



Ministry of Science, Research & Technology
Iranian Research Organization
for Science and Technology

Research paper

Synthesis and characterization of Ni-doped CaTiO₃ nano-powders and their potential for the removal of Cd from wastewaters

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HIGHLIGHTS

- A simple method was applied for the construction of Ni-doped CaTiO₃ nano-powders from commercial CaCO₃ and TiO₂.
- The as-prepared sample was characterized by XRD, FE-SEM, and FT-IR techniques.
- The sample composed of small grains with an average size of 78 nm.
- The method could be a useful, inexpensive and efficient tool for the preparation of Ni-doped CaTiO₃ nano-powders.
- The Ni-doped CaTiO₃ nano-powder was most efficient for the removal of Cd²⁺ from water media.

ARTICLE INFO

Article history:

Received 8 June 2022

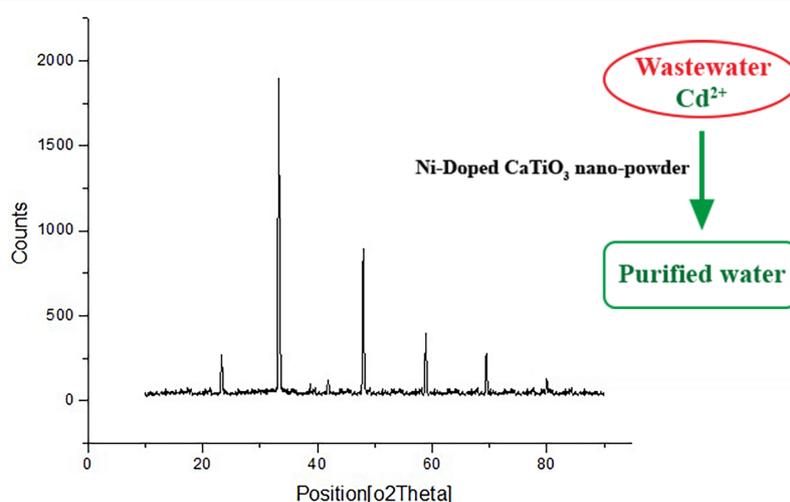
Revised 11 October 2022

Accepted 15 October 2022

Keywords:

CaTiO₃ Nano-powders
Ni-Doped CaTiO₃
Cd²⁺ Removal
Wastewater
Adsorption experiment

GRAPHICAL ABSTRACT



ABSTRACT

A simple method was applied to construct Ni-doped CaTiO₃ nano-powders from commercial CaCO₃ and TiO₂, characterized by XRD, FE-SEM, and FT-IR. The sample was composed of small grains with an average size of 78 nm. This method could be a useful, inexpensive, and efficient tool for the preparation of Ni-doped CaTiO₃ nano-powders. The prepared sample was used for the removal of Cd²⁺ from water media. Results indicated that Cd²⁺ removal by Ni-doped CaTiO₃ nano-powders was very efficient (100% removal yield) when the pH was adjusted to 4.5, the catalyst dosage amounted to 0.05 g, and the Cd²⁺ solution concentration was 60 mg.L⁻¹. A pseudo-second-order kinetic model described the kinetics of Cd²⁺ removal.

1. Introduction

Pollution is one of the most important factors leading to the wastage of water resources due to the discharge of domestic, urban, and industrial wastewater. Industrial activities have increased the presence of heavy metals in urban wastewater. Industrial effluents contain significant amounts of metals such as chromium, nickel, cadmium, and zinc, which cause many environmental problems if not decomposed. Wastewater contaminated with heavy metals threaten human health and plant and animal ecosystems if it enters the environment. Limited water resources and the risk of a water shortage crisis make it necessary to correct contaminated water [1-4]. Cadmium is a highly toxic metal due to its effects on vital human organs, such as lungs, kidneys, and bones, that cause congenital disabilities and human deaths. Cadmium enters the aquatic ecosystems through soil and bedrock erosion, atmospheric pollution, wastewater, contaminated sludge areas, and the use of fertilizers in agriculture. With the proliferation of different industries, wastewater produced by industrial processes has become a significant threat to the environment. The pollution of wastewater by heavy metals such as cadmium ions has a devastating effect on human health, organisms, and the human food chain. Refining industrial wastewater is necessary due to the detrimental environmental effects of cadmium [3,5-8].

Many methods are used to remove heavy metal ions, including filtration, coagulation, adsorption, oxidation, reverse osmosis, ion exchange, precipitation, etc. Among these methods, the adsorption process is widely used due to the abundance and availability of adsorbents such as clay, activated carbon, zeolites, etc. However, the high cost of some adsorbents, such as activated carbon, makes the removal method too expensive to be practical. The adsorption technique is widely used for simple operations, low power consumption, easy maintenance, and greater efficiency for wastewater treatment. In recent years, the use of nanomaterial sorbents with remarkable results in pollution removal has been increasing. Nanomaterials have a high surface area and more active sites to adsorb heavy metals [9-12]. Calcium titanate (CaTiO_3) is a ferroelectric perovskite structure oxide with the general formula of ABO_3 , in which A is a divalent metal ion and B is a tetravalent metal ion. The remarkable dielectric and magnetic properties and unique electrical characteristics have

led to their widespread use in different fields, including materials science, geology, chemistry, and physics. CaTiO_3 has a good potential to be used as a microwave resonator because of its high dielectric constant of $\epsilon = 180$ at room temperature. CaTiO_3 can be widely used in electronic ceramics and catalyzes the partial oxidation of light hydrocarbons. Initially, calcium titanate was prepared by a conventional solid-state reaction between titanium dioxide (TiO_2) and calcium oxide (CaO) or calcium carbonate (CaCO_3). However, the thermal stability of CaO and TiO_2 makes this method too difficult to use. On the other hand, the heterogeneity of the sample, contamination with impurities, the high temperature necessary, the presence of coarse particles with different sizes, and non-uniform distribution are the main disadvantages of this method [13-18].

In this study, we first report a cost-effective, and eco-friendly method for preparing Ni-doped CaTiO_3 by applying NiO, CaCO_3 , and TiO_2 . Then, the catalytic removal of Cd^{2+} from wastewater was investigated.

2. Materials and methods

All reagents were purchased from Merck and Aldrich and used without further purification. The powder X-Ray diffraction patterns were measured with D8, Advance, Bruker, axs, and diffractometer using $\text{Cu-K}\alpha$ irradiation. Field emission scanning electron microscope (FE-SEM) images were obtained on HITACHI S-4160. Dynamic light scattering (DLS) was measured using a Malvern Zetasizer Nano ZS (ZEN 3600) instrument.

2.1. Preparation of Ni-doped CaTiO_3 nano-powders

In a 100 ml alumina crucible, NiO (0.5 mmol), CaCO_3 (20 mmol, 2 g), TiO_2 (20 mmol, 1.6 g), and aminoethanol (80 mmol, 4.88 g) were mixed. Next, the mixture was placed in an electric furnace and calcined at 1000 °C for 2 h. Then, CaTiO_3 was obtained as a white powder (2.6 g, 96 % yield). Lastly, the mixture was powdered and analyzed.

2.2. Adsorption experiments

$\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ was used as the source of cadmium ions. Each of the solutions was prepared by first dissolving the required amount of $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ in distilled water. Then, an indirect batch equilibrium method was used

to estimate the adsorption parameters at ambient conditions. Results showed that the most effective parameters affecting the sorption process were initial metal concentrations, initial pH, and the amount of Ni-doped CaTiO_3 adsorbent.

2.2.1. Step 1: Effect of pH

A series of Cd^{2+} solutions (30 ml, 60 mg.L^{-1} , initial pH = 5.8) was prepared to evaluate the effect of pH on the removal percentage of Cd^{2+} ions on Ni-doped CaTiO_3 . The pH values of the solutions were then adjusted from 3 to 6 using dilute HCl and NaOH. Next, the samples were stirred in contact with Ni-doped CaTiO_3 (0.05 g) under ambient conditions for 180 min. At 20 min intervals, the concentration of Cd^{2+} was determined using the atomic absorption technique (Varian Spectra A 250 Plus). All experiments were done in acidic media because of Cd precipitation as $\text{Cd}(\text{OH})_2$ at a pH > 7.

The removal percentage (R) was determined as Eq. (1).

$$R = [(C_0 - C_t)/C_0] \times 100 \quad (1)$$

where C_0 (mg.L^{-1}) is the initial Cd^{2+} concentration and C_t (mg.L^{-1}) is the concentration at time t (min).

2.2.2. Step 2: Effect of Cd^{2+} solution concentration and Catalyst dosage

Four different Cd^{2+} solutions with concentrations of 30, 60, 90, and 120 mg.L^{-1} (pH $\approx 5.1 - 5.8$) were mixed with 0.05 g of Ni-doped CaTiO_3 nano-powders, and the mixture was stirred at room temperature (24°C) for 3 h. The concentration of the Cd^{2+} solution was determined using the atomic absorption technique. The same study was performed with different catalyst dosages of 0.01, 0.025, 0.05, and 0.1 g of catalyst while the Cd^{2+} solution (30 mL , 60 mg.L^{-1}) was constant.

3. Results and discussion

3.1. Adsorbent characterization

Fig. 1 shows the FE-SEM photographs of Ni-doped CaTiO_3 nano-powders. The observation results obtained by FE-SEM showed that the sample was composed of small grains less than 100 nm and of uniform shapes. The TEM photograph of Ni-doped CaTiO_3 nano-

powders confirms the nano-sized particles consist of small spherical shaped grains whose dimensions do not exceed 100 nm. Furthermore, the electron diffraction X-ray (EDX) analysis showed the presence of Ni, Ca, Ti, and O, which agrees with our aim to synthesize Ni-doped CaTiO_3 nano-powders (Fig. 1).

The dynamic light scattering (DLS) technique was used to determine the particle size distribution of the Ni-doped CaTiO_3 nano-powders. Before analysis, 1 g of nano-powder was dispersed in 20 ml of ethanol by

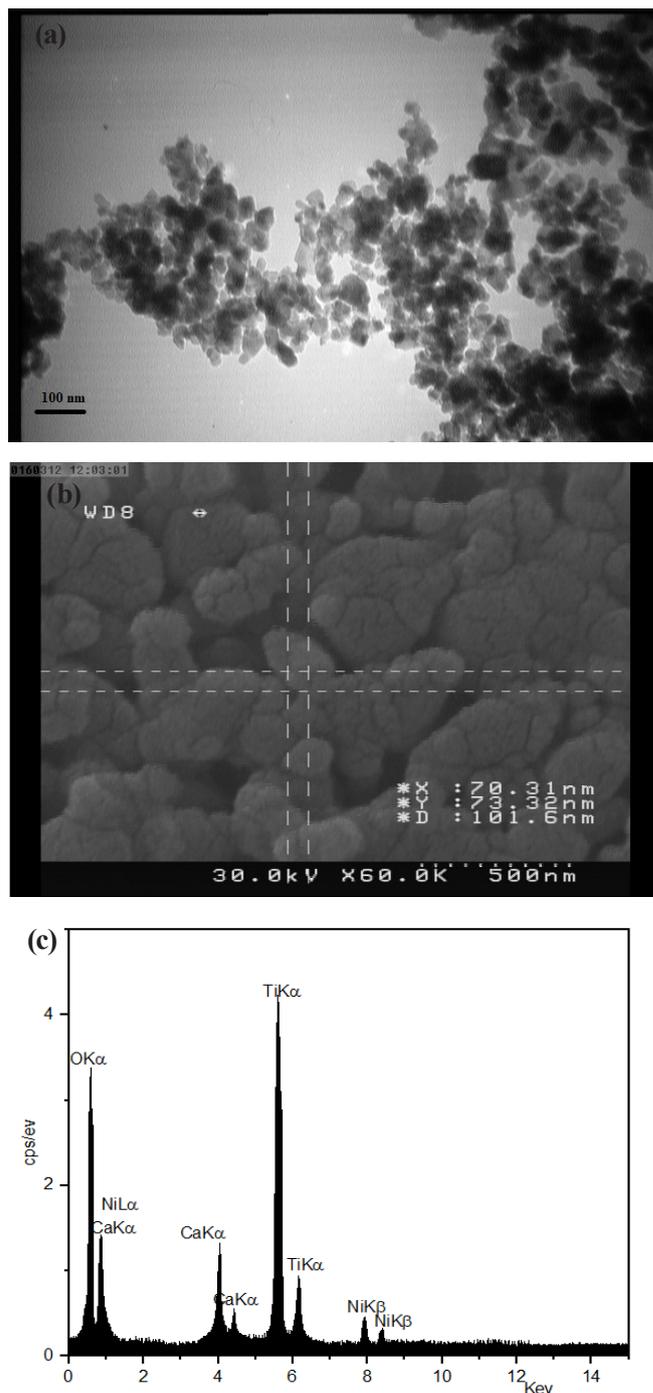


Fig. 1. (a) FE-SEM and (b) TEM micrographs and (c) EDX analysis of Ni-doped CaTiO_3 nano-powders.

ultrasonic irradiation for 30 min. According to DLS measurement, the nanoparticles have an average size of 76 nm (Fig. 2). XRD pattern was used to identify the phase and crystallite size of Ni-doped CaTiO₃ nano-powders (Fig. 3). The pattern is well-matched with the orthorhombic structure of Ni-doped CaTiO₃. Dominant peaks at $2\theta = 23.3, 33.2, 41.8, 47.9, 58.8, 69.4,$ and 79.9 correspond to the (101), (00 2), (040), (321), and (400) planes of orthorhombic CaTiO₃. The crystallite size (D) was calculated from the XRD pattern using Scherrer's equation (Eq. (2)).

$$D = K\lambda / (\beta \cos \theta) \quad (2)$$

where D is the crystal size (nm), θ is the Bragg angle, λ is the Cu-K α cathode wavelength ($\lambda = 0.154\ 056$ nm), β is the full width of the XRD peak with the highest intensity ($2\theta = 33.2$) at half height (radian), and K is a shape factor (≈ 0.9). The average crystallite size was estimated by Scherrer's equation and found to be 79 nm.

The nitrogen adsorption-desorption isotherms and pore size distribution analysis of Ni-doped CaTiO₃ nano-powders are shown in Fig. 4. The N₂ adsorption-desorption isotherms show hysteresis loops of type H₃ with a pattern of type IV, indicating the presence of pores materials. The specific surface area of Ni-doped CaTiO₃ nano-powders was measured using the BET method and determined to be 6.3 m².g⁻¹ (Fig. 4). The BJH method was used to calculate the pore size distribution of the sample, and the pore volume was found to be 0.0487 cm³.g⁻¹. The FT-IR spectrum of Ni-doped CaTiO₃ nano-powders is shown in Fig. 4. The broad peak ranging from 400 to 600 cm⁻¹ is due to the metal-oxygen vibration modes and others at 3200-3500 cm⁻¹ can be attributed to adsorbed water.

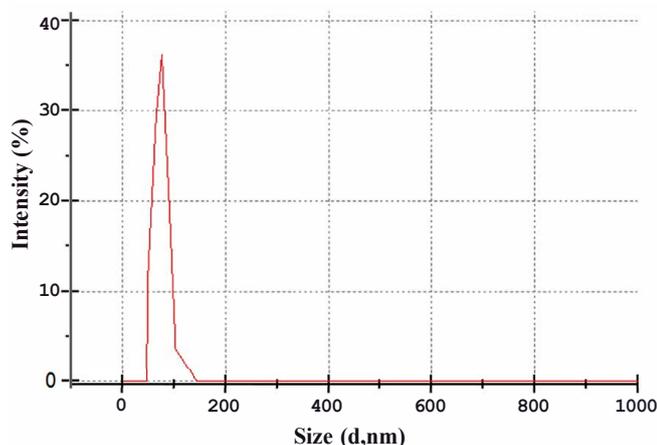


Fig. 2. The DLS analysis of Ni-doped CaTiO₃ nano-powders.

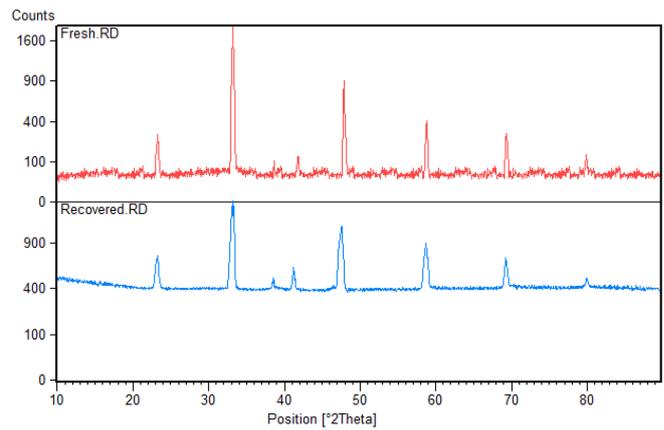


Fig. 3. The XRD pattern of freshly prepared and recovered Ni-doped CaTiO₃ nano-powders.

3.2. Evaluation of Ni-doped CaTiO₃ nano-powders for Cd²⁺ removal

This work investigates the potential of using Ni-doped CaTiO₃ nano-powders to absorb Cd²⁺ ions from water. The effect of different parameters, including pH, Cd²⁺ concentration, and adsorbent dosages, were studied. Each experiment was repeated twice, and the results were reported as an average. The related values are summarized in Table 1.

3.2.1. Effect of pH

The pH value has a significant impact on the removal yield since it determines the surface charge of the Ni-doped CaTiO₃ and the degree of ionization of the cadmium in the solution. In a slightly basic medium

Table 1. The investigated parameters and their values used for the adsorption of Cd²⁺ ions.

pH	Cd ²⁺ Concentration (mg.L ⁻¹)	Adsorbent (g)
3	60	0.05
4.5	60	0.05
6	60	0.05
4.5	60	0.01
4.5	60	0.025
4.5	60	0.05
4.5	60	0.1
4.5	30	0.05
4.5	90	0.05
4.5	120	0.05

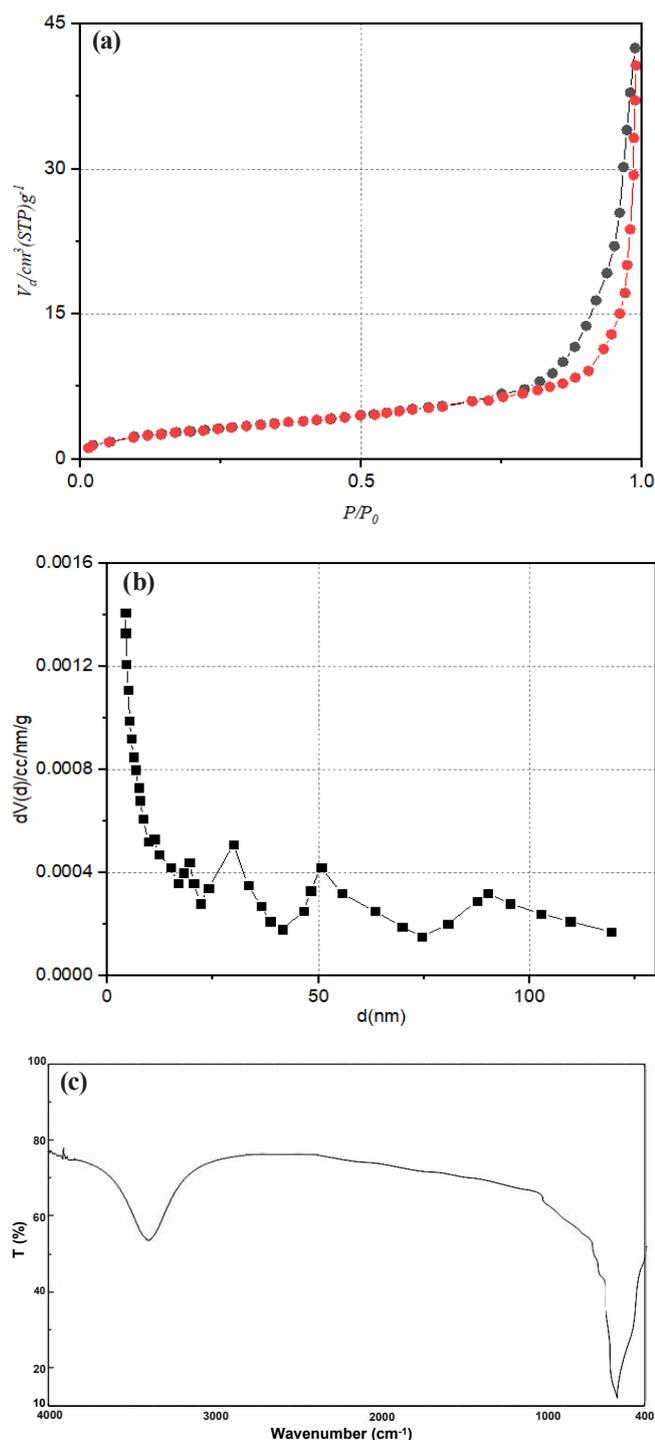


Fig. 4. (a) N_2 adsorption-desorption isotherms, (b) pore size distribution analysis, and (c) FT-IR spectra of Ni-doped CaTiO_3 nano-powders.

($\text{pH} > 7$), the solubility of Cd^{2+} decreased, and $\text{Cd}(\text{OH})_2$ precipitated from the reaction mixture. In a highly acidic media ($\text{pH} < 3$), Ni-doped CaTiO_3 nano-powders decomposed. Thus, the most suitable media had a pH ranging from 3.5 to 6. Keeping this in mind, we examined the role of pH in removing Cd^{2+} ions from an aqueous solution of Cd^{2+} ($60 \text{ mg}\cdot\text{L}^{-1}$) in a pH range of 3.5 to 6, and the results are summarized in Fig. 5.

The complete removal of Cd^{2+} was achieved when the pH value was adjusted to 4.5. The complete removal implies that the catalyst works as an efficient sorbent for Cd^{2+} removal.

3.2.2. Effect of Cd^{2+} solution concentration

The effect of the initial Cd^{2+} concentration was examined using different concentrations of the Cd^{2+} solution, including 30, 60, 90, and 120 $\text{mg}\cdot\text{L}^{-1}$, at an optimum pH value (Fig. 6). The results show that the removal yield increased when the Cd^{2+} solution concentration increased up to 60 $\text{mg}\cdot\text{L}^{-1}$. However, at higher concentrations, the removal decreased. Cd adsorption decreased due to the saturation of the catalyst surface at higher concentrations [19,20].

3.2.3. Effect of catalyst dosage

Generally, as the catalyst concentration increases, the removal rate rapidly increases. So, the effect of catalyst dosage on the removal percentage of Cd^{2+} was investigated ($60 \text{ mg}\cdot\text{L}^{-1}$, $\text{pH} = 4.5$). The catalyst concentration was varied from 0.01 to 0.1 g (Fig. 7). As shown in Fig. 7, the removal percentage of Cd^{2+} was increased from 30 % to 100 % by increasing the catalyst dosages from 0.01 to 0.05 g. A decrease in the removal rate was observed at the higher amount of catalyst dosage. This may be due to the agglomeration of catalyst particles and the reduced specific surface area of the catalyst [19].

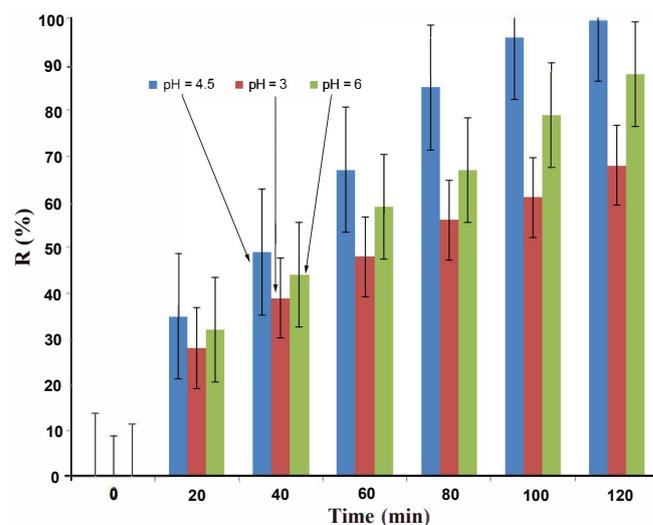


Fig. 5. Effect of pH and contact time on Cd^{2+} adsorption by Ni-doped CaTiO_3 nano-powders [Cd^{2+} concentration: $60 \text{ mg}\cdot\text{L}^{-1}$; catalyst dosage: 0.05 g ($1.7 \text{ g}\cdot\text{L}^{-1}$); solution volume: 30 ml].

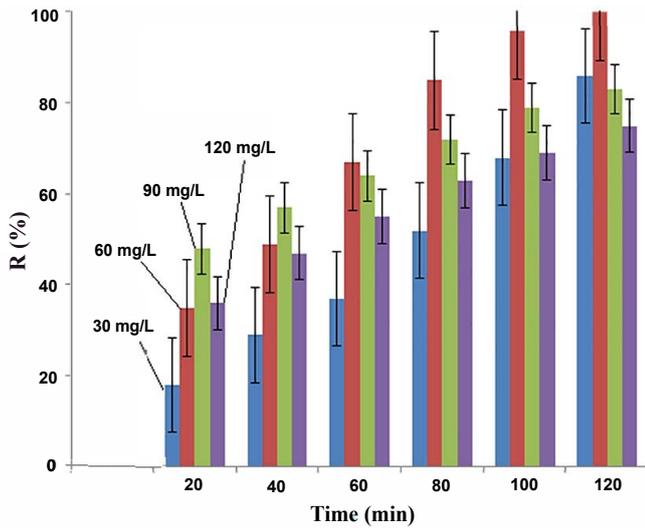


Fig. 6. Effect of Cd²⁺ solution concentration on the adsorption percentage by Ni-doped CaTiO₃ nano-powders [pH = 4.5; catalyst dosage: 0.05 g (1.7 g.L⁻¹); solution volume: 30 ml].

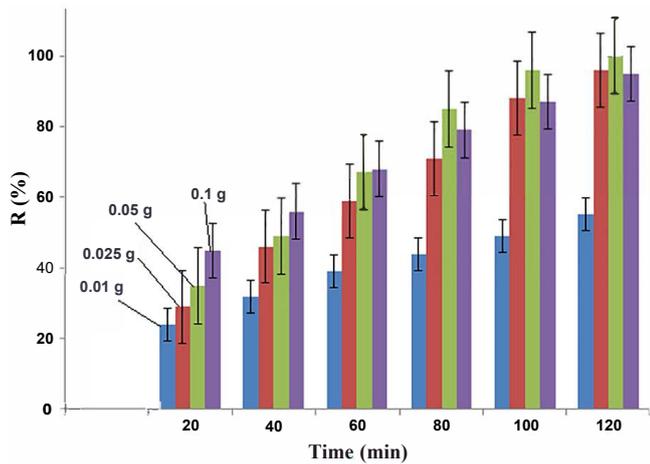


Fig. 7. Effect of catalyst dosage on the adsorption percentage by Ni-doped CaTiO₃ nano-powders [pH = 4.5; Cd²⁺ solution concentration; 60 mg.L⁻¹; solution volume: 30 ml].

3.2.4. Investigation of the adsorption kinetics

The data were fitted to pseudo-first-order and pseudo-second-order models to investigate the sorption kinetics of Cd²⁺ onto the Ni-doped CaTiO₃ nano-powders. The related equations are given as Eqs. (3) and (4) [19].

$$\log (q_e - q_t) = \log q_e(-k_1 t / 2.303) \quad \text{pseudo-first order} \quad (3)$$

$$(t / q_t) = (1 / k_2 q_e^2) + (t / q_e) \quad \text{pseudo-second order} \quad (4)$$

$$q_e = [(C_0 - C_e)V/m]$$

$$q_t = [(C_0 - C_t)V/m]$$

where:

- q_e is the equilibrium adsorption capacity (mg.g⁻¹),
- q_t is the adsorption capacity at time t (mg.g⁻¹),
- k_1 is the pseudo-first order reaction rate constant (min⁻¹),
- k_2 is the pseudo-second order reaction rate constant (g.mg⁻¹.min⁻¹),
- t is the time (min),
- C_0 is the initial concentration at $t = 0$,
- C_e is the concentration at equilibrium time,
- C_t is the concentration at time t .

The k_1 , k_2 , q_e , and R^2 parameters were calculated from first-order and second-order kinetic models as revealed in Figs. 8 and 9. The results are presented in Table 2. Comparing the results of the kinetics models shown in Table 2 showed the pseudo-second order model better fitted to describe the adsorption results.

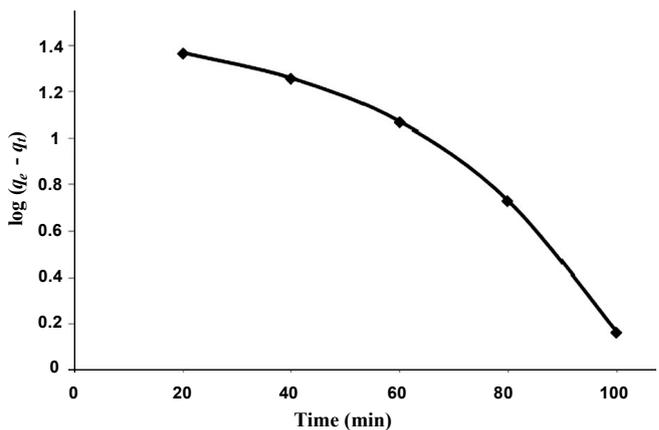


Fig. 8. First-order kinetic model for the Cd²⁺ adsorption by Ni-doped CaTiO₃ nano-powders [pH = 4.5; Cd²⁺ solution concentration; 60 mg.L⁻¹; solution volume: 30 ml; catalyst dosage: 0.05 g (1.7 g.L⁻¹)].

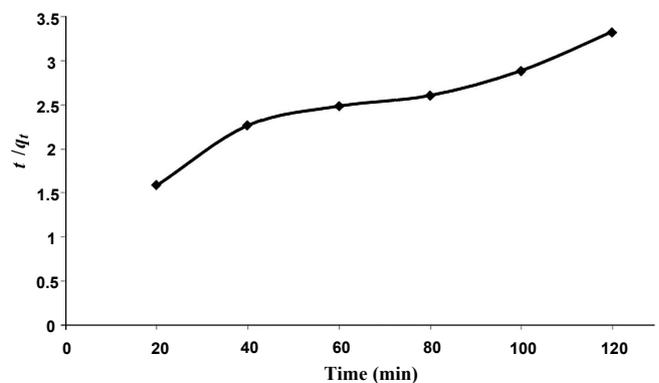


Fig. 9. Second-order kinetic model for the Cd²⁺ adsorption by Ni-doped CaTiO₃ nano-powders [pH = 4.5; Cd²⁺ solution concentration; 60 mg.L⁻¹; solution volume: 30 ml; catalyst dosage: 0.05 g (1.7 g.L⁻¹)].

Table 2. Kinetics parameters of the Cd²⁺ adsorption onto Ni-doped CaTiO₃ nano-powders calculated from first-order and second-order kinetic models (Figs. 8 and 9).

Model	Parameter	Value
Pseudo-first-order	k_1	0.032
	q_e	36
	R^2	0.911
Pseudo-second-order	k_2	1.54×10 ⁻⁴
	q_e	66.7
	R^2	0.942

3.3. Adsorbent reusability and desorption investigations

In order to recover the Cd²⁺ ions and reuse the Ni-doped CaTiO₃ nano-powders, diluted HNO₃ (5 %) was used as a desorption agent. The adsorption-desorption experiments were done three times with 100, 99, and 98 % of Cd removal in the 1st, 2nd, and 3rd runs respectively. The results indicated that the adsorbent could be regenerated and reused efficiently.

3.4. Comparison results

It was found that Ni-doped CaTiO₃ nano-powders perform excellent adsorption for Cd²⁺ ions (100 %), which is comparably higher than various previously reported adsorbents in the literature (Table 3).

4. Conclusions

This study highlights the Ni-doped CaTiO₃ nano-powders potential for removing Cd²⁺ from aqueous media. The sorption process was highly pH-dependent, and an optimum removal of 100 % of Cd²⁺ was observed

at a pH of 4.5 using 0.05 g of catalyst and 60 mg.L⁻¹ concentration of the Cd²⁺ solution. The Cd²⁺ adsorption kinetic was well fitted to the pseudo-second order kinetic model.

Acknowledgments

The authors are indebted to the Islamic Azad University, Najafabad Branch for financial support of this research.

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Table 3. Comparison results with other adsorbents.

Adsorbent	Contact time (min)	Elimination yield (%)	Reference
Ni-Doped CaTiO ₃	120	100	This work
CaTiO ₃	120	87	This work
Clay of Ain Dorrij Ouezzane Morocco	120	75	21
Clay of Sale Morocco	150	79	22
Alkali-Modified Agricultural Waste	180	85	23
CuO/Hydroxyethyl cellulose membrane	120	97.14	24
Al ₂ O ₃ -NaA Zeolite membrane	12 h	99.9	25

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