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The electrochemical solid phase nano extraction of melamine on $Bi(OH)_3$ colloidal modified carbon paste electrode by cyclic voltammetry

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ABSTRACT

Electrochemical solid phase nano extraction (ESPNE) of melamine from aqueous solution on bismuth hydroxide colloidal modified carbon paste electrode was studied by cyclic voltammetry. The extraction kinetics under optimal conditions follows a Gaussian model. The initial potential serves as the pre-concentration of bismuth cations by negative electrode field with an apparent first-order rate constant of $0.0749 s^{-1}$, and is favorable for the final reduction of bismuth. The extraction thermodynamics follows Langmuir adsorption model with adsorption constant of 1.2852. The initial potential in the ESPNE process controls the oxidation state of the the extractent, bithmus hydroxide nano particles, and is fovorable for the extraction and monitoring processes.

KEYWORDS

Electrochemical solid phase nano extraction;
Melamine;
Bithmus hydroxide;
Carbon paste electrode;
Cyclic voltammetry.

INTRODUCTION

Melamine (2,4,6-triamino-1,3,5-triazine), as an important chemical raw material, has been widely used in the production of plastics[1-4], of finishers for paper[5], of flame retardant[6], and in the manufacture of wrinkle-free textiles[7] as well as nanomaterials[8-10]. Recent cases of the discovery of melamine in pet food, animal feed, milk and protein sources including wheat gluten, rice protein concentrate, and corn gluten created an urgent need for rapid methods for detecting melamine in food[11-13]. The common methods for detection of melamine has been recommended as GC/MS[14], LC/MS[15-16], as well as the specific antigen-antibody reaction and immune chromatography analysis technology[17-19]. Melamine is electrochemically inactive, and cannot be directly determined by electrochemical method. The key step in the electrochemical detection is the separation and pre-concentration of melamine from the complex systems on electrochemically active substance. Solid phase micro extraction (SPME) offers a green sample preparation method for the separation and pre-concentration of analyte[20, 21]. The combination of SPME with Electrochemistry and nano materials is called electrochemical solid phase nano extraction (ESPNE)[21], and had been used in the detection of inorganic and organic compounds in complex systems.

Electrochemically deposited bismuth electrodes have been widely used in electroanalytical chemistry[22], the well defined oxidation and reduction peaks of bismuth offers a chance for the indirectly determination of electrochemical inactive substance[23, 24].

In the present paper, The ESPNE of melamine on the $Bi(OH)_3$ colloidal nanoparticle modified carbon paste electrode was studied by cyclic voltammetry based redox behaviour of bismuth hydroxide. Some interesting results were reported here.

EXPERIMENTAL

Instruments and agents

The electrochemical experiments were carried out on an Electrochemical Analyzer (model CHI620, Shanghai Chen Hua Instrument Co.) with three-electrode system, a piece of platinum wire as counter electrode, a home-made solid state graphite-epoxy composite electrode as the working electrode, a KCl saturated calomel electrode (SCE) as the reference electrode. All potentials were reported here was respect to this reference electrode.

Bismuth nitrite, analytical pure, was prepared into 1.0mM stock solution for the modification of electrode. Potassium nitrate, analytical pure, was prepared into 1.0M stock solution as the electrolyte solution. Graphite powder (spectroscopy pure), silicon oil (analytical pure) were used as working electrode raw materials without further purifications. Disodium hydrogen phosphate and citric acid, analytical pure, were prepared into 0.2 mol/L for pH buffer solution in the range of 2.2-8.0. All solutions were prepared with ultrahigh pure water (>18.2 MΩ from mili-Q water system). All electrolyte solution was dearodezed with high purity nitrogen gas to remove oxygen prior to use.

The preparation of working electrode

The basic electrode was prepared as the previous described[21].

Bismuth nitrate colloidal solution was prepared by hydrolysis of 10 mM bismuth nitrate aqueous solution with slowly heating into a collosol.

The 1.0 mL collosol was diluted with water, and mixed with 1.0 g graphite powder in 50.0 mL beaker. The water in mixture was evaporated by heating the beaker and stirring with glass rod into a powder again, the bismuth hydroxide colloidal modified graphite powder was obtained.

The modified graphite powder was mixed with silicone oil at the weight ratio of 1:1 into a paste. The paste was filled into the cavity in the basic electrode, and polished on a glassy paper into mirror like-surface as the working electrode. The electrode can be easily renewed by replacing the used paste with new one.

RESULTS AND DISCUSSIONS

Cyclic voltammetric behavior of the modified electrode

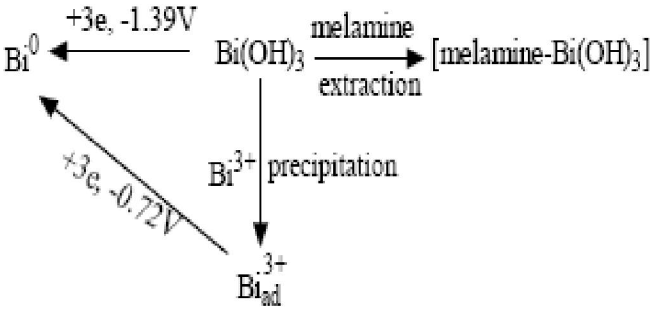
The electrodes including bismuth hydroxide colloidal modified carbon paste electrode were set into a 0.50 M KNO_3 electrolyte solution (pH 5.0). The cyclic voltametric experiments were performed in the potential range of -0.4 V—-1.6 V at accumulation time of 130 s and quiet time of 100 s, and the obtained CV curves were shown in Figure 1. The modified electrode shows two irreversible reduction peaks at -0.72 V (with the peak current of 64.81 μA) and -1.39V (with the peak current of 375.0 μA) in curve 1 of Figure 1. The later belongs to the reduction of bismuth in bismuth hydroxide, the former belongs to the bismuth ion adsorbed on the bismuth hydroxide during the precipitation process. The dissociation constant of bismuth hydroxide can be calculated from the reduction peak potentials of bismuth ion and bismuth hydroxide as 3.2×10^{-33}. The formation of the hydroxide needs the hydroxide ion the solution pH is about 6.0. The reduction peak current (i_{pc}/μA) at -1.39 V was plotted against scan rate ($v/(V.s^{-1})$), a straight linear was obtained with a regression equation of,

$$i_{pc}/\mu A=-12.40+531.8v/(V.s^{-1}) \quad (1)$$

The correspondence coefficient of R=0.9986, and standard deviation of SD=1.22 were obtained in the regression. This result indicates that the reduction process is a surface controlled one, and the bismuth hydroxide particles were well distributed on the surface of the electrode, while in an electrolyte solution including 1.0 μM melamine, a similar CV curve with two smaller reduction peaks was obtained as shown in curve 2 of Figure 1. The one at -0.72 V belongs to bismuth ion in solution decreases about 9.26 μA, but the one at -1.39 V decreases greatly about 166.7 μA.

Melamine is a polar molecule with three –N= atoms and three $-NH_2$ groups, and its pk_a=5.35[25]. at pH 6.0 the main form of melamine is nutrael one, which is likely to be interacted with hydroxide group by hydrogen bondings, and adsorbed or extracted on the surface of bismuth hydroxide nano particle surfaces from solution. This adsorption of melamine results in the inhibition of the bismuth in the bismuth hydroxide nano particles taking part in the electrochemical reduction, and results in the decrease of the reduction peak current at -1.39 V.

But the bismuth ion adsorbed at the bismuth hydroxide precipitate particles was only slightly influenced by the melamine. So the reduction peak current at -0.72 V only smaller decreased. So the electrochemical solid phase nano extraction mechanism of melamine on bismuth hydroxide nano particles may be described as the following,



Scheme 1 : The mechnism of melamine adsorption and bismuth redox reactions

The influence of the amount of extractant

The amount of nano particles of bismuth hydroxide in the colloidal solution is the important factor influencing the extraction, which is determined by the volume or concentration of the colloidal solution. In practice, 1.0 mL of the colloidal solution was used in the modification of 1.0 g graphite powder. The concentration of colloidal solution was controlled by dilution of the originally prepared colloidal solution with ultra pure water as ratio of the dilution. The CV experiments were performed at 0.10V/s scan rate with the carbon paste electrode of different ratio of dilution in electrolyte solution. The obtained reduction peak current at -1.39V was plotted against the logarithm of dilution ratio. A one-peak curve with the peak point located at logR=4.0 was obtained as shown in Figure 2.

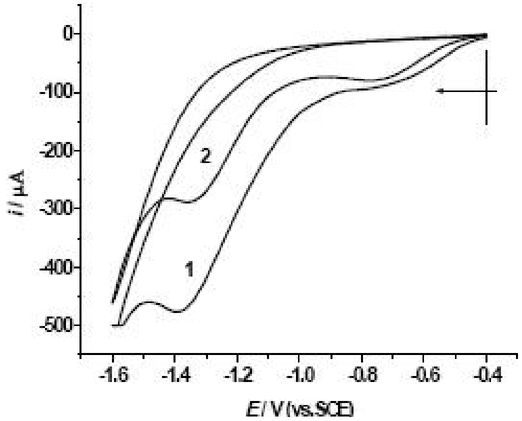


Figure 1 : The CV curves of bismuth hydroxide modified carbon paste electrode in 0.50M KNO_3 electrolyte solution with (2) and without melamine (1). The at the accumulation time of 130s initial potential of -0.40V for 100s; and the melamine concentration of 1.0μM; solution pH: 5.0.

This result indicates that the original colloidal solution was diluted for 10^4 times, and then modified on 1.0 g graphite powder surface for the extraction of melamine, which can gives out effective reduction peak current of the bismuth hydroxide nano particles. The increase of R will decreases the amount of nano particle for the solid phase extraction, but decrease of R will increase of nano particles, which may increase the amount of sites for solid phase extraction, but decrease the efficiency of the reduction of bismuth hydroxide during the interaction and aggregation of the nano particles. In practice, $R=10^4$ was chosen as the optimal amount of extractant.

The effect of solution pH

Solution pH is another important factor, especially in the case of metal hydroxide as the solid phase extractant. The solution pH was controlled by phosphate buffer system (PBS) in the range of 3.0-8.0. The CV experiments were performed as before in the solution with different solution pH, the obtained reduction peak current was plotted against solution pH, and a curve was obtained with the peak point at pH 5.0 as shown in Figure 3. In practice, pH 5.0 was chosen as the optimal solution pH.

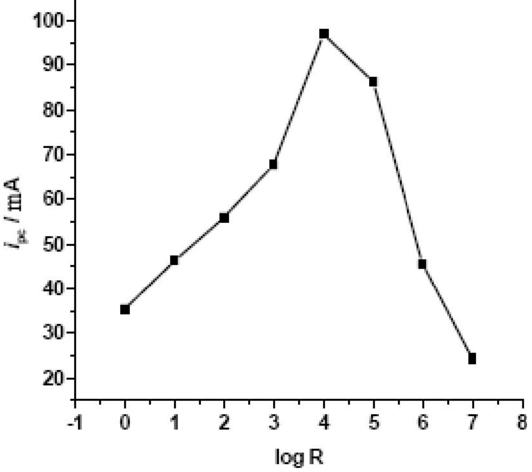


Figure 2 : The relationship between reduction peak current and diluted ratio of bismuth hydroxide colloidal solution. The other experimental conditions were the same as those in Figure 1.

The extraction dynamics of melamine

The modified electrode was set in 0.50 M KNO_3

(pH 5.0) electrolyte solution including 1.0×10^{-6} M melamine, and CV experiments were performed at initial potential of -0.40V for quiet time of 100 s and scan rate of 0.10V/s after extraction for different time. The obtained reduction peak current plotting against extraction time was a sigmoidial curve as shown in Figure 4.

The curve was regressed as a Gaussian model with a regression equation of,

$$\mathbf{i_{pc} = 58.96\times\exp\left[-\frac{(t+7.704)^2}{3428}\right]} \qquad (2)$$

R=0.992, SD=2.15

This means that the extraction of melamine on the surface of bismuth hydroxide particles follows a Gaussian model, and was controlled by interaction energy of the adsorption sites. In this step melamine and bismuth hydroxide strongly interacted by $^{+}NH_3$-OH or OH-NH_2 hydrogen bandings, which decreases the reduction activity of bismuth hydroxide, and corespondence with the results in Figure 1. In practice, the optimal extraction time was set at 40 s.

The extraction dynamics with initial potential

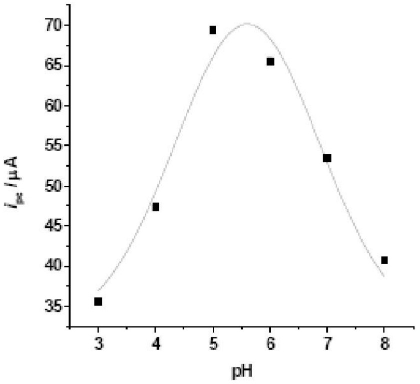


Figure 3 : The relationship between reduction peak current and solution pH. The other experimental conditions were the same as those in Figure 1.

Quiet time is the time interval between applying initial potential to the electrodes and the beginning of potential scan. If the extraction is related to the initial potential then the quiet time will greatly influenced the peak current of bismuth hydroxide. The modified electrode was set in 0.50 M KNO_3 (pH 5.0) electrolyte solution including 1.0×10^{-6} M melamine, then CV experiments were performed from the initial potential of -0.40V for different quiet time of 2-110 s at scan rate of 0.10V/s. The obtained reduction peak current plotting against quiet time, and a sigmoidial curve was obtained as shown in Figure 5.

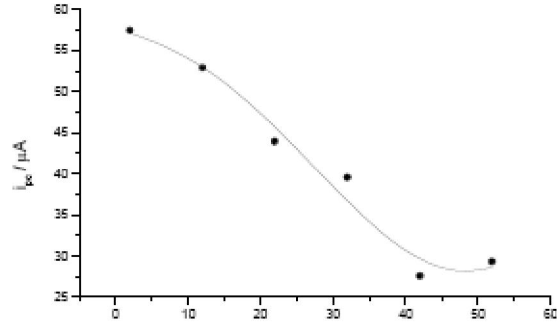


Figure 4 : The relationship between reducion peak current and extraction time. The other experimental conditions were the same as those in Figure 1.

The curve was regressed a boltzman function of,

$$\mathbf{i_{pc} / \mu A = 58.4 - \frac{41.1}{1+\exp\left[\frac{-(t/s-54.7)}{13.35}\right]}} \qquad (4)$$

X^2=1.027. The apparent first order rate constant was obtained as 0.075 s^{-1}. From Figure 1, it can be seen that the negative initial potential of -0.40 V is before the first reduction peak at -0.72 V, which may collect the bismuth cation aroound graphite powder by electric field, and increase the reduction peak current at -1.39 V. The optimal quiet time was chosen as 100s.

The thermodynamics of the extraction

Under the optimal conditions, the extraction of melamine on the surface of bismuth hydroxide nano particles at different melamine concentration was monitored by cyclic voltammetry. The surface coverage at ith step can be obtained from the reduction peak current at different melamine concentration as,

$$\mathbf{\theta_i = \frac{i_{pc,0} - i_{pc,i}}{i_{pc,0}}} \qquad (5)$$

Here $i_{pc,0}$ was the reduction peak current without melamine (375 μA), $i_{pc,i}$ was in the ith step with melamine concentration of c_i. The extraction isothermal equation was the plot of θ against concentration of melamine as shown in Figure 6.

The curve was regressed as an extended Langmuir adsorption equation[26],

$$\theta = \mathbf{\frac{1}{(0.3859 + 1.2852c^{(0.9466-1)})}} \qquad (6)$$

R=0.9993,SD=6.07×10^{-3}

From the regression equation (7), it can be seen, the adsorption constant, b=1.2852>1, which means the adsorption of melamine on bismuth hydroxide surface is thermodynamic favourable adsorption, and occurs

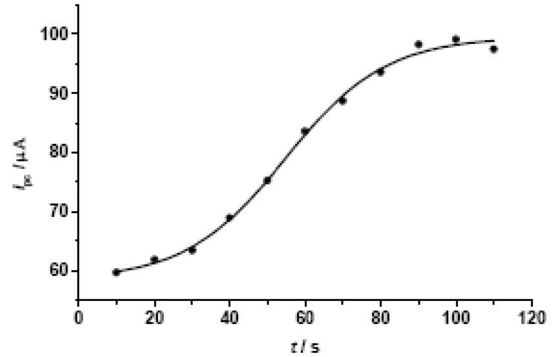


Figure 5 : The relationship between reducion peak current and quiet time . The other experimental conditions were the same as those in Figure 1.

automatically.

CONCLUSIONS

As a summary of this work, a carbon paste electrode was modified by bismuth hydroxide colloidal as a solid phase nano extractant extracting melamine from aqueous solution with the help of electrochemistry. The melamine extraction was carried out in pH 5.0 aqueous solution. The extraction including diffusion controlled physical adsorption and hydrogen bonding related chemical adsorption, and follows extended Longmuir adsorption model in the isothermal equation. The initial potential serves as the pre-concentration of the bismuth ion, and increases the activity of the final reduction of bismuth hydroxide. The chemical carbon paste electrode was proved as a new plantform for electrochemical solid phase nano extraction and electrochemical determination of electrochemically inactive species in solutions.

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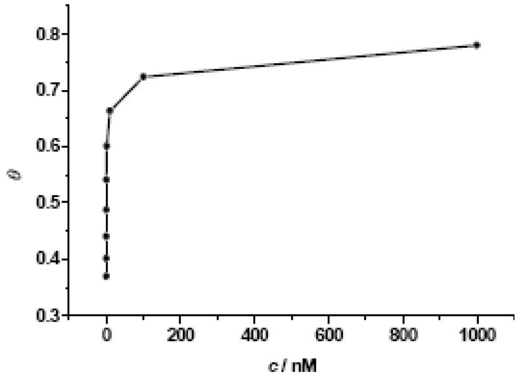

Figure 6 : The relationship between surface coverage and melamine concentration. The other experimental conditions were the same as those in Figure 1.

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