



PHYSICAL CHEMISTRY 2006

Proceedings

*of the 8th International Conference
on Fundamental and Applied Aspects of
Physical Chemistry*

September 26-29,
Belgrade, Serbia

ISBN 86-82139-26-X
Title: Physical Chemistry 2006. (Proceedings)
Editors Prof. dr A. Antić-Jovanović
Published by: The Society of Physical Chemists of Serbia, Studentski trg 12-16, P.O.Box 137, 11001 Belgrade, Serbia
Publisher: Society of Physical Chemists of Serbia
For publisher: Prof. dr S. Anić, president of the Society of Physical Chemists of Serbia
Printed by: "Jovan" Printing and Published Comp;
250 Copies; Number of Pages: x + 442; Format B5;
Printing finished in September 2006.
Text and Layout: Aleksandar Nikolić
250 – copy printing

STUDY OF COPPER ADSORPTION ON AMINOFUNCTIONALIZED MACROPOROUS POLY(GMA-co-EGDMA)

A. Nastasović¹, Z. Sandić², Lj. Malović³,
D. Jakovljević¹ and J. Marković⁴

¹*ICTM -Center for Chemistry, Studentski trg 12-16, Belgrade, Serbia.
(anastaso@chem.bg.ac.yu)*

²*Faculty of Science, Mladena Stojanovića 2, Banja Luka, BIH.*

³*Faculty of Forestry, Kneza Višeslava 1, Belgrade, Serbia.*

⁴*Vinča Institute of Nuclear Sciences, P.O. Box 522, Belgrade, Serbia.*

Abstract

Macroporous crosslinked copolymer of glycidyl methacrylate and ethylene glycoldimethacrylate (PGME) was synthesized by suspension copolymerisation and modified by ring-opening reaction of epoxy groups with ethylene diamine, diethylene triamine and triethylene tetramine. The uptake of copper ions by amino-functionalized macroporous PGME from aqueous solutions was investigated in batch experiments. The equilibrium data fitted well with the Langmuir model.

Introduction

Metal adsorption through precipitation and ion exchange/chelation is a common approach for reducing the toxicity of the wastewater streams of hydro-metallurgical and other industries [1]. Chelating copolymers that consist of crosslinked copolymer (solid support) and ligand with O, N, S and P atoms that coordinate different metal ions, are often used for that purposes. Amino-functionalized macroporous glycidyl methacrylate copolymers, obtained by reaction of epoxy groups of the copolymer with amines possess high capacity and good selectivity for heavy metal ions, combined with chemical and mechanical stability [2,3]. In this study, macroporous crosslinked copolymer of glycidyl methacrylate and ethylene glycoldimethacrylate (PGME) was modified with ethylene diamine (PGME-en), diethylene triamine (PGME-deta) and triethylene tetramine (PGME-teta). Amino-functionalized samples were used for copper sorption. The experimental data were analysed by the Langmuir model of adsorption.

Experimental

Macroporous PGME (surface area $36 \text{ m}^2 \text{ g}^{-1}$, pore diameter 87 nm, particle size 150-500 μm) was prepared by suspension copolymerisation [6]. PGME-en was obtained by heating the mixture of 4.0 g of PGME, 10.0 g of ethylene diamine and 100 ml of toluene at 80 °C for 6 h. PGME-deta was obtained by heating the mixture of 3.6 g of PGME, 15.7 g of diethylene triamine and 100 ml of toluene at 80 °C for 6 h. PGME-teta was obtained by heating the mixture of 5.0 g of PGME, 7.75 g of triethylene tetramine and 30 ml of toluene. After the reaction, samples were filtered, washed with

ethanol and dried. Sorption of Cu(II) ions was studied by contacting 0.1 g of copolymer with 50 ml of metal salt solution. After 3 h, samples were filtered and the Cu(II) concentration in filtrate was determined by atomic absorption spectrometry (AAS, SpectrAA Varian Instruments). The sorption capacity was calculated from expression:

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

where C_0 and C are the concentrations of the metal ions in the initial solution and in the aqueous phase after treatment for certain period of time, respectively, V is the volume of the aqueous phase and m is the amount of the copolymer beads used for the experiment.

Results and Discussion

The adsorption isotherms of Cu(II) on amino-functionalized samples are shown in Fig. 1. The maximum uptake for PGME-en, PGME-deta and PGME-teta are 1.38, 2.20 and 2.62 mmol g^{-1} . Obviously, the Cu(II) uptake increases with the increase of equilibrium concentration until reaching the saturation value, after which the concentration no longer affects the uptake capacity. The affinity of the adsorbent towards the metal ions may be verified by plotting the adsorption data according to Langmuir adsorption model [5]:

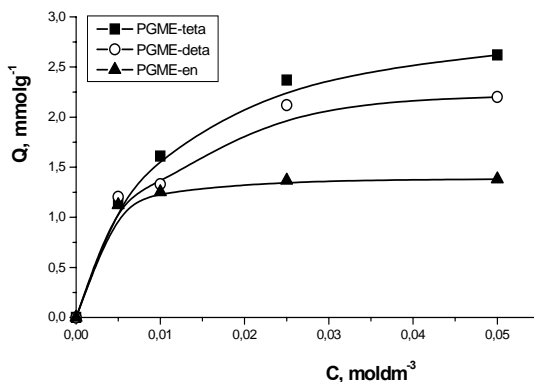


Fig. 1. Adsorption isotherms of Cu(II) on PGME-en, PGME-deta and PGME-teta at pH 4 and 25 °C.

$$\frac{C_e}{q_e} = \frac{C_e}{q_s} \frac{1}{Kq_s} \quad (2)$$

where C_e is the equilibrium concentration of metal ions in solution, q_e the adsorbed value of metal ions at equilibrium concentration, q_s the saturated adsorbing capacity and K is the binding constant, related to the energy of adsorption. Plots C_e/q_e vs. C_e gave a straight line, indicating that the adsorption corresponds to Langmuir isotherm. The values of q_s and K for adsorption of Cu(II) on PGME-en, PGME-deta and PGME-teta were obtained from the slopes and intercepts of the lines in Fig. 2 and reported in Table 1. The value of correlation coefficient (r^2) and experimental value of saturation capacity, $q_{e, \text{exp}}$, indicate that the Langmuir isotherm

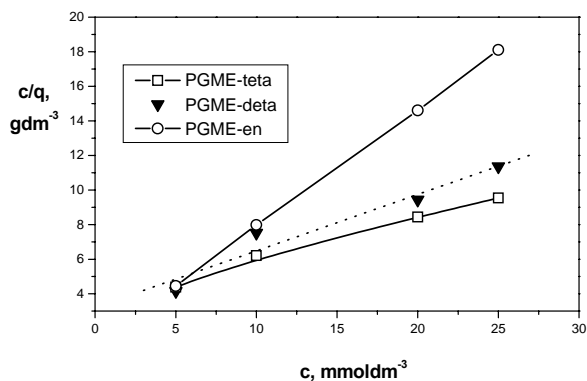


Fig. 2. Langmuir isotherms for Cu(II) adsorption on PGME-en, PGME-deta and PGME-teta.

has been best fitted for Cu(II) sorption on PGME-en. The lowest value of correlation coefficient (0.970) indicate deviation from Langmuir model in the case of Cu(II) uptake on PGME-deta.

Table 1. Parameters of Langmuir adsorption isotherm for the Cu(II) adsorption on amino-functionalized samples at 25 °C.

Sample	$q_{e,exp}$, mmolg ⁻¹	q_s , mmolg ⁻¹	K dm ³ mmol ⁻¹	r^2
PGME-en	1.38	1.47	0.62	0.999
PGME-deta	2.20	3.06	0.10	0.970
PGME-teta	2.62	3.98	0.07	0.994

Conclusion

The obtained results show that the equilibrium distribution of Cu(II) between the sorbent and solution phases can be described using the Langmuir model of monomolecular layer adsorption. The best fit for the Cu(II) adsorption data was observed for PGME sample modified with ethylene diamine.

Acknowledgement

This work was supported by the Serbian Ministry of Science and Environmental Protection.

References

- [1] S. D. Smith, S. D. Alexandratos, *Solvent Extr. Ion Exch.*, 2000, **18**, 779-807.
- [2] F. Švec, H. Hrudkova, D. Horak, J. Kalal, *Angew. Makromol. Chem.*, 1977, **63**, 23-36.
- [3] A. Nastasović, S. Jovanović, D. Đorđević, A. Onjia, D. Jakovljević, T. Novaković, *React. Funct. Polym.*, 2004, **58**, 139-147.
- [4] S. Jovanović, A. Nastasović, N. Jovanović, K. Jeremić, *Mater. Sci. Forum*, 1996, **214**, 155-162.
- [5] A. Atia, A. M. Donia, K. Elwakeel, *Sep. Purif. Technol.*, 2005, **43**, 43-48.
- [6] P. K. Malik, *J. Hazard Mater.*, 2004, **B113**, 81-88.