Research Article/Chemical, Food, and Environmental Engineering http://doi.org/10.15446/ing.investig.114741

Activation of Coal Fly Ash for Cadmium Wastewater Remediation

Activación de ceniza volante de carbón para la remediación de aguas residuales contaminadas con cadmio

Yareli Ginalis Medina [1] and Roberto Flores [2]

ABSTRACT

Industrial wastewater contamination by heavy metals is a major environmental issue. Various techniques and materials have been proposed to address this problem, including those related to the adsorption process. However, new, improved, and low-cost materials must be developed and proposed in order for these strategies to be competitive. This study aims to investigate the remediation of water contaminated with cadmium, *i.e.*, Cd(II), using activated coal fly ash, a low-cost sorbent, as it is the byproduct of an industrial process. Coal fly ash was chemically treated in acidic and alkaline mediums and activated using ultrasonic energy to enhance the materials and increase the uptake of Cd(II). Controlling the pH was found to be crucial, as the maximum sorption capacity occurred at pH 6. The materials activated in an alkaline medium with ultrasound were able to adsorb more significant amounts of Cd(II) under the studied experimental conditions and over four cycles of adsorption experiments. Finally, the kinetics of the adsorption process were analyzed, and some mathematical kinetics models were proposed to simulate the experimental data. After statistical discrimination, the Elovich isotherm was selected to represent the adsorption of Cd(II) in the different materials studied.

Keywords: coal fly ash, ultrasonic activation in alkaline mediums, cadmium wastewater remediation, pH effect, kinetics parameter estimation, Elovich isotherm

RESUMEN

La contaminación de aguas residuales industriales por metales pesados es un problema medioambiental importante. Se han propuesto varias técnicas y materiales para abordar esta problemática, incluyendo aquellas relacionadas con el proceso de adsorción. No obstante, es necesario desarrollar y proponer materiales nuevos, mejorados y de bajo costo para que estas estrategias sean competitivas. Este estudio tiene como objetivo investigar la remediación de agua contaminada con cadmio, *i.e.*, Cd(II), utilizando cenizas volantes de carbón activado, un sorbente de bajo costo, pues es un subproducto de un proceso industrial. Las cenizas volantes de carbón se trataron químicamente en medios ácidos y alcalinos y se activaron mediante energía ultrasónica para mejorar su capacidad de adsorción de Cd(II). El control del pH resultó crucial, ya que la máxima capacidad de adsorción se produjo a un pH de 6. Los materiales activados en medio alcalino mediante ultrasonido pudieron adsorber cantidades más significativas de Cd(II) bajo las condiciones experimentales estudiadas y en cuatro ciclos de adsorción. Finalmente, se analizó la cinética del proceso de adsorción y se propusieron algunos modelos cinéticos matemáticos para simular los datos experimentales. Después de una discriminación estadística, se seleccionó la isoterma de Elovich para representar la adsorción de Cd(II) en los diferentes materiales estudiados.

Palabras clave: ceniza volante de carbón, activación con ultrasonido en medio alcalino, remediación de agua de desecho con cadmio, efecto de pH, estimación de parámetros cinéticos, isoterma de Elovich

Received: May 29th, 2024
Accepted: May 8th, 2025

Introduction

Cadmium – Cd(II) – contamination in agricultural soils has been shown to affect plant growth and health [1]–[5]. High levels of Cd(II) significantly reduce crop yield, potentially resulting in plant mortality. Cd(II) also alters plant height, root length, and the fresh weight of roots, stems, and leaves. In addition, it changes the uptake and transport of essential nutrients, resulting in nutrient deficiencies within the plants. Cd(II) toxicity impedes seed germination, plant growth, photosynthetic efficiency, and plant protein homeostasis, and it has the propensity to induce oxidative damage and generate reactive oxygen species within plant tissues.

Soil Cd(II) pollution significantly affects microbial communities and ecological processes, leading to soil microbial diversity and composition alterations. Bacterial diversity is more severely impacted compared to fungal diversity [6], [7]. The accumulation of Cd(II) in the soil also impedes the uptake and translocation of water and essential nutrients in plants, adversely affecting their health and

[1] PhD in Engineering – Chemical Engineering, Texas A&M University, USA. Affiliation: Associate profesor, Universidad Autónoma del Estado de Morelos, Facultad de Ciencias Químicas e Ingeniería, México. Email: roberto.flores@uaem.mx

[2] BSc in Engineering – Chemical Engineering, Universidad Autónoma del Estado de Morelos, México. Email: yareli.medina@uaem.edu.mx

development. This is attributed to the harmful modulation of genes associated with metal resistance, carbon fixation, nitrification, and denitrification [3], [8]. The consequences of Cd(II) contamination extend beyond chemical toxicity and influence complex biological interactions and ecological dynamics within the soil's ecosystem.

Cd(II) pollution impacts human health, with occupational and environmental exposure leading to various ailments and diseases, including nephrotoxicity, osteotoxicity, teratogenicity, endocrine disruption, hepatotoxicity, and cancers of the breast, lung, prostate, nasopharynx, pancreas, and kidney [9], [10]. Cd(II) disrupts the body's antioxidant defense system, inducing oxidative stress and cellular or molecular alterations, thus contributing to liver and kidney diseases [11], [12].

The maximum concentration limit of Cd(II) in wastewater varies depending on the source and prevailing regulatory standards. Generally, permissible Cd(II) concentrations in wastewater fall within the limits set by regulatory bodies such as the WHO and the EPA [13]. OSHA has established a legal exposure limit of 5 μg m^{-3} of Cd(II) as an eight-hour time-weighted average. In Mexico, NOM-201-SSA1-2015, referencing the WHO, sets the maximum permissible limits for Cd(II) in water for human consumption at 0.003 mg L^{-1} .

Wastewater contaminated with Cd(II) can originate from various sources such as mining, residues from industrial activity (*e.g.*, pharmaceuticals), atmospheric deposition, metal plating, sedimentation, agricultural activities, and stormwater runoff [12], [14]–[16].

Several technologies have been developed for the remediation of Cd(II)-contaminated waters, including adsorption [17]–[21], biosorption [22]–[24], electrochemical precipitation [25]–[27], ion exchange [28]–[30], and bioremediation [16], [24], [31]. However, Cd(II) wastewater remediation faces various challenges. Firstly, as a non-biodegradable heavy metal, Cd(II) persists in the environment, making its removal a challenging task. Additionally, conventional Cd(II) removal techniques, such as chemical precipitation and ion exchange, are costly and produce toxic sludges as secondary contaminants. Furthermore, the methods of existing wastewater treatment plants need to be improved to effectively remove Cd(II).

Cd(II)-containing wastewater can be remediated using fly ash as an adsorbent. Numerous studies have investigated the use of modified fly ash – either through acid or alkaline activation, or combined with other species – for cadmium removal from aqueous solutions, demonstrating its significant potential with efficiencies exceeding 90% [32]–[34].

Fly ash offers several advantages for wastewater remediation as a low-cost, recyclable material that can be easily obtained as a byproduct of thermal power plants. Its high porosity, surface area, and chemical composition make it an efficient material for removing contaminants such as heavy metals, organic compounds, and dyes from wastewater [35], [36]. The acid activation of fly ash significantly affects its properties by increasing Si/Al ratios, eliminating impurities and dealuminations, and increasing the total pore volume and surface area [37], [38]. On the other hand, the alkaline activation of fly ash leads to the formation of a sodium aluminosilicate geopolymer with enhanced heavy metal adsorption capacity compared to normal ash [39], [40]. Another alternative to improving fly ash properties for heavy metal sorption corresponds to the application of ultrasonic energy [41]–[43].

This study investigates the potential use of coal fly ash as an adsorbent material for treating wastewater contaminated with Cd(II). Coal fly ash has been chosen because it is a waste product from thermoelectric power plants that could be utilized as a raw material in a new process, which aligns with the principles of the circular economy. The coal fly ash used in this work was treated with ultrasound and chemicals in acidic and alkaline media to increase its reactivity.

Materials and methods

Our coal fly ash was obtained from a pulverized coal-fired power plant in the north of Mexico, and it underwent multiple washes with distilled water to remove all soluble compounds. Afterwards, it was dried at 120 °C overnight and stored at room temperature. Its chemical composition has been reported elsewhere [42].

A set of coal fly ash samples was subjected to ultrasonic treatment for 4 h at room temperature using a Cole Parmer 8890R-MTH ultrasonic bath. 10 g of fly ash were placed in 100 mL of distilled water. Ultrasonic energy was applied at a frequency of 47 kHz and an intensity of 147 W for 20 min on and 20 min off. Following ultrasonic treatment, the samples were dried at 120 °C overnight and stored at room temperature.

Another group of samples was activated in an acidic medium by suspending 10 g in a 100 mL 5 M nitric acid (HNO_3) solution for 4 h, with continuous mechanical stirring or ultrasonic energy. After activation, the samples were washed several times with distilled water to remove all remaining chemicals. Then, they were dried at 120 °C overnight and stored at room temperature.

The last set of samples was subjected to alkaline activation by mixing 10 g in a 100 mL 5 M sodium hydroxide (NaOH) solution. This process was similar to the acidic activation method, with the only difference being that NaOH was used instead of an HNO_3 solution. The samples were prepared using either mechanical stirring or ultrasonic energy.

Synthetic wastewater was prepared by dissolving $Cd(NO_3)_2.4H_2O$ (purchased from Aldrich and used as received) in distilled water to obtain a nominal Cd(II) composition of 500 ppm, simulating mining wastewater that is highly contaminated before it reaches freshwater bodies.

The experiments were conducted in duplicate as follows. 100 mL of synthetic wastewater solution were mixed with 5 g of sorbent material in a beaker for 60 min. At different time intervals, 1 mL aliquots were taken and analyzed in accordance with the ASTM D 4691-02 Method (*Standard practice for measuring elements in water by flame atomic absorption spectrophotometry*) to determine the Cd(II) concentration in the solution. Different pH conditions were studied and adjusted using a 20 wt% HNO_3 solution.

The CD(II) sorption (q_t) in mg Cd g^{-1} sample was estimated as follows:

$$q_t = \frac{(C_i - C_t)\cdot V}{m} \quad (1)$$

where C_i is the initial Cd(II) concentration in mg L^{-1}; C_t is the Cd concentration in mg L^{-1} at time t; V is the volume of Cd(II) solution in mL; and m is the weight of the sorbent in g.

Results

Effect of pH on normal and ultrasonically activated fly ash

Cd(II) adsorption experiments were conducted on the original fly ash at different pH levels. In these experiments, samples of the contaminated water were taken at various intervals (between 0 and 60 min), and the Cd(II) concentration was measured. Through the calculations explained earlier, the quantity of Cd(II) adsorbed on the fly ash per unit of mass was determined. The results are presented in Fig. 1. A slight increase is observed as the pH increases from 4 to 6. At a pH of 6, the adsorption reaches its maximum, and, after 60 min, the amount adsorbed on the fly ash is 2.9 mg Cd g^{-1} of fly ash. When the pH increases to 7, the amount of Cd(II) adsorbed decreases, and, after 60 min, the adsorbed amount is 2.4 mg Cd g^{-1} of fly ash. This is consistent with the results presented in previous studies, which have shown the adsorption of Cd(II) in fly ash to be most effective for pH values between 4 and 7 [12], [44]–[46].

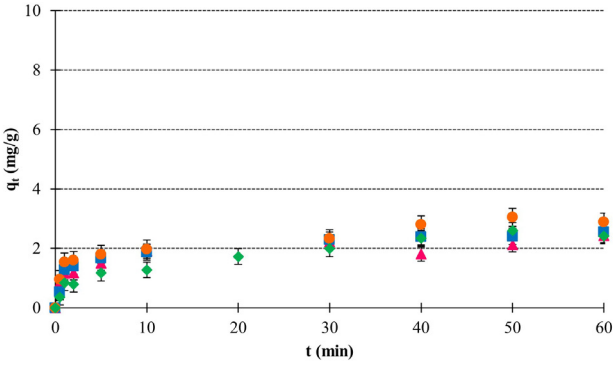

Figure 1. Experimental results of Cd adsorption on Normal fly ash. ▲ pH 4, ■ pH 5, ● pH 6, ◆ pH 7.
Source: Authors

When fly ash was activated with ultrasonic energy, the amount of Cd(II) adsorbed increased significantly in comparison with its normal counterpart (Fig. 2). However, the behavior of the solution's pH was similar to that observed with normal fly ash. As the pH increased from 4 to 6, the adsorbed amount of Cd(II) increased, reaching a maximum of 9.8 mg Cd g^{-1} of fly ash after 60 min. When the pH increased to 7, the adsorbed amount of Cd(II) decreased, and, after 60 min, it was 6.7 mg Cd g^{-1} of fly ash. The cavitation phenomenon, which enhances the textural characteristics of fly ash, is responsible for the observed increase in the adsorption capacity of Cd(II) in fly ash when activated with ultrasonic energy, as previously observed [41]–[43].

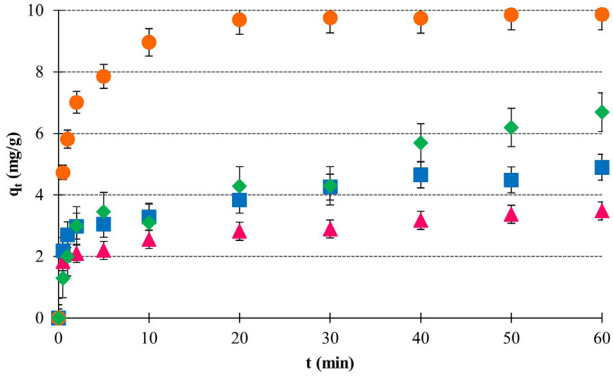

Figure 2. Experimental results of Cd adsorption on fly ash activated with ultrasonic energy. ▲ pH 4, ■ pH 5, ● pH 6, ◆ pH 7.
Source: Authors

Activation of fly ash in acidic and alkaline medium by applying ultrasonic energy

As previously explained, fly ash samples were also activated in both acidic and alkaline mediums. Two activation methods were used: in one method, the samples were mechanically shaken, and, in the other, ultrasonic energy was applied during activation. After this process, the samples were dried at 120 °C overnight. The Cd(II) adsorption capacity of the fly ash samples prepared at pH values of 6 and 7 was studied, as these pH levels had shown the best Cd(II) adsorption results in the original fly ash and in the samples activated with ultrasonic energy alone. The results obtained are presented in Figs. 3 and 4.

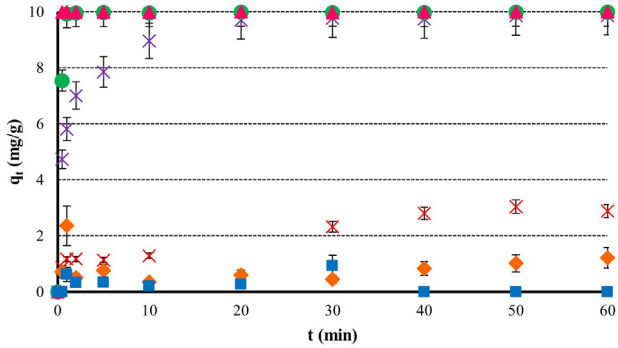

Figure 3. Experimental results of Cd adsorption at pH 6. × Normal fly ash; ✳ US fly ash, ◆ Normal fly ash + HNO_3, ■ US fly ash + HNO_3, ● Normal fly ash + NaOH, ▲ US fly ash + NaOH.
Source: Authors

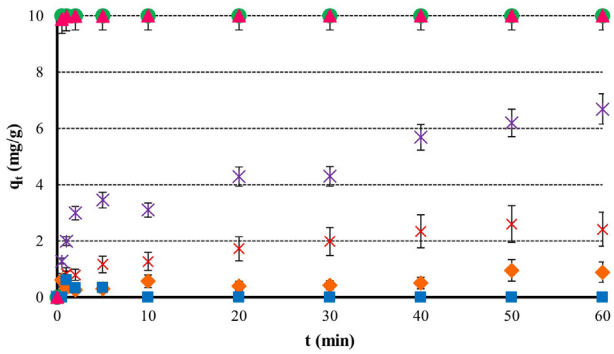

Figure 4. Experimental results of Cd adsorption at pH 7. × Normal fly ash; ✳ US fly ash, ◆ Normal fly ash + HNO_3, ■ US fly ash + HNO_3, ● Normal fly ash + NaOH, ▲ US fly ash + NaOH.
Source: Authors

According to the experimental results, the treatment with HNO_3 significantly reduces the adsorption capacity of Cd(II) in fly ash when compared to normal fly ash and that activated solely with ultrasound. In the experiments conducted at pH 7, adsorption was almost non-existent. Previous studies indicate that the acid treatment of fly ash increases its porosity and surface area, making it more effective in adsorbing contaminants. This treatment also promotes dealumination and increases the concentration of silanol groups on the surface, creating more acidic sites [47], [48]. However, these changes make it difficult for Cd(II) to be adsorbed onto the surface of the fly ash.

On the other hand, it was observed that fly ash treated with NaOH can adsorb almost all the Cd(II) present in an aqueous solution. According to the material balance, if the 5 g of adsorbent material can adsorb all the Cd(II) present in the 100 mL of solution, the load is 10 mg g^{-1}. The method used to treat the fly ash, *i.e.*, mechanical stirring or ultrasonic energy, did not affect the adsorption capacity of Cd(II). Both methods showed a practically immediate adsorption of Cd(II). The behavior of both materials was also similar at pH values of 6 and 7; all the Cd(II) was adsorbed at the beginning of the experiment. Previous studies have reported that the alkaline activation of fly ash can lead to the formation of $NaAlSiO_2$ polymorphs that can quickly transform into zeolite structures. Furthermore, when combined with ultrasonic energy, zeolite A is produced, with improved crystallinity and a smaller particle size. This technology can effectively treat contaminated wastewater [49], [50].

Reuse of adsorbent materials

The materials activated in an alkaline medium were used in four adsorption cycles at pH 6. The results obtained are shown in Figs. 5 and 6. The materials prepared with mechanical stirring showed a gradual loss of adsorption after each cycle. The maximum adsorption of 10 mg g^{-1} was achieved in less than 1 min during cycle 1. However, during cycle 2, it took 60 min to reach the same level of adsorption. Similarly, in cycle 3, the adsorption achieved was 5 mg g^{-1} within 60 min; in cycle 4, it was only 2 mg g^{-1}.

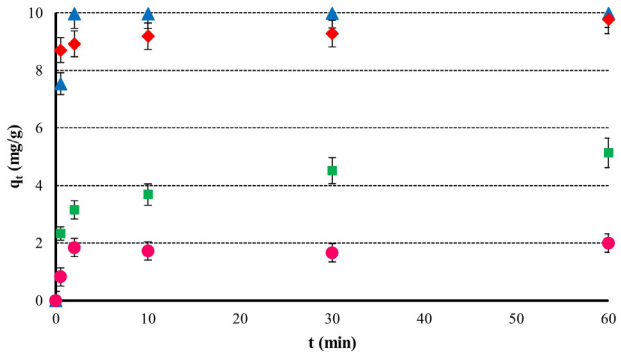

Figure 5. Reuse cycles of activated fly ash in alkaline medium with mechanical stirring at pH 6. ▲ cycle 1, ◆ cycle 2, ■ cycle 3, ● cycle 4.
Source: Authors

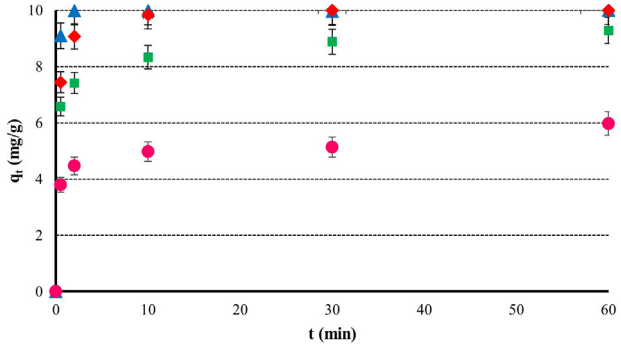

Figure 6. Reuse cycles of fly ash activated in alkaline medium with ultrasonic energy at pH 6. ▲ cycle 1, ◆ cycle 2, ■ cycle 3, ● cycle 4.
Source: Authors

When fly ash is activated in an alkaline medium using ultrasonic energy, it shows a greater adsorption capacity in each of the cycles. The maximum adsorption capacity of 10 mg g^{-1} was achieved in less than 10 min in cycles 1 and 2. Additionally, the adsorption achieved in cycle 3 was 9.4 mg g^{-1} in 60 min. In cycle 4, it was 6 mg g^{-1}, which is significantly greater than the value achieved with fly ash activated via mechanical agitation.

Kinetic studies of Cd(II) adsorption on fly ash

Experimental data were analyzed to determine the adsorption kinetics of Cd(II) on normal fly ash and ultrasound-activated fly ash. The kinetic study was not carried out on fly ash activated in an alkaline medium because the adsorption process was nearly instantaneous in the initial cycles. Table I presents the selected kinetic models already integrated and linearized. The first-order Lagergren model assumes that the limiting stage of the adsorption process is the mass transfer of Cd(II) ions from the solution to the adsorbent's surface, where there are homogeneous active sites. Therefore, the adsorption is uniform and involves physical forces. The second-order Lagergren model explains that adsorption occurs at specific sites on the adsorbent surface, and that the probability of occupying these sites is proportional to the square of the fraction of unoccupied sites. This model also assumes that the intraparticular diffusion of Cd(II) through the adsorbent material's pores is the limiting stage of the adsorption process. On the other hand, the Elovich model

is derived from the Langmuir theory, but it differs in that the active sites of the adsorbent are heterogeneous and exhibit different activation energies. This means that the rate of adsorption of a solute molecule at a given active site depends on the activation energy of that site.

Table I. Kinetics models proposed for the heavy metal sorption on solid materials

Name of the model	Integrated model
First-order Lagergren	$q_t = q_e \cdot \left[1 - e^{(-k \cdot t)}\right]$
Second-order Lagergren	$q_t = \dfrac{t}{\dfrac{1}{k \cdot q_e^2} + \dfrac{t}{q_e}}$
Elovich	$q_t = k_1 + k_2 \cdot \ln(t)$

Source: Authors

The experimental data were analyzed using the PolymathPlus software, and nonlinear regression was performed for each proposed model. The R^2 *adjusted criterion* for the sorption of Cd(II) on coal fly ash materials is presented in Table II. The results show that the Elovich adsorption isotherm is the kinetic model that best fits the experimental data. The fittings of the Elovich isotherm with the experimental data shown in Figs. 7 and 8 provide compelling evidence of their strong correlation.

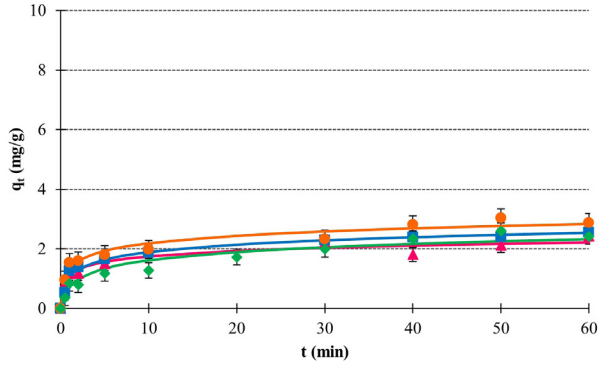

Figure 7. Fitting experimental data for Cd adsorption on normal fly ash with the Elovich isotherm. ▲ pH 4, ■ pH 5, ● pH 6, ◆ pH 7.
Source: Authors

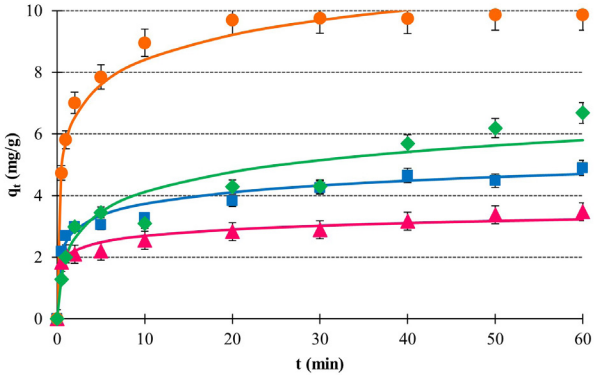

Figure 8. Fitting experimental data for Cd adsorption on fly ash activated with ultrasonic energy with the Elovich isotherm. ▲ pH 4, ■ pH 5, ● pH 6, ◆ pH 7.
Source: Authors

Table II. $R^2_{adjusted}$ *criterion* for the sorption of Cd(II) on coal fly ash materials

Model	$R^2_{adjusted}$								Average
	Normal fly ash				Activated fly ash				
	pH = 4	pH = 5	pH = 6	pH = 7	pH = 4	pH = 5	pH = 6	pH = 7	
First-order Lagergren	0.8432	0.9014	0.7990	0.8668	0.7682	0.7700	0.9364	0.8668	0.8440
Second-order Lagergren	0.9146	0.9602	0.8891	0.9146	0.8760	0.8563	0.9853	0.8371	0.9042
Elovich	0.9456	0.9569	0.9604	0.9359	0.9694	0.9555	0.9806	0.9132	0.9522

Source: Authors

Discussion

Effect of pH on adsorption capacity

The pH of the solution affects the surface charge of the adsorbent, which in turn influences the adsorption capacity. At lower pH values, the adsorbent surface is more positively charged, leading to a reduced adsorption of positively charged Cd(II) ions due to electrostatic repulsion. However, as the pH increases, the surface charge becomes increasingly negative, leading to a more significant electrostatic attraction of Cd(II) ions [51], [52]. The adsorption capacity of the fly ash is enhanced as the pH increases from 4 to 6 and decreases at pH 7 (Figs. 1 and 2). At low pH levels, the active sites of fly ash are subjected to an intense competition from H^+ and Cd(II) ions for adsorption. In a similar manner, the surface of fly ash can receive a partially positive charge, causing it to repel Cd(II) ions. The latter is due to the presence of SiO_2 and Al_2O_3 in the fly ash structure, whose charge depends on the pH of the medium. The number of H^+ ions decreases as the pH of wastewater increases, resulting in less competition for the active sites of the fly ash with Cd(II) ions. Similarly, with the increase in pH, the surface charge of the fly ash tends to be negative, which attracts Cd(II) ions [17], [18], [20], [21], [51]. On the other hand, at greater pH levels (>6) there is the possibility of forming $Cd(OH)_2$, which may precipitate and negatively affect its adsorption by blocking active sites [37], [51].

Activation of fly ash in an acidic medium

The activation of fly ash in an acidic medium has been used to improve different physical, chemical, and textural properties of fly ash [53]. The acidic medium helps to remove impurities, such as unburned carbon residues, sulfur, and volatile compounds. It also increases the surface area by dissolving metal oxides and increasing the pore size. However, in this work, the acid activation of fly ash was ineffective in improving the Cd(II) adsorption capacity, regardless of whether ultrasonic energy was applied. The low adsorption capacity is similar to that reported in previous studies [37]. This may be due to the acidic character that fly

ash acquires after acid treatment, making it unattractive to Cd(II) ions, which, according to these studies, behave like soft Lewis acids.

Activation of fly ash in an alkaline medium and its reuse

The activation of fly ash with NaOH, a process that induces structural changes on its surface by destroying its glass phase structure and increasing its surface area, has significant practical implications. The chemical interactions between NaOH and the active species of Al_2O_3 and SiO_2 make them more susceptible to increasing their adsorption capacity. For instance, once activation has been carried out, the Al sites tend to have a negative charge and quickly attract positive ions [18], [40]. This has led to a significant improvement in the adsorption capacity of fly ash, particularly regarding Cd(II) ions, and it is the main reason for the high adsorption efficiency of the materials synthesized in this work. Said efficiency is maintained for up to four reuse cycles, a situation that has also been noted in other studies [19], [54], [55].

Activation of fly ash using ultrasonic energy

On the other hand, it was demonstrated that using ultrasonic energy on fly ash significantly enhances its ability to adsorb chemical compounds, even when it has been treated in an acidic solution – where its effectiveness in removing Cd(II) is minimal. Several studies have demonstrated that activating fly ash with ultrasonic energy effectively removes contaminants from wastewater. These studies consistently show a significant increase in the adsorption capacity of fly ash after ultrasound treatment, regardless of the specific contaminant (*e.g.*, heavy metals, dyes, and toxic organic chemicals), the pH, the temperature, and the amount of adsorbent used in the wastewater [43], [56], [57]. The improvement in the characteristics of fly ash can be ascribed to the acoustic cavitation produced when ultrasonic energy is applied. Ultrasonic waves generate gas micro-bubbles in the liquid, which rapidly expand and burst in response to varying sound pressure. During the collapse of the microbubbles, there are microjets and extremely high local pressure and temperature conditions (exceeding 1000 atm and 5000 °C). These conditions lead to significant changes in the structure and morphology of the fly ash, causing it to break down into smaller particles. This results in an increase in surface area, pore size, and the availability of active sites. Consequently, the external resistance to mass transfer during the adsorption process is reduced. Additionally, sonic cavitation can aid in the elimination of contaminants within the material which hinder the organization of active sites [57], [58]. Additionally, the use of ultrasonic energy can significantly enhance the reactions between fly ash and NaOH in an alkaline environment. At specific points where high pressure and temperature conditions are reached, a synergistic effect is triggered. This effect is a result of the combination of alkaline activation and ultrasound, which plays a crucial role in increasing the surface area and forming fused Na-fly ash species with negative charge. Consequently, the adsorption capacity is significantly enhanced.

Kinetics studies of Cd(II) adsorption on fly ash

When carrying out kinetic studies of Cd(II) adsorption on fly ash, the Elovich model exhibited a better statistical fit with the experimental data than the pseudo-first order and pseudo-second order models. Elovich's theory demonstrates the heterogeneity of the active sites in fly ash. Some these sites may be derived from Al and others from Si, and each of them can have different ionic strengths, thus exhibiting different activation energies. Other studies have fitted the experimental data to the pseudo-second order model [17], [19], [37], [51], [54], [59]. However, they did not raise the possibility of fitting the data to the Elovich model. It is important to note that the pseudo-second-order model also considers that adsorption occurs at specific sites on the surface of the adsorbent, but it does not include the variation in these sites' activation energy.

This is in line with the characterization results reported by some authors [17]–[20], [54]. FTIR characterization identified that Cd(II) ions adsorb by ion exchange with the -OH, Si-O, and Al-O species, forming Si-O-Cd species – this was confirmed through XRD spectra. However, they did not relate these findings to the Elovich model, which considers that adsorption takes place in various heterogeneous sites with different activation energies, and adjustments were made mainly with the Lagergren first- and second-order models.

Based on the above-presented results, the following reaction mechanism was proposed by [20], where the presence of more than one adsorbent species is observed, again in accordance with the Elovich model, with multiple active site with different activation energies:

$$\text{-M-OH} + OH^- \rightarrow \text{-MO}^- + H_2O \quad \text{(M: Si, Al)} \tag{2}$$

$$2\text{-MO}^- + Cd(II) \rightarrow \text{-M-O-Cd-O-M} \quad \text{(M: Si, Al)} \tag{3}$$

$$Cd(II) + H_2O \leftrightarrow Cd(OH)^- + H^+ \tag{4}$$

$$\text{-M-OH} + Cd(OH)^- \leftrightarrow MCd(OH)_2^0 \quad \text{(M: Si, Al)} \tag{5}$$

Conclusions

This study shows that coal fly ash, a cost-effective material, can remove cadmium from industrial wastewater. However, the activation of coal fly ash in an acidic medium is ineffective; after this chemical treatment, the material did not adsorb cadmium. Activating coal fly ash by applying ultrasonic energy in an alkaline medium enhances its adsorption capacity. pH plays a critical role in adsorption, with the highest cadmium uptake occurring at pH 6. Statistical analysis indicates that the Elovich isotherm provides a better fit for the experimental data on cadmium adsorption across all studied materials and under various experimental conditions.

CRediT author statement

Roberto Flores conceived the idea, developed the methodology, and supervised the experimental work. Yareli G. Medina conducted the experimental work, collected the experimental data, and validated the results. Both authors collected bibliographic information, formally analyzed the experimental results, and provided critical feedback. Roberto Flores contributed to writing the definitive version of the manuscript.

Conflicts of interest

The authors declare that they have no conflict of interest that could influence the contents of this manuscript.

References

[1] T. El Rasafi *et al.*, "Cadmium stress in plants: A critical review of the effects, mechanisms, and tolerance strategies," *Crit. Rev. Environ. Sci. Technol.*, vol. 52, no. 5, pp. 675–726, Mar. 2022. https://doi.org/10.1080/10643389.2020.1835435

[2] Y. Huang, S. Mubeen, Z. Yang, and J. Wang, "Cadmium contamination in agricultural soils and crops," in *Theories and Methods for Minimizing Cadmium Pollution in Crops*, Z. Yang, C. He, and J. Xin, Eds., Singapore: Springer Nature Singapore, 2022, pp. 1–30. https://doi.org/10.1007/978-981-16-7751-9_1

[3] U. Zulfiqar *et al.*, "Cadmium phytotoxicity, tolerance, and advanced remediation approaches in agricultural soils; A comprehensive review," *Front. Plant Sci.*, vol. 13, art. 773815, Mar. 2022. https://doi.org/10.3389/fpls.2022.773815

[4] M. Tunçtürk *et al.*, "Safflower (*Carthamus tinctorius* L.) response to cadmium stress: Morpho-physiological traits and mineral concentrations," *Life*, vol. 13, no. 1, art. 135, Jan. 2023. https://doi.org/10.3390/life13010135

[5] W. Fan *et al.*, "The rhizosphere microbiome improves the adaptive capabilities of plants under high soil cadmium conditions," *Front. Plant Sci.*, vol. 13, art. 914103, Oct. 2022. https://doi.org/10.3389/fpls.2022.914103

[6] Y. Guo *et al.*, "Copper and cadmium co-contamination affects soil bacterial taxonomic and functional attributes in paddy soils," *Environ. Pollut.*, vol. 329, art. 121724, Jul. 2023. https://doi.org/10.1016/j.envpol.2023.121724

[7] Q. Meng, T. Diao, L. Yan, and Y. Sun, "Effects of single and combined contamination of microplastics and cadmium on soil organic carbon and microbial community structural: A comparison with different types of soil," *Appl. Soil Ecol.*, vol. 183, art. 104763, Mar. 2023. https://doi.org/10.1016/j.apsoil.2022.104763

[8] N. Verma, R. Gill, K. Priya, and A. Kumar, "Plants and microbes assisted remediation of cadmium-contaminated soil," in *Hazardous and Trace Materials in Soil and Plants*, M. Naeem, T. Aftab, A. A. Ansari, S. Singh Gill, and A. Macovei, Eds. Cambridge, MA, USA: Academic Press, 2022, pp. 283–296. https://doi.org/10.1016/B978-0-323-91632-5.00008-2

[9] G. Genchi, M. S. Sinicropi, G. Lauria, A. Carocci, and A. Catalano, "The effects of cadmium toxicity," *Int. J. Environ. Res. Public. Health*, vol. 17, no. 11, art. 3782, May 2020. https://doi.org/10.3390/ijerph17113782

[10] I. Suhani, S. Sahab, V. Srivastava, and R. P. Singh, "Impact of cadmium pollution on food safety and human health," *Curr. Opin. Toxicol.*, vol. 27, pp. 1–7, Sep. 2021. https://doi.org/10.1016/j.cotox.2021.04.004

[11] K. Bhattacharyya *et al.*, "Pathophysiological effects of cadmium(II) on human health-a critical review," *J. Basic Clin. Physiol. Pharmacol.*, vol. 34, no. 3, pp. 249–261, May 2023. https://doi.org/10.1515/jbcpp-2021-0173

[12] H. Thu Ha, T. Dinh Minh, and H. Minh Nguyet, "Application of green nanocomposite to adsorb cadmium ion in wastewater," *VNU J. Sci. Earth Environ. Sci.*, vol. 37, no. 1, Mar. 2021. https://doi.org/10.25073/2588-1094/vnuees.4564

[13] Y. Deng *et al.*, "Purification and water resource circulation utilization of Cd-containing wastewater during microbial remediation of Cd-polluted soil," *Environ. Res.*, vol. 219, art. 115036, Feb. 2023. https://doi.org/10.1016/j.envres.2022.115036

[14] M. Irfan, X. Liu, K. Hussain, S. Mushtaq, J. Cabrera, and P. Zhang, "The global research trend on cadmium in freshwater: A bibliometric review," *Environ. Sci. Pollut. Res.*, vol. 30, no. 28, pp. 71585–71598, Apr. 2021. https://doi.org/10.1007/s11356-021-13894-7

[15] M. A. Irshad *et al.*, "Green and eco-friendly synthesis of TiO_2 nanoparticles and their application for removal of cadmium from wastewater: reaction kinetics study," *Z. Für Phys. Chem.*, vol. 236, no. 5, pp. 637–657, May 2022. https://doi.org/10.1515/zpch-2021-3171

[16] Z. Yuan *et al.*, "Tracing anthropogenic cadmium emissions: From sources to pollution," *Sci. Total Environ.*, vol. 676, pp. 87–96, Aug. 2019. https://doi.org/10.1016/j.scitotenv.2019.04.250

[17] X. Zhao *et al.*, "Effect and mechanisms of synthesis conditions on the cadmium adsorption capacity of modified fly ash," *Ecotoxicol. Environ. Saf.*, vol. 223, art. 112550, Oct. 2021. https://doi.org/10.1016/j.ecoenv.2021.112550

[18] H. Zhao *et al.*, "Possibility of removing cadmium pollution from the environment using a newly synthesized material coal fly ash," *Environ. Sci. Pollut. Res.*, vol. 27, no. 5, pp. 4997–5008, Feb. 2020. https://doi.org/10.1007/s11356-019-07163-x

[19] X. Huang *et al.*, "Optimization of preparation technology for modified coal fly ash and its adsorption properties for Cd2+," *J. Hazard. Mater.*, vol. 392, art. 122461, Jun. 2020. https://doi.org/10.1016/j.jhazmat.2020.122461

[20] R. Qiu, F. Cheng, and H. Huang, "Removal of Cd2+ from aqueous solution using hydrothermally modified circulating fluidized bed fly ash resulting from coal gangue power plant," *J. Clean. Prod.*, vol. 172, pp. 1918–1927, Jan. 2018. https://doi.org/10.1016/j.jclepro.2017.11.236

[21] L. Ma *et al.*, "Removal of cadmium from aqueous solutions using industrial coal fly ash-nZVI," *R. Soc. Open Sci.*, vol.

5, no. 2, art. 171051, Feb. 2018. https://doi.org/10.1098/rsos.171051

[22] B. Devi and H. P. Sarma, "Equilibrium isotherm and kinetic study of biosorption of cadmium from synthetic water using wastes leaves of Averrhoa carambola," *J. Appl. Nat. Sci.*, vol. 15, no. 2, pp. 826–843, Jun. 2023. https://doi.org/10.31018/jans.v15i2.4598

[23] S. Gupta, D. Garg, and A. Kumar, "Cadmium biosorption using *Aloe. barbadensis* Miller leaves waste powder treated with sodium bicarbonate," *Clean. Waste Syst.*, vol. 3, art. 100032, Dec. 2022. https://doi.org/10.1016/j.clwas.2022.100032

[24] A. Rezaee and S. Ahmady-Asbchin, "Removal of toxic metal Cd (II) by *Serratia bozhouensis* CdIW2 using in moving bed biofilm reactor (MBBR)," *J. Environ. Manage.*, vol. 344, art. 118361, Oct. 2023. https://doi.org/10.1016/j.jenvman.2023.118361

[25] Y. Kim, K. Kim, H. H. Eom, X. Su, and J. W. Lee, "Electrochemically-assisted removal of cadmium ions by redox active Cu-based metal-organic framework," *Chem. Eng. J.*, vol. 421, art. 129765, Oct. 2021. https://doi.org/10.1016/j.cej.2021.129765

[26] R. Rajumon, S. P. Aravind, S. Bhuvaneshwari, J. Ranjitha, and P. Mohanraj, "Removal of cadmium heavy metal ions from wastewater by electrosorption using modified activated carbon felt electrodes," *Water Sci. Technol.*, vol. 82, no. 7, pp. 1430–1444, Oct. 2020. https://doi.org/10.2166/wst.2020.425

[27] M. A. Salem and N. Majeed, "Removal of cadmium from industrial wastewater using electrocoagulation process," *J. Eng.*, vol. 26, no. 1, pp. 24–34, Dec. 2019. https://doi.org/10.31026/j.eng.2020.01.03

[28] M. M. Abou-Mesalam, M. R. Abass, E. S. Zakaria, and A. M. Hassan, "Metal doping silicates as inorganic ion exchange materials for environmental remediation," *Silicon*, vol. 14, no. 13, pp. 7961–7969, Aug. 2022. https://doi.org/10.1007/s12633-021-01568-5

[29] Z. Qing, L. Guijian, P. Shuchuan, and Z. Chuncai, "The simultaneous removal of cadmium (II) and lead (II) from wastewater with the application of green synthesized magnesium silicate hydrate," *Front. Earth Sci.*, vol. 10, art. 1074687, Jan. 2023. https://doi.org/10.3389/feart.2022.1074687

[30] Y. Zalim, A. Benayada, and Z. El Ahmadi, "Cadmium removal from cadmium-containing apatites by ion-exchange reactions," *ChemistrySelect*, vol. 7, no. 35, art. e202201862, Sep. 2022. https://doi.org/10.1002/slct.202201862

[31] V. Ponia, H. Kumar, S. Ishtiyaq, R. Goswami, and S. Bhadauria, "Remediation of cadmium ions from the contaminated aqueous media by using dead biomass of *Bacillus subtilis*," *Int. J. Adv. Res.*, vol. 10, no. 05, pp. 344–359, May 2022. https://doi.org/10.21474/IJAR01/14715

[32] P. Chen, J. Wu, L. Li, Y. Yang, and J. Cao, "Modified fly ash as an effect adsorbent for simultaneous removal of heavy metal cations and anions in wastewater," *Appl. Surf. Sci.*, vol. 624, art. 157165, Jul. 2023. https://doi.org/10.1016/j.apsusc.2023.157165

[33] A.-E. Segneanu *et al.*, "Highly efficient engineered waste eggshell-fly ash for cadmium removal from aqueous solution," *Sci. Rep.*, vol. 12, no. 1, art. 9676, Jun. 2022. https://doi.org/10.1038/s41598-022-13664-6

[34] K. Singh, A. K. Singh, A. Kumar, and A. Agarwal, "Fly ash and TiO2 modified fly ash as adsorbing materials for removal of Cd(II) and Pb(II) from aqueous solutions," *J. Hazard. Mater. Adv.*, vol. 10, art. 100256, May 2023. https://doi.org/10.1016/j.hazadv.2023.100256

[35] N. B. Singh, A. Agarwal, A. De, and P. Singh, "Coal fly ash: An emerging material for water remediation," *Int. J. Coal Sci. Technol.*, vol. 9, no. 1, art. 44, Dec. 2022. https://doi.org/10.1007/s40789-022-00512-1

[36] V. K. Yadav, A. Amari, A. Gacem, N. Elboughdiri, L. B. Eltayeb, and M. H. Fulekar, "Treatment of fly-ash-contaminated wastewater loaded with heavy metals by using fly-ash-synthesized iron oxide nanoparticles," *Water*, vol. 15, no. 5, art. 908, Feb. 2023. https://doi.org/10.3390/w15050908

[37] G. Buema *et al.*, "Eco-friendly materials obtained by fly ash sulphuric activation for cadmium ions removal," *Materials*, vol. 13, no. 16, art. 3584, Aug. 2020. https://doi.org/10.3390/ma13163584

[38] Z. Hussain *et al.*, "Modification of coal fly ash and its use as low-cost adsorbent for the removal of directive, acid and reactive dyes," *J. Hazard. Mater.*, vol. 422, art. 126778, Jan. 2022. https://doi.org/10.1016/j.jhazmat.2021.126778

[39] A. Fernández-Jiménez, M. Monzó, M. Vicent, A. Barba, and A. Palomo, "Alkaline activation of metakaolin–fly ash mixtures: Obtain of Zeoceramics and Zeocements," *Microporous Mesoporous Mater.*, vol. 108, no. 1–3, pp. 41–49, Feb. 2008. https://doi.org/10.1016/j.micromeso.2007.03.024

[40] A. Purbasari, D. Ariyanti, and S. Sumardiono, "Preparation and application of fly ash-based geopolymer for heavy metal removal," presented at the *2nd Int. Conf. Chem. Process Prod. Eng.*, Semarang, Indonesia, 2020, art. 050006. https://doi.org/10.1063/1.5140918

[41] S. Boycheva, I. Marinov, S. Miteva, and D. Zgureva, "Conversion of coal fly ash into nanozeolite Na-X by applying ultrasound assisted hydrothermal and fusion-hydrothermal alkaline activation," *Sustain. Chem. Pharm.*, vol. 15, art. 100217, Mar. 2020. https://doi.org/10.1016/j.scp.2020.100217

[42] R. Flores, "Kinetics studies on the process of zn removal from wastewater using ultrasonically activated sorbents," *Chem. Biochem. Eng. Q.*, vol. 31, no. 1, pp. 123–130, Apr. 2017. https://doi.org/10.15255/CABEQ.2015.2267

[43] B. Ileri and D. Sanliyuksel Yucel, "Metal removal from acid mine lake using ultrasound-assisted modified fly ash at different frequencies," *Environ. Monit. Assess.*, vol. 192, no. 3, art. 185, Mar. 2020. https://doi.org/10.1007/s10661-020-8150-4

[44] P. Kucharski, B. Białecka, and M. Thomas, "Removal of cadmium ions from polluted waters using low-cost adsorbents: process optimization study," *Desalination Water Treat.*, vol. 256, pp. 114–124, Apr. 2022. https://doi.org/10.5004/dwt.2022.28375

[45] T. T. Nguyen, T. M. L. P. Thi, T. N. Thi, T. T. Le, C. T. N. Thi, and N. H. Nguyen, "Adsorption optimization for the removal of cadmium in water by aluminum (hydr)oxide on cation exchange resin," *Curr. Appl. Sci. Technol.*, vol. 23, no.

2, Jul. 2022. https://doi.org/10.55003/cast.2022.02.23.012

[46] Y. Xu, H. Xia, Q. Zhang, G. Jiang, W. Cai, and W. Hu, "Adsorption of cadmium(II) in wastewater by magnesium oxide modified biochar," *Arab. J. Chem.*, vol. 15, no. 9, art. 104059, Sep. 2022. https://doi.org/10.1016/j.arabjc.2022.104059

[47] A. Chatterjee, X. Hu, and F. L.-Y. Lam, "Modified coal fly ash waste as an efficient heterogeneous catalyst for dehydration of xylose to furfural in biphasic medium," *Fuel*, vol. 239, pp. 726–736, Mar. 2019. https://doi.org/10.1016/j.fuel.2018.10.138

[48] N. Wang, L. Hao, J. Chen, Q. Zhao, and H. Xu, "Adsorptive removal of organics from aqueous phase by acid-activated coal fly ash: Preparation, adsorption, and Fenton regenerative valorization of 'spent' adsorbent," *Environ. Sci. Pollut. Res.*, vol. 25, no. 13, pp. 12481–12490, May 2018. https://doi.org/10.1007/s11356-018-1560-y

[49] Z. Adamczyk, M. Cempa, and B. Białecka, "The influence of ultrasound on fly ash zeolitisation process efficiency," *Miner. Process. Extr. Metall. Rev.*, vol. 43, no. 4, pp. 427–439, May 2022. https://doi.org/10.1080/08827508.2021.1897585

[50] M. Echeverri-Aguirre, J. Molina, A. A. Hoyos-Montilla, H. H. Carvajal, and J. S. Rudas, "Heat flow modelling of the alkaline activation of fly ash with sodium hydroxide in the presence of portlandite," *Constr. Build. Mater.*, vol. 357, art. 129248, Nov. 2022. https://doi.org/10.1016/j.conbuildmat.2022.129248

[51] F. A. Al-Khaldi, B. Abu-Sharkh, A. M. Abulkibash, and M. A. Atieh, "Cadmium removal by activated carbon, carbon nanotubes, carbon nanofibers, and carbon fly ash: a comparative study," *Desalination Water Treat.*, vol. 53, no. 5, pp. 1417–1429, Feb. 2015. https://doi.org/10.1080/19443994.2013.847805

[52] K. Seffah, A. Zafour-Hadj-Ziane, A. T. Achour, J.-F. Guillet, P. Lonchambon, and E. Flahaut, "Adsorption of cadmium ions from water on double-walled carbon nanotubes/iron oxide composite," *Chem. J. Mold.*, vol. 12, no. 2, pp. 71–78, Nov. 2017. https://doi.org/10.19261/cjm.2017.412

[53] S. K. Malpani and A. Rani, "A greener route for synthesis of fly ash supported heterogeneous acid catalyst," *Mater. Today Proc.*, vol. 9, pp. 551–559, 2019. https://doi.org/10.1016/j.matpr.2018.10.375

[54] G. Buema *et al.*, "Performance assessment of five adsorbents based on fly ash for removal of cadmium ions," *J. Mol. Liq.*, vol. 333, art. 115932, Jul. 2021. https://doi.org/10.1016/j.molliq.2021.115932

[55] N. Mladenović Nikolić *et al.*, "Adsorption efficiency of cadmium (ii) by different alkali-activated materials," *Gels*, vol. 10, no. 5, art. 317, May 2024. https://doi.org/10.3390/gels10050317

[56] B. Çalışkan and E. Şayan, "A brief overview of the effects of ultrasound on the adsorption/desorption process: A review," *Int. J. Environ. Anal. Chem.*, vol. 104, no. 16, pp. 3821–3851, Dec. 2024. https://doi.org/10.1080/03067319.2022.2093641

[57] A. Mary Ealias and M. P. Saravanakumar, "A critical review on ultrasonic-assisted dye adsorption: Mass transfer, half-life and half-capacity concentration approach with future industrial perspectives," *Crit. Rev. Environ. Sci. Technol.*, vol. 49, no. 21, pp. 1959–2015, Nov. 2019. https://doi.org/10.1080/10643389.2019.1601488

[58] O. Dere Ozdemir and S. Piskin, "A novel synthesis method of zeolite x from coal fly ash: Alkaline fusion followed by ultrasonic-assisted synthesis method," *Waste Biomass Valor.*, vol. 10, no. 1, pp. 143–154, Jan. 2019. https://doi.org/10.1007/s12649-017-0050-7

[59] F. A. Olabemiwo, B. S. Tawabini, F. Patel, T. A. Oyehan, M. Khaled, and T. Laoui, "Cadmium removal from contaminated water using polyelectrolyte-coated industrial waste fly ash," *Bioinorg. Chem. Appl.*, vol. 2017, pp. 1–13, 2017. https://doi.org/10.1155/2017/7298351