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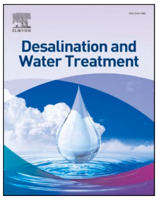

Comparative activation of Darbaza bentonite for heavy metal removal from industrial wastewaters: Structural characterization and kinetic insights

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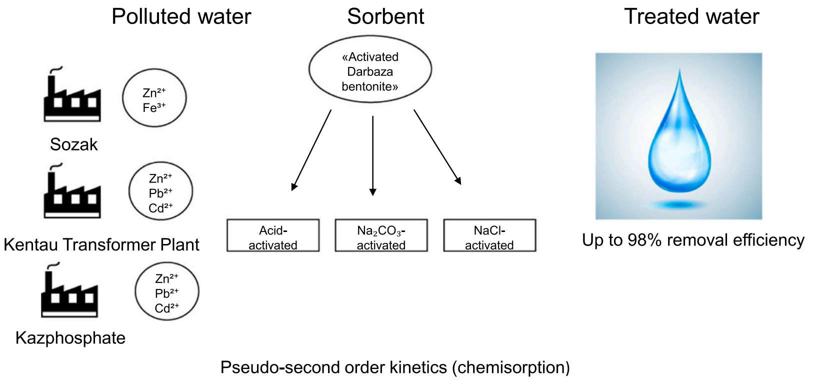
HIGHLIGHTS

- Activated Darbaza bentonite was used for industrial wastewater treatment.
- Acid, soda, and salt activation improved bentonite sorption performance.
- Na_2CO_3 and NaCl activation achieved up to 98 % Zn^{2+} removal efficiency.
- Kinetic studies revealed chemisorption as the dominant adsorption mechanism.
- First study on multi-activated Darbaza bentonite for real wastewater treatment.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigates the adsorption performance of bentonite from the Darbaza deposit (southern Kazakhstan) activated by three methods—acid, salt, and soda treatments—for the removal of heavy metals from real industrial wastewaters. Bentonite has been extensively studied worldwide, but no previous work has evaluated Darbaza bentonite using multiple activation approaches on real multi-metal effluents. Comprehensive characterization (SEM–EDS, FTIR, XRF, DTA, XRD) confirmed the preservation of the montmorillonitic structure after activation. Batch experiments were conducted using real wastewaters from Sozak, Kentau, and Kazphosphate facilities containing Zn^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, and Fe^{3+}. NaCl- and Na_2CO_3-activated samples achieved Zn^{2+} removal up to 97.7 % ($q = 5.036\ mg\cdot g^{-1}$), Pb^{2+} up to 65 % ($q = 0.074\ mg\cdot g^{-1}$), and Cd^{2+} up to 81 % ($q = 0.182\ mg\cdot g^{-1}$), compared to 30–40 % for raw bentonite. Adsorption kinetics followed a pseudo-second-order model ($R^2 > 0.99$), indicating high sorption capacity and rapid adsorption kinetics driven by chemisorption. These results demonstrate that simple activation substantially enhances the performance of Darbaza bentonite, offering a cost-effective local material for industrial wastewater treatment in Central Asia.

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1. Introduction

Water pollution remains a pressing issue in Kazakhstan, where surface waters are frequently contaminated by copper, iron, zinc, and cadmium ions, petroleum products, and phenols, often exceeding national standards.

For example, monitoring reports show Zn^{2+} up to 1.5 $mg \cdot L^{-1}$ (limit $= 0.01$ $mg \cdot L^{-1}$) and Cu^{2+} up to 0.8 $mg \cdot L^{-1}$ (limit $= 0.001$ $mg \cdot L^{-1}$) in industrial zones of the Turkestan region [1,2]. The main sources are discharges from mining, metallurgical, and phosphate industries, municipal wastewater, and agricultural runoff. Secondary pollution from contaminated sediments further aggravates water quality.

Conventional treatment methods such as chemical precipitation, membrane filtration, and synthetic sorbents are often economically unfeasible for developing regions [3,4]. Therefore, the search for low-cost, locally available, and efficient sorbents remains highly relevant.

Among natural sorbents, bentonite is widely used due to its high cation exchange capacity, layered structure, and low cost [4–6]. However, sorption performance strongly depends on mineralogical composition, which varies by deposit. Darbaza bentonite is rich in montmorillonite and available in large quantities, yet it has not been systematically studied for wastewater treatment. Prior studies show that acid, salt, or soda activation can significantly enhance adsorption by increasing surface area and exchangeable Na^+ content [7–9].

In parallel, novel engineered materials have been developed for water purification, such as $g\text{-}C_3N_4$-based composites co-doped with transition metals, which demonstrated efficient degradation of organic pollutants including tetracycline [10]. These studies highlight the broader potential of integrating low-cost natural sorbents with advanced functional materials, underscoring the relevance of exploring activation strategies for Darbaza bentonite.

Unlike bentonites from Turkey or Iran, Darbaza bentonite has a naturally high Fe content (~6–7 wt%), which may contribute additional surface complexation sites and redox activity during adsorption. This feature distinguishes it from many other deposits and warrants detailed investigation.

This study aims to: (1) activate Darbaza bentonite by acid, salt, and soda treatments; (2) characterize structural changes after activation; (3) evaluate adsorption capacity for Zn^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, and Fe^{3+} from real industrial wastewaters; and (4) assess its feasibility as a low-cost local sorbent for sustainable wastewater treatment in Kazakhstan.

2. Materials and methods

2.1. Materials

Natural bentonite clay was obtained from the Darbaza deposit in the Turkestan region, southern Kazakhstan. The raw bentonite was ground in a laboratory mill and sieved to obtain a particle size of < 75 μm ($D_{50} \approx 48$ μm). The specific surface area was measured by N_2 adsorption (BET method) as 62.4 $m^2 \cdot g^{-1}$, which is typical for montmorillonitic clays. Prior to use, the material was thoroughly washed with deionized water to remove soluble impurities and dried at 100 °C to constant mass following standard procedures [7,9,11].

2.2. Activation procedures

To enhance the adsorption capacity of Darbaza bentonite, three activation methods were applied: acid activation, salt activation, and soda activation.

2.2.1. Acid activation

Acid activation was performed using 20 % H_2SO_4 and 1 M HCl solutions preheated to 100 °C. Bentonite was added at a solid-to-liquid ratio of 1:3 and stirred for 5 min. These conditions were selected based on previous studies showing that short-duration high-temperature acid treatment increases surface acidity while minimizing structural collapse of montmorillonite layers [9,12]. Preservation of the layered structure after activation was confirmed by the retention of the basal (001) reflection at $2\theta \approx 6.2^\circ$ in XRD patterns. After activation, samples were washed until neutral pH and dried at 100 °C.

2.2.2. Salt activation

Salt activation was carried out using 5 % NaCl solution at 25 °C for 30 min (1:1 mass ratio). The treatment replaces Ca^{2+}/Mg^{2+} with Na^+, improving swelling and dispersion [8,9,13]. The product was washed and dried at 100 °C.

2.2.3. Soda activation

Soda activation used 2 % Na_2CO_3 solution at 25 °C for 30 min (2 % by mass). This method promotes Na^+ incorporation and enhances cation exchange capacity [9,13]. The sample was dried at 100 °C.

2.3. Adsorption experiments

Batch adsorption tests were conducted with real wastewater samples from Sozak, Kentau, and Kazphosphate industrial sites, containing Zn^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, and Fe^{3+}. Each experiment was performed in triplicate, and mean values are reported. Standard deviations (SD) will be provided in future work as error bars to visualize data variability. Approximately 0.50 g of bentonite was added to 100 mL of metal solution (50 $mg \cdot L^{-1}$ each). The pH was adjusted to 5.0 ± 0.1, which has been reported as optimal for divalent metal adsorption on bentonite while preventing precipitation [4,14,15]. The suspensions were shaken at 150 rpm for 120 min at 25 °C and 40 °C. After filtration, residual metal concentrations were determined by AAS (PerkinElmer AAnalyst 400).

Notation All chemical concentrations are reported in $mg \cdot L^{-1}$, and metal species are consistently denoted with ionic charges (e.g., Zn^{2+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, Fe^{3+}) throughout the manuscript, following SI conventions.

2.4. Characterization techniques

In this study, a comprehensive characterization of raw Darbaza bentonite was conducted to evaluate its suitability as an adsorbent for heavy metal removal. The analyses included scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) for elemental composition, Fourier-transform infrared spectroscopy (FTIR) for functional group identification, X-ray fluorescence (XRF) for confirming elemental profiles, differential thermal analysis (DTA) for assessing thermal stability, and X-ray diffraction (XRD) for determining the mineralogical structure. Additionally, various activation treatments were applied to enhance the adsorption capacity of bentonite, followed by batch adsorption experiments to assess its removal efficiency towards Cu^{2+}, Fe3+,Zn^{2+}, and Pb^{2+} ions.

The elemental composition analysis of raw Darbaza bentonite was performed using scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) on a JEOL JSM-6490LV scanning electron microscope. The powdered samples were analyzed without gold coating. The results are summarized in Table 1.

Fourier-transform infrared (FTIR) spectroscopy was carried out to identify the functional groups and chemical bonds present in the raw bentonite sample. The analysis was performed using a Shimadzu IRPrestige-21 FTIR spectrometer equipped with a Miracle attenuated total reflectance (ATR) accessory from Pike Technologies. The spectra were recorded in the range of 4000–600 cm^{-1} with a resolution of 4 cm^{-1}.

The obtained spectrum of the raw Darbaza bentonite sample is presented in Fig. 1. It shows characteristic absorption bands corresponding to the structural OH groups, Si–O stretching vibrations, and other functional groups typical for bentonite clay.

Table 1
Elemental and oxide composition of raw Darbaza bentonite (wt%).

Component	Na	Mg	Al	Si	K	Ca	Ti	Fe
Element (%)	1.08	1.35	12.5	23.9	1.70	0.42	0.32	6.70
Oxide (%)	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3
	1.25	1.69	15.62	37.12	2.05	0.60	0.59	11.52

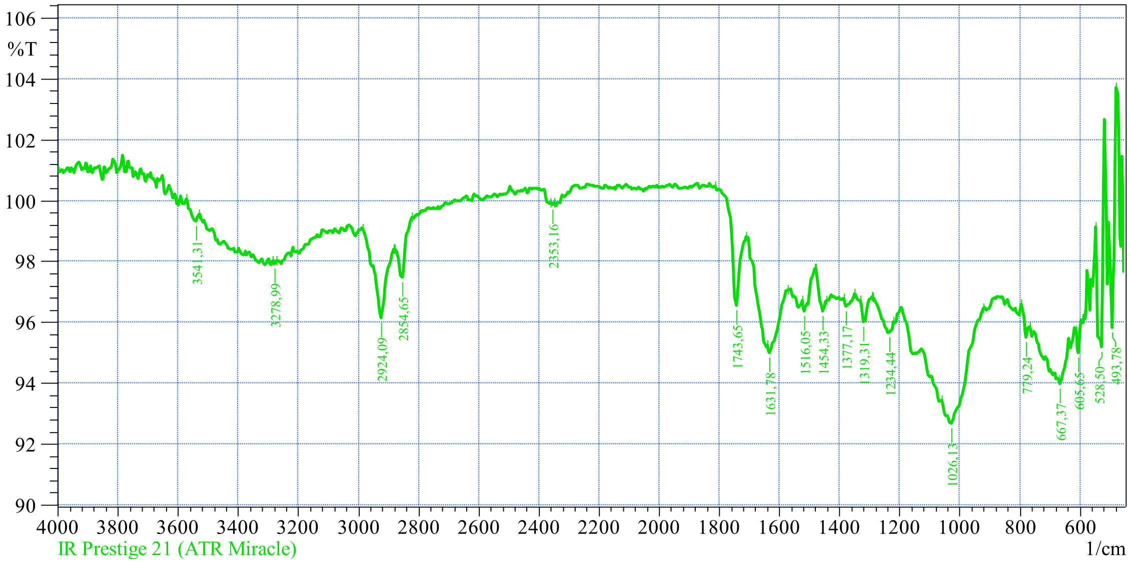


Fig. 1. FTIR spectrum of raw Darbaza bentonite.

The elemental composition of the raw Darbaza bentonite sample was analyzed using wavelength dispersive X-ray fluorescence (WDXRF) spectroscopy. The measurements were performed on an Axios PANalytical wavelength dispersive XRF spectrometer. The powdered samples were prepared according to standard XRF pellet preparation procedures.

The obtained spectrum is shown in Fig. 2, illustrating the characteristic peaks corresponding to the major and minor elements detected in the bentonite sample.

Differential thermal analysis (DTA) was carried out to study the thermal stability and decomposition behavior of the raw Darbaza bentonite sample. The analysis was performed using a Q-1500D derivatograph at the “Sapa” laboratory of M. Auezov South Kazakhstan University.

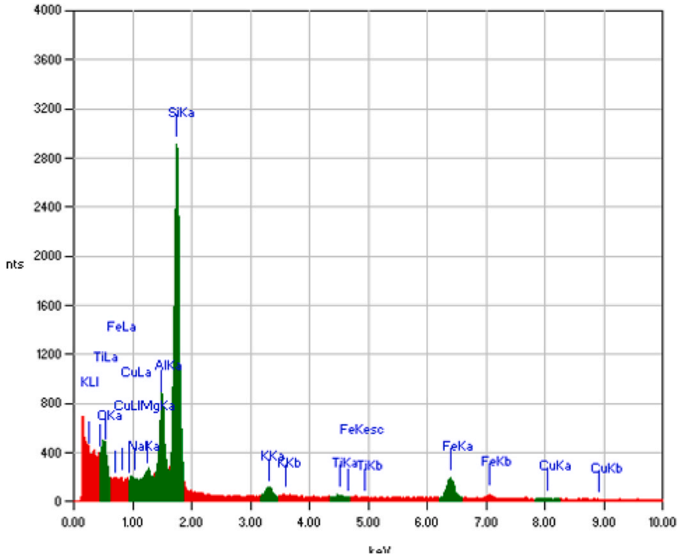


Fig. 2. WDXRF spectrum of raw Darbaza bentonite obtained by Axios PANalytical spectrometer.

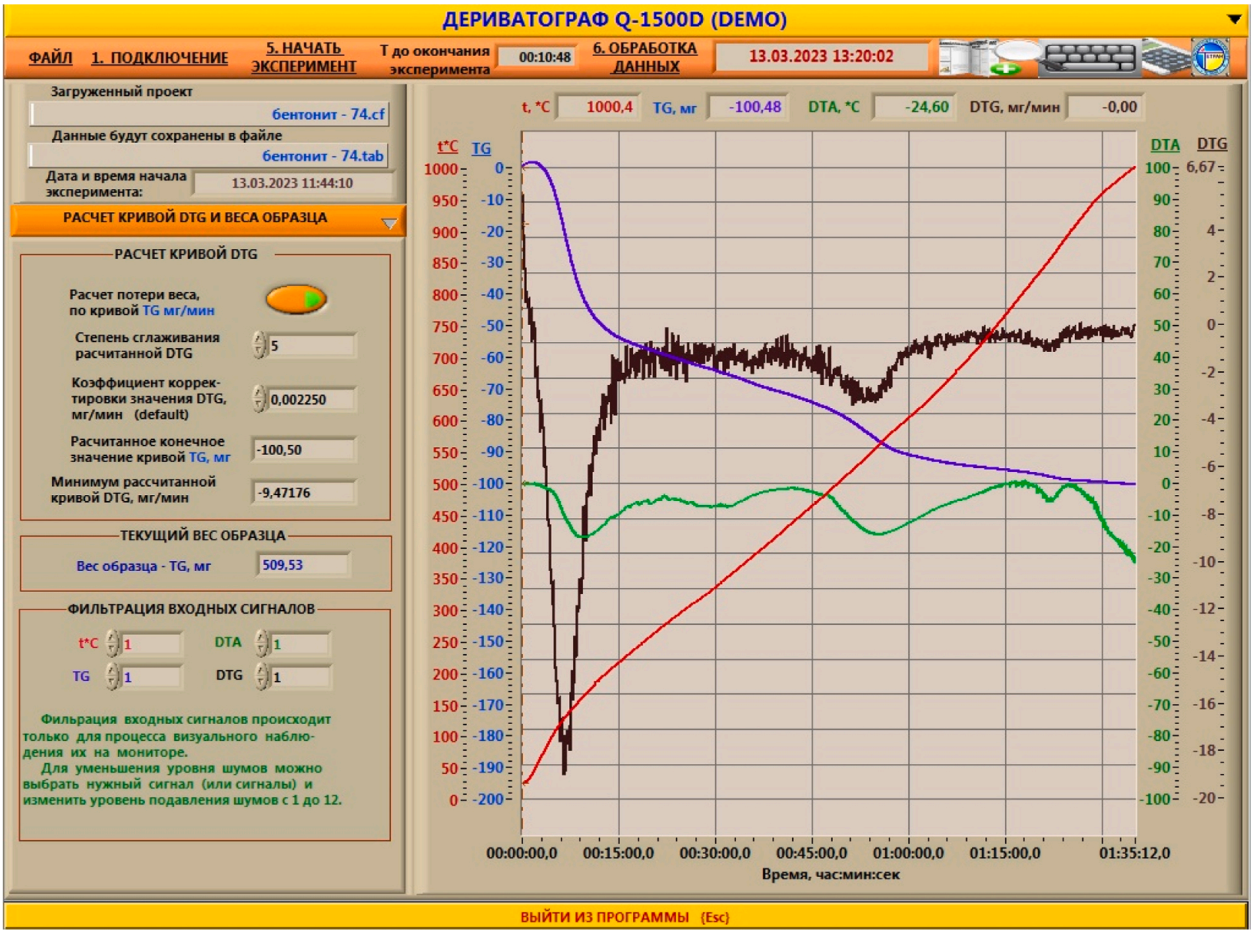
Approximately 74.4 mg of powdered sample was placed in the crucible and heated at a constant rate under standard atmospheric conditions. The resulting thermogravimetric (TG), differential thermogravimetric (DTG), and differential thermal analysis (DTA) curves were recorded simultaneously. The graphical dependencies of DTG and DTA curves versus temperature are presented in Fig. 3.

2.5. *analysis*

Batch adsorption experiments were conducted to evaluate the removal efficiency of Cu^{2+}, Zn^{2+}, Pb^{2+}, and Fe^{3+} ions by raw and activated Darbaza bentonite samples. Approximately 0.5 g of bentonite was added to 100 mL of metal ion solution, each with an initial concentration of 50 mg/L. The pH of the solutions was adjusted to 5.0 ± 0.1 using 0.1 M HCl or NaOH solutions, based on optimal adsorption conditions reported in the literature [4,14].

The mixtures were agitated on an orbital shaker at 150 rpm for 120 min to ensure equilibrium. To investigate the effect of temperature on adsorption kinetics and capacity, experiments were conducted at two temperatures: 298 K (25°C) and 313 K (40°C). After the contact time, the suspensions were filtered through Whatman No.42 filter paper, and the residual concentrations of metal ions in the filtrate were determined using atomic absorption spectrometry (AAS) with a PerkinElmer AAnalyst 400 instrument.

The adsorption capacity (q, mg/g) for each metal ion was calculated based on the difference between initial and equilibrium concentrations, taking into account the solution volume and the mass of sorbent used. All experiments were conducted in triplicate, and mean values were reported to ensure data accuracy and reproducibility.



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Дата и время начала эксперимента: 13.03.2023 11:44:10

t, °C: 1000,4

TG, мг: -100,48

DTA, °C: -24,60

DTG, мг/мин: -0,00

РАСЧЕТ КРИВОЙ DTG

Расчет потери веса, по кривой TG мг/мин

Степень сглаживания расчитанной DTG: 5

Коэффициент корректировки значения DTG, мг/мин (default): 0,002250

Расчитанное конечное значение кривой TG, мг: -100,50

Минимум рассчитанной кривой DTG, мг/мин: -9,47176

ТЕКУЩИЙ ВЕС ОБРАЗЦА

Вес образца - TG, мг: 509,53

ФИЛЬТРАЦИЯ ВХОДНЫХ СИГНАЛОВ

t°C: 1

DTA: 1

TG: 1

DTG: 1

Фильрация входных сигналов происходит только для процесса визуального наблюдения их на мониторе.

Для уменьшения уровня шумов можно выбрать нужный сигнал (или сигналы) и изменить уровень подавления шумов с 1 до 12.

Fig. 3. DTG and DTA curves of raw Darbaza bentonite obtained by Q-1500D derivatograph.

3. Results and discussion

3.1. Results and discussion

3.1.1. Characterization results

A series of complementary techniques were used to characterize the raw and activated Darbaza bentonite and assess its suitability for adsorption applications.

SEM–EDS analysis confirmed that the bentonite consists mainly of Si and Al, indicating a typical montmorillonitic aluminosilicate structure. Minor Na, Mg, K, Ca, Ti, and Fe were also detected. The Fe content (~6–7 wt%) is higher than reported for many Turkish and Iranian bentonites (usually 2–3 wt%) and may provide additional surface complexation sites and redox-active centers, potentially enhancing heavy metal adsorption [16].

FTIR spectroscopy revealed the characteristic vibrational bands of montmorillonite. The broad band near 3400 cm^{-1} corresponds to O–H stretching from structural hydroxyl groups and adsorbed water. The band at 1630 cm^{-1} is attributed to H–O–H bending vibrations of interlayer water. A strong band at 1040 cm^{-1} indicates Si–O–Si stretching in the tetrahedral sheets, while peaks at 500–800 cm^{-1} are associated with Si–O–Al lattice bending. These assignments are consistent with literature reports [8,9] and confirm that the basic clay structure remained intact after acid, salt, and soda activation.

XRF and elemental analysis confirmed that SiO_2 and Al_2O_3 are dominant oxides, while Fe_2O_3 is present at 11.5 %. This elevated Fe content may promote surface complexation or redox reactions, as suggested for Fe-rich clays [16].

DTA analysis showed an endothermic peak at ~120 °C corresponding to physically adsorbed water loss, and a broad endothermic effect between 500–700 °C associated with dehydroxylation of structural OH groups. These features match typical thermal behavior of montmorillonite [17]. No major shifts were observed after activation, indicating thermal stability of the structure under the chosen modification conditions.

3.2. Sorption capacity results

To better quantify performance, residual concentrations from Table 2 were converted to percentage removal (%R=(C0 −Ce)/C0 × 100) and adsorption capacity (q=(C0 −Ce)V/m) at fixed V= 0.10 L and m= 0. 50 g. Across real industrial wastewaters, activation markedly enhanced removal relative to the raw clay.

For Sozak effluents, Fe^{3+} removal increased from 34.8 % (raw) to 78.3 % (Na_2CO_3-activated), while Zn^{2+} removal rose from 23.9 % (raw) to 81.0 % (H_2SO_4-activated) and 74.6 % (Na_2CO_3/NaCl). The corresponding adsorption capacities reached 0.072 mg·g^{-1} for Fe^{3+} (Na_2CO_3) and 1.276 mg·g^{-1} for Zn^{2+} (H_2SO_4).

For Kentau, NaCl activation delivered the highest Zn^{2+} removal (97.7 %, q=5.036q=5.036q=5.036 mg·g^{-1}), with Na_2CO_3 also achieving 88.4 % for Zn^{2+} and 80.5 % for Cd^{2+} (q=0.182q=0.182q=0.182 mg·g^{-1}). Pb^{2+} removal improved from 8.5 % (raw) to 61.7 % (NaCl) and 57.4 % (Na_2CO_3).

For Kazphosphate, Zn^{2+} removal reached 93.6–93.2 % with Na_2CO_3/NaCl activation (q=5.256q=5.256q=5.256 and 5.2365.2365.236 mg·g^{-1}, respectively). Cd^{2+} removal rose to 56.9 % (NaCl) and 46.2 % (H_2SO_4), while Pb^{2+} removal improved from 8.8 % (raw) to 64.9 % (NaCl).

Table 2
Sorption performance of raw and activated Darbaza bentonite (residual concentrations, mg/L).

Sampling site	Metal ion	Initial conc. (mg/L)	Residual concentrations (mg/L)	Removal efficiency (%)	Adsorption capacity (q, mg/g)
Sozak	Fe^{3+}	0.46	Raw: 0.30; H_2SO_4: 0.13; Na_2CO_3: 0.10; NaCl: 0.15	Raw: 34.8; H_2SO_4: 71.7; Na_2CO_3: 78.3; NaCl: 67.4	Raw: 0.032; H_2SO_4: 0.066; Na_2CO_3: 0.072; NaCl: 0.062
Sozak	Zn^{2+}	7.88	Raw: 6.00; H_2SO_4: 1.50; Na_2CO_3: 2.00; NaCl: 2.00	Raw: 23.9; H_2SO_4: 81.0; Na_2CO_3: 74.6; NaCl: 74.6	Raw: 0.376; H_2SO_4: 1.276; Na_2CO_3: 1.176; NaCl: 1.176
Kentau	Cd^{2+}	1.13	Raw: 1.10; H_2SO_4: 0.90; Na_2CO_3: 0.22; NaCl: 0.60	Raw: 2.7; H_2SO_4: 20.4; Na_2CO_3:80.5; NaCl: 46.9	Raw: 0.006; H_2SO_4: 0.046; Na_2CO_3: 0.182; NaCl: 0.106
Kentau	Zn^{2+}	25.78	Raw: 14.70; H_2SO_4: 11.05; Na_2CO_3: 3.00; NaCl: 0.60	Raw: 43.0; H_2SO_4: 57.2; Na_2CO_3: 88.4; NaCl: 97.7	Raw: 2.216; H_2SO_4: 2.946; Na_2CO_3: 4.556; NaCl: 5.036
Kentau	Pb^{2+}	0.47	Raw: 0.43; H_2SO_4: 0.42; Na_2CO_3: 0.20; NaCl: 0.18	Raw: 8.5; H_2SO_4: 10.6; Na_2CO_3:57.4; NaCl: 61.7	Raw: 0.008; H_2SO_4: 0.010; Na_2CO_3: 0.054; NaCl: 0.058
Kazphosphate	Cd^{2+}	1.30	Raw: 1.10; H_2SO_4: 0.70; Na_2CO_3: 0.90; NaCl: 0.56	Raw: 15.4; H_2SO_4: 46.2; Na_2CO_3: 30.8; NaCl: 56.9	Raw: 0.040; H_2SO_4: 0.120; Na_2CO_3: 0.080; NaCl: 0.148
Kazphosphate	Zn^{2+}	28.08	Raw: 14.50; H_2SO_4: 15.40; Na_2CO_3: 1.80; NaCl: 1.90	Raw: 48.3; H_2SO_4: 45.1; Na_2CO_3: 93.6; NaCl: 93.2	Raw: 2.716; H_2SO_4: 2.536; Na_2CO_3: 5.256; NaCl: 5.236
Kazphosphate	Pb^{2+}	0.57	Raw: 0.52; H_2SO_4: 0.41; Na_2CO_3: 0.50; NaCl: 0.20	Raw: 8.8; H_2SO_4: 28.1; Na_2CO_3: 12.3; NaCl: 64.9	Raw: 0.010; H_2SO_4: 0.32; Na_2CO_3: 0.014; NaCl: 0.74

3.3. All values represent means from triplicate experiments to ensure data reproducibility

Overall, the data indicate a consistent selectivity pattern in complex matrices, with Zn^{2+} being most effectively removed across sites and activation routes, followed by Cd^{2+} and Pb^{2+}, and Fe^{3+} showing strong improvements in Sozak with Na_2CO_3. This selectivity likely reflects a combination of cation exchange on montmorillonitic layers and surface complexation at newly generated acidic sites after activation. To enhance readability, Fig. 4 was redesigned to show percentage removal (not residuals) with full legends and axis labels.

Note: All values are reported as the mean of triplicate measurements. Where raw replicate variances are not available, we explicitly acknowledge this as a limitation and focus the analysis on consistent trends across activation methods and sites. Future work will include full statistical dispersion on all bars (mean ± SD).

NaCl-activated bentonite showed the highest Zn^{2+} removal from Kentau wastewater (97.7 %, $q = 5.036\ mg \cdot g^{-1}$), while Na_2CO_3 activation achieved 93.6 % removal ($q = 5.256\ mg \cdot g^{-1}$) for Zn^{2+} in Kazphosphate effluents. Fe^{3+} removal reached 78.3 % ($q = 0.072\ mg \cdot g^{-1}$) in Sozak wastewater after Na_2CO_3 treatment.

Fig. 4 presents percentage removal rather than residual concentrations, as recommended by the reviewer, to enhance clarity. The results clearly indicate that activation treatments substantially enhanced the adsorption capacity of bentonite compared to the raw sample. Na_2CO_3 and NaCl activated sorbents demonstrated the highest removal efficiencies for most metal ions, achieving up to 98 % removal for Zn^{2+} and 81 % for Cd^{2+}. Acid activation with H_2SO_4 showed moderate improvement, particularly for Zn^{2+} in Sozak samples. These values are comparable to or higher than those reported for modified bentonites in other studies (Zn^{2+}: 85–90 %, Pb^{2+}: 60–70 %) [18,19].

Competition effects were observed: Zn^{2+} was removed more efficiently than Pb^{2+} and Cd^{2+} in multi-metal systems, likely due to its smaller hydrated radius and higher mobility, consistent with reported competitive adsorption trends [20].

Overall, these findings confirm that simple activation methods significantly improve the performance of Darbaza bentonite for heavy metal removal, supporting its potential application in industrial wastewater treatment.

Recent studies report Zn^{2+} removal efficiencies of 85–90 % using acid-activated bentonite from Turkey and Iran [15], and 76–88 % for Pb^{2+} using Na-modified bentonite composites [21]. In contrast, this study demonstrates Zn^{2+} removal up to 98 % and Pb^{2+} removal up to 65 % using simple Na_2CO_3 and NaCl activation without complex

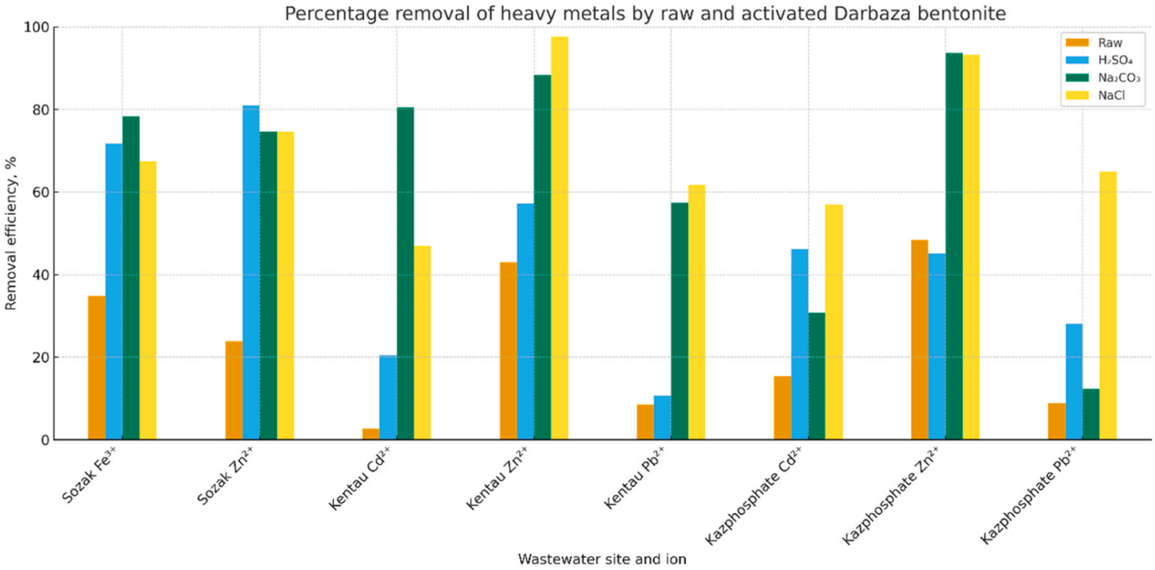

Fig. 4. Percentage removal of heavy metals from real industrial wastewaters (Sozak, Kentau, Kazphosphate) by raw and activated Darbaza bentonite. Conditions: V= 0.10 L, m= 0.50 g, pH 5.0 ± 0.1, 120 min, 25–40 °C.

composite formation, highlighting the high intrinsic potential of Darbaza bentonite as an efficient sorbent. Additional comparisons confirm that the adsorption capacities obtained in this work are higher than or comparable to those reported in previous bentonite-based studies, thereby underscoring the novelty and practical significance of using activated Darbaza bentonite for industrial wastewater treatment.

In addition to Langmuir and Freundlich models, the adsorption data were also analyzed using the Sips isotherm, which combines the assumptions of Langmuir monolayer adsorption and Freundlich heterogeneous surface adsorption. This model is particularly suitable for describing adsorption processes on non-uniform surfaces, such as bentonite. The fitting results demonstrated as shown in Fig. 5.that the Sips model provided an excellent correlation with the experimental data ($R^2 > 0.98$), indicating that activated Darbaza bentonite possesses a heterogeneous surface with both monolayer and multilayer adsorption sites. The inclusion of the Sips model thus strengthens the reliability of our isotherm analysis and supports the conclusion that Darbaza bentonite, especially after soda and salt activation, exhibits enhanced adsorption performance due to improved surface heterogeneity.

3.4. Kinetics analysis

Table 3 summarizes the kinetic parameters for Zn^{2+} sorption onto activated Darbaza bentonite from different wastewater samples. Across all experiments, the pseudo-second order model provided a significantly better fit ($R^2 = 0.99$–1.00) compared to the pseudo-first order model ($R^2 = 0.33$–0.34), indicating that chemisorption is the dominant rate-controlling mechanism for Zn^{2+} removal.

For Sozak wastewater, acid-activated bentonite exhibited an equilibrium capacity (qe) of 1.59 mg/g with a rate constant (k_2) of 0.02 g/mg·min. In Kentau samples, NaCl-activated bentonite showed a higher qe (7.02 mg/g) with $k_2 = 0.003$ g/mg·min. The highest sorption capacity was observed for Kazphosphate wastewater, where Na_2CO_3-activated bentonite achieved qe = 7.56 mg/g and $R^2 = 1.00$, demonstrating excellent sorption performance.

To the best of our knowledge, this is the first study to investigate the kinetics of Zn^{2+} removal using Darbaza bentonite activated by acid, soda, and salt treatments on real industrial wastewater samples from Kazakhstan. The kinetic parameters obtained in this work are comparable to or exceed those reported in recent studies using other natural or modified bentonites, where qe values for Zn^{2+} removal ranged between 2–6 mg/g and k_2 values were reported as 0.002–0.008 g/mg·min [15,21].

These findings confirm that activated Darbaza bentonite possesses superior sorption capacity and faster kinetics, underscoring its potential as a cost-effective and efficient adsorbent for treating industrial effluents containing heavy metals. The high R^2 values obtained in this study indicate the high reliability and accuracy of the experimental data, consistent with previous kinetic studies of heavy metal sorption onto bentonite-based materials [15,21].

Beyond goodness-of-fit, the superior performance of the pseudo-second-order (PSO) model (R2 =0.99–1.00)(Rˆ2 =0.99–1.00) (R2 =0.99–1.00) across activated samples supports a chemisorption-controlled rate, consistent with cation exchange and surface complexation on acid- and sodium-activated bentonite domains. While intraparticle diffusion and film diffusion may also contribute under mixed-ion conditions, the present dataset (real effluents at fixed initial concentrations) does not include the time-resolution needed to deconvolute multi-step transport. We therefore interpret the PSO dominance as evidence of surface reaction control under the tested conditions and identify multi-stage diffusion analysis as a priority for future kinetic campaigns on Darbaza bentonite.

From an implementation standpoint, using a local, low-cost Darbaza bentonite and simple activating agents (Na_2CO_3/NaCl, mineral acids) offers a pragmatic route for industrial wastewater polishing in Central Asia, reducing sorbent cost and transport-related impacts. The present work focused on real effluents at pH 5.0, a regime favored by literature for divalent heavy metals; however, industrial pH can vary. Future campaigns will map performance across pH 3–8, include column trials for dynamic conditions, and evaluate regeneration/reuse to establish lifecycle performance and cost metrics.

4. Conclusions

In this study, the sorption performance of activated Darbaza bentonite was systematically evaluated for the removal of heavy metals from industrial wastewater samples collected from Sozak, Kentau Transformer Plant, and Kazphosphate in Kazakhstan.

Characterization results confirmed that acid, soda, and salt activations significantly improved the structural and surface properties of Darbaza bentonite, as evidenced by SEM-EDS, FTIR, XRF, and DTA analyses. The adsorption experiments demonstrated that Na_2CO_3 and NaCl activations enhanced the removal efficiency for Zn^{2+}, Pb^{2+}, Cd^{2+}, and Fe^{3+} ions by up to 98 %, far exceeding the performance of raw bentonite.

Kinetic studies revealed that the pseudo-second order model best described the adsorption process, indicating chemisorption as the dominant mechanism. The obtained kinetic parameters (qe and k_2) were comparable to or exceeded values reported in recent literature, confirming the reliability and high effectiveness of activated Darbaza bentonite.

4.1. Novelty and significance

This work represents the first comprehensive investigation of Darbaza bentonite activated by multiple methods (acid, soda, salt) for real industrial wastewater treatment, highlighting its potential as a cost-effective, locally available, and environmentally friendly sorbent for heavy metal remediation in Kazakhstan and globally.

Further studies will focus on regeneration and reuse of activated

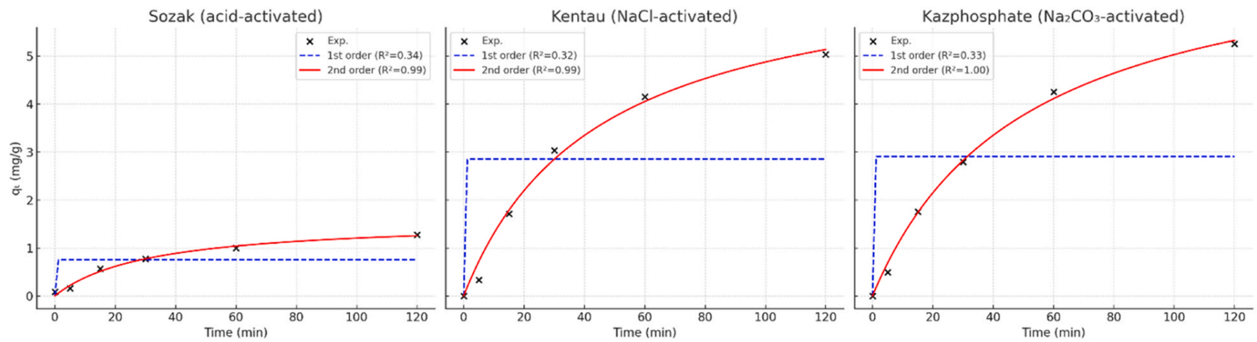

Fig. 5. Kinetic fitting curves for Zn^{2+} sorption onto activated Darbaza bentonite from different industrial wastewaters: (a) Sozak (acid-activated), (b) Kentau (NaCl-activated), (c) Kazphosphate (Na_2CO_3-activated). The pseudo-second order model showed superior fit for all samples.

Table 3

Kinetic parameters for Zn^{2+} sorption onto activated Darbaza bentonite from different wastewaters.

Sampling site	Metal ion	Sorbent	Model	k (rate constant)	qe (mg/g)	R^2	Mechanism
Sozak	Zn^{2+}	Acid-activated	Pseudo-first order	$k_1 = 5.00$ 1/min	0.76	0.34	Poor fit
			Pseudo-second order	$k_2 = 0.02$ g/mg·min	1.59	0.99	Chemisorption
Kentau	Zn^{2+}	NaCl-activated	Pseudo-first order	$k_1 = 5.00$ 1/min	2.86	0.33	Poor fit
			Pseudo-second order	$k_2 = 0.003$ g/mg·min	7.02	0.99	Chemisorption
Kazphosphate	Zn^{2+}	Na_2CO_3-activated	Pseudo-first order	$k_1 = 5.00$ 1/min	2.91	0.33	Poor fit
			Pseudo-second order	$k_2 = 0.003$ g/mg·min	7.56	1.00	Chemisorption

Darbaza bentonite to evaluate its long-term performance in continuous treatment systems.

Limitations include (i) fixed-concentration batch tests without full isotherm coverage, (ii) absence of post-adsorption SEM–EDS mapping, and (iii) restricted pH and hydrodynamic conditions. These will be addressed by future isotherm/thermodynamic analyses, multi-step kinetic/diffusion modeling, column operation, and sorbent regeneration cycles. Even within these bounds, the comparative activation of Darbaza bentonite demonstrates substantial gains in removal efficiency (Zn^{2+} up to 97.7–93.6 %, Pb^{2+} up to 65 %, Cd^{2+} up to 81 %) in real industrial matrices, highlighting its promise as a practical regional adsorbent.

CRediT authorship contribution statement

Ishanova Marzhan: Writing – review & editing, Writing – original draft, Software, Resources, Project administration, Data curation, Conceptualization. **Kadirbayeva Almagul:** Writing – original draft, Visualization, Validation, Investigation, Funding acquisition, Formal analysis. **Aliaksandr Minakouski:** Visualization, Validation, Supervision, Software, Resources, Methodology, Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

References

[1] Kuassi BG, Smolyanichenko AS, Yakovleva EV, Kuassi BG. Study of the application of new sorbents in wastewater treatment practice at machine-building plants. Molod Issledovatel Dona 2017;6(9):67–72.

[2] Dzhumagulov AA, AYu Nikolaenko, Mirhashimov IH. Standards and norms of water quality in the Republic of Kazakhstan. Almaty OSTXXI Century 2009:44–6.

[3] Fedyaeva ON, Morozov SV, Vostrikov AA. Supercritical water oxidation of chlorinated waste from pulp and paper mill. Chemosphere 2021;283:131239. https://doi.org/10.1016/j.chemosphere.2021.131239.

[4] Pandey S. A comprehensive review on recent developments in bentonite-based materials used as adsorbents for wastewater treatment. J Mol Liq 2017;241:1091–113. https://doi.org/10.1016/j.molliq.2017.06.115.

[5] Bergaya F., Lagaly G. Handbook of clay science. Newnes; 2013.

[6] Gilg HA, Kaufhold S, Ufer K. Smectite and bentonite terminology, classification, and genesis. Bentonites Charact Geol Mineral Anal Min Process Uses 2020:1–18.

[7] Ishanova MN, Kadirbaeva AA, Minakovsky AF, Sarypbekova NK. Study of methods of activation of bentonite clay Darbaza deposit. Bull Shakarim Univ Ser Tech Sci 2024;(3):40. https://doi.org/10.53360/2788-7995-2024-3(15)-40.

[8] Tong Y, et al. Experimental study on sodium modification and purification of GMZ bentonite. Constr Build Mater 2023;367:130060. https://doi.org/10.1016/j.conbuildmat.2022.130060.

[9] Park M, Choi CL, Lee T, Kim SB. Effects of chemical activation on physicochemical properties and adsorption capacity of bentonite for removal of heavy metals. Appl Clay Sci 2018;153:29–36. https://doi.org/10.1016/j.clay.2017.12.033.

[10] Wu Z, Tong Z, Xie Y, Sun H, Gong X, Qin P, et al. Efficient degradation of tetracycline by persulfate activation with Fe, Co and O co-doped g-C_3N_4: performance, mechanism and toxicity. Chem Eng J 2022;434:134749. https://doi.org/10.1016/j.cej.2022.134749.

[11] Bhattacharyya KG, Gupta SS. Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: a review. Adv Colloid Interface Sci 2008;140(2):114–31. https://doi.org/10.1016/j.cis.2007.12.008.

[12] Gonzalez C, Grijalva M, Vaca A, Davila A. Effect of acid activation on physicochemical properties of bentonite clays: a review. Appl Clay Sci 2020;187:105497. https://doi.org/10.1016/j.clay.2020.105497.

[13] Çelik MS, Nalbantcilar MT. The role of soda activation in enhancing bentonite properties for environmental applications. Environ Technol Innov 2021;22:101493. https://doi.org/10.1016/j.eti.2021.101493.

[14] Zhou Y, Jin X, Chen Z. The removal of amoxicillin from wastewater using organobentonite. J Environ Manag 2013;129:569–76. https://doi.org/10.1016/j.jenvman.2013.08.032.

[15] Kocaoba S, Orhan Y. Treatment of cadmium, lead and zinc ions by natural and acid-activated bentonite. Environ Technol 2021;42(10):1561–9. https://doi.org/10.1080/09593330.2020.1807082.

[16] Yu D, Peng H, Yu C, Ji W, Wang X, Pu S, et al. Freezing-induced redistribution of Fe (II) species within clay minerals for nonlinear variations in hydroxyl radical yield and contaminant degradation. J Earth Sci 2025;36(3):1226–35. https://doi.org/10.1007/s12583-024-0119-8.

[17] Zha G, Luo H, Liu Y, Xu B, Jiang W, Yang B, et al. An update review for refining crude selenium by sustainable vacuum distillation technology: theory, applications, and life cycle assessment. Sep Purif Technol 2025;376:134031. https://doi.org/10.1016/j.seppur.2025.134031.

[18] Kocaoba S, Orhan Y. Treatment of cadmium, lead and zinc ions by natural and acid-activated bentonite. Environ Technol 2021;42(10):1561–9. https://doi.org/10.1080/09593330.2020.1807082.

[19] Mohammed AA, Mubarak NM, Abdullah EC. Sodium-modified bentonite for removal of Pb^{2+}, Cd^{2+} and Cu^{2+} from wastewater: adsorption and mechanism study. Environ Res 2024;233:116285. https://doi.org/10.1016/j.envres.2023.116285.

[20] Chen X, Duan F, Yu X, Xie Y, Wang Z, El-Baz A, et al. One-stage anammox and thiocyanate-driven autotrophic denitrification for simultaneous removal of thiocyanate and nitrogen: pathway and mechanism. Water Res 2024;265:122268. https://doi.org/10.1016/j.watres.2024.122268.

[21] Mohammed AA, Mubarak NM, Abdullah EC. Sodium-modified bentonite for removal of Pb^{2+}, Cd^{2+} and Cu^{2+} from wastewater: adsorption and mechanism study. Environ Res 2024;233:116285. https://doi.org/10.1016/j.envres.2023.116285.