Characterization and adsorption performance of surfactant-modified zeolite for chromium(VI) removal from aqueous solutions

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ABSTRACT

This study examined the surface modification of natural zeolite sourced from Pangasinan, Philippines to assess its potential as an adsorbent for Cr(VI) removal. The natural zeolite (NZ) and surfactant-modified zeolite (SMZ) were characterized to evaluate their composition and alterations in surface properties. Characterization revealed a reduction in specific surface area (SSA) from 165.84 m² g⁻¹ to 37.68 m² g⁻¹ and a reversal in zeta potential from -16.9 mV to +46.73 mV, enabling Cr(VI) adsorption. Adsorption performance was investigated under varying conditions, including adsorbent dosage, contact time, solution pH, ionic strength, competing ions, and dissolved organic matter (DOM). Optimal Cr(VI) adsorption occurred at pH 3, with equilibrium reached rapidly, favoring the univalent $HCrO_4^-$ species over the divalent CrO_4^{2-} species prevalent at higher pH levels. Increased ionic strength and competing ions reduced Cr(VI) adsorption, while the presence of DOM had no significant effect. SMZ exhibited a maximum adsorption capacity of 13.603 mg g⁻¹, as described by the Langmuir isotherm model (R^2 = 0.970), indicating a uniform monolayer adsorption mechanism. Comparative performance tests demonstrated Cr(VI) removal efficiencies of 61.52% for SMZ, 73.82% for powdered activated carbon (PAC), and 1.03% for NZ. Although the removal efficiency of SMZ is lower than PAC, it offers a cost-effective, resource-efficient alternative with potential scalability. The study has shown its applicability in wastewater treatment, particularly under acidic conditions, with proper management of ionic strength and competing ions. Future research should investigate regeneration capabilities and evaluate the SMZ performance in real-world conditions.

Keywords: hexavalent chromium, surfactant-modified zeolite, adsorption studies.

INTRODUCTION

Environmental contamination is a consequence of industrial processes that discharge huge quantities of wastewater, polluting soil and water bodies. Textile and metallurgical sectors are recognized to release wastewater with high concentrations of heavy metals, which are highly toxic pollutants of various microorganisms, plants, and even humans. Chromium is a heavy metal frequently seen in industrial effluents, particularly in the wastewater generated by activities, such as electroplating, leather tanning, mining, and textile manufacturing (Coetzee et al., 2018; Bolaños-Benítez et al., 2020; Younas et al., 2022; Iyer et

al., 2023). Hexavalent chromium, Cr(VI), is a form of chromium that significantly endangers the environment and public health due to its carcinogenic and mutagenic effects. The elimination or reduction of Cr(VI) from contaminated sources has become a critical area for environmental research and engineering (Asgari et al., 2013).

Globally, stringent regulations have been imposed to manage Cr(VI) pollution. For instance, the European Union banned the use of Cr(VI) in surface treatments with Registration, Evaluation, Authorization, and Restriction of Chemicals (REACH) in 2017 and phased out corrosion-resisting paint additives by 2019 (Carneiro et al., 2021). In the Philippines, the Administrative

Order #2021-09, a Chemical Control Order (CCO) for Cr(VI) compounds, was issued by the Department of Environment and Natural Resources (DENR) on October 26th, 2021. CCO mandates strict regulation of Cr(VI) in activities such as the manufacture of pigments, inks, textile dyes, protective coatings, stainless steel, and electronic equipment, as well as in laboratory operations and tanneries. The entities engaged in the importation, manufacture, distribution, or industrial use of Cr(VI) compounds are required to register with and obtain clearances from the Environmental Management Bureau (EMB). This regulatory framework stresses the need for innovative and locally available solutions to manage the Cr(VI) contamination in the country.

Traditional techniques for eliminating Cr(VI), including chemical precipitation, ion exchange, and membrane technologies, are often costly and energy-intensive, limiting their practicality for large-scale use or in low-income settings (Misaelides, 2011; Ghanizadeh et al., 2012). Consequently, adsorption using natural or modified low-cost materials has emerged as an efficient and economically feasible alternative. Adsorption has been extensively studied due to its versatility. Natural and synthesized materials possessing high adsorption capacity, like zeolites, have been used for heavy metal adsorption.

Natural zeolites, like clinoptilolite, heulandite, and mordenite, have attracted interest for their ability to eliminate contaminants from water owing to their high cation-exchange capacities and porous structures (Li and Bowman, 2001; Mier et al., 2001). Zeolites are commonly utilized due to their affordability and excellent adsorption capabilities. However, their net negative structural charge, caused by isomorphous substitution within the crystal lattice, results in minimal affinity for anions, such as Cr(VI). To overcome this issue, surface modification has been explored using cationic surfactants.

Cationic surfactants form an organic layer on the zeolite surface, modifying its chemistry to enable the adsorption and removal of anionic pollutants (Bowman, 2003; Apreutesei et al., 2008; Inglezakis and Zorpas, 2012). Modifying zeolite surfaces with cationic surfactants like hexadecyltrimethylammonium bromide (HDTMA-Br) improves their ability to adsorb anionic pollutants (Leyva-Ramos et al., 2008). A surfactant-modified zeolite (SMZ) possesses positive surface charges, which facilitate the Cr(VI) adsorption through electrostatic interactions (Asgari et al., 2013). Previous research on different modified natural zeolites demonstrated their effectiveness in adsorbing anionic pollutants (Warhol et al., 2006; Wingenfelder et al., 2006; Li et al., 2007; Zhang et al., 2007; Guan et al., 2010). Cr(VI) adsorption efficiency is greatly affected by factors like the quantity of competing ions in the solution, ionic strength, and pH levels (Hommaid and Hamdo, 2014; Yalçın et al., 2022). The adsorption mechanism typically involves a combination of surface anion exchange and chemisorption, as confirmed by isotherm and kinetic studies across multiple modified zeolite systems (Asgari et al., 2013; Yalçın et al., 2022). SMZs were also found to be effective in the sorption of volatile petroleum hydrocarbons (Karapanagioti et al., 2005; Torabian et al., 2010) and phenolic compounds (Dong et al., 2010).

In the context of the Philippines, the abundance of natural zeolites presents a promising opportunity to develop cost-effective sorbents for environmental remediation. The Philippine zeolite has been studied for Cu, As, Ni, and Pb adsorption (Olegario-Sanchez and Pelicano, 2017; Olegario-Sanchez et al., 2019). Despite its potential, limited research has investigated the use of Philippine zeolites to remove Cr(VI) in contaminated soil and water. This study involved the surface modification of a Philippine natural zeolite, followed by characterization and examination of its Cr(VI) adsorption capacity. Key parameters, including adsorbent dose, contact time, solution pH, ionic strength, competing ions, and dissolved organic matter were evaluated to provide insights into the adsorption conditions and advance its potential application for industrial effluent treatment. Furthermore, the adsorption capability of SMZ for Cr(VI) was evaluated in comparison to that of the natural zeolite and activated carbon.

MATERIAL AND METHODS

Materials and chemical reagents

The natural zeolite (NZ, 0.074–0.044 μm) originating from an open pit mine in Pangasinan, Philippines was sourced from Saile Industries Incorporated. The zeolite samples were rinsed with dH_2O and oven-dried at 105°C for 24 hours. Other chemicals used in the study were analytical reagent grade, including calcium chloride ($CaCl_2$),

sodium chloride (NaCl), potassium chloride (KCl), and sodium hydroxide (NaOH), potassium dichromate ($K_2Cr_2O_7$), potassium sulfate (K_2SO_4), sodium phosphate (Na_3PO_4), hexadecyltrimethyl ammonium bromide (HDTMA-Br), diphenylcarbazide ($C_{13}H_{14}N_4O$), sulfuric acid (H_2SO_4), and hydrochloric acid (HCl). Suwanee River Fulvic/ Humic Acid (SRFA-II/SRHA-II) standards were from the International Humic Substances Society (USA). The commercial adsorbent powdered activated carbon (PAC WPH-1000) was obtained from Calgon Carbon Corporation.

Surface modification

Before surface modification, the cation exchange capacity (CEC) was measured using the method outlined by Chapman (1965), while the external cation exchange capacity (ECEC) was determined following Bouffard (1998). To prepare SMZ, zeolite samples were mixed with HDTMA-Br solutions prepared in an amount equal to 150% of ECEC of the zeolite in a 250 mL Erlenmeyer flask. The suspensions were agitated in an orbital shaker for 8 hours at room temperature and then allowed to rest overnight to achieve equilibrium. Afterwards, the mixture was filtered, and the solid residue was left to air-dry for 48 hours. The samples were pulverized and placed in a desiccator.

Material characterization

Natural zeolite and SMZ were both characterized to provide better insights on surface modification. Surface morphology and elemental composition were analyzed using a scanning electron microscope (SEM, FEI ESEM Quanta 450 FEG Philips-XL20) equipped with an Oxford Ultim Max EDS detector. The crystallinity and mineral composition were analyzed through X-ray diffraction (XRD) using a Philips PW1710 microprocessor-controlled PW1050 instrument. Functional groups and chemical structures were characterized with Fourier-transform infrared spectroscopy (FTIR) on a Perkin Elmer Spectrum One spectrometer.

The methylene blue (MB) dye adsorption technique was used to measure the specific surface area (SSA) with a Shimadzu UV-2600 UV-Vis spectrophotometer set at 664 nm. Fifteen mg of the adsorbent was combined with 150 mL of 20 mg L^{-1} MB solution and agitated at 100 rpm for 60 hours to achieve equilibrium and maximum dye uptake. Post-centrifugation, the supernatants were assessed using UV-Vis spectrophotometry at 664 nm, and the MB absorbed was calculated by comparing the results to the control samples. Equation 1 was used to calculate SSA:

$$SSA = \frac{N_A A_{MB}(C_A - C_B)V_{MB}}{M_{MB}m_s} \qquad (1)$$

where: C_A – the initial MB concentration, C_B – equilibrium MB concentration, V_{MB} – volume of solution, m_s – adsorbent mass, M_{MB} – molecular mass of MB, N_A – Avogadro's number, and A_{MB} – area covered per MB molecule (1.35 nm^2).

The surface charge (zeta potential) was measured using 0.1% w/v suspensions prepared in Milli-Q water. Furthermore, for SMZ, zeta potential measurements were performed in a pH range (2–10). The suspensions were agitated for 48 hours before the zeta potential measurement using dynamic light scattering with a Malvern Zetasizer NanoZS.

Sorption studies

Batch adsorption experiments were performed in 50 mL polypropylene tubes with 200 mg SMZ and 20 mL of 50 mg L^{-1} Cr(VI) solution. Mixtures were shaken using an end-over-end shaker for a day, followed by centrifugation (4000 rpm, 20 minutes) to separate the liquid and solid phases. Supernatants were collected and analyzed for Cr(VI) concentration at 540 nm using a UV-Vis spectrophotometer (Shimadzu UV-2600). All experiments were conducted in triplicate.

Adsorption tests were done by varying individual parameters while maintaining all other conditions constant to evaluate their effects. The effect of contact time was assessed by examining various contact durations (0.5–48 hours). Solution pH effect was investigated by adjusting the solution pH by minimal addition (<50 μL) of diluted HNO_3/NaOH solutions to achieve the desired pH values (3, 5, 7, and 9). The ionic strength effect at 0.01, 0.05, 0.1, and 0.5 M NaCl, KCl, and $CaCl_2$ was also investigated. Subsequently, the influence of competing ions (SO_4^{2-} and PO_4^{3-}), applied as K_2SO_4 and Na_3PO_4, in 25, 50, and 100 mg L^{-1} and DOM, applied as SRHA-II and SRFA-II in 1, 5, 10 mg L^{-1} were examined. Equation 2 was used to determine the adsorption capacity of SMZ.

$$q_e = \frac{(C_i - C_f)V}{m} \qquad (2)$$

where: q_e – solid phase sorbate concentration (equilibrium) (mg g^{-1}), V – volume of solution (L), m – adsorbent quantity (g), C_i – initial Cr(VI) concentration (mg L^{-1}), C_f – final Cr(VI) concentration (mg L^{-1}).

The adsorption test was performed in a wide variety of Cr(VI) concentrations ranging from 10 to 1000 mg L^{-1}. Both the Langmuir (Equation 3) and Freundlich (Equation 4) isotherm models were utilized to account for the adsorption parameters.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \qquad (3)$$

$$q_e = K_F C_e^{\frac{1}{n}} \qquad (4)$$

where: q_e – equilibrium Cr(VI) concentration in SMZ (mg g^{-1}), C_e – equilibrium Cr(VI) concentration in solution (mg L^{-1}), q_m – maximum sorption capacity of SMZ (mg g^{-1}), K_F – Freundlich constant, K_L – Langmuir constant, and $1/n$ – heterogeneity factor.

Adsorption efficiency benchmarking

The ability of SMZ to adsorb Cr(VI) was assessed in comparison with NZ and powdered activated carbon (PAC), a standard commercial adsorbent. For this, 200 mg of each adsorbent was combined with 20 mL Cr(VI) solution (50 mg L^{-1}) in 50 mL polypropylene tubes. Adsorption efficiency is expressed as Cr(VI) removal from the solution (%) (Equation 5).

$$Removal\ (\%) = \frac{C_i - C_f}{C_i} \times 100 \qquad (5)$$

where: C_i – initial Cr(VI) concentration (mg L^{-1}), C_f – final Cr(VI) concentration (mg L^{-1}).

RESULTS AND DISCUSSION

Material characterization

Surface morphology and elemental composition

The scanning electron micrographs are presented in Figure 1. Natural zeolitic material exhibited thin, plate-like crystals of mordenite, heulandite, and clinoptilolite, as shown in Figure 1a. After modification, the SEM micrograph of SMZ revealed that the crystal structure was obscured by the presence of HDTMA-Br, indicating organic layer development on the surface (Figure 1b). EDS analysis of SMZ detected significant amounts of C, O, Si, and Al, confirming the aluminosilicate composition of the zeolite and the carbon-based nature of HDTMA-Br (Figure 2).

Crystallinity and mineral composition

The XRD analysis indicated that the natural material consists of mordenite, montmorillonite, heulandite, calcite, and quartz (Figure 3a). Comparable mineral compositions were identified in SMZ following surfactant treatment (Figure 3b). Zeolite showed diffraction peaks similar to those of the crystalline structure reported in previous studies (Olegario-Sanchez and Pelicano, 2017).
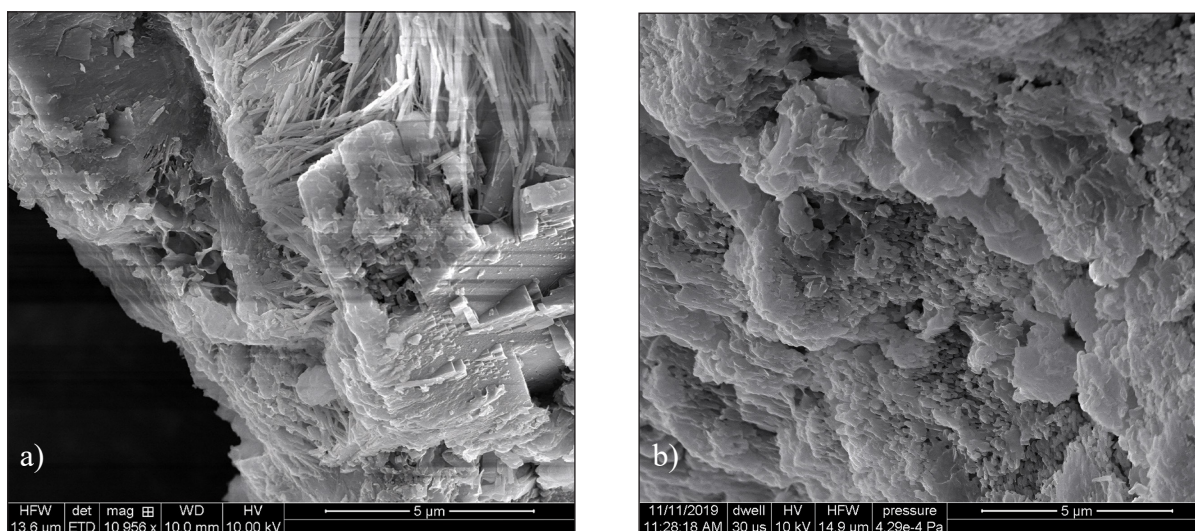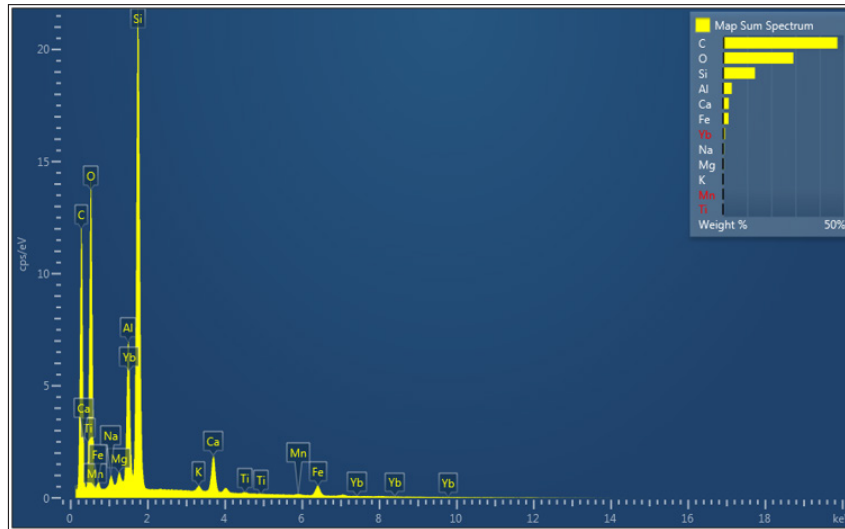

Figure 1. SEM images of (a) NZ and (b) SMZ

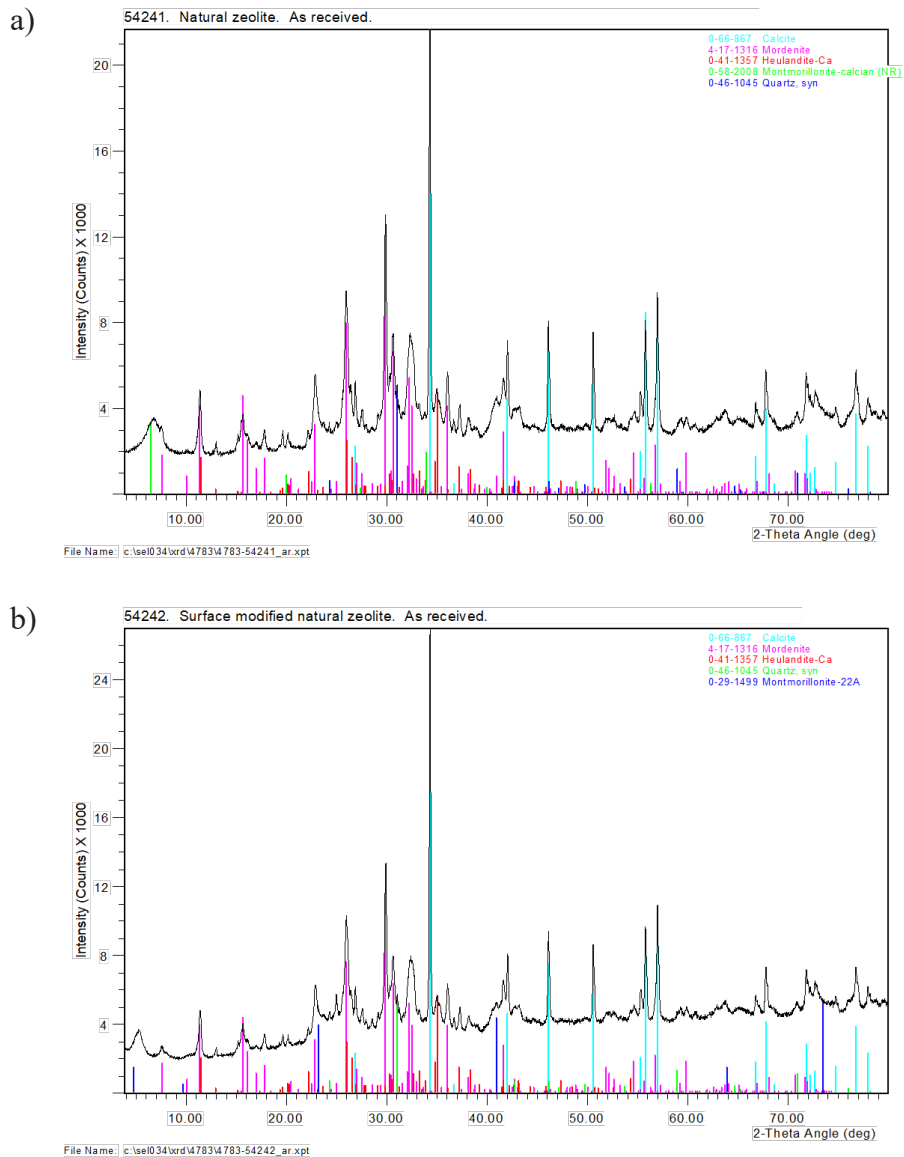**Figure 2.** EDS peaks of elements present in the map sum spectrum of SMZ

Figure 3. XRD profiles of (a) NZ and (b) SMZ

Functional groups identification

The FTIR spectra of NZ and SMZ, along with HDTMA-Br, are shown in Figure 4. The SMZ spectrum exhibited characteristic bands at 1120 and 494 cm^{-1}, corresponding to T-O stretching and bending vibrations, respectively. Additional bands were observed at 1642 cm^{-1} for water bending vibrations, 3408 cm^{-1} for hydrogen bonding water, and 3600 cm^{-1} for isolated OH stretching. Two new bands at 2922 and 2852 cm^{-1} due to the antisymmetric and symmetric C-CH$_2$ stretching of the alkyl chain are associated with the surfactant HDTMA (Warchol et al., 2006). The FTIR findings were consistent with earlier studies on natural zeolites and SMZ (Karadag et al., 2007; Zeng et al., 2010). According to Breck (1974), zeolite FTIR spectra bands are class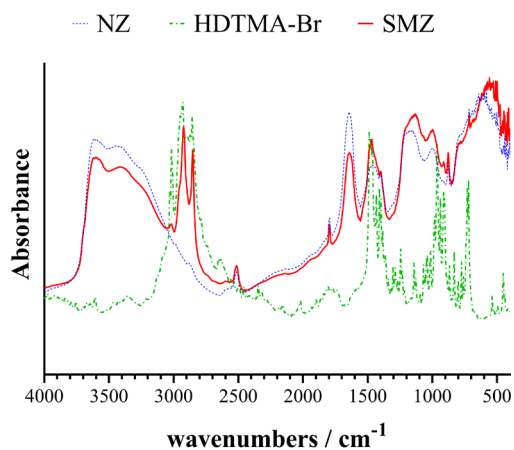ified as follows: a) Si–O–Al and Si–O–Si vibrations: These occur in the ranges 420–500 cm^{-1} and 1200–950 cm^{-1}. The most prominent vibration band common to all zeolites, 1200–950 cm^{-1} range, is attributed to T–O stretching from internal tetrahedra. The second strongest band, 420–500 cm^{-1} range, corresponds to T–O bending. b) Pseudo-lattice vibration bands: These appear in the 500–800 cm^{-1} region and are unaffected by the Si/Al ratio or the type of channel cations. c) Water-related bands in zeolites: Three typical bands are identified: isolated OH stretching (a sharp band around 3619 cm^{-1}), hydrogen-bonded OH groups (a broad band near 3440 cm^{-1}), and a bending vibration of water at approximately 1640 cm^{-1}.

Specific surface area and charge

Surface area and charge are both important in adsorption processes. The SSA of NZ and SMZ were 165.84 and 37.68 m^2 g^{-1}, respectively. The results demonstrate that surface modification with HDTMA-Br, a large molecular compound, significantly reduced SSA. This reduction adversely affects the ability of SMZ to adsorb Cr(VI) species, as less adsorption sites are available. The surface charge (reported as zeta potential) of the NZ is -16.9 mV. Having a net negative charge indicates that natural zeolite is not able to adsorb anionic contaminants like CrO$_4^{2-}$. In contrast, due to the surfactant modification, the surface charge of SMZ was +46.73 mV. At various pH levels, SMZ retained a net positive zeta potential allowing Cr(VI) adsorption in a wide range of pH (Figure 5). The positive zeta potential allows SMZ to
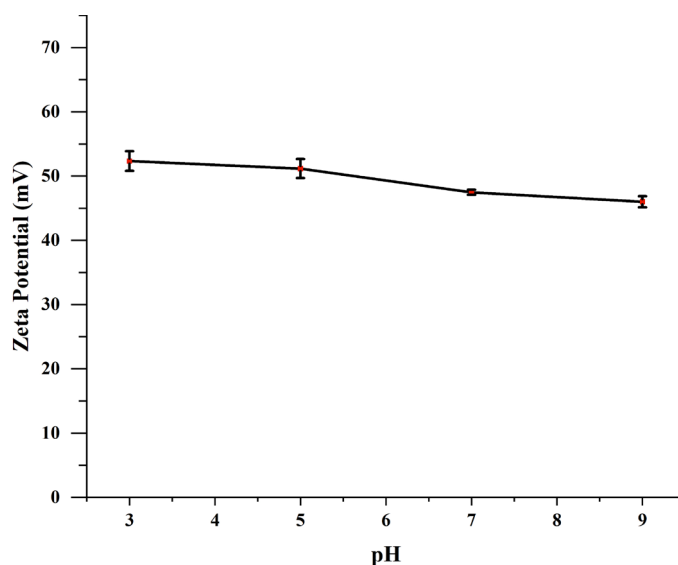

Figure 4. FTIR spectra of NZ, SMZ and HDTMA-Br

Figure 5. Surface zeta potential measurements of SMZ at different pH

adsorb anionic Cr(VI) species. The charge reversal indicates the formation of the organic layer of the ionic surfactant. This occurs through cation exchange, followed by hydrophobic interactions facilitating surfactant attachment. Surfactant molecules, when present in quantities that are higher than the critical micelle concentration, result in the formation of a bilayer, known as an admicelle, on the surface (Chen et al., 1992). The outer layer is held in place through hydrophobic interactions resulting in a shift in the surface charge of SMZ from negative to positive, enabling it to exhibit anion exchange capacity (Zanin et al., 2016).

Adsorption studies

Effect of SMZ dose, contact time, and pH

The effect of adsorbent dosage on Cr(VI) adsorption is shown in Figure 6a. The removal efficiency is highly dependent on the amount of adsorbent that is utilized. Increasing dosage results in a decreasing amount of Cr(VI) ions adsorbed per unit of adsorbent. The amount of Cr(VI) adsorbed decreased from 4.24 mg g^{-1} to 1.71 mg g^{-1} as the SMZ dosage increased from 100 mg to 500 mg. This outcome is within expectations, as a fixed initial Cr(VI) concentration combined with an increased adsorbent quantity offers a greater surface area and more available adsorption sites for ion binding, indicating relation adsorption dependence leading to dilution effect becoming more apparent where the limited amount of Cr(VI) ions is insufficient to occupy all available adsorption sites at higher dosages. Increasing the adsorbent dosage resulted in a lower adsorption capacity as a greater number of adsorption sites remained unutilized during the process (Radnia et al., 2012). Similar results were reported on Cr(VI) adsorption on various adsorbents (Rengaraj et al., 2001; Hommaid and Hamdo, 2014; Jorfi et al., 2017; Tsafam et al., 2019).

The quantity of adsorbed Cr(VI) (mg g^{-1}) due to contact time is presented in Figure 6b. The results indicated that Cr(VI) was rapidly adsorbed onto SMZ, and equilibrium was reached within a short period of time. Rapid Cr(VI) adsorption is considered a beneficial characteristic of SMZ for its practical applications. The findings demonstrate that a duration of 30 minutes was adequate for the adsorption process to reach equilibrium.

Adsorption experiments were carried out at pH levels of 3, 5, 7, and 9 as presented in Figure 6c. The findings indicated that an increase in

solution pH led to a reduction in Cr(VI) adsorption, with the maximum amount of Cr(VI) sorbed onto SMZ occurring at pH 3. Under acidic conditions, H$^+$ dominates the environment; while under alkaline conditions, OH$^-$ ions are abundant decreasing Cr(VI) sorption efficiency. Moreover, the dominant Cr(VI) species in the environment, along with the exchange capability of the SMZ for different species, affects the adsorption process.
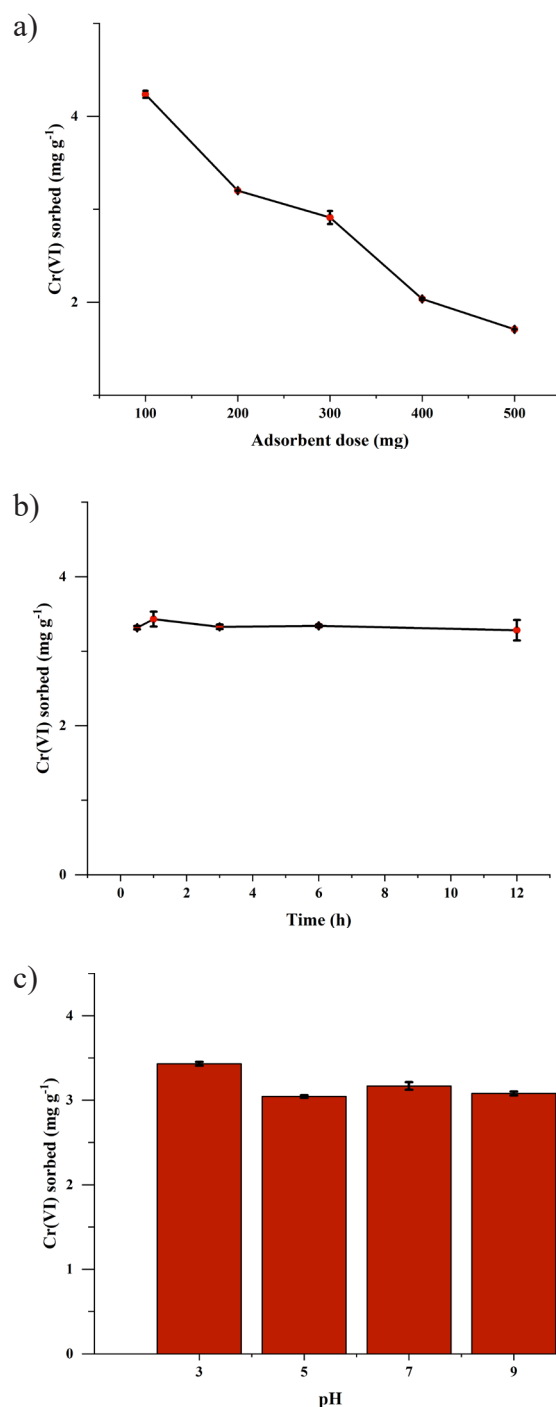

Figure 6. Cr(VI) sorbed (mg g^{-1}) due to the effect of (a) adsorbent dosage, (b) contact time, and (c) pH

Depending on the solution pH, Cr(VI) exists in the forms of $HCrO_4^-$, CrO_4^{2-}, and $Cr_2O_7^{2-}$. Visual MINTEQ speciation results revealed that 93.5% of the Cr(VI) species is $HCrO_4^-$ at pH 3, 90.9% is $HCrO_4^-$ at pH 5, 77.8% and 21.6% are CrO_4^{2-} and $HCrO_4^-$ at pH 7, while 99.4% occur as CrO_4^{2-} at pH 9. At lower pH values (pH 3 and 5), the univalent form is predominant, requiring one exchange site for every $HCrO_4^-$ ion. At higher pH value (pH 9), Cr(VI) species exist as divalent anion (CrO_4^{2-}), requiring two exchange sites. The results of this investigation corroborate earlier research, as the highest adsorption of Cr(VI) was also noted at pH 3 with HDTMA-modified zeolite-rich tuff (Salgado-Gomez et al., 2014), HDMTA-modified synthesized zeolite Y (Malek and Nizam, 2007), zeolite/chitosan hybrid composite (Pang et al., 2015), and HDTMA-treated natural Anatolian zeolite (Yalcin et al., 2022). Another potential factor affecting the adsorption is the surface charge. The zeta potential of SMZ slightly decreases as pH increases, affecting its affinity to adsorb Cr(VI) anions.

Effect of ionic strength, dissolved organic matter, and competing ions

Wastewater from different industries often contains different ions and dissolved salts, contributing to elevated ionic strength. The adsorption efficiency of SMZ can be substantially influenced by higher ionic strength, which reduces Cr(VI) adsorption, as shown in Figure 7. The Cr(VI) sorption using dH2O was 3.13 mg g^{-1}. In contrast, at CaCl2 concentrations of 0.01, 0.05, 0.1, and 0.5

M, the adsorption levels were 2.19, 0.94, 0.39, and 0.19 mg g^{-1}, respectively. A similar decreasing trend is observed when using either NaCl or KCl solution. The effect of ionic strength on the Cr(VI) adsorption is generally associated with the competitive dynamics between background electrolyte anions and Cr(VI) for available adsorption sites (Li, 2004; Zeng et al., 2010). The chloride ions (Cl$^-$) engage in competition with chromate ions for the available sorption sites. These findings align with similar studies observing an inverse relationship between ionic strength and Cr(VI) adsorption (Gładysz-Płaska et al., 2011; Jing et al., 2011; Castro-Castro et al., 2020).

Increasing the background electrolyte concentrations increases the corresponding electrical conductivity (EC) of the Cr(VI) solutions. For example, with 0.01, 0.05, 0.1, and 0.5 M CaCl2 background electrolyte concentrations, the EC values were 0.12, 4.78, 8.66, and 29.20 dS m^{-1}, respectively. The extensive EC values encompassed a broad spectrum of environmental circumstances, providing practical significance. For example, irrigation water having EC values between 0.7–3.0 dS m^{-1} is subject to slight to moderate usage restrictions. In contrast, water exceeding 3.0 dS m^{-1} faces severe limitations due to its impact on crop water availability (Ayers and Westcot, 1985). Meanwhile, saline soils typically have a saturated soil extract exceeding 4 dS m^{-1} (Richards, 1954), while landfill leachates may present the EC values ranging from 5 to 17 dS m^{-1} (Marttinen et al., 2002). The capability of SMZ to adsorb Cr(VI)
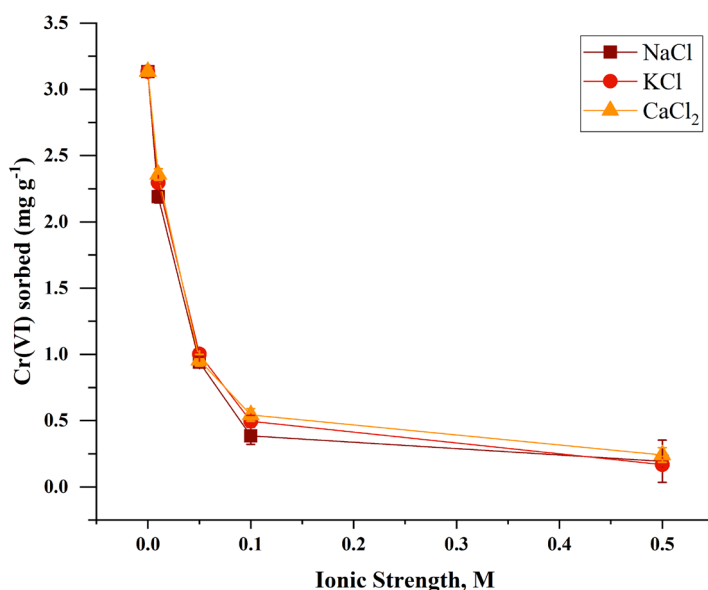

Figure 7. Cr(VI) adsorption on SMZ at various ionic strength values

across a wide range of EC levels suggests potential application to various problem areas in both soil and water.

Competing ions such as SO_4^{2-} and PO_4^{3-} reduced Cr(VI) adsorption onto SMZ, as shown in Figure 8a. In the absence of these ions, Cr(VI) adsorption was 3.17 mg g^{-1}. The addition of sulfate at concentrations of 25 to 100 mg L^{-1} lowered Cr(VI) adsorption from 2.56 to 2.16 mg g^{-1}. Similarly, increasing phosphate concentrations from 25 to 100 mg L^{-1} reduced Cr(VI) adsorption from 2.62 to 2.26 mg g^{-1}. Sulfate and phosphate ions compete with Cr(VI) species to occupy the finite number of

SMZ adsorption sites. Competing anions can negatively affect Cr(VI) adsorption subject to specific competing anions, the initial Cr(VI) concentrations, and relative surface affinities (Rai and Zachara, 1986).

Meanwhile, the presence of HA and FA in the initial solution had no impact on Cr(VI) adsorption onto SMZ, as shown in Figure 8b. Without any DOM, Cr(VI) adsorption was 3.17 mg g^{-1}. With 1–10 mg L^{-1} of HA, adsorption ranged from 3.20 to 3.14 mg g^{-1}. Similarly, the presence of 1–10 mg L^{-1} of FA resulted in adsorption values between 3.22 and 3.12 mg g^{-1}. Previous research has shown that the Cr(VI) reduction rate
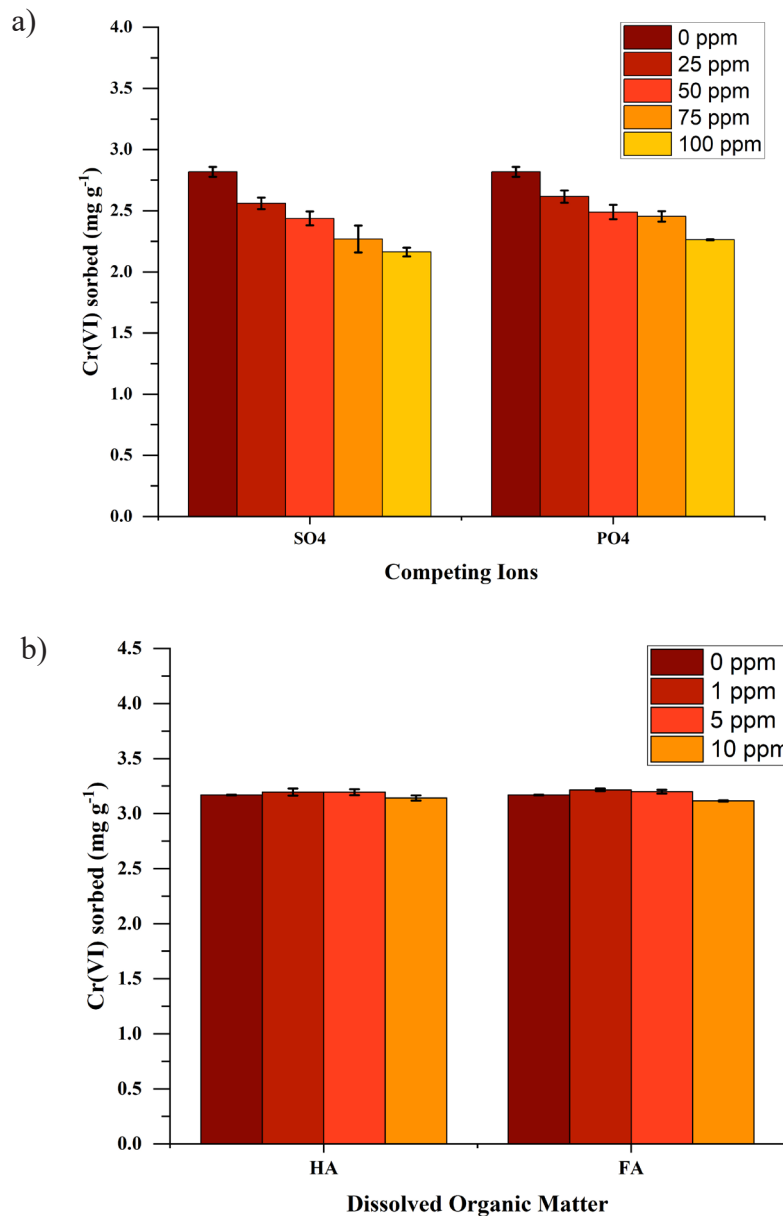

Figure 8. Cr(VI) adsorption on SMZ at various concentrations of (a) competing ions and (b) dissolved organic matter

is positively correlated with the concentration of soil humic substances, as observed in the cases of HA and FA (Palmer and Puls, 1994). Additionally, the reduction is enhanced under lower pH conditions (Bloomfield and Pruden, 1980). In this particular study, it is possible that the reduction did not occur during the 24-hour test period due to the inherent alkalinity of SMZ (pH 7.82), resulting in a high solution pH after mixing. The pH of the test solutions after mixing was around 8.02 to 8.19 which is not conducive to spontaneous Cr(VI) reduction. According to Eckert et al. (1990), Cr(VI) reduction by humic acids has a half-life of approximately three days under extremely low pH, while at pH levels between 4 and 7, the process takes several days to complete.

Adsorption isotherm

A comparison between the experimental data and the theoretical predictions of the Langmuir and Freundlich isotherm models is shown in Figure 9. These models yield critical insights into sorption mechanisms, affinity of the sorbent, and surface characteristics. The parameter values derived from the isotherm models are presented in Table 1. Analysis of the adsorption data revealed a better fit with the Langmuir isotherm model compared to the Freundlich model with a high correlation coefficient ($R^2 = 0.970$) which indicates that the Langmuir model provides a better fit for the experimental data, implying the sorption process follows a homogeneous surface adsorption, suggesting a monolayer adsorption mechanism where Cr(VI) ions bind uniformly to the surface of SMZ. The maximum adsorption capacity (q_m) of SMZ for Cr(VI) was calculated to be 13.603 mg g^{-1}, while the Langmuir constant (K_L) was determined to be 0.017. The Freundlich model, characterized by a Freundlich constant (K_f) of 1.818 and an adsorption intensity (n) of 3.339, describes sorption on a heterogeneous surface with varied energy sites. Although the Freundlich model fits the data reasonably well ($R^2 = 0.881$), its lower correlation coefficient compared to the Langmuir model suggests that Cr(VI) sorption onto SMZ is better represented by a uniform, monolayer adsorption process rather than a multi-layered or heterogeneous one. Similarly, other studies have reported the Langmuir isotherm model as the best-fit model for Cr(VI) adsorption onto various zeolites (Asgari et al., 2012; Bolortamir et al., 2011; Yalcin et al., 2022).

Table 1. Parameters of the Langmuir and Freundlich models for Cr(VI) adsorption onto SMZ

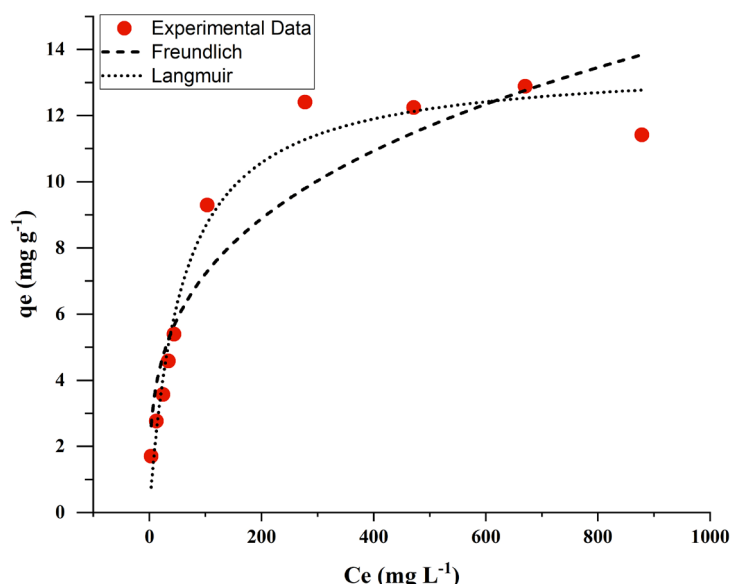| Parameter	Langmuir			Freundlich		
	q_m	K_L	R^2	n	K_f	R^2
SMZ	13.603	0.017	0.970	3.339	1.818	0.881

Figure 9. Cr(VI) adsorption fitted to Langmuir and Freundlich isotherm models

Benchmark of adsorption efficiency

The benchmarking adsorption test results showed that SMZ had removed 61.52% of Cr(VI), PAC achieved a higher removal rate of 73.82%, and NZ showed minimal effectiveness, removing only 1.03%. The relatively lower adsorption capacity of SMZ compared to PAC may be due to differences in pore structure and higher surface area. Activated carbon is known for its high surface area and extensive pore network, which enhances its ability to absorb various contaminants including Cr(VI). SMZ, while modified to enhance its adsorption properties, may not possess the same level of surface complexity, which could explain the differences observed in the removal efficiency. However, SMZ may present certain advantages over PAC, including a lower cost of production from natural zeolite, and its modification process may be less resource-intensive compared to the production of activated carbon, which often requires significant energy inputs.

Practical application and limitations

Repeated exposure to contaminated water may reduce its adsorption efficiency over time. Thus, the regeneration potential of SMZ also needs to be considered for real-world usage. Zeng et al. (2010) successfully demonstrated the regeneration of SMZ using methods such as sodium carbonate extraction and hydrochloric acid treatment, as observed in chromate-saturated hexadecylpyridinium bromide (HDPB) modified chabazite-Ca and clinoptilolite. Successful regeneration of SMZ after removal of other contaminants such as organic contaminants (Hashemi et al., 2018), various pesticides (Andrunik et al., 2023) was also observed.

The translation of laboratory results to real-world applications presents several challenges and considerations. In controlled laboratory settings, factors such as pH, ionic strength, and competing ions are carefully regulated, enabling optimal conditions for Cr(VI) adsorption by SMZ. However, in natural environments or industrial effluents, these parameters can vary significantly, affecting adsorption efficiency. As demonstrated in this study, the Cr(VI) adsorption capacity of surfactant-modified zeolites is pH-sensitive and adsorption capacity decreases in the presence of high ionic strength and competing ions. Industrial effluents with elevated

levels of other ions can compete with Cr(VI) ions for active sites on the SMZ, thereby reducing its efficacy. Additionally, natural waters with high alkalinity or pH can diminish the adsorption of Cr(VI), possibly necessitating pre-treatment steps to adjust the solution chemistry before effective SMZ application.

Real-world wastewater often contains diverse contaminants, including heavy metals, organic pollutants, and varying concentrations of dissolved salts, which may reduce the adsorption capacity of SMZ due to competitive adsorption and complexation effects. This study did not involve chromate-contaminated industrial wastewater and to the authors' knowledge, no existing studies have been conducted on this subject. However, few studies have tested various SMZs in other contexts with industrial wastewater, demonstrating its potential for broader applications. Ozdemir et al. (2009) employed SMZ in a fixed-bed column reactor to successfully remove color from real textile wastewater, while Solińska and Bajda (2021) effectively used HDTMA-Br-modified clinoptilolite in removing inorganic compounds, such as ammonium, nitrate, and sulfate from wet flue gas desulfurization wastewater. Also, surfactant-modified zeolite Y has shown significant efficacy in removing organic contaminants from olefin plant wastewater, reducing total organic carbon by up to 89% through hydrophobic and electrostatic interactions (Hashemi et al., 2019).

CONCLUSIONS

The surfactant-modified Philippine zeolite (SMZ) was characterized and investigated for Cr(VI) adsorption. The characterization revealed significant changes in surface morphology, charge properties, and adsorption capacity of SMZ compared to the natural zeolite (NZ). While the surface area was reduced due to the large molecular size of HDTMA-Br, the zeta potential reversal from negative to positive facilitated efficient adsorption of Cr(VI) anions across a wide pH range. The formation of an HDTMA-Br bilayer on the zeolite surface through cation exchange and hydrophobic interactions enabled this transformation.

The study examined the effectiveness of SMZ for Cr(VI) adsorption under various environmental conditions. The equilibrium adsorption was reached rapidly and the optimal

adsorption was achieved at pH 3. The pH significantly influenced adsorption, with acidic conditions favoring the univalent $HCrO_4^-$ species, which requires fewer adsorption sites compared to the divalent CrO_4^{2-} species predominant at higher pH levels. Ionic strength adversely affected Cr(VI) uptake primarily due to competition from chloride ions. Similarly, competing ions like sulfate and phosphate reduced Cr(VI) adsorption, while dissolved organic matter, such as humic and fulvic acids, had no effect due to the high pH of the SMZ solution, which was not conducive to Cr(VI) reduction. These findings demonstrate the potential of SMZ as an effective adsorbent for Cr(VI) removal, particularly under acidic conditions and with careful management of ionic strength and competing ions in wastewater treatment applications.

The adsorption studies reveal that SMZ follows a Langmuir isotherm model, indicating a uniform monolayer adsorption mechanism for Cr(VI). The Langmuir model provides a better representation of the adsorption process compared to the Freundlich model, which describes heterogeneous adsorption. Benchmarking tests showed the Cr(VI) removal efficiencyof SMZ was lower than that of PAC. Although PAC exhibited higher removal efficiency due to its greater surface area and pore complexity, SMZ offers a cost-effective and resource-efficient alternative, leveraging its modified natural zeolite structure to achieve significant adsorption performance. Future research may explore optimizing the surfactant modification process to enhance adsorption capacity further and the regeneration and reuse potential of SMZ in long-term applications. Additionally, studies could investigate its effectiveness in real-world scenarios, including its application in complex wastewater matrices and its performance under varying environmental conditions to establish broader utility in remediation efforts.

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