

Construction of Hierarchically Porous Dealuminated ZSM-5 Zeolite for Enhanced Anionic Dye Adsorption: A Case Study of Xylenol Orange

Shuyan Zang

Shenyang University of Chemical Technology

Yupeng Zhang

Shenyang University of Chemical Technology

Xiangpeng Wang

Weifang University of Science and Technology

Yujie Feng

Weifang University of Science and Technology

Shuhan Chai

Weifang University of Science and Technology

Ziyan Liu

Weifang University of Science and Technology

Wenjing Zhao

Weifang University of Science and Technology

Wenxu Wang

Shenyang University of Chemical Technology

Zhihao Fang

wfsgfzh@163.com

Weifang University of Science and Technology

Juan Wang

Shenyang University of Chemical Technology

Research Article

Keywords: Hierarchically porous ZSM-5 zeolite, Dealumination engineering, EFAI species, Surface coordination, Anionic dye

Posted Date: September 23rd, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10556050/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.
[Read Full License](#)

Additional Declarations: No competing interests reported.

**Construction of Hierarchically Porous Dealuminated ZSM-5 Zeolite
for Enhanced Anionic Dye Adsorption: A Case Study of Xylenol
Orange**

Shuyan Zang ^a, Yupeng Zhang ^a, Xiangpeng Wang ^b, Yujie Feng ^b, Shuhan Chai ^b, Ziyang Liu ^b, Wenjing Zhao ^b, Wenxu Wang ^a, Zhihao Fang ^{b,*}, Juan Wang ^{a,*}

^a College of Science, Shenyang University of Chemical Technology, Shenyang 110142, China

^b Shandong Higher Education Institution Collaborative Innovation Center of Starch-Based Materials and Biomanufacturing between Universities and Enterprises, Weifang University of Science and Technology, Weifang 262700, PR China

The corresponding authors: Zhihao Fang, wfsgfzh@163.com; Juan Wang, wangjuanl@syuct@163.com

Abstract

The persistent accumulation of synthetic anionic dyes in industrial wastewater constitutes a severe environmental challenge, whereas the fundamental limitation of conventional adsorbents lies in the difficulty of reconciling surface charge incompatibility with inadequate mass transfer kinetics. Here, we surmount this limitation via a dual-modification strategy-cetyltrimethylammonium bromide (CTAB)-directed recrystallization followed by HCl-mediated dealumination. XRD, FTIR, and SEM confirmed that the framework topology (MFI) was retained and a hierarchical pore architecture was successfully constructed. Brunauer-Emmett-Teller (BET) analysis quantitatively revealed a substantial enhancement in surface area and mesopore volume, which directly reflects improved active site utilization. Spectroscopic evidence further confirms the emergence of Lewis-acidic extra-framework aluminum (EFAI) species. This paradigm shifts the adsorption mechanism from passive electrostatic capture to synergistic surface coordination, wherein coordinatively unsaturated Al centers act as potent anchoring nodes for xylenol orange (XO) anions. Under optimal conditions (pH 5, initial XO concentration 150 mg/L, adsorption time 60 min, temperature 298 K, adsorbent dosage 2.0 g/L), the obtained Meso-Z5-DeAl achieved an outstanding adsorption capacity of 72.24 mg/g and a removal efficiency of 96.32%, showing competitive performance compared with previously reported zeolite-based adsorbents of the same class. Moreover, equilibrium was reached within 60 min, significantly outperforming conventional systems. Kinetic and isotherm analyses unequivocally established a monolayer coverage mechanism

dominated by chemisorption (pseudo-second-order kinetics, $R^2 > 0.99$; Langmuir fitting). Interfering ion experiments demonstrated strong anti-interference capability toward anions, and over 90% of the initial capacity was retained after five regeneration cycles. The long-standing activity-stability trade-off was resolved through precise defect engineering. This study provides a scalable and cost-effective strategy for the treatment of anionic dye wastewater, and sheds light on the rational design of next-generation zeolite-based adsorbents—where the key lies in achieving the synergistic integration of targeted surface-site regulation and hierarchical transport channels.

Keywords: Hierarchically porous ZSM-5 zeolite; Dealumination engineering; EFAI species; Surface coordination; Anionic dye

1. Introduction

Industrial effluents containing synthetic dyes have become a persistent water-quality concern because large volumes are discharged from textile, printing, papermaking, and related manufacturing processes during ongoing industrial and urban development (Din et al., 2024). Once introduced into aquatic systems, many dye molecules are difficult to biodegrade and may lower water transparency, alter light penetration, and disturb ecological processes (Akhouri et al., 2019). Their environmental significance is also linked to toxic dye residues and degradation products, some of which are carcinogenic and therefore relevant to human-health risk. In parallel, colored wastewater can suppress photosynthesis in receiving waters and interfere with the stability of aquatic communities and food-chain relationships (Huang et al., 2021). For these reasons, effective decolorization before discharge remains an important issue

in water-environment management.

A variety of treatment routes have been explored for removing dyes from aqueous solutions, including coagulation (Tsoutsas et al., 2024), membrane filtration (Alakhras et al., 2020), photocatalysis (Ghaemi et al., 2015), and adsorption (Bulgariu et al., 2019). The practical value of each route depends on factors such as energy demand, cost, selectivity, ease of recovery, and the possibility of secondary pollution (Ouachtak et al., 2020). Among these methods, adsorption is frequently regarded as an attractive option because it combines operational simplicity with high removal efficiency and relatively limited environmental burden (Abdallah and Alprol, 2024). This has encouraged the development of adsorbents such as metal-organic frameworks (MOFs) (Duo et al., 2019; Wang et al., 2023), porous polymer (He et al., 2022), imidazolate zeolite frameworks (ZIFs) (Jia et al., 2024), layered double hydroxide (Su et al., 2022), and surfactant-modified zeolites (Bagheri et al., 2024). Zeolites are especially appealing because of their low cost, structural stability, and tunable surface chemistry (Al-Wasidi et al., 2022; Nguyen et al., 2023). ZSM-5 zeolite has therefore received considerable attention for adsorption of organic dyes, heavy metal ions, and other water pollutants (Al-Jubouri et al., 2022; Radoor et al., 2026). However, the framework substitution of Si by Al gives natural ZSM-5 a negatively charged surface, which weakens its affinity toward anionic dyes (Hu et al., 2024). This limitation reduces its usefulness for treating wastewater containing anionic azo dyes such as methyl orange. Surface engineering that adjusts both charge properties and hydrophobicity has consequently become a key strategy for improving ZSM-5 adsorption performance. In this context, modification with cationic

surfactants is particularly useful because it is experimentally straightforward and can introduce positively charged adsorption domains on the zeolite surface.

CTAB is a representative cationic surfactant that can anchor on zeolite surfaces through electrostatic interaction (Bi et al., 2025; Javad Kalbasi and Eghbalian, 2022). Such anchoring compensates the intrinsic negative charge of the zeolite and simultaneously supplies long hydrophobic alkyl chains, thereby generating surface microdomains favorable for anionic-dye capture (Yu et al., 2024). Existing studies have shown that the adsorption behavior of CTAB-modified zeolites depends strongly on surfactant loading and the arrangement of the surface coverage layer (Bagheri et al., 2024; Hamoud et al., 2023). Nevertheless, further experimental evidence is still needed to clarify how wastewater-relevant variables, including pH variation and coexisting ions, affect removal efficiency, as well as how regeneration and reuse influence practical applicability.

Dealumination represents a well-established post-synthetic methodology for zeolites, involving the extraction of aluminum from the zeolite framework via chemical agents or hydrothermal treatment (Wei et al., 2015). The principal objective of dealumination is to modulate the Si/Al ratio within the zeolite framework and consequently its acidity, whereas the resulting pore architecture can be influenced to varying extents depending on the specific treatment conditions. A notable drawback of dealumination lies in the potential blockage of zeolite micropores by weakly acidic EFAl species. Although the presence of such EFAl entities and their synergistic interplay with Brønsted acid sites may enhance the catalytic performance of zeolites in

certain reactions (Bekele et al., 2026; Schallmoser et al., 2014) they can also promote substantial carbonaceous deposition, thereby accelerating catalyst deactivation (Hartmann et al., 2016). Depending on the treatment regimen, dealumination may induce pronounced alterations in the acidic characteristics of zeolites, including the density and strength of both Brønsted and Lewis acid sites (Ma et al., 2024). Conversely, dealumination facilitates the removal of aluminum-rich moieties (which typically exhibit inferior Brønsted acidity), thereby mitigating severe coke formation and pore blockage during catalytic reactions. Consequently, the implementation of dealumination techniques constitutes an ideal strategy for the rational design of hierarchical zeolites featuring an optimal balance of microporosity, crystallinity, and acid site distribution.

In this work, dealuminated CTAB-modified ZSM-5 zeolites were prepared for the enhanced removal of xylenol orange (XO) from wastewater. XRD, FTIR, and SEM were employed to examine the phase structure, functional groups, and morphology of the prepared composite. The adsorption behavior was assessed through batch experiments in which contact duration, temperature, initial dye loading, and solution pH were systematically varied. Kinetic, isotherm, and thermodynamic analyses were further applied to interpret the adsorption mechanism. The findings indicate that dealuminated CTAB-modified ZSM-5 can serve as a cost-effective, scalable, and environmentally compatible adsorbent.

2. Materials and methods

2.1 Reagents and materials

Ammonium chloride was purchased from Beijing Innochem Co., Ltd. (China). Sodium aluminate (NaAlO_2), tetrapropylammonium hydroxide (TPAOH), XO was purchased from Xilong Scientific Co., Ltd. (China), and CTAB was obtained from Tianjin Kermel Chemical Reagent Co., Ltd. (China). All chemicals used in this work were analytical-grade reagents.

2.2 Preparation of ZSM-5

In a typical synthesis, 0.0550 g of NaAlO_2 was first dissolved in a mixed solution comprising 40.00 g of 20 wt% TPAOH solution and 26.00 g of deionized water. After complete dissolution of the aluminate source under stirring, 6.00 g of solid silica gel was introduced as the silicon source. The mixture was continuously stirred at ambient temperature for 4 h to yield a homogeneous precursor gel. The resulting gel was then transferred into a Teflon-lined stainless steel autoclave and subjected to hydrothermal crystallization at 453K for 48 h. The crystalline product was recovered by centrifugation or filtration, thoroughly washed with deionized water until the washings reached near-neutral pH, and subsequently calcined at 550 °C for 6 h to eliminate the organic template. The calcined sample (5.00 g) was dispersed in 150.0 mL of 1 mol/L NH_4Cl solution and ion-exchanged at 80 °C, and the exchange was repeated twice, followed by a final calcination at 550 °C for 5 h to afford the proton-form ZSM-5.

2.3 Modification of ZSM-5 zeolite with CTAB

A surfactant-directed recrystallization route was adopted to obtain the micro-mesoporous ZSM-5 composite zeolite using CTAB as the template (Fig. 1). Complete

dissolution of the alkaline medium was first achieved by dispersing 1.80 g of NaOH in 30.0 mL of deionized water under stirring at room temperature. Thereafter, 6.00 g of ZSM-5 zeolite powder was introduced, and stirring was maintained for 1 h to generate a homogeneous alkaline precursor suspension, denoted as solution A. In a separate preparation, 20.00 g of CTAB was dissolved in 180.0 mL of deionized water, and the mixture was vigorously stirred at room temperature until a clear template solution was obtained, which was designated as solution B. Finally, 75.0 mL of solution B was added dropwise to solution A, and the mixed system was stirred for another 1 h at room temperature to promote contact between CTAB and ZSM-5 and to facilitate interfacial reorganization.

For the preliminary construction of mesoporous features, the fully mixed suspension was sealed in a PTFE-lined stainless-steel autoclave, with the filling ratio controlled below 80%, and subjected to static hydrothermal crystallization at 110 °C for 24 h. After cooling to room temperature, the product was transferred to a beaker. A 2.0 mol/L HCl solution was then introduced dropwise under stirring until the pH stabilized at 8.5, allowing neutralization of excess NaOH and adjustment of the surface charge state. The suspension was subsequently returned to the autoclave for a second hydrothermal treatment at 110 °C for 24 h, during which the micro-mesoporous composite structure was further optimized by directed recrystallization. The crystallized solid was separated by centrifugation at 8000 rpm for 10 min and washed repeatedly with deionized water until the filtrate was neutral, thereby removing residual salts and unreacted species.

The washed solid was dried at 100 °C for 10 hours and then transferred to a muffle furnace. Calcination was carried out in air at 550 °C for 6 h to remove the CTAB mesopore-directing template, thereby exposing the newly generated mesoporous structure. The powder obtained after calcination was designated as Meso-Z5 composite zeolite.

HCl was used as the dealumination agent in the subsequent treatment. Specifically, 5.00 g of Meso-Z5 zeolite was dispersed in 100.0 mL of 0.1 mol/L HCl solution, and the suspension was refluxed with stirring at 90 °C in a constant-temperature oil bath for 24 h. After the reaction, the product was washed several times with deionized water and collected by centrifugation. The recovered solid was dried at 110 °C for 12 hours and calcined in air at 550 °C for 6 hours, giving the HCl-treated partially dealuminated zeolite sample, denoted as Meso-Z5-DeAl, representing the dealuminated derivative of the mesoporous ZSM-5 parent.

2.4 Characterization

The phase structure of Meso-Z5-DeAl was examined on an Empyrean X-ray diffractometer (XRD) (PANalytical, the Netherlands) using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Data were collected at 40 kV and 40 mA with a scanning rate of $13^\circ \text{ min}^{-1}$, a step size of 0.03° , and a 2θ range of 5° - 60° . Surface functional groups were analyzed by transmission Fourier-transform infrared spectroscopy (FT-IR) using a Nicolet iS 60 spectrometer (Thermo Fisher Scientific, USA). Spectra were acquired at a resolution of 4 cm^{-1} over 400 - 4000 cm^{-1} and 2700 - 3200 cm^{-1} , with 32 scans recorded for each sample. Sample morphology and particle size were characterized with a JSM-8800F

field-emission scanning electron microscope (SEM) (JEOL, Japan). Before observation, the samples were dehydrated, dried, uniformly deposited on smooth silicon wafers, and fixed to a copper stage. Platinum sputter coating was applied to enhance surface contrast. The acceleration voltage and working distance were 3 kV and 8 mm, respectively. The specific surface area and pore characteristics were evaluated by nitrogen adsorption-desorption isotherms using the Brunauer-Emmett-Teller (BET) method (ASAP 2010, Micromeritics, USA). The zeta potential of Meso-Z5-DeAl was measured using a dynamic light scattering analyzer (Nano ZS90, Malvern Instruments, UK). Lastly, high-performance liquid chromatography (HPLC, Agilent 1260 Infinity II, Agilent Technologies, USA) was used to determine the concentration of XO in aqueous solution.

2.5 Adsorption experiments

Subsequently, the suspensions were filtered through a membrane filter, and the residual XO concentrations in the filtrates were quantified by HPLC. Chromatographic separation was performed on a conventional C18 reversed-phase column (250 mm × 4.6 mm, 5 μm) using acetonitrile/water (65/35, v/v) as the mobile phase at a flow rate of 1.0 mL/min. The detection wavelength was set at 435 nm and the column temperature was maintained at 303 K. Under these conditions, the XO retention time was approximately 3.4 min. The removal efficiency (η) and adsorption capacity (Q) of Meso-Z5-DeAl for XO were calculated using Equations (1) and (2), respectively.

$$Q = \frac{(C_0 - C_t)V}{m} \quad (1)$$

$$\eta = \frac{(C_0 - C_t)}{C_0} \times 100\% \quad (2)$$

where Q is the adsorption capacity (mg/g), V is the solution volume (L), C_0 is the initial XO concentration (mg/L), C_t is the residual XO concentration in the solution after adsorption at time t (mg/L), η is the removal efficiency (%), and m is the mass of the adsorbent (g).

2.6 Kinetic studies

The effect of contact time was evaluated by adding 0.10 g of adsorbent to 50.00 mL of an XO solution at pH 5 with an initial concentration of 150 mg/L at 298-318K. The suspensions were magnetically stirred for predetermined durations, after which adsorption capacities were calculated according to Eq. (1). To investigate the effect of contact time on adsorption performance, six parallel experiments were conducted with adsorption times of 10, 20, 30, 40, 50, and 60 min, while keeping other conditions unchanged. To determine the rate-controlling behavior, time-dependent kinetic data were fitted with the pseudo-first-order (Eq. (3)) and pseudo-second-order models. The intraparticle diffusion model was then used to further assess diffusion-related contributions and estimate the corresponding rate constant.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

The following parameters are defined:

In these equations, q_t represents the amount of adsorbate taken up at time t (mg/g), q_e is the equilibrium adsorption capacity (mg/g), k_1 is the pseudo-first-order rate constant (min^{-1}), k_2 is the pseudo-second-order rate constant ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$), and t is the contact time (min).

2.7 Adsorption isotherms

The dependence of adsorption on initial XO concentration was studied by mixing 0.10 g of Meso-Z5-DeAl with 50.00 mL of XO solutions at pH 5, with concentrations ranging from 100 to 200 mg/L. After magnetic stirring for 60 minutes at 298 K-318 K, the mixtures were filtered, and the equilibrium XO concentration C_e in the filtrate was determined by high-performance liquid chromatography (HPLC) under the chromatographic conditions described above. The XO concentration was quantified from the chromatographic peak area using the established calibration curve. Langmuir and Freundlich isotherm models were applied to the resulting equilibrium data to describe the adsorption behavior.

$$\frac{C_e}{q_e} = \frac{1}{k_L q_{max}} + \frac{C_e}{q_{max}} \quad (5)$$

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \quad (6)$$

The following parameters are defined:

Here, C_e denotes the equilibrium adsorbate concentration in solution (mol/L), q_e is the equilibrium adsorption capacity (mg/g), k_L is the Langmuir constant, q_{max} is the maximum adsorption capacity (mg/g), k_F is the Freundlich constant, and n is the adsorption intensity exponent.

3. Results and discussion

3.1 Characterization of the adsorbent

The XRD pattern of Meso-Z5-DeAl is presented in Fig. 2A, which exhibits the

characteristic diffraction peaks of the MFI framework at $2\theta = 7.98^\circ$, 8.82° , 23.14° , 23.96° , and 24.44° (Yang et al., 2021). The absence of additional peaks corresponding to impurity phases confirms that the MFI structure was well preserved after the modification.

FTIR spectra of pristine ZSM-5 and Meso-Z5-DeAl are compared in Fig. 2B. For the zeolite samples, the absorption band at 1101 cm^{-1} is assigned mainly to internal asymmetric stretching of the SiO_4 tetrahedron together with Si-O bending. The bands at 1224 cm^{-1} and 794 cm^{-1} correspond to external asymmetric and symmetric stretching vibrations, respectively (Du et al., 2017). The band near 545 cm^{-1} is associated with double five-membered rings (D5R) and is therefore a fingerprint of the MFI framework (Ma et al., 2024). The FTIR spectrum of Meso-Z5-DeAl exhibited characteristic bands at 2845 cm^{-1} and 2918 cm^{-1} , corresponding to the symmetric and asymmetric C-H stretching vibrations, respectively. These bands were absent in the spectrum of ZSM-5, confirming the successful incorporation of CTAB-directed zeolite (Xu et al., 2014). Because the 546 cm^{-1} band remained visible for all samples, retention of the MFI topology was confirmed (Airi et al., 2021). The broad O-H stretching feature centered at 3651 cm^{-1} is attributed to terminal silanol groups (Si-OH), while its broadening and shifts arise from hydrogen-bonding effects that influence overlapping O-H stretching vibrations (Atugoda et al., 2021). The absence of obvious shifts in the characteristic ZSM-5 bands after CTAB treatment suggests that CTAB was mainly adsorbed on the external surface and did not destroy the intrinsic Si-O and Al-O bonds.

The morphological evolution of ZSM-5 upon modification is illustrated by the

SEM images in Fig. 3. The pristine ZSM-5 (Fig. 3a) displays rectangular crystallites with aggregated stacking, characteristic of the MFI-type zeolite framework. In contrast, the modified Meso-Z5-DeAl (Fig. 3b) largely preserves the primary crystal morphology, yet the particle edges become noticeably rounded instead of sharp, suggesting surface etching occurred during the treatment. The modified particles also present smoother edges than the sharp-edged pristine ZSM-5 crystals. The elemental analysis of Meso-Z5-DeAl is shown in Fig. 3(c). The dominant Si, Al, and O signals are consistent with the aluminosilicate composition of the zeolite. Together with the SEM observations, these results indicate that the overall morphology and elemental framework of ZSM-5 were largely retained after alkaline-assisted recrystallization and acid treatment. The aforementioned findings indicate that the original grain morphology was largely preserved during the modification process, with no significant deterioration observed. These results suggest that the original grain morphology was largely preserved after the modification, with no significant deterioration observed.

The textural properties of pristine ZSM-5 and Meso-Z5-DeAl were characterized by N₂ adsorption-desorption measurements, as presented in Fig. 4. Upon modification, the BET specific surface area exhibited a modest increase from 382.43 m²/g to 409.75 m²/g. More notably, the external surface area, determined by the t-plot method, increased substantially from 74.65 m²/g to 288.56 m²/g, whereas the micropore surface area decreased from 307.78 m²/g to 121.19 m²/g. A concomitant reduction in micropore volume was observed, from 0.1346 cm³/g to 0.0561 cm³/g. In contrast, the BJH mesopore area (adsorption branch) rose from 13.70 m²/g to 125.62 m²/g, alongside an

increase in mesopore volume from 0.04 cm³/g to 0.3127 cm³/g. These results clearly reveal a pronounced redistribution of the pore architecture, confirming that the modification strategy effectively enhanced the mesoporosity of the parent microporous ZSM-5, yielding a hierarchical material with coexisting micropores and mesopores (Meng et al., 2017).

The development of secondary porosity is primarily attributable to alkaline desilication, followed by surfactant-assisted hydrothermal reconstruction (Wen et al., 2025). During the alkaline treatment, OH⁻ ions preferentially attack Si-O-Si bonds and extract framework silicon species, thereby generating structural defects, voids, and secondary pores. The positively charged CTA⁺ aggregates interact with negatively charged silicate and aluminosilicate species, serving as mesopore-directing agents under hydrothermal conditions (Yu et al., 2023). The ensuing neutralization and hydrothermal treatment facilitate the recondensation and reorganization of dissolved species around the surfactant aggregates. Upon calcination to remove CTAB, the newly formed mesopores and external surface area are exposed. Subsequent acid treatment promotes dealumination and the removal or redistribution of pore-blocking aluminum-containing species, while modifying the local coordination environment of aluminum and consequently affecting pore accessibility (Roth et al., 2025). Collectively, the increased external and mesopore surface areas, along with the partial reduction in micropore surface area, corroborate the successful construction of hierarchical Meso-Z5-DeAl, rather than a mere uniform enlargement of the total specific surface area.

3.2. Adsorption experiments

3.2.1 Effect of adsorbent dosage

Adsorbent dosage is an important operating variable because excessive material use increases treatment cost and may also introduce secondary environmental concerns (Shah et al., 2025). To evaluate dosage effects, 0.8, 1.2, 1.6, 2.0, 2.4, and 2.8 g/L of pristine ZSM-5 or Meso-Z5-DeAl (corresponding to 0.04-0.14 g added to 50 mL of solution) were used, with an initial XO concentration of 150 mg/L in a 50 mL volume. The adsorption results are summarized in Fig 5A.

Compared with ZSM-5, Meso-Z5-DeAl improved both XO adsorption capacity and removal efficiency. As the amount of Meso-Z5-DeAl increased from 0.8 g/L to 1.2 g/L, the removal efficiency rose from 84.45% to 91.65%; when the dosage was further increased to 2.4 g/L, the removal efficiency reached 97.13%. The substantial increases in specific surface area, pore volume, and total content of surface functional groups available for binding lead to a reduction in the equilibrium concentration of the adsorbate in the liquid phase, thereby promoting the transfer of more adsorbate molecules from the solution to the adsorbent surface. Concurrently, the proliferation of adsorption sites facilitates the capture of XO molecules, thus enhancing the removal efficiency (Adeoye et al., 2023). The improvement is attributable to the increased number of accessible adsorption sites at higher adsorbent loadings. By contrast, the adsorption capacity per unit mass decreased from 158.36 mg/g to 51.05 mg/g as dosage increased, this is attributable to the fact that as the removal efficiency approaches its maximum, the equilibrium concentration in the solution decreases to nearly 0 mg/L; under such conditions, further increasing the adsorbent dosage merely elevates the

fraction of unsaturated active sites, thereby resulting in a decline in adsorption capacity. Although the adsorption capacity per unit mass decreased with increasing adsorbent dosage, the removal efficiency increased as more adsorption sites became available. At a dosage of 2.0 g/L, Meso-Z5-DeAl already exhibited a relatively high removal efficiency, while further increasing the dosage provided only a limited additional improvement in removal performance and led to a further decrease in adsorbent utilization efficiency. Therefore, considering the balance between removal performance and adsorbent consumption, 2.0 g/L was adopted as the working dosage for subsequent experiments.

3.2.2 Effect of initial concentration

The influence of initial XO concentration on the adsorption performance of Meso-Z5-DeAl is depicted in Fig. 5B. As the initial concentration was elevated from 100 to 200 mg/L, the equilibrium adsorption capacities of both adsorbents increased progressively, attributable to the enhanced concentration gradient between the bulk solution and the adsorbent surface, which strengthened the mass-transfer driving force and facilitated the migration of XO molecules toward the external surface and internal pores (Choudhary et al., 2025). Notably, the adsorption capacity of ZSM-5 exhibited only a limited increase, whereas that of Meso-Z5-DeAl rose markedly from 47.44 to 90.86 mg/g. In contrast, the removal efficiency of Meso-Z5-DeAl displayed a slight decline from 94.89% to 90.86% with increasing initial concentration, while the parent ZSM-5 showed substantially lower removal efficiency throughout. This trend can be rationalized by the fact that, at a fixed adsorbent dosage, a higher substrate

concentration creates a steeper concentration gradient, driving more XO molecules toward the adsorption sites and thus increasing the pollutant loading per unit mass of adsorbent. However, upon doubling the initial concentration to 200 mg/L, the total amount of XO molecules requiring removal also doubled, whereas the number of available adsorption sites remained unchanged. Although the enhanced mass transfer driven by the elevated concentration gradient promoted the adsorption capacity, the site occupancy rapidly approached saturation, resulting in an elevated residual XO concentration in the solution and a consequent reduction in removal efficiency (Nodehi et al., 2020). Over the entire concentration range investigated, Meso-Z5-DeAl consistently outperformed pristine ZSM-5 in both adsorption capacity and removal efficiency, confirming that the dealumination and mesoporosity modification broadened the mass-transfer pathways and increased the number of accessible active sites. On the basis of these findings, and in consideration of economic feasibility, an initial XO concentration of 150 mg/L was selected as the optimal value.

3.2.3 Effect of temperature

The influence of temperature on the adsorption of XO by Meso-Z5-DeAl is presented in Fig. 5C. Within the investigated temperature range, the adsorption performance showed only a weak dependence on temperature. The removal efficiency varied slightly from 91.11% at 298 K to 87.78% at 318 K, while the adsorption capacity remained relatively stable over 298-338 K. Temperature can exert competing effects on adsorption: increasing temperature enhances the molecular mobility and mass-transfer rate of the adsorbate, whereas it may simultaneously alter adsorbate–surface

interactions and the interfacial equilibrium. The limited variation observed in the present system therefore suggests that these effects largely offset each other within the investigated temperature range, resulting in only a minor net influence on XO adsorption. Notably, the slight variation in removal efficiency should not be interpreted as evidence of an exothermic adsorption process; the thermodynamic analysis discussed below indicates a positive ΔH , confirming the overall endothermic nature of XO adsorption on Meso-Z5-DeAl. Considering the comparable adsorption performance and the lower energy requirement, 298 K was selected as the operating temperature for subsequent experiments.

3.2.4 Effect of contact time

The relationship between contact time and adsorption performance was used to determine the equilibrium time (Fig. 5D). The rapid adsorption in the initial stage is attributed to the abundant surface active sites and the strong electrostatic attraction between the anionic XO species and the cationic components of the adsorbent. During dealumination, extra-framework aluminum species in cationic forms are generated, which are anchored on the framework as Lewis acid sites and serve as powerful positive adsorption centers. Therefore, for anionic XO, a large number of XO molecules occupy these high-affinity sites, macroscopically manifested as a rapid increase in adsorption capacity (Hamad et al., 2024). A slight fluctuation in the measured adsorption performance was observed upon further extending the contact time; however, no systematic improvement was obtained after 60 min. Therefore, 60 min was considered sufficient for adsorption equilibrium and was selected for subsequent experiments.

Moreover, the adsorption capacity of Meso-Z5-DeAl was consistently higher than that of ZSM-5 at any tested contact time. The mesoporous structure constructed in the modified sample shortened the diffusion path of dye molecules, facilitating the rapid access of XO to internal adsorption sites. Therefore, 60 min was adopted as the equilibrium contact time for subsequent experiments.

3.2.5 Effect of pH

The solution pH can simultaneously modulate the surface charge properties of the adsorbent, the speciation of surface active sites, and the protonation/dissociation speciation of XO dye, thereby significantly altering the solid-liquid interfacial adsorption interactions. As shown in Fig. 6A, within the investigated pH range of 3-11, Meso-Z5-DeAl consistently maintained excellent adsorption performance toward XO, with the removal efficiency stably remaining above 90%, and the overall adsorption performance was significantly superior to that of pristine ZSM-5.

Within the pH range of 3-5, the XO removal efficiency of Meso-Z5-DeAl remained at a high level, with the optimal removal performance of 96.77% achieved at pH 5—only a marginal improvement over that at pH 3 (95.56%), and the difference between the two values was negligible within the experimental error. Combined with the Zeta potential results shown in Fig. 6B, the isoelectric point of Meso-Z5-DeAl was determined to be 5.96; hence, the overall surface of the material was positively charged at pH 3 and 5, which favored the capture of negatively charged XO species in solution. As revealed by the XO speciation distribution in Fig. 6C (Li et al., 2025b), in a strongly acidic environment, XO predominantly existed in a highly protonated form with a

relatively low effective negative charge density, which to some extent restricted its electrostatic interaction with the positively charged sites on the adsorbent. As the pH increased to 5, XO underwent progressive deprotonation, resulting in an enhanced negative charge density; meanwhile, the adsorbent surface remained positively charged, further strengthening the electrostatic attraction between the solid and liquid phases, thereby leading to a slight improvement in adsorption performance.

As the pH further increased to the range of 5.96-11, the XO removal efficiency gradually decreased from 96.77% to approximately 90.67%. Within this pH range, XO underwent further dissociation, and its negative charge intensity continued to increase; meanwhile, the surface of Meso-Z5-DeAl switched from positively to negatively charged once the pH exceeded the isoelectric point, leading to weakened electrostatic attraction at the macroscopic level and the emergence of electrostatic repulsion between the solid phase and the dye. Concurrently, in near-neutral and alkaline environments, extra-framework aluminum species are prone to hydrolysis, hydroxylation, and even polymerization, gradually generating $\text{Al}(\text{OH})_3$ -type oxyhydroxides (An et al., 2021). The continuous deprotonation of Al-OH sites on the material surface progressively reduced the number of positively charged sites available for binding anions, further diminishing the electrostatic binding affinity toward anionic XO (Xie et al., 2025). In addition, the abundant OH^- ions in alkaline media compete with XO anions for the limited adsorption sites, further contributing to the decline in adsorption capacity.

It is noteworthy that, even though electrostatic adsorption was significantly suppressed under high pH conditions, Meso-Z5-DeAl still achieved an XO removal

efficiency exceeding 90%. This phenomenon demonstrates that the adsorption of XO onto Meso-Z5-DeAl is not driven solely by electrostatic interactions; non-electrostatic interactions such as pore confinement and enrichment, surface coordination, and intermolecular hydrogen bonding also contribute to the adsorption process. Taking both adsorption capacity and removal efficiency into consideration, pH 5 was selected as the optimal initial pH condition for subsequent static adsorption experiments.

3.2.6 Effect of coexisting ions on adsorption

The adsorption stability of Meso-Z5-DeAl toward XO in complex aqueous environments was evaluated through coexisting competing ion experiments. As shown in Fig. 7A, common anions present in water bodies, including Cl^- , NO_3^- , H_2PO_4^- , and SO_4^{2-} , were selected for gradient interference experiments to assess whether Meso-Z5-DeAl could maintain its high adsorption capacity for XO under actual wastewater conditions. As illustrated in Fig. 7A, the coexisting anions compete with XO molecules for the limited positively charged adsorption sites on Meso-Z5-DeAl, while simultaneously weakening the electrostatic interactions, thereby inhibiting adsorption (Zhang et al., 2026). The experimental results confirmed that the competitive effect intensity of different anions followed the order: $\text{Cl}^- \approx \text{NO}_3^- < \text{H}_2\text{PO}_4^- < \text{SO}_4^{2-}$. Monovalent anions with lower charge density exhibited only limited competitive ability, whereas SO_4^{2-} , as a divalent anion with higher charge density and stronger electrostatic attraction, caused more pronounced interference with XO adsorption (Chen et al., 2012). Among the four anions investigated, only high concentrations exhibited significant competitive effects, while the remaining inorganic anions had limited impact on the

adsorption performance. This result indicates that the interaction between Meso-Z5-DeAl and XO cannot be simply attributed to electrostatic attraction; if the adsorption relied entirely on electrostatic interactions, the abundant coexisting anions in the system would substantially occupy the positively charged adsorption sites and drastically reduce the XO adsorption capacity. Furthermore, it confirms that Meso-Z5-DeAl exhibits favorable anti-interference capability in complex water matrices containing multiple inorganic anions, demonstrating considerable potential for practical application.

3.2.7 Reusability

Evaluating the regeneration performance of Meso-Z5-DeAl toward XO is essential for effectively mitigating XO contamination and facilitating its practical application. After each adsorption experiment, the spent Meso-Z5-DeAl was subjected to desorption using 0.1 mol/L NaOH solution. The material was thoroughly rinsed with deionized water until the pH of the washing solution reached neutrality, and the regenerated Meso-Z5-DeAl was then employed in the subsequent adsorption cycle. As illustrated in Fig. 7B, the adsorption capacity in the first cycle was 72.14 mg/g, which declined to 65.42 mg/g after five cycles, corresponding to 90.68% retention of the initial capacity. During the desorption process, NaOH preferentially etched the mesopore walls and the silica-rich defect sites on the surface, leading to a continuous decrease in specific surface area and pore volume, and consequently a reduction in active sites. The reusability performance of Meso-Z5-DeAl was evaluated through five consecutive adsorption-desorption cycles. After five cycles, the adsorption capacity exhibited a

gradual but sustained declining trend; although a certain degree of decrease was observed in the fifth cycle compared with the first, the material still maintained a relatively high adsorption capacity. Overall, Meso-Z5-DeAl can be reused for multiple cycles; however, the regeneration process cannot fully restore its initial performance.

3.3 Adsorption kinetics

Adsorption kinetics were analyzed to clarify how XO interacts with the adsorbent surface over time. Batch adsorption tests were conducted to evaluate the time-dependent uptake process, and the resulting data were fitted with pseudo-first-order and pseudo-second-order kinetic models to identify the dominant rate behavior. The pseudo-first-order model and pseudo-second-order model, which are commonly associated with physisorption and chemisorption, respectively, were used for kinetic interpretation.

The kinetic fitting results are presented in Fig. 8, and the parameters calculated from Eqs. (3)-(4), including k_1 and k_2 , are listed in Table 1. Comparison of the determination coefficients (R^2) and the differences between calculated and experimental equilibrium adsorption capacities (q_e) shows that the pseudo-second-order model fits the experimental data better than the pseudo-first-order model. The kinetic parameters therefore indicate that XO adsorption on Meso-Z5-DeAl follows pseudo-second-order behavior. This result supports the contribution of chemisorption, which may arise from specific interactions between surface functional groups on Meso-Z5-DeAl and ionic XO species (Chang et al., 2022).

3.4 Equilibrium study

Equilibrium adsorption data were fitted with the Langmuir and Freundlich models to further interpret the adsorption mechanism. As shown in Fig. 9 and summarized in Table 2, the Langmuir fitting consistently produced higher determination coefficients (R^2) than the Freundlich fitting.

These results indicate that XO adsorption by Meso-Z5-DeAl is more appropriately represented by the Langmuir isotherm. The adsorption process can therefore be interpreted as monolayer coverage occurring on a relatively homogeneous adsorbent surface.

3.5 Proposal of adsorption mechanisms

As illustrated in Fig. 10, the adsorption mechanism of Meso-Z5-DeAl is governed by the synergistic interplay of surface coordination chelation, multiple hydrogen-bonding interactions, and local electrostatic guidance. According to the relationship between Zeta potential and pH (Fig. 6B), the isoelectric point of the material is determined to be approximately pH 5.96; consequently, the material surface carries a net positive charge at around pH 5, indicating favorable adsorption performance toward anionic species (Li et al., 2025a). At pH 5.0, the sulfonic acid groups of XO are predominantly deprotonated to the sulfonate form ($-\text{SO}_3^-$), while most of its carboxyl groups are also deprotonated to $-\text{COO}^-$. Owing to the coupled protonation equilibria among the carboxylate, tertiary amine, and phenolic groups, several adjacent

protonation states may coexist; thus, XO can be regarded as a multiply charged anionic species (Magnaghi et al., 2023).

Dealumination proceeds via hydrolysis and cleavage of framework Al-O-Si bonds, leading to the removal of tetrahedral framework aluminum and the generation of silanol-rich defect sites or silanol nests (Grajales-González et al., 2024; Wang et al., 2024). A portion of the extracted aluminum is retained as EFAl species within the pores or on the external surface, in forms such as hydrated, hydroxylated, or partially framework-bound species (Chang et al., 2022). These EFAl species can generate coordinatively unsaturated Lewis acid sites or localized positive charge regions (Batool et al., 2024; Mancuso and Van Speybroeck, 2024). The Lewis acid sites associated with EFAl species can coordinate with the -COO^- and >NH^+ groups of the iminodiacetic acid moieties of XO, potentially forming a five-membered N,O-chelate-like surface complex between the iminodiacetic acid unit and the coordinatively unsaturated aluminum center (Askarli et al., 2024). In addition, the phenolic hydroxyl groups and other oxygen-containing groups of XO can form hydrogen bonds with surface silanol (Si-OH), aluminol (Al-OH), and deprotonated oxygen sites. The locally positively charged or ligand-exchange-active EFAl sites can facilitate the approach and subsequent coordination of XO molecules, thereby enabling specific surface complexation to overcome unfavorable long-range electrostatic repulsion.

3.6 Comparison with other adsorbents

Table 3 compares the maximum adsorption capacities q_e of Meso-Z5-DeAl and other cationic surfactant-modified adsorbents toward XO, and details the corresponding

key experimental parameters, including adsorbent dosage and adsorption equilibrium time. In contrast, the Meso-Z5-DeAl prepared in this study achieved a high adsorption capacity of 72.24 mg/g at a low dosage of merely 2.0 g/L and within a short equilibrium time of 60 min, demonstrating distinct advantages in both adsorption capacity and adsorption rate.

4. Conclusion

In this study, ZSM-5 zeolite was modified through CTAB surface functionalization followed by HCl-assisted dealumination. Characterization by FTIR, XRD, SEM, and EDS confirmed successful CTAB-directed on the ZSM-5 molecular sieve while preserving the zeolite framework features. Batch adsorption experiments showed that XO removal was affected by Meso-Z5-DeAl dosage, contact duration, initial pH, and initial XO concentration. The adsorption mechanism was associated with electrostatic interaction, hydrogen bonding, hydrophobic effects, and cation- π interaction. Kinetic analysis demonstrated that the pseudo-second-order model provided the best description of the adsorption process, whereas equilibrium fitting favored the Langmuir model, indicating monolayer adsorption on relatively homogeneous sites. With its straightforward preparation and favorable adsorption performance, Meso-Z5-DeAl shows potential as an effective adsorbent for remediation of XO-contaminated water.

Author contributions

Shuyan Zang: Conceptualization, investigation, methodology, validation, formal analysis, writing - original draft, writing - review & editing. **Yupeng Zhang and Zhihao Fang:** Methodology, data curation, formal analysis, writing - review & editing. **Xiangpeng Wang and Juan Wang:** Investigation, data curation, resources, project administration. **Wenxu Wang:** Project administration, Supervision. **Yujie Feng and Shuhan Chai:** Methodology, project administration, validation. **Ziyan Liu and Wenjing Zhao:** visualization. All authors have read and approved the final version of the manuscript.

Data availability

The data supporting this study can be accessed upon reasonable request.

Declaration of competing interest

The authors confirm the absence of any recognized conflicting financial interests or personal affiliations that might conceivably have been perceived as influencing the research presented in this manuscript.

Acknowledgements

The authors express their gratitude to the National Natural Science Foundation of China (No. 52570204) for financial support.

References

- Abdallah, M. A. M. & Alprol, A. E.: 2024, 'Utilization of aquatic biomass as biosorbent for sustainable production of high surface area, nano- microporous, for removing two dyes from wastewater', *Scientific Reports*, *14*, 4471.
- Adeoye, J. B., Balogun, D. O., Etemire, O. J., Ezech, P. N., Tan, Y. H. & Mubarak, N. M.: 2023, 'Rapid adsorptive removal of eosin yellow and methyl orange using zeolite Y', *Scientific Reports*, *13*, 21373.
- Airi, A., Signorile, M., Bonino, F., Quagliotto, P., Bordiga, S., Martens, J. A. & Crocellà, V.: 2021, 'Insights on a Hierarchical MFI Zeolite: A Combined Spectroscopic and Catalytic Approach for Exploring the Multilevel Porous System Down to the Active Sites', *ACS Applied Materials & Interfaces*, *13*, 49114–49127.

- Akhouairi, S., Ouachtak, H., Addi, A. A., Jada, A. & Douch, J.: 2019, 'Natural Sawdust as Adsorbent for the Eriochrome Black T Dye Removal from Aqueous Solution', *Water, Air, & Soil Pollution*, 230, 181.
- Al-Jubouri, S. M., Al-Jendeel, H. A., Rashid, S. A. & Al-Batty, S.: 2022, 'Antibiotics adsorption from contaminated water by composites of ZSM-5 zeolite nanocrystals coated carbon', *Journal of Water Process Engineering*, 47, 102745.
- Al-Kazragi, M. A., Al-Heetimi, D. T. A. & Al-Khazrajy, O. S. A.: 2019, 'Xylenol orange removal from aqueous solution by natural bauxite (BXT) and BXT-HDTMA: kinetic, thermodynamic and isotherm modeling', *Desalination and Water Treatment*, 145, 369–377.
- Al-Wasidi, A. S., Saad, F. A., AlReshaidan, S. & Naglah, A. M.: 2022, 'Facile Synthesis of ZSM-5/TiO₂/Ni Novel Nanocomposite for the Efficient Photocatalytic Degradation of Methylene Blue Dye', *Journal of Inorganic and Organometallic Polymers and Materials*, 32, 3040–3052.
- Alakhras, F., Alhajri, E., Haounati, R., Ouachtak, H., Addi, A. A. & Saleh, T. A.: 2020, 'A comparative study of photocatalytic degradation of Rhodamine B using natural-based zeolite composites', *Surfaces and Interfaces*, 20, 100611.
- An, G., Yue, Y., Wang, P., Liu, L., Demissie, H., Jiao, R. & Wang, D.: 2021, 'Deprotonation and aggregation of Al¹³ under alkaline titration: A simulating study related to coagulation process', *Water Research*, 203, 117562.
- Askarli, S., Mukhambetov, I., Chung, S.-H., Awwad, M., Almeida, J. N., Komaty, S., Navarro de Miguel, J. C., Li, T. & Ruiz-Martínez, J.: 2024, 'Influence of Extra-Framework Aluminum Species on the Catalytic Properties of Acidic USY Zeolite in (Hydro)cracking

Reactions', *ACS Catalysis*, *14*, 13630–13639.

Atugoda, T., Gunawardane, C., Ahmad, M. & Vithanage, M.: 2021, 'Mechanistic interaction of ciprofloxacin on zeolite modified seaweed (*Sargassum crassifolium*) derived biochar: Kinetics, isotherm and thermodynamics', *Chemosphere*, *281*, 130676.

Bagheri, A., Khabbaz, S. H. & Rafati, A. A.: 2024, 'Comparison of the natural and surfactant-modified zeolites in the adsorption efficiency of sunset yellow food dye from aqueous solutions', *Scientific Reports*, *14*, 22511.

Batool, S. R., Sushkevich, V. L. & van Bokhoven, J. A.: 2024, 'Factors Affecting the Generation and Catalytic Activity of Extra-Framework Aluminum Lewis Acid Sites in Aluminum-Exchanged Zeolites', *ACS Catalysis*, *14*, 678–690.

Bekele, B. T., Kragt, N., Loch, H., Hibbitts, D. & Gounder, R.: 2026, 'Proximal Brønsted Acid Sites in Zeolites Cooperate to Stabilize Transition States via Hydrogen Bonding and Multi-Ion-Pair Interactions', *ACS Catalysis*, *16*, 12094–12109.

Bi, J., Zhan, Q., Chen, Y., Liang, Z., Liu, N., Zhang, X., Wang, Z. & Han, Y.: 2025, 'Dynamic switch of CTAB as the sole template for the synthesis hierarchically porous ZSM-5 through a straightforward conventional static hydrothermal method', *Microporous and Mesoporous Materials*, *397*, 113768.

Bulgariu, L., Escudero, L. B., Bello, O. S., Iqbal, M., Nisar, J., Adegoke, K. A., Alakhras, F., Kornaros, M. & Anastopoulos, I.: 2019, 'The utilization of leaf-based adsorbents for dyes removal: A review', *Journal of Molecular Liquids*, *276*, 728–747.

Chang, A.-L., Nguyen, B.-S., Nguyen, V.-H. & Hu, C.: 2022, 'Adsorption kinetics of methyl blue using metal-modified barium lanthanum titanate as an effective absorbent', *Materials*

Chemistry and Physics, 276, 125363.

Chebotarev, A. N., Guzenko, E. M., Barbalat, D. O. & Snigur, D. V.: 2018, 'MODIFICATION OF THE ORGANO-POLYMERIC ANIONITES SURFACE WITH XYLENOL ORANGE BY SORPTION', *Вісник Одеського національного університету. Хімія*, 23, 78–85.

Chen, H., Zhong, A., Wu, J., Zhao, J. & Yan, H.: 2012, 'Adsorption Behaviors and Mechanisms of Methyl Orange on Heat-Treated Palygorskite Clays', *Industrial & Engineering Chemistry Research*, 51, 14026–14036.

Choudhary, M., Chakinala, N., Saini, P., Surolia, P. K. & Chakinala, A. G.: 2025, 'Carbon foams derived from biomass with ultra-high adsorption capacity for the removal of tetracycline', *Materials Advances*, 6, 7450–7468.

Din, M. I., Khalid, R., Hussain, Z., Arshad, M. & Khan, S. A.: 2024, 'A critical review on application of organic, inorganic and hybrid nanophotocatalytic assemblies for photocatalysis of methyl orange dye in aqueous medium', *Reviews in Chemical Engineering*, 40, 67–91.

Du, S., Sun, Q., Wang, N., Chen, X., Jia, M. & Yu, J.: 2017, 'Synthesis of hierarchical TS-1 zeolites with abundant and uniform intracrystalline mesopores and their highly efficient catalytic performance for oxidation desulfurization', *Journal of Materials Chemistry A*, 5, 7992–7998.

Duo, H., Tang, H., Ma, J., Lu, X., Wang, L. & Liang, X.: 2019, 'Iron-based metal–organic framework as an effective sorbent for the rapid and efficient removal of illegal dyes', *New Journal of Chemistry*, 43, 15351–15358.

- Fouda, S. R. & Hassan, S. A.: 2024, 'Impact of LaZnFe₂O₄ supported NiWO₄@D400-MMT@CMS/MMA nanocomposites as a catalytic system in remediation of dyes from wastewater', *Scientific Reports*, *14*, 11644.
- Garrudo-Guirado, M. I., Blanco-Flores, A., Toledo-Jaldin, H. P., Sánchez-Mendieta, V. & Vilchis-Néstor, A. R.: 2018, 'Reuse of sustainable materials for xylenol orange dye and copper (II) ion ammoniacal removal', *Journal of Environmental Management*, *206*, 920–928.
- Ghaemi, N., Madaeni, S. S., Daraei, P., Rajabi, H., Shojaeimehr, T., Rahimpour, F. & Shirvani, B.: 2015, 'PES mixed matrix nanofiltration membrane embedded with polymer wrapped MWCNT: Fabrication and performance optimization in dye removal by RSM', *Journal of Hazardous Materials*, *298*, 111–121.
- Grajales-González, E., Monge-Palacios, M., Brunialti, S. & Sarathy, S. M.: 2024, 'Mechanistic Insights into the Dealumination of an H-ZSM-5 Zeolite Using Reactive Molecular Dynamics Simulations', *ACS Catalysis*, *14*, 14110–14126.
- Hamad, N., Galhoum, A. A., Saad, A. & Wageh, S.: 2024, 'Efficient adsorption of cationic and anionic dyes using hydrochar nanoparticles prepared from orange peel', *Journal of Molecular Liquids*, *409*, 125349.
- Hamoud, M. A., Abo-Zahra, S. F., Attia, M. A., Someda, H. H. & Mahmoud, M. R.: 2023, 'Efficient adsorption of cesium cations and chromate anions by one-step process using surfactant-modified zeolite', *Environmental Science and Pollution Research*, *30*, 53140–53156.
- Hartmann, M., Machoke, A. G. & Schwieger, W.: 2016, 'Catalytic test reactions for the

evaluation of hierarchical zeolites', *Chemical Society Reviews*, 45, 3313–3330.

He, Y., Bao, W., Hua, Y., Guo, Z., Fu, X., Na, B., Yuan, D., Peng, C. & Liu, H.: 2022, 'Efficient adsorption of methyl orange and methyl blue dyes by a novel triptycene-based hyper-crosslinked porous polymer', *RSC Advances*, 12, 5587–5594.

Hu, Y., Ju, S., Luo, J. & Pan, H.: 2024, 'Facile preparation of cellulose nanofiber/ZSM-5 zeolite/polyethyleneimine aerogel for selective adsorption of Cu²⁺ in wastewater', *Journal of Solid State Chemistry*, 337, 124751.

Huang, C., Liao, H., Ma, X., Xiao, M., Liu, X., Gong, S., Shu, X. & Zhou, X.: 2021, 'Adsorption performance of chitosan Schiff base towards anionic dyes: Electrostatic interaction effects', *Chemical Physics Letters*, 780, 138958.

Javad Kalbasi, R. & Eghbalian, F.: 2022, 'Dynamic light scattering investigation of CTAB/swelling agent/water mixture for designing of hierarchical ZSM-5 zeolites with favorable mesoporosity', *Journal of Materials Science*, 57, 8676–8686.

Jia, X., Kanbaiguli, M., Zhang, B., Huang, Y., Peydayesh, M. & Huang, Q.: 2024, 'Anisotropic Chitosan-nanocellulose/Zeolite imidazolate frameworks-8 aerogel for sustainable dye removal', *Journal of Colloid and Interface Science*, 676, 298–309.

Li, Y., Wang, W., Bai, M., Li, X., Li, Y., Liu, H., Fang, Z. & Sang, J.: 2025a, 'Organically modified sodium montmorillonite for enhanced adsorption of xylenol orange from aqueous solutions: kinetic, thermodynamic, and mechanistic study', *Environmental Geochemistry and Health*, 48, 63.

Li, Y., Yu, K., Li, H., Li, S., Han, J., Guo, D.-Y., Chen, S. & Pan, Q.: 2025b, 'Colorimetric Xylenol Orange: A Long-Buried Aggregation-Induced Emission Dye and Restricted

Rotation for Dual-Mode Sensing of pH and Metal Ions', *Analytical Chemistry*, 97, 1845–1852.

Ma, J.-T., Meng, T.-F., Chen, Z.-Y., Zhu, Y.-J., Lian, C., Wang, P., Liu, D.-H. & Zhao, Y.-P.: 2024, 'Catalytic performance and mechanism study of the isomerization of 2,5-dichlorotoluene to 2,4-dichlorotoluene', *RSC Advances*, 14, 8709–8717.

Magnaghi, L. R., Zaroni, C., Alberti, G. & Biesuz, R.: 2023, 'The colorful world of sulfonephthaleins: Current applications in analytical chemistry for “old but gold” molecules', *Analytica Chimica Acta*, 1281, 341807.

Mancuso, J. L. & Van Speybroeck, V.: 2024, 'The nature of extraframework aluminum species and Brønsted acid site interactions under catalytic operating conditions', *Journal of Catalysis*, 429, 115211.

Meng, L., Mezari, B., Goesten, M. G., Wannapakdee, W., Pestman, R., Gao, L., Wiesfeld, J. & Hensen, E. J. M.: 2017, 'Direct synthesis of hierarchical ZSM-5 zeolite using cetyltrimethylammonium as structure directing agent for methanol-to-hydrocarbons conversion', *Catalysis Science & Technology*, 7, 4520–4533.

Nguyen, N.-A., Nguyen, D.-K., Dinh, V.-P., Duong, B.-N., Ton-That, L., Hung, N. T. & Ho, T.-H.: 2023, 'Effective adsorption of Pb(II) ion from aqueous solution onto ZSM-5 zeolite synthesized from Vietnamese bentonite clay', *Environmental Monitoring and Assessment* 195, 1530.

Nodehi, R., Shayesteh, H. & Kelishami, A. R.: 2020, 'Enhanced adsorption of congo red using cationic surfactant functionalized zeolite particles', *Microchemical Journal*, 153, 104281.

Ouachtak, H., Akhouairi, S., Haounati, R., Addi, A. A., Jada, A., Taha, M. L. & Douch, J.: 2020,

- '3,4-Dihydroxybenzoic acid removal from water by goethite modified natural sand column fixed-bed: experimental study and mathematical modeling', *Desalination and Water Treatment*, 194, 439–449.
- Radoor, S., Karayil, J. & Kim, H.: 2026, 'Recent advances in ZSM-5 zeolite for multi-pollutant removal from water: A mini review', *Microporous and Mesoporous Materials*, 399, 113841.
- Roth, W. J., Gil, B., Tarach, K. A. & Góra-Marek, K.: 2025, 'Top-down engineering of zeolite porosity', *Chemical Society Reviews*, 54, 7484–7560.
- Schallmoser, S., Ikuno, T., Wagenhofer, M. F., Kolvenbach, R., Haller, G. L., Sanchez-Sanchez, M. & Lercher, J. A.: 2014, 'Impact of the local environment of Brønsted acid sites in ZSM-5 on the catalytic activity in n-pentane cracking', *Journal of Catalysis* 316, 93–102.
- Shah, H. H., Amin, M., Pepe, F., Mancusi, E. & Fareed, A. G.: 2025, 'Overview of environmental and economic viability of activated carbons derived from waste biomass for adsorptive water treatment applications', *Environmental Science and Pollution Research*, 32, 19084–19109.
- Su, X., Chen, Y., Li, Y., Li, J., Song, W., Li, X. & Yan, L.: 2022, 'Enhanced adsorption of aqueous Pb(II) and Cu(II) by biochar loaded with layered double hydroxide: Crucial role of mineral precipitation', *Journal of Molecular Liquids*, 357, 119083.
- Tsoutsas, E. K., Tolkou, A. K., Kyzas, G. Z. & Katsoyiannis, I. A.: 2024, 'An Update on Agricultural Wastes Used as Natural Adsorbents or Coagulants in Single or Combined Systems for the Removal of Dyes from Wastewater', *Water, Air, & Soil Pollution*, 235, 178.
- Wang, C., Brenig, A., Xu, J., Deng, F., Paunović, V. & van Bokhoven, J. A.: 2024, 'Evidence of

- Preferential Aluminum Site Loss during Reaction-Induced Dealumination', *Journal of the American Chemical Society*, 146, 34279–34284.
- Wang, C., Feng, X., Shang, S., Liu, H., Song, Z. & Zhang, H.: 2023, 'Adsorption of methyl orange from aqueous solution with lignin-modified metal–organic frameworks: Selective adsorption and high adsorption capacity', *Bioresource Technology*, 388, 129781.
- Wei, Y., Parmentier, T. E., de Jong, K. P. & Zečević, J.: 2015, 'Tailoring and visualizing the pore architecture of hierarchical zeolites', *Chemical Society Reviews*, 44, 7234–7261.
- Wen, T.-H., You, C.-Y., Liu, T.-H., Goldsmith, B. R. & Lin, Y.-C.: 2025, 'Accelerating Hierarchical ZSM-5 Engineering via Bayesian Optimization-Guided Discovery', *ACS Materials Au*, 6, 415–424.
- Xie, K., Xie, J., Zhao, Z., Meng, X. & Chen, B.: 2025, 'Synthesis of iron-modified montmorillonite/Al₂O₃ composite adsorbents and their phosphorus adsorption performance study', *Scientific Reports*, 15, 34873.
- Xu, D., Feng, J. & Che, S.: 2014, 'An insight into the role of the surfactant CTAB in the formation of microporous molecular sieves', *Dalton Transactions*, 43, 3612–3617.
- Yang, K., Yan, S., Sang, Y., Liu, J., Yu, L., Yang, X. & Huang, S.: 2021, 'Construction of hierarchical ZSM-5 zeolites by chelating-alkaline medium', *Materials Today Sustainability*, 13, 100070.
- Yu, L., Xu, C., Zhou, Q., Fu, X., Liang, Y. & Wang, W.: 2023, 'Facile synthesis of hierarchical porous ZSM-5 zeolite with tunable mesostructure and its application in catalytic cracking of LDPE', *Journal of Alloys and Compounds*, 965, 171454.
- Yu, W., Wu, X., Mi, R., Zai, H., Fang, M., Min, X., Liu, Y. & Huang, Z.: 2024, 'Synthesis of

ZSM-5 zeolite from fly ash by one-pot hydrothermal method for methylene blue removal',
Journal of the American Ceramic Society, 107, 5298–5312.

Zhang, L., Liu, X., Liu, W., Du, H. & Guo, J.: 2026, 'Hierarchical porous biochar with Fe/Zn co-activation derived from orange waste: enhanced methylene blue adsorption and mechanistic insights', *Biochar X*, 2, e004.

Captions for figures and tables

Fig.1 Schematic diagram of the synthesis of Meso-Z5-DeAl.

Fig. 2. (A) XRD patterns of the samples: (a) ZSM-5, (b) Meso-Z5-DeAl. (B) IR patterns of the samples: (a) ZSM-5, (b) Meso-Z5-DeAl.

Fig. 3. SEM images of: (a) ZSM-5, (b) Meso-Z5-DeAl, (c) EDS mapping of Meso-Z5-DeAl with Si, O, Al, N, Na element, respectively.

Fig 4 N₂ adsorption-desorption isotherms and pore size distribution curves of (A) ZSM-5, (B) Meso-Z5-DeAl.

Fig. 5. Adsorption efficiency of XO on Meso-Z5-DeAl and ZSM-5 adsorbents under varied parameters: (A) Effect of pristine and Meso-Z5-DeAl dosage. (Condition: 298 K, pH 5.0, 60 min, XO initial concentration 150 mg/L) (B) initial XO concentration (Condition: 298 K, pH 5.0, 60 min, 2.0 g/L both adsorbents), (C) temperature (Condition: pH 5.0, 60 min, 2.0 g/L both adsorbents, XO initial concentration 150 mg/L), and (D) contact time (Condition: 298 K, pH 5.0, 2.0 g/L both adsorbents, XO initial concentration 150 mg/L).

Fig. 6. (A) Effect of initial pH on XO adsorption by pristine and Meso-Z5-DeAl. (Condition: 298 K, 2.0 g/L both adsorbents, 60 min, XO initial concentration 150 mg/L) (B) Zeta potential

diagram of Meso-Z5-DeAl. (as a function of pH in water at 1 g/L, 298 K; pH adjusted with HCl and NaOH). (C) Species distribution diagram of XO as a function of pH.

Fig. 7. (A) Influence of coexisting ions on XO adsorption by Meso-Z5-DeAl. (B) Influence of adsorption-desorption cycles on the adsorption capacity of Meso-Z5-DeAl for XO (Condition: 298 K, pH 5.0, 60 min, 2.0 g/L Meso-Z5-DeAl, XO initial concentration 150 mg/L).

Fig. 8. (A) Pseudo-first-order kinetic model for XO adsorption onto Meso-Z5-DeAl, (B) pseudo-second-order kinetic model for XO adsorption onto Meso-Z5-DeAl. Conditions: pH 5.0, 2.0 g/L Meso-Z5-DeAl, XO initial concentration 150 mg/L.

Fig. 9. Adsorption Isotherm curves of XO on Meso-Z5-DeAl with (A) Langmuir model and (B) Freundlich model.

Fig. 10. Adsorption Mechanism of Meso-Z5-DeAl for XO.

Table 1 The kinetics parameters of XO adsorption onto Meso-Z5-DeAl.

Table 2 Adsorption Isotherm Fitting Parameters for XO adsorption onto Meso-Z5-DeAl.

Table 3 Comparison of adsorption performance of various adsorbents for XO removal.

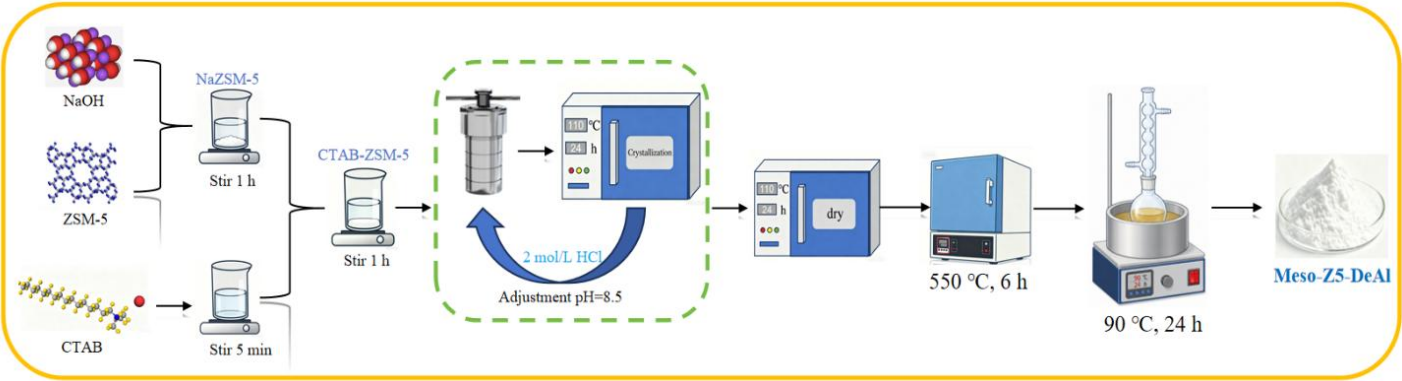


Fig.1 Schematic diagram of the synthesis of Meso-Z5-DeAl.

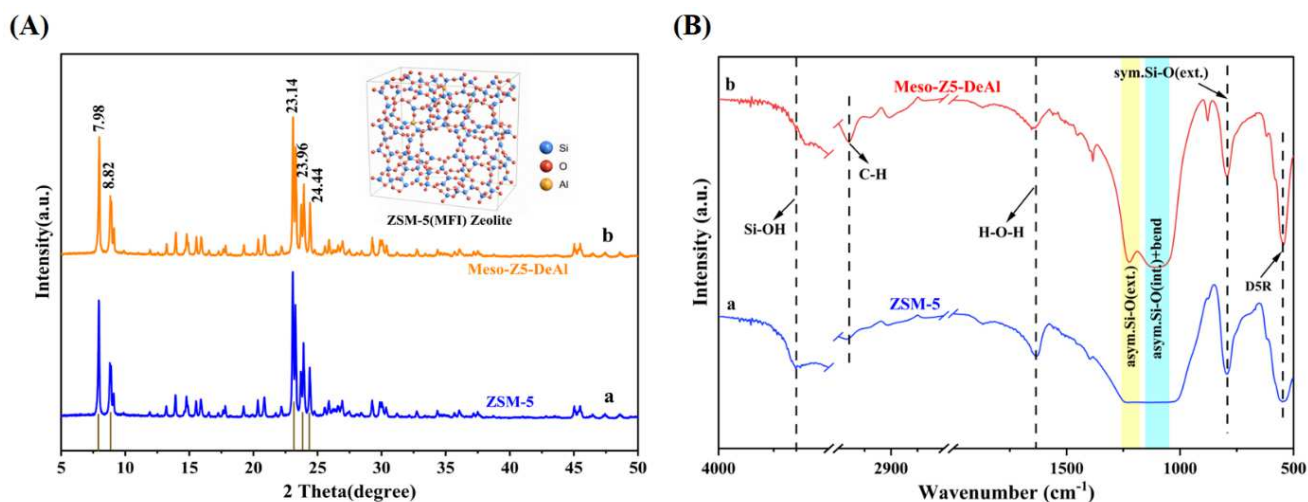


Fig. 2. (A) XRD patterns of the samples: (a) ZSM-5, (b) Meso-Z5-DeAl. (B) IR patterns of the samples: (a) ZSM-5, (b) Meso-Z5-DeAl. Note: sym. is symmertric, asym. is asymmetric, int. is internal, ext. is external, D5R is double five-membered ring (MFI fingerprint).

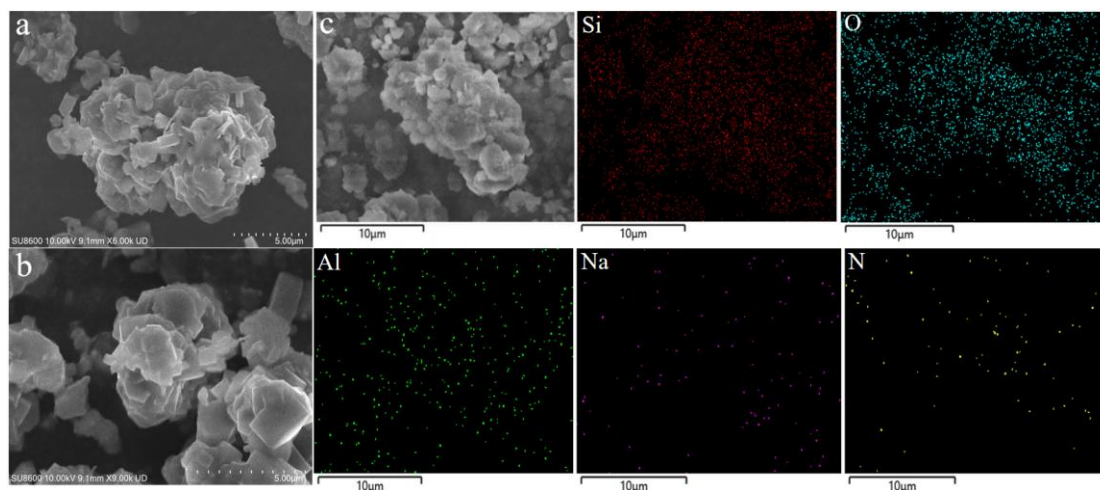


Fig. 3. SEM images of: (a) ZSM-5, (b) Meso-Z5-DeAl, (c) EDS mapping of Meso-Z5-DeAl with Si, O, Al, N, Na element, respectively.

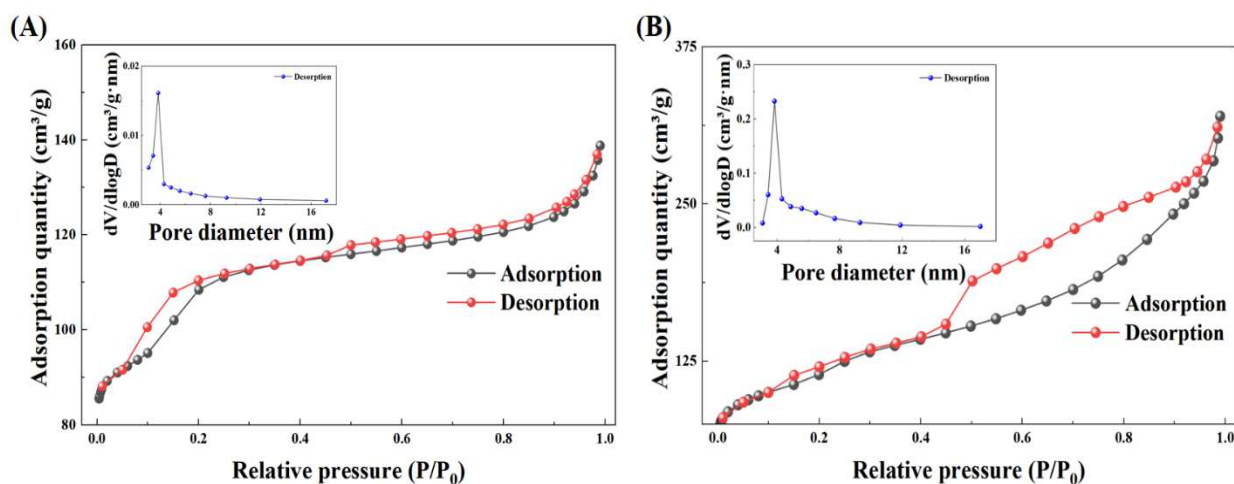


Fig 4 N_2 adsorption-desorption isotherms and pore size distribution curves of (A) ZSM-5, (B) Meso-Z5-DeAl.

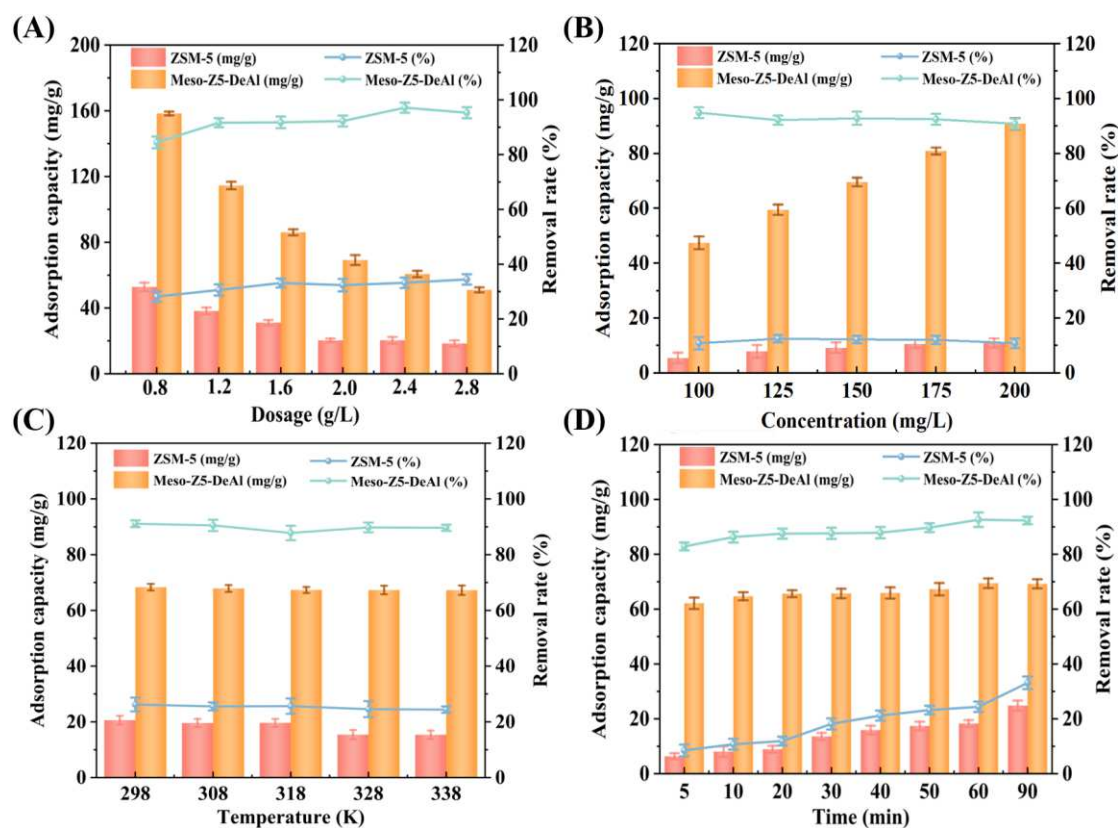


Fig. 5. Adsorption efficiency of XO on Meso-Z5-DeAl and ZSM-5 adsorbents under varied parameters: (A) Effect of pristine and Meso-Z5-DeAl dosage. (Condition: 298 K, pH 5.0, 60 min, XO initial concentration 150 mg/L) (B) initial XO concentration (Condition: 298 K, pH

5.0, 60 min, 2.0 g/L both adsorbents), (C) temperature (Condition: pH 5.0, 60 min, 2.0 g/L both adsorbents, XO initial concentration 150 mg/L), and (D) contact time (Condition: 298 K, pH 5.0, 2.0 g/L both adsorbents, XO initial concentration 150 mg/L).

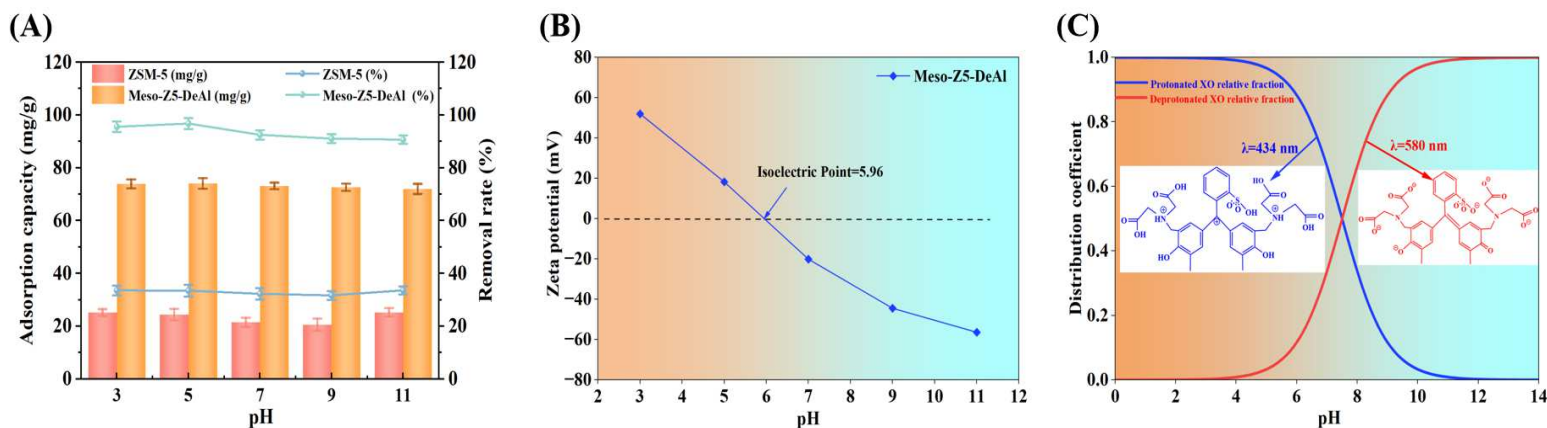


Fig. 6. (A) Effect of initial pH on XO adsorption by pristine and Meso-Z5-DeAl. (Condition: 298 K, 2.0 g/L both adsorbents, 60 min, XO initial concentration 150 mg/L) (B) Zeta potential diagram of Meso-Z5-DeAl. (as a function of pH in water at 1 g/L, 25 °C; pH adjusted with HCl and NaOH). (C) Species distribution diagram of XO as a function of pH.

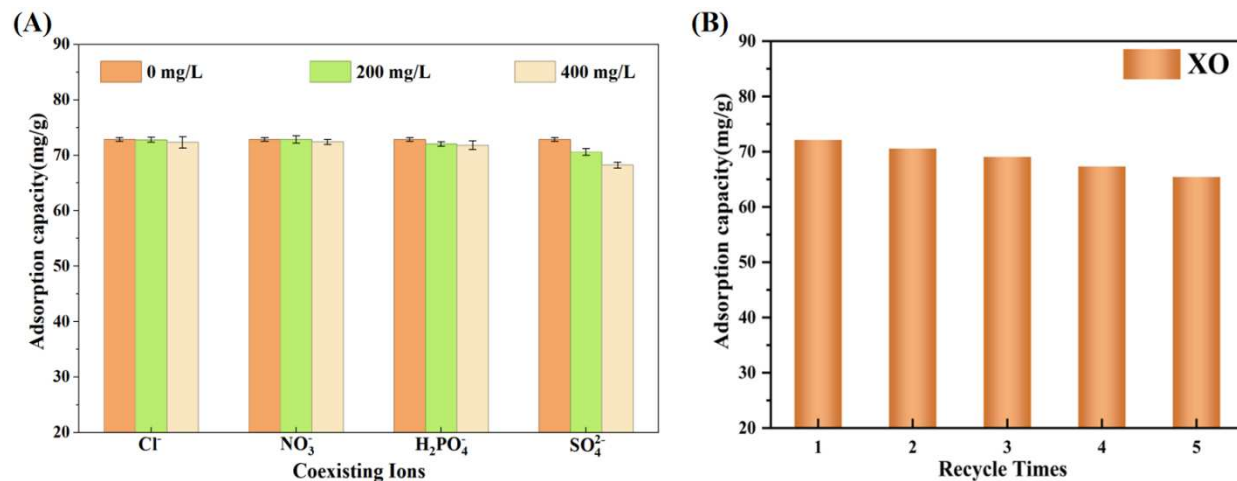


Fig. 7. (A) Influence of coexisting ions on XO adsorption by Meso-Z5-DeAl. (B) Influence of adsorption-desorption cycles on the adsorption capacity of Meso-Z5-DeAl for XO (Condition: 298 K, pH 5.0, 60 min, 2.0 g/L Meso-Z5-DeAl, XO initial concentration 150 mg/L).

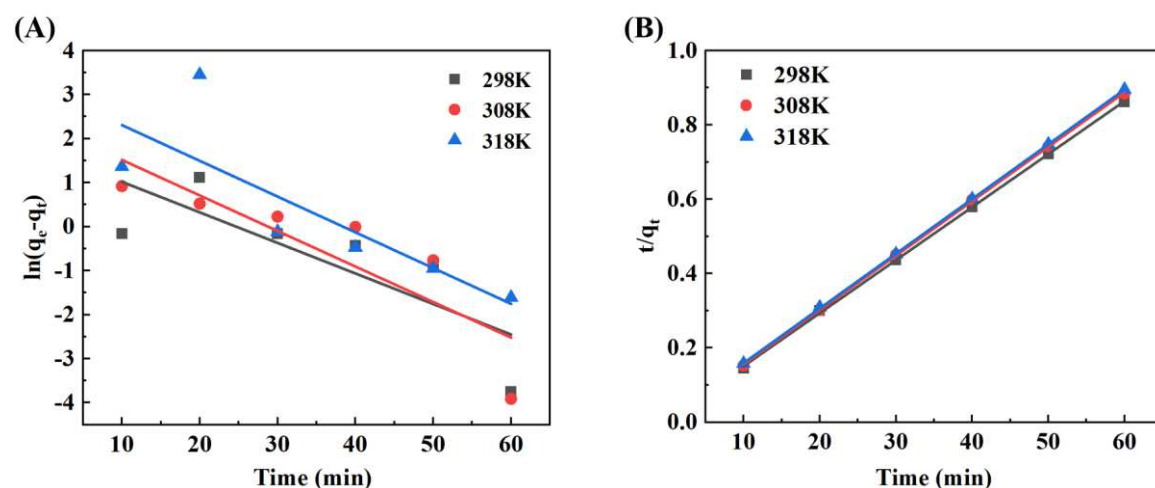


Fig. 8. (A) Pseudo-first-order kinetic model for XO adsorption onto Meso-Z5-DeAl, (B) pseudo-second-order kinetic model for XO adsorption onto Meso-Z5-DeAl. Conditions: pH 5.0, 2.0 g/L Meso-Z5-DeAl, XO initial concentration 150 mg/L.

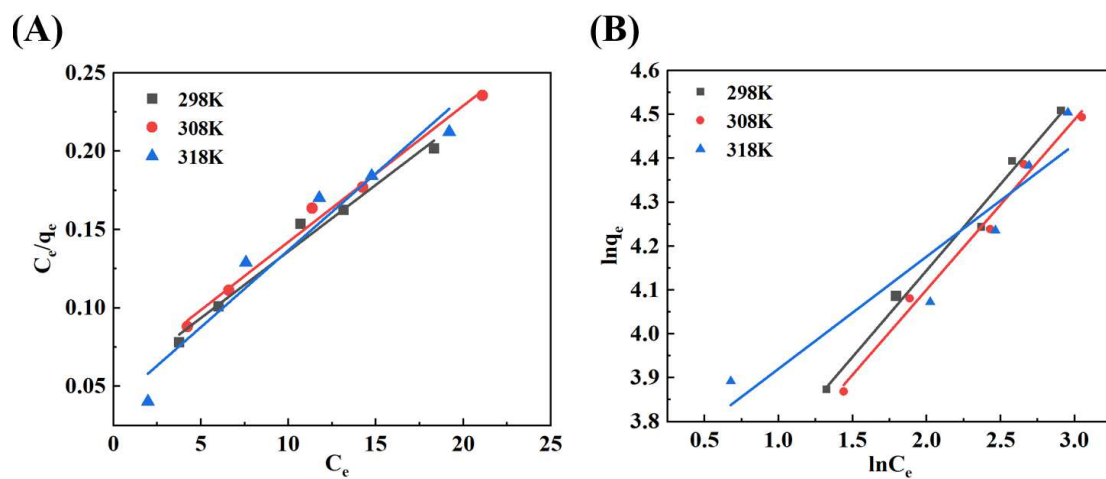


Fig. 9. Adsorption isotherm curves of XO on Meso-Z5-DeAl with (A) Langmuir model and (B) Freundlich model.

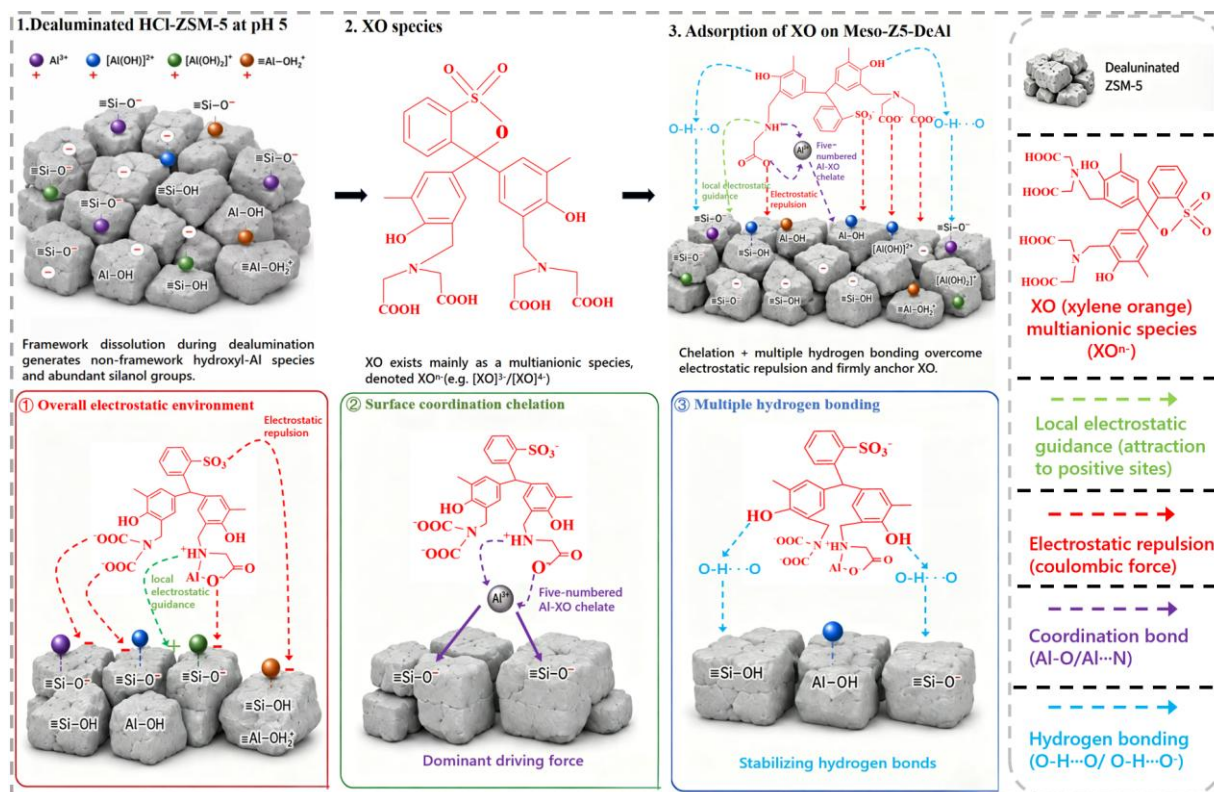


Fig. 10. Adsorption Mechanism of Meso-Z5-DeAl for XO.

Table 1 The kinetics parameters of XO adsorption onto Meso-Z5-DeAl

Models	Temperature (K)		
	298	308	318
Pseudo-first-order			

K_1	0.0941	0.0807	0.0812
$q_{e \text{ cal}}$	5.547	10.21	22.65
R^2	0.6336	0.7336	0.6778
Pseudo-second-order			
K_2	0.024	0.023	0.0178
$q_{e \text{ cal}}$	70.13	68.35	67.98
R^2	0.9998	0.9991	0.9997

Table 2 Adsorption Isotherm Fitting Parameters for XO adsorption onto Meso-Z5-DeAl

T (K)	Langmuir			Freundlich		
	$q_{\max}$ (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)	n	R^2
298	117.6	0.166	0.9911	28.69	2.538	0.9871
308	115.1	0.157	0.9908	27.81	2.579	0.9886
318	101.8	0.254	0.9815	37.05	2.729	0.8884

Table 3 Comparison of adsorption performance of various adsorbents for XO removal

Adsorbent	q_e (mg/g)	Contact time	Dosage	Ref.
Aquatic-biomass-derived biosorbent	17.58	180 min	0.5 g/L	(Abdallah and Alprol, 2024)
BXT-HDTMA	5.376	30 min	10 g/L	(Al-Kazragi et al., 2019)
Granion AWA-G1 organopolymeric anion exchanger	41.1	60 min	0.6 g	(Chebotarev et al., 2018)
LaZnFe ₂ O ₄ @Ni WO ₄ @D400-MMT@CMS/M	44.05	220 min	0.5 g/L	(Fouda and Hassan, 2024)

MA “S ₃ ”				
Vitreous tuff (VT)	45.17	50 min	1.0 g/L	(Garrudo-Guirado et al., 2018)
Meso-Z5-DeAl	72.24	60 min	2.0 g/L	This work