ABSTRACT

of dissertation for the doctor of Philosophy degree (PhD)
6D072000 – "Chemical technology of inorganic substances"

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Sorption and catalytic characteristics of composite materials based on natural raw materials

The dissertation work is devoted to the synthesis of new composite materials based on natural raw materials with sorption and catalytic properties. Protocols of synthesis are developed, physico-chemical characteristics of obtained materials are studied and the features of the sorption of heavy metal ions and the catalytic processes of nitrophenol reduction and hydroxidation of yellow phosphorus are investigated. All received data is new, the results are presented in the form of 2 articles in journals reviewed by the Web of Science and Scopus, and are protected by 2 utility model patents.

Relevance of the research topic. The relevance of this work is determined by the need for experimental development of new composite materials based on natural raw materials for use in wastewater treatment. Also for use as catalysts in nitrophenol reduction and butoxylation reactions of yellow phosphorus.

Composite material (CM) is a material consisting of two or more components (phases), where one of them, at least, is a solid, with a special property that can not be achieved by any of the components separately or even not just their sum. The properties of the composites are achieved through the interaction of individual phases, which is called the synergistic effect. Composite materials are widely used in medicine, construction, shipbuilding, sorption, catalysis, as well as in many other branches of science and technology. In this regard, the synthesis and study of the properties of composite materials is of theoretical and practical interest.

Currently, more and more countries, including the Republic of Kazakhstan, are faced with a global environmental problem - environmental pollution, in particular, natural, drinking and waste waters with heavy metals. It is well known that they directly affect the human body, changing its functions and properties, that is, they are able to accumulate in the body and affect the natural metabolism processes.

Therefore, one of the current priorities in the field of environmental protection is the search for effective and environmentally friendly composite materials for wastewater treatment.

In addition, CMs are actively used in various catalytic reactions. In this work, as a model reaction, the processes of reduction of nitro groups, butoxilation and hydroxidation of yellow phosphorus are investigated. The process of reducing nitro groups in amines plays an important role in organic, pharmaceutical and synthetic chemistry. Amine hydrogenation products are widely used as dyes, agrochemical and pharmaceutical products, as well as intermediate products for the preparation of diazonium salts, acylated aminophenols, quinones. It is known that for this process there are a number of catalysts based on noble metals, the disadvantage of which is the high cost of raw materials and the complexity of their synthesis. Natural materials of clay, vegetable and sea origin are the most available reagents for the synthesis of CM with various applied properties.

The catalytic properties of the obtained CMs were also investigated in model reactions — production of phosphoric acid from yellow phosphorus. Phosphoric acid H_3PO_4 is the most important intermediate in the production of concentrated phosphate fertilizers. In addition, phosphoric acid is used in the production of various technical salts, organophosphorus compounds, including insecticides, semiconductors, ion exchange resins, as well as to create protective coatings on metals. Purified or so-called food phosphoric acid is used in the food industry for the preparation of feed concentrates and pharmaceuticals. Currently, the most common method is an acid decomposition of ores containing more than 25 % P_2O_5. Phosphoric acid is formed directly by dissolving the ore, i.e. direct extraction of phosphorus compounds by extraction. Hence the name of the product - extraction phosphoric acid (EPA). Thermal acid is obtained from poorer ores. The process is based on the recovery of phosphorus from natural phosphates by coke at high temperatures and the further production of H_3PO_4 from phosphorus. These methods have such disadvantages as the formation of acidic waste formed during the reaction. At present, the industrial production of trialkyl phosphates includes, in the first stage, the oxidation of yellow phosphorus P_4 with molecular chlorine. As a result of the reaction, all the chlorine, during the whole process, spent on obtaining PCl_3, turns into a very difficult to utilize chlorine-containing waste. Therefore, the relevance of this work is due to the need to search for alternative "chlorine-free" processes for the synthesis of organic phosphorus compounds (OPC) from yellow phosphorus due to the insufficient development of catalytic chemistry P_4, the lack of production of yellow phosphorus into valuable phosphorus-containing products in Kazakhstan and increased environmental requirements.

Aim of the work – is to obtain cost-effective, efficient composite materials based on natural raw materials, which have a high sorption capacity for heavy metal ions from aqueous solutions and catalytically

activity in the reactions of reduction of 4-nitrophenol and the butoxylation of yellow phosphorus.

Research tasks. To achieve this it was necessary to solve the following tasks:

- to synthesize and determine the optimal conditions for the production of composite materials based on natural raw materials: clay, plant origin and various polymer modifiers (PEG, PVP);
- to establish the physico-chemical and textural characteristics of the obtained composite materials;
- to determine the optimal conditions for the sorption of Cu^{2+}, Cd^{2+}, Pb^{2+}, Ni^{2+} heavy metal ions by obtained CM;
- to determine the catalytic characteristics of supported copper-polymer catalysts in the reduction reaction of 4-nitrophenol to 4-aminophenol;
- to determine the catalytic properties of supported copper-polymer catalysts in the oxidation of yellow phosphorus in an aqueous solution in an oxygen atmosphere to produce phosphoric acid;
- establish optimal conditions for catalytic oxidation of yellow phosphorus to phosphoric acid in the presence of homogeneous copper-polymer catalysts in an aqueous medium in an oxygen atmosphere.

Objects of the study: composite materials based on bentonite clays, zeolite, orange and mandarine peel, and polymer modifiers (PEG, PVP).

Subject of the study: synthesis of composite materials; sorption extraction of HM ions from aqueous solutions by obtained CM; catalytic reduction reactions of 4-nitrophenol and hydroxylation of yellow phosphorus.

Novelty of the work. The scientific novelty of the research is to develop optimal conditions for the synthesis of new polymer-inorganic composite materials. For the first time, the possibility of using the obtained CM in water purification from heavy metal ions by the sorption method is shown. The first synthesized copper-containing CMs were investigated as catalysts in the reactions of hydrogenation of 4-nitrophenol and oxidation of yellow phosphorus, followed by the production of phosphoric acids.

Scientific and practical significance. Production of CM contributes to sustainable environmental development of the Republic of Kazakhstan. Studies conducted in the course of work allow us to open up prospects for the use of the materials obtained as effective, affordable and cheap sorbents for the purification of industrial wastewater. Also, the studied reduction reactions of 4-nitrophenol in the presence of in situ Cu_2O nanoparticles immobilized on natural bentonite and zeolite, functionalized with polyethylene glycol, are highly efficient and affordable. Kazakhstan has extensive reserves of phosphate ores. In this regard, obtaining phosphorus-containing products is a priority for the country. Phosphoric acid is used in

the production of various technical salts, organophosphorus compounds, including insecticides, semiconductors, ion exchange resins, as well as to create protective coatings on metals. The catalytic properties of new polymer-metal catalysts based on copper (II) ions and polyethylene glycol (PEG) in the reactions of phosphoric acid production was showed in this work. In addition, the study investigated the reaction of oxidative butoxylation of yellow phosphorus in the presence of heterogeneous catalysts — supported $CuCl_2$-PVP, which, due to their high catalytic activity and selectivity, can be recommended for the synthesis of valuable phosphoric esters directly from yellow phosphorus under mild conditions. It should be noted that the obtained results have theoretical interest for the development of physical chemistry (thermodynamics and kinetics of heterogeneous processes: sorption, catalysis) and chemistry of coordination compounds.

Investigation methods. The following physico-chemical methods of analysis were used in this work: X-ray phase analysis, IR spectrometry, electron microscopy, BET, atomic absorption spectroscopy, UV spectrophotometry.

Connection of the topic with the research plan and various government programs. The work was performed in the framework of the project “Development of the Scientific Basis for Producing Phosphorus-Containing Compounds Based on Technogenic Mineral Raw Materials" - 2015-2017 (№ 0115PK00515), funded by the MES RK.

The main statements to be defended:

- The results of physico-chemical studies of the composition and structure of the synthesized composite materials;
- Optimal conditions for purification of aqueous solutions from the Cu^{2+}, Cd^{2+}, Pb^{2+}, Ni^{2+} ions by composites based on natural raw materials;
- The results of the study of the catalytic reduction of 4-nitrophenol in the presence of a composite material – in situ Cu_2O/PEG-bentonite (zeolite);
- The results of the study of the catalytic oxidation of yellow phosphorus in the presence of homogeneous catalyst $[Cu(PEG)_2Cl_2]$;
- The results of the study of the catalytic oxidation of yellow phosphorus in the presence of composite materials - $CuCl_2$-PVP-substrate.

Approbation of the work results. The main results of the work were presented and discussed at international conferences and seminars: V All-Russian Scientific Youth School-Conference "Chemistry under the sign of sigma: research, innovation, technology" (Omsk, May 15-20, 2016); International Scientific Conference "Innovative development and relevance of science in modern Kazakhstan" (Almaty, October 20-21, 2016); International scientific conference of students and young scientists "Farabian readings" (Almaty, April 11-14, 2016); International scientific

conference of students and young scientists "Farabian readings" (Almaty, April 11-12, 2017); 4th International Russian-Kazakh Scientific and Practical conference “Chemical Technology of Functional Materials” (Almaty, 12-13 April 2018); International scientific conference of students and young scientists "Farabian readings" (Almaty, April 9-10, 2018); XXVIII Russian youth scientific conference "Problems of theoretical and experimental chemistry" (Ekaterinburg, 25-27 April 2018).

Publications. The results of the thesis were published in 22 papers, including:

- 2 articles published in international scientific journals, indexed by Scopus and Web of Science: Studia UBB Chemia with IF = 0.305 and Bulletin of Materials Science with IF = 0.925;
- 2 utility model patents;
- 6 articles published in journals recommended by the Committee on the Control of Education of the Ministry of Education and Science of the Republic of Kazakhstan;
- 14 materials of International, Republican scientific seminars and conferences.

The personal contribution of the author consists in the formulation and conduction of experiments, interpretation of the theoretical and experimental solution of the problems, discussion and generalization of the obtained results.

The structure and scope of the thesis. The thesis work consists of introduction, literature review, experimental part, results and discussion, conclusion, list of references and application. The total amount of the thesis is 92 pages, includes 45 figures and 28 tables. List of references contains of 204 names.