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Polyaniline/FeZSM-5 composites – Synthesis, characterization and their high catalytic activity for the oxidative degradation of herbicide glyphosate

Maja Milojević-Rakić[a,*], Danica Bajuk-Bogdanović[a], Bojana Nedić Vasiljević[a], Aleksandra Rakić[a], Sandra Škrivanj[b], Ljubiša Ignjatović[a], Vera Dondur[a], Slavko Mentus[a], Gordana Ćirić-Marjanović[a]

[a] Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12-16, 11158, Belgrade, Serbia
[b] Faculty of Chemistry, University of Belgrade, Studentski trg 12-16, 11158, Belgrade, Serbia

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ABSTRACT

Semiconducting composites of nanostructured and granular polyaniline (PANI) with FeZSM-5 zeolite were synthesized by the oxidative polymerization of aniline with ammonium peroxydisulfate in water, without added acid and in an aqueous H_2SO_4 solution, in the presence of FeZSM-5, by using initial weight ratios aniline/FeZSM-5 of 1/1 and 1/5. These novel composite materials, in their as-synthesized (protonated) and deprotonated forms, were characterized by elemental, thermogravimetric and differential thermal analysis, scanning electron microscopy, FTIR and Raman spectroscopy, X-ray powder diffraction and conductivity measurements. The catalytic activity of the PANI/FeZSM-5 composites towards the oxidation of herbicide glyphosate with hydrogen peroxide has been investigated. A significant improvement of the catalytic activity of PANI/FeZSM-5 composites compared to that of pure PANI and FeZSM-5 was observed, manifested by the almost one order of magnitude more efficient oxidative degradation of glyphosate with hydrogen peroxide. The maximum of oxidized/decomposed amount of glyphosate was achieved in the presence of PANI/FeZSM-5 composite synthesized using an initial aniline/FeZSM-5 = 1/5 wt ratio. It has been shown that the method of synthesis and interactions between PANI and zeolite in this complex composite system, leading to more efficient electron transfer and hydrogen peroxide decomposition, are crucial for the catalytic properties of tested PANI/FeZSM-5 materials. It is shown that new PANI/FeZSM-5 composites present advanced catalyst materials for enhanced green catalytic degradation of pesticide/herbicide pollutants in environmental remediation systems.

1. Introduction

There is a growing interest in the development of conductive polymers/zeolites (nano)composites in order to obtain new materials with synergistic or complementary properties for various applications [1]. A special attention was paid to the synthesis and characterization of polyaniline (PANI) composites with zeolites [2–32]. The preparation of PANI/zeolite composites was accomplished by the oxidation of aniline within the zeolite (Y, HY, HZ, HS, MCM-41, ZSM-5, *β*-zeolite) channel system [2–4,6,7,12,22], by chemical [5,8,9,15–19,23–27,29–32], electrochemical [5,28], emulsion [10], and enzymatic [20] oxidative polymerizations of aniline in the presence of various zeolites (e.g., MCM-41, 13X, *β*-zeolite, FUYB, Y, HY, NaY, ZSM-5, amine-functionalized ZSM-5, clinoptilolite, and erionite), by dry mixing of PANI powder with zeolites such as Y, HY, 13X, MCM-41, and LTA [13,14,27], and by the addition of some zeolites (e.g., Zenith-N, LTN) to the PANI solution [11,21]. Plenty of experimental spectroscopic evidences (FTIR, UV–Vis, Raman, EPR, etc.) indicated that PANIs synthesized within the zeolite channel system [2–4,6,7,12,22] or at the zeolite surface [5,8–10,15–20,23–32] exist in the conducting emeraldine salt form, which depending on synthetic conditions and isolation procedures contains localized/delocalized polarons and bipolarons in various proportions (Scheme 1). The applicability of PANI composites with zeolites for solid state pH electrodes [17], gas (CO, CO_2, NO_2, NH_3, H_2O, alkylamines) sensors [13,14,19,27,31], sensors for epinephrine [33], paracetamol [33], folic acid [33], lindane [34], acetylcholine [30], organophosphates [30], hydrazine [35], and phenylhydrazine [35], as well as the usability of PANI/zeolite composites as antiferromagnetic materials [9], cathodes in a primary cell (battery) [11,21], curing agents for epoxy resin [10], corrosion inhibitors [24,28], membranes [26], catalysts [36], components of electrorheological fluids [37], sorbents for multiresidue analysis of pesticides [32], and adsorbents [38], was also thoroughly investigated.

PANI/zeolite composites were proved to be efficient adsorbents for environmental pollutants, e.g., herbicide glyphosate [N-(phosphonomethyl)

* Corresponding author.
E-mail address: maja@ffh.bg.ac.rs (M. Milojević-Rakić).

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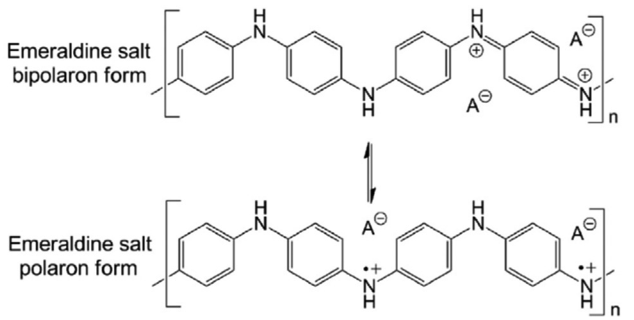

Scheme 1. Bipolaron and polaron form of PANI emeraldine salt. An anion (counter-ion, e.g. hydrogensulfate) is denoted by A^-.

glycine] which is toxic to aquatic life with long lasting effects [39], and Cr (VI) compounds (chromates, dichromates, etc.) [29] which show both the acute and chronic toxicity to aquatic organisms [39]. The potential application of PANI/zeolite composites for efficient removal of herbicide and other pesticide pollutants from wastewaters looks especially promising and interesting. The efficient removal of pesticide pollutants, which accumulate in the environment because more than 99.9% of pesticides actually do not reach the intended target pests [40], represents a significant scientific challenge over the past three decades. One of the current problems is the unloading and cleaning of pesticide/herbicide containers which lead to the contamination of ground and underground waters [41]. Wastewaters usually contain rather high quantities of pesticide/herbicide molecules (order of magnitude being mgL^{-1}) while in water flows these concentrations are in the order of μgL^{-1}. In the case of the well-known post-emergence, non-selective, systemic herbicide glyphosate, which is extensively implemented in agricultural and urban environments [42], it was revealed that glyphosate quantities detected in ground water in certain cases were somewhat above its maximum contaminant level of $700\,\mu gL^{-1}$ [43] according to the ecological U.S. standards. It should be noted that glyphosate quantities detected in ground water were 3–4 orders of magnitude higher than its maximum contaminant level of $0.1\,\mu gL^{-1}$ according to the much more rigorous ecological EU regulation [44]. Therefore, a development of the efficient remediation techniques for the removal of glyphosate became an emerging task for the scientific community in recent years. An efficient adsorption technique for the glyphosate removal from aqueous solutions, by using the nanostructured and granular PANIs and their composites with zeolite HZSM-5 as adsorbents, has been developed by our research group [25]. However, it should be noted that it is generally expected that only combination of adsorption techniques and chemical methods could give satisfactory results in pesticide/herbicide removal from wastewaters with different levels of contamination, because adsorption techniques for pesticide/herbicide removal require additional step of the regeneration/recovery or destruction of pollutant-containing adsorbents, while chemical methods often result in incomplete removal or unwanted side products [45].

Advanced oxidation processes for pesticide/herbicide removal from wastewaters often include Fenton reactions in systems for catalytical decomposition of H_2O_2 which produce hydroxyl radicals in the presence of ferrous ions or hydroperoxyl radicals in the presence of ferric ions. This reaction could be employed for oxidation and removal of various organic compounds [46]. Amongst heterogeneous Fenton catalysts, special attention was given to zeolites with iron present as framework and extra-framework ions [47,48].

Based on (i) the fact that chemical catalytic processes comprising hydrogen peroxide as oxidant were successfully utilized in the glyphosate decomposition/removal [41,49], (ii) the finding that Fe-doped-zeolites (FeZSM-5, etc.) were successfully used as catalysts in the oxidative degradation of some organic pollutants with hydrogen peroxide (H_2O_2) [47,50], and (iii) our study showing excellent adsorption properties of PANI and PANI/HZSM-5 composites towards glyphosate [25], here we present the investigation of catalytic properties of FeZSM-5 zeolite, PANI, and novel PANI/FeZSM-5 composites in the oxidative degradation of pesticide glyphosate with hydrogen peroxide.

2. Experimental

2.1. Materials

Aniline (p.a., Centrohem, Serbia) was distilled under reduced pressure and stored in argon, prior to use. Sulfuric acid (H_2SO_4) 96% (p.a., Centrohem, Serbia), ammonium peroxydisulfate (APS) (p.a., Centrohem, Serbia), H_2O_2 30% (p.a., Centrohem, Serbia), iron(III) citrate (Acros Organics, USA), and zeolite HZSM-5 (Zeolyst International, $SiO_2/Al_2O_3 = 30$, $S_{BET} = 400\ m^2g^{-1}$) were used as received.

2.2. Synthesis of FeZSM-5 zeolite

FeZSM-5 zeolite was prepared via ion-exchange of HZSM-5 zeolite [51]. The ion exchange procedure was conducted in suspension comprising 20 g HZSM-5 zeolite and 3×10^{-4} M iron(III) citrate in total volume of 2 L. The suspension was stirred for 15 days and subsequently the resulting FeZSM-5 was filtered, washed with deionized water and dried at 110 °C.

2.3. Synthesis of PANIs and PANI/FeZSM-5 composites

Based on the procedure for preparation of PANI/ZSM-5 nanocomposites by the oxidative polymerization of aniline with APS in water without added acid in the presence of ZSM-5 [23,25], in order to obtain PANI/FeZSM-5 composite using the initial weight ratio aniline/FeZSM-5 = 1/1, aqueous suspension comprising FeZSM-5 (1.86 g) and aniline (1.86 g; 0.02 mol) was prepared, in a total volume of 50 mL. The FeZSM-5/aniline aqueous suspension was stirred 10 min, subsequently the 50 mL of APS solution in water (5.7 g; 0.025 mol) was poured to the FeZSM-5/aniline aqueous suspension, and after constant stirring for 2 h at 23 °C the resulting PANI/FeZSM-5 composite material, denoted as PFeZ1/1, was collected on a filter, washed with 0.005 M H_2SO_4, and then dried in vacuo at 60 °C for 3 h. Similarly, the PANI/FeZSM-5 composite sample denoted as PFeZ1/5 was prepared by using the initial weight ratio aniline/FeZSM-5 = 1/5. In both experiments, the molar ratio aniline/APS was 1:1.25 and zeolite content in a reaction mixture was set to 1.86 g. Pure PANI was synthesized by the same method without the presence of zeolite. The initial pH values for FeZSM-5/aniline suspensions were 8.72 and 8.80, for PFeZ1/1 and PFeZ1/5, respectively. The pH values of reaction mixtures at the end of polymerization, after 45 min for PFeZ1/1 and 24 h for PFeZ1/5, were 0.7 and 1.8, respectively. In order to investigate the influence of the initial acidity of reaction mixture on catalytic properties of prepared composites, PANI/FeZSM-5 composites were also prepared, using the same synthetic procedure, by the chemical oxidative polymerization of aniline in aqueous FeZSM-5 suspension acidified by H_2SO_4, i.e., the starting FeZSM-5/aniline aqueous suspension was made in 0.2 M H_2SO_4 instead of water. Composite samples obtained in acidified medium using the initial weight ratios aniline/FeZSM-5 = 1/1 and 1/5 are denoted as PFeZ1/1S and PFeZ1/5S, respectively, while PANI sample obtained in acidified medium without the presence of FeZSM-5 is denoted as PANI/S. The initial pH values for FeZSM-5/aniline/H_2SO_4/APS suspensions were 2.4 and 1.3, for composites with the initial weight ratio zeolite/aniline = 1 and 5, respectively. The overall time of polymerization, t_{pol}, of 25 min was set in order to achieve a value of pH = 0.5–0.8 at the end of the reaction.

A portion of all prepared samples was treated with an excess of 5% NH_4OH for 3 h, to transform as-synthesized protonated PANI (salt) form to deprotonated (base) form. The samples obtained by the base treatment were collected on a filter, rinsed with 5% NH_4OH, and dried in vacuo at 60 °C for 3 h. Samples in deprotonated form were labeled with suffix *d*.