

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

I. Equilibrium and Batch Adsorptions

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Abstract

The two-step surface modifications of activated carbon was carried out to improve the adsorption capacity of toxic heavy metal ions in liquid phase. Physical and chemical properties of the as-received activated carbon (AC) and two kinds of surface-modified activated carbons (1stAC and 2ndAC) were evaluated through the BET analysis, surface acidity, and oxides measurements. Specific surface area and pore volume did not significantly change, but surface oxide-group remarkably increased by the surface modification. Equilibrium and batch adsorptions of the various metals, such as Pb, Cd, and Cr, using AC, 1stAC, and 2ndAC were performed at initial pH 5. The adsorption capacity and rate of 2ndAC were higher than those of AC and 1stAC. The carboxylic/sodium carboxylate complex groups were developed from the two-step surface modification of activated carbon, which strongly affected the adsorption of metal ions.

Keywords : Activated Carbon, Two-step, Surface Modification, Metal Ion, Adsorption Equilibrium, Batch adsorption

1. Introduction

Heavy metal pollution in industrial wastewater is extremely serious environmental problem due to its difficult degradation to a harmless product, unlike organic wastewater. Many workers have made efforts to remove heavy metals from industrial wastewater using various kinds of processing method such as chemical precipitation, evaporation, ion exchange, cementation electrolysis, and reverse osmosis [1]. The selection of suitable process for identifying practical and cost-effective means to remove such heavy metals is very difficult due to secondary generation problems of unexpected metal-bearing sludge [2].

Recently, numerous studies have been conducted to connect the surface characteristics of oxidized carbon or fiber with the adsorption capacities of these materials for toxic gases and organic or metal pollutants in waste. Carbon surface can be modified by the heat treatment in oxidizing gases such as air, carbon dioxide, and oxygen, and the oxidation in acidic solution. The nature and the capacity of surface oxides formed on the treatment with oxygen depend on the nature of the carbon and the history of its formation. In case of oxidative treatments in solutions, the major reaction is the formation of the surface oxygen compounds. The formation of these surface compounds using various types of carbon and using different oxidative treatments in gaseous and liquid phases has been studied by a large number of investiga-

tors and has been well reviewed [5-7]. The effect of oxidative 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. According to many workers, the adsorption sites of metal ions on activated carbon are known as oxide groups such as carboxyl and phenolic groups and increased by surface acid treatment [5-7]. However, the acidic carbon leads the decreases of solution pH during adsorption of the metal ions. Generally, it is well known that adsorption capacity of metal ions on activated carbon decreases at a low pH [8]. According to the works of Netzer, metal adsorption is inversely proportional to metal solubility in aqueous solutions [3]. Most metals become less soluble and form hydroxides and oxides as the solution pH increases [4]. Therefore, a controlling of solution pH to favorable adsorption region of metal ions is very important.

In this study, the two-step surface modification of activated carbon to enhance the adsorption capacity of metal ion in liquid phase was applied. The first surface modification was performed using HNO₃ solution (hereafter, abbreviation as the 1stAC) and followed the subsequent second surface treatment of 1stAC in a mixed alkaline solution (hereafter, abbreviation as the 2ndAC). Pb, Cd, and Cr existing in industrial wastewater are selected as the adsorbates. Both the

equilibrium and batch adsorption of the metals on the as-received activated carbon (AC), the 1stAC, and the 2ndAC were carried out to estimate the removal capacities and adsorption rate at solution pH of 5. This work aims to investigate the practical applicability of two-step surface modification method of activated carbon on removal of the metal ions in aqueous solution.

2. Experiment

2.1. Preparations of Material

The AC produced from Samchulri Co. in Korea was used in this work. The granules of the AC were ground and then sieved to give a particle size of 16~30 meshes (average particle diameter of 0.85 mm). After sieved, the particles were washed with deionized water to free of dust and dried at 110°C in a vacuum oven. The first surface modification of AC was carried out in a 7 N nitric acid solution. After pouring AC into a volumetric flask, it was shaken slowly at a temperature of 80~90°C for 10 hours in water bath. At this time, the ratio of solution to AC was fixed to 6.0 ml/g. This activated carbon obtained from the first surface modification procedure was abbreviated as the 1stAC. The subsequent second surface modification of the 1stAC was performed in a mixed alkaline solution. Based on the optimal condition of the previous study [10], the alkaline solution was prepared with mixing 1 N NaOH and 1 N NaCl solution. The 1stAC was immersed in the mixed alkaline solution at a ratio of 20 ml/g-carbon and shaken slowly at a temperature of 30°C for 48 hours in water bath. This activated carbon obtained from the second surface modification procedure was abbreviated as the 2ndAC.

2.2. Characterization of Surface

The physical properties of three kinds of carbons, such as BET surface areas and total pore volume were measured by BET N₂ adsorption (Micromeritics ASAP 2400). The pHs of the point of zero charge (pH_{ZPC}) for these carbons were determined by the following method. Each of carbon 5 g was added to two identical portions of 500 ml solutions containing known concentrations of sodium perchlorate (NaClO₄). These were agitated for 20 hours with low speed at 30°C. Samples were titrated directly with 0.1 M HCl and 0.1 M NaOH, and the pH values were noted until equilibrium after adding a 0.1 µl drop of the acid or alkali solution, respectively. The electrophoretic mobility was measured using a zeta potential analyzer (Zetaplus, BIC). The method proposed by Boehm *et al.* [5] was selected to determine the surface acidity. The carbon sample was added to the excess standard bases, which are sodium bicarbonate (NaHCO₃), sodium carbonate (Na₂CO₃), sodium hydroxide (NaOH) and sodium ethoxide (NaOC₂H₅) in 0.1 N concentration. Carbon samples dried at 150°C were used so as to be free from any

physically adsorbed gases and vapors. A weighed capacity of 1 g of each carbon was placed into several 250 ml double-stopper flasks. 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 hours and allowed to stand for 48 hours 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.

2.3. Equilibrium Adsorption

Adsorption isotherms of the heavy metal ions on three kinds of carbons were obtained in wide concentration ranges of 10~1000 ppm. The initial solution pH in all experiments was adjusted to pH 5. The solution adjusted to specified concentration was placed into glass bottle containing weighted carbon sample. The solid to solution ratio in isotherm experiment was 2.5 g/l. The bottle was shaken slowly in water bath at 30°C for 7 days. After reaching adsorption equilibrium, the final solution pH was directly measured in nitrogen atmosphere and a small capacity of solution for concentration analysis was withdrawn from the supernatant by 0.45 mm membrane filters. The concentrations of metal ions in solution were measured by Atomic Absorption Spectrophotometer (Perkin Elmer 51000 PC).

2.4. Batch Adsorption

In order to compare adsorption rates of the carbons for the metal ions, the agitated bath reactor was used in this experiment. Each of stock solutions of the metal ions was prepared with the concentration of 1,000 mg/l. The initial concentration of metal ions was adjusted to 50 ppm by dilution of these stock solutions, and then adjusted to pH 5 using NaOH and HCl solution. 5 g of each carbon was placed in vessel containing 2 l of the solution and then the impeller was rotated at 200 rpm. At this time, the reactor was maintained at 30°C in a water bath.

3. Results and Discussion

3.1. Adsorption Isotherms

Figs. 1~3 show the adsorption isotherms of the selected heavy metals on the three kinds of carbons. The variations in solution pH at equilibrium state as a function of the equilibrium concentration was plotted in Fig. 4.

These adsorption isotherms were favorable types I according to adsorption isotherm classification [13]. In overall, the 1stAC showed a significantly increased adsorption capacity of metal ions in all equilibrium concentrations, compared to the AC. The adsorption capacity of the 2ndAC had the highest value among three carbons. It is well known that metal adsorption is inversely proportional to metal solubility in aqueous solutions and profitable in some alkaline solutions

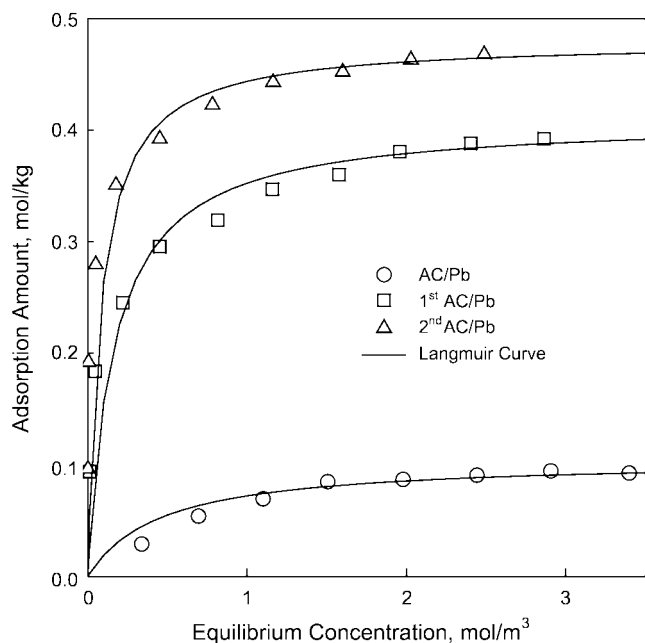


Fig. 1. Adsorption isotherm of Pb on various carbons at initial solution pH 5 and temperature 303 K.

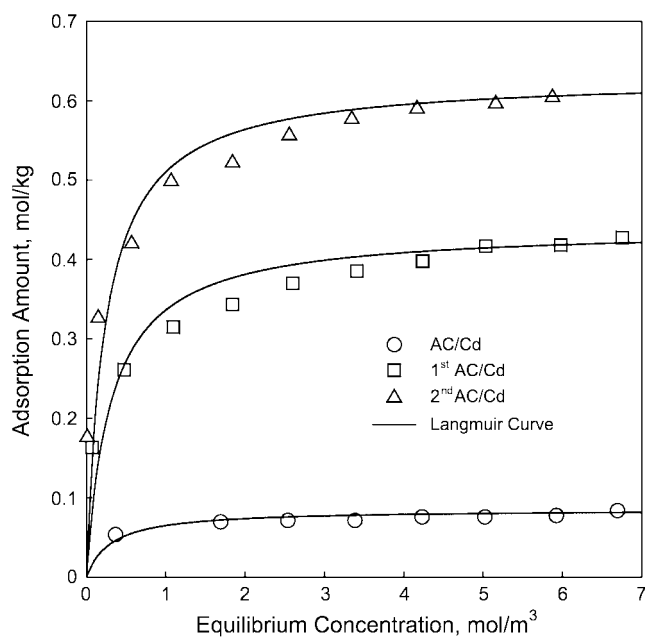


Fig. 2. Adsorption isotherm of Cd on various carbons at initial solution pH 5 and temperature 303 K.

before precipitating range [14]. As shown in Fig. 4, although the solution pH at equilibrium on the AC was the highest, the adsorption capacity was the lowest. It was attributed to insufficient amount of surface functional groups such as carboxyl and phenolic groups related to metal adsorption. The adsorption capacity of the 2ndAC was slightly superior to that of the 1stAC. The analysis of this result would be men-

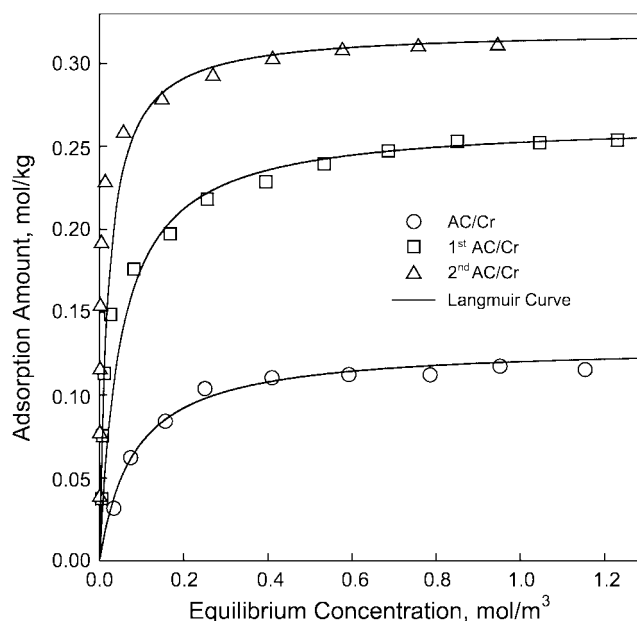


Fig. 3. Adsorption isotherm of Cr on various carbons at initial solution pH 5 and temperature 303 K.

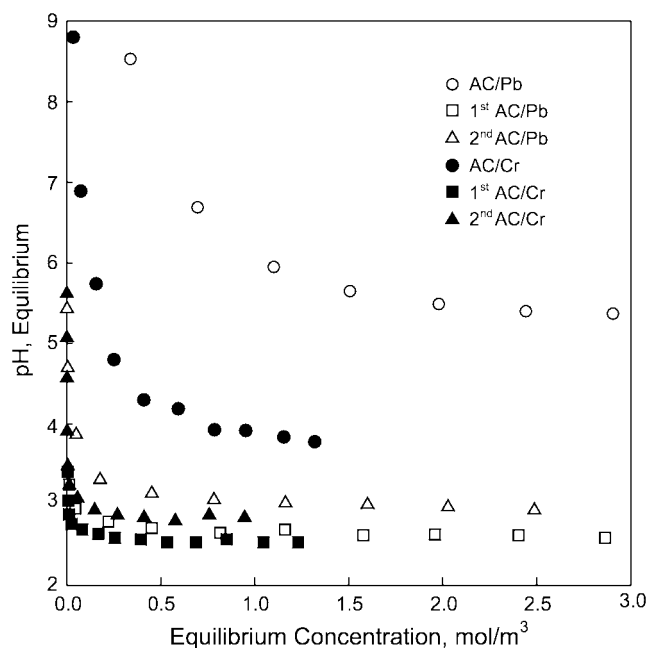


Fig. 4. Equilibrium pH on various carbons in metal solution at initial solution pH 5 and temperature 303 K.

tioned in next section of 3.2.

Langmuir curves estimated by approximated method were drawn in the figures. The curves were well fitted to experimental data and the Langmuir parameters were listed in Table 1. However, the Langmuir curves had a little deviation to the data in the lower concentration range.

3.2. Characteristics of Carbon Surface

Table 1. Langmuir Parameters for Metal Ions on Various Carbons at 30°C. [$q = q_m BC / (1 + BC)$, q_m : mol/kg, B: m³/mol]

Adsorbents	Parameters	Pb	Cd	Cr
AC	q_m	0.12	0.08	0.13
	B	2.98	3.21	12.21
1 st AC	q_m	0.41	0.44	0.26
	B	6.13	3.24	20.13
2 nd AC	q_m	0.48	0.52	0.32
	B	12.24	4.25	50.21

Table 2. Physical Properties of AC and Modified Carbons

Physical properties	Unit	AC	1 st AC	2 nd AC
Particle density	g/cm ³	0.70	0.68	0.65
Total pore volume	cm ³ /g	0.74	0.71	0.65
Micropore volume	cm ³ /g	0.64	0.59	0.53
Average pore diameter	Å	19.3	20.8	21.8
BET surface area	m ² /g	1530	1360	1150

Table 3. Estimated Acidic Oxide Groups on Various Carbon Surfaces. [Unit : meq/g]

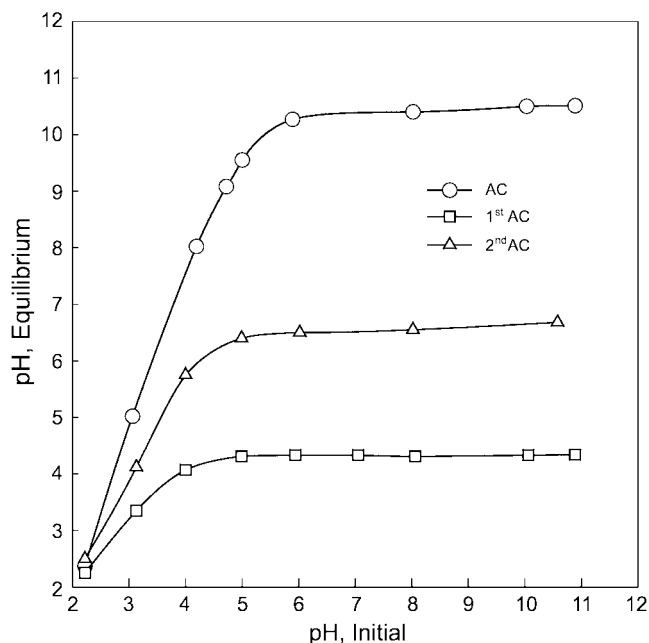
Carbons	Type of oxide groups					Total amount
	I	II	III	IV	V	
AC	0.031	0.01	0.335	0.058	–	0.434
1 st AC	0.705	0.213	2.148	0.183	–	3.249
2 nd AC	0.693	0.205	2.016	0.162	0.173	3.249

I: Strongly acidic carboxyl group, II: Weakly acidic carboxyl group, III: Phenolic group, IV: Carbonyl group, V: Estimated groups (Carboxylic/ Sodium Carboxylate).

Physical properties of three kinds of carbons by BET N₂ adsorption are listed in Table 2. The AC has extended surface area and many micropores. The properties of both surface-modified carbons except average pore diameter decreased as compared with the AC. Although the apparent surface areas and pore volumes appear to decrease with the surface modifications, the variations are nominal. It has been reported that the treatment of carbons with HNO₃ did not affect their physical morphology but altered their surface chemical properties [10].

The changes of surface acidity by treatment with HNO₃ and alkaline solutions can be detected classically with Boehm's titration measurement and the results are shown in Table 3. Although this interpretation is not universally accepted, it gives a semi-quantitative measure of the surface functionalities [12].

The characteristics of carbon surface could also be analyzed by pH_{ZPC} test [11]. In this study, it was measured that pH_{ZPC} for the AC is 7.5, 4.5 for the 1stAC, and 5.8 for the 2ndAC, respectively. In order to investigate the release of

**Fig. 5.** pH variations of distilled water on various carbons at temperature 303 K.

sodium ion from the 2ndAC surface, ICP analysis was conducted together with the AC and 1stAC. The AC and 1stAC had about 0.09 wt% of sodium and 2ndAC showed about ten times higher sodium content than the AC and 1stAC. It might be indicated that some of the hydrogen ions on surface function groups of the 1stAC would exchanges with sodium ions by the second surface modification (Type V oxide group) and also sodium ions would be adsorbed on the carbon surface.

As shown in Table 3, the 1stAC has a many acidic groups, especially carboxyl and phenolic groups. Although the oxide groups on the 1stAC are not identified precisely, the total capacity of the oxide groups are remarkably increased by the first modification. In case of the 2ndAC, the amount of oxide groups were decreased a little, but it had considerably many oxide groups.

Fig. 5 showed the pH variations after reaching adsorption equilibrium when three kinds of carbons were put into distilled water. In the initial pH ranges of 3~6, the final pH increased remarkably when the AC was used. The AC has a plateau at about the equilibrium pH 10. It means that the AC has a basic characteristics. Considered basic carbon, the AC used in this work would has a large quantity of electron by activated process because usual activations are performed in a hot steam condition [8]. In contrast, the equilibrium pH of the 1stAC dropped from the initial pH, and its plateau was formed at the equilibrium pH 4. The acid groups such as carboxyl and phenolic groups lead a decrease in solution pH by releasing hydrogen ions into bulk solution. However, the 2ndAC has the higher plateau value of pH 6.5 than the 1stAC. This result would indicates that the 2ndAC has an amphoteric

characteristics, which represents an intermediate character between the AC and 1stAC in the extended pH ranges.

As mentioned before, the 2ndAC showed the highest adsorption capacity of metal ions among three carbons in all equilibrium concentrations. The enhanced adsorption capacity of the 2ndAC would be explained by following two factors.

The first is that the amount of surface function groups on the 2ndAC is slightly lower than that of the 1stAC as shown in Table 3. This means that two carbons would have a similar adsorption site, based on the assumption that type V oxide group is also responsible for the adsorption reaction. If the type I and II oxide groups on the 1stAC are available for the adsorption of metal ions, the maximum adsorption capacities (q_m) of divalent ions (Pb, Cd) and trivalent ion (Cr) calculated from the amount of oxide groups (Table 3) are 0.38 mol/kg and 0.253 mol/kg, respectively. It is thought that the calculated values for Pb and Cr ions are similar to the experimental data as shown in Table 1. However, in case of the 2ndAC, this calculation becomes more complex due to the characteristics of surface oxide groups.

In this study, the solution pH was not controlled during adsorption process. It is well known that the adsorption process of surface modified activated carbons was controlled by ion-exchange mechanism, because hydronium ions on ion-exchange sites (function groups) are displaced as the metal ions adsorb onto the site, leading to a decrease in pH during adsorption process. Our study has also identified a similar phenomena as shown in Fig. 4. The equilibrium pH on the 1stAC varied from 4.2 to 2.6 as equilibrium concentration increased, but the pH variation on the 2ndAC ranged from 6.2 to 3.0. Therefore, the second factor is that the decrease in solution pH after equilibrium on the 1stAC provides further support for a competition adsorption between metal ions and hydronium ions. However, the 2ndAC showed a slight increase of solution pH after adsorption equilibrium, which would provide a favorable solution pH conditions for metal ion adsorption. However, the detailed instrument analysis will be required to identify this proposed mechanism.

3.3. Adsorption Rate

The concentration profiles for the adsorption of various metal ions with time in batch reactor are plotted as a function of time in Figs. 6–8. The concentration profiles on both the 1stAC and the 2ndAC more sharply decreased than those on the AC, and the 2ndAC also showed a higher adsorption capacity than the 1stAC. Fig. 9 represented a variations in solution pH during the metal adsorption process using three kinds of carbons. Comparing the pH profiles in batch reactor on the 1stAC and the 2ndAC, the 1stAC led a sharp decrease in pH with time, but the 2ndAC maintained the initial pH. It was reported that the isotopic exchange reactions between metal ion and the acidic carbon was very fast in the initial stages at high pH values and the slow exchange reactions at

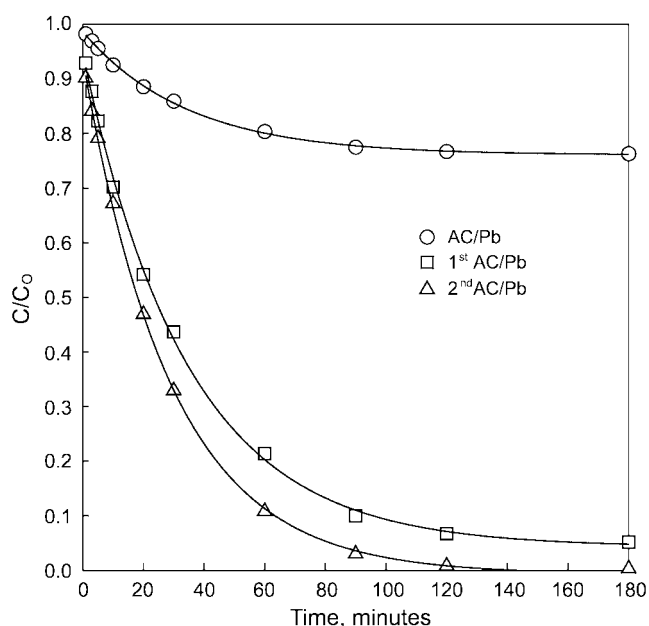


Fig. 6. Concentration profiles of Pb in bath reactor at initial solution pH 5 and temperature 303 K ($C_0=0.241 \text{ mol/m}^3$, $m=5 \text{ g}$, $V=2 \text{ L}$).

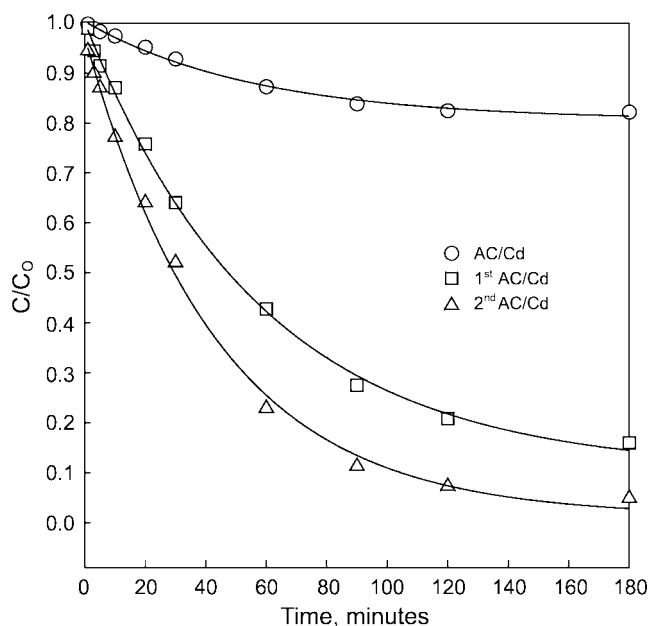


Fig. 7. Concentration profiles of Cd in bath reactor at initial solution pH 5 and temperature 303 K ($C_0=0.455 \text{ mol/m}^3$, $m=5 \text{ g}$, $V=2 \text{ L}$).

low pH values was observed [8]. Based on the data of these figures, the adsorption rates of the metals by the 1stAC decreased faster than the 2ndAC with decreasing the solution pH. It was not attributed to insufficiency of surface functional groups because the 1stAC and 2ndAC had almost the same amount of surface functional groups, as shown the Table 3. Therefore, it would be inferred that the decrease of

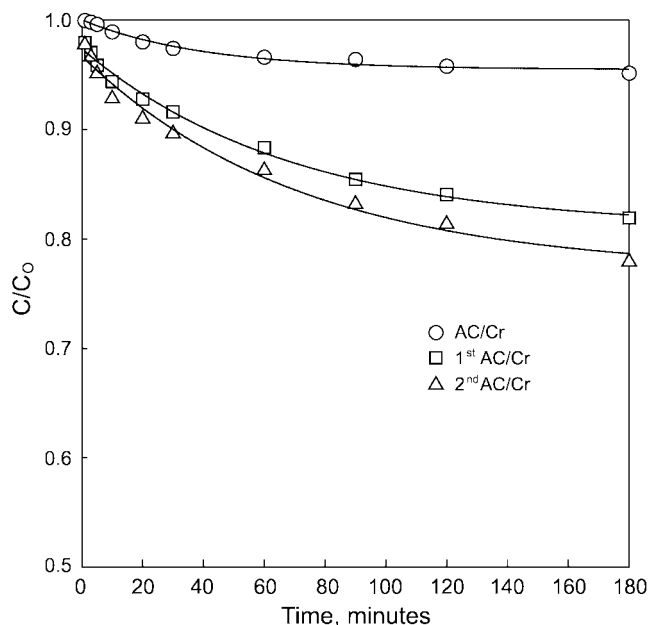


Fig. 8. Concentration profiles of Cr in bath reactor at initial solution pH 5 and temperature 303 K ($C_0=0.962 \text{ mol/m}^3$, $m=5 \text{ g}$, $V=2 \text{ L}$).

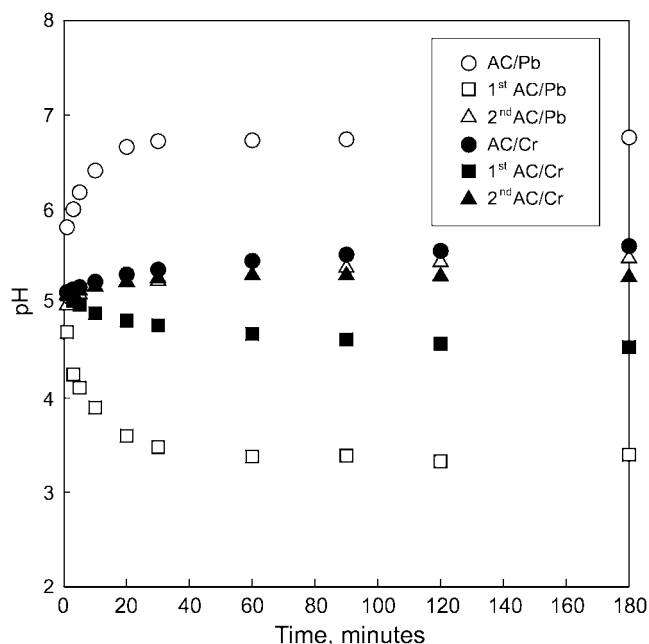


Fig. 9. Solution pH with adsorption time in bath reactor at initial solution pH 5 and temperature 303 K.

solution pH caused to the decrease of adsorption rate in company with the decrease of adsorption capacity.

The rates by the 2ndAC was faster than the 1stAC with maintaining the initial pH. A kinetics of ion-exchange reaction is very fast as mentioned before. The reaction rate of the functional group on the 2ndAC surface would be almost corresponded to that the 1stAC. The difference between both

surface-modified carbons is the amount of hydronium ions produced into bulk solution. Based on the pH variations in the batch reactor, the released capacity of hydronium ions from the 2ndAC was less than the 1stAC. A higher concentration of hydronium ions would interrupt the metal adsorption [8]. From these results, the second modification is very useful for not only the adsorption capacity but also the adsorption rate of the metal ions in the acidic solution. The order of adsorption rate of the metal ions was found as the 2ndAC > 1stAC >> AC. These effects combining the higher adsorption rate and capacity through the two-step surface modification would produce an effective adsorption condition in a fixed bed.

4. Conclusion

The two-step surface modification of activated carbon using the acidic and alkaline solution was performed to enhance the removal capacity of the heavy metal ions. The adsorption capacity and rate by the second surface-modified activated carbon (2ndAC) were obviously higher than those of as-received activated carbon (AC) and the first surface-modified activated carbon (1stAC). The carboxylic/sodium carboxylate complex groups were developed through two steps surface modification of activated carbon, which strongly affected the adsorption of metal ions. From the measurement of both the concentration profiles and the variations of solution pH during adsorption process in batch reactor, it would be inferred that 2ndAC showed a higher adsorption capacity and rate of metal ions. Although the capacity of surface function groups on the 2ndAC is slightly lower than that of the 1stAC, the contribution of functional groups of the 2ndAC on metal adsorption would be sufficient, compared to that of 1stAC. The decrease in solution pH during adsorption process on the 1stAC provides further support for a competition adsorption between metal ions and hydronium ions. However, the 2ndAC showed a slight increase of solution pH after adsorption equilibrium, which would provide a favorable solution pH conditions for metal ion adsorption.

Acknowledgments

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