



## 12-Tungstophosphoric acid/BEA zeolite composites – Characterization and application for pesticide removal

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### ARTICLE INFO

#### Keywords:

Composites  
BEA zeolite  
Heteropoly acid  
Raman spectroscopy  
Adsorption  
Nicosulfuron

### ABSTRACT

Tungstophosphoric acid and BEA zeolite composites were synthesized by wetness impregnation, followed by ultrasonication and calcination. Composites were characterized using Raman spectroscopy, thermal analysis and pH-dependent zeta potential. Spectroscopic measurements indicated the interaction of acid and the support by binding of polyanion terminal oxygens and BEA extra framework H<sup>+</sup> via hydrogen bonds. Evaluation of prepared composites revealed their higher efficiency in nicosulfuron adsorption, in comparison to parent zeolite. All prepared composites showed excellent adsorption properties for pesticide removal in the range 12.1–25.8 mg of nicosulfuron per gram of investigated sample. Better adsorption capacity was found for sonicated samples in comparison to as-synthesized and calcined ones. It was found that the amount of polyanion in the composites and the extent of the particles surface charge are not crucial for the adsorption application, it is rather the uniformity of the zeolite surface coverage with the polyanion that is more important.

### 1. Introduction

Advanced composite materials often exhibit improved properties when compared to starting components and are, therefore, the scope of interest in a number of scientific studies [1]. Heteropoly acids are extensively investigated compounds due to their various, highly applicable, physico-chemical properties, stability, low cost and simple synthesis procedures. The unique structure of tungstophosphoric acid (HPW) is providing a number of possible interactions and preparation routes for obtaining different composite materials for various applications. The basic structure unit of HPW is the Keggin anion (PW<sub>12</sub>O<sub>40</sub>)<sup>3-</sup> consisting of the central PO<sub>4</sub> tetrahedron surrounded by twelve WO<sub>6</sub> octahedra which form four linked W<sub>3</sub>O<sub>13</sub> units. The oxygen atoms belong to one of the four types [2,3]. The four O<sub>a</sub> atoms are linking the PO<sub>4</sub> tetrahedron to three octahedra of a group, twelve O<sub>b</sub> atoms in W-O-W bridges between two different W<sub>3</sub>O<sub>13</sub> groups, twelve O<sub>c</sub> atoms in W-O-W bridges within the same W<sub>3</sub>O<sub>13</sub> group, and twelve O<sub>d</sub> atoms in terminal (unshared) positions.

Depending mainly on the pH value of the solution and concentration of HPW, the several molecular species originated from HPW can persist in the equilibrium [4,5]. Accordingly, the nature of HPW supported on carriers is highly dependent on the concentration in the impregnating

solutions, the solvent used, the solution pH, the acid/base nature of the carrier and the preparation procedure.

Among different inorganic carriers used in order to overcome polyanion low surface area and high solubility, zeolites are in the investigation focus because of their ordered pore structures, high thermal stability and large surface area [1]. In our previous contribution, zeolite BEA was selected due to its good stability in acidic medium thus convenient as HPW carrier. The Keggin anion cannot fill the zeolite voids and is therefore deposited on the external surface of the crystallites [6]. The influence of HPW/BEA ratio and different modification routes on properties and catalytic activities of the composites was considered [7]. As there are only few contributions dealing with this type of composite materials [6,8–10], the intention of the present work was to give detailed insight in HPW interaction with the support and to point out possibility for a new composite application.

Raman spectroscopy is a useful technique for investigation of heteropoly acids [2,3,11]. However, for the first time employed in the study of this type of composite materials, Raman spectroscopy enables consideration of molecular species of HPW and their possible interactions with the zeolite support. In addition, the synthesized composite materials were characterized by pH-dependent zeta potential measurements, and thermal analysis.

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In this work, an attempt was made to investigate HPW/BEA composites as adsorbents for the removal of pesticide from aqueous solutions by means of High Performance Liquid Chromatography (HPLC) method. Adsorption is the most widespread technology used for the removal of pesticides. The adsorption properties of the resulting composite samples were examined by adsorption of nicosulfuron, as a probe pesticide molecule. This pesticide belongs to the class of the sulfonylurea herbicides used to control annual grass weeds in maize crops because of their high herbicidal activity and low mammalian toxicity [12]. These are relatively novel, environmentally compatible compounds which represent one of the most useful classes of herbicides [13]. The main investigation of the effect that pesticides have on agricultural soils is summarized in examination of their adsorption on different types of soil [14,15]. When the investigation of potential removal by adsorption on specific adsorbents is in question, to the best of our knowledge, it was reported only for activated carbon monolith [14]. However, due to the fact that sulfonylurea herbicides have high solubility in water, high mobility and slow degradation, there are definite concerns about environmental risk [12]. The Freundlich and Langmuir-Freundlich equations were used to model the adsorption isotherms in order to identify the specific factors governing adsorption of the considered pesticide.

## 2. Experimental

### 2.1. Materials

BEA zeolite was obtained from Zeolyst International (CP814E). The  $\text{SiO}_2/\text{Al}_2\text{O}_3$  mole ratio is 25, extra framework ion is ammonium and declared surface area is  $680 \text{ m}^2/\text{g}$ . The as-received zeolite was thermally treated at  $550 \text{ }^\circ\text{C}$  for 4 h with the purpose of obtaining its hydrogen form [16]. The 12-tungstophosphoric acid hexahydrate,  $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot\text{nH}_2\text{O}$  (HPW), was synthesized according to the literature method [17], subsequently recrystallized, and dried at  $80 \text{ }^\circ\text{C}$  to obtain hexahydrate form. The ultrapure MilliQ water obtained from purification system Milipore was used throughout. The nicosulfuron secondary standard was obtained from Galenika a.d. (Serbia).

The composite preparation routes were previously reported in detail [7]. Three suspensions of BEA zeolite in water were prepared by mixing 10 g of zeolite with 150 mL of deionized water. After zeolite particles were suspended, precise HPW amount was added to each suspension in order to achieve the particular HPW/BEA weight ratio. Initial HPW concentrations in suspensions were 4.5, 8.9 and  $11.2 \text{ mmol/L}$ , respectively (HPW/BEA weight ratio was 20, 40 and 50 wt%). Suspensions were stirred with magnetic stirrer for 4 h and left to age for the next 24 h. The next day each suspension was divided into three parts. One part was dried at  $80 \text{ }^\circ\text{C}$  for 12 h, and these samples were marked as BPW20, BPW40 and BPW50. The BPW20U, BPW40U and BPW50U samples were additionally treated, after aging, with the ultrasound for 30 min in a continuous wave ultrasound reactor VC 750 Ultrasonic Processor (Sonics and Materials) equipped with 13 mm solid probe. The maximum net power output was 750 W at a frequency of 20 kHz and amplitude of 40 %. After sonication the samples were dried at  $80 \text{ }^\circ\text{C}$  for 12 h. The samples marked as BPW20C, BPW40C and BPW50C were calcinated at  $300 \text{ }^\circ\text{C}$  for 4 h after drying.

### 2.2. Characterization

Raman spectra excited with a 532 nm diode laser were collected on a DXR Raman microscope (Thermo Scientific, USA), equipped with an optical microscope and a CCD detector. The Raman spectra of suspensions were recorded with exposure time of 10 s, number of exposures of 10 for the small volume ( $5 \text{ } \mu\text{L}$ ) of sample on a gold support. Solid samples were recorded on microscope glass slide under the same conditions. Supports with the sample were placed on an X-Y motorized sample stage and the laser beam was focused on the sample using the

objective magnification of  $10\times$ . The scattered light was analyzed by the spectrograph with a grating  $900 \text{ lines mm}^{-1}$  and spectrograph aperture of  $50 \text{ } \mu\text{m}$  slit. Laser power was kept at 10 mW.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the samples were performed on a Netzsch STA 409 EP instrument. The samples were heated from 25 to  $1000 \text{ }^\circ\text{C}$  in the air atmosphere with a heating rate of  $10 \text{ }^\circ\text{C}/\text{min}$ . The samples were kept in a desiccator at a relative humidity of 23 %, prior to analyses.

The zeta potentials of the BEA zeolite and prepared composites were studied using a Zetasizer Nano ZS90 (Malvern Instruments). Aqueous suspensions ( $0.1 \text{ mg/mL}$ ) of the test materials were dispersed in an ultrasonic bath and an average of 20 measurements were taken as the measured potential. Prior to the measurements, the operating conditions were adjusted and confirmed using a calibrated latex dispersion supplied by the instrument manufacturer (zeta potential  $42 \pm 3 \text{ mV}$ ). The zeta potential measurements were conducted at two pH values: pH = 2 (the highest initial acidity of the suspensions for composites preparation) and pH = 5 (the adjusted acidity for pesticide adsorption study).

The concentrations of the nicosulfuron remaining in the aqueous solutions after adsorption on the BPW samples were determined by means of HPLC method. Nicosulfuron standard solution was prepared in water with concentration of  $100 \text{ mg/L}$ , and pH value was adjusted to 5, while working solutions were prepared by further diluting. For determination of the adsorption isotherms, dispersions comprising 30 mL of nicosulfuron solution ( $10\text{--}100 \text{ mg/L}$ ) and 50 mg of BPW composite samples and BEA zeolite were allowed to equilibrate for 24 h at  $23 \text{ }^\circ\text{C}$ . After equilibration period the dispersions were centrifuged at 13,400 rpm (Minispin, Eppendorf), filtered through a  $0.45 \text{ } \mu\text{m}$  Phenex nylon syringe filter (Phenomenex) and the amount of pesticide in the supernatant was measured by HPLC method. The amount of adsorbed nicosulfuron was calculated per gram of investigated adsorbent and plotted as a function of equilibrium concentration of nicosulfuron remaining in the supernatant.

The Bischoff chromatograph system consists of a HPLC Compact Pump Model 2250 fitted with the LC-CaDI 22-14 Interface, sample injector and Gastorr TG-14 Degasser. The system and the data management were controlled by MacDACq integral software. The stationary phase column was ProntoSil C18 AQ plus (Bischoff),  $150 \times 4.6 \text{ mm}$ ,  $10 \text{ } \mu\text{m}$  particle diameter. The nicosulfuron determination was performed by injecting  $50 \text{ } \mu\text{L}$  of solution into the chromatograph, and the absorbance at 254 nm was then measured using UV/VIS Lambda 1010 detector. The eluent was water/acetonitrile (60:40, v/v; pH = 2.5) isocratic mixture with a flow rate of  $1.5 \text{ mL}/\text{min}$ . All solvents and analytes for HPLC were filtered through a  $0.45 \text{ } \mu\text{m}$  nylon membrane filters.

### 2.3. Adsorption isotherm models

The equilibrium sorption data for nicosulfuron adsorption on BPW samples were fitted using Langmuir, Freundlich and Langmuir-Freundlich isotherm models. The isotherms were obtained when the amounts of nicosulfuron adsorbed per weight unit of each adsorbent ( $\text{mg/g}$ ) were presented as the function of equilibrium concentrations of the nicosulfuron in the suspension ( $\text{mmol/L}$ ).

The Langmuir isotherm model (LM) is widely used for a number of sorption processes from solutions. However, the real pesticide sorption systems usually require a model that takes adsorption site density as exponentially decaying function with respect to the adsorption heat [18]. This empirical, Freundlich model (FM) [19] presumes heterogeneous site distribution  $q = KC^{1/n}$ , where  $q$  is the amount of solute adsorbed by the adsorbent ( $\text{mg/g}$ ),  $C$  is equilibrium concentration ( $\text{mg/L}$ ), while  $K$  and  $n$  are constants that represent adsorptive capacity and intensity, respectively. In order to keep some level of heterogeneous distribution of active sites, but eventually, to avoid indefinite increase of adsorption with concentration, it is rather useful to apply Langmuir-

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