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# Removal of Zn (II) Cations from Water Media by Carbonaceous Derived from Origanum Majorana: Kinetic Studies

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# إزالة كاتيونات الزنك من الأوساط المائية بواسطة مشتق كربوني من نبات البردقوش ***Origanum Majorana***: دراسة الحركية

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**Abstract:**

This research evaluates the capability of carbonized Origanum Majorana leaf powder to remove Zn(II) ions from contaminated water through batch adsorption experiments. The process was optimized using an initial Zn(II) concentration of 300 mg/L, pH of 4, a temperature of 30 °C, and a contact duration of 75 minutes. Maximum removal efficiency occurred at pH 4, while higher pH values led to decreased performance, likely due to the formation of insoluble zinc hydroxide. To understand the adsorption behavior, three kinetic models were applied: pseudo-first-order, pseudo-second-order, and intra-particle diffusion. The adsorption process was best described by the pseudo-first-order model, suggesting that the interaction predominantly occurred on the external surface of the adsorbent. Additionally, the intra-particle diffusion model indicated a dual mechanism-initial surface binding followed by diffusion within the pores. The study highlights that carbonized Origanum Majorana leaves serve as a low-cost, eco-friendly material for removing Zn(II) from water, making them a promising alternative to conventional activated carbon in sustainable water treatment technologies.

**Keywords**: Adsorption Process, Natural Adsorbent, Marjoram Leaves, Zinc Ion, Kinetic Modeling.

**الملخص**

تهدف هذه الدراسة إلى تقييم كفاءة مسحوق أوراق المردقوش ***(Origanum Majorana)*** المكربن في إزالة أيونات الزنك الثنائية ($Zn^{2+}$) من المياه الملوثة باستخدام تجارب الامتزاز على دفعات. تم تحديد الظروف المثلى للتجربة عند تركيز ابتدائي للزنك قدره 300 ملغم/لتر، ودرجة حموضة (pH) تبلغ 4، ودرجة حرارة 30 درجة مئوية، ومدة تلامس 75 دقيقة. أظهرت النتائج أن أعلى كفاءة للإزالة تحققت عند$pH = 4$ ، بينما انخفضت الكفاءة عند درجات حموضة أعلى بسبب احتمال ترسيب الزنك على شكل هيدروكسيد غير ذائب. تم تحليل البيانات التجريبية باستخدام ثلاثة نماذج حركية: النموذج الزائف من الدرجة الأولى، والنموذج الزائف من الدرجة الثانية، ونموذج الانتشار داخل الجزيئات. وأظهر النموذج الزائف من الدرجة الأولى تطابقاً أفضل مع النتائج، مما يشير إلى أن عملية الامتزاز تتركز بشكل أساسي على السطح الخارجي للسطح الممتزة. كما أوضح نموذج الانتشار داخل الجزيئات وجود آلية ثنائية تشمل الامتزاز السطحي في المرحلة الأولى، يتبعها انتشار الأيونات داخل مسام المادة. تشير نتائج البحث إلى أن مسحوق أوراق المردقوش يُعد مادة منخفضة التكلفة وصديقة للبيئة وفعالة في إزالة الزنك من المياه، مما يجعله بديلاً واعداً للفحم المنشط في تطبيقات معالجة المياه القائمة على مبادئ الكيمياء الخضراء.

**الكلمات المفتاحية:** عملية الامتزاز، الماص الطبيعي، أوراق المردقوش، أيونات الزنك، النموذجة الحركية.

## Introduction

Water contamination is a growing environmental issue with far-reaching effects on both human health and aquatic ecosystems. Among various pollutants, heavy metals are particularly concerning due to their persistence, bioaccumulation, and toxicity, often reaching humans through the food chain. Rapid industrialization, increased agricultural usage of chemicals, and transportation activities have significantly contributed to the presence of harmful substances in freshwater sources [1]. Activities like marine shipping and the widespread use of fertilizers and pesticides further intensify the degradation of water quality [2].

Heavy metals may also infiltrate the environment through atmospheric deposition. Emissions from industrial plants release metal particles into the air, which can eventually settle on land and water surfaces [3]. In soil, improperly discarded metal waste may corrode and leach into groundwater, contaminating drinking water sources and affecting agricultural productivity. Moreover, Zinc (Zn), while necessary in small amounts for biological functions, can pose health risks when present in excess. High concentrations are linked to symptoms such as fever and pulmonary distress [4]. Major sources of zinc pollution include effluents from galvanizing industries and mining operations [5]. Traditional zinc removal methods, such as ultrafiltration, ion exchange, and chemical precipitation, are often costly and technically demanding, making them less suitable for widespread use, especially in low-income settings [6].

In this direction, Adsorption is gaining recognition as an effective and affordable solution for removing heavy metals from aqueous systems. This technique relies on the interaction of dissolved metal ions with the surface of a solid material, known as the adsorbent, where these ions become bound or immobilized [7,8]. The simplicity of adsorption methods, combined with their efficiency, makes them particularly advantageous for environmental remediation, especially in areas with limited technological resources [9]. There are two primary types of adsorptions: physical (physisorption) and chemical (chemisorption). Physisorption involves weak, reversible forces and typically results in multilayer adsorption. In contrast, chemisorption forms strong, irreversible chemical bonds between the adsorbent and the metal ions, often in a monolayer arrangement [12,13]. Factors such as pH, contact duration, surface characteristics, and temperature can significantly influence the efficiency of the adsorption process [11].

Although activated carbon is a common adsorbent due to its high surface area and porosity, its cost and difficulty in regeneration limit its application in economically constrained settings [14]. This limitation has driven the search for eco-friendly, low-cost alternatives such as plant-derived adsorbents. One such promising material is Origanum Majorana (marjoram), an aromatic herb with natural adsorption potential when carbonized.

The present study aims to evaluate the effectiveness of carbonized Origanum Majorana leaves in removing Zn(II) ions from water. It will further investigate the adsorption kinetics and determine the influence of factors such as pH, temperature, and contact time, with the ultimate goal of proposing a green, cost-efficient alternative for water purification.

## Material and methods

### Chemicals and Instruments

All reagents utilized in this study were of analytical grade to ensure accuracy and reliability of results. Zinc acetate, EDTA (ethylenediaminetetraacetic acid), xylenol orange dye, and hexamethylenetetramine were sourced from Merck (Germany). Diethyl ether was acquired from Riedel-de Haën (Germany), while hydrochloric acid and sodium hydroxide were supplied by Fluka (Germany). Sulfuric acid was purchased from BDH (United Kingdom). To prepare the zinc working solution, zinc acetate was dissolved in deionized water to yield a Zn(II) concentration of 300 mg/L.

The pH levels of all working solutions were measured using a digital pH meter (Jenway 3205, USA). Adsorption experiments were carried out in a temperature-controlled shaker water bath (Clifton, Italy). A high-temperature muffle furnace (Naber, Germany) was employed for adsorbent preparation via carbonization, and all weighing procedures were conducted using a precision analytical balance (Mettler, China).

### Preparation of the Adsorbent

Fresh leaves of Origanum Majorana were gathered from the Sabha region in southern Libya. The leaves were initially rinsed with tap water, followed by deionized water to eliminate surface contaminants. They were then air-dried at ambient temperature for approximately 24 hours. Once completely dried, the leaves were manually ground using a mortar and pestle to produce a fine powder. To remove volatile substances, the powder was subjected to solvent extraction using diethyl ether.

Subsequently, the plant powder underwent thermal carbonization at 500 °C for one hour in a muffle furnace. After cooling, the material was sieved to obtain particles smaller than 125 micrometers [15].

The processed carbonaceous powder was stored in airtight containers and used as the adsorbent for zinc removal in the following experiments.

## Batch Adsorption Experiments

To evaluate the adsorption capacity of the prepared carbonized Origanum majorana powder for Zn(II) ions, a series of batch experiments were performed [16]. The concentrations of Zn(II) before (Co) and after (Ce) adsorption were determined via complexometric titration using 0.0005 M EDTA. Xylenol orange served as the indicator, with sulfuric acid and hexamethylenetetramine added as part of the buffering system, according to the method described by Ackacha (2010).

Adsorption experiments were carried out under fixed parameters: an initial pH of 4, Zn(II) concentration of 300 mg/L, adsorbent dose of 0.04 g in 100 mL of solution, agitation at 300 rpm, and a contact time of 60 minutes at 30 °C. To determine the initial metal ion concentration (Co), a 10 mL aliquot of the zinc solution was titrated prior to the addition of the adsorbent. After the contact period, the supernatant was separated and titrated again to measure the equilibrium concentration (Ce) of Zn(II). The amount of Zn(II) adsorbed per unit mass of adsorbent (qe, mg/g) was calculated using the following formula:

$$q_e = \frac{(C_o - C_e) \times V}{W} \qquad (1)$$

Where: V (l) is the volume of solution and W is the weight of adsorbent (g).
CoC_o = initial Zn(II) concentration (mg/L)
CeC_e = equilibrium Zn(II) concentration (mg/L)
VV = volume of solution (L)
WW = mass of adsorbent (g)

## Results and discussion

### Effect of pH

The influence of pH on the adsorption capacity of Zn(II) ions onto carbonized Origanum majorana leaf powder was investigated in the range of pH 2 to 5. Experiments were carried out under the following optimized conditions: initial Zn(II) concentration of 300 mg/L, adsorbent dose of 0.04 g/100 mL, particle size <125 μm, contact time of 60 minutes, and temperature of 30 °C. As shown in Figure 1, the adsorption capacity peaked at pH 4, reaching 187.96 mg/g. A decline in efficiency was observed at pH 5, likely due to the precipitation of Zn(II) as hydroxide species, reducing the number of free Zn(II) ions available for adsorption [17].

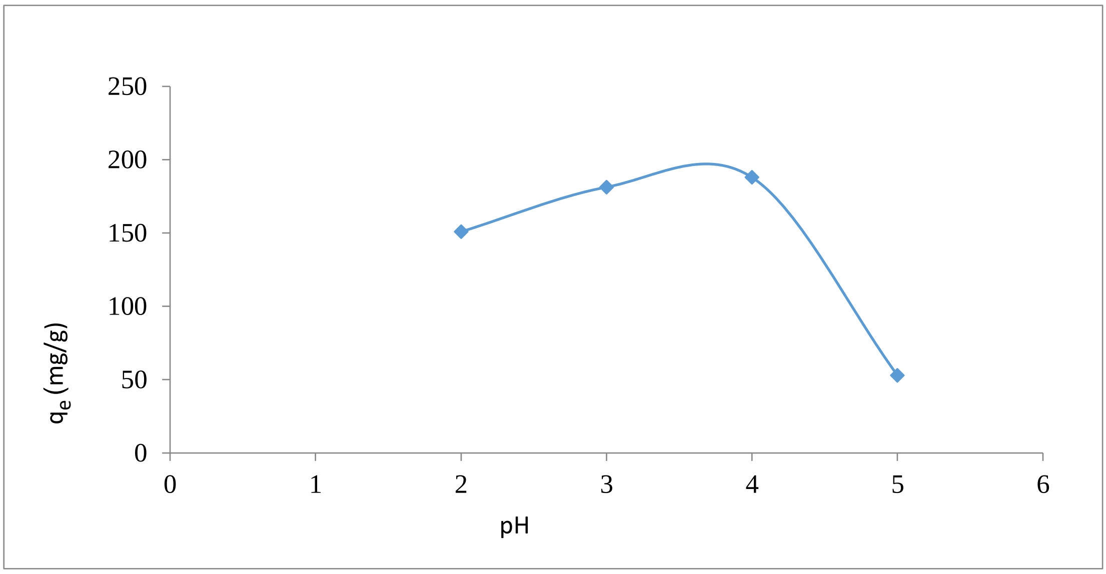

**Figure 1**. Effect of pH on Zn(II) adsorption by carbonized Origanum Majorana powder.

### Effect of Contact Time

The impact of contact time on Zn(II) removal efficiency at 30 °C is illustrated in Figure 2. Using a constant pH of 4, Zn(II) concentration of 300 mg/L, adsorbent dose of 0.04 g, and agitation speed of 300 rpm, the adsorption capacity increased progressively with time. The maximum observed value was 305.8 mg/g at 75 minutes. Continued adsorption beyond this point suggested extended surface interaction, although the rate of adsorption slowed due to site saturation.

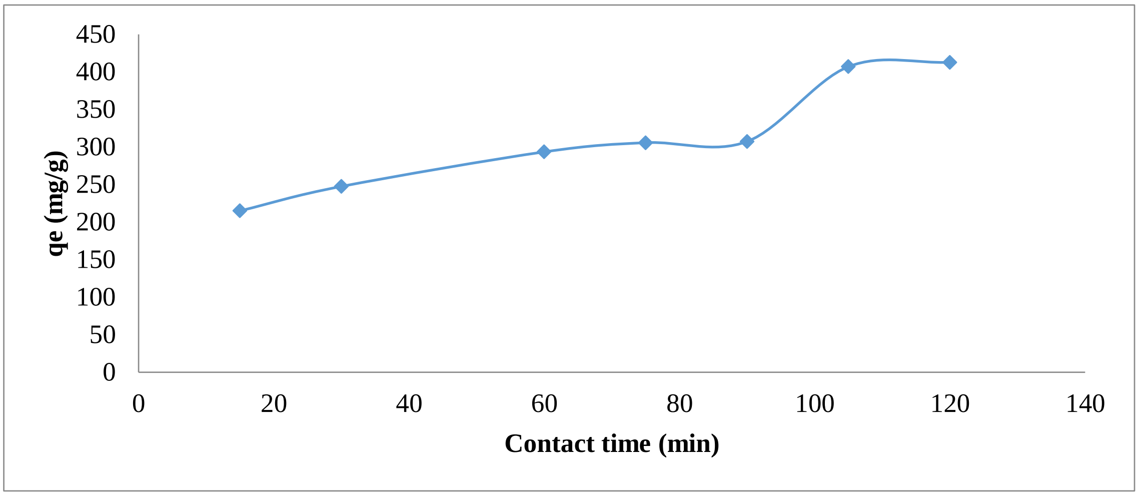

**Figure 2**. Effect of contact time on Zn(II) adsorption efficiency.

### Kinetic Studies

To interpret the adsorption behavior and mechanism, three kinetic models were applied: pseudo-first-order, pseudo-second-order, and intra-particle diffusion.

### Pseudo-First-Order Model

The pseudo-first-order model by Lagergren was used to describe the time-dependent uptake of Zn(II). The linear form is given by:

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (2)$$

where qtq_t is the amount of Zn(II) adsorbed at time tt, qeq_e is the adsorption at equilibrium, and k1k_1 is the rate constant. From the slope and intercept of the plot in Figure 3, the kinetic parameters were obtained and summarized in Table 1. A high correlation coefficient ($R^2 = 0.984$) and the agreement between experimental and calculated qeq_e values indicate that this model describes the system well.

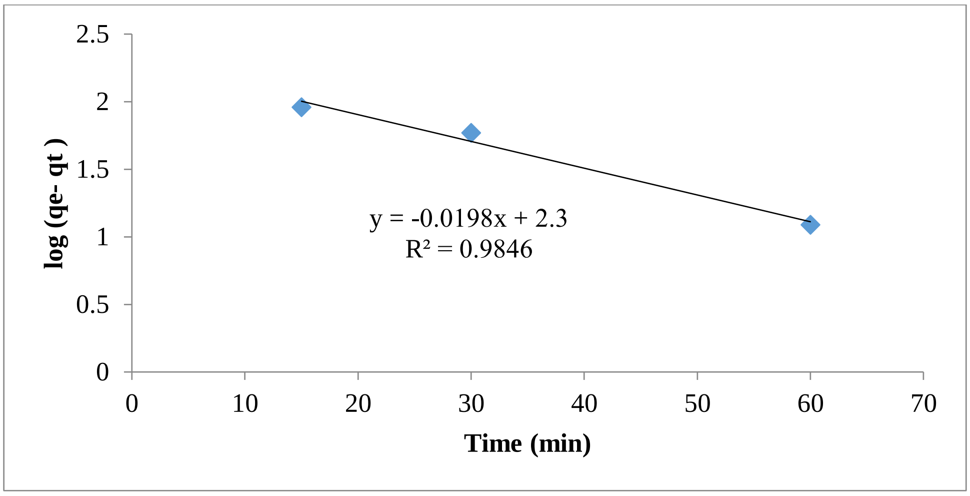

**Figure 3**. Pseudo-first-order kinetics for Zn(II) adsorption.

### Pseudo-Second-Order Model

The pseudo-second-order equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{K_2 {q_e}^2} + \frac{1}{q_e} t \qquad (3)$$

where k2k_2 is the second-order rate constant. Although Figure 4 demonstrates a linear relationship, the lower R² value (0.934) and the large deviation between experimental and calculated qeq_e values suggest that the adsorption does not follow pseudo-second-order kinetics precisely.

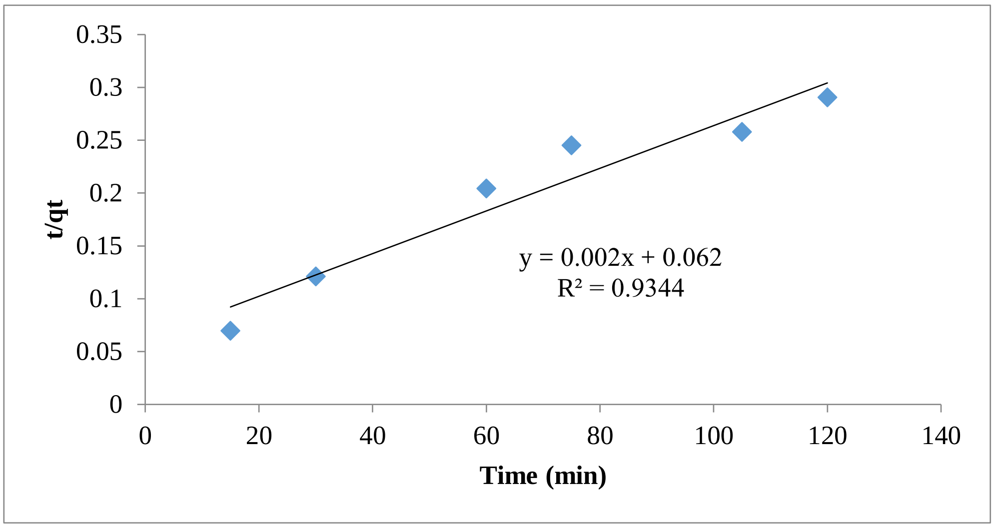

**Figure 4**. Pseudo-second-order kinetics for Zn(II) adsorption.

### Intra-Particle Diffusion Model

To assess the possibility of diffusion-controlled adsorption, the Weber-Morris intra-particle diffusion model was applied:

$$q_t = K_p \, t^{1/2} + C \qquad (4)$$

where kpk_p is the diffusion rate constant and CC indicates boundary layer effects. As illustrated in Figure 5, the linear plot does not pass through the origin, implying that intra-particle diffusion is not the sole rate-limiting step. Adsorption likely occurs in multiple stages, including film diffusion and pore diffusion [20].

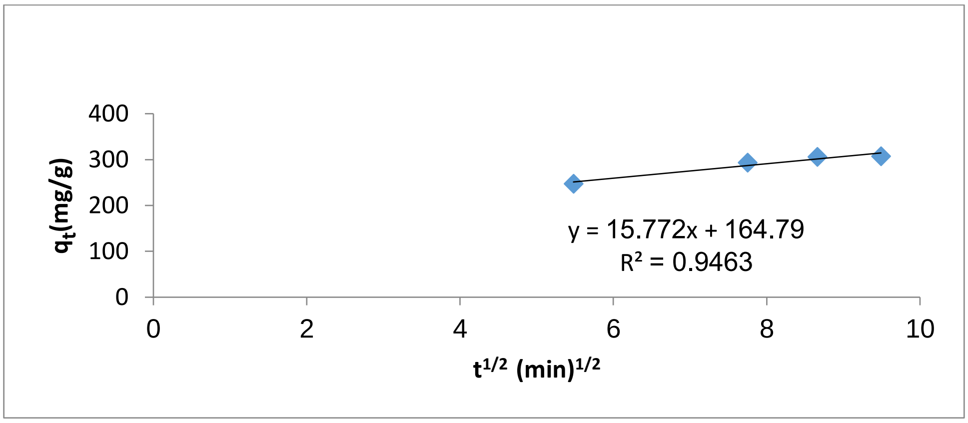

**Figure 5**. Intra-particle diffusion model for Zn(II) adsorption.

**Table 1:** Comparison of Kinetic Models for Zn(II) Adsorption onto Carbonized Origanum Majorana Leaves Powder.

| **Model** | **$q_e$, exp. (mg/g)** | **$q_e$, calc. (mg/g)** | **Rate Constant** | **$R^2$** |
|---|---|---|---|---|
| Pseudo-First Order | 305.8 | 199.5 | 0.04376 l/min | 0.984 |
| Pseudo-Second Order | 305.8 | 500.0 | 0.0000645 g/mg·min | 0.934 |
| Intra-Particle Diffusion | — | — | 15.77 mg/g·$min^{1/2}$ | 0.946 |
| Model | $q_e$, exp. (mg/g) | $q_e$, calc. (mg/g) | Rate Constant | $R^2$ |

The kinetic data presented in Table 1 evaluates the adsorption of Zn(II) ions onto carbonized *Origanum majorana* leaves powder using three commonly applied models: pseudo-first-order, pseudo-second-order, and intra-particle diffusion. Among these, the pseudo-first-order model provides the best statistical fit, with a high correlation coefficient ($R^2 = 0.984$). However, a notable discrepancy exists between the experimental adsorption capacity ($q_e$, exp = 305.8 mg/g) and the calculated value ($q_e$, calc = 199.5 mg/g), suggesting that while the model describes the kinetics well, it may underestimate the actual equilibrium adsorption capacity. In contrast, the pseudo-second-order model yields a significantly higher calculated $q_e$ (500.0 mg/g) compared to the experimental value, accompanied by a lower $R^2$ of 0.934. This overestimation indicates that the pseudo-second-order model does not accurately reflect the adsorption process in this system, despite its common association with chemisorption mechanisms. The intra-particle diffusion model, although lacking $q_e$ values, shows a relatively strong correlation ($R^2 = 0.946$), suggesting that diffusion within the adsorbent's pores plays a significant role in the adsorption process. The rate constant for this model (15.77 mg/g·$min^{1/2}$) supports the hypothesis that the process may be governed by more than one rate-limiting step. Overall, the kinetic results suggest that the adsorption mechanism likely follows a multi-stage pathway involving both rapid surface adsorption and slower intra-particle diffusion. While the pseudo-first-order model offers the best statistical fit, the intra-particle diffusion model provides valuable mechanistic insight, indicating the complex nature of Zn(II) uptake onto the carbonized plant material. Further investigation using complementary kinetic models could help confirm the dominant mechanism and validate the role of internal diffusion.

## Conclusion

This study demonstrates that carbonized Origanum Majorana leaf powder is a promising, eco-friendly, and cost-effective adsorbent for the removal of Zn(II) ions from aqueous media. Optimal adsorption occurred at pH 4, with a contact time of 75 minutes at 30 °C. Among the kinetic models evaluated, the pseudo-first-order model best described the adsorption process, indicating that surface interactions govern the uptake mechanism. Additionally, the intra-particle diffusion model revealed a two-step adsorption process involving both boundary layer and pore diffusion. These results support the potential application of plant-based adsorbents as sustainable alternatives to conventional methods for heavy metal removal, contributing to environmentally responsible water treatment practices.

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