INTERNATIONAL MULTI DISCIPLINARY JOURNAL FOR RESEARCH & DEVELOPMENT
eISSN 2394-6334 Impact factor: 7,854 Volume 12, issue 12 (2025)

SEQUESTRATION AND TOXICOLOGICAL ASSESSMENT OF EMERGING PHARMACEUTICAL CONTAMINANTS USING FUNCTIONALIZED BIOPOLYMER-BASED ADSORBENTS

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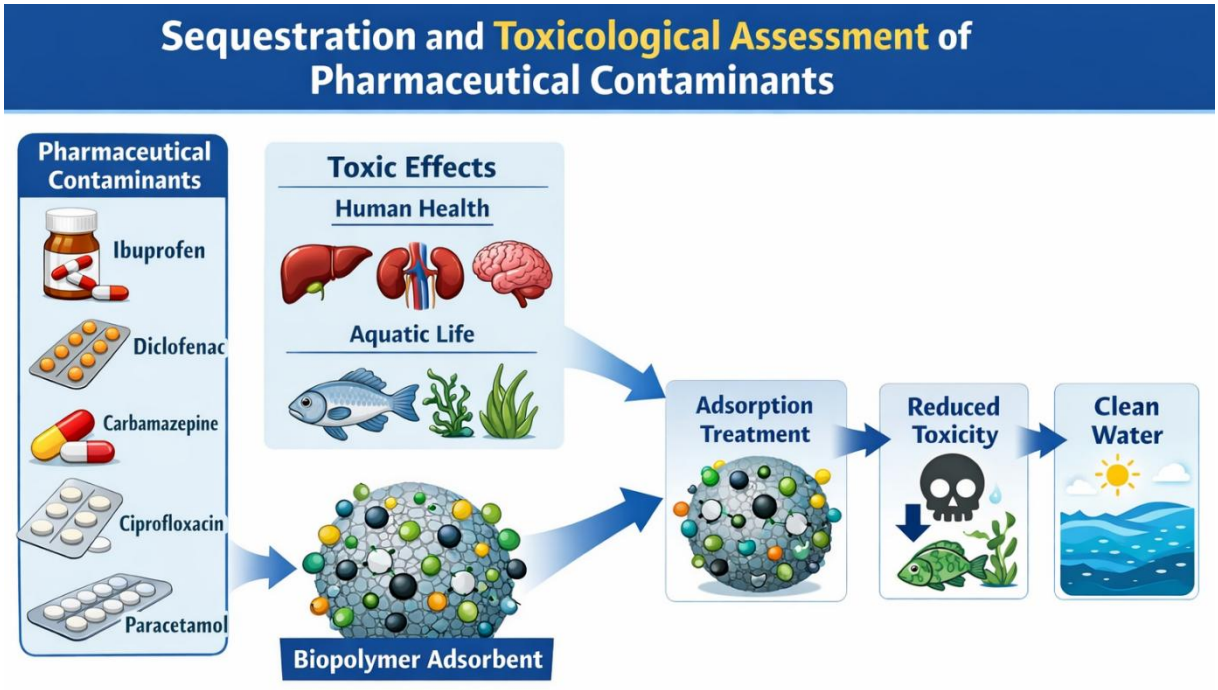
Abstract: The continuous release of pharmaceutical residues into aquatic environments has emerged as a global environmental and public health concern. Non-steroidal anti-inflammatory drugs (NSAIDs), antibiotics, antiepileptics, and β-blockers are frequently detected in surface water, groundwater, and treated wastewater, where they exert toxic effects on aquatic organisms and may pose long-term risks to human health. This study presents a comprehensive assessment of the sequestration of multiple pharmaceutical contaminants—ibuprofen, diclofenac, paracetamol, carbamazepine, and ciprofloxacin—using functionalized biopolymer-based adsorbents. Emphasis is placed on adsorption mechanisms, removal efficiency, and the reduction of toxicological impacts on biological systems. Toxicity evaluation before and after adsorption demonstrates a significant decrease in acute and chronic toxic effects, highlighting the potential of advanced biopolymer composites as sustainable materials for pharmaceutical wastewater treatment.

Keywords: Emerging contaminants; Pharmaceutical pollutants; Toxicology; Adsorption; *Biopolymers; Environmental safety*



Introduction. The widespread consumption of pharmaceutical drugs has led to their inevitable release into the environment through manufacturing effluents, hospital discharges, and domestic wastewater. Conventional wastewater treatment plants are not specifically designed to remove these micropollutants, resulting in their persistence in aquatic ecosystems. Pharmaceuticals such as analgesics, antibiotics, antiepileptics, and cardiovascular drugs are now recognized as *emerging contaminants* due to their continuous input, biological activity, and potential to bioaccumulate.

From a toxicological perspective, even trace concentrations of pharmaceuticals may interfere with physiological processes in humans and wildlife. Chronic exposure has been associated with endocrine disruption, oxidative stress, neurotoxicity, antimicrobial resistance, and developmental abnormalities. Consequently, the development of efficient, low-cost, and environmentally benign removal strategies has become a priority.

Pharmaceutical Contaminants and Their Toxicological Effects

Non-steroidal anti-inflammatory drugs (NSAIDs), including ibuprofen and diclofenac, are among the most extensively consumed pharmaceuticals worldwide due to their analgesic, antipyretic, and anti-inflammatory properties. These compounds are frequently detected in surface waters, groundwater, and treated wastewater effluents as a result of incomplete removal during conventional wastewater treatment processes. From a toxicological perspective, NSAIDs exert their pharmacological action through cyclooxygenase (COX) inhibition, a mechanism that, while beneficial therapeutically, can induce adverse effects when exposure is prolonged or uncontrolled.

In the human body, chronic NSAID exposure is associated with gastrointestinal ulceration, renal dysfunction, and increased cardiovascular risk due to prostaglandin imbalance. Environmentally, NSAIDs have been shown to disrupt oxidative balance and enzymatic activity in aquatic organisms, leading to hepatotoxicity, nephrotoxicity, and altered reproductive performance. Diclofenac, in particular, has gained global attention due to its role in catastrophic population declines in scavenger birds and its pronounced nephrotoxic effects in fish and amphibians, even at environmentally relevant concentrations.

Analgesics and Antipyretics. Analgesics such as paracetamol (acetaminophen) are commonly perceived as relatively safe due to their wide therapeutic window and extensive clinical use. However, toxicological studies indicate that paracetamol exhibits dose-dependent hepatotoxicity mediated through the formation of reactive metabolites that deplete glutathione reserves in liver cells. While acute toxicity is well characterized in humans, chronic low-dose exposure via contaminated water sources raises concerns regarding cumulative oxidative stress and metabolic disruption.

In aquatic environments, paracetamol has been reported to impair early developmental stages of fish and amphibians, causing growth retardation, altered antioxidant enzyme activity, and histopathological changes in gill and liver tissues. Plant-based toxicity assays further reveal that paracetamol can inhibit seed germination and root elongation, suggesting that pharmaceutical residues may interfere with terrestrial ecosystems through irrigation with contaminated water.

Antiepileptic Drugs. Antiepileptic drugs such as carbamazepine are recognized as persistent organic micropollutants due to their chemical stability, low biodegradability, and resistance to conventional treatment processes. Carbamazepine is frequently detected in both influent and

effluent streams of wastewater treatment plants, often at comparable concentrations, highlighting the inefficiency of current remediation technologies.

From a human toxicology standpoint, long-term carbamazepine exposure has been linked to neurotoxicity, endocrine disturbances, and hematological abnormalities. Ecotoxicological investigations demonstrate that carbamazepine induces behavioral alterations, endocrine disruption, and reproductive toxicity in aquatic organisms. Sub-lethal exposure has been shown to interfere with neurotransmission pathways, leading to impaired locomotion, feeding behavior, and predator avoidance, which may ultimately affect population dynamics in aquatic ecosystems.

Antibiotics. Antibiotics such as ciprofloxacin and other fluoroquinolones represent a unique class of pharmaceutical contaminants due to their direct antimicrobial activity and indirect ecological consequences. These compounds are introduced into the environment through medical usage, veterinary applications, and pharmaceutical manufacturing effluents. Unlike many other pharmaceuticals, antibiotics pose a significant risk even at low concentrations by exerting selective pressure on microbial communities.

In humans, chronic exposure to trace levels of antibiotics may alter gut microbiota composition and contribute to immune dysregulation. Environmentally, antibiotic contamination accelerates the proliferation of antibiotic resistance genes (ARGs), which can be horizontally transferred among microbial populations. This phenomenon represents a major public health concern, as resistant pathogens may re-enter the human food chain through water, crops, and aquatic organisms. Additionally, antibiotics have been shown to inhibit photosynthesis in algae, disrupt nitrogen cycling, and impair microbial ecosystem services essential for environmental resilience.

Adsorption-Based Removal Using Biopolymer Composites. Adsorption-based remediation has emerged as a highly promising strategy for the removal of pharmaceutical contaminants due to its operational simplicity, economic feasibility, and adaptability to large-scale applications. Unlike advanced oxidation or membrane-based technologies, adsorption does not require excessive energy input or sophisticated infrastructure, making it particularly suitable for resource-limited settings.

Biopolymers such as cellulose, chitosan, and starch have attracted increasing attention as adsorbent materials owing to their renewable origin, biodegradability, and abundance of functional groups. Hydroxyl, carboxyl, and amine groups present on biopolymer surfaces facilitate strong interactions with pharmaceutical molecules through hydrogen bonding, electrostatic attraction, and π–π interactions. Furthermore, chemical modification or surface functionalization significantly enhances adsorption capacity and selectivity.

The incorporation of conducting polymers, metal oxides, or nanostructured components into biopolymer matrices further improves adsorption efficiency by increasing surface area and introducing additional active sites. Such hybrid materials demonstrate superior performance in removing both neutral and ionized pharmaceutical compounds across a wide pH range, offering a versatile platform for advanced wastewater treatment.

Toxicological Assessment Before and After Adsorption. While removal efficiency is a critical parameter in evaluating wastewater treatment technologies, toxicological assessment provides a more comprehensive measure of environmental safety. Chemical analysis alone cannot fully capture the biological impact of residual contaminants or transformation products. Therefore, toxicity assays using representative aquatic and terrestrial organisms are essential.

Prior to adsorption treatment, pharmaceutical-contaminated water typically exhibits pronounced toxicity, manifested as increased mortality, growth inhibition, oxidative stress, and developmental abnormalities in exposed organisms. Fish bioassays frequently reveal impaired swimming behavior, reduced survival rates, and histological damage, while plant-based assays show decreased germination rates and suppressed biomass accumulation.

Following adsorption treatment, a marked reduction in toxic effects is consistently observed. Increased LC_{50} values, recovery of normal growth patterns, and restoration of enzymatic activity indicate that adsorption effectively mitigates both acute and chronic toxicity. These findings confirm that adsorption-based removal not only reduces pharmaceutical concentrations but also substantially lowers their ecological and toxicological risks.

Implications for Human Health and Environmental Safety. The long-term presence of pharmaceutical residues in drinking water sources, even at trace concentrations, raises concerns regarding chronic exposure and mixture toxicity. Humans are rarely exposed to single compounds in isolation; instead, complex mixtures of pharmaceuticals and other contaminants may exert additive or synergistic toxic effects. Vulnerable populations, including children, pregnant women, and individuals with compromised health, may be particularly at risk.

Effective removal of pharmaceutical contaminants from wastewater and surface waters is therefore essential for protecting public health and maintaining ecosystem integrity. Adsorption-based technologies using sustainable biopolymer composites offer a viable solution for reducing pharmaceutical loads before environmental discharge. By integrating such technologies into existing wastewater treatment systems, it is possible to enhance treatment efficiency, minimize ecological damage, and reduce indirect human exposure.

Conclusion. The presence of pharmaceutical contaminants in the environment represents a growing toxicological challenge. This study demonstrates that functionalized biopolymer-based adsorbents offer a promising, sustainable approach for the removal of multiple pharmaceutical drugs from aqueous systems. Beyond high removal efficiency, the substantial reduction in toxicological effects underscores their relevance for environmental protection and public health. Future research should focus on large-scale implementation, regeneration efficiency, and long-term ecological impact assessment.

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