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Surface modification of activated carbon via HCl or NH_4OH treatment to enhance the removal of Cr(VI) from aqueous solution

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ABSTRACT

Surface-modified activated carbon (AC) was fabricated using different concentration of HCl or NH_4OH to enhance its adsorption capacity for the removal of Cr(VI) from aqueous solution. Surface-modified ACs were also characterized by analyzing their morphologies, specific surface area, zeta potential, elemental composition, and functional groups. Batch adsorption experiments revealed that the modification of AC with HCl was more effective for increasing Cr(VI) removal by AC than NH_4OH. Cr(VI) adsorption onto AC treated with 20% HCl (20H-AC) under different contact times followed the pseudo-second-order model, indicating that chemisorption limited the rate of Cr(VI) adsorption. The determination coefficient of the Langmuir model fit was higher than that of the Freundlich model. The maximum adsorption capacity of 20H-AC for Cr(VI) was 177.9 mg/g, which was comparable to adsorbents listed in other literatures. A thermodynamic study showed that Cr(VI) adsorption onto 20H-AC is an endothermic and spontaneous reaction and chemisorption. An increase in solution pH from 2 to 10 resulted in a significant decrease in the adsorption amount of Cr(VI), that is from 78.37 to 28.40 mg/g. The negative influence of HCO_3^- on the Cr(VI) adsorption was higher than that of SO_4^{2-} and NO_3^-. Therefore, this study reveals that the modification of AC using HCl is effective in enhancing the removal efficiency of Cr(VI).

Keywords: Cr(VI) removal; Surface-modification; Activated carbon; Acid treatment; Base treatment

1. Introduction

Chromium (Cr) occurs in three abundant forms, Cr(0), Cr(III), and Cr(VI). Cr(0) is a metal chromium that is used for making steel; both Cr(VI) and Cr(III) are used for chrome plating, and in dyes and pigments, leather tanning, and wood preserving [1]. Cr(III) is an essential heavy metal for humans and animals. However, its hexavalent form can easily penetrate the cell wall, leading to various cancers [2]. Cr(VI) affects skin, causes stomach ulceration after short-term exposure, and leads to the damage of liver,

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kidney, and nerve tissue due to long-term exposure [3,4]. Due to its toxic and carcinogenic nature, the maximum concentration of Cr in wastewater discharge is set at 5 mg/L for Cr(III) and at 0.05 mg/L for Cr(VI) [5]. Cr can be introduced into the aqueous environment through its discharge by a variety of industrial processes. Thus, industrial wastewaters containing Cr(VI) need to be treated before being discharged into surface waters.

Several methods, such as adsorption, biosorption, reduction, membrane filtration, ion-exchange, foam flotation, and electrolysis have been investigated for Cr(VI) removal [1]. Among these technologies, adsorption has many advantages, such as availability, profitability, ease of operation, high efficiency, and low cost [1,6–8]. Activated carbon (AC) is widely used as an adsorbent for water treatment because of its high specific area, large porosity, excellent internal microporosity, and a variety of surface functional groups [9–11]. AC is a carbonaceous material with a well-developed pore structure and a large surface area, which allows for more binding sites for adsorption [12]. AC has been proven to be an effective adsorbent in the removal of a wide variety of organic and inorganic pollutants from aqueous solutions, especially the removal of organic contaminants due to the hydrophobic nature of its surface [13,14]. Although unmodified AC also exhibits high adsorption for organic compounds, it is not nearly as effective at removing inorganics and metals from aqueous solutions [14,15]. Therefore, its adsorption capacity and feasible removal rate must be substantially boosted by modification of the sorbent with suitable techniques.

The techniques for the modification of AC can be categorized into chemical, physical, and biological modification. The chemical modification includes sub-categories of acidic treatment, basic treatment, and impregnation of foreign material [14]. The surface functional groups on AC produced by modifications led to enhanced or reduced adsorption capacity and the selectivity of a certain adsorbate in the gaseous or liquid phase [16]. Acid treatment of unmodified AC with HNO_3, H_2SO_4, and HCl reportedly increased the number of functional groups, such as carboxyl, quinone, carbonyl, lactone, hydroxyl, and carboxylic anhydride, which further improved its ability to remove the metal cations from water by complex formation [14]. On the other hand, basic treatment was mainly carried out to improve the ability of AC in removing organic contaminants, and only a few papers have reported the removal of metal contaminants by basic treatment [14,17,18]. Besides, most researches have been conducted to modify the surface functional groups of AC with different O-containing acid solutions, including HNO_3 [19–21], H_2SO_4 [5,22], H_3PO_4 [23], and H_2O_2 [24], but few studies [17,25] examined non-O-containing acid solution, such as HCl.

The objective of this study is to modify the surface of AC via acid or base treatment to enhance the adsorption capacity of AC for Cr(VI). Batch adsorption experiments were performed to evaluate the Cr(VI) removal by surface-modified AC fabricated under different conditions. Further experiments including kinetic, equilibrium, and thermodynamic studies were performed with surface-modified AC, which had the highest removal percentage for Cr(VI). The adsorption equilibrium and dynamics were also characterized using theoretical models to design and control the adsorption process units. Equilibrium adsorption data were applied to Langmuir and Freundlich adsorption models and pseudo-first-order and pseudo-second-order rate equations were used to describe adsorption kinetics. Thermodynamic properties, including enthalpy, entropy, and Gibbs free energy were also calculated from the results obtained under different reaction temperatures. Moreover, the adsorption of Cr(VI) onto surface-modified AC was evaluated under different chemical conditions, such as pH and presence of competing anions.

2. Materials and methods

2.1. Surface modification of activated carbon

Commercial granular AC was purchased from Kaya Carbon Co., Ltd., (Republic of Korea). Ammonium hydroxide solution (NH_4OH), hydrochloric acid (HCl), sodium hydroxide (NaOH), potassium dichromate ($K_2Cr_2O_7$), acetone (CH_3COCH_3), and diphenylcarbazide ($C_{13}H_{14}N_4O$) were purchased from Sigma-Aldrich Co. (US), and were used as received. A 1,000 mg/L of Cr(VI) stock solution was obtained by dissolving potassium dichromate. The purchased granular AC was sieved to obtain a uniform size (0.85–1.18 mm) of granules. Surface-modified AC was prepared by acid or base treatment. Sieved AC was treated with different concentrations of HCl (5%, 10%, 15%, and 20% w/w) for acid treatment, and the samples were labeled as 5H-AC, 10H-AC, 15H-AC, and 20H-AC, respectively. Different concentrations of NH_4OH (5%, 10%, 15%, and 20% w/w) were used for the base treatment and the resultant samples were labeled as 5N-AC, 10N-AC, 15N-AC, and 20N-AC, respectively. A sample of 10 g AC was stirred in 100 mL of the corresponding acid or base solution at 25°C for 24 h at 100 rpm. The treated AC was washed with deionized water until there was no further change in the pH; furthermore, it was oven-dried at 65°C for 24 h. The modified AC was stored in a desiccator before use. Untreated AC (0-AC) was used for comparison and washed with deionized water before use.

2.2. Characterization of surface-modified activated carbon

The physical and chemical properties of ACs were investigated under different concentrations of HCl or NH_4OH by using various methods. A field emission scanning electron microscopy (FE-SEM; S-4700, Hitachi, Japan) was used to investigate the surface morphologies of the surface-modified AC. N_2 adsorption–desorption experiments were performed to measure the specific surface area of AC using a surface area analyzer (Quandrasorb SI, Quantachrome Instrument, USA). Before the measurement of the specific surface area, the samples were degassed at 350°C for 6–7 h. The surface charge of unmodified and modified ACs was analyzed with an electrophoretic light scattering spectrophotometer (ELS-8000, Otsuka Electronics, Japan). Electrophoretic mobility was determined for the AC particles in deionized water and converted to zeta potentials using the Smoluchowski equation. Using the N_2 adsorption–desorption isotherms, the specific surface area was determined via Brunauer–Emmett–Teller analysis.

The functional groups on the surface of AC were analyzed using a Fourier transform infrared spectroscopy (FT-IR) (Nicolet iS10, Thermo Scientific).

2.3. Cr(VI) adsorption experiments

The removal of Cr(VI) was evaluated using surface-modified ACs that were synthesized under different concentrations of HCl or NH_4OH under batch conditions. The batch experiments to quantify the Cr(VI) removal of the surface-modified ACs were performed by reacting 0.150 g of the ACs with 30 mL of 100 mg/L Cr(VI) solution in a 50 mL Falcon tube for 24 h. The tubes were agitated in a shaking incubator (SJ-808SF, Sejong Scientific Co., Korea) at 100 rpm and at 25°C. After the reaction, the samples were filtered using Whatman GF/C filter paper (pore size = 1.2 μm). The filtered solution was subjected to colorimetric analysis using 2-diphenylcarbazide method [26]. Cr(VI) concentration was determined using a UV-visible spectrophotometer (Optizen, Mecasys Corporation, South Korea) at 540 nm. All batch experimental conditions were identical to those described above unless otherwise stated. The experiments were performed in triplicate.

Kinetic, equilibrium, and thermodynamic adsorption experiments were performed with 20H-AC to investigate the fundamental characteristics of Cr(VI) adsorption, as it was found to be the most efficient surface-modified AC for Cr(VI) removal. Kinetics experiments were performed with two different initial Cr(VI) concentration of 100 and 400 mg/L. The adsorbent (0.15 g) was shaken in 30 mL of Cr(VI) solution at 100 rpm and 25°C for different reaction times (0.25, 0.5, 1, 2, 3, 6, 12, and 24 h). In equilibrium adsorption experiments, the initial Cr(VI) concentration was varied from 25 to 2,500 mg/L, and the dosage and reaction time of 20H-AC were fixed to 0.15 g and 24 h, respectively. The thermodynamic adsorption experiments were performed under 15°C, 25°C, and 35°C by reacting 0.15 g of 20H-AC with 30 mL of 100 mg/L Cr(VI) solution.

The effect of pH on Cr(VI) removal by 20H-AC was investigated by varying the pH of 400 mg/L Cr(VI) solution. The pH of the solution was adjusted to 2, 4, 6, 8, and 10 using 0.1 M of HCl or NaOH solution. Cr(VI) removal was also investigated in the presence of three different concentrations (1, 10, and 100 mM) of each anion, such as nitrate (NO_3^-), sulfate (SO_4^{2-}), and bicarbonate (HCO_3^-), respectively. 20H-AC was reacted with 400 mg/L Cr(VI) solution, which was prepared by dissolving corresponding concentration of $NaNO_3$, Na_2SO_4, and $NaHCO_3$, respectively.

2.4. Data analysis

The kinetic data can be analyzed using the following pseudo-first-order and pseudo-second-order models:

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \tag{1}$$

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

where q_t is the amount of Cr(VI) removed at time t (mg-Cr(VI)/g), q_e is the amount of Cr(VI) removed at equilibrium (mg-Cr(VI)/g), k_1 is the pseudo-first-order rate constant (1/h), and k_2 is the pseudo-second-order rate constant (g/mg-Cr(VI)/h).

The equilibrium data can be analyzed using the Langmuir (Eq. (3)) and Freundlich (Eq. (4)) models:

$$q_e = \frac{Q_m K_L C}{1 + K_L C} \tag{3}$$

$$q_e = K_F C_e^{\frac{1}{n}} \tag{4}$$

where C is the concentration of Cr(VI) in the aqueous solution at equilibrium (mg-Cr(VI)/g), K_L is the Langmuir constant related to the binding energy (L/mg-Cr(VI)), Q_m is the maximum amount of Cr(VI) removed per unit mass of dolomite (mg-Cr(VI)/g), K_F is the distribution coefficient (L/g), and n is the Freundlich constant.

The thermodynamic properties of the experimental results were analyzed using the following equations:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{5}$$

$$\Delta G^\circ = -RT\ln K_e \tag{6}$$

$$\ln K_e = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{7}$$

$$K_e = \frac{\alpha q_e}{C_e} \tag{8}$$

where ΔG° is the change in Gibbs free energy (kJ/mol), ΔS° is the change in entropy (J/K/mol), ΔH° is the change in enthalpy (kJ/mol), K_e is the equilibrium constant (–), and α is the amount of adsorbent (g/L).

3. Results and discussion

3.1. Characterization of surface modified AC

The physical and chemical properties, including surface morphologies, specific surface area, surface charge, and chemical functional groups of unmodified AC and modified AC were investigated using different concentration of NH_4OH or HCl. The surface morphologies of the prepared AC samples were characterized using FE-SEM. Compared to unmodified AC, the surface of 10N-AC did not show a distinct difference; however, an increase in the NH_4OH concentration up to 20% led to the appearance of pores in AC (Fig. 1c). Micropores were also observed in the sample of 10H-AC, indicating that the pores on the surface of AC were produced even under a low concentration of HCl treatment. An increase in the concentration of HCl up to 20% produced debris on the surface of AC, which destructed the pores by severe oxidation [14].

The specific surface area of surface-modified AC is presented in Table 1. Except in the case of 15% NH_4OH treatment, a lower specific surface area was observed in the AC modified with NH_4OH than that of

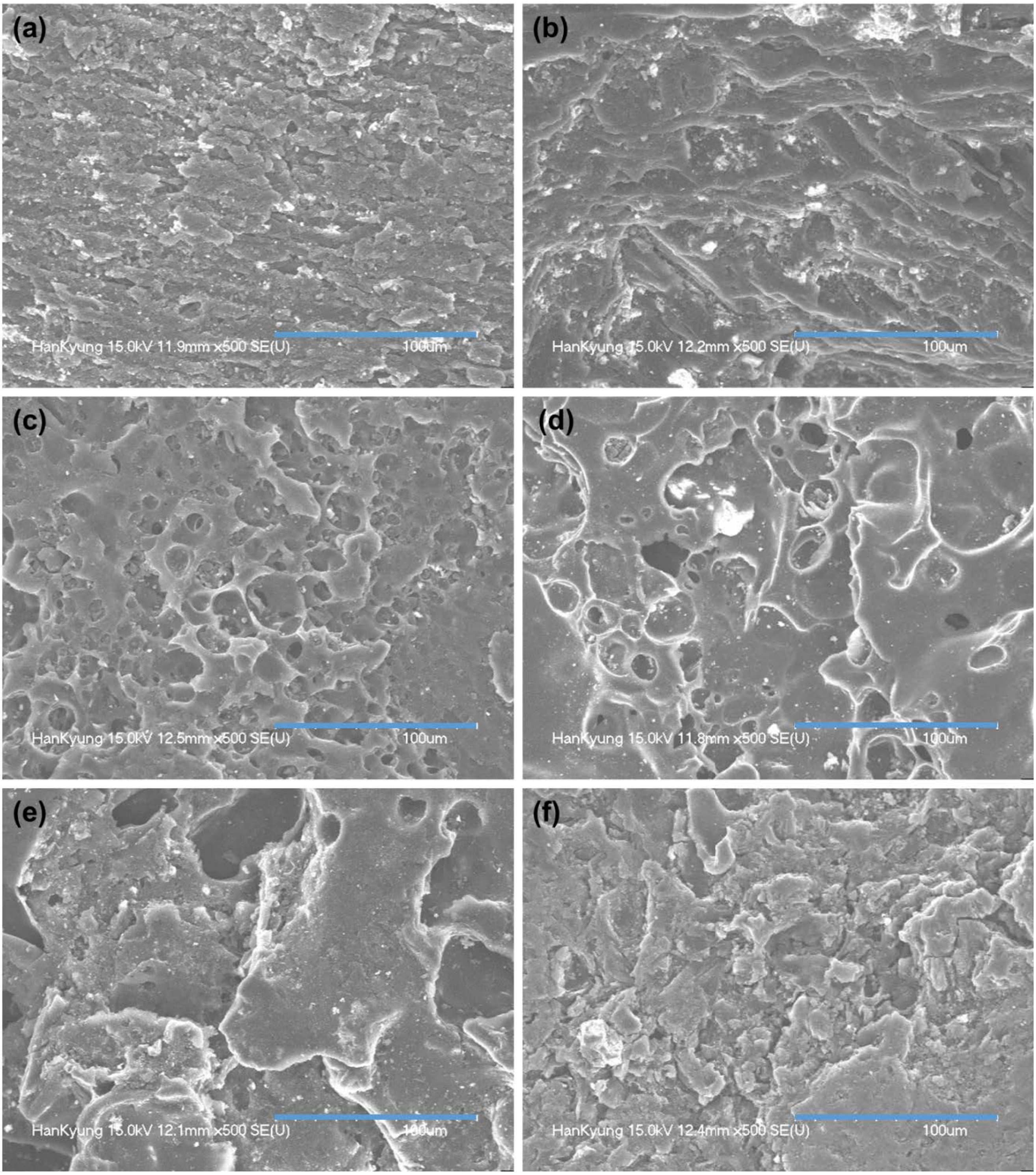

Fig. 1. FE-SEM images of surface-modified AC samples: (a) 0-AC, (b) 10N-AC, (c) 20N-AC, (d) 10H-AC, (e) 20H-AC before Cr(VI) adsorption, and (f) 20H-AC after Cr(VI) adsorption. Scale bar: 100 μm.

unmodified AC, and a reduction in specific surface area (11.4%) was observed in the treatment of AC with 20% NH_4OH. A decrease in the surface area can be attributed to the blockage in the carbon matrix induced by the functional groups, which are generated during the reaction with NH_4OH [27]. Specific surface area of HCl modified AC decreased from 1,125.7 to 953.4 m^2/g, as the concentration of HCl increased from 5% to 20%, and the specific surface area of 20H-AC was 15.2% less than that of unmodified AC. This result is consistent with the morphologies obtained from FE-SEM,

Table 1
Specific surface area, zeta potential, and elemental composition of ACs modified under difference concentration of HCl or NH_4OH

Adsorbents	Specific surface area (m^2/g)	Zeta potential (mV)	Elemental composition			
			C (%)	H (%)	N (%)	S (%)
0-AC	1,123.7	–12.4	73.1	0.49	0.25	0.46
5N-AC	1,029.7	–17.3	72.74	0.49	0.32	0.49
10N-AC	1,077.9	–15.0	71.84	0.54	0.35	0.42
15N-AC	1,122.6	–16.6	72.69	0.48	0.34	0.41
20N-AC	995.7	–19.4	71.86	0.52	0.39	0.43
5H-AC	1,125.7	23.6	71.84	0.60	0.18	0.47
10H-AC	1,046.2	25.5	71.32	0.53	0.24	0.48
15H-AC	990.9	20.7	70.89	0.45	0.21	0.50
20H-AC	953.4	34.6	68.89	0.69	0.20	0.44

which revealed that the surface of 20H-AC had less pores. The reduction of the specific surface area of AC by strong acid oxidizers, such as HNO_3 and HCl was also observed by some researchers. Singha et al. [28] also observed that the specific surface area of AC was decreased by HCl treatment and reported that the reason is due to the blocking of narrow pores by the surface functional groups introduced by acid treatments. Dobrowolski and Otto [20] suggested that the treatment of strong acid, that is HNO_3 caused carbon digestion, which led to the loss of pore walls and the destruction of some micropores on the surface of AC. The total, micro-, meso-, and macro- pore volume of the unmodified AC were 0.545, 0.328, 0.171, and 0.046 cm^3/g, respectively. Based on this classification of the International Union of Pure and Applied Chemistry [29], the average pore size of the unmodified AC was 2.18 nm, which corresponds to the boundary between micropores (diameter < 2 nm) and mesopores (2 nm < diameter < 50 nm).

The specific surface charge of nascent AC used in this study was negatively charged in deionized water. The commercial AC has both positive and negative charge at neutral pH depending on raw material and activation method. The surface charge of AC treated with NH_4OH ranged from –15.0 to –19.4 mV, slightly lower than that of unmodified AC. HCl treatment altered the surface charge of AC from negative to positive because the surface of AC was protonated by HCl treatment [28].

FT-IR spectroscopy was used to identify the functional groups present on the surface-modified AC and the results are shown in Fig. 2. Acid and base treatment did not change the identity of functional groups present on the surface of AC; however, changes in the intensity of the peaks signified an effect on the relative concentration of functional groups [30]. The peak at about 2,950–2,970 cm^{-1} and at 1,100 and 1,260 cm^{-1} was due to C–H stretching and C–O stretching vibration, respectively [31]. The bands between 3,200 and 3,500 cm^{-1} can be attributed to O–H vibrations, which indicate the presence of surface hydroxyl groups and physically absorbed water [32]. After HCl treatment, peaks at about 780 and 1,100 cm^{-1} gradually increased with an increase in HCl concentration. The peak at about 780 cm^{-1} due to C–Cl stretching [33] was distinctly observed in AC treated with a high concentration of HCl (20H-AC). The C–Cl bonding could be produced in 20H-AC via the nucleophilic substitution, the Hell-Volhard-Zelinsky reaction, and the Markovnikov addition [32]. This result is consistent with the elemental composition (Table 1), in which a higher H percentage of 20H-AC was observed, compared to the other surface modified ACs. A peak at 1,100 cm^{-1} could be due to the HCl treatment, which increases the amount of oxygen functional groups, such as carboxylate groups, phenols, ethers, and lactones, which are the commonly found functional groups having a C–O bond [30,32]. Chen and Wu [32] also reported that HCl treatment on AC resulted in an increase in the amount of single-bonded oxygen functional groups. Chiang et al. [34] reported that basic treated AC also increased carboxylate groups, phenols, and lactones groups. Thus, a peak at 1,100 cm^{-1} was predicted in this study after basic treatment. However, there have no specific changes in the spectra on the basic treated ACs (5N-AC, 10N-AC, 15N-AC, and 20N-AC) as compared with 0-AC.

3.2. Cr(VI) removal under different surface modification and its removal mechanism

Surface modification of AC samples were performed under different concentration of NH_4OH or HCl, and Cr(VI) adsorption by different surface-modified ACs is shown in Fig. 3. The amount of adsorbed Cr(VI) onto 5N-AC was 10.8% higher than non-treated AC; however, an increase in NH_4OH concentration decreased the amount of adsorbed Cr(VI) onto AC. Cr(VI) adsorption by AC decreased by up to 14.8% after treatment with 20% NH_4OH solution, as compared to that of 0-AC. HCl treatment improved the amount of adsorbed Cr(VI) onto AC, and the highest adsorption capacity of 17.8 mg/g was obtained from AC treated with 20% HCl (20H-AC). Cr(VI) adsorption increased by up to about 50% after treatment with 20% HCl. These results infer that HCl treatment improved the adsorption capacity of AC for Cr(VI) but NH_4OH was not effective in enhancing the Cr(VI) adsorption of AC.

From the specific surface area values obtained and the results of the batch adsorption studies described above, it is clear that the change in the specific surface area did not contribute significantly to Cr(VI) adsorption onto

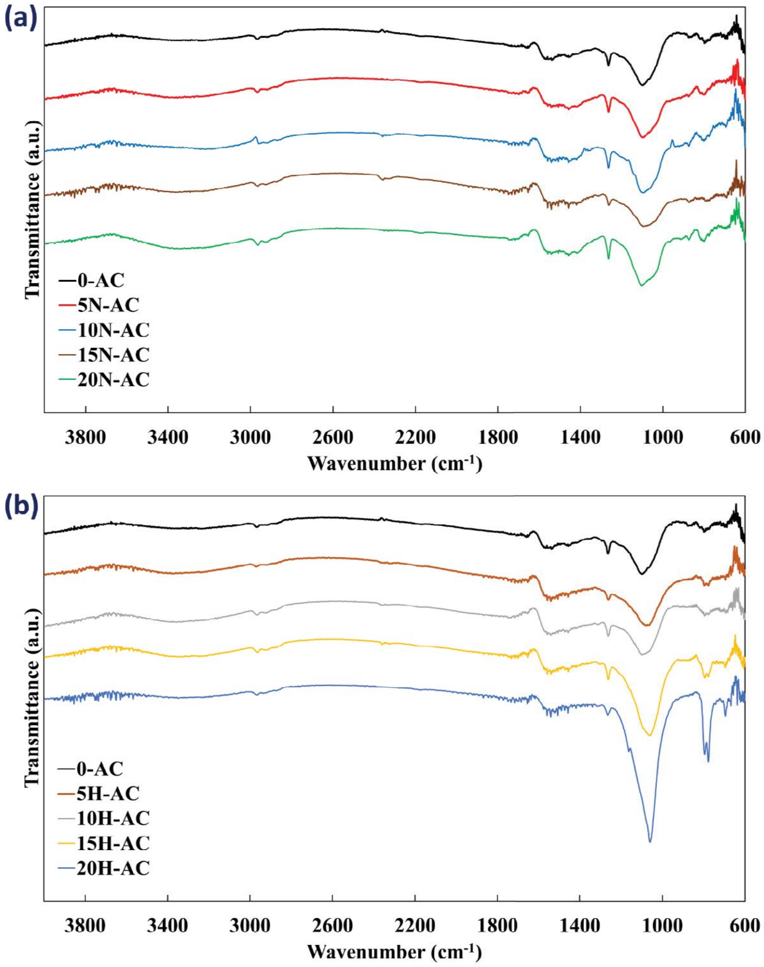

Fig. 2. FT-IR spectra of ACs modified under difference concentration of (a) NH_4OH and (b) HCl.

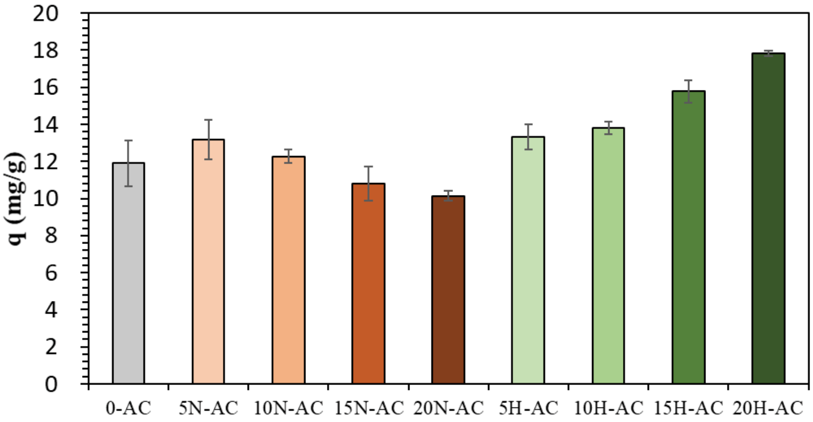

Fig. 3. Cr(VI) adsorption onto ACs modified under difference concentration of HCl or NH_4OH (initial Cr(VI) concentration: 100 mg/L; pH: 7.0; adsorbent dosage: 5 g/L; reaction time: 24 h; agitation speed: 100 rpm; temperature: 25°C).

surface-modified AC. Improvement in Cr(VI) adsorption capacity is primarily caused by the change in surface functional groups produced by the modification of AC using NH_4OH or HCl. This result suggests that the mechanism of Cr(VI) adsorption is surface complexation and electrostatic attraction between the Cr(VI) ions and the surface of the adsorbent [35]. Upon treating the AC sample with NH_4OH, its surface becomes more negatively charged. A similar result was also observed by Park and Jang [17] who reported that the adsorption of Cr(VI) by

NaOH-treated AC was less than that by unmodified AC. This can be explained by the presence of OH^- ion produced under alkaline environment, which reacts with the surface functional groups of AC [14]. Chiang et al. [34] verified that AC treated with NaOH showed a major increase in the concentration of hydroxyl and carboxyl groups on the surface of NaOH-treated AC, which became more negatively charged. Electrostatic interactions of the negatively charged NH_4OH-treated AC with the negatively charged chromate or dichromate ions allows electrostatic repulsion, providing more unfavorable conditions for adsorption [17,36].

In contrast to the NH_4OH treatment, HCl treatment resulted in a positively charged AC surface. Cr(VI) is present in the aqueous medium as chromate (CrO_4^{2-}) and bi-chromate ($HCrO_4^-$). These anions can be attracted to the protonated forms of the hydrous carbon surface. Thus, the removal mechanism can be explained on the basis of attraction between the anions and the positively charged AC surface sites. Oxygenated functional groups (carboxyl (−COOH), carbonyl (=C=O), and lactonic and phenolic/hydroxyl (−OH) can behave like acids and can make the carbon surface more acidic, which then can be protonated easily by attracting a proton (H^+) from the aqueous solution [28]. The formation of protonated functional groups, such as $-COOH_2^+$, OH_2^+, and $C-OH^+$ [5] provides favorable condition for the adsorption of Cr(VI) onto modified AC [17,36]. These positively charged surface sites of the HCl-modified AC get bonded with the $HCrO_4^-$ and CrO_4^{2-} present in the solution by the attraction of electrostatic force, forming coordinate complexes [28].

3.3. Kinetic, equilibrium, and thermodynamic study of Cr(VI) adsorption onto 20H-AC

Cr(VI) adsorption onto 20H-AC as a function of reaction time was performed at two different concentrations, that is 100 and 400 mg/L. Fig. 4 shows the plot of experimental data with two kinetic models of pseudo-first-order and pseudo-second-order. The calculated parameters for two kinetic models are presented in Table 2. At a low initial concentration of Cr(VI) (100 mg/L), Cr(VI) adsorption reached equilibrium within 6 h; however, a fourfold larger time period, that is 24 h was required to reach equilibrium at 400 mg/L of initial Cr(VI) concentration. The determination coefficients for both concentrations are closer to unity in the pseudo-second-order model, indicating that pseudo-second-order model is better fitted to kinetic experimental data. Thus, the adsorption of Cr(VI) onto 20H-AC is mainly governed by chemical adsorption due to pseudo-second-order model, suggesting that the adsorption process involves chemisorption mechanism [37,38]. Similar results have been also observed by several researchers [23,38], who observed that pseudo-second-order model fitted the data for Cr(VI) adsorption onto AC.

The relationship between the adsorbed Cr(VI) onto 20H-AC (q_{eq}) and its aqueous concentration (C_e) at equilibrium is plotted in Fig. 5, and the parameters obtained from Langmuir and Freundlich isotherm models are

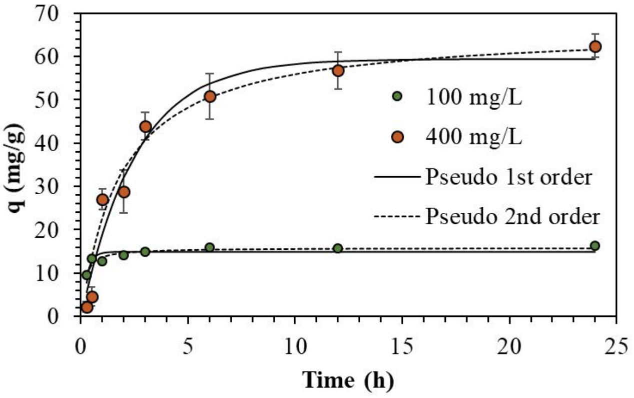

Fig. 4. Effect of contact time on Cr(VI) adsorption onto 20H-AC with model fits of pseudo-first-order and pseudo-second-order model (initial Cr(VI) concentration: 100 and 400 mg/L; pH: 7.0; adsorbent dosage: 5 g/L; reaction time: 0.25–24 h; agitation speed: 100 rpm; temperature: 25°C).

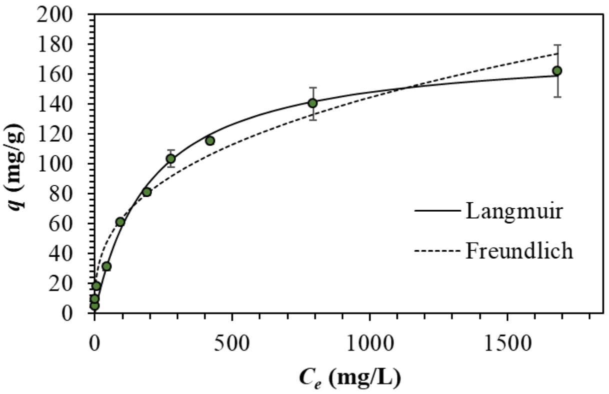

Fig. 5. Effect of initial concentration on Cr(VI) adsorption onto 20H-AC with model fits of Langmuir and Freundlich isotherm models (initial Cr(VI) concentration: 25–2,500 mg/L; pH: 7.0; adsorbent dosage: 5 g/L; reaction time: 24 h; agitation speed: 100 rpm; temperature: 25°C).

Table 2
Model parameters for the pseudo-first-order and pseudo-second-order models obtained from the kinetic sorption experiments for Cr(VI) adsorption onto 20H-AC

Initial Cr(VI) concentration (mg/L)	Pseudo-first-order kinetic model parameters			Pseudo-second-order kinetic model parameters		
	q_e (mg/g)	k_1 (1/h)	R^2	q_e (mg/g)	k_2 (g/(mg h))	R^2
100	14.94	3.991	0.766	15.91	0.402	0.886
400	59.34	0.391	0.959	66.34	0.008	0.970

presented in Table 3. Fig. 5 shows that the adsorption capacity of 20H-AC was increased with increasing the Cr(VI) concentration in the aqueous phase. It can be explained by that more Cr(VI) adsorption at higher its initial concentration was achieved by the higher driving force to facilitate the ion diffusion from the solution phase to the surface of adsorbents and more collision between Cr(VI) and active sites of the adsorbents [39]. The R^2 value of the Langmuir model ($R^2 = 0.9886$) was higher than that of the Freundlich model ($R^2 = 0.9747$) and standard error of estimate (SEE) of Langmuir model (6.40) was lower than that of the Freundlich model (9.53), indicating that Cr(VI) adsorption onto 20H-AC occurs in a single layer on the homogeneous surface containing finite number of adsorption sites. Furthermore, it suggests that the energies of adsorption are uniform and that there is no transmigration of adsorbed Cr(VI) in the skeleton of the adsorbing surface [35]. The $1/n$ value of the Freundlich model was calculated to be 0.355, which is less than 0.5, indicating a strong binding between Cr(VI) and 20H-AC [40]. Maximum adsorption capacity (Q_m) and the Langmuir constant (K_L) obtained from the Langmuir model were 177.9 mg/g and 0.00487 L/mg, respectively.

The maximum adsorption capacity of 20H-AC for Cr(VI) was comparable to that of other AC published by Owlad et al. [1] for Cr(VI) removal from water and wastewater. Of the 37 AC listed by Owlad et al. [1], 36 had a lower Cr(VI) adsorption capacity than 20H-AC. Only powder AC had a higher adsorption capacity than 20H-AC [41] as it has a larger specific surface area than that of 20H-AC. We also compared the adsorption capacity of 20H-AC for Cr(VI) to that of other AC published in recent literature (Table 4). Cr(VI) adsorption capacity of 20H-AC was found to be superior than that of the adsorbents listed in Table 4, of which ranged from 2.05 to 125 mg-Cr(VI)/g. It is worth mentioning that 20H-AC is granular size, it can be easily separated from the water after treatment. Moreover, it is easily modifiable and cheap.

Thermodynamic parameters obtained under different temperatures (15°C, 25°C, and 35°C) are provided in Table 5. A positive value of standard enthalpy change ($\Delta H°$) indicated that the adsorption of Cr(VI) on 20H-AC was an endothermic process. The enthalpy change ($\Delta H°$) was high, at 42.7980 kJ/mol, indicating that complexation or chemisorption may be responsible for Cr(VI) adsorption onto 20H-AC. The enthalpy change of chemical adsorption was >29 kJ/mol and that of complexation ranged from 8 to 60 kJ/mol [38,48]. The negative values of the standard Gibb's energy change ($\Delta G°$) at 15°C, 25°C, and 35°C indicated that the adsorption

Table 3
Model parameters for the Freundlich and Langmuir models obtained from the equilibrium sorption experiments for Cr(VI) adsorption to 20H-AC

Model	Parameters		R^2	SEE
Langmuir	Q_m (mg/g) 177.9	K_L (L/mg) 0.00487	0.989	6.40
Freundlich	K_F ((mg-Cr(VI)/g)·(L/mg-Cr(VI))$^{1/n}$) 12.43	$1/n$ 0.355	0.975	9.53

R^2: determination coefficient; SSE: standard error of estimate.

Table 4
Comparison of the maximum adsorption capacity (q_m) of several adsorbents for Cr(VI) removal

Adsorbent	Particle size	q_m (mg/g)	Reference
HCl-modified granular AC	0.850–1.18 mm	177.9	This study
Bamboo waste AC	150 μm	125	[42]
AC/f-MWCNTs	Powder	113.29	[35]
AC/f-CNSs	Powder	105.48	[35]
Powdered AC-FeO/Ag	Powder	100.0	[43]
H_2SO_4-AC	NA[a]	54.11	[22]
Coffee husk AC	150 μm	52.6	[44]
Unmodified corncorb AC	NA	22.82	[22]
PEI-palm shell granular AC	1–2 mm	20.5	[45]
Oxidiezed AC from peanut shell	37–88 μm	13.48	[46]
Palm shell granular AC	1–2 mm	12.6	[45]
H_2SO_4-treated waste AC	2–3 mm	10.929	[5]
AC-CNTs	50 μm	9.0	[47]
Mango kernel H_3PO_4 AC	710–1,000 μm	7.8	[23]
HNO_3-treated waste AC	NA	7.485	[19]
HNO_3-treated AC	Powder	6.92	[20]
High temperature outgassed AC	Powder	2.05	[20]

[a] Not available.

Table 5
Changes in enthalpy, entropy, and Gibb's energy for Cr(VI) adsorption onto 20 H-AC

T (°C)	ΔH° (kJ/mol)	ΔS° (kJ/mol K)	ΔG° (kJ/mol)
15	42.7980	0.1599	–3.2880
25			–4.8874
35			–6.4868

of Cr(VI) onto 20H-AC is spontaneous under these experimental conditions.

3.4. Effect of solution pH and competing anions

The adsorption of Cr(VI) onto 20H-AC under different pH conditions is shown in Fig. 6. With an increase in pH from 2 to 10, the adsorption of Cr(VI) onto 20H-AC decreased from 78.4 to 28.4 mg/g at 400 mg/L of Cr(VI) and from 19.8 to 15.9 mg/g at 100 mg/L of Cr(VI). The reduction in Cr(VI) adsorption by 20H-AC with the increase of pH was more distinct at a higher initial concentration of Cr(VI). Lower adsorption of Cr(VI) at higher pH was reported in previous works using other adsorbents [23,45,49,50]. Lower adsorption at higher pH can be explained by larger electrostatic repulsion between the negatively charged 20H-AC and divalent CrO_4^{2-} [38]. The surface of 20H-AC becomes more negatively charged due to deprotonation. Cr(VI) can exist as hydrogen chromate ($HCrO_4^-$), chromate (CrO_4^{2-}), or dichromate (CrO_4^{2-}) depending upon the pH; Cr(VI) exists as hydrogen chromate anions ($HCrO_4^-$) between pH 1.0 and pH 6.5 and as CrO_4^{2-} above pH 6.5 [38]. Cr(VI) exists as CrO_4^{2-} above pH 6.5, which can be more repulsive to negatively charged surface, than $HCrO_4^-$. This is also consistent with the fact that Cr(VI) adsorption onto 20H-AC decreased sharply with an increase in pH from 6 to 8 (Fig. 6). Another reason for lower adsorption of Cr(VI) onto 20H-AC at higher pH can be explained due to the competitiveness between chromate and hydroxyl ions for favorable adsorption sites of 20H-AC. This can be supported with the information that Cr(VI) adsorption at a lower initial concentration (100 mg/L) is less dependent on pH than a higher initial concentration (400 mg/L).

The effects of common competing ions, including NO_3^-, SO_4^{2-}, and HCO_3^- were also investigated and the results are shown in Fig. 7. The presence of NO_3^-, SO_4^{2-}, and HCO_3^- reduced the uptake of Cr(VI) by 20H-AC and a greater reduction in the adsorption of Cr(VI) was observed at a higher competing anion concentration. These results indicate that NO_3^-, SO_4^{2-}, and HCO_3^- compete with the dichromate ions for adsorption onto the active sites. A large decrease in adsorption capacities in the presence of HCO_3^- suggests that it has a greater effect on the adsorption of Cr(VI). The shared charge of CO_3^- ion is 1.33, less than that of NO_3^- and SO_4^{2-}, indicating that a higher effective negative charge on each O atom leads to stronger ionic bonding [51]. Higher pH of the solution in the presence of HCO_3^- is also attributed to the poor adsorption of Cr(VI) by 20H-AC.

4. Conclusions

The surface modification of AC via acid and base treatment was performed to enhance its efficiency for Cr(VI) removal. With an increase in HCl concentration, a decrease in the specific surface area of AC was observed due to the destruction of some micropores of AC. FT-IR spectroscopy results showed that the peak related to C–Cl was formed on the surface of AC by the treatment of 20% HCl. The HCl treatment on AC enhanced its adsorption capacity for Cr(VI) ion but NH_4OH treatment was not effective on the adsorption of Cr(VI). The enhancement of Cr(VI) adsorption by the surface modification of AC using HCl was due to the protonation of AC by the HCl treatment. Kinetic studies indicated that the rate of Cr(VI) adsorption onto 20H-AC was limited mainly by chemisorption. Equilibrium adsorption data were better described by the Langmuir model than by the Freundlich model, indicating that Cr(VI) adsorption onto 20H-AC occurred via monolayer. The maximum adsorption capacity of 20H-AC obtained from Langmuir model fitting was 177.9 mg/g, which was superior to that of other AC reported in other literatures. Cr(VI) adsorption onto 20H-AC decreased with an

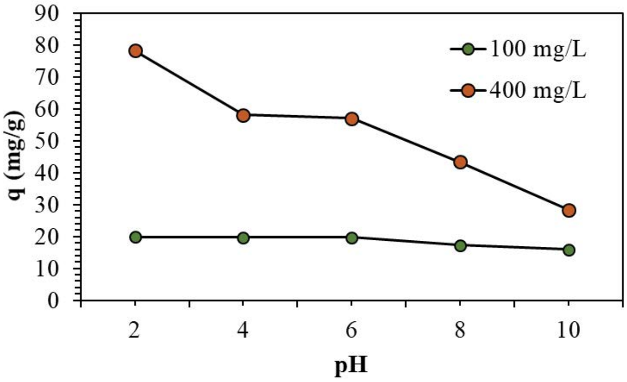

Fig. 6. Effect of solution pH on Cr(VI) adsorption onto 20H-AC (initial Cr(VI) concentration: 100 and 400 mg/L; initial pH of solution: 2.0–10.0; adsorbent dosage: 5 g/L; reaction time: 24 h; agitation speed: 100 rpm; temperature: 25°C).

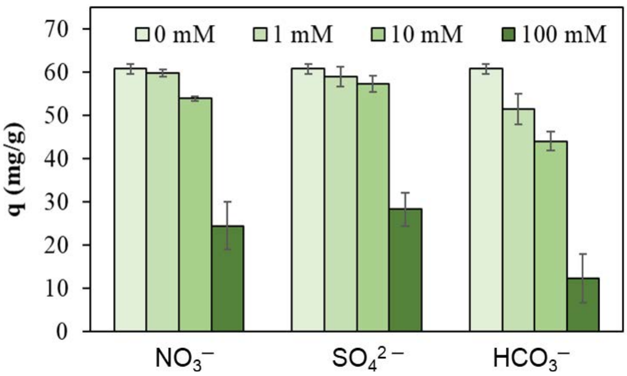

Fig. 7. Effect of competing anions on Cr(VI) adsorption in 20H-AC (initial Cr(VI) concentration: 400 mg/L; pH: 7.0; adsorbent dosage: 5 g/L; reaction time: 24 h; agitation speed: 100 rpm; temperature: 25°C).

increase in pH due to larger electrostatic repulsion at higher pH. The presence of competing anions, such as NO_3^-, SO_4^{2-}, and HCO_3^- interfered with the uptake of Cr(VI) by 20H-AC. Thus, this study demonstrates that HCl-modified granular AC is an efficient adsorbent for the removal of Cr(VI) in water.

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