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Treatment of Oil Refinery Wastewater Polluted by Heavy Metal Ions via Adsorption Technique using Non-Valuable Media: Cadmium Ions and Buckthorn Leaves as a Study Case

Salem Jawad Alhamd
Department of Petroleum Engineering, College of Engineering, Kerbala University, Kerbala, Iraq

Mohammed Nsaif Abbas
Environmental Engineering Department, College of Engineering, Mustansiriyah University, Baghdad, Iraq, mohammed.nsaif.abbas@uomustansiriyah.edu.iq

Mehrdad Manteghian
Department of Petroleum Engineering, Faculty of Chemical Engineering, Tarbiat Modares University, Tehran, Iran;

Thekra Atta Ibrahim
Department of Biology, College of Education for Pure Science, University of Diyala, Diyala, Iraq

Karar Dawood Salman Jarmondi
Environmental Engineering Department, College of Engineering, Mustansiriyah University, Baghdad, Iraq

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Abstract

This study focuses on the removal of cadmium ions generated by oil refinery wastewater, employing an agricultural by-product. Buckthorn leaves, sourced from Baghdad and Diyala provinces, underwent preparation, including washing, drying, crushing, and sieving before being utilized in experiments. Batch experiments were conducted using simulated solutions to assess the impact of six key adsorption design parameters: pH, cadmium concentration, agitation speed, contact time, adsorbent dosage, and temperature. The highest adsorption efficiency, reaching 94.4367%, was directly correlated with contact time, adsorbent dosage, pH value, and agitation speed, and inversely related to other variables. Morphological studies on the treated adsorbent, indicated structural changes during the adsorption process, manifested as shifts in FTIR and XRD peaks, and observed pore alterations through SEM analysis. The BET test revealed a surface area of 36 m^2/g, with less than 68% utilization through adsorption. Adsorption behavior was analyzed in three parts: isothermal analysis, exhibiting a strong fit to the Langmuir model; kinetic study, favoring the pseudo-second-order model; and thermodynamic characterization as exothermic, of low entropy, and spontaneous. The study also investigated the regeneration of spent adsorbent, highlighting physical activation as the more effective method, providing four reuse cycles compared to chemical activation's two. The paper extended its investigation to real oil refinery wastewater, assessing the ability of the adsorbent to compete with other contaminants. Buckthorn leaves exhibited an efficiency of 50-75% in remediating real wastewater, similar to simulated solutions. Consequently, this research proposes an environmentally sound, cost-effective means of sustainably repurposing agricultural waste to achieve zero-residue levels.

Keywords

Adsorption, buckthorn leaves, cadmium ions, oil refinery wastewater, zero residual level (ZRL)

Cover Page Footnote

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RESEARCH PAPER

Treatment of Oil Refinery Wastewater Polluted by Heavy Metal Ions via Adsorption Technique using Non-valuable Media: Cadmium Ions and Buckthorn Leaves as a Study Case

Salem J. Alhamd [a], Mohammed N. Abbas [b,*], Mehrdad Manteghian [c], Thekra A. Ibrahim [d], Karar D.S. Jarmondi [b]

[a] Department of Petroleum Engineering, College of Engineering, Kerbala University, Kerbala, Iraq
[b] Environmental Engineering Department, College of Engineering, Mustansiriyah University, Baghdad, Iraq
[c] Department of Petroleum Engineering, Faculty of Chemical Engineering, Tarbiat Modares University, Tehran, Iran
[d] Department of Biology, College of Education for Pure Science, University of Diyala, Diyala, Iraq

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1. Introduction

Contamination of environmental resulted from numerous pollutants is an important issue, primarily due to their release to the environment via various industrial or agricultural applications [1], discharged into the soil [2], or emitted into the air [3] in various types and varying quantities depending on the industry, such as mining, dyes, batteries, glass, and others [4]. Various heavy metals, such as nickel, vanadium, cadmium, lead, mercury, chromium, and others, are present in crude oil [5]. During the different refining processes of crude oil, such as pretreatment, heating, separation, and

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* Corresponding author.
E-mail address: mohammed.nsaif.abbas@uomustansiriyah.edu.iq (M.N. Abbas).
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production of oil derivatives, a proportion of these metals is disposed of in the oil refineries' wastewater [6]. Like vitamins, the human body needs some kinds of heavy metals in small and very limited amount every day [7]. Ions of heavy metals such as cadmium, lead, copper, zinc, chromium, nickel and mercury are toxic and non-biodegradable [2]. They can easily reach the waterway; accumulate in the bodies of living organisms and from there to humans, causing many health problems such as kidney failure, oral ulcers, anemia, and sometimes types of cancer, in addition to problems and dangers for animals, plants and the environment alike [6]. Cadmium is one of the heavy metals that contaminate the environment and is classified among the toxic elements [8]. Cadmium ions pose a detrimental threat to the environment by entering the food chain, which can result in severe health risks to humans. This includes potential damage to the kidneys and bones, and long-term exposure may contribute to the development of conditions such as high blood pressure [9]. It affects living organisms by reacting with the nucleic acids (DNA and RNA) of the cell and thus affects the genetic genes [10]. It affects the metabolic processes, life cycles and growth of animals and plants in aquatic environments [11]. Cadmium is used in many industries, including batteries, phosphate fertilizers, dyes, alloys, and sheet metal [1]. It is also possible to enter water bodies from the discharge of oil refinery waste into them, due to the fact that all kinds of crude oil contain different percentages of cadmium [12]. The permissible concentration of cadmium ion in drinking water is 0.005 mg/l [9], while it is 0.04 mg/l in river water [13], according to the parameters of the World Health Organization and 0.03 mg/l according to Iraqi standard [9]. Due to these concentration values, the cadmium ions must be completely disposed of or reduced to the lowest possible level before disposing the wastewater into the various waterways, whether surface or underground, and working to prevent the mixing of polluted wastewater with rainwater [9]. From reviewing the literature, the treatment of water contaminated with cadmium ions has been studied using various methods including chemical precipitation, ion exchange, ultrafiltration, reverse osmosis membranes, coagulation and flocculation, solvent extraction and others [1]. All of the above methods include obstacles that may be economic or lead to accumulate of toxic substances being left behind after the end of the process, or require complex systems, require high energy, or have limited efficiency compared to their cost [14]. Thus, all these traditional methods are ineffective in treating low concentrations of heavy metals in general and cadmium in particular [15]. Adsorption technology is considered one of the best methods used in treating water contaminated with heavy metals due to its appropriate efficiency, especially in low concentrations [16]. On the other hand, it does not require complex systems or high operating costs, nor does it consume high energy [17]. One of the most important materials used as an adsorption media is activated carbon. Activated carbon has aroused the interest of researchers in the field of adsorption due to its high surface area, efficiency and possibility of reuse [18]. However, the high cost of its preparation and the loss of between 10 and 15 % of its weight in each reactivation process prompted researchers to reconsider its use and search for other cheaper alternatives to produce it or to use it as direct adsorbents instead [17]. Among the most important materials that have been proposed as alternatives to activated carbon are agricultural waste and solid waste such as rice husks [19], not only for cadmium also for thallium removal [20] hardness [21], cobalt [22] lead [23], inorganic contaminants [24], selenium [25], cadmium [26], cyanide [27], antimony [28], dyes

Nomenclature:

b	Adsorption heat constant ($J.mol^{-1}$)
C	Constant related with the thickness of boundary layer in intra-particle diffusion model ($g.mg^{-1}$)
C_e	Equilibrium concentration of adsorbent ($mg.l^{-1}$)
C_i	Initial concentrations of adsorbent ($mg.l^{-1}$)
C_f	Final concentrations of adsorbent ($mg.l^{-1}$)
K_F	Freundlich Constant $[(mg.g^{-1}).(l.mg^{-1})^{1/n}]$
K_L	Constant of Langmuir isotherm model ($l.mg^{-1}$)
K_T	Temkin Constant ($l.g^{-1}$)
k_1	1st order rate constant (min^{-1})
k_2	2nd order rate constant ($g.mg^{-1}.min^{-1}$)
k_{ad}	Adsorption equilibrium coefficient (–)
k_P	Intra-particle diffusion Rate constant ($g.mg^{-1}.min^{-0.5}$)
m	Mass of adsorbent media (g)
n	Adsorption intensity of Freundlich isotherm model (–)
q_e	Capacity of adsorption at equilibrium ($mg.g^{-1}$)
q_{max}	Maximum capacity of adsorption ($mg.g^{-1}$)
q_t	Capacity of adsorption at any time ($mg.g^{-1}$)
R	is the percentage removal (–)
R	Universal gas constant (8.3144 $J\ mol^{-1}\ K^{-1}$)
SE	Standard Error of Mean (–)
T	Absolute temperature (K)
t	Time of adsorption (min)
V	Volume of solution (l)
α	Initial rate of adsorption ($mg.g^{-1}.min^{-1}$)
β	Desorption constant ($g.mg^{-1}$)
ΔH	Enthalpy change ($J.mol^{-1}$)
ΔS	Entropy change ($J.mol^{-1}.K^{-1}$)
ΔG	Gibbs free energy ($kJ.mol^{-1}$)

[29], groups of heavy metals [30], phenol [31], and zinc [32]. The agricultural wastes not used for treated the contaminated water [33], but also treated crude oil [34] and soil [35] as well as produced a benefit material [36] in addition to nanoparticles [37]. For the last three decades, there are many applications for the use of these wastes in the field of polluted water treatment using adsorption technology [38], as they are available materials with negligible toxicity and cheap price, in addition to their efficiency due to their acceptable performance [39]. Therefore, the purpose of this paper is to shed light on the importance of agricultural waste (including tree leaves) and its use in a beneficial and environmentally friendly manner, up to the zero residues level (ZRL). The concept of (ZRL) is achieved in this study by disposing of more than one type of waste simultaneously in a useful method [40] such as concrete additives [41], radiation-absorbent material [42], fertilizer [43], and rodenticide due to its toxic effect [44]. The removing of cadmium ions from aquatic media was investigated from different previous studies. Almond shells were examined for their potential by Mehrasbi et al., 2009 [45] to adsorb Cd(II) ions from aqueous solutions. The shells were pretreated with different solutions, including NaOH, HNO_3, and distilled water, and their adsorption capacities were compared. The batch adsorption experiments considered initial ion concentration, pH, and adsorbent dosage. The results indicated that alkali-modified almond shells had higher adsorption capacities for Cd(II) compared to acid- and water-pretreated shells. The Langmuir model provided the best fit for the adsorption isotherms, suggesting a strong affinity of almond shells for Cd(II) adsorption. The optimal pH for adsorption was found to be in the range of 5−6. The orange peel was used as a low-cost and eco-friendly adsorbent to remove Cd(II) ions from water by Akinhanmi et al., 2020 [46]. Surface properties were characterized via SEM, XRD, and FT-IR tests. Optimal conditions obtained were 2 h of contact time, 240 mg/l initial Cd(II) concentration, 0.04 g/l adsorbent dosage, 45 °C temperature, and pH 5.5. Langmuir isotherm analysis was the best model to describe the process and 128.23 mg/g the adsorption capacity. Kinetic data followed the pseudo-first-order model, while the endothermic adsorption process had an enthalpy of 0.0046 kJ mol^{-1} and entropy of −636.865 J mol^{-1} K^{-1}. Increasing adsorbent dosage and decreasing Cd(II) ion concentration improved removal efficiency, demonstrating the potential of orange peel for Cd(II) ion removal from water. Agricultural waste-derived activated carbons, specifically pomegranate peel (PPAC) and date pit (DPAC) activated carbon, were examined by Al-Onazi et al., 2021 [47] for their potential to remove Cd(II) from aqueous solutions. The study investigated the impact of various parameters, including solution pH, adsorbent dosage, initial Cd(II) concentration, and contact time, on the adsorption process. PPAC exhibited higher adsorption efficiency and a greater maximum adsorption capacity (q_{max}) for Cd(II) compared to DPAC. The Langmuir isotherm model and pseudo-second-order kinetics were found to describe the adsorption behavior well. This research underscores the effectiveness of PPAC as an eco-friendly and cost-efficient sorbent for Cd(II) removal from water. Thus, this paper investigates the study of cadmium ion removal from simulated and real oil refinery wastewater using buckthorn leaves and determining the optimal operating conditions that achieve the greatest removal of cadmium ions. Moreover, predicting the isothermal, kinetic and thermodynamic behaviors of adsorption.

2. Materials and methods

2.1. Materials

The materials utilized in this study included tetrahydrate cadmium nitrate of a chemical formula $Cd(NO_3)_2 \cdot 4H_2O$, having a purity of 98.5 %, which was supplied by Labogens company, India. The solutions of pH adjustment, i.e., sodium hydroxide (NaOH) pellets with a purity of 99.99 % and hydrochloric acid (HCl) with a purity of 37 % were purchased from MERCK company, Germany. Acetone (CH_3COCH_3) was obtained from MERCK company, Germany. All of these materials were used without further treatment. Double distilled water used in the experimental procedures was prepared in the laboratory using a distillation unit (2014 GFL Double distiller apparatus, Germany) at room temperature.

2.2. Preparation of buckthorn leaves

Buckthorn Leaves used in this research were collected from buckthorn tree residues in the city of Baghdad and Baquba District in Diyala Governorate. Then the leaves were washed several times with an excess tap water to get rid of any impurities and dirt stuck before drying them naturally for three days in outdoor using sunlight in the spring season, where the temperature ranges between 25 and 30 °C. Then the dried leaves were firstly washed with distilled water for once, and after that dried using a drying oven (Drying oven, TR 450, Nabertherm, Germany) at a temperature starting from the laboratory temperature and gradually increasing until it reaches 50 °C. The drying process was continuing until the weight of leaves was stable. Clean and dried leaves were crushed manually using a laboratory ceramic mortar (200 ml volume and 75 mm height ceramic mortar and pestle of rough friction surface, Rotilabo®, Carl ROTH, Germany) and sieved using sieve analysis to determine crust size. The sizes of the resulting crushed leaves from crushing ranged between 2.36 and 1.18 mm for passing through sieves No. 8 and 16, respectively. Finally, the leaves were kept in amber glass containers in a cool dry place until they were used in conducting experiments. Fig. 1 represents the leaves of the buckthorn tree used in this study.

2.3. Stock solution of cadmium ions

The adsorption capacity of buckthorn leaves for cadmium ions was determined using simulated aqueous solutions containing specific concentrations of cadmium metal. This procedure was employed to ensure the accuracy of the experimental results, preventing potential interference from other heavy metals, substances, or compounds that might be present in the real wastewater of oil refineries.

A stock solution of 1000 mg/l concentration was achieved by dissolving precisely 2745 mg of tetrahydrate cadmium nitrate, in exactly 1000 ml of double distilled water. The mixing was carried out using magnetic stirrer at 100 rpm and lab temperature. The mixing process was uninterrupted until dissolved of all $Cd(NO3)2 \cdot 4H2O$ completely. The final solution produced, called stock solution, served as the source for preparing of the required aqueous solutions used in subsequent adsorption experiments.

Fig. 1. Crushed buckthorn leaves used in this Study.

2.4. Calibration curve

For detecting the cadmium content in adsorption aqueous solutions, Atomic Absorption Spectroscopy (AAS) instrument (Shimadzu AA-7000, Japan) was employed, which operated at a wavelength of 326.1 nm. A calibration curve for cadmium ions was constructed by analyzing multiple samples with known and specific concentrations of cadmium, correlating each concentration with its corresponding absorbance value. Fig. 2 shows the preparing calibration curve for cadmium achieved via AAS analysis in this particular study.

2.5. Collecting of real oil refinery wastewater

Several samples were collected from wastewater of three Iraqi oil refineries according to the method described by (Abbawi and Hassan, 1990) [48] through taking a clean and sterile 1l beaker and submerging it in the refinery wastewater collection basin. The sample taking covered tightly, then wrapping it by two layers of aluminum foil, recording the sample number and the date of its withdrawal. The samples were taken from wastewater discharged from Baiji refinery, Al-Doura refinery, and Basra refinery; in Northern, central and southern of Iraq, respectively. The samples collected were transported as soon as possible to the laboratory for analysis of their composition. The laboratory test of the cadmium heavy metal was performed accurately and triplicate, and the average of measurements was taken. The analysis of

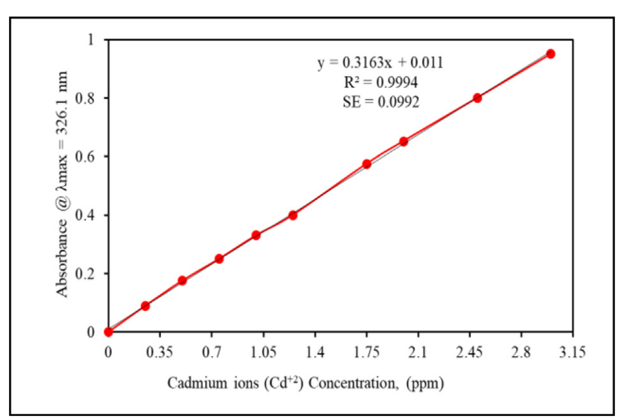

Fig. 2. Calibration curve of cadmium ions using AAS.

cadmium concentration in the real wastewater has been observed that it was less than 5 mg/l. Thus, the range of Cd^{+2} investigated in this study is 0.1−10 mg/l.

2.6. Adsorption unit

The adsorption unit used to study the susceptibility of buckthorn leaves to adsorb the cadmium ions from simulated aqueous solutions was of the batch type, which is a shaking water bath unit (Thermo Scientific MaxQ SHKE7000 Benchtop, Model 4303). Experiments were carried out using 150 ml borosilicate glass conical flasks (IndiaMART, India), each flask contains a certain amount of buckthorn leaves, which represents the adsorbent media, in addition to 100 ml of controlled pH cadmium solution of a specified initial concentration. The pH of the solution was adjusted using 0.1 N hydrochloric acid (HCl) and sodium hydroxide (NaOH) solutions. After setting the temperature of the adsorption unit, the sample is placed in the water bath shaker, the agitation speed is adjusted to the required value, and the adsorption process starts and continues for specified contact time. Then the filtration process is carried out using filter paper (Whatman™ No.1 Grade Circular Filter Papers, 110 mm Diameter- B8A61979) and filtering unit (Filtering Kit 250 ml, Vacuum Pump with Gauge, KT3003-3 Science Lab Supplies/UK). Then the filtered samples were examined using the AAS instrument, and the residual cadmium concentration in the sample is determined by the calibration curve. From knowing the initial concentration, the percentage removal of cadmium ions and adsorption capacity of buckthorn leaves can be calculated through equations (1) and (2), respectively:

$$R = \left(1 - \frac{C_\circ}{C_i}\right) \times 100 \quad (1)$$

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

3. Results and discussion

3.1. Effect of pH changing

Fig. 3 illustrates the impact of varying the pH on the removal efficiency of divalent cadmium ions from simulated aqueous solutions when utilizing buckthorn leaves as the adsorbent. The pH variation was the first design parameter tested, ranging from 1 to 14, while maintaining other operational conditions at constant values of 1 mg/l initial concentration, 180 min of contact time, 0.5 g of adsorbent dose, 300 rpm agitation speed, and 25 °C temperature. As depicted in Fig. 3, the removal efficiency exhibits a gradual, consistent, and closely proportional increase with rising solution pH, starting at 22.9661 % at pH 1 and peaking at 69.3758 % at pH 6. This trend can be elucidated by the positively charged surface of the adsorbent resulting from H^{+} ions at lower pH levels. This positive charge creates a significant repulsion force between the adsorbent surface and the diffusing Cd^{+2} ions in the solution, leading to diminished removal efficiency. Furthermore, the increased presence of hydrogen ions in the solution competes with cadmium ions for the available active sites on the surface of buckthorn leaves. Conversely, higher pH values mitigate the positive charge on the adsorbent's surface, thereby reducing the resistance to Cd^{+2} ion adsorption and, consequently, enhancing efficiency. Upon increasing the pH value beyond 6 (from 7 to 14), two significant observations were documented. First, removal efficiency exhibited a sharp and rapid ascent until it reached the optimum level. The second observation entailed the precipitation of cadmium ions at the base of the experimental flask. This phenomenon signifies that the escalation in removal efficiency beyond 69.3758 % results from a precipitation process, rather than adsorption. In this precipitation process, cadmium ions linger in the solution, even as their diffusion is restricted, and removal efficiency attains its peak. However, this behavior does not equate to the removal of the target ions but merely neutralizes their activity.

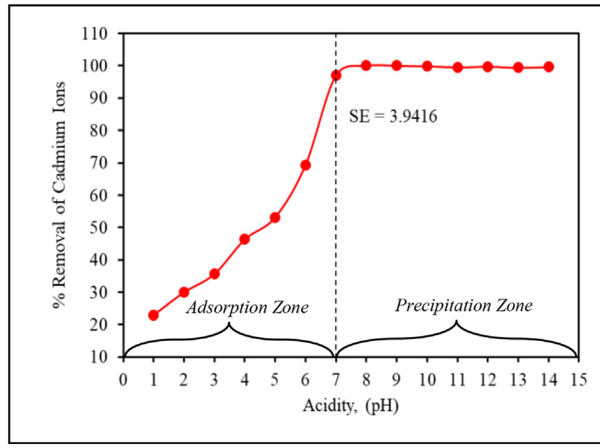

Fig. 3. Effect of pH on the % removal of Cd^{+2} ions using buckthorn leaves.

Should the pH value decrease due to alterations in the ambient conditions, there is a potential for these ions to reintroduce contamination to the solution, leading to a cycle of pollution. Such an outcome contradicts the core objective of this study, which seeks a definitive purification of polluted water rather than a temporary treatment. In contrast, the adsorption method ensures that cadmium ions cannot easily return to the solution because they become bound to functional groups at the active sites distributed on the adsorbent medium's surface. Therefore, the optimal pH for cadmium ion removal was determined to be 6, rather than 7 or higher, despite the elevated efficiency achieved at the latter pH value. This determination aligns with the primary aim of the study, which focuses on confirming the capacity of buckthorn leaves to exclusively remove cadmium ions from aqueous solutions through the process of adsorption. This result agrees with [26].

3.2. Effect of agitation speed changing

*Special description of the title. (dispensable)

The agitation speed is one of the most important factors to be studied to know the behavior of the adsorption media, as it is always related to the concept of diffusivity. Therefore, the effect of this variable on the efficiency of the treatment process was studied within a range of 100−500 rpm, while the values of the acidity function, initial concentration, contact time, and adsorbent dose were fixed at 6, 1 mg/l, 180 min, 0.5 g, respectively and at laboratory temperature. As illustrated in Fig. 4, changing the agitation speed values has a pronounced and direct effect on the efficiency of cadmium removal from simulated aqueous solutions when utilizing buckthorn leaves as the adsorption material. Notably, there is an approximate 48 % increase in removal efficiency when the agitation speed increases from 100 to 350 rpm.

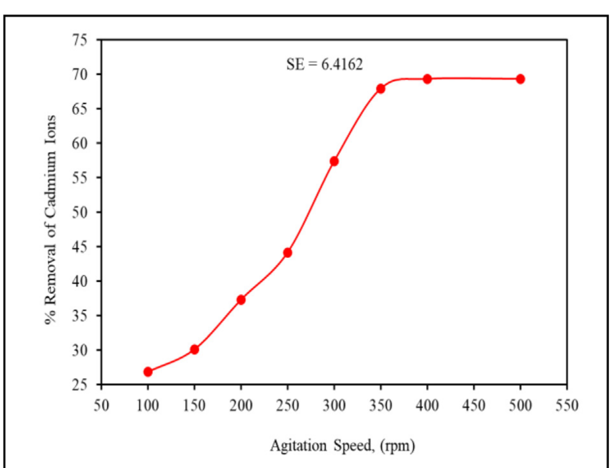

Fig. 4. Effect of agitation speed on the % removal of Cd^{+2} ions using buckthorn leaves.

Beyond this point, however, the removal efficiency is kept constant, showing no further noteworthy change. The reason for this is due to the increase in the diffusion of cadmium ions in the solution as a result of increasing the agitation speed, which leads to an increase in the chance of those ions reaching the functional groups dispersed on the surface of the adsorbent. Also, increasing the agitation speed may be led to destroy any film layer might be formed on the surface of the buckthorn leaves, thus reducing the resistance to adsorption of cadmium ions. The relationship between agitation speed and ion mass can be considered, where higher speeds tend to displace lighter hydrogen and hydroxide ions from the surface of adsorbent. This displacement facilitates the access of heavier cadmium ions to the active sites, resulting in an augmented adsorption of ions. Consequently, by elevating the agitation speed, the treatment process's efficiency can be enhanced through an increased number of adsorbed ions. This result is consistent with [17].

3.3. Effect of initial concentration changing

Within a range between 0.1 and 10 mg/l, the removal efficiency was studied as a result of changing the initial concentration of cadmium ions in simulated aqueous solutions, while the other operational factors were fixed at pH = 6, contact time 180 min, adsorbent dose 0.5 g, agitation speed 300 rpm, and at laboratory temperature. The results of the study of this variable showed that the removal efficiency is inversely proportional to the value of the initial concentration, as it decreases from 77.1428 % to 15.971 % when the concentration increases from 0.1 to 10 mg/l, respectively.

In contrast, the adsorption capacity of buckthorn leaves increases gradually until reaches its maximum value at a concentration of 4 mg/l. Iincreasing the initial concentration means increases the mass of Cd^{+2} when the volume at constant aqueous solution, and this leads to a competition that becomes more intense with an increase in the concentration value due to the stability of the adsorbent dose. The adsorbent has a fixed surface area including stable active sites with finite functional groups that can bond with a certain number of cadmium atoms. By increasing the concentration, the unadsorbed Cd^{+2} ions will be more, reducing the efficiency. Fig. 5 shows the result of the effect of changing the initial concentration on the efficiency of adsorption of cadmium ions from aqueous

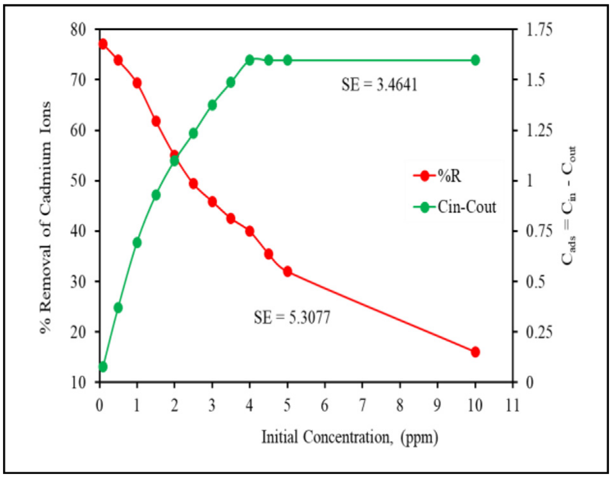

Fig. 5. Effect of initial concentration on the % removal of Cd^{+2} ions using buckthorn leaves.

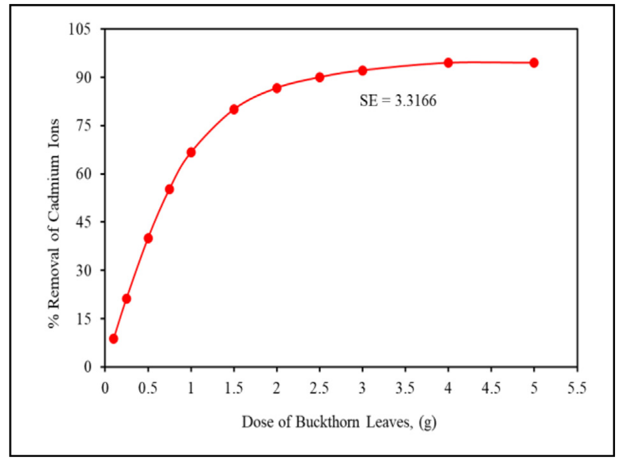

Fig. 6. Effect of buckthorn leaves dose on the % removal of Cd^{+2} ions using buckthorn leaves.

solutions by buckthorn leaves. Study of [28] showed similar results to the results of the current study.

3.4. Effect of adsorbent dose changing

The dose of the adsorption media is the main factor in any adsorption process. Therefore, determining the optimum dose that achieves the greatest removal of the adsorbent material is a vital matter that must be determined in any study of surface phenomena in general and adsorption in particular. The study of the adsorption dose factor and its effect on the efficiency of the treatment process was carried out by conducting a set of laboratory experiments at constant operating conditions. pH, initial concentration, agitation speed, contact time and temperature of 6, 4 mg/l, 350 rpm, 180 min, and 25 °C respectively. The range of the studied adsorbent dose ranges between 0.01 and 5 g of buckthorn leaves. The obtained results showing the effect of the adsorbent dose were represented in Fig. 6.

This result shows that the relationship between the two variables was a direct relationship. As explained in the effect of the initial concentration above, the adsorbent material has a specific surface area per unit mass. When the adsorbent dose is increased, the surface area value that is in contact with the polluted solution will increase, which means providing additional active sites that can adsorb more cadmium ions. As a result of initial concentration stability, which means the stability of the mass of cadmium dispersed in the solution, the chance of cadmium ions reaching the active sites will be greater, which means that the adsorption of ions increases with the increase. Fig. 6 also shows that the adsorption efficiency will remain constant at 94.4367 % without change after the value of 4 g of buckthorn leaves despite the increase in the dose. The reason is due to the adsorption process reaching a state of equilibrium, which means that the substance is not able to adsorb any additional amount of cadmium ions as a result of the saturation state. Similar results have been reported by [31].

3.5. Effect of contact time changing

The optimum time to achieve the best removal efficiency of cadmium ions in was determined through a set of experiments at lab temperature. All other design variables were fixed at 6, 4 mg/l, 4 g, 350 rpm, which represent the pH, the initial concentration of cadmium ions, the adsorbent dose, and the agitation speed, respectively. It is noticed from the Fig. 7 which represents the results obtained for

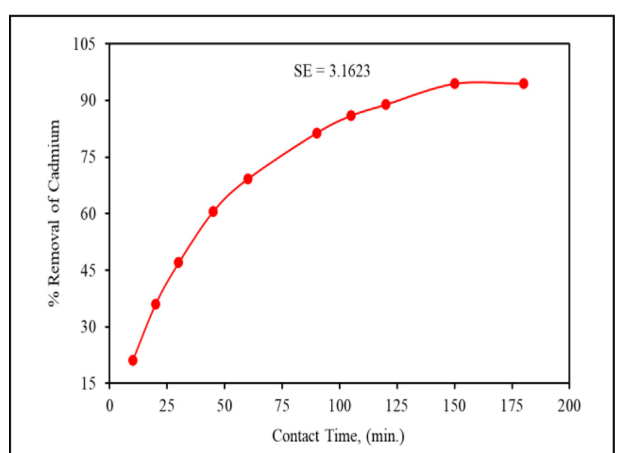

Fig. 7. Effect of contact time on the % removal of Cd^{+2} ions using buckthorn leaves.

varying the contact time between 10 and 180 min. The increase in the contact time has a clear effect on increasing the efficiency of the treatment process.

The percentage removal increased from 21.1337 % to 94.4367 % as a result of increasing the contact time from 10 min to 150 min, respectively, which shows that there is a direct relationship between treatment time and efficiency within this range. The observed outcome can be attributed to the prolonged contact time, wherein an extended duration allows cadmium ions more time to interact with the adsorbent. With all other variables maintained at their optimal settings, this extended contact period enhances the likelihood of cadmium ions accessing active sites on the adsorbent's surface. Consequently, the potential for ion adsorption increases, resulting in improved removal efficiency. After exceeding the time period of 150 min, it is noted that the removal rate remains constant and does not change as a result of the adsorption process reaching a state of equilibrium and the inability to capture other molecules under the current operating conditions. An identical result was concluded by [27].

3.6. Effect of temperature changing

It is not possible to determine the important thermodynamic properties of any physical or chemical process, including the adsorption process, except by studying the effect of temperature. Through which, it is possible to know spontaneous of adsorption on the surface of the adsorbent material. The impact of temperature on the removal process efficiency was investigated over a temperature range of 20−50 °C, while all other operational parameters remained at their optimal settings. Fig. 8 illustrates that the adsorption process is exothermic, with removal efficiency decreasing as temperature rises.

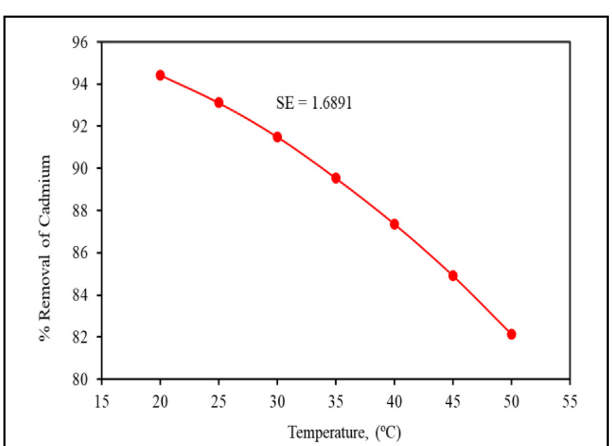

Fig. 8. Effect of temperature on the % removal of Cd^{+2} ions using buckthorn leaves.

The highest recorded percentage removal, 94.4367 %, was achieved at standard laboratory temperature. This result can be attributed to the fact that the forces controlling the adsorption process are weak forces and that increasing the temperature in the mentioned range breaks the forces that cross-link cadmium ions. The adsorption surface, which helps to release them and stimulates the return of ions to the aqueous solution, thus reducing the adsorption efficiency. It is noted that the decrease in efficiency increases significantly with increasing temperature, which means an increase in the speed of liberation of particles from bonding with the surface of buckthorn leaves. It is possible that the increase in temperature has an effect on increasing the kinetic energy of the cadmium ions adsorbed on the adsorbing surface, which leads to them having the necessary energy to break free from the forces that bind them to the surface and return to the aqueous solution again. This pattern of change indicates that the adsorption forces are van der Waals forces and that the rate of desorption of cadmium ions is higher than the adsorption rate and thus the adsorption process is of a physical type. These results are consistent with many results such as [28].

3.7. Effect of coexisting ions

In general, the ability to adsorb cadmium ions from real wastewater of three Iraqi oil refineries using buckthorn leaves as an adsorbent was lower than that observed when using simulated aqueous solutions prepared in the laboratory. Even though the adsorption process carried out at optimal operating conditions that give the highest efficiency in simulated aqueous solutions, a decrease in efficiency occurred in the real wastewater samples.

This decrease can be primarily attributed to the presence of other heavy metal ions, as well as numerous organic and inorganic substances. In this complex mixture, cadmium ions faced competition with various substances during the adsorption process using buckthorn leaves. Real wastewater comprises a multitude of different compounds, not limited to cadmium alone. Fig. 9 illustrates that the efficiency of buckthorn leaves in adsorbing cadmium ions from Al-Doura oil refinery wastewater is higher than that from Basra refinery, and the latter is, in turn, higher than that from Baiji refinery. Although the difference in cadmium concentration in the wastewater of the three refineries was not significant, the removal efficiency varied considerably. This variation may be attributed to the fact that

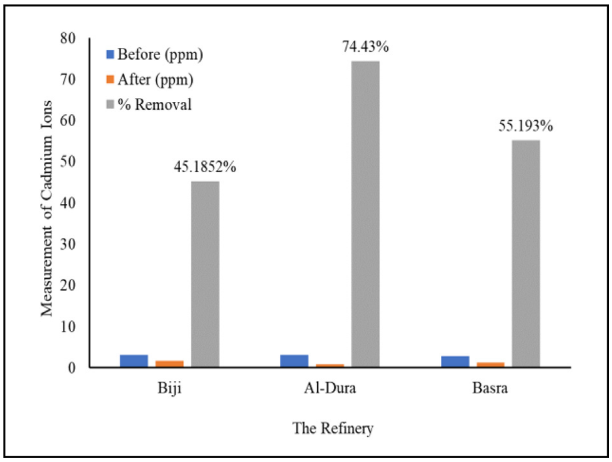

Fig. 9. Removal of Cd^{+2} ions from real refinery wastewater using buckthorn leaves.

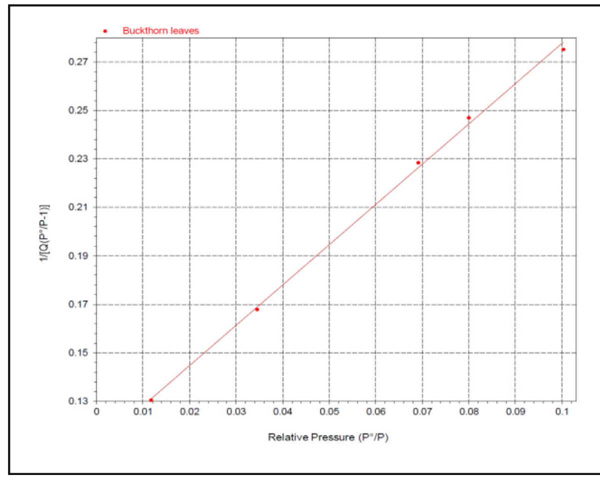

Fig. 10. BET Surface Area Plot of Buckthorn Leaves.

Basra and Baiji refinery wastewater contains higher concentrations of other compounds and heavy elements. This, in turn, intensifies the competition between these compounds and cadmium for the limited number of active sites available on the surface of buckthorn leaves. Consequently, this competition reduces the opportunity for cadmium ions to access these sites and remain in the solution, thus lowering the overall adsorption efficiency.

4. Characterization of buckthorn leaves before and after adsorption of cadmium

4.1. BET surface area (S_{BET})

The surface area is an important parameter to evaluate the operational characteristics of catalysts, adsorbents and any other porous media. In this study, the surface area was determined for buckthorn leaves before and after cadmium adsorption.

The measurement process involved physical adsorption–desorption analysis of nitrogen gas at a constant temperature equivalent to the boiling point of liquid nitrogen −77K The adsorption process initially saturated the micropores of the material at a ratio of $P/P^{\circ} = 0.34513$, followed by the filling of mesopores with multilayers of nitrogen gas. Remarkably, the specific surface area of the buckthorn leaves has a value of 36.1766 m^2/g before adsorption and negligible value after treatment with cadmium heavy metal. Fig. 10 show the BET surface area plot of buckthorn leaves.

4.2. X ray diffraction (XRD)

The crystalline structure of the adsorbent media investigated using X-ray diffraction analysis. The XRD analysis was conducted at room temperature, employing CuKα (1.5406 Å) radiation and covering a 2θ range from 20 to 70°. Fig. 11 illustrates the XRD patterns obtained for the buckthorn leaves before and after adsorption of cadmium. The XRD diffractograms before adsorption exhibited a broad intense peak centered at 44° and 64°, indicating the presence of calcium oxalate ($CaC_2O_4 \cdot nH_2O$) and calcium carbonate ($CaCO_3$) which are common crystalline phases found in plant tissues. After adsorption, new peaks are appeared at 22°, and 24° which suggest the formation of new crystalline phases due to treatment with cadmium. The compounds corresponding to these peaks are cadmium oxide (CdO) and cadmium hydroxide ($Cd(OH)_2$), respectively. These compounds are formed as a result of the interaction between cadmium ions and other chemical constituents in the buckthorn leaves. The presence of a peak at 30° indicates alterations in the crystal lattice of leaf constituents.

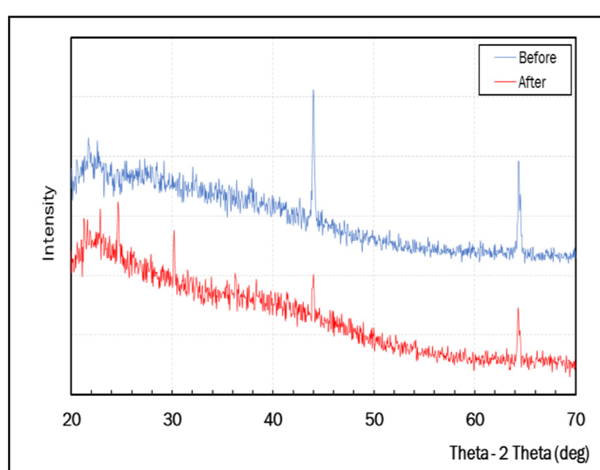

Fig. 11. XRD of Buckthorn Leaves Before and After Adsorption.

Cadmium ions have been affected the lattice, affecting the arrangement of secondary metabolites like flavonoids or phenolic compounds. The molecules of these compounds arrange themselves into a highly ordered, repeating, three-dimensional structure as a result of introducing the cadmium ions into plant tissues. Despite the adsorption of cadmium, the peaks at 44° and 64° remain largely unchanged. These peaks continue to represent the crystalline phases of calcium oxalate (at 44°) and calcium carbonate (at 64°). These phases appear to be less affected by the cadmium adsorption process, suggesting a lower affinity for cadmium ions or greater stability due to less affected by the adsorption process. Notably, no other important diffraction peaks were observed, suggesting the absence of any additional crystalline phases in the adsorbent. The obtained peaks were found to be in agreement with the reference JCPDS file No. 05−0586 for calcium oxalate, JCPDS file No. 00-005-0623 for calcium carbonate, JCPDS file No. 00-005-0642 for cadmium oxide and JCPDS file No. 00-035-0819 for cadmium hydroxide.

4.3. Fourier Transform Infrared (FTIR) spectroscopy test

The chemical composition and functional groups present in the adsorbent media were examined using Fourier Transform Infrared (FTIR) spectroscopy. FTIR analysis was performed under ambient conditions, employing a spectrometer with infrared radiation. Spectral data were collected over a wavenumber range typically from 4000 to 400 cm-1, allowing for the identification of characteristic vibrational modes and functional groups within the material.

The FTIR spectra before and after cadmium adsorption on the buckthorn leaves reveal information about the chemical components and structural changes in adsorbent. While many peaks remain relatively stable, shifts or changes in specific peaks indicate interactions between cadmium and functional groups in the leaves, highlighting the adsorption effects on the plant leaves. As seeing from Figs. 12 and 13 show that the peaks at 3288.56, 2919.70, 1608.06, 1316.03, 1239.35, 1028.20, 514.11, and 405.85 cm^{-1} are nearly constant and little shifted to 3297.08, 2922.72, 1618.35, 1316.61, 1239.54, 1028.62, 509.92, and 413.53 cm-1, respectively. These peaks refer to O−H stretching, C−H stretching, C]O carbonyl, NO_2 stretch, C−O stretching in polysaccharides, C−N in aliphatic amines, C−Br bond, and C−H in aromatic compound, respectively. However, there are some peaks are disappeared from the spectrum of buckthorn leaves before

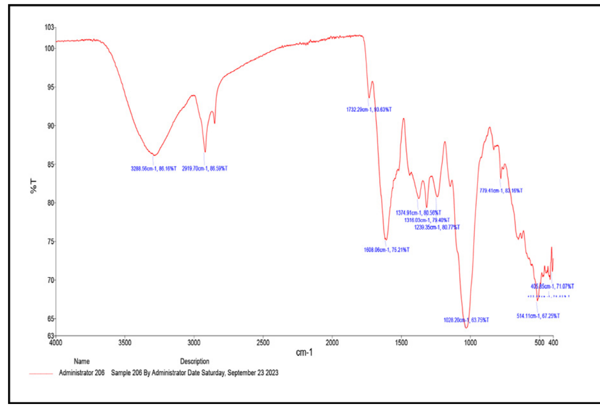

Fig. 12. FTIR of Buckthorn Leaves Before adsorption.

adsorption at 1732.29, 1374.91, 779.41, and 422.98 cm-1, in addition to appear a new peak at 649.07 cm-1 which refer to C−Cl bond due to the interaction between cadmium and the chlorophyll found in the buckthorn leaves. These changes in the FTIR spectra after cadmium adsorption suggest that chemical interactions between cadmium ions and functional groups on the surface of buckthorn leaves has occurred. The appearance of new peaks and shifts in existing peaks may be attributed to the formation of cadmium complexes or the adsorption of cadmium onto the leaf surface.

4.4. Scanning Electron Microscopy (SEM) test

Scanning Electron Microscopy (SEM) is a technique used to investigate the surface morphology and microstructure of materials at a high magnification. When applied to the analysis of Buckthorn leaves before and after adsorption of cadmium, SEM can reveal some observations into how the surface characteristics and structure of the leaves have changed due to the adsorption process. Before

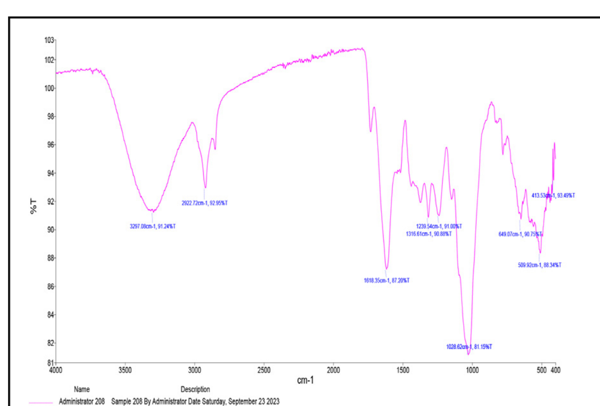

Fig. 13. FTIR of Buckthorn Leaves After adsorption.

adsorption of cadmium, the Fig. 14 shows the natural surface morphology of the leaves. This includes features such as the epidermal cells of leaf, stomata, trichomes (hair-like structures), and the overall texture of the leaf surface.

The surface appears relatively clean and free from any foreign materials or deposits, with the presence of clear random and thick lines like-hair surface structures. SEM image of Buckthorn leaves after adsorption of cadmium i.e., Fig. 15, reveals more roughing and the hair-like structures become more clearly but more regular. In addition, some of pores closed due to agglomeration of cadmium ions on these gaps.

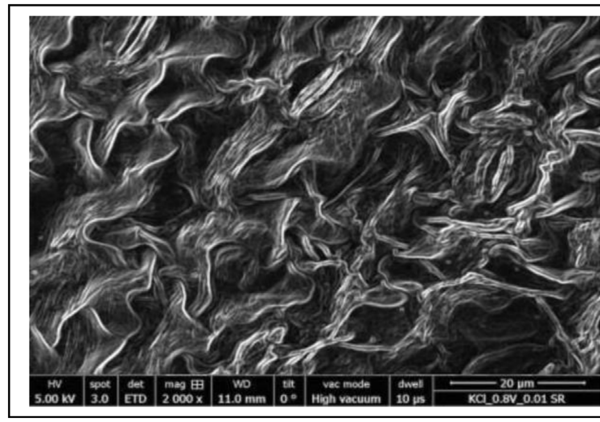

Fig. 15. SEM of Buckthorn Leaves After adsorption.

5. Adsorption behavior

5.1. Isothermal study

At a constant temperature, the relationship between the concentration and the amount of the adsorbent when equilibrium state occurs has a relationship called the adsorption isotherm. The importance of the adsorption isothermal study is it: 1) determines the method of bonding the adsorbent material to the surface of the adsorbate media, through important data that describe the nature of adsorption by determining the best operating conditions and 2) shows how the adsorbent and adsorbate molecules are distributed when they reach the equilibrium state. There are many models that represent the adsorption isotherm, including Freundlich, Langmuir, Temkin, Dubinin-Radushkevich (D-R), Redlich-Peterson (R–P), Spis, Toth and Khan models. Since they represent the most important and well-known adsorption models, Langmuir, Freundlich and Temkin models will be used to represent the experimental results obtained in this paper. The model closest to representing the data is determined by converting the model equation to linear form and assigning the correlation coefficient. Figs. 16–18 show the isotherms of Langmuir, Freundlich and Temkin for the adsorbent material (buckthorn leaves) for cadmium metal ions constants. Table 1 shows the details of the isothermal models used in the current study, while Table 2 shows the values of these isotherm. These data show that the degree of agreement of the experimental results with these models takes the following form: Langmuir > Timkin > Freundlich models for cadmium according to the value of the correlation coefficient, which was 0.9999, 0.9983 and 0.9704 respectively. It is clear that the adsorption process of cadmium using buckthorn leaves as an adsorbent is subject to Langmuir's isotherm better than other models due to the high correlation coefficient value. This means that the adsorption occurs on a monolayer surface with a finite number of identical sites and the adsorption process is preferred according to the value of the separation factor, which was 0.7740. On the other hand, Timken

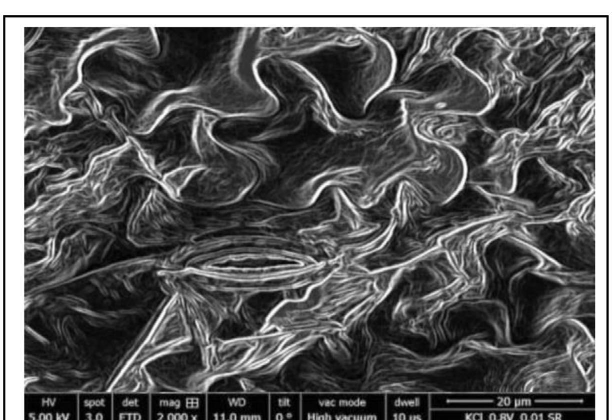

Fig. 14. SEM of Buckthorn Leaves Before Adsorption.

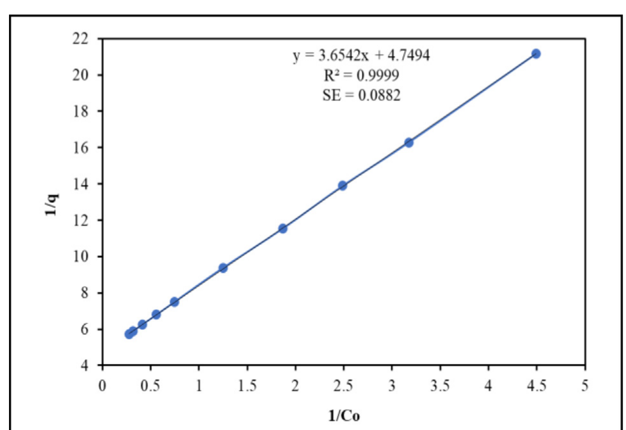

Fig. 16. Langmuir Isotherm of Cd^{+2} Adsorption using buckthorn leaves.

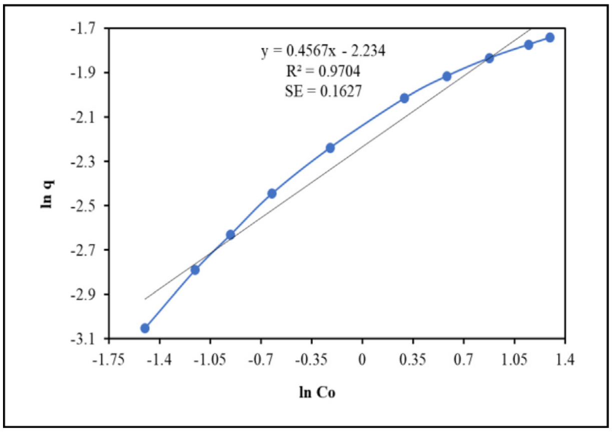

Fig. 17. Freundlich Isotherm of Cd^{+2} Adsorption using buckthorn leaves.

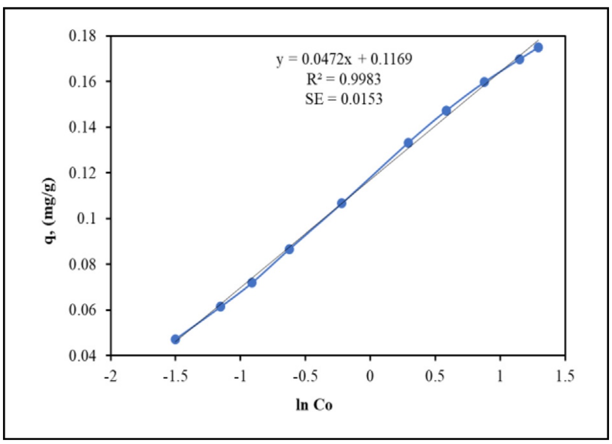

Fig. 18. Temkin Isotherm of Cd^{+2} Adsorption using buckthorn leaves.

model was very efficient in representing the data according to the correlation coefficient of 0.9983, which is not far from the Langmuir model.

While the Freundlich model represented the results with the least efficiency, as the results matched with this model with the lowest value of the correlation coefficient which is 0.9704 and this indicates that the obtained results are not subjected to the last two models.

5.2. Kinetic study

The purpose of adsorption kinetics is to characterize how quickly adsorbent ions or molecules migrate towards the surface of the adsorption material over time. This is achieved by plotting time-based data using curves or straight lines under specific operational conditions. A crucial aim of adsorption kinetics is to discern the adsorption mechanism on the surface of adsorbent material by comparing the results with various kinetic models that represent the adsorption process. Several kinetic models are available for describing adsorption, with key ones including the pseudo-first order, pseudo-second order, Elovich, and intra-particle diffusion models, all employed in this study and elaborated in Table 3. Figs. 19–22 display the data acquired from the kinetic investigation into the removal of cadmium ions from aqueous solutions using buckthorn leaves. Table 4 outlines the coefficients for the four kinetic models used to analyze the study's results. Notably, the most suitable model for representing this data is the pseudo-second order model, closely followed by the pseudo-first order model, as indicated by their higher correlation coefficients compared to other models. This outcome suggests that the available effective sites on the adsorbent material's surface, specifically buckthorn leaves, are directly proportional to the quantity of adsorbed cadmium ions according to the pseudo-second-order model, whereas adsorption occurs in a single layer, following the pseudo-first order model. This result finds further support in the almost ideal match between the isotherm study results and the Langmuir model, which posits that adsorption transpires in a single layer.

As for the Elovich kinetic model, the results of the kinetic study matched with it with a lower correlation coefficient than the previous two models. This confirms the obtained practical results as the percentage of adsorption of cadmium ions gradually decreases with increasing concentration, and this is exactly the hypothesis of the Elovich model. On the other hand, the Intra-particle diffusion model was the least consistent with the results, according to the correlation coefficient shown in Table 4. This is due to the assumptions of this model contradict the practical results obtained under optimal conditions. The reason of this result is that the boundary layer has little effect on the surface of the adsorbent

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

Model	General Form	Linear Form	Slop	Intercept	Augmented Parameter
Langmuir	$q_e = \frac{q_{max}.K_L C_e}{1+K_L C_e}$	$\frac{\mathbf{1}}{q_e} = \frac{1}{q_{max}K_L}\frac{\mathbf{1}}{C_e} + \frac{1}{q_{max}}$	$\frac{1}{q_{max}K_L}$	$\frac{1}{q_{max}}$	$R_L = \frac{1}{1+K_L C_e}$
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. The values of constants of isotherm models.

Model	Constant	Value
Langmuir Isotherm Mode	q_{max}	0.20859
	K_L	1.31192
	R_L	0.7740
	R^2	0.9999
	SE	0.0882
Freundlich Isotherm Mode	K_F	0.1071
	n	2.1896
	R^2	0.9704
	SE	0.1627
Timkin Isotherm Model	b	52,519
	K_T	1
	R^2	0.9983
	SE	0.0153

media and the ions can reach the active sites easily and with less resistance due to the high agitation speed. Based on the correlation coefficient values, the degree of agreement of the kinetic models used with the results of this study takes the following form: pseudo-second order > pseudo-first order > Elovich > intra-particle diffusion models.

5.3. Thermodynamic study

The values of thermodynamic functions are very important in explaining many reactions (especially the adsorption process). Through their properties, it is possible to distinguish the nature of the dominant forces and the direction of the course of interactions, as well as giving a good description of the nature of the molecules organization in different systems resulting from molecular interventions of all kinds. The value of heat or enthalpy (ΔH) represents a direct measure of the interaction forces between the adsorbent molecule and the adsorbing surface, while the value of the entropy (ΔS) represents a measure of the disorder and randomness of the molecules on the surface of the adsorption, and the compressive energy (ΔG) is the function through which it is possible to identify spontaneity or not spontaneous interaction. These thermodynamic variables are calculated using the Van-'t-Hoff equation, which is represented mathematically by the following equation:

$$\ln k_{ad} = -\frac{\Delta H}{R}\frac{1}{T} + \frac{\Delta S}{R} \quad (3)$$

Where k_{ad} can be calculated from the following equation:

$$k_{ad} = \frac{q_e}{C_e} \quad (4)$$

By plotting the linear relation between ln k_{ad} and 1/T the values of ΔH and ΔS can be concluded from slop and intercept of line respectively. From these obtained values, the Gibbs free energy property can be calculated and determine the spontaneity of the adsorption according to equation 1

$$\Delta G = \Delta H - T\Delta S \quad (5)$$

Fig. 23 represents the results of the thermodynamic study, while the values of the three thermodynamic functions were included in the Table 5. As it is known, the thermodynamic functions (ΔG, ΔH and ΔS) are an important indicator to estimate the spontaneity of the process and to describe the adsorption mechanism of ions and molecules on the surface of the adsorbing medium. On the other hand, it is an accurate way to describe the state of overlap between the two surfaces of the solid phase and the liquid phase. The data from figures and tables representing the process of adsorption of cadmium on the surface of buckthorn leaves indicated that the thermodynamic equilibrium coefficient k_{ad} decreases with increasing temperature of the adsorption system.

The increase in temperature triggers a disruption of the bonds between adsorbent metal ions and their respective active sites on the adsorption surface. Consequently, this disruption leads to the release of ions back into the solution. Notably, all enthalpy changes were found to be negative, signifying that the adsorption of the examined heavy metal ions onto the adsorption material's surfaces is an exothermic process. Additionally, the adsorption of cadmium using buckthorn leaves was characterized as a physical process, with an enthalpy value below 40 kJ/mol. The negative change in entropy across all adsorption experiments indicates a

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

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

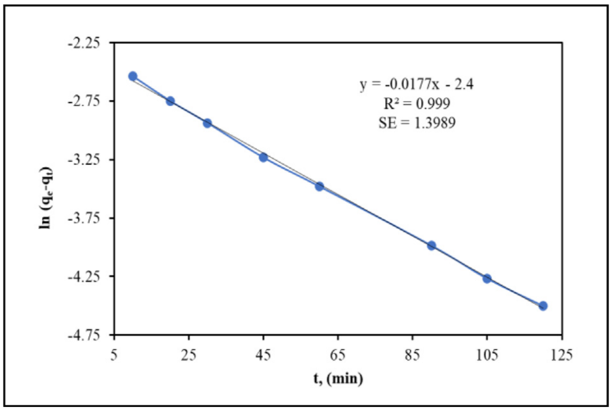

Fig. 19. Pseudo-first-order kinetic model of Cd^{+2} adsorption using Buckthorn leaves.

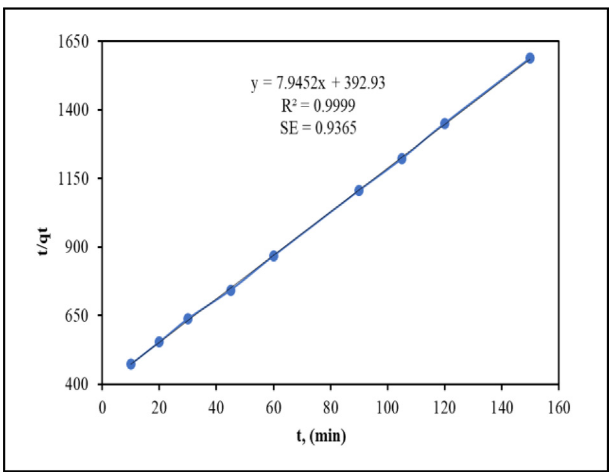

Fig. 20. Pseudo-second-order kinetic model of Cd^{+2} adsorption using Buckthorn leaves.

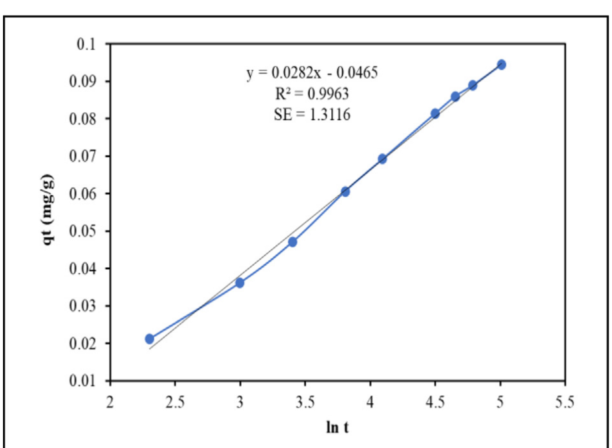

Fig. 21. Elovich kinetic model of Cd^{+2} adsorption using Buckthorn leaves.

reduction in randomness at the interface between the solid and liquid phases during the adsorption process. This reflects the strong affinity of buckthorn leaves' surfaces for cadmium ion adsorption. The negative entropy suggests that adsorbed molecules exhibit greater uniformity compared to their state in solution, arising from the exchange of heavy element ions with less mobile ions on the material's surface. This exchange results in reduced entropy during adsorption. Furthermore, the adsorption process of cadmium ions using these materials was determined to be spontaneous under the studied experimental conditions, as evidenced by the negative values for the change in free energy. This suggests that the adsorption of cadmium ions onto the adsorption sites in the adsorbent material, buckthorn leaves, is a self-sustaining process that doesn't necessitate external energy to complete. The decrease in the negative value of the Gibbs free energy with increasing system temperature indicates a decline in spontaneity, implying that adsorption is more favorable at lower temperatures.

6. Regeneration and reusability

As the cadmium adsorption process using buckthorn leaves was of physical adsorption type, it lends itself to regeneration since the adsorbed ions are chiefly bound to functional groups on the adsorption surface via weak van der Waals forces. Consequently, this study investigates the physicochemical reactivation process of buckthorn leaves, employed as an economical adsorption media for the removal of cadmium from simulated wastewater, mimicking oil refinery effluents. Physical activation involves subjecting the cadmium-laden buckthorn leaves to thermal treatment in an oven. This treatment occurs in five cycles, with each cycle entailing exposure to a temperature of 50 °C for 10 min, followed by immersion in distilled water (at a ratio of 1 g of leaves to 10 ml of distilled water) for 5 min. The slurry is then filtered and subjected to further heat treatment for a total of five cycles. Remarkably, the color of leaves changes noticeably after the fifth heat treatment, signifying alterations in their properties, and by the seventh cycle, they begin to char. Chemical activation, on the other hand, entails treating the cadmium-laden adsorption medium with a 0.1 M acetone solution (at a ratio of 1 g of leaves to 1 ml of acetone solution). This mixture is placed in a magnetic stirrer for 1 h, stirred at room temperature (with a speed not exceeding 100 revolutions per minute), washed with distilled water, and dried at 50 °C for 10 min. This process is repeated to achieve chemical activation. Physically and chemically activated

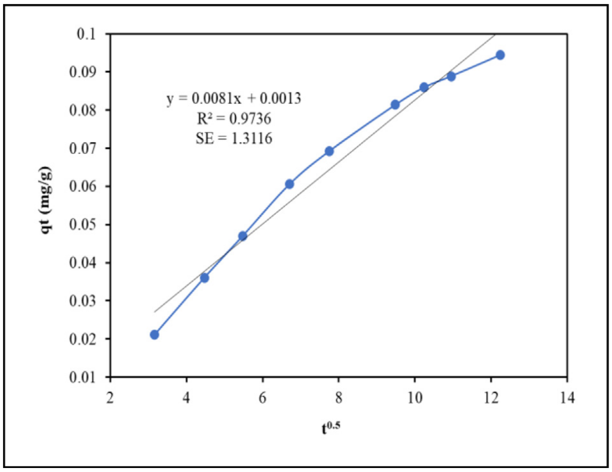

Fig. 22. Intra-particle diffusion kinetic model of Cd^{+2} adsorption using Buckthorn leaves.

Table 4. The values of constants of kinetic models.

Model	Constants			
Pseudo-first-order	k_1	q_e	R^2	SE
	0.023	0.095	0.9971	1.3989
Pseudo-second-order	k_2	q_e	R^2	SE
	0.161	0.1257	0.9999	0.9365
Elovich	α	β	R^2	SE
	0.0054	33.461	0.9963	1.3116
Intra-particle diffusion	k_p	C	R^2	SE
	0.0081	0.0013	0.9736	1.3116

buckthorn leaves were subsequently evaluated for their potential to adsorb cadmium from aqueous solutions once again. The same batch system utilized in previous experiments was employed, maintaining the operational conditions that had yielded the highest cadmium percentage removal from polluted simulated solutions. These conditions included pH of 6, an agitation speed of 350 rpm, an initial cadmium concentration of 4 mg/l, 4 g of leaves, a contact time of 150 min, and a laboratory temperature. The results indicated that the adsorbent material, physically activated via thermal treatment, could be effectively reused up to four times. Conversely, leaves treated with acetone as a chemical activation method demonstrated a limited reusability, with only two cycles feasible before a complete loss of adsorption capacity occurred. Fig. 24 presents the impact of the number of reactivation cycles on the efficiency of cadmium removal using regenerated buckthorn leaves as an adsorbent.

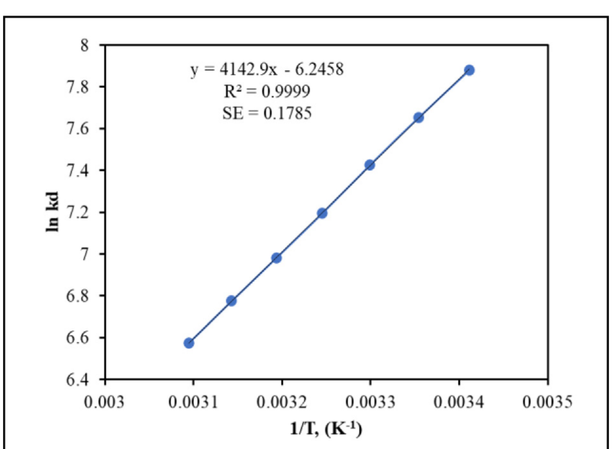

Fig. 23. Effect of temperature on adsorption constant.

Table 5. The values of thermodynamic properties constants.

T(°C)	ΔH (kJ/mol)	ΔS (kJ/mol.K)	ΔG (kJ/mol)
20	-34.446	-0.05193	-19.2226
25			-18.9629
30			-18.7033
35			-18.4436
40			-18.1840
45			-17.9243
50			-17.6650

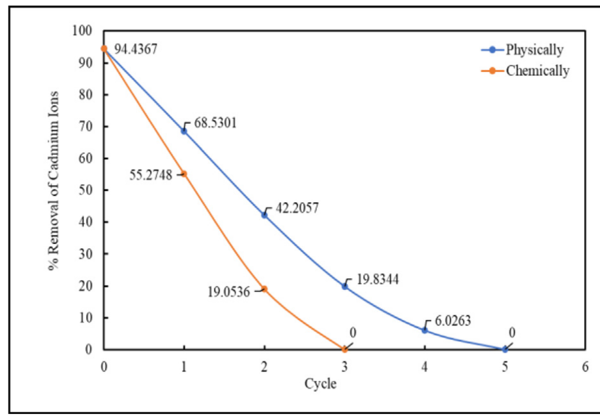

Fig. 24. Effect of Regeneration on the Efficiency of Cd^{+2} ions Removal.

Table 6. Summary of cadmium adsorption efficiency of various adsorbents.

Adsorbent	%R	Reference
Watermelon rinds	100	[26]
Almond shells	91.5	[45]
Orange peels	88.34	[46]
Pomegranate peel activated carbon (PPAC)	91.3	[47]
Date pit activated carbon (DPAC)	91.1	[47]
Acid modified banana peels	99.95	[49]
Rice husk	100	[50]
Tea waste	100	[50]
Cassava	94.9	[51]
Modified clinoptilolite	98.9	[52]
Fly ash	78.21	[53]
Ash/GO/Fe_3O_4	98.68	[54]
Fe_3O_4 NPs	100	[55]
Potato peels	76	[56]
Eggshells	89.7	[57]
Buckthorn leaves	94.4367	This study

7. Comparison between this study and the other

While this study is concerned with investigating the ability of buckthorn leaves to recover cadmium from both simulated contaminated aqueous solutions and real wastewater, numerous researchers also delved into the possibility of removing cadmium ions from simulated and real wastewater using different adsorbents. Table 6 presents a comparative analysis of the findings between this study and previous studies conducted by various researchers.

8. Conclusions

Agricultural waste presents an ongoing environmental challenge due to its continuous accumulation resulting from indispensable farming activities. This study introduces an innovative approach to harness one such significant agricultural waste, specifically buckthorn tree leaves. Buckthorn trees, deciduous in nature, shed large quantities of leaves, representing a sustainable resource for water treatment if optimally utilized. The research findings indicate that buckthorn leaves, of nearly 36 m^2/g surface area, possess a remarkable capacity to recover cadmium ions, a type of heavy metal, from aqueous solutions under various operating conditions. The removal efficiency exhibited a direct correlation with several key factors: pH, buckthorn leaf quantity, contact time, and agitation speed. Conversely, it displayed an inverse relationship with temperature and the cadmium ion concentration in the solution. The highest percentage removal, reaching 94.4367 %, was achieved under specific conditions: pH 6, a contact time of 150 min, a temperature of 25 °C, 4 g of buckthorn leaves, an initial cadmium concentration of 4 mg/l, and an agitation speed of 350 rpm. Furthermore, isotherm study revealed that the Langmuir model aptly represents the adsorption process, which conforms to the pseudo-second order model based on an impressive correlation coefficient (R^2) value of 0.9999 for both models. Thermodynamically the results show that the adsorption is exothermic, accompanied by a decrease in entropy, as evident from the enthalpy and entropy values of −34.446 and −0.0519, respectively. Consequently, adsorption is deemed spontaneous, supported by negative values for all Gibbs free energy function across various temperatures. The morphological investigations were carried out on both pristine and exhausted buckthorn leaves, with further characterization involving FTIR, XDR, and SEM analyses. According to BET analysis, the adsorption process occupied less than 68 % of the surface area post-treatment. The FTIR test results indicated that adsorption played a significant role, leading to the disappearance and shift of numerous peaks in the spectrum. XRD analysis provided clear evidence of the notable impact on lattice and structural changes in plant tissues, primarily attributed to the introduction of new phases. SEM test observations elucidated the influence of cadmium adsorption on the closure of pores within the buckthorn leaves. The spent adsorption medium underwent physical activation at 50 °C and chemical activation using a 0.1 M acetone solution. Subsequently, it was reused to recover cadmium from contaminated simulated aqueous solutions within the same batch system under optimal operating conditions. Results demonstrated that physical activation significantly outperformed chemical activation, with heat-treated leaves exhibiting reusability for up to four cycles, while leaves treated with acetone could be used for a maximum of two cycles. In a comprehensive exploration, this study also assessed the feasibility of cadmium removal from real wastewater sourced from three Iraqi oil refineries: Baiji, Al–Dora, and Basra. Notably, the recovery efficiency of cadmium from real wastewater was marginally lower compared to simulated aqueous solutions, achieving approximately 74 %, 55 %, and 45 % for the Daura, Basra, and Baiji refinery models, respectively.

Conflicts of interest

The authors have no conflicts of interest to disclose.

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