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Research Article

A Comprehensive study on adsorption kinetics and equilibrium: Utilizing olive mill by-products as a sustainable biosorbent for cobalt (II) removal

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ABSTRACT

Aiming to remove cobalt from wastewater in a sustainable manner, this work marks a major advancement in industrial and technological advancements. We study if dried olive mill solid residues (DOMSR), a byproduct of the olive oil business, may effectively remove Co(II) ions from aqueous solutions by acting as a biosorbent. We have been able to offer useful insights by carefully analyzing the adsorption process and optimizing crucial variables such contact time, pH levels, initial metal concentration, and adsorbent dosage. Our experimental results demonstrate that higher initial cobalt concentrations increased the adsorption capacity, reaching a maximum of 120 mg/L. At pH 6.0, the maximum removal percentage was 82%, and the optimum adsorption achieved after 40 min of contact time. The adsorption process was best described by the pseudo-second-order model, according to kinetic studies, suggesting that chemisorption is the rate-limiting stage. The best fit was given by the Langmuir isotherm model (R^2=0.9948), which indicated homogenous active sites and a maximal sorption capacity (Q_m) of 41.84 mg/g. This research underscores the potential of agricultural waste-based biosorbents like OMSR for efficient cobalt removal, thereby offering a valuable contribution to sustainable wastewater treatment practices and environmental conservation.

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INTRODUCTION

The industrial and digital revolutions have marked significant milestones in human history, leading to an increasing demand for specialty elements like cobalt across various industries. This demand has been particularly driven by the growth of electronic devices, electric vehicles, and renewable energy technologies, all of which rely heavily on cobalt for the production of lithium-ion batteries and other essential components. As a result, heavy metal ions such as cobalt, copper, nickel, and zinc are frequently detected in the waste streams from industries such as electronics manufacturing, electroplating, petrochemicals, mining operations, tanneries, and textile production. The widespread use of these metals in modern industrial processes underscores the importance of developing efficient methods for their removal from wastewater to mitigate environmental impact [1].

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It was predicted that the price of cobalt would rise around five times between 2015 and 2018 due to the high demand, particularly from the automotive and technology sectors [2]. Because of increasing demand and value for cobalt, the mining sector has grown to be extremely profitable for governments and investors around the world [3]. According to projections, the world's cobalt demand is predicted to rise dramatically from 50 kT yearly in 2007 to 110 kT annually by 2030[4]. However, research has revealed that the present supply chains and mining practices for cobalt are not only unsustainable but also seriously dangerous for the environment because of uncontrolled industrial processes, depleted reserves, and unequal resource distribution [5]. These methods have resulted in the depletion of limited raw resources and water contamination, exceeding the permissible cobalt thresholds for both human (above 0.05 mg/L) and livestock (above 1 mg/L) consumption in irrigation water [6,7]. The World Health Organisation (WHO) has established that 2 μg/L is the highest level of cobalt ions that can be present in drinking water [3]. The development of workable and effective methods for removing cobalt (II) ions from water sources that are contaminated and cleaning and sanitising industrial effluent requires quick action [8].

To remove heavy metals, a variety of technologies are frequently used, including coagulation, chemical precipitation, adsorption, nanofiltration, ion exchange with resins, and other methods [9–20]. Among these, adsorption is considered the most effective method. Adsorption is a physicochemical process where mass transfers between a solid surface and a fluid phase, effectively removing metals at low concentrations. This technique is particularly suitable for extracting and recovering metal ions from wastewater, as it is user-friendly, cost-effective, and allows for the regeneration of the adsorbent through various methods [21]. Extensive research has been conducted on various adsorbents for wastewater purification, including carbonaceous, cellulose, biochar materials, and different agricultural wastes [22-30]. Because of its pore structure, which offers a lot of surface area for physical adsorption, and its innate functional groups, which may allow for chemical adsorption of heavy metal ions, biochar in particular has grown in popularity [31]. Additionally, there is a rising trend in using biosorbent materials for metal recovery due to their natural abundance, cost-effectiveness, and sustainability. This could reduce the overall cost of the adsorption process and enhance its overall value [32].

The effective use of waste products from both the agricultural and industrial industries has had a significant impact on the development of efficient and sustainable adsorption treatment methods. As a result, numerous adsorbents have been developed [33]. Waste from agriculture that are widely accessible and can be sourced responsibly have shown promise as viable and affordable substitutes for removing cobalt ion contaminants [34]. These agricultural waste materials have not only demonstrated their efficacy in effectively eliminating cobalt ions but also provided an environmentally friendly solution, thereby significantly contributing to the use of sustainable practices.

Numerous studies have focused on the removal of Co(II) ions from aqueous solutions using a variety of adsorbent materials, each offering unique benefits and mechanisms. Amoo et al. [3] explored the use of cow bone (CB), cow bone char (CBC), and activated cow bone carbon (ACBC) as adsorbents, finding that these materials, characterized by mesoporosity and hydroxyapatite properties, effectively removed Co^{2+} ions. The adsorption process for ACBC was driven by strong electrostatic attraction, with a pseudo second-order kinetic model indicating chemisorption. Thermodynamic analysis revealed different behaviors, with ACBC showing endothermic and non-spontaneous adsorption, while CB and CBC exhibited exothermic and physisorptive properties. Similarly, Demirbas [7] studied the adsorption of Co(II) using activated carbon derived from hazelnut shells. The process followed a pseudo-second-order kinetic model and was pH-dependent, with optimal adsorption capacity observed at 13.88 mg Co(II)/g. The thermodynamic analysis also indicated an endothermic nature of adsorption. Elsherif et al. [13] investigated tea and coffee powders as low-cost and environmentally friendly adsorbents, with adsorption influenced by various factors such as contact time and pH. The Langmuir isotherm model best described the equilibrium data, showing high maximum adsorption capacities of 244 mg/g for both adsorbents. Conte et al. [21] optimized the synthesis of mesoporous activated carbon using a factorial design, identifying conditions that enhanced cobalt removal through the formation of surface oxygenated groups. The rapid adsorption process reached equilibrium in just 15 minutes, and desorption studies highlighted the potential for effective cobalt recovery using sulfuric acid. Ghanavati et al. [22] explored the potential of MgO nanoparticles deposited on chitosan for Co(II) ion removal. Their study, involving a batch adsorption test system, showed that the adsorption process followed both first and second-order kinetic models and was effectively described by Freundlich and Langmuir isotherms. Thermodynamic analysis further demonstrated the suitability of this adsorbent for heavy metal remediation. Together, these studies underscore the diverse approaches and materials available for efficient Co(II) ion removal from aqueous environments.

This study sought to assess the efficacy of Dried Olive Mill Solid Residues (DOMSR), a by-product of the olive oil industry, as a novel and sustainable adsorbent for cobalt removal from aqueous solutions. Unlike conventional adsorbents, DOMSR offers an environmentally friendly and cost-effective alternative by utilizing waste material, thereby contributing to waste valorization and sustainable water treatment practices. The research effort focused on optimizing key parameters that govern the cobalt adsorption process, including contact time, pH, initial metal concentration, and adsorbent dosage. In addition, this study provides a comprehensive evaluation of the adsorption behavior by employing various adsorption isotherms and kinetic models, which were rigorously applied to accurately depict the equilibrium and kinetic data obtained from experimental trials. This innovative approach not only addresses the pressing issue of industrial wastewater management but also demonstrates the potential of DOMSR as a highly effective adsorbent for heavy metal removal, setting the stage for future applications in environmental remediation

MATERIALS AND METHODS

Chemicals and Regents

The chemicals used in this experiment were carefully provided by Sigma-Aldrich Co. (Merck, Darmstadt, Germany). These chemicals, including sodium hydroxide pellets (≥98.0-100.5%), hydrochloric acid (37%), nitric acid (70%), and potassium thiocyanate (99%), were of the highest quality. Deionized water, crucial for maintaining the purity of the solutions, was obtained from a Labtech Ultra-Pure Water Deionizer. The stock solution of Cobalt (II) ions, a key component of our study, was prepared with utmost care using Cobalt(II) chloride hexahydrate (98%), also purchased from Sigma-Aldrich Co. (Merck, Darmstadt, Germany). All compounds used in the study were of analytical grade, ensuring the accuracy and reliability of our results. The solutions were freshly prepared and stored at room temperature (25°C).

Preparation of adsorbents

For this study, we collected olive mill solid residue from local mills in Msallata, Libya. This solid residue was then processed into a powder called DOMSR (Dried Olive Mill Solid Residue), which served as our adsorbent material. There were multiple phases required in getting DOSR ready. To get rid of any contaminants, we first rinsed the solid olive residue with distilled water. After that, we dried it for a full day at 70°C in an electric oven. Following the drying process, the residues were ground and sieved to create a fine powder with an average particle size of less than 125 μm. After that, the powder was carefully kept in glass vials that were sealed until it was time to employ it as an adsorbent to extract cobalt ions. A digital photograph, shown in Fig. 1, provides a visual depiction of the sieved biosorbent. The photograph includes (a) the Olive Mill Solid Residues (OMSR) after cleaning, and (b) the prepared powder (DOMSR), which serves as the biosorbent.

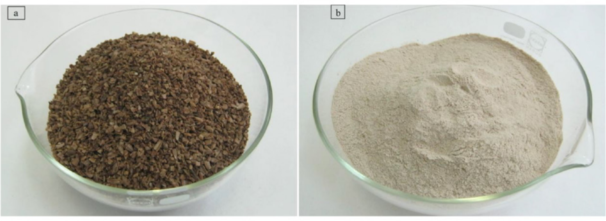

Figure 1. a) Olive mill solid residues (OMSR) and b) the prepared powder (DOMSR)

Metal ion determination

The concentrations of metal ions in the solutions and their levels in the aqueous solutions before and after adsorption were measured using the state-of-the-art JENWAY Molecular Absorption Spectrophotometer 6305. Another cutting-edge instrument used to regulate the pH of the solution—a crucial component of our experiment—was the JENWAY pH Metre 3505. The method described in an earlier publication [13] was used to determine cobalt (II) as a thiocyanate complex, guaranteeing the accuracy and repeatability of our findings. A blue colored complex was formed by adding 2.0 mL of (4M) concentrated potassium thiocyanate solution to a 5.0 mL Co(II) solution. To ensure the stability of the cobalt-thiocyanate complex, the solution was prepared in a 1:1 mixture of water and acetone since the complex is not stable in pure water. Additionally, the solution was acidified with 10% nitric acid (1 mL) to maintain the required acidic environment for optimal complex formation. The resulting solution's absorbance was measured at 620 nm using a spectrophotometer [13]. To enhance the accuracy of our measurements, calibration curves for metal ions were developed using stock solutions with concentrations ranging from 5 to 40 mg/L.

Adsorption procedure

The batch adsorption technique was used to adsorb cobalt(II) ions from an aqueous solution. Here's a detailed explanation of the process: A known initial concentration of Co(II) in a 50-mL solution was combined with a preset amount of DOMSR in 150-mL Erlenmeyer flasks. A blank solution devoid of Co ions was also added to account for adsorption by the adsorbent. Each flask was then covered with parafilm to prevent any external contamination. The mixture was then shaken at 175 rpm for a specific amount of time in a temperature-controlled incubator set at 25°C with a shaking platform. The supernatant and adsorbent were separated via filtration. The Co(II)-SCN complex was measured with a UV-VIS spectrophotometer to ascertain the beginning and ultimate concentrations of cobalt(II). Finally, the adsorption efficiency (%R) and capacity (Qe) were calculated. as follows:

$$\%R = \frac{C_0 - C_e}{C_0} \text{ x } 100 \tag{1}$$

$$Q_e = \frac{(C_0 - C_e) \text{ x } V}{M} \tag{2}$$

In the equations, Co and Ce (in mg/L) stand for the initial and ultimate equilibrium concentrations of Co(II). The mass of the biosorbent is specified as M (in g), and the volume of the solution is stated as V (in L). Three runs of the experiments were made, and the average values are shown here with the matching standard deviations.

The investigation examined the effects of adsorbent dose, starting concentration, pH, and contact time on the extraction of CO_2+ ions from aqueous solutions. Ideal numbers were found and applied to the kinetics and equilibrium investigations. The adsorbate suspension was supplemented with 0.1 M HCl or 0.1 M NaOH as needed to adjust values within the pH range of 2 to 9. On the other hand, solution samples were obtained for the kinetics analyses at regular intervals (0–60 min), and the cobalt (II) ion concentration was tracked throughout time. To optimise the design of an adsorption system for the removal of adsorbate, equilibrium adsorption data must be recorded. 50 mL of Co(II) solutions were mixed with the same amount of DOMSR to get the equilibrium adsorption isotherm data. Co(II) ions concentrations in the tests ranged from 10 mg/L to 120 mg/L, and 150 mL Erlenmeyer flasks with the proper pH were used for the studies. It was also looked at how different adsorbent doses, from 0.05 g to 1.00 g, affected the removal of Co(II) ions through adsorption.

RESULTS AND DİSCUSSİON

Influence of pH on adsorption

The rate at which surface reactions occur is largely dependent on the pH level of the solution. The primary reason for the variations in adsorption capacity within a designated pH range is the impact of pH on the surface adsorption characteristics of DOMSR. The change in Co(II) ion removal effectiveness from 2 to 9 pH values is shown in Fig. 2. At pH 2.0, the observed elimination percentage was just 71%. On the other hand, elimination efficiency increased significantly from pH 2.0 to 6.0 (82%). Because the binding locations were positively charged by H+ ions, the adsorption of Co(II) ions was restricted at low pH values, such as 2.0. Electrostatic repulsion prevented the Co(II) ions from attaching to the adsorbent surface as a result of the positive charge on the binding sites. Furthermore, Co(II) species are exclusively found in the divalent ionic form within this pH range. reduced pH values resulted in reduced Co(II) absorption because H+ ions and CO_2+ ions competed for the negatively charged adsorption sites [35, 36].

The concentration of H+ ions in the solution dropped as the pH rose to 5–6. As a result, there were more negatively charged binding sites available for adsorption, and because of their electrostatic attractions, the absorption of CO_2+ increased significantly [37]. This explains why elimination increased steadily beginning at pH 3.0. The maximum clearance percentage of 82% was noted at pH 6.0, suggesting that pH 6.0 is the ideal value for the elimination of Co(II).

However, the overall efficacy of Co(II) ion removal is decreased in the high pH zone (7-9) when several ionic forms of Co(II) are present, such as Co(OH)3, Co(OH)2, and Co(OH)+[7,38]. The adsorption effectiveness keeps rising as the pH rises above this threshold, continuing until the metal ions precipitate (pH > 8) as a result of the precipitate of cobalt hydroxide forming.

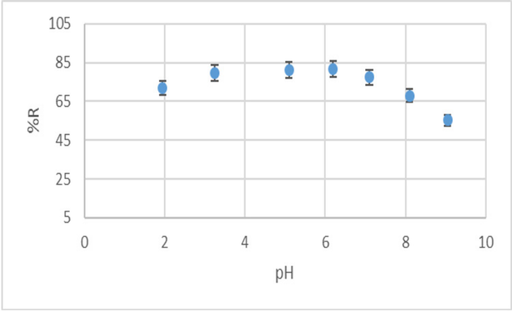

Figure 2. Impact of pH on Co(II) adsorption

Influence of adsorbent dosage

The dose of the adsorbent is important in the field of adsorption research. It establishes the highest amount of metal ions that the adsorbent is capable of removing for a specific solution concentration. Fig. 3 illustrates how increasing the adsorbent dosage from 0.05 to 1 g/50 mL results in an increase in the percentage of Co(II) removal from 66.20% to 84.80%. But from 26.50 mg/g to 1.70 mg/g, the adsorption capability drops. The greater surface area of the adsorbent and the existence of more binding sites are responsible for the higher percentage removal. On the other hand, the adsorbent particles' tendency to aggregate may be the cause of the decline in adsorption capacity, which leads to the overlapping of adsorption sites and a decrease in the surface area that is available for Co(II). Co(II) has a longer diffusion path to the adsorption sites as a result [13, 14]. It is noteworthy that despite a nearly twofold increase in DOMSR dosage (0.6 to 1 g/50 mL), there was no discernible increase in the elimination %. It barely went up to 84.80% from 82.20%. As a result, 0.5 g/50 mL is the most economical adsorbent dosage.

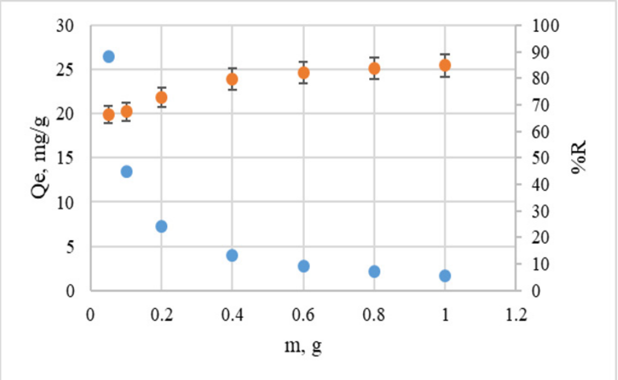

Figure 3. Impact of adsorbent dosage on Co(II) adsorption

Influence of contact time

Determining the equilibrium time is crucial in adsorption studies as it defines the point at which the adsorbent reaches its maximum sorption capacity. This information is essential for designing adsorption systems with appropriate residence times and making informed decisions about time-dependent variables related to the adsorption process [39, 40]. Fig. 4 illustrates the effect of contact duration on the removal efficiency of Co^{2+} ions by the adsorbents. The results indicate a rapid increase in Co^{2+} ion removal during the first 30 minutes, which is attributed to the high concentration gradient between the Co^{2+} ions in the solution and the available sorption sites on the adsorbent [41, 42]. After this initial period, the removal rate begins to decline and eventually levels off. This plateau is primarily due to the gradual saturation of the adsorbent's active sites, leading to a reduced removal rate as the system approaches equilibrium. Fig. 4 confirms that after 40 minutes, the adsorbents achieve saturation, and the percentage of Co^{2+} ions removed stabilizes [43]. This equilibrium is largely a result of the diminishing van der Waals forces between the Co^{2+} ions and the adsorbent's active sites as the adsorption sites become increasingly occupied [44].

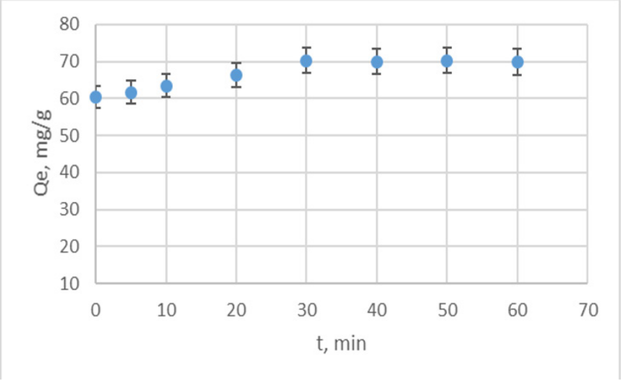

Figure 4. Impact of contact time on Co(II) adsorption

Influence of initial concentration

This study aimed to investigate cobalt's adsorption on the DOMSR adsorbent to determine the equilibration time for maximum uptake and understand the kinetics of the adsorption process. Fig. 5 illustrates the relationship between cobalt concentration and adsorption. Since it provides the required driving power to overcome mass-transfer barrier between the aqueous and solid phases, the initial concentration of cobalt is an important consideration. Consequently, a greater starting metal concentration raises DOMSR's sorption capacity. Fig. 5 shows that when the initial metal concentration rises, the equilibrium adsorption capacity increases linearly and reaches a maximum of 120 mg/L for cobalt ions. The graph indicates that as the initial cobalt concentration rises from 10 to 120 mg/L, the amount absorbed varies from 2.80 to 39.00 mg/g. As the initial concentration rises, the available adsorption sites become limited, leading to a decrease in adsorption percentage. This is because, at a fixed adsorbent dose, the total available adsorption sites are constrained, resulting in similar amounts of the adsorbate being adsorbed. Consequently, the adsorption percentage decreases as the initial adsorbate concentration increases [45,46]. The higher initial concentrations increase the adsorption capacity due to the stronger concentration gradient that drives greater interaction between the Co(II) ions and the binding sites of the adsorbent [47].

Experimental parameters overview

Table 1 provides a comprehensive comparison between the findings of our current study and previous research outcomes.

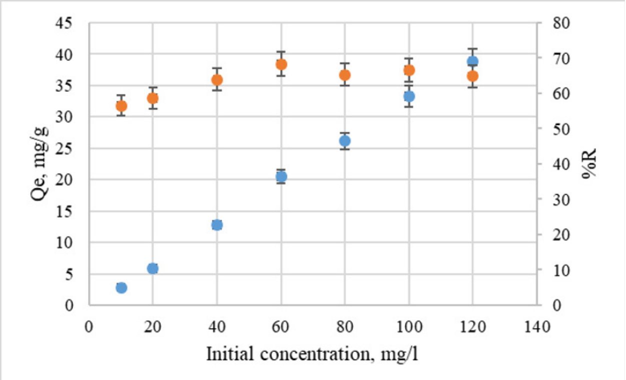

Figure 5. Impact of initial concentration on Co(II) adsorption

The table encompasses crucial information related to the adsorbent material, contact time, pH levels, adsorbent dosage, and initial concentration.

In terms of contact time, the present study found that the optimal adsorption of cobalt ions on olive mill solid residues occurred after 40 min of contact time. This falls within the range reported in previous studies (15-200 min). However, it suggests that our process may yield comparable results in a shorter period of time. The results of our investigation regarding pH indicate that a pH of 6 is the most suitable for the adsorption of cobalt ions onto the powder derived from olive mill solid residues. This discovery is consistent with several previous studies that identified optimal pH ranges of 5-5.5, 5.5-6, and 6. However, it differs from other studies that identified broader pH ranges of 4-5 and 4-9 as optimal. Additionally, the current study used a dosage of 0.5 g/50 ml of solution for the olive mill solid residues powder. While this dosage is similar to some previous studies (0.14g/50mL, 0.22g/50mL), it differs from others that employed different concentrations (0.5g/100mL, 2.0mg/L, 0.1g/50mL, 0.2g/50mL, 1.0g/L, 200mg/L). The optimal dosage can be influenced by various factors, such as the specific surface area of the adsorbent and the initial concentration of the contaminant[17]. Finally, the examination of cobalt ions' initial concentration indicates the highest adsorption capacity at 120mg/L. It is worth noting that this falls within the concentration range (30-600 mg/L) that has been previously studied, indicating that our chosen concentration is representative. Nonetheless, future studies may want to consider examining a wider range of initial concentrations in order to determine the maximum adsorption capacity of the olive mill solid residues powder.

The findings of the present study are consistent with certain prior investigations; however, notable discrepancies do exist. These discrepancies could potentially be attributed to several factors, including the type of surface. The surface characteristics of the adsorbent may vary based on the source material and the activation process employed [37,7]. Furthermore, the specific experimental conditions employed in each study may exert an influence on the observed outcomes.

Table 1. Comparison of the current study with some previous studies

The study	Adsorbent	Contact time (min)	pH	Dosage	Initial concentration (mg/l)
Present study	**Olive mill solid residues powdered**	**40**	**6**	**0.5 g/ 50 ml**	**120**
Amoo et al. [3]	Cow bone (CB), cow bone char (CBC), and activated cow bone carbon (ACBC)	150 for CB, 180 for CBC, 200 for ACBC	4, 5, and 5 for the ACBC, CBC, CB	0.14 g/50 ml, 0.22 g/50 ml, 0.26 g/50 ml for the CB, CBC, ACBC	250
Elsherif et al. [13]	Coffee and tea powder	40	5.5-6.0	1.0 g/l	240
Elsherif et al. [14]	Orange peels powder	30	4.0-5.0	0.1 g/50 ml	600
Ghanavati et al. [22]	MgO nanoparticles deposited on chitosan	50	5.0	0.1 g/50 ml	50
Swelam et al. [35]	Magnetic nano-hydroxyapatite	180	4.0-9.0	0.2 g/50 ml	30
Kolvankar [36]	Activated carbon prepared from coconut tree roots	60	7	0.5 g/100 l	240
Elsherif et al. [39]	Olive leaves powder	30	5.0-5.5	0.1 g/50 ml	150
Nadaroglu and Kalkan [45]	Red mud	15	5.5	2.0 mg/l	50
Narwade and Khairnar [48]	Nano-hydroxyapatite matrix	30	6	200 mg/l	2000

Isotherms models

In order to understand the relationship between the adsorbate and the adsorbent surface, adsorption isotherms are essential. The four most often used models for adsorption isotherm data analysis were Freundlich, Langmuir, Temkin, and Dubinin-Radushkevich (D-R) [13]. By utilising these models on the data, parameters were obtained that provide important information about the sorption mechanism, the adsorbent's surface characteristics, and its affinity. Figs. 6a, 6b, 6c, and 6d show these models' linear graphs. Table 2 contains comprehensive details on the linear equations and parameters for every model.

Table 2. Isotherms models equations and parameters [13,16]

Eq. No.	Isotherms model	Linear equation	Parameters
1	Langmuir	$\frac{1}{Q_e} = \frac{1}{Q_m} + \frac{1}{b\, Q_m\, C_e}$	Qe (mg/g): adsorption capacity Ce (mg/L): equilibrium concentration Qm (mg/g): maximal adsorption capacity b (L/mg): Langmuir constant
2	Freundlich	$\log Q_e = \log K_F + \frac{1}{n} \log C_e$	KF (mg/g (L/mg)1/n): Freundlich adsorption constants n: Empirical constant characterizing the heterogeneity of the adsorbent surface
3	Temkin	$Q_e = B_T \ln K_T + B_T \ln C_e$	BT (J/mol): Temkin adsorption constant KT (L/mg): Temkin isotherm constant
4&5	D-R	**log Qe = log Qm – β ε2** $\varepsilon = RT \operatorname{Log} (1+ \frac{1}{C_e})$	β (mol^2/J^2): Dubinin-Radushkevich constant ε (J/mol): Polanyi potential R (kJ/mol K): The gas constant T (K): The absolute temperature

Using four isotherm models, the adsorption of Co+2 ions onto the DOMSR adsorbent was investigated. Of these models, the Freundlich model came in second (R2=0.9896), while the Langmuir model showed the best fitting (R2=0.9948). Table 3 shows that the Temkin model had the lowest fitting value (R2=0.9294) and the D-R model had the lowest fitting value (R2=0.8052).

This result implies that the adsorbent's active sites are uniform. It was found that the maximal sorption capacity (Qm) was 41.84 mg/g. The equilibrium parameter, RL, is a dimensionless constant that describes the fundamental properties of the Langmuir isotherm:

$$R_L = \frac{1}{1+b\,C_0} \tag{6}$$

The isotherm's shape is evaluated using RL; values larger than 1 signify an unfavourable shape, RL=1 a linear shape, values between 0 and 1 a favourable shape, and RL=0 an irreversible shape [6]. Table 3 displays RL values that are less than 1 and larger than 0 (0.87-0.36), suggesting that CO_2+ has a favourable adsorption onto the DOMSR adsorbent.

The parameter that characterises the heterogeneity of the adsorbent surface is represented by the constant (n) in the empirical Freundlich model. Favourable adsorption is indicated by a value of $0 < n < 1$, whereas unfavourable adsorption is indicated by a value of $n > 1$. Linear adsorption is represented by a value of $n = 1$. The adsorption process is irreversible if $n = 0$ [49]. The present investigation revealed that the Freundlich constant (n) was not equal to unity (0.52), suggesting that the adsorption process escalated with an increase in ion concentration. This is explained by the DOMSR adsorbent's increasing surface coverage [50].

The following formula can be used to find the adsorption energy values in the Dubinin-Radushkevich (D-R) model, denoted as E:

$$E = \frac{1}{\sqrt{2\beta}} \tag{7}$$

E is the equivalent of the reaction mechanism. The sorption process is controlled by ion exchange if E is between 8 and 16 kJ/mol. The sorption mechanism may be influenced by physical forces when E is less than 8.0 kJ/mol. The computed E value for CO_2+ adsorption was 0.224 kJ/mol (Table 3). This suggests that physical sorption is the primary mode of sorption.

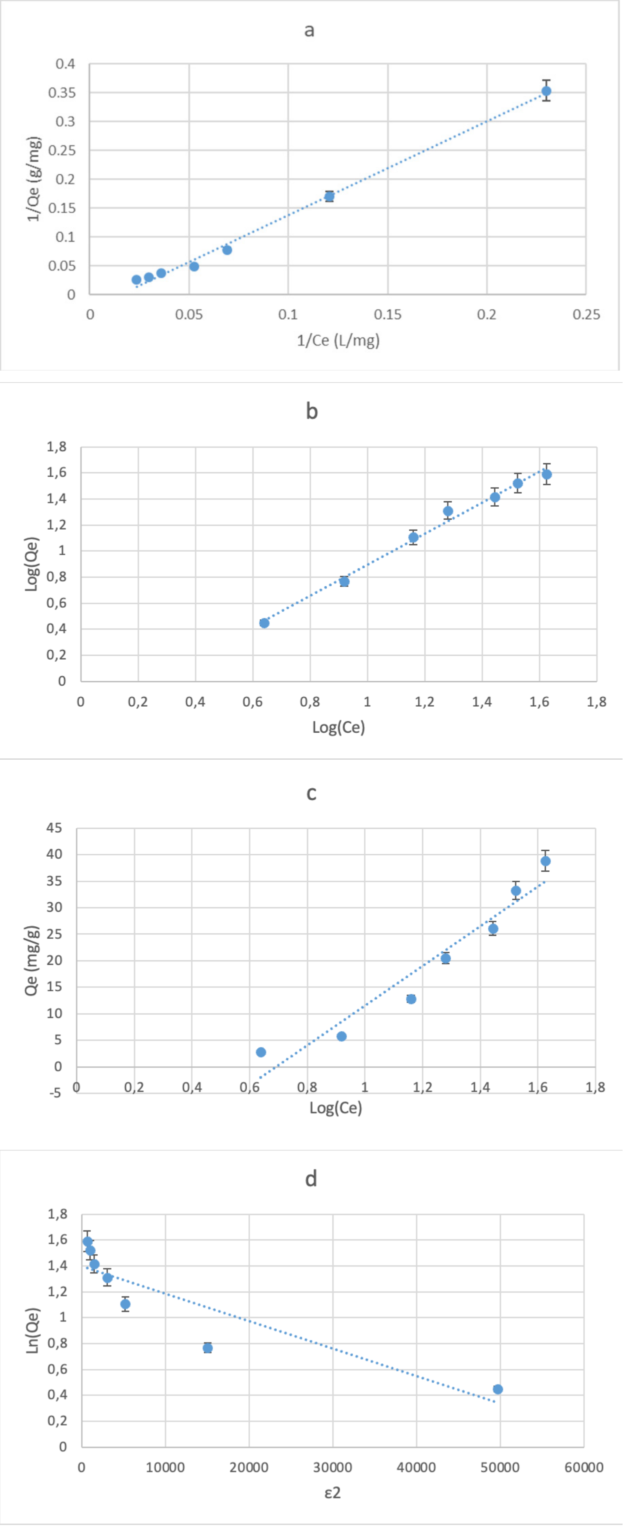

Figure 6. Linear graphs for a) Langmuir model, b) Freundlich model, c) Temkin model, d) D-R model plot of Co(II) adsorption

Table 3. Parameters of Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherm models for the adsorption of Co(II) on DOMSR

Model	Parameter	Value
Langmuir	b (L/mg)	0.015
	Qm (mg/g)	41.84
	R2	0.9948
Freundlich	KF (mg/g (L/mg)1/n)	1.970
	n	2.039
	R2	0.9896
Temkin	BT (J/mol)	37.404
	KT (L/mg)	1.996
	R2	0.9294
Dubinin-Radushkevich	Qm (mg/g)	24.93
	β (mol^2/J^2)	2x10-5
	E (kJ/mol)	0.224
	R2	0.8052

Kinetic models

The concentration of the adsorbate is known to fluctuate over time, as observed in the kinetic process [3]. By studying the kinetics of adsorption, we can understand how the adsorption process evolves from its initial state to equilibrium. This understanding allows us to create predictive models that determine the status of the process at different points in time [51]. Adsorption is the physical process in which ions or atoms of the sorbate move from a less stable region in an aqueous solution to a more stable one. This movement is influenced by Van der Waals forces and/or electrostatic physical forces [40]. In our study, we investigated the kinetics of the produced adsorbent (DOMSR) and compared the results with three kinetic models: Elovich, pseudo-first-order, and pseudo-second-order [3,13,19]. These models were then used to analyze the adsorption data we collected. Understanding the kinetics involved in the adsorption process enables us to design adsorption systems that can effectively remove a targeted percentage of the adsorbate (R%) or optimize the adsorption capacity of the derived adsorbent (Qe). For more detailed information, please refer to Table 4, which provides the linear equations and associated parameters for each model.

Table 4. Kinetic models equations and parameters [13,16]

Eq. No.	Kinetic model	Linear equation	Parameters
8	Pseudo-first-order	$\ln(Q_e - Q_t) = \ln(Q_e) - \frac{k_1}{2.303} \times t$	Qt (mg/g): Adsorbed quantities at t time Qe (mg/g): Adsorbed quantities at equilibrium k1 (min-1): The adsorption rate constant
9	Pseudo-second-order	$\frac{t}{Q_t} = \frac{1}{k_2 \times Q_e^2} + \frac{t}{Q_e}$	k2 (g/mg.min): The adsorption rate constant
10	Elovich	$Q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t)$	α (mg/g.min): The initial adsorption rate β (g/mg): The desorption constant

Several kinetic models were used in the analysis of adsorption investigations on the removal of CO_2+ metal ions from an aqueous solution, as shown in Table 4. As shown in Figs. 7a, 7b, and 7c, the goodness of fit of each model was assessed by comparing its correlation coefficient (R2) to unity (1). Table 5 presents the computed kinetic parameters and their accompanying coefficients of determination (R2 values).

As shown in Fig. 7a, the pseudo-first-order kinetic model did not provide a satisfactory fit for the adsorption data, with a coefficient of determination (R^2) of 0.822. The estimated adsorption capacity (Qe(calc)) was 2.67 mg/g, while the experimentally observed adsorption capacity (Qe(exp)) was 70.32 mg/g. Despite the R^2 value being relatively close to 1, this substantial discrepancy between the calculated and experimental capacities indicates a poor fit between the pseudo-first-order model and the experimental data. This suggests that the pseudo-first-order model does not accurately represent the adsorption kinetics in this system.

The pseudo-second-order kinetic model demonstrates an outstanding correlation coefficient of 0.9995, indicating the best fit for the adsorption kinetics of Co^{2+} ions onto the DOMSR adsorbent, as shown in Fig. 7b. This high correlation coefficient, which is close to 1, reflects a strong agreement between the model and the experimental data. Further support for this model's accuracy is provided in Table 5, which compares the calculated adsorption capacity (Qe(calc)) of 14.18 mg/g with the experimental adsorption capacity (Qe(exp)) of 14.10 mg/g. The close match between these values confirms that the pseudo-second-order model is the most suitable for describing the adsorption process. This indicates that chemisorption is the rate-limiting step in the adsorption of Co^{2+} ions onto the prepared adsorbents [3].

The kinetic parameters for the Elovich model are detailed in Table 5, and the corresponding data are illustrated in Fig. 7c. The Elovich model achieves a respectable correlation coefficient (R^2) of 0.8806, with a model constant (α) of 12.34 mg/g·min. Despite these relatively high correlation values, the Elovich model does not adequately fit the experimental data for Co^{2+} ion adsorption onto the DOMSR adsorbent. This suggests that, although the Elovich model shows some correlation, it is not the most suitable model for describing the kinetics of Co^{2+} ion adsorption in this case.

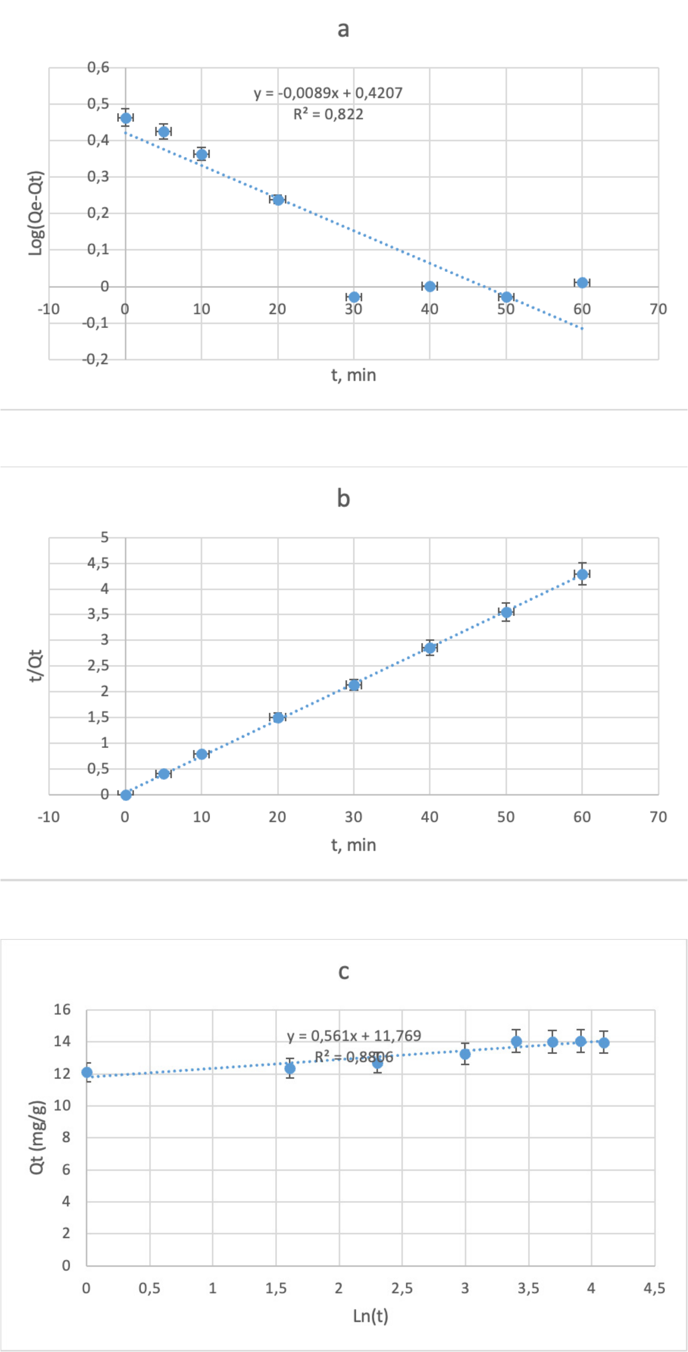

Figure 7. Kinetic model plots of Co(II) adsorption onto DOMSR: a) Pseudo-First-Order model, b) Pseudo-Second-Order model, c) Elovich model

Table 5. Kinetic parameters for Co(II) adsorption onto DSOR

Pseudo-First-Order			
k_1 (min^{-1})	Q_e (Cal.) (mg/g)	R^2	Q_e (Exp.) (mg/g)
0.020	2.67	0.8220	14.10
Pseudo-Second-Order			
k_2 (g/mg.min)	Q_e (Cal.) (mg/g)	R^2	Q_e (Exp.) (mg/g)
0.106	14.18	0.9995	14.10
Elovich			
β (g/mg)	α (mg/g.min)	R^2	Q_e (Exp.) (mg/g)
0.085	12.34	0.8806	14.10

CONCLUSIONS

In summary, the increasing demand for cobalt due to advancements in industry and technology demands long-term strategies for removing the metal from aqueous solutions. This study examined the possibility of using olive mill solid waste (DOMSR) as a cost-effective and environmentally friendly adsorbent to remove Co(II). In order to improve the cobalt absorption efficiency, tests with adsorbent dose, pH levels, and elemental metal concentrations are conducted. According to the data obtained under these particular conditions, DOMSR is a promising biosorbent for applications involving water purification since it shows a high adsorption capacity for cobalt ions. Kinetic investigations indicate that the pseudo-second-order model best describes adsorption., suggesting that chemisorption is the rate-limiting process. The equilibrium data demonstrated monolayer adsorption at the homogenous adsorbate sites by following the Langmuir isotherm. The Elovitch model fit better than the pseudo-second-order model, although exhibiting a respectable connection. This study emphasises the potential of biosorbents derived from agricultural waste, such DOMSR, for the remediation of heavy metal pollution. The outcomes also showed how successful OMSR is as a long-term cobalt removal method. These critically important breakthroughs have the potential to greatly improve water treatment and save the environment.

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DATA AVAILABILITY STATEMENT

The author confirm that the data that supports the findings of this study are available within the article. Raw data that support the finding of this study are available from the corresponding author, upon reasonable request.

CONFLICT OF INTEREST

The author declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

USE OF AI FOR WRITING ASSISTANCE

Not declared.

ETHICS

There are no ethical issues with the publication of this manuscript.

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