Hakim Sabzevari University

JOURNAL OF HEAVY METAL RESEARCH

انجمن زمین شناسی ایران ۱۳۷٤ 1995 GEOLOGICAL SOCIETY OF IRAN

https://jhmr.hsu.ac.ir Journal of Heavy Metal Research, 2026, vol 1, Issue 1, 7-16

Original Article

Adsorption of heavy metals from industrial wastewater in Iran using modified natural minerals

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Received: 20 October 2025
Revised: 30 October 2025
Accepted: 06 November 2025
Published: 01 February 2026

Publisher: Hakim Sabzevari University

Citation: Taghavi Sani, H. A., Mafi, A. and Emami, M. (2026). Adsorption of heavy metals from industrial wastewater in Iran using modified natural minerals. (e233671). Journal of Heavy Metal Research, *1*(1), 7–16.

Abstract

The escalating issue of heavy metal contamination in industrial effluents, particularly from Iran's burgeoning petrochemical and metallurgical sectors, necessitates the development of cost-effective and sustainable remediation technologies. This study investigates the potential of natural and modified minerals sourced from significant Iranian deposits for the adsorptive removal of heavy metals from synthetic industrial wastewater. Clinoptilolite-rich zeolite from Semnan Province and vermiculite from Gilan Province were subjected to a novel blended modification, combining acid (H_2SO_4) and surfactant (CTAB) treatments to create a multi-functional adsorbent. The performance of these materials was evaluated for the removal of Cr(III), Cr(VI), Cu(II), Ni(II), Cd(II), Pb(II), and Zn(II) ions from an initial concentration of 10 mg/L for each metal. Batch adsorption experiments were conducted by varying key parameters, including adsorbent concentration (10 g/L), pH (4, 6, 8), and the ratio of natural to modified minerals. Characterization using XRD, FTIR, and BET analysis confirmed structural and surface chemical changes post-modification, leading to enhanced surface area and active site availability. Results demonstrated that modified vermiculite was exceptionally effective, achieving removal efficiencies exceeding 98% for Pb(II) and Cr(VI) under optimal conditions (pH 6, 60:40 a cost-effective 60:40 natural-to-modified mineral ratio). Modified zeolite also showed significant removal capabilities, particularly for Cu(II) and Zn(II). Kinetic studies indicated rapid initial adsorption, with equilibrium reached within 60-90 minutes for most metals. Multiple regression analysis yielded robust predictive models ($R^2 > 0.97$) for the tested parameter space, linking final pollutant concentrations to variables such as removal percentage and mineral adsorption capacity. This research highlights the immense potential of locally sourced, geochemically characterized Iranian minerals as a sustainable solution for industrial wastewater treatment, offering a practical pathway to mitigate environmental pollution and support circular-economy principles in the region, while acknowledging the need for further validation under more complex, competitive conditions.

Keywords: Heavy metal removal; Adsorption; Iranian zeolite; vermiculite; Industrial wastewater; Blended modification

1. Introduction

Rapid industrialization and population growth have placed unprecedented stress on global freshwater resources. A direct consequence of this development is the generation of vast quantities of industrial wastewater, often laden with toxic and persistent pollutants. Among these, heavy metals are of particular concern due to their non-biodegradability, tendency to bioaccumulate, and severe toxicity to ecosystems and human health, even at

https://doi.org/10.22034/jhmr.2025.554551.1003

trace concentrations (Fu & Wang, 2011). Long-term exposure to heavy metals such as lead (Pb), cadmium (Cd), chromium (Cr), and nickel (Ni) through contaminated water and food chains is linked to a range of adverse health effects, including neurological disorders, renal failure, and various cancers (Jaishankar et al., 2014; Liu et al., 2023). The metals selected for this study—Cr, Pb, Cu, Ni, Cd, and Zn—are representative pollutants commonly found in the effluents of key Iranian industries, including petrochemicals, steel manufacturing, mining, and electroplating, making their removal a national priority.

In Iran, a nation with significant industrial sectors, including petrochemicals, steel manufacturing, and mining, the management of heavy-metal-contaminated wastewater is a critical environmental challenge. The common practice of using treated or untreated wastewater for agricultural irrigation to conserve scarce freshwater resources further exacerbates the problem, leading to the accumulation of heavy metals in soils and crops, thereby posing a direct threat to food safety and public health (Muchuweti et al., 2006; Yazdanpanah et al., 2014). Consequently, there is an urgent need for efficient, economically viable, and environmentally benign technologies for the removal of heavy metals from industrial effluents before their discharge or reuse.

A variety of methods have been developed for this purpose, including chemical precipitation, ion exchange, membrane filtration, and electrochemical treatment. However, many of these techniques are associated with high operational costs, significant energy consumption, or the generation of secondary toxic sludge, limiting their widespread application, especially in developing economies (e.g., Shrestha et al., 2021). In this context, adsorption has emerged as a promising alternative due to its simplicity of design, high efficiency, and the potential for utilizing low-cost, naturally abundant materials as adsorbents (Tripathi et al., 2025).

Natural minerals such as zeolites and clays (e.g., vermiculite, bentonite) have garnered substantial attention as potential adsorbents. These aluminosilicate minerals possess unique properties, including a porous structure, high specific surface area, and significant cation exchange capacity (CEC), which make them effective at sequestering heavy metal ions from aqueous solutions (Velarde et al., 2023; Wang & Peng, 2010). Furthermore, their surface properties can be readily enhanced through chemical modification—such as acid/base treatment, surfactant impregnation, or metal oxide coating—to improve their adsorption capacity and selectivity for specific pollutants (Rathi et al., 2024; Jiménez-Castañeda & Medina, 2017).

Iran is endowed with extensive deposits of high-quality natural minerals. Significant reserves of clinoptilolite-rich zeolitic tuffs are located in the Semnan and East Azerbaijan provinces, formed from the alteration of volcanic glass in saline-alkaline lake systems during the Eocene (IZA, 2016). Similarly, vermiculite deposits are known to exist, for instance, in the Gilan Province (Bobrowski et al., 2021). The specific geochemical and mineralogical characteristics of these deposits can significantly influence their adsorption properties, making a region-specific investigation highly relevant. While previous studies have explored the use of these minerals globally, research focusing on the systematic modification and comparative evaluation of Iranian-sourced zeolite and vermiculite for treating complex industrial wastewater is limited (e.g., Najafi et al., 2016). This study introduces a novel approach to advance the practical application. The primary innovation lies in the development and systematic evaluation of a dual-strategy adsorbent system: (1) a blended modification technique, combining acid and surfactant treatments to create a single, multi-functional adsorbent material, and (2) a blended adsorbent application, mixing this modified material with its natural, low-cost counterpart to optimize performance and economic viability. The central hypothesis is that this blended modification strategy will create a versatile adsorbent with enhanced porosity and surface area from acid treatment, combined with tailored surface chemistry from surfactant modification to simultaneously target both cationic (e.g., Pb^{2+}, Cu^{2+}) and anionic (e.g., Cr(VI) as CrO_4^{2-}) heavy metals, a common challenge in real industrial effluents.

This study aims to bridge this gap by providing a comprehensive investigation into the use of natural and modified zeolite and vermiculite from prominent Iranian deposits for the removal of a suite of heavy metals (Cr, Pb, Cu, Ni, Cd, Zn) from synthetic petrochemical wastewater. The primary objectives are: (1) to characterize the geological and physicochemical properties of the natural minerals and their modified forms; (2) to systematically evaluate the effects of critical operational parameters, such as pH and the ratio of natural-to-modified mineral, on adsorption efficiency; (3) to elucidate the underlying adsorption mechanisms through kinetic and statistical modeling; and (4) to assess the practical potential of these materials as a sustainable and localized solution for industrial wastewater management in Iran. This work provides a novel perspective by integrating geochemical context with a pragmatic engineering approach focused on cost-performance optimization.

2. Geological Context and Materials

The selection of adsorbents for this study was based on their abundance within Iran and their known potential for cation exchange. The specific geological origin and inherent mineralogical composition of these materials are fundamental to understanding their baseline adsorption behavior and their response to chemical modification.

2.1. Study Site and Experimental Design

Natural Zeolite (NZ): The zeolite used in this study is a clinoptilolite-rich tuff sourced from the Aftar region in Semnan Province, Northern Iran. Geologically, these deposits are part of the Eocene Karaj Formation, which consists predominantly of green tuffs and shales. The formation of these extensive zeolite deposits is attributed to the devitrification of rhyolitic volcanic glass in a shallow, saline-alkaline marine environment. The high pH and salinity of the depositional environment provided ideal conditions for the alteration of volcanic ash into zeolites (IZA, 2016). The raw material appears as a light-green to creamy-white rock. Semi-quantitative analysis of our XRD data (Section 4.1) estimated the clinoptilolite content to be in the range of 85-95%, confirming its high purity.

Natural Vermiculite (NV): The vermiculite was obtained from a deposit in the Gilan Province, located in northern Iran near the Caspian Sea. Vermiculite is a 2:1 type hydrous phyllosilicate mineral that undergoes significant expansion when heated. Geologically, vermiculite deposits are typically formed by the hydrothermal alteration or weathering of biotite or phlogopite micas. The distinct chemical composition of the Gilan vermiculite, particularly its high Fe_2O_3 and MgO content, was hypothesized to provide a high density of surface hydroxyl groups and a significant structural charge, potentially enhancing its affinity for heavy metal cations through surface complexation and ion exchange mechanisms.

2.2. Mineralogical and Chemical Characterization

The raw minerals were crushed, ground, and sieved to a particle size of 100-200 mesh (75-150 µm) for all experiments. The bulk chemical composition of the natural zeolite (NZ) and natural vermiculite (NV) was determined by X-ray Fluorescence (XRF) spectrometry. The results, presented in Table 1, provide a quantitative overview of the major oxides present in the minerals.

The high SiO_2/Al_2O_3 ratio in the zeolite is characteristic of clinoptilolite. The vermiculite is characterized by high concentrations of MgO and Fe_2O_3, consistent with its origin from the alteration of ferromagnesian micas.

Table 1. Chemical composition (wt.%) of natural zeolite (NZ) and natural vermiculite (NV) from Iranian deposits as determined by XRF analysis.

Oxide	Natural Zeolite (NZ)	Natural Vermiculite (NV)
SiO_2	68.54	39.81
Al_2O_3	12.31	15.52
Fe_2O_3	1.45	12.88
CaO	2.98	5.65
MgO	1.02	14.31
Na_2O	2.55	0.21
K_2O	3.10	1.05
TiO_2	0.18	1.49
Loss on Ignition (LOI)	7.87	9.08
Total	**100.00**	**100.00**
Si/Al Ratio	**5.57**	**2.56**

3. Methodology

The experimental procedure was designed to systematically assess the adsorption performance of natural and modified Iranian minerals under various conditions relevant to industrial wastewater treatment.

3.1. Adsorbent Preparation and Modification

The sieved natural zeolite (NZ) and natural vermiculite (NV) powders were washed with deionized water to remove impurities and dried at 105 °C for 24 hours. A portion of each mineral was then subjected to chemical modification to create modified zeolite (MZ) and modified vermiculite (MV). To introduce novelty and explore different surface alterations, two modification methods were employed, and the resulting materials were blended.

- **Acid Modification:** 50 g of the natural mineral was treated with 500 mL of 0.5 M H_2SO_4 solution. The slurry was stirred at 60 °C for 4 hours to remove exchangeable cations and impurities, and to potentially increase surface area through partial dealumination.
- **Surfactant Modification:** 50 g of the natural mineral was treated with 500 mL of 0.1 M Cetyltrimethylammonium bromide (CTAB) solution. The mixture was stirred at room temperature for 24

hours. This process aims to modify the surface charge from negative to positive, enhancing the adsorption of anionic species (like Cr(VI) as CrO_4^{2-}).

After each modification process, the materials were thoroughly washed. The washing procedure involved centrifuging the slurry, decanting the supernatant, and resuspending the mineral in fresh deionized water. This cycle was repeated until the pH of the supernatant stabilized to a neutral value (6.8-7.2) and its conductivity dropped below 10 µS/cm, ensuring the complete removal of residual acid, CTAB, and displaced ions that could interfere with subsequent adsorption experiments. The washed materials were then dried at 80 °C.

The final modified adsorbents (MZ and MV) used in the experiments were a 50:50 (w/w) blend of the acid-treated and surfactant-treated materials. This novel blended modification was designed to create a multi-functional adsorbent. The acid-treated portion contributes enhanced porosity and surface area for general adsorption, while the surfactant-treated portion introduces positively charged functional groups (from CTAB) specifically to target anionic species. The 50:50 ratio was selected as a balanced approach to ensure significant contributions from both modification types, creating a versatile material capable of handling complex wastewater containing both cationic and anionic pollutants.

To investigate a cost-effective application, mixtures of natural and modified minerals were tested. The ratios of 100:0 (purely natural), 80:20, and 60:40 (natural: modified) were selected to systematically evaluate the performance improvement gained per unit of modified material, aiming to identify an optimal blend that balances enhanced efficiency with the added cost of modification.

3.2. Adsorbent Characterization

The natural and modified minerals were characterized using several analytical techniques:

- **X-ray Diffraction (XRD):** Mineralogical phases were identified using a Bruker D8 Advance diffractometer with Cu-Kα radiation, scanned from 5° to 70° 2θ.
- **Fourier-Transform Infrared Spectroscopy (FTIR):** Surface functional groups were analyzed using a PerkinElmer Spectrum Two spectrometer in the range of 400-4000 cm^{-1}.
- **Scanning Electron Microscopy (SEM):** Surface morphology and microstructure were observed using a TESCAN VEGA3 microscope after gold-sputter coating the samples.
- **Brunauer-Emmett-Teller (BET) Analysis:** Specific surface area, pore volume, and pore size distribution were determined from N_2 adsorption-desorption isotherms at 77 K using a Quantachrome NOVA 2200e analyzer.

3.3. Wastewater Preparation and Batch Adsorption Studies

A synthetic wastewater was prepared to simulate the effluent from a typical petrochemical complex, such as those found in the Asaluyeh region of Iran. The base composition of the wastewater is detailed in Table 2. This matrix was then spiked with a stock solution containing multiple heavy metals—Cr(III), Cr(VI), Cu(II), Ni(II), Cd(II), Pb(II), and Zn(II)—to achieve an initial concentration of 10 mg/L for each metal ion. The salts used were of analytical grade (Merck), including $Cr(NO_3)_3$, $K_2Cr_2O_7$, $Cu(NO_3)_2$, $Ni(NO_3)_2$, $Cd(NO_3)_2$, $Pb(NO_3)_2$, and $Zn(NO_3)_2$.

Batch adsorption experiments were conducted in 250 mL Erlenmeyer flasks. In each flask, a fixed amount of adsorbent (to achieve a concentration of 10 g/L) was added to 100 mL of the metal-spiked synthetic wastewater. The flasks were agitated on an orbital shaker at 150 rpm at room temperature (25 ± 2 °C). The key variables investigated were:

- **Effect of pH:** The initial pH of the solution was adjusted to 4, 6, and 8 using 0.1 M HCl or 0.1 M NaOH.
- **Effect of Natural-to-Modified Mineral Ratio:** Adsorbents were tested as 100% natural (100:0), and mixtures of 80:20 and 60:40 (natural: modified).
- **Adsorption Kinetics:** Samples were collected at predetermined time intervals (5, 15, 30, 60, 90, 120 min) to study the rate of adsorption.

After agitation, the samples were filtered through a 0.45 µm membrane filter. The final concentrations of the heavy metals in the filtrate were analyzed using Atomic Absorption Spectrometry (AAS, PerkinElmer PinAAcle 900T).

The removal efficiency (%) and adsorption capacity at equilibrium (q_e, mg/g) were calculated using the following equations:

$$\text{Removal Efficiency (\%)} = [(C_0 - C_e) / C_0] \times 100 \quad (1)$$

$$q_e = [(C_0 - C_e) \times V] / m \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentrations of the metal ion (mg/L), V is the volume of the solution (L), and m is the mass of the adsorbent (g).

Table 2. Characteristics of the synthetic petrochemical wastewater used in the experiments.

Parameter	Value	Unit
pH	7.2 ± 0.2	-
Conductivity	25.5	mS/cm
Chemical Oxygen Demand (COD)	2500	mg/L
Total Organic Carbon (TOC)	35.2	mg/L
Total Nitrogen (TN)	15.8	mg/L
Sulfate (SO_4^{2-})	1500	mg/L
Chloride (Cl^-)	4500	mg/L
Phenols	0.15	mg/L

3.4. Statistical Analysis

To evaluate the significance of the experimental parameters, an Analysis of Variance (ANOVA) was performed. Furthermore, multiple linear regression analysis was conducted using SPSS (v.25) to develop a predictive model for the final pollutant concentration. The dependent variable was the final metal concentration (C_e), and the independent variables included initial concentration (C_0), pH, mineral ratio, contact time, removal efficiency (%), and adsorption capacity (q_e).

4. Results

4.1. Adsorbent Characterization

XRD Analysis: The XRD patterns confirmed that the primary mineral in the NZ sample was clinoptilolite, with minor amounts of quartz and feldspar. The MV sample was identified as vermiculite, with associated biotite and chlorite phases. After modification, the main crystalline structures of both minerals remained intact, indicating that the treatments did not destroy the mineral framework. However, a slight decrease in the intensity of some peaks was observed in the modified samples, suggesting partial dissolution or surface amorphization, particularly with the acid treatment.

FTIR Analysis: The FTIR spectra of NZ showed characteristic bands for zeolites, including a broad band around 3450 cm⁻¹ (O-H stretching of water molecules), 1630 cm⁻¹ (H-O-H bending), and a strong asymmetric stretching band for T-O-T (T=Si or Al) linkages around 1050 cm⁻¹. For NV, bands at 3400 cm⁻¹ (structural OH) and 1010 cm⁻¹ (Si-O stretching) were prominent. In the modified samples (MZ and MV), the appearance of new weak bands around 2920 and 2850 cm⁻¹ confirmed the successful grafting of CTAB's aliphatic chains onto the mineral surfaces. The intensity of the hydroxyl bands also shifted, indicating interaction with the modifying agents.

SEM Analysis: SEM micrographs revealed that the natural zeolite (NZ) consisted of tabular, coffin-shaped crystals typical of clinoptilolite. The natural vermiculite (NV) exhibited a characteristic lamellar, plate-like structure. After modification, the surfaces of both minerals appeared rougher and more porous. In the surfactant-modified samples, an organic film was visible on the mineral surfaces, while acid treatment led to the formation of small etch pits, suggesting an increase in surface heterogeneity.

BET Surface Area: The results of the BET analysis are summarized in Table 3. The modification process led to a significant increase in the specific surface area and total pore volume for both minerals. The acid treatment was particularly effective in increasing porosity by clearing blocked pores and creating new micropores. This enhanced surface area is expected to provide more active sites for metal adsorption, contributing to the enhanced removal efficiencies observed. However, as discussed in Section 5, this physical change is coupled with crucial changes in surface chemistry, which also play a dominant role in the overall performance improvement.

Table 3. BET surface area and pore characteristics of natural and modified minerals.

Adsorbent	Specific Surface Area (m²/g)	Total Pore Volume (cm³/g)	Average Pore Diameter (nm)
Natural Zeolite (NZ)	38.5	0.112	11.6
Modified Zeolite (MZ)	75.2	0.205	10.9
Natural Vermiculite (NV)	15.8	0.045	11.4
Modified Vermiculite (MV)	42.1	0.128	12.2

4.2. Effect of pH on Heavy Metal Adsorption

The pH of the aqueous solution is a master variable in adsorption processes, as it affects both the surface charge of the adsorbent and the speciation of metal ions. The effect of initial pH on the removal of Pb(II) and Cr(VI) was investigated at pH 4, 6, and 8, using the 60:40 mineral mixture. As shown in Figure 1, the removal of the cationic metal, Pb(II), increased significantly as the pH rose from 4 to 6 for both adsorbents. This is because at lower pH, the adsorbent surface is protonated (positively charged), leading to electrostatic repulsion with Pb^{2+} ions. As pH increases, the surface becomes more negatively charged, enhancing electrostatic attraction. A slight decrease in removal was observed at pH 8, likely due to the precipitation of Pb(OH)$_2$. Conversely, the removal of the anionic Cr(VI), which exists as HCrO$_4^-$ or CrO$_4^{2-}$, was highest at the acidic pH of 4. At this pH, the positively charged adsorbent surface strongly attracts the chromate anions. As pH increases, the surface becomes negative, leading to repulsion and decreased removal. Based on the overall performance for the suite of metals, a pH of 6 was selected as the optimal condition for further experiments, as it provided a good balance for removing both cationic and anionic species.

4.3. Effect of Natural-to-Modified Mineral Ratio

To balance cost and performance, the effect of mixing natural and modified minerals was studied. Figure 2 shows the removal efficiency for Cu(II) and Ni(II) using 100% natural mineral (100:0), an 80:20 mix, and a 60:40 mix of natural-to-modified mineral. The results clearly indicate that increasing the proportion of the modified mineral significantly enhances removal efficiency. For vermiculite, the removal of Ni(II) increased from 45% with NV to over 85% with the 60:40 mixture. While the 100% modified mineral would likely yield the highest removal, the 60:40 ratio provides a substantial performance boost over the natural material at a lower cost than using only modified minerals. This ratio was therefore identified as the optimal blend for practical applications under the tested conditions.

4.4. Effect of Natural-to-Modified Mineral Ratio

The adsorption kinetics for all six heavy metals were studied under the optimized conditions (pH 6, 60:40 ratio). The results are presented in Figure 3. Adsorption was rapid for all metals, with over 70% of the total removal occurring within the first 30 minutes. This is attributed to the abundance of readily available active sites on the adsorbent surfaces. Equilibrium was generally reached within 60-90 minutes. Modified vermiculite (MV) consistently outperformed modified zeolite (MZ) for most metals, especially Pb(II), Cr(VI), and Ni(II). The final removal efficiencies at 120 minutes are summarized in Table 4. MV achieved remarkable removal rates of 98.5% for Pb(II) and 95.2% for Cr(VI). MZ showed strong affinity for Cu(II) (92.4%) and Zn(II) (88.1%). The removal of Cd(II) was comparatively lower for both adsorbents, but still significant.

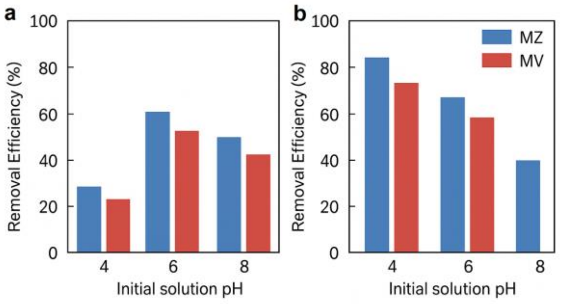

Figure 1. Effect of initial solution pH on the removal efficiency of Pb(II) (a) and Cr(VI) (b) by modified zeolite (MZ) and modified vermiculite (MV) mixtures (60:40 ratio). Conditions: C$_0$ = 10 mg/L, adsorbent dose = 10 g/L, time = 120 min.

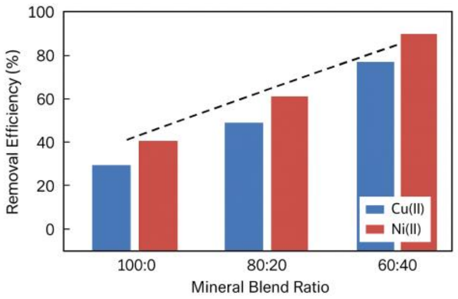

Figure 2. Effect of the natural-to-modified mineral ratio on the removal efficiency of Cu(II) and Ni(II). Conditions: pH = 6, C$_0$ = 10 mg/L, adsorbent dose = 10 g/L, time = 120 min.

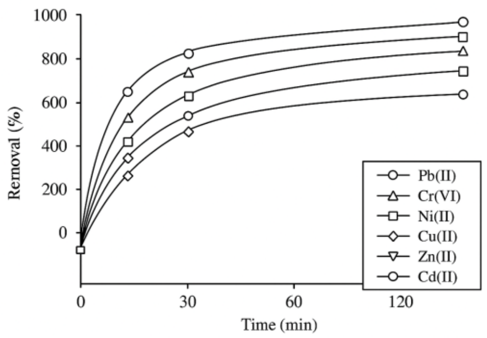

Figure 3. Adsorption kinetics for various heavy metals using the 60:40 modified vermiculite (MV) mixture. Conditions: pH = 6, C$_0$ = 10 mg/L, adsorbent dose = 10 g/L.

4.5. Statistical Modeling

ANOVA results (Table 5) confirmed that pH, mineral type, and modification ratio had a statistically significant effect ($p < 0.05$) on the removal efficiency of all tested metals. The interaction between pH and mineral type was also significant, highlighting that the optimal pH differs for zeolite and vermiculite.

Multiple linear regression analysis was used to develop predictive models for the final pollutant concentration (C_e) within the tested parameter space. The models for the modified vermiculite and zeolite mixtures are shown in Equations (3) and (4), respectively. The high R^2 values indicate that the models can accurately predict the final concentration based on the key operational parameters under these specific experimental conditions. These models serve as a useful tool for process optimization within this study's scope, but would require validation with external data sets before broader application.

For Modified Vermiculite (MV):

$$C_e = 10.52 - 0.102 * n - 0.085 * q_e - 0.25 * pH \quad (3)$$

$(R^2 = 0.981)$

For Modified Zeolite (MZ):

$$C_e = 11.20 - 0.110 * n - 0.077 * q_e - 0.18 * pH \quad (4)$$

$(R^2 = 0.973)$

where C_e is the final concentration (mg/L), n is the removal percentage, q_e is the adsorption capacity (mg/g), and pH is the initial solution pH.

4.6. Acknowledgment of Experimental Limitations

It is important to note that the high removal efficiencies reported were achieved under controlled laboratory conditions using synthetic wastewater with an initial metal concentration of 10 mg/L. Real industrial effluents are far more complex, often containing higher and more variable pollutant concentrations, a mixture of competing ions, and diverse organic and inorganic ligands. These factors can significantly impact adsorbent performance by competing for active sites and altering metal speciation. Therefore, the results presented here represent an optimized potential under idealized conditions. They serve as a crucial proof-of-concept but should not be interpreted as directly transferable to all real-world scenarios without further validation. Future work must address performance in competitive multi-metal systems and actual industrial wastewater to fully assess the practical applicability of these materials.

Table 4. Maximum removal efficiencies (%) for heavy metals using modified mineral mixtures (60:40 ratio) and comparison with literature values

Metal Ion	Modified Zeolite (MZ) - This Study	Modified Vermiculite (MV) - This Study	Literature Value (Zeolite-based)[a]	Literature Value (Vermiculite-based)[b]
Pb(II)	94.6	**98.5**	~99%	~95%
Cr(VI)	85.3	**95.2**	~80%	~90%
Cu(II)	**92.4**	89.8	~90%	~85%
Ni(II)	81.5	**88.6**	~75%	~80%
Zn(II)	**88.1**	82.3	~85%	~78%
Cd(II)	70.2	**75.4**	~70%	~72%

[a] Based on various studies on modified zeolites (e.g., Faustino et al., 2024; Rathi et al., 2024).

[b] Based on studies on modified vermiculite (e.g., Malandrino et al., 2006). Values are approximate for comparison.

Table 5. Summary of ANOVA results for the effect of different parameters on Pb(II) removal.

Source of Variation	Sum of Squares	df	Mean Square	F-value	P-value (Significance)
Mineral Type (Zeolite vs. Vermiculite)	1850.4	1	1850.4	45.8	< 0.001 (Significant)
pH (4, 6, 8)	2430.8	2	1215.4	30.1	< 0.001 (Significant)
Ratio (100:0, 80:20, 60:40)	3155.2	2	1577.6	39.0	< 0.001 (Significant)
Error	1455.1	36	40.4		
Total	**8891.5**	**41**			

5. Discussion

5.1. Role of Modification and Mineralogy in Adsorption

The superior performance of the modified minerals over their natural counterparts can be directly attributed to the physicochemical changes induced during the treatment process. The BET analysis (Table 3) showed a near doubling of the specific surface area for both zeolite and vermiculite after modification. This increase provides a greater number of accessible sites for metal ion binding. The SEM and FTIR results further support this, showing a roughened surface morphology and the successful incorporation of functional groups from the CTAB surfactant. The acid treatment likely contributed by removing pore-blocking impurities and creating new micropores, while the surfactant modification altered the surface charge, creating a dual-functionality adsorbent capable of binding both cations and anions.

The difference in performance between vermiculite and zeolite, even after modification, is rooted in their fundamental crystal structures and chemical compositions (Table 1). Vermiculite, a 2:1 phyllosilicate, has a high layer charge originating from isomorphic substitution in the tetrahedral sheet, resulting in a very high cation exchange capacity (CEC), often higher than that of clinoptilolite. The superior performance of MV, particularly for Pb(II) (98.5% removal) and Ni(II) (88.6% removal), can be partly attributed to its unique chemical makeup. The Gilan vermiculite contains significantly higher Fe_2O_3 (12.88%) and MgO (14.31%) compared to the zeolite. This ferromagnesian character likely results in a higher density of surface hydroxyl sites (Fe-OH, Mg-OH), which, upon deprotonation at pH 6, act as strong Lewis bases, forming stable inner-sphere complexes with cations like Pb^{2+} and Ni^{2+}. This chemical advantage, combined with its high CEC, provides a more robust explanation for its outperformance than structural factors alone, underscoring the importance of selecting minerals with favorable inherent geochemistry.

5.2. Adsorption Mechanisms and Influence of pH

The adsorption of heavy metals onto aluminosilicate minerals is a complex process involving multiple mechanisms, including ion exchange, surface complexation, and electrostatic attraction. The strong pH dependency observed in this study (Figure 1) provides insight into these mechanisms.

For cationic metals like Pb^{2+}, Cu^{2+}, and Ni^{2+}, the primary mechanism is likely a combination of ion exchange with native cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) in the mineral structure and surface complexation with deprotonated silanol ($Si\text{-}O^-$) and aluminol ($Al\text{-}O^-$) groups on the mineral surface. As pH increases from 4 to 6, these functional groups deprotonate, increasing the negative surface charge and enhancing the attraction of metal cations. The exceptional affinity of MV for Pb^{2+} suggests that surface complexation with the abundant Fe-OH and Mg-OH sites on the vermiculite surface is a dominant mechanism, in addition to ion exchange within its interlayer spaces. This is consistent with findings from other studies on vermiculite and zeolite (Malandrino et al., 2006).

For Cr(VI), which exists as an anion ($HCrO_4^-/CrO_4^{2-}$), the mechanism is fundamentally different. The high removal at acidic pH (pH 4) is due to strong electrostatic attraction between the negatively charged chromate anions and a positively charged adsorbent surface. This positive charge is generated from two sources: the protonation of surface hydroxyl groups (e.g., $Si\text{-}OH_2^+$) and, more importantly, the quaternary amine headgroups ($\text{-}N^+(CH_3)_3$) of the CTAB molecules grafted onto the mineral surface during the surfactant modification step. This demonstrates the success of our blended modification strategy, as the CTAB-modified portion of the adsorbent creates dedicated sites for anion binding, enabling the simultaneous removal of pollutants with opposite charges.

5.3. Practical Implications for Industrial Application in Iran

The findings of this study have significant practical implications for wastewater management in Iran. The high removal efficiencies achieved using locally sourced and minimally processed minerals present a compelling case for their adoption as a low-cost, sustainable alternative to conventional, more expensive treatment methods. The abundance of zeolite and vermiculite deposits in Iran ensures a reliable and inexpensive supply of raw materials. The proposed modification process is relatively simple and does not require sophisticated equipment, making it feasible for on-site implementation at industrial facilities.

The development of a 60:40 natural-to-modified mineral mixture represents a pragmatic, cost-optimized solution. It significantly boosts performance while keeping material costs lower than a fully modified system. The rapid kinetics, with equilibrium reached in about an hour, suggest that these materials could be effectively used in continuous flow systems, such as packed bed columns, which are common in industrial settings. The robust statistical models (Eq. 3 & 4) can serve as a valuable tool for process design and optimization, allowing engineers to predict the performance of the treatment system under varying influent conditions within the tested range.

By valorizing its own geological resources, Iran can develop a circular economy approach to environmental management, turning a natural resource into a high-value product for pollution control. This not only addresses the critical issue of water pollution from key industries but also promotes local economic development and reduces reliance on imported technologies.

5.4. Future Perspectives and Practical Challenges

While this study demonstrates high adsorption potential, the practical, long-term application hinges on addressing the lifecycle of the adsorbent. Future research must focus on two critical areas: regeneration and disposal. Regeneration studies should explore the desorption of heavy metals using appropriate eluents (e.g., dilute acids like HCl or HNO_3 for cations, or basic solutions for anions) to potentially recover the metals and restore the adsorbent's capacity. The economic feasibility of regeneration versus single-use application needs to be rigorously assessed, considering the cost of chemicals and the potential degradation of the adsorbent over multiple cycles. For disposal, spent adsorbents laden with toxic metals must be managed as hazardous waste. Stabilization/solidification techniques, such as vitrification or cement encapsulation, should be investigated to immobilize the metals and prevent their long-term leaching into the environment, ensuring the overall process is environmentally sound. Addressing these challenges is paramount to transitioning this promising technology from the laboratory to full-scale industrial deployment.

6. Conclusions

This study successfully demonstrated the high potential of natural and modified zeolite and vermiculite sourced from major Iranian deposits for the adsorptive removal of heavy metals from industrial wastewater. The key conclusions are as follows:

1. Mineral performance: Both Iranian zeolite (from Semnan) and vermiculite (from Gilan) are effective adsorbents. Modified vermiculite, in particular, exhibited exceptional performance, achieving over 98% removal for Pb(II) and 95% for Cr(VI) under optimized conditions, which is attributed to its superior intrinsic CEC and favorable surface chemistry (high Fe/Mg content).

2. Effectiveness of blended modification: A novel chemical modification via a combined acid and surfactant treatment significantly enhanced the minerals' adsorption capacity by increasing surface area and creating a dual-functional surface capable of binding both cations and anions.

3. Optimal conditions: The optimal conditions for broad-spectrum heavy metal removal from a 10 mg/L solution were identified as a pH of 6 and an adsorbent mixture containing a 60:40 ratio of natural-to-modified mineral. This blend offers a practical compromise between performance and cost.

4. Rapid kinetics: The adsorption process was rapid, with equilibrium largely achieved within 60-90 minutes, making these materials suitable for application in continuous treatment systems.

5. Predictive modeling: Robust statistical models ($R^2 > 0.97$) were developed for the tested conditions, providing a reliable tool for predicting treatment efficiency and aiding in the design of application systems.

This research provides a strong foundation for the development of a sustainable, low-cost wastewater treatment technology tailored to the Iranian industrial context. Future work should focus on pilot-scale testing in continuous flow column reactors to validate these batch-scale findings. Additionally, comprehensive studies on the regeneration, safe disposal, and economic lifecycle of the spent adsorbents are crucial for ensuring the long-term environmental sustainability and viability of this promising technology.

Acknowledgements

The authors gratefully acknowledge the technical staff at the Central Laboratory of Amirkabir University of Technology for their assistance with the XRD, SEM, and AAS analyses. We thank the anonymous reviewers for their constructive comments that helped improve the manuscript.

Declarations

Data and code availability

All data generated or analyzed during this study are available from the corresponding author upon reasonable request. No computational code was used in this study.

Conflicts of interest

The authors announced that they have no known conflicts of interest or personal relationships that could have appeared to influence the work reported in this manuscript.

Ethical approval

The authors declare no ethical issues; the research was carried out in full agreement with ethical standards. Also, this paper is neither under Review nor published elsewhere.

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