

Study on Adsorption of Heavy Metals Cd and Pb by Poly(γ -glutamic acid)

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ABSTRACT

The objective of this study was to investigate the effects of addition concentration of various poly(γ -glutamic acid (PGA) and pH of Cd and Pb heavy metal solutions on adsorption (chelation) of Cd²⁺ and Pb²⁺ by PGA. Three types of PGA, high molecular weight (MW) Na-PGA [Na-PGA(H)], low MW Na-PGA [Na-PGA(L)], 6%1M cross-linked PGA [6%1M PGA], were donated by Vedan Enterprise Co., Taichung County, Taiwan, ROC. One of PGA, [S-PGA], was obtained by my laboratory. The adsorption of Cd²⁺ in 10ppm Cd aqueous solution (pH ? 9.0) by addition of 40mg/L Na-PGA(H) or Na-PGA(L) was about 9ppm (90%). This result was 0.225g Cd²⁺/g PGA by another unit. The adsorption percentage of Cd²⁺ by addition of 4mg/L PGA was also about 90% (another unit was 2.25g Cd²⁺/g PGA) when pH of Cd aqueous solution was equal to or more than 11.0 or 10.0 for 6%1M PGA or S-PGA, respectively. When pH of Pb aqueous solution was 9.0, the best uptake of Pb²⁺ on PGA was obtained. The adsorption percentage of Pb²⁺ by addition of 40mg/L Na-PGA(H) or S-PGA or 4mg/L 6%1M PGA was about 90%, while that by 120mg/L Na-PGA(L) addition was only 80% (another unit was 0.066g Pb²⁺/g PGA). The uptakes of Cd²⁺ and Pb²⁺ on PGA little increased as the molecular weight (MW) of PGA used in heavy metal aqueous solution increased. The adsorption of Cd²⁺ and Pb²⁺ on PGA could be affected by the various type and MW of PGA and pH of heavy metal aqueous solution. This may be due to the chemical structure of the various type of PGA.

Keywords : poly(γ -glutamic acid (PGA) ; heavy metal (Cd and Pb) ; adsorption (chelation)

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REFERENCES

王一雄，1997，土壤環境污染，國立編譯館，台北，229-260。 2. 呂文凱，2003，利用回應曲面法尋求苔蘚桿菌生產聚穀胺酸之培養基最適化，大葉大學食品工程研究所碩士論文。 3. 阮國棟，1989，水處理技術-有害成分去除法，科技出版社，新竹，24-30；54-68。 4. 胡筱敏、羅茜、劉述波，1998，微生物絮凝劑的研究與應用，國外金屬礦選礦，16-18。 5. 宮小燕、弈兆坤、王曙光、黎澤華，2001，微生物絮凝劑絮凝特性的研究，環境化學，550-556。 6. 陳靜生，1992，水環境化學，曉園出版社，台北，131-146。 7. 陳永甡編著，1998，環境保護法規，文經圖書，台北，168-182。 8. 陶茂林、施大林、王蕾、陳金林，1997，微生物絮凝劑的製備及絮凝條件的研究

究，食品與發酵工業，26-28。9. 章裕民，1998，環境工程化學，文京圖書，台北，471-472。10. 許世興、顏棋鑫，2003，幾丁聚糖顆粒吸附之有害重金屬之探討，國家圖書館，台北。11. 黃志彬，1995，利用幾丁聚醣吸附水中微量重金屬之研究，國立交通大學環境工程研究所，國科會研究計畫報告。12. 蔡永興、陳見財、張啟達、潘建成、朱昱學，1997，電鍍業減廢回收與污染防治，經濟部工業局，台北，59-90。13. Bhattacharya D., J. A. Hestekin, P. Brushaber, L. Cullen, L. G. Bachas, and S. K. Sikdar, 1998, Novel poly-glutamic acid functionalized microfiltration membranes for sorption of heavy-metals at high capacity. *J. Memb. Sci.* 141(1):121-135. 14. Cardenas G., P. Orlando, and T. Edelio, 2001, Synthesis and applications of chitosan mercaptanes as heavy metal retention agent. *Intern. J. Bio. Macromol.* 28:167-174. 15. Cheng C., Y. Asada, and T. Aida, 1989, Production of γ -polyglutamic acid by *Bacillus subtilis* A35 under denitrifying conditions. *Agric. Biol. Chem.* 53:2369-2375. 16. Chun L., D. F. Yu, A. Newman, F. Cabral, C. Stephens, N. Hunter, L. Milas, and S. Wallace, 1998, Complete regression of well-established tumors using novel water-soluble poly (L-glutamic acid)-paclitaxel conjugate. *Cancer Res.* 58:2404-2409. 17. Chun L., J. E. Price, L. Milas, N. R. Hunter, S. Ke, W. Tansey, C. Charnsagavej, and S. Wallace, 1999, Antitumor activity of poly (L-glutamic acid)-paclitaxel on syngeneic and xenografted tumors. *Clin. Cancer Res.* 5:891-897. 18. Daninippon Pharmaceutical Co. Ltd., 1972, Ice cream stabilizer, Japanese Patent. 19735/72. 19. Domard A, Rinaudo M, 1983, International Journal of biological Macromolecules, Vol. 5, pp.49. 20. East G, and Qin Y, 1993, Journal of applied polymer science. Vol. 50, pp. 1773. 21. Goto A., and M. Kunioka, 1994, Biosynthesis and hydrolysis of Poly(γ -glutamic acid) from *Bacillus subtilis* IFO3335. *Biosci. Biotechnol. Biochem.*, 56:1031-1035. 22. Jeuniaux C, 1996, Advanced Chitin, Sci. 1, Vol. 1. 23. Konno A., T. Taguchi, and T. Yamaguchi, 1989, New use of polyglutamic acid for foods. European Patent Application EPO284386A1. 24. Kunioka. M., 1995, Biosynthesis of poly (γ -glutamic acid) from L-glutamine, citric acid and ammonium sulfate in *Bacillus subtilis* IFO3335. *Appl. Microbiol. Biotechnol.* 44:501-506. 25. Kunioka. M., 1997, Biosynthesis and chemical reactions of poly(amino acid)s from microorganisms. *Appl. Microbial. Biotechnol.* 47:469-475. 26. Kurane R., and H. Matsuyama, 1994, Production of a bioflocculant by mixed culture. *Biosci. Biotech. Biochem.* 58:1589-1594. 27. Kurane R., K. Takeda, and T. Suzuki, 1986, Screening and characteristics of microbial flocculants. *Agric. Biol. Chem.* 50:2301-2307. 28. Kurane R. and Y. Nohata, 1991, Microbial flocculation of waste liquids and oil emulsion by a bioflocculant from *Alcaligenes latus*. *Agric. Biol. Chem.* 55:1127-1129. 29. Lee S. H., S. O. Lee, K. L. Jang, and T. H. Lee, 1995, Microbial flocculant from *Arcuadendron* sp. TS-49. *Biotech. Lett.* 17: 95-100. 30. Li C., D. F. Yu, R. A. Newman, F. Cabral, L. C. Stephens, N. Hunter, L. Milas, and S. Wallace, 1998, Complete regression of well-established tumors using a novel water-soluble poly(L-glutamic acid)-paclitaxel conjugate. *Cancer Research* 58:2404-2409. 31. McLean R. J. C., D. Beauchemin, L. Clapham, and T. J. Beveridge, 1990, Metal-binging characteristics of the gamma-glutamyl capsular polymer of *Bacillus licheniformis* ATCC 9945. *Appl. Environ. Microbiol.* 56(12):3671-3677. 32. Mitsuiki M., A. Mizuno, H. Tanimoto, and M. Motoki, 1998, Relationship between the antifreeze activities and the chemical structures of oligo- and poly(glutamic acid)s. *J. Agric. Food Chem.* 46(3): 891-895. 33. Multani A. S., C. Li, M. Ozen, M. Yadav, D. F. Yu, S. Wallace, and S. Pathak, 1997, Paclitaxel and water-soluble poly(L-glutamic acid)-paclitaxel, induce direct chromosomal abnormalities and cell death in a murine metastatic melanoma cell line. *Anticancer Research.* 17:4269-4274. 34. Muzarelli R, 1977, Chitin. Pergamon Press. New York. 35. Muzarelli R, 1973, Naturally Chelating Polymer Pergamon Press. New York. Chap.5. 36. Nestle N., and R. Kimmich, 1996, Heavy metal uptake of alginate gels studied by NMR microscopy. *Colloids & Surface.* 115: 141-147. 37. Onsoyen E., and O. Skaugrud, 1990, " Metal Recovery Using Chitosan ", *J. Chem. Tech. Biotechnol.* 49:395-404. 38. Ontni Y., Y. Tabata, and Y. Ikada, 1996, A new biological glue from gelatin and ploy(L-glutamic acid). *J. Biomed. Meter. Res.*? 31:157-1391. 39. Salehizadeh A., and S. A. Shojaosadati, 2001, Extracellular biopolymeric flocculants: Recent trends and biotechnological importance. *Biotech. Adv.* 19:371-385. 40. Salehizadeh A., M. Vossoughi, and I. Alemzadeh, 2000, Some investigations on bioflocculant producing bacteria. *Biochem. Eng. J.* 5:39-44. 41. Suh H., G. S. Kwon, C. H. Lee, H. S. Kim, H. M. Oh, and B. D. Yoon, 1997, Characterization of bioflocculant produced by *Bacillus* sp. DP-152. *J. Ferment. Bioeng.* 84(2): 108-112. 42. Takeda M., J. Koizumi, H. Matsuoka, and I. Nakamura, 1991, A protein bioflocculant produced by *Rhodococcus erythropolis*. *J. Ferment. Bioeng.* 74:408-409. 43. Takeda M., J. Koizumi, H. Matsuoka, and M. Hikuma, 1992, Factors affecting the activity of a protein bioflocculant produced by *Nocardia amarae*. *Agric. Biol. Chem.* 55:2663-2664. 44. Toeda K., and R. Kurane, 1991, Microbial flocculant from *Alcaligenes cupidus* KT201. *Agric. Biol. Chem.* 55:2793-2799. 45. Troy F.A., 1993, Chemistry and biosynthesis of the poly(γ -D-gluramyl)capsule in *Bacillus subtilis*, 1. Properties of the membrane-mediated biosynthetic reaction. *J. Biol. Chem.* 48:305-315. 46. Wang Z., K. Wang, and Y. Xie, 1995, Bioflocculant-producing microorganisms. *Acta Microbiol. Sin.* 35(2): 121-129. 47. Yokoi H., T. Arima, J. Hirose, S. Hayashi, and Y. Takasaki, 1996, Flocculation properties of poly(γ -glutamic acid) produced by *Bacillus subtilis*. *J. Ferment. Bioeng.* 82(1): 84-87. 48. Yokoi H., T. Yoshida, S. Mori, J. Hirose, S. Hayashi, and Y. Takasaki, 1997, Biopolymer flocculant produced by an *Enterobacter* sp. *Biotech. Lett.* 19(6): 569-573. 49. Yokoi H., O. Natsuda, J. Hirose, S. Hayashi, and Y. Takasaki, 1995, Characteristics of biopolymer flocculant produced by *Bacillus* sp. PY-90. *J. Ferment. Bioeng.* 79: 378-380.