

CHROMIUM

*Environmental, Medical
and Materials Studies*

Margaret P. Salden
Editor

Chemical Engineering Methods and Technology

NOVA

CHEMICAL ENGINEERING METHODS AND TECHNOLOGY

**CHROMIUM: ENVIRONMENTAL,
MEDICAL AND MATERIALS STUDIES**

MARGARET P. SALDEN
EDITOR



Nova Science Publishers, Inc.
New York

Copyright © 2011 by Nova Science Publishers, Inc.

All rights reserved. No part of this book may be reproduced, stored in a retrieval system or transmitted in any form or by any means: electronic, electrostatic, magnetic, tape, mechanical photocopying, recording or otherwise without the written permission of the Publisher.

For permission to use material from this book please contact us:

Telephone 631-231-7269; Fax 631-231-8175

Web Site: <http://www.novapublishers.com>

NOTICE TO THE READER

The Publisher has taken reasonable care in the preparation of this book, but makes no expressed or implied warranty of any kind and assumes no responsibility for any errors or omissions. No liability is assumed for incidental or consequential damages in connection with or arising out of information contained in this book. The Publisher shall not be liable for any special, consequential, or exemplary damages resulting, in whole or in part, from the readers' use of, or reliance upon, this material. Any parts of this book based on government reports are so indicated and copyright is claimed for those parts to the extent applicable to compilations of such works.

Independent verification should be sought for any data, advice or recommendations contained in this book. In addition, no responsibility is assumed by the publisher for any injury and/or damage to persons or property arising from any methods, products, instructions, ideas or otherwise contained in this publication.

This publication is designed to provide accurate and authoritative information with regard to the subject matter covered herein. It is sold with the clear understanding that the Publisher is not engaged in rendering legal or any other professional services. If legal or any other expert assistance is required, the services of a competent person should be sought. FROM A DECLARATION OF PARTICIPANTS JOINTLY ADOPTED BY A COMMITTEE OF THE AMERICAN BAR ASSOCIATION AND A COMMITTEE OF PUBLISHERS.

Additional color graphics may be available in the e-book version of this book.

LIBRARY OF CONGRESS CATALOGING-IN-PUBLICATION DATA

Chromium : environmental, medical, and materials studies / editors, Margaret P. Salden.
p. cm.

Includes bibliographical references and index.

ISBN 978-1-61122-656-0 (hardcover : alk. paper) 1. Chromium. I. Salden, Margaret P.

TP245.C6C47 2011

620.1'8934--dc23

2011013647

Published by Nova Science Publishers, Inc. / New York

Chapter 8

**MACROPOROUS AND NON-POROUS
AMINO-FUNCTIONALIZED GLYCIDYL
METHACRYLATE BASED COPOLYMERS
FOR HEXAVALENT CHROMIUM SORPTION**

*Aleksandra B. Nastasović¹, Zvezdana P. Sandić²,
Danijela D. Maksin³, Antonije E. Onjia³,
Aleksandra D. Milutinović-Nikolić⁴ and Dušan M. Jovanović⁴*

¹Institute of Chemistry, Technology and Metallurgy, Center for Chemistry,
Polymer Department, University of Belgrade, Studentski trg 12-16,
Belgrade, Republic of Serbia

²Faculty of Science, Mladena Stojanovića 2, Banja Luka,
Bosnia and Hercegovina, Republic of Srpska

³Vinča Institute of Nuclear Sciences, University of Belgrade, P.O. Box 522,
Belgrade, Republic of Serbia

⁴Institute of Chemistry, Technology and Metallurgy, Center for Catalysis
and Chemical Engineering, University of Belgrade, Njegoševa 12,
Belgrade, Republic of Serbia

ABSTRACT

Two porous samples and one non-porous sample of crosslinked poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate) [abbreviated PGME] were synthesized by suspension copolymerization and functionalized by ring-opening reaction of the pendant epoxy groups with diethylene triamine (deta). Initial PGME, as well as amino-functionalized samples, were characterized by FT-IR spectroscopy, mercury porosimetry, scanning electron microscopy and elemental analysis. The kinetics of Cr(VI) sorption by amino-functionalized PGME was investigated in batch experiments under non-competitive conditions. It was found that the porosity of PGME-deta samples plays an important role in Cr(VI) uptake. Cr(VI) sorption by macroporous amino-functionalized

samples was rapid, with the uptake capacity higher than 80% after 30 minutes. Two kinetic models (the pseudo-first and the pseudo-second order) were used to determine the best-fit equation for chromium(VI) sorption by PGME-deta.

Keywords: Chromium(VI) sorption, Glycidyl methacrylate based copolymer, Porosity, Pseudo-second order kinetic model

1. INTRODUCTION

The existence of extremely toxic heavy metals in the environment presents environmental hazard, since they accumulate in living tissues throughout the food chain causing serious health problems [1]. Chromium, which is on the top-priority list of toxic pollutants defined by the U.S. Environmental Protection Agency (EPA), exists in nature primarily in two valence states, trivalent chromium [Cr(III)] and hexavalent chromium [Cr(VI)] [2]. Even though Cr(III) is less toxic than Cr(VI), it can be oxidized over a range of oxic conditions in natural waters and sediments [3], so the removal of chromium of both oxidation states from industrial wastewater is of great importance.

Major sources of chromium contamination are electroplating, metal finishing industries, tanneries, paints and pigments industry, fungicide industry and ceramic or glass manufacturing [4].

The hexavalent form, reported to be five hundred times more toxic than the trivalent one [5], is classified as a known human carcinogen that modifies the DNA transcription process causing important chromosomal aberrations [6,7]. Also, it can cause kidney and gastric damage and epidermal irritation. Because of the detrimental effect on human health, the maximum permissible levels of Cr(VI) in drinking water and wastewater were set by EPA at 20 and 200 $\mu\text{g/L}$, respectively [2].

The most common conventional method for Cr(VI) removal is reduction to Cr(III) at pH 2.0 and precipitation of Cr(OH)_3 with lime at pH 9–10 [8]. The disadvantage of chromium precipitation is the necessity for disposal of the solid waste. Alternative approaches, like adsorption, reverse osmosis, electrolytic recovery techniques, ion exchange and liquid–liquid extraction were also proven to be effective for chromium removal from industrial effluents and waters. Among these approaches, adsorption is one of more popular methods for the removal of chromium from wastewaters [1]. A number of different types of adsorbents such as lignocellulosic materials [6], activated carbon [7-9], chitin and chitosan [10], commercial ion-exchanges [11], clay [12,13] and synthetic polymer adsorbents [1,2,7,14-19] were shown to remove chromium from waste water.

Chelating copolymers offer some advantages and have excellent potential applications for selective removal and/or recovery of toxic heavy metal ions from waste solutions. They consist of a stable and insoluble crosslinked copolymer, having suitable active groups that interact with the sorbate analyte (ligands). In a relatively simple process, the chelating copolymer is contacted with the contaminated solution, loaded with metal ions, and stripped with appropriate eluent. After sorption, the copolymer is filtered, regenerated and reused, which reduces costs. The acrylic-based adsorbents are considered as almost ideal chelating sorbents for removal of heavy metals, being very stable in the range of buffers from pH 1.0 to 11.0, and resistant to microbial degradation and a number of chemicals [1]. Macroporous

crosslinked copolymers based on glycidyl methacrylate, GMA, produced by radical suspension copolymerization, in the shape of regular beads of required size and porosity, were already successfully used for heavy and precious metals sorption [20-24], as adsorbents and column packings in gas chromatography (GC) [25-27], supports for classical catalysts as well as enzymes [28,29]. Due to their hydrophilicity, easiness of use, high capacity, fast kinetics and good selectivity, combined with chemical stability, GMA based copolymers are more frequently utilized than well known and commercially available hydrophobic poly(styrene-*co*-divinylbenzene). Furthermore, the advantage of these copolymers over ion exchange resins for removal and/or recovery of heavy metal ions from wastewater streams lies in the fact that, depending on pH, they can both coordinate metals and act as basic ion exchangers, binding them as chloro complexes [30].

In this chapter, two samples of poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate) [abbreviated PGME)] with different porosity parameters (specific pore volume, specific pore area and pore diameter) were synthesized by suspension copolymerization in the presence of inert component, while the third sample was synthesized in the same manner but without inert component. All three samples were additionally functionalized via ring-opening reaction of the pendant epoxy groups with diethylene triamine. The amino-functionalized copolymers were tested as chromium(VI) adsorbents, in a batch system, under non-competitive conditions. Kinetic data were analyzed using two sorption kinetic models (the pseudo-first and the pseudo-second order) to determine the best fit equation for chromium sorption onto amino-functionalized PGME.

2. EXPERIMENTAL

2.1. Materials

All the chemicals used were analytical grade products and used as received: glycidyl methacrylate (GMA) (Merck), ethylene glycol dimethacrylate (EGDMA) (Fluka), ethylene diamine (EDA) (Fluka), diethylene triamine (DETA) (Merck), 2,2'-azobisisobutyronitrile (AIBN) (Merck), poly(N-vinyl pyrrolidone) (Kollidone 90, BASF), cyclohexanol (Merck), dodecanol (Merck). Chromium(VI) solutions were prepared from reagent grade potassium dichromate salt (Sigma-Aldrich), using deionized water.

2.2. Analysis and Spectroscopy

The copolymer samples were analyzed for their carbon, hydrogen and nitrogen content using the Vario EL III device (GmbH Hanau Instruments, Germany). Elemental analysis was calculated from multiple determinations within $\pm 0.2\%$ agreement. The Fourier transform infrared attenuated total reflectance (FTIR-ATR) spectra were measured by Thermo Nicolet 6700 FT-IR Spectrophotometer, equipped with an ATR Smart Orbit accessory, in the spectral range of 4000-400 cm^{-1} .

The pore size distributions of the initial and the functionalized samples were determined by a high pressure mercury intrusion porosimeter Carlo Erba Porosimeter 2000, operating in

the interval of 0.1-200 MPa. Sample preparation was performed at room temperature and pressure of 0.5 kPa.

The specific surface areas (S_{BET}) of samples PGME3 and PGME3-deta were determined by the BET method from the low-temperature nitrogen adsorption isotherms obtained by Sorptomatic 1990 Thermo Finningen at $-196\text{ }^{\circ}\text{C}$. Samples were outgassed at 323 K and 1 mPa for 6 h.

The concentrations of Cr(VI) were determined by flame atomic absorption spectroscopy (FAAS) (PerkinElmer 3100 ZL). Standard statistical methods were used to determine the mean values and standard deviations for each set of data.

Surface and interior morphology of the unmodified and modified PGME beads was investigated by a scanning electron microscope (SEM; JEOL, JSM-6460 LV, Tokyo, Japan).

2.3. Preparation of PGME

Three PGME samples, two macroporous and one non-porous, were prepared by a radical suspension copolymerization. The reaction mixture for macroporous copolymer synthesis consisted of the monomer phase (75.0 g) containing monomer mixture (19.5 g GMA i 13.0 g EGDMA for sample PGME1 and 26.0 GMA i 6.5 g EGDMA for sample PGME2), AIBN as initiator (0.3 g) and 45.2 g of inert component (34.0 g of cyclohexanol and 8.5 g of tetradecanol), which was suspended in the aqueous phase consisting of 225.0 g of deionized water and 2.25 g poly(N-vinyl pyrrolidone). The copolymerization was carried out at $70\text{ }^{\circ}\text{C}$ for 2h and at $80\text{ }^{\circ}\text{C}$ for 6h with a stirring rate of 300 rpm. The non-porous sample PGME3 was synthesized without inert component; the monomer phase consisting of 39.0 g GMA and 26.0 g EGDMA and containing 0.65 g of AIBN, was suspended in the aqueous phase containing 200.0 g of distilled water and 2.00 g of poly(N-vinyl pyrrolidone). The temperature program, the duration and the stirring conditions were the same as for the macroporous samples. After completion of the reaction, the copolymer particles were washed with water and ethanol kept in ethanol for 12 h and dried in vacuum at $40\text{ }^{\circ}\text{C}$. The synthesized samples were purified by Soxhlet extraction with ethanol. The resulting crosslinked beads were sieved and the fraction with average particle diameter (D) in the range 150-300 μm was used in the subsequent reactions.

2.4. Functionalization of PGME with Diethylene Triamine

All synthesized PGME samples were functionalized with diethylene triamine in the same manner. A mixture of 7.2 g of copolymer sample, 31.4 g of diethylene triamine and 300 ml of toluene was left at room temperature for 24h and then heated for 6 h at $80\text{ }^{\circ}\text{C}$ at a stirring rate of 250 rpm. The modified samples were filtered, washed with ethanol, dried and labeled as PGME1-deta, PGME2-deta and PGME3-deta (additional label -deta designates functionalization with diethylene triamine).

2.5. Chromium Sorption Batch Experiments

The sorption of Cr(VI) ions from aqueous solutions (initial metal concentrations 0.01, 0.02, 0.05 and 0.1 M; pH=1.8) was investigated in batch experiments under non-competitive conditions, at room temperature. The reproducibility of the sorption experiments results was verified in triplicate. Standard statistical methods were used to determine the mean values and standard deviations for each set of data.

For the determination of Cr(VI) sorption rates, 0.50 g of copolymer was contacted with 50 cm³ of metal salt solution. In each experiment, 0.5 cm³ of aliquots were removed at appropriate times (1, 5, 15, 30, 60, 90 and 180 min) and diluted to 50 cm³. The concentrations of chromium(VI) ions in the aqueous phases were measured by flame atomic absorption spectroscopy (AAS).

The amount of metal ions sorbed onto unit mass of copolymer beads (sorption capacity, mmol g⁻¹) was calculated from:

$$Q = \frac{(C_0 - C) \cdot V}{m} \quad (1)$$

Where C_0 and C are the concentrations of the metal ions in the initial solution and in the aqueous phase after treatment for a certain period of time, respectively (in mmol dm⁻³), V is the volume of the aqueous phase (in dm³) and m is the amount of the PGME amino-functionalized beads used for the experiment (in g).

3. RESULTS AND DISCUSSION

3.1. Synthetic Aspects

Macroporous copolymers are prepared in the presence of a pore forming agent (inert component, porogen), having a permanent well-developed porous structure even in the dry state [31]. As initially proposed by Kun and Kunin [32], the beads present agglomerates of microspheres (100-200 nm). Each microsphere consists of smaller nuclei (10-20 nm) which are often fused. The most substantial contributions to the surface area come from micropores with diameters smaller than 2 nm and mesopores ranging from 2 to 50 nm. Conversely, large macropores with diameters over 50 nm, which are located in between agglomerates, insignificantly influence the surface area.

The sorption capacity, selectivity, diffusion and flow properties of macroporous chelating copolymers, and thus their applicability, to a great extent, among other factors, depend on their porosity. For that reason, the knowledge of the mechanism of porous structure formation and the possibility of optimization of porosity parameters is needed in order to design a chelating copolymer with the desired sorption performances and selectivity towards individual metal ions. The macroporous morphology and the formation of porous copolymers have been extensively investigated and described in the literature [31-44].

Macroporous structure appears as the result of phase separation, which occurs during the polymerization of a monomer mixture containing appropriate amounts of both crosslinking

monomer and inert component, being a low-molecular weight substance (good solvent, a poor solvent for synthesized copolymer or their binary mixture), or a linear polymer. The inert component should mix very well with monomers and should not dissolve the copolymer obtained. In that way, it is easier to separate copolymer particles as the new phase from the reaction mixture, as well as form porous structures.

When the inert component is a poor solvent (non-solvent) for the synthesized copolymer, phase separation takes place and macroporous structure is formed. When the copolymer is obtained in the presence of a good solvent, the result can be one of two kinds of pore structure-gel or macroporous. When mixtures of good and poor solvents are used, the obtained copolymers possess intermediary characteristics. Consequently, the proper selection of inert component is important for optimization of the porous structure of synthesized beads. In general, the porous structure of macroporous copolymers can be controlled by the type and the amount of the inert component and the type and the amount of crosslinking monomer in the reaction mixture [34-41].

Copolymers with different epoxy group content were synthesized by changing the amount of the crosslinking monomer, EGDMA. The content of EGDMA in two porous copolymer samples, PGME1 and PGME2, was 40 and 20 wt.%, respectively. The content of the inert component was kept constant (80 wt.% of cyclohexanol and 20 wt.% of 1-tetradecanol). Non-porous sample PGME3 was synthesized in the same manner and with the same amount of EGDMA as sample PGME1 (40 wt.% of EGDMA), but without the inert component. All samples, non-porous and porous, were further chemically modified with diethylene triamine, in order to obtain chelating copolymers containing amino groups capable of chromium sorption.

The elemental analysis data for initial and amino-functionalized PGME samples are presented in Table 1. From the elemental analysis data, the degree of conversion of epoxy groups, the ligand concentration, C_{LIG} , and the amino group concentration in amino-functionalized PGME samples, C_{AG} , were calculated and presented in Table 2.

The elemental analysis data for initial samples are in fair agreement with the theoretical values, with acceptable variations, within the limits expected for suspension polymerization. The epoxy group content in initial copolymer samples (PGME1, PGME2 and PGME3) is therefore as designed.

Table 1. Elemental analysis data for initial and amino-functionalized PGME samples

Sample	Elemental analysis ^a					
	Found			Calculated		
	% C	% H	% N	% C	% H	% N
PGME1	59.0	6.5	-	59.8	7.1	-
PGME2	58.7	7.4	-	59.5	7.1	-
PGME3	58.8	7.1	-	59.8	7.1	-
PGME1-deta	53.3	8.1	7.0	56.3	8.2	8.4
PGME2-deta	51.8	8.3	8.8	55.0	9.0	14.3
PGME3-deta	58.9	7.2	0.9	56.3	8.2	8.4

^a Elemental analysis was calculated from multiple determinations within $\pm 0.2\%$ agreement.

Table 2. Conversion of epoxy groups, ligand concentration and amino group concentration in amino-functionalized PGME samples

	Conversion of epoxy groups, %	Ligand concentration, mmolg ⁻¹	Amino group concentration, mmolg ⁻¹
PGME1-deta	39.3	1.66	4.98
PGME2-deta	37.1	2.09	6.27
PGME3-deta	4.98	0.21	0.63

The nitrogen content is lower than calculated for all amino-functionalized samples. To a certain extent it is anticipated, since some part of epoxy groups usually remain inside the crosslinked copolymer, not being accessible for subsequent reactions and analytical determinations [42]. The conversion of epoxy groups for sample PGME1-deta of approximately 40% is in accordance with our previous results [17].

However, high discrepancies are observed for samples PGME2 and PGME3. The sample PGME2 was synthesized with higher amount of GMA than PGME1, i.e. with higher amount of epoxy groups capable of chemical modification, in order to introduce chelating amino groups. However, the nitrogen content in PGME2-deta was slightly higher than for PGME1-deta, and 1.6 times lower than calculated. On the other hand, sample PGME3-deta synthesized with the same amount of GMA as PGME1, has very low nitrogen content (below 1%) and consequently, a lower degree of conversion of epoxy groups and a lower amino group concentration. It seems that in the case of non-porous PGME3, the majority of epoxy groups are situated in the core of beads formed during copolymerization, remaining inaccessible for functionalization.

The FTIR-ATR spectra of all synthesized and amino-functional samples were recorded. As an illustration, FTIR spectra of initial PGME1 and PGME1-deta were presented in Figure 1. The assignation of FTIR-ATR bands to specific chemical bonds is given in Table 3.

The data clearly shows the presence of both epoxy and ester carbonyl groups in the unmodified copolymers and also the amino groups in the modified copolymers.

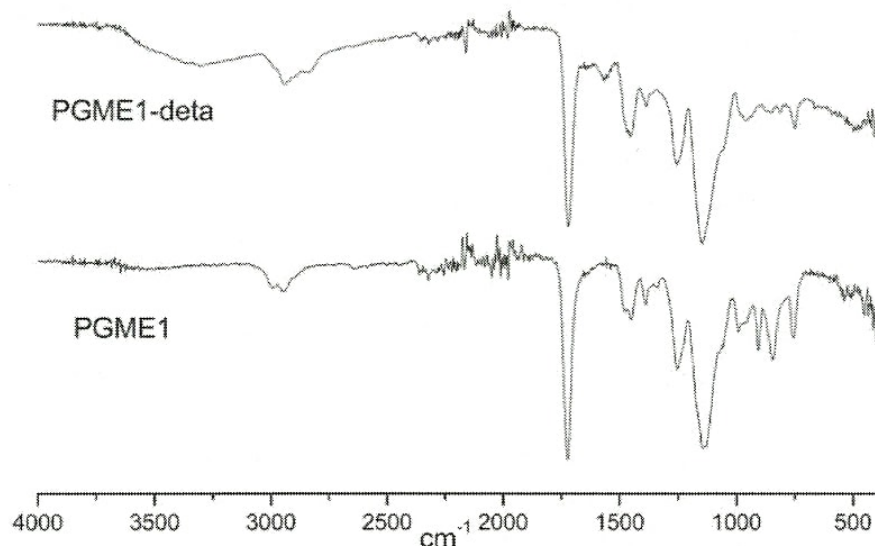


Figure 1. FTIR-ATR spectra of poly(GMA-co-EGDMA) (sample PGME1) and amino-functionalized sample PGME1-deta.

Table 3. FTIR-ATR spectra assignment

Sample	epoxy ring vibration, cm ⁻¹		δ(CH) epoxy cm ⁻¹		crosslinked copolymers vibrations, cm ⁻¹ ν (CH) ν(CO) >C=O			ν(NH ₂) cm ⁻¹	δ(NH) cm ⁻¹	ν(NH) cm ⁻¹
	PGME1	907	844	1253	1453	2994-2949	1147	1725		
PGME1-deta	854	815	1257	1452	2955	1149	1725	3300	1569	1389

δ-bending vibration, ν-stretching vibration

The presence of epoxy groups shows that GMA has been incorporated into the copolymer chain. The band at 2994-2949 cm⁻¹ is assigned to the stretching vibration of C-H bond, the strong band at 1147 cm⁻¹ is assigned to the stretching vibration of the C-O ester bond, and the strong band at 1720 cm⁻¹ is assigned to the stretching vibration of >C=O.

The bands characteristic for crosslinked copolymers (except of the intensities of the epoxide ring vibrations) were not changed in the modified samples. This indicates that the structure of the copolymer, with the exception of the epoxy group, remained unchanged in the process of modification with diethylene triamine.

The bands assigned to the epoxide ring vibrations at 907 and 844 cm⁻¹ in the spectrum of PGME1 have not completely disappeared in the spectrum of the modified sample PGME1-deta, although their intensity became very low and they were shifted to lower frequencies (from 854 to 815 cm⁻¹). The result of the conversion of epoxy groups is the appearance of the new bands in the spectra of amino-functionalized copolymers, due to the presence of amino groups (ν(NH₂), δ(NH) and ν(NH)).

The porosity parameters (specific pore volume, V_s, specific surface area, S_{Hg}, and pore diameter which corresponds to the half of the pore volume, d_{v/2}) for the initial and the amino-functionalized PGME samples were calculated from the cumulative pore volume distribution curves, except for PGME3 and PGME3-deta. The non-porous nature of these two samples suggested that the more appropriate characterization technique was nitrogen physisorption that enables detection of smaller pores than mercury porosimetry. The results of nitrogen physisorption confirmed the absence of any porous structure since S_{BET} < 1 m²/g for both PGME3 and PGME3-deta. The porosity parameters for the macroporous samples are presented in Table 4.

It is obvious that the samples PGME1 and PGME2, synthesized with 60 and 80 wt.% GMA have considerably different porosity parameters. With the increase of GMA content in the monomer mixture, the pore size distribution curves of the synthesized samples were shifted towards larger pores, accompanied by the decrease in the specific surface area. Also, it can be concluded that amino-functionalization causes alteration of porosity parameters of PGME samples by decreasing specific surface area and shifting toward larger pores.

The surface morphology and the bulk structure of the copolymer particles were investigated by scanning electron microscopy (Figures 2-4). The copolymer beads of PGME1 and PGME2 and their amino-functionalized samples (Figures 2 and 3) had a rough surface, due to the pores formed during the copolymerization process, while non-porous samples PGME3 and PGME3-deta had a smooth and featureless surface. The non-porous beads had an almost ideal spherical shape (Figures 4a and 4b), while the porous ones (Figures 2a, 2b, 3a and 3b) showed certain irregularities.

Table 4. Porosity parameters of the initial and functionalized PGME samples

Sample	$S_{Hg}, m^2 g^{-1}$	$V_S, cm^3 g^{-1}$	$d_{V/2}, nm$
PGME1	59	0.96	74
PGME2	40	0.96	148
PGME1-deta	55	0.91	96
PGME2-deta	29	0.89	184

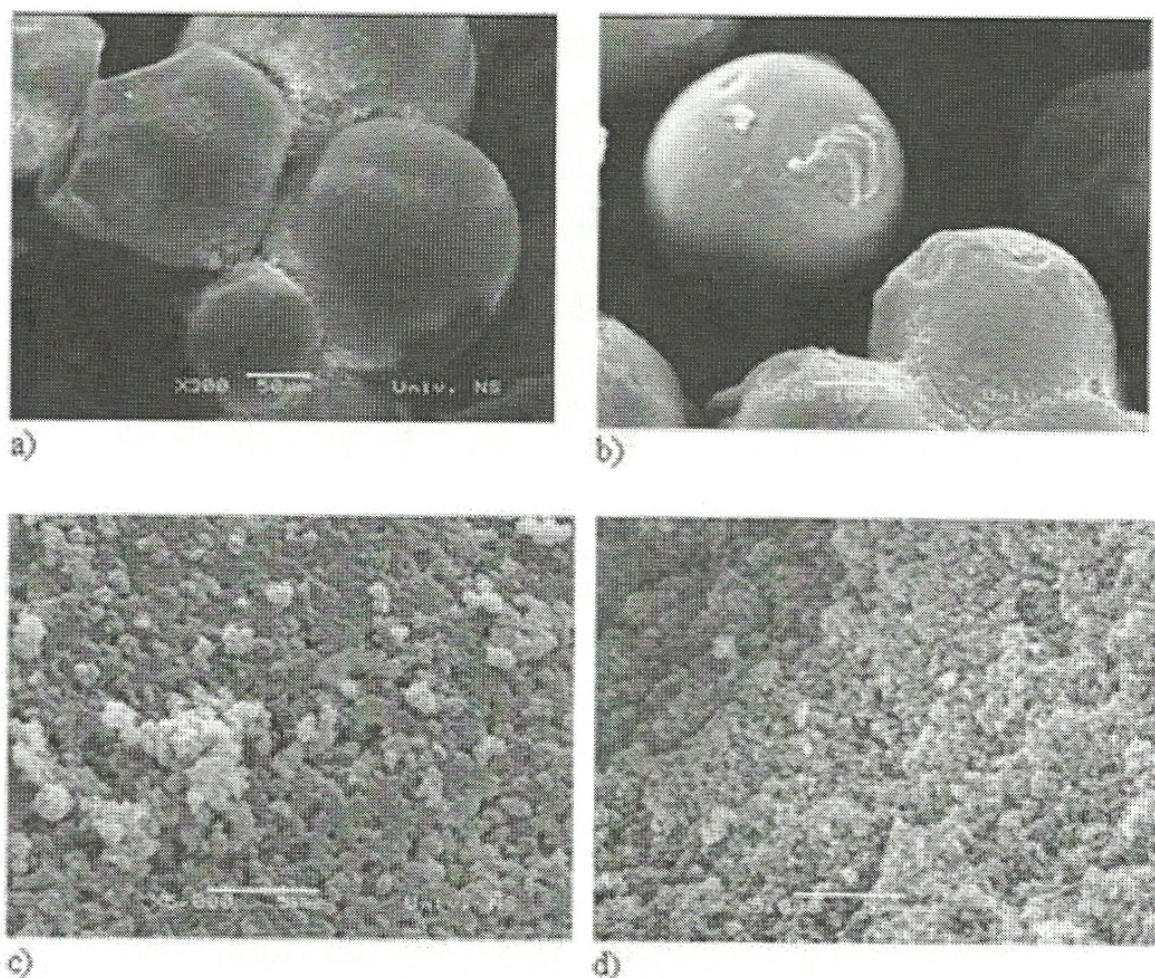


Figure 2. SEM photographs of beads: a) PGME1 and b) PGME1-deta [magnifications: 300x (a) and 200x (b)]; and cross-section of the beads: c) PGME1 and d) PGME1-deta [magnifications: 5000x (c) and 1000x (d)].

The cross-section of the samples revealed differences between porous and non-porous beads. The porous beads, both modified and unmodified, had pores formed between globular agglomerated structures. No pores were identified in the cross-sections of the non-porous samples (Figures 4c and 4d). Only brittle fracture appearance, which is characteristic of non-porous epoxy polymers was observed [43].

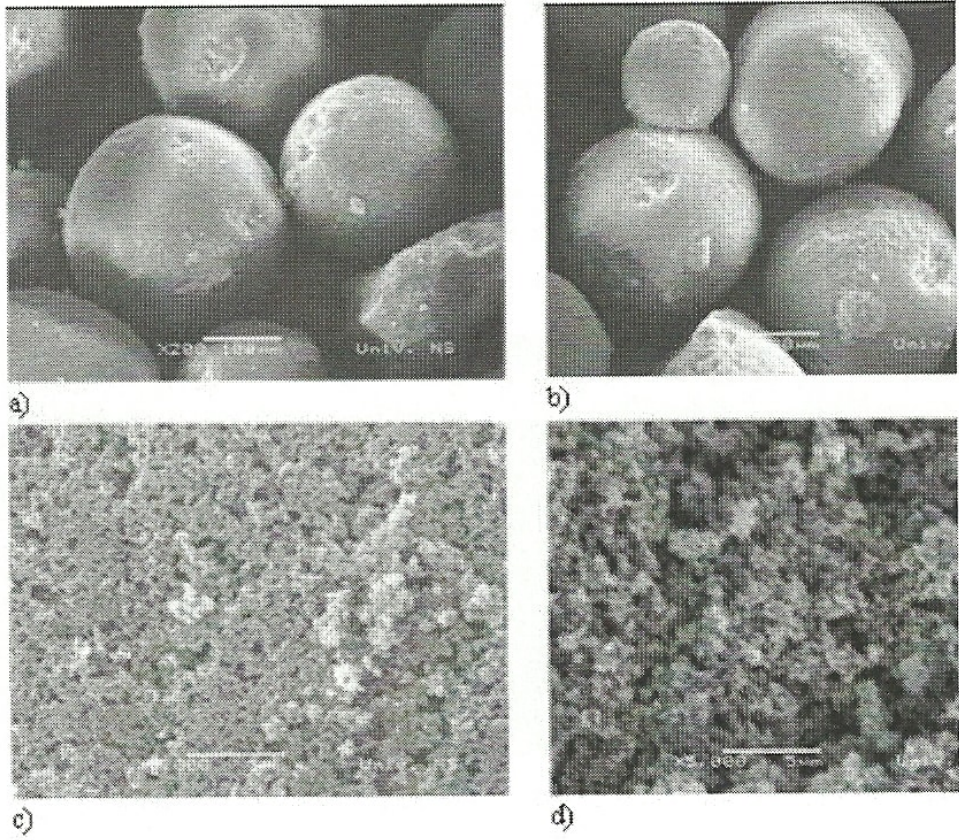


Figure 3. SEM photographs of beads (magnification 200x): a) PGME2 and b) PGME2-deta; cross-section of the beads (magnification 5000x): c) PGME2 and d) PGME2-deta.

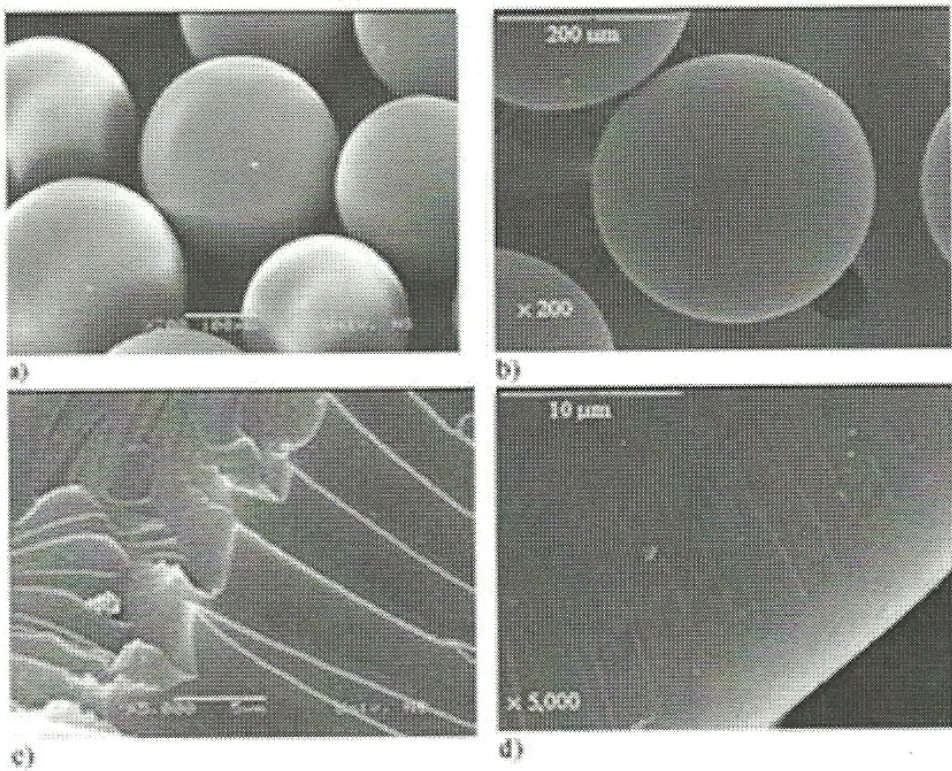


Figure 4. SEM photographs of beads (magnification 200x): a) PGME3 and b) PGME3-deta; cross-section of the beads (magnification 5000x): c) PGME3 and d) PGME3-deta.

3.2. Chromium(VI) Sorption on Amino-Functionalized PGME

From the standpoint of potential application of functionalized PGME copolymers, rapid sorption of metal ions would be beneficial, providing a short solution-sorbent contact time in the actual process.

The sorption of Cr(VI) species is dependent on total concentration of Cr(VI) and pH of the equilibrium solution [44]. The hexavalent species may be in the form of dichromate ($\text{Cr}_2\text{O}_7^{2-}$), hydrochromate (HCrO_4^-) or chromate (CrO_4^{2-}) depending on chromium concentration and pH. The dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$) is a dimer of HCrO_4^- , which is formed when the concentration of chromium exceeds approximately 1 g/l. In neutral solutions, Cr(VI) will be present in the form of HCrO_4^- and CrO_4^{2-} at low concentrations.

In this chapter, the experiments were performed at pH 1.80, which is favorable for maximum Cr(VI) sorption by PGME [16]. At low pH, protonated amino groups attached to the crosslinked copolymer attract the negatively charged chromium species, leading to higher sorption rates and capacities [45]. Cr(VI) sorption rates for three PGME-deta samples were determined as a function of initial Cr(VI) concentration. The results are presented in Figures 5-7.

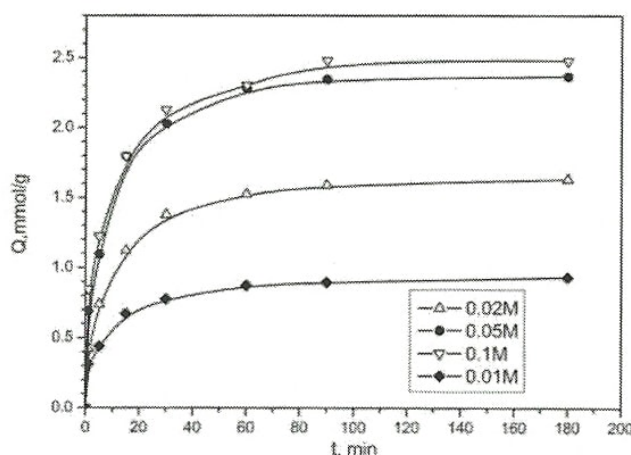


Figure 5. Sorption of Cr(VI) ions vs. time on PGME1-deta.

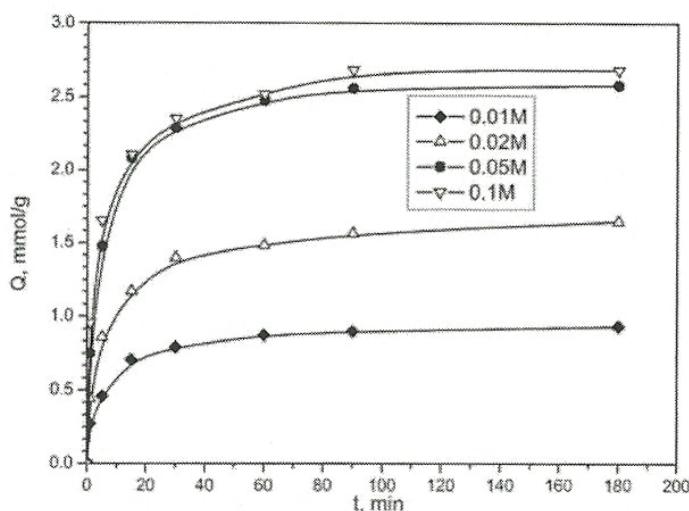


Figure 6. Sorption of Cr(VI) ions vs. time on PGME2-deta.

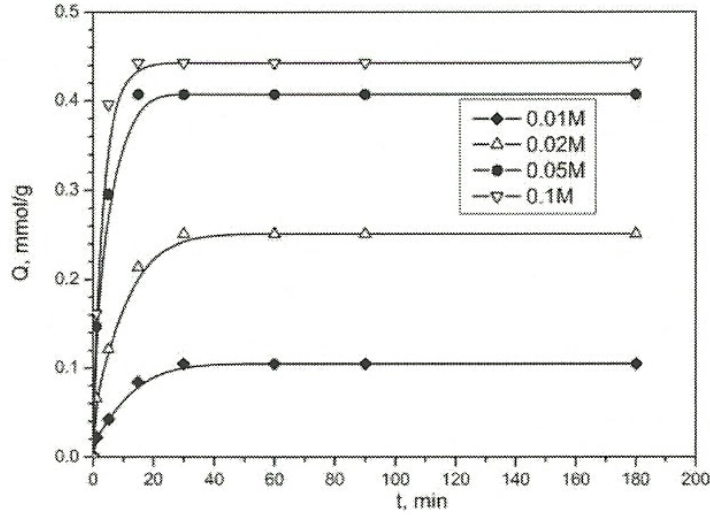


Figure 7. Sorption of Cr(VI) ions vs. time on PGME3-deta.

Table 5. Sorption capacities after 5 minutes (Q_5) and 30 minutes (Q_{30}), maximum sorption capacities (Q_{max}) and maximum ligand occupation (L_{max}) for metal sorption on amino-functionalized PGME samples

Sample	$C_{Cr(VI)}$, M	Sorption properties				
		Q_5 , $mmol\ g^{-1}$ (%)	Q_{30} , $mmol\ g^{-1}$ (%)	Q_{max} , $mmol\ g^{-1}$	Q_{max} , $g\ g^{-1}$	L_{max} , %
PGME1-deta	0.01	0.54 (47)	0.87 (83)	0.93	0.05	55.8
	0.02	0.74 (45)	1.38 (84)	1.63	0.08	97.7
	0.05	1.09 (46)	2.03 (86)	2.37	0.12	142
	0.1	1.22 (49)	2.13 (86)	2.48	0.13	148
PGME2-deta	0.01	0.46 (49)	0.83 (85)	0.93	0.05	42.9
	0.02	0.86 (52)	1.34 (85)	1.65	0.08	75.9
	0.05	1.47 (57)	2.29 (88)	2.58	0.13	119
	0.1	1.65 (62)	2.35 (88)	2.68	0.14	124
PGME3-deta	0.01	0.042 (40)	0.10 (100)	0.10	0.005	49.9
	0.02	0.12 (48)	0.25 (100)	0.25	0.013	119
	0.05	0.30 (73)	0.41 (100)	0.41	0.021	194
	0.1	0.40 (89)	0.44 (100)	0.44	0.023	211

Since the investigated samples have different ligand concentrations, in order to provide a more appropriate comparison, maximum ligand occupation, L_{max} , was calculated [46]:

$$L_{max} = \frac{Q_{max}}{C_{LIG}} \cdot 100 \quad (2)$$

The values of maximum ligand occupation (L_{max}), maximum sorption capacities (Q_{max}) and sorption capacities after 5 min (Q_5) and 30 min (Q_{30}), read from Figures 5-7, are given in Table 5.

Generally, three consecutive mass transport steps are associated with the sorption of a solute from solution by porous sorbents [43]. Firstly, sorbate migrates through the solution to the exterior surface of the sorbent particles by molecular diffusion, i.e. film diffusion, which is followed by solute movement from the particle surface into the interior by pore diffusion, and finally sorbate is adsorbed onto the active sites at the interior of the sorbent particle. This phenomenon takes relatively long contact time.

The literature data on Cr(VI) removal with a wide variety of sorbents, natural or synthetic, were obtained under different experimental conditions, so that they are almost impossible to compare. However, just for the sake of comparison, we will mention some of those results. High sorption rates of hexavalent chromium at the onset, and then plateau values gradually reached within 15 min, were observed for macroporous basic anion exchange resins containing tertiary amine groups, Lewatit MP 62 and Lewatit M 610 [44]. Bayramoglu et al. also observed high initial Cr(VI) sorption rate at pH 2, with time required to attain the equilibrium of 120 min, both for crosslinked poly(glycidyl methacrylate-*co*-methyl methacrylate) with attached ethylene diamine ($Q_{\max} = 137.7$ mg/g) [45] and magnetic poly(GMA-*co*-EGDMA) synthesized in the presence of Fe₃O₄ nano-powder, with immobilized poly(ethyleneimine) ($Q_{\max} = 22.9$ mg/g) [1]. Baran et al. reported that sorption of Cr(VI) attained an optimum at 30 min for chitosan, 50 min for chitin, 30 and 40 min for macroporous strongly acidic poly(styrene-*co*-divinylbenzene) based ion-exchangers Purolite CT-275 and Purolite MN-500; and 30 min for Amberlite XAD-7 [10]. The maximum sorption capacities were found to be 153.85 mg/g for chitosan, 126.56 mg/g for Purolite II; 89.29 mg/g for Purolite I and 70.42 mg/g for chitin.

The sorption capacities of the investigated amino-functionalized copolymers increased with increasing initial concentration of chromium ions in the medium. The obtained maximum sorption capacities of 130 mg/g for PGME1-deta, 140 mg/g for PGME2-deta and 23 mg/g for PGME3-deta are comparable with the literature data. The porous samples exhibit even superior sorption capacities than some types of reported sorbents. Figures 5-7 show high initial Cr(VI) sorption rate, which is more pronounced for higher metal concentrations. It suggests that the sorption process occurs predominantly at the surface of the highly crosslinked amino-functionalized beads. After that, the sorption rate becomes slower and saturation was gradually reached. The mechanism of intrapore diffusion (i.e. diffusion phenomenon where the rate of interaction is controlled by porosity parameters of the copolymer and the diffusion of the metal ions through the pores to interact with the internal surface) is represented by the slower sorption rates, which were noticed after 20 min of the initial sorption [44].

From the results in Table 5, it can be seen that eventhough the sample PGME2-deta has somewhat higher amino group concentration (6.27 mmol/g), than PGME1-deta (4.98 mmol/g), the values of maximum sorption capacities for macroporous samples are similar, indicating that beside amino group concentration other sorbent properties affect there sorption performance. After 30 minutes more than 80% for PGME1-deta, and almost 90% for PGME2-deta of the maximum sorption capacity was reached. This result suggests that although both sorbents are fast, the latter being somewhat faster. Also, ligand occupation values were higher than 100% for all the samples, which suggests that more than one amino group per ligand (and possibly hydroxyl group) are involved in Cr(VI)sorption.

The literature data show that the process of pore diffusion and the surface area in the pores determine sorption rate and capacity, respectively. The porous surface structure is considered to be an important factor in providing an increase in surface area. In addition, the pores reduce the mass transfer resistance and facilitate the intrapore diffusion of metal ions because of high internal surface area with low diffusional resistance in the copolymer beads (imply high adsorption capacity and rate) [1]. Different sorption behaviour of samples PGME1-deta and PGME2-deta could be expected bearing in mind that they have completely different parameters of porous structure. Namely, sample PGME1-deta has almost twice higher specific surface and lower pore diameter ($S_{Hg} = 55 \text{ m}^2/\text{g}$, $d_{V/2} = 96 \text{ nm}$) than PGME2-deta ($S_{Hg} = 29 \text{ m}^2/\text{g}$, $d_{V/2} = 184 \text{ nm}$). However, in the case of very fast sorption, it seems that the influences of the pore surface area and the pore diameter in porous chelating copolymers are interrelated and not so easy to explain. Apart from the influence of the ligand type and amount, the accessibility of functional groups is also an important parameter which should be taken into consideration.

The initial Cr(VI) sorption onto non-porous PGME3-deta is faster than for PGME1-deta and PGME2-deta, but maximum sorption capacities are very low, up to 0.44 mmol/g. Since the majority of epoxy groups are trapped in the core of the copolymer beads and they cannot be functionalized, the non-porous PGME is not suitable for metal ions sorption.

3.3. Kinetic Models

In order to examine the controlling mechanism of sorption processes, such as mass transfer and chemisorption, kinetic models were used to test the experimental data. Two kinetic models (the pseudo-first and the pseudo-second order) were used to determine the best-fit equation for the metals sorption by the PGME-deta samples with different porosity. The most commonly used is Lagergren's equation for pseudo-first order rate [48,49]:

$$\log(Q_{eq} - Q_t) = \log Q_{eq} - \frac{(k_1 t)}{2.303} \quad (3)$$

Where k_1 is the rate constant of pseudo-first-order sorption (min^{-1}), Q_{eq} and Q_t denote the amounts of sorbed metal ions at equilibrium and at time t (mmol g^{-1}), respectively. A plot of $\log(Q_{eq} - Q_t)$ versus t should give a straight line to confirm the applicability of the kinetic model. In a true first-order process, $\log(Q_{eq})$ should be equal to the intercept of a plot $\log(Q_{eq} - Q_t)$ against t .

A pseudo-second order equation is given as [48,49]:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_{eq}^2} + \frac{1}{Q_{eq}} t \quad (4)$$

Where k_2 ($\text{g}^{-1}\text{mmol}^{-1}\text{min}^{-1}$) is the rate constant of the pseudo-second order sorption. A plot of t/Q_t versus t should give a linear relationship for the second-order kinetics.

The rate constants k_1 and k_2 , equilibrium sorption capacity, Q_{eq} , and the correlation coefficient, R^2 , calculated from the values of intercepts and slopes of corresponding plots for the pseudo-first and the pseudo-second order equations are given in Table 6.

As an illustration, plots $\log(Q_{eq} - Q_t) - t$ (pseudo-first order) and $t/Q_t - t$ (pseudo-second order) for Cr(VI) sorption by PGME1-deta were shown in Figure 8.

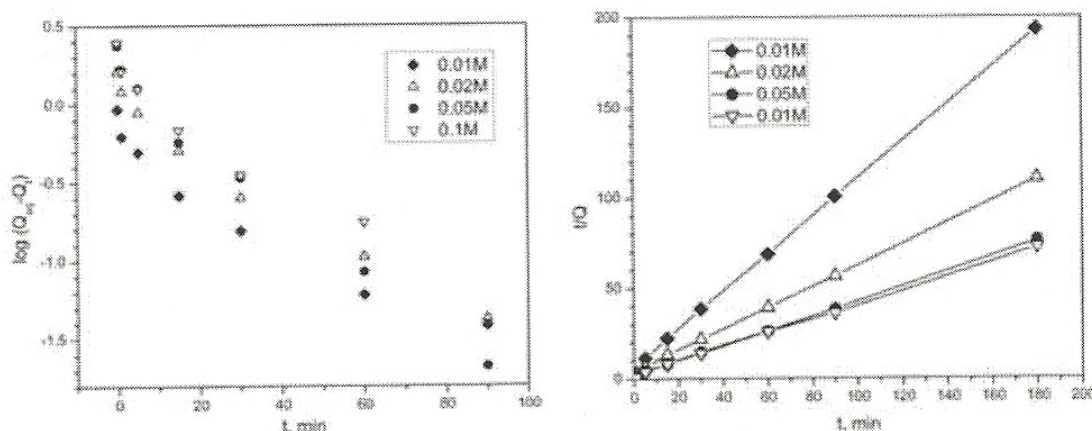


Figure 8. Pseudo-first (a) and pseudo-second order kinetics (b) of the Cr(VI) uptake by PGME1-deta.

Table 6. Kinetic data for Cr(VI) sorption on PGME-deta samples

Samples	Experimental		Models					
			Pseudo-first order kinetics			Pseudo-second order kinetics		
	$C_{\text{Cr(VI)}}, \text{M}$	$Q_{e \text{ exp}}, \text{mmol g}^{-1}$	k_1, min^{-1}	$Q_e, \text{mmol g}^{-1}$	R^2	$k_2, \text{g mmol}^{-1} \text{min}^{-1}$	$Q_e, \text{mmol g}^{-1}$	R^2
PGME1-deta	0.01	0.93	0.034	0.38	0.9208	0.194	0.96	0.9992
	0.02	1.63	0.039	1.13	0.9619	0.102	1.68	0.9994
	0.05	2.37	0.050	1.68	0.9830	0.088	2.43	0.9995
	0.1	2.48	0.041	1.66	0.9020	0.081	2.55	0.9992
PGME2-deta	0.01	0.93	0.035	0.57	0.8706	0.249	0.95	0.9997
	0.02	1.65	0.030	1.05	0.9154	0.249	1.68	0.9997
	0.05	2.58	0.051	1.81	0.9619	0.113	2.63	0.9998
	0.1	2.68	0.045	1.79	0.8625	0.113	2.73	0.9994
PGME3-deta	0.01	0.11	0.104	0.10	0.9892	2.42	0.11	0.9885
	0.02	0.25	0.122	0.23	0.9876	1.42	0.26	0.9992
	0.05	0.41	0.246	0.37	0.9505	2.58	0.41	0.9998
	0.1	0.44	0.449	0.44	0.9990	3.69	0.44	0.9999

The theoretical Q_{eq} values estimated from the first-order kinetic model gave significantly different values compared to the experimental ones, and the correlation coefficients are found to be rather low. This indicates that the first-order kinetic model is not applicable to the sorption of chromium on amino-functionalized samples.

On the other hand, the theoretical Q_{eq} values for chromium(VI) ions show good agreement with the experimental data for second-order kinetics, with correlation coefficients higher than 0.9990 (with one exception, for PGME3-deta and the lowest Cr(VI) concentration). This suggests that chromium sorption by PGME functionalized with diethylene triamine obeys the pseudo-second order kinetics, meaning that sorption depends both on the properties of the metal and the chelating copolymer.

CONCLUSION

Two porous samples and one non-porous sample of poly(GMA-co-EGDMA) [abbreviated PGME] were synthesized by suspension copolymerization and functionalized with diethylene triamine. The possibility of Cr(VI) removal from aqueous solutions was tested under non-competitive conditions. After 30 minutes, more than 80% for PGME1-deta, and almost 90% for PGME2-deta of maximum sorption capacity was attained. Also, the ligand occupation values were higher than 100% for all the samples, which suggests that more than one amino group per ligand (and possibly hydroxyl group) is involved in the Cr(VI) sorption.

The obtained maximum sorption capacities of 130 mg/g for PGME1-deta, 140 mg/g for PGME2-deta and 23 mg/g for PGME3-deta are comparable with the literature data. The porous samples exhibit even superior sorption capacities than some types of reported sorbents. The results show that the influences of surface pore area and pore diameter in porous chelating copolymers are interrelated and not so easy to explain. Apart from the influence of the ligand type and the amount, the accessibility of functional groups is also an important parameter which should be taken into consideration.

From the analysis of the two kinetic models it was concluded that the sorption of chromium(VI) by amino-functionalized PGME obeys the pseudo-second order kinetics, meaning that sorption depends both on the properties of the metal and the chelating copolymer.

ACKNOWLEDGMENTS

This work was supported by the Ministry of Science and Technological Development of the Republic of Serbia (Projects ON 142039 and ON 166001).

REFERENCES

- [1] Bayramoglu, G; Arica, MY. *Chem. Eng. J.*, 2008, 139, 20–28.
- [2] Kumar, PAI; Ray, M; Chakraborty, S. *Chem. Eng. J.*, 2009, 149(1-3), 340-347.
- [3] Graham, MC; Farmer, JG. *Chemistry of Freshwaters*, in: Harrison, R. M. ed. *Principles of Environmental Chemistry*; RSC Publishing: Cambridge, UK. 2007. (Inc. Chapter 3, 80-169 (2007)).
- [4] Costa, M. *Toxicol. Appl. Pharm.*, 2003, 188(1), 1-5.
- [5] U.S. Environmental Protection Agency: *Toxicological Review of Hexavalent Chromium*. National Center for Environmental Assessment, Office of Research and Development, Washington, DC. 1998.
- [6] Miretzky, P; Fernandez Cirelli, A. *J. Hazard. Mater.*, 2010, 180(1-3), 1-19.
- [7] Kaušpėdienė, D; Kazlauskienė, E; Gefenienė, A; Binkienė, R. *J. Hazard. Mater.*, 2010, 179(1-3), 933-939.
- [8] Mohan, D; Singh, KP; Singh, VK. *J. Hazard. Mater.*, 2006, 135(1-3), 280-295.
- [9] Yue, Z; Bender, SE; Wang, J; Economy, J. *J. Hazard. Mater.*, 2009, 166(1), 74-78.
- [10] Baran, A; Bıçak, E; Baysal, ŞH; Önal, S. *Bioresour. Technol.*, 2006, 98, 661–665.
- [11] Alguacil, FJ; Alonso M; Lozano, LJ. *Chemosphere*, 2004, 57, 789–793.
- [12] Ali Khan, S; Riaz-ur-Rehman; Ali Khan, M. *Waste Manage.*, 1995, 15(4), 271-282.
- [13] Da Fonseca, MG; De Oliveira, MM; Arakaki, LNH. *J. Hazard. Mater.*, 2006, 137(1), 288-292.
- [14] Yigitoglu, M; Arslan, M. *Polym. Bull.*, 2005, 55, 259-268.
- [15] Eisazadeh, H. *J. Appl. Polym. Sci.*, 2007, 104, 1964-1967.
- [16] Çaykara, T; Çakar F; Demirci, S. *Polym. Bull.*, 2008, 61, 311–318.
- [17] Nastasović, A; Sandić, Z; Suručić, Lj; Maksin, D; Jakovljević, D; Onjia, A. *J. Hazard. Mater.*, 2009, 171(1-3), 153-159.
- [18] Uğuzdoğan, E; Denkbaş, EB; Kabasakal, OS. *J. Hazard. Mater.*, 2010, 177(1-3), 119-125.
- [19] Neagu, V; Mikhalovsky, S. *J. Hazard. Mater.*, 2010, doi:10.1016/j.jhazmat.2010.07.057 .
- [20] Nastasović, A; Jovanović, S; Đorđević, D; Onjia, A; Jakovljević, D; Novaković, T. *React. Funct. Polym.*, 2004, 58(2), 139-147.
- [21] Nastasović, A; Jovanović, S; Jakovljević, D; Stanković S; Onjia, A. *J. Serb. Chem. Soc.*, 2004, 69(6), 455-460.
- [22] Nastasović, A; Đorđević, D; Jakovljević, D; Novaković, T; Vuković, Z; Jovanović, S. *Heavy metal ions removal with macroporous poly poly(4-vinyl pyridine-co-ethylene glycol dimethacrylate)*, in: Bregg R. K. ed. *Leading Edge Polymer Research*; Nova Science publishers: New York. 2006. Chapter 7, 213-234.
- [23] Nastasović, A; Jakovljević, D; Sandić, Z; Đorđević, D; Malović, Lj; Kljajević, S; J. Marković, J; Onjia, A. *Amino-functionalized glycidyl methacrylate based macroporous copolymers as metal ion sorbents*, in: Barroso M. I. ed. *Reactive and Functional Polymers Research Advances*; Nova Science Publishers New York. 2007, Chapter 2, 79-112.
- [24] Malović, Lj; Nastasović, A; Sandić, Z; Marković, J; Đorđević, D; Vuković, Z. *J. Mater. Sci.*, 2007, 42(10), 3326-3337.