



Removal of Cadmium (II) from Water by Adsorption on Olive Leaves

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Abstract

The removal of a high level of cadmium in drinking water by olive leaves as a natural material is a simple way to produce high quality water. The study revealed that olive leaves were able to effectively remove a significant percentage of cadmium. Using a 0.5 gm sample size of ground olive leaves could remove 91.3% of cadmium with an initial concentration of 100 ppm within 120 min. A significant increase in the removal of Cd (II) with an increase in the olive dosage and increase in temperature could be observed.

Keywords: Adsorption, Cadmium, olive leaves, pH

1. Introduction

Water is one of the most important substances on earth. All plants and animals must have water to survive. If there is no water, there would be no life on earth. The world is entering the third millennium; the water issue has become one of the most important issues which take the concern of the whole world. Besides, water pollution affects the international relations between countries that share water resources and may cause wars. Water covers about 71% of the earth's surface, but only 2.5% of the earth's water is freshwater (1). World Health Organization WHO has reported that water scarcity is affecting a third of people in the world and the problem is continuously increasing because of the rising water demand (2). Therefore, people depend on polluted water which causes many diseases. The dependence of humans is mainly on their ability to manage the natural resources; therefore, new methods should be provided to purify water and increase its quality to encounter overpopulation. Water pollution came from any change in its chemical or physical properties and make it inappropriate for various usage (3). There are different causes of water pollution like 1-Sewage and wastewater 2-Mining activities 3-Globalwarming 4-Industrial waste (4). The sources of water pollution are different from one place to another (surface water pollution, Groundwater pollution, Nutrients pollution, microbiological pollution, Chemical water pollution and, pollution by metals). The inorganic contamination of water is different from organic one because they cannot be metabolized, therefore removal of inorganic contaminates depends on the formation of bonds between them and a solid surface (5). There many techniques used for removing of inorganic contaminates the removal process must be simple, effective, and inexpensive (6). example for the removal methods are (Chemical precipitation, Ion exchange, Cementation, coagulation and flocculation, Membrane filtration, Ultrafiltration, Reverse osmosis, and Adsorption (7). The adsorption method offers flexibility in design and operation. Also, adsorption is economically effective for a dilute solution, and sometimes it is a reversible process (8). Cadmium compounds have varying degrees of solubility ranging from very soluble to nearly insoluble (9). the solubility affects their absorption and toxicity. The average concentration of cadmium in the earth's crust is between 0.1 and 0.5 (ppm) It was discovered in 1817

simultaneously by Stormier and Hermann as an impurity in zinc carbonate. Cadmium is listed in the European Restriction of Hazardous Substances (10). because of its toxicity and nickel-cadmium batteries have been replaced with nickel-metal hydride and lithium-ion batteries. Cadmium is an extremely toxic industrial and environmental pollutant classified as a human carcinogen (Group 1) - according to International Agency for Research on cancer. According to Environmental Protection Agency (EPA); and 1B carcinogen classified by European Chemical Agency (ECHA). Cadmium and its salts are severe lung and gastrointestinal irritants that can be fatal by inhalation and ingestion. Acute ingestion of as little as 10 mg of cadmium chloride can cause pulmonary toxicity, such as pulmonary edema, emphysema, and bronchitis (11-13). This research aims to study the removal of Cd^{2+} which is a hazardous element in the environment at a high concentration by adsorption using Guava leaves as a natural, low-cost adsorbent. The parameters affecting the adsorption process as Cd^{2+} initial concentration, adsorbent doses, pH, temperature, and rate of stirring.

2. Experimental

Chemicals and Reagents

This chapter describes materials and chemical reagents used in this work in addition to the methods that were followed to fulfill the aim of work. Methodology contains details about gathering the natural adsorbents, preparation, characterization and its application with heavy metals.

Reagents

1. Hydrochloric acid (HCl) 37%, Nitric acid (69 %), Sodium hydroxide (MW40), were obtained from ACROS Organics, New Jersey, USA
2. Spectroscopic grade heavy metal Cadmium acetate were obtained from ACROS Organics, New Jersey, USA
3. Spectroscopic grade solvents obtained from Fisher Scientific, UK.

Apparatus

1. Analytical Scanning Electron Microscope (SEM: JSM- 6360LA, JEOL, Japan).
2. Fourier Transform Infrared Spectrophotometer; FTIR-8400S, Shimadzu, Japan.
3. Atomic Absorption (AA)
4. Water Deionizer.
5. PH Meter
6. Oven
7. Shaker (BT 4010, Biotech company, Egypt)
8. Heating Magnetic Stirrer

3. Preparation of Solutions

Preparation of Cadmium [II] Stock Solutions

Stock solution of 500-ppm cadmium [II] solution as cadmium acetate is prepared by dissolving the appropriated weight (1209.6 mg) of cadmium acetate in one-liter measuring flask and the final volume completed up to one liter using deionized water. Further concentrations required obtained via dilution from the stock solution.

Collection and Preparation of Natural Adsorbents

The natural adsorbents used in this work collected from the available best environment source. The Olive leaves (Ol), was collected mainly from Siwa oasis, Matrouh Governorate, EGYPT,

Preparation of Olive Leaves

Olive leaves (Ol) was selected as adsorbent for removal of Cd^{2+} ions in this study. The (Ol) was collected and washed thoroughly under running tap water to remove sand, dust and /or any adhering particles then was soaked by distilled water for 12 hours. The (Ol) was then dried under sunlight for a few days and then in oven at 70 °C until it became crisp. The dried (Ol) crushed and blended to fine powder form using a blender. The grinding (Ol) in the form of powder was washed with excessive amounts of distilled water; several washings were performed to remove dust and soluble materials; the powder was then dried under sunlight and then in an oven at 70°C for a period of 1.5 hour and kept in airtight container.



4. Instruments and Working Procedures

FTIR Measurements

Fourier transform infrared (FTIR) spectra of the natural adsorbents under investigation were recorded between 400 and 4000 cm^{-1} with a 4 cm^{-1} resolution from KBr pellets on a LX 18-5255 Perkin Elmer Spectrum BX 11 FTIR system.

Scanning Electron Microscopy (SEM)

The surface Morphology of each adsorbent was analyzed by scanning electron microscope (SEM, JSM- 6360LA, JEOL, Japan) which produces images of adsorbents surface with focused beam of electrons this electrons interact with atoms in adsorbents producing various signals that contain information about adsorbents surface, the peaks position is combined with the detected single to produce an image.

Batch Experiments

A) Effect of Rotating Time:

To investigate the effect of rotating time on the adsorption process, eight bottles were prepared; each contains 100 ml of (50ppm) (Co) of Cadmium [II] solution. For each bottle, 0.75 gm of each the adsorbent under investigation is added and closed. The bottles let on shaker at room temperature to rotate for period times; 15, 30, 60, 90, 120, 150, 180 and 1440 minutes, then the solution take for filtration and the filtrates is used to determine the final concentration (C) via AA instrument.

The Removal percentage (R) calculated according to formula;

$$R = \frac{C^{\circ} - C_i}{C^{\circ}} * 100\%$$

The equilibrium adsorption capacity of the adsorbent; q_e (mg/g) calculated using the formula:

$$q_e = \frac{C^{\circ} - C_i}{w} * v$$

Where, C° initial concentration of the metal (mg/l), C_i is the equilibrium concentration of the metal (mg/l). v is the volume of the solution (L) and w is the weight of the adsorbent used

B) Effect of pH

To investigate the effect of pH on the adsorption process, five bottles were prepared; each contains 100 ml of (50ppm) (Co) Cadmium [II] solution. For each bottle, 0.75 gm of each the adsorbent under investigation is added and closed after the pH of bottles adjusted for different values via pH-meter (2 – 6.5) using NaOH, HCl, then the final solution is filtrated and the filtrates is used to determine the final concentration of Cadmium metal (C) using Atomic Absorption AA instrument.

C) Effect of Metal Concentration

To investigate the effect of metal concentration on the adsorption process, five bottles were prepared; each contains 100 ml of different concentrations of (25, 50, 75, 100, and 125 ppm) Cadmium [II] solution. For each bottle, 0.75 gm of each the adsorbent under investigation is added. The bottles closed for 120 minutes until reach equilibrium at room temperature then the solution is filtrated, the filtrates used to determine the final concentration of Cadmium metal (C) using Atomic Absorption AA instrument.

D) Effect of Adsorbent Dose

To investigate the effect of adsorbent dose on the adsorption process, five bottles were prepared; each contains 100 ml of 50 ppm of Cadmium [II] solution, then different adsorbent doses 0.25, 0.50, 0.75 .1.00 and 1.5 gm added to each bottle and let for 120 minutes at room temperature before filtering the result solution. The filtrates used to determine the final concentration of Cadmium metal (C) using Atomic Absorption AA instrument.

E) Effect of Temperature:

To investigate the effect of temperature on the adsorption process, three bottles were prepared; each contains 100 ml of 50 ppm of Cadmium [II] solution, for each bottle, 0.75 gm of each the adsorbent under investigation is added and

the bottles closed. The bottles let to rotate at different temperature 250C, 350C, and 450C on magnetic shake for 120 minutes before filtrate the resulting solution and the filtrates is used to determine the final concentration (C) via AA instrument

5. Results and Discussion

Characterization of the Natural Adsorbents under Investigation:

Olive leaves were introduced recently into Pharmacopeia as potential natural remedies due to the presence of **Oleuropein** (a **polyphenolic iridoid glycoside**) and its derivatives such as **hydroxytyrosol** and **tyrosol** [238-240]. Olive leaves characterized as one of the most powerful antioxidants containing herbs as compared to other many natural herbs (14-15). It was reported that Oleuropein present in olive leaves possess the highest level of antioxidant and free radical scavenging capacity (1 – 14%) as compared to the Olive Oil content of Oleuropein (0.005 – 0.12%) among various parts of olive tree (16). Table (1) illustrate the Chemical Structures of the main Phenolic Compound in the Leaf of Olive.

Table 1. Chemical Structures of the main Phenolic Compound in the Leaf of Olive

Phenolic Compound	Chemical Formula	Chemical Class
Oleuropein	C ₂₅ H ₃₂ O ₁₃	Secoiridoids
Hydroxytyrosol	C ₈ H ₁₀ O ₃	Phenolic alcohol
Verbascoside	C ₂₉ H ₃₆ O ₁₅	Flavonoids
Apigenin-7-glucoside	C ₂₁ H ₂₀ O ₁₀	Flavonoids

Phenolic acids found in olive leaf extracts are derivatives of hydroxycinnamic, and hydroxybenzoic acids. Triterpenic acids are another group of phytochemicals in Olive leaf extracts. They are pentacyclic terpene acids present diverse biological activities The most abundant triterpenic acid is oleanolic acid, which represents up to 79–89%, followed by maslinic acid with 14–20% of triterpenic acid content. Ursolic acid, uvaol and erythrodiol have also been identified in olive leaf extracts [245, 246]. Olive **phenolics** are much more concentrated in the leaves compared with Olive fruit or Olive Oil: 1450 mg total phenolics/100 g fresh leaf vs. 110 mg/100 g fruit and 23 mg/100 ml extra virgin olive oil (17-18). The phenolic composition of olive leaf extract OLEs varies according to plant variety, harvesting season and method, leaf maturity, storage conditions and extraction method. For example, in case of Tofahy and Shemlali OLEs, the O–H stretching overlapping with N–H at wavenumbers of 3276 and 3256 cm⁻¹ and C = O stretching of a carboxylic acid at 1697 and 1695 cm⁻¹ in Tofahy and Shemlali OLEs, respectively (19). These vibrations were accompanied by C–O stretching peak at 1260 and 1262 cm⁻¹ and OH bending at 927 and 922 cm⁻¹ in Tofahy and Shemlali, respectively. While, the stretching peaks for C = C in the aromatic ring of the phenolic compounds observed at 1624 cm⁻¹ (Tofahy) and 1600.98 cm⁻¹ (Shemlali) also, the glycosidic C–O group in Oleuropein observed at 1069 cm⁻¹ (Tofahy) and located at 1069 cm⁻¹ (Shemlali) (20). These functional groups reflect that, the oleuropein, apigenin-7-glucoside, and luteolin-7-glucoside are the phytochemicals in olive leaf extracts OLEs (21). Moreover, the symmetric stretching vibration for a methylene group (CH₃) observed at 2925 (Tofahy) and at 2916 cm⁻¹ (Shemlali), followed by C-H scissoring at 1437 cm⁻¹ in Tofahy, C-H rocking at 1381 (Tofahy) and at 1386 cm⁻¹ (Shemlali), and in-plane bending vibrations of CH₂ at 766 and 764 cm⁻¹ in Tofahy and Shemlali, respectively. These stretching and bending vibrations indicate the presence of an alkane. As well as noticed the amide II or N–H stretching that located at 1518 cm⁻¹ and 1521 cm⁻¹ and C–N at 1018 cm⁻¹ and 1021 cm⁻¹ due to vibrations of amines (22). Consequently, Olive leaves contain organic functional groups such as alkanes, aromatic compounds, and amide linkages of protein and amine (23).

In the present work, the Fourier Transforms Infrared Spectra (FTIR) of Olive leaves, Fig. (1), Table (2) shows a number of absorption peaks mostly complying with the most literature's data of FTIR of Olive leaves extracted OLEs.

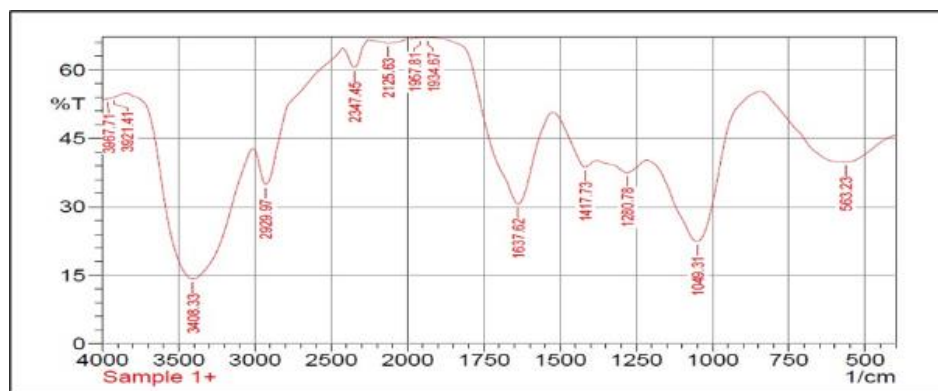


Figure 1: FTIR of Olive leaf under investigation

The FT-IR spectrum of Olive leaves before its reaction with 50 ppm of Cadmium solution listed in Table (2). Several characteristic bands, with the intensity of (54.0), were observed at 3967, 3921, and 3408 cm^{-1} . The first two peaks are corresponding to symmetric and asymmetric stretching vibration of N-H, O-H, while the third peak attributed to the Stretching vibration of C-H or $-\text{NH}_2$ bonds in clear evidence for the existence of different types of organic compounds such as aldehydes, ketones, carboxylic acids, acid halides, amides, ester, etc. Two characteristic absorption peaks, with the same intensity observed at 1957, 1934 cm^{-1} assigned to stretching symmetric and asymmetric vibration of C-O of amides, COOH, esters etc. The observed peaks at (2929 cm^{-1} , 2347 cm^{-1} , and 2125 cm^{-1}), with intensity (34.9, 60.5, and 65.9), respectively, could be attributed to the C-H stretching vibrations of CH_3 (alkane), Stretching vibration of $\text{C}\equiv\text{C}$, $\text{C}\equiv\text{N}$, or $\text{C}=\text{S}$ and Stretching vibration of C-C, C-N, respectively. The stretching vibration of C-N bond that observed suggesting that the organic compounds with C-N bonds also be present. The peak observed at 1634 cm^{-1} (intensity 30.6) assigned to $\text{C}=\text{O}$ stretching carbonyl group of carboxylic acid or $\text{C}=\text{N}$ stretching. While, the observed peaks at 1417, 1280, and 1049 cm^{-1} assigned to C-O stretching vibration of phenolic groups, Stretching, bending vibrations of ethylene systems $-\text{CH}=\text{CH}$, and Stretching vib. of C-C, C-N, C-O-C ether, respectively. The peak observed at 563 cm^{-1} is characteristic of stretching C-Cl, stretching vibration of halogenated compounds (24-30).

Table 2: FTIR of Olive leaves before reaction with Cd^{+2} solution.

No	Peak	Intensity	Functional group
1	3967	53.65	N-H / O-H symmetric stretching
2	3921	54.06	N-H / O-H asymmetric stretching
3	3408	14.21	C- H Stretching / $-\text{NH}_2$
4	2929	34.90	C-H stretching vibration of CH_3 (alkane)
5	2347	60.49	Stretching vibration of $\text{C}\equiv\text{C}$, $\text{C}\equiv\text{N}$, $\text{C}=\text{S}$
6	2125	65.88	Stretching vibration of C-C, C-N
7	1957	67.08	Stretching symmetric of C-O of amides, COOH, esters etc.
8	1934	67.06	Stretching asymmetric of C-O of amides, COOH, esters etc.
9	1637	30.64	$\text{C}=\text{O}$ stretching carbonyl of $-\text{COOH}$, or $\text{C}=\text{N}$ stretching.
10	1417	38.71	C-O stretching vibration of phenolic groups
11	1280	37.48	Stretching, bending vibrations of ethylene systems $-\text{CH}=\text{CH}$.
12	1049	22.47	Stretching vib. of C-C, C-N, C-O-C ether
13	563	39.79	C-Cl, stretching vibration of halogenated compounds.

After reaction of Olive leaves with cadmium solution as natural adsorbent for (Cd^{+2}) ions, the FTIR results depicted at Fig (2) shows a different behavior compared to that before reaction with Cadmium solution. Were new peaks has observed, as well as peaks shifted or change their intensities and positions, while other some peaks are faded. The

FTIR results are compared with those of the Olive leaves (ligand) (L) in order to determine the coordination sites that may involve in chelation. There are some guide peaks, in the spectra of the ligand, which are of good help for achieving this goal. The position and /or the intensities of some peaks expected to be changed upon chelation. The obtained results, as listed in Table (3), confirm the formation of chelating complexes in between the Cadmium ion (Cd^{+2}) and the Olive leave's compounds that leads to a change restricts the bending and stretching vibrations of the functional groups and disappears the spectrum bands.

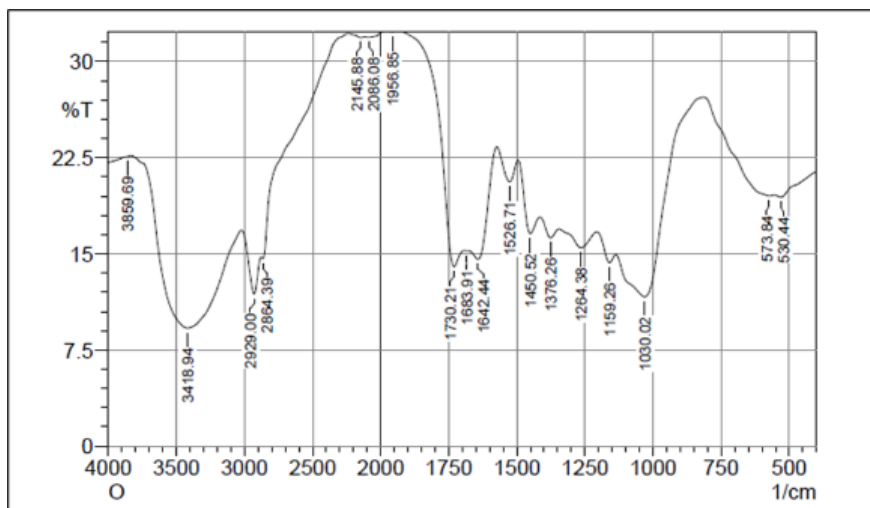


Figure 2: FTIR of Olive leaf after interaction with Cd^{+2} solution.

Table 3: FTIR of Olive leaves after reaction with Cd^{+2} solution.

No	Peak	Intensity	Functional group
1	3859	22.57	N-H stretching of amino group and OH of alcohol.
2	3418	9.21	Stretching C-H, $-\text{NH}_2$
3	2929	11.87	C- H stretching vibrations of CH_3
4	2864	14.63	C-H stretching vibration of CH_3 (alkane)
5	2145	31.87	C-N symmetric stretching of amino groups
6	2086	31.88	C-N stretching asymmetric of amino group
7	1956	32.31	Stretching vibration of C-O of amides, COOH, esters
8	1730	14.01	C-O stretching in carboxyl coupled to the amide I linkage
9	1683	15.23	Side C=O stretching carbonyl group of carboxylic acid
10	1642	14.57	Ring C=O stretching carbonyl group of carboxylic acid
11	1526	20.62	Stretching symmetric vibration of NO_3
12	1450	16.58	-O- CH_3 deformation
13	1376	16.25	Stretching asymmetry vibration of NO_3 .
14	1264	15.47	C-O stretching vibration of phenolic groups.
15	1159	14.31	Stretching vibration of C-O-C of ether
16	1030	11.65	Stretching vib. of C-C, C-N
17	573	19.53	Coordinate N \rightarrow M bond
18	530	19.42	stretching O- M bond

The peaks as 3998, 3967 cm^{-1} (N-H / O-H symmetric and asymmetric stretching) disappeared due to their participation in complexation with Cd^{+2} ions. These band's vanish in complexes is a worth noting suggesting that the metal ions coordinate with phenolic oxygen by deprotonation. The stretching frequency of (C=N), which is present

in free ligands, changes to a value of 111 cm^{-1} lower when complexes are present. In this case, the coordination of the metal ion with the nitrogen of the leaves compounds. While a new peak observed at 3859 cm^{-1} with intensity (22.6) attributed to stretching of -NH_2 bond of amino groups, and the fading of the hydroxyl (-OH) group due to its involving in acidic bonds with cadmium ion. The peak at 3408 cm^{-1} shifted to be at 3418 cm^{-1} . The peaks at (2929 cm^{-1} , 2864 cm^{-1} and 2145 cm^{-1}) characteristic the C-H stretching vibrations of CH_3 and CH_2 groups, C-H symmetric vibration of CH_2 and C-H bending, respectively, which did not participate in the complex formation. While the peak at 2086 cm^{-1} assigned to C-N stretching of amino group. The peak observed at 1730 cm^{-1} could attributed to C=O stretching in carboxyl coupled to the amide, while the peaks at 1683 , 1642 cm^{-1} assigned to side and ring C=O stretching carbonyl group which lead to presence of aldehydes, ketones and carboxylic acids. The phenolic (C-O) frequency decreased from 1417 cm^{-1} to 1264 cm^{-1} , in contrast to the ligand's frequency of 1417 cm^{-1} , lending credence to this theory. Peaks observed at 1526 cm^{-1} and 1376 cm^{-1} assigned to Stretching symmetric and asymmetric vibration of NO_3 , respectively. The peak located at 1159 cm^{-1} Stretching vibration of C-O-C of ether. Moreover, the peak observed at 573 cm^{-1} assigned to the coordination bond $\text{N}\rightarrow\text{M}$, while the band observed at 530 cm^{-1} assigned to the stretching O-M bonds. According to the observed results, one can say that, the Cadmium ion (Cd^{+2}) has reacted with Olive leaves to form a coordination bond with the Nitrogen of ligand and with Oxygen in keto-form via (C=O), as well as the Olive leaves (ligand) is behaves as a neutral bidentate or tridentate ligand to forming strong M-O chemical bond.

6. The Morphology of Adsorbents Under Investigation

In order to link the mechanical properties of natural adsorbents under investigation with their morphology and microstructure, the scanning electron microscopy (SEM) was used. Samples has coated with gold layer and images taken by scanning electron microscope model (JEOL JSM-5300). The morphology of the adsorbents is at magnification of 50,000x. For all compounds under investigation, size scale is smaller than 100nm. Fig. (3-7) shows scanning electron micrographs of the Olive leaves.

SEM studies indicated that, the samples were found with almost spherical globular porous morphology with some of the agglomeration of nanoparticles (may be due to presence of the capping agent) were also found. It was observed from these photographic imaging, that a homogeneous structural morphology with few micro porosities of free volume in the neat adsorbents structure.

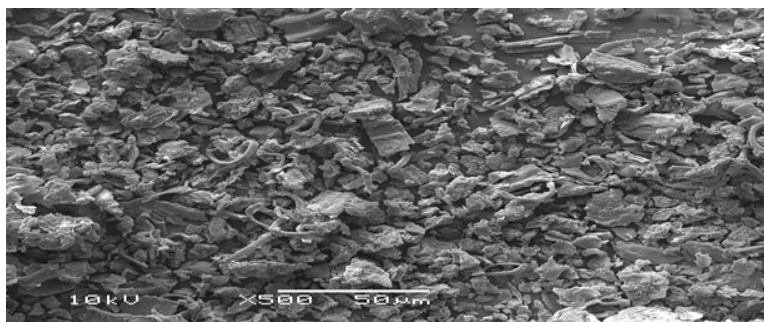


Figure 3: SEM of Olive leaves at magnification of 500x

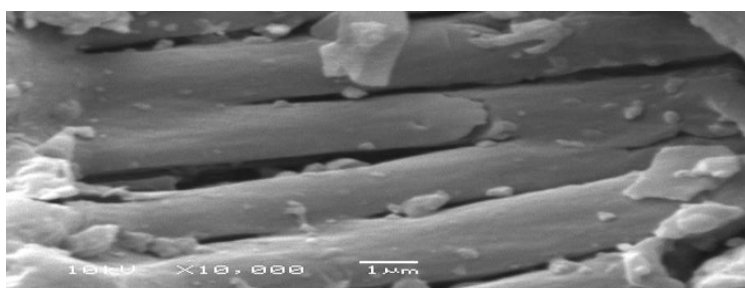


Figure 4: SEM of Olive leaves at magnification of 10,000

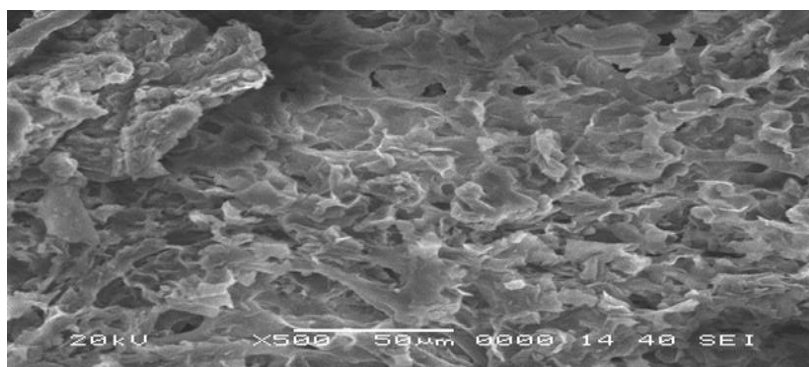


Figure 5: SEM of Olive leaves- Cd^{+2} at magnification of 500x

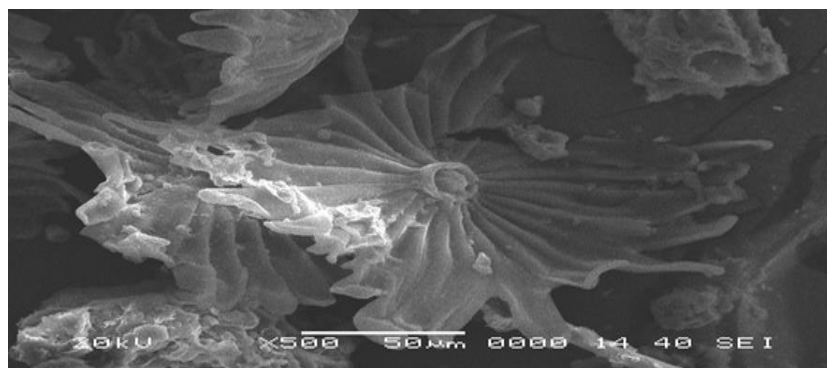


Figure 6: SEM of Olive leaves- Cd^{+2} at magnification of 500x

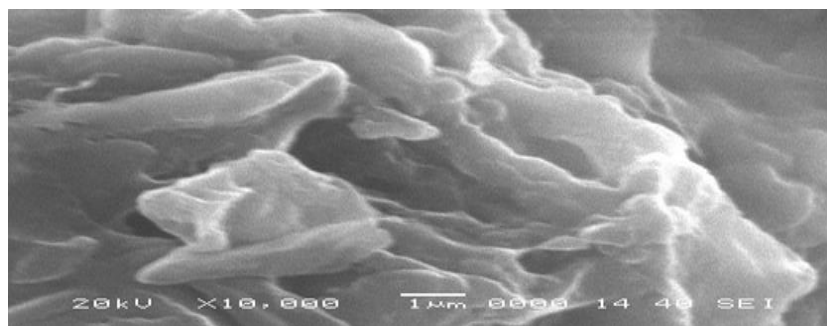


Figure 7: SEM of Olive leaves- Cd^{+2} at magnification of 10,000

Figs (3-7) represents SEM images of Olive leaves at different magnification (500 – 10,000x). It was observed from these photographic imaging, that a homogeneous structural morphology with few micro porosities of free volume in the neat adsorbents structure. The Cadmium molecules are clearly adsorbed at spongy surfaces of Olive leaves.

7. The Removal of Cadmium Ions

Batch Experiments

Batch Experiments' technique has selected to estimate and determine the removal of cadmium ion from synthetic polluted solution. As well as to study the effect of (rotating time, solution's pH, metal concentration, adsorbent's dose, and temperature) on the cadmium removal efficiency. To estimate the evaporation losses of cadmium, a control blank sample simultaneously placed in the same shaker. Similar results between control and treated samples indicated no losses due to evaporation. The batch experiments carried out by using a mechanical shaker at a speed of 150 rpm for different time (5- 1440 min) with specific amount of the adsorbents in contact with 100 ml of aqueous

synthetic polluted solution of cadmium ions. In the present work the effect of the rotating time, pH, metal concentration, adsorbent dose and the temperature were assessments as the followings:

A) Effect of Contact Time

To investigate the effect of contact (rotating) time on the adsorption process, eight bottles were prepared; each contains 100 ml of (50ppm) (C_0) of Cadmium [II] solution. For each bottle, 0.75 gm of each the adsorbent under investigation is added and closed. The bottles let on shaker at room temperature to rotate for period times; 15, 30, 60, 90, 120, 150, 180 and 1440 minutes, then the solution take for filtration and the filtrates is used to determine the final concentration (C) via AA instrument to determine the removal % of Cadmium ions from the aqueous solution. The sorbed concentration of Cd^{+2} into sorbents as well as the removal efficiency or sorption percent of cadmium and distribution coefficient (K) were evaluated by using the isotherm models; Langmuir, Freundlich and Dubinin-Radushkevich were applied to describe adsorption in this work. The removal (R) % is observed by equation (1) while the amount of adsorbate uptake by the adsorbent is given in equation (2) and the distribution coefficient of the cadmium ions by the adsorbent is given in equation (3).

$$\text{Removal \%} = [(C_0 - C_e)/C_0] \times 100. \quad (1)$$

$$q = [(C_0 - C_e)/m] \times V. \quad (2)$$

$$K = q/C_e. \quad (3)$$

Where:

q is the amount of adsorbed cadmium (mmol/g)

C_0 is the initial metal concentration in contact with the adsorbent (mmol/l)

C_e is the Cd^{+2} concentration (mmol/l) after the batch adsorption procedure,

V is the volume of metal solution (l) in contact with the adsorbent, and m is the mass (g) of adsorbent,

K is the distribution coefficient of the cadmium ions between the adsorbent and the aqueous phase. The observed data are collected in Table (4), and Fig (8– 14).

Table 4: Removal % of Cd^{+2} using Olive leaves (OL)

No	Time (min)	Olive leaves			
		Ce	R%	Q	K
1	15	33.50	33.00	2.20	0.07
2	30	24.51	50.98	3.40	0.14
3	45	21.45	57.10	3.81	0.18
4	60	16.80	66.40	4.43	0.26
5	120	15.50	69.01	4.60	0.30
6	150	25.00	50.00	3.33	0.13
7	180	28.00	44.00	2.93	0.10
8	240	30.00	40.00	2.67	0.09
9	1440	35.00	30.00	2.00	0.06

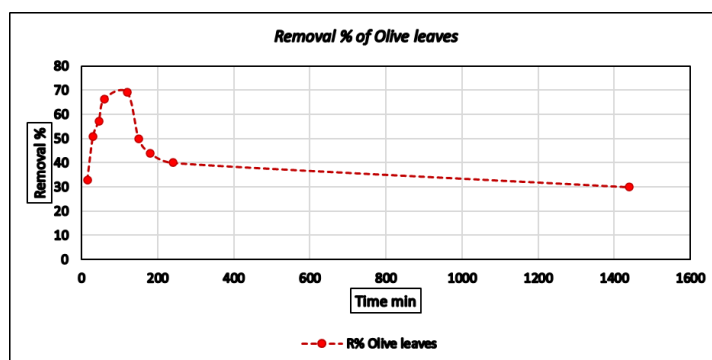


Figure 8: Removal % of Cadmium using Olive leaves

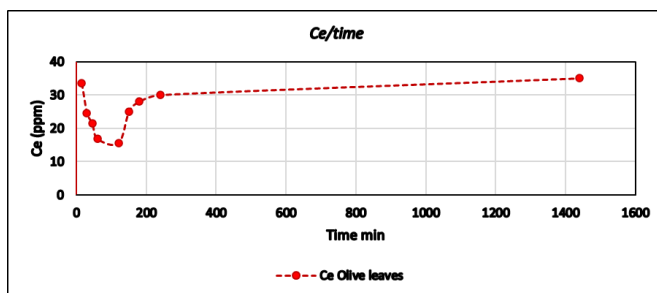


Figure 9: Equilibrium conc. of Cadmium - Time (min)

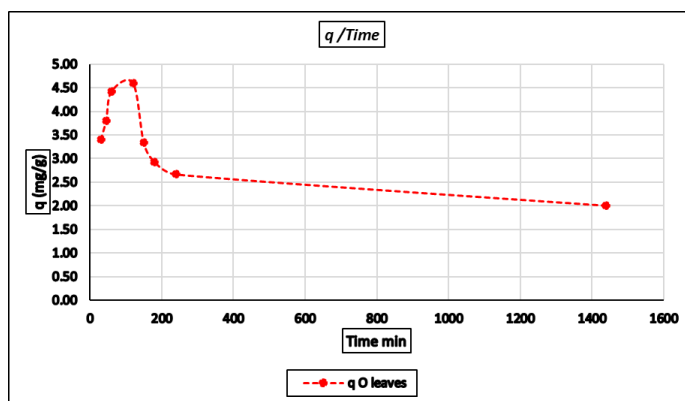


Figure 10: Adsorption capacity (mg/g) – time of Olive leaves, Branches

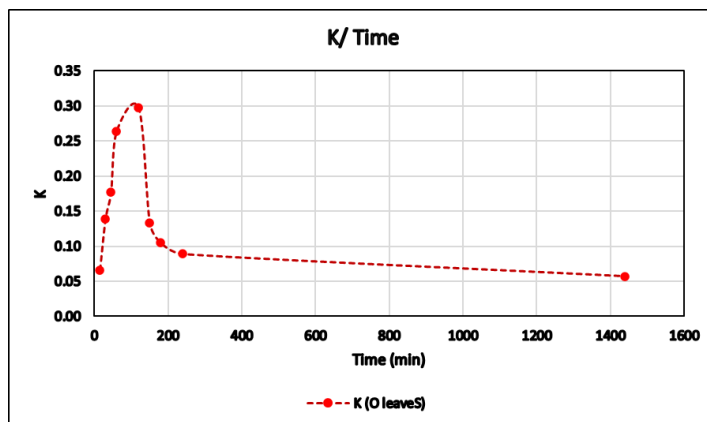


Figure 11: Distribution coefficient (K) of Cd²⁺ ions - Olive leaves

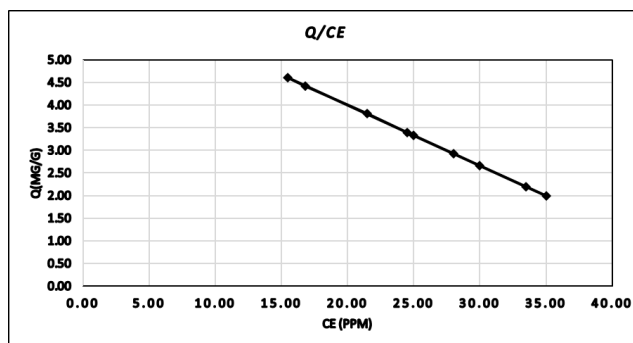


Figure 12: Eq. Conc. "Ce" - adsorption capacity "q" of Olive leaf

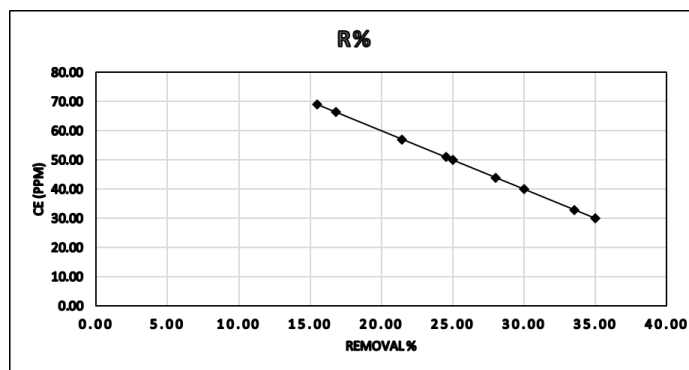


Figure 13: Eq. Conc. "Ce" - Removal % of Cd^{+2} - Olive leaves

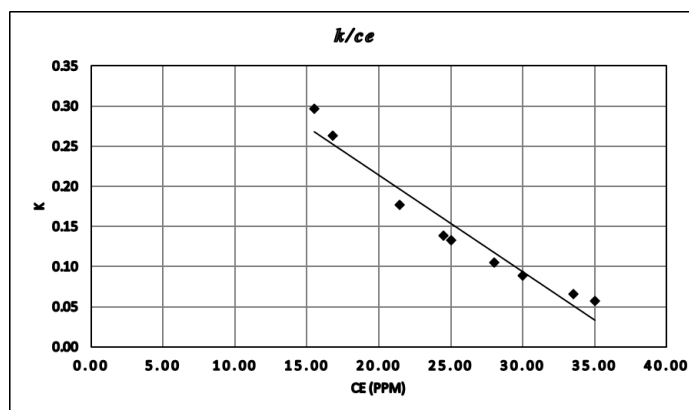


Figure 14: Eq. Conc. "Ce" - Distribution coefficient (K) of Cd^{+2} - Olive leaves

The removal % of Olive leaves, whereas the values start with a value of 33.0, reaching their maximum value at 69.01, and then they begin to decrease as well, reaching 30.0, The adsorption capacity "q" and the distribution coefficient constant "k" with differences in values as is clear. On the contrary, it was observed that the equilibrium concentration "Ce" values start at 33.5 "Ol", then reach their lowest values at 15.5, and then rise again to reach 35, On other hand, straight lines with different slopes were observed when studying the relationship between adsorption capacity "q", Equilibrium concentration "Ce", Removal %, and the distribution coefficient constant K of both Olive leaves to indicates the existence of a direct, linear relationship between these variables. Generally, either Olive leaves could be consider as a natural adsorbent has the capability to remove (adsorb) cadmium ions in aqueous solutions, whereas adsorbents show up suitable removal % (69.01). In addition to close values of adsorption capacity (4.6).

B) Effect of pH

To investigate the effect of pH on the adsorption process, five bottles were prepared; each contains 100 ml of (50-ppm) (C_0) Cadmium [II] solution. For each bottle, 0.75 gm of each the adsorbent under investigation is added and closed after the pH of bottles adjusted for different values via pH-meter (2 – 6.5) using NaOH, HCl, then the final solution is filtrated and the filtrates is used to determine the final concentration of Cadmium metal (C) using Atomic Absorption AA instrument.

Table 5: Removal % of Cd^{+2} using Olive Leaves at different pH values

No	pH	Olive leaves			
		Ce	R%	q	K
1	2.58	22.71	45.42	3.64	0.160
2	3.06	25.03	50.06	3.33	0.133

3	3.99	29.12	58.24	2.78	0.096
4	4.49	32.23	64.46	2.37	0.074
5	5.55	34.57	69.14	2.06	0.060
6	6.12	36.21	72.42	1.84	0.051

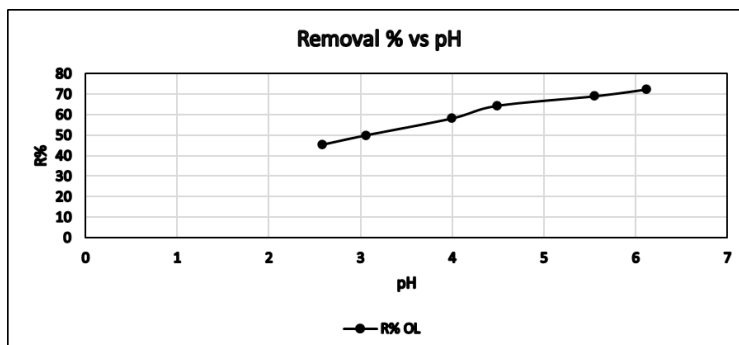


Figure 15: Effect of pH on the removal % of Cd^{+2} (50ppm) - olive leaves

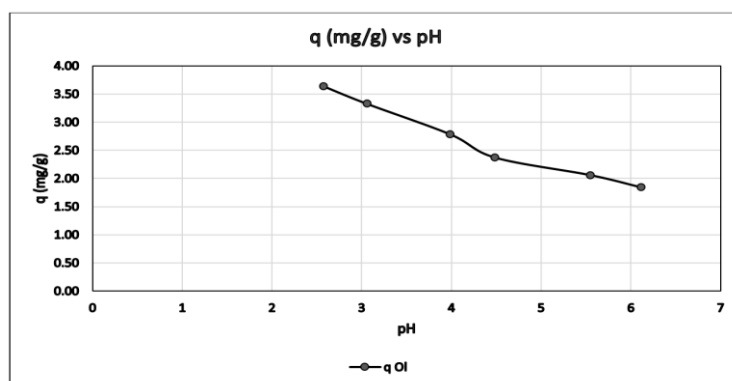


Figure 16: Effect of pH on the adsorption Capacities "q" (mg/g) of Cd^{+2} (50ppm) on olive leaves

C) Effect of Metal Concentration

To investigate the effect of metal concentration on the adsorption process, five bottles were prepared; each contains 100 ml of different concentrations of (25, 50, 75, 100, and 125 ppm) Cadmium [II] solution. For each bottle, 0.75 gm of each the adsorbent under investigation is added. The bottles closed for 120 minutes until reach equilibrium at room temperature then the solution is filtrated, the filtrates used to determine the final concentration of Cadmium metal (C) using Atomic Absorption AA instrument. The observed results listed in Table (6), Fig (17- 18) as following.

Table 6: Removal % of Cd^{+2} using Olive leaves & Olive branches at different Cd^{+2} ion concentration values (ppm)

No	Conc. ppm	Olive leaves (OL)			
		Ce	R%	q	K
1	25	2.18	91.30	3.04	1.40
2	50	14.00	72.00	4.80	0.34
3	75	22.18	70.43	7.04	0.32
4	100	53.00	47.00	6.27	0.12
5	125	69.75	44.20	7.37	0.11

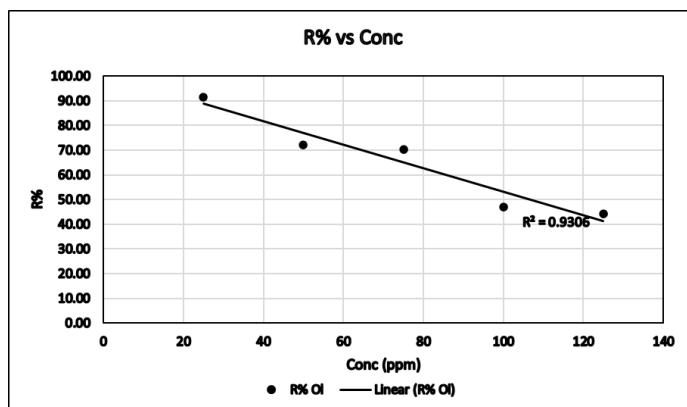


Figure 17: Effect of Cd^{2+} Concentration on the Removal % (R %) using Olive leaves.

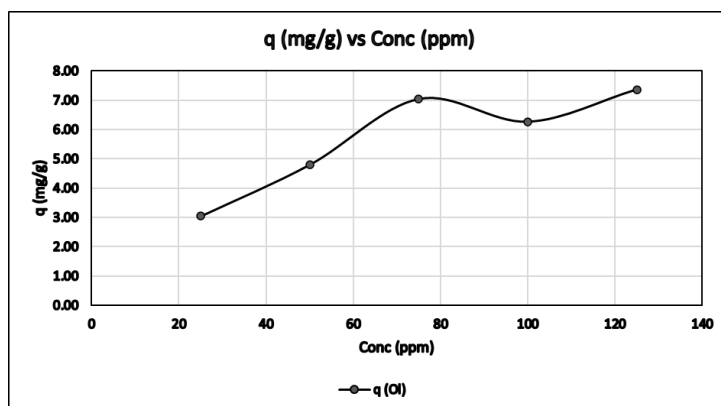


Figure 18: Effect of Cd^{2+} Concentration on the adsorption Capacities (q) using Olive leaves.

D) Effect of Adsorbent Dose

To investigate the effect of adsorbent dose on the adsorption process, five bottles were prepared; each contains 100 ml of 50 ppm of Cadmium [II] solution, then different adsorbent doses 0.25, 0.50, 0.75, 1.00 and 1.5 gm added to each bottle and let for 120 minutes at room temperature before filtering the result solution. The filtrates used to determine the final concentration of Cadmium metal (C) using Atomic Absorption AA instrument. The observed results are depicted in Table (7).

Table 7: Effect of adsorbents dose on the removal % & adsorption capacities of Cadmium ions on Olive leaves

No	Dose (mg).	Olive leaves			
		Ce	R%	q	K
1	0.25	45.64	8.72	1.74	0.04
2	0.5	38.10	23.80	2.38	0.06
3	0.75	22.11	55.77	3.72	0.17
4	1	20.00	60.00	3.00	0.15
5	1.5	18.82	62.36	2.08	0.11

E) Effect of Temperature:

To investigate the effect of temperature on the adsorption process, three bottles were prepared; each contains 100 ml of 50 ppm of Cadmium [II] solution, for each bottle, 0.75 gm of each the adsorbent under investigation is added and the bottles closed. The bottles let to rotate at different temperature 250C, 350C, and 450C on magnetic shake for 120

minutes before filtrate the resulting solution and the filtrates is used to determine the final concentration (C) via AA instrument. The observed results are depicted in Table (8) and Fig (19).

Table 8: Effect of Temperature on the removal % & adsorption capacities of Cadmium ions on Olive leaves.

No	Temp	Olive leaves			
		Ce	R%	q	K
1	25	31.10	37.80	2.52	0.08
2	35	29.24	41.52	2.77	0.09
3	45	20.70	58.60	3.91	0.19

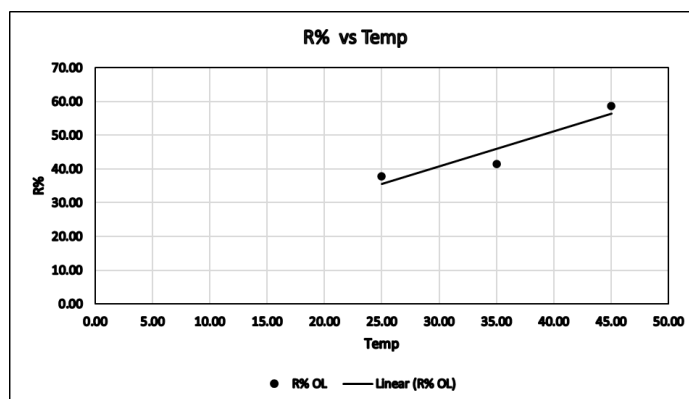


Figure 19: Effect of Temperature on the Removal % (R %) using Olive leaves.

In general, the effect of pH, metal concentration, adsorbent dose, and the temperature on the adsorption process, consequently, the maximum removal % values (R%), and the adsorption capacity “q” (mg/g) can be compared in order to achieve the best conditions for using these natural materials to remove cadmium ions from aqueous solutions, Table (9).

Table 9: The summary of the Removal % values.

Adsorbent	R% before any effect	R% after the effect of			
		pH	Metal conc.	Adsorbent dose	Temp.
Ol	69.01	7.242	91.30	62.36	58.60

Olive leaves (Ol):

The Removal percentage (R %) value was affected when controlling the metal concentration values, recording its highest value (91.30), while recording 72.42 at pH (6.12), while it did not have any significant change when studying the effect of temperature or the adsorbent dose.

7. Conclusion

The adsorption behavior of cadmium ions onto the natural adsorbents such as Olive leaves has studied. The obtained results indicated that; the removal of heavy metals such as Cd+2 through the adsorption on the natural adsorbents is highly effective, promising, and cost effective, as well as confirm that the adsorption is a strong choice for removing the heaviest metals from wastewater.

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