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COLUMN MODE STUDY TO EVALUATE THE BEHAVIOR OF METAL ADSORPTION OF PHOSPHORIC ADSORBENT SYNTHESIZED BY RADIATION INDUCED GRAFT POLYMERIZATION

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ABSTRAK

STUDI MODE COLUMM UNTUK MENGEVALUASI SIFAT PENGUAPAN LOGAM OLEH ABSORBENT DENGAN GUGUS FUNGSI PHOSPHOR YANG 01 SINT ASI SECARA POLIMERISASI CANGKOK DENGAN INDUKSI RADIASI. Studi mode column dilakukan untuk mengevaluasi sifat-sifat dari adsorbent serat yang memiliki gugus fungsi phosphor. Serat adsorbent disintesis langsung dengan cara polimerisasi cangkok monomer 2-hydroxyethyl methacrilate Phosphoric acid pada serat polipropilene yang di coating poliethylene dengan menggunakan radiasi. Parameter yang diteliti adalah pengaruh dari pH, tipe adsorbent, konsentrasi logam, kecepatan alir dan persen grafting. Persen grafting tertinggi yang diperoleh adalah 427% setara kandungan phosphor sebanyak 5.2 mmol. Adsorpsi metoda column dengan menggunakan column packing yang mengandung adsorbent bergugus fungi phosphor untuk logam Pb diperoleh pH optimum adalah 6 dan breakthrough dari adsorbent tipe Na dan H adalah sarna atau keduanya memiliki kesamaan kinetika penyerapan.Kurva dan titik breakthrough tidak secarakuat dipengaruhi oleh kecepatan alir, hal ini menandakan adsorbent memiliki kecepatan penyerapan yang tinggi. Adsorben memiliki kemampuan penyerapan yang baik terhadap Pb, Cd, Co dan Zr. Kapasitas penyerapan tertinggi adalah 4.2 mrnol/gram penyerap untuk Pb dan Zr.

ABSTRACT

COLUMN MODE STUDY TO EVALUATE THE BEHAVIOR OF METAL ADSORPTION OF PHOSPHORIC ADSORBENT SYNTHESIZED BY RADIATION INDUCED GRAFT POLYMERIZA TION. Column mode study were performed to evaluate the behavior of fibrous adsorbent having phosphoric function prepared by directly synthesis of 2-hydroxyethyl methacrylate phosphoric acid onto polypropylene coated polyethylene by radiation induced graft polymerization. The parameter observed was effect of pH, adsorbent form, metal concentration, flow rate and degree of grafting. The higher degree of grafting obtained was 427 % which correspond to 5.2 mmol phosphoric content. In the column mode adsorption of Pb by using column packed with phosphoric adsorbent, the optimum pH found was 6 and the breakthrough curve Na and H form of adsorbent was similar, meaning the same behavior of adsorbent kinetics. The breakthrough point and curve do not strongly depend on flow rates which indicate that the adsorbent has a high adsorption rate. The adsorbent also has good ability to adsorb Pb, Cd, Co and Zr. The highest adsorption capacity obtained was 4.2 mmol/g adsorbent for Pb and Zr.

Key word: Phosphoric adsorbent, chelating fiber, column mode study, breakthrough capacity, toxic metals

INTRODUCTION

Ion exchange fibers became interesting because of their characteristic metal ion selectivity, high capacity and exchange rate, a variety form allowing many possibility for their use.[1-6]

Extensive investigation were carried out with chelating exchanger containing phosphoric group. Ion exchanges (resins or fiber) having phosphoric acid functional reported have good selectivity and ability to absorbed lanthanides and actinides, Pb and Ba, Zn, and to metal ion classified into hard Lewis acid such as Fe (III), Zr (IV), Mo (IV), and U (IV). Due to these hard Lewis cation to form sparingly soluble hydroxides, they exist as soluble species in strongly acidic pH region.[7-19]

Jyo, A.et.all. were studied to develop cation exchange using polypropylene coated by polyethylene fiber having phosphoric acid or phosphonic groups. Reaction used was two steps, first grafted poly (glacidyl methacrylate) orpoly (cloromethylstyrene) onto polypropylene coated by polyethylene fiber. Second step was phosphorylation. These fibers exhibit extremely rapid adsorption rate in divalent heavy metals ion such as Pb and Cu from weak acidic pH solution (pH ca. 5_6).[20-21] However, their main disadvantages were two step reaction, using chemical initiator to graft of phosphoric monomer and their capacity of uptake metal rather low because of low degree of grafting (30% degree of grafting).

The aim of the present work to column mode study is to perform the behavior of toxic metals adsorption of fibrous adsorbent having phosphoric function prepared by directly synthesis of 2-hydroxyethyl methacrylate phosphoric acid onto polypropylene coated polyethylene by radiation induced graft polymerization. The parameter observed was effect of pH, adsorbent form, metal concentration, flow rate and degree of grafting. While trunk polymer used was polypropylene coated polyethylene non woven fiber (PPPE), 2-hydroxyethyl methacrylate phosphoric acids (HMPA) were used as monomer. PPPE fiber was excellent matrix for membrane development due to its chemical resistance, not cross-linked and large surface area. The advantages are that the diffusion of ion would not be hindered by cross-linking in the resin and improvement of exchange rate would result because of a large surface area. Radiation induced graft polymerization have advantages because clean technology and the grafting achieved can be controlled to be desired extensively.

EXPERIMENT MATERIALS

Non-woven cloth composed of polypropylene coated polyethylene fiber (FPPPE, Kurashiki MFG Co. Osaka, Japan) was used as a trunk polymer.

2-hydroxyethyl methacrylate phosphoric acids (HMPA) as Phosphoric monomer were purchased from Kyoeisha.Co. Osaka, Japan. The monomer is mixture of mono (50%) and diester (50%) . Their chemical structures were shown in figure 1.

METHODS

Electron beam irradiation

PPPE non-woven cloth sample was cut into rectangular shape (7 cm x 15 em). Its initial weight, Wo, was measured and it was placed into polyethylene bags. After air in the bags was displaced by nitrogen and the samples were then irradiated with electron beam (2 Mev, 1 rnA) for 20 min (totals dose 200 kGy). Irradiated sample was stored in an electric refrigerator at -80°c. . The electron accelerator used was a cascade type one (Dynamitron, named accelerator No.2) at Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute. (JAERI).

Graf polymerization of phosphoric acid monomer

20 (wt %) solution of phosphoric acid monomer were prepared in 10: 90 % MeOH /H_2O mixture solvent and 0.05 mmol/l Mohr salt. Nitrogen was bubbled into monomer solution for 30 min to expel dissolved oxygen. The irradiated sample was taken into a glass ampoule, and air in the ampoule was eliminated by a vacuum pump. The monomer was then sucked into the ampoule and resulting reaction mixture was maintained at 60°C reaction temperatures for given reaction time. At the completion of grafting, the graft copolymer was washed by adding DMF sample into reaction mixture. The graft copolymer was then washed by methanol and dried under vacuum at 40°C for 12 hours.

The Degree of grafting was calculated using the following equation:

Degree of grafting (%)= (Wg-Wo) x 100/Wo.

where Wo and Wg represent the weight of initial and grafted polymers, respectively.

Column mode adsorption

The phosphoric adsorbent had 160 % degree of grafting (0.05 g) swollen in water and was packed into column packed into column (i.d. 7mm) and the column was then washed by water. The volume of the adsorbent bed was 0.4 ml which was as the standard to convert flow rate in ml/h into space velocity in h^{-1}.The feeding solution was 10 mM metal (Pb, Cd, Co) unbuffer solution. After the feeding solution, the column was washed by water and metal was eluted by 1M hydrocloric acid and then washed by water for the next run. Column effluent for adsorption process were collected on fraction collector. The concentration in each fraction was measured by inductive plasma mass spectroscopy. In this work breakthrough curve was plotted between C/Co versus bed volume of feeding solution and C and Co represent concentration of metal in column effluent and the feeding solution, respectively

RESULT AND DISCUSSION

Graft polymerization

The grafting process was conducted by using 20 % HMPA in 10-90 methanol-water mixed solvent, 60° C for desired reaction time (1-24h). The grafting obtained was shown in figure 1. The degree of grafting increased with the reaction times and achieved 427 % at 24 reaction time which corresponds with 5.2 meq/g of phosphoric content and acid capacity 4.9 meq/g adsorbent. The degree of grafted sample used were 160 and 400 % .

Column mode study

Effect of pH on metal adsorption

Effect of pH on lead absorption shows in figure 2. The increase of pH value from 1-6 the amount of lead adsorbed were increased from 0.63 and 4.6 mg (0.025 mg adsorbent) and the optimum pH was 6. The decrease of lead sorption corresponded to low pH value (pH<5) is apparent due to an increase in competition for adsorption site by H+ at the higher pH (pH > 6), the lead tends to precipitate. The result obtained was similar with the other result conducted by batch method. Un-buffered lead solution has pH value above 5 and to minimize other interference, un-buffered solution was used for the late experiment

Effect of adsorbent form

Column Na form was condition by feeding successively 2 M sodium hydroxide, water, I M hydrochloric acid, water and repeated and then the last feeding with sodium hydroxide and water. For hydrogen form, the same their method was conducted except for using sodium hydroxide. The concentration lead used was 10 mmol un-buffered solution. The result of the breakthrough behavior experiment (Figure 3) showed that the breakthrough point is about 25 bed volume. The lead adsorbed (value of C/Co) become increased fast up to C/Co value 0.6 after the breakthrough point and litle decrease of adsorbent speed until 0.9 , and then become slow after the value of C/Co above 0.9. The breakthrough capacity and total capacity for Na form were 1.9 and 2.9 mmol/g adsorbent and for H+ form 1.9 and 3.1 mmol/g adsorbent.. The breakthrough curve of Na and W forms of phosphoric adsorbent was similar indicating the same behavior of adsorption kinetic.

Effect of metal concentration on breakthrough curve

Effect of various lead (Pb) concentration on breakthrough curve shown in figure 4. The feeding solution was 1, 2 and 10 mrnol/L Un-buffer solution. While the increase of concentration from 1, 2 and 10, the breakthrough point decrease from around 42, 33 and 25 bed volume. The breakthrough curve shifted toward left with increasing metal concentration and at 10 mmol/L metal concentration after breakthrough point the value ClCo increased fast up to saturation end. The total capacity were increased 0.84, 1.25 and 3.1 mmol *lg* adsorbent of lead with increasing metal concentration.

Effect of flow rate on breakthrough curve

The breakthrough curves for different flow rates (75 , 250 and 1250 hoi) showed in figure 4. The breakthrough capacity of all flow rates almost gave the same value of 24 bed volume. After the breakthrough point, at all flow rates, the curve was similar tendency, the adsorbed metal (value of C/Co) become increased fast up to ClCo value 0.6 and become slow after ClCo value 0.9. The breakthrough capacity for 75 ,250 and 1250 hoi were 1,8, 1,9 and 1,9 mrnol/ g adsorbent respectively and the total capacity were 2.9, 3.1 and 3,1 mmol/g, respectively. The breakthrough capacity does not strongly depend on flow rate. At the fastest flow rate 1250 hoi, nearly equal to upper limit of our present column system, the breakthrough capacity is not decreased, indicating that the adsorbent has fast reaction rate.

Effect of metal ion

When breakthrough curve was investigated for 4 kinds of metal ions, the feeding solution wasl0 mM Pb, Cd and Co un-buffered, Zr at pH 1 and flow rate was of 250 hoi. For Co, Cd and Pb, it was used adsorbent with 160 % degree of grafting and for Zr, it was used 400% degree of grafting. The result gave almost the same breakthrough point at capacity of 25 bed volume. The breakthrough curves for three metals showed almost the same tendency increased fast up until ClCo value 0.96 and then slow. The total capacity achieved Co, Cd, Zr and Pb were 2.8, 2.7, 4.1 and 3.1 mmol/gram adsorbent, respectively.

Effect of degree of grafting

Effect of degree of grafting on breakthrough curve was shown in figure 7. The degree of grafting of phosphoric adsorbent used was 160% and 400%. The result showed that the breakthrough capacity obtained was 1.9 and 2.1 mmol/g adsorbent and total capacity was 3.1 and 4.1 mmol/g adsorbent respectively. The breakthrough capacity showed little increase because the feeding solution was enough high concentration (10 mmol/L). After ClCo value 0.8 for 400% degree of grafting, the exchange rate is slower than 160%. The phenomena appeared because at higher degree of grating, the degree of crosslinking of phosphoric adsorbent was also high.

CONCLUSION

Column mode study were performed and it was concluded that fibrous adsorbent having phosphoric group have high adsorbent rate and high capacity for Pb, Cd, Co and Zr. Indeed the highest adsorption capacity obtained was 4.2 mmol/g adsorbent for Pb and Zr.

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Figure and Table Caption

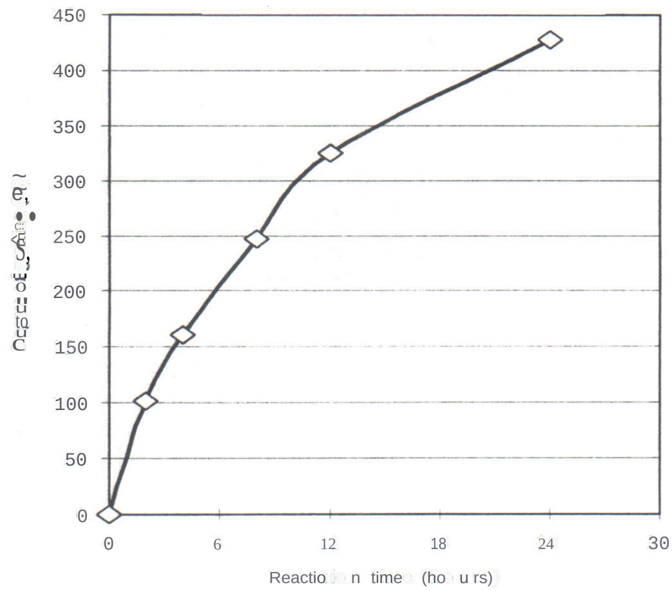

Figure 1. The degree of grafting on various reaction time (total dose 200kGy, 60°C and 20% of HMPA in mixed solvent 10/90 ofMeOH/H_2O ,w/w%, 0.05 mmol/L Mohr salt).

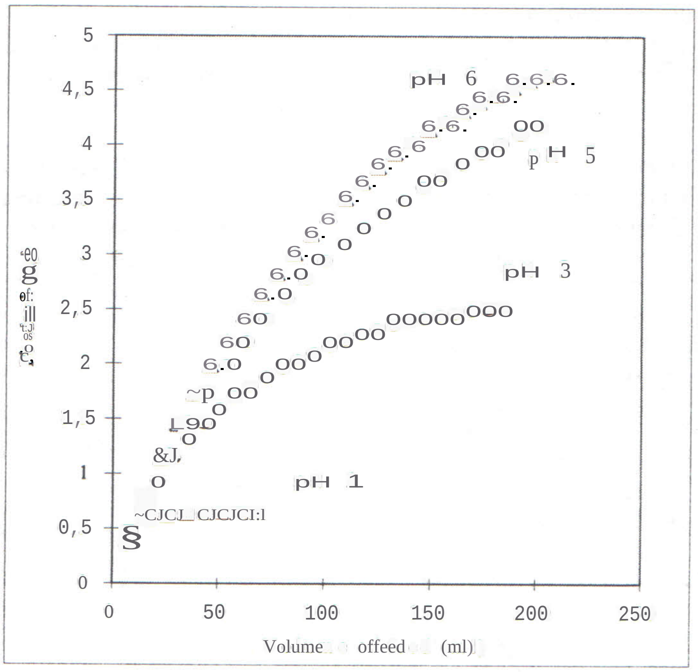

Figure 2. Effect of pH on adsorption ofPb
(100 ml/min, 50 ppm, 0.025 g adsorbent

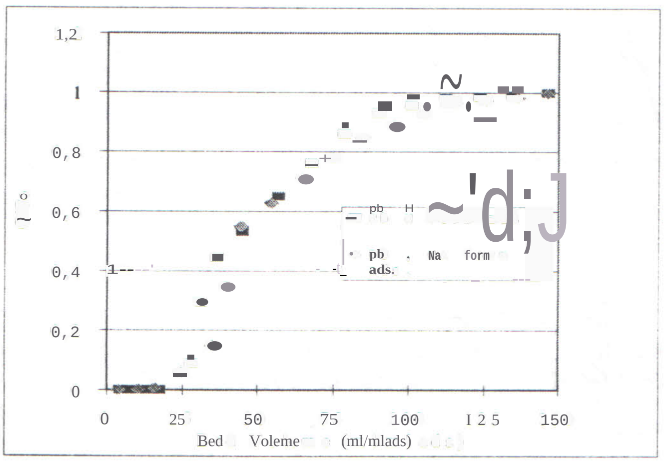

Figure 3. Effect of different form of adsorbent on breakthrough curve (0.05 g adsorbent, 10 mM of Pb unbuffered solution, flow rate 100 mllmin)

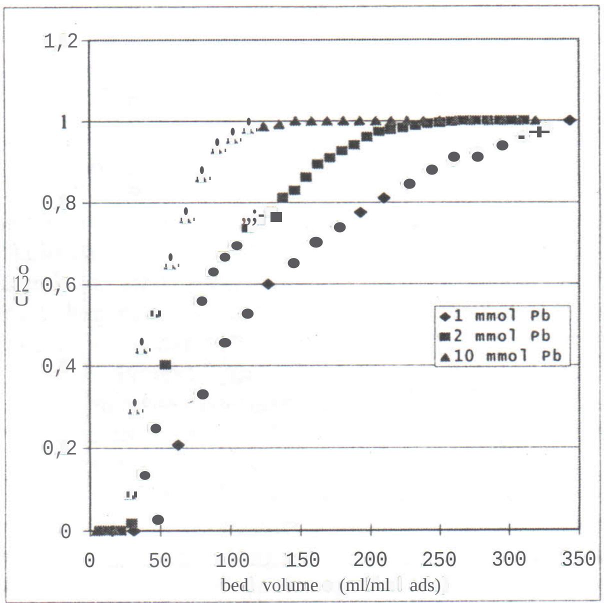

Figure 4. Effect of metal concentration on breakthrough curve (0.05 g adsorbent, 100 ml/min)

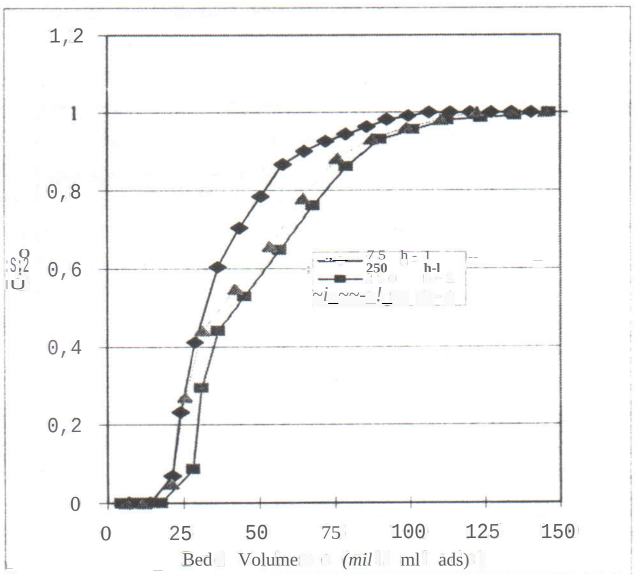

Figure 5. Effect of flow rate on breakthrough curve (0.05 g adsorbent, 10 mmol unbuffered solution)

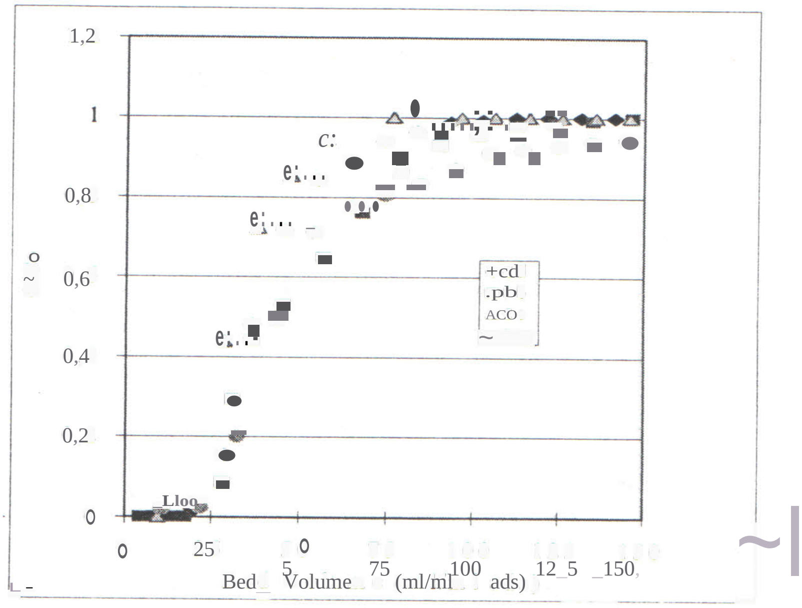

Figure 6. Effect of different metal on breakthrough curve (0.05 g adsorbent, Pb, Co and Cd 10 mmol metal unbuffered solution and Zr 10 mmol at pH 1)

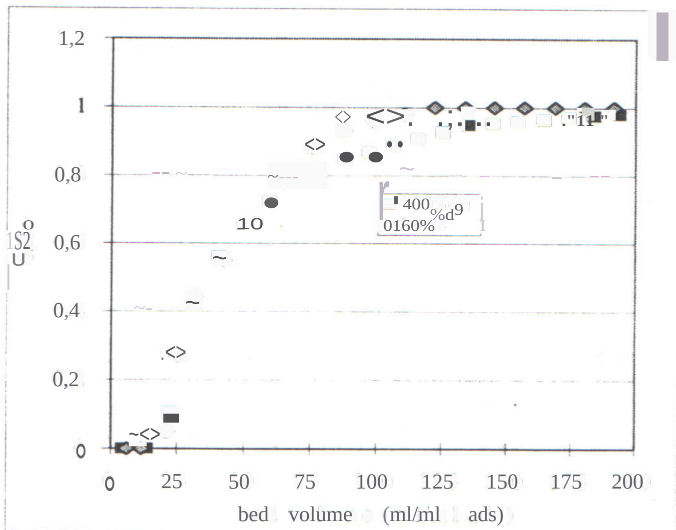

Figure 7. Effect of degree of grafting on breakthrough curve (0.05 g adsorbent, 10 mmol metal unbuffered solution)