

Using of Christ's Thorn Jujube Leaves as an Efficient Material for Two Eco-Friendly Applications

Teba Tariq khaled (✉ teba.t.khaled@gmail.com)

University of Mustansiriyah <https://orcid.org/0000-0001-5479-115X>

Suha Anwer Ibrahim

Mustansiriyah University

Mohammed Nsaif Abbas

Mustansiriyah University

Thekra Atta Ibrahim Zaid

Mustansiriyah University

Research Article

Keywords: Zinc, Christ's thorn jujube leaves, adsorption, batch-mode unit, and ZRL

Posted Date: November 16th, 2023

DOI: <https://doi.org/10.21203/rs.3.rs-3474390/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

USING OF CHRIST'S THORN JUJUBE LEAVES AS AN EFFICIENT MATERIAL FOR TWO ECO-FRIENDLY APPLICATIONS

ABSTRACT

Despite the benefits provided by zinc element, there are damages that may result from it in the event of an increase in its percentage in the human body. In this case, its impact will be negative and harmful to health as well as environmental pollution impact. Because this element is a multi-use element in all fields, many activities throw zinc in their waste, which can reach humans through the food chain. Therefore, zinc ions must be removed from polluted aqueous media if they exceed the permissible limits according to international standards. The current paper aims to remove zinc ions from polluted water by means of adsorption technology and to investigate the susceptibility of Christ's thorn jujube (CTJ) leaves [of scientific name *Ziziphus spina-christi*] as a low-cost natural adsorption medium. The effect of a multi-operating condition that is directly related to the adsorption process was studied within specific ranges to determine the optimal conditions for the treatment process, where the percentage of zinc removal is the highest possible. The study was conducted using a batch-mode unit. The studied operational conditions were represented by the acidity function (pH), the initial zinc ions concentration, the quantity of raw CTJ leaves used, contact time, temperature, and the agitation speed. The obtained results showed that about 77% of zinc ions were recovered and that the percentage of removal is directly proportional to the acidity function (pH), agitation speed, contact time, CTJ dose, and temperature and inversely with the initial zinc ion concentration. The residues of CTJ leaves loaded with zinc ions were investigated for their utilization by studying its use as a type of organic fertilizer for white beans after determining the amount of zinc ions adsorbed by CTJ leaves. The results showed that the mass of bean pods obtained from the soil treated with CTJ leaves loaded with zinc was approximately 9% more than the mass of beans produced from the soil treated with CTJ leaves alone and the untreated soil, where the mass of the resulting crop was approximately equal. Thus, this paper proposed one of the innovative methods of solid waste management and water purification simultaneously in an efficient, economical, and environmentally friendly manner.

Keywords: Zinc, Christ's thorn jujube leaves, adsorption, batch-mode unit, and ZRL

1. Introduction

Heavy metals are defined as elements that are naturally present in the earth's crust, and generally have a large atomic weight and physical properties such as transition metals, some metalloids, lanthanides, actinides, and their density are at least five times greater than that of water (Hashem et. al., 2021). 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. The light metals had a density of 0.860 to 5.0 g/cm³ and 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 (Bharagava, 2017). 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 (Ghulam et. al., 2020). Today, heavy metals are used in industry, agriculture, construction, weapons, entertainment, and others and the examples to use of these metals are many (Al-Hermizy et. al., 2022). Iron (Fe) is used in the construction of buildings, cadmium (Cd) and lead (Pb) in the manufacture of batteries, nickel (Ni) in electroplating, antimony (Sb) in the manufacture of glass and ceramics, chromium (Cr) in the production of metal alloys, arsenic (As) is a component of agricultural pesticides, and copper (Cu) is a basic material in the manufacture of electrical wires and other countless uses (Ibrahim et. al., 2016). Some heavy metals such as copper, selenium, zinc...etc are considered necessary to maintain the metabolism of the human body, but in certain concentrations (Khaleel et. al., 2022). However, at concentrations higher than permissible levels, they can lead to poisoning, at which point they are called toxic metals. 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 (Al-Ali et. al., 2023). In view of the great state of pollution that the planet is currently experiencing with all its basic components, soil, air, and water, the treatment of these components has become an urgent necessity and an important issue that cannot be abandoned in any of human activities in order to preserve human health (Abdullah et. al., 2023). One of the most important heavy elements is the vital and essential zinc element for human, plant, and animal life (Al-

Hermizy et. al., 2022). This element is an important and necessary component that must be taken by humans but in specific concentrations. The recommended daily dose of zinc that a person needs varies according to age and gender and generally ranges between 2 mg to 12 mg per day (**IOM, FNB, 2001**). The highest permissible concentration of zinc in drinking water should not exceed 15 and 5 mg/l in surface and drinking water, respectively, according to the parameters of the World Health Organization (WHO) (**Al-Hermizy et. al., 2022**) and the US Environmental Agency (EPA) (**ATSDR, 2005**), respectively. Therefore, any concentration higher than the aforementioned concentration in drinking water is unacceptable because it will lead to harm to humans. Symptoms of an acute zinc increase are nausea and vomiting, stomach pain and diarrhea, as well as flu-like symptoms, while the symptoms of chronic increase are low levels of high-density lipoprotein or good cholesterol in the body, decreased immune function, copper deficiency in the body, 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 (**Agnew and Slesinger, 2022**). These symptoms occur within a few hours through acute inhalation of zinc and usually, this condition 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 (**Abbas et. al., 2020**). These methods differ in their effectiveness in removing zinc, and although some of them are recent, they include many limitations that make the treatment issue need study and review. Among these obstacles are the high cost, their need for special systems, their high energy consumption, the require a large space to complete the treatment process, or they are inefficient in treating low concentrations or the accumulation of toxic waste after the completion of the treatment process (**Ibrahim et. al., 2016**). In comparison with the previous methods, adsorption technology is one of the most promising methods in the field of water purification, as it does not require high operational costs or sophisticated systems and does not consume much energy and at the same time is highly efficient in removing pollutants that may reach the ideal ratio (**Al-Ali et. al., 2023**). 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 (**Maddodi et. al., 2020**). The problem of the activated carbon cost was overcome by using low materials with a suitable surface area, either as a source to prepare activated carbon or by using them directly as adsorption media. One of these materials of wide use instead of activated carbon are agricultural wastes, such as rice husks to remove cobalt (**Abbas and Abbas, 2013a**), barium (**Abbas and Abbas, 2013b**), manganese (**Abbas and Abbas, 2013c**), thallium (**Alalwan et. al., 2018**), humic acid (**Abbas and Abbas, 2014**), and hardness elements (**Ibrahim et. al., 2021**), banana peels to remove heavy metals (**Abdullah et. al., 2023**), tea leaves to remove copper element (**Al-Ali et. al., 2023**), watermelon rinds (**Abbas and Nussrat, 2020**), lemon peels (**Alalwan et. al., 2020**), orange peels to remove antimony (**Hasan et. al., 2021**), egg shell to remove antimony (**Ali et. al., 2020**), pomegranate peels to remove selenium (**Al-Ali et. al., 2023**) and dyes (**Alalwan et. al., 2021**) from wastewater, water hyacinths (**Ali and Abbas, 2020**), algae to remove phenol (**Abbas et. al., 2019a**), aluminum foil to remove cobalt and dye (**Ghulam et. al., 2020**) and others. These materials have proven their effectiveness in removing heavy metals from crude oil (**Abbas and Alalwan, 2019; Abbas and Ibrahim, 2020; Ali et. al., 2021**) and soil (**Abbas et. al., 2021a**), as well as organic matter (**Abbas et. al., 2019b**), and not only from polluted water. The adsorption can be applied in the live body to adsorb different things such as drugs or toxic (**Ibrahim et. al., 2020**). As for the problem of toxic waste accumulation, it has been eliminated by several environmentally friendly methods, up to the concept of zero residual level (ZRL) (**Abbas et. al., 2021b**). One of these methods is its use as raw materials for the preparation of catalysts (**Alwan et. al., 2021**) or as a rodenticide due to its toxicity (**Abd ali et. al., 2018; Ibrahim et. al., 2020**) or as a good additive to enhance the concrete mixture (**Abbas et. al., 2022; Abdulkareem et. al., 2023**) or as a raw substance for nano-material (**Alminshid et. al., 2021**). Another method is to produce a cheap fertilizer for the soil (**Abbas, 2015**) or in the preparation of useful materials (**Abbas et. al., 2020**). This paper deals with the study of the use of Christ's thorn jujube (CTJ) leaves of the scientific name (*Ziziphus spina-christi*) as a kind of tree leaves as an adsorbent for zinc from aqueous solutions and to determine the optimal conditions to achieve the highest purification efficiency of polluted water in the first stage. The second stage included a study of the use of the remaining residues from the treatment process as an organic fertilizer for the bean plant directly without any treatment as one of the types of environmentally friendly treatments. Thus, the main research objective is achieved, which is to reach the concept of the zero residual level (ZRL) with the highest efficiency, lowest cost, and best returns.

2. Experimental procedure

The experimental work of this paper includes two parts. The first part deals with studying the ability of CTJ leaves for the adsorption of zinc ions in batch mode unit from simulated aqueous solutions previously prepared with known concentrations and under different operating conditions. In this part, the optimum operating conditions are determined from the acidity function (pH), temperature (T), contact time (t), adsorbent amount (m), initial concentration of zinc ions (C_0), and mixing speed (A_s) achieving the highest adsorption efficiency. The second part investigates the utilization of the adsorption residues accumulate 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, in order to achieve the principle of zero residue level (ZRL).

3. Adsorbent media

Freshly fallen Christ's thorn jujube (CTJ) leaves of the scientific name (*Ziziphus spina-christi*) shown in **Figure 1** were collected from a number of orchards in Diyala Governorate, Kanaan District in the period between 03 November 2020 to 15 April 2021. The collected leaves were characterized by being thin, simple, greenish-yellow, oval in shape, their upper surface smooth, and the lower covered with fuzz, sharp-headed, and their veins prominently visible. The collected leaves were washed with an excess of tap water until the dirt and dust stuck to them were removed, and then the clean leaves were washed with distilled water once. The washed leaves were dried naturally using fresh air and sunlight only and kept in their usual form in opaque glass containers at room temperature until use. The surface area of these CTJ leaves was measured by Branueur-Emmet-Teller (BET) analysis using nitrogen gas physical adsorption isotherm at a temperature of 77 K using ASAP 2020, Micromeritics Co., USA device. The surface area of used CTJ leaves was 3.6138 m²/g.

4. Stock solution

In order to study the ability of Christ's thorn jujube leaves to adsorb zinc ions from polluted water, suitable aqueous solutions were prepared to simulate real solutions avoiding any interaction with other elements and compounds present in the real polluted water and 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 mg/L concentration of zinc ions was prepared from dissolving an appropriate amount of zinc nitrate hexahydrate [$Zn(NO_3)_2 \cdot 6H_2O$] salt of 297.49 g/mol molecular weight and a purity $\leq 99.0\%$, 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, Loo3015) at room temperature. When zinc nitrate is completely dissolved, then the volume was completed to 1 liter using double distilled water. This solution was used in preparing aqueous solutions used in adsorption experiments of different concentrations using the dilution law, as each 1 ml of the stock solution contains 1 mg of zinc ions.

5. Calibration curve

Instrumental analysis is used for the purpose of determining the unknown concentration of the substance in the sample. One of the advantages of this analysis is that it is fast, does not require a long time, and it 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 gives an absorbance reading, which must be converted into concentrations. In order to determine zinc ions in the solution resulting from adsorption experiments using CTJ leaves, solutions of known concentrations of zinc must be prepared and tested at a wavelength of 214 nm. After that, the absorbance of each concentration was detected and the results of the concentration versus the absorbance were plotted to achieve the calibration curve of zinc ions. The spectroscopic examinations of zinc standard solutions were carried out using Shimadzu AA-7000, Japan device, and the resulting calibration curve of Zinc ions (shown in **Figure 2**) was drawn and the correlation coefficient was calculated using the statistical method described in (Ali et. al., 2020).



Figure 1. CTJ leaves used in this study

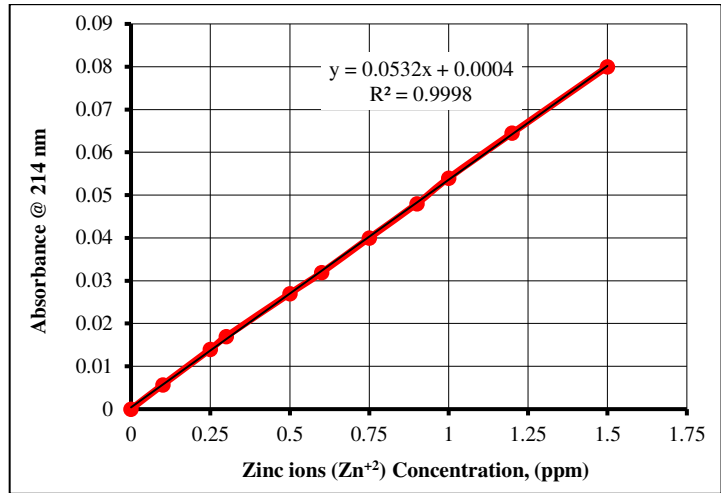


Figure 2. AAS Calibration Curve of Zinc Ions

6. Adsorption unit

The adsorption unit used in the current study is a batch-type unit represented by a Water Bath Shaker of type (Thermo Scientific MaxQ 7000 SHKE7000 Benchtop Model 4303, 2011, USA). 100 ml of zinc solution was used in each of the studied concentrations and poured into Erlenmeyer Conical Flasks of 150 ml capacity, airtight, and the flasks were completely covered 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 certain amount of CTJ leaves prepared previously was added to the sample flasks. The flasks were placed in the water bath, the time, temperature, and mixing speed were set, and the system was turned on. The ranges of operational conditions used were 1-10, 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, CTJ leaves quantity, contact time and temperature, respectively. At the end of the specified period, the unit turns off automatically and the samples are extracted and filtered in two stages, first one using filter paper (Whatman™ No.1 Grade Circular Filter Papers, 110 mm Diameter- B8A61979) and then using 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 equations 1, 2, and 3, respectively:

$$C_{ads} = C_o - C_f \quad \dots (1)$$

$$\%R = \frac{C_{ads}}{C_o} \times 100 \quad \dots (2)$$

$$q = \frac{V}{m} \times C_{ads} \quad \dots (3)$$

Where: C_o 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 CTJ leaves (ppm); V : is the volume of solution used in treatment process (liter); m : is the amount of CTJ leaves used in treatment process (g); q : is the adsorption capacity (mg/g) and $\%R$: is the percentage of adsorption

7. Benefiting from the residues of the adsorption process

For the safe disposal of CTJ leaves loaded with adsorbed zinc ions from aqueous solutions in a beneficial manner, its use as an effective and cheap organic fertilizer for bean plant was investigated, up to the concept of 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 CTJ 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 CTJ 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) and (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, CTJ 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 CTJ leaves to be an organic fertilizer for clay soil was tested by applying it to the white bean plant because it is fast-growing and does not require many preparations. The mass of bean seeds was chosen to be 0.325 exactly to determine the effect of treatment accurately. Unabsorbed virgin CTJ leaves were also used and prepared in the same way as before for the adsorbed leaves to compare the results with clay soil only. The soil used for growing beans was divided into 5 sections, the first section was only clay soil free of any additives, and the second section was clay soil mixed with unabsorbed virgin CTJ leaves, while the third, fourth, and fifth sections included clay soil mixed with CTJ leaves adsorbed with zinc ions at a ratio of 0.3, 0.9, 3.0 mg/g, respectively. The amount of CTJ leaves used were fixed in each section and mixed with 5 mg of zinc/kg of clay soil. All soils were watered with the water of same quality which was pH 7.21, turbidity 1 NTU, TDS=62 ppm, CaCO₃ 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, 5 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.

8. Results and discussion:

8.1. Adsorption of zinc ions using CTJ leaves

After conducting the experimental work for 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 detected. In this section, the results obtained of the first part of the experimental procedure and the scientific reasons for the behavior of the adsorbent material (CTJ) 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 CTJ leaves as an adsorbent.

8.2. Impact of an acidity function

The acidity function is one of the most important factors that directly affect the adsorption process, due to its effect on the ions dispersed in the solution and also for its effect on the surface of the adsorbent material. The effect of pH on the zinc adsorption process in CTJ leaves was studied within a range of 1-10, keeping all other variables constant at the optimal values. It is noted from Figure 3 that the effect of varying the pH was direct, as the adsorption efficiency increases by increasing the acidity function from a value of 1 until it reaches its highest value at pH = 6, while the efficiency decreases after that with an increase in pH. The reason for the increase in efficiency at acidic values is that the surface of CTJ 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 CTJ. By increasing the pH value, the concentration of hydrogen ions (H⁺) will gradually decrease, and with it the resistance to the positive heavy element ions (Zn⁺²) will decrease, and the surface of CTJ 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 largest 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 will increase, which may lead to the effect of the effective groups and change their behavior. 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 (Al-Hermizy et. al., 2022) in their study of zinc adsorption using lemon peels.

8.3. 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.

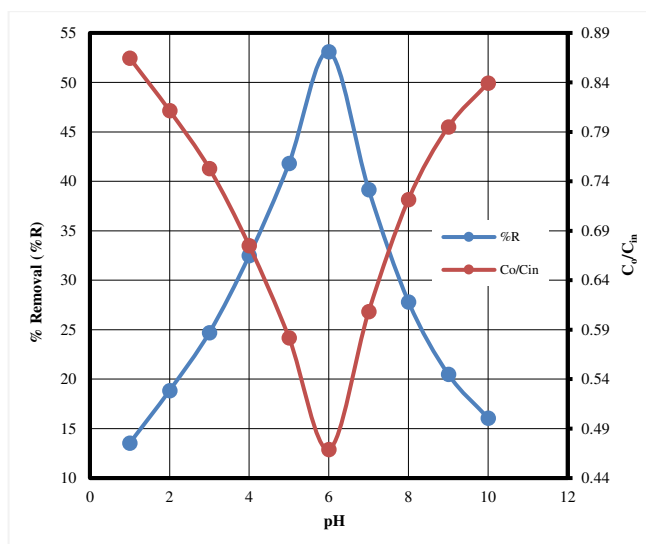


Figure 3. pH impact on the adsorption behavior of zinc ions using CTJ leaves

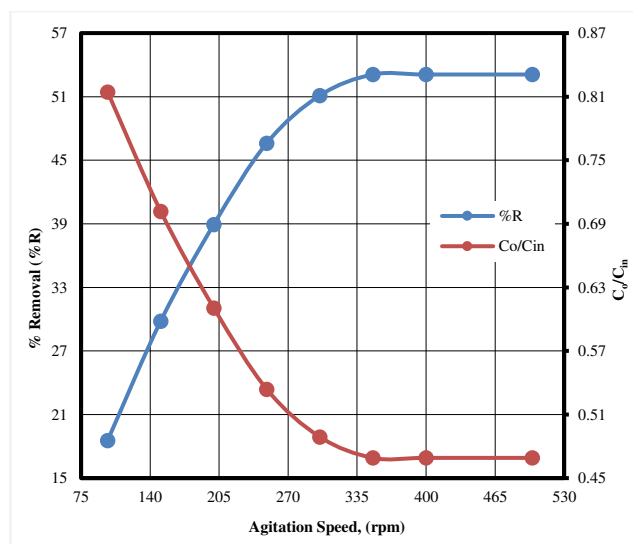


Figure 4. Agitation speed impact on the adsorption of zinc ions using CTJ leaves

Figure 4 shows the effect of changing the agitation speed on the efficiency of zinc ions adsorption by CTJ leaves, with other operating conditions keeping constant at optimum conditions. During the studied range of 100-500 revolutions per minute, it appears that the adsorption efficiency increases by increasing the agitation speed to reach its maximum value at 350 rpm, and then the adsorption efficiency is established at that value without change despite the increase in the agitation speed. This result can be explained by the fact that the speed of agitation contributed to increasing the chance of zinc ions reaching the active sites spread on the surface of CTJ leaves, which contributed to increasing the adsorption efficiency. Therefore, the ions will remain in the solution and the adsorption efficiency will remain unchanged. Similar results were obtained by (Hasan et. al., 2021) when they studied the adsorption process of antimony as a heavy metal using orange peels.

8.4. Impact of Initial Concentration

Figure 5 shows the effect of altering the initial concentration on the susceptibility of CTJ leaves to the adsorption of zinc ions (Zn^{+2}). It is clear that 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 CTJ leaves have a specific surface area through which they can adsorb a specific 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. This means that the amount of non-adsorbed substance will increase with increasing the initial concentration because the volume of the solution is constant and therefore the efficiency will decrease. On the other hand, it is noted from the same figure that the amount of the adsorbent substance zinc ions (Zn^{+2}) increases by increasing the value of the initial concentration until it reaches a specific value and then remains constant without change. This is because the amount of adsorbed material depends on the surface area, which is fixed at a specific number. Therefore, the number of adsorbed zinc ions increases with increasing concentration (the number of ions in the solution) until it reaches the maximum value and does not change afterward despite the increase in concentration. The current results are in agreement with the result of (Ghulam et. al., 2020).

8.5. Impact of adsorbent dose

The adsorption process depends mainly on the presence of an adsorbent media with certain properties that performs the adsorption process. The quantity of this substance has a significant impact, as determining the optimum amount of it to achieve the maximum removal efficiency is a necessary and important issue because it will detect the designed capacity of the adsorption unit.

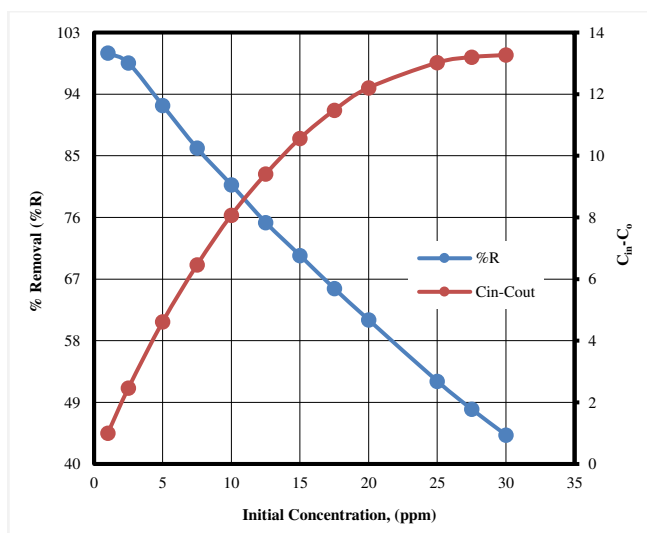


Figure 5. Initial concentration impact on the adsorption of zinc ions using CTJ leaves

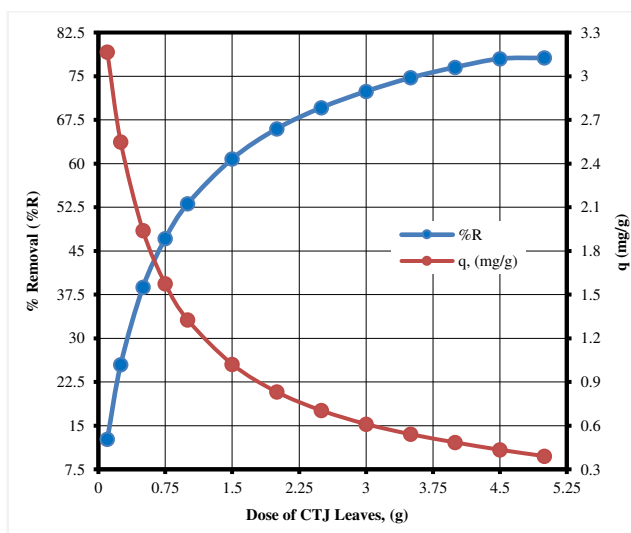


Figure 6. Adsorbent dose impact on the adsorption of zinc ions using CTJ leaves

whether it is in a batch or continuous unit. Within the range of 0.5-5 g, the behavior of CTJ leaves as adsorption media for zinc ions from contaminated aqueous solutions was studied, while the other operating parameters were kept constant at optimum values. The results of studying this operating factor showed that the percentage of adsorption increases with an increase in the dose of adsorbent material with constant initial concentration and that the highest efficiency was achieved at 4.0 g. Despite the increase in the dose, the adsorption efficiency remained constant 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 lead 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 not able 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 the greatest possible. Figure 6 shows the effect of the amount of adsorbent on the adsorption of heavy element ions. (Alwan et. al., 2021) indicated results that are identical to the results of the current study.

8.6. Impact of Contact time

To realize the kinetics of the adsorption process in a comprehensive way, 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 CTJ leaves, a set of adsorption experiments were carried out with different time periods ranging from 10-180 minutes, while the rest of the operating conditions were kept at optimal conditions. Figure 7 epitomizes the results of the experiments of changing the contact time on the adsorption efficiency for the current study. It is noted from the above figure that the percentage of zinc removal is directly proportional to the contact time and that 120 minutes was the equilibrium time, after which the efficiency remains constant and does not change according to the specific operational conditions. Increasing the contact time leads to an increase in the probability of ions reaching the active sites, thus reducing the number of ions dispersed in the solution, and ultimately increasing the efficiency. It is noted that the adsorption efficiency is high in the initial time periods, and the increase begins to decrease gradually until reaching the maximum value. The reason for this result is that the adsorbent material is initially virgin and free of any polluted substance, so the adsorption will be more intense, and with the passage of time the material gradually begins to saturate. Progressively, the substance reaches the state of equilibrium and is not able to adsorb any additional quantity, despite the presence of vacant effective sites, and the reason for this may be the operational conditions, the design of the adsorption system, and its absorptive capacity. Most of the previous studies had results consistent with the obtained result, such as (Ibrahim et. al., 2016).

8.7. 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. This operational factor was studied in this investigation within a sufficient range between 20-60°C to determine the optimum temperature to achieve the best adsorption efficiency. The results shown in Figure 8 showed that raising the temperature from 20 to 45°C leads to an increase in the percentage of adsorption of zinc ions from 10-77%, respectively, and that the relationship within this range is direct. 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, which means that a larger number of zinc ions can be adsorbed and their number decreases in the solution. 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.

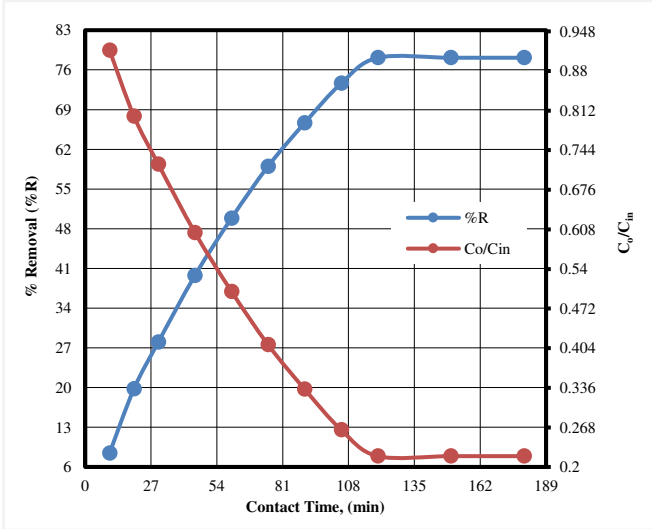


Figure 7. Contact time impact on the adsorption of zinc ions using CTJ leaves

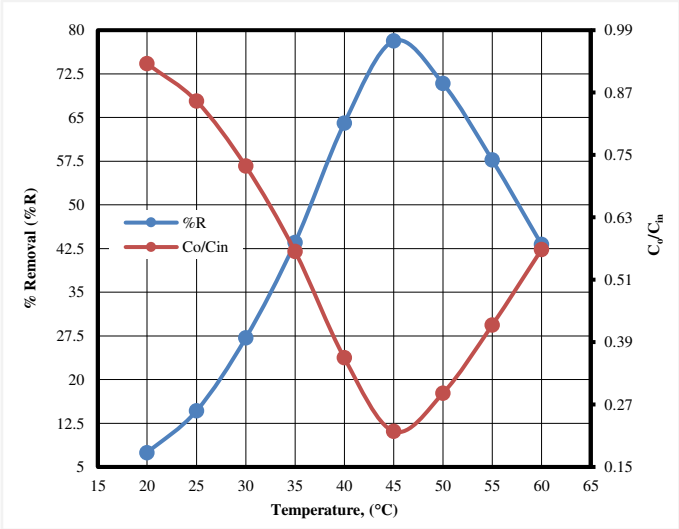


Figure 8. Temperature impact on the adsorption of zinc ions using CTJ leaves

On the other hand, increasing the temperature leads to an increase in the kinetic energy of zinc ions, which makes their arrival to the active sites require less time and thus increases the number of zinc ions adsorbed on the surface of the CTJ leaves and thus increases 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 be freed from the forces associated with it 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 had the same practical results that are identical to the results of the current study, including (Ibrahim et. al., 2021).

8.8.Benefiting from the adsorption residues

The results obtained from the use of Zinc-laden CTJ leaves as an organic fertilizer (according to the method shown previously) showed that it had a clear 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 CTJ 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 is of great importance in terms of the ability of growth regulators to maneuver in the plant body and for 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 major role in the growth of flower nodes. On the other hand, zinc enters the synthesis of enzymes that synthesize plant auxins. It also plays an important role in the process of oxidation of sugars in plants and has a key role in the formation of chlorophyll and in 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, apples, and it is one of 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 CTJ leaves, especially since the soil (according to the value of its acidic function) is classified among the soils with a low level of zinc.

Table 1. results of using the residues of zinc adsorption as fertilizer for 0.325 g bean seed

Growing bean seeds

Type of Soil	Mass (mean $\pm$ SD)	% increase
Virgin Clay soil	0.3282 $\pm$ 0.02941	0.9723
Clay soil + CTJ only	0.3284 $\pm$ 0.00885	1.0462
Clay soil + CTJ of 0.3 mg/g Zinc	0.3338 $\pm$ 0.01928	2.7076
Clay soil + CTJ of 0.9 mg/g Zinc	0.3382 $\pm$ 0.01844	4.2523
Clay soil + CTJ of 3.0 mg/g Zinc	0.3542 $\pm$ 0.00845	8.9723

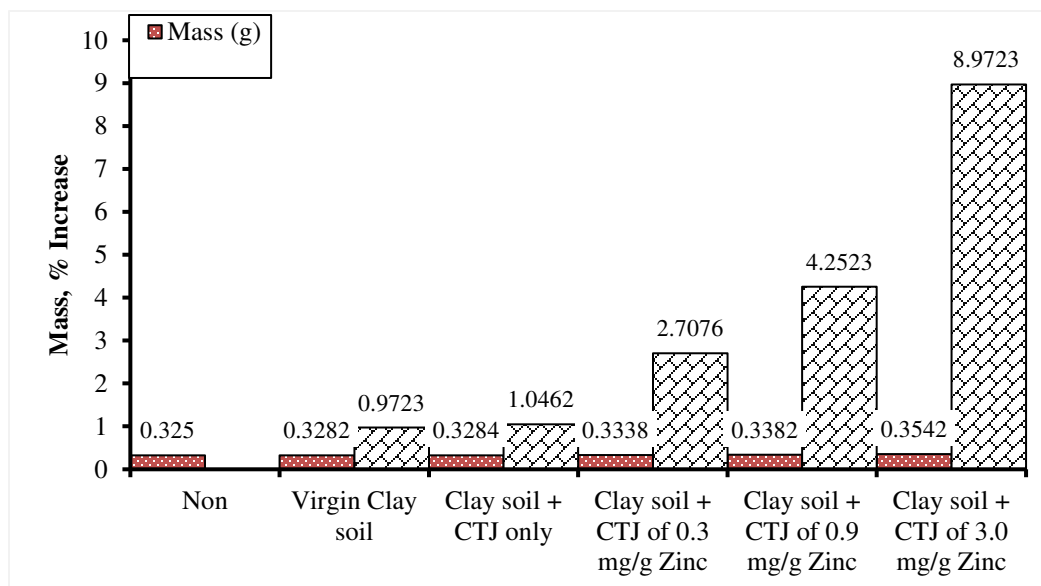


Figure 9. Behavior of using adsorbent residues as a fertilizer compared with other type of soils

9. Conclusions

The current study discussed the ability of CTJ leaves to treat zinc-contaminated water in a batch-mode adsorption unit and at a set of operating conditions. The studied operational conditions included the acidity function, mixing speed, the initial concentration of zinc, the quantity of CTJ leaves, the contact time, and finally the temperature of the adsorption unit. The results showed that the maximum adsorption efficiency was 77%, and it was achieved at an acid function of 6, agitation speed of 350 rpm, an initial concentration of 35 ppm, and 4.0 g of CTJ leaves, an equilibrium time of two 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 in general, the acidity function, and the temperature after the optimum value. The objectives of the study were completed by reaching the concept of zero residue level by converting zinc-contaminate CTJ leaves residues into an activated organic fertilizer. This fertilizer was applied to the bean plant in zinc-poor soil and in simple experimental conditions. These residues showed the ability to compete with other types of fertilizers, as the treatment of the soil with these residues led to an increase in the mass of beans planted in it in proportions directly proportional to the amount of zinc loaded on it, and it reached 9%. From the foregoing, it concludes that agricultural waste, including tree leaves, which represent a varying percentage of municipal waste, is an important source for sustainable development by treating environmental pollutants and disposing of them in beneficial ways other than the traditional methods of burning and burial.

References:

- Abbas F. S., Abdulkareem W. S. and Abbas M. N., (2022), "Strength Development of Plain Concrete Slabs by the Sustainability Potential of Lead-Loaded Rice Husk (LLRH)", *Journal of Applied Engineering Science*, Volume 20, Number 1, pp: 160-167. <https://doi:10.5937/jaes0-32253>
- Abbas M. N. and Abbas F. S., (2013a), "Iraqi Rice Husk Potency to Eliminate Toxic Metals from Aqueous Solutions and Utilization from Process Residues", *Advances in Environmental Biology*, Volume 7, Number 2, pp: 308-319.
- Abbas M. N. and Abbas F. S., (2013b), "The Feasibility of Rice Husk to Remove Minerals from Water by Adsorption and Avail from Wastes", *Research Journal of Applied Sciences*, WSEAS Transactions On Environment and Development, Volume 9, Issue 4, October, pp:301-313.

363 Abbas M. N. and Abbas F. S., (2013c), "The Predisposition of Iraqi Rice Husk to Remove Heavy Metals from
364 Aqueous Solutions and Capitalized from Waste Residue", Research Journal of Applied Sciences,
365 Engineering and Technology, Volume 6, Issue 22, pp: 4237-4246.

366 Abbas M. N. and Abbas F. S., (2014), "Application of Rice Husk to Remove Humic Acid from Aqueous Solutions
367 and Profiting from Waste Leftover", WSEAS Transactions on Biology and Biomedicine, Volume 11, 2014,
368 Art. #9, pp. 62-69.

369 Abbas M. N. and Alalwan H. A., (2019), "Catalytic Oxidative and Adsorptive Desulfurization of Heavy Naphtha
370 Fraction", Korean Journal of Chemical Engineering, Volume 12, Issue 2, pp: 283-288. November.
371 <http://doi.org/10.9713/kcer.2019.57.2.283>

372 Abbas M. N. and Ibrahim S. A., (2020), "Catalytic and thermal desulfurization of light naphtha fraction", Journal
373 of King Saud University - Engineering Sciences, Volume 32, Issue 4, pp: 229-235.
374 <https://doi.org/10.1016/j.jksues.2019.08.001>

375 Abbas M. N. and Nussrat T. H., (2020), "Statistical Analysis of Experimental Data for Adsorption Process of
376 Cadmium by Watermelon Rinds in Continuous Packed Bed Column", International Journal of Innovation,
377 Creativity and Change, Volume 13, Issue 3, pp: 124-138.

378 Abbas M. N., Ali S. T. and Abbas R. S., (2020), "Rice Husks as a Biosorbent Agent for Pb⁺² Ions from Contaminated
379 Aqueous Solutions: A Review", Biochemical and Cellular Archives, Volume 20, Number 1, pp: 1813-1820.
380 <https://doi.org/10.35124/bca.2020.20.1.1813>

381 Abbas M. N., Al-Madhhachi A. T. and Esmael S. A., (2019b), "Quantifying soil erodibility parameters due to
382 wastewater chemicals", International Journal of Hydrology Science and Technology, Volume 9, Issue 5, pp:
383 550-568. <http://doi.org/10.1504/IJHST.2019.10016884>.

384 Abbas M. N., Al-Tameemi I. M., Hasan M. B., and Al-Madhhachi A. T., (2021a), "Chemical Removal of Cobalt and
385 Lithium in Contaminated Soils using Promoted White Eggshells with Different Catalysts", South African
386 Journal of Chemical Engineering, Volume 35, pp: 23-32. <https://doi.org/10.1016/j.sajce.2020.11.002>

387 Abbas M. N., Ibrahim S. A., Abbas Z. N. and Ibrahim T. A., (2021b), "Eggshells as a Sustainable Source for Acetone
388 Production", Journal of King Saud University - Engineering Sciences,
389 <https://doi.org/10.1016/j.jksues.2021.01.005>

390 Abbas M. N., Al-Hermizy S. M. M., Abudi Z. N., and Ibrahim T. A., (2019a), "Phenol Biosorption from Polluted
391 Aqueous Solutions by Ulva lactuca Alga using Batch Mode Unit", Journal of Ecological Engineering, Volume
392 20, Issue 6, July, pp: 225-235. <https://doi.org/10.12911/22998993/109460>

393 Abbas, M.N., (2015), "Phosphorus removal from wastewater using rice husk and subsequent utilization of the
394 waste residue", Desalination and Water Treatment, Volume 55, Issue 4, pp: 970-977.
395 <https://doi.org/10.1080/19443994.2014.922494>

396 Abd ali I. K., Ibrahim T. A., Farhan A. D. and Abbas M. N., (2018), "Study of the effect of pesticide 2,4-D on the
397 histological structure of the lungs in the albino mice (Mus musculus)" Journal of Pharmaceutical Science
398 and Research, Volume 10, Issue 6, pp: 1418-1421, August.

399 Abdulkareem W.S., Aljumaily H.S.M., Mushatat H.A., Abbas M.N., (2023), "Management of Agro-Waste by Using
400 as an Additive to Concrete and Its Role in Reducing Cost Production: Impact of Compressive Strength as a
401 Case Study", International Journal on "Technical and Physical Problems of Engineering" (IJTPE), Issue 54,
402 Volume 15, Number 1, pp: 62-67.

403 Abdullah W. R., Alhamadani Y. A. J., Abass I. K., and Abbas M. N., (2023), "Study of chemical and physical
404 parameters affected on purification of water from inorganic contaminants", Periodicals of Engineering and
405 Natural Sciences, Volume 11, Number 2, pp: 166-175. <http://dx.doi.org/10.21533/pen.v11i2.3508>

406 Agnew U. M. and Slesinger T. L., (2022), "Zinc Toxicity", [Updated 2022 Jan 6]. In: StatPearls [Internet]. Treasure
407 Island (FL): StatPearls Publishing; 2022 January. Available from:
408 <https://www.ncbi.nlm.nih.gov/books/NBK554548/>

409 Al-Ali S. I. S., Abudi Z. N. and Abbas M. N., (2023), "Modelling and Simulation for the use of Natural Waste to
410 Purified Contaminated Heavy Metals", Journal of the Nigerian Society of Physical Sciences, Volume 5, Issue
411 1, 1143. <https://doi.org/10.46481/jnsps.2023.1143>

412 Al-Ali S. I. S., Ibrahim S. A., Abbas M. N., and Ibrahim T. A., (2023), "Mathematical Modelling of Selenium
413 Adsorption using Pomegranate Peel", Tikrit Journal of Engineering Sciences, under publishing.

414 Alalwan H. A., Abbas M. N., Abudi Z. N. and Alminshid A. H., (2018), "Adsorption of thallium ion (Tl^{+3}) from
 415 aqueous solutions by rice husk in a fixed-bed column: Experiment and prediction of breakthrough curves",
 416 Environmental Technology and Innovation, Volume 12, November, pp: 1-13.
 417 <https://doi.org/10.1016/j.eti.2018.07.001>

418 Alalwan H. A., Abbas M. N., and Alminshid A. H., (2020), "Uptake of Cyanide Compounds from Aqueous Solutions
 419 by Lemon Peel with Utilising the Residue Absorbents as Rodenticide", Indian Chemical Engineer, Volume
 420 62, Issue 1, pp: 40-51 <https://doi.org/10.1080/00194506.2019.1623091>

421 Alalwan, H. A., Mohammed, M. M., Sultan, A. J., Abbas, M. N., Ibrahim, T. A., Aljaafari, H. A. S., Alminshid, A. A.,
 422 (2021), "Adsorption of methyl green stain from aqueous solutions using non-conventional adsorbent media:
 423 Isothermal kinetic and thermodynamic studies", Bioresource Technology Reports, 14, 100680.
 424 <https://doi.org/10.1016/j.biteb.2021.100680>

425 Al-Hermizy S. M. M., Al-Ali S. I. S., Abdulwahab I. A. and Abbas M. N., (2022), "Elimination of Zinc Ions (Zn^{+2})
 426 from Synthetic Wastewater Using Lemon Peels", Asian Journal of Water, Environment and Pollution,
 427 Volume 19, No. 5, pp: 79-85. <https://doi.org/10.3233/AJW220073>

428 Ali G. A. A. and Abbas M. N., (2020), "Atomic Spectroscopy Technique Employed to Detect the Heavy Metals from
 429 Iraqi Waterbodies Using Natural Bio-Filter (Eichhornia crassipes) Thera Dejla as a Case Study", Systematic
 430 Reviews in Pharmacy, Volume 11, Issue 9, pp: 264-271. <https://doi.org/10.31838/srp.2020.9.43>.

431 Ali G. A. A., Ibrahim S. A. and Abbas M. N., (2021), "Catalytic Adsorptive of Nickel Metal from Iraqi Crude Oil
 432 using non-Conventional Catalysts", Innovative Infrastructure Solutions, Volume 6, Article number: 7, 9
 433 pages. <https://doi.org/10.1007/s41062-020-00368-x>

434 Ali S. A. K., Almhana N. M., Hussein A. A. and Abbas M. N., (2020), "Purification of Aqueous Solutions from Toxic
 435 Metals using Laboratory Batch Mode Adsorption Unit Antimony (V) Ions as a Case Study", Journal of Green
 436 Engineering (JGE), Volume 10, Issue 11, pp: 10662-10680, November.

437 Alwan E. K., Hammoudi A. M., Abd I. K., Abd Alaa M. O., and Abbas M. N., (2021), "Synthesis of Cobalt Iron Oxide
 438 Doped by Chromium Using Sol-Gel Method and Application to Remove Malachite Green Dye",
 439 NeuroQuantology, Volume 19, Issue 8, pp: 32-41 <http://doi:10.14704/nq.2021.19.8.NQ21110>

440 Bharagava R. N., (2017), "Environmental Pollutants and Their Bioremediation Approaches", CRC Press; ISBN:
 441 978-1-138-62889-2, 1138628891

442 Ghulam N. A., Abbas M. N. and Sachit D. E., (2020), "Preparation of synthetic alumina from aluminium foil waste
 443 and investigation of its performance in the removal of RG-19 dye from its aqueous solution", Indian
 444 Chemical Engineer, Volume 62, Issue 3, pp: 301-313. <https://doi.org/10.1080/00194506.2019.1677512>

445 Hasan M. B., Al-Tameemi I. M., and Abbas M. N., (2021), "Orange Peels as a Sustainable Material for Treating
 446 Water Polluted with Antimony", Journal of Ecological Engineering, Volume 22, Issue 2, pp: 25-35.
 447 <https://doi.org/10.12911/22998993/130632>

448 Hashem N. S., Ali G. A. A., Jameel H. T., Khurshid A. N. and Abbas M. N., (2021), "Heavy Metals Evaluation by
 449 Atomic Spectroscopy, for Different Parts of Water Hyacinth (Eichhornia crassipes) Plants Banks of Tigris
 450 River", Biochemical and Cellular Archives, Volume 21, No. 2, pp: 3813-3819,
 451 <https://connectjournals.com/03896.2021.21.3813>

452 <https://www.atsdr.cdc.gov/ToxProfiles/tp60-c1-b.pdf>, August, 2005

453 Ibrahim T. A., Abbas M. N. and Abbas F. S., (2016), "Detoxification of Pesticides Wastewater by Adsorption
 454 Technique Feasibility of Agricultural Waste Utilization", LAMBERT Academic Publishing, ISBN-10:
 455 365983243X, ISBN-13: 978-3659832437

456 Ibrahim T. A., Mahdi H. S., Abbas R. S. and Abbas M. N., (2020), "Study the Effect of Ribavirin Drug on the
 457 histological structure of the testes in Albino mice (Mus musculus)", Journal of Global Pharma Technology,
 458 Volume 12, Issue 02 (Suppl.), pp: 142-146.

459 Ibrahim T. A., Mohammed A. M., Abd ali I. K. and Abbas M. N., Hussien S. A., (2020), "Teratogenic Effect of
 460 Carbamazepine Drug on the Histological Structure of Testes in the Albino Mouse (Mus musculus)", Indian
 461 Journal of Forensic Medicine & Toxicology, Volume 14, Number 4, pp: 1829-1834
 462 <https://doi.org/10.37506/ijfomt.v14i4.11809>

463 Ibrahim, S. A., Hasan, M. B., Al-Tameemi, I. M., Ibrahim, T. A., Abbas, M. N., (2021), "Optimization of adsorption
 464 unit parameter of hardness remediation from wastewater using low-cost media", Innovative Infrastructure
 465 Solutions, Volume 6, Issue 4, Article number: 200. <https://doi.org/10.1007/s41062-021-00564-3>

466 Institute of Medicine, Food and Nutrition Board (IOM, FNB), (2001), "Dietary Reference Intakes for Vitamin A,
 467 Vitamin K, Arsenic, Boron, Chromium, Copper, Iodine, Iron, Manganese, Molybdenum, Nickel, Silicon,
 468 Vanadium, and Zinc", Washington, DC: National Academy Press, Cited by
 469 <https://ods.od.nih.gov/factsheets/Zinc-HealthProfessional/#en2>

470 Khaleel L. R., Al-Hermizy S. M., and Abbas M. N. (2022), "Statistical Indicators for Evaluating the Effect of Heavy
 471 Metals on Samaraa Drug Industry Water Exposed to the Sun and Freezing", Tropical Journal of Natural
 472 Product Research, Volume 6, Issue 12, pp: 1969-1974. <http://www.doi.org/10.26538/tjnpr/v6i12.12>

473 Maddodi S. A., Alalwan H. A., Alminshid A. H. and Abbas M. N., (2020), "Isotherm and computational fluid
 474 dynamics analysis of nickel ion adsorption from aqueous solution using activated carbon", South African
 475 Journal of Chemical Engineering, Volume 32, April, pp: 5-12. <https://doi.org/10.1016/j.sajce.2020.01.002>