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ORIGINAL PAPER

Determination of cadmium (II) using H_2O_2-oxidized activated carbon modified electrode

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Abstract Pristine activated carbon (AcC) was oxidized by H_2O_2 under ultrasonic conditions. Compared with pristine AcC, the H_2O_2-oxidized AC possesses higher accumulation ability to trace levels of Cd^{2+}. Based on this, a highly sensitive, simple and rapid electrochemical method was developed for the determination of Cd^{2+}. In 0.01 mol L^{-1} $HClO_4$ solution, Cd^{2+} was effectively accumulated at the surface of H_2O_2-oxidized AcC modified paste electrode, and then reduced to Cd under −1.10 V. During the following potential sweep from −1.10 to −0.50 V, reduced Cd was oxidized and a sensitive stripping peak appears at −0.77 V. The stripping peak current of Cd^{2+} changes linearly with concentration over the range 5.0×10^{-8} to 5.0×10^{-6} mol L^{-1}. The limit of detection was found to be 3.0×10^{-8} mol L^{-1} for 2-min accumulation. Finally, this new sensing method was successfully used to detect Cd^{2+} in waste water samples.

Keywords Cadmium · Determination · Oxidized activated carbon · Modified electrode

1 Introduction

Cadmium is highly toxic and carcinogenic for humans [1–3] and is listed as the sixth most poisonous substance jeopardizing human health. Exposure to lower amounts of cadmium may cause renal dysfunction, bone degeneration, lung insufficiency, liver damage and hypertension in humans. Hence, there is an urgent need for developing a highly sensitive, rapid, reliable and simple method for the analysis of Cd^{2+}.

The extensively-used analytical methods for Cd^{2+} include atomic absorption spectrometry (AAS) [4] and inductively coupled plasma-atomic emission spectrometry (ICP-AES) [5]. In addition to these, various electrochemical methods utilizing different modified electrodes have been reported for the determination of Cd^{2+} since electrochemical method possesses high sensitivity, good selectivity, low cost, simplicity and easy data read-out. For example, a SWNT/Nafion film-modified GCE with limit of detection (LOD) of 1.0×10^{-8} mol L^{-1} after 5-min accumulation [6], a *p*-tert-butylthiacalixarene LB film modified GCE with LOD of 2.0×10^{-8} mol L^{-1} after 5-min accumulation [7], a zirconium phosphated-silica-modified carbon paste electrode with LOD of 2.6×10^{-8} mol L^{-1} after 2-min accumulation [8], a stannum film electrode with LOD of 9.8×10^{-9} mol L^{-1} after 3-min accumulation [9], a clay nanoparticle and anthraquinone complexly modified GCE with LOD of 3.0×10^{-9} mol L^{-1} after 5-min accumulation [10], a carbamoylphosphonic acid modified carbon paste electrode with LOD of 8.9×10^{-8} mol L^{-1} after 2-min accumulation [11], and a polycyclodextrin-modified carbon paste electrode with LOD of 2.0×10^{-6} mol L^{-1} [12], have been reported for the determination of Cd^{2+}. However, to the best of our knowledge, electrochemical determination of trace levels of Cd^{2+} using a H_2O_2-oxidized activated carbon (AcC) modified paste electrode is reported for the first time in this work.

The main objective of the current work is to develop a sensitive and convenient electrochemical method for the determination of Cd^{2+} using the excellent properties of H_2O_2-oxidized AcC. AcC is a carbon-based material with porous structure, large surface area and strong adsorptive

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ability. Pristine AcC was oxidized by 30% H_2O_2 under ultrasonic conditions for 2, 6 and 10 h. The electrochemical response of Cd^{2+} at different electrodes such as unmodified, AcC modified and various H_2O_2-oxidized AcC modified electrodes was investigated by anodic stripping voltammetry (ASV). Compared with the unmodified and AcC modified paste electrodes, the H_2O_2-oxidized AcC modified paste electrode remarkably enhances the stripping peak current of Cd^{2+}. The oxidation treatment imparts some useful properties to AcC, such as smaller particle size, larger surface area, numerous micro-pores and oxygenous group. Therefore, H_2O_2-oxidized AcC exhibits higher accumulation efficiency to Cd^{2+} and greatly improves the stripping peak current. Based on this, a novel, highly sensitive, rapid and convenient electrochemical method was developed for the determination of Cd^{2+}, which was successfully employed to determine Cd^{2+} in waste water samples.

2 Experiment

2.1 Reagents

$Cd(NO_3)_2$, virgin activated carbon, graphite powder (spectral reagent) and paraffin oil were purchased from Shanghai Reagent Corporation (Shanghai, China). A stock solution of 1.00×10^{-2} mol L^{-1} Cd^{2+} was prepared by dissolving $Cd(NO_3)_2$ into redistilled water and then diluted to desired concentrations using redistilled water. Other chemicals were analytical reagent grade. All chemicals were used without further purification.

2.2 Apparatus

The electrochemical measurements were performed using an 830B Electrochemical Analyzer (CH Instruments, USA). A conventional three-electrode system consisting of an oxidized-AcC modified paste working electrode, a saturated calomel reference electrode (SCE) and a platinum wire auxiliary electrode, was employed. Atomic absorption spectrometric measurements were conducted with AA-6300 atomic absorption spectrophotometer (SHIMADZU, Japan).

2.3 Oxidation treatment of AcC

The oxidation of pristine AcC was performed as follows: 2.0 g of pristine AcC was added into 30.0 mL 30% H_2O_2, then ultrasonicated at room temperature for different times, namely 2, 6 and 10 h. The H_2O_2-oxidized AcCs (denoted as AcC-2, AcC-6 and AcC-10) were then collected on a filter membrane, washed with redistilled water and finally dried at 120 °C.

2.4 Preparation of modified paste electrode

Firstly, 200.0 mg H_2O_2-oxidized AcC (AcC-2, AcC-6 or AcC-10) was homogeneously mixed with 600.0 mg graphite powder and 240.0 μL paraffin oil to give a uniform modified paste. The resulting paste was pressed into the end cavity (3 mm in diameter, 1 mm in depth) of the electrode body and the surface was polished on a smooth paper. The unmodified and AcC modified paste electrodes were also prepared by the same procedure. The amount of paraffin oil was carefully controlled because excessive oil will lower the conductivity, while insufficient oil is not beneficial to obtain uniform carbon paste.

2.5 Determination of Cd^{2+}

Unless stated otherwise, 0.01 mol L^{-1} $HClO_4$ solution was used as medium for the determination of Cd^{2+}. The analysis of Cd^{2+} includes two steps: accumulation and stripping. Firstly, Cd^{2+} in the bulk solution was preconcentrated onto the modified paste electrode surface, then reduced to Cd under −1.10 V for 2 min. Secondly, the reduced Cd was oxidized to Cd^{2+} during the following anodic sweep from −1.10 to −0.50 V, yielding a stripping peak at −0.77 V. The stripping peak current was measured and served as the analytical signal for Cd^{2+}.

3 Results and discussion

3.1 Electrochemical response of Cd^{2+}

The electrochemical response of Cd^{2+} in different supporting electrolytes was examined using anodic stripping voltammetry (ASV). After 2-min accumulation under −1.10 V, the square wave voltammograms were recorded from −1.10 to −0.50 V. The supporting electrolytes include HCl, $HClO_4$, NaAc, NaCl, NaH_2PO_4 (0.1 and 0.01 mol L^{-1}), pH 3.6, 4.0, 4.6, 5.0, 5.6 HAc-NaAc buffer (0.1 mol L^{-1}). It was found that the electrochemical behavior of Cd^{2+} shows great difference in different supporting electrolytes. In 0.01 mol L^{-1} $HClO_4$ solution, the anodic stripping peak current of Cd^{2+} is higher and the peak shape is well-defined. Therefore, 0.01 mol L^{-1} $HClO_4$ was used in the following studies for the determination of Cd^{2+}.

Figure 1 shows the anodic stripping voltammograms of 5.0×10^{-7} mol L^{-1} Cd^{2+} at different electrodes such as the unmodified paste electrode, the AcC, AcC-2, AcC-6, AcC-10 modified paste electrodes. At the unmodified paste electrode (curve a), a stripping peak is observed after 2-min accumulation in 0.01 mol L^{-1} $HClO_4$. The peak potential is at −0.77 V, and the peak current is very low. However, the stripping current of Cd^{2+} obviously increases at the AcC

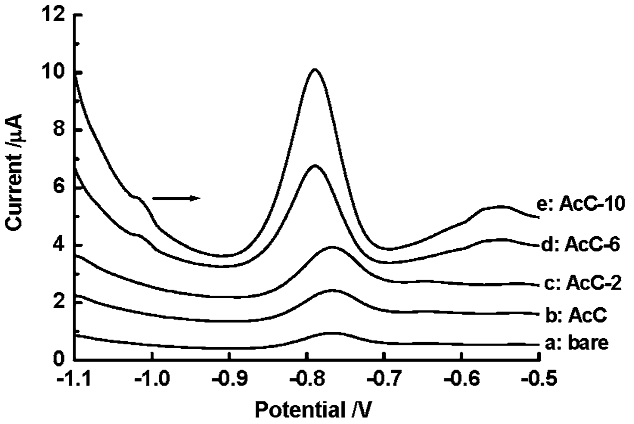

Fig. 1 Anodic stripping voltammograms of 5.0 × 10^{-7} mol L^{-1} Cd^{2+} in 0.01 mol L^{-1} $HClO_4$. (a) Unmodified paste electrode; (b–e) AcC, AcC-2, AcC-6, AcC-10 modified paste electrode. Accumulation potential = −1.10 V, accumulation time = 2 min, pulse amplitude = 25 mV, pulse width = 10 ms, scan rate = 100 mV s^{-1}

modified paste electrode under the identical conditions (curve b). Compared with graphite, AcC possesses larger surface area and stronger adsorption ability to Cd^{2+}. Therefore, the stripping peak current of Cd^{2+} obviously increases at the AcC-modified paste electrode.

Curves (c), (d) and (e) illustrate the anodic stripping voltammetric response of Cd^{2+} at the AcC-2, AcC-6 and AcC-10 modified paste electrodes, respectively. From the comparison, it is clear that the stripping peak current of Cd^{2+} increases at the H_2O_2-oxidized AcC modified paste electrode. When the AcC was oxidized by H_2O_2 under successive ultrasonic conditions, the particle size decreased and the surface area greatly increased. Additionally, more and more oxygenous groups such as carboxyl and hydroxyl are introduced. The larger surface area and numerous oxygenous groups provide more active sites for Cd^{2+} binding, and enhance the accumulation efficiency for Cd^{2+}. As a result, the anodic stripping peak current of Cd^{2+} significantly increases at the H_2O_2-oxidized AcC modified paste electrode. Additionally, the anodic stripping peak current of Cd^{2+} at the H_2O_2-oxidized AcC modified electrodes obeys the following order: AcC-10 > AcC-6 > AcC-2. Therefore, the AcC-10 modified paste electrode is employed to achieve higher sensitivity.

3.2 Optimization of detection

From Fig. 1 the AcC-10 increases the anodic stripping peak current of Cd^{2+}. However, the mass ratio between AcC-10 and graphite powder was found to influence the stripping peak current of Cd^{2+}, as shown in Fig. 2. When the mass percentage of AcC-10 increased from 0% to 25%, the peak current of Cd^{2+} increased linearly due to the higher accumulation efficiency and the existence of many more active sites. However, when the mass percentage is higher than 25%, the peak current begins to decrease, maybe caused by the fact that the electrical conductivity and electron exchange ability decrease when the content of AcC-10 is too high. Thus, the mass content of AcC-10 was selected as 25% in this work.

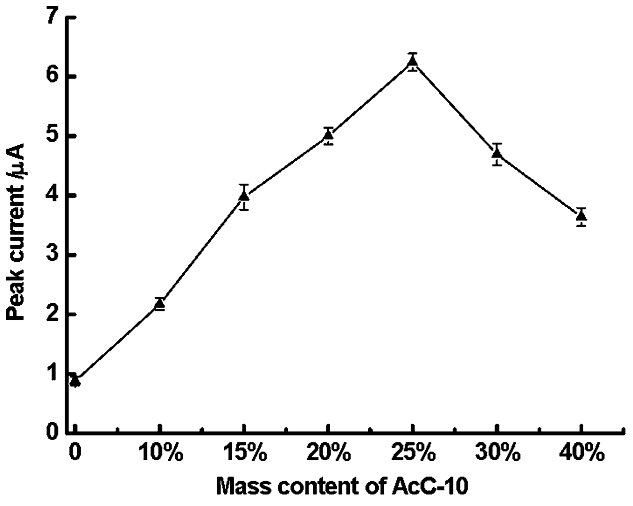

Fig. 2 Effect of the content of AcC-10 on the stripping peak current of 5.0 × 10^{-7} mol L^{-1} Cd^{2+}

In ASV, accumulation potential and accumulation time are two important parameters since they significantly influence the determining sensitivity. Figure 3 depicts the stripping peak current of 5.0(10^{-7} mol L^{-1} Cd^{2+} after 2-min accumulation under different accumulation potentials. When the accumulation potential shifts negatively from −0.90 to −1.10 V, the stripping peak current of Cd^{2+} increases linearly. With further negative shift of the accumulation potential from −1.10 to −1.30 V, the stripping peak current of Cd^{2+} remains almost unchanged, suggesting that the determining sensitivity has not been improved. Furthermore, more negative accumulation potential will

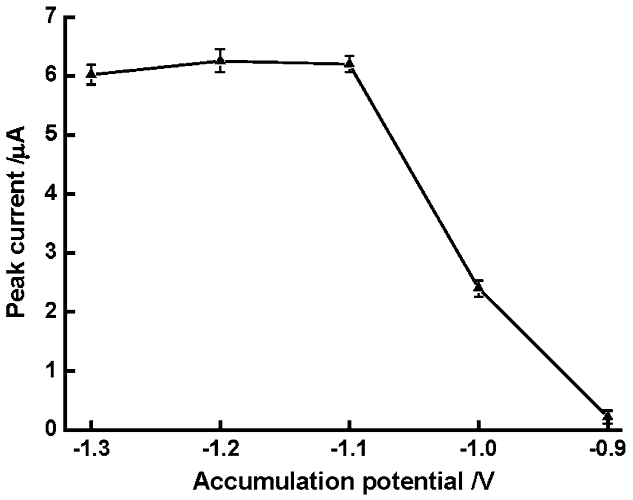

Fig. 3 Influence of accumulation potential on the stripping peak current of 5.0 × 10^{-7} mol L^{-1} Cd^{2+}

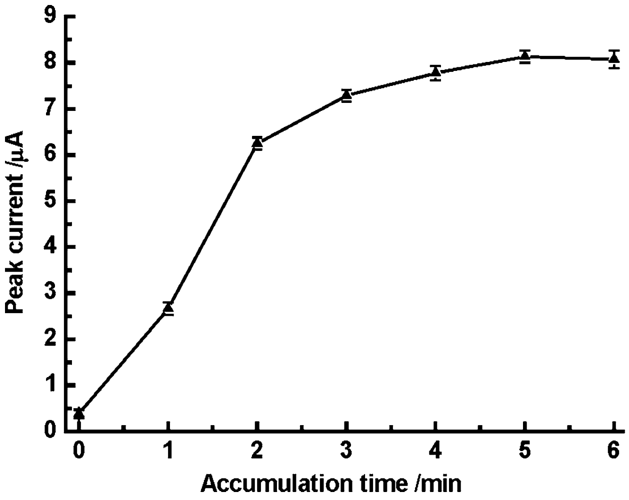

Fig. 4 Influence of accumulation time on the stripping peak current of 5.0 × 10^{-7} mol L^{-1} Cd^{2+}

cause other metal ions or H^+ to be reduced, causing interference to the determination of Cd^{2+}. So, the accumulation potential was fixed at −1.10 V in this system.

Figure 4 shows the influence of accumulation time on the anodic stripping peak current of Cd^{2+}. Increasing the accumulation time from 0 to 2 min causes the stripping peak current to increase markedly; this may be attributed to the fact that the amount of Cd^{2+} at the modified electrode surface greatly increases. Further increase in accumulation time from 2 min to 5 min causes the peak current of Cd^{2+} to increase slightly and the plot becomes curved. If the accumulation time increases from 5 to 6 min, the peak current of Cd^{2+} remains almost unchanged and the plot becomes a straight line, revealing that the amount of Cd^{2+} accumulated at the modified electrode surface tends to a limiting value. In order to shorten analysis time and achieve higher sensitivity 2-min accumulation was used.

3.3 Reproducibility

After each measurement the AcC-10 modified paste was removed from the end cavity and a new AcC-10 modified paste electrode was prepared. The reproducibility between multiple electrodes was estimated by comparing the anodic stripping peak current of 5.0 × 10^{-7} mol L^{-1} Cd^{2+}. The relative standard deviation (RSD) was 6.8% for 10 AcC-10 paste electrodes, revealing that this method possesses excellent reproducibility.

3.4 Interference

To evaluate the interference of foreign cations on the determination of Cd^{2+}, a systematic study was carried out. The stripping peak currents of 5.0 × 10^{-7} mol L^{-1} Cd^{2+} in the absence and presence of various concentrations of foreign cations were measured. When the peak current change exceeded 10%, it was considered that this particular cation caused obvious interference, and the corresponding concentration was defined as the tolerance level. The results are listed in Table 1, suggesting that 10,000-fold concentration of Al^{3+}, Zn^{2+}, Ca^{2+}, Fe^{3+}, Ba^{2+}; 1,000-fold concentration of Pb^{2+}, Ni^{2+}; 500-fold concentration of As^{3+}, 100-fold concentration of Hg^{2+}, Cu^{2+}; have almost no influence.

Table 1 Interferences of foreign cations on the stripping peak current of 5.0 × 10^{-7} mol L^{-1} Cd^{2+}

Foreign cations	Tolerance level (mol L^{-1})
Al^{3+}, Zn^{2+}, Ca^{2+}, Fe^{3+}, Ba^{2+}	5.0 × 10^{-3}
Pb^{2+}, Ni^{2+}	5.0 × 10^{-4}
As^{3+}	2.5 × 10^{-4}
Hg^{2+}, Cu^{2+}	5.0 × 10^{-5}

3.5 Linear range and limit of detection

The relationship between the anodic stripping peak current (i_p) of Cd^{2+} and concentration (*C*) was studied under the optimized conditions as shown in Fig. 5. The i_p is proportional to *C* over the range 5.0 × 10^{-8} to 5.0 × 10^{-6} mol L^{-1}, obeying the regression equation: $i_p = -0.4215 + 1.3104 \times 10^7 C$ (i_p in μA, *C* in mol L^{-1}, $r = 0.998$).

Additionally, the limit of detection was estimated using the method of gradually decreasing the concentration of Cd^{2+}. When the concentration of Cd^{2+} decreased to 3.0 × 10^{-8} mol L^{-1}, an observable stripping peak was observed after 2-min accumulation. With further decrease in concentration, the stripping peak almost disappeared. So, the limit of detection was evaluated as 3.0 × 10^{-8} mol L^{-1} for 2-min

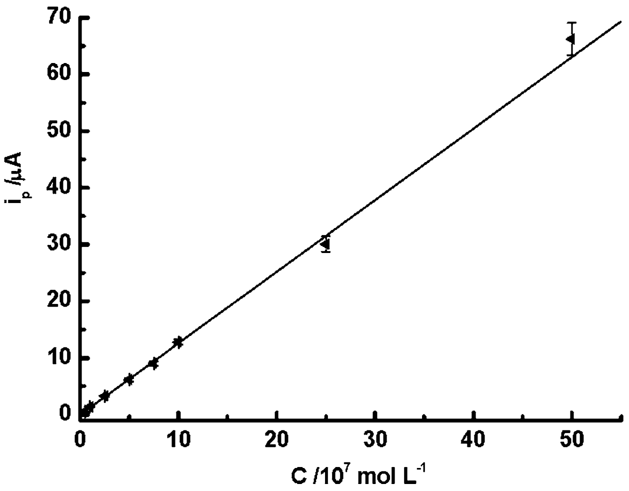

Fig. 5 Calibration curve for Cd^{2+}

Table 2 Determination of Cd^{2+} in water samples

Samples	By AAS (mol L^{-1})	By this method (mol L^{-1})	RSD (%)	Recovery (%)
A	7.66×10^{-8}	8.09×10^{-8}	4.4	101.0
B	9.02×10^{-7}	8.84×10^{-7}	3.7	98.2
C	9.53×10^{-6}	9.49×10^{-6}	2.5	105.0
D	8.06×10^{-6}	8.83×10^{-6}	4.1	98.1

accumulation. The limit of detection will decrease with increased accumulation time. For example, the limit of detection was as low as 5.0×10^{-9} mol L^{-1} for 6-min accumulation.

3.6 Determination of Cd^{2+} in water samples

The newly proposed method was employed to detect Cd^{2+} in water samples to verify its potential application and the results shown in Table 2. Firstly, 5.00 mL of water sample was added in 5.00 mL 0.02 mol L^{-1} $HClO_4$ solution. Secondly, the square wave anodic stripping voltammograms were recorded after 2-min accumulation and the peak current was measured for Cd^{2+}. The concentration of Cd^{2+} in the sample was obtained by the standard addition method and each sample solution underwent three parallel detections. The value of RSD was below 5%, indicating good reproducibility. Additionally, different concentrations of Cd^{2+} standard solution were added to the sample solution and the recovery was subsequently evaluated. It was found that the recovery was between 98.1% and 105.0%, suggesting that this new analytical method is effective and feasible. The concentration of Cd^{2+} in water samples was also determined by atomic absorption spectrometry (AAS) in order to test the accuracy of the new method. The results obtained by AAS and the present new method were in good agreement, indicating that the method has good accuracy and potential application in practical sample analysis.

4 Conclusions

Activated carbon was oxidized by H_2O_2 under ultrasonic conditions, producing large surface area, numerous micropores and more oxidizing groups. Therefore, H_2O_2-oxidized activated carbon exhibits higher accumulation ability to Cd^{2+} and greatly improves sensitivity for the determination of Cd^{2+}.

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