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Abstract

The doctoral thesis describes research focusing on the use of MOF materials as adsorbents for uremic toxins and psychoactive substances such as amphetamine, methamphetamine, cocaine and MDMA, drug carriers for levofloxacin (LVX), progesterone (P4) and acriflavine (ACF) and catalysts for oxidation reactions. The interdisciplinary nature of the work consists in combining the synthesis of these materials, their characteristics and the study of their sorption abilities, drug release profiles or catalytic abilities.

The experimental part of the dissertation was divided into three parts. In the first part of the work, effective Zr-MOF adsorbents for uremic toxins: hippuric acid and 3-indoleacetic acid and psychoactive substances were developed. For uremic toxins, a series of UiO-66 materials was obtained, supported by modulatory synthesis and functional groups. Nine different materials with the same topology, differing in surface area and pore size, were obtained. In addition, 4 materials differed in the number of amino groups. This approach allowed to obtain maximum adsorption for both uremic toxins. The use of two extreme amounts of amino groups (25% and 100%) in the UiO-66 material without the use of modulated synthesis allowed for the highest efficiency in the case of hippuric acid sorption. For 3-indole acetic acid, apart from introducing functional groups into the material, an important aspect was the use of hydrochloric acid as a modulator. For the sorption of psychoactive substances, a series of Zr-MOFs was obtained: NU-1000, UiO-67 and MOF-808. The sorption tests carried out allowed to obtain a maximum of nearly 100% for amphetamine and cocaine using NU-1000 as an adsorbent. The conducted physicochemical and sorption tests showed that the ratio of the pore size of the materials to the size of the adsorbed molecule has a significant impact on the sorption capacity of these substances.

In the second part of the work, drug carriers were developed. For progesterone, a series of UiO-66 materials was prepared, during which various modulators were used. Additionally, one material contained amine functional groups. Obtained materials UiO-66,

UiO-66 25% HCl, UiO-66 NH_2(75%) 25% HCl and UiO-66 Benz. showed different specific surfaces and pore sizes, which allowed to obtain different drug loading values. It was noted that the presence of functional groups and the modulator used also affect the rate of drug release from the composite. In addition, a method for obtaining the LVX@Uio-66 25% HCl@SILK composite was developed. The drug release profile from the LVX@UiO-66 25% HCl@SILK composite does not differ significantly from the drug release profile from the LVX@UiO-66 25% HCl composite. which may indicate that the addition of a silk matrix does not interfere with the release of LVX in the composite. For progesterone, a series of UiO-66 materials was prepared, for which synthesis with a modulator of hydrochloric acid in various concentrations was used. The obtained materials: UiO-66, UiO-66 12.5% HCl and UiO-66 25% HCl differed in pore size and surface area. The increase in the modulator concentration clearly increased the specific surface area, which allowed for a greater amount of drug charge in the material. Progesterone release profiles from the composites showed no major changes. A series of Zr-MOF materials was prepared for acriflavine: NU-1000, UiO-67, UiO-66 25% HCl and MOF-808. Due to the use of materials with different topologies and pore sizes, different amounts of drug loading into the material were obtained. For the ACF@NU-1000 and ACF@UiO-67 composites, the influence of the pH of the environment on the drug release profile was investigated. Changing the environment from deionized water into which acriflavine was released from composites to PBS (pH = 5.5) and SBF (7.4) resulted in a decrease in its release capacity. The acriflavine release profile from ACF@(UiO-67) to SBF clearly differs from the other release profiles, indicating that the UiO-67 structure is more sensitive to environmental pH changes.

In the third part of the work, catalysts for the oxidation reaction were developed. This part is also divided into three subsections. In the first one, MM-HKUST-1-son catalysts were obtained. and MM-HKUST-1-son.-def. (MM=Cu, CuPd) using ultrasounds (son.) and crystal etching in the final stage of the synthesis with orthophosphoric acid (def.). The obtained diffraction patterns did not show the presence of palladium nanoparticles on the surface of the MOF, suggesting the incorporation of this metal into the structure of HKUST-1. The addition of orthophosphoric acid did not reduce the crystallinity of the samples, and the BET tests indicate that a mesoporous surface was obtained. Catalytic tests of the cyclohexene

oxidation reaction using the synthesized catalysts were carried out. The main products of this reaction include: 2-cyclohexenol, 2-cyclohexenone, trans-1,2-cyclohexanediol and 3-cyclohexen-1-ol, and the conversion rate obtained is almost 50% for Cu-HKUST-1-son., Cu - HKUST-1-son.-def., CuPd-HKUST-1-son. and 96% for CuPd-HKUST-1-son.. In the next subsection, Cu-HKUST-1-kl materials were deposited on ceramic foams. and CuPd-HKUST-1-kl. by the solvothermal method. The analysis of the diffraction patterns showed no decrease in the crystallinity of the deposited MOF materials on the foams. No additional reflections indicating the presence of metallic palladium were observed for CuPd-HKUST-1-class, which may indicate its incorporation into the MOF structure. Catalytic tests of cyclohexene and benzyl alcohol oxidation reactions were carried out for MOF and MOF powders deposited on foams. In the case of the cyclohexene oxidation reaction, slight changes can be seen in the degree of reaction conversion for materials in the form of powders and those deposited on ceramic foams. For Cu-HKUST-1-class the value of the conversion rate drops from 75% to 65% and for CuPd-HKSUT-1-kl. increases from 62% to 67%. For the benzyl alcohol oxidation reaction, a significant increase in the degree of conversion is seen for catalysts with copper and palladium. In the last section, a series of NP@Zr-MOF catalysts were obtained. UiO-66 was synthesized using 3 different modulators: acetic acid, hydrochloric acid (in two different concentrations and benzoic acid) and NU-1000. Copper, silver, and palladium nanoparticles were deposited by impregnation of sonicated alcohol solutions on MOF materials and subjected to physicochemical tests and catalytic texts of the cyclohexene oxidation reaction. Impregnation did not affect the degree of crystallinity of the materials. The use of a modulator during the synthesis and the type of metal affected the distribution of nanoparticles and their size, which was confirmed by TEM images. For all catalysts, the degree of conversion higher than 50% was obtained in the cyclohexene oxidation reaction. For AgUiO-66, this result was about 96%.

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