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PROSPECTS FOR THE PRACTICAL APPLICATION OF AMINOCARBOXYPHOSPHONATES AND THEIR METAL COMPLEXES (review).

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The review article summarizes and systematizes many years of literature data on possible areas of application of aminocarboxyphosphonic acids and metal complexes based on them. It is shown that aminocarboxyphosphonates, due to their wide range of functional properties, in particular, such as photoluminescence, magnetic properties, biological activity, can find application in a wide variety of areas. Both aminocarboxyphosphonic acids themselves and their complexes can serve as the basis for biologically active substances in agronomy - as synthetic growth regulators, as effective preparations for increasing extracted sugar from various plants (sugar cane, sweet potato, sugar beet, melon, etc.) and preparations for accelerating fruit ripening under adverse weather conditions. One of the most interesting areas of use of aminocarboxyphosphonates and nanoparticles based on them for biomedical purposes is the creation of precursors for the development of new antitumor drugs. Due to their high porosity, these materials can be used in ecology for the purification of soil and/or drinking water from heavy metals. The approaches to the modification of the coordination environment, variations in the nature of metals and ligand environment highlighted in the work can be used as a model for the development of new coordination polymers and MOFs structures as environmentally friendly depressants for selective flotation separation of minerals (dolomite, galena, sphalerite). Aminocarboxyphosphonates of metals as a subclass of coordination polymers, due to the presence of such groups in the molecules as POH, COOH, N^+-H, demonstrate acidic properties, the combination of which with electrocatalytically active transition metals makes them very attractive in the field of fuel cells and electrolyzers. They can be used as potential proton conductors and/or precursors of electrocatalysts, heterogeneous catalysts in the Knoevenagel condensation with high selectivity.

Keywords: complexes, aminocarboxyphosphonates, 3-d, 4-f metals, biological activity, catalyst, purification from heavy metals, practical application.

INTRODUCTION. Complexones are organic compounds that contain basic and acidic centers, the mutual arrangement of which determines the formation of stable chelate cycles upon coordination with metal ions. The first representatives of complexones are aminocarboxylic acids - nitrilotriacetic acid (H_3NTA) and ethylenediaminetetraacetic acid (H_4EDTA), in the molecules of which there are several aminoacetate fragments -NHCH$_2$COOH [1, 2]. To solve a wide range of practical problems, the range of complexones has significantly increased. Today, in addition to classical polyaminopolycarboxylic acids, this group also includes aminocarboxyphosphonic acids (ACPhA), which contain two different types of acid moieties near the donor nitrogen atom - carboxyl and phosphonic groups: H_2PO_3-NCH$_2$-R (R = -H, -CH$_2$COOH, -CH$_2$PO$_3$H$_2$). The presence of two different acid groups in the molecules of aminocarboxyphosphonic acids, which differ significantly in basicity, charge, electron-donating ability, stereochemistry, and size, ensures their high coordination capacity and selectivity towards metals of various natures. Aminocarboxyphosphonic acids, combining the properties of aminocarboxylic and phosphonic/aminophosphonic acids, compared to their carboxyl- or phosphorus-containing analogues, form a much larger set of differently protonated metal complexes in solutions and polynuclear structures of unusual structure in the solid state due to the formation of additional chelate cycles. Due to the presence of different types of coordination sites in their molecules, aminocarboxyphosphonate metal complexes have higher solubility, which facilitates their crystallization compared to aminocarboxylate and/or phosphonate analogues [3–5].

Earlier, in review articles [6, 7], literature data on the structure and physicochemical properties of both aminocarboxyphosphonic acids themselves and metal complexes (3-d, 4-f metals) based on them were summarized. Through the analysis of numerous works, including those from the last 5 years, this article examines the prospects for the application of aminocarboxyphosphonic acids and their metal complexes in various industries for the creation of multifunctional materials.

EXPERIMENT AND DISCUSSION OF THE RESULTS. Aminocarboxyphosphonates, unlike their carboxyl- and/or phosphorus-containing analogues, are a relatively poorly studied class of compounds that are not yet widely used in industry. But in the last 30 years, this class of compounds has attracted significant attention from researchers around the world due to the wide potential of their practical use as plant growth regulators and herbicides, as well as the potential application of their metal complexes in materials chemistry as functional materials due to the presence of a number of useful properties (high porosity, photoluminescence, catalytic, nonlinear optical, magnetic properties, etc.) [8–11].

Biological activity of aminocarboxyphosphonates

Aminocarboxyphosphonates exhibit biological activity, are non-toxic to mammals and, importantly, are capable of fairly rapid degradation in the environment. The biological properties of aminocarboxyphosphonic acids and biometal complexes based on them are due to the fact that they are structural phosphorus-containing analogues of natural amino acids, therefore they can participate in the mechanisms of many bioprocesses, have low toxicity and high solubility in the natural en-

vironment [1, 4, 12]. Studies in recent decades have shown that aminocarboxyphosphonates exhibit herbicidal and growth-stimulating properties [5, 13–16]. Among all aminocarboxyphosphonates, the most studied organophosphonate, which is widely used in practice, is N-(phosphonomethyl)glycine (H_3PMG) - a phosphonomethyl derivative of the amino acid glycine, and is known worldwide as the non-selective herbicide «Glyphosate» (the original agricultural product «Roundup»). It has a strong phyllocid effect, which causes disruption of enzymatic processes in plants. In the soil, glyphosate is microbiologically decomposed and deactivated. This process is inhibited by the binding of glyphosate to metal cations present in the soil. N-(phosphonomethyl)glycine is able to selectively inhibit the synthesis of the enzyme 5-enelpyruvoylshikimate-3-phosphate synthase (EPSPhS), which, although absent in higher organisms, is necessary for the synthesis of aromatic amino acids in plants and microorganisms. Glyphosate-based preparations exhibit a universal effect when in contact with green plants at low rates of application (~0.8–1.7 kg/ha), have low phytotoxicity and are rapidly decomposed in the environment under aerobic and anaerobic conditions with the formation of the main metabolite - aminomethylphosphonic acid [17–19].

In [20], the effect of Glyphosate on microbial biomass and soil activity was investigated. It was shown that it significantly stimulates soil microbial activity by mineralizing C and N, but does not affect soil microbial biomass. C mineralization, as well as the rate of mineralization, increases with increasing glyphosate application rates (Fig. 1). Moreover, the rate of C mineralization increases on the first day after glyphosate addition and continues for 14 days. It was found that Glyphosate directly and rapidly decomposes microbes, even at high rates of application, without negatively affecting their activity.

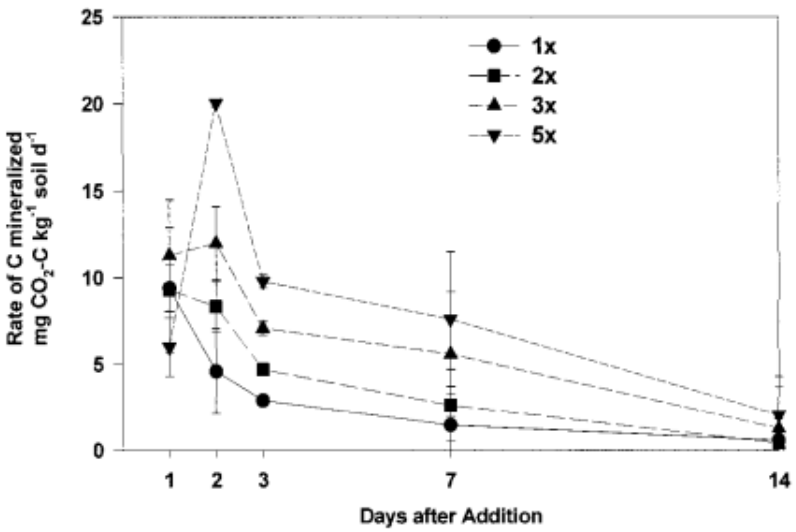


Fig. 1. Effect of glyphosate addition rate on soil C mineralization.
(1×–5× are rates of glyphosate addition to soil at doses of 47, 94, 140, and 234 mg, respectively.
Error bars indicate one standard deviation [20]).

An analogue of N-(phosphonomethyl) glycine – N,N-bis(phosphonomethyl)glycine (H_5BPMG) – known as the drug «Glyphosin», is a synthetic growth regulator and is used mainly to increase the extracted sugar from various plants (sugar cane, sweet potato, sugar beet, melon, etc.) and is effective for accelerating fruit ripening under adverse weather conditions. Thus, N,N-bis(phosphonomethyl)glycine has been recognized as a chemical ripener of sugar cane in small replicated field plots and on a commercial scale to determine optimal rates and timing of application [176, 177]. It was shown that the use of Glyphosine at doses of 2.24, 4.48 and 6.72 kg/ha 6 weeks after application contributed to a significant increase in the percentage (>15%) of sucrose in sugarcane compared to the untreated control. A greater increase in sugar was observed for the dose of 6.72 kg/ha. Trials of Glyphosine on a commercial scale (application rate – 3.36 kg/ha) showed an increase in sugar from 9 to 15% compared to the control already 4 weeks after application.

In [21], aqueous solutions of N,N-bis(phosphonomethyl)glycine (were tested on cantaloupe plantings. It was shown that the increase in melon yield under the influence of BPMG was 6.6%, and the sugar content increased by approximately 10%, regardless of the concentration of glyphosate.

The biological properties of ACPhA are due to the presence in their molecule of a covalent C—P bond that is resistant to photolysis, chemical hydrolysis, and temperature, but capable of being destroyed by the enzymatic action of microorganisms [20, 22–25].

The ability to biodegrade compounds with a C-P bond has been demonstrated in many bacteria of the genera *Escherichia*, *Pseudomonas*, *Agrobacterium*, *Klebsiella*, *Arthrobacter*, *Bacillus*, *Rhizobium*, and *Rhizobium* [26, 27]. Some strains (e.g., *Pseudomonas* sp. LBr and *Flavobacterium* sp.) transform most of the N-(phosphonomethyl)glycine into aminomethylphosphonate or glyphosate oxidoreductase [28, 29]. The metabolism of N-phosphonomethylglycine by *Pseudomonas* sp. LBr, a bacterium isolated from waste from the glyphosate production process, was investigated by a combination of ^{13}C NMR and phosphonate analysis of the culture medium. *Pseudomonas* sp. LBr is capable of removing 20 mM glyphosate from the culture medium, which is approximately 20 times more than any other microorganism. The bacterium degrades high levels of glyphosate primarily by converting it to aminomethylphosphonate with subsequent release into the culture medium. Only a small amount of aminomethylphosphonate (about 0.5–0.7 mM), which is necessary to provide phosphorus for growth, could be metabolized by the microorganism. NMR analysis of *Pseudomona*s sp. LBr grown on 1 mM glyphosate showed that about 5% of H_3PMG was degraded by a separate pathway involving its cleavage to glycine.

That is, the main role in the biodegradation of H_3PMG in soils, after its use as a herbicide, is played by bacteria (Fig. 2) or enzymes of some microorganisms (for example, glyphosate oxidoreductase) (Fig. 3) [28–30].

At low concentrations, H_3PMG does not affect the vital activity of soil microorganisms, but an increase in its concentration up to 100 times causes a decrease in bacterial population cultures and diversity [31, 32].

Toxicological studies have shown that H_3PMG has low toxicity after oral, dermatological and inhalation administration and does not exhibit genotoxic, carcinogenic, neurotoxic, tera-

togenic effects. The LD_{50} of N-(phosphonomethyl)glycine for mammals is 2100 mg/kg [11, 33]. In the body of laboratory animals, 23–36% of H_3PMG is absorbed, it is well distributed in tissues with the formation of the main metabolite - aminomethylphosphonic acid [34, 35].

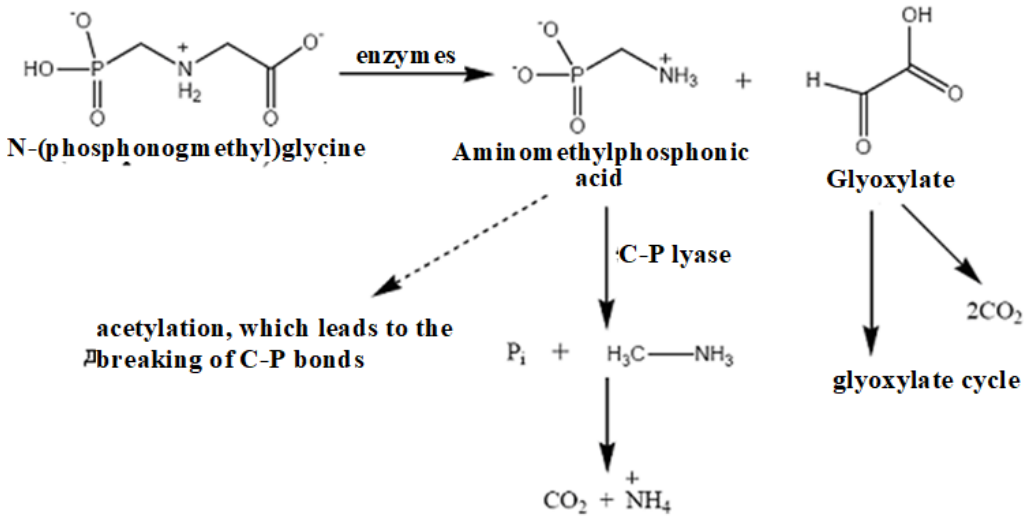


Fig. 2. Scheme of biodegradation of N-(phosphonomethyl)glycine in soils.

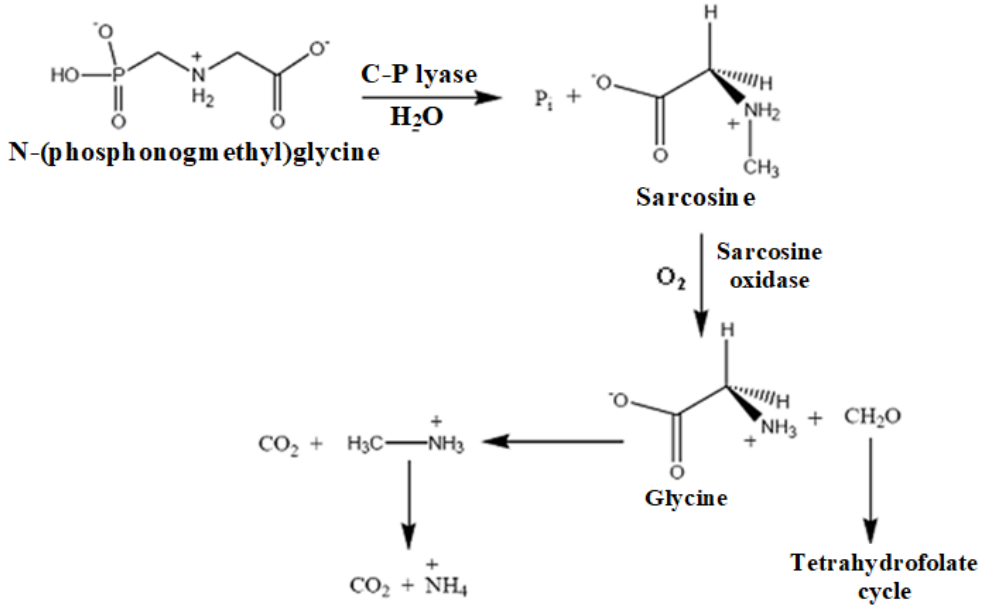


Fig. 3. Scheme of biodegradation of N-(phosphonomethyl)glycine under the action of enzymes.

Particular attention is drawn to the stimulating effect of aminocarboxyphosphonates on the growth of microorganisms used in biotechnology. It is known that the influence of *Pseudomonas* sp. on the development of agricultural crops can be both positive and negative. Some bacterial strains are phytopathogenic, others, for example, saprophytic pseudomonads, which widely inhabit the rhizosphere of plants, play an important role in their protection. Bacterial antagonists from the genus *Pseudomonas* are used as means of biological control of plant diseases of bacterial and mycological etiology. Also, saprophytic representatives of the genus *Pseudomonas* are producers of a large number of biologically active compounds, such as pigments, antibiotics, amino acids, polysaccharides, toxins, vitamins, as well as other organic substances used in immunology, medicine and agriculture [36–38].

In studies conducted at the V.I. Vernadsky Institute of General and Inorganic Chemistry of the NAS of Ukraine, the growth-stimulating activity of N-(phosphonomethyl)aminosuccinic and N,N′-bis(phosphonomethyl)aminosuccinic acids and 3d-metal complexes based on them was established against non-pathogenic bacterial strains of *Pseudomonas* cultures (*Pseudomonas fluorescens*, *Pseudomonas aureofaciens*) and microorganisms *Escherichia coli ATCC 25922* [6, 39]. The interest in the mentioned *Pseudomonas* species is connected, first of all, with manifestation of useful properties for plants, since these bacteria are able to stimulate their growth and development, to act as antagonists of phytopathogenic fungi and bacteria. Substances, which have the property to activate growth of such microorganisms, in turn, become potential objects for development of biological preparations for agrobiotechnology. On the other hand, some species of microorganisms of the genus *Pseudomonas* are able to assimilate organic, including phosphorus-containing compounds, to final ecologically clean decomposition products, which becomes actual in practical use of carboxyaminophosphonates without their accumulation in the environment [40–44]. It has been proven that N-(phosphonomethyl) aminosuccinic and bis(phosphonomethyl)aminosuccinic acids and 3d-metal complexes based on them exhibit growth-stimulating activity against strains of gram-negative microorganisms of the genus Pseudomonas. At the same time, the growth-stimulating effect of the M^{II}PMAS complexes, depending on the 3d-metal ion, increases in the following order: **Cu(II) > Zn(II) > Ni(II) > Co(II).** The maximum stimulating effect on the growth of bacterial cultures is exhibited by bis(phosphonomethyl)aminosuccinate Co(II), which is able to initiate the synthesis of one of the most important growth hormones - heteroauxin.

In addition to agronomy, the use of aminocarboxyphosphonates has been proposed to reduce the toxicity of heavy metals in soils during their purification [45, 46], to create a protective film during steel corrosion [47], to obtain surface-modified nanoparticles that have antitumor activity [48, 49], as an additive to cosmetic compositions [50, 51], etc.

Use of aminocarboxyphosphonates for the removal of heavy metals.

The variety and quantity of waste discharged into the environment are the main disadvantages of industrialization. The activities of industrial enterprises, automobile exhausts and other attributes of civilization, unfortunately, negatively affect the state of ecology, the quality of water, air, soil, etc. Heavy metals are

one of the most toxic pollutants of anthropogenic origin. The danger of heavy metals entering the environment is determined by the fact that, unlike organic pollutants, they do not break down, but pass from one form to another, in particular, they are included in the composition of salts, oxides, organometallic compounds. The term «heavy metals» is used for metals whose specific gravity exceeds 5 g/cm^3 or atomic number is more than 20. Among them, the most toxic are metal ions - Cu, Cd, Pb, Cr, Mn, Hg, Fe, Al, Se, Sn, rare-earth elements (REE), etc.

Water pollution by heavy metal ions is of serious concern due to their toxicity to many life forms. In order to reduce the impact of heavy metals on the environment, various water purification technologies are being studied, such as: chemical precipitation, ion exchange, redox processes. The trend is to find a universal and economical method for removing heavy metals from wastewater. One of the water purification methods that is effectively used to remove heavy metal ions from drinking water and wastewater is adsorption. Adsorption is a separation process that consists in the adhesion of metal ions dissolved in aqueous solutions to the surface of an adsorbent. The mechanisms of metal ion separation from water by adsorption are influenced by both their characteristics and the characteristics of the adsorbent, which are determined by the interaction between them. These interactions can be of a physical nature, caused by low-energy forces (for example, Van der Waals-type forces). In this case, metal ions are adsorbed in the pores of the adsorbent without the participation of electron transfer. In this case, the process is reversible, and the metal ion molecules retained on the surface of the adsorbent can be removed by desorption, regenerating the adsorbent. If the interaction between metal ions and adsorbents involves electron transfer and the formation of chemical bonds, the process is called chemical adsorption, or chemisorption. In this case, the metal ions are not attracted to the entire surface of the adsorbent materials, but only to the active zones, which contain functional groups that react with the metal using more energy than in physical adsorption, a fact that explains the greater selectivity of chemical adsorption. In adsorption processes, the adsorbent material used is an important element for obtaining an effective separation. Porous activated carbons, zeolites, bioadsorbents, carbon nanotubes are often used to remove heavy metals. However, these materials have limited practicality due to low adsorption capacity, low efficiency, or high cost. The best adsorbents are compounds with well-ordered structures, such as metal-organic frameworks (MOFs) and coordination macromolecular compounds (Coordination Polymers, CPs), which are currently being intensively studied to create new materials. The main advantages of MOFs and CNs in adsorption processes over other adsorbent materials are their large specific surface area, well-organized unique structures, and stable pores with uniform size, which ensure their high adsorption capacity over a wide pH range for the removal of heavy metals from wastewater [52–55].

N,N-bis(phosphonomethyl)glycine, which has excellent chelating ability, was used for wastewater treatment from heavy metals in [53, 55]. Metallophosphonate organic frameworks of Ni(II) were synthesized by hydrothermal method using $Ni(CH_3COO)_2 \cdot 4H_2O$ and phosphonic acids (phosphonoacetic acid, vinylphosphonic acid (VP) and N,N-bis(phosphonomethyl)glycine (Gly)). The adsorption properties

of these materials in the process of removing heavy metals (Cr(VI), Cd(II), Pb(II)) from aqueous solutions at different pH values, contact time and initial adsorbate concentration were investigated (Fig. 4.).

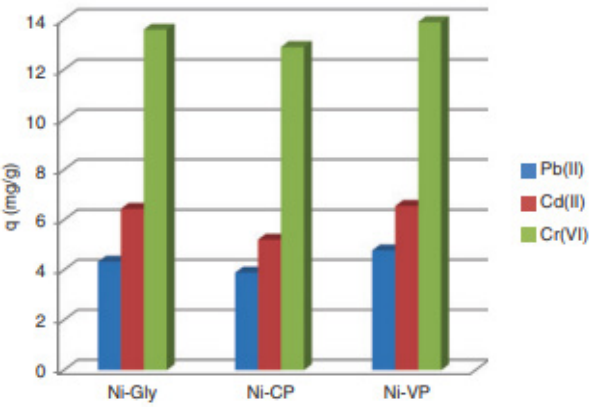


Fig. 4. Adsorption capacity of metallophosphonate organic Ni(II) frameworks in the process of removing heavy metal ions from aqueous solutions. (C_i=30 mg/l, S:L=2 g/l, t=60 min. [53]).

As can be seen from Fig. 4, metal organic frameworks based on Ni(II) phosphonates showed the highest adsorption capacity in the process of Cr(VI) removal compared to the removal of divalent metal ions. Detailed studies of the removal of Cr(VI) from aqueous solutions showed that the highest adsorption capacity of all materials is at pH 2.5 (Fig. 5), and the adsorption efficiency of the studied materials in the process of removing Cr(VI) ions from aqueous solutions is in the following order:

Ni-CP<Ni-Gly≤Ni-VP.

In [56], two coordination network polymers based on N,N-bis(phosphonomethyl)glycine Co–Gly and Ni–Gly were used as adsorbents for the removal of Cd(II) ions from aqueous solutions, which contain as the main structural units $[M(HO_3PCH_2)_2N(H)CH_2COO)(H_2O)_2]$ (M= Ni, Co). Adsorption of cadmium on the studied compounds was carried out in a batch mode at different pH, initial concentration, contact time, temperature and mass of the sorbent. It was found that the Ni–Gly sample has a larger specific surface area and pore volume (45 m^2/g, 0.85 cm^3/g) compared to the Co–Gly sample (32 m^2/g, 0.25 cm^3/g), and exhibits higher adsorption capacity in removing Cd(II) ions from aqueous solutions.

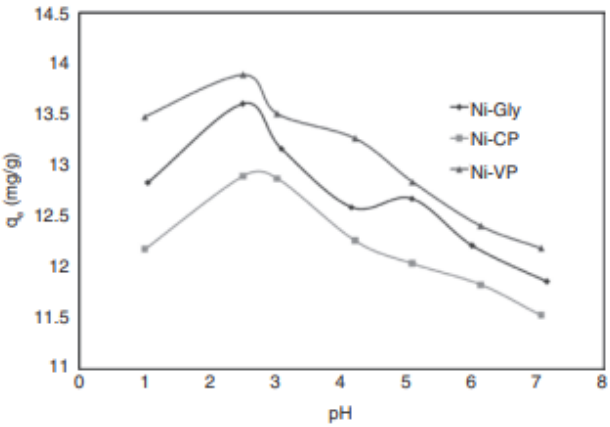


Fig. 5. Effect of initial pH on the adsorption capacity of Ni(II) metallophosphonate organic frameworks in the process of removing Cr(VI) ions from aqueous solutions [53].

The maximum adsorption capacity for Co-Gly and Ni-Gly was 51.5 mg/g and 58.1 mg/g, respectively. The higher specific surface area and pore volume of Ni–Gly together with the higher negative partial charges of Ni in the polymer network increase the electrostatic attraction between Ni-Gly and the positively charged Cd^{2+} ions, which causes a higher adsorption capacity of Ni-Gly. In addition, the adsorbent materials can be easily regenerated and recycled without significant loss of cadmium adsorption capacity.

Of no less concern is the contamination of

ground and/or drinking water with high concentrations of arsenic. Therefore, the need to find new appropriate methodologies capable of removing this pollutant is relevant today. An important aspect to consider is the possibility of finding arsenic in different chemical forms, which may require different approaches for its removal. To this end, speciation analysis is crucial for a better understanding of the behavior of arsenic species in aqueous solutions, especially in the presence of compounds with pronounced chelating properties. In recent years, the interest of scientists has focused on the increasing use of phosphonates in the industrial field and on their binding capacity. This class of ligands is characterized by a stable covalent carbon-phosphorus bond, and the most used compounds have structures similar to the known aminopolycarboxylates, such as ethylenediaminetetraacetate and nitrilotriacetate. Italian scientists have studied the interaction of As(III) with three phosphonic acids: N-(phosphonomethyl)iminodiacetic (H_4PMIDA), tri(nitrilotri(methyl)phosphonic (NTA_3P) acids and N,N-bis-(phosphonomethyl)glycine (H_5BPMG) [54]. In-depth potentiometric and calorimetric studies depending on pH allowed the authors to determine the formation of complexes of the composition ML, MLHi and ML(OH) in solutions and to propose the use of aminocarboxyphosphonates for arsenic removal. Based on the analysis of the values of the coefficient $pL_{0.5}$ (the concentration of the ligand capable of removing 50% of metal ions present in trace amounts), it was shown that all ligands demonstrate good sequestering ability in fresh water conditions, which varies in the series $NTA_3P > H_5BPMG > H_4PMIDA$.

Aminocarboxyphosphonate-based metal-organic frameworks can be used to extract or separate rare earth elements from solutions. Rare earth elements are a group of valuable metals with growing demand and widespread applications. Mineral ores, traditional sources of REE, require significant capital investment, and their processing is a source of environmental pollution. Industrial and natural fluids containing REE are potential alternative sources of these metals. REE, being toxic in nature, accumulate in water bodies as their industrial use increases exponentially, so their effective separation is of great importance.

In [57], the efficiency of polymer resin beads functionalized with H_5BPMG for the selective extraction of REE from saline solutions in fixed-bed adsorption columns was investigated. Competitive adsorption experiments were performed with different metals (Nd, Gd, Ho, Al, Fe, Co, Ni, Ba, Pb, Th, and U). BPMG-functionalized resins showed improved performance after 1–2 cycles of use or after an acid pre-rinse cycle, and REE adsorption was consistent for at least five cycles. At the same time, the adsorbent materials showed a slight preference for heavier REEs (qHo > qNd), although the overall adsorption of REEs on the amine resin was insignificant. Experiments with multi-element mixtures containing REEs and competing ions showed that the absorption of REEs by BPMG-functionalized resins was 137 times higher and more selective than for unfunctionalized amine resins. BPMG resin granules did not experience a significant decrease in REE adsorption capacity upon addition of other metals, whereas the performance of the aminated resin granules deteriorated at high concentrations. The REE and Pb removal efficiency was 10 times higher for BPMG-functionalized resins than for aminated resins in both REE-only and REE + competing metal mixtures (Fig. 6a).

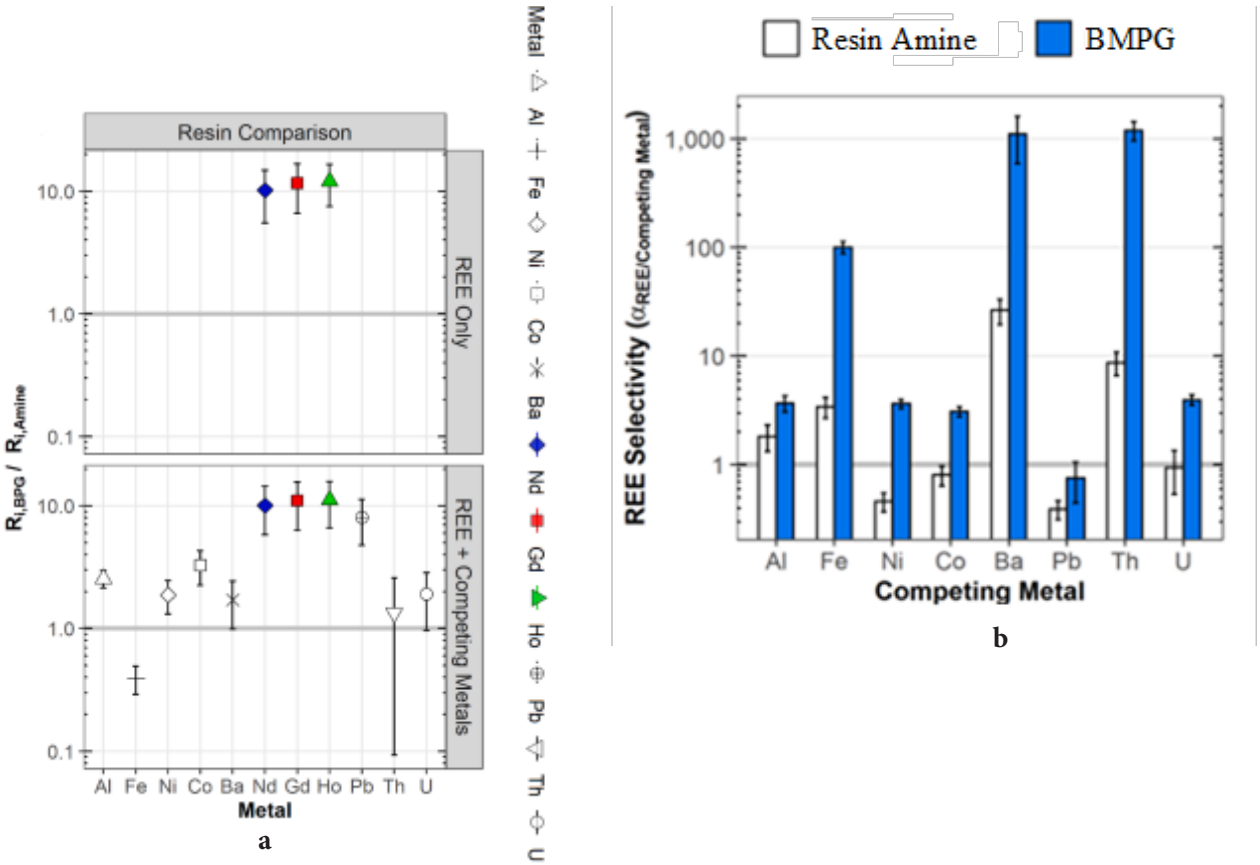


Fig. 6. Improvement of metal extraction for BMPG resins compared to aminated resins (a) and separation coefficients (αREE/competing metal) for REE (average value for Nd, Gd and Ho) for each competing metal in the mixture (b) [57].

The average separation coefficients for the BMPG-functionalized resins were highest for REE/Ba and REE/Th (αREE/competing metal > 1000) and were ≈ 137 times higher than for the aminated resins (Fig. 6b). A multi-element column test showed that the BMPG resin granules adsorbed ~15 times more REE than the granules of the unfunctionalized aminated resin (1.99 mg-REE/g BMPG resin vs. 0.137 mg-REE/g Amine resin). The aminated resins adsorbed mainly actinides (Th and U) with minor uptake of other metals.

Elution with the BMPG column yielded the following order of recovery: Ni > Ho > U/Co > Gd > Nd > Pb≫Ba/Th. The recovered concentrations were low for Pb, which is related to the low concentration of HNO_3 (0.75 M) used for elution. This study highlights the potential of these new materials for REE recovery and provides new insights into their performance under a range of conditions.

For the selective adsorption of La(III) from wastewater, an iron-benzenetricarboxylic acid-based polyacrylonitrile polymer (Fe-BTC) functionalized with N-(phosphonomethyl)iminodiacetic acid (PMIDA) was used [58] (Fig. 7).

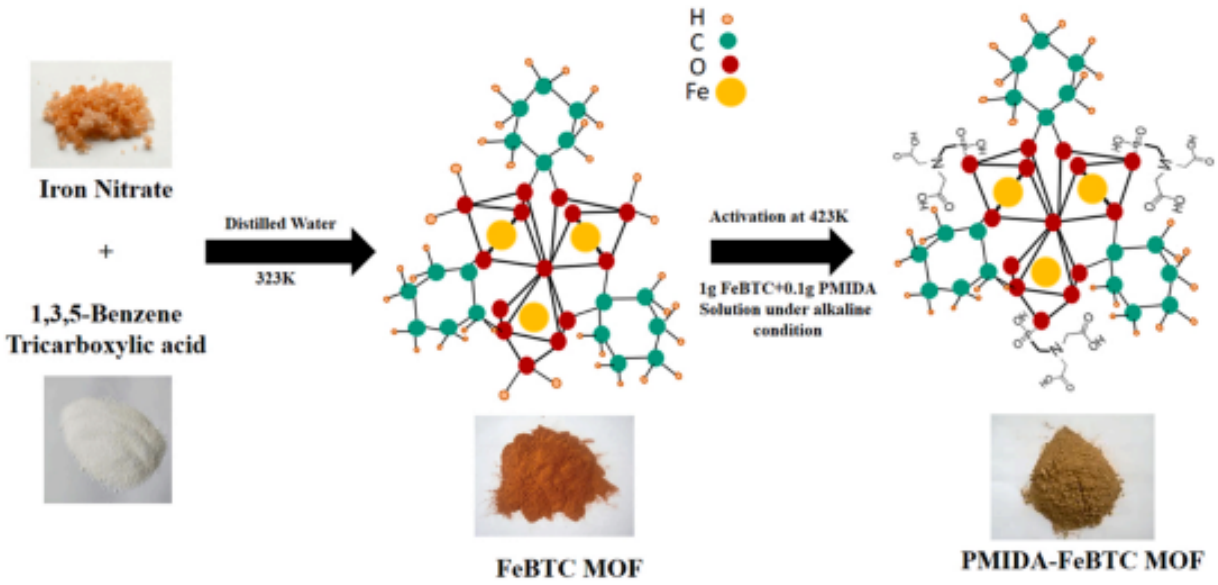


Fig. 7. Scheme of the synthesis of functionalized FeBTC with PMIDA molecules [58].

According to the authors, such research is necessary because La(III) due to its properties is used for various purposes: for the removal of phosphates in water purification, for improving special optical properties of glass, as an automotive catalytic converter, as a catalyst for biodiesel production and oil refining, etc. [59–61]. And what is more important is that La has wide application in nuclear technologies for controlling neutrons in control rods [62]. In this regard, scientists are making great efforts to develop processes for the extraction of lanthanum from alternative resources (such as acid mine drainage, brines, wastewater, etc.) to increase the availability of lanthanum and minimize the pressure on exhaustible resources. The extraction of La is also necessary because lanthanum, being toxic in nature, causes environmental damage and contaminates the food chain when accumulated [63, 64]. Considering these points, several separation methods, such as ion exchange, solvent extraction, chemical precipitation, adsorption and membrane separation, are currently used in industry to remove, separate and preconcentrate La from waste streams. These processes are successful but energy-intensive, which affects the scalability, ease of operation and cost-effectiveness of the process. Adsorption methods for lanthanum extraction are cost-effective and user-friendly. The adsorption of lanthanum from aqueous solutions (sewage, wastewater, brines, acid mine drainage, etc.) has been investigated using a wide range of adsorbents, which are mainly functionalized inorganic, carbonaceous (including nanoparticles), and organic-inorganic composites: magnetic silica P507 [65], cysteine-modified Fe_3O_4 nanoparticles [66], HESI-SBA15 [67], Cu-Al intercalated with EDTA [68], etc. However, low adsorption capacity, limited surface-to-mass ratio, and low selectivity are the main problems faced by these adsorbents.

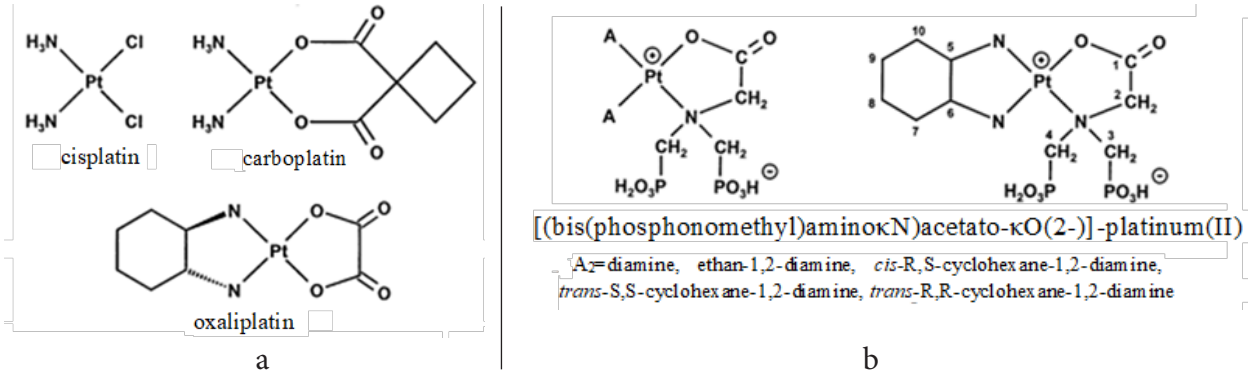
To overcome these difficulties, the authors [58] proposed the use of polymer beads based on a functionalized metal-organic framework, since they have a high specific surface area and have a great potential for the extraction of lanthanum from water sources. It was shown that the functionalization of MOF with PMIDA chelate groups leads to an increase in La^{3+} adsorption (over 95%) compared to FeBTC, which is due to the formation of bidentate coordination bonds of lanthanum with the surface carboxyl groups of PMIDA, which is confirmed by NMR, high-resolution IR spectroscopy, X-ray photoelectron spectroscopy, etc. In addition, the interaction of PMIDA with carboxyl groups changes the effective surface charge, which also contributes to the improvement of the adsorption characteristics of functionalized MOFs. The adsorption capacity of the functionalized MOF and composite granules was 232.5 mg/g and 77.51 mg/g. It was found that the adsorption characteristics of PMIDA-FeBTC for La^{3+} depend on the pH of the solution and the dosage of the adsorbent. When the pH increases from 2 to 8, the adsorption capacity increases, but at pH>6, insoluble hydroxide $La(OH)_3$ can be formed, which significantly reduces its adsorption. Therefore, the authors proposed to maintain the pH of the solutions at ~4.0 for effective extraction of La, at which the surface potential does not change, which contributes to faster diffusion of various forms of La^{3+} to the surface of the adsorbent.

When the sorbent dosage is increased from 2.5 g/l to 3 g/l for a La^{3+} concentration of 750 mg/l, its adsorption increases from 60% to 98.35%, while the adsorption capacity decreases from 302.8 mg/g to 257 mg/g. However, above 3 g/l, the adsorption percentage remains unchanged due to the limited amount of adsorbate. Therefore, 3 g/l can be chosen as the optimal adsorbent dosage at a layer height of 12 cm and a flow rate of 10 ml/min.

Prospects for the use of aminocarboxyphosphonates as antitumor agents.

Despite the worldwide success of platinum complexes (1-4 cis-diamindichloroplatinum(II) - cisplatin, carboplatin, cis-diamine-(1,1-cyclobutanedicarboxylato)platinum(II), oxaliplatin (trans-R,R-cyclohexane-1,2-diamine)oxalatoplatinum(II)) as some of the best agents in clinical cancer chemotherapy, researchers around the world continue to make efforts to find new anticancer drugs to overcome the serious side effects caused by platinum drugs, improve clinical efficacy, and expand the spectrum of use of newly created compounds. For the synthesis of platinum complexes with selective activity in primary and secondary malignant bone neoplasms (osteosarcoma and bone metastases of tumors with other primary localizations), a series of stereoisomeric platinum(II) complexes based on bis(phosphonomethyl)aminoacetic acid and cyclohexane-1,2-diamine ligands (chxn), - [(bis(phosphonomethyl)aminoκN) acetato-κO(2-)]-platinum(II) with (Fig. 8) was synthesized in [69], the antitumor activity of which was studied on human ovarian cancer cells (CH1) using the colorimetric microculture assay (MTT assay).

The antitumor activity of the synthesized complexes in vitro was compared with the similar action of cisplatin, carboplatin, and oxaliplatin (Fig. 9, Table 1).



a b

Fig. 8. Structural formulas of known antitumor Pt(II) complexes (a) and synthesized in [69] (b).

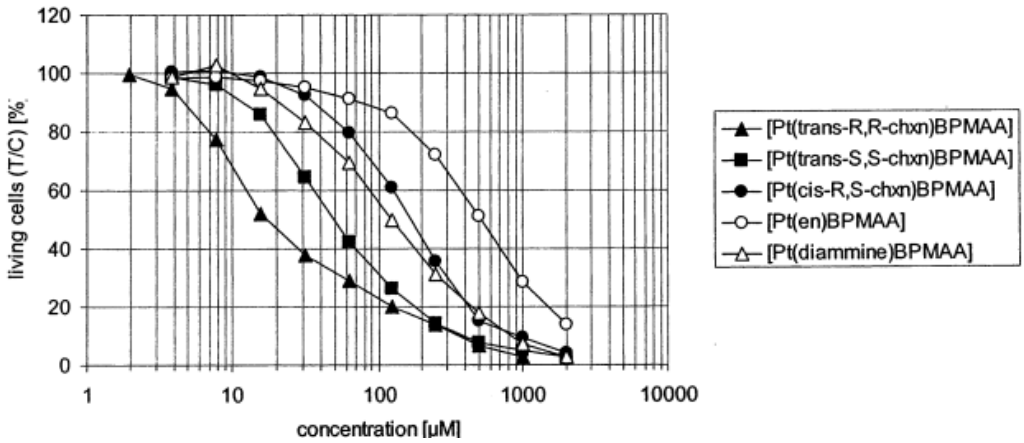


Fig. 9. Concentration-response curves of [(bis(phosphonomethyl)amino-κN)acetato-κO(2-)]platinum(II) complexes in ovarian cancer cells (CH1) after exposure for 96 h (T/C - ratio of live cells to tumor cells) [69].

Table 1.

Antiproliferative activity of [(bis(phosphonomethyl)amino-*κ*N)acetato-*κ*O(2-)]platinum(II) complexes in comparison with known platinum-based anticancer drugs on the CH1 ovarian cancer cell line [69].

Complex	IC_{50}, μM
[Pt(NH_3)$_2$BPMAA]	128 ± 22
[Pt(en)BPMAA	532 ± 154
[Pt(*cis*-R,S-chxn)BPMAA]	169 ± 56
[Pt(*trans*-S,S-chxn)BPMAA]	52.4 ± 10.9
[Pt(*trans*-R,R-chxn)BPMAA]	20.6 ± 1.1
cisplatin	0.15 ± 0.01
carboplatin	2.5 ± 0.4
oxaliplatin	0.27 ± 0.07

Both compounds [Pt(*trans*-chxn)BPMAA] demonstrate higher antitumor activity than the corresponding analogue [Pt(*cis-R*,Schxn) BPMAA], and the complex [Pt(*trans-R,R*-chxn)BPMAA] is the most active among the three isomers. This is consistent with the effectiveness of the oxaliplatin isomers. In addition, both complexes [Pt(*trans*-chxn)BPMAA] demonstrate significantly higher activity compared to [Pt(NH_3)$_2$BPMAA] and [Pt(en) BPMAA], while the *cis*-isomer [Pt(*cis*-R,S-chxn)BPMAA] has either similar or even slightly lower activity than [Pt(NH_3)$_2$BPMAA]. Thus, the antitumor activity of the studied complexes decreases in the following order: [Pt(*trans*-R,R-chxn)BPMAA] > [Pt(*trans*-S,S-chxn)BPMAA] > [Pt(NH_3)$_2$BPMAA] ≥ [Pt(-*cis*-R,S-chxn)BPMAA] > [Pt(en)BPMAA].

The advantage of [Pt(*trans*-R,R-chxn) BPMAA] was also confirmed when studying the *in vivo* effect of the synthesized complexes on white mice infected with murine leukemia L1210. In this tumor model, the survival of experimental animals is significantly increased by the administration of [Pt-(*trans*-R,R-chxn) BPMAA], which is reflected in T/C values >250% at the optimal dosage.

The authors believe that the activity of BPMAA complexes with chxn will be preserved also in these cisplatin-resistant cells and relevant tumor models *in vivo*.

In recent years, with the development of modern nanotechnology, interest has arisen in the synthesis and study of metal nanoparticles (NPs) with biological activity. The size of nanoparticles or nanosystems used in chemistry, medicine, and biotechnology is of great importance, since it determines the permeability, activity, solubility, and toxicity of nanoparticles [70, 71]. A feature of such particles is that they easily form complex compounds with organic ligands, which have new properties compared to macrocompounds. Thus, nanoparticles can bind to nucleic acids, proteins, integrate into membranes, penetrate into cellular organelles, changing the functions of biostructures. A number of works have been devoted to the study of the properties of metals in the ultradisperse range in the form of powders, solutions and suspensions [72, 73]. It has been shown that non-aggregated metal nanoparticles have antimicrobial, antiviral, and antioxidant activity [75–76]. A number of authors have shown that the biological activity of metal nanoparticles is determined not only by their size, but also by their shape. For example, dendritic and spindle-shaped nanoparticles have higher cytotoxicity than spherical ones [77]. Thus, the totality of the above facts indicates that metal nanoparticles have biological activity, the severity of which depends on their size, shape, surface structure, aggregate state, chemical composition, solubility and a number of other factors [66, 78]. Among the various forms of nanoscale materials, solutions of metal nanoparticles are of interest. Their advantage lies in a relatively narrow size distribution (up to 12 nm) and shape (mostly spherical) and a long retention time of biological activity. Therefore, the use of stable metal nanoparticles in aqueous solutions is promising in various fields of biology, veterinary medicine and medicine. In this regard, the search for new ways to form monodisperse systems with controlled nanoparticle size is relevant.

One of the most interesting chemical elements used as nanoparticles for biomedical purposes is cobalt Co(II) and its oxide. Despite its physiological role as a cofactor of vitamin B_{12}, cobalt cannot be considered only as an es-

sential element. Cobalt-based nanoparticles in general and cobalt oxide nanoparticles in particular are currently attracting great interest due to their unique properties, which depend on size, shape and potential applications in pigments, catalysis, sensors, electrochemistry, magnetism, energy storage, etc. [79]. Cobalt nanoparticles have the ability to penetrate cells very quickly [80], which has attracted the attention of researchers to biomedical application systems based on cobalt nanoparticles. However, the use of cobalt nanoparticles is limited due to their toxicity, and this problem can be overcome by coating magnetite/maghemite nanoparticles with polymeric organophosphorus compounds [81, 82]. The binding of organophosphorus molecules to the inorganic phase occurs as a result of the formation of strong M-O-P bonds through heterocondensation and coordination. Homocondensation with the formation of P-O-P bridges is unlikely, and such bridges are unstable in the presence of water. Organophosphorus coupling agents react specifically with metal oxide surfaces and promote only the formation of a monolayer. The resulting monolayers are highly stable under physiological conditions.

Using this approach, Chattopadhyay and colleagues [83] investigated the prospects of using surface-modified cobalt oxide (CoO) nanoparticles as carriers of cancer antigens in human macrophages. N-Phosphomethyliminodiacetic acid used to modify the CoO surface in order to overcome the toxic effect of CoO nanoparticles. In this case, the phosphonate group of PMIDA acts as a surface anchoring agent, and the two -COOH groups bind nonspecifically to tumor-associated antigens. Cytotoxicity studies, flow cytometric analysis, and scanning electron micrographs showed that PMIDA-coated nanoparticles significantly enhance the cellular uptake of nanoparticles and thus promote apoptosis of cancer cells.

The conjugation of PMIDA with CoO nanoparticles studied by IR spectroscopy (Fig. 10).

In the IR spectra, a decrease in the intensity of the ν(OH) band at 3440 cm^{-1} is observed, indicating the conjugation of the phosphonic group of PMIDA on CoO NPs. The presence of bands at 1750 cm^{-1} and 1050 cm^{-1}, which correspond to M–O–P and P–O vibrations, respectively, confirms the conjugation of PMIDA on the surface of the nanoparticles.

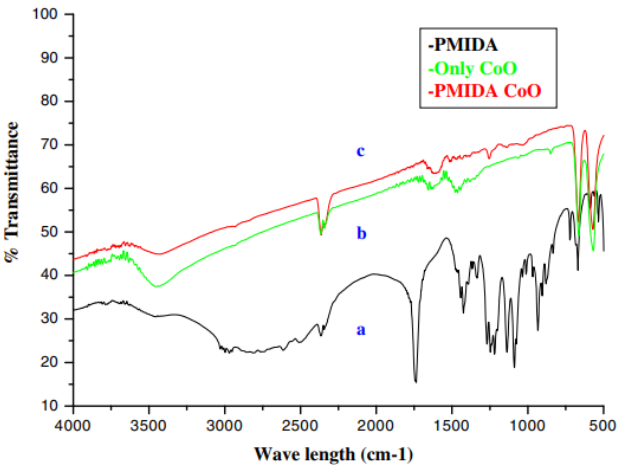


Fig. 10. IR spectra of PMIDA (a), CoO (b) and CoO nanoparticles coated with PMIDA (c) [83].

The authors carried out a study of the toxicity of CoO-PMIDA nanoparticles towards normal human lymphocytes and oral squamous epithelial cells *in vitro*. The experiments were conducted in comparison with the well-known anticancer drug doxorubicin. The study revealed no significant difference between the effects of CoO-PMIDA nanoparticles and doxorubicin: doxorubicin killed Jurkat cells (lymphoma T-cell lines) and KB cells (oral carcinoma) by 15.64%, 25.28%, 40.52% and 17.08%, 30.80%,

42.73%, respectively, at doses of 1, 5 and 10 μg/ml, while CoO-PMIDA nanoparticles killed Jurkat and KB cells by 14.2%, 21.80%, 34.28% and 12.20%, 23.58%, 35.78%, respectively. However, PMIDA-coated CoO nanoparticles did not have a toxic effect on normal human lymphocytes and oral epithelial cells, while doxorubicin had a toxic effect on normal cells. This selectivity significantly enhances the therapeutic potential of nanoparticles by cells, and thus facilitates cancer cell apoptosis.

The authors proposed a model in which cytotoxicity against oral cancer is manifested by activation of normal human macrophages using the CL-PMIDA-CoO complex (Fig. 11).

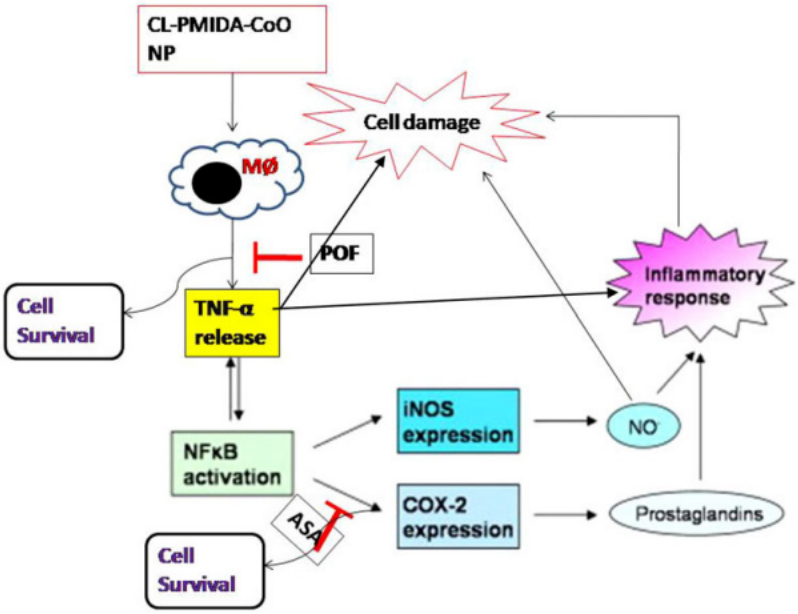
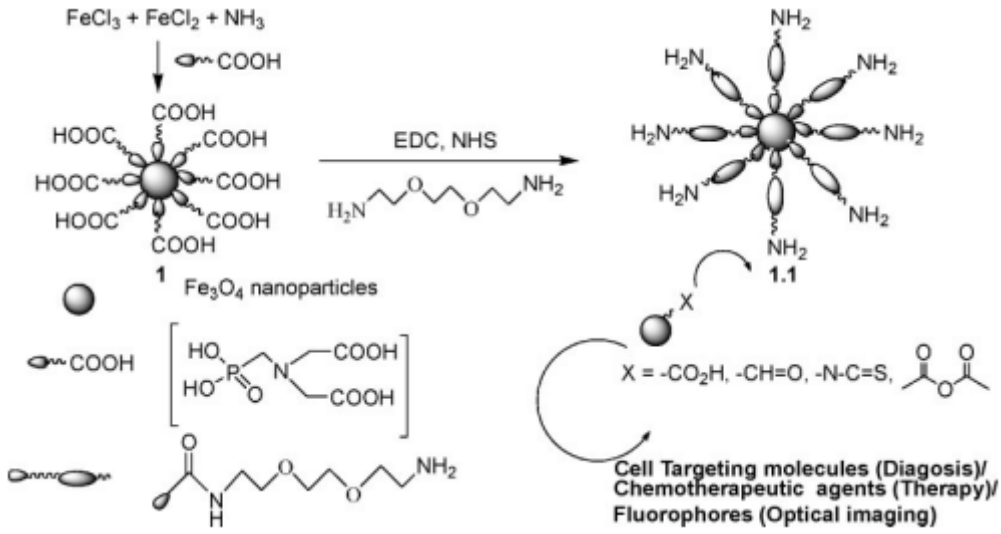


Fig. 11. Proposed pathway of action of CL–PMIDA–CoO nanoparticles as antitumor agents [83].

This model allows for basic studies of tumor lysate delivery to macrophages and immunostimulation mediated by activated macrophages against oral cancer cells. To identify factors involved in anticancer activity, the researchers used pentoxifylline (POF), a potent TNF-α blocker, in the experiment (TNF-α – tumor necrosis factor extracellular protein and multifunctional pro-inflammatory cytokine synthesized by monocytes and macrophages). It was found that TNF-α is responsible for the destruction of KB cells, and in the presence of aminocarboxyphosphonate, the production of NO, which is responsible for the destruction of cancer cells, is increased. From this perspective, the authors believe that CL–PMIDA–CoO_{NPs} indirectly stimulate TNF-α and thus exhibit anticancer immunotherapy (Fig. 12). Functionalization of the CoO surface with –COOH and $–NH_2$ groups facilitates the conjugation of nanoparticles with anticancer drugs through amide bonds, which are effectively taken up by cancer cells. Thus, PMIDA-coated CoO nanoparticles may have great promise for cancer treatment due to the lack of lethal toxicity to normal (living) cells.



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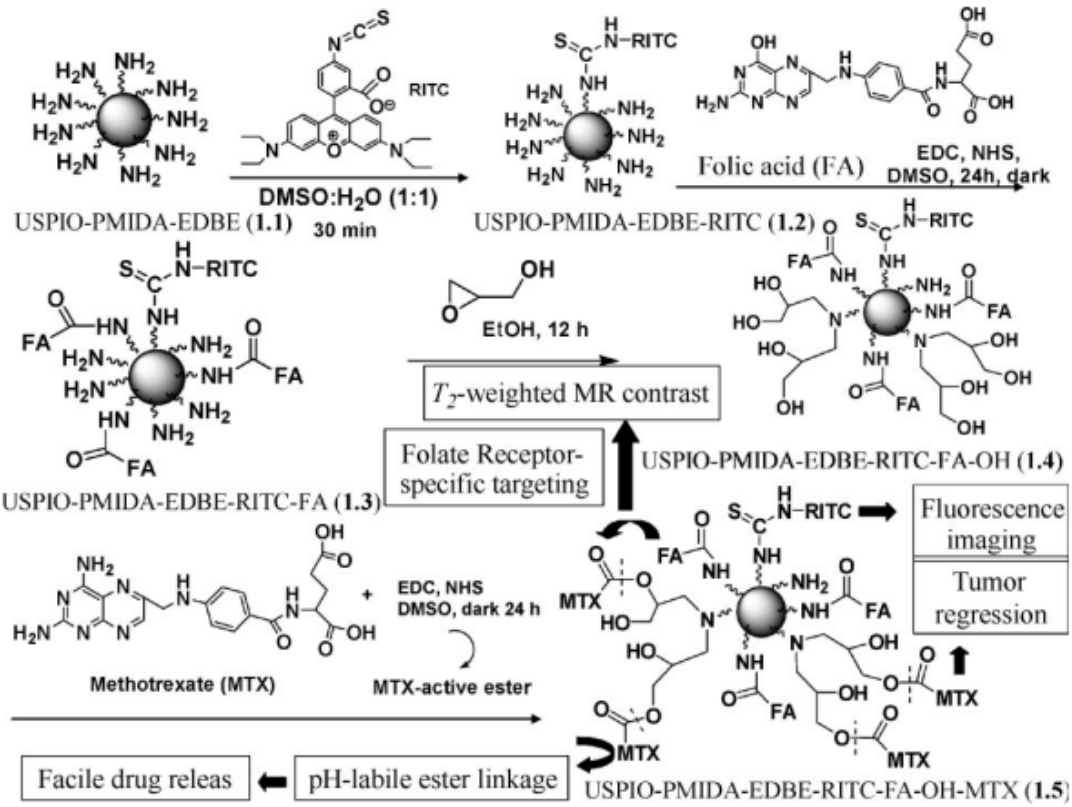

b

Fig. 12. Scheme of the synthesis of functionalized paramagnetic magnetite nanoparticles (a) and a multifunctional nanomedical platform for magnetic resonance/optical imaging of cancer cells (b) [84].

No less interesting results were obtained in the study of a nanosystem based on an ultrasmall superparamagnetic iron oxide nanocore (USPIO) modified with a hydrophilic, biocompatible and biodegradable coating - N-phosphonomethyliminodiacetic acid to create a multifunctional nanoprobe that can selectively target, detect and kill cancer cells [84]. The synthesis of the nanosystem consists of 4 stages. First, ultrasmall superparamagnetic magnetite nanoparticles were synthesized by alkaline chemical co-precipitation of Fe^{3+} and Fe^{2+} in the presence of PMIDA (Fig. 12, a).

PMIDA-coated magnetite nanoparticles (USPIO-PMIDA, 1) served as the base material to enable magnetically guided drug delivery and to enhance magnetic resonance contrast. Then, a fluorescent dye, rhodamine B isothiocyanate (RITC), was linked to the amino-derivative substrate of USPIO-PMIDA (1.1) to provide optical imaging capabilities. In step 3, folic acid (FA) was conjugated to 1.1 to target cancer cells overexpressing the folate receptor (FR). Finally, the folate analog methotrexate (MTX) was linked to the nanoparticle surface via a pH-labile ester linkage to facilitate drug release within acidic tumor endosomes and to initiate apoptosis (Fig. 12, b).

The synthesized USPIO–PMIDA–EDBE–RITC–FA–OH–MTX (1.5) nanoparticles are biocompatible and biodegradable because they are composed of biodegradable and biocompatible components. These functional nanoparticles are stable in aqueous buffer solutions, have good cellular targeting ability, and their relatively simple synthesis process is scalable.

To further demonstrate the anticancer potential of USPIO-PMIDA-EDBE-RITC-FA-OH-MTX, in vitro cell uptake experiments were performed. FR-positive human cervical carcinoma HeLa cells were selected as the target cell line. Magnetic-activated cell sorting (MACS) was used to preliminarily quantify the uptake of nanoparticles into target cells.

Cellular uptake of conjugates containing folic acid as the targeting molecule was significantly improved compared to their non-targeted controls, demonstrating active targeting of magnetite nanoparticles through the interaction between folate groups on the surface of the nanoparticles and receptors of HeLa cells (Fig. 13).

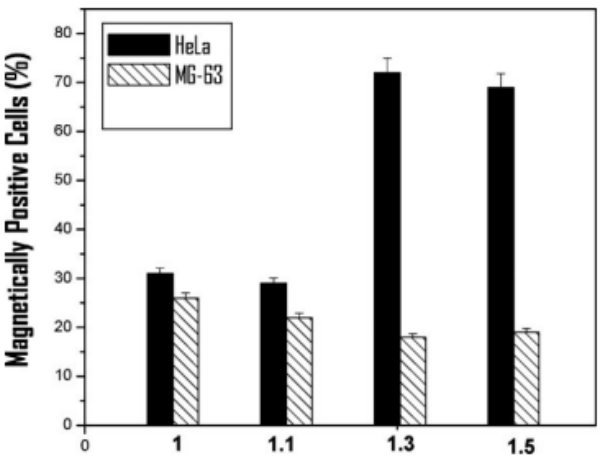

Fig. 13. Quantitative assessment of the uptake of USPIO–PMIDA–EDBE–RITC–FA–OH–MTX nanoparticles by FR-positive HeLa and FR-negative MG-63 cell lines [84].

To confirm receptor specificity for the conjugate, the uptake of 1.5 by HeLa cells was also compared with that of the FR-negative human osteosarcoma cell line MG-63. The uptake of nanoparticles by HeLa cells was much greater than that of their non-targeted counterparts. In contrast, the uptake of folate-targeted nanoparticles by MG-63 cells was significantly lower and similar to that of non-targeted controls.

Magnetic resonance phantom imaging was used to assess the detectability by MRI and to further confirm the association of these nanoparticles with FR-overexpressing HeLa cells. HeLa cells cultured with FA-functionalized nanoparticles had a shorter T_2 relaxation time (higher relaxivity) than those cultured with the unfunctionalized counterpart due to the enhanced magnetism. The results presented here show the high potential of the obtained nanocarriers as a cancer-targeting MRI probe.

In vitro drug release experiments of 1.5 conducted at different pH values (pH = 2.0 - 7.4) showed that the release rate was much higher in the lower pH range (pH 2–5) with negligible drug release at physiological pH. This suggests that USPIO-PMIDA-EDBE-RITC-FA-OH-MTX would be released more in acidic tumor regions than in normal tissues. When particles accumulate inside cells via FR-mediated endocytosis, reduced pH values may induce further accelerated release within acidic endosomes of tumor cells.

When exposed to drug-modified nanoparticles at low concentrations (0.01 mg/ml) after 24 hours, cancer cells showed a noticeable trend towards decreased viability. To test whether USPIO–PMIDA–EDBE–RITC–FA–OH–MTX could induce cell death by initiating apoptosis, HeLa cells were exposed to 1.0 mg/ml USPIO–PMIDA–EDBE–RITC–FA–OH–MTX for 0.5 h and incubated at 37°C for 24 h. The results showed intense red fluorescence in the cytoplasm of cells treated with folate-targeted nanoparticles, demonstrating cellular internalization via receptor-mediated endocytosis. To examine nuclear morphology and identify nuclear alterations associated with cell death, cells were additionally stained with 4'-6-diamidino-2-phenylindole (DAPI), a nuclear dye that exhibits strong blue fluorescence upon binding to DNA. Cells treated with USPIO-PMIDA-EDBE-RITC-FA-OH-MTX exhibited typical apoptotic morphology, which included condensed nuclei, membrane blebs, and the formation of apoptotic bodies.

Other areas of application of aminocarboxyphosphonates.

Aminocarboxyphosphonates have promising applications for flotation separation of minerals [85–87]. For example, [86, 87] proposed the use of N,N-bis(phosphonomethyl) glycine as a highly effective dolomite depressant for the flotation of magnesite from dolomite using sodium oleate (NaOL) as a collector. Using an optimized reagent system consisting of 80 mg/L NaOL, 30 mg/L BPMG, and pH 10.0, concentrates with MgO and CaO contents of 42.81% and 4.35%, respectively, were obtained with their recoveries of 80.85% and 23.67%, respectively. Both single mineral and binary mixed mineral tests clearly confirm the exceptional depressant capabilities of BPMG in dolomite flotation, while demonstrating negligible impact on magnesite flotation. At the same time, the depressant effect of BPMG on dolomite demonstrates excellent selectivity, ensuring maximum MgO recovery with minimal CaO recovery.

Contact angle measurements demonstrate hydrophobic limitations inherent to the natural minerals magnesite and dolomite. However, adsorption of NaOL on mineral surfaces enhances the hydrophobic characteristics of both minerals. In the presence of BPMG, the differential adsorption behavior of NaOL on mineral surfaces gives magnesite and dolomite distinct wetting properties. Zeta potential measurements showed that both magnesite and dolomite have negative zeta potentials

under alkaline conditions (pH≈10.0). Therefore, BPMG must overcome electrostatic repulsion during adsorption on mineral surfaces. BPMG exhibits increased adsorption affinity to the surface of dolomite minerals, which can be attributed to the difference in atomic radii of calcium and magnesium in the semi-closed state on the mineral surface. Fourier transform infrared spectroscopy analysis confirmed that the strong interaction between BPMG and dolomite can be attributed to the chemical interaction between the phosphonic groups in BPMG and the metal atoms on the surface of the dolomite mineral. XPS analysis confirmed the specific interaction of BPMG with calcium rather than magnesium sites on the dolomite surface. Coordination between the $-PO_3$ groups in BPMG and the calcium sites leads to the formation of Ca–BPMG complexes, thereby facilitating selective adsorption on mineral surfaces.

Based on the conducted studies, the authors proposed possible adsorption models for BPMG and NaOL on dolomite and magnesite (Fig. 14).

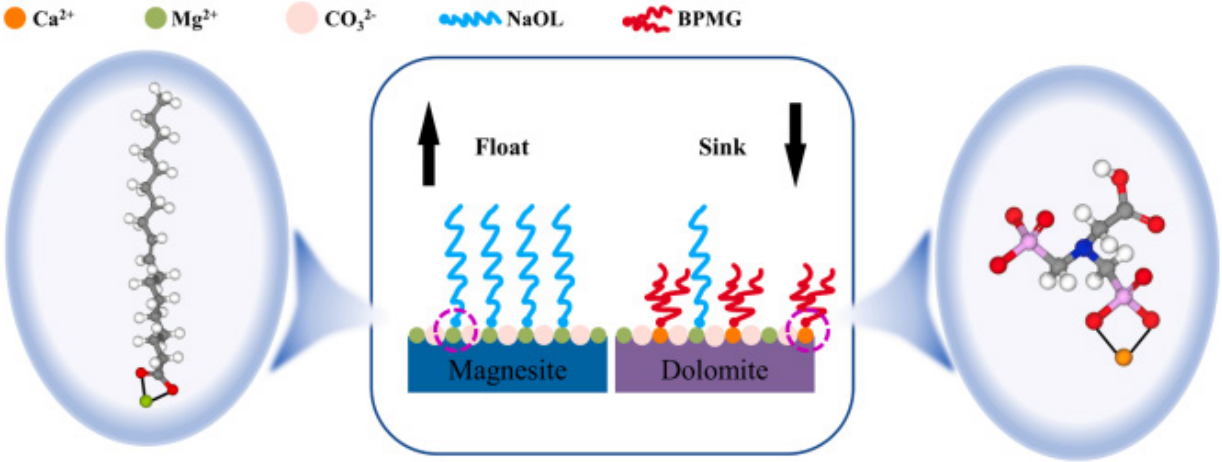

Fig. 14. Model of adsorption of BPMG and NaOL on magnesite and dolomite [86].

BPMG is intensively chemisorbed on the dolomite surface through calcium sites. In addition, the weak interaction between BPMG and magnesite has little effect on the adsorption of NaOL on the magnesite surface, maintaining the excellent flotation of magnesite. For dolomite, the high adsorption of BPMG on its surface and the formation of Ca-BPMG chelates, which accumulate on the dolomite surface, possibly due to steric hindrance, significantly reduce the adsorption of NaOL.

In [87], the use of N-(phosphonomethyl) iminodiacetic acid (PMIDA) as an environmentally friendly depressant for the selective flotation of galena and sphalerite was investigated. PMIDA microflotation tests were performed to evaluate its effectiveness. In addition, the mechanism of PMIDA depression was analyzed using solution chemistry calculations, zeta potential measurements, contact angle determination, X-ray photoelectron spectroscopy, and density functional theory calculations. Solution chemistry calculations showed that the presence of PMIDA in the pulp (C_{PMIDA} =

120 mg/l, pH = 8) in the form of $PMIDA^{3-}$ ions optimized the depressive effect on the sphalerite surface, while galena demonstrated excellent flotation. The addition of PMIDA increased the hydrophilicity of the sphalerite surface and made it difficult for xanthate to adsorb on the sphalerite surface. However, the introduction of PMIDA had minimal effect on the surface hydrophilicity and adsorption of xanthate on galena, thereby promoting the selective separation of sphalerite and galena. Zeta potential measurements showed that the adsorption capacity of xanthate on the sphalerite surface was significantly reduced after PMIDA treatment. X-ray photoelectron spectroscopy analysis showed that the adsorption of PMIDA on the sphalerite surface was associated with the formation of a stable chemical bond between the oxygen atoms of the phosphonic acid group and the surface zinc atoms of sphalerite. That is, PMIDA exhibited a higher adsorption affinity for the sphalerite surface compared to the galena surface, thereby selectively inhibiting the flotation of sphalerite.

Metal phosphonates, as a subclass of coordination polymers, exhibit acidic properties due to the presence of groups such as POH, SO_3H, COOH, N^+-H in their molecules. The combination of these properties with electrocatalytically active transition metals makes them very attractive in the field of fuel cells and electrolyzers, as potential proton conductors and/or precursors of electrocatalysts [88, 89]. The authors [90] obtained a series of Co^{2+} and Sn^{4+} phosphonates based on glycine-N,N-bis(methylene)phosphonic acid (BPMGLY) by hydrothermal synthesis. In the case of the tin derivative, the amorphous compound $Sn(C_4H_{11}O_8NP_2)_{0,75}Cl_{2,5}(H_2O)_{2,5}$($Sn^{4+}$-BPMGLY) is formed. Its pyrolytic treatment at 700 °C in air led to the formation of amorphous pyrophosphate (Sn^{4+}-BPMGLY-700). As for cobalt phosphonates, three crystalline phases with the composition $[Co(C_4H_{11}O_8NP_2(H_2O)_2]\cdot nH_2O$ (n = 0; 2) were obtained. All synthesized compounds were studied as proton conductors in a wide range of temperatures and humidity conditions. Sn^{4+} derivatives at 95°C and 95% relative humidity showed the highest conductivity values of $7.99\cdot10^{-4}$ and $6.63\cdot10^{-3}$ $S\cdot cm^{-1}$ for Sn^{4+}-BPMGLY and Sn^{4+}-BPMGLY-700, respectively, and cobalt aminocarboxyphosphonates were used as precursors for base metal catalysts by pyrolysis of the complexes at different temperatures in a 5%-H_2/Ar atmosphere and investigated as electrocatalysts for oxygen and hydrogen evolution reactions (OER or HER), and oxygen reduction reactions (ORR).

A group of Indian scientists led by B.V. Appa Rao first conducted a series of studies on the protection of carbon steel surfaces from corrosion using a synergistic mixture of environmentally friendly N,N-bis(phosphonomethyl)glycine and zinc ions [48, 91]. In [91], published in 2008, a study of an environmentally friendly ternary inhibitor composition consisting of the binary BPMG-Zn^{2+} system as the primary synergist and ascorbate ions as a secondary synergist for protecting carbon steel from corrosion in a low chloride environment was presented. The fact is that N,N-bis(phosphonomethyl)glycine in combination with Zn^{2+} in almost neutral aqueous media, although an effective corrosion inhibitor, requires relatively high concentrations of both BPMG and Zn^{2+} (≥ 80 ppm). Therefore, to improve the inhibition efficiency of this system at lower concentrations, sodium ascorbate was added as a second synergist, since the ascorbate ion contains five hydroxyl and one

carboxyl group and forms strong complexes with Fe^{3+}. It turned out that the effect of adding ascorbate was quite significant. While the binary system BPMG-Zn^{2+} (BPMG:Zn^{2+} = 1:4, $C_{BPMG} = C_{Zn2+}$ = 40 ppm) inhibited the corrosion of carbon steel with an inhibition efficiency (IE) of 90%, the addition of only 25 ppm of ascorbate to the above system provided an IE of 95%. The ternary inhibitor composition was found to be effective in the pH range of 5–11 and even at pH=11 it had excellent inhibition efficiency, a condition at which all other phosphonate-based systems fail.

Potentiostatic polarization studies of the ternary inhibitor system showed that the corrosion potential shifts from -350 to -371 mV in the cathodic direction, and the corrosion current decreases from 6.16 mA·cm^{-2}, observed in the case of the control solution, to 0.94 mA·cm^{-2} in the presence of the inhibitor. Such a significant decrease in the corrosion current indicates a decrease in the corrosion rate in the presence of the inhibitor. Comparison of the Fourier transform infrared spectra of pure BPMG and ascorbic acid with the corresponding IR spectra of surface films formed in the presence of the inhibitor showed the formation of Fe(III) complexes with BPMG and ascorbate on the steel surface (bathochromic shift of the ν(COO^-) vibration from 1732_{BPMG} ($1676_{ascorbate}$) cm^{-1} to 1623 cm^{-1} in the film; shift of ν(PO_3) 1181 cm^{-1} → 1140 cm^{-1}). A small peak at 1323 cm^{-1} indicates the formation of $Zn(OH)_2$ on the film surface.

Based on the results of the research, the authors proposed a plausible mechanism for corrosion inhibition:

1. Carbon steel undergoes initial corrosion with the formation of Fe^{2+} ions at the anodic sites: $Fe \rightarrow Fe^{2+} + 2e^-$;

2. Then $Fe2^+$ undergoes oxidation in the presence of oxygen: $Fe^{2+} + O_2 \rightarrow Fe^{3+} + e^-$;

3. A reduction reaction occurs at the cathode in a neutral and alkaline environment: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$;

4. Before the formation of a protective film, iron oxides, namely γ-Fe_2O_3 and Fe_3O_4, are formed on the metal surface;

5. BPMG and ascorbate ions react with Zn^{2+} ions present in the bulk of the solution to form a complex [Zn(II)–BPMG–ascorbate] and this complex diffuses to the metal surface. The formed zinc complex then reacts with Fe^{3+} ions available at the anode sites to form hetero- and polynuclear complexes [Fe(III)–BPMG–ascorbate];

6. Zn^{2+} ions released in the previous reaction combine with OH- ions present at the cathode, forming a precipitate $Zn(OH)_2$: $Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2\downarrow$;

7. Thus, the ternary inhibitor system suppresses corrosion by controlling both the anodic and cathodic reactions. A protective film is formed on the metal surface, which consists of iron oxides, $Zn(OH)_2$ and [Fe(III)–BPMG–ascorbate].

The effectiveness of this ternary inhibitor composition at high pH environments is due to the stability of the [Fe(III)–BPMG–ascorbate] complex formed on the metal surface and the presence of optimal amounts of $Fe(OH)_3$ and $Zn(OH)_2$ in the surface film.

Continuing their research, the authors found that the binary BPMG-Zn^{2+} system is an effective corrosion inhibitor for carbon steel in low-chloride aqueous media in the pH range of 5 to 8, which is commonly used for cooling water systems. The inhibitor mixture acts as a mixed-type inhibitor, controlling both anodic and cathodic reactions [48].

In [92], four 3d–4f heterometallic coordination polymers based on N-(phosphonomethyl) iminodiacetic acid were synthesized: [$LnFe^{III}Fe^{II}_6(HPMIDA)_6]\cdot 2H_2O$ (Ln = Eu, Dy, Ho, Y), which were investigated as heterogeneous catalysts in the Knoevenagel condensation. This is an important reaction of the C–C coupling of a carbonyl group with a compound containing an activated methylene group and is widely used for the synthesis of fine chemicals and pharmaceuticals.

The Eu complex was tested as a heterogeneous catalyst in the Knoevenagel condensation of benzaldehyde with malononitrile in 1.0 ml of toluene at 60°C (Fig.15).

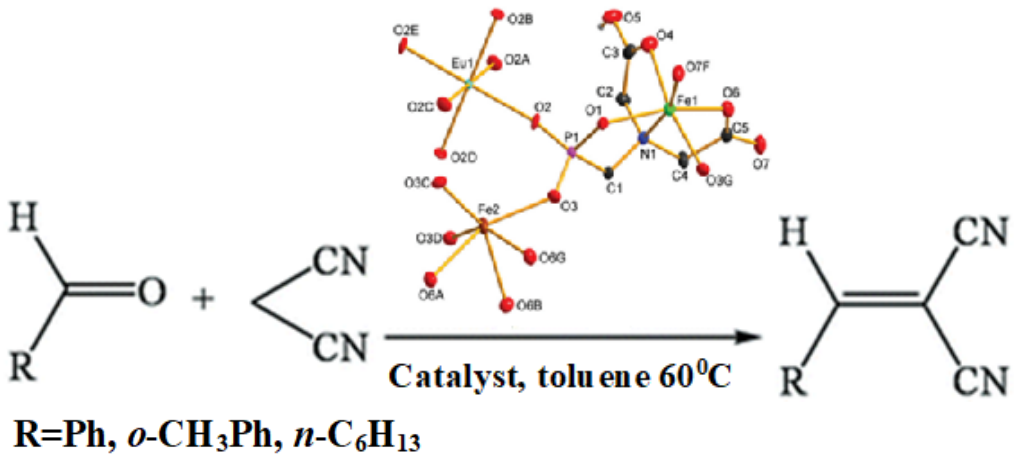

Fig.15. Scheme of heterogeneous catalysis in the Knoevenagel condensation of benzaldehyde with iminodiacetic acid [92].

The material showed catalytic activity in this reaction compared to a control experiment performed using the same conditions but without the addition of catalyst. After 27 hours of reaction, the conversion of benzaldehyde was 27%, while in the control experiment the conversion was only 7%. In this case, the yield of the main product in the reaction with the catalyst was 98%, while in the condensation reaction without the catalyst the yield was 89%. Benzoic acid was formed as a minor product. After the reaction, the heterogeneous catalyst was filtered, washed with toluene, and used in a second catalytic cycle under the same experimental conditions. After 27 hours, the benzaldehyde conversion was 32%, and in the third and fourth catalytic cycles using [$EuFe^{III}Fe^{II}_6(HPMIDA)_6$], the benzaldehyde conversion was 28% and 8%, respectively. Thus, the synthesized heterometallic complex can be recycled and reused for at least two more catalytic cycles without loss of catalytic activity. The substrate scope was also extended to o-tolualdehyde and heptaldehyde. The reaction with *o*-tolualdehyde and malononitrile gave an aldehyde conversion of 20% in 4.0 mL toluene at 60°C. No side products were detected, indicating that the reaction was selective for the Knevenagel condensation product. The reaction of malononitrile with heptanoaldehyde in 1.0 mL of toluene at 60 °C

gave 57% conversion of the aldehyde, but the reaction was not selective, as heptanoic acid was formed as a by-product. Complexes with Dy, Ho, and Y show similar catalytic activity, but the europium-containing complex is the most effective.

The authors proposed a mechanism for the catalytic activity of the complexes. The synthesized MOFs contain only Lewis acid centers, and the Knoevenagel condensation is traditionally catalyzed by basic catalysts. However, the organometallic framework $LnFe^{III}Fe^{II}_6(HPMIDA)_6$ works as a Brønsted base in the reaction and deprotonates the active methylene group of malononitrile. Thus, a defec Brønsted acid site is formed in the MOF, which, together with the neighboring Lewis acid (iron and rare earth ions), facilitates the activation of both reagents in the Knevenagel condensation. The deprotonated active methylene group of malononitrile attacks the aldehyde, and then, after re-protonation and dehydration of the adduct, the Knoevenagel condensation product is formed. The catalytic properties of heterometallic complexes indicate that these types of compounds are heterogeneous catalysts for the Knoevenagel condensation with high selectivity.

CONCLUSIONS. The polydentate nature of aminocarboxyphosphonate ligands due to their diverse coordination sites and different affinities for different metal centers allows for the preparation of new compounds with a number of unique properties. This opens up prospects for obtaining a large number of highly stable complexes of various cyclic structures, both in composition and shape, in particular heteronuclear complexes, the internal coordination sphere of which includes two or more different metals simultaneously. In the synthesis of heteronuclear complexes based on complexones, the conformational ability of ligands to bind metals of different natures (for example, d- and f-elements) into a single coordination site is used. The effectiveness of such compounds as materials for new technologies and medicines is obvious. In recent years, aminocarboxyphosphonic acids and their metal complexes have attracted significant attention from researchers around the world due to their broad potential for practical use. Aminocarboxyphosphonates of transition metals are currently used in agronomy as plant growth regulators and herbicides. Their potential application in materials chemistry as functional materials has also been revealed due to the presence of a number of useful properties: high porosity, photoluminescence, catalytic, nonlinear optical, and magnetic properties, etc. Due to these properties, aminocarboxyphosphonates can be used for the removal of heavy metals (Cd, Pb, Cr, La, As) from wastewater or groundwater, for the production of surface-modified nanoparticles with antitumor activity, for flotation separation of minerals, for the creation of a protective film during steel corrosion, for chelation therapy, molecular imaging and catalysis.

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ПЕРСПЕКТИВИ ПРАКТИЧНОГО ЗАСТОСУВАННЯ АМІНОКАРБОКСИФОСФОНАТІВ ТА ЇХНІХ МАТАЛОКОМПЛЕКСІВ (огляд)

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В оглядовій статті узагальнено та систематизовано багаторічні літературні дані щодо можливих сфер застосування амінокарбоксифосфонових кислот та металокомплексів на їхній основі. Показано, що амінокарбоксифосфонати з огляду на їхній широкий спектр функціональних властивостей, зокрема таких як фотолюмінесценція, магнітні властивості, біологічна активність, можуть знайти застосування у найрізноманітніших сферах. Як самі амінокарбоксифосфонові кислоти, так і їхні комплекси здатні виступати основою для біологічно активних речовин в агрономії – як синтетичні регулятори росту, як ефективні препарати для збільшення екстрагованого цукру з різних рослин (цукрова тростина, солодка картопля, цукровий буряк, диня та ін.) та препарати для прискорення дозрівання плодів за несприятливих погодних умов. Однією з найцікавіших сфер використання амінокарбоксифосфонатів та наночастинок на їхній основі для біомедичних цілей є створення прекурсорів для розроблення нових протипухлинних препаратів. Завдяки високій пористості ці матеріали можна використовувати в екології для очищення ґрунтової та/або питної води від важких металів. Висвітлені в роботі підходи щодо модифікації координаційного середовища, варіації природи металів і лігандного оточення можуть бути використані як модель для розроблення нових координаційних полімерів та MOF-структур як екологічно чистих депресантів для селективної флотаційної сепарації мінералів (доломіту, галеніту, сфалериту). Амінокарбоксифосфонати металів як підклас координаційних полімерів завдяки наявності в молекулах таких груп, як POH, COOH, N^+-H демонструють кислотні властивості, поєднання яких з електрокаталітично-активними перехідними металами робить їх привабливими в області паливних елементів і електролізерів. Вони можуть бути використані як потенційні протонопровідники та/або прекурсори електрокаталізаторів, гетерогенні каталізатори у конденсації Кневенаґеля з високою селективністю.

Ключові слова: комплекси, амінокарбоксифосфонати, 3d-, 4f-метали, біологічна активність, каталізатор, очищення від важких металів, практичне застосування.

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