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Heulandite Nanocomposites for Wastewater Treatment: A Critical Review

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Abstract

The contamination of wastewaters by toxic heavy metal ions and persistent organic pollutants is one of the most serious global threats to human health and ecological security. Natural zeolites, especially heulandite (HEU framework), are promising low-cost and environmentally friendly materials for water purification due to their well-defined crystalline pore networks, high cation exchange capacity (CEC) and excellent thermal stability. However, pristine heulandite suffers from significant physical disadvantages including limited mesoporosity, absence of visible-light absorption, significant mass-transfer limitations for macromolecular contaminants, and challenging phase separation in slurry systems. To overcome these limitations, recent studies have focused on the rational design, synthesis and functional surface modification of novel heulandite nanocomposites. In this review, a comprehensive and critical synthesis of the state-of-the-art advances in heulandite nanocomposites is presented. We systematically review different synthesis methods such as hydrothermal in-situ crystallization, sol-gel deposition, chemical co-precipitation, organosilane/surfactant grafting and polymer hybridization. The structural retention, interface band engineering and active site distribution are elucidated by evaluating the advanced diagnostic characterization techniques (PXRD, FE-SEM/HR-TEM, EDX, FTIR, BET/BJH N_2 physisorption, XPS, UV-Vis DRS and PL spectroscopy). In addition, this review extensively covers heavy metal removal (Pb^{2+}, Cd^{2+}, Cu^{2+}, Cr(VI), Hg^{2+}, Ni^{2+}) in terms of operating parameters, comprehensive adsorption isotherm models (Langmuir, Freundlich, Dubinin-Radushkevich), kinetics (Pseudo-First-Order, Pseudo-Second-Order, Intraparticle Diffusion) and thermodynamics. Solar photocatalytic degradation of persistent organic pollutants (dyes, antibiotics, pesticides) is elaborately discussed with emphasis on band alignment, charge separation pathways, Direct Z-scheme/S-scheme heterojunctions and reactive oxygen species (ROS: .OH, $.O^{2-}$, h^{+}) generation. Finally, bifunctional simultaneous removal, magnetic catalyst recovery, long-term cyclic stability, leaching risks, techno-economic feasibility, and industrial scale-up challenges are critically discussed to guide future research directions.

Keywords: *Heulandite nanocomposites; Natural zeolites; Heavy metal adsorption; Photocatalytic degradation; Heterojunction architecture; Adsorption kinetics & isotherms; Synergistic wastewater remediation.*

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Executive Summary & Key Highlights

- **Structural Superiority:** Natural heulandite (HEU topology) possesses a unique 2D/3D intersecting channel system (10-MR Channel A, 8-MR Channels B & C) with high cation exchange capacity (CEC = 2.2–2.8 meq/g), rendering it an ideal inorganic matrix for nanocomposite engineering.
- **Multi-Functional Hybridization:** Recent advances integrate transition metal oxides (TiO_2, ZnO, BiOBr), magnetic iron oxides (Fe_3O_4), carbon allotropes (g-C_3N_4, GO), and biopolymers (chitosan, alginate) into HEU matrices, overcoming raw zeolite limitations such as low mesoporosity and wide optical bandgaps.
- **Bifunctional Performance:** Optimized Heulandite nanocomposites display exceptional heavy metal sorption capacities (e.g., q_{max} = 285.4 mg/g for Pb^{2+}, 210.8 mg/g for Cd^{2+}, and 175.2 mg/g for Cr(VI)) and solar photocatalytic degradation efficiencies (greater than 98% within 60 min for tetracycline, ciprofloxacin, and methylene blue).

- **Dual-Action Synergism:** Simultaneous removal systems demonstrate that photo-generated electrons reduce toxic Cr(VI) to Cr(III), which subsequently exchanges into HEU cation channels, while photogenerated holes and reactive oxygen radicals (·OH, $\cdot O_2^-$) degrade organic co-pollutants.
- **Thermodynamics & Kinetics:** Heavy metal adsorption overwhelmingly follows Pseudo-Second-Order kinetics and Langmuir isotherm models (chemisorption, $\Delta H° > 0$, $\Delta G° < 0$), while photocatalytic degradation obeys Langmuir-Hinshelwood pseudo-first-order kinetics.

1. Introduction And State-Of-The-Art

Rapid industrialization, intensification of agriculture and urban expansion have produced huge amounts of complex wastewater containing toxic inorganic heavy metals (e.g., Pb^{2+}, Cd^{2+}, Cr (VI), Hg^{2+}, Cu^{2+}, Ni^{2+}, As(V)) and recalcitrant organic micro-pollutants (e.g., synthetic azo dyes, pharmaceuticals, personal care products, pesticides and endocrine-disrupting chemicals) [1-3]. Heavy metals are non-biodegradable, highly bioaccumulative and extremely toxic even at trace levels (part-per-billion), leading to severe neurological damage, renal failure, carcinogenicity and ecological collapse [4]. Meanwhile, persistent organic pollutants are resistant to natural attenuation and biodegradation and pose serious threats to aquatic photosynthesis and human metabolic systems [5]. In real-world industrial effluents (e.g., electroplating, textile, tannery and pharmaceutical wastewater), heavy metals and organic pollutants are often present simultaneously, resulting in synergistically complex toxicity that poses serious problems for conventional treatment systems [6].

Conventional methods for wastewater treatment include chemical precipitation, coagulation-flocculation, solvent extraction, membrane filtration, ion exchange resins and activated carbon adsorption [7,8]. These technologies, despite their efficiency under some conditions, have several important technical and economic limitations, such as high energy and operational costs, membrane fouling, low selectivity, incomplete removal of pollutants at trace concentrations and the generation of secondary toxic sludge which has to be disposed of in a hazardous way [9]. Semiconductor photocatalysis (TiO_2, ZnO, BiOBr, g-C_3N_4) in Advanced Oxidation Processes (AOPs) provides a sustainable route for total mineralization of toxic organic molecules into harmless H_2O, CO_2 and mineral acids under light irradiation [10]. However, suspended benchmark photocatalysts suffer from the rapid recombination of photogenerated electrons and holes, limited use of solar light, small specific surface area, low adsorption capacity for non-polar molecules and high recovery costs from treated effluents [11].

In this regard, natural aluminosilicate zeolites have been attracting great scientific and industrial interest as versatile supports and active components for hybrid environmental nanomaterials [12]. Zeolites are three-dimensional framework structures of corner-sharing $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra, creating uniform molecular-scale channels, cages and high negative framework charges balanced by extra-framework exchangeable cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) [13]. Heulandite (HEU framework topology) is a unique member of the family of natural zeolites because of its crystallographic pore geometry, high structural stability, availability in volcanic ash deposits worldwide and better theoretical Cation Exchange Capacity (CEC = 2.2-2.8 meq/g) [14].

Despite these inherent advantages, raw natural heulandite has fundamental limitations for direct use in sophisticated wastewater treatment. First, the narrow microporous channels (0.3–0.7 nm) and severe molecular diffusion limitations may prevent bulky organic pollutants (such as tetracycline, Rhodamine B, and reactive dyes) from entering the internal structure. They may limit adsorption to external surface sites. Photochemically, the material is optically inactive in the visible region due to a large bandgap greater than 4.2 eV, making it completely inactive for direct solar-driven photocatalysis. As a chemical property, its net negative framework charge makes it strongly electrostatically repulsive or non-affinitive toward toxic anionic species such as Cr (VI) ($Cr_2O_7^{2-}$, $HCrO^{4-}$), As(V) (H_2AsO^{4-}) and anionic dyes, while it has a high affinity toward cationic pollutants. Finally, from an operational point of view, heulandite fine powder slurries exhibit poor settling characteristics in water; thus, post-treatment separation is difficult, and there is a risk of secondary particulate contamination unless the zeolite is magnetically functionalized or immobilized on a substrate.

To overcome these intrinsic challenges, material scientists have led the design of novel Heulandite Nanocomposites. By embedding transition metal oxide semiconductors (TiO_2, ZnO, BiOBr, Fe_2O_3), magnetic nanoparticles (Fe_3O_4), metal-organic frameworks (MOFs), conductive polymers (polyaniline, polypyrrole, chitosan) and two-dimensional carbon materials (graphene oxide, g-C_3N_4) on modified surfaces of HEU, multifunctional hybrid materials have been developed [15-18]. These nanocomposites have large adsorption capacity, improved electron-hole separation due to interfacial heterojunctions, enhanced light harvesting and fast magnetic recovery.

The present comprehensive review discusses recent developments in heulandite nanocomposites in a critical manner. Herein, we systematically explore the structural architecture of the HEU framework, novel synthesis routes, advanced characterization techniques, heavy metal adsorption behaviour (kinetics, isotherms, thermodynamics, and ion-exchange/complexation mechanisms), photocatalytic degradation of organic pollutants (heterojunction dynamics, ROS generation), dual-functional simultaneous remediation, catalyst regeneration, and techno-economic industrial feasibility.

2. Crystallographic Architecture And Physicochemical Properties Of Heulandite

Heulandite is a member of the group 7 zeolites with HEU framework topology and crystallizes in the monoclinic system (space group C2/m) [19]. The basic structural building blocks are 4-4-1 secondary building units (SBUs) consisting of corner-sharing $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra. Structural net negative charge is produced by isomorphous substitution of Si^{4+} by Al^{3+} in the silicate framework, which is charge-balanced by hydrated extra-framework alkali and alkaline earth cations (mainly Ca^{2+}, Na^{+}, K^{+}, and Mg^{2+}) within the pore channels together with zeolitic water molecules [20].

The ideal chemical formula of pristine natural heulandite is written as:

$$(Na, K)\ Ca_4\ [Al_9\ Si_{27}\ O_{72}]\ 24\ H_2O \quad \ldots\ldots\ldots\ldots\ldots\ (1)$$

The main characteristic difference of the HEU topology is the two-dimensional intersecting channel system, which is composed of three different crystallographic pore channels. Channel A is a 10-membered ring (10-MR) channel parallel to the c-axis with crystallographic free dimensions of about 0.75 nm × 0.31 nm. Channel B is an 8-membered ring (8-MR) channel which is also parallel to the c-axis and has dimensions of 0.46 nm × 0.36 nm. Finally, Channel C is an 8-membered ring (8-MR) channel parallel to the a-axis with dimensions of 0.47 nm x 0.28 nm, which is intersected by Channels A and B. It is important to make a scientific distinction between heulandite and clinoptilolite since they both share the same HEU framework topology. The main difference is the Si/Al atomic ratio and thermal stability of the framework [21]. Heulandite has a Si/Al ratio less than 4.0 (typically 2.8-3.8), which means it has more Al, a higher density of structural charge, and a higher theoretical Cation Exchange Capacity (CEC = 2.2-2.8 meq/g) than clinoptilolite (Si/Al ≥ 4.0, CEC = 1.6-2.2 meq/g). However, high-aluminum heulandite experiences a structural phase change (Heulandite-A to Heulandite-B) and channel collapse when heated above 250–350°C as a consequence of rapid dehydration, while silica-rich clinoptilolite is thermally stable up to 750°C [22]. Therefore, the synthetic processing of heulandite materials and calcination of the composites should be strictly controlled below 300 °C to keep the structural pore integrity.

3. Design And Synthesis Methodologies For Heulandite Nanocomposites

The synthesis method has great importance for the performance of heulandite nanocomposites, which determines the dispersion of nanoparticles, the interfacial contact, the porosity, the surface area and the chemical stability. Several physical, chemical and hybrid synthetic routes have been developed for the fabrication of high-performance HEU nanocomposites.

3.1 Pre-treatment, Acid Leaching, and Cation Conditioning

Raw natural heulandite ore contains mineral impurities (quartz, feldspar, smectite clays, iron oxides) and mixed extra-framework cations (Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}) that block channels and prevent ion exchange. Mechanical crushing, sieving to a particle size of 75–150 μm, washing with deionized water and chemical conditioning make up the pre-treatment [23]. The controlled

acid leaching with dilute mineral acids (0.1–1.0 M HCl or H_2SO_4) selectively removes the soluble carbonate impurities and causes partial dealumination, generating the secondary mesopores (2–10 nm) on the zeolite surface without framework collapse of HEU. Then the zeolite is converted to a homogeneous Na-exchanged form (Na-HEU) by homo-ionic conditioning using 1.0 M NaCl solution. Na^+ has a lower hydration energy and a weaker electrostatic framework binding, with much faster subsequent cation exchange kinetics with heavy metal ions or metal precursors [24].

3.2 Hydrothermal In-Situ Crystallization

Hydrothermal synthesis is the in-situ growth of inorganic semiconductor nanoparticles (TiO_2, ZnO, BiOBr, SnO_2, CdS, etc.) directly in or on the surface of pre-conditioned heulandite particles at elevated temperature (120–180°C) and autogenous pressure in a Teflon-lined stainless-steel autoclave [25]. Precursor salts (e.g., titanium isopropoxide, zinc nitrate, bismuth nitrate) are dissolved in an aqueous or alcoholic slurry in which HEU microparticles are dispersed. Hydrothermal aging can form strong chemical bonds (e.g. Si-O-Ti or Al-O-Zn bonds) at the host-guest interface. The hydrothermal parameters (pH, temperature, reaction time, precursor-to-zeolite ratio) dictate the crystallite phase (e.g. pure anatase TiO_2 versus rutile) and the spatial distribution of the nano-photocatalysts.

3.3 Sol-Gel Deposition & Alkoxide Hydrolysis

The sol–gel technique involves the hydrolysis and condensation of metal alkoxides (e.g., titanium tetrabutoxide, zinc acetate) in the presence of suspended heulandite particles. Hydrolysis of the alkoxide gives fine clusters of metal oxide sol that condense on the external surfaces of the zeolite host, which are rich in hydroxyl groups (-Si-OH, -Al-OH) [26]. Following solvent evaporation, low-temperature calcination (200–300°C) resulted in the formation of highly dispersed, ultra-small oxide nanoparticles supported on the HEU framework. The sol-gel synthesis provides excellent control of stoichiometry, high purity and uniform nanometer-scale film coatings.

3.4 Chemical Co-Precipitation for Magnetic Functionalization

Heulandite is functionalized with superparamagnetic iron oxide nanoparticles (Fe_3O_4 or γ-Fe_2O_3) for rapid magnetic separation from the treated water. Chemical co-precipitation is carried out by dissolving ferrous (Fe^{2+}) and ferric (Fe^{3+}) salts in stoichiometric ratios (1:2 molar ratio) in an aqueous slurry of HEU, followed by rapid alkaline precipitation with NaOH or NH_4OH at pH 10–11 under an inert nitrogen atmosphere [27]. The resulting Fe3O4@HEU nanocomposite has a considerable magnetic response (saturation magnetization M_s = 25–45 emu/g) and could be separated from the solid-liquid mixture within seconds by an external neodymium magnet.

3.5 Organic-Inorganic Polymer Hybridization & Bead Immobilization

To overcome dust hazards and continuous column clogging due to fine powders, the heulandite nanocomposites are often encapsulated into biopolymer matrices (e.g., chitosan, sodium alginate, polyvinyl alcohol (PVA), polyaniline (PANI)). The hybridization of the polymer is carried out by cross-linking the polymer chains with glutaraldehyde, epichlorohydrin, or $CaCl_2$ in the presence of HEU powders [28]. Polymeric functional groups (amine -NH_2, hydroxyl -OH, carboxyl -COOH) provide additional binding sites for heavy metals and stabilize the zeolite particles into mechanical macroscopic beads or membranes suitable for continuous packed-bed operations.

3.6 Surface Organosilane and Surfactant Grafting

To convert the inherently hydrophilic and negatively charged surface of heulandite into an organophilic and positively charged surface for the capture of anionic heavy metals ($Cr_2O_7^{2-}$, $HCrO^{4-}$, H_2AsO^{4-}) and organic contaminants, organosilane coupling agents (e.g.,3-aminopropyltriethoxysilane, APTES) or cationic surfactants (e.g., hexadecyltrimethylammonium bromide, HDTMA-Br) are grafted onto HEU. Cationic surfactant molecules intercalate into external surface sites via ion exchange, forming organic admicelles and monolayers with positive surface potential [29].

Table 1. Comprehensive Comparison of Synthesis Methodologies for Heulandite Nanocomposites.

Synthesis Methodology	Nanocomposite System	Key Reaction Conditions	Structural & Functional Advantages	Limitations / Challenges
Hydrothermal In-Situ	TiO_2/HEU, BiOBr/HEU, SnO_2/HEU	120–180°C, 6–24 h, autogenous pressure, pH 2–10	High crystallinity, strong interfacial chemical bonding (Si-O-Ti), uniform distribution	Requires autoclaves; potential partial phase transformation if T > 200°C
Sol-Gel Deposition	ZnO/HEU, TiO_2-SiO_2/HEU	Alkoxide hydrolysis, room T aging, calcination <300°C	Precise stoichiometry control, ultra-fine particle size (<10 nm), high surface area	Requires expensive metal alkoxides and organic solvents; calcination needed
Chemical Co-Precipitation	Fe_3O_4@HEU, γ-Fe_2O_3/HEU	Fe^{2+}:Fe^{3+} = 1:2, pH 10–11 (NH_4OH/NaOH), N_2 purge, 60–80°C	Superparamagnetic properties (M_s > 30 emu/g), ultra-fast magnetic separation	Fe_3O_4 prone to air oxidation to non-magnetic α-Fe_2O_3 without nitrogen inerting
Biopolymer Cross-linking	Chitosan/HEU, Alginate/HEU beads	Polymer dissolution, glutaraldehyde/$CaCl_2$ cross-linking	Flexible macro-bead formatting, abundant -NH_2/-COOH sites, zero powder loss	Reduced mass transfer diffusion rate inside thick hydrogel beads
Surfactant / Silane Grafting	HDTMA-HEU, APTES-HEU	Surface grafting with APTES or HDTMA-Br at 60–80°C	Surface charge reversal (negative to positive), high anionic sorption (Cr(VI))	Surfactant leaching at extreme pH or high ionic strength

4. Advanced Characterization Techniques And Diagnostic Signatures

Comprehensive characterization is essential to verify nanocomposite formation, crystal phase integrity, morphological distribution, surface chemistry, textural porosity, and optoelectronic properties.

4.1 Powder X-Ray Diffraction (PXRD)

The PXRD indicates that the HEU framework maintains its structure after modification. Characteristic reflections for natural heulandite are observed at 2θ ≈ 9.8° (020), 11.1° (200), 19.0° (002), and 22.4° (151) [30]. Loading of semiconductor nanoparticles (TiO_2, ZnO) leads to the appearance of the characteristic diffraction peaks of anatase TiO_2 (101 at 25.3°) or wurtzite ZnO (100, 002, 101 at 31.7°, 34.4°, 36.2°) without decreasing the intensity of the reflection of heulandite. The average crystallite size (d) of supported nanoparticles is estimated using the Scherrer equation:

$$d = \frac{K \cdot \lambda}{\beta \cdot \cos\theta} \qquad (2)$$

where K is the shape factor (0.9), λ is the X-ray wavelength (0.15406 nm for Cu-Kα), β is the full width at half maximum (FWHM) in radians, and θ is the Bragg diffraction angle.

4.2 Electron Microscopy (FE-SEM, HR-TEM) and EDX Mapping

Field-Emission Scanning Electron Microscopy (FE-SEM) shows the classical tabular, coffin-shaped or lamellar plate morphology of natural heulandite crystals (1–10 μm). High-Resolution Transmission Electron Microscopy (HR-TEM) confirms the decoration of small oxide nanoparticles (5-20 nm) onto the smooth zeolite basal planes. HR-TEM lattice fringe analysis clearly shows the interplanar d -spacings (e.g., d = 0.352 nm for the (101) plane of anatase TiO_2, and d = 0.253 nm for the (311) plane of Fe_3O_4). Energy Dispersive X-ray Spectroscopy (EDX)

elemental mapping confirms the spatial distribution of Si, Al, Ti, Fe and target adsorbed metal ions without macro segregation.

4.3 Fourier-Transform Infrared Spectroscopy (FTIR)

FTIR diagnostic absorption bands provide crucial structural insights into framework T-O-T bonds, where T represents silicon or aluminum. Within the spectrum, the absorption range of 1050–1080 cm^{-1} corresponds to the internal asymmetric stretching vibrations of (Si, Al) O_4 tetrahedra, while external symmetric stretching vibrations are observed at 790–800 cm^{-1} and 600–620 cm^{-1}. Lower frequency modes at 450–470 cm^{-1} represent T-O bending within the tetrahedral framework, whereas bands at 1635 cm^{-1} and 3400–3500 cm^{-1} are assigned to the H-O-H bending and -OH stretching modes of zeolitic water and silanol (-Si-OH) groups. Additionally, in TiO_2/HEU or BiOBr/HEU nanocomposites, a new absorption feature appears at 920–940 cm^{-1} corresponding to Ti-O-Si heterojunction cross-linking bonds, confirming successful chemical coupling rather than simple physical blending.

4.4 Nitrogen Physisorption (BET & BJH Analysis)

N_2 adsorption-desorption isotherms at 77 K are used to determine specific surface area (S_{BET}), pore volume and pore size distribution. Natural heulandite exhibits a Type IV isotherm with an H_3 hysteresis loop, indicating that the mesopores are slit-like pores formed by aggregation of primary crystallites. The raw HEU has a small surface area (S_{BET} = 25–45 m^2/g). S_BET is greatly increased to 80-180 m^2/g, and mesopore volume (V_{meso} from 0.04 to 0.22 cm^3/g) is enlarged by BJH calculations due to acid leaching and semiconductor functionalization, greatly improving the mass transport of large pollutant molecules.

4.5 X-Ray Photoelectron Spectroscopy (XPS)

XPS determines elemental oxidation state and shifts in chemical bonding. The formation of the composite induces small shifts (0.3-0.6 eV) in the binding energies of core-level scans of Si 2p (102.8 eV) and Al2p (74.2 eV), indicative of a redistribution of electron density throughout the interface. XPS can determine the target metal valency of spent adsorbents. For example, photo-reduction of toxic Cr (VI) (Cr $2p_{3/2}$ peak at 579.2 eV) to non-toxic Cr (III) (peak at 576.8 eV).

4.6 Optical Spectroscopy (UV-Vis DRS, PL, and EIS)

UV-Vis diffuse reflectance spectroscopy (DRS) is used to determine the range of light absorption. The raw HEU has almost no absorption for wavelengths larger than 300 nm, while the semiconductor nanocomposites show strong absorption in the visible spectrum (400–600 nm). The optical band gap energy (E_g) is calculated using Tauc's relation:

$$(\alpha\, h\nu)^n = A\,(h\nu - E_g) \qquad (3)$$

where α is the absorption coefficient, hν is the photon energy, A is a constant and n = 2 for direct bandgap or n = 0.5 for indirect bandgap transition. The PL emission intensity is directly related to the electron-hole recombination rates. The PL intensities of HEU nanocomposites are consistently quenched relative to pure semiconductors, indicating the zeolitic matrix functions as an electron sink suppressing charge recombination.

Table 2. Diagnostic Characterization Signatures and Physical Information for Heulandite Nanocomposites.

Analytical Technique	Measured Parameter	Diagnostic Signature for HEU Nanocomposites	Key Structural Information Derived
PXRD	Diffraction angles (2θ), peak FWHM	HEU peaks at 9.8°, 11.1°; Anatase TiO_2 at 25.3°; Fe_3O_4 at 35.4°	Crystal phase identification, crystalline preservation, Scherrer particle size
FE-SEM / HR-TEM	Surface morphology, lattice fringes	Tabular HEU slabs (1–5 μm) decorated with 5–15 nm oxide nanoparticles	Nanoparticle dispersion, spatial distribution, lattice d-spacing, interfacial contact
FTIR	Vibrational frequencies (cm^{-1})	T-O-T bands at 1050 and 460 cm^{-1}; new Ti-O-Si band at 930 cm^{-1}	Framework structural integrity, surface functional group grafting, chemical linkages
BET / BJH N_2	Adsorption volume vs. relative pressure P/P_0	Type IV isotherm, H3 hysteresis, S_{BET} increasing from 35 to 145 m^2/g	Specific surface area, micropore/mesopore size distribution, total pore volume

XPS	Core-level Binding Energies (eV)	Binding energy shifts in Si 2p, Ti 2p, Cr 2p (579.2 → 576.8 eV)	Elemental surface composition, oxidation states, electron transfer vectors
UV-Vis DRS	Diffuse reflectance / Absorbance spectra	Red-shift of absorption edge from 320 nm (UV) to 480 nm (Visible)	Optical absorption edge, optical bandgap calculation (E_g via Tauc plot)
PL Spectroscopy	Fluorescence emission intensity	Significant quenching of emission peak compared to pure TiO_2/ZnO	Suppression of photogenerated electron-hole recombination rate

5. Heavy Metal Adsorption: Operational Factors, Isotherms, Kinetics, And Mechanisms

The surface phenomena involved in removing heavy metals using heulandite nanocomposites are chemically and physically complex. Optimization of remediation systems demands systematic evaluation of operational parameters, equilibrium isotherms, kinetic rates and thermodynamic properties.

5.1 Influence of Key Operational Parameters

Solution pH serves as the single most critical variable governing heavy metal adsorption by controlling both the surface charge of the nanocomposite governed by its point of zero charge and the speciation of dissolved metal ions. At acidic conditions below pH 3.0, high concentrations of hydronium ions (H_3O^+) compete vigorously with divalent cations such as Pb^{2+}, Cd^{2+}, and Cu^{2+} for zeolite exchange sites, while protonated silanol groups (-Si-OH_2^+) induce electrostatic repulsion. As the pH shifts into a moderately acidic range of 4.5 to 6.5, surface deprotonation yields negatively charged sites (-Si-O-), fostering strong electrostatic attraction and cation exchange. Conversely, oxyanionic species like hexavalent chromium ($HCrO^{4-}$ and $Cr_2O_7^{2-}$) adsorb most effectively at a lower pH range of 2.0 to 3.0, where positive surface protonation is maximized. Once the pH exceeds 7.5, heavy metal removal is dominated by the chemical precipitation of insoluble hydroxides ($M(OH)_2$), masking genuine adsorption mechanisms.

Adsorbent dosage similarly dictates the balance between overall removal efficiency and individual site utilization. Increasing the total mass of nanocomposite enhances the overall percentage of heavy metal removal by providing a higher volume of surface-active sites and accessible cation-exchange channels. However, this higher mass leads to a lower equilibrium uptake capacity. This trade-off stems primarily from particle aggregation and the spatial overlapping of active binding sites at elevated dosages, which reduces the effective surface area available per unit mass of the adsorbent.

Finally, ionic strength and the presence of background matrix ions introduce significant interference in practical industrial wastewater treatment. Co-existing non-target cations, including Na^+, K^+, Ca^{2+}, and Mg^{2+}, compete directly for available exchange channels based on their hydrated ionic radii and charge densities. For natural HEU zeolites, the relative affinity hierarchy proceeds as $Pb^{2+} > Cd^{2+} > Cu^{2+} > Ca^{2+} > Mg^{2+} > Na^+$. High background ionic strength can screen surface charges and compress the electrical double layer, altering target heavy metal uptake in complex aquatic environments.

5.2 Equilibrium Adsorption Isotherm Modeling

Adsorption isotherms describe how metal ions partition between the liquid and solid phases at equilibrium. Three primary isotherm models are widely applied:

5.2.1 Langmuir Isotherm Model

The Langmuir model assumes monolayer adsorption onto a finite number of energetically equivalent, identical active sites without lateral interaction between adsorbed species:

$$q_e = \frac{(q_m K_L C_e)}{(1 + K_L C_e)} \qquad (4)$$

where q_e is equilibrium adsorption capacity (mg/g), C_e is equilibrium metal concentration (mg/L), q_m is maximum theoretical monolayer capacity (mg/g), and K_L is the Langmuir affinity constant (L/mg). The essential dimensionless separation factor R_L indicates adsorption favorability:

$$R_L = \frac{1}{(1 + K_L\ C_0)} \quad (5)$$

where R_L values between 0 and 1 confirm favourable adsorption.

5.2.2 Freundlich Isotherm Model

The Freundlich model describes multilayer adsorption on heterogeneous surfaces with non-uniform energy distribution:

$$q_e = K_F \cdot C_e^{(1/n)} \quad \textbf{(6)}$$

where K_F is the Freundlich capacity factor ((mg/g) (L/mg) $^{(1/n)}$) and 1/n is the heterogeneity factor. Values of 1/n less than 1 denote favourable surface adsorption.

5.2.3 Dubinin-Radushkevich (D-R) Isotherm Model

The D-R model differentiates between physical and chemical adsorption mechanisms based on mean free energy (E):

$$q_e = q_d\ \ exp^{(-\beta\varepsilon^2)} \quad \textbf{(7)}$$

where q_d is D-R monolayer capacity (mg/g), β is an activity coefficient constant (mol²/kJ²), and ε is the Polanyi potential (ε = R T ln (1 + 1/C_e)). The mean free energy of adsorption E (kJ/mol) is calculated as:

$$E = \frac{1}{\sqrt{(2 \cdot \beta)}} \quad \textbf{(8)}$$

An E value less than 8.0 kJ/mol indicates physical adsorption (physisorption), E between 8.0 and 16.0 kJ/mol signifies ion-exchange chemisorption, and E greater than 16.0 kJ/mol denotes strong covalent chemical bonding.

5.3 Adsorption Kinetics and Rate-Limiting Steps

Kinetic modeling is useful to understand the rate of metal ion uptake and to determine the rate-controlling mechanisms involved in adsorption processes. The Pseudo-First-Order (PFO) or Lagergren kinetic model is based on the fact that the rate of adsorption is proportional to the number of free sites remaining and can be written as

$$\ln (q_e - q_t) = \ln (q_e) - k_1 t \quad (9)$$

In contrast, the Pseudo-Second-Order (PSO) model proposed by Ho and McKay assumes chemisorption (sharing or transfer of electrons between adsorbent and adsorbate) as the rate-limiting step. It obeys the straight-line equation

$$\frac{t}{qt} = \frac{1}{(k^2\ q_e^2)} + \frac{t}{q_e} \quad (10)$$

where k_2 represents the PSO rate constant expressed in g/(mg·min). To evaluate internal mass transfer kinetics, the Weber-Morris Intraparticle Diffusion model uses the expression

$$q_t = k_p * t_{0.5} + C \quad (11)$$

where k_p is the intraparticle diffusion rate constant, and C reflects boundary layer resistance.

The Pseudo-Second-Order kinetic model is generally known to fit the adsorption of heavy metals onto HEU nanocomposites with correlation coefficients higher than 0.99 ($R^2 > 0.99$) in the published literature. The strong fit indicates that the rate-limiting steps in metal removal are chemical ion-exchange and surface complexation, not simple film diffusion.

5.4 Adsorption Thermodynamics

Thermodynamic parameters Standard Gibbs Free Energy change (ΔG°), Enthalpy change (ΔH°), and Entropy change (ΔS°) are derived using the van 't Hoff equations:

$$K_d = \frac{q_e}{C_e} \quad (12)$$

$$\Delta G° = -R \cdot T \cdot \ln(K_d) \quad (13)$$

$$\ln(K_d) = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (14)$$

Negative ΔG° values confirm the spontaneous nature of heavy metal uptake. Positive ΔH° values verify an endothermic process where temperature elevation enhances intra-crystalline channel diffusion and cation desolvation, while positive ΔS° reflects increased randomness at the solid-solution interface during ion exchange.

5.5 Primary Sequestration Mechanisms

Heavy metal capture by heulandite (HEU) nanocomposites occurs through four complementary mechanisms: ion exchange, surface complexation, electrostatic attraction, and reductive precipitation. Ion exchange is driven by isomorphous Al^{3+} framework substitutions that yield negative charges balanced by mobile extra-framework cations like Na^+ and Ca^{2+}, allowing toxic metals to replace them via $2(HEU\text{-}Na^+) + M_2+ \rightleftharpoons (HEU)_2\text{-}M_{2+} + 2\ Na^+$. Simultaneously, surface complexation takes place as metal ions form inner- or outer-sphere coordination complexes with surface silanol (-Si-OH), aluminol (-Al-OH), or grafted functional groups ($-NH^2$, -COOH) through reactions such as $\text{-Si-OH} + M^{2+} \rightleftharpoons \text{-Si-O-}M^+ + H^+$.

Furthermore, deprotonated nanocomposite surfaces exert strong Coulombic attraction toward positively charged divalent ions like Pb^{2+}, Cd^{2+}, and Cu^{2+}. In modified materials such as polyaniline or zero-valent iron nanocomposites (e.g., PANI/HEU, nZVI@HEU), reductive precipitation provides an additional pathway: highly toxic Cr(VI) species ($HCrO^{4-}$) are electrostatically drawn to protonated amine groups and reduced to less toxic Cr(III) via electron transfer, ultimately precipitating as $Cr(OH)_3$ within the zeolite pore matrix.

Table 3. Heavy Metal Sequestration Performance Metrics and Isotherm/Kinetic Fits for Heulandite Nanocomposites.

Target Metal	HEU Nanocomposite System	Optimum pH	q_max (mg/g)	Best-Fit Isotherm	Kinetic Model	Primary Removal Mechanism
Pb(II)	Chitosan/HEU Composite	5.5	285.4	Langmuir	Pseudo-Second-Order	Ion exchange + $-NH_2$ surface complexation
Cd(II)	Na-HEU / Fe_3O_4 Hybrid	6.0	210.8	Langmuir	Pseudo-Second-Order	Cation exchange in Channel A/B + electrostatic attraction
Cr(VI)	PANI/HEU Nanocomposite	2.0	175.2	Langmuir	Pseudo-Second-Order	Electrostatic attraction + chemical reduction to Cr(III)
Cu(II)	APTES-Grafted HEU	5.5	142.6	Langmuir	Pseudo-Second-Order	Inner-sphere silanol/amino coordination complexation
Hg(II)	Thiol-Functionalized HEU	4.0	198.5	Langmuir	Pseudo-Second-Order	Strong covalent soft-soft S-Hg chelation
Ni(II)	Hydrothermal TiO_2/HEU	6.5	118.3	Langmuir	Pseudo-Second-Order	Ion exchange + surface hydroxyl complexation

6. Photocatalytic Degradation Of Organic Pollutants

Integrating semiconductor photocatalysts with heulandite creates high-performance photocatalysts that combine pollutant adsorption with photo-oxidation.

6.1 Photocatalytic Reaction Kinetics

Photocatalytic degradation of organic pollutants in dilute aqueous solutions generally follows the Langmuir-Hinshelwood (L-H) kinetic model:

$$r = \frac{-dC}{dt} = \frac{(k_r \cdot k_a \cdot C)}{(1 + Ka \cdot C)} \qquad (15)$$

where r is the oxidation rate, C is the pollutant concentration, k_r is the intrinsic reaction rate constant, and K_a is the adsorption equilibrium constant. At low initial pollutant concentrations (K_a C << 1), equation 12 simplifies to a pseudo-first-order kinetic expression:

$$\ln \frac{C_0}{C_t} = k_{app}\, t \qquad (16)$$

where k_{app} is the apparent pseudo-first-order rate constant (min^{-1}), and C_0 and C_t are pollutant concentrations at time 0 and t, respectively.

6.2 Mechanism and Reactive Oxygen Species (ROS) Generation

The photocatalytic process on HEU nanocomposites starts with photogeneration and proceeds through a sequence of elementary steps. When the incident energy of the light is greater than the bandgap of the semiconductor, $h\nu \geq E_g$, the nanocomposite absorbs the energy of the light and excites electrons (e^-) from the valence band to the conduction band, creating conduction band electrons (eCB^-) and valence band holes (hVB^{+}), as shown below:

$$\text{Nanocomposite} + h\nu \rightarrow eCB^- + hVB^+.$$

During the subsequent interfacial charge transfer, the non-conductive and negatively charged aluminosilicate framework of HEU acts as an electron acceptor and trap. The photogenerated eCB^- quickly transfers to framework defects or iron impurities, thus effectively suppressing charge recombination with hVB^+.

Thereafter, ROS are produced by concurrent redox pathways. The trapped electrons reduce dissolved oxygen (O_2) to produce superoxide radical anions ($eCB^- + O_2 \rightarrow \cdot O_2^-$), and the photogenerated holes oxidize adsorbed water or hydroxyl ions to generate highly reactive hydroxyl radicals
($hVB^+ + H_2O \rightarrow \cdot OH + H^+$).

Finally, during the mineralization stage, these non-selective, highly oxidative ROS ($\cdot OH$ at E° = +2.80 V vs. NHE and $\cdot O_2^-$ at E° = -0.33 V vs. NHE) attack the adsorbed organic pollutants (e.g., dyes and antibiotics) to cleave aromatic rings and intermediate fragments, leading to their complete degradation into CO_2, H_2O, and mineral acids.

6.3 Advanced Heterojunction Architectures (Z-Scheme and S-Scheme)

Direct Z-Scheme or S-Scheme heterojunctions (e.g. BiOBr/g-C_3N_4/HEU or ZnO/Bi_2S_3/HEU) have recently been employed in HEU nanocomposites to enhance solar light harvesting and increase redox potential. In a Direct Z-Scheme, photogenerated electrons with a lower reduction potential in semiconductor I are recombined with photogenerated holes with a lower oxidation potential in semiconductor II. Such spatial separation keeps the high-energy e^- in the most negative CB and the high-energy h^+ in the most positive VB, maximizing the radical generation and simultaneously stabilizing both species on the HEU matrix.

Table 4. Photocatalytic Degradation Performance Metrics of Organic Pollutants using Heulandite Nanocomposites.

Target Pollutant	Pollutant Class	Nanocomposite System	Light Source	Degradation Efficiency (%)	k_app (min^{-1})	Dominant ROS
Tetracycline (TC)	Antibiotic	BiOBr/g-C_3N_4/HEU	Visible (λ > 420 nm)	98.4% (60 min)	0.0642	$\cdot O_2^-$ and h^+
Ciprofloxacin (CIP)	Antibiotic	TiO_2/Fe_3O_4@HEU	Simulated Solar	95.2% (90 min)	0.0381	$\cdot OH$ and $\cdot O_2^-$
Methylene Blue (MB)	Azo Dye	ZnO/HEU Nanocomposite	UV Light (254 nm)	99.1% (45 min)	0.0895	$\cdot OH$
Rhodamine B (RhB)	Xanthene Dye	BiOCl/HEU Hybrid	Visible Light	96.8% (60 min)	0.0524	h^+ and $\cdot OH$
Bisphenol A (BPA)	Endocrine Disruptor	CuS/g-C_3N_4/HEU	Visible Light	92.5% (120 min)	0.0215	$\cdot O_2^-$ and $\cdot OH$
2,4-Dichlorophenol	Pesticide	Fe_2O_3/TiO_2/HEU	Solar Light	91.0% (150 min)	0.0168	$\cdot OH$

7. Dual-Functional Removal Systems And Synergistic Mechanisms

Wastewater streams from industry often contain mixtures of heavy metals and organic dyes or pharmaceuticals. Synergistic interactions in dual-functional heulandite nanocomposites enable simultaneous heavy metal reduction/adsorption and organic photo-oxidation in a single reactor.

A typical example is the coexistence of toxic Cr(VI) and the antibiotic tetracycline (TC). Photogenerated conduction band electrons are individually consumed by Cr(VI) reduction, and valence band holes are individually consumed by TC oxidation. In single-pollutant systems,

electron-hole accumulation leads to recombination. In the dual-pollutant systems over TiO_2/HEU or BiOBr/HEU nanocomposites, Cr(VI) is an efficient electron acceptor and TC is a hole scavenger:

$$Cr_2O_7^{2-} + 14\,H^+ + 6\,e^- \rightarrow 2\,Cr^{3+} + 7\,H_2O \quad (17)$$

$$Tetracycline + h^+ / \cdot OH \rightarrow Intermediates \rightarrow CO_2 + H_2O + NH_4^+ \quad (18)$$

Mutual consumption promotes the separation of photogenerated charge carriers, leading to the increase of Cr(VI) reduction and TC degradation efficiencies by 2.1 to 3.5 times compared with the single-pollutant solutions. Importantly, the newly formed less toxic Cr^{3+} cations are immediately captured by heulandite via cation exchange into its exchangeable channel networks, thus avoiding secondary heavy metal release.

8. Catalyst Regeneration, Reusability, And Environmental Safety

Long-term cyclic durability, regeneration efficiency, and structural safety are critical determinants of industrial feasibility.

8.1 Desorption and Regeneration Protocols

The regeneration of heavy-metal-loaded nanocomposites was performed by using the dilute mineral acids (0.1 M HCl or HNO_3) or chelating agents (0.05 M EDTA-2Na). Desorbing the adsorbed heavy metals from HEU channels with protons (H^+) or Na^+ ions is done to recover the metals from the concentrated wash solution. Residual surface-adsorbed organic intermediates in organic-fouled photocatalytic nanocomposites are completely degraded by simple visible-light irradiation in water (photocatalytic self-cleaning) or ethanol washing, and the original activity is recovered.

8.2 Cyclic Stability and Structural Integrity

The magnetic Fe_3O_4@HEU composites show good reusability with >92% adsorption capacity and >90% photocatalytic degradation efficiency after 8 successive operational cycles. The post-reaction PXRD and FTIR analyzes confirm that the HEU framework retains its monoclinic crystal structure without any framework dealumination or phase collapse. ICP-MS analysis of treated water confirms that metal leaching (Fe, Ti, Al, Si) is well below WHO drinking water standards (<0.05 mg/L), showing excellent environmental safety.

9. Techno-Economic Feasibility, Scale-Up Challenges, And Future Perspectives

While lab results for heulandite nanocomposites are excellent, moving to industrial uptake involves addressing a number of key technological and economic bottlenecks. One, natural heulandite deposits exhibit marked differences in purity, Si/Al ratio and cation composition from one geographic location to another. Standardized protocols for acid pre-treatment and sodium exchange are needed to ensure batch-to-batch consistency for commercialization. Operationally, processing systems should transition from batch slurry reactors to continuous-flow packed-bed columns or 3D-printed monolithic zeolite ceramics, avoiding severe pressure drops and particulate loss in high-throughput facilities.

Other issues are energy efficiency and overall cost-effectiveness. The engineering of narrow-bandgap heterojunctions, such as S-scheme $Bi_2O_2CO_3$/BiOBr/HEU, enables the nanocomposites to efficiently harvest visible solar light (400–700 nm) without the requirement of energy-intensive artificial UV lamp systems. Finally, comprehensive Life Cycle Assessment (LCA) and rigorous techno-economic modeling are needed to evaluate the full-scale environmental impacts and to prove the long-term cost superiority over the established commercial adsorbents such as activated carbon and synthetic ion-exchange resins.

10. Conclusions

Heulandite nanocomposites are a breakthrough in the chemistry of environmental materials, a marriage of natural mineralogy of zeolites and nano-semiconductor technology. The unique 2D/3D intersecting channel system of the HEU framework provides an ideal platform for dispersing functional nanoparticles enhancing mass transport and stabilizing photogenerated charge carriers. These nanocomposites overcome the intrinsic limitations of pristine zeolite by rational surface engineering, such as hydrothermal growth, sol-gel deposition, magnetic functionalization, and polymer hybridization. They show excellent heavy metal sequestration (q max > 280 mg/g) by ion-exchange and surface complexation, and superior solar photocatalytic

mineralization (> 98%) of recalcitrant organic pollutants. For the dual-pollutant wastewater, the simultaneous heavy metal reduction and organic oxidation are significantly enhanced by the synergistic electron/hole scavenging. The heulandite nanocomposites show excellent cyclic stability, low leaching and easy and fast recovery by a magnet, which makes them very promising as sustainable and cost-effective materials for advanced purification of wastewater from industrial effluents.

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