

## Removal Efficiency of Toxic Heavy Metal Ions in Wastewater by Double Surface-Modified Activated Carbon

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Adsorption capacities of toxic heavy metal ions using as-received carbon(AC), single and double surface-modified activated carbon(OAC and DSMC) in wide pH ranges are extensively evaluated. Physical and chemical properties of surface-modified activated carbons are evaluated through BET analysis, surface acidity and oxides measurements. Based on the adsorption isotherms of Pb, Cd and Cr ions by AC, OAC and DSMC, the adsorption amount on DSMC was obviously higher than that on the other carbons. Breakthrough behaviors of ternary metal ions in a column packed with three kinds of carbon were also characterized with respect to the variations of the influent pH and concentration. The adsorption capacity of DSMC in a fixed bed stood a favorable comparison with that of as-received carbon.

Keywords: Activated carbon, Double surface-modification, Heavy metal, Adsorption.

### Introduction

Heavy metal pollution of groundwater is an extremely serious environmental problem due to its difficult degradation to a harmless end product, unlike organic wastes. Industrial wastewater containing heavy metal ions needs an advanced treatment process to reduce metal ion contaminants to levels that allow them to be safely discharged according to an environmentally permissible concentration. Industrial wastewaters are generally classified as organic waste, inert inorganic waste and heavy metal waste. Representative heavy metal ions to be removed are lead, cadmium, chromium mercury and cyanide, etc. Various technologies have been used to treat industrial wastewater, such as chemical precipitation, sorption and neutralization, and advanced process. Controlling the release of these species depends on the design of the treatment process within each particular system. Among those processes, sorption technology using both an organic ion-exchanger and inorganic sorbent has shown its effectiveness [1~2]. Ion exchange resin offered prospects for extended useful life for treatment of heavy metal ions, but the cost of resin is relatively high. Although activated carbon has low adsorption efficiency for removing metal ions in wastewater, it has been widely used as a final cleaning material in the industrial wastewater treatment process due to low cost. If the adsorption efficiency of activated carbon to remove the toxic heavy metals is enhanced by the surface modification technique, the operation cost and secondary waste volume can be significantly reduced.

In general, the adsorption extent of heavy metals on inorganic adsorbent in aqueous solution is influenced by many factors[3~6]. These include the properties of sorbents, solution pH, concentration of co-ions (cation, anion and electrolytes), complexing agents, etc. Among these parameters, it has been recognized that pH has a significant effect on the sorption efficiency of respective species to be removed. Recently, numerous studies have

been conducted to connect the surface characteristics of oxidized carbon or fiber with the influence in the adsorption capacities of toxic gases and organic or metal pollutants in waste on these sorbents[6~12]. The effect of oxidation treatment is often manifested on the removal of heavy metal ion from aqueous solutions. These results may lead to the conclusion that both pore structure and the surface chemistry of carbon affects significantly the adsorption characteristics of inorganic and organic polar molecules. In our laboratory, adsorption characteristics of uranium and cobalt ions in an acid solution on oxidized activated carbon were extensively studied [13, 14].

In previous study, surface modification of activated carbon using nitric acid solution, and second surface modification with alkali solution (NaOH, NaCl, NaNO<sub>3</sub> solution) at various solution concentrations was carried out [15]. In this paper, double surface-modified activated carbon is manufactured by double surface treatment of as-received activated carbon using an acid/alkali solution for the purpose of testing its adsorption efficiency of heavy metal ions in wastewater. Lead, cadmium and chromium ions as adsorbate in waste generated from industrial process are selected. Extensive experiments were performed to evaluate adsorption efficiencies of double surface-modified activated carbon and to obtain adsorption equilibrium isotherms for each ion. The surface characteristics for surface-modified activated carbon were analyzed. Also, the capacity factor using surface-modified activated carbon for the removal of toxic metal ions was compared with that of the as-received activated carbon and commercial organic ion exchange resin, based on the results obtained from fixed bed runs.

### Experiment

#### Materials

This study aims to investigate the adsorption characteristics of double surface-modified activated

carbons for removal of heavy metal ions in aqueous solutions. Activated carbon obtained from Samchulri Co. was used as the raw adsorbent (*hereafter, activated carbon, and abbreviation as AC*). The granules of activated carbon was ground, sieved to give a particle size of 16 ~ 30 meshes (average particle diameter : 0.85 mm). Sieved particles were used after being washed free of dust with deionized water and dried at 110 °C in a vacuum drying and then stored in a vacuum desiccator at room temperature. First surface-modification of carbon was carried out by heating in 7 N nitric acid solution at a temperature of 80~90 °C for 10 hours in a volumetric flask [16,17]. The first modified-activated carbons (*hereafter, oxidized carbon, and abbreviation as OAC*) were then exhaustively washed with distilled water and dried in a vacuum oven at 100 °C. Second surface-modification of OAC (*hereafter, double surface-modified AC, and abbreviation as DSMC*) was carried out by immersing it in a mixed alkaline solution (0.05N NaOH-NaCl concentration) at room temperature for 48 hrs. The physical properties of these adsorbents, measured by BET-N<sub>2</sub> analyses (Micromeritics ASAP 2400), are shown in Table 1. The pore size distribution of the OAC and DSMC is slightly different from that of the AC [15].

Table 1. Physical properties of AC, OAC and DSMC

Physical properties	AC	OAC	DSMC
Particle density, g/cm <sup>3</sup>	0.70	0.685	0.655
Total pore volume, cm <sup>3</sup> /g	0.74	0.71	0.65
Micropore volume, cm <sup>3</sup> /g	0.64	0.59	0.53
Average pore diameter, Å	19.3	20.8	21.8
BET surface area, m <sup>2</sup> /g	1,530	1,360	1,150
Micropore area, m <sup>2</sup> /g	1,460	1,300	1,080

#### Surface characterization

The pH of the zero point of charge (pH<sub>zpc</sub>) for three kinds of activated carbons was determined by the following method. 0.5 g of carbon is added to each of two identical portions of 500 mL solutions containing known concentrations of sodium chloride (NaClO<sub>4</sub>), respectively. Samples were agitated for 20 hr at low speed. Samples for analysis were titrated directly with 0.1M HCl and 0.1M NaOH, and pH values were noted until equilibrium after each aliquot of acid (or alkali) addition. The electrophoretic mobility was measured using a zeta potential analyzer (Zetaplus, BIC). It was measured that the pH<sub>zpc</sub> for AC is 7.5, 4.5 for OAC, and 5.8 for DSMC, respectively.

The method proposed by Boehm et al. was selected to determine the surface acidity. The carbon sample was added to the excess standard bases, which are sodium bicarbonate, sodium carbonate, sodium hydroxide and sodium ethoxide in 0.1N concentration. Carbon samples dried at 150°C were used so as to be free from any physically adsorbed gases and vapors. A weighed amount of 1 g of each carbon was placed into several 250 ml double-stoppered flasks, and 100 ml of excess base

solutions after purging with nitrogen gas were added to them and sealed in a nitrogen environment. The mixtures were shaken mechanically for 48 hr and allowed to stand for 48 hr at 30 °C. The mixture was then filtered through membrane filter. The base consumption in 50 ml of the filtrate was measured by back-titration with 0.1 N HCl, using a pH meter. The total number of milliequivalents of acid oxide per gram of sample was determined by acid equivalent. Surface acidity data measured by the above method are summarized in Table 3.2. It was found that the treatment of activated carbon with nitric acid caused total surface acidity to be increased significantly, and the carboxyl and phenolic hydroxyl groups is over ten times that of as-received carbon. Also, double surface modification of OAC led to slightly decrease the surface function groups and the total acidity, compared to OAC.

Table 2. Acidic oxide groups on various carbon surface  
Unit : meq/g

Carbons	I	II	III	IV	Total Acidity
AC	0.031	0.01	0.335	0.058	0.655
OAC	0.705	0.213	2.148	0.183	3.249
DSMC	0.693	0.205	2.016	0.162	2.167

(I) : Strongly acidic carboxyl group, (II) : Weakly acidic carboxyl group, (III) : Phenolic group, (IV) : Carbonyl group.

#### Adsorption efficiency and isotherms

The initial concentration of metal ions, Pb, Cd and Cr, was adjusted by the dilution of these stock solutions containing 1000 mg/l. All the reagents used were GR grade, which are Pb(NO<sub>3</sub>)<sub>2</sub>, CdCl<sub>2</sub>·2.5H<sub>2</sub>O, CrCl<sub>3</sub>·6H<sub>2</sub>O. The effect of solution pH on adsorption efficiency was evaluated in the initial pH ranges from 2.5 to 8. The initial pH (pH<sub>0</sub>) of solutions was adjusted with GR-graded HCl and NaOH. The solution pH, however, was not controlled during the adsorption process. At relatively high pH ranges, adjustment of pH was conducted in nitrogen atmosphere to avoid the contact with carbon dioxide. However, the ionic strength was not controlled in this study. The standard method was used for the determination of adsorption efficiency and isotherms. 40 ml of the solution adjusted to specific concentration and pH<sub>0</sub> was placed into a 100 ml glass bottles containing previously weighed samples of adsorbent. The bottle was then capped with silicon rubbers and shaken for specified periods that the maximum contact time was 7 days. After reaching equilibrium, a small amount of solution for concentration analysis was then withdrawn from the supernatant out of individual bottles using a 0.45mm micro membrane filter. No interference due to adsorption onto glass bottle and filter was observed through blank tests. The solid-to-solution ratio (g/l) in isotherm experiment ranged from 1.25 to 2.5. The final pH (pH<sub>eq</sub>) of suspension after equilibrium was measured in nitrogen atmosphere. The measurement of solution pH was performed using an Orion Model 920A pH-meter. The adsorption efficiency and the total adsorption amount of

metal ions per unit mass of adsorbent( $x/m$ ) is obtained by the following relationship :

$$\text{Adsorption Efficiency} = (q \times m)/(C_o \times V) \times 100$$

$$\text{Adsorption amount, } q \text{ (mg/g)} = (C_o - C_e) \times V/m$$

where  $C_o$ (mg/l) and  $C_e$ (mg/l) are the initial and equilibrium concentrations of metal ion,  $m/V$  is the ratio of the mass of adsorbent(g) to the volume of solution(l).

### Fixed bed runs

The adsorption experiments in a fixed bed were carried out using a glass column of 0.01m inside diameter and 0.3 m in length. Carbon samples were soaked in distilled and demineralized water adjusted to the same pH of the influent over 24 hrs. A micro-metering pump was used to maintain the constant down-flow of 2 ml/min. Stock solutions adjusted to a desired pH were prepared in a glass-made tank of 3 L volume, and the tank was immersed in a constant-temperature water bath. A silicon cap was used to avoid the contact of carbon dioxide with the solution. A fraction collector collected effluent from the column periodically, and the pH of collected samples was directly measured, except for over-night runs.

An atomic Absorption Spectrophotometer (Moel : Perkin Elmer 5100 PC) was used to measure the residual concentration of metal ions as well as the initial concentration. The initial or residual concentrations in the mixture used for multi-component adsorption were measured by ICP-AES (Model : JOBIN-YVON JY50).

## Results and Discussion

### Influence of pH on adsorption efficiency

It is well known that the adsorption of metal cations onto adsorbents is strongly dependent on the solution pH[3,6,18,19] In order to make a thorough investigation of the influence of pH on the adsorption capacity of heavy metal ions by a double surface-modification of carbon, preliminary adsorption experiments using AC, OAC and DSMC were carried out in the initial pH ranges of 2.5 ~ 8. The solid-to-solution ratio was fixed at 2.0 for the three adsorbents. Fig. 1 showed the removal efficiency of single metal ions, Pb(II), Cd(II) and Cr(III), over a wide range of equilibrium pH at 20 mg/l of initial concentration.

In general, the adsorption characteristics of metal ions in aqueous solution are analyzed in terms of adsorption edge, which indicates a specified pH range in which adsorption efficiency is sharply increased as pH increases. For a cationic metal ion, the magnitude of adsorption increases abruptly at a specified pH, which is called  $pH_{abr}$ . On keeping initial concentration of uranium at 20mg/l, three adsorbents showed the typical trend of the adsorption efficiency of a metal ion in solution to the extent that metal ion removal becomes higher as pH increases. On comparing the adsorption capacities of the three adsorbents, AC showed very low adsorption efficiency in

a low pH range. However, OAC and DSMC have good removal efficiencies even at a relatively low pH range.

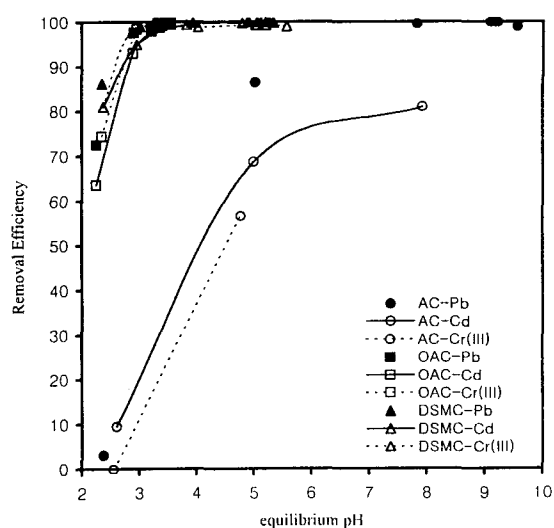


Fig. 1. Variations in removal efficiencies of various metal ions as a function of equilibrium pH at an initial concentration of 20 mg/l,  $m/V=2.0$ .

In particular, the adsorption efficiency of metal ions using DSMC was slightly superior to that of OAC over wide ranges of pH. This phenomenon can be explained by the following two facts. First, adsorption efficiency is closely related to pH variations after equilibrium. Second, that greater amounts of surface oxides, such as the carboxyl and the phenolic hydroxyl groups, lead to an increase of the adsorption capacity of metal ions. The pH after the addition of adsorbent into a solution, in principle, tends to vary toward the direction of the sorbent's  $pzc$ [3]. The final pH at the equilibrium was considerably influenced by the adsorbents used, as shown in Fig. 2.

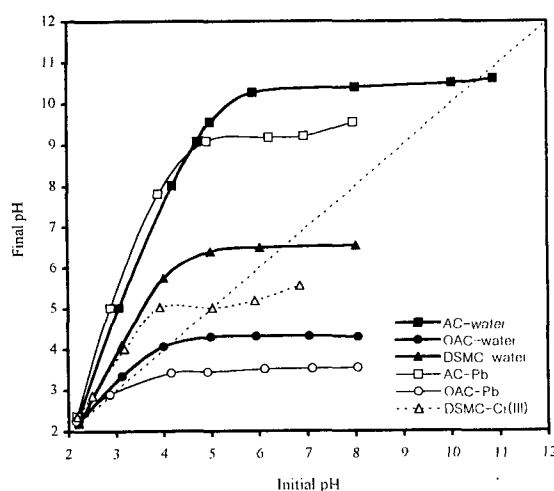


Fig. 2. Comparison of initial pH with the final pH after adsorption equilibrium using three kinds of carbons at an initial concentration of 20 mg/l,  $m/V=2.0$

In low pH ranges (< pH 3), significant variations of the solution pH were not observed. On the other hand, in the

pH ranges of 3 ~ 8, the final pH increased when AC was used as the adsorbent. In contrast, OAC showed that the final pH decreased when compared with the initial pH, and DSMC has an intermediate trend between AC and OAC in pH variation. Therefore, it is thought that the combination of its surface acidity and greater oxide would lead to the higher adsorption efficiency of DSMC.

Fig. 3 shows the influence of adsorbent amount on the removal efficiency of three kinds of metal ions at initial solution pH=3 and a concentration of 20 mg/l. Overall, the dosage of OAC and DSMC for obtaining 100% adsorption efficiency of metal ion is about four times below that of AC. The adsorption efficiencies of Pb and Cd ions using AC are higher than that of the Cr(III) ion. In general, the chromium ion in industrial wastewater exists as the Cr(VI) type, which is difficult to remove by adsorption. Although Cr(III) is effectively removed by OAC or DSMC, further study for the adsorption characteristic analysis of Cr(VI) ion on DSMC will be necessary.

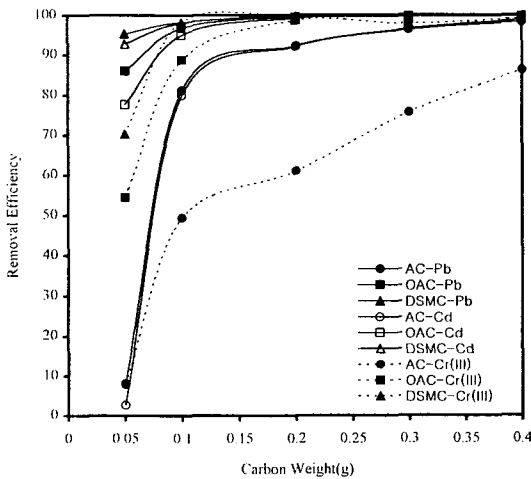


Fig. 3. Influence of carbon amount used on metal ions adsorption at an initial concentration of 20 mg/l, pH=3 and V=40 ml

#### Adsorption isotherms of metal ions

The adsorption isotherms of Pb, Cd and Cr ions on AC, OAC and DSMC at initial solution pH 5 were shown in Figs. 4 ~ 6, respectively. These isotherms were represented as a function of the total concentration of metal ions, and correlated by the Langmuir or Freundlich isotherm equation. Parameters obtained from various isotherm equations are summarized in Table 3.

The maximum adsorption amounts of Pb and Cr ions on the OAC were almost four times higher than that on the AC. In addition, the adsorption amount on DSMC was obviously higher than that on the OAC. As mentioned before, the final pH (equilibrium pH) values depend on the adsorbent types used, even though initial solution pH is fixed to be the same. In this study, solution pH was not controlled during the adsorption process. The variation of the final pH (equilibrium pH) at each equilibrium concentration is represented in Figs. 4 ~ 6.

Table 3. Freundlich and Langmuir parameters for metal ions on various carbons at 30°C.

Isotherm	Adsorbent	Parameters	Pb	Cd	Cr(III)
Freundlich	AC	K	1.22	3.53	1.44
		n	2.32	6.96	2.02
	OAC	K	25.26	12.35	7.51
		n	5.33	4.76	6.86
	DSMC	K	41.19	20.41	12.32
		n	6.95	5.14	13.32
Langmuir	AC	q <sub>m</sub>	28.09	9.07	6.31
		B	0.00	0.05	0.45
	OAC	q <sub>m</sub>	84.75	50.51	13.42
		B	0.03	0.02	0.47
	DSMC	q <sub>m</sub>	97.09	70.42	16.18
		B	0.08	0.03	1.55

\*Unit - q<sub>m</sub> : mg/g, B : l/mg

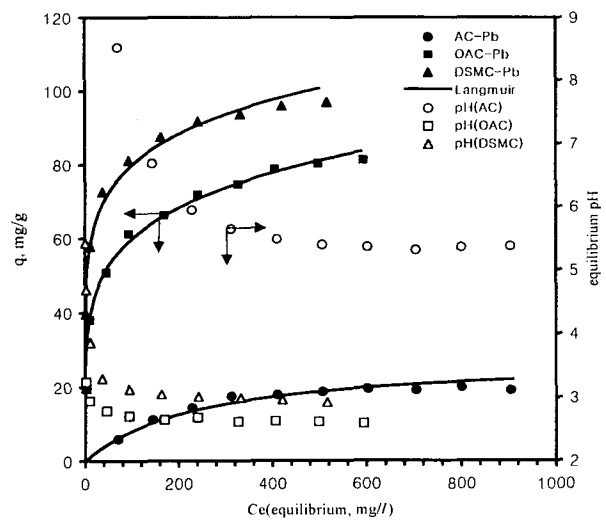


Fig. 4. Adsorption isotherms of Pb on various carbons at initial solution pH 5 and variation in equilibrium pH as a function of equilibrium concentration.

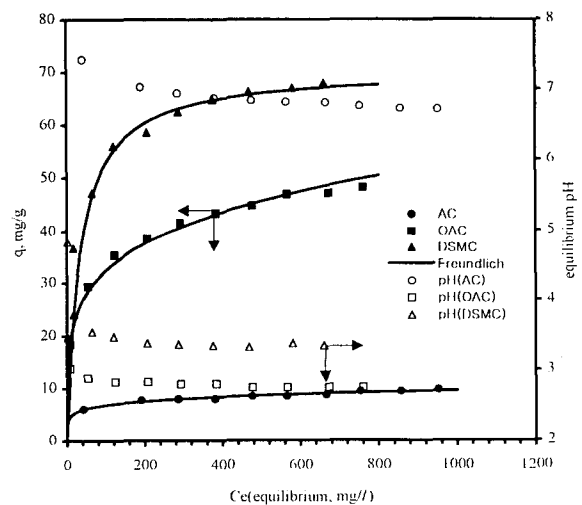


Fig. 5. Adsorption isotherms of Cd on various carbons at initial solution pH 5 and variation in equilibrium pH as a function of equilibrium concentration.

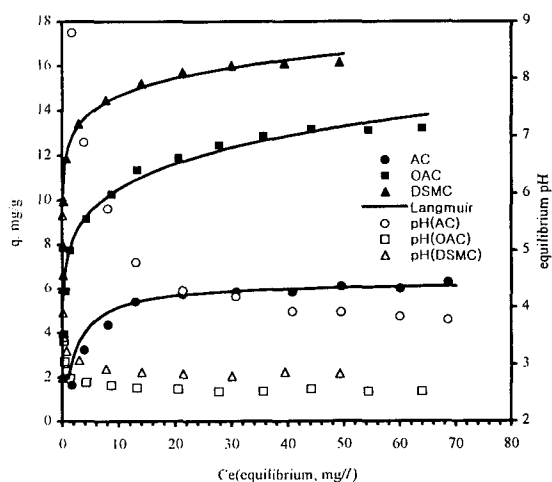


Fig. 6. Adsorption isotherms of Cr on various carbons at initial solution pH 5 and variation in equilibrium pH as a function of equilibrium concentration.

On the whole, equilibrium pH sharply decreased at low equilibrium concentration ranges, and leveled off to constant values as equilibrium concentration increased. Especially, when AC was used as adsorbents, the equilibrium pH values were increased over whole concentration ranges, compared to initial pH. But OAC and DSMC showed reverse characteristics. Supposing that a buffer solution of specified pH is used, these variations may become diminished. Abbasi et al. [16] and Park et al. [13] investigated adsorption of uranium or cobalt ions in aqueous solutions on the oxidized carbon, and proposed the ion-exchange mechanism for uranium sorption. The carboxyl groups with a pK value of 4~5 or phenolic group are largely responsible for the ion exchange of divalent ions or other hydrolyzed ionic species from solution. It is thought that the decrease in pH reflects metal ion removal by an ion-exchange mechanism. That is, the hydronium ions on ion-exchange sites, mainly a surface functional group, are displaced as the metal ions are adsorbed onto this site, leading to a pH decrease with adsorption time. Actually, the oxidized carbon has a great amount of surface functional groups. Among these groups, the weakly or strongly acidic carboxyl group at a relatively low pH is available in the adsorption of metal ions, because the pK value of the phenolic group is about 10 ~ 12 [16]. It was reported that the competitive adsorption between cadmium and the hydronium ions on the chitosan was identified from the pH measurement during the adsorption process [20]. These behaviors are clearly different from those in the metal ions-OAC or DSMC adsorption system.

#### Evaluation of removal capacity in a fixed bed

In general, solution pH of industrial wastewater ranges from 5 to 6. Breakthrough curves for ternary adsorption of Pb(44 ppm), Cd(44 ppm) and Cr(4 ppm) ions on various carbons at an influent solution pH of 3.2 and 4.9 were experimentally obtained, as show in Fig. 7(pH=4.9).

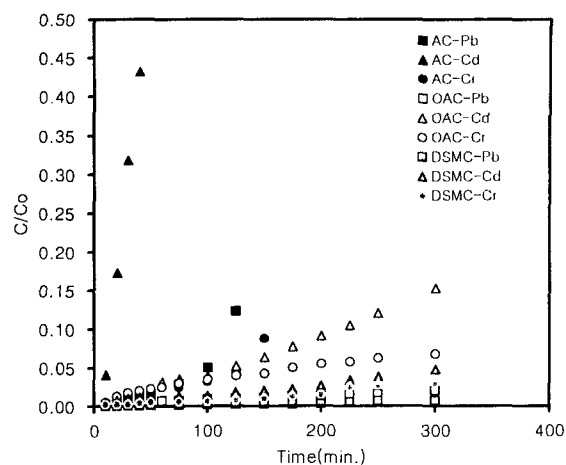


Fig. 7. Effect of carbon type on breakthrough curves for ternary ions adsorption(Pb:44 ppm, Cd:44 ppm, Cr: 4 ppm) at influent pH 4.9.

The adsorption capacity of the DSMC had a favorable comparison with that of AC and OAC even in a low pH condition, including in a neutral aqueous solution. Based on the breakthrough time and the maximum discharge concentration of toxic heavy metal ions that is 1 ppm for the Pb and Cd ion and 0.5 ppm for Cr, the capacity factor for the removal of metal ions using three kinds of carbons (AC, OAC, DSMC) is defined as follows.

$$\text{Capacity factor} = \frac{\text{Total treated waste volume}}{\text{Bed volume}}$$

In this study, the bed volume was fixed at 7.8 ml and the carbon weight used in the fixed bed run was about 3 g. As shown in Fig. 8 obtained at influent pH 4.9, capacity factors of DSMC for the removal of various metal ions are superior to those of AC or OAC. Quantitative analysis of capacity factors for each ion showed that the adsorption capacity of DSMC increased by 9 times for lead, 30 times for cadmium, 3 times for chromium as compared to that of AC at pH 5. The price of activated carbon is about 3 thousand won/kg and is very low compared to that of organic ion exchange resin (about 0.1 million won/kg). Hence the use of DSMC material seems very economical in the treatment of wastewater even if the cost of surface modification is considered. DSMC would efficiently remove toxic heavy metals in industrial wastewater as well as radionuclides in radioactive liquid waste [13]. And the treatment cost and secondary waste volume would be greatly reduced compared to those in the treatment process adopting costly organic ion exchange resins or as-received activated carbons. It is concluded that the double surface-modified activated carbon can be utilized to treat decontamination wastewater.

#### Conclusion

Adsorption capacities of toxic heavy metals, such as lead, cadmium and chromium, using double surface-modified activated carbon (DSMC) in wide pH ranges are extensively evaluated. Physical and chemical properties of

surface-modified activated carbons are evaluated through BET analysis, surface acidity and oxides measurements. Variations in adsorption efficiencies of heavy metal ions on various activated carbons were evaluated in wide pH ranges of 2.5 ~ 8. The adsorption capacity of DSMC is shown to be comparable to that of the as-received carbon(AC) even in a low pH range. Based on the adsorption isotherms, the maximum adsorption amount of Pb and Cr ions on the oxidized carbon(OAC) was almost four times higher than that on the AC. In addition, the adsorption amount on DSMC was obviously higher than that on the OAC. Breakthrough behaviors of various metal ions in a column packed with three kinds of carbon were also characterized with respect to the variations of the influent pH and concentration. Capacity factors of DSMC for the removal of various metal ions are superior to those of AC or OAC. Quantitative analysis of capacity factors for each ion showed that the adsorption capacity of DSMC increased by 9 times for lead, 30 times for cadmium, 3 times for chromium as compared to that of AC at pH 5.

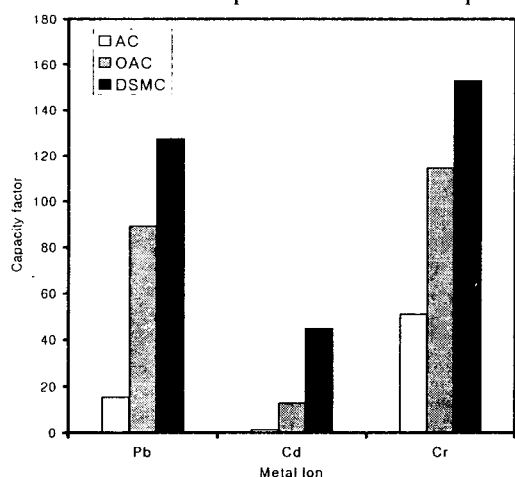


Fig. 8. Comparison of capacity factors for the removal of various metal ions using three kinds of carbons at influent pH 4.9.

### Acknowledgment

This project has been carried out under the Nuclear R&D Program by MOST

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