Removal of copper ions from wastewater by adsorption/electrosorption on modified activated carbon cloths

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ABSTRACT

Adsorption and electrosorption of copper ions (Cu^{2+}) from wastewater were investigated with variously modified activated carbon fiber (ACF) cloth electrodes. Commercial polyacrylonitrile-based ACF cloths were modified by nitric acid or impregnated with chitosan solution. The surface characteristics of ACFs before and after modification were evaluated by nitrogen adsorption–desorption isotherms, zeta potential, Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and cyclic voltammetry. Adsorption and electrosorption capacities of Cu^{2+} on ACF cloths without and with a bias potential were measured, respectively, and the electrosorption isotherms were also investigated. The initial pH of the copper ion solution was adjusted to 4.0. Experimental results showed that electrosorption effectively increases adsorption capacity. The adsorption/electrosorption isotherms of Cu^{2+} on ACF cloths were in good agreement with Langmuir and Freundlich equations. The equilibrium adsorption capacity at 0.3 V was 0.389 mmol/g, which is two times higher than that at open circuit. The maximum electrosorption capacity of Cu^{2+} on chitosan impregnated ACF cloths was 0.854 mmol/g, which is about 2.2 times higher than that on the pristine cloths.

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1. Introduction

Copper ion (Cu^{2+}) is a common hazardous pollutant in wastewater and is often released by metallurgical, plating, printing circuits, fertilizer and refining industries. Prolonged oral administration of excess quantity of Cu^{2+} may result in liver damage and acute poisoning to the human body. The tolerance limit for Cu^{2+} for discharge into inland surface waters is 3.0 mg/L and in drinking water is 0.05 mg/L [1]. Higher Cu^{2+} concentrations in wastewater can be easily decreased by various methods including electrochemical operations, reverse osmosis, or chemical treatment processes [2]. However, the application of methods mentioned above becomes costly at lower concentrations of Cu^{2+}. Adsorption by porous adsorbent such as zeolite [3] or activated carbon [4–6] is one of the alternatives. It is well known that the surface area and pore size distribution of adsorbents play an important role during the adsorption processes. In addition to the nature of the pore structure, the capacity and rate of adsorption on porous adsorbents depend on the surface functional groups [5].

Electrosorption is generally defined as potential polarization-induced adsorption on the surface of electrodes, and is a non-Faraday process [7]. After the polarization of the electrodes, the polar molecules or ions can be removed from the electrolyte solution by the imposed electric field and adsorbed onto the surface of the electrode. Because of its low energy consumption and environmentally friendly advantage, electrosorption has attracted a wide interest in the adsorption processes for treatment of wastewater [7–10] and the purification of supplied water [11]. Although electrosorption has been shown as a promising treatment process, it has been limited by the performance of electrode material. Activated carbon fiber cloth with high specific surface area and high conductivity is one of the commonly used electrode materials. The surface chemistry of activated carbon fiber has been recognized as a key parameter in the control of the adsorption process. To increase the adsorption capacity, a number of modification methods have been employed [12–15]. In this study, polyacrylonitrile-based ACF cloths were modified by nitric acid or impregnated with chitosan solution. The physicochemical properties of ACF cloths, such as BET surface area, pore size distribution, the surface zeta potential and surface functional groups, were analyzed to better understand the mechanism of adsorption/electrosorption. The objective of this study is to investigate the effect of surface modification on the adsorption/electrosorption capacity of Cu^{2+} on ACF cloths.

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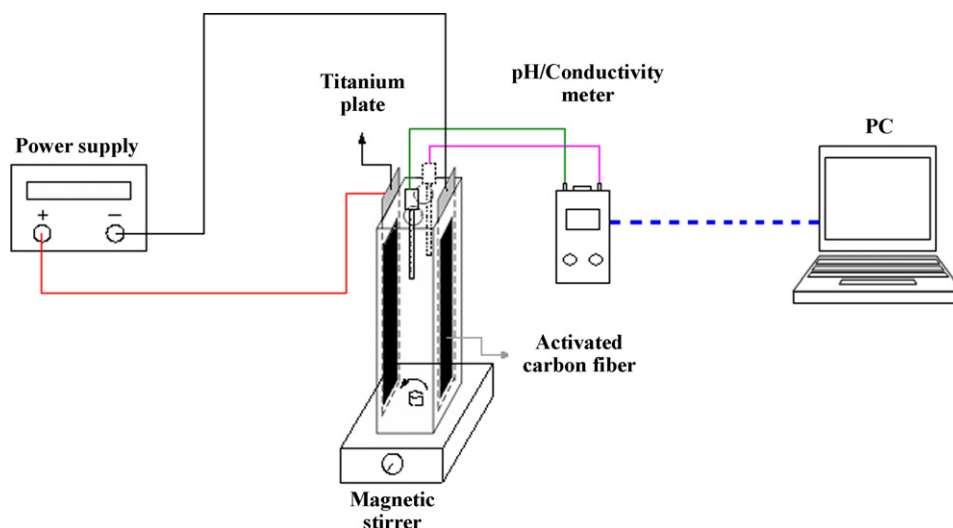
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Fig. 1. Schematic diagram of static state adsorption/electrosorption apparatus.

2. Materials and experiments

2.1. Pretreatment of ACF cloths

Polyacrylonitrile (PAN)-based ACF cloths (AW, obtained from Taiwan Carbon Technology Co., Ltd.) were used in this study. Prior to the experiments the ACF cloths were first heated in boiling deionized (DI) water. Then washed by DI water several times and dried at 105 °C for 24 h and kept in a desiccator for further use.

2.2. Modification of ACF cloths

Chitosan solution was prepared by dissolving 3 wt.% of chitosan powder in acetic acid. The pretreated ACF cloths were submersed in chitosan solution for 24 h. After filtration the ACF cloths were immersed in 1N NaOH solution for 24 h. Then, they were washed by large amounts of DI water and dried at 105 °C for 24 h. The modified ACF cloths are denoted as AW-CH.

The pretreated AW ACF cloths were also modified by immersing in 3N nitric acid solution at 50 °C for 24 h. Washed with DI water and dried at 105 °C for 24 h. The modified ACF cloths are denoted as AW-NA.

2.3. Characterization of ACF cloths

The BET specific surface area and pore size distribution of ACF cloths before and after modification were determined by an automated gas sorption system (Quantachrome Autosorb-1), using N_2 as adsorbate at 77 K. The pore size was calculated using the BJH model in the range 1.4–200 nm and the DFT model in the range 0.3–10 nm. The Fourier transform infrared spectroscopy (FTIR, Perkin-Elmer Instruments Spectrum One) analysis was performed after grinding the carbon samples and mixing them with KBr powder to prepare sample-KBr pellets. Surface zeta potentials of ACF cloths were determined by a Brookhaven Instruments Corp. 90plus Particle Size Analyzer. Three solutions of 50 mg/L of ground ACF cloths were prepared in bottles with CO_2-free DI water with 1 mmol/L KCl. The pH of the solution was adjusted between 2 and 12 by adding HCl and NaOH.

X-ray photoelectron spectrum (XPS) experiments were performed on a Kratos Axis Ultra DLD photoelectron spectrometer. There is a 180° hemispherical sector electron energy analyzer with a 165 mm mean radius with MCP stack and delay-line detector. The equipment was operated with an achromatic Mg/Al X-ray source at 450 W. The binding energy scale was calibrated to 284.6 eV for the main C 1s peak. The full width at half maximum of each deconvoluted C 1s spectrum was 0.68 eV. Prior to XPS measurements all ACF samples were dried in a vacuum oven at 100 °C for 6 h. The vacuum in the analysis chamber was always better than 5×10^{-10} Pa. The high-resolution scans were performed over the 280–294, 395–407, 527–540 ranges for C 1s, N 1s and O 1s spectra, respectively. Curve fitting was performed using a non-linear least-squares algorithm and assumed a mixed Gaussian/Lorentzian peak shape of variable proportion.

Cyclic voltammetric (CV) measurements were performed using an electrochemical analyzer (CH Instruments CHI608B, USA). The three-electrode cell consisted of Ag/AgCl as the reference electrode, Pt as the counter electrode and the prepared ACF cloth electrode as the working electrode. All CV measurements were undertaken with a 100 ppm copper nitrate solution. The electrolytes were degassed with purified nitrogen gas before CV measurements and nitrogen was passed over the solution during all the measurements. The solution temperature was maintained at 25 °C by means of circulating water thermostat (HAAKE DC3 and K20, Germany). The sweep rates were set at 50, 100 and 200 mV/s.

2.4. Adsorption/electrosorption capacity measurements

A conventional three-dimensional electrode system was adopted in the adsorption/electrosorption investigation in both open circuit and electrochemical polarization experiments. A schematic diagram of the static state adsorption/electrosorption system is shown in Fig. 1. Experimental apparatus included an electrosorption tank, a pH meter, a conductivity meter, and a DC power supply. The working electrode was a piece of ACF cloth connected by a titanium plate. The initial concentration of the Cu^{2+} ions in the solution ranged from 40 to 200 mg/L. The initial pH of the solution was adjusted to 4.0 by adding either 0.1 M nitric acid or 0.1 M sodium hydroxide solution. The concentrations of copper ions were determined by an atomic absorption spectrometry (Hitachi Z-6100). The quantity of ions adsorbed per unit mass of used ACF cloth was calculated from the equation

$$q = \frac{(C_0 - C)V}{m} \tag{1}$$

where C_0 and C are the concentrations at the beginning and at any time, respectively, V is the volume of the solution, and m is the mass of the ACF cloth module.
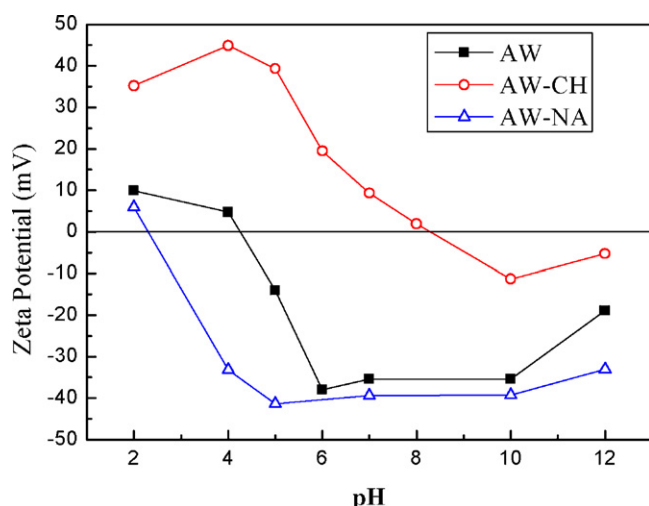
Fig. 2. Zeta potential of original and modified ACF cloths as a function of pH.

Fig. 3. FTIR spectra of various ACF cloths. (a) AW, (b) AW-CH and (c) AW-NA.

3. Results and discussion

3.1. Characterization of ACF cloths

The chitosan content of coated ACF cloths (AW-CH) was determined using a thermogravimetric analyzer (TA Instruments, TGA2050). The sample was heated up to 900 °C at a rate of 10 °C/min under nitrogen flow (40 mL/min). The chitosan started to decompose at 200 °C and burnt out completely at 550 °C. It was found that about 3.0 wt.% of chitosan was coated on the ACF cloths.

Fig. 2 shows the surface zeta potential of the original and modified ACF cloths as a function of solution pH. The point of zero charge (PZC) is defined as the pH value at which surface charge is zero at a particular aqueous solution composition. From Fig. 2, the PZCs of the original AW, modified AW-CH and AW-NA ACF cloths are at pH 4.3, 8.2 and 2.2, respectively. Rangel-Mendez and Streat [16] reported the PZC points of KoTHmex TC-66C (PAN-based) ACF and one oxidized by nitric acid are at pH 4.2 and 2.4, respectively. Jha et al. [17] also reported a PZC value of 8.5 for chitosan flake. Because the amine group ($-NH_2$) becomes $-NH_3^+$ in acid solution, the surface of the AW-CH ACF cloth impregnated by chitosan solution is positively charged and the PZC is higher than that of the original cloth. The PZC value of AW-NA is shifted to a lower pH value after the surface of the ACF cloth was oxidized by nitric acid. Some acidic surface oxides such as acidic groups such as carboxylic, phenolic, carbonyl, and lactonic enhanced after oxidation. The surface of ACF cloths is positively charged at the solution pH values below the PZC. On the other hand, as solution pH values are greater than the PZC, the carbon surface becomes more negative due to dissociation of weakly acidic oxygen-containing groups. Thus, the adsorbent surface is able to attract and exchange cations in solution.

Fig. 3 shows the FTIR spectra of various ACF cloths. The FTIR spectra of all ACFs displayed the following bands: 1077, 1172, 1630–1780, and 3200–3400 cm^{-1} for $=$C–OH (bending), –C–N
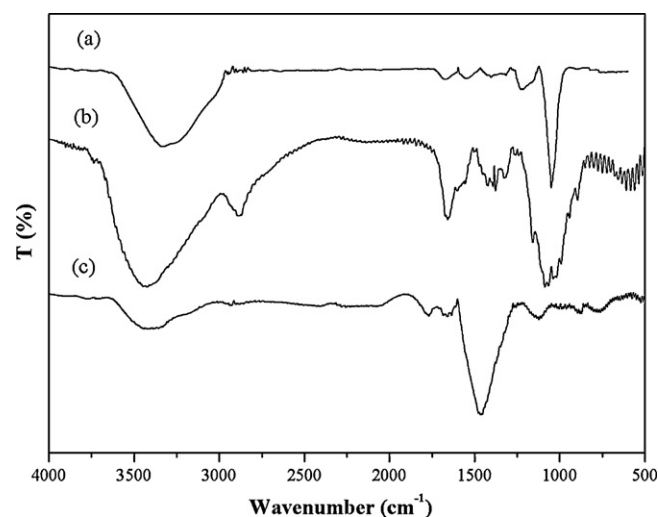
(stretching), C$=$O (stretching), and free O–H stretches, respectively [18]. As shown in Fig. 3, the IR spectrum of AW-CH after impregnation by chitosan shows peaks assigned to the saccharide structure at 1152, 1082, 1028, and 897 cm^{-1}, and a strong amino characteristic peak at around 3420, 1655 and 1325 cm^{-1} are assigned to amide I and III bands, respectively [19]. The FTIR spectrum of the ACF after nitric acid oxidation (AW-NA) displayed additional peaks around 1712 cm^{-1} (C$=$O, stretching vibration) [20] and around 1383 cm^{-1} (NO_3^-) [21].

Table 1 lists physical characteristics of ACF cloths. The BET surface areas were determined to be 1294, 1123, and 1209 m^2/g for AW, AW-CH and AW-NA, respectively. After being impregnated with chitosan the ACF cloth surface area slightly diminished. It is interesting to note that for AW cloth 74.0% of total pore volume is attributed to micropores, however, the micropore pore volume of modified cloth slightly decreased. Fig. 4 shows the micropores size distribution of ACF cloths. It is found that most of the pores of ACF cloths are smaller than 2 nm. The micropore volumes of AW-CH and AW-NA ACF cloths were slightly reduced after modification. From Table 1, there is no significant change in surface morphology for AW-CH and AW-NA cloths, though a few surface areas are lost due to blockage of the pores by chitosan or erosion by nitric acid oxidation.

XPS analysis was used for evaluations of the changes in the chemical bonding states and concentrations of surface functional groups formed by chemical surface modification. Fig. 5 shows the C 1s, O 1s, and N 1s core-level spectra of AW, AW-CH, and AW-NA ACF cloths. It may be noted that the C 1s and N 1s spectra of AW-CH have significant differences in binding energy compared to those of AW. The main functional groups of chitosan (amine and hydroxyl) appear at the XPS spectra of AW-CH. In other words, chitosan was definitely coated on ACF cloth after impregnation with chitosan solution. All C 1s and O 1s spectra of AW-NA are similar to those of AW. There is a peak at 405.5 eV observed on the N 1s

Table 1
Physical characteristics of activated carbon cloths.

Activated carbon cloth	Specific surface area (m^2/g)	V_T[a] (cm^3/g)	V_{micro}[b] (cm^3/g)	V_{meso}[c] (cm^3/g)
AW	1294.3	0.742	0.55	0.192
AW-CH	1123.3	0.655	0.47	0.185
AW-NA	1209.3	0.694	0.50	0.195

[a] Total pore volume was determined from N$_2$ isotherm at $P/P_0 = 0.995$.
[b] Micropore volume was calculated by Dubinin–Radushkevithch (D–R) equation.
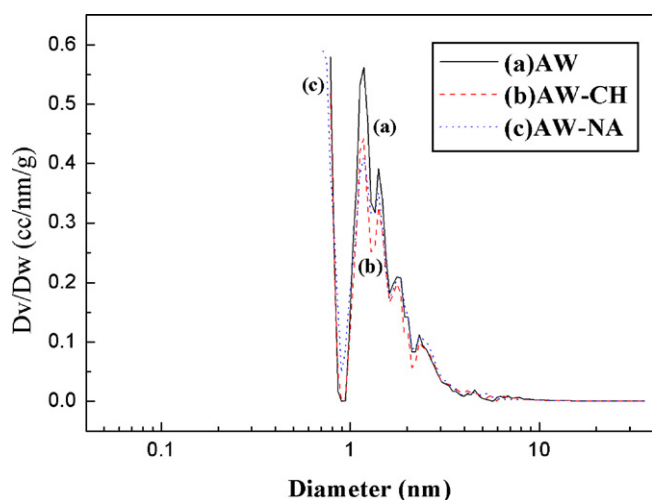[c] $V_{meso} = V_T - V_{micro}$.

Fig. 4. Micropore size distribution of ACF cloths.

spectrum of AW-NA, indicating that nitrate appears after nitric acid modification.

The high-resolution scans of C 1s, N 1s and O 1s spectra were deconvoluted by curve fitting using a non-linear least-squares algorithm. The C 1s spectra were deconvoluted into four components with chemical shifts corresponding to graphite (284.6 eV), hydroxyl (286.3 eV), carbonyl (287.4 eV), and carboxyl (288.9 eV) groups [11]. The O 1s spectra were fitted by five component peaks corresponding to C=O at 530.6 eV, carbonyl oxygen atoms in esters, amides, anhydrides and oxygen atoms in hydroxyls or ethers at 532.3 eV, the ether oxygen atoms in esters and anhydrides at 533.5 eV, the oxygen atoms in carboxyl groups at 534.3 eV, and adsorbed water molecules at 536.3 eV [22]. The N 1s spectra were deconvoluted into five component peaks corresponding to N-6 pyridine (398.9 eV), amine (399.4 eV) [23], N-5 pyrrole (400.4 eV), N-Q (401.5 eV), and nitrogen oxides (405.5 eV) [15]. The surface elemental compositions as well as the relative content of different functional groups from C 1s, O 1s, and N 1s XPS spectra deconvolution are listed in Table 2. After impregnation with chitosan, the total oxygen and nitrogen surface concentrations increase from 10.33%
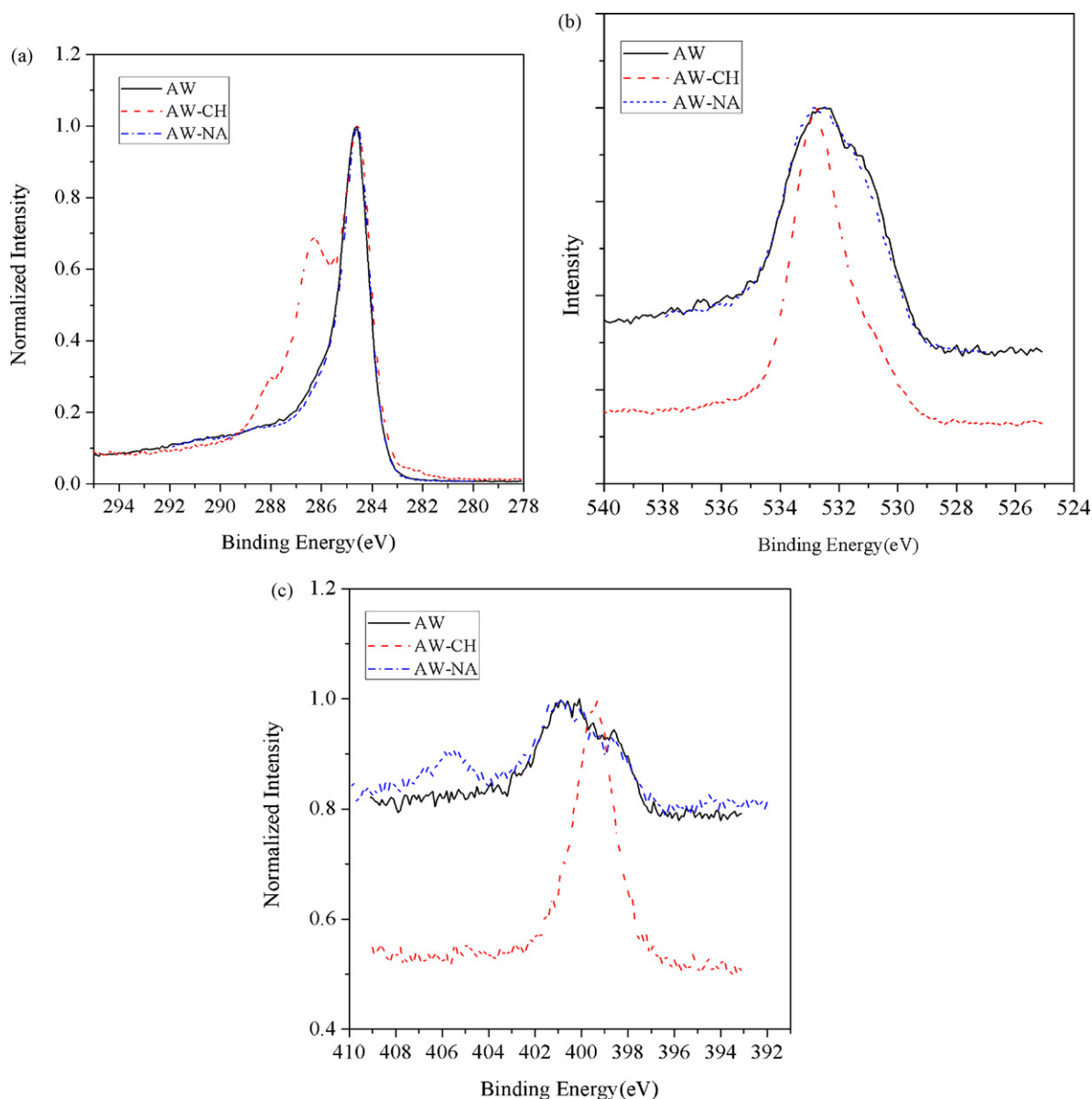

Fig. 5. XPS spectra of (a) C 1s, (b) O 1s, and (c) N 1s for pristine and modified ACF cloths.

Table 2
Relative content of surface groups determined by C 1s, O 1s, and N 1s spectra from XPS for ACF cloths.

ACF (atomic conc.%)	Surface concentration from C 1s peak of (at.%)			
	Graphite (284.6 eV)	Hydroxyl (286.3 eV)	Carbonyl (287.4 eV)	Carboxyl (288.9 eV)
AW (87.15)	69.74	18.72	6.07	5.47
AW-CH (75.06)	52.55	32.32	9.99	5.14
AW-NA (89.47)	77.62	13.02	2.3	7.06
	Surface concentration from O 1s peak of (at.%)				
	C=O (530.6 eV)	C–O (532.3 eV)	C–O–C (533.5 eV)	C=N–O (534.4 eV)	Adsorbed water (536.3 eV)
AW (10.33)	34.58	41.97	16.04	5.18	2.23
AW-CH (19.91)	18.61	49.08	27.59	3.69	1.03
AW-NA (7.98)	31.94	41.15	19.81	6.08	1.02
	Surface concentration from N 1s peak of (at.%)				
	N-6 pyridine (398.9 eV)	Amine (399.4 eV)	N-5 pyrrole (400.4 eV)	N–Q (401.5 eV)	–NOx (405.5 eV)
AW (2.52)	26.45	2.92	36.52	26.2	7.91
AW-CH (5.03)	9.43	73.43	13.46	3.15	0.53
AW-NA (2.55)	19.31	2.27	28.25	27.27	22.9

and 2.52% to 19.91% and 5.03%, respectively. The deconvolution of C 1s spectrum in Table 2 indicates that hydroxyl and carbonyl functional groups on pure carbon surface sites are increased after being impregnated by chitosan. The peak at 532.3 eV from deconvolution of O 1s spectrum implies that amide and hydroxyl functional groups are increased for AW-CH. The increase of the binding energies (399.4 ev) provides evidence that noteworthy amine groups exist on AW-CH cloth surface after being impregnated with chitosan. The presence of surface amines, amides and hydroxyl groups can be confirmed by the FTIR spectra. As can be seen in Table 2, however, hydroxyl and carbonyl functional groups did not change significantly after nitric acid treatment at room temperature. Oh et al. [11] reported the surface carboxyl functional groups on pure carbon surface sites were increased by surface modification in nitric acid solution at 90–100 °C. From Table 2, the peak at 405.5 eV from deconvolution of N 1s spectrum reveals that nitrogen oxides are remarkably increased for AW-NA.

In order to ensure that the copper was not oxidized or reduced during the electrosorption process, the electrosorptive bias potential must be controlled. The cyclic voltammetries of copper solution were measured by electrochemical workstation at various sweep rates, and the results are shown in Fig. 6. Steady increases and decreases observed in current with electric potential in copper nitrate soluti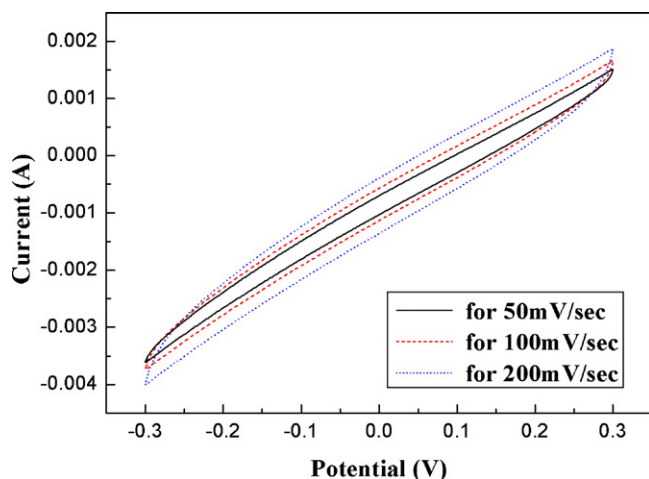on indicate that no oxidation or reduction occurs in the range between −0.3 and 0.3 V. Therefore, the electrosorption was carried out in this potential range to prevent the copper from being reduced or oxidized.

3.2. Adsorption/electrosorption isotherms

The adsorption and electrosorption isotherms of $CuNO_3$ on different ACF cloths were determined at open circuit and 0.3 V bias potential, respectively. The initial pH value of Cu^{2+} solution was set at pH 4. The removal of Cu^{2+} increases with time and attains equilibrium at 12 h for the initial Cu^{2+} concentration of 100 mg/L. Fig. 7 illustrates adsorption isotherms of Cu^{2+} on ACFs at open circuit. It is found that the maximum amounts of Cu^{2+} adsorbed on AW, AW-CH, and AW-NA cloths after 12 h are 0.210, 0.380, and 0.289 mmol/g, respectively. Afkhami et al. [13] reported that the maximum adsorption of copper ion on Spectracarb 2225 C-cloth is 0.127 mmol/g. Kadirvelu et al. [5] reported 0.174 mmol/g adsorption capacity on a rayon-based ACF cloth (CS 1501). Experimental results reveal that AW-CH cloth possesses the highest copper ion adsorption capacity at open circuit. The reason can be attributed to copper ion chelating with the lone pair of electrons on the amine group of chitosan. The mechanism of sorption on AW-CH cloth is possibly an ion exchange of the Cu^{2+} ions with hydrogen ions pro-

Fig. 6. Cyclic voltammograms for AW ACF cloth in 100 ppm $CuNO_3$ at various sweep rates.
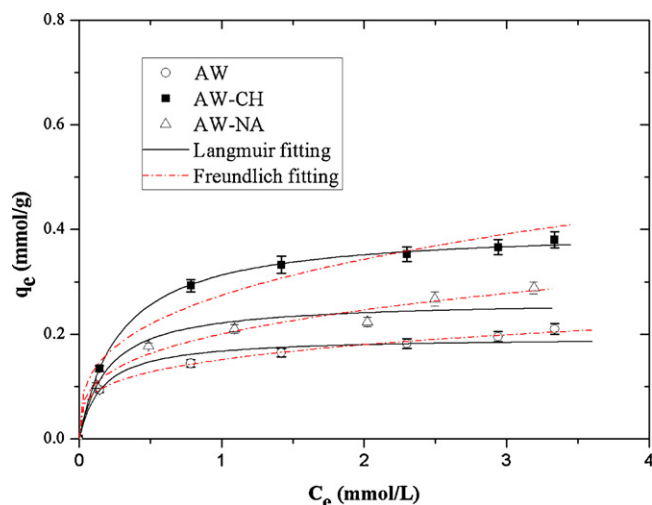

Fig. 7. Adsorption isotherm data of copper ions on ACF cloths with Langmuir and Freundlich models correlated at open circuit.

Table 3
Parameters of Langmuir and Freundlich equations for Cu^{2+} adsorption/electrosorption on ACF cloths at pH 4.

ACF	q_m (mmol/g)	Freundlich			Langmuir		
		K (mmol$^{1-1/n}$ L$^{1/n}$/g)	$1/n$	R^2	q_e (mmol/g)	b (L/mmol)	R^2
0 V							
AW	0.210	0.152	0.246	0.996	0.186	6.411	0.950
AW-CH	0.380	0.274	0.323	0.946	0.371	3.518	0.999
AW-NA	0.289	0.201	0.297	0.970	0.251	5.193	0.972
0.3 V							
AW	0.389	0.267	0.282	0.955	0.386	5.630	0.834
AW-CH	0.854	0.794	0.351	0.833	0.969	3.594	0.906
AW-NA	0.516	0.358	0.319	0.938	0.482	3.072	0.989

tonating the amine end groups. It was well known that carboxyl and hydroxyl functional groups promote adsorption of inorganic ion in solution by ion-exchange reaction as hydrophilic compounds. According to FTIR and XPS analyses, amine and hydroxyl functional groups exist on the surface of AW-CH cloths. For AW-NA cloth, as aforementioned the adsorbent surface is negatively charged at pH values higher than the PZC due to the dissociation of weakly acid oxygen-containing groups. Therefore, positively charged copper ions will ion exchange with oxygenated surface functional groups at pH 4. Since the solution pH value is greater than the PZC (2.2), the AW-NA cloth surface becomes more negative due to dissociation of weakly acidic oxygen-containing groups. This renders the AW-NA carbon cloth capable of adsorbing trace copper ions from an aqueous solution at pH value about 4.

The isotherm data were correlated by Langmuir and Freundlich models. The general form of Langmuir isotherm is

$$q = \frac{q_e b C_e}{1 + b C_e} \tag{2}$$

where q represents the amount adsorbed at equilibrium, C_e is the equilibrium concentration of copper solution; q_e is the maximum amount of solute adsorbed, b is a constant.

The Freundlich empirical model is represented by

$$q = k C_e^{1/n} \tag{3}$$

where C_e is the equilibrium concentration, k and $1/n$ are Freundlich constants depending on the temperature and the given adsorbent–adsorbate couple.

The parameters of Langmuir and Freundlich models for Cu^{2+} adsorption/electrosorption on ACF cloths at different bias potentials and pH 4 are listed in Table 3. From Langmuir model regression results, the maximum amounts of copper ion adsorbed (q_e) at open circuit are 0.186, 0.371, and 0.251 mmol/g on AW, AW-CH, and AW-NA cloths, respectively. The regressed values are closed to experimental maximum adsorption capacities.

Fig. 8 shows electrosorption isotherms of Cu^{2+} on original and modified ACF cloths as well as both Langmuir and Freundlich model regressions at 0.3 V bias potential. It is found that the electrosorption isotherms obey both Langmuir and Freundlich models. As 0.3 V potential loaded, the maximum adsorption capacities are 0.389, 0.854, and 0.516 mmol/g on AW, AW-CH, and AW-NA cloths, respectively. The comparison of the adsorption capacity of AW-CH ACF cloths at open circuit and at 0.3 V bias potential is shown in Fig. 9. After the polarization of electrodes, the copper ions move around the electrode by the imposed electric field and are adsorbed onto the surface of electrode. The results show that the adsorption capacity of copper ions onto ACF cloths can be effectively enhanced by polarization potential. The maximum adsorption capacity at 0.3 V bias potential is two times higher than that at open circuit.
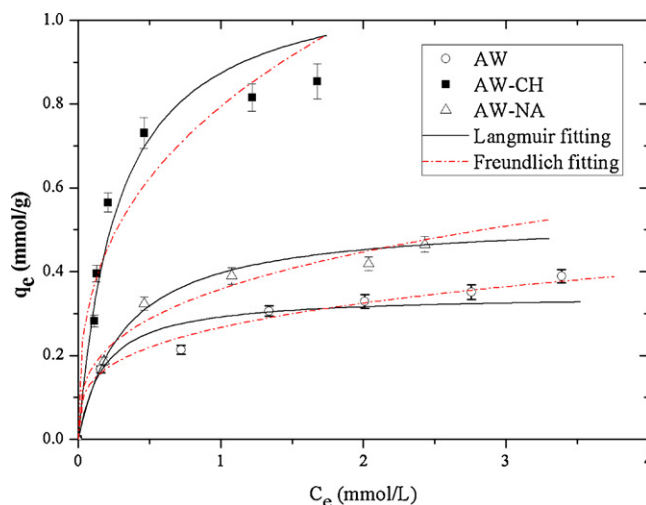

Fig. 8. Adsorption isotherm data of copper ions on ACF cloths with Langmuir and Freundlich models correlated at 0.3 V bias potential.
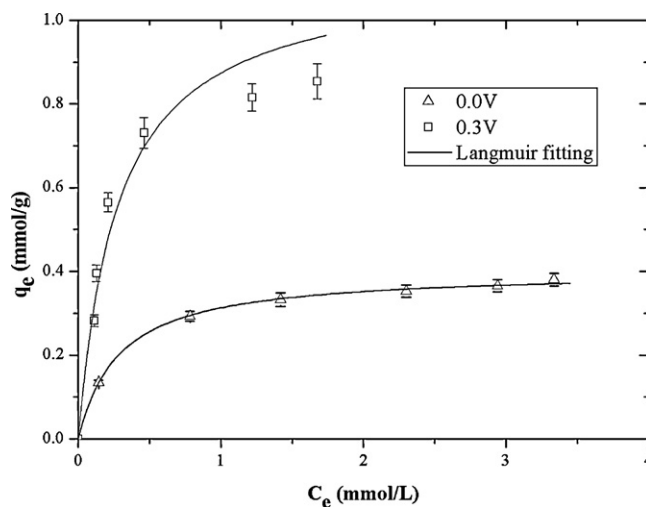

Fig. 9. Comparison of adsorption isotherms of copper ions on AW-CH ACF cloths at 0.3 V bias potential and at open circuit.

4. Conclusions

Polyacrylonitrile-based ACF cloth was modified by nitric acid and impregnated by chitosan. Pristine and modified ACF cloths were used to remove Cu^{2+} from aqueous solution. Adsorption and electrosorption capacities of copper ions on modified ACF cloths were measured under open circuit and at 0.3 V bias potential, respectively. According to FTIR and XPS analyses, a few chitosan had been impregnated on the AW-CH and the AW-NA cloth sur-

faces were slightly chemically modified by nitric acid. Experimental results show that electrosorption capacity significantly higher than adsorption capacity. At 0.3 V potential loading, the equilibrium adsorption capacity is about twofold large at open circuit. The adsorption/electrosorption capacity of Cu^{2+} on ACF cloths follows the sequence AW-CH > AW-NA > AW. The electrosorption capacity of Cu^{2+} on AW-CH ACF cloth, which only 3.0 wt.% chitosan impregnation, is about two times higher than that on the pristine one. Experimental isotherm data for adsorption/electrosorption of Cu^{2+} on pristine and modified ACF cloths can be well simulated by both Langmuir and Freundlich models.

Acknowledgments

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