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(Review Article)

Sustainable remediation of dye pollutants using ash-based photocatalytic nanocomposites: A Comprehensive Review

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Abstract

Rapid industrialization and human activities have resulted in severe issues with organic pollutants, particularly dyes, that increase challenges in the management of wastewater. This review focuses on the sustainability and cost-effectiveness of ash-based photocatalytic nanocomposites in the removal of dyes from wastewater. Ash is the most abundant by-product derived from industrial and agricultural practices. Due to its remarkable adsorption capacity and interesting physicochemical properties, ash has emerged as one of the promising support materials for photocatalysts. The nanocomposites show enhanced degradation efficiency for various dyes by exploiting the synergistic effects of ash's adsorption capabilities and the photocatalytic activity of semiconductor materials. This review discusses synthesis methods, characterization techniques, and photocatalytic performance of ash-based nanocomposites in detail and discusses the challenges associated with stability, reusability, and practical implementation in industrial applications. Highlighting the "waste to wealth" strategy, the review underscores the dual benefits of mitigating environmental issues associated with ash disposal and advancing sustainable wastewater treatment solutions. Future research directions are proposed to optimize performance and scalability.

Keywords: Photocatalytic; Nanocomposites; Dyes; Flyash; Zeolites

1. Introduction

Water pollution, especially from synthetic dyes, has become a crucial environmental issue that increases with the expansion of industries [1]. A wide range of water resources has been contaminated by inadequately treated industrial effluents from textile, leather, paper, and plastic industries. Synthetic dyes, with complicated chemical structures and bright colours, are known to be notoriously resistant to degradation in conventional wastewater treatment processes. These dyes persist in the environment, giving them considerable risks to aquatic life and humans through their potential toxicity, carcinogenicity, and allergenic properties [2,3]

Relentless investigation into developing productive, economical, and sustainable methods for dye removal has been a great forcing function for advanced treatment technologies. Among these, photocatalysis stands out as a promising approach for organic pollutant degradation, including dyes, whereby light energy is used to activate semiconductor materials to break down complex dye molecules into less harmful substances [4]. Nevertheless, practical applications of photocatalysis are hampered by related issues such as low stability of the photocatalysts, rapid recombination of photogenerated electron-hole pairs, and difficulties in catalyst recovery and reuse.

Using abundant industrial, agricultural [5], and power generation process by-products such as ash to support photocatalysts promises a good solution. Ashes—such as coal fly ash (CFA), bottom ash, and biomass ash—are rich in aluminosilicates and other minerals, making them materials of high surface area, porosity, and ion-exchange capacity

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[6]. These properties make ash an excellent adsorbent for pollutants, and when combined with photocatalysts, it significantly enhances dye degradation through synergistic effects [7].

Ash-based photocatalytic nanocomposites are a new concept for overcoming the dual problem of dye pollution and ash disposal. These nanocomposites take advantage of the adsorptive properties of ash and the photocatalytic capabilities of semiconductor materials to create systems that simultaneously adsorb dye molecules and catalyze their breakdown under light irradiation. This dual functionality offers several advantages, including improved degradation efficiency, reduced catalyst deactivation, and potential for catalyst reuse, making these materials suitable for large-scale industrial applications.

Ash-based photocatalytic nanocomposites development and optimization involve various synthesis techniques such as sol-gel processes, hydrothermal methods, and impregnation [8]. These methods fine-tune the physical and chemical properties of the composites, including surface area, porosity, and the distribution of active sites to optimize the photocatalytic performance [7]. The structural and compositional versatility of ash allows designing nanocomposites with tailored properties for particular applications that improve their effectiveness in removing dyes [9].

2. Antibiotics: Classification and Mechanisms of Action

Antibiotics are essential chemotherapeutic agents that inhibit the growth or prevent the microorganisms, like bacteria, fungi, protozoa, and viruses, at small concentrations [10,11]. They are grouped depending on their chemical configuration, mode of action, and spectrum. The major ones include:

- Quinolones and Fluoroquinolones: Interference with bacterial DNA gyrase or topoisomerase.
- Aminoglycosides: Interference of protein synthesis through interaction with ribosomal RNA.
- Glycopeptides: It inhibits the synthesis of cell wall of Gram-positive bacteria.
- Macrolides: They bind to the 50S ribosomal subunit and inhibit bacterial protein synthesis.
- Tetracyclines: They interfere with protein synthesis by binding to the 30S ribosomal subunit.
- Sulfonamides: They inhibit bacterial folic acid synthesis.

Understanding the mechanisms of action and classifications of antibiotics is crucial for developing effective remediation strategies for antibiotic pollutants [12-15].

2.1. Environmental Impact of Textile Dye Pollution

One of the major environmental issues is the discharge of textile dyes into water bodies. Textile effluent contains a variety of dyes, chemicals, and organic and inorganic compounds like toxic metals like chromium, arsenic, copper, and zinc [16, 17]. Such pollutants affect aquatic and human life. One of the major sources of industrial effluent pollution is textile dyeing and finishing, and over 100,000 types of commercially available dyes exist, a large percentage of which find their way into various industrial applications [18].

2.2. Release of Unfixed Dyes During Textile Processing

In textile dyeing and finishing processes, part of the dyes fails to fix onto the fabrics, and it finds its way into the environment due to incomplete exhaustion and dye hydrolysis. This leads to high dye concentration in textile effluents. The persistence of these dyes in the environment and possibly their toxicity [19] calls for efficient treatment technologies to mitigate dye pollution.

2.3. Environmental Hazards of Dye-Contaminated Effluents

The discharge of dye-contaminated effluents into natural water resources poses severe environmental risks. Even trace amounts of dye can significantly affect the photosynthetic function of aquatic plants by blocking sunlight and disrupting the food chain. Dye pollutants also increase the Biological Oxygen Demand (BOD5) of receiving water bodies, reducing the reoxygenation process and threatening aquatic life [19,20].

2.4. Health Risks Associated with Recalcitrant Dyes

Recalcitrant dyes, which include carcinogens and other harmful compounds, are risks to human health and the environment over the long term [19]. For instance, triphenylmethane dyes are reported to be phytotoxic, cytotoxic, and potentially carcinogenic [18]. Prolonged exposure to such dyes leads to different health issues, such as skin and eye abnormalities, respiratory problems, and allergic reactions [21].

2.5. Necessity for Effective Treatment of Textile Effluents

The environmental and health risks associated with dye pollution necessitate the development of effective treatment technologies [16-18,22]. Advanced treatment methods are crucial to mitigate the hazards of dye contamination, protect water quality, and ensure the sustainability of natural resources [23].

3. Dye Treatment Techniques

Dye treatment methodologies include physical, chemical, and biological techniques [23-26]. Physical methods such as adsorption and filtration are widely used due to their efficiency but may require further post-treatment to address secondary waste [27]. Chemical methods like coagulation-flocculation are also employed but are limited by high costs and excessive chemical use. Conventional biological treatments often fall short due to the stable nature of persistent dyes.

Advanced Oxidative Processes (AOPs) have garnered significant attention for their effectiveness in non-selectively degrading dyes through the generation of reactive oxygen species (ROS) [28-30]. Among these, photocatalysis stands out as a promising green technology for dye degradation, offering high efficiency in mineralizing complex organic pollutants into harmless by-products under solar irradiation [31].

3.1. Historical Background and Definition of Zeolites

Zeolites, discovered by Swedish mineralogist Alex Fredrick Cronsted in 1758, are microporous crystalline aluminosilicates known for their ability to selectively adsorb molecules based on size and shape [32-34]. Their structure comprises interconnected $[SiO_4]_4$- and $[AlO_4]_5$- tetrahedra, forming a three-dimensional network with pore openings ranging from 0.3 to 1.0 nm [35-36].

3.2. Structural Composition of Zeolites

Zeolites consist of TO4-type tetrahedra, where T represents silicon and/or aluminum. The difference in valence between silicon (+4) and aluminum (+3) creates an excess negative charge balanced by cations. The typical chemical formula is Ma/b [(AlO2)a (SiO2)y].cH2O [37].

3.3. Physicochemical Properties

- **Pore Structure and Surface Area**: Zeolites feature micro-pores with diameters between 0.3 and 1.0 nm and exhibit large internal surface areas, crucial for adsorption.[38]
- **Ion Exchange Capacity**: Influenced by the Si/Al ratio, low-silica zeolites demonstrate high ion exchange capabilities.[38]
- **Thermal Stability and Acidity**: These properties are related to the Si/Al ratio, affecting thermal stability and catalytic activity.[38]
- **Hydrophilicity and Catalytic Activity**: Zeolites' hydrophilicity and surface-active centers contribute to their exceptional catalytic activity.[38]

3.4. Classification of Zeolites

Zeolites are categorized based on pore size and Si/Al ratio into small, medium, large, and very large pore sizes, as well as low, intermediate, and high silica types. Each category has specific applications and performance characteristics in environmental remediation [39-40].

3.5. Environmental Remediation Applications

Zeolites have been widely used in environmental remediation because of its adsorption and ion exchange capabilities [41]. They are utilized for the removal of heavy metals, radionuclides and organic pollutants from contaminated water and soil. Their application for wastewater treatment, especially dye removal, is an area of research activity [42]

3.6. Fly Ash Properties

Fly ash, a coal combustion by-product in power plants, is comprised of silica, alumina, iron oxides, and other minerals. This composition varies according to the source of the coal and its combustion conditions [43]. Fly ash has been classified as Class F, low calcium type, and Class C, high calcium type, due to differences in the properties of each type to be used for different applications.

3.7. Physical and Chemical Properties of Fly Ash

- Particle Size and Distribution: Fly ash particles are relatively fine, with a spherical shape that helps in its dispersion.
- Surface Area and Porosity: High surface area and porosity of fly ash increase its adsorption capacity.
- Chemical Composition: The presence of different oxides affects its reactivity and interaction with pollutants [44].

3.8. Zeolites Obtained from Fly Ash

Fly ash can be converted into zeolites by hydrothermal synthesis, with resultant materials nearly equivalent to natural zeolites. These zeolites show a high adsorption capacity for pollutants and have been used in many environmental applications [43].

3.9. Composition of Fly Ash-Based Zeolites

Fly ash-based zeolites are primarily composed of aluminosilicates, with varying Si/Al ratios depending on the synthesis conditions and starting materials [44-45]. These materials offer significant potential for wastewater treatment due to their tailored adsorption and ion-exchange properties [46].

3.10. Advanced Techniques for Dye Removal

Photocatalytic degradation is an advanced technique involving semiconductor photocatalysts, which has shown great potential in the effective degradation of dyes under light irradiation [47-48]. Innovations in photocatalyst materials, including composite systems and doped photocatalysts, have improved their performance and applicability in dye removal [48].

3.11. Photocatalysts and Their Mechanism of Action

Photocatalysts are generally semiconductors, like TiO2, ZnO, and Fe2O3, which under irradiation produce reactive oxygen species, leading to the degradation of organic pollutants. The performance is highly dependent on the intensity of light, the surface area of the catalyst, and the type of pollutant [49-51].

4. Conclusion and Future Perspectives

This review has covered extensive discussions on the potential and development of ash-based photocatalytic nanocomposites and zeolite-based materials for addressing environmental pollution, especially in terms of contaminants related to dyes and antibiotics. The integration of the ubiquitous by-product ash resulting from industrial and agricultural processes with photocatalysts appears promising for sustainable wastewater treatment. The ash-based photocatalytic nanocomposites with their improved adsorption capacity and photocatalytic activity can provide a dual functionality to significantly enhance the efficiency of dye degradation. Several synthesis methods, characterization techniques, and performance analyses point to the potential of such nanocomposites as promising and cost-effective solutions in wastewater treatment.

Similarly, zeolites, with their specific physicochemical properties, have shown significant efficiency in environmental remediation, especially in the removal of antibiotics from wastewater. Zeolite-based composites, such as Fe(III)-modified synthetic zeolite 13X and MoS_2@Zeolite, have excellent adsorption capacities and photocatalytic activities under different light sources. The ability of these materials to address antibiotic pollution highlights their versatility and effectiveness in combating a broad spectrum of pollutants.

The review also discussed the environmental and health hazards of dye and antibiotic pollutants and highlighted the importance of developing advanced and sustainable treatment technologies. Ash-based and zeolite-based materials present significant advantages: cost-effectiveness, high performance, and the possibility of valorizing waste.

Future Perspectives

- Affordable Technologies Development There is the need to conduct research to develop scalable and cost-effective technologies that will remove emerging contaminants, including new classes of dyes and antibiotics. Innovations should target decreased production costs and enhanced practical applicability of the materials.

- Tighter Environmental Control: There is a need to enforce stricter controls over the concentration of pharmaceutical pollutants in aquatic environments. This way, pollution will be better controlled and ecosystems protected from the damaging effects of these contaminants.
- Sophisticated Detection Methods: There is also a need for the development of sophisticated detection methods that are effective in monitoring pharmaceutical pollutants. These methods should be capable of detecting trace levels of contaminants, especially in areas undergoing rapid industrialization.
- Research on Granulation Processes: Zeolite-based materials might be stabilized and have better performance in column flow applications if the granulation processes are explored. The granulated forms may facilitate easier handling and efficiency in large-scale wastewater treatment plants.
- Research on Regeneration Methods: There is a need to develop effective regeneration methods for zeolite-based adsorbents that maintain their sorption capacity and selectivity over several uses. Regeneration methods should be optimized to ensure long-term usability and cost-effectiveness.
- Advancement of Photocatalytic Effectiveness: Future studies need to focus on the advancement of both ash-based and zeolite-based materials in enhancing their photocatalytic effectiveness. This includes improving efficiency under natural sunlight and creating new photocatalytic systems to handle a wider range of pollutants.
- Affordable Production Technologies: Focus on the development of low-cost and environmentally friendly production methods will enhance the practical utility of photocatalytic and adsorbent materials. In this regard, innovations in production technologies should focus on environmental sensitivity and resource efficiency.
- Integration of Multifunctional Materials: Future research could be focused on the integration of multifunctional materials that combine photocatalytic, adsorptive, and catalytic properties. Such multifunctional materials could offer an integrated approach to wastewater treatment by addressing different pollutants in a single step.

In summary, while much progress was made in the development of ash-based and zeolite-based materials for environmental remediation, one can say that there is still work to be done. Challenging the current aspects and pursuing novel approaches toward these materials will enhance its effectiveness and applicability as a solution for pollution control and environmental protection

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

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