

Electrosorption and Separation of Co^{2+} and Sr^{2+} Ions from Decontaminated Liquid Wastes

Jun-Soo Kim, Chong-Hun Jung*[♠], Won-Zin Oh* and Seung-Kon Ryu

Dept. of Chemical Engineering, Chungnam National University, Taejeon 305-764, Korea

*Korea Atomic Energy Research Institute, P.O. Box 105, Taejeon 305-600, Korea

[♠]e-mail: *nchjung@kaeri.re.kr*

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Abstract

A study on the electrosorption of Co^{2+} and Sr^{2+} ions onto a porous activated carbon fiber (ACF) was performed to treat radioactive liquid wastes resulting from chemical or electrochemical decontamination and to regenerate the spent carbon electrode. The result of batch electrosorption experiments showed that applied negative potential increased adsorption kinetics and capacity in comparison with open-circuit potential (OCP) adsorption for Co^{2+} and Sr^{2+} ions. The adsorbed Co^{2+} and Sr^{2+} ions are released from the carbon fiber by applying a positive potential on the electrode, showing the reversibility of the sorption process. The possibility of application of the electrosorption technique to the separation of radionuclides was examined. The result of a selective removal experiments of a single component from a mixed solution showed that perfect separation of Co^{2+} and Sr^{2+} ions was possible by the electrosorption process.

Keywords : *Electrosorption, Separation, Cobalt, Strontium, Activated Carbon Fiber, Regeneration*

1. Introduction

In the view of the recycling of wastes generated from nuclear facilities, the electro-decontamination or chemical-decontamination of salt has been known to be effective. However, it is necessary to perfectly treat the secondary wastes occupying about 40% of the decontamination cost for the efficiency of decontamination technology.

Ion exchange, precipitation, and evaporation processes have been used to treat the secondary wastes resulting from decontamination [1-3]. But they have been restricted in wide application because of their disadvantages and limitations. Therefore, intensive investment in the research and development of the electrochemical method, which is effective in treatment of secondary wastes, has been conducted [4-6].

Electrodeposition of metals using porous carbon electrodes has been extensively investigated. Electrodeposition can be used as a useful technology in treatment of metal-bearing wastes because hazardous metals deposited can be recovered as a resource [7]. Earlier studies showed that the treatment of copper, lead, cadmium and nickel by electrodeposition on a variety of carbon materials (carbon nanofiber monoliths, glass carbon, and coal-derived carbon foams, etc) was very effective [8]. For some metals like strontium and cesium, electrodeposition is not a practical approach because of the high reduction potential of these cations.

An alternative to electrodeposition is electrosorption, that is, adsorption of the metal cations onto a negatively charged

carbon surface. The technique of electrosorption, which is an added electrical driving force to the traditional adsorption and ion exchange mechanism, has reversible characteristics of purifying waste solution by adsorption and concentrating contaminants by desorption [9-10]. Because adsorbents are regenerated by desorption, the secondary wastes are not regenerated. Electrosorption takes advantage of a combination of the high surface area and the electrical conductivity of porous carbons. It has been suggested as a minimally polluting, energy-efficient, and potentially cost-effective method for ion exchange, reverse osmosis, electrodialysis, and evaporation [11].

The selection of a proper electrode for an efficient removal of trace components from a solution is of high importance in the design of an electrochemical system. The basic requirements for an efficient electrode material are chemical and electrochemical inertness for a wide variety of chemicals and a wide range of potentials; high specific surface area (to achieve this requirement the electrode should be porous and the pores should be accessible by the electrochemically active species); high fluid permeability of the pore system; easily shapable as required by cell design considerations; high electronic conductivity and continuity of the electronic contact throughout the electrode bed; and inexpensive.

Carbon-based materials (activated carbon and activated carbon fibers etc.) satisfy the requirements described above well and have good radiation and chemical resistance. Especially ACF, which can be easily made in a variety of types

(textures or sheet), has a high specific surface area and good fluid permeability.

This study performed the batch experimental on the adsorption of Co^{2+} and Sr^{2+} , using ACF felt as an electrode. The adsorption behaviors were investigated, with changing pH, applied potential, and the concentration of electrolytes. The result was compared with the adsorption behavior when the potential is not applied. Also, the desorption behavior was investigated by reversing the applied potential. In order to confirm the degree of continuous regeneration of ACF, cycling experiments consisting of adsorption and desorption steps were carried out. For the radionuclides which do not have the same half-lives, it is safe and convenient method to separate the radionuclides and manage respectively. In this study, we conducted selective separation for binary components solution containing Co^{2+} and Sr^{2+} ions to investigate the application possibility of the electrosorption technique for the separation of radionuclides.

2. Experimental

2.1. Electrosorption electrode and reagents

2.1.1. Electrosorption electrode

The electrosorption electrode used in this study, which has the thickness of 3~7 mm, was pitch-based ACF felts. Table 1 shows the physicochemical properties of ACF felt. ACF has a large BET specific surface area, and most of the pores can be classified as a micropore which has an average pore radius of about 7.1 Å. It is known that the electrical conductivity of carbons used in the electrochemical process is in the range from 0.1 to $1.0(\Omega\text{-cm})^{-1}$, and a good carbon electrode has electrical conductivity values more than $1.0(\Omega\text{-cm})^{-1}$. The electrical conductivity values of ACF felt used in this experiment was $7.2(\Omega\text{-cm})^{-1}$. Therefore ACF felt can be used as a good conductive electrosorption adsorbent.

2.1.2. Reagents

Various solutions were prepared by diluting a concentrated CoCl_2 (or SrCl_2) solution with sodium chloride and deionized water (over $16\text{ M}\Omega\text{-cm}$). 0.1 N NaCl was used as electrolyte solution and the concentration of CoCl_2 and SrCl_2 was 0.5 mM. The pH of the solution was adjusted by adding 0.1 M NaOH and/or 0.1 M HCl as required. The solutions of

Table 1. Physical and chemical characteristics of ACF felts

Physical property		Electro/chemical property	
Specific S/A (m^2/g)	1680	Conductivity ($\text{ohm}\cdot\text{cm}$) ⁻¹	7.2
Total pore vol. (cm^3/g)	0.86	pH	6.4
Micro pore vol. (cm^3/g)	0.84	Surface acidity (meq/g)	0.38

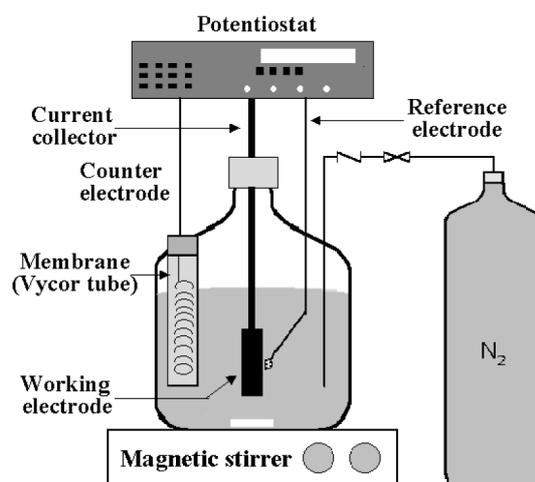


Fig. 1. Schematic diagram of batch adsorber.

Co and Sr were purged by nitrogen gas for 30 min prior to the experiment because of the easy reduction of dissolved oxygen in the solution.

2.2. Electrochemical cell

A small lab-scale three-electrode electrochemical cell was used for this study. Fig. 1 shows the apparatus. The experimental system consists of a potentiostat (EG&G Model 273), a working electrode (ACF), and an electro-chemical cell (EG&G Model G0096). The reference, counter, and working electrodes were dipped in the cell. A saturated calomel electrode (SCE) was used as the reference electrode. All potentials described in this paper are based on this reference electrode. The counter electrode used a platinum wire representing a non-corrosive surface for the gas evolution reaction and was separated from the working electrode by a Vycor membrane (Vycor No 7930).

2.3. Electrosorption and desorption

Electrosorption tests were conducted using the electrochemical cell in a batch mode. A constant amount of ACF felt was wound around a graphite rod, which was used as a current collector and dipped in the concentration of 0.5 mM solution with constant stirring of the electrolyte. The pH of the solution was continuously measured during the electrosorption experiments. The solution was sampled by autopipette with time. The adsorption behavior was investigated at various potentials, solution pHs, and concentrations of electrolytes and it was compared with the adsorption behavior at OCP. Also, the desorption behavior test for a fully saturated ACF was tested by applying the positive potential.

The concentration of Co^{2+} and Sr^{2+} in the solution was analyzed with an Atomic Absorption Spectrophotometer (Perkin Elmer 1100B). The pH was measured for each sample with a pH meter (Metrohm titroprocessor M682).

3. Results and Discussion

3.1. Electro-sorption behavior in the batch experiment

General adsorption-desorption processes are controlled by pressure (concentration in liquid phase adsorption) or temperature, while the electro-sorption process could be governed by the electric potential. When the electric potential is loaded, the electric double layer generated at the surface of the electrode are charged or discharged. Using this phenomenon, the electro-sorption can be accomplished. The adsorption of ionic species or non-ionic species in the solution should be influenced by the electric potential at the surface of electrode and electric properties of electrode materials. Therefore, the adsorption capacity can be controlled. When the electro-sorption process is applied in the treatment of a waste solution containing an ion species, they can be adsorbed in the electric double layer of the electrode electrostatically without phase change.

As shown in Table 1, ACF has various oxidized functional groups, which are amphoteric, hence, the possibility of cation-ion exchange can be expected.

The protonation/deprotonation equilibrium which is generally used to describe the surface charge development on surfaces containing an amphoteric oxygenated group can be written as:

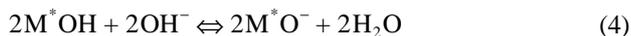


where MOH represents an oxygenated surface group on the carbon surface. Depending on the properties of MOH groups on the carbon surface, the net charge will either be positive, neutral, or negative when the carbon is placed in an aqueous environment maintained at a given pH.

During electro-sorption, an H^+ ion was adsorbed on a carbon surface charged with anion selectively [10].



where H_{ads} is considered to be a hydrogen atom bound to the surface. The basic environment in some local region about the cathode provides conditions favorable for ionization of acid groups that are not ionized by the prevailing proton concentration in the bulk solution. Thus



where M^*OH are representative of such neutral groups.

Reaction (4) introduces a new pathway for cobalt removal from solution by



Meanwhile, a reaction mechanism for the counter electrode can be predicted as follows:

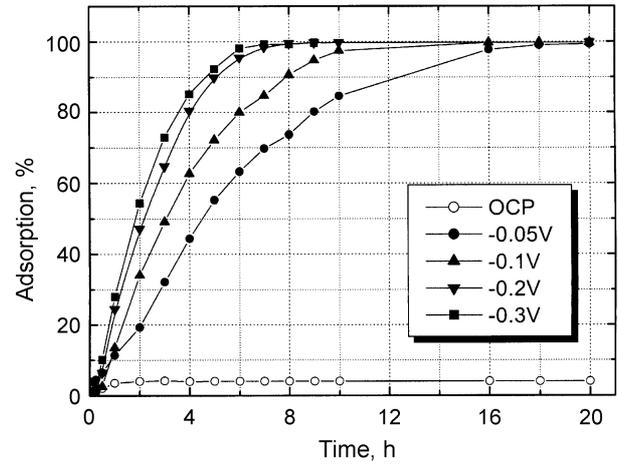


Fig. 2. Electro-adsorption % of Co^{2+} with variation of potentials at 0.5 g ACF.



3.1.1. Effect of potentials

(1) Electro-sorption of Co^{2+} ion

Electro-sorption of Co^{2+} onto the ACF felt was carried out at various negative potentials in the range of -0.05 to -0.3 V (vs. SCE). The adsorption % of Co^{2+} with variation of potentials using approximately 0.5 g of ACF felt is shown in Fig. 2. In comparison, a conventional adsorption (i.e., adsorption without an externally applied negative potential on the carbon electrode) test was performed, the results are also included in Fig. 2. It can be seen that Co^{2+} is effectively removed by electro-sorption at all applied negative potentials, while no Co^{2+} is removed by OCP adsorption. The Co^{2+} ion is removed 100% from a solution when a negative potential is applied to the carbon electrode. Adsorption kinetics increased at more negative potentials. Comparing the electro-sorption kinetics, the initial electro-sorption kinetics at -0.3 V is slightly faster than that at -0.2 V. However, the electro-sorption equilibrium is reached after 7 h for these two values of electric potentials (-0.3 and -0.2 V). From the results, we determined the potential of 0.2 V as an optimum electro-sorption potential, taking into account electric energy consumption.

Table 2. Data for adsorption of Co^{2+} on ACF electrode at various potential

Applied potential (vs. SCE)	OCP	-0.05 V	-0.1 V	-0.2 V	-0.3 V
Amount of adsorbed ($\text{mg}_{\text{cobalt}}/\text{g}_{\text{ACF}}$)	1.5	22.8	31.2	34.7	36.3

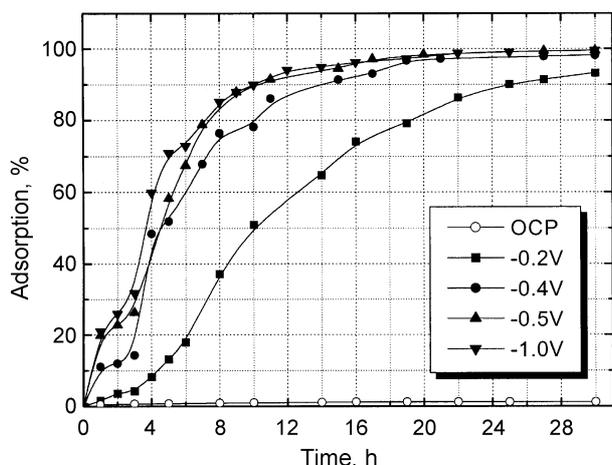


Fig. 3. Electro-adsorption % of Sr^{2+} with variation of potentials at 0.5 g ACF.

The capacity for Co^{2+} calculated at various potentials was represented in Table 2. The difference of the amount adsorbed in OCP and the applied potential -0.05 V was $21.3 \text{ mg}_{\text{cobalt}}/\text{g}_{\text{ACF}}$. Apparently, the external negative potential exerted on the carbon fiber has a great impact on the adsorption capacity of the carbon fiber. The increase of adsorption capacity for cation is due to electrostatic attraction by Coulomb's interaction. Many researchers reported that the adsorption capacity of carbon-based material was increased by an applied potential [13-15].

(2) Electrosorption of Sr^{2+} ion

The adsorption % of Sr^{2+} at various negative potentials and OCP were investigated. As shown in Fig. 3, no Sr^{2+} ion was removed at OCP, but 100% of the Sr^{2+} ions were adsorbed on the electrode surface in all ranges of the investigated negative electric potential except at -0.2 V. Because the time to reach adsorption equilibrium is long at -0.4 V, the condition of 0.5 V is chosen as an optimal adsorption electrical potential of Sr^{2+} ion.

3.1.2. Effect of pH

(1) Electrosorption of Co^{2+} ion

It has been reported that the solution pH has a considerable influence on liquid adsorption of heavy metal ions by ion exchange resins or inorganic adsorbents. Adsorption tests were carried out at a potential of -0.1 V and -0.2 V respectively to examine explicitly the effects of solution pH on the Co^{2+} adsorption.

The adsorption behavior of Co^{2+} with a variation of solution pH at -0.1 V and -0.2 V is shown in Fig. 4. The adsorption behavior was similar at the initial pH above 5. But it took a longer time to remove Co^{2+} ion completely in the condition of pH 3.5. It is presumably due to the mutual repulsion of H_3O^+ and Co^{2+} . As the applied negative potential became lower, the adsorption kinetics showed a greater difference.

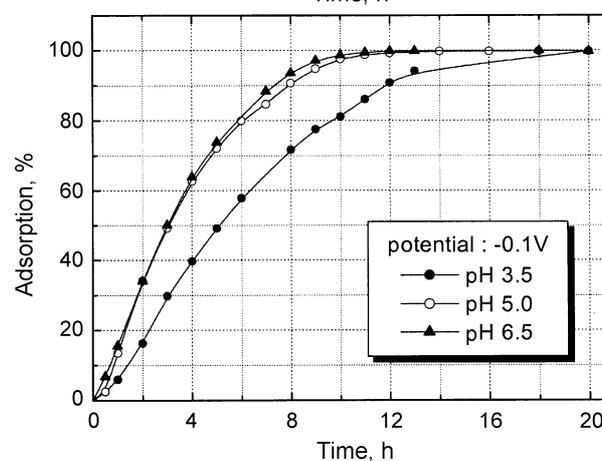
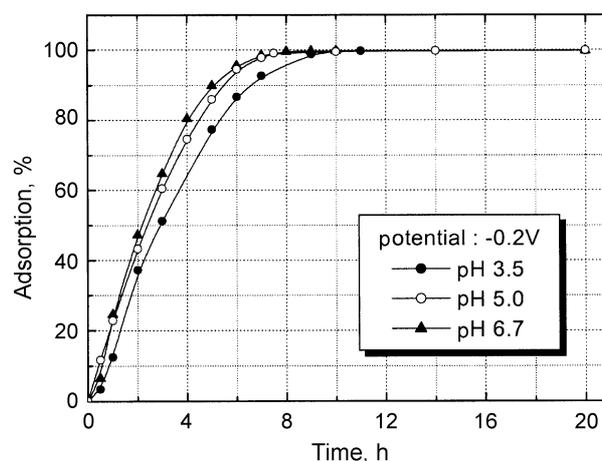


Fig. 4. Electro-adsorption % of Co^{2+} with variation of pH.

(2) Electrosorption of Sr^{2+} ion

The adsorption behavior of Sr^{2+} with variation of solution pH at -0.5 V is shown in Fig. 5. The adsorption kinetics increased with the increase in solution pH. The increase of pH to 7 gave very limited effects except for Sr^{2+} ion removal

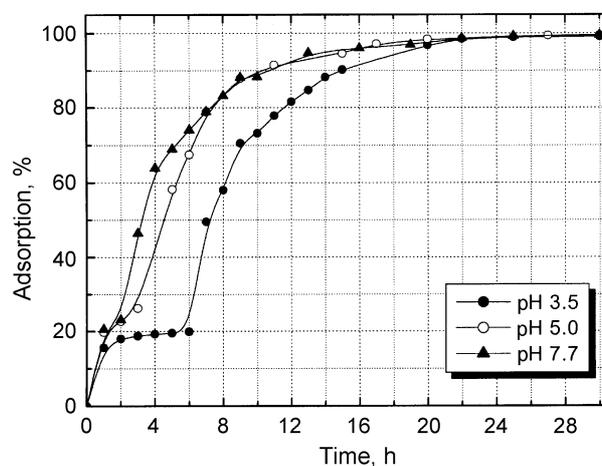


Fig. 5. Electro-adsorption % of Sr^{2+} with variation of pH.

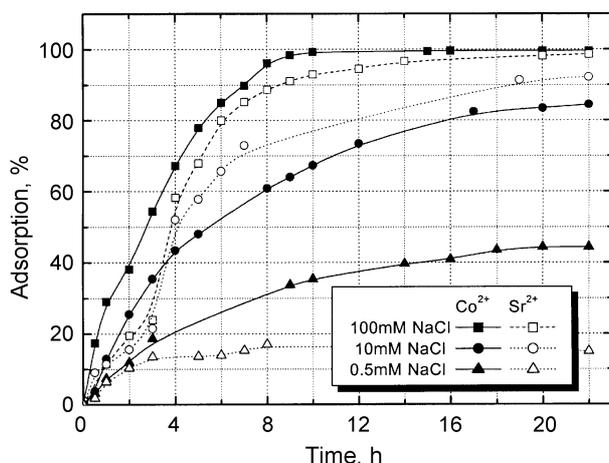


Fig. 6. Electro-adsorption % of Co^{2+} and Sr^{2+} with variation of electrolyte concentration.

during the first 6h. The adsorption behavior of Sr^{2+} with pH is similar to that of Co^{2+} .

3.1.3. Effect of electrolyte concentration

The effect of electrolyte concentration was studied and the results are shown in Fig. 6. It can be seen that adsorption kinetics increased with increasing the electrolyte concentration. It is due to the increase of ion mobility and decrease of ohmic voltage drop occurring because of the increase of electrolyte concentration. When the potential is applied to the electrode immersed in solution, electric conduction occurred by ion transfer playing the role of charge carrier. As electrolyte concentration becomes higher, ion concentration becomes more dense and charge transfer becomes active, which is favorable in electroadsorption reaction.

3.2. Desorption

When the electroadsorption and desorption process is conducted as one cycle, the separation of chemical species from electrolytic solution may be practiced by changing the electric potential applied to the adsorbent periodically. When the negative potential is applied during the first half of the cycle, the adsorbate is removed from the solution streaming through the adsorption electrode. After that, the adsorbent is applied by the positive potential and a fresh solution is passed through the adsorbent during the second half of the cycle. This solution is drawn off by a separation process in the state of concentrated adsorbate. The regeneration of adsorbent, which is an attractive feature of the electroadsorption process, can be accomplished simultaneously. The periodic electroadsorption and regeneration of spent adsorbent can be achieved when the desorption is reversible.

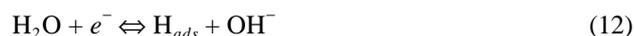
When the current is reversed, the carbon acts as the anode and



which results in a localized low pH and facilitates the reaction



whereas the predicted reaction on the counter electrode is as follows:



Evans and Hamilton explained for demineralization of water with the upper reaction mechanism [16].

(1) Effect of potentials and pH

Desorption was examined by applying the reversing potential to ACF adsorbent saturated with Co^{2+} ions. The desorption % of Co^{2+} with the variation of initial solution pH and applied potential is shown in Fig. 7. From the result, we see the desorption process occurs easily with the increase of the positive potential and the decrease of the solution pH. The comparison of the desorbed portion of Co^{2+} ions at +0.5 V indicated that the desorption at pH 3.5 was better than that at pH 6.5. However, the desorption of Co^{2+} ions did not occur completely. The comparison of the desorbed portion of Co^{2+} ions at +0.7 V, the desorption at pH 6.7 occurs easily. From the result, the determining factor for desorption is the applied electric potential rather than the solution pH. The optimum desorption potential and solution pH were determined to be +0.7 V and 5.0, respectively.

The desorption % of Sr^{2+} with the variation of initial solution pH and applied potential is shown in Fig. 8. In case of Sr^{2+} , the initial desorption kinetics had a slight change with initial pH at +0.3 V and desorption of Sr^{2+} was not attained completely. But, all Sr^{2+} ions were desorbed at +0.75 V within 5h. The optimum desorption potential and solution pH were determined to be +0.75 V and 5.0, respectively.

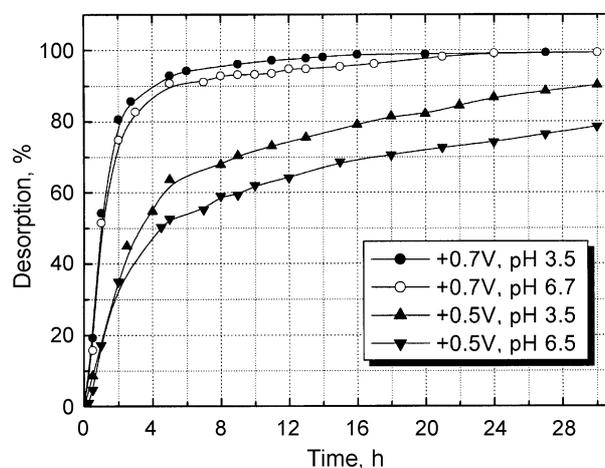


Fig. 7. Desorption % of Co^{2+} with variation of pH and potentials.

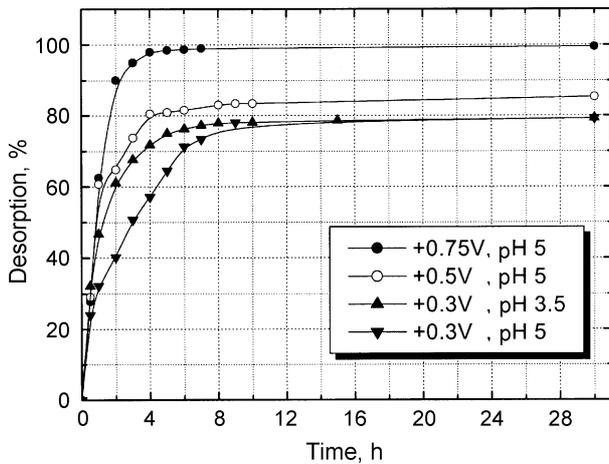


Fig. 8. Desorption % of Sr^{2+} with variation of pH and potentials.

3.3. Regeneration of adsorbent

To confirm the continuous use of electroadsorbents, cycling experiments consisting of an adsorption step at -0.2 V and desorption steps at $+0.7$ V were performed. Fig. 9 shows the residual concentration of Co^{2+} ions with variations of adsorption and desorption step in each cycle. For three cycling experiments, little difference appeared in the kinetics of adsorption and desorption, but a similar adsorption/desorption behavior was represented for three cycling times without a change in the amount of adsorption/desorption. It could be considered that the surface functional group of the ACF was removed by a partial reaction and then the property of the electrode surface was changed after the first cycle, or the Co^{2+} ion adsorbed on the inner pores of the

ACF was not removed completely after the desorption process and it caused the change of the pore structure. These results indicate that reversing the potential of ACF electrode results in the electrodesorption of adsorbate ions while regenerating the ACF electrode. Also we ascertained the possibility of the repetitive recycling process. Also, it was confirmed that the recycling process of adsorption/desorption could be conducted for several periods over three times.

3.4. Binary components

Most radioactive wastes contain various radionuclides which have different radioactivities, half lives, and toxicities. Therefore, it is necessary to examine the effects of the pres-

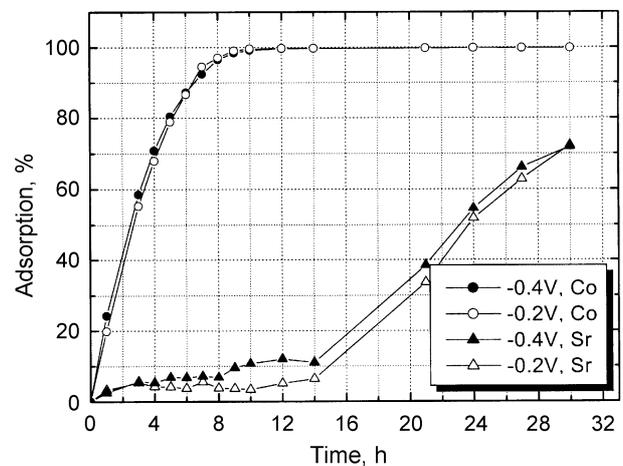


Fig. 10. Electro-adsorption % of Co^{2+} and Sr^{2+} with variation of potentials at binary systems.

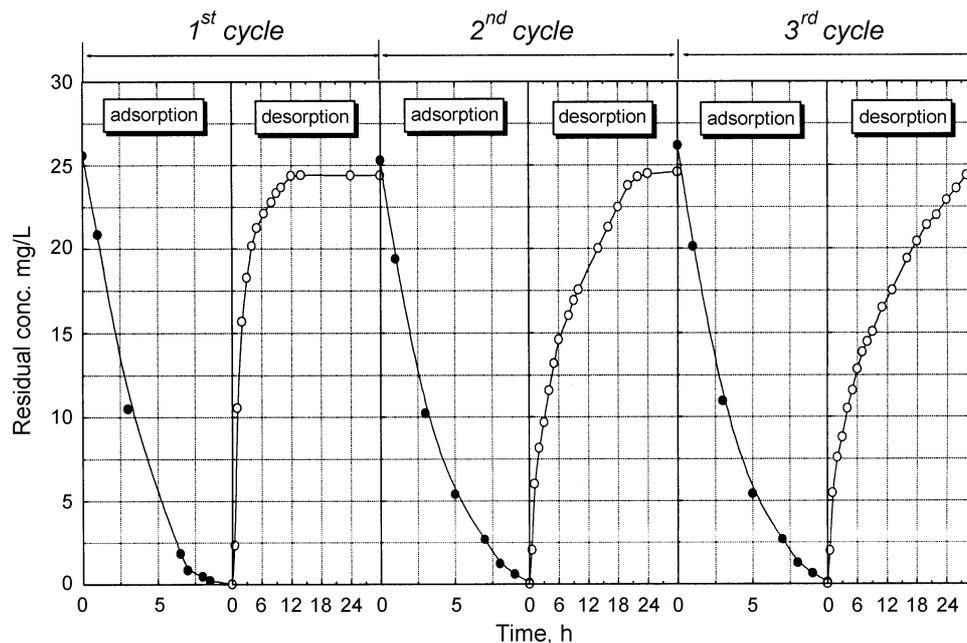


Fig. 9. Electro-adsorption and regeneration behaviors of ACF electrode for Co^{2+} .

ence of competing ions for the selection of optimal adsorption conditions. The adsorption using an ACF electrode is conducted for a binary component solution containing Co^{2+} and Sr^{2+} ions.

Fig. 10 shows the removed portion of Co^{2+} and Sr^{2+} ions from the binary component solution against the applied electric potential. Almost 100% removal of Co^{2+} is obtained, which is similar to the singular component system in which only Co^{2+} ions exist. However, only about 10% removal of Sr^{2+} is reached during the first 10h, and the sorption process of Sr^{2+} ions occurs after the adsorption reaction of Co^{2+} ions proceeds. From these results, it was found that Co^{2+} ions are more competitive than Sr^{2+} ions in the sorption on the active sites of a ACF adsorbent, and that Co^{2+} and Sr^{2+} ions are easily separated by the electrosorption process. Because the adsorption characteristics of Co^{2+} and Sr^{2+} ions are similar at -0.2 V and -0.4 V, the electrosorption process will be beneficial at the applied electric potential of -0.2 V.

4. Conclusions

From this study, the following conclusions can be drawn.

(1) Co^{2+} and Sr^{2+} ions in liquid waste resulting from wet decontamination are effectively removed by electrosorption on an electrode made of pitch-based activated carbon fibers.

(2) The adsorbed Co^{2+} and Sr^{2+} ions on an ACF electrode are easily desorbed by reversing the applying potential.

(3) The electric regeneration of carbon electrode more than three times by reversibility of electrosorption process were confirmed.

(4) Complete separation of Co^{2+} and Sr^{2+} ions is possible by electrosorption since high selectivity of electrosorption of Co^{2+} and Sr^{2+} ions is achieved.

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