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Reversible Electrosorption of Thiocyanate Anions by Active Carbon Felt

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Abstract: Adsorption of thiocyanate anions (SCN^-) induced by electrochemical polarization on active carbon felt (ACF) electrode was measured in a three-electrode cell by UV spectroscopy for the application of the electrosorption technique in the removal of SCN^- in water. Positive polarization of the ACF electrode causes a dramatic increase in the adsorption of SCN^- and negative polarization causes desorption of most of SCN^- from the ACF electrode. The reversibility of electrosorption is remarkably affected by current intensity, solution pH, and the co-existed ions. The fully reversible electrodesorption of SCN^- occurs in basic solution with pH 9.68. Electrochemical oxidation of partial SCN^- decreases this reversibility under stronger polarization. The stronger adsorption of SCN^- on open circuit in acid solution and the competition of SO_4^{2-} with SCN^- also results in the decreased reversibility of electrosorption.

Keywords: Active carbon felt (ACF), electrical double layer (EDL), eletrosorption, regeneration, thiocyanate anions (SCN^-)

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INTRODUCTION

The adsorption technique of porous active carbon material with high specific area is widely used for environment protection and remediation. However, the regeneration of the adsorbent usually requires high temperature or strong basic solvent, which consumes much energy, causes secondary pollution, and strongly influences the economical performance of adsorption process. A novel reversible electrosorption technique has shown advantages of solving these problems in a more environmentally friendly way with less energy cost, a smaller amount of secondary waste, and more convenient operation conditions (1). Electrosorption is generally defined as potential-induced adsorption by applying galvanostatic or potentiostatic polarization on the electrode. When the electrode is polarized, charges on the electrode are compensated by the ions with countercharges. So, ions in solution are assembled in the electric double layer (EDL) formed between the electrode and the electrolyte. After the electrodes become saturated with salt or impurities, the electrodes are regenerated by electrical discharge, allowing the captured ions to be released into a relatively small volume solution again for concentration. Due to this reversibility, electrosorption can not only increase the adsorption ability of the adsorbent, especially in the dilute solution, but also change the adsorption tendency by controlling the direction of electric polarization to reach an adsorption-desorption cycle. And it provides the attractive approach to regenerate the adsorbent in situ and reduces or avoids using a large amount of acid or bases, thereby substantially reducing the secondary pollution. The reversible electrosorption, therefore, plays a promising role in its practical industry application, such as water deeper purification, solvent recycle, and the enrichment of valuable substance. Removal of heavy metals and other inorganic ions by electrosorption has already been tried to purify various contaminated water and to desalinate water (2–6).

Thiocyanate is one kind of noxious ion that might be present in some industrial waste water and needs to be removed. It is also known to be among the anions most strongly adsorbed at Hg owing to its strong electron pair donator. Recently, the electrosorption technique of high-area carbon cloth materials has been found to be effective for the removal of thiocyanate from waste water, and the adsorptive effectiveness was related to the hydration properties in water (7,8).

In this paper, we chose activated carbon felt (ACF) as the electrosorption electrode because of its large adsorption capacity, convenient operational conditions, and better electric conductivity than granular active carbon. Our work focused on the effects of solution pH, current intensity, and coexisted anions on SCN$^-$ electrosorption reversibility on active carbon felt electrode.

EXPERIMENTAL

Materials

Carbon felt made by active carbon fiber used in the present work was kindly provided by LiaoYuan Chemical Engineering Corp. KSCN, NaOH, KOH, H_2SO_4, HNO_3, and KNO_3 were the reagent grade chemicals. Deionized water was used in adsorption and electrosorption experiments.

Pretreatment of Carbon Felt

Before use, the carbon felt underwent a deionization clean procedure to avoid the release of the undesired ions from the carbon felt due to its surface functional groups or any ions adventitiously introduced in the preparation of the carbon felt into the solution during the adsorption measurement. In this procedure, a carbon felt sample cut in an accurately desired dimension and weight was placed in the conical flask and washed repeatedly with boiled deionized water, until the conductance of outcoming water from each batch reached a stable value. The cleaned carbon felt modules were kept in deionized water to avoid the air bubbles trapped in the pores before the adsorption experiment.

Surface Area and Porosity

The BET surface area of active carbon felts was determined by nitrogen (99.99% purity) adsorption/desorption at 77 K using a Micomeritics ASAP 2010 surface analyzer. The adsorbents were degassed at 423.15 K under vacuum. Porosity distribution was deduced from the experimental data using the BJH method.

Scanning Electron Micrography (SEM)

The surface morphology and the structure of ACF was visualized at accelerating voltage of 12.5 kV by a Philips Instrument FEI Quanta 200 F scanning electron microscope.

pH_{PZC} and Surface Charge Distribution of ACF

Batch equilibrium method for determination of pH of the point of zero charge (PZC) was described by Babić et al. (9). Accordingly, the samples of ACF (0.2 g) were shaken in PVC vials, for 24 h, in 40 ml of 0.01 or 0.1 mol L^{-1} KNO_3, at different pH values. Initial pH values were obtained by adding some amount of KOH or HNO_3 solution (0.1 mol L^{-1}), keeping the ionic strength constant. The amount of H^+ or OH^- ions adsorbed by ACF was calculated from the difference between the initial and the final concentration of H^+ or OH^- ions, and determined from the initial and the final pH values (pH_i and pH_f, respectively).

Surface charge densities of ACF, in aqueous solutions of KNO_3, were determined by potentiometric titration. The titration started from pH corresponding to PZC of ACF. Two runs were carried out:

a. in the presence of ACF (0.2 g of ACF in 200 ml of 0.01 or 0.1 mol L^{-1} KNO_3),
b. in the absence of ACF in the same electrolyte (blank). A 0.01 mol L^{-1} solution of HNO_3 or NaOH was used as the titrant in the pH range below or above that of PZC, respectively.

A dose of titrant, 0.05–20 ml, dependent on the solution pH and the electrolyte concentration, was added successively every 10 min. During the titration, solutions were stirred with a magnetic stirrer and purified N_2 was bubbled through the system, preventing any CO_2 or O_2 adsorption from the air. Experiments were carried out at 298 K. The difference in acid or base quantities, used to reach the same pH in solutions with ACF and the blank, was taken to represent the association or dissociation of H^+ ions from ACF surface. Then the surface charge density can be calculated by

$$\sigma_0 = \frac{\Delta V \cdot C \cdot F}{S \cdot M}$$

Where σ_0 (coulomb m^{-2}) is the surface charge density, ΔV is the difference of the titrant volumes used for the solution with ACF and the blank solution, respectively, at given pH values, C is the molar concentration of titrant, F is the Farady constant (96 500 C), S is the specific surface area of ACF (m^2 g^{-1}), and M is the mass of ACF used for titration.

Electrosorption Measurements

The electrosorption isotherms and electrosorption kinetics measurements were carried out in an electrolytic cell. The adsorbent electrode was a piece of carbon felt serving as the working electrode and held in place by a Pt wire; the counter electrode was a Pt plate (10 × 5 mm). A saturated calomel electrode was used as a reference electrode. Working, counter and reference electrodes were connected to a potentiostat/galvanostat. The carbon felt with the accurate weight was attached to the Pt wire and placed in 50 ml different initial concentration KSCN dilute solution in the electrolytic cell. Because of the difficulties of feedback control of the potentiostatic mode for very high area electrodes having large double-layer capacitances (7), a small and constant positive current was applied through the cell by employing the galvanostatic mode to polarize the carbon felt electrode in the polarization experiments. The solution is stirred for 3 h (sometimes overnight or longer) to attain equilibrium under polarization.

The change in the concentration of the thiocyanate solution due to the adsorption of ions on electrodes was monitored using an UV/visible spectrophotometer at 214 nm. In the equilibrium experiment, the adsorption capacity is defined as the quantity of ion adsorbed per unit mass of carbon felt at equilibrium, calculated by

$$q_e = \frac{(C_0 - C_e)V}{M}, \tag{1}$$

where C_0 and C_e are the concentrations at the beginning and the equilibrium adsorption states, respectively, V is the volume of the solution, and M is the mass of the carbon felt module. In kinetic experiments, the amount of adsorption at time t, q_t was calculated by

$$q_t = \frac{(C_0 - C_t)V}{M}, \tag{2}$$

where C_t is the liquid-phase concentration at time t.

The open-circuit adsorption was accomplished by the same experimental setup with the electrochemical polarization turning off.

In reversible electrosorption experiment in situ, after ACF adsorbed SCN^- to reach equilibrium, it was polarized, and the influence of electrosorption can be clearly shown by the increase or decrease of the adsorption capacity of ACF with comparison of the original adsorption capacity of ACF.

RESULTS AND DISCUSSION

Surface Morphology and Porosity

The SEM micrographs of ACF were shown in Fig. 1. The well-shaped ACF has lower electrical resistance than granular active carbon serving for electrosorption material. ACF has a BET surface area of 1367 m^2 g^{-1}. The pore size distribution of ACF was shown in Fig. 2. The ACF

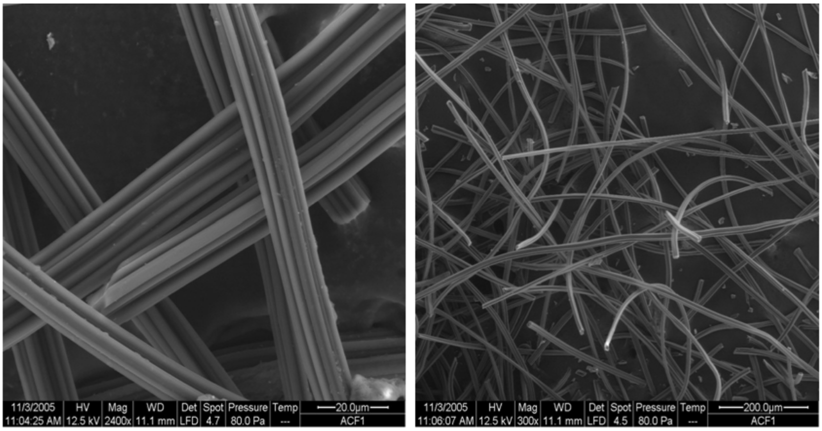

Figure 1. SEM micrographs of ACF at two magnifications.

adsorbent is highly microporous with a BJH desorption average pore diameter of 2.5 nm.

pH$_{PZC}$ and Surface Charge Distribution of ACF

pH$_f$ readings for pH$_{PZC}$ determination were plotted as a function of pH$_i$ in Fig. 3. The pH$_f$ plateau observed corresponds to pH at which there is

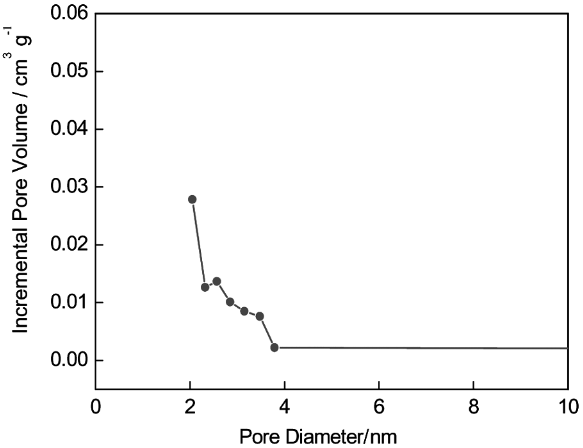

Figure 2. Pore size distribution of ACF.

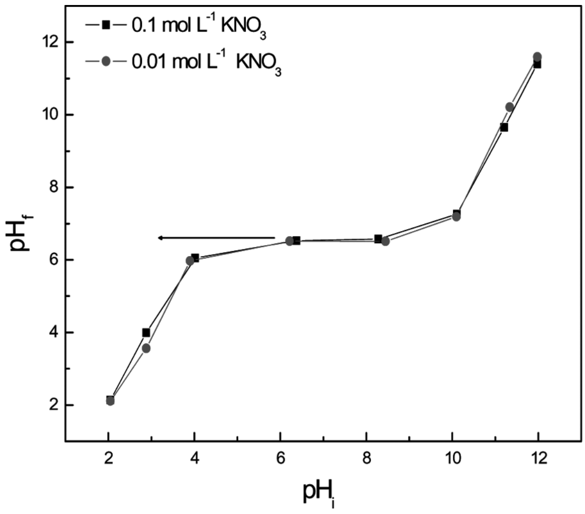

Figure 3. Determination of pH_{PZC} of ACF in KNO_3 solutions (pH_i, initial value; pH_f, final value).

no net H^+ or OH^- adsorption. At this pH, the difference between the initial and the final $[H^+]$ or $[OH^-]$ is zero. This pH was determined to be 6.5 and taken as the pH_{PZC} of ACF.

The carbon surface charge distribution was shown in Fig. 4. It is known that the net charge on carbon surface is positive at a solution pH lower than pH_{PZC} of the surface and is negative at a solution pH higher than pH_{PZC}.

Effect of Polarization Intensity on Reversible Electrosorption of SCN^-

Positive polarization of the ACF electrode by passing a current galvanostatically caused a dramatic increase in adsorption due to the electrostatic attraction between SCN^- anions and the ACF electrode polarized in the positive direction. However, reversal of the polarization by passing a negative current galvanostatically, resulted in desorption of some electroadsorbed SCN^- anions from the carbon interface into solutions, which shows reversibility of electrosorption of SCN^- to some extent. Figure 5 was our work shown in reference (10) to display the dependence of the different current intensities on the reversibility of electrosorption of SCN^- of ACF electrode in near neutral solution pH 6. The extent

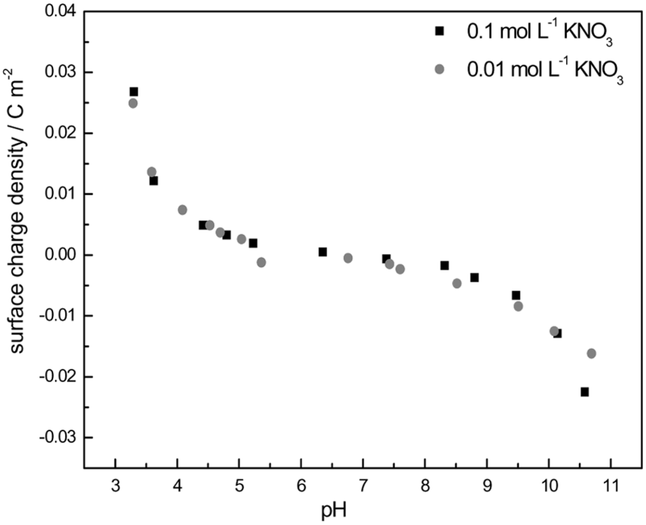

Figure 4. Surface charge densities of ACF at different ionic strengths as a function of pH.

of reversibility of electrosorption weakened with the increased polarization current intensity. The two reasons are discussed more here: one is that a small fraction of the electroadsorbed SCN$^-$ ions remains adsorbed at sites that became accessible upon polarization of the carbon felt (7); the other is that oxidation of part of SCN$^-$ happened at high current intensity or high potential when carbon felt was positively polarized. The irreversible oxidation of thiocyanate on the surface of the small dimensional ACF electrode is observed at potentials higher than 0.77 V vs. S.C.E(SCE) (10). However, this oxidation peak occurs depending on the experimental conditions. It is difficult to observe the oxidation peak on the lager dimensional ACF electrode which is used in adsorption and electrosorption because the charging current of EDL of the porous active carbon felt electrode is large. That is the reason why galvanostastic polarization is applied in this work. It is speculated that more positive polarization, such as +1.2 mA, caused more electroadsorbed SCN$^-$ to be oxidized. Thus, the electrodesorption quantity of the later negative polarization remarkably decreased.

Effect of pH on Reversible Electrosorption of SCN$^-$

It is reported that treatment of activated carbon material with base or acid changed the adsorption capacity for the adsorption of cations and

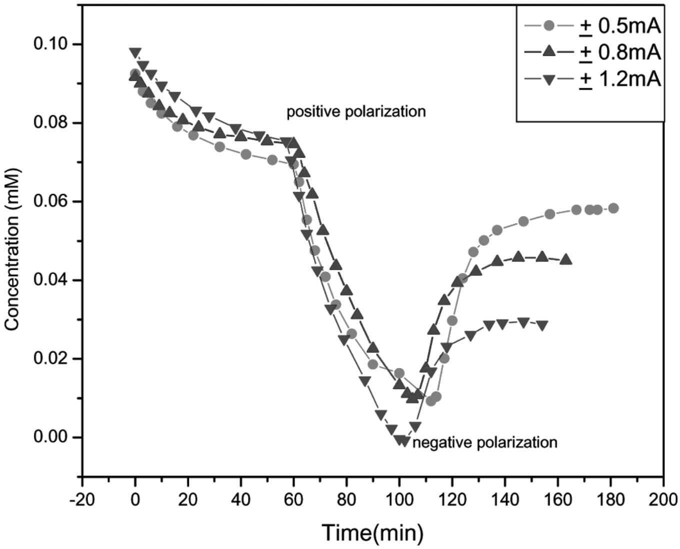

Figure 5. Effect of different current intensities on the electrosorption of SCN^- on active carbon felt at pH 6.

anions (11,12). And that pH changes resulted in an almost reversible desorption of bentazone on activated carbon cloth in electrochemical regeneration is also reported (13). These indicated that solution pH is an important factor in ions removal efficiency by adsorption and electrosorption. However, the underlying mechanism may be correlated not only with the carbon surface area but also with the physicochemical properties of carbon surface and adsorbate, especially when the adsorbate is organic chemicals in electorsorption. The variations of SCN^- electrosorption reversibility in different pH solutions are shown in Fig. 6 (reflected by the change of SCN^- concentration). All the experiments were conducted with the same procedure—the active carbon felt was immersed in 0.2 mmol L^{-1} SCN^- solution for adsorption on open circuit for 60 min, and then it was polarized by +0.1 mA for 60 min, and later it was polarized by −0.1 mA for the same duration. The reversibility of SCN^- electrosorption was strongly influenced by pH. At pH 1.12, the concentration of SCN^- decreased slightly under positive polarization, but this decrease was not attenuated by negative polarization, and the concentration of SCN^- continued to decrease in the later 60 min negative polarization. The electrosorption of SCN^- was totally irreversible. At pH 2.4, the concentration of SCN^- decreased under positive polarization, but was nearly unchanged under the negative

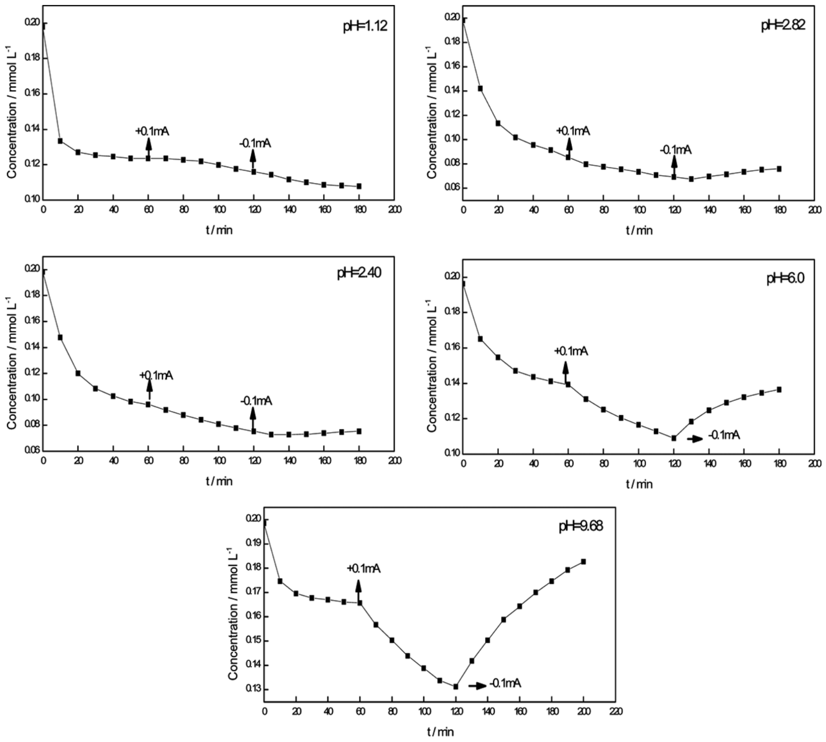

Figure 6. Effect of pH on the electrosorption reversibility of SCN^- on active carbon felt.

polarization. At pH 2.82, negative polarization slightly increased the concentration of SCN^-, which means that part of SCN^- was desorbed by negative polarization. At about pH 6, most electroadsorbed SCN^- was desorbed by negative polarization. At pH 1~6, the adsorption of SCN^- on open circuit is nearly not influenced by electrodesorption under negative polarization, which is shown by the concentration of SCN^- under negative polarization increased to the levels all below the levels corresponding to the open-circuit adsorption.

However, in basic solution, e.g. pH 9.68, the concentration of SCN^- increased under negative polarization and surpassed the amount before the beginning of positive polarization, which implied that some adsorbed SCN^- on open circuit owing to specific adsorption and physisorption caused by Van der Waals forces were also desorbed under negative polarization. It is shown that the reversibility of electrosorption of SCN^- of the ACF electrode in neutral and basic solution is much better than that in acidic solution.

The corresponding potential recorded in pH 1.12 ~ 9.68 varied from 0.6 to 1.4 V vs. S.C.E. in positive polarization, depending on current intensity, solution pH, and the contact resistance of the ACF electrode. If the SCN^- anions are oxidated, it cannot be detected by UV spectrum. So, the increase of concentration of SCN^- detected by UV spectrum in negative polarization still showed the desorption of SCN^-,even though electrooxidation of thiocyanate in positive polarization could not be excluded totally .

The reversibility of electrosorption is affected by several factors including adsorbate concentration, solubility, as well as electrostatic and dispersion interactions between the electrode and the adsorbates. In spite of the complexity of the phenomena, some trends are observed. For example, the reversibility for charged molecules is generally higher than that observed for similar neutral molecules. Furthermore, adsorbates which have stronger adsorption tendencies (or stronger non-electrostatic adsorbate/adsorbent interactions) are more likely to exhibit reduced electrosorption reversibility (3,14).

The inhibition of the reversibility of electrosorption of SCN^- under positive polarization in acidic solution can be attributed to the competition of adsorption on open-circuit with electrosorption. According to the classical electric double layer (EDL) theory, the total amount of anions in EDL under a certain potential is the sum of anions by contact adsorption and electrostatic adsorption (15). It is shown in Fig. 7 that the adsorption of SCN^- on ACF on open-circuit under acidic conditions with pH from 1 to about 3 is much stronger than that in basic conditions with pH from 6 to 10, in a wide pH range. So, the anions by electrostatic adsorption under positive polarization in acidic solution were smaller than that in basic solution.

It is easily understood that the increased adsorption capacity of SCN^- by positive polarization (electrosorption) is smaller, and then the possible decreased adsorption capacity of SCN^- by negative polarization (electrodesorption) is also small as a result of the electrostatic force. The change of adsorption capacity of SCN^- caused by electrosorption and electrodesorption at different pH is shown in Fig. 8. In acidic solution, the increased adsorption capacity of SCN^- by +0.1 mA polarization is small and the decreased adsorption capacity of SCN^- by −0.1 mA polarization is also small. And in basic solution, the increased adsorption capacity of SCN^- by +0.1 mA polarization enhanced, so the decreased adsorption capacity of SCN^- by −0.1 mA polarization enhanced too. Because some adsorbed SCN^- on open circuit are also desorbed by negative polarization, the decreased adsorption capacity of SCN^- by −0.1 mA polarization is bigger than the increased adsorption capacity of SCN^- by +0.1 mA polarization at pH 9.68.

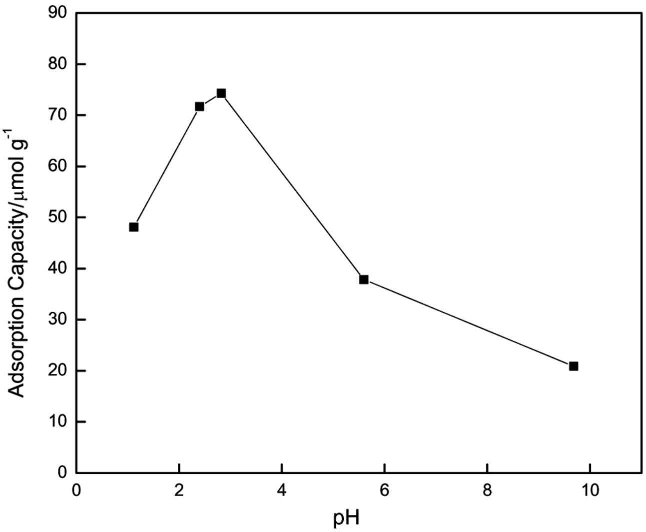

Figure 7. Effect of pH on the adsorption of SCN^- on open circuit on active carbon felt.

As for the reason of strong adsorption tendencies of SCN^- on ACF on open-circuit in acidic solution and weak adsorption tendencies of SCN^- on ACF on open-circuit in basic solution, it is attributed to the change of surface charge of ACF at different pH as shown in Fig. 4. It is well known that the most common functional groups on the active carbon surface are carboxyl, lactonic, carbonyl, and phenolic. At pH lower than pH_{PZC} 6.5 the surface is positively charged because of strongly adsorbed protons on the surface oxygen-containing functional groups of ACF:

$$S_2C = O + H^+ == S_2C = OH^+$$

And at pH values higher than pH_{PZC} 6.5 the surface is negatively charged due to the dissociation of weakly acidic oxygen-containing groups:

$$SCO_2H == SCO_2^- + H^+$$

So, the attraction between SCN^- and the positively charged surface increases, leading to the stronger adsorption of SCN^- on ACF on open-circuit in acidic solution. However, the repulsion between SCN^-

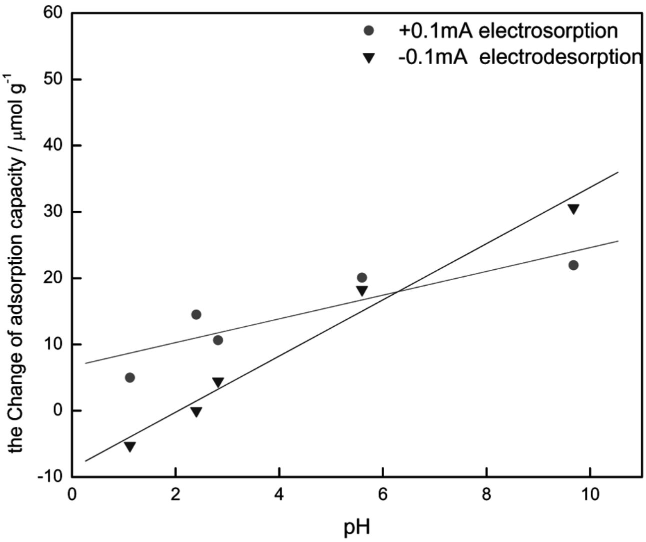

Figure 8. Effect of pH on electrosorption and electrodesorption of SCN^- on active carbon felt.

and the negatively charged surface increases, leading to the less adsorption SCN^- on ACF on open-circuit in basic solution. Furthermore, the negatively charged carbon felt in basic solution might increase the repulsive forces at interface with the adsorbed SCN^- upon negative polarization, because more negative charges exist on ACF. As a consequence, almost all adsorbed SCN^- on open circuit are also desorbed by negative polarization at pH 9.68.

Effect of SO_4^{2-} on Reversible Electrosorption of SCN^-

Another reason for the inhibition of the reversibility of electrosorption of SCN^- under positive polarization in acidic solution is possibly the competition of the SO_4^{2-} and SCN^- in the electrosorption process because H_2SO_4 is used to adjust pH. It is speculated that SO_4^{2-} might take part in the adsorption and electrosorption on ACF by competition with the SCN^-. The dependence of different concentrations of SO_4^{2-} on the reversibility of electrosorption SCN^- is shown in Fig. 9. The electrosorption of SCN^- is attenuated with more SO_4^{2-} anions, showing that the other anions co-existing in solution have a negative effect on the electrosorption of SCN^-.

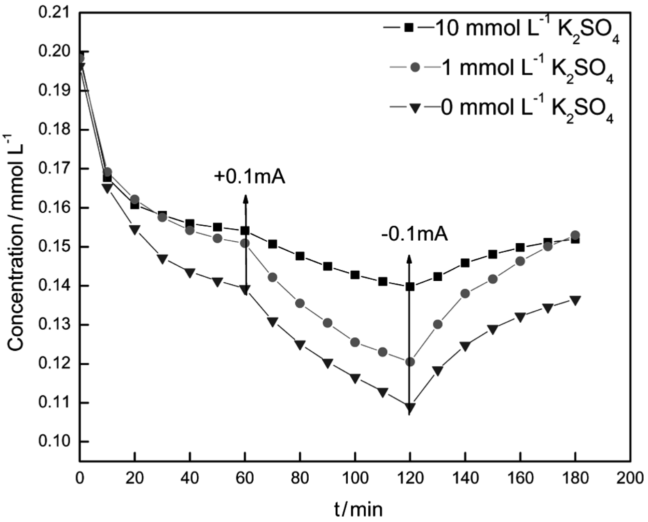

Figure 9. Effect of SO_4^{2-} on the electrosorption of SCN$^-$ on active carbon felt at pH 6.

CONCLUSION

Positive polarization remarkably increases the adsorption of SCN$^-$ on the ACF electrode and negative polarization can realize the desorption of SCN$^-$ on the ACF electrode. This reversible electrosorption of SCN$^-$ on ACF electrode is strongly affected by pH and polarization. In weakly acidic and neutral solution, negative polarization usually desorbs the SCN$^-$ caused by positive polarization easily, but nearly not influences the firmness of SCN$^-$ by the adsorption on the open circuit. And, in the basic solution, the negative polarization of the ACF electrode can accomplish the nearly total desorption of SCN$^-$, including the adsorption of SCN$^-$ on open circuit. This is probably because the intensity of the chemical bond like interaction of SCN$^-$ with ACF in specific adsorption and the Van der Waals force of the adsorption are further lessened with repulsive forces at the interface with the adsorbed SCN$^-$ increasing under negative polarization in basic conditions owing to more negative charges on ACF. So, SCN$^-$ adsorbed on open circuit can be released from the surface of ACF into solution to realize the regeneration of ACF in situ. Electrochemical oxidation of partial SCN$^-$ and competition of SO_4^{2-} with SCN$^-$ also caused the decrease of the reversibility under strong electric polarization. However, the electrosorption process with reversibility to some extent indicates the considerable potential for the ACF as an adsorbent for water purification.

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