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CONTENT

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APPLICATION OF MACROPOROUS NANOCOMPOSITE IN MICROEXTRACTION OF AROMATIC AMINE FROM WATER

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ABSTRACT
Magnetic macroporous poly(glycidyl methacrylate-*co*-trimethylolpropane trimethacrylate) nanocomposite was synthesized by suspension copolymerization. The obtained nanocomposite was characterized by Fourier transform infrared spectroscopy (FT-IR), mercury porosimetry and scanning electron microscopy (SEM). Such magnetic nanocomposite was applied as sorbent for a dispersive solid-phase microextraction (DSPME) for aniline preconcentration from water samples. The parameters affecting the microextraction were optimized. The screening of DSPME parameters was determined using Plackett-Burman design (PBD). For the optimization of the most important factors Central Composite Design (CCD) was used. The analysis of the results showed that the pH value and temperature of desorption were the most significant factors.

INTRODUCTION
Aniline is a major raw material in the production of textile dye, herbicides, pesticides, fungicides, plastics and pharmaceuticals [1]. Its considerable consumption in industrial processes has led to the release of aniline in the environment. Aniline is a priory environmental pollutant due to its high toxicity and suspected carcinogenicity and numerous health problems such as vomiting, liver damage and even cyanosis [2]. Because aniline is present in real environmental samples in low concentrations, most analytical techniques rely on some type of preconcentration of samples before analysis. For that reason, DSPME has gained special attention, due to its simplicity, low consumption of sorbent and organic solvent, short extraction time, and high enrichment factor [3]. However, the type of sorbent plays a significant role in the DSPME method. Among different types of sorbents used in DSPME, magnetic polymer nanocomposites have attracted much attention due to their large surface area, chemical, magnetic and physical properties, reusability, and high efficiency and selectivity in the extraction of the target analyte. In this study, magnetic polymer nanocomposite based on glycidyl methacrylate (GMA) was prepared and applied as a potential sorbent for the development of a relatively fast and effective dispersive solid-phase microextraction for aniline preconcentration. The affecting factors on the microextraction recovery were optimized through Design of Experiment (DoE).

EXPERIMENTAL
Magnetic macroporous nanocomposite based on GMA (with 60 wt.% of crosslinker, trimethylolpropane trimethacrylate) was synthesized by radical suspension copolymerization in the presence of 10 wt.% magnetic nanoparticles [4]. FTIR spectra were taken in ATR (attenuated total reflection) mode using a Nicolet 380 spectrometer with a Smart OrbitTM ATR attachment. Pore size distributions were collected by a high-pressure mercury intrusion porosimeter Carlo Erba Porosimeter 2000. SEM micrographs were obtained on JEOL JSM-6460LV instrument. The

DSPME procedure with magnetic nanocomposite sorbent prior to HPLC-MS was used for the detection of aniline according to the procedure described in the literature [5]. A PBD was applied in order to evaluate the significance of eleven variables on the microextraction recovery for the DSPME procedure. Variables were tested at two levels, a high (+1) and a low (-1) level: pH (X_1, 2-10), mass of sorbent (X_2, 10-50 mg), ion strength (X_3, 0-1 wt. %), type of extraction (X_4, vortex-ultrasonic), extraction time (X_5, 1-5 min), extraction temperature (X_6, 10-40 °C), type of eluent (X_7, methanol or acetonitrile), eluent volume (X_8, 200-700 μL), type of desorption (X_9, vortex-ultrasonic), desorption temperature (X_{10}, 10-40 °C) and desorption time (X_{11}, 1-5 min). In the next step, a CCD was used for optimization of the most significant parameters (pH and temperature of desorption) at five levels. For the analysis of the experimental data the statistical software MINITAB was used.

RESULTS AND DISCUSSION

In the FTIR spectrum (Figure 1a), the absorption bands for GMA based nanocomposite at 2995 cm^{-1} and 2950 cm^{-1} (C-H symmetric and asymmetric stretching vibrations), 1730 cm^{-1} (C=O stretching vibrations), 1145 cm^{-1} (stretching vibrations of C-O-C), ~ 1250, ~910 and ~ 840 cm^{-1} (stretching vibrations of C-O) were observed. The absorption band at 640 cm^{-1} (vibrations of Fe–O bonds) indicates the successful incorporation of magnetic nanoparticles in polymer [4]. Values of specific pore volume, V_p, specific surface area, S_{Hg}, and pore diameter which corresponds to half of pore volume, $D_{V/2}$ were 0.77 cm^3/g, 65 m^2/g and 83 nm, respectively. The porosity parameters calculated from the cumulative pore volume distribution curve (Figure 1b) confirmed macroporous structure ($D_{V/2}$> 50 nm).

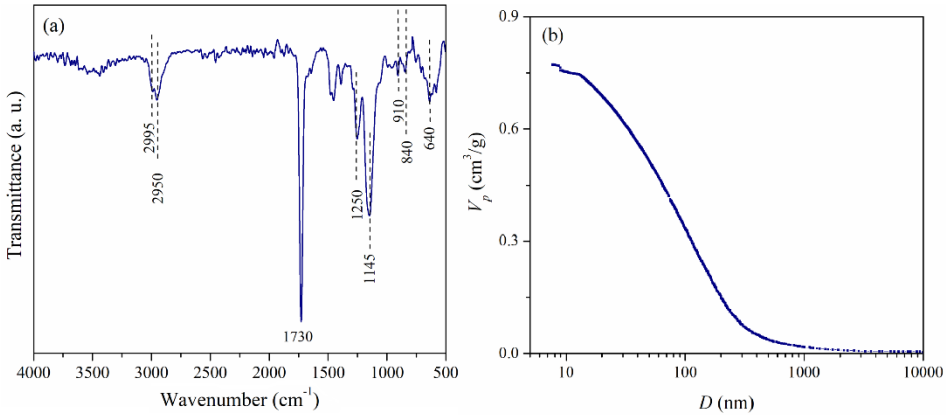

Figure 1.FTIR spectrum (a) and the cumulative pore size distribution curve (b) of magnetic macroporous nanocomposite.

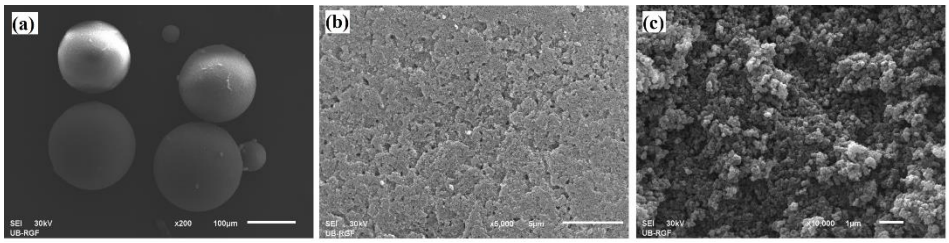

Figure 2. SEM microphotographs of (a) beads (magnification 200×), (b) particle surface (magnification 5000×) and (c) cross-section (magnification 10000×) for obtained nanocomposite.

The appearance and morphology of the surface and cross-section for obtained nanocomposite were investigated by SEM (Figure 2). It can be noticed that nanocomposite has the shape of beads with rough surfaces and porous structures.

The PBD was chosen to screen the eleven independent variables on the microextraction recovery of aniline in 12 runs. The obtained results are presented in Figure 3.

According to the obtained screening results,pH and the temperature of desorption were the most significant variables with a positive effect, while other independent variables had no significant effect on the microextraction recovery. For each factor with no significant effect, the factor level with the optimal response was selected based on the main effects plot (Figure 3). The main effect plot analysis revealed that increaseof the mass of sorbent, extraction time and temperature, and eluent volume as well as decrease of the ion strength and time of desorption led to an increase in microextraction recovery. The optimum for non-significant variables were set as: 50 mg of the sorbent mass, without ion strength, ultrasonic as type of extraction, 5 min for extraction time, 10 °C for extraction temperature, 700 µl of eluent volume, vortex as type of desorption, 1 min for desorption time and acetonitrile as eluent. Two significant factors were selected for the optimization step by CCD.

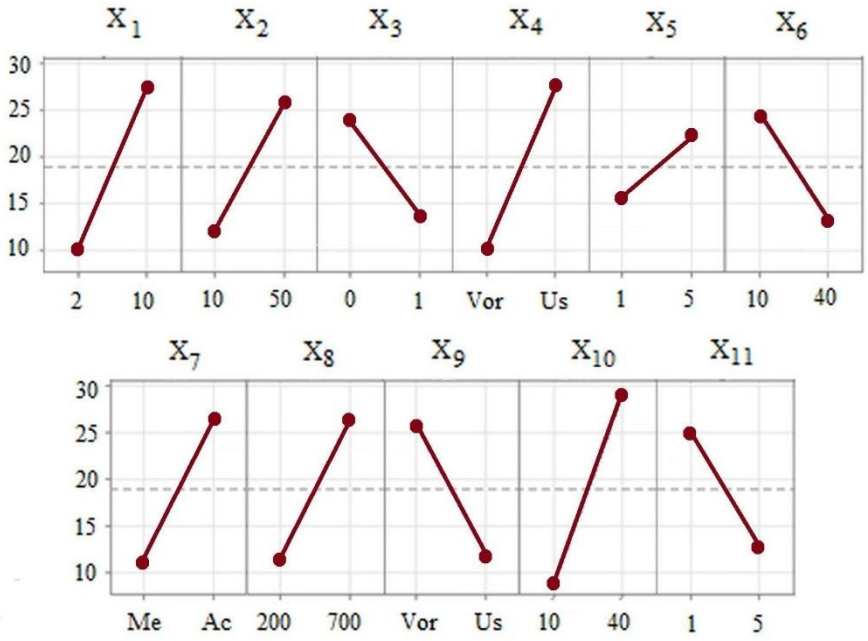

Figure 3. Main effect plot obtained for the PBD of screening experiment.

The CCD design was established to optimize the important factors to obtain the best response. Thirteen experiments were investigated at five levels. The elliptical contours of the contour plot (Figure 4) showed the combined influence of the significant variables on the microextraction recovery. The plot also indicates that the maximum microextraction recovery percent value was found in the middle of the range for each variable. The optimum microextraction recovery for aniline was found at pH 9 and desorption temperature of 20 °C.

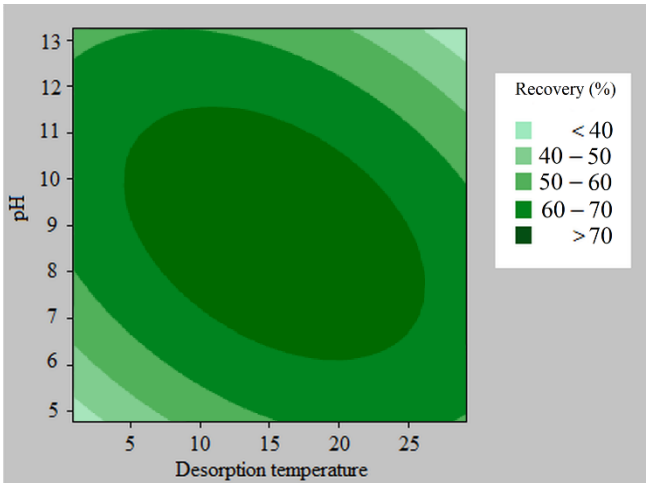

Figure 4. Contour plot desorption temperature – pH obtained for the CCD optimization step.

CONCLUSION

In the present study, a macroporous magnetic nanocomposite was synthesized by suspension copolymerization and used as a sorbent in dispersive solid-phase microextraction of aniline before its determination by HPLC-MS. The synthesized nanocomposite was characterized by FTIR spectroscopy, mercury porosimetry and SEM. FTIR analysis confirmed the presence of magnetite nanoparticles in the polymer matrix, while mercury porosimetry confirmed macroporous structure. The porosity of obtained nanocomposite was proved by SEM. Eleven affecting factors on the extraction recovery were optimized in two steps using the PBD as the screening step and the CCD as the optimization step. Application of DSPME procedure previously optimized with DoE resulted in the successful determination of aniline with good sensitivity, and short extraction and separation time.

Acknowledgment

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