005)

UTILIZING FROM THE Bi^{3+} LOADED POMEGRANTE PEELS RESIDUES

When the adsorption process of bismuth ended, a considerable amount of polluted pomegranate peels was remnant. This Bi^{3+} loaded residue was collected and sorted due to its content of bismuth, trying to dispose it in benefit, economic and eco-friendly manner. The get ridding style was performed according to zero residue level concept.

One of the proposed methods involves using this waste as a rodenticide for Sprague Dawley rats (*Rattus norvegicus domestica*) by following the procedure described by (Ibrahim et al., 2020a), which includes preparing the animal cages and feeding regimen. Upon completion of the laboratory experiments, the half-lethal dose (LD_{50}) was determined and compared with values reported in the literature, confirming it was within the expected range. Table 1 presents the half-lethal dose (LD_{50}) for rats using both normal and contaminated pomegranate peels. Although bismuth is considered one of the least toxic heavy metals, the rats fed Bi^{+3}-pomegranate peels displayed a range of adverse effects that intensified with increasing doses, eventually leading to mortality at higher concentrations (Al-Latif et al., 2023). Observed physical changes in the rats during the treatment period included decreased levels of albumin and protein in the urine, the onset of diarrhea, and progressively severe skin infections (Abd Ali et al., 2024). Anatomical examination of the rats that succumbed to bismuth-loaded peels revealed kidney atrophy, with the severity of this condition worsening at higher treatment doses (Ibrahim et al., 2020b).

CONCLUSIONS

The major target of this investigation is treating polluted water using agricultural residues and dispose of toxic residues in a way that is beneficial to the environment, up to the zero residue level. The practical side and the experimental results of this study reached several conclusions that can be included in the following form: at first, the adsorption process showed that the pomegranate peel is an adsorbent with good effectiveness and a clear efficiency in the adsorption of bismuth from polluted aqueous solutions. The maximum removal percentage was achieved (74.79%) at pH of 7.350 rpm agitation speed, 38 mg/L initial concentration, 5 g of adsorbent dose, contact time of 2.4 h, and at laboratory temperature. The remaining pomegranate peels (the peels loaded with the adsorbent metal) showed a high ability to be used as a rodenticide for rats, and the evidence for this is that the half lethal dose (LD_{50}) was identical to what was recorded in the previous studies. According to the obtained results, the main goal was achieved: implementing a sustainability approach through the zero residual level concept.

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