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Effect of Two-step Surface Modification of Activated Carbon on the Adsorption Characteristics of Metal Ions in Wastewater II. Dynamic Adsorption

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Abstract

Based on the previous results of the equilibrium and batch adsorptions, the removal efficiency of the two-step surface-modified activated carbon (2^{nd}AC) for heavy metal ions such as Pb, Cd, and Cr in fixed column was evaluated by comparing with that of the as-received activated carbon (AC) and the first surface-modified activated carbon (1^{st}AC). The order of metal removal efficiency was found as 2^{nd}AC > 1^{st}AC >> AC, and the efficiency of the 2^{nd}AC maintained over 98% from the each metal solution. Increase of the removal efficiency by the second surface modification was contributed to maintain favorable pH condition of bulk solution during adsorption process. The removal of the heavy metals on the 2^{nd}AC was selective with Pb being removed in preference to Cr and Cd in multicomponent solutions and slightly influenced by phenol as the organic material.

Keywords : *Carbon, Surface Modification, Metal Ions, Phenol, Multicomponent, Fixed Bed*

1. Introduction

Many workers have made efforts to remove heavy metals from industrial wastewater using various kinds of processing methods such as chemical precipitation, evaporation, ion exchange, cementation electrolysis, and reverse osmosis [1, 2]. These conventional technologies appear to be useful, but often create some problems such as the separation of sludge and the generation of secondary waste [3, 4]. The concept of adsorption of metals by activated carbon was first demonstrated in 1929 [5]. Up to approximately 1970, the use of activated carbon for metal removal was confined to improve the efficiency of metallurgical recovery [6]. In 1970, the United States became alarmed about the widespread contamination of surface waters by mercury. Filters were subsequently developed and were effective in removing mercury from caustic solutions. One component of these filters was activated carbon. This was reported to be the first use of carbon for the sole purpose of trace metal removal from wastewater. Sigworth and Smith showed the relationship between the solution pH and adsorption of inorganic compound by activated carbon [7]. They showed that metal adsorption was inversely proportional to metal solubility in aqueous solutions and the better adsorption can be expected when conditions render the compound less soluble. Most metals become less soluble and form hydroxides and oxides with increasing of the solution pH [8]. Therefore, the control of solution pH is very important to remove heavy metals.

Carbons can be oxidized by heat treatment in air, carbon dioxide or oxygen. Many workers reported that the nature and the amount of surface oxides formed on treatment with oxygen depend on the nature of the carbon, the history of its formation, its surface area, and the temperature of treatment. In case of oxidative modification in solutions, the major reaction is the formation of the surface compounds, although some gasification may also occur depending on the strength of the oxidative modification and the severity of the experimental conditions. The formation of the surface oxygen compounds using various types of carbon and using different oxidative modifications in gaseous and liquid phases has been studied by a large number of investigators and has well been reviewed [9, 10].

From the previous our works of part I (Equilibrium and Batch adsorption), the adsorption site of metal ions on activated carbon were oxide groups such as carboxyl and phenolic and increased by the surface modification. But the acidic carbon lead a decrease in solution pH during adsorption of the heavy metal ions. Generally, adsorption capacity of metal ions on activated carbon was relatively low at lower pH ranges [11]. In order to overcome the decrease of adsorption capacity with decreasing solution pH, two steps of surface modification of activated carbon was performed. The adsorption capacity of the second surface-modified activated carbon (2^{nd}AC) showed the remarkable increase in adsorption capacity of metal ions.

In industrial fields, various kinds of fixed bed have been used to remove metal ions of low concentration in final wastewater treatment. Therefore, adsorption behavior in fixed bed should be investigated to obtain data for a control of adsorption process. In this work, extensive experiments were focused to obtain the breakthrough curves of the various metal ions (Pb, Cd and Cr) adsorption on three kinds of activated carbons (AC, 1stAC, 2ndAC) in single component and three component systems. The breakthrough behaviors in four component system made by introducing phenol to the three component system were also obtained to investigate the influence of organic material which is co-existed with metal ions in wastewater.

2. Experimental

2.1. Materials

The AC as a raw material was received from Samchori Co. in korea, which was made of coconut shell. The 1stAC was prepared with the acidic modification of the AC in 7 N nitric acid solution at 80^{o}C. The 2ndAC was made by the subsequent modification of the 1stAC in alkaline solution, which was prepared with mixing 1 N NaOH and 1 N NaCl solution, and then diluted to 0.05 N solution. Its surface modification condition obtained from previous study was also applied [13].

Reagent grade $Pb(NO_3)_2$, $CdCl_2 \cdot 2.5H_2O$, and $CrCl_3 \cdot 6H_2O$ were used to prepare the metal solutions. The concentration of metal ions was measured by Atomic Adsorption Spectrophotometer (Perkin Elmer 51000 PC), and UV Spectrometer was used to measure the concentration of phenol according to the Standard Method [14].

2.2. Fixed Experiment

To estimate adsorption behaviors of the metal ions and phenol in flowing fluid, fixed bed experiments were performed in various kinds of solutions. The solutions adjusted to pH 5 were prepared in glass-made tank of 3 L volume and then immersed in constant-temperature water bath. Each of the carbons was packed in a glass column of 0.01 m in inside diameter and 0.3 m in length. Bed height in packed column was controlled with packed mass of carbon, which ranged from 3 cm (mass: 1 g) to 6 cm (mass: 2 g). Micrometering pump was used to maintain the constant downflow. These carbons were immersed in distilled water for about ten hours to remove air in pores of carbon so as to prevent influence of a bubble during the adsorption in column. Glass beads were packed the upper and lower of carbon bed to prevent a channeling effect in the column, and then distilled water was flowed by the micro-metering pump for 2 hours. Afterward, prepared solutions of the metal ions and phenol were flowed with constant flow rate of 1~2 ml/min.

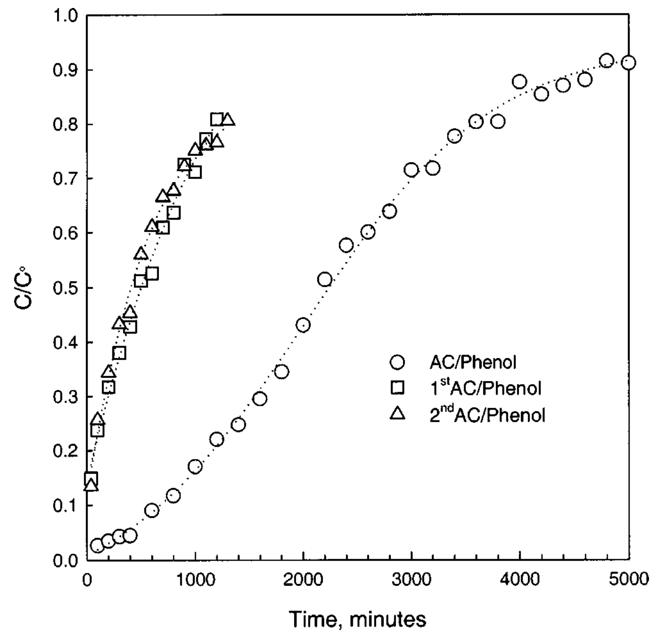

Fig. 1. Breakthrough curves of phenol in fixed bed packed with three kinds of carbons at input solution of pH 5 and temperature 303 K [Co: 0.531 mol/m^3, F.R. (Flow Rate): 1 ml/min, Packed Mass: 1 g].

All the experiments were conducted at 30^{o}C. Effluent from the fixed bed was collected periodically using a fraction collector. The solution pH of collected sample was directly measured. In this study, adsorption experiments for multi-component system as well as single component were carried out. Metal ion concentrations in the three components solution were 0.241 mol/m^3 (50 mg/l) of Pb, 0.445 mol/m^3 (50 mg/l) of Cd, 0.096 mol/m^3 (5 mg/l) of Cr, respectively. Four components solution was made by introducing 0.531 mol/m^3 (50 mg/l) of phenol to the three component system. Its composition of multicomponent solutions followed the yearbook of Environment Statement by Ministry of Environment in Korea. The concentration of metal ions in multicomponent solution was measured by ICP-AES (Model: JOBIN-YVON JY50).

3. Results and Discussion

3.1. Single Component Solution

Figs. 1~4 show the breakthrough curves for adsorption of phenol and three metal ions on the three kinds of carbons in single component solution at initial pH 5. Fig. 5 represents the pH variations of effluent from the packed column.

The breakthrough curve of phenol on the AC, as shown in Fig. 1, was a typical S-shape curve so as to effectively remove phenol in fixed bed. Breakthrough times of phenol on the 1stAC and 2ndAC were shorter than that on the AC. The reduction of removal efficiency of phenol on the two

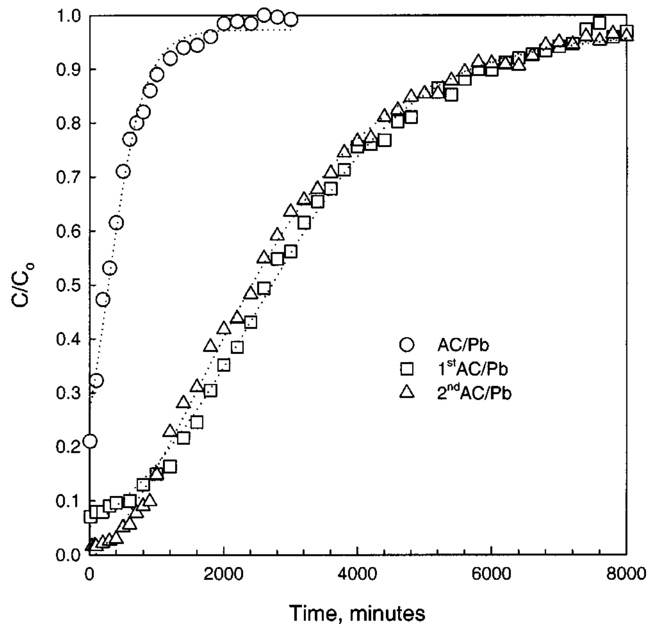

Fig. 2. Breakthrough curves of Pb in fixed bed packed with three kinds of carbons at input solution of pH 5 and temperature 303 K [C_o: 0.241 mol/m^3, F.R.: 1 ml/min, Packed Mass: 1 g].

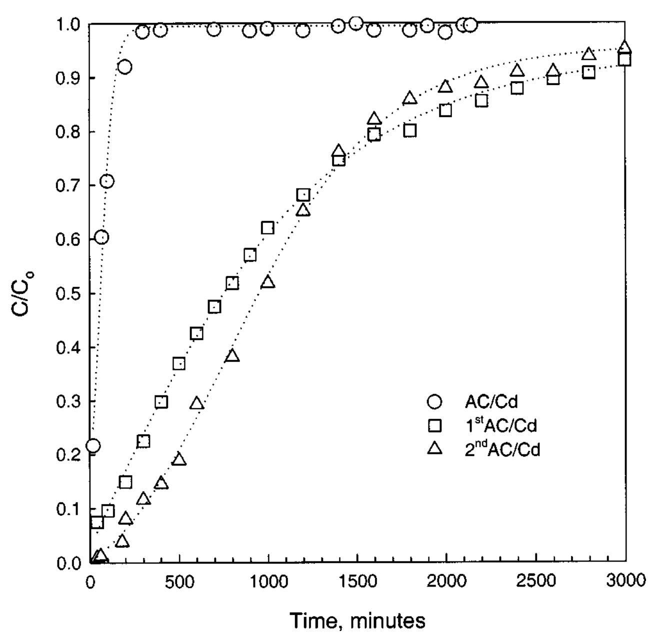

Fig. 3. Breakthrough curves of Cd in fixed bed packed with three kinds of carbons at input solution of pH 5 and temperature 303 K [C_o: 0.445 mol/m^3, F.R.: 1 ml/min, Packed Mass: 1 g].

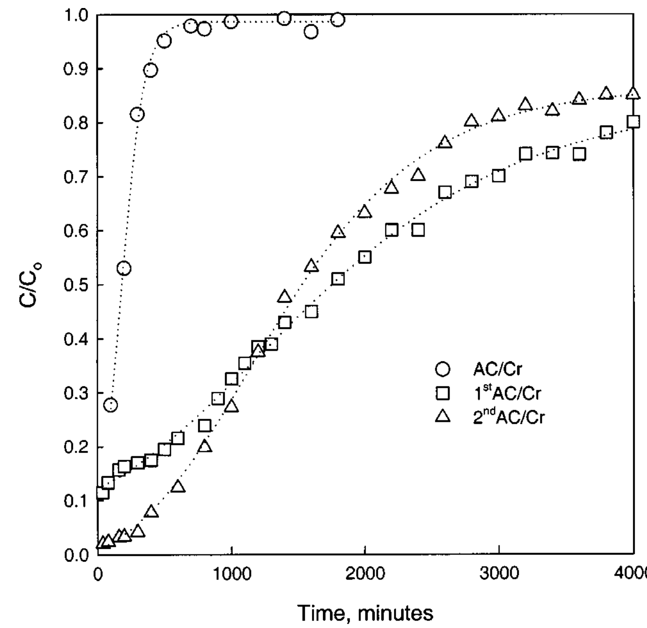

Fig. 4. Breakthrough curves of Cr in fixed bed packed with three kinds of carbons at input solution of pH 5 and temperature 303 K [C_o: 0.096 mol/m^3, F.R.: 1 ml/min, Packed Mass: 1 g].

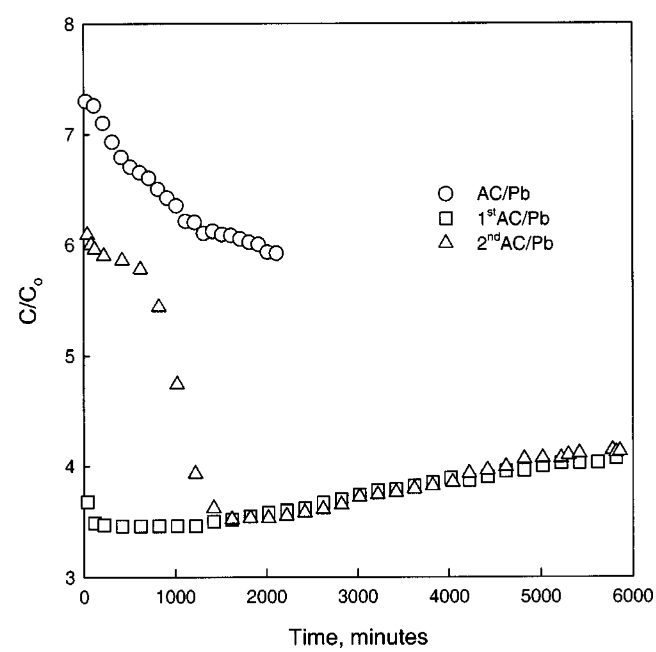

Fig. 5. Variations of Effluent pH in fixed bed packed with three kinds of carbons in single component solution at input solution of pH 5 and temperature 303 K.

kinds of surface-modified carbons would be contributed to deplete the adsorption sites for phenol molecules during the surface modifications. The adsorption of phenol on activated carbon was found to depend on the surface area of the carbon, as well as being influenced by the presence of oxygen complexes. It was also reported that chemisorbed oxygens reduced the dispersion forces of adsorption, and the adsorption capacity of phenol was decreased [11].

In Figs. 2~4, all breakthrough curves of three metal ions adsorption on the AC packed column (hereafter, AC-column) increased rapidly at earlier adsorption time. However, the 2ndAC packed column (hereafter, 2ndAC-column) showed more extended breakthrough time curves than the 1stAC packed column (hereafter, 1stAC-column), in a viewpoint of removal efficiency at the beginning point and treatment time until the relative concentration, C/C_o of 0.1. As shown in Fig. 5, the pH variations of effluent in the 2ndAC-column was maintained about the value of 6 at earlier adsorption time. However, the 1stAC-column sharply decreased in initial adsorption period and leveled off to about 3.5. Considering the increase of effluent pH in the AC-column, the carbons prepared by the various pyrolytic processes were like poly-condensed aromatic hydrocarbons, which are known to be Lewis bases (electron donor) and which can preferentially exchange H^+ ions to OH^- ions from water or aqueous solutions [15]. This would leave the surrounding liquid with excess OH^- ions, giving rise to the basic character. Although the higher solution pH enhance the metal adsorption, the lower removal efficiency of metals in the AC-column would be attributed to the insufficiency of the surface functional groups relating to ion-exchange with metal ion. The surface functional groups were remarkably increased by the first modification as shown in the previous works. Ultimately, the increased pH in the AC-column might be influenced by the releasing electron from the AC as well as some physical adsorption of acid [11]. In the case of the 2ndAC-column, the higher effluent pH condition at earlier time would provide an effective adsorption condition for the removal of metal ions adsorption, which was attributed to surface characteristic of the 2ndAC as shown in the Surface Characterization of Part I. Therefore, the second modification of the 1stAC produced oxide groups including sodium as mentioned by Boehm [8]. The groups on the 2ndAC could change the initial solution pH toward the pH_{PZC}. From the figure, the solution pH decreased with adsorption time and then identified with that of the 1stAC-column. It would consider that the functional groups on the 2ndAC was returned to acid group by exchanging with hydrogen ion.

Based on the results from the single component solution, two step surface modification of activated carbon revealed to be useful method for the removal of metal ions, because the removal efficiency achieved over 98% at initial time and the breakthrough time at C/C_o of 0.1 was about two times longer than that for the 1stAC.

3.2. Three Components Solution

Breakthrough curves of the metal ions in fixed bed packed with three kinds of carbons in three components solution [Pb (0.241 mol/m^3: 50 ppm), Cd (0.445 mol/m^3: 50 ppm), Cr (0.096 mol/m^3: 5 ppm)] at input solution pH of 5 are represented in Figs. 6~8, and Fig. 9 shows variations in effluent pH with adsorption time.

As shown in Fig. 7 and 8, the removal efficiencies of Pb in both the 1stAC and 2ndAC-column were much higher than those of the other metal ions, but it was difficult to remove Cd ion effectively in three component system. When weakly and strongly adsorbable components are contained in the fluid entering an adsorbent column, the latter replaces the former if these components have an identical adsorption

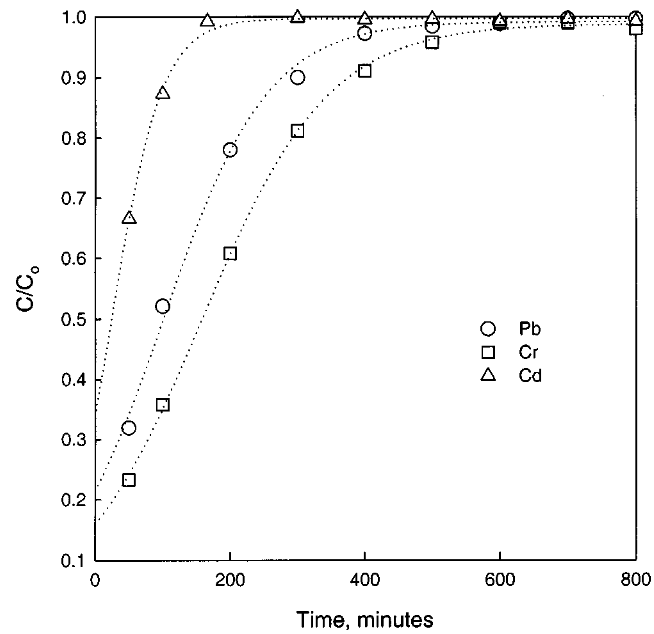

Fig. 6. Breakthrough curves of various metal ions in fixed bed packed with AC in three component system at input solution of pH 5 and temperature 303 K [C_o: Pb (0.241 mol/m^3), Cd (0.445 mol/m^3), Cr (0.096 mol/m^3), F.R.: 2 ml/min, Packed Mass: 2 g].

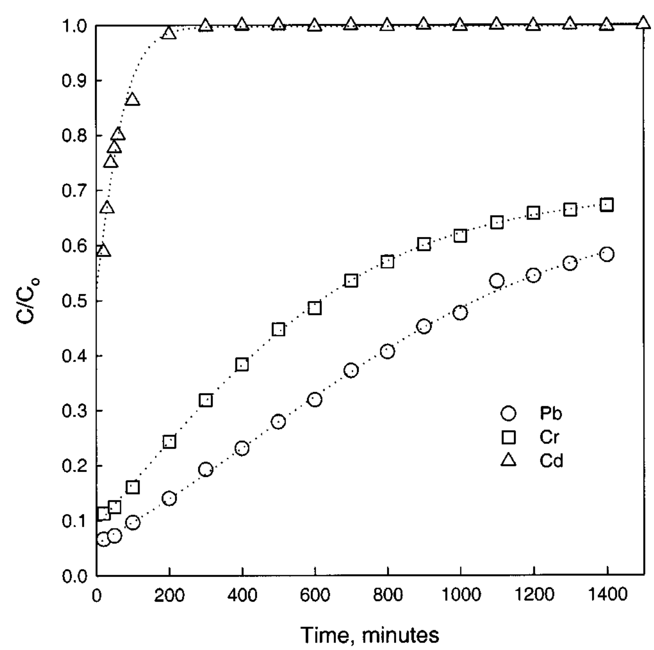

Fig. 7. Breakthrough curves of various metal ions in fixed bed packed with 1stAC in three component system at input solution of pH 5 and temperature 303 K [C_o: Pb (0.241 mol/m^3), Cd (0.445 mol/m^3), Cr (0.096 mol/m^3), F.R.: 2 ml/min, Packed Mass: 2 g].

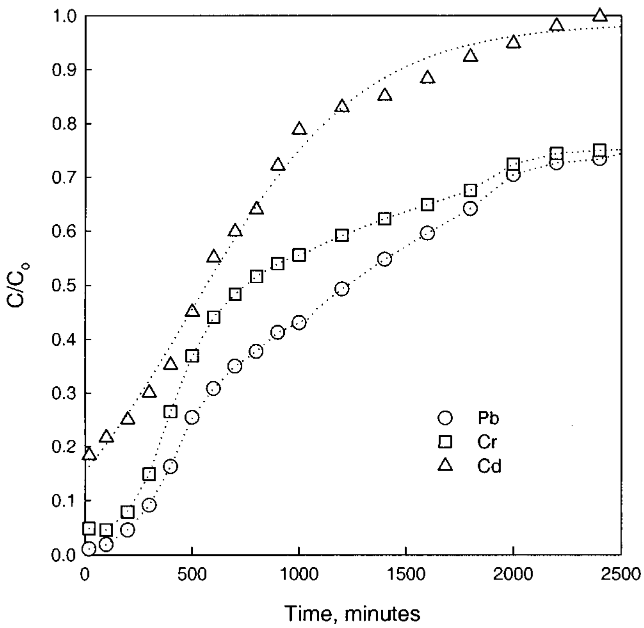

Fig. 8. Breakthrough curves of various metal ions in fixed bed packed with 2nd AC in three component system at input solution pH 5 and temperature 303 K [C_o: Pb (0.241 mol/m^3), Cd (0.445 mol/m^3), Cr (0.096 mol/m^3), F.R.: 2 ml/min, Packed Mass: 2 g].

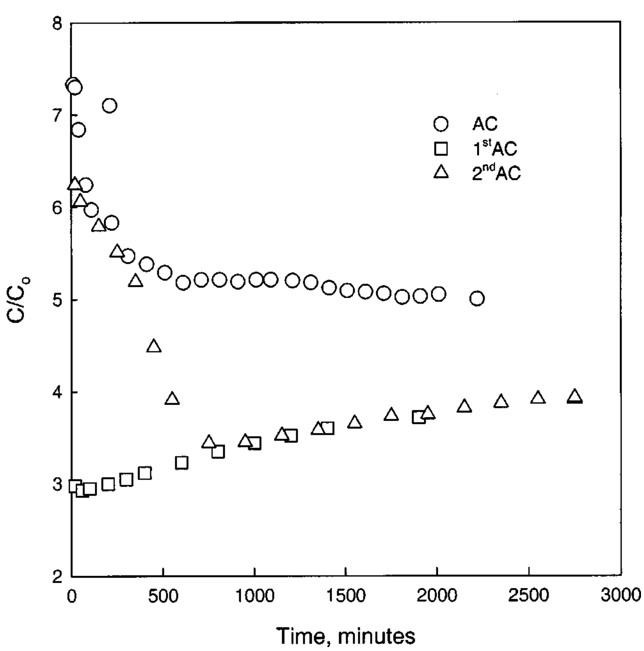

Fig. 9. Variations of Effluent pH in fixed bed packed with three kinds of carbons in three component system at input solution of pH 5 and temperature 303 K.

sites. In this case, after a certain length of traveling path in a column, the concentration profiles of these components are established as several mass transfer zone corresponding to the number of components [16]. From the breakthrough curves, the order of removal efficiencies was found as Pb > Cr > Cd. However, the concentration of Cr in the solution was much lower than other metals. Therefore, it could consider that competition between Pb and Cd dominated the adsorption processing in this packed column. If Pb was strongly component, the mass transfer zone of Cd (abbreviation as MTZ-Cd) should be established after MTZ-Pb in the column. Also, if length of the MTZ-Cd was not enough to remove Cd ion, a complete concentration profile, at least decline of C/C_o=0.1, would not form. As shown in Fig. 7 and 8, the curve for Cd ion from the 1stAC-column was very steep, but the curve from the 2ndAC-column was a little more effective for removal efficiency than that from the 1stAC. In the case of 1stAC, the condition in MTZ-Cd was changed unfavorable to adsorption because of decreasing pH due to adsorbed Pb and Cr in the MTZ-Pb, as shown in Fig. 9. Since the pH of effluent from the 2ndAC-column was maintained about value of 6 at earlier time, it can be estimated that a capacity of the 2ndAC to prevent the decreasing of solution pH contributes the narrow MTZ-metals in multi-component system. From the breakthrough curves, the 2ndAC was more useful than the 1stAC as a point of view that the removal efficiency (99% to Pb, 96% to Cr, and 80% to Cd) at initial adsorption time and the achieving treatment time until the C/C_o of 0.1 for Pb and Cr, as compared with 1stAC-column.

3.3. Four Components Solution

The breakthrough curves of each component in the four

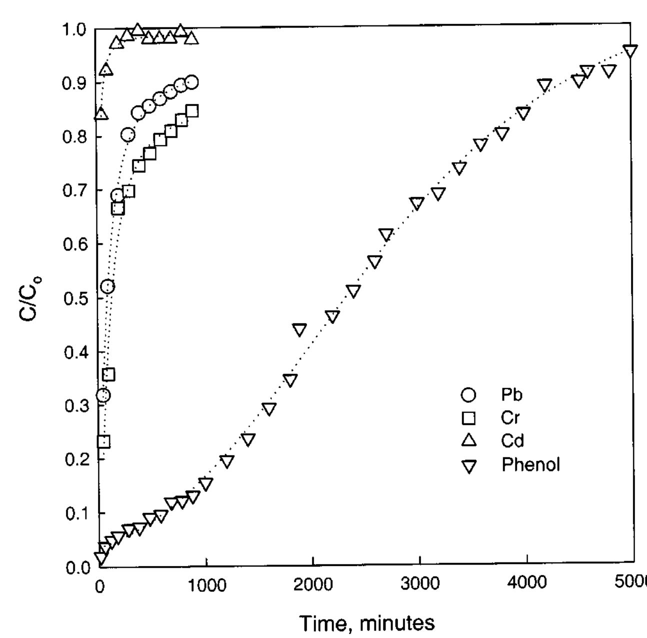

Fig. 10. Breakthrough curves of various metal ions in fixed bed packed with AC in four component system at input solution of pH 5 and temperature 303 K [C_o: Pb (0.241 mol/m^3), Cd (0.445 mol/m^3), Phenol (0.531 mol/m^3), Cr (0.096 mol/m^3), F.R.: 2 ml/min, Packed Mass: 2 g].

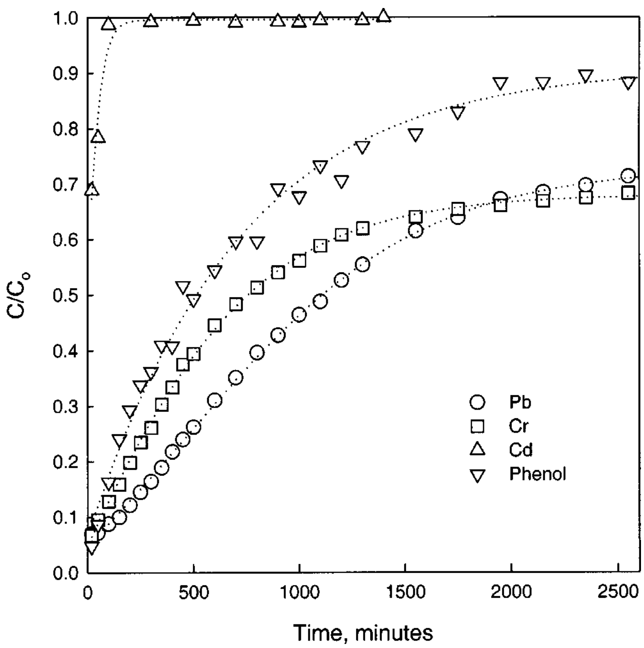

Fig. 11. Breakthrough curves of various metal ions in fixed bed packed with 1stAC in four component system at input solution of pH 5 and temperature 303 K [C_o: Pb (0.241 mol/m^3), Cd (0.445 mol/m^3), Phenol (0.531 mol/m^3), Cr (0.096 mol/m^3), F.R.: 2 ml/min, Packed Mass: 2 g].

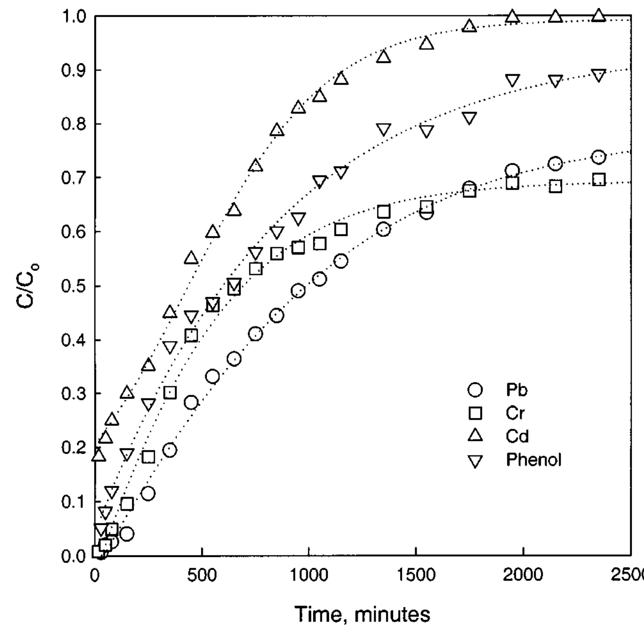

Fig. 12. Breakthrough curves of various metal ions in fixed bed packed with 2ndAC packed column in four component system at input solution of pH 5 and temperature 303 K [C_o: Pb (0.241 mol/m^3), Cd (0.445 mol/m^3), Phenol (0.531 mol/m^3), Cr (0.096 mol/m^3), F.R.: 2 ml/min, Packed Mass: 2 g].

components solution including 0.531 mol/m^3 (50 ppm) of phenol are shown in Figs. 10~12, and Fig. 13 represents the variations of effluent pH with time. As shown in Fig. 10, the removal of phenol in the AC-column was effective and the removal efficiency was similar to in the single component solution. Both the treatment time and the process time from C/C_o=0.1 to C/C_o=0.9 were almost equal to that in the single component curve of Fig. 1. Therefore, it could be analyzed that the effect of competitive adsorption of other metal ions in the multicomponent system on the phenol adsorption by AC was minimal. Also, the length of MTZ-phenol was identical to that in single component solution.

In Fig. 11, the breakthrough curves of metal ions the 1stAC-column were almost identical those in Fig. 7 as if phenol is not exist and the phenol curve was much like in Fig. 1. The behaviors of metal ions in the 1stAC-column were not influenced by phenol as the behavior of phenol was not influenced by the metal ions. Moreover, the breakthrough behaviors of the metal ions in the 2ndAC-column, as represented in Fig. 12, had a like tendency as the 1stAC, and the increased removal efficiency was not affected by the change of fluid condition with adding phenol. Compared the effluent pH in Fig. 13 with that in Fig. 9, these pH variations in the 1stAC and 2ndAC-column were very similar without any influence of phenol adsorption. From these results, the higher removal efficiencies of metal ions by the 2ndAC were maintained regardless of the kinds of solutions.

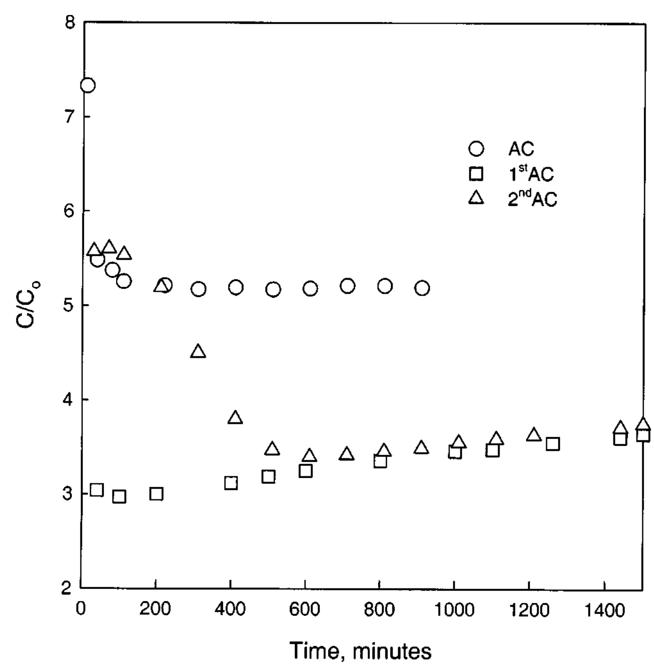

Fig. 13. Variations of Effluent pH in fixed bed packed with three kinds of carbons in four component system at input solution of pH 5 and temperature 303 K.

4. Conclusion

The two-step surface modification of activated carbon for the removal of heavy metals in fixed bed was experimentally evaluated. It was also identified that the 2ndAC showed a higher removal efficiency for Pb, Cd, and Cr ions in the single component solution, as compared with those of both as-received activated carbon (AC) and the first surface-modified activated carbon (1stAC). The breakthrough behaviors of metal ions using 2ndAC in the multicomponent system also exhibited a higher removal efficiency than those of 1stAC and AC, and was slightly influenced by the presence of phenol. Based on the pH variations of effluent as adsorption proceed, the increase of removal efficiency was caused by that the 2ndAC would control the solution pH to favorable adsorption range for the removal of heavy metals in the fixed bed. Therefore, the two-step surface modification method of activated carbon using the acidic and alkaline solutions would be useful for effective purification of industrial wastewater.

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