ABSTRACT AND REFERENCES

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INVESTIGATION OF THE STRUCTURE AND SORPTION PECULIARITIES OF COBALT AND URANIUM IONS BY NANOCOMPOSITES BASED ON MONTMORILLONITE AND TETRAETHOXYSILANE (p. 6-11)

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The structure and adsorption characteristics of silica- and montmorillonite-based nanocomposites are investigated. Tetraethoxysilane was used as a source of silica. The porous structure was investigated by the method of low-temperature nitrogen adsorption.

According to the research results, it was found that a small amount of silica in nanocomposite samples (14 % SiO_2) contributes to the formation of material with a larger specific surface area and greater number of meso- and macropores compared to original montmorillonite. This, in turn, leads to a better diffusion of ions of different nature into the nanocomposite structure. An increase in the silica content (up to 57 % SiO_2) allows obtaining microporous samples with a large specific surface area.

It was determined that the increase of the montmorillonite content in the investigated samples contributes to the improvement of the adsorption properties of nanocomposites in relation to the removal of cobalt(II) ions from the aqueous medium. At an optimum silica content (3–14 % SiO_2), the experimental samples retain high values of maximum cobalt adsorption (14 mg/g), as well as original montmorillonite. It was also found that an increase in the silica concentration in the samples increases the efficiency of removal of uranium(VI) ions from the aqueous medium (from 12 mg/g in original montmorillonite to 25 mg/g for nanocomposites with a silica content of 57 %). This is due to, first, an increase in the specific surface area of the samples, and secondly – an increase in the number of surface hydroxyl groups, which more selectively remove uranium from solutions. Thus, selection of the chemical composition of nanocomposites based on silica gel and montmorillonite allows regulating porous structures and surface chemistry, and thus increasing the sorbent efficiency depending on the task.

Keywords: porous structure, template-free synthesis, aluminosilicate adsorbents, structural modification, cobalt adsorption, uranium adsorption.

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"THE POPCORN EFFECT": OBTAINING OF THE HIGHLY ACTIVE ULTRAFINE NICKEL HYDROXIDE BY MICROWAVE TREATMENT OF WET PRECIPITATE (p. 12-20)

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Nickel hydroxide is widely used as an active material of supercapacitors. The most active are samples of $Ni(OH)_2$ with (α+β) layered structure synthesized in a slit diaphragm electrolyzer. However, the processes that occur during filtering and drying, negatively impact electrochemical activity. The influence of microwave treatment of different times (from 0.5 to 5 min) on the structure, surface morphology and porous structure, and also on the electrochemical properties of nickel hydroxide samples prepared in a slit diaphragm electrolyzer, has been studied. A hypothesis was proposed on the existence of the "popcorn effect": short-term high-power microwave irradiation of the wet sample would result in water boiling and internal explosion of the sample. Treated and untreated samples were studied by means of X-ray diffraction analysis, scanning electron microscopy and BET nitrogen adsorption-desorption. Electrochemical characteristics were studied by means of galvanostatic charge-discharge cycling in the supercapacitor regime. The existence of the "popcorn effect" has been confirmed by increased sample thickness after microwave treatment by 1.94 times, specific surface area 2.13 times, pore volume by 2.66 times, and average pore diameter by 1.46 times, It was discovered, that increasing treatment duration to 2–5 min leads to microwave drying. XRD results revealed the occurrence of ageing (crystallization) processes of nickel hydroxide during thermal drying and their absence upon realization of the "popcorn effect". This results in the formation of X-ray amorphous samples. Comparative analysis of electrochemical characteristics of treated and untreated $Ni(OH)_2$ samples was performed. An increase of specific capacity at high current densities (80 and 120 mA/cm^2) for treated samples was observed: by 10.9 % upon microwave drying, 24–42 % upon realization of the "popcorn effect". The maximum capacity of 231.1 F/g has been observed for the sample, in which the "popcorn effect" was realized the most. However, microwave treatment resulted in lower capacities at low cycling current density. This is related to the thermal treatment of the particle surface, caused by rapid boiling of water. A magnetron of a higher power is required for avoiding this negative effect.

Keywords: nickel hydroxide, specific capacity, supercapacitor, microwave treatment,specific surface area, ageing.

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ESTABLISHING THE PATTERNS IN THE FORMATION OF OXIDE FILMS ON THE ALLOY TI6AL4V IN CARBONIC ACID SOLUTIONS (p. 21-26)

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This paper reports results of studying the features of the formation of thin interference-colored oxide films on the alloy Ti6Al4V alloy in solutions of carboxylic acids. It has been established that a change in voltage on the cell corresponding to the molding dependence of the alloy depends on the anodic current density. At current densities <0.5 $A\cdot dm^{-2}$, a continuous oxide film is not formed at the alloy surface and the assigned voltage value is not reached. An increase in current density to values higher than 0.5 $A\cdot dm^{-2}$ predetermines a linear change in voltage over time with followed by reaching the assigned magnitude U. The maximum film thickness for these conditions is defined by the voltage magnitude and does not depend on the electrolysis mode. Color of the oxide film is defined by the specified value for the molding voltage and does not depend on current density, nature and concentration of carboxylic acid. A match between the molding dependences of oxidation obtained in different electrolytes suggests that the formation of oxide proceeds in line with the same mechanism. The obtained data are explained by the fact that the formation of oxide under the galvanic static mode takes place under conditions of the presence of a constant potential gradient in the oxide film. An increase in the voltage magnitude applied to the cell predetermines a proportional increase in the maximum oxide thickness, since it leads to an increase in the amount of electricity passed through the cell and a corresponding increase in the mass of the oxidized metal. Results of the study into determining the effect of the nature of carboxylic acid on the formation process of an oxide film on the alloy Ti6Al4V using the method of electrochemical oxidation have demonstrated that the nature of the electrolyte does not affect the characteristics of its formation. The obtained data allow us to suggest that the choice of an electrolyte for the development of a technology for electrochemical oxidation of titanium implants should be based on the results of studying the functional properties of the obtained coatings.

Keywords: anodic polarization, electrochemical oxidation, oxide film, molding dependence, potential gradient.

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STUDYING THE EFECT OF NANOLIQUIDS ON THE OPERATIONAL PROPERTIES OF BRICK BUILDING STRUCTURES (p. 27-32)

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The study reported here has established that the ceramic facing brick is characterized by capillary porosity that increases indicators of water absorption and capillary pull, as well as efflorescence formation at its surface. In order to protect the surface of such a brick and to provide it with the improved performance properties, we have used hydrophobizing substances. We have determined experimentally that the application of the PMPhS- and AP-based hydrophobizing agents leads to a decrease in porosity by 1.2–1.3 times, in water absorption – by 1.2–2.3 times, in water absorption at capillary pull – by 1.1–3.2 times. Research into frost resistance has found that for the ceramic brick, covered with PMPhS, it increases by 15 cycles, and when treating a brick surface with AP – by 20 cycles, compared to the untreated brick (F50). By employing an electron microscopy, it was determined that the alternating freeze-thawing leads to that the brick's surface, treated with PMPhS and AP, demonstrates the formation of microcracks (in this case, water absorption increased by 42 and 28 %). By applying a method of mathematical planning of the experiment, it was found that the most effective hydrophobizing substance is the modifier that contains the nano-Al_2O_3 powder (a nano-liquid). It was determined that when treating the surface with a nano-liquid (the amount of nano-Al_2O_3 is 0.8 %), its water absorption decreases to 1.2–1.6 %, its water absorption indicator at capillary pull – to 0.08–0.12 $kg/m^2 \cdot h^{0.5}$. Using a method of defectoscopy, applying the Karsten tube, it was found that water absorption for the brick whose surface was coated with a nano-liquid reduced from 0.15 to 0.002 ml/cm^2, indicating a high level of hydrophobization. The electron microscopy method confirmed that the modification of the ceramic brick surface by the hydrophobizing nano-fluids makes it possible to compact the structure through the colmatation of pores and microcracks, which reduces the capillary pull of the brickwork. That also leads to the improved atmospheric and frost resistance of brick building structures.

Thus, there is a reason to argue about the possibility of improving the physical and technical indicators of the brick building structure by modifying the surface of the ceramic facing brick by a nano-fluid.

Keywords: ceramic facing brick, porosity, water absorption, hydrophobizing substance, nano-liquid.

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CONSTRUCTION OF A MATHEMATICAL MODEL OF EXTRACTION PROCESS IN THE SYSTEM "SOLID BODY – LIQUID" IN A MICROWAVE FIELD (p. 33-43)

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We have analyzed the extraction process in the technology of oilseed processing. This paper describes the original provisions, specificity, modern scientific schools, and the level of representation of the classic extraction process. The specificity of mathematical modeling of the extraction process, given the introduction of an additional driving force that significantly affects the kinetics of extraction in an electromagnetic field of ultra-high frequency, is considered from the classical theory of the process.

We have constructed the extraction kinetics calculation formulae, in microwave field, which develop the theory of extraction kinetics in an electromagnetic field. The paper gives an analysis of variants for the representation of a mathematical notation of the extraction process of disperse materials in an electromagnetic field of ultra-high frequency. A complete model of the mass exchange processes during extraction in a microwave field in the differential form will make it possible to generate conditions for conducting comprehensive experimental studies, which would fully define the extraction process of oilseeds.

We have theoretically substantiated the process of heat and mass exchange between the all defining objects inside an extraction unit with an electromagnetic field of ultra-high frequency. Based on material balances, we derived equations describing the basic dynamic characteristics of oil extraction mode in an extraction unit. Since the precise analytical solution to the presented mathematical model in the form of a system of differential equations in particular derivatives does not exist, the approximate solution has been proposed. It makes it possible to identify the distribution of an extractant depending on the size of fractions of raw materials, the existence and magnitude of power of the pulsed electromagnetic field of ultra-high frequency, the extractant's hydro-module, temperature, solvents, for any point in time.

Based on the experimental research into extraction of oilseed material, it was established that under the action of microwave radiation a value for the mass release coefficient during extraction of oilseed raw materials grows by an order of magnitude ($\beta=1\cdot10^{-5}$) compared to extraction without the effect of MW field ($\beta=1\cdot10^{-6}$). Oil extraction under the action of a microwave field increases to 30 %, while electricity consumption decreases by 93–97 %. The application of a microwave field would not only improve production efficiency, but reduce energy costs during process by an order of magnitude.

Keywords: extraction, microwave field, heat and mass exchange, material balance, differential equations.

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OXIDATION OF 4BROMETYLBENZENE BY OZONE IN ACETIC ACID (p. 44-50)

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The kinetics and the mechanism of ozonation of 4-bromethylbenzene in acetic acid was studied. The constants of the rate of reaction of ozone with 4-bromethylbenzene and 4-bromacetophenone at different temperatures were determined. We showed the possibility of conducting the process not only by the aromatic ring of the substrate in accordance with the Krige mechanism, but also with the formation of 4-bromacetophenone, which will be used when creating new methods of synthesis of oxygen-containing derivatives of ethylbenzene.

It was established that oxidation of 4-bromethylbenzene by ozone in acetic acid flows mainly by the aromatic ring with the formation of ozonides – peroxide products of aliphatic nature. Up to 35 % of 4-bromacetophenone and trace amounts of 1-(4-bromphenyl)ethanol were identified among the products of oxidation reaction by the side chain. The reaction of ozone with 4-bromethylbenzene in acetic acid at temperatures of up to 30 °C has the first

order by initial components and the value of constant of reaction rate does not depend on the concentration of reactants. With increasing temperature, constant of reaction rate begins to depend on the concentration of reagents, and in this case, ozone consumption increases significantly. This indicates that under experimental conditions, ozone is consumed simultaneously at different stages of oxidation. It was proved that ozonation of 4-bromethylbenzene is a complicated process, in which the substrate is oxidized by the non-chain mechanism. Ozone is consumed in two directions: in the reaction with the substrate by non-chain mechanism and by the chain mechanism at the stage of chain continuation in the reaction with the products of thermal decomposition of ozonides. This fact gives grounds to argue that at an increase in temperature, unproductive consumption of ozone will grow rapidly and, vice versa, under conditions of prevention of ozonolysis, ozone will participate in the reaction with formation of the target aromatic product.

Thus, the experimentally obtained data are the basis for the development of the process of oxidation of derivatives of ethylbenzene and creation of the foundations of technology of 4-bromacetophenone synthesis with the help of ozone. This will considerably simplify the apparatus design of the process, enhance the output of the target product and will contribute to subsequent improvement of the method of oxidative processing of reagents.

Keywords: ozone-oxygen mixture, 4-bromethylbenzene, ozonolysis, 4-bromacetophenone, acetic acid, rate constant.

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"GREEN" SYNTHESIS OF NANOPARTICLES OF PRECIOUS METALS: ANTIMICROBIAL AND CATALYTIC PROPERTIES (p. 51-58)

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The paper presents the use of agricultural products, namely grape skins, in the "green" synthesis of monometallic (Au, Ag) and bimetallic (Au–Ag) nanoparticles (NPs) from aqueous solutions of metal ions of the corresponding precursors. At present, there exist urgent problems of utilization of waste from the agro-industrial complex, rational use of nature and transition to the use of environment-friendly and energy-efficient technologies. Therefore, there is a tendency to use "green" technologies in obtaining nanomaterials that are considered environment-friendly and resource-saving.

The study has proved the efficiency of using food waste (grape skins) as a reducing and stabilizing agent in forming nanoparticles of precious metals of mono- and bimetallic structures. Biological raw materials were extracted in an aqueous medium under a short-term effect of low-temperature plasma discharges. On the basis of the complex analysis of the extract composition, it was proved that the hydroxyl, carbonyl and carboxyl functional groups of the organic compounds of the grape skin extract are responsible for the recovery of the metal ions and stabilization of the resulting NPs.

The research has proved that mono- and bimetallic NPs are formed with the following peaks: for Ag^0 (λ_{max}=440 nm), Au^0 (λ_{max}=540 nm), and Ag–Au (λ_{max}=510 nm). The size and stability of the nanoparticles obtained by the "green" synthesis were assessed in comparison with the same parameters for the plasmochemical method of nanoparticles' formation. The study has revealed antibacterial, catalytic and anti-corrosion properties of the synthesized nanoparticles. The resulting monometallic (Au, Ag) and bimetallic (Au–Ag) nanoparticles show excellent catalytic activity while recovering p-nitrophenol (4-NPh) to p-aminophenol (4-APh) in the presence of $NaBH_4$. The synthesized NPs demonstrate their antibacterial activity against gram-positive and gram-negative bacteria. The findings allow to expand the practical application of metal nanoparticles in various industries and enhance the processing and reuse of non-liquid waste.

Keywords: aqueous extract, componential composition, grapes, recovery, nitrophenol, antibacterial properties, antioxidant activity.

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STUDYING THE PHOTOCATALYTIC OXIDATION OF HYDROXYBENZENE IN AQUATIC MEDIUM ON THE PHOTOCATALIZERS SnO_2, ZnO, TiO_2 (p. 59-67)

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This paper reports results of research into photocatalytic activity of oxides SnO_2, ZnO, TiO_2 in the process of hydroxybenzene degradation in an aqueous medium with the separately considered properties of the allotrope modifications of titanium oxide (IV): anatase and rutile. The relationship has been substantiated between a decrease in the value for the width of the restricted area and an increase in the photocatalytic activity of the examined oxides. The effect has been established of the organization of agitation on an increase in the degree of hydroxybenzene degradation in an aqueous medium, which is 10–15 % on average. We have studied the influence of ratio of anatase to rutile in a photocatalyst on the hydroxybenzene degradation efficiency. It has been shown that the results obtained in the course of the study are consistent with data from the scientific literature, while opening up additional possibilities to increase the degree of hydroxybenzene oxidation in a joint application of anatase and rutile. It was established that the greatest degree of oxidation with and without agitation at an irradiation time of 60 minutes can be achieved at the content ratio of anatase to rutile of 75/25 % and is 23 % and 37 %, respectively. The use of such a composition makes it possible to increase the degree of hydroxybenzene oxidation in an aqueous medium by 11–18 %, which is 1.5–1.9 times larger in comparison with pure rutile and anatase. The results obtained led to the conclusion on that in order to reduce the time required to achieve the maximal indicators for the process of hydroxybenzene degradation, it is necessary to increase the ratio of the irradiated surface to the height of the device and to increase the Re number of the agitation process. Based on the obtained experimental data, we have established the optimum composition of a photocatalyst, which makes it possible to reach the maximal degree of hydroxybenzene recovery from solution.

Keywords: wastewater treatment, hydroxybenzene, photocatalytic activity, titanium dioxide, anatase, rutile.

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