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Buckthorn Leaves as an Efficient Material for Simultaneously Multi Eco-Friendly Purposes

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Abstract

Zinc, an essential element, offers numerous benefits; however, an excessive accumulation of zinc within the human body can pose detrimental effects. This study endeavors to mitigate zinc contamination in water sources through an adsorption process utilizing buckthorn leaves as a cost-effective, natural adsorbent. The investigation examined various operational parameters that affect the adsorption process, including pH levels, initial zinc ion concentrations, buckthorn leaf dosage, contact duration, temperature, and agitation speed. The results showed that 78% was the maximum removal of zinc ions, achieved at the optimum conditions of 6, 25 ppm, 4.5 g, 120 min, 45 °C, and 350 rpm, respectively. Furthermore, the residual buckthorn leaves, laden with zinc ions, were evaluated for potential utilization as an organic fertilizer for white beans. The investigation entailed determining the zinc ion content adsorbed by the leaves. Subsequent cultivation trials demonstrated a noteworthy enhancement in bean pod yield from soil treated with zinc-loaded leaves, exhibiting a 9% increase compared to soil treated solely with raw leaves or left untreated. Notably, the resulting crop mass was equivalent across all treatment groups. Thus, this study presents an innovative approach to simultaneously manage solid waste and purify water, offering an efficient, cost-effective, and environmentally sustainable solution.

Keywords: Adsorption; Alum sludge; Batch mode; Nano-zeolite; Vanadium

1. Introduction

Heavy metals are defined as elements that are naturally present in the earth's crust. Generally, they have a large atomic weight and physical properties, such as those of transition metals, some metalloids, lanthanides, and actinides, and their density is at least five times greater than that of water [1]. The use of the term heavy metals dates back to as early as the nineteenth century, specifically in 1817, when the German chemist Leopold Gmelin divided the elements into nonmetals, light metals, and heavy metals [2]. The light metals had a density ranging from 0.860 to 5.0 g/cm³, and the heavy metals had a density ranging from 5.308 to 22.000 g/cm³. The term was later associated with elements with a high atomic number. Since their discovery in ancient eras, including iron, copper, gold, silver, and lead, it has become rare for any human activity that does not use heavy elements [3]. Today, heavy metals are used in various industries, including agriculture, construction, and entertainment, among others, and there are numerous examples of these metals [4]. Iron is used in the construction of buildings, while cadmium and lead are used in the manufacture of batteries. Nickel is utilized in electroplating, antimony is used in the manufacture of glass and ceramics, while chromium is used in the production of metal alloys. Arsenic is a component of agricultural pesticides, and copper is a basic material in the manufacture of electrical wires and for numerous other uses [5]. Some heavy metals, such as copper, selenium, and zinc, are considered necessary for maintaining the human body's metabolism, but only in certain concentrations [6]. However, at concentrations higher than permissible levels, they can lead to poisoning, at which point they are called toxic metals [7]. The danger of heavy metals is that they tend to bioaccumulation, which is the increase in the concentration of a chemical substance in an organism biologically over time. These elements enter the human body through contaminated drinking water, food, and air [8]. Given the great state of pollution that the planet is currently experiencing with all its basic components, soil, air, and water. The treatment of these elements has become an urgent necessity and a crucial issue that cannot be overlooked in any human activity to preserve human health [9]. One of the most important heavy elements is the vital and essential zinc element for human, plant, and animal life [2]. This element is an important and necessary component that humans must consume in specific concentrations. The recommended daily dose of zinc that a person needs varies according to age and gender, generally ranging between 2 mg and 12 mg per day [10]. The highest permissible concentration of zinc in drinking water should not exceed 15 mg/l according to the World Health Organization (WHO) [4] and 5 mg/l due to the US Environmental Agency (EPA) [11] in surface and drinking water, respectively. Therefore, any concentration higher than the aforementioned concentration in drinking water is unacceptable because it will lead to harm to humans [12]. Symptoms of an acute zinc increase are nausea and vomiting, stomach pain and diarrhea, as well as flu-like symptoms. The symptoms of chronic inflammation include low levels of high-density lipoprotein (HDL, or "good cholesterol") in the body, decreased immune function, copper deficiency, and changes in taste. In the case of inhaling high concentrations of zinc through dust or fumes, as in the case of metal smoke fever, which can affect people who work in metals, such as welding, the person suffers from chills, sweating, weakness, fever, muscle pain, chest pain, cough and shortness of breath [13]. These symptoms occur within a few hours after acute inhalation of zinc, and the condition usually lasts for no more than two days. Through the literature review, there are several methods used to treat heavy metals (including zinc element) contaminated water, such as coagulation-flocculation, anaerobic biological-chemical process, micro-electrolysis, membranes, chemical precipitation, ion exchange, nanomaterials, Oxygen-plasma, Ozonation process, reverse osmoses (RO), Photocatalytic process, adsorption and others [14]. These methods differ in their effectiveness in removing zinc, and although some of them are recent, they have many limitations that make the treatment issue a subject that needs study and review [15]. Among these obstacles are the high cost, the need for specialized systems, high energy consumption, and the requirement for a large space to complete the treatment process. Also, they are inefficient in treating low concentrations or the accumulation of toxic waste after the completion of the treatment process [5]. In comparison with previous methods, adsorption technology is one of the most promising methods in water purification. It does not require high operational costs or sophisticated systems, consumes minimal energy, and, at the same time, is highly efficient in removing pollutants, achieving an ideal percentage [16]. However, this method also includes some obstacles, such as the high cost of activated carbon, the main material in the adsorption process due to its unique properties and high surface area, as well as the accumulation of often toxic residues that require additional treatment to reduce its toxicity or environmentally friendly ways to get rid of it [17]. The problem of the activated carbon cost was overcome by using low-cost materials with a suitable surface area, either as a source to prepare activated carbon or by using them directly as adsorption media [18]. One of these materials of wide use instead of activated carbon are agricultural wastes, such as rice husks to remove cobalt [19], nickel [20], zinc [21], dye [22], aminomethyl phosphonic acid [23], and hardness elements [24], watermelon rinds [25], lemon peels [26], orange peels [27], and eggshell [28], pomegranate peels for removing dyes [29] from wastewater, water hyacinth [30], algae to heavy metals [31], and others. These materials have proven effective in removing heavy metals from crude oil [32-34] and soil [35], as well as organic matter [36], not only in polluted water. The adsorption can be applied in the live body to adsorb different things such as drugs or toxic. The issue of toxic waste accumulation has been addressed through several environmentally friendly methods. It is used as a raw material for the preparation of catalysts [37], as a rodenticide due to its toxicity [38], or as an additive to enhance the concrete mixture [39]. This paper examines the use of buckthorn leaves as an adsorbent for zinc removal from aqueous solutions and determines the optimal conditions for achieving the highest purification efficiency of polluted water in the first stage. The second stage involved a study of utilizing the remaining residues from the treatment process as an organic fertilizer for the bean plant, directly without any additional treatment, as one of the environmentally friendly options. Thus, the primary research objective is achieved, which is to attain the concept of a zero residual level (ZRL) with the highest efficiency, lowest cost, and best returns.

2. Experimental Procedure

The experimental work presented in this paper consists of two parts. The first part involves studying the ability of buckthorn leaves to adsorb zinc ions in a batch mode unit from simulated aqueous solutions of known concentrations and under various operating conditions. In this part, the optimum operating conditions are determined by the acidity function (pH), temperature (T), contact time (t), adsorbent amount (m), initial concentration of zinc ions (C0), and mixing speed (As), which achieve the highest adsorption efficiency. The second part investigates the utilization of the adsorption residues accumulated in the previous part after they were collected, classified, and sorted according to the concentration of adsorbed zinc, in a beneficial, economical, and environmentally friendly manner, to achieve the principle of zero residue level (ZRL).

2.1. Adsorbent Media

Freshly fallen buckthorn leaves of the scientific name (*Ziziphus spina-christi*) shown in Fig. 1 were collected from several orchards in Diyala Governorate, Kanaan District, in the period between 03 November 2020 to 15 April 2021. The collected leaves were characterized as being thin, simple, greenish-yellow, and oval in shape, with a smooth upper surface and a lower surface covered with fuzz. They were sharp-headed, and their veins were prominently visible. The collected leaves were washed with an excess of tap water until the dirt and dust stuck to them were removed. Then, the clean leaves were washed with distilled water once. The washed leaves were dried naturally in fresh air and sunlight and then stored in their original form in amber glass jars at room temperature until use. The surface area of these buckthorn leaves was measured using a Branueur-Emmet-Teller (BET) analysis, which involved nitrogen gas physical adsorption isotherms at a temperature of 77 K, on an

ASAP 2020 device from Micromerities Co., USA. The surface area of used buckthorn leaves was 36.138 m^2/g.

Figure 1. Buckthorn leaves were used in this study.

2.2. Stock Solution

To study the ability of buckthorn leaves to adsorb zinc ions from polluted water, suitable aqueous solutions were prepared and simulated to resemble real solutions, thereby avoiding any interaction with other elements and compounds present in the real polluted water. On the other hand, to determine the operating conditions required to remove zinc ions only in high accuracy. To achieve these two goals, a stock solution of 1000 ppm concentration of zinc ions was prepared from dissolving an appropriate amount of zinc nitrate hexahydrate [Zn $(NO_3)_2.6H_2O$) salt of 297.49 g/mol molecular weight and a purity ≤ 99.0%, supplied from Sigma-Aldrich Company] in one liter of distilled water. The preparation process was carried out using a magnetic stirrer hotplate (CH-2093-001, Libdirect, Australia) by dissolving the specified amount of zinc nitrate hexahydrate in a 1.5 l flask (PYREX Erlenmeyer Conical Flask Narrow Mouth with Heavy Duty Rim, Jada Scientific Inc., USA of 1.5L) and by adding a sufficient amount of double distilled water produced using a distillation apparatus type (Water Distiller GFL 2008 8 l/h, L003015) at room temperature. When zinc nitrate was completely dissolved, the volume was then completed to 1 liter using double-distilled water. This solution was used in preparing aqueous solutions for adsorption experiments at different concentrations, utilizing the dilution law, as each 1 mL of the stock solution contains 1 mg of zinc ions.

2.3. Calibration Curve

Instrumental analysis is used to determine the concentration of an unknown substance in a sample. One of the advantages of this analysis is that it is fast, does not require a long time, and can be done using a small volume of sample. It is suitable for complex samples, in addition to being highly sensitive and reliable results. The analysis was used by an Atomic Absorption Spectrophotometer (AAS), as this test is considered one of the optical methods that depend on measuring the quantity of light energy absorbed by the sample to be analyzed at a specific wavelength. Accordingly, a calibration curve must be prepared for the sample, as the device provides an absorbance reading that must be converted into concentrations. To determine the zinc ions in the solution resulting from adsorption experiments using buckthorn leaves, solutions of known zinc concentrations must be prepared and tested at a wavelength of 214 nm. After that, the absorbance of each concentration was measured, and the results were plotted to form a calibration curve of zinc ions versus concentration. The spectroscopic examinations of zinc standard solutions were carried out using a Shimadzu AA-7000, a Japanese device. The resulting calibration curve of zinc ions (shown in Fig. 2) was drawn, and the correlation coefficient was calculated using the statistical method described in [40].

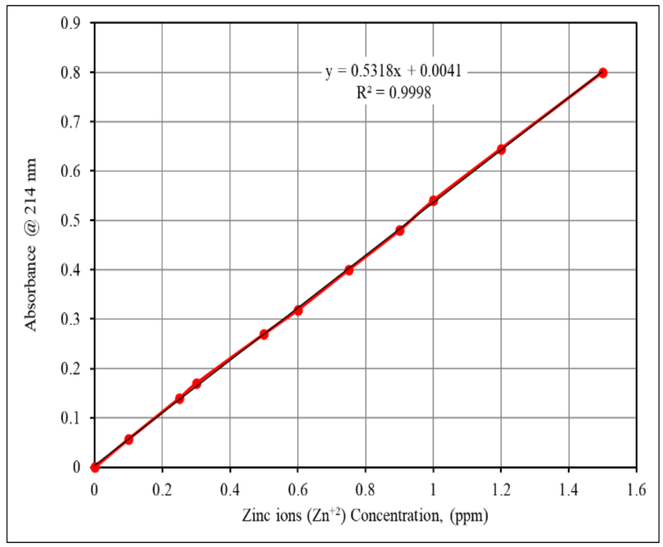

Figure 2. AAS Calibration Curve of Zinc Ions.

2.4. Adsorption Unit

The adsorption unit used in the current study is a batch-type unit, represented by a Thermo Scientific MaxQ 7000 SHKE7000 Benchtop Water Bath Shaker (Model 4303, 2011, USA) [41]. According to the methods described by [42], a 0.1-liter zinc solution was used in each of the studied experiments and poured into 150 ml capacity, airtight Erlenmeyer conical flasks. The flasks were then covered entirely with aluminum foil to ensure that the light did not affect the experimental samples. The pH of the solutions was adjusted using pre-prepared 0.1 M solutions of hydrochloric acid (HCl) and sodium hydroxide (NaOH) supplied by Sigma-Aldrich company. A previously prepared amount of buckthorn leaves was added to the sample flasks. The flasks were placed in the water bath, and the time, temperature, and mixing speed were set. The system was then turned on. The ranges of operational conditions used were 1-10 rpm, 100-500 rpm, 1-30 ppm, 0.1-5 g, 10-180 min, and 20-60°C for the acidity function, agitation speed, initial concentration, buckthorn leaves quantity, contact time, and temperature, respectively. At the end of the specified period, the unit automatically turns off. The samples are carefully extracted and filtered in two stages. The first stage uses filter paper (Whatman™ No. 1 Grade Circular Filter Papers, 110 mm Diameter - B8A61979), and the second stage employs a filtering system (Filtering Kit 250ml, Vacuum Pump with Gauge, KT3003-3 Science Lab Supplies/UK). The amount of residual concentration is determined by testing the samples using AAS with the assistance of a pre-prepared calibration curve for zinc. The amount of adsorption concentration, adsorption efficiency, and adsorption capacity are determined using (1), (2), and (3), respectively [43]:

$$C_{ads} = C_o - C_f \tag{1}$$

$$\%R = \frac{C_{ada}}{C_o} \tag{2}$$

$$q = \frac{V}{m} \times C_{ads} \tag{3}$$

Where: $C_\circ$ and C_f: are the concentrations of zinc ions before and after treatment process (ppm), respectively; C_{ads}: is the concentration of zinc adsorbed using buckthorn leaves (ppm); V: is the volume of solution used in treatment process (liter); m: is the amount of buckthorn leaves used in treatment process (g); q: is the adsorption capacity (mg/g) and $\%R$: is the percentage of adsorption.

3. Benefiting From the Residues of the Adsorption Process

For the safe disposal of buckthorn leaves loaded with adsorbed zinc ions from aqueous solutions in a beneficial manner, their use as an effective and inexpensive organic fertilizer for bean plants was investigated, aiming for a zero-residue level. This process was carried out in the following procedure: after completing the adsorption process and calculating the amount of adsorbed material by buckthorn leaves in each experiment, these residues were collected and dried using a drying oven (TR 450, Nabertherm, Germany), starting with a room temperature and gradually increased at a rate of 1°C/5 minutes up to 50°C and for an hour and a half until the samples dry. After that, the buckthorn leaves were classified according to the amount of adsorbed zinc into three groups: A, B, and C, and the amount of zinc loaded on them ranged between (0.3-0.59), (0.6-0.9) and (1-3) mg/g respectively, the kept the classified leaves in dark containers until use. Before using it as an organic fertilizer, buckthorn leaves were crushed using an electric mill, sieved, and large parts were crushed again to obtain a powder measuring 1.18 mm to pass through sieve No. 16. Clay soils were prepared whose composition consisted of 65% clay, while the values of acidity function, percentage of organic matter, electrical conductivity and cation exchange capacity (CEC) were 8.14, 2.322%, 6.08 ms/cm, 24.746 meq/100g, respectively. The ability of buckthorn leaves to serve as an organic fertilizer for clay soil was tested by applying them to white bean plants, as they are fast-growing and require minimal preparation. The mass of the bean seeds was chosen to be 0.325 exactly to determine the effect of the treatment accurately. Unabsorbed virgin buckthorn leaves were also used and prepared in the same manner as before to compare the results with those from clay soil only. The soil used for growing beans was divided into five sections: the first section consisted of pure clay soil, free of any additives, and the second section was clay soil mixed with unabsorbed virgin buckthorn leaves.

In contrast, the third, fourth, and fifth sections included clay soil mixed with buckthorn leaves, adsorbed with zinc ions at ratios of 0.3, 0.9, and 3.0 mg/g, respectively. The amount of buckthorn leaves used was fixed in each section and mixed with 5 mg of zinc per kilogram of clay soil. All soils were watered with water of the same quality, which was pH 7.21, turbidity 1 NTU, TDS=62 ppm, $CaCO_3$ hardness 36 ppm, sodium 9 ppm, chloride 2.65 ppm, magnesium 37 ppm, zinc nil ppm sulfate 6.13 ppm, and EC 2.04 ds/m. In each of these five sections, five bean seeds are placed in a zigzag shape, separated by 2 cm between each line. The ripe beans were carefully harvested and weighed from each section separately to determine the efficiency of the fertilizer used.

4. Results and Discussion

After conducting experimental work on the process of zinc removal from contaminated aqueous solutions using the adsorption technique, the results for each set of specific operating conditions were determined, and the optimal conditions for the adsorption process were identified. In this section, the results obtained from the first part of the experimental procedure and the scientific reasons for the behavior of the adsorbent material (buckthorn leaves) will be discussed based on the obtained efficiency and similar literature, despite the absence of any paper dealing with the removal of heavy elements using buckthorn leaves as an adsorbent.

4.1. Impact of Acidity Function (pH)

The acidity function is one of the most critical factors that directly affect the adsorption process due to its impact on the ions dispersed in the solution and its effect on the surface of the adsorbent material. The effect of pH on the zinc adsorption process in buckthorn leaves was studied within a range of 1-10, keeping all other variables constant at 25 ppm, 1 g, 350 rpm, 180 min., and 45°C for initial concentration of zinc, the mass of buckthorn leaves, agitation speed, contact time, and temperature, respectively. Fig. 3 shows that the effect of varying the pH is direct, as the adsorption efficiency increases with increasing acidity function from a value of 1 until it reaches its highest value at pH = 6. In contrast, the efficiency decreases after that with further increases in pH. The reason for the increase in efficiency at acidic values is that the surface of buckthorn leaves is affected by hydrogen ions (H^+), whose value is as high as possible at pH = 1, which makes the surface charged with a positive charge that repels the positive zinc ions (Zn^{+2}) as well and prevents them from reaching the active sites on buckthorn. By increasing the pH value, the concentration of hydrogen ions (H^+) decreases gradually. With it, the resistance to the positive heavy element ions (Zn^{+2}) will decrease. The surface of buckthorn leaves will be able to absorb more of the positive ions, thus reducing the concentration of zinc ions (Zn^{+2}) in the solution and increasing the efficiency. When the value of the acid function reaches 6, the resistance will become as low as possible, the most significant number of zinc ions

(Zn^{+2}) will reach the adsorption surface, and the efficiency will reach its maximum value. As for increasing the pH above the neutralization value, the basicity increases, which may alter the behavior of the effective groups. This means that the adsorbed zinc ions (Zn^{+2}) return to the solution again as a result of their liberation from van der Waals forces, thus reducing the adsorption efficiency. This result agrees with [44] and [45] in their study of zinc and nickel using lemon peels and waste tea leaves, respectively.

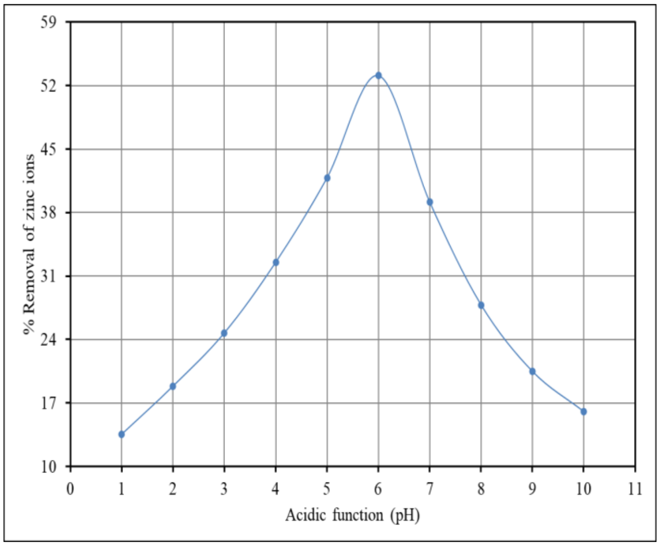

Figure 3. pH impact on the adsorption behavior of zinc ions using buckthorn leaves.

4.2. Impact of Agitation Speed

The agitating applied to the polluted aqueous solutions contributes to shortening the time required for the pollutants to reach the adsorbent material and vice versa. It also contributes to improving the adsorption efficiency. Fig. 4 shows the effect of changing the agitation speed on the efficiency of zinc ions adsorption by buckthorn leaves, with other operating conditions keeping constant at 25 ppm, 1 g, 6, 180 min., and 45°C for the initial concentration of zinc, the mass of buckthorn leaves, the acidity of the solution, contact time, and temperature, respectively. Within the studied range of 100-500 rpm, it appears that the adsorption efficiency increases with increasing agitation speed, reaching its maximum value at 350 rpm. Subsequently, the adsorption efficiency remains constant at this value, regardless of the increase in agitation speed. This result can be attributed to the fact that the speed of agitation increased the likelihood of zinc ions reaching the active sites on the surface of buckthorn leaves, thereby enhancing the adsorption efficiency. Therefore, the ions will remain in the solution, and the adsorption efficiency will remain unchanged. Similar results were obtained by [36] when they studied the adsorption process of antimony as a heavy metal using orange peels and ferric ion adsorption by almond shell achieved by [47].

4.3. Impact of Initial Concentration

Fig. 5 shows the effect of altering the initial concentration on the susceptibility of buckthorn leaves to the adsorption of zinc ions (Zn^{+2}), keeping other operating parameters constant at 6, 1 g, 350 rpm, 180 min., and 45°C for the acidity of the solution, the mass of buckthorn leaves, agitation speed, contact time, and temperature, respectively. There is an inverse relationship between the adsorption efficiency and the initial concentration value, as the percentage removal of the adsorption decreases with increasing concentration. This result can be elucidated depending on the surface area of the adsorbent, as buckthorn leaves have a specific surface area through which they can adsorb a particular number of zinc ions (Zn^{+2}). However, by increasing the concentration, the functional groups present in the active sites cannot adsorb additional amounts of zinc ions, as the amount of adsorbent is constant [48]. This means that the amount of non-adsorbed substance will increase with an increase in the initial concentration because the volume of the solution is constant; therefore, the efficiency will decrease. On the other hand, it is noted from the exact figure that the amount of the adsorbent substance, zinc ions (Zn^{+2}), increases with the initial concentration until it reaches a specific value, after which it remains constant without change. This is because the amount of adsorbed material depends on the surface area, which is fixed to a particular number. Therefore, the number of adsorbed zinc ions increases with increasing concentration (i.e., the number of ions in the solution) until it reaches a maximum value, after which it remains constant despite further concentration increases. The current results are in agreement with the results of [49] and [50].

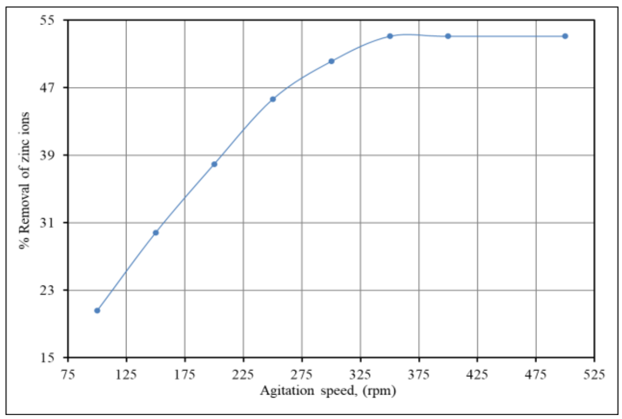

Figure 4. The agitation speed affects the adsorption of zinc ions using buckthorn leaves.

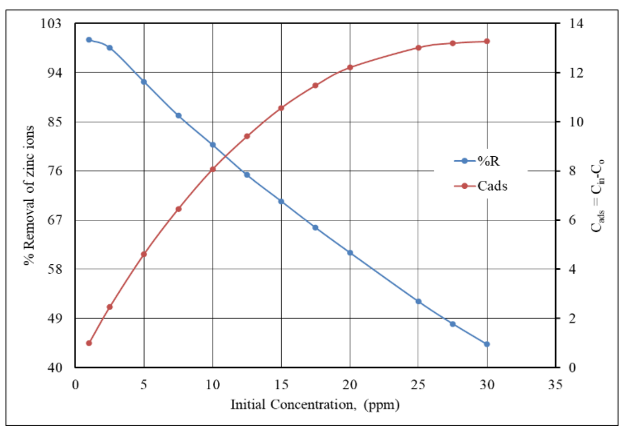

Figure 5. Initial concentration impact on the adsorption of zinc ions using buckthorn leaves.

4.4. Impact of Adsorbent Dose

The adsorption process depends mainly on the presence of an adsorbent media with specific properties that perform the adsorption process. The quantity of this substance has a significant impact, as determining the optimum amount to achieve maximum removal efficiency is a crucial issue, as it will reveal the designed capacity of the adsorption unit. Whether it is in a batch or continuous unit. Within the range of 0.5-5 g, the behavior of buckthorn leaves as adsorption media for zinc ions from contaminated aqueous solutions was studied. At the same time, the other operating parameters were kept constant at 25 ppm, 6, 350 rpm, 180 min., and 45°C for the initial concentration of zinc, acidity of the solution, agitation speed, contact time, and temperature, respectively. The results of studying this operating factor showed that the percentage of adsorption increases with an increase in the dose of adsorbent material, maintaining a constant initial concentration and that the highest efficiency was achieved at a dose of 4.0 g. Despite the increase in the dose, the adsorption efficiency remained steady and did not change. The adsorbent material possesses functional groups within the active sites dispersed on the adsorption surface, i.e., the increase in the dose of adsorbent leads to an increase in the surface area subjected to adsorption, which increases the chance of binding the ions of the polluted ions with the functional groups, and thus the adsorption capacity increases. When the saturation state is reached, the material is unable to adsorb any additional dose of zinc ions, according to the operational conditions, and thus, a state of equilibrium occurs, where the adsorption capacity is at its most excellent possible level. Fig. 6 shows the effect of the amount of adsorbent on the adsorption of heavy metal ions [51], indicating results that are consistent with those of the current study.

4.5. Impact of Contact Time

To realize the kinetics of the adsorption process comprehensively, it is indispensable to investigate the behavior of the contact time, through which it is possible to determine the time required to reach the equilibrium state at which the adsorption capacity has reached its ultimate. To find out the effect of time on the adsorption of zinc ions by buckthorn leaves, a set of adsorption experiments were carried out with different periods ranging from 10-180 minutes, while the rest of the operating conditions were kept at 25 ppm, 4.5 g, 350 rpm, 6, and 45°C for initial concentration of zinc, mass of buckthorn leaves, agitation speed, acidity of the solution, and temperature, respectively. Fig. 7 illustrates the results of the experiments on changing the contact time and its effect on the adsorption efficiency for the current study. As shown in the above figure, the percentage of zinc removal is directly proportional to the contact time, with 120 minutes representing the equilibrium time. After this point, the efficiency remains constant and does not change under varying operational conditions. Increasing the contact time leads to an increase in the probability of ions reaching the active sites, thereby reducing the number of ions dispersed in the solution and ultimately enhancing efficiency [46]. It is noted that the adsorption efficiency is high in the initial period, and the increase begins to decrease gradually until it reaches a maximum value. The reason for this result is that the adsorbent material is initially virgin and free of any polluted substances, allowing for more intense adsorption. Over time, the material gradually begins to saturate. Progressively, the substance reaches a state of equilibrium and is unable to adsorb any additional quantity despite the presence of vacant effective sites. The reason for this may be the operational conditions, the design of the adsorption system, or its absorptive capacity. Most previous studies have yielded results consistent with the obtained result, as seen in [51] and [52].

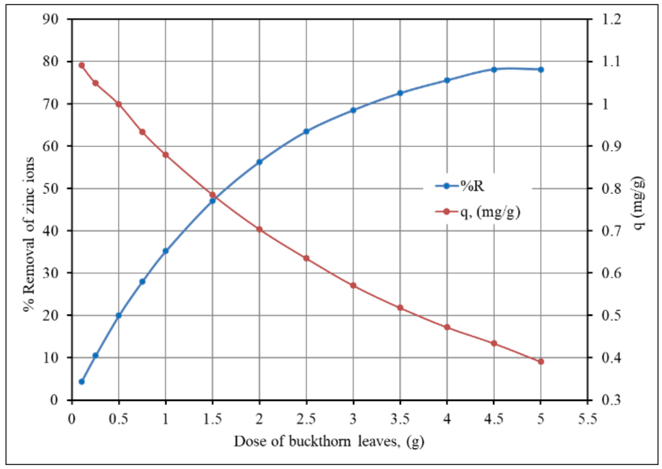

Figure 6. Adsorbent dose impact on the adsorption of zinc ions using buckthorn leaves.

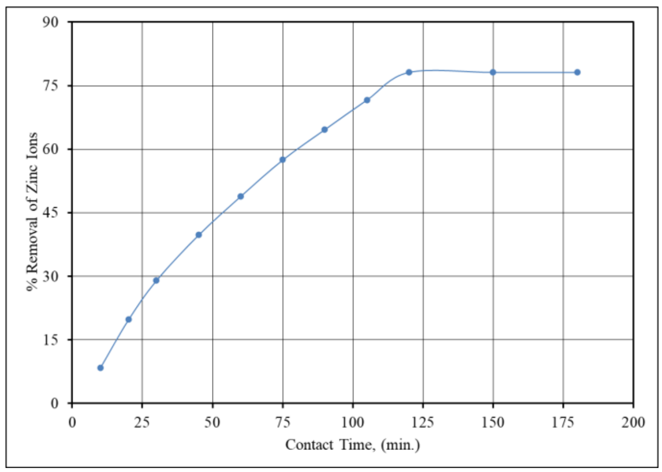

Figure 7. Contact time impact on the adsorption of zinc ions using buckthorn leaves.

4.6. Impact of Temperature

Temperature is closely related to surface phenomena in general and the adsorption process in particular. It is always the determinant of spontaneity, enthalpy, and entropy of adsorption, as well as predicting the type of adsorption that occurs. This operational factor was studied in this investigation within a sufficient range of 20-60°C to determine the optimum temperature for achieving the best adsorption efficiency. At the same time, the other parameters were kept constant at 25 ppm, 4.5 g, 350 rpm, 180 min., and 6 for the initial concentration of zinc, the mass of buckthorn leaves, agitation speed, contact time, and acidity of the solution, respectively. The results shown in Fig. 8 indicate that increasing the temperature from

20 to 45°C leads to a corresponding increase in the percentage of zinc ion adsorption, from 10% to 77%, respectively, and that this relationship is direct within this range. Then, the adsorption efficiency starts to decrease after exceeding this range until it reaches 39% at 60°C. Raising the temperature leads to an increase in the dissolution of the pollutant, as it is known that zinc nitrate increases its solubility with increasing temperature, allowing a larger number of zinc ions to be adsorbed, and their concentration in the solution decreases. There is a possibility of expanding the dimensions of the active sites on the surface of the adsorbent material as a result of heating, which leads to the entry of a larger number of zinc ions and thus increases the adsorption efficiency.

On the other hand, increasing the temperature leads to an increase in the kinetic energy of zinc ions, which reduces the time required for their arrival at the active sites and thus increases the number of zinc ions adsorbed on the surface of the buckthorn leaves, thereby enhancing the adsorption efficiency. After the temperature exceeds 45°C, the adsorbent begins to lose the adsorbed ions on its surface as a result of obtaining the necessary energy to break free from the forces associated with the functional groups. Or, increasing the temperature leads to dissociation of the adsorbent itself (and this is what was observed from practical experience), and in both cases, the adsorbed molecules return to the solution, and the efficiency of adsorption decreases. Similar studies have yielded similar beneficial results, which are consistent with those of the current research, as reported in [49]-[52].

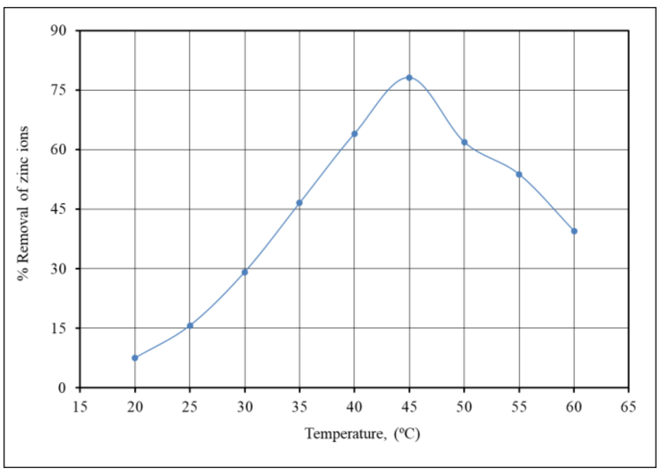

Figure 8. Temperature impact on the adsorption of zinc ions using buckthorn leaves.

4.7. Adsorption Isothermal Study

This study contributes to measuring the ability of buckthorn leaves to recover zinc ions under known parameters, which enables the planning of constructing more effective adsorption units. There are various models used to represent the isotherm behavior of the adsorption process, such as the Langmuir isotherm model, which assumes that adsorption occurs on similar sites, with the assumption that each site can be adsorbed by one particle of the contaminant and, therefore, the adsorbed particles are independent [48]. The other model is the Freundlich isotherm model, which is based on the assumption that the adsorption sites are heterogeneous, as the adsorption is distributed on the surface of the adsorbent gradually according to the adsorption strength, which decreases with distance. Moreover, the Temkin isotherm model is based on the assumption of interactions between adsorbed molecules on the surface, taking into account the thermal effects that may occur during adsorption [53]. Table 1 shows the details of the isothermal models used in the current study. Fig. 9 to Fig. 11 represent the results of applying isothermal models to the results obtained from the adsorption of zinc ions using the buckthorn leaves as an adsorbent. At the same time, Table 2 shows the values of the constants of these models. The results of the isothermal study show the application of three main models, Langmuir, Freundlich, and Temkin, which provide multiple insights into the adsorption mechanism and the nature of the interaction between the adsorbent and the pollutant [54]. For the Langmuir model, which is based on the assumption that adsorption occurs on a homogeneous surface with equal energy sites, the value of q_{max} represents the maximum adsorption capacity, i.e., the maximum mass of zinc that can be adsorbed by the buckthorn leaves when all sites are saturated. K_L is the Langmuir constant, indicating the affinity of the contaminant to the adsorbent surface. A low value here shows a relatively weak interaction between the adsorbent and vanadium, suggesting that the ions do not bind easily or strongly to the surface of the buckthorn leaves. For the Freundlich model, which assumes that the surface is heterogeneous and adsorption occurs across sites of varying energy, the value of K_F represents the adsorbent's ability to adsorb at a given concentration, with a low value indicating limited adsorption capacity. The value of n is a nonlinear indicator reflecting the intensity of adsorption; being greater than one indicates that adsorption is favorable but follows a heterogeneous distribution across the adsorbed sites, indicating that the surface is not homogeneous and that there are sites with higher adsorption capacity than others [54]. For the Temkin model, which considers the interactions between adsorbent molecules and thermal effects, the K_T value represents the interaction strength between the adsorbent and the pollutant, indicating relatively strong interactions.

On the other hand, the b value reflects the changes in thermal energy during adsorption. It indicates that the adsorption efficiency increases with an increase in the concentration of the zinc pollutant, suggesting a significant thermal effect on the adsorption process. When comparing the models, the Langmuir model best represents the data according to the high correlation coefficient value (0.9996), indicating that the adsorption process mainly occurs on a homogeneous surface with equally efficient sites. In contrast, the Freundlich model (R^2 = 0.9963) reflects the nature of a heterogeneous surface with diverse energy sites, whereas the Temkin model (R^2 = 0.9961) highlights the effects of thermal interactions, but it is less accurate in representing the data. The separation coefficient R_L indicates the suitability of adsorption, with a value between 0 and 1, meaning that adsorption is of the preferred type [54].

4.8. Benefiting from the Adsorption Residues

The results obtained from using zinc-laden buckthorn leaves as an organic fertilizer (as shown in Table 3 and Fig. 12) demonstrated an apparent effect on the mass of the plant growing in the treated soil. Where the bean seeds resulting from the soil treated with leaves as fertilizer had a greater mass than their counterparts in the soil treated with buckthorn leaves only, and the mass of the resulting bean seed was close to that obtained from the non-treated soil. Zinc is a trace mineral vital to plant growth and development, and it plays a crucial role in the ability of growth regulators to regulate processes within the plant body and in plant enzymatic hydrolysis. It is also a necessary component for the formation of tryptophan, the amino acid that makes up indole-3-acetic acid (IAA), which plays a significant role in the growth of flower nodes. On the other hand, zinc is involved in the synthesis of enzymes that produce plant auxins. It also plays a crucial role in the oxidation of sugars in plants and is essential for the formation of chlorophyll and the process of photosynthesis. Zinc is absorbed in the form of the element ion (Zn^{+2}). The plants most responsive to zinc fertilization are corn, beans, grapes, and apples, and they are among the plants most sensitive to zinc deficiency. Therefore, the increase in the mass of the bean seeds came as a result of the absorption of zinc carried on the buckthorn leaves, mainly since the soil (according to the value of its acidic function) is classified among the soils with a low level of zinc.

Table 1. Details of isothermal models used in this study.

Model	General Form	Linear Form	Slop	Intercept	Augmented Parameter
Langmuir	$q_e = \frac{q_{max}.K_L C_e}{1+K_L C_e}$	$\frac{1}{q_e} = \frac{1}{q_{max}K_L}\frac{1}{C_e} + \frac{1}{q_{max}}$	$\frac{1}{q_{max}K_L}$	$\frac{1}{q_{max}}$	$R_L = \frac{1}{1+K_L C_e}$
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	$q_e = \frac{RT}{b} ln\ K_T C_e$	$q_e = \frac{RT}{b} ln\ K_T + \frac{RT}{b} ln\ C_e$	$\frac{RT}{b}$	$\frac{RT}{b} ln\ K_T$	–

Table 2. Constants of isothermal models used in the current study.

Langmuir isotherm model				Freundlich isotherm model			Temkin isotherm model		
q_{max}	K_L	R_L	R^2	K_F	n	R^2	K_T	b	R^2
1.9106	0.0539	0.4262	0.9996	0.1581	1.6268	0.9963	0.4658	6.0636	0.9961

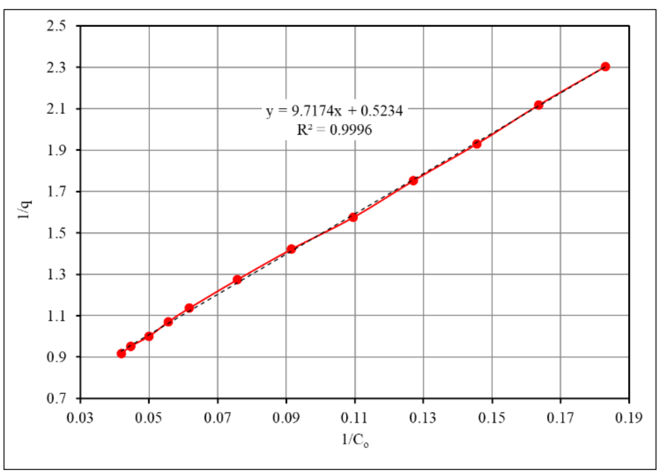

Figure 9. Langmuir isotherm model of zinc adsorption using buckthorn leaves.

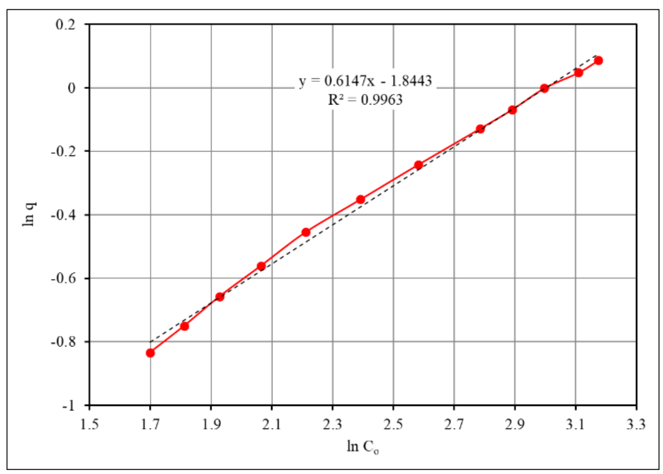

Figure 10. Freundlich isotherm model of zinc adsorption using buckthorn leaves.

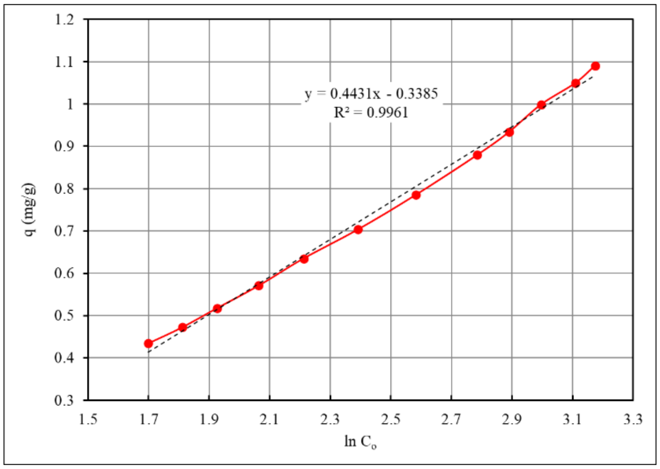

Figure 11. Temkin isotherm model of zinc adsorption using buckthorn leaves.

Table 3. Results of using the residues of zinc adsorption as fertilizer for 0.325 g bean seed.

Type of Soil	Growing bean seeds	
	Mass, (mean ± SD)	% increase
Virgin Clay soil	0.3282±0.02941	0.9723
Clay soil + buckthorn leaves only	0.3284±0.00885	1.0462
Clay soil + buckthorn leaves of 0.3 mg/g Zinc	0.3338±0.01928	2.7076
Clay soil + buckthorn leaves of 0.9 mg/g Zinc	0.3382±0.01844	4.2523
Clay soil + buckthorn leaves of 3.0 mg/g Zinc	0.3542±0.00845	8.9723

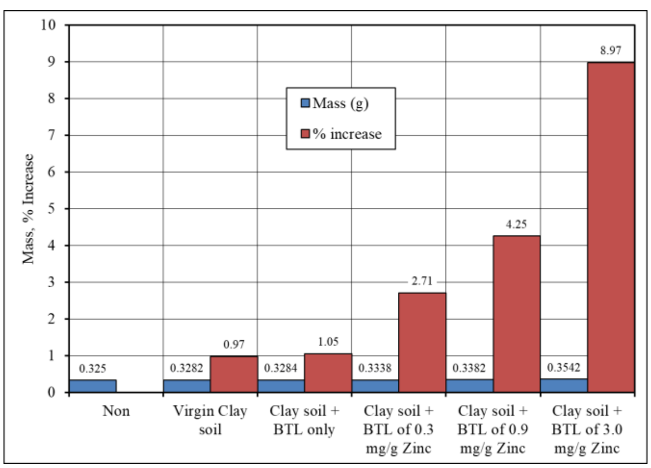

Figure 12. The behavior of using buckthorn leaves (BTL) residues as a fertilizer compared with other types of soils.

5. Conclusions

The current study examined the ability of buckthorn leaves to treat zinc-contaminated water in a batch-mode adsorption unit under a set of operating conditions. The studied operational conditions included the acidity function, mixing speed, initial zinc concentration, number of buckthorn leaves, contact time, and the temperature of the adsorption unit. The results showed that the maximum adsorption efficiency was 77%, achieved at an acid function of 6, an agitation speed of 350 rpm, an initial concentration of 35 ppm, 4.0 g of buckthorn leaves, an equilibrium time of 2 hours, and a temperature of 45°C. Experimental work indicated that the adsorption efficiency of zinc is directly related to all variables except for the initial concentration of zinc, the acidity function, and the temperature after the optimum value. The objectives of the study were achieved by reaching a zero-residue level through the conversion of zinc-contaminated buckthorn leaf residues into an activated organic fertilizer. This fertilizer was applied to bean plants in zinc-poor soil under simple experimental conditions. These residues demonstrated the ability to compete with other types of fertilizers, as the treatment of the soil with these residues increased the mass of beans planted in it, in proportions directly proportional to the amount of zinc applied, reaching 9%. From the foregoing, it can be concluded that agricultural waste, including tree leaves, which represent a significant percentage of municipal waste, is a crucial source for sustainable development by treating environmental pollutants and disposing of them in beneficial ways, rather than the traditional methods of burning and burial.

Conflict of interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Author Contribution Statement

Suha Anwer Ibrahim executed the experiments and performed lab work.

Alanood A. Alsarayreh's technical writing of the manuscript.

Teba Tariq Khaled discussed the results and contributed to the preparation of the final manuscript.

Mohammed Nsaif Abbas proposed the research problem and supervised the findings of this work.

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