



# Performance of fluoride electrosorption using micropore-dominant activated carbon as an electrode



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## ABSTRACT

Fluoride electrosorption using micropore-dominant activated carbon (AC) as an electrode was developed. The parameters of voltage, flow rate, and electrode gap were optimized to be 1.6 V, 10 mL/min and 2 mm, respectively. The electrosorption isotherm conforms to the Langmuir model, indicating the monolayer adsorption of the fluoride ions. The saturated electrosorption capacity for fluoride ions under the optimized parameters was 16.8 mg/g (AC). The high saturated electrosorption capacity of this micropore-dominant AC was attributed to its high specific surface area of 2130 m<sup>2</sup>/g, which was mainly contributed by the micropores. The saturated electrosorption capacity has a linear relationship to the square of the applied voltage. The fluoride electrosorption occurred only when the voltage was higher than the electro-capillary maximum voltage of 0.14 V for this AC. The charge efficiency reached a high value of 0.98 for the micropore-dominant AC, indicating that only counterions existed in the micropores.

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## 1. Introduction

Fluorine is an essential trace element for the human body and helpful to enhance bone and tooth strength. However, excessive intake of fluoride will cause damage to the human body [1,2]. The fluoride that enters the human body mainly comes from drinking water, and the fluoride concentration limit of the World Health Organization (WHO) is 0.5–1.5 mg/L [3]. However, the fluoride concentration in groundwater is often much higher than this value [4]. The chronic intake of drinking water containing excessive fluoride will lead to dental and skeletal fluorosis [5,6], so fluoride removal from drinking water is very important.

Adsorption is the most widely used method, and a large number of adsorbents have been synthesized for fluoride removal from drinking water [7]. Cost-effective adsorbents such as diatomaceous earth, bone char, and zeolites [8], usually have low adsorption capacity. Compared with natural adsorbents, metal oxide adsorbents, such as nano-alumina [9] and granular ferric hydroxide [10], have higher adsorption capacity. To further increase the adsorption capacity, composite metal adsorbents such as Fe-Ti [11], Fe-Zr [12], and Fe-Cr [13] have been synthesized. Expensive rare earth metals are also often used for increasing the adsorption capacity, such as Fe-Al-Ce [14], Ce-Ti [15], Mn-Ce [16], which entails a high cost.

Practically, cheap adsorbents usually suffer from low adsorption capacity [12], and the high-capacity adsorbents usually suffer from high costs. In addition, the regeneration of the adsorbents introduces an additional cost. Because the fluoride is usually chemically adsorbed on the adsorbents, alkali washing is usually used to remove the adsorbed fluoride, followed by acid washing to neutralize the pH in the regeneration solution. This not only increases the costs but also produces more waste water and causes secondary pollution to the environment. Metal adsorbents are also inevitably dissolved into water in the fluoride adsorption process, causing ion pollution of the water [17].

Electrosorption is a clean and economical method that generates no secondary pollution [18]. Carbon materials with a high specific surface area, such as activated carbon (AC) [19–21], carbon fibers [22,23], carbon aerogels [24], carbon nanotubes [25], graphene [26,27], mesoporous carbon [28], and carbon composite materials [29,30], have been used to produce electrodes for electrosorption. After applying a voltage, the two electrodes are positively and negatively charged, respectively. When aqueous solution flows through the gap between the electrodes, cations move to the negative electrode and anions move to the positive electrode under the action of the electric field, forming an electric double layer on the electrode surface. The ions in the solution are gradually moved onto the electrode surface and stored in the electric double layer, decreasing the bulk concentration of the solution [31]. Upon shorting the electrodes, the adsorbed ions are released back into the bulk solution, which causes the electrodes to be

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regenerated. Electrosorption is a non-Faradaic process, and the ions are fixed by the Coulomb force instead of chemical bonds on the electrode surface, so acid or alkali washing is not needed for the regeneration of the electrodes [21].

Electrosorption has the advantages of high energy efficiency, high removal efficiency, low cost and easy regeneration. Electrosorption has been studied in many works for removing NaCl [21,28,32] and other ions such as  $\text{Cr}^{2+}$  [33],  $\text{Cu}^{2+}$  [34],  $\text{Fe}^{3+}$  [35], and  $\text{NO}_3^-$  [36]. However, there have been few reports on fluoride removal by electrosorption. Tang et al. [37] studied the fluoride and nitrate removal from water by electrosorption using the activated carbon electrodes, the energy consumption was calculated by assuming the charge efficiency as 1. Some similar research about desalination using the activated carbon electrodes indicated the charge efficiency was below 0.5 [38]. The charge efficiency directly affects the energy consumption, which needs to be studied. The applied voltage is the key parameter in the electrosorption, and higher applied voltage leads to higher desalting capacity due to stronger electrostatic interaction. Hou et al. reported that the removal efficiency of ferric ions increased with the applied voltage below 2.0 V. However, when the electrical voltage was increased to 2.2 V, the removal efficiency gradually decreased due to the electrolysis of water [35]. The electrolysis of water was also observed at an applied voltage of 1.4 V in other report [19].

AC is widely used to produce electrodes due to its large specific surface area and low cost. The high specific surface area brings a high electrical double-layer capacitance, which results in a high electrosorption capacity [39]. Han et al. also reported that the AC electrode with the higher micropore porosity and specific surface area was preferable to obtain the higher electrosorption capacity [38]. In this paper, a micropore-dominant AC with narrow pore size was used as the electrode material. The effects of the applied voltage on the electrosorption capacity were studied. The applied voltage, flow rate, and electrode gap were optimized for high electrosorption efficiency. The electrosorption mechanism was studied by analyzing the electrosorption isotherm and the charge efficiency.

## 2. Materials and methods

### 2.1. Fabrication of AC electrode

AC with a specific surface area of  $2130 \text{ m}^2/\text{g}$  (Fuzhou Yi-Huan Carbon, China) was used as the electrode material. To fabricate the carbon electrode, a carbon slurry was prepared by mixing AC powder, carbon black (Fuzhou Yi-Huan Carbon, China), and the solution of poly(vinylidene fluoride) (PVDF, MW = 275,000, Sigma-Aldrich, USA) dissolved in di-methylacetamide (DMAc, Beijing Chemical Reagents, China). The slurry was stirred for 3 h to ensure homogeneity and then coated on a graphite plate. The coated plate was dried in an oven at  $80^\circ\text{C}$  for 6 h and then put in a vacuum oven at  $50^\circ\text{C}$  for 2 h to completely remove the organic solvent remaining in the micropores of the coated layer. The obtained AC electrode consists of 80% AC, 10% carbon black as conductive material, and 10% PVDF as binder. The AC electrodes were then assembled into an electrosorption cell.

### 2.2. Characterization of AC electrode

The Brunauer-Emmett-Teller (BET) surface area and pore size distribution (PSD) were measured by nitrogen adsorption at 77 K using a surface area analyzer (Autosorb-iQ, Quantachrome Instruments USA). The PSD was calculated by density functional theory (DFT) from the adsorption isotherm.

An electrochemical workstation (CHI 600 D, Shanghai CH Instrument Company, China) with a three-electrode system was used to analyze the characteristics of the capacitance, electrical adsorption, and desorption of the fabricated carbon electrode. The carbon electrode was fixed as the working electrode, and a platinum electrode and Ag/AgCl electrode were used as the counter and reference electrodes, respectively. 1.0 M NaCl solution was used as the electrolyte, and the water temperature in all measurements were kept at  $25^\circ\text{C}$ . The cyclic voltammetry (CV) performance was measured at different scan rates from 1 to 50 mV/s, and the electrical potential range was set from  $-0.6 \text{ V}$  to  $0 \text{ V}$  (vs Ag/AgCl electrode). The capacitance was calculated from the current-voltage curves according to Eq. (1),

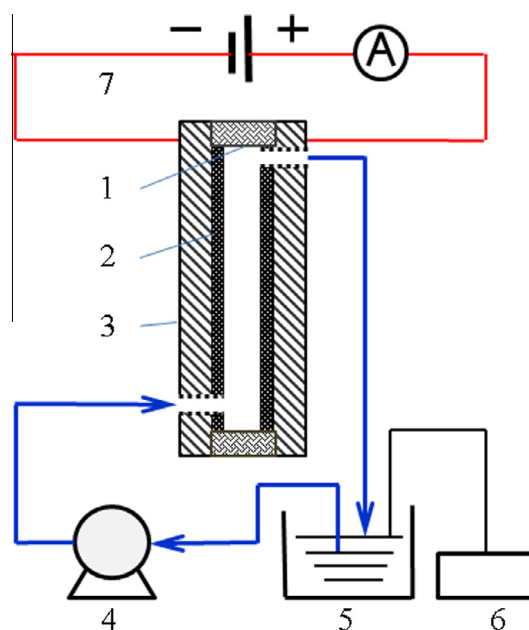
$$C = \frac{\int IdV}{vmV} \quad (1)$$

where  $C$  is the specific capacitance ( $\text{F/g(AC)}$ ),  $I$  is the response current (A),  $V$  is the instantaneous potential (V),  $v$  is the scan rate of the electrical potential (V/s), and  $m$  is the mass of AC on the electrodes (g) in this work.

### 2.3. Electrosorption apparatus and experiments

A schematic diagram of the electrosorption cell is shown in Fig. 1. The AC electrode had a size of  $60 \times 60 \times 0.2 \text{ mm}$ , and a hole with a diameter of 6 mm was opened for water to flow through. An insulated spacer was used to separate the two electrodes to avoid short circuits and also as a water flow path. The electrodes were fixed using a Plexiglas plate, and both of them had a hole with a diameter of 6 mm for water to flow through.

A stock solution with a fluoride concentration of 500 mg/L was prepared using NaF reagent (AR, Beijing Chemical Reagents, China) and deionized water and was diluted to different concentrations. The fluoride concentration of the effluent was measured using a conductivity meter, and the correlation of the conductivity ( $\mu\text{S}/\text{cm}$ ) to the concentration (mg/L) was calibrated prior to the experiment. The conductivity of the fluoride solution had an excellent linear relationship with the fluoride concentration. Before each



**Fig. 1.** Schematic diagram of the experimental apparatus 1. insulated spacer; 2. AC electrode; 3. graphite plate; 4. peristaltic pump; 5. feed tank; 6. conductivity meter; 7. potentiostat.

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