Solid phase microextraction and determination of dichromate in aqueous solution based on pine needle powder-modified carbon paste electrode by potentiometry

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Received: 27 January 2013 / Accepted: 6 May 2013 / Published online: 21 May 2013
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Abstract Pine needle is a low-cost natural biopolymer, and $\text{Cr}_2\text{O}_7^{2-}$ is a poisonous anions in the environment. In the present paper, pine needle powder was used as a solid phase microextractant in the modification of carbon paste electrode for extraction and determination of $\text{Cr}_2\text{O}_7^{2-}$ anions. The extraction process was monitored by an open circuit potential method, and an apparent first-order rate constant of 0.06474 s^{-1} was obtained from a Richard model. The extraction isothermal curve follows a logarithm adsorption model with a adsorption equilibrium constant of 5.95. Under the optimal conditions, the concentration of $\text{K}_2\text{Cr}_2\text{O}_7$ in river water of Shenyang Normal University campus was determined by the potentiometric method in the concentration range of 1.0×10^{-6} – $1.0 \times 10^{-2} \text{ M}$ with a detection limit of $1.0 \times 10^{-7} \text{ M}$ (the signal to noise Ratio was 3:1), relative standard deviation of 3.44 %, and standard addition recovery in the range of 94.70–103.5 %. The large amounts of common existing ions such as Cr^{3+} , Cu^{2+} , and SO_4^{2-} showed no interference with the molar ratio up to 100:1, but CrO_4^{2-} , Pb^{2+} ions showed a great interference in the detection of $\text{Cr}_2\text{O}_7^{2-}$ due to the transformation from CrO_4^{2-} to $\text{Cr}_2\text{O}_7^{2-}$ and precipitations of PbCrO_4 and PbCr_2O_7 , respectively.

Keywords Dichromate anion · Pine needle powder · Open circuit potential · Carbon paste electrode · Solid phase microextraction · Potentiometry

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Introduction

Cr(VI), mainly considered as chromate anion and dichromate anion, are the important environmental pollutants from electrochemical plating, and the paper and leather industries. They may induce mutations and cause cancer [1] in human, and are more harmful than Cr(III). One way to reduce the toxicity of Cr(VI) in the environment is to reduce Cr(VI)–Cr(III) with chemical agents [2]. Recently, the transformation from Cr(VI) to Cr(III) with low-cost natural biomaterials has been investigated [3–5]. Among the many natural biomaterials, pine needles were reported as a powerful natural biomaterial with microporous structure of resin ducts containing reduction groups, such as phenol, hydroxyl, amino, and terpenoid [6, 7]. The adsorption of Cr(VI) and transformation from Cr(VI) to Cr(III) by pine needles has been reported as several hundreds times higher than other natural biomaterials, so it was considered as a good biomaterial in the effective removal of Cr(VI) pollutants in the aqueous solutions [8].

The analytical methods commonly used for the determination of Cr(VI) are atomic absorption spectrometry (AAS) [9], fluorescence spectrometry [10], and electrochemical measurements [11]. If these analytical methods are combined with the microextraction of pine needle powder for the determination of Cr(VI), the sensitivity and selectivity must be increased, and the detection of limit must be decreased. But in practice, how to induce an electrochemical inactive species into the electrode surface is a key problem. A chemically-modified carbon paste electrode has been proved as a powerful tool in electrochemistry and electroanalysis [12, 13]. Pine needle powder can be easily mixed into graphite powder to make a suitable pine needle powder-modified carbon paste electrode. Pine needle powder is an electrochemically inactive species. The introduction of pine needle powder may increase the extraction capability of Cr(VI), but decrease the conductivity and reactivity of the carbon paste electrode, so the common amperometric methods such as cyclic voltammetry and pulse differential voltammetry, may not be suitable for the detection. Open circuit potential (OCP) is a potentiometric method, commonly used in monitoring the potential at the working electrode surface without interference from the applied potential or current, and has been widely used in many areas such as electrochemical research [14], environmental monitoring [15], bioinstrumentation [16], and material analysis [17].

Even though, in our studies, the natural pine needle powder has shown two functions including adsorption and transformation of Cr(VI)–Cr(III) [6, 7] only the adsorption of the Cr(VI) function can be found and monitored in the carbon paste electrode case. The second function of the transformation from Cr(VI) to Cr(III) can be monitored with spectrophotometry. In the present paper, the natural pine needle powder modified the carbon paste electrode as the solid phase microextractant for dichromate from aqueous solution. The dynamics and thermodynamics of the microextraction process were investigated by open circuit potential measurement. The solid phase microextraction was also used in the determination of dichromate in aqueous solution with some interesting results.

Experimental

Instruments and reagents

Electrochemical experiments were carried out on a CHI620B electrochemical system (CHI, USA) with a two-electrode, home-made pine needle powder-modified carbon paste electrode (PCPE) as the working electrode, and a KCl-saturated calomel electrode (SCE, model 232) as the reference electrode. All potentials reported here were with respect to this reference electrode.

Brown pine needles, as the natural microextractant, were collected from the ground under the matured *Pinus koraiensis* trees (over 15 years old) in Shenyang Normal University campus in the spring season. Graphite powder (spectrophotometric pure) and silicone oil were used for the carbon paste electrode. Potassium dichromate ($K_2Cr_2O_7$) and potassium chromate (K_2CrO_4) were used as target materials. Disodium hydrogen phosphate (Na_2HPO_4) and citric acid were used as the buffer solution system. Potassium nitrate (KNO_3), hydrochloric acid (HCl), chromium chloride ($CrCl_3$), potassium sulfate (K_2SO_4), lead sulfate ($PbSO_4$) and copper sulfate ($CuSO_4$) were all analytical pure (purchased from Shenyang Chemical) and used for electrolyte and interference substances. All solutions were prepared with ultrapure water ($18.2\text{ M}\Omega\text{ cm}^{-1}$) obtained from Milli-Q system (Billerica, MA, USA).

Preparation of the working electrode

The basic electrode was prepared with graphite powder, polyamide resin, and epoxy resin, mixed into a paste with a weight ratio of 4:1:1, tightly filled into a clean glass tube (inner diameter about 4 mm) with a copper wire at the other end as the electrode lead, and solidified in air for 72 h. The upper end of the prepared electrode was scraped out to produce a 1-mm cavity for carbon paste.

The collected dried brown pine needles were successively cleaned with drinking water and ultrapure water, and ground into powder (about 600#) with a grinder. The carbon paste was prepared with 0.003 g pine needle powder, 1.0 g graphite powder, and 0.60 g silicone oil, filled tightly into the cavity in the basic electrode, and polished on glass-paper as the pine needle powder-modified carbon paste electrode (PCPE). The paste in the working electrode cavity can be renewed for new measurements after usage. The prepared carbon paste can be stored in air for several months without loss of its activity.

Experimental procedure

The open circuit potential experiment on the different electrodes was in 5.0 mL 0.3 M KNO_3 electrolyte solution and 5.0 mL disodium hydrogen phosphate–citric acid buffer solution (pH = 2.4) in the time range of 0–600 s. The 5.0 mL $K_2Cr_2O_7$ with different concentrations was added into the solution at 300 s, and the experiment was continued until the saturated adsorption stage was reached at about 600 s.

Results and discussion

The open circuit potential curves of $\text{Cr}_2\text{O}_7^{2-}$ on PCPE

Open circuit potential experiments were performed in 0.3 M KNO_3 electrolyte solution including phosphate/citrate buffer solution at pH 2.4 and 1.0×10^{-4} M $\text{K}_2\text{Cr}_2\text{O}_7$ solution at the PCPE and bare CPE as described in Sect. 2.3. The potential–time curves were obtained as shown in Fig. 1. The PCPE responses to the electrolyte solution with the open circuit potential decreased from 0.339 V at 0 s to 0.2975 V at 300 s, and then to 0.2884 V at 600 s, shown as curve 3 in Fig. 1. The addition of 1.0×10^{-4} M $\text{K}_2\text{Cr}_2\text{O}_7$ at 300 s made the open circuit potential sharply increase with a larger potential difference of 0.3780 V between that at 600 s and that at 300 s, shown as curve 1 in Fig. 1. The bare CPE responses to the addition of 1.0×10^{-4} M $\text{K}_2\text{Cr}_2\text{O}_7$ solution at 300 s produced a small potential difference of 0.0458 V between that at 600 s and that at 300 s. The potential response of PCPE to $\text{K}_2\text{Cr}_2\text{O}_7$ was 8.3 times larger than that of CPE. This result indicates that PCPE shows an efficient microextraction and was a good sensor for monitoring the $\text{K}_2\text{Cr}_2\text{O}_7$ species.

The pine needle powder is a natural biomaterial with microporous structures. Inside the pores, there are many kinds of phenol, hydroxyl, and amino groups, which serve as the active adsorption sites for the solid phase microextractant of dichromate [7]. The microextraction kinetics can be obtained from the potential–time curve in the time interval of 300–400 s (curve 1 in Fig. 1), which shows a transition process of the adsorption. The transition process can be regressed as a Richards function to describe the accumulation growth model and adsorption model [18, 19], from which the apparent first-order extraction rate constant was obtained as 0.06474 s^{-1} , and inflection time as 316.4 s.

Fig. 1 The potential–time curves of potassium dichromate at electrodes with dichromate (1), without dichromate (2), and bare CPE (3) with dichromate in 0.3 M KNO_3 electrolyte solution including 1.0×10^{-4} M $\text{K}_2\text{Cr}_2\text{O}_7$ at pH = 2.4. The curve (3) is the potential of PCPE in the absence of dichromate ions

$$E/V = 0.6511 / \left(1 + \exp(16.35 - 0.0647t)^{1/0.06434} \right), R^2 = 0.9957, SD = 0.0055 \quad (1)$$

After 400 s, the process tends to the saturated stage and gives out an open circuit potential of the system at 600 s. The potential–time curve of dichromate anions at the CPE electrode (curve 2 in Fig. 1) shows the similar Richards model, but with different parameters as,

$$E/V = 0.3271 / \left(1 + \exp(8.348 - 0.02923t)^{1/5.649} \right), R^2 = 0.9905, SD = 0.000769 \quad (2)$$

The apparent first-order microextraction rate constant of 0.02923 s^{-1} and inflection time of 308.4 s were obtained, which are smaller than that for PCPE. The inflection times are similar, but the extraction rate constant at PCPE was one times larger than that at CPE, and the exponential index of $1/0.06434$ at PCPE was also 87 times larger than that at CPE ($1/5.649$), both of which are responsible for the fast and efficient extraction of dichromate from aqueous solution.

The potential–time curve of PCPE in the electrolyte solution without dichromate shows a Gaussian function curve (curve 3 in Fig. 1) as,

$$E/V = 0.2978 \exp\left(-(t - 183)^2 / 5080000\right); R^2 = 0.9998, SD = 0.0000084 \quad (3)$$

This regression equation indicates that, in the electrolyte solution without dichromate, the ions in the solution distribute at the electrode–solution interface according to the zero charge potential of the electrode [20]. The open circuit potential difference ($\Delta E/V$) of PCPE in electrolyte solution with and without dichromate at 600 s can be used to optimize the experimental conditions and to determine the concentration of dichromate in the solution.

The optimal conditions for determination of $\text{K}_2\text{Cr}_2\text{O}_7$ at PCPE

The influence of the amount of extractant (pine needle)

In order to investigate the influence of the amount of the extractant on the extraction process of dichromate, the different amount of the pine needle powder was mixed with 1.00 g graphite powder for preparation of the PCPE. The OCP experiments were performed under the same experimental conditions. The open circuit potential difference (ΔE) was plotted against the weight ratio of pine needle powder and graphite powder ($r = w_{\text{pine needle}}/w_{\text{graphite}}$) as shown in Fig. 2. The curve of $\Delta E - r$ was regressed into a quadratic equation as,

$$\Delta E = 44.85 - 27.76r - 0.1043/r^2, R^2 = 0.9934, SD = 1.579 \quad (4)$$

This curve shows that, with the increase of modification ratio of pine needle powder to graphite powder from 0.0 %, the open circuit potential deference increases sharply, reaching the maximum point of 44.8 mV (the constant term in Eq. 4) at 0.3 %, and then decreases linearly. The third term is responsible for the sharp decrease in $r < 0.3$ %, which indicates the effective extraction of dichromate from aqueous

Fig. 2 The plot of open circuit potential difference against the mixing ratio of pine needle powder to graphite in the PCPE. The other experimental conditions were the same as those in Fig. 1

solution. The second term is responsible for the linear decrease in the range of $r > 0.3$ %, which means that, with the increase of extractant, the effective extraction points resulting in the open circuit potential changes were decreased. In practice, the mixing ratio of 0.3 % was chosen as the optimal amount of pine needle powder.

The influence of solution pH

The solution pH is an important factor, which influences not only the existing forms of Cr(VI) [21] but also the extraction ability of pine needle powder. The solution pH was controlled by hydrochloric acid in the range of 1.0–2.2 and disodium hydrogen phosphate–citric acid buffer system in the range of 2.2–4.2. The OCP experiments were performed in 0.3 M KNO_3 electrolyte solution including 1.0×10^{-4} M $\text{K}_2\text{Cr}_2\text{O}_7$. The plot of the open circuit potential difference against solution pH was a complex curve as shown in Fig. 3.

The curve can be regressed into a Gaussian distribution function with the central pH of 2.44 as,

$$\Delta E = 0.3095 \exp\left(-(\text{pH} - 2.44)^2 / 1.144\right), R^2 = 0.993, \text{SD} = 0.0103 \quad (5)$$

In acidic solution, dichromate becomes a complex system. The association constant of hydrogen dichromate anions was $\text{p}K_{a2} = 1.8$ [21]. The reaction can be expressed as,

With the increase of the solution pH ($\text{pH} > 2.44$), the hydrogen dichromate was dissociated according to the reaction shown in Eq. (7) into hydrogen chromate

Fig. 3 The relationship between the open circuit potential difference and solution pH. Other experimental conditions were the same as those in Fig. 1

anions, which are not suitable species for the extraction, and responsible for the decrease of the potential.

With the decrease of solution pH ($\text{pH} < 2.4$), the main species in the region of solution are $\text{HCr}_2\text{O}_7^{2-}$, $\text{H}_2\text{CrO}_4^{2-}$, $\text{HCr}_4\text{O}_{13}^-$, and $\text{HCr}_3\text{O}_{10}^-$ due to the following reactions [7, 21]. These reactions cannot be extracted effectively, and are responsible for the decrease of open circuit potential in this pH region.

In practice, the optimal pH was chosen as $\text{pH} = 2.4$. These results also indicate that hydrogen dichromate anions is the suitable species for the microextraction from aqueous solution into the pine needle powder-modified carbon paste electrode surface.

The influence of the concentration of potassium dichromate

Under the optimal experimental conditions, the open circuit potential experiments were performed in KNO_3 electrolyte solution including different concentrations of $\text{K}_2\text{Cr}_2\text{O}_7$. The obtained open circuit potential difference was plotted against concentrations of $\text{K}_2\text{Cr}_2\text{O}_7$ as shown in Fig. 4a, which can be regressed into an exponential function of,

$$\Delta E = 0.774 + 0.1217 \text{ pc}, \text{ pc} = -\log(c, M), R^2 = 0.988, \text{ SD} = 0.0209 \quad (11)$$

The exponential relationship of potential difference with concentration of dichromate anions is the isothermal extraction curve.

The extraction process can be expressed as the following equation,

The open circuit potential can be expressed according to the Nerstian equation [22].

During the adsorption process, the dichromate anions interact with the pine needle powder and form a new membrane with pine needle–dichromate species, and can be described as,

$$E = E^0 - \frac{0.05916}{n} \log(c^m, \text{M}) = E^0 + m \times 0.05916 \log(c, \text{M}) \quad (13)$$

From this equation, $m \times 0.05916 = 0.1217$, then $m = 2.057$. This result indicates each of the adsorption sites in the pine needle powder can adsorb two of the hydrogen dichromate anions, and belongs to the super-Nerstian responses [23].

The adsorption belongs to a logarithm adsorption model [24]. The equilibrium constant for this adsorption reaction (Eq. 12) can be obtained from the intersection of Eq. (13) as $K_{\text{eq}} = 2.29 \times 10^6$, which is favorable for the extraction results.

Fig. 4 **a** The plot of open circuit potential difference against dichromate concentration; **b** the plot of open circuit potential difference against the logarithm of dichromate concentration. The other experimental conditions were the same as those in Fig. 1

Determination of dichromate

The working curve, detection limit and deviation

The Eq. (12) can also serve as the working curve for the analysis of dichromate anions in the concentration range of 1.0×10^{-6} – 1.0×10^{-2} M in aqueous solution with a detection limit of 1.0×10^{-7} M (signal to noise ratio of 3:1). The 5.00×10^{-5} M potassium dichromate was determined 8 times under the optimal conditions, the average potential difference was obtained as 0.2018 V, the standard deviation is 0.00695, and the relative standard deviation is 3.44 %.

Interference experiment

Some anions and cations were selected as the interference ions. CrO_4^{2-} and Cr^{3+} ions are the same element with different valences and forms. Cu^{2+} and Pb^{2+} ions are easy to form a precipitates with chromates. SO_4^{2-} is an anion with the same charge as chromate. Monovalent NO_3^- is a common anion, but it has been used as the electrolyte in the studies. The interference of these ions was investigated by the open circuit potential method. The molar ratios of the interference ions to $\text{K}_2\text{Cr}_2\text{O}_7$ (1.0×10^{-4} M) were chosen as 0.1:1, 1:1, 10:1, and 100:1. The experiments were performed under optimal conditions. The relative standard deviation (RSD) for the detection of dichromate in the presence of interference ions were obtained as listed in Table 1

The Cr^{3+} , Cu^{2+} , and SO_4^{2-} ions show a very little influence on the determination of $\text{Cr}_2\text{O}_7^{2-}$ with the maximum permissible molar ratio of 100:1. CrO_4^{2-} ion shows a small influence at the molar ratio below 1:1, but a larger influence with the increase of molar ratio from 10:1 to 100:1 due to the transformation between dichromate and chromate in strong acidic solution [21]. Pb^{2+} ion shows a great influence on the detection of dichromate anions due to the immediate formation of precipitation with dichromate and chromate anions.

The standard addition in domestic wastewater

The standard addition experiments were performed under the optimal conditions with the wastewater in the Shenyang Normal University campus. The dichromate ion was detected by the reported method. The average concentration of dichromate

Table 1 The effects of interference ions on the determination of dichromate

Molar ratio	CrO_4^{2-} (%)	Cr^{3+} (%)	Cu^{2+} (%)	SO_4^{2-} (%)	Pb^{2+}
0.1:1	0.30	0.10	0.05	0.08	18.90 %
1:1	4.80	0.20	0.20	2.50	56.90 %
10:1	35.80	3.40	1.20	3.70	–
100:1	48.51	4.80	2.30	4.75	–

was 10.52 μM ($n = 10$) with relative deviation of 3.0 %. The standard addition experiments in the wastewater with 10.0 μM standard dichromate solution, the average concentration were detected as 20.58 μM ($n = 10$), and the recovery was obtained in the range of 94.70–103.5 %.

Conclusions

As the summary of this paper, the solid phase microextraction and detection of dichromate at a pine needle powder-modified carbon paste electrode were studied by potentiometry. Some important results were obtained as follows.

1. Pine needles as an important natural biomaterial can be used in the modification of a carbon paste electrode for the solid phase microextraction of dichromate anions.
2. There are several species of Cr(VI), which transfer between them in acidic solution, and show a sharp response to solution pH, and interference with the detection of dichromate.
3. The microextraction process and the concentration of dichromate anions can be directly monitored by the open circuit potential method not only for extraction thermodynamics and kinetics but also for the detection of dichromate anions from solution.
4. The extraction–potentiometric method was proved to be a sensitive and a powerful method for the detection of dichromate anions in the concentration range of 1.0×10^{-6} – 1.0×10^{-2} M with the detection limit of 1.0×10^{-7} M, the relative standard deviation of 3.44 %, and standard addition recovery of 94.70–103.5 %.

Acknowledgments The author would like to acknowledge the financial support of the Chinese National Science Foundation (20875063), Liaoning education minister Foundation (2004-c022) and Shenyang Sciences and Technology Bureau Foundation (2007-GX-32).

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