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Article

Efficiency of heat-treated sepiolite in the adsorption of Cd, Zn, and Co from aqueous solutions: A low-cost approach for wastewater treatment

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Abstract: This study investigated the adsorption of Cd, Co, and Zn ions onto unmodified and heat-treated sepiolite, focusing on the effect of contact time, initial pH, and heat pretreatments. Kinetic experiments were conducted in triplicate, and equilibrium experiments indicated that Co^{2+} had the highest adsorption preference, followed by Zn^{2+} and Cd^{2+}. The adsorption efficiency for Co^{2+} significantly increased with higher initial pH, whereas Zn^{2+} and Cd^{2+} showed optimal adsorption at lower pH levels. Heat-treated sepiolite at 250 °C exhibited a higher surface area and adsorption capacity in comparison with unmodified and 150 °C-treated sepiolite, which indicated the importance of heat pretreatment. The pseudo-second-order kinetic model better described the adsorption process, and it was confirmed chemisorption as the rate-limiting step. By increasing the contact time, adsorption rates enhanced, with equilibrium achieved within 480 min for all systems. Higher initial solute concentrations led to an increase in adsorption processes, with Co ions consistently showing higher adsorption efficiency in competitive multi-ionic solutions. Adsorption percentages varied with pH and thermal treatment, indicating the importance of these parameters in optimizing sepiolite's adsorption capacity for heavy metal removal.

Keywords: sepiolite; kinetic models; heavy metals; adsoption

1. Introduction

Ever-increasing industrialization brings about essential decisions to protect the environment and specifically conserve water resources by developing cost-effective wastewater treatment methods [1]. The application of clay and modified clays to remove toxic heavy metals from wastewater has attracted attention in recent decades [2,3]. Due to the high adsorption capacity of clays and their easy accessibility in nature, clay minerals have received more attention from researchers for adsorption experiments [4]. To improve their adsorption capacity, there are various methods like heat and acid treatment that are applied by many researchers [5]. The removal of toxic heavy metal ions and their lethal effects on the environment and industrial wastewater using different adsorbents has received more attention recently [6]. Sepiolite ($Si_{12}O_{30}Mg_8(OH)_4(H_2O)_4 \cdot 8H_2O$) is a natural, fibrous clay mineral with fine microporous channels [7]. The Sepiolite's high adsorption capacity suggests its effectiveness in removing heavy metals from polluted/waste waters. Sepiolite in aqueous suspensions can acquire a surface charge through the adsorption and desorption of potential-determining ions, particularly protons, on its surfaces [8]. Sepiolite's crystal-chemical features allow it to retain heavy metals through adsorption and/or cation exchange reactions [9].

The adsorption process can occur on the oxygen ions of the tetrahedral sheets, on the water molecules at the edges of the octahedral sheet, and on Si-OH (silanol groups) along the direction of the fibers, whereas cationic exchanges occur by substituting the solvated ions inside the channels and/or inside the octahedral on the edges of the channels [10,11]. This unique structure leads to the study of this mineral for many experimental applications, such as membranes for ultrafiltration, catalyst carriers [12–14], fillers in polymer composites [15], adsorbents for organic molecules and heavy metals [16], and inorganic templates [17].

Numerous studies have explored the efficient use of sepiolite, both natural (without heat pre-treatment) and modified (heat pre-treatment), for the removal of some selected heavy metals, including Cd, Zn, and Co, from industrial and municipal wastewater [18–20]. Specifically, the study assessed the effectiveness of both unmodified and heat-treated sepiolite in removing heavy metals from aqueous solutions, considering various factors such as solution pH, heavy metal concentration, and contact time (ranging from 5 to 2880 min). To gain a deeper understanding of the adsorption mechanism and kinetics, the experimental data was analyzed using the intraparticle diffusion, pseudo-first order, and pseudo-second order kinetic models. This analysis will help elucidate the rate-limiting step and the overall adsorption process involved in heavy metal removal by both unmodified and heat-pretreated sepiolite.

2. Material and methods

2.1. Materials

2.1.1. The sorbent

The sepiolite sample used in this study was obtained from a mine near the town of Fariman in the Khorasan region of Iran. All samples were ground using an electric mill, processed by a ball mill, and then sieved to obtain particle sizes smaller than 0.05 mm (<53 μm). By obtaining this size of sepiolite samples, all the sepiolite required for use as an adsorbent to remove Cd, Zn, and Co from aqueous solutions was saturated with calcium ions [21].

2.1.2. Chemicals

For the saturation process, a 0.5 M $CaCl_2$ solution was prepared using $CaCl_2$ from Merck, Darmstadt, Germany. 55.45 g of $CaCl_2$ dissolved in one liter of deionized distilled water to make this concentration of calcium. We ought to saturate all surfaces of this mineral with Ca^{2+} to start the sorption and desorption of heavy metals. So 5 g of sieved minerals were taken in centrifuge tubes, and 25 ml of $CaCl_2$ 0.5 M were added to them, and then the samples were shaken at 350 rpm for 30 min. After that, the suspensions were centrifuged at 3000 rpm for 10 min, and the limpid solutions of all these tubes were gathered to measure the EC. These steps were repeated until the EC of the clear solutions reached a stable value. Then the saturated samples in the extremity of tubes were gathered and were taken into the oven for 72 h at 75 °C to be dried completely, and then we started flouring and ball-milling again, same as sieving before, to obtain the 0.05 mm (<53 μm) sizes of mineral.

Sorption studies of cadmium (Cd), zinc (Zn), and cobalt (Co), along with the desorption of magnesium (Mg), were investigated using batch experiments. The adsorbent that is used in this study is prepared in three temperature treatments, including room temperature (22.5 ± 0.2 ℃), 150 ℃, and 250 ℃ heat pre-treatments. Sample pre-treatments of 150 ℃, and 250 ℃ of adsorbents were taken in an electrical kiln for 4 h. Since the kiln temperature was raised to the targeted warmth, the removal of the present (existent) zeolitic water, which was bound in the mineral structure, changed the adsorption capacity of this mineral for heavy metals in aqueous solutions. Therefore, the needed amounts of this mineral were taken in the kiln for 4 h at 150 ℃ and the same was done for the heat pre-treatment at 250 ℃. After this period, the kiln was cooled to room temperature, and the samples were extracted and stored in a desiccator to prevent the possible adsorption of air moisture on the surfaces of the heat-treated (modified) sepiolite [22].

To create multi-ion solutions, the following metal concentrations were used: 20 ppm Cd, 20 ppm Co, and 20 ppm Zn for the 60-ppm solution; 80 ppm Cd, 80 ppm Co, and 80 ppm Zn for the 240-ppm solution; and 160 ppm Cd, 160 ppm Co, and 160 ppm Zn for the 480-ppm solution. The materials used to make these solutions were $CdCl_{2\cdot 2½}H_2O$ obtained from BDH Company (England) and $CoCl_2$ and $ZnCl_2$ from Merck, Darmstadt, Germany. To make the desired solutions with high punctuality, at first, 1000 ppm concentrations of each of the heavy metals as a stock solution in a single component solution were made. To prepare 1000 ppm solutions of Cd, Co, and Zn, 2.031 g of $CdCl_{2\cdot 2½}H2O$, 2.084 g of $ZnCl_2$, and 2.203 g of $CoCl_2$ were weighed, and each was dissolved in 1 liter of deionized water to obtain 1000 ppm solutions of these heavy metals. All solutions were made by using deionized water. In the presence of some Zn^{+2} complexes, such as the zincate complex [$Zn\ (OH)_4^{2-}$], we had to reduce the stock solution pH by using the HCl 0.5N to prevent the deposition of those complexes and to get a sleek stock solution. This was due to the low solubility of $ZnCl_2$ in deionized water, and the Ksp of Zn^{2+} is close to 1.2×10^{-17}. Finally, the produced multi-component solutions were conducted at pH 4 and pH 5. For adjusting the solutions at these pHs, if necessary, HCl 0.2N and NaOH 0.2N were used [23].

2.2. Methods

2.2.1. Batch experiments

A batch experiment is a simple method commonly used to assess the adsorptive capacities of natural and modified sorbents. Besides the ease of using this technique, it helps to provide important information about the efficiency of the sorbent in removing adsorptive species under static conditions [24]. Thus, batch techniques are widely used for environmental studies, especially for the removal of heavy metals from municipal and industrial wastewater [25].

To start this part of the experiments, 0.3 g of adsorbent was precisely weighted for each unmodified and the heat-pretreated sepiolite into polyethylene containers, then 30 cc of multi-component solutions were added to them (1:100 solid to liquid ratio) with three repetitions for each anticipated temperature treatment at the three specified concentrations: 60 ppm, 240 ppm, and 480 ppm, comprising adequate amounts of cadmium, cobalt, and zinc. All the above-mentioned stages were conducted for eleven contact times, including: 5, 10, 20, 30, 60, 120, 240, 480, 720, 1440, and 2880 min.

2.2.2. Kinetic experiments

Kinetic experiments were done by mixing 0.3 g of weighted samples from modified and unmodified sepiolite by heat treatments in polyethylene containers at three repetitions with 30 cc of multi-component solutions. So, we had 27 suspension containers for each contact time, which included 9 containers for adsorbents without heat treatment, 9 containers for the heat treatment of 150 °C, and even 9 containers for the heat treatment of 250 °C. Total sorption and desorption processes by eleven contact times, including 5, 10, 20, 30, 60, 120, 240, 480, 720, 1440, and 2880 min, were investigated. So, we had 298 suspension containers for the kinetic experiments. Each of the 27 containers related to each experimental contact time was shaken at an agitation speed of 350 rpm in the shaker for any of the mentioned contact times. Then these suspensions were centrifuged for about 10 min at 3000 rpm to separate the adsorbent from multi-ionic solutions, and after that, the clear solutions were passed through filter paper, poured into new containers, and prepared for atomic adsorption readings (model: SavantAA-GBC). Several kinetic models are available to investigate the adsorption kinetic mechanisms and potential rate-controlling steps such as chemical reactions and mass transport processes [26].

The adsorbed metal concentrations were determined by the difference between the initial and final concentrations in the aqueous solutions after the adsorbing process, using the equation below.

$$Q_e = \frac{C_0 - C_e}{m}.V \tag{1}$$

where the Q_e is the amount of metal absorbed per mass unit of adsorbent. The C_0 and C_e are the initial and equilibrium concentrations (mg.kg^{-1}), respectively, m is the mass of the adsorbent (g) and V is the volume of the solution (L) [27].

In this experiment three kinetics models including Pseudo-first and Pseudo-second order model and Intraparticle diffusion model have been investigated to examine the controlling mechanism of the adsorption processes and to understand the behavior of the adsorbent and to test the experimental data.

The Pseudo-first order model that was presented by Lagergren, is expressed as follows:

$$\frac{d_q}{d_t} = k_1(q_e - q_t) \tag{2}$$

where the q_e and q_t are the amounts of adsorbed ions onto the sepiolite at equilibrium and at any time *t*, respectively. The K_1 is the rate constant of first-order adsorption [28].

The linear form of this equation is expressed as follows:

$$ln(q_e - q_t) = lnq_e - k_i.t \tag{3}$$

The plots of ln (q_e–q_t) against *t*, give a linear relationship from which k_1 and q_e values can be determined from the slope and intercept of this equation, respectively [29].

The pseudo-second order model was also used to describe the sorption of metal ions. The equation for the reaction is expressed as follows:

$$\frac{d_q}{\mathrm{d_t}} = k_2(q_e - q_t)^2 \tag{4}$$

where k_2 is rate constant for pseudo-second-order adsorption (g.mg^{-1} min). q_e and q_t are the sorption capacity (mg/g) of ions at equilibrium and at a time *t*, respectively [30].

Also, the linear form of this equation is represented as follows:

$$\frac{\mathrm{t}}{\mathrm{q_t}} = \frac{1}{\mathrm{k_2 . q_e}} + \frac{\mathrm{t}}{\mathrm{q_e}} \tag{5}$$

The plots of t/q_t against t give a linear relationship in which k_1 and q_e values can be calculated from the slope and intercept of this equation, respectively [31].

The sorption data was also analyzed in terms of Intraparticle diffusion mechanism that can be described as following Equation (6):

$$q_t = k_i . \sqrt{t} + C \tag{6}$$

where q_t (mg. g^{-1}) is the concentration of cations absorbed at time *t* by the adsorbent, and k_i (mg. g. t$^{-0.5}$) is the intraparticle rate constant [31].

3. Result and discussion

This study delves into the molecular structure and composition of sepiolite, a mineral characterized by its unique fibrous arrangement. Sepiolite's structure consists of alternating sheets of tetrahedra and octahedra, forming a network of channels that house coordinated water molecules bonded to magnesium centers. Additionally, zeolitic water resides within the mineral's porous channels (**Figure 1a**).

Transmission Electron Microscopy (TEM) images revealed the elongated, needle-like morphology of sepiolite, confirming its fibrous crystal structure and any potential defects (**Figure 1b**). X-ray Diffraction (XRD) patterns further validated the mineral's phase identity, providing insights into its crystalline arrangement and purity (**Figure 1c**). Energy Dispersive X-ray Spectroscopy (EDAX) analysis confirmed the presence of magnesium, silicon, and other key elements within the sepiolite structure (**Figure 1d**).

By combining TEM imaging, XRD, and EDAX, this comprehensive study provides a detailed understanding of sepiolite's structural and compositional characteristics. This knowledge is essential for evaluating its adsorption properties and exploring its potential applications.

The kinetic experiments were done in triplicate under the same conditions for each heat-treated sepiolite and for any of the contact times studied. The remaining concentrations of metal ions in the aqueous phase were computed from the averages of experimentally determined adsorbate concentrations after adsorption, using Equation (1). These values were then used in the analysis of data and for graph fitting by some kinetic models.

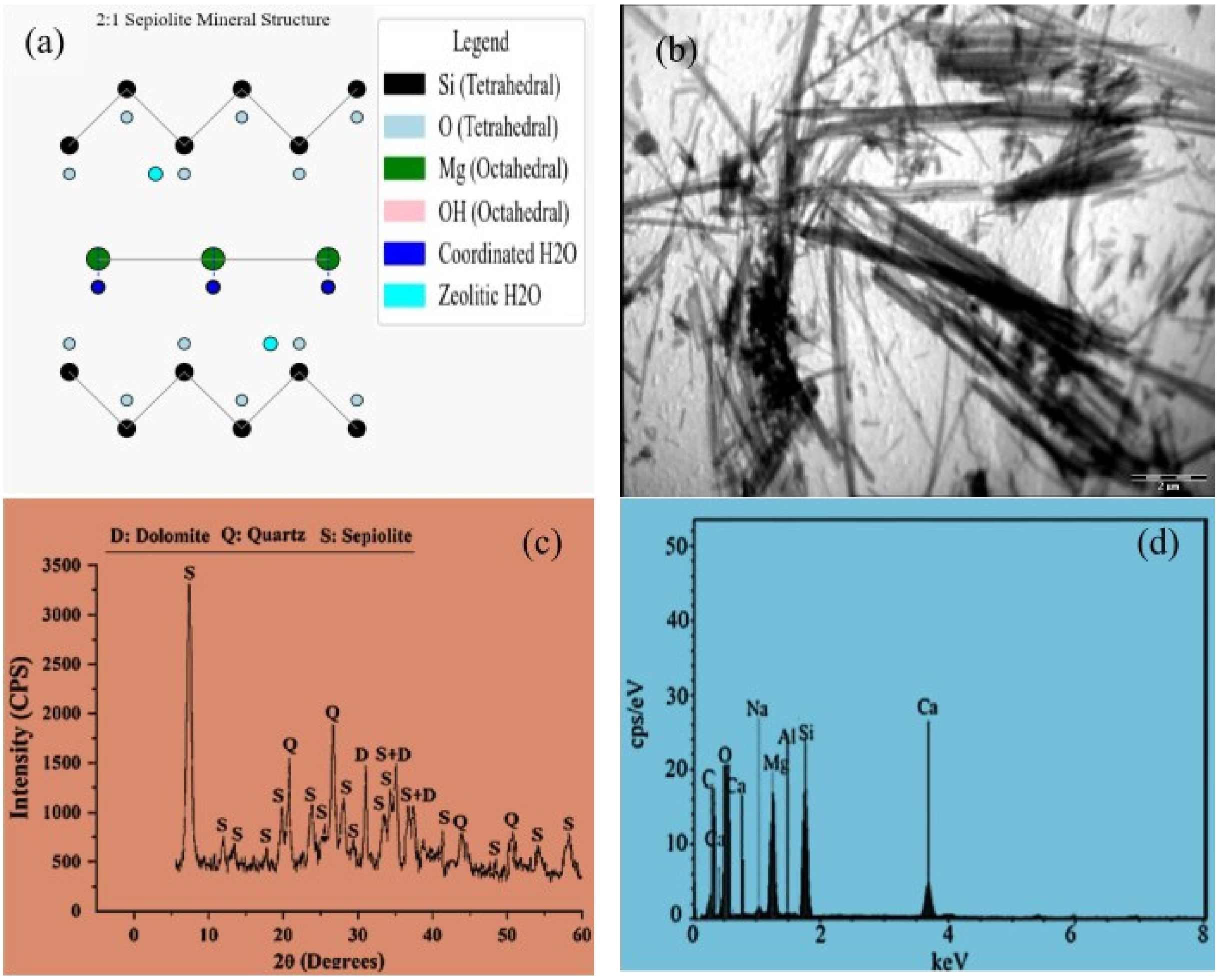
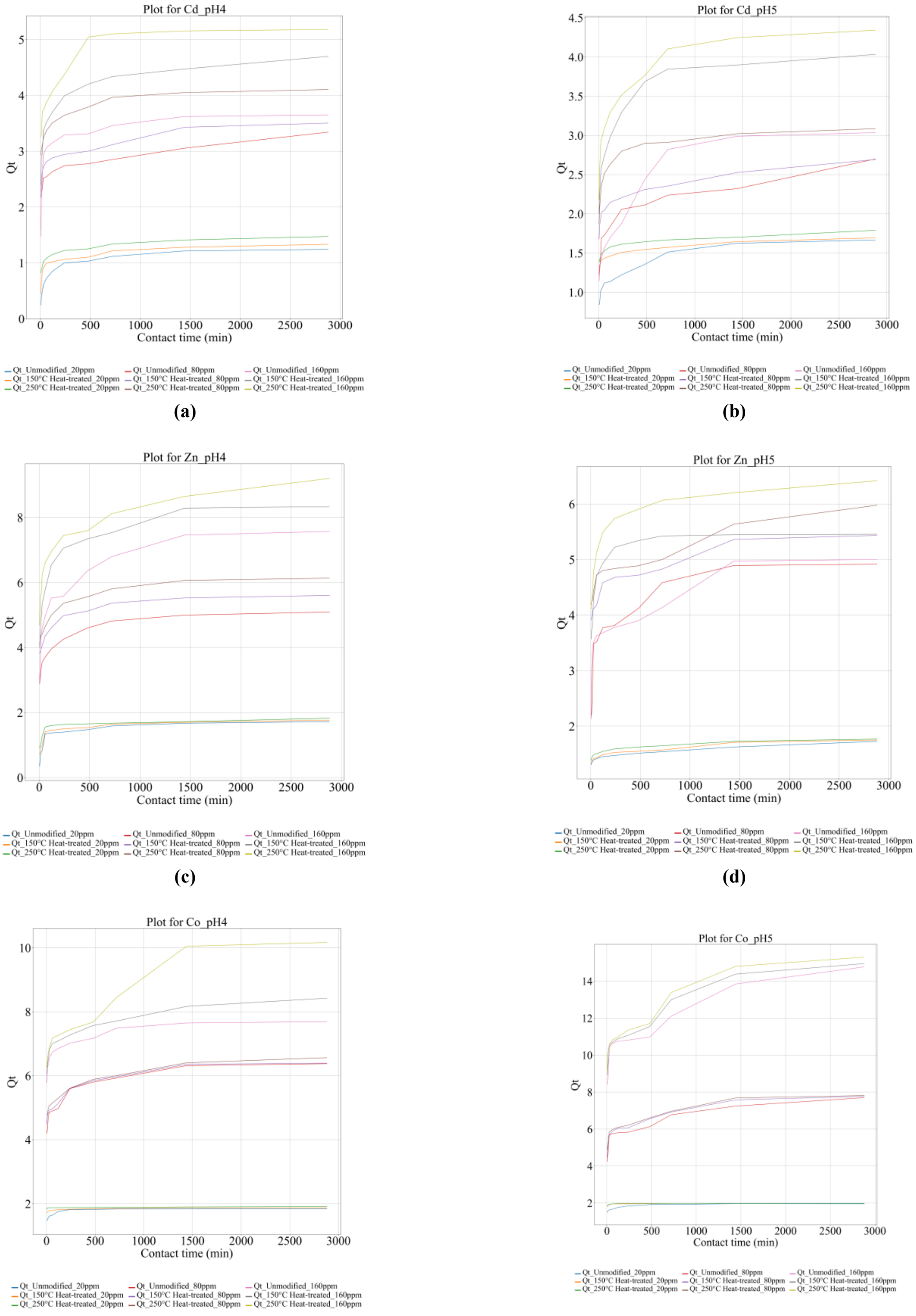


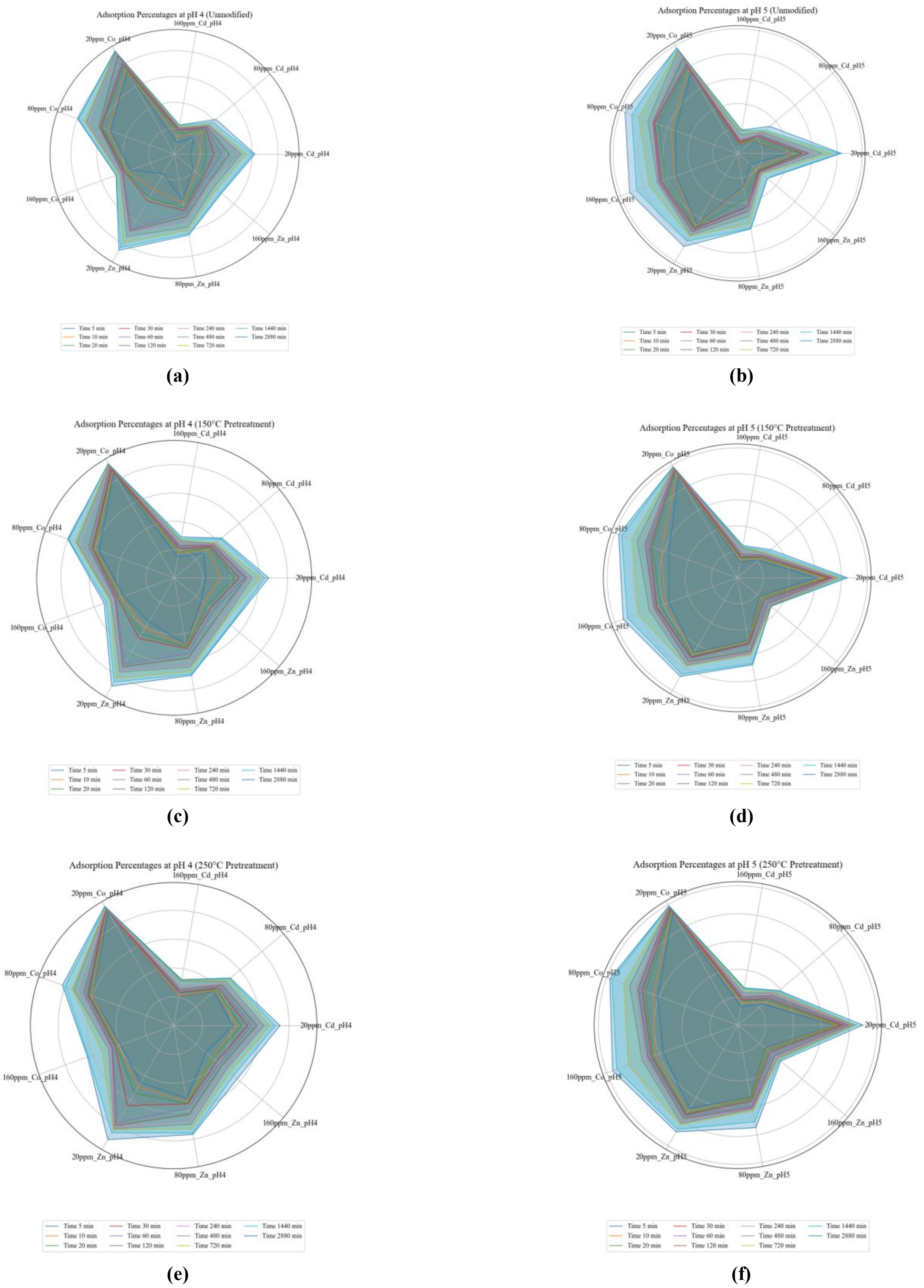
Figure 1. (a) 2:1 mineral structure; **(b)** TEM images; **(c)** XRD pattern; **(d)** EDAX spectrum of applied sepiolite.

Equilibrium experiments were done, and the kinetic curves obtained for the sorption of Cd, Co, and Zn by sepiolite are presented. **Figure 2** shows the heavy metal adsorption on unmodified and modified (heat-treated) sepiolite samples in various solution concentrations and different pH values. Also, **Figure 3** shows the adsorption percentages of the investigated heavy metals on unmodified and modified sepiolite samples. The number of milligrams absorbed per gram of unmodified and heat-treated sepiolite as an adsorbent versus the number of milligrams at equilibrium per volume of solution is illustrated for Cd, Co, and Zn cations. Equilibrium was strongly favorable for Co^{2+}. According to the equilibrium kinetics, the selectivity series is $Co^{2+} > Zn^{2+} > Cd^{2+}$. The adsorption capacity of natural and heat-treated sepiolite was higher for cobalt than for the other two cations in all experiments and both studied pH solutions. It could be attributed to the atomic and adsorbing properties of cobalt that this element formed fewer complexes in multi-component solutions at pH 4 and 5 than other existing elements. And the adsorbing properties of natural and modified sepiolite refer to the crystalline structure and morphology of this mineral to substituting the existing cations in liquid phase with the leached Mg^{2+} from octahedral sheets under acidic conditions [32,33].



(a) **(b)** **(c)** **(d)** **(e)** **(f)**

Figure 2. Heavy metal adsorption on unmodified and modified sepiolite samples under different solution concentrations and pH values: **(a)** Cd at pH 4; **(b)** Cd at pH 5; **(c)** Zn at pH 4; **(d)** Zn at pH 5; **(e)** Co at pH 4; **(f)** Co at pH 5.



Adsorption Percentages at pH 4 (Unmodified)

Adsorption Percentages at pH 5 (Unmodified)

Adsorption Percentages at pH 4 (150°C Pretreatment)

Adsorption Percentages at pH 5 (150°C Pretreatment)

Adsorption Percentages at pH 4 (250°C Pretreatment)

Adsorption Percentages at pH 5 (250°C Pretreatment)

(a) **(b)** **(c)** **(d)** **(e)** **(f)**

Figure 3. Adsorption percentages of the investigated heavy metals on unmodified and modified sepiolite samples: **(a)** Unmodified sepiolite at pH 4; **(b)** Unmodified sepiolite at pH 5; **(c)** 150°C heat-pretreated sepiolite at pH 4; **(d)** 150°C heat-pretreated sepiolite at pH 5; **(e)** 250°C heat-pretreated sepiolite at pH 4; **(f)** 250°C heat-pretreated sepiolite at pH 5.

3.1. Effect of initial pH value

Adsorption usually directly depends on the amounts of H^+ and OH^- in solutions. The pH values have an important effect on the surface charge of an adsorbent, such as protonation and deprotonation of surface functional groups, and affect the interaction between chemical species of metal ions present in the solution [34]. A decrease in pH value increased the competition between H^+ and other cationic species for adsorptive sites on the surface and edges of sepiolite. On the other hand, interaction of positive charges with sepiolite at lower pHs should be decreased [35]. As can be seen in **Figures 1** and **2**, the efficiency removal of cobalt ions increased considerably when the pH value of initial solutions increased from 4 to 5 in all concentrations of multi-component studied solutions, and it occurs for Zn and Cd in multi-component solutions at concentrations less than 60 ppm. Although the adsorption of zinc and cadmium was decreased by increasing the initial pH values, it could justify that pH 4 was not the optimum adsorption pH value for these two elements. Similarly, Guerra et al. [36] have investigated the absorption of arsenic (V) on sepiolite and modified sepiolite in the pH range of 1.0–8.0. They reported that the maximum values of adsorption of arsenic ions were observed in pH < 4. Factors such as concentration, metal recovery procedures, the formation of soluble metal complexes, and subsequently their stability in aqueous solutions are considerably affected by changes in pH values. In this study, it's been clearly demonstrated that the surface charge of the adsorbent can be modified by charging the pH of the solution, and this parameter affected the chemical species in the solution [37]. The reason for diminished adsorption capacity of zinc and cadmium by natural and heat-treated sepiolite at pH 5 in comparison with pH 4 at the high concentrations is the positively charged cationic species that are present in solution and the competition between the excess OH groups in multi-component solutions. On the top side, higher acid concentrations suppress the hydrolysis of the Zn and Cd ions (See **Figures 1** and **2**). The analysis of contact time and Q_t data across multiple pH values and heavy metal concentrations revealed consistent trends in the behavior of the measured parameters. Each plot represents a clear relationship between contact time and the quantity of substance adsorbed (Q_t), with varying slopes and intercepts indicating different kinetic behaviors across the datasets. This consistency across plots facilitates straightforward comparisons between different concentrations and various heat treatments, highlighting any outliers or anomalies that warrant further investigation.

The observed trends suggested that the adsorption kinetics follow a predictable pattern, with most investigated batch systems and displaying a linear or near-linear relationship between contact time and Q_t. This indicates that the adsorption process reaches equilibrium within the studied time frames. Future studies should focus on extending the contact time to explore the possibility of reaching a new equilibrium or identifying any potential secondary kinetics that may occur beyond the observed timeframe. Additionally, replicating this analysis with different substances (e.g., various clay minerals or organo-minerals) could validate the general applicability of the observed trends and further our knowledge of the adsorption mechanisms.

3.2. The effect of heat pre-treatment

The effect of heat pre-treatment on sepiolite was investigated, and it was observed that the specific surface area of sepiolite samples that were heated before application as an adsorbent dominantly increased. Sepiolite heated at 250 °C exhibits a larger surface area compared to sepiolite heated at 150 °C. As observed across all systems, the adsorption capacity of natural and heat-treated sepiolite follows the order: SEP 250 °C > SEP 150 °C > natural SEP. Natural sepiolite contains a significant amount of water in its structure, which is located mostly in channels and is known in terms of zeolitic water [38]. This kind of water can be considered free since it's exposed to heat treatment. By heat treating this mineral, the zeolitic water will be lost, and the specific surface area of this mineral should be increased in comparison to natural sepiolite [39]. The adsorption capacity of heat-treated sepiolite was considerably greater than that of natural sepiolite, e.g., up to 90% of Co ions in the 60 ppm multi-component solutions adsorbed by heat-treated minerals at both pHs 4 and 5 during a short time, and the needed time for adsorbing this amount of Co by natural sepiolite at the same conditions was about 48 h.

Table 1. the results of kinetic adsorption models by natural sepiolite in multi-component solutions at pH 4 and 5.

Temperature treatment	**pH**	**Concentration (ppm)**	**Element**	**Intraparticle diffusion**			**Pseudo-first order**			**Pseudo-second order**		
				K_i	C	R^2	K_1	Q_e	R^2	K^2	Q_e	R^2
22.5 ± 0.2	4	20	Cd	0.018	0.5	0.752	0.001	0.584	0.907	0.021	1.256	0.999
	4	20	Co	0.006	1.151	0.623	0.001	0.149	0.658	0.223	1.845	1
	4	20	Zn	0.022	0.811	0.638	0.001	0.674	0.851	0.027	1.730	0.999
	4	80	Cd	0.023	2.199	0.728	0.00	1.144	0.887	0.026	3.311	0.996
	4	80	Co	0.042	4.546	0.853	0.00	0.054	0.894	0.044	6.410	0.999
	4	80	Zn	0.042	3.289	0.826	0.001	1.496	0.862	0.039	5.128	0.999
	4	160	Cd	0.029	2.461	0.543	0.001	0.854	0.873	0.053	3.663	0.999
	4	160	Co	0.032	6.304	0.794	0.001	1.141	0.921	0.081	7.752	0.999
	4	160	Zn	0.084	3.965	0.821	0.001	3.062	0.945	0.024	7.633	0.998
Temperature treatment	pH	Concentration (ppm)	Element	Intraparticle diffusion			Pseudo-first order			Pseudo-second order		
				K_i	C	R^2	K_1	Q_e	R^2	K^2	Q_e	R^2
22.5 ± 0.2	5	20	Cd	0.016	0.931	0.895	0.002	0.733	0.996	0.023	1.680	0.998
	5	20	Co	0.009	1.601	0.750	0.002	0.216	0.566	0.125	1.960	1
	5	20	Zn	0.007	1.341	0.968	0.00	0.414	0.976	0.037	1.718	0.998
	5	80	Cd	0.025	1.432	0.875	0.00	1.200	0.940	0.018	2.660	0.993
	5	80	Co	0.057	4.925	0.847	0.001	2.609	0.969	0.024	7.692	0.997
	5	80	Zn	0.05	2.814	0.755	0.001	1.670	0.893	0.029	4.975	0.998
	5	160	Cd	0.041	1.26	0.890	0.001	1.499	0.872	0.016	3.096	0.997
	5	160	Co	0.112	9.078	0.908	0.00	5.596	0.977	0.019	14.705	0.995
	5	160	Zn	0.043	2.997	0.783	0.001	1.831	0.866	0.021	5.050	0.996

Table 1 shows the statistical analysis for the kinetic adsorption results of unmodified sepiolite in multi-ionic solutions at pH 4 and 5. The adsorption of Cd, Co,

and Zn was evaluated at three different concentrations (20 ppm, 80 ppm, and 160 ppm) and analyzed using the mentioned kinetic models, including intraparticle diffusion, pseudo-first order, and pseudo-second order. At pH 4, the pseudo-second-order model provided the highest R^2 values across all concentrations and ions, indicating that this model best describes the adsorption process. For instance, at 20 ppm, the R^2 values for Cd, Co, and Zn were 0.999, 1, and 0.999, respectively. This suggests that the rate-limiting step might involve chemisorption. Similarly, at pH 5, the pseudo-second-order model again showed superior fitting, with R^2 values consistently close to 1. For instance, at 80 ppm, the R^2 values for Cd, Co, and Zn were 0.998, 0.998, and 0.998, respectively. The intraparticle diffusion model, while not the best fit, indicated that intraparticle diffusion might also play a role, especially for higher concentrations.

Table 2. the results of kinetic adsorption models by 150 °C heat treated sepiolite in multi-component solutions at pH 4 and 5.

Temperature treatment	**pH**	**Concentration (ppm)**	**Element**	**Intraparticle diffusion**			**Pseudo-first order**			**Pseudo-second order**		
				k_i	C	R^2	K_1	Q_e	R^2	K_2	Q_e	R^2
150 °C heat treated	4	20	Cd	0.013	0.758	0.688	0.001	0.478	0.902	0.027	1.335	0.998
	4	20	Co	0.002	1.757	0.752	0.001	0.080	0.774	0.365	1.866	1
	4	20	Zn	0.018	0.990	0.674	0.001	0.608	0.798	0.033	1.770	0.999
	4	80	Cd	0.021	2.516	0.833	0.001	0.905	0.943	0.035	3.508	0.998
	4	80	Co	0.038	4.736	0.890	0.001	1.445	0.940	0.048	6.451	0.999
	4	80	Zn	0.037	4.008	0.833	0.001	1.298	0.912	0.051	5.618	0.999
	4	160	Cd	0.039	3.013	0.771	0.00	1.464	0.855	0.036	4.695	0.999
	4	160	Co	0.042	6.450	0.895	0.00	1.816	0.965	0.044	8.475	0.999
	4	160	Zn	0.082	4.891	0.788	0.001	2.821	0.921	0.033	8.403	0.999
Temperature treatment	pH	Concentration (ppm)	Element	Intraparticle diffusion			Pseudo-first order			Pseudo-second order		
				k_i	C	R^2	K_1	Q_e	R^2	K_2	Q_e	R^2
150 °C heat treated	5	20	Cd	0.007	1.342	0.831	0.001	0.320	0.966	0.053	1.692	0.999
	5	20	Co	0.009	1.601	0.750	0.001	0.050	0.663	0.695	1.976	1
	5	20	Zn	0.008	1.363	0.944	0.00	0.378	0.959	0.042	1.751	0.999
	5	80	Cd	0.017	1.864	0.899	0.001	0.786	0.976	0.030	2.680	0.998
	5	80	Co	0.056	5.156	0.869	0.001	2.375	0.955	0.029	7.812	0.998
	5	80	Zn	0.03	4.00	0.916	0.001	1.324	0.952	0.037	5.464	0.998
	5	160	Cd	0.039	2.395	0.806	0.00	1.388	0.788	0.035	4.048	0.999
	5	160	Co	0.113	9.435	0.938	0.001	5.296	0.970	0.021	15.151	0.997
	5	160	Zn	0.035	4.125	0.627	0.002	0.774	0.828	0.120	5.494	1

Tables 2 and **3** present the kinetic adsorption results of heat-treated sepiolite, respectively, for 150 °C and 250 °C. The pseudo-second-order model continued to exhibit the highest R^2 values, indicating its suitability in describing the adsorption kinetics of heat-treated sepiolite. At pH 4 and 80 ppm, the R^2 values for Cd, Co, and Zn were 0.998, 0.999, and 0.999, respectively, for sepiolite treated at 150°C. Similarly, for heat-treated sepiolite at 250 °C, the R^2 values were 0.999 for Cd, Co, and Zn,

confirming the dominance of the pseudo-second-order kinetics. Interestingly, the heat treatment seemed to enhance the adsorption capacity (Q_e) of sepiolite, specifically by increasing the heat treatment temperature and by increasing the concentrations. For example, at 160 ppm and pH 4, the Q_e values for Cd increased from 3.663 mg. g^{-1} in natural sepiolite to 5.236 mg. g^{-1} in sepiolite treated at 250 °C. This enhancement suggests that heat treatment modifies the sepiolite structure, potentially increasing the number of active sites available for contaminant adsorption. The intraparticle diffusion model's k_i values also increased with heat treatment, indicating improved diffusion rates within the sepiolite matrix. Overall, these results highlighted the significant impact of heat treatment and pH on the adsorption kinetics of heavy metals by Iranian sepiolite.

Table 3. the results of kinetic adsorption models by 250 °C heat treated sepiolite in multi-component solutions at pH 4 and 5.

Temperature treatment	**pH**	**Concentration (ppm)**	**Element**	**Intraparticle diffusion**			**Psudo-first order**			**Psudo-second order**		
				k_i	C	R^2	K_1	Q_e	R^2	K_2	Q_e	R^2
250 °C heat treated	4	20	Cd	0.012	0.935	0.842	0.001	0.476	0.926	0.031	1.473	0.998
	4	20	Co	0.001	1.859	0.655	0.00	0.054	0.894	0.344	1.912	1
	4	20	Zn	0.015	1.186	0.602	0.001	0.495	0.787	0.041	1.818	0.999
	4	80	Cd	0.023	3.121	0.832	0.001	0.809	0.926	0.061	4.115	0.999
	4	80	Co	0.036	4.867	0.935	0.001	1.567	0.988	0.04	6.579	0.999
	4	80	Zn	0.041	4.347	0.859	0.001	1.496	0.896	0.046	6.173	0.999
	4	160	Cd	0.040	3.560	0.785	0.001	1.120	0.792	0.057	5.236	0.999
	4	160	Co	0.078	6.337	0.944	0.001	3.807	0.952	0.019	10.309	0.995
	4	160	Zn	0.077	5.634	0.853	0.00	3.560	0.890	0.026	9.174	0.998
Temperature treatment	pH	Concentration (ppm)	Element	Intraparticle diffusion			Psudo-first order			Psudo-second order		
				k_i	C	R^2	K_1	Q_e	R^2	K_2	Q_e	R_2
250 °C heat treated	5	20	Cd	0.007	1.446	0.873	0.00	0.339	0.916	0.054	1.782	0.999
	5	20	Co	0.001	1.915	0.467	0.001	0.026	0.573	1.566	1.976	1
	5	20	Zn	0.007	1.440	0.910	0.00	0.317	0.938	0.058	1.770	0.999
	5	80	Cd	0.020	2.221	0.722	0.001	0.687	0.833	0.057	3.096	0.999
	5	80	Co	0.054	5.328	0.900	0.001	2.279	0.939	0.030	7.874	0.998
	5	80	Zn	0.033	4.243	0.944	0.00	2.063	0.951	0.026	5.952	0.997
	5	160	Cd	0.038	2.681	0.819	0.001	1.378	0.903	0.033	4.367	0.999
	5	160	Co	0.115	9.686	0.940	0.00	5.425	0.959	0.022	15.384	0.997
	5	160	Zn	0.043	4.571	0.764	0.00	1.586	0.813	0.050	6.410	0.999

3.3. Effect of contact time

The effect of contact time on the adsorption of Cd, Co, and Zn was analyzed kinetically over a range of 5 min to 48 h. The parameter of contact time is an important factor because it can reflect the adsorption kinetics of an adsorbent for a given initial concentration of the adsorbate [40]. The experimental data showed that by lapsing the contact time from 5 min to 48 h, the adsorption of heavy metals on natural and heat-treated sepiolite samples increased. Although the sorption equilibrium for each system was different from the others, the equilibrium was achieved within the initial 480 min (**Figures 1** and **2**). clearly indicates that the sorption of Cd, Co, and Zn at different concentrations in all systems increased instantly at the initial stage of the adsorption process and then increased gradually until the equilibrium was reached and after that remained constant. Similar results have been reported in research done by Bektas et al. [41], when they studied the removal of Lead from aqueous solutions by natural sepiolite [41]. Shirvani et al., indicated that by increasing contact time between the mineral adsorbent and heavy metals, the adsorption was increased [42].

3.4. Effect of initial solute concentration

The removal amounts of Cd, Co and Zn were calculated in term of q_t and the value of q_t against the contact times for all multi-component solutions showed that by increasing the initial concentrations from 60 ppm to 240 ppm and then to 480 ppm, the amounts of adsorbed heavy metals on adsorbent increased. It was clear that, due to the high adsorption capacity of sepiolite, by increasing the solute concentrations, the sorption equilibrium will be reached at higher qt values. However, by increasing concentrations in initial solutions, the interactions between cationic species with each other and competitions for adsorption sites will be increased. Similar results have been reported by other researchers [43].

3.5. The effect of heavy metals competition in aqueous solutions

Experimental data showed that the adsorption of Cobalt ions by natural and heat-treated sepiolite at all concentrations and for both investigated pH solutions was greater than the adsorption of Cd and Zn. The reason for this difference must be attributed to the atomic characteristic of Co and to the adsorption properties of sepiolite for adsorbing cations in multi-component solutions [44]. The Co with atomic number of 27, has smaller cationic size compared to Zn and Cd, with atomic numbers of 30 and 48, respectively. Under the same conditions, the quantity of absorbed heavy metal by natural and modified sepiolite layer increases for smaller cations [45]. This increase can be supported by this hypothesis that small cations are adsorbed in channels and on the exchangeable structural sites of the sepiolite [46]. Similar results have been reported by Brigatti et al. [47], where they studied the removal of heavy metals Co^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} by sepiolite and they showed that the amount of heavy metal sorbed by sepiolite layer increases for smaller cations [47]. Also, Kocaoba and Akyuz, studied the effect of pH, concentration, stirring time, stirring speed and sorption amount on adsorption, thus they indicated that the adsorption of Co by natural sepiolite was more than Ni, at all those factors [48].

3.6. Adsorption percentages

As can be seen in **Figure 3**, the adsorption experiments conducted under various conditions revealed distinct adsorption efficiencies for the sepiolite mineral. At pH 4, the unmodified sepiolite showed varying adsorption percentages for Cd, Co, and Zn, demonstrating a gradual increase over time. The treatment at 150 °C significantly enhanced the adsorption capacity, particularly for Co and Zn, indicating a possible modification of the mineral's surface properties that facilitated better adsorption. The 250 °C pretreatment, however, showed a different trend, with the adsorption percentages for Cd remaining relatively high while those for Co and Zn plateaued, suggesting that higher temperatures might lead to structural changes in the sepiolite, affecting its adsorption behavior differently for each metal. These results underscore the importance of both pH and thermal pretreatment in optimizing the adsorption efficiency of sepiolite for heavy metal removal.

The varying adsorption efficiencies observed under different conditions highlight the complex interplay between pH, temperature, and the mineral's adsorption capacity. The increased efficiency at pH 4 and 150 °C suggests that moderate thermal activation enhances the active sites available for adsorption, possibly by increasing the surface area or altering the surface chemistry to favor heavy metal interaction. However, the plateau observed at 250 °C indicates a potential limit to thermal activation, beyond which structural integrity might be compromised, reducing the number of effective adsorption sites. This finding aligns with previous studies that suggest optimal adsorption conditions are specific to the type of heavy metal and the physicochemical properties of the adsorbent [49]. Future research could further elucidate the mechanisms behind these observations, providing deeper insights into optimizing adsorption processes for environmental remediation.

3.7. Kinetic analysis

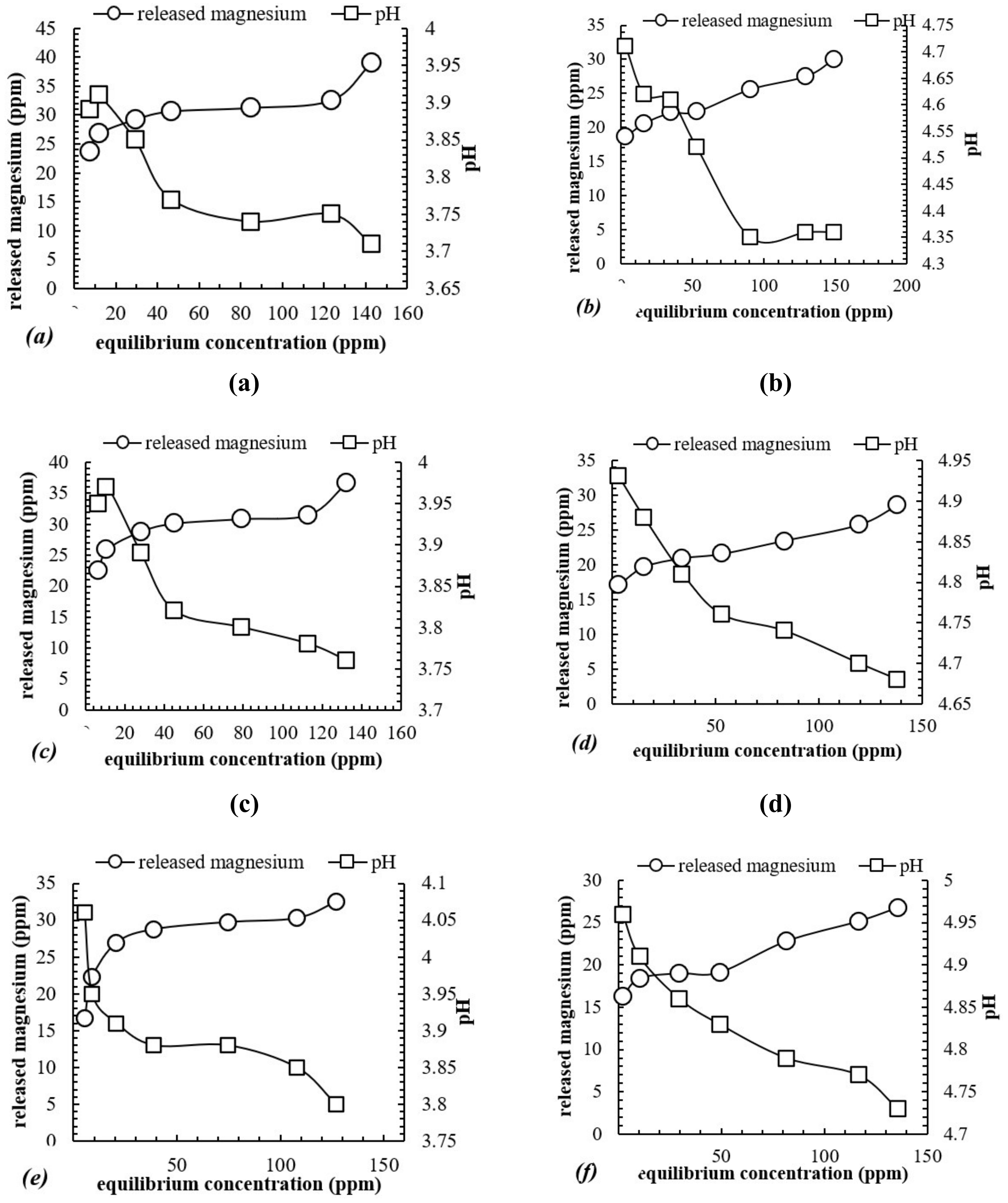
Sorption data have been interpreted via Pseudo-first and Pseudo-second order and the Intra-particle diffusion kinetic models. From the testing of plots which, q_t versus $t^{1/2}$, ln (q_e−q_t) versus t and (t/q_t) versus t, the rate constants k_i, k_1, and k_2, and correlation coefficients are calculated in **Tables 1–3** for the unmodified, 150 °C, and 250 °C heat treated sepiolite, respectively and a good correlation coefficient (R^2) obtained for the pseudo-second order kinetic model. It was reported that the Pseudo-second order model with the ($R^2 \geq 0.999$) yields the best linearity model than the Pseudo-first and the Intra-particle diffusion model as R^2 values are compared [30,50].

The adsorption kinetic data were analyzed by an intraparticle diffusion model to determine the rate and the quantity of adsorbing cations in the adsorption process. Furthermore, the Intra-particle diffusion kinetic model suggests that the adsorption process could be controlled by the internal diffusion with a partial effect of the external diffusion [51]. The fitted data via this model showed correlation coefficients mostly less than 0.9 and revealed the fact that the Intraparticle diffusion model couldn't adequately support the adsorption process in these experiments. Similar results reported by Dada et al. [52], which investigated the parameters for modeling the kinetics with statistical validity, desorption and adsorption of Cu (II) ions onto zerovalent iron nanoparticles [52]. Also, Wang et al. [53] demonstrated that Interparticle diffusion model is not the controlling factor in determining the kinetics of Cd adsorption on clay minerals [53]. Also from the comparison data of Pseudo-first and the Pseudo-second order models, this fact clarified that all investigated parameters in the Pseudo-second order including adsorption capacity at time t (Q_e), the rate constant (k_2) and correlation coefficient (R^2) were more than adsorption capacity at time t (Q_e), the rate constant (k_1) and correlation coefficient (R^2) in Pseudo-first order which indicated that the adsorption kinetic process was well supported by the Pseudo-second order model. Other scientists reported that the adsorption from liquid solutions has been extensively studied, with a wealth of experimental data focusing on the adsorption capabilities of various materials towards different solutes. While many studies include both equilibrium and kinetic data, a common practice involves fitting the kinetic data to empirical models. Among these, the pseudo-first and pseudo-second order models are widely used, particularly in their linearized forms. Even though the pseudo-second order model often achieves excellent fitting quality, it lacks a physical basis and is inconsistent with the understanding that diffusion processes govern adsorption kinetics [54]. The present study demonstrates, through examples and analysis, that the apparent success of the Pseudo-second order model in fitting data is better compared to the two other employed kinetic models.

3.8. Released magnesium

In this study, the release of Mg^{2+} from the sepiolite structures into the solutions was investigated, along with the pH changes in the final solutions. Atomic adsorption measurements indicated that more Mg^{2+} was released from unmodified sepiolite compared to heat-treated samples, with minerals heated at 150 °C releasing more Mg^{2+} than those heated at 250 °C. These findings suggest cation exchange between the investigated heavy metals and structural Mg^{2+}. The differences in released magnesium quantities are due to the increased surface area and adsorption capacity of heated samples in comparison with natural ones. The magnesium at the edges of the octahedral sheets in 250 °C heated minerals, influenced by zeolitic water and increased surface area, was less than in 150 °C heated and unmodified mineral samples. Therefore, magnesium at the edges of octahedral sheets in natural sepiolite exchanged more with existing cationic ions in experimental solutions. Lazarevic et al. [35] reported that acid-treatment on sepiolite led to magnesium leaching from octahedral sheets and exchange with lead (Pb) ions in solutions. Miura et al. [33] observed that thermal, acid, and base treatments degraded sepiolite's fibrous morphology, with high-temperature or long-term treatments and acid treatments increasing the sepiolite surface area.

Figures 3 shows the changes in pH values and released magnesium corresponding to heavy metal concentrations. At low equilibrium concentrations, the acidic content of the solutions, the freedom effect of solute ions, and the high adsorption ability of sepiolite resulted in high Mg^{2+} release, which interacted with OH^- ions, brought about decreasing °C the final pH of the solution. Since the initial heavy metal concentrations increased, pH values decreased, and magnesium release increased smoothly. Continued increases in heavy metal concentrations led to significant Mg^{2+} release and pH decreases due to the exchangeable effect of magnesium with the investigated positive charge ions (See **Figure 4a–f**).



(a) **(b)**

(c) **(d)**

(e) **(f)**

Figure 4. The changes in pH values and released magnesium correspond to heavy metal concentrations. **(a)** Natural sepiolite in solution with pH 4 values; **(b)** Natural sepiolite in solution with pH 5 values; **(c)** heat pretreated sepiolite at 150 °C in solution with pH 4 values; **(d)** heat pretreated sepiolite at 150 °C in solution with pH 5 values; **(e)** heat pretreated sepiolite at 250 °C in solution with pH 4 values; **(f)** heat pretreated sepiolite at 250 °C in solution with pH 5 values.

The ability to regenerate and reuse sepiolite adsorbent is crucial for its sustainability and economic viability in real-world applications. While this study focused on sepiolite's capacity to remove Cd, Co, and Zn ions, the thermal pretreatment at 250 °C that enhanced its adsorption also opens the door for efficient regeneration. Previous research has shown that heat-treated absorbents can often be restored through simple thermal or chemical processes, which release bound ions and reactivate adsorption sites [55]. Given sepiolite's stability at moderate temperatures, it's likely that the material can be regenerated and reused multiple times without significant performance loss. Although, according to the natural condition of sepiolite constitution, the mineral's original structure will be changed but the adsorption capacity for future uses will remain.

Future studies should explore the regeneration potential of heat-treated sepiolite through desorption experiments. These experiments should assess both the adsorbent's efficiency over multiple cycles and its long-term structural integrity. Such investigations are essential for confirming sepiolite's suitability for large-scale environmental remediation as a sustainable adsorbent. On the other hand, given the abundant and low-cost availability of sepiolite in Iran, these methods and minerals present viable options for use in wastewater treatment.

4. Conclusion

The present study successfully indicates the enhanced adsorption capacities of heat-treated sepiolite for the removal of contaminant heavy metals from wastewaters. The findings indicated that heat pretreatment at 250 °C considerably increased the potential surface area and adsorption efficiency of sepiolite, specifically for Co^{2+} ions. The pseudo-second order kinetic model best fitted the experimental data and suggested chemisorption as the primary adsorption mechanism. The effect of pH on adsorption efficiency showed the importance of optimizing solution conditions for effective heavy metal removal. These understandings can inform low-cost and sustainable approaches for wastewater treatment, to provide readily available and easily modified natural adsorbents like sepiolite. Moreover, future research can focus on exploring the long-term stability of heat-treated sepiolite in various environmental conditions and its scalability for industrial applications.

Although the present study primarily focused on Cd, Co, and Zn, the kinetic experiments were performed in multi-ionic solutions that reflect real-world conditions. The influence of additional ions, including H^+ and OH^- at varying pH levels, was considered, particularly in the analysis of adsorption behavior. However, it would be acknowledged that a more comprehensive investigation involving a wider range of competing ions (e.g., Na^+, Ca^{2+}, Mg^{2+}) could provide deeper insights into competitive adsorption dynamics. Future work should extend these findings by examining the impact of these common ions in multi-component solutions to better understand their role in metal ion adsorption efficiency and adsorption site competition. This would provide a more complete understanding of the adsorption mechanisms in complex environmental matrices.

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writing—review and editing, AL; visualization, RS and SH; supervision, AL; project administration, RS; funding acquisition, AL. All authors have read and agreed to the published version of the manuscript.

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