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Adsorption characteristics of lithium ions on coconut-based activated carbons modified with acids

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ABSTRACT

The adsorption characteristics of lithium ions on virgin and modified activated carbons with three different acids (acetic acid, sulfuric acid, and nitric acid) were studied. Although the surface modification by acids decreased pore surface area and volume, the increased acidity and oxygen-containing functional groups on the surface improved the equilibrium adsorption capacity of activated carbons. Especially, the modification by nitric acid increased the adsorption capacity of lithium ions by 45.5% compared with virgin activated carbons, despite the loss of Brunauer-Emmett-Teller specific area and total pore volume by 34% and 39%, respectively. Langmuir isotherm model provided the best fit to the adsorption isotherm data of virgin (AC) and modified activated carbons with nitric acid (NAC) and the calculated maximum adsorption capacities were 2.48 and 5.64 mg/g for AC and NAC, respectively. The adsorption energies calculated based on D–R equation for AC and NAC were 7.90 and 10.91 kJ/mol, respectively, suggesting that lithium ion adsorption on AC and NAC are characterized by ion exchange. Meanwhile, the adsorption kinetics obeyed the pseudo-second-order rate model more reliably than the pseudo-first-order rate model.

Keywords: Activated carbon; Adsorption; Lithium ion; Surface modification; Acetic acid; Sulfuric acid; Nitric acid

1. Introduction

Lithium is a material with a high energy storage capacity and has been used as a raw material in a wide variety of fields such as secondary batteries, ceramics, catalysts, and pharmaceuticals. In recent years, it has also drawn much attention as a nuclear fusion energy source [1]. Commercialization of high-capacity batteries and electric vehicles in the near future will further increase the demand of lithium and/or lithium compounds. However, land reserves such as mines and salt lakes contain only about 14 million tons of lithium. To overcome this insufficiency, an alternative source of seawater which contains 2,300 hundred million tons of lithium has been developed [2].

It is known that separation and recovery methods of lithium from seawater are ion exchange [3], extraction [4], membrane [5], and adsorption [6]. Among these methods, adsorption is widely used because of its convenient operation, effectiveness, and relatively low costs [7]. In the adsorption process, activated carbons are proven to be an effective adsorbent for metal removal and recovery due to their exceptionally high surface areas, well-developed internal microporous structures as well as the presence of a wide spectrum of surface functional groups that increases the stability of adsorption [8]. Recently, many studies have placed emphasis on surface modification of activated carbons to increase their adsorption efficiencies by adding favorable adsorption sites [7,8].

Common methods for surface modification of activated carbons are impregnation [9], thermal treatment [10], and acidification/basification [7,11]. Impregnation usually destroys the surface and some parts of the pores of the activated carbons,

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leading to a decrease in specific surface area and pore volume. Thermal treatment is also disadvantageous in that the oxygen functional groups are destroyed at high temperature, which decreases the adsorption ability of activated carbons. Meanwhile, surface modification by acidification/basification produces diverse functional groups on the surface, which increases the adsorption ability for metal ions [12]. Virgin activated carbons are generally modified with nitric acid [7], sulfuric acid [13], acetic acid [14], and phosphoric acid solutions [15]. The surface oxidation of activated carbons with nitric acid solution increased a number of acidic groups on the surface [7]. Many researchers have thus used activated carbons modified by acids to achieve efficient separation and recovery of heavy metal ions [16]. Moreover, Seron et al. [6] and Alfarra et al. [17] used activated carbons modified with phosphoric acid and nitric acid for lithium ion adsorption, respectively.

The objective of this study is to comprehensively investigate the effect of surface modification on the lithium ion adsorption by activated carbons. Three representative acids, i.e., acetic acid, sulfuric acid, and nitric acid, were used for surface modification of activated carbons and the change of surface characteristics was evaluated by measuring morphology, acidity, elemental compositions, and compositions of functional groups of virgin and modified surfaces. Then, lithium ion adsorption characteristics on virgin and surface-modified activated carbons were compared according to chemical changes of the surface. Batch-type experiments were employed to obtain adsorption isotherms, adsorption kinetics, and pH effects.

2. Materials and methods

Coconut-based granular activated carbons with the particle size of 40–60 mesh were obtained from Calgon, USA. Activated carbons were washed with pure water, and dried at 80°C overnight and cooled down in a desiccator to room temperature for subsequent acid surface modification. Prepared activated carbons were modified by agitating with 5 vol% CH_3COOH (acetic acid), 5 vol% H_2SO_4 (sulfuric acid), and 5 vol% HNO_3 (nitric acid) solutions for 12 h at 80°C. Virgin activated carbons were denoted by AC and modified activated carbons with acetic acid (0.88 mol/L), sulfuric acid (0.94 mol/L), and nitric acid (1.20 mol/L) solutions were denoted by AAC, SAC, and NAC, respectively. A 0.5 g AC and 200 mL acid solution were put into 500 mL Erlenmeyer flask, and then the solution was stirred at 200 rpm for 12 h at 80°C. The acid solution containing AC was neutralized by using 0.05 N NaOH solution for 30 min, and activated carbons modified by acids (AAC, SAC, and NAC) were washed with deionized water and dried at 85°C for 24 h. The pH of the solution for surface modification was controlled by a 0.1 N HCl solution and a 0.1 N NaOH solution in the pH range of pH 2–10.

The morphology of activated carbons before and after surface modification was observed by a scanning electron microscope (SEM, HITACHI, S-2700). Their acidity and surface potential were measured by a Boehm titration [18] and by a zeta potential analyzer (Brookhaven, zeta plus), respectively. Elemental analysis for the surface of activated carbons was carried out by an X-ray photoelectron spectroscopy (XPS, Thermo VG Scientific, MultiLab 2000). Brunauer-Emmett-Teller (BET) specific surface area and total pore volume were measured by a BET analyzer (Quantachrome, Nova 1000e).

Batch-type adsorption experiments were performed. Lithium chloride (LiCl, Shinyo, EP) was diluted with deionized water to obtain a stock solution of 1,000 mg/L lithium ion. The concentration of lithium ion was measured by an ion chromatography (DX-120, Dionex). The pH of the lithium ion solution was measured by a pH meter (Orion, Model 420A). The adsorption capacity q_t (mg/g) at time t was calculated by:

$$q_t = \frac{\left(C_0 - C_t\right)V}{m} \tag{1}$$

The adsorption capacity q_e (mg/g) at equilibrium was calculated by:

$$q_e = \frac{\left(C_0 - C_e\right)V}{m} \tag{2}$$

where C_0, C_t, and C_e are initial concentration and the concentration of lithium ion, at the initial time, at any time t, and at equilibrium (mg/L), respectively. V is the volume of the solution (L) and m is the mass of activated carbons (g).

3. Results and discussion

3.1. Effects of surface modification by acids on characteristics of activated carbons

The change of characteristics of virgin and surface-modified activated carbons was summarized in Table 1. The results showed that BET specific surface area and total pore volume of activated carbons decreased with surface modification by acids. When compared with AC, the BET specific surface area of AAC, SAC, and NAC was gradually reduced by about 7%, 28%, and 34%, respectively. And the same trend was valid for the total pore volume by about 7%, 28%, and 39%, respectively. Fig. 1 shows the surface morphologies of AC, AAC, SAC, and NAC measured by SEM. There was no peculiar difference in the surface structures of AAC, SAC, and NAC compared with AC. Therefore, it proposes that surface functional groups created by acids would not block the entrance of the pores, but rather infiltrate to the inner surface of the pores. The result of pore narrowing leads to the reduction of the pore surface area and volume, as shown in Table 1. Pak et al. [18] reported when a commercial AC was modified by sulfuric acid, the BET area and the pore volumes decreased, however, the micropore surface area and volume tended to increase slowly after acid modification. These phenomena might be due to the formation of new functional groups by oxidation reactions and the clogging of some pores by the erosion of the carbon skeleton [19].

Table 1
Comparison of characteristics of virgin and surface-modified activated carbons

Activated carbons	BET specific surface area (m^2/g)	Total pore volume (cm^3/g)
AC	1,595	0.659
AAC	1,484	0.612
SAC	1,151	0.472
NAC	1,057	0.402

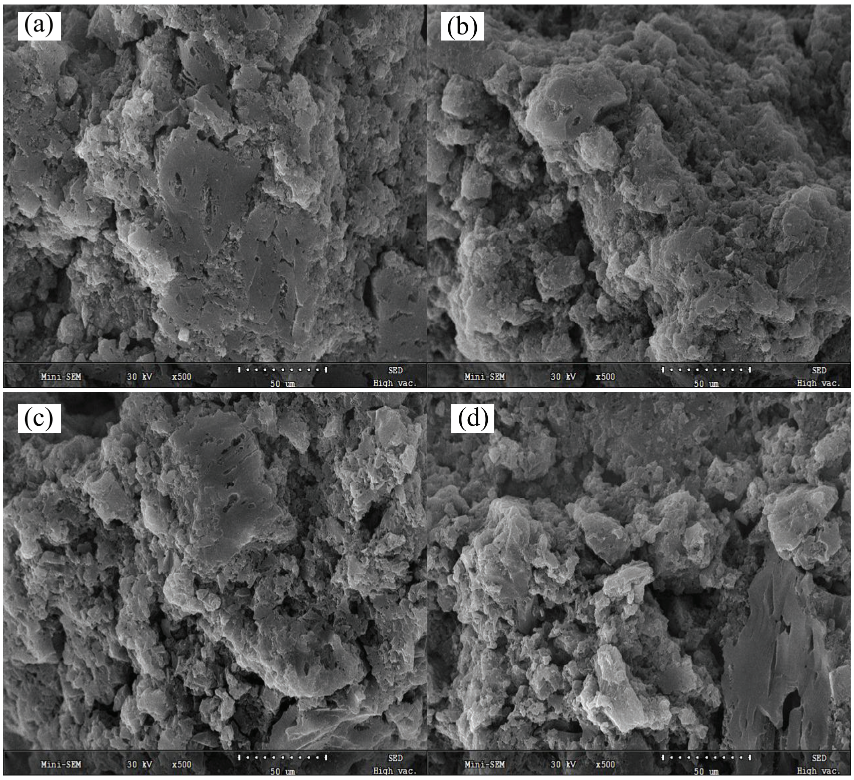


Fig. 1. Comparison of SEM images of the surface of virgin and modified activated carbons with three different acids: (a) AC, (b) AAC, (c) SAC, and (d) NAC.

Fig. 2 shows the variations of surface acidity of activated carbons by acid modification. The acidity was calculated by Boehm's titration method [20]. The acidity increased gradually from 0.2 mmol/g of AC, to 0.6 mmol/g of AAC, to 0.75 mmol/g of SAC, and finally to 2.57 mmol/g of NAC. The increase of surface acidity was about 12.8 times from virgin to surface-modified activation carbons by nitric acid. It is inversely proportional to the change of pore surface area and volume. These tendencies are in good consistence with the reported concentration of the surface functional group of the modified AC by citric acid. It was 0.32 mmol/g, which was higher than that of a commercial AC, 0.19 mmol/g, by Chen et al. [21]. The surface site density on the surface of AC is increased by acid modification [22], indicating that the modified AC (AAC, SAC, and NAC) would greatly enhance its metal adsorption capacity.

XPS analysis was conducted to investigate the difference of elemental compositions on the surface of the activated carbons modified with three different acids more explicitly. The results were compared in Fig. 3. Carbon, nitrogen, and oxygen contents are known to have their peaks at 285, 402, and 533 eV, respectively. Elemental compositions were then summarized in Table 2 for the surface of virgin and surface-modified activated carbons. All modified samples showed an increase in the oxygen content. It is noted that oxygen content increased gradually from 8.25% (AC) to 12.01% (NAC), but carbon content decreased gradually from 91.0% (AC) to 86.5% (NAC). Nitric acid modification increased oxygen content on the surface of activated carbons by 45.5%. It is consistent with other results that AC modification by nitric acid increases hydroxyl/anhydrides and carboxylic groups and the reconstruction of the O1s peak from 531.1 to 534.2 eV on the nature of the surface oxygen groups [23]. The total oxygen to total carbon ratio, O/C ratio, indicated the degree of surface oxidation. The O/C ratio also showed that oxygen is the most present on the surface modified by nitric acid. Therefore, it suggests that oxygen-containing functional groups increase with surface-modification of activated carbons by acids, especially by nitric acid.

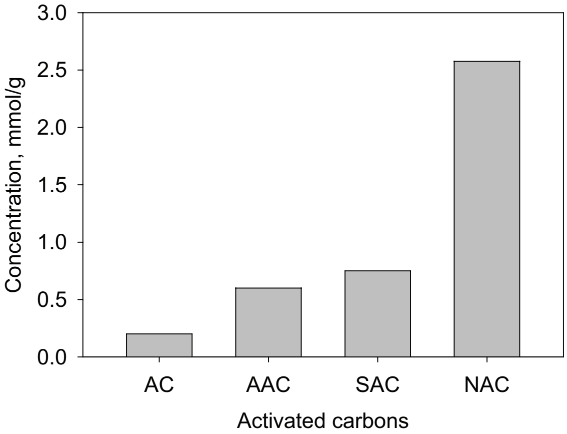


Fig. 2. Variations of surface acidity of virgin and surface-modified activated carbons.

Oxygen-containing functional groups, such as C–O, C=O, and O=C–O, are generated by the penetration of oxygen into the graphite structure during the manufacturing process of activated carbons and the subsequent formation of carboxyl, lactone, and hydroxyl groups on the surface. The compositional difference of surface functional groups was then investigated by the deconvolution of C1s peaks from the XPS spectra into functional groups for virgin and surface-modified activated carbons as shown in Fig. 4. The presence of surface oxygen groups and chemisorbed species on the surface is identified by the chemical shift of the C1s peak. The deconvoluted peaks indicate C–C, C–O/C=O, O=C–O bonds at 284.9, 286–287, and 288–289 eV, respectively. Quantitative compositions of functional groups were summarized for comparison in Table 3. As expected,

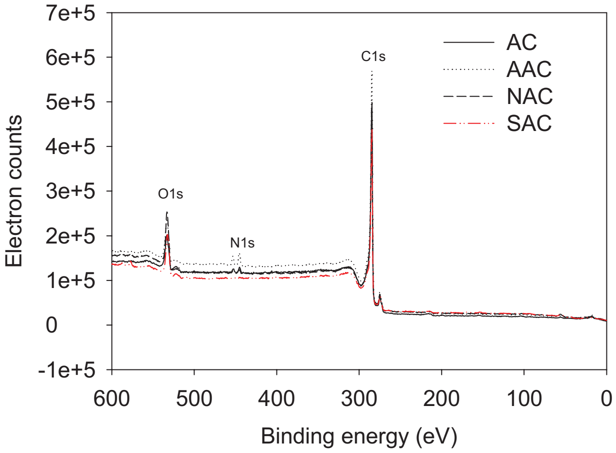
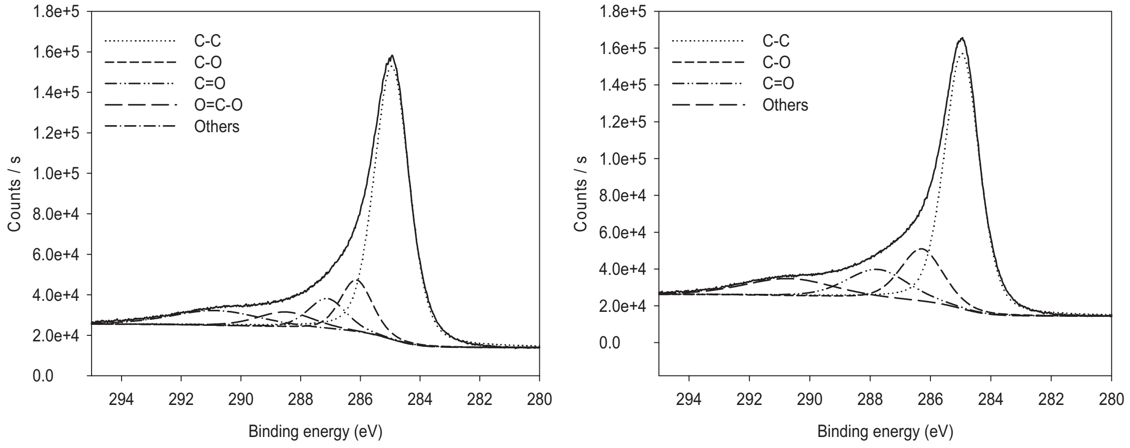


Fig. 3. Comparison of XPS spectra of virgin and surface-modified activated carbons.

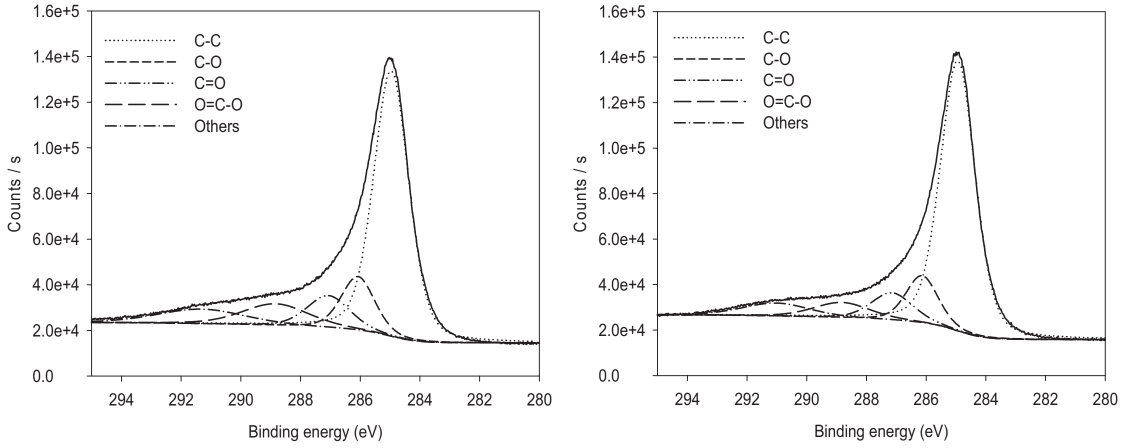
Table 2
Comparison of elemental compositions on the surface of virgin and surface-modified activated carbons

Activated carbons	Elemental composition (%)			
	C1s	O1s	N1s	O/C
AC	91.00	8.25	0.75	0.09
AAC	90.79	8.86	0.34	0.10
SAC	87.97	10.58	1.45	0.12
NAC	86.50	12.01	1.48	0.14



(a) AC

(b) AAC



(c) SAC

(d) NAC

Fig. 4. Deconvolution of C1s peaks from the XPS spectra into functional groups for virgin and surface-modified activated carbons.

the proportions of C–C and C–H groups were the most, followed by the C–O group. Despite the inconsistency for AAC, the data showed a general trend that acid modification decreased the proportions of C–C and C–H groups and increased the proportions of C=O and O=C–O groups. Especially, the comparison between virgin (AC) and surface-modified activated carbons by nitric acid (NAC) were solidly consistent with the other relevant result in Table 2.

3.2. Effects of surface modification by acids on adsorption capacity of lithium ions

The effects of surface modification by acids on the adsorption capacity of lithium ions were studied. Equilibrium adsorption capacities of lithium ions on virgin and surface-modified activated carbons with acids were compared in Fig. 5. The equilibrium adsorption capacity of lithium ions was calculated by measuring the residual lithium ion concentrations of the batch reactor. NAC had the highest equilibrium adsorption capacity, while AC had the lowest value. The equilibrium adsorption capacities increased gradually from 0.62 mg/g of AC, to 0.66 mg/g for AAC, to 0.99 mg/g for SAC, and finally to 2.29 mg/g for NAC. The increase of the equilibrium adsorption capacity was about 3.7 times from virgin to surface-modified activation carbons by nitric acid. In general, the adsorption capacity of activated carbons is proportional to their specific surface area. Thus, NAC with lowest specific surface area (Table 1) was expected to have the lowest lithium ion adsorption capacity, but the result was the opposite. Combined with the results of Table 1, Fig. 2, and Table 3, it suggests that the highest acidity and the richest functional groups on modified surfaces of activated carbons by nitric acid compensated the loss of their specific surface area and contributed to the great increase of the lithium ion adsorption capacity.

Table 3
Compositions of functional groups obtained from the deconvolution of C1s peaks for virgin and surface-modified activated carbons

Activated carbons	Functional group (%)				
	C–C and C–H	C–O	C=O	O=C–O	Others
AC	65.72	11.51	7.99	5.88	8.90
AAC	61.82	15.48	12.22	–	10.47
SAC	68.42	11.00	8.10	6.29	6.19
NAC	61.40	11.87	8.97	9.42	8.34

3.3. Effects of pH on the adsorption capacity of lithium ions

In most cases, the pH is one of the influential factors in adsorption. As the pH of solution changes, the ionic forms of adsorbates in aqueous environments and the surface electric charges of adsorbents also change. The variations of electrical charges on the surfaces of AC and NAC according to pH value were compared in Fig. 6. The surface charges of AC and NAC were positive at below pH 4.5 and pH 2.5, respectively. In other words, isoelectric points of AC and NAC were placed at pH 4.5 and pH 2.5, correspondingly. Considering that many carboxylic groups are formed when activated carbons are treated with nitrate, the lower isoelectric point of NAC is due to the dissociation of carboxylic groups at pH 2–6 [7].

The effect of pH values on the adsorption capacity of lithium ions on AC and NAC was compared in Fig. 7. The lithium ion adsorption on AC and NAC were not activated below pH 2. In the range of pH 4–10, equilibrium adsorption capacities of lithium ions were then maintained at 0.6 and 2.3 mg/g for AC and NAC, respectively. These results explain that lithium ion adsorption works better on NAC than AC at lower pH values because NAC has a lower isoelectric point [11].

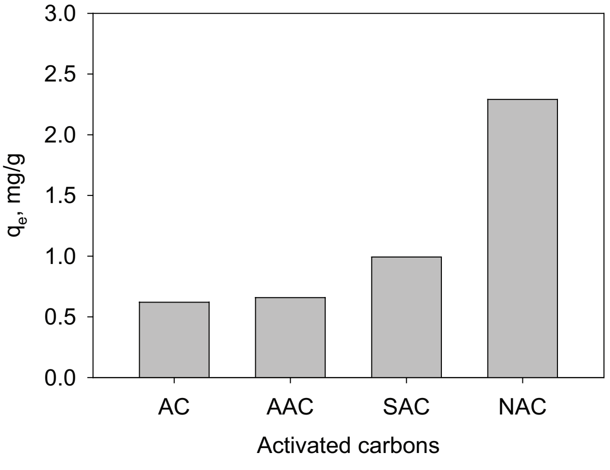


Fig. 5. Variations of the adsorption capacity of lithium ions. The initial concentration of lithium ions, the amount of activated carbons, and the operating temperature were 10 mg/L, 0.5 g, and 20°C, respectively.

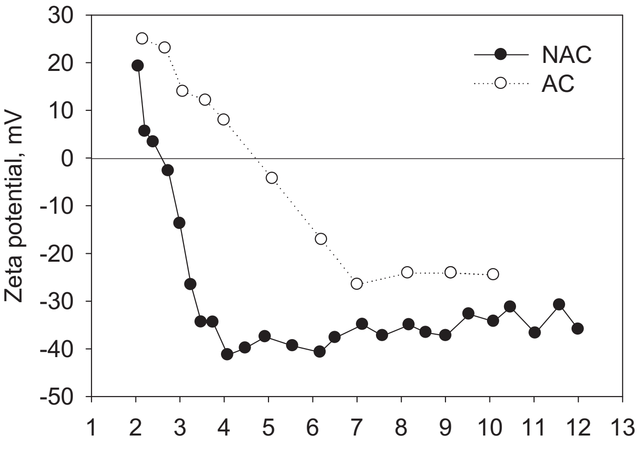


Fig. 6. Variations of zeta potentials according to pH value.

3.4. Adsorption isotherms

Freundlich, Langmuir, and Dubinin–Radushkevich (D–R) isotherm models were applied to fit the experimental data of lithium ion adsorption on activated carbons.

The linearized form of the Freundlich isotherm model is given by:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \tag{3}$$

where K_F is the Freundlich constant (L/mg), q_e is the equilibrium adsorption capacity (mg/g), and $1/n$ is the adsorption strength constant.

The linearized form of the Langmuir isotherm model is given by:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}K_L} + \frac{C_e}{q_{\max}} \tag{4}$$

where K_L is the Langmuir constant (L/mg), and $q_{\max}$ is the maximum lithium ion adsorption capacity (mg/g).

The Dubinin–Radushkevich (D–R) isotherm model [24] is expressed as follows:

$$\ln q_e = \ln q_{\max} - \beta \in^2 \tag{5}$$

where $q_{\max}$ is the maximum adsorption capacity (mol/g), β is the adsorption energy constant (mol^2/kJ), and ε is the Polanyi potential which is calculated by the following equation:

$$\varepsilon = RT\ln\left(1 + 1/C\right) \tag{6}$$

where R is the ideal gas constant (kJ/mol·K), T is the absolute temperature (K). E is the average adsorption energy (kJ/mol), calculated as follows:

$$E = \frac{1}{\sqrt{2\beta}} \tag{7}$$

Adsorption isotherms of lithium ions on AC and NAC were compared in Fig. 8. As expected, equilibrium adsorption capacity increased in proportion to the equilibrium lithium ion concentration of the solution. The experimental data in Fig. 8 were fitted to Eqs. (3)–(5), and the parameters calculated by regression were listed in Table 4. Adsorption isotherms of lithium ions on AC and NAC satisfied the Langmuir equation well. Correlation coefficients (R^2) between the Langmuir isotherm and the experimental data were over 0.99. Maximum adsorption capacities ($q_{\max}$) calculated by the Langmuir equation for AC and NAC were 2.48 and 5.64 mg/g, respectively. NAC had 2.27 times bigger $q_{\max}$ than AC. Seron et al. [6] and Jeong et al. [25] reported that the adsorption capacities of lithium ions using an activated carbon and the activated carbons modified from H_3PO_4 were 1.0 and 1.8–6.0 mg/g, respectively. The maximum adsorption capacity ($q_{\max}$), 5.64 mg/g, of lithium ion with the NAC in this study was closed to the high range of values as compared with their adsorption capacities by the kinds of activated carbons (Table 5). It is suggested that activated carbons to be modified by acid solutions is required to obtain a superior adsorption capacity of lithium ion. Other researches for lithium ion adsorption using a zeolite substituted Na ion and an extractant, which is a solvent impregnated resin containing both 1-phenyl-1,3-tetradecanedione and tri-*n*-octylphosphine oxide, suggested maximum adsorption capacities were 3.2 and 1.26–3.78 mg/g, respectively [3,26]. The adsorption energies (E) of the D–R equation for AC and NAC were 7.90 and 10.91 kJ/mol, respectively. Considering that these values were in the range of 8–16 kJ/mol, lithium ion adsorption on AC and NAC are characterized by ion exchange [27].

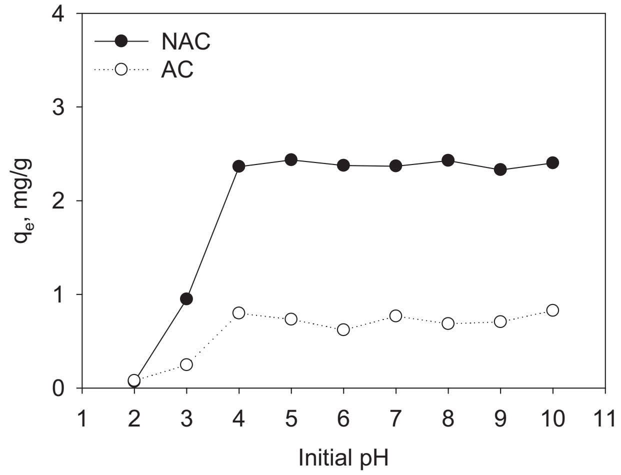


Fig. 7. Effects of initial pH on the adsorption capacity of lithium ions. The initial concentration of lithium ions, the amount of activated carbons, and the operating temperature were 10 mg/L, 0.5 g, and 20°C, respectively.

3.5. Adsorption kinetics

The pseudo-first-order rate model in the adsorption process is defined as follows [21]:

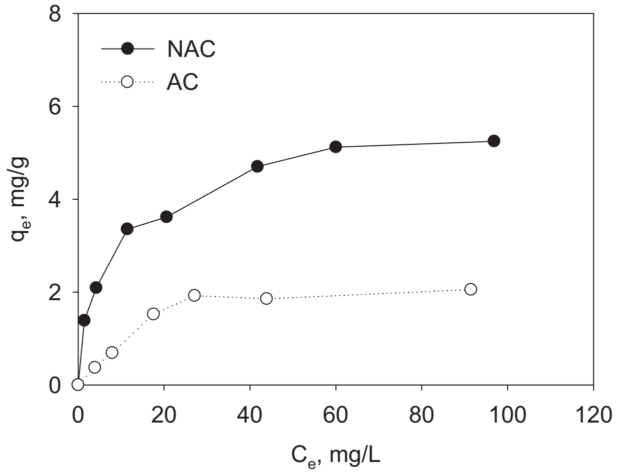


Fig. 8. Comparison of adsorption isotherms of lithium ions. The amount of activated carbons and the operating temperature were 0.5 g and 20°C, respectively.

$$\log\left(q_e - q_t\right) = \log\left(q_e\right) - \frac{k_1 t}{2.303} \tag{8}$$

where q_t is the adsorption capacity of lithium ions at any time t (mg/g) and k_1 is the pseudo-first-order kinetics constant (1/min).

The pseudo-second-order rate model is defined as follows [28]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{9}$$

where k_2 is the rate constant of pseudo-second-order model (g/mg·min).

Variations of the adsorption capacity of lithium ions on AC and NAC were shown in Fig. 9, according to adsorption time. The initial concentration of lithium ions was 10 mg/L, and the adsorption time in a batch reactor was carried out for 60 min. The progress of lithium ion adsorption on AC and NAC was almost finished within 10 min, and the adsorption capacity hardly increased after 20 min. The $q_{\max}$ on AC and NAC during the adsorption time were 0.62 and 2.10 mg/g, respectively. NAC had 3.4 times bigger equilibrium adsorption capacity than AC. The experimental data in Fig. 9 were fitted to Eqs. (8) and (9), and the parameters calculated by regression were listed in Table 6. The adsorption kinetics for AC and NAC obeyed the pseudo-second-order rate model more reliably than the pseudo-first-order rate model.

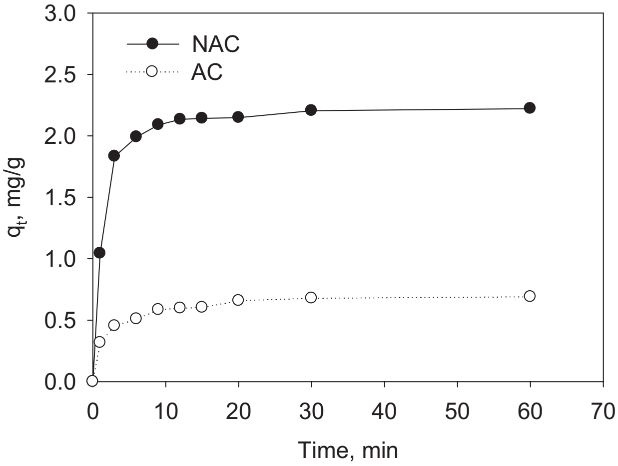


Fig. 9. Variations of adsorption capacity of lithium ions according to adsorption time. The amount of activated carbons and the operating temperature were 0.5 g and 20°C, respectively.

4. Conclusion

The effects of surface modification by three different acids on the adsorption of lithium ions on activated carbons were studied. The surface modification by acids decreased the BET specific surface area and total pore volume of the activated carbons. Especially, the modification with nitric acid reduced them by 34% and 39% compared with AC, respectively. On the other hand, the nitric acid modification increased the acidity and oxygen content on the surface of

Table 4
Comparison of parameters of isotherm models for adsorption of lithium ions

Adsorbent	Freundlich			Langmuir			D–R		
	n	K_F (mg/g)	R^2	$q_{\max}$ (mg/g)	K_L (L/g)	R^2	$q_{\max}$ (mol/g)	E (kJ/mol)	R^2
AC	0.2216	0.5634	0.8547	2.48	0.00351	0.9962	0.0010	7.90	0.9051
NAC	1.313	0.3292	0.9727	5.64	0.1689	0.9962	0.0013	10.91	0.9905

Table 5
Comparison of the NAC and other typical sorbents from adsorption capacities of lithium ions

Sorbents	$q_{\max}$ (mg/g)	pH	Temperature (°C)	Reference
AC	1.00	6.0	20	[6]
AC modified from H_3PO_4	1.80–6.00	6.0–8.0	20	[25]
Na-A zeolite	3.20	6.0	10–40	[3]
Solvent impregnated resin	1.26–3.78	–	20	[26]
AC modified from HNO_3 (NAC)	5.64	5.5	20	In this study

Table 6
Comparison of parameters of kinetic models for adsorption of lithium ions

Adsorbent	Pseudo-first-order model			Pseudo-second-order model		
	k_1 (1/min)	q_e (mg/g)	R^2	k_2 (g/mg·min)	q_e (mg/g)	R^2
AC	0.1248	0.4314	0.9617	0.9064	0.7048	0.9984
NAC	0.1421	0.8527	0.8636	0.5381	2.2548	0.9999

the activated carbons greatly. XPS analysis demonstrated the increase of C=O and O=C–O functional groups on the surface by acid modification. The highest surface acidity and richest oxygen-containing surface functional groups rendered NAC to have the highest equilibrium adsorption capacity of lithium ions, about 3.7 times higher than that of AC, despite its loss of pore surface area and volume.

Meanwhile, the investigation on the pH effect showed that the optimum operational pH range was 4–10 for lithium ion adsorption. Adsorption isotherm data of AC and NAC were then found to be best fitted to the Langmuir model and the calculated maximum adsorption capacities (q_{max}) were 2.48 and 5.64 mg/g for AC and NAC, respectively. The adsorption energy (E) obtained by the D–R equation for AC and NAC were 7.90 and 10.91 kJ/mol, respectively, and it suggested that the lithium ion adsorption on AC and NAC are characterized by ion exchange. The adsorption kinetics for AC and NAC obeyed the pseudo-second-order rate model, while the progress of lithium ion adsorption on AC and NAC was almost finished within 10 min and reached equilibrium states after 20 min. The results posed a possibility of NAC as an efficient adsorbent for recovering lithium ions from seawater.

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