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Zeta-potentials of Oxygen and Nitrogen Enriched Activated Carbons for Removal of Copper Ion

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Abstract

The oxygen and nitrogen enriched activated carbons were obtained from modification of commercial activated carbon by using nitric acid, sodium hydroxide and urea. Zeta-potentials of modified activated carbons were investigated in relation to copper ion adsorption. The structural properties of modified activated carbons were not so much changed, but the zeta-potentials and isoelectric points were considerably changed. The zeta-potential of nitric acid modified activated carbon was the most negative than other activated carbons in the entire pH region, and the pH_{IEP} was shifted from pH 4.8 to 2.6, resulted in the largest copper ion adsorption capacities compare with other activated carbons in the range of pH 3 ~ 6.5. In case of urea modified activated carbon, copper ion adsorption was larger than that of the as-received activated carbon from pH 2 to pH 6.5 even though the pH_{IEP} was shifted to pH 6.0, it was due to the coordination process operated between nitrogen functional groups and copper ion. The adsorption capacity of copper ion was much influenced by zeta-potential and pH_{IEP} of carbon adsorbent.

Keywords : *Zeta-potential, Activated carbon, Copper ion adsorption*

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1. Introduction

Adsorption of metal ions on activated carbon (AC) from aqueous solution is depending on the surface chemistry and pH of solution. Surface chemistry of carbon materials was influenced by acidic, basic or neutral functional groups. Many researchers studied oxygen and nitrogen surface functional groups for removal of metal ions [1-8].

Various oxidizers have been used to improve the oxygen functional groups on carbon surface. Among the oxidizers, nitric acid has been the most widely used to increase the total acidity in wet oxidation treatments [1-7]. Most process for improving nitrogen functional groups on carbon surface has been limited in ammonia treatment [7, 8], but another chemical was needed because the ammonia has toxicity. Adib *et al.* [9] reported that amides, NH and NH_2 or NH_4^+ species were developed on the surface of AC by impregnation of AC in urea solution, and then heat treated it up to 450°C in N_2 surrounding. This AC was very effective in removal of gaseous adsorbates. These oxygen and nitrogen functional groups of AC are protonated in solution and the AC surface is being charged negatively or positively. The chemical adsorption is being operated between these charged surface and metal ion. Therefore, measuring the surface charge of carbon is important in metal adsorption.

One of useful methods to measure the surface charge of solid is the zeta-potential measurement. Many researchers have measured the zeta-potentials and isoelectric point (pH_{IEP}) to characterize carbon materials [6, 10-16], however only a few studies have mentioned in relation to the removal of metal ions from aqueous solution.

In this work, zeta-potentials of oxygen and nitrogen enriched ACs were studied in relation to removal of copper ion from aqueous solution. To obtained the purpose; i) commercial AC was surface modified by impregnation in nitric acid (HNO_3), sodium hydroxide (NaOH) and urea ($CO(NH_2)_2$) to enrich the oxygen, and nitrogen functional groups, ii) characterization of modified ACs was performed by using nitrogen adsorption, acid-base neutralization titration techniques, elemental analysis, and zeta-potential measurements, and iii) the pH-dependent adsorption of copper ion on modified ACs were carried out to investigate the effect of zeta-potential.

2. Experimental

2.1. Modification of AC

Coconut-based commercial AC (Hanil Green Tech. Co., Korea) was used in this study. Before the modification, the AC was washed with distilled water and dried at 110°C for 24 h and denoted as-received R-AC. A part of R-AC was

Table 1. Modification conditions of ACs

AC	Chemicals	Temperature (°C)	Time (h)
R-AC (as-received)	-	-	-
A-AC (acid modified)	1 M HNO_3	80	2
B-AC (base modified)	1 M NaOH	80	2
U-AC (urea modified)	1 M $CO(NH_2)_2$	25/450	2
H-AC (annealing of A-AC)	-	1000/N_2	2

modified with 1 M HNO_3 and 1 M NaOH solution (1 g of carbon /10 ml of solution) at 80°C for 2 h. The modified ACs were then washed with distilled water until the pH became constant and dried at 110°C for 24 h. The HNO_3 and NaOH modified ACs were denoted as A-AC and B-AC, respectively. In order to prepare the nitrogen enriched AC, a part of R-AC was impregnated with 1 M $CO(NH_2)_2$ solution (1 g of carbon/ 10 ml solution) at room temperature for 2 h, and then annealing was applied in quartz tube: the furnace temperature was raised up to 450°C at 10°C/min in N_2, and maintained for 1 h, then cooled down to room temperature, which was denoted as U-AC. H-AC was prepared by annealing of A-AC at 1000°C in N_2 to remove the surface functional groups. Table 1 shows the modification conditions of ACs.

2.2. Characterization of modified ACs

Structural properties were measured by using a surface area analyzer (Micromeritics ASAP 2010) from N_2 adsorption at 77 K. Elemental analysis was carried out by using EA1110 (CE instrument). Surface functional groups of each modified activated carbons were measured by Boehm method. Zeta-potential was measured by using zeta-potential analyzer (Otasuka Electronic Co. ELS-6000). Approximately 50 mg of AC was dispersed in 1 *l* of NaCl solution (electrolyte) to ensure ionic strength. In order to obtain CO_2-free NaCl solution, N_2 was bubbled through NaCl solution until the pH of the solution became 7.0. The pH of solution was adjusted by adding either 0.1 M HCl or 0.1 M NaOH followed by agitation at 200 rpm for 24 h at 20°C to make a equilibrium.

2.3. Copper ion adsorption

Adsorptions of copper ion on as-received and modified ACs were performed by changing the solution pH. The copper solution was prepared by mixing 1 mM $CuCl_2$ under N_2 pursing. The pH of solution was adjusted by using 0.1 M HCl and 0.1 M NaOH. Then, 1 g of AC was added to 100 mL of the solution and agitated at 200 rpm for 24 h at 20°C. The copper ion solution was filtered with microsyringe filter and the concentration of copper ion was measured by using inductively coupled plasma (ICP) atomic emission spectrometer (TJA, Atomscan25, USA). The amounts of adsorbed copper ion on AC were determined by the difference of the copper ion concentrations before and after adsorption.

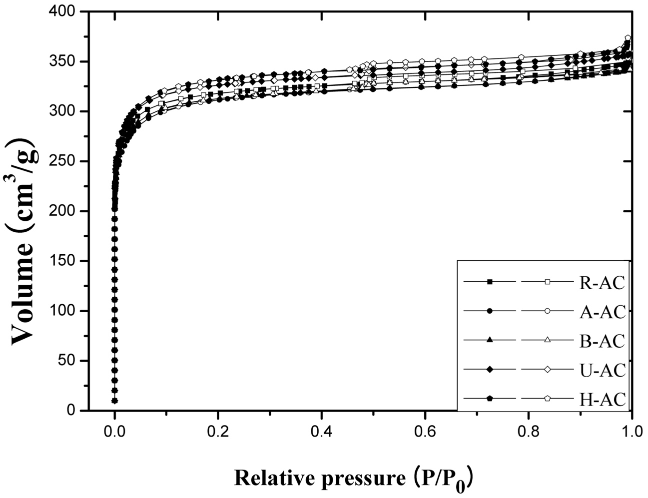

Fig. 1. Nitrogen adsorption isotherms of modified ACs. (solid = adsorption; open = desorption)

3. Results and discussion

3.1. Textural properties of ACs

Nitrogen adsorption isotherms and structural properties of modified ACs were shown in Fig. 1 and summarized in Table 2. All the isotherms of modified ACs were type I showing that pores developed were micropores. The specific surface areas of modified ACs have shown only a little change within 3%. Wang *et al.* [4] reported that the surface area of the AC increased by acid and base treatment. On the other hand, Shim *et al.* [1] and Adib *et al.* [9] reported that some of the micropores were blocked by functional groups introduced by the chemical modification, resulted in the decrease of surface area as welll as micropore volume. The appearance of hysteresis loops in the adsorption isotherms were due to the existence of some mesopores and slit-shaped pores of ACs.

3.2. Surface chemical analysis of ACs

The changes of the surface acidity and basicity of modified ACs were summarized in Table 3. The total acidity increased about 4 times by HNO_3 treatment, especially lactone groups increased about 12 times, while total basicity decreased 34%. For B-AC, total acidity decreased about 60%, but lactone groups increased 2.4 times than that of R-AC. Chen *et al.* [3] also reported that HNO_3 treatment generated a large amount of oxygen containing functional groups, especially the NaOH treatment changed carbonyl

Table 2. Structural properties of modified ACs

AC	S_{BET} (m^2/g)	S_{micro} (m^2/g)	V_t (cm^3/g)	D_{pore} (Å)
R-AC	1247	1219	0.54	17.39
A-AC	1198	1169	0.55	18.25
B-AC	1217	1191	0.53	17.39
U-AC	1277	1248	0.56	17.46
H-AC	1283	1255	0.56	17.46

Table 3. Surface acidic and basic contents of modified ACs

	Phenol	Lactone	Carboxyl	Total acidity	Total basicity
R-AC	0.19	0.05	0.15	0.39	0.35
A-AC	0.55	0.61	0.40	1.56	0.23
B-AC	0.02	0.12	0.01	0.15	0.53
U-AC	0.12	0.04	0.07	0.23	0.57
H-AC	0.01	N	N	0.01	0.52

Table 4. Elemental analysis of modified ACs

	C (wt%)	H (wt%)	N (wt%)	O^a (wt%)	O/C
R-AC	86.04	1.31	0.20	11.45	0.13
A-AC	77.30	3.10	0.63	18.97	0.25
B-AC	87.55	2.14	0.17	10.14	0.12
U-AC	87.12	1.17	2.04	9.67	0.11
H-AC	93.45	1.19	0.20	5.16	0.06

a : obtained by difference

and carboxyl groups to lactone groups instead of new functional groups generation.

When the AC was modified by impregnation with $CO(NH_2)_2$ and heat treated up to 450°C, the acidity decreased about 40% and basicity increased about 68%. Adib *et al.* [9] reported that basic nitrogen functional groups such as -NH, $-NH_2$, $-NH_4^+$ were enhanced by $CO(NH_2)_2$ treatment.

Elemental analysis of the modified ACs was summarized in Table 4. R-AC has about 11% oxygen whereas A-AC contains 66% higher amounts of oxygen than that of R-AC. However, the oxygen contents of other three ACs decreased due to the removal of acidic oxygen functional groups.

3.3. Zeta-potentials of ACs

Zeta-potential was influenced by solution pH and electrolyte concentration. Therefore, zeta-potentials of R-AC at different NaCl (electrolyte) concentration were investigated and the results were shown in Fig. 2. The pH_{IEP} was shifted to acidic region and zeta-potentials was also lowered by decrease of ionic strength.

Zeta-potentials of modified ACs were shown in Fig. 3. The zeta-potential became more negative as the pH value increased because of the deposition of more OH^- on the surface of ACs [17]. The A-AC showed the most negative zeta-potentials than others over entire pH region and the pH_{IEP} was shifted from pH 4.8 to 2.6. Similar observations for zeta-potential curves of HNO_3 treated carbons were reported in literatures [10-12]. It was due to the increase of negatively charged site on carbon surface by deprotonation of produced strong acidic functional groups such as carboxyl group. Harry *et al.* [18] reported that deprotonation of carboxyl group mainly occurred in the range from pH 2 to 6, so the zeta potential of electrochemically oxidized activated carbon fiber steeply increased as the increase of pH, then the zeta-potential curve was plateau above pH 6, and the pH_{IEP} was shifted from pH 3 to pH 1.2. Because the amount of carboxyl group decreased, zeta-potentials of B-AC showed less negatively charged than R-AC and the pH_{IEP} shifted to pH 6.3 in spite of the increase of lactone group. The pH_{IEP} of the U-AC was shifted to pH 6.0 due to the decrease of acidity and the increase of basicity. The zeta-potential and pH_{IEP} of the U-AC compared with the R-AC were not much changed, because the nitrogen-containging groups (amides, NH and NH_2 or NH_4^+ species) were behaved as either bases or strong(carboxylic) or weak(phenols) acids, and they are able to behave weak acidic groups [9].

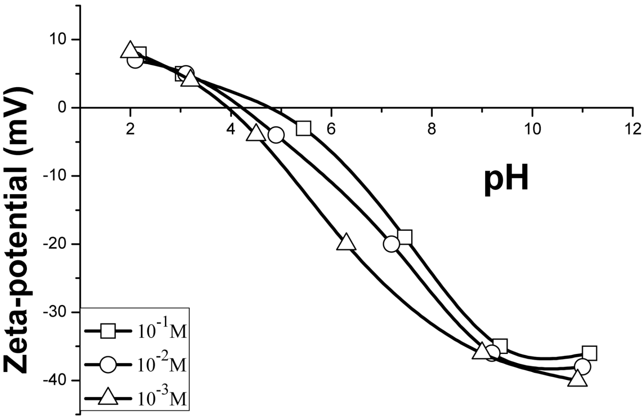

Fig. 2. Zeta-potentials of as-received AC in 10^{-1} ~ 10^{-3} M NaCl solution.

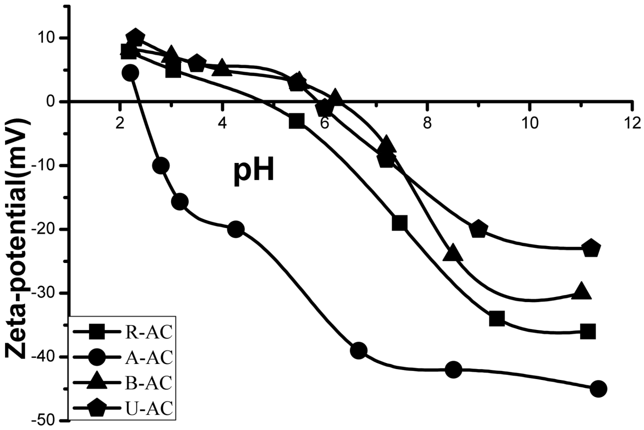

Fig. 3. Zeta-potentials of modified ACs in 10^{-1} M NaCl solution.

If oxygen functional groups were removed, what will be

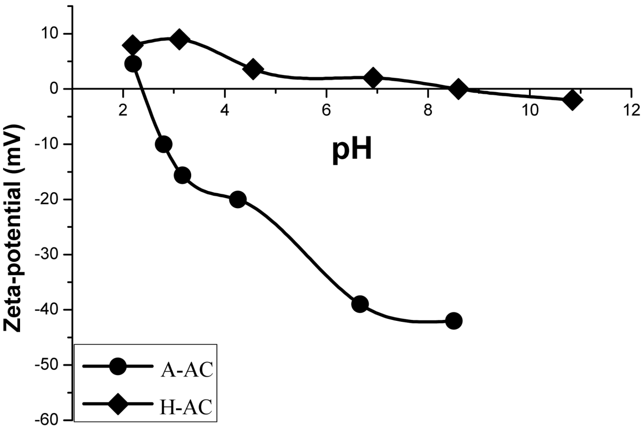

Fig. 4. Zeta-potentials of surface functional groups removed AC in 10^{-1} M NaCl solution.

happened to zeta-potential. The results were shown in Fig. 4. Heat treated AC was changed to more basic, so the pH_{IEP} of H-AC shifted from acid (pH 2.5) to base (pH 8.6), but the zeta-potentials get close to zero over the entire pH region. Yanagisawa *et al.* [14] reported very similar results that the zeta-potentials of AC were closed to zero over the entire pH region when the AC was heat treated at 1800°C, because there was a correspondence between the acidic functional group amount and the zeta-potential value, and the surface functional groups were almost decomposed above 1500°C.

The changes of pH_{IEP}s in relation to the amount of carboxyl group which was strong acid were shown in Fig 5. The pH_{IEP}s were shifted to more acidic as the increase of the amount of carboxyl group.

3.4. Copper ion adsorption

The copper ion adsorption capacities of the modified ACs were shown as a function of the initial (before adsorption) pH in Fig. 6. The adsorption capacities of copper ion increased as the increase of initial pH from 1.5 to 6. Fig. 7 shows the changes of solution pH before and after adsorption. The final (after adsorption) pH was much higher than the initial pH (except for A-AC). In case of A-AC, the final pH was not so much changed compared with the initial pH due to the acidic surface of A-AC. But for other ACs which have basic surface, the final pH was much higher than the initial pH because of the strong adsorption of hydrogen ions on ACs [3]. These pH changes can be influence the copper ion adsorption capacity because of the competitive adsorption of hydrogen ion with copper ion in low pH region, in addition the zeta-potential measured after equilibrium for 24 h. Therefore the copper ion adsorption capacities of the modified ACs were shown as a function of the final

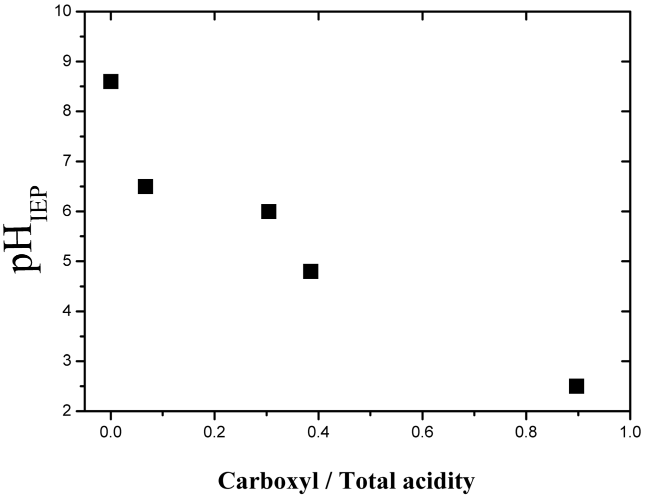

Fig. 5. The pH_{IEP} changes as a function of carboxyl/total acidity.

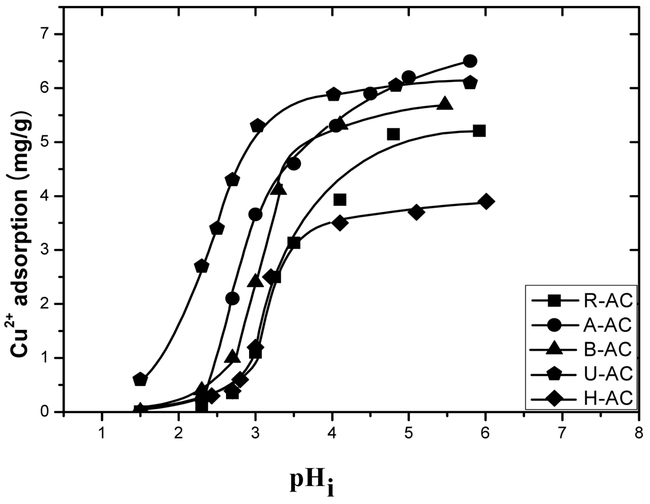

Fig. 6. Adsorption of copper ion as a function of pH_i on modified ACs.

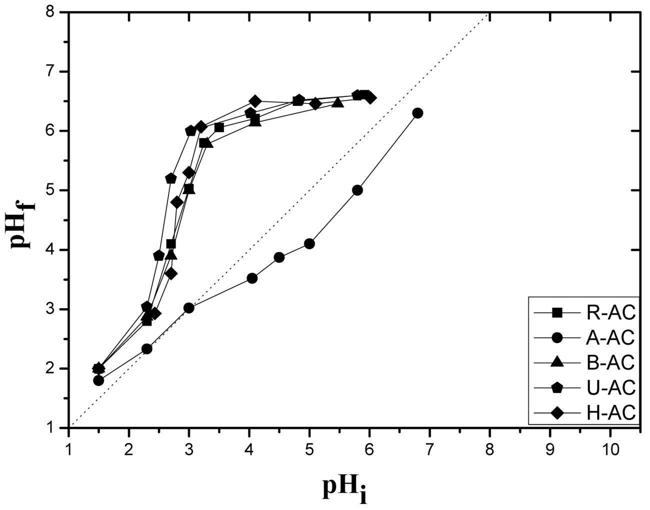

Fig. 7. The pH change of the solution before and after adsorption of copper ion on modified ACs. (pH_i = before adsorption, pH_f = after adsorption)

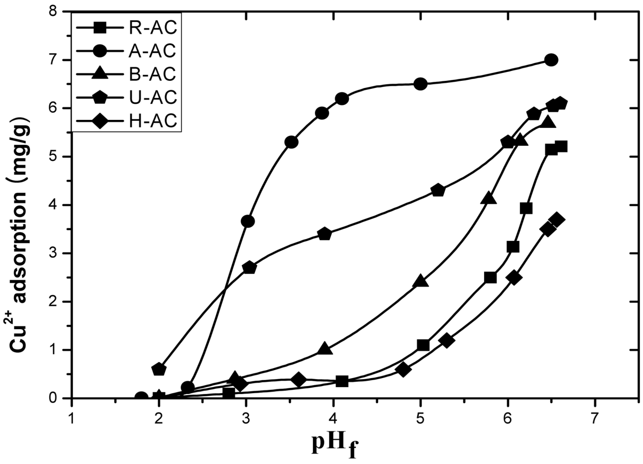

Fig. 8. Adsorption of copper ion as a function of pH_f on modified ACs.

pH in Fig. 8. The adsorption capacities of copper ion increased as the increase of pH from 2 to 6.5, because the increase of negatively charged sites and the decrease of positively charged sites which favored the adsorption of copper ion, but the curve shapes were different from each other. The adsorption capacities of copper ion on R-AC increased slightly from 0 to 1.1 mg/g until pH 5, and rapidly increased to 5.15 mg/g until pH 6.5. B-AC and H-AC were shown similar trend of curve shapes to R-AC. But on A-AC, the adsorption capacities of copper ion increased rapidly from pH 2.3 to 4 then slightly increased until pH 6.5. The pH_{IEP} of A-AC was pH 2.4, so the surface of A-AC was negatively charged which favored the adsorption of copper ion. The pH_{IEP} of other samples were pH 4.8, 6.3, 6.0 and 8.6, so they were less favored the copper ion adsorption than A-AC. In case of U-AC, although the pH_{IEP} was more basic and zeta-potentials were lower than R-AC in the entire pH region, the adsorption capacities of copper ion were larger than R-AC in the entire pH region. Furthermore, the adsorption capacities of copper ion were larger than A-AC in below pH 3. Yantasee *et al.* [19] reported that nitrogen functional groups such NH_2 adsorbed the metal ions through not only ion-exchange process but also coordination process.

4. Conclusions

The results presented in this paper clearly showed the importance of zeta-potential of carbon adsorbents for removal of metal ion from aqueous solution. The structural properties of ACs were not so much changed by modification using HNO_3, NaOH and $CO(NH_2)_2$, while the surface chemistry and zeta-potential were considerably changed. The HNO_3 treated AC showed the largest copper ion adsorption capacities compare with other 4 ACs in the range of pH 3~6.5, because the zeta-potential of this AC was the most negative than other ACs in the entire pH region, and the pH_{IEP} was shifted from pH 4.8 to pH 2.6. In case of the $CO(NH_2)_2$ treated AC, copper ion adsorption was larger than the as-received AC from pH 2 to pH 6.5 even though the pH_{IEP} was shifted to pH 6.0, it was due to the coordination process operated between nitrogen functional groups and copper ion, but the copper ion adsorption increased as the solution pH increased and closed to pH_{IEP}.

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