

# **PHYSICAL CHEMISTRY 2016**

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## A NOVEL Tc <sup>99m</sup> SORBENT BASED ON MACROPOROUS MAGNETIC POLYMER

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### ABSTRACT

A novel magnetic macroporous poly(glycidyl-*co*-ethylene glycol dimethacrylate) (mPGME) synthesized by suspension copolymerization and functionalized with diethylene triamine (mPGME-deta) was evaluated as sorbent for pertechnetate ion (TcO<sub>4</sub><sup>-</sup>) removal from aqueous solutions. Atomic force microscopy (AFM) was used for characterization. The kinetics of TcO<sub>4</sub><sup>-</sup> adsorption onto mPGME-deta is relatively fast and depends on pH.

### INTRODUCTION

Magnetic polymers have been used in biomedical applications like cell separation [1], affinity chromatography [2], targeted drug delivery [3], etc. In this study, magnetic macroporous mPGME microspheres were prepared by suspension polymerization, functionalized with diethylene triamine (mPGME-deta) and tested as technetium-99 sorbent from aqueous solutions.

### EXPERIMENTAL

#### *mPGME synthesis and amino-functionalization*

Macroporous mPGME was prepared by suspension copolymerization of glycidyl methacrylate (GMA) and ethylene glycol dimethacrylate (EGDMA, crosslinker), in the presence of inert component and suspended magnetite nanoparticles prepared via improved chemical coprecipitation method [4]. The aqueous phase consisting of 225.0 g of water and 2.25 g poly(*N*-vinyl pyrrolidone) was placed in polymerization reactor and heated to 70 °C. The monomer phase containing monomer mixture (19.5 g GMA and 29.1 g EGDMA), AIBN as initiator (0.5 g), 63.8 g of inert component (51.0 g of cyclohexanol and 12.8 g of tetradecanol) and 1.15 g of magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles was sonicated for 30 min at 300/600 W within an ultrasonic water bath (Sonic 12GT). The resulting mixture was dropped into polymerization reactor. The reaction mixture was stirred at 350 rpm during

the monomer addition and heating was started. The copolymerization was carried out under nitrogen atmosphere at 75 °C for 2 h and at 80 °C for 2 h with a stirring rate of 250 rpm. After the reaction, the magnetic copolymer beads (mPGME) were washed with water and ethanol, kept in ethanol for 12 h, and dried in vacuum at 50 °C. The mPGME was additionally functionalized with diethylene triamine as described elsewhere [5] and labeled as mPGME-deta.

The pore size distribution of mPGME was determined by mercury porosimetry (Carlo Erba 2000, software Milestone 200). The surface morphology of mPGME was studied by atomic force microscopy (AFM). Measurements were performed in air with AutoProbe CP-Research SPM (TM Microscopes-Bruker). Bruker Phosphorus (n) doped silicon Tap300 metrology probes, model MPP-11123-10 with Al reflective coating and symmetric tip Nominal spring constant of these cantilevers is 40N/m, while their resonance frequency is around 300 kHz. Due to the nature of the samples non-contact mode was applied. Both topography and “error signal” AFM images were taken and later analysed using the software Image Processing and Data Analysis Version 2.1.15 and SPMLab Analysis software from VEECO DI SPMLab NT Ver. 6.0.2.

#### **Sorption of Tc <sup>99m</sup>**

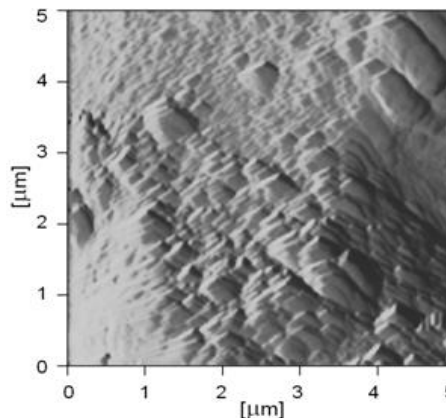
The pH-dependent sorption of TcO<sub>4</sub><sup>-</sup> by mPGME-deta was studied in aqueous buffer solutions at pH range 2-8. Aqueous buffer solutions were prepared from reagent grade chemicals and deionized water (Milli-Q Millipore 18 MΩcm<sup>-1</sup> conductivity). Batch experiments were performed at room temperature by mixing 50 mg of mPGME-deta, 4.9 ml of buffer solution and 0.1 ml of pertechnetate solution with activity of *ca* 10 MBq in a vial. The blanks were prepared in the same way but without mPGME-deta. The calculated amount of pertechnetate ions (<sup>99</sup>Tc + <sup>99m</sup>Tc) in every vial was *ca* 8.987·10<sup>11</sup>. Aliquots of 100 μl were drawn at predefined time points from the vials containing mPGME-deta as well as from the blanks. The aliquot activity was measured in well-type NaI (TI) gamma counter (2470 WIZARD2, *PerkinElmer, USA*). Relative measurements of adsorbed radioactivity were obtained using the following equation:

$$R = \frac{R_b - R_s}{R_b} \cdot 100\% \quad (1)$$

where R is the adsorbed <sup>99m</sup>Tc activity (%), R<sub>b</sub> is the measured activity of the blank aliquot (counts per min) and R<sub>s</sub> is the activity of the supernatant aliquot from the vials containing mPGME-deta (counts per min).

## RESULTS AND DISCUSSION

The specific surface area of the magnetic mPGME particles ( $92 \text{ m}^2 \text{ g}^{-1}$ ) was calculated as the sum of incremental specific surface areas from the pore size distribution curves as described in the literature [6]. The surface morphology of mPGME-deta was studied by atomic force microscopy (AFM). The measurements were performed at  $(5 \times 5) \mu\text{m}^2$  scan size with the resolution of  $(256 \times 256)$  data points per image. The Figure 1 shows 2D “error signal” AFM image of the top view of mPGME-deta. As can be seen, the sample surface is covered with a layer of absorbed magnetite.

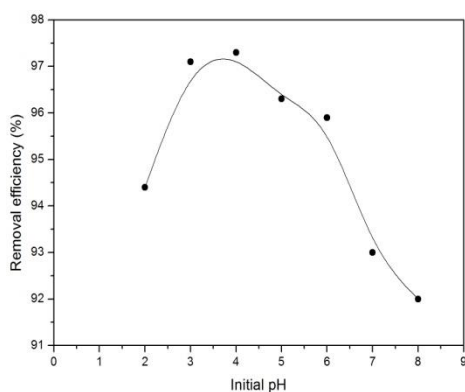


**Figure 1.** The 2D AFM image of the mPGME-deta

The average roughness ( $R_a$ ) and root mean square roughness ( $R_q$ ) were used for studying the sample morphology. The average roughness,  $R_a$ , and root mean square roughness,  $R_q$ , values were calculated to be  $0.181 \mu\text{m}$  and  $0.231 \mu\text{m}$ , respectively.

### The effect of pH on $\text{TcO}_4^-$ sorption

The solution pH is crucial parameter that affects the surface charge of the sorbent, the protonation-deprotonation of surface functional groups, metal speciation in the aqueous solution and consequently, the sorbate/sorbent interactions [7]. Thus, the effect of solution pH on  $\text{TcO}_4^-$  removal by mPGME-deta was investigated (Figure 2). Since previous experiments



**Figure 2.** The effect of pH on the  $\text{TcO}_4^-$  removal efficiency,  $t=180 \text{ min}$

showed rapid sorption, with 90% of  $\text{TcO}_4^-$  sorbed within the first 5 min, the equilibrium time of 180 min was chosen for experiments in this study. The  $\text{TcO}_4^-$  sorption by mPGME-deta was pH-dependent, with optimal sorption pH between 3.0 and 6.0 and maximum at  $\text{pH} \sim 4.0$ . In acidic medium, the interactions between the protonated amino groups of mPGME-deta and negatively charged  $\text{TcO}_4^-$  anions promote high pertechnetate



removal. However, at  $\text{pH} \geq 6$ , the  $\text{TcO}_4^-$  sorption sharply decreased due to the decrease of the number of protonated amino groups in mPGME-deta.

### CONCLUSION

A novel magnetic macroporous mPGME was tested as sorbent for pertechnetate ion ( $\text{TcO}_4^-$ ) removal from aqueous solutions. AFM measurement showed mPGME surface covered with a layer of absorbed magnetite. The  $\text{TcO}_4^-$  sorption onto mPGME-deta was fast and pH-dependent, with high removal efficiency of 96% for 180 min in the pH range 3.0-6.0.

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