ISSN: 2394-3122 (Online)
ISSN: 2394-6253 (Print)
Impact Factor: 6.03
Volume 10, Issue 9, September 2023
SK International Journal of Multidisciplinary Research Hub
Journal for all Subjects
e-ISJN: A4372-3088
p-ISJN: A4372-3089
Research Article / Survey Paper / Case Study
Published By: SK Publisher *(www.skpublisher.com)*

Exploring the Coordination Chemistry of Metal–Organic Frameworks for Sensing, Adsorption, and Photocatalytic Breakdown of Tetracycline Antibiotics and Emerging Pollutants

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Abstract: The widespread use of tetracycline antibiotics (TCs) has led to their persistent presence in aquatic environments, posing ecological and health risks such as antibiotic resistance and toxicity. Metal–organic frameworks (MOFs), constructed via coordination bonds between metal ions/clusters and organic ligands, have emerged as versatile materials for environmental remediation. Their tunable porosity, large surface area, and diverse coordination environments enable applications in detection, adsorption, and photocatalytic degradation of antibiotics. This paper provides a comprehensive analysis of coordination chemistry principles governing MOFs, their structure–property relationships, and recent advances (2020–2023) in tetracycline removal. Mechanistic insights, challenges, and future perspectives are also discussed.

I. INTRODUCTION

1.1 Environmental Impact of Tetracycline Antibiotics

Tetracyclines (TC, CTC, DOX, OTC) are among the most widely used antibiotics globally. Their excessive use results in:

- Persistence in water systems
- Development of antimicrobial resistance
- Toxicity to aquatic organisms

They exhibit:

- High solubility (313–8600 mg/L)
- Stability in acidic conditions
- Complexation ability with metal ions

1.2 Emergence of MOFs in Environmental Remediation

Metal–organic frameworks (MOFs) are crystalline porous materials formed via **coordination bonds** between:

- Metal nodes (Fe, Zr, Cu, Al)
- Organic linkers (carboxylates, imidazolates)

Key advantages:

- Ultra-high surface area (>1000 m^2/g)
- Tunable pore size
- Functionalizable active sites

These features make MOFs highly effective for:

- Adsorption
- Catalysis
- Sensing

II. FUNDAMENTALS COORDINATION CHEMISTRY IN MOFS

2.1 Coordination Bonding and Structure

MOFs are built through:

- Metal–ligand coordination bonds
- Secondary building units (SBUs)

Types of coordination:

- Octahedral (e.g., Fe^{3+})
- Tetrahedral (e.g., Zn^{2+})
- Paddlewheel structures (Cu^{2+} dimers)

2.2 Structural Features

(i) Porosity

- Microporous (<2 nm)
- Mesoporous (2–50 nm)

(ii) Open Metal Sites (OMS)

- Provide strong binding sites for pollutants

(iii) Functional Groups

- $-NH_2$, $-COOH$ enhance adsorption

2.3 Host–Guest Interactions

Key interactions governing adsorption:

- π–π stacking
- Hydrogen bonding
- Electrostatic attraction
- Metal–ligand coordination

III. MOFs FOR DETECTION OF TETRACYCLINE ANTIBIOTICS

3.1 Fluorescent MOF Sensors

Mechanism:

- Fluorescence quenching/enhancement upon TC binding

Detection pathways:

- Photoinduced electron transfer (PET)
- Förster resonance energy transfer (FRET)

3.2 Electrochemical Detection

- MOFs as electrode modifiers
- High sensitivity and selectivity

3.3 Colorimetric Detection

- Visible color change upon antibiotic interaction

3.4 Detection Performance

Method	Detection Limit
Fluorescence	ng/L level
Electrochemical	µg/L level

IV. ADSORPTION OF TETRACYCLINE USING MOFs

4.1 Adsorption Mechanisms

(i) π–π Interaction

- Between aromatic rings of MOFs and TC molecules

(ii) Hydrogen Bonding

- Between –OH/–NH groups

(iii) Electrostatic Interaction

- Depends on pH and surface charge

(iv) Coordination Interaction

- Metal ions interact with TC functional groups

4.2 Adsorption Performance

Recent MOFs show:

- Adsorption capacity up to **428 mg/g**
- Fast kinetics and high selectivity

4.3 Factors Affecting Adsorption

- pH
- Temperature

- Initial concentration
- MOF pore size

4.4 Isotherm Models

Langmuir:

qe=qmaxbCe1+bCeq_e = \frac{q_{max} b C_e}{1 + b C_e}qe=1+bCeqmaxbCe

Freundlich:

qe=KfCe1/nq_e = K_f C_e^{1/n}qe=KfCe1/n

V. PHOTOCATALYTIC DEGRADATION OF TETRACYCLINE

5.1 Photocatalytic Mechanism

1. Light absorption
2. Electron excitation (VB → CB)
3. Formation of reactive oxygen species (ROS):
    - •OH
    - O_2^-
4. Degradation into CO_2 and H_2O

5.2 MOF-Based Photocatalysts

Types:

- Ti-based MOFs
- Zr-based MOFs (UiO series)
- Fe-based MOFs

5.3 Advanced Systems

(i) MOF-Derived Catalysts

- Pyrolysis → metal/oxide-carbon composites

(ii) MOF-on-MOF Heterojunctions

- Improved charge separation
- Enhanced photocatalytic efficiency

5.4 Catalytic Efficiency

    - 90% degradation within 60–120 min
- Enhanced stability and recyclability

VI. INTEGRATED ADSORPTION–PHOTOCATALYSIS SYSTEMS

MOFs enable **synergistic removal**:

- Adsorption concentrates pollutants

- Catalysis degrades them

Advantages:

- High efficiency
- Reduced secondary pollution

VII. BEYOND TETRACYCLINE: BROADER APPLICATIONS

7.1 Other Antibiotics

- Sulfonamides
- Fluoroquinolones

7.2 Heavy Metal Removal

- Pb^{2+}, Hg^{2+}, Cd^{2+}

7.3 Organic Pollutants

- Dyes
- Pesticides

MOFs are versatile platforms for **multi-pollutant removal**

VIII. RECENT ADVANCES (2022–2023)

8.1 High-Performance MOFs

- Adsorption capacities >400 mg/g
- Improved stability

8.2 MOF-Derived Catalysts

- Enhanced catalytic activity via pyrolysis

8.3 AI-Assisted Design

- Predictive modeling of degradation efficiency

IX. CHALLENGES

1. Stability in aqueous environments
2. Metal ion leaching
3. High synthesis cost
4. Scalability issues

X. FUTURE PERSPECTIVES

- Green synthesis of MOFs
- Hybrid MOF-based nanocomposites
- Solar-driven photocatalysis
- Real wastewater applications

- Smart sensing platforms

XI. CONCLUSION

The coordination chemistry of MOFs provides a powerful foundation for designing advanced materials capable of detecting, adsorbing, and degrading tetracycline antibiotics. Their tunable structure, multifunctionality, and high efficiency position them as promising candidates for next-generation water treatment technologies. Continued research into stability, scalability, and hybrid systems will further enhance their practical applicability.

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