ABSTRACT

for the dissertation work of Saparbek Tugelbay on the topic

“ Mechanochemical synthesis of silver phosphate nanocomposites and their photocatalytic and antibacterial properties ”, submitted for the degree of Doctor of Philosophy (PhD) in the educational program 8D05301 – Chemistry.

The dissertation is presented in the form of a series of published articles in accordance with paragraph 5-1 of the Rules for awarding academic degrees, approved by Order No. 7 of the Minister of Science and Higher Education of the Republic of Kazakhstan dated January 9, 2023.

General characteristics of the study

The study is focused on the mechanochemical synthesis of silver phosphate and silver halide nanoparticles, as well as Ag_3PO_4/AgCl nanocomposites, exhibiting high photocatalytic and light-sensitive antibacterial activity for water purification from organic and microbial contaminants.

Relevance of the study

Contamination of water bodies by persistent organic compounds and pathogenic microorganisms represents a serious environmental and social challenge, as such pollutants, including nitrofuran antibiotics (Nitrofurazone and Furagin), can remain in aquatic environments for long periods, promoting antibiotic resistance and posing a direct threat to human health. Conventional water treatment methods do not ensure complete degradation of these substances, which necessitates the development of efficient functional materials for their removal. In recent years, photocatalytic nanomaterials have been actively investigated; however, most conventional photocatalysts (e.g., TiO_2, ZnO) exhibit low activity under visible light, rapid charge carrier recombination, and limited long-term stability. In this context, silver phosphate (Ag_3PO_4) has emerged as a promising visible-light-active photocatalyst, demonstrating high efficiency through the generation of reactive oxygen species and the effective degradation of persistent organic pollutants.

Degree of research development

Promising compounds include photocatalytic materials based on silver phosphates and silver halides. Silver phosphate (Ag_3PO_4) possesses a narrow band gap (2.41 eV) and the ability to generate reactive oxygen species under visible-light irradiation, making it an effective photocatalyst and antibacterial agent. Moreover, the fabrication of nanocomposites based on Ag_3PO_4 and silver halides represents a promising approach to improving stability and functional properties. Existing methods for synthesizing nanocomposites (hydrothermal methods, co-precipitation methods, etc.) require significant time and energy consumption and are not always suitable for producing nanocomposites in large quantities. Mechanochemical synthesis, based on solid-state interactions of reactants under intensive milling, represents an environmentally friendly, energy-efficient, and optimal method for producing nanostructured powders in large volumes. However, information on the mechanochemical synthesis of Ag_3PO_4 nanoparticles and silver halides remains limited (Nobuya Machida et al.). In addition, existing studies pay insufficient attention to the development of hybrid nanocomposites based on silver phosphate and silver halides, particularly Ag_3PO_4/AgCl, capable of combining photocatalytic stability, high charge transfer efficiency, and pronounced antibacterial activity. Especially few studies are devoted to the light-stimulated antibacterial activity of Ag_3PO_4/AgCl nanocomposites under visible-light irradiation.

Research objective

The objective of this study is to obtain nanoparticles and nanocomposites based on silver phosphate via a mechanochemical method and to investigate their photocatalytic and antibacterial activity.

To achieve this objective, the following tasks were defined:

1. Mechanochemical synthesis of silver phosphate (Ag_3PO_4) nanoparticles and silver halides (AgCl, AgBr, AgI) using a planetary ball mill.
2. Evaluation of the photocatalytic properties of the obtained Ag_3PO_4, AgCl, AgBr, and AgI nanoparticles in the degradation of persistent organic pollutants (Nitrofurazone and Furagin).
3. Systematization and critical analysis of studies on the light-sensitive antibacterial activity of Ag_3PO_4-based nanocomposites.
4. Mechanochemical synthesis of heterostructured Ag_3PO_4/AgCl nanocomposites.
5. Investigation of the effect of component ratios in Ag_3PO_4/AgCl nanocomposites on photocatalytic activity and determination of the optimal composition providing maximum efficiency of organic compound degradation.
6. Evaluation of the antibacterial activity of the obtained Ag_3PO_4-based nanoparticles and nanocomposites against test bacterial strains.
7. Determination of the light-stimulated antibacterial activity of Ag_3PO_4/AgCl nanocomposites.

Object of the study

Silver phosphate (Ag_3PO_4) nanoparticles, silver halides (AgCl, AgBr, AgI), and hybrid Ag_3PO_4/AgCl nanocomposites.

The subject of the study comprises the physicochemical, photocatalytic, and antibacterial properties of the obtained nanomaterials based on silver phosphate and silver halides.

Research methods

Mechanochemical synthesis was carried out using a planetary ball mill. The structural and morphological characteristics of the obtained materials were investigated using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive spectroscopy (EDS), ultraviolet–visible spectroscopy (UV–Vis), and photoluminescence (PL). Antibacterial activity was evaluated against model microorganisms E. coli, S. aureus, P. aeruginosa, and Candida albicans. Photocatalytic activity was assessed based on the degradation of persistent organic pollutants, namely nitrofuran antibiotics (Nitrofurazone and Furagin) and an organic dye (methylene blue), under visible-light irradiation.

Scientific novelty of the dissertation research

The dissertation presents experimental data confirming the high photocatalytic activity of Ag_3PO_4 and AgCl nanoparticles under visible-light irradiation, manifested by the efficient degradation of the antibiotics Nitrofurazone and Furagin in aqueous solutions. For the first time, Ag_3PO_4/AgCl nanocomposites were synthesized via a mechanochemical method, and their light-sensitive antibacterial activity against Pseudomonas aeruginosa ATCC 9027 and Escherichia coli ATCC 8739 strains was determined for the first time.

The scientific novelty of the dissertation research is defined by the following main provisions submitted for defense:

1. Among the studied silver halide and silver phosphate nanoparticles, AgCl exhibits the highest photocatalytic activity in the visible-light region toward furagin, while Ag_3PO_4 shows the highest activity toward Nitrofurazone.
2. Mechanochemical activation of precursors (silver nitrate, sodium phosphate, and sodium chloride) in the presence of a solid diluent (sodium nitrate) in a planetary ball mill at 400 rpm for 30 min leads to the formation of Ag_3PO_4/AgCl nanocomposites.
3. Ag_3PO_4/AgCl nanocomposites with a composition of 75:25 exhibit light-stimulated antibacterial activity against Pseudomonas aeruginosa ATCC 9027 and Escherichia coli ATCC 8739 strains.

Scientific results:

In the first article entitled "Scalable synthesis of AgX (Cl, Br, I, PO_4) nanophotocatalysts for efficient visible-light degradation of persistent antibiotics from aqueous environments", silver phosphate (Ag_3PO_4) and silver halide (AgCl, AgBr, AgI) nanoparticles were synthesized using a mechanochemical method with a planetary ball mill. The obtained nanoparticles exhibit predominantly spherical morphology; the particle size of silver phosphate is less than 300 nm, while that of silver halides (AgCl, AgBr, AgI) is approximately 1 μm. Photocatalytic studies under visible-light irradiation demonstrated that the synthesized Ag_3PO_4 and AgCl nanoparticles effectively degrade persistent antibiotics, Nitrofurazone and Furagin, achieving significant pollutant degradation within 90 min at an initial concentration of 10 mg/L. AgCl degrades Nitrofurazone by ~90% ($k = 0.020 \pm 0.005$ min^{-1}) and Furagin by ~99% ($k = 0.060 \pm 0.005$ min^{-1}). Ag_3PO_4 degrades Nitrofurazone by ~97% ($k = 0.037 \pm 0.005$ min^{-1}) and Furagin by ~95% ($k = 0.035 \pm 0.005$ min^{-1}).

In the second article, " Ag_3PO_4-based composites as next-generation antibacterial nanomaterials: A review of light-induced synergistic effects", a systematic review of data on the light-sensitive antibacterial activity of Ag_3PO_4-based nanocomposites was conducted for the first time. The study provides a detailed analysis of antibacterial mechanisms, including the generation of reactive oxygen species (ROS) and the role of Ag^+ ions, thereby filling existing gaps in scientific research. The obtained results have significant practical relevance for medicine, biomaterials development, and the design of environmentally safe technologies.

In the third article, "Enhanced photocatalytic antibacterial Ag_3PO_4/AgCl nanocomposites for water purification from organic and microbial contaminants", hybrid Ag_3PO_4/AgCl nanocomposites were synthesized for the first time using a mechanochemical approach. The formation of a stable interfacial contact in Ag_3PO_4/AgCl nanocomposites was established and confirmed by transmission electron microscopy. Interfacial interactions lead to changes in thermal properties: the melting and crystallization temperatures for all studied nanocomposite compositions are approximately 376 °C.

The ability of the obtained nanocomposites to simultaneously degrade organic pollutants and inhibit bacterial growth was evaluated. Among the studied Ag_3PO_4, AgCl nanoparticles and Ag_3PO_4/AgCl nanocomposites, the Ag_3PO_4/AgCl (75:25) nanocomposite exhibited the highest photocatalytic activity under visible-light irradiation. The degradation rate constant of the organic dye was twice as high as that of Ag_3PO_4 and four times higher than that of AgCl. For Ag_3PO_4/AgCl (75:25), the degradation degree of methylene blue reached 98% within 3 h ($k = 0.021 \pm 0.005$ min^{-1}). Among all investigated Ag_3PO_4 and AgCl nanoparticles and Ag_3PO_4/AgCl nanocomposites, the Ag_3PO_4/AgCl (75:25) nanocomposite demonstrated the most pronounced and stable antibacterial and fungicidal activity. The Ag_3PO_4/AgCl (75:25) nanocomposite exhibits pronounced light-stimulated antibacterial activity against Pseudomonas aeruginosa ATCC 9027 and Escherichia coli ATCC 8739 strains.

In the fourth article, "Visible-light-responsive Ag_3PO_4 -based photocatalysts for water treatment and wastewater remediation: Advances, challenges, and future directions", a systematic analysis of modern Ag_3PO_4 -based photocatalytic materials for visible-light-driven water purification was carried out. For the first time, the photocatalytic performance of Ag_3PO_4 toward various classes of pollutants (dyes, antibiotics, pharmaceuticals, pesticides, and microplastics) was comprehensively compared, taking into account the conditions of real aquatic systems. The key photocatalytic mechanisms, including charge transfer, generation of reactive oxygen species, and Ag^+ photocorrosion, were analyzed, and the effectiveness of heterostructures (Ag_3PO_4 /g-C_3N_4, Ag_3PO_4 /TiO_2, etc.) in enhancing activity and stability was demonstrated. The obtained results provide a scientific basis for the development of sustainable and scalable water treatment technologies.

Theoretical and practical significance of the study

The theoretical significance of the study lies in the advancement of scientific understanding of the photocatalytic and antibacterial activity of nanoparticles and nanocomposites based on silver

phosphate. A mechanistic scheme for the degradation of nitrofurans by Ag_3PO_4 nanoparticles and silver halides (AgCl, AgBr, AgI) is proposed, emphasizing the key role of valence band holes and superoxide radicals. For the first time, Ag_3PO_4 nanoparticles and Ag_3PO_4/AgCl nanocomposites were systematically classified and experimentally investigated, and new data were obtained on the influence of interfacial interactions on the efficiency of organic pollutant degradation under visible-light irradiation, as well as on the mechanisms of light-stimulated antibacterial action through the generation of reactive oxygen species (ROS) and Ag^+ ions.

The practical significance consists in the development of an environmentally friendly and scalable mechanochemical method for the synthesis of nanomaterials based on silver phosphate and silver halides, as well as their composites exhibiting high photocatalytic and antibacterial activity. The obtained materials are promising for wastewater and natural water purification, the development of antimicrobial coatings, filtration systems, and biomedical technologies.

Approbation of practical research results

The main results of the study were presented at the following conferences:

1. the International Scientific Conference of Students and Young Scientists “INESS, 13th Int. Conf. on Nanomaterials & Advanced Energy Storage Systems”, Astana, Kazakhstan, August 06–08, 2025;
2. the international scientific conference “245th The Electrochemical Society (ECS Meeting)”, San Francisco, USA, May 24 – June 2, 2024;
3. the international scientific conference “11th International Congress on Energy Efficiency and Energy Related Materials (ENEFM)”, Ölüdeniz, Muğla, Turkey, October 21–27, 2025;
4. the international scientific conference “48th World Conference on Applied Science, Engineering & Technology (WCASET)”, Kuala Lumpur, Malaysia, November 17–18, 2025.

Publications and personal contribution of the author to the research

Based on the results of the study, four scientific articles have been published.

***Tugelbay, S.,** Volobuyeva, V., Abilkhan, A., Tatykayev, B. Scalable synthesis of AgX (Cl, Br, I, PO_4) nanophotocatalysts for efficient visible-light degradation of persistent antibiotics from aqueous environments. J. Photochem. Photobiol. A: Chem. 472 (2026) 116748. https://doi.org/10.1016/j.jphotochem.2025.116748 . Journal of Photochemistry & Photobiology A: Chemistry, journal impact factor - 4.7, WoS quartile - Q2, Scopus percentile - 85%.

In this work, the doctoral candidate acted as the first author and made the main contribution to the research: formulated the concept and idea of the study, performed the mechanochemical synthesis of silver halides and silver phosphate, conducted structural characterization (XRD, Raman, SEM, TEM, UV–Vis), carried out experimental investigations of antibiotic degradation, analyzed the obtained results, and prepared the manuscript for publication.

***Tugelbay, S.,** Yergaliuly, G., Abilkhan, A., Khan, N., Tatykayev, B. Ag_3PO_4-based composites as next-generation antibacterial nanomaterials: A review of light-induced synergistic effects. Chem. Eng. J. 522 (2025) 167818. https://doi.org/10.1016/j.cej.2025.167818 . Chemical Engineering Journal; journal impact factor - 13.2, WoS quartile - Q1, Scopus percentile - 97%.

In this work, the doctoral candidate served as the first author, proposed the scientific idea of the study, developed the manuscript structure, collected and analyzed the literature data, conducted a comparative discussion of photocatalytic and antibacterial mechanisms, wrote the manuscript text, and performed its editorial revision.

Tugelbay, S., Shalabayev, Z., Khan, N., Mukhanbetzhanov, N., Jumagaziyeva, A., Sultanov, F., Kozhakhmetov, S., Kushugulova, A., Shevelkov, A.V., Mucsi, G., Tatykayeva, U., Daniyeva, N., Burkitbayev, M., Tatykayev, B. Enhanced photocatalytic antibacterial Ag_3PO_4/AgCl nanocomposites for water purification from organic and microbial contaminants. J. Environ. Chem. Eng. 13 (2025) 118753. https://doi.org/10.1016/j.jece.2025.118753 . Journal of Environmental Chemical Engineering; journal impact factor - 7.2, WoS quartile - Q1, Scopus

percentile - 95%. The doctoral candidate actively participated in the development of the synthesis protocol for Ag_3PO_4/AgCl nanocomposites using a planetary ball mill and conducted comprehensive investigations of their photocatalytic activity.

***Tugelbay, S.,** Bakbolat, B. Visible-light-responsive Ag_3PO_4-based photocatalysts for water treatment and wastewater remediation: Advances, challenges, and future directions. J. Environ. Chem. Eng. 13 (2025) 120339. https://doi.org/10.1016/j.jece.2025.120339. Journal of Environmental Chemical Engineering; Impact Factor - 7.2, WoS Quartile - Q1, Scopus Percentile - 95%. In this work, the doctoral researcher served as the first author, proposed the scientific concept and structure of the review, conducted a systematic collection and critical analysis of contemporary literature, performed a comprehensive comparison of photocatalytic mechanisms and properties of Ag_3PO_4-based materials, developed key scientific illustrations and tables, wrote the main text of the manuscript, and carried out the complete process of scientific editing and preparation of the paper for publication.

Tugelbay Saparbek is the first author in all four published articles and the corresponding author in three of them. His scientific contribution includes formulation of the research concept, development and implementation of nanostructure synthesis, design and execution of experiments, detailed analysis of the obtained data, and preparation of scientific publications.

Relationship of the research with governmental scientific programs

– Grant funding of the Ministry of Science and Higher Education of the Republic of Kazakhstan for scientific and (or) scientific-technical projects for 2025–2027 on the topic "Advanced Ag_3PO_4-based nanocomposites with photocatalytic and photo-enhanced antibacterial activity", IRN AP26198675;

– Grant funding of the Ministry of Science and Higher Education of the Republic of Kazakhstan for scientific and (or) scientific-technical projects for 2022–2024 on the topic "Photocatalysts based on g-C_3N_4 and metal sulfides: solid-state synthesis and hydrogen generation performance", IRN AP13068426;

– Program-targeted funding of the Ministry of Science and Higher Education of the Republic of Kazakhstan for scientific and (or) scientific-technical projects for 2018–2020 on the topic "Development and testing of technologies for the production of new sulfur-containing nanocomposites and preparations", IRN BR05234566