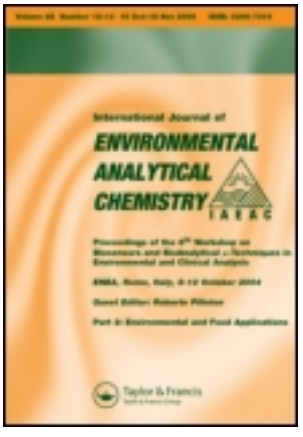

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An electrochemical sensor for p-aminophenol based on the mesoporous silica modified carbon paste electrode

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An electrochemical sensor for *p*-aminophenol based on the mesoporous silica modified carbon paste electrode

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A mesoporous silica was synthesised and used to modify the surface of carbon paste electrode (CPE). The electrochemical behaviours of *p*-aminophenol were investigated. Compared to the unmodified CPE, the mesoporous silica-modified CPE obviously lowers the oxidation potential of *p*-aminophenol, and remarkably increases its oxidation peak current. The effects of pH value, amount of mesoporous silica, accumulation potential and time were examined. As a result, a sensitive, rapid and convenient electroanalytical method was developed for *p*-aminophenol. The linear range is from 0.025 mg L^{-1} to 3 mg L^{-1}, and the limit of detection is 0.01 mg L^{-1} after 2-min accumulation. Finally, the method was successfully used to determine *p*-aminophenol in water samples.

Keywords: aminophenol; detection; mesoporous silica; electrochemical sensor

1. Introduction

p-Aminophenol is a commercially important intermediate for the manufacture of analgesic and antipyretic drugs. Otherwise, it is also widely used in photography and chemical dye industries. Because its structural is similar to aniline and phenol, *p*-aminophenol is considered as a highly toxic pollutant. Therefore, it is important to develop rapid and sensitive method for the determination of *p*-aminophenol.

Until now, various methods have been reported for the determination of *p*-aminophenol, including spectrophotometry [1–5], quartz crystal microbalance sensor [6], high-performance liquid chromatography [7,8], capillary electrophoresis [9], chemiluminescence [10] and fluorescence [11]. Due to its high sensitivity, short analysis time, field-deployability, low power consumption and inexpensive equipment, electrochemical determination has received much attention and has been widely used in environmental monitoring. *p*-Aminophenol is electrochemical active, so electrochemical methods such as single-wall carbon nanotube film-modified electrode [12] were also reported for its determination. However, to the best of our knowledge, electrochemical determination of *p*-aminophenol using mesoporous silica-modified electrode has not been reported.

Since the first discovery of mesoporous silica in 1992 [13], the interest in this field has expanded all over the world. With the characteristics such as highly uniform porous channels, large surface area, narrow pore-size distribution, tunable pore sizes over a wide range, and so on, mesoporous materials have obtained wide applications in catalysis as

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well as in other realms of chemistry [14–18]. We first developed a sensitive and rapid electroanalytical method for *p*-aminophenol using the excellent properties of mesoporous silica. At the mesoporous silica-modified electrode, the oxidation signals of *p*-aminophenol remarkably increase. Therefore, the sensitivity of determination of *p*-aminophenol is greatly improved when using mesoporous silica. Compared with other reported methods for *p*-aminophenol, this new method exhibits high sensitivity, rapid response and excellent simplicity.

2. Experimental

2.1 *Reagents*

All the chemicals were of analytical grade and used directly without purification. *p*-Aminophenol, *o*-aminophenol, *m*-aminophenol, cetyltrimethylammonium bromide (CTAB), tetraethyl orthosilicate (TEOS), graphite powder and paraffin oil were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China).

2.2 *Instruments*

All the electrochemical measurements were carried out using CHI 650B Electrochemical Workstation (Chenhua Instrument Co., Shanghai, China). A conventional three-electrode system, consisting of a mesoporous silica-modified carbon paste working electrode, a saturated calomel reference electrode (SCE) and a platinum wire auxiliary electrode, was employed.

Scanning electron microscopy (SEM) was performed with a FEI-Quanta 200 microscope.

2.3 *Synthesis of mesoporous silica*

Mesoporous silica was synthesised according to the published work using CTAB as the template [19]. A solution of CTAB in NaOH solution was prepared and stirred at 298 K. After that, the silica source (TEOS) was added to this solution under stirring to give gel mixture with following molar compositions: 1 SiO_2/0.25 NaOH/0.1 CTAB/100 H_2O. After 30 min of stirring at 298 K, the mixture was sealed and heated at 343 K for 24 h under the static conditions. The resulting solid precipitate was recovered by filtration, washed with redistilled water and dried at 80°C overnight. Finally, the dried solid precipitate was calcined at 823 K for 6 h to remove CTAB.

The morphology and the grain size of synthesised mesoporous silica were characterised using SEM, which is shown in Figure 1. From the SEM image, it is very clear that the synthesised mesoporous silica is composed of well-dispersed spherical nanoparticles, and the diameter is about 15–25 nm. Furthermore, the specific surface area (S), pore volume (V) and pore diameter (D) of mesoporous silica were measured using nitrogen sorption isotherms. The values of S, V and D are 826 $m^2 g^{-1}$, 0.59 mL g^{-1} and 3.4 nm, suggesting that the synthesised mesoporous silica possesses large surface area and specific mesoporous channels.

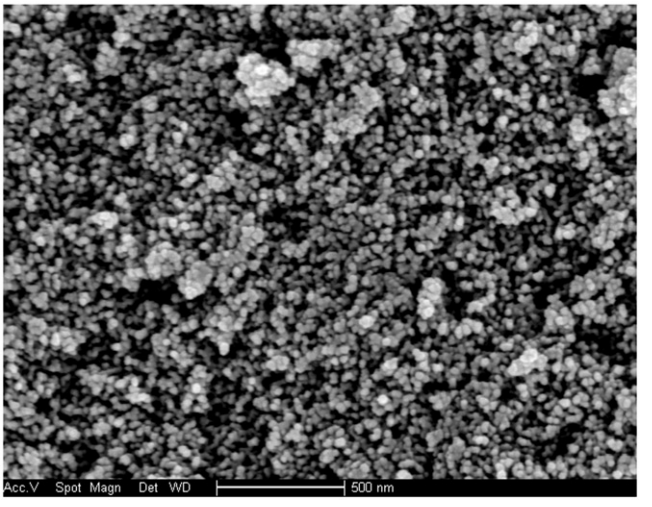


Figure 1. SEM image of mesoporous silica.

2.4 *Preparation of mesoporous silica sensor*

The synthesised mesoporous silica (0.15 g) was mixed with graphite powder (0.85) and paraffin oil (0.3 mL) to give a homogenous mesoporous silica-modified carbon paste. After that, the resulting carbon paste was pressed into the end cavity (3-mm in diameter) of the electrode body, and the surface was polished using a smooth paper. The carbon paste sensor was prepared according to the same procedure but without mesoporous silica.

2.5 *Analytical procedure*

Unless otherwise stated, pH 5.6 HAc-NaAc buffer ($0.1\,\mathrm{mol\,L^{-1}}$) was used as the supporting electrolyte for the determination of *p*-aminophenol. After 2-min accumulation, the differential pulse voltammetry (DPV) curves were recorded with the following parameters: pulse amplitude = 50 mV, pulse width = 40 ms, scan rate = $40\,\mathrm{mV\,s^{-1}}$. Finally, the oxidation peak current at 0.11 V was measured for *p*-aminophenol.

3. Results and discussion

3.1 *Electrochemical behaviours of p-aminophenol*

The electrochemical behaviours of *p*-aminophenol at CPE and mesoporous silica-modified CPE were examined using cyclic voltammetry (CV). Figure 2 depicts the cyclic voltammograms of *p*-aminophenol in pH 5.6 HAc-NaAc buffer. At the unmodified CPE (curve a), a pair of redox peak was observed during the cyclic sweep from −0.30 V to 0.50 V. The oxidation peak potential (E_{pa}) is 0.37 V, and the reduction peak potential (E_{pc}) is 0.08 V. So, the peak potential separation ($\Delta E_p = E_{pa} - E_{pc}$) is as large as 290 mV, suggesting that the reversibility of oxidation of *p*-aminophenol is very poor at the unmodified CPE. However, the oxidation peak of *p*-aminophenol shifts negatively to 0.18 V, and the reduction peak shifts positively to 0.14 V at the mesoporous silica-modified CPE (curve b). The value of ΔE_p decreases to 40 mV, clearly indicating that the oxidation

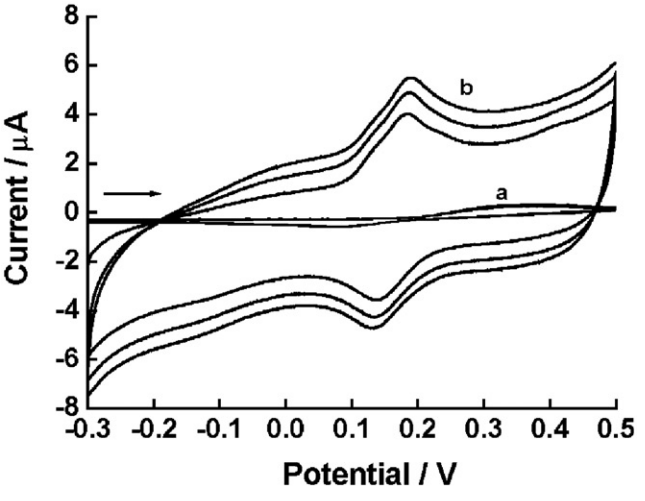


Figure 2. Cyclic voltammograms of 2 mg L^{-1} *p*-aminophenol in pH 5.6 HAc-NaAc buffer at CPE (a) and mesoporous silica-modified CPE (b). Scan rate: 100 mV s^{-1}.

of *p*-aminophenol becomes more reversible at the mesoporous-modified CPE. According to Nicholson's theory [20], the decrease of ΔE_p indicates that the electron transfer rate increases. So, the electron transfer rate of *p*-aminophenol greatly increases at the mesoporous silica-modified CPE, indicative of highly efficient catalytic activity.

In addition, it was found that the oxidation peak current of *p*-aminophenol remarkably increases at the mesoporous silica-modified CPE. This suggests that mesoporous silica possesses notable surface enhancement effect to *p*-aminophenol. Mesoporous silica has specific mesoporous channels, large surface area and numerous active sites; therefore, mesoporous silica-modified CPE exhibits high accumulation efficiency to *p*-aminophenol, greatly improving the surface concentration as well as the oxidation signals of *p*-aminophenol.

3.2 *DPV responses of low concentration of p-aminophenol*

In order to develop an analytical method for trace levels of *p*-aminophenol, the electrochemical responses of low concentration of *p*-aminophenol at CPE and mesoporous silica-modified CPE were studied using DPV. Figure 3 shows the DPV curves of 0.2 mg L^{-1} *p*-aminophenol in pH 5.6 HAc-NaAc buffer. At the unmodified CPE (curve a), a very small oxidation peak appears at 0.21 V. The negligible oxidation signals indicate that the determining sensitivity of *p*-aminophenol is very poor at the unmodified CPE. However, a very sensitive oxidation peak is observed at the mesoporous silica-modified CPE (curve c). The oxidation peak potential shifts negatively to 0.11 V, and the oxidation peak current remarkably increases. Therefore, the mesoporous silica-modified CPE greatly improves the sensitivity of detection of *p*-aminophenol. Otherwise, the DPV curves of mesoporous silica-modified CPE in pH 5.6 HAc-NaAc buffer without *p*-aminophenol were also given in curve (b) for better comparison. The blank curve is smooth and no oxidation peak appears, revealing that the oxidation peak in curve (c) is attributed to *p*-aminophenol.

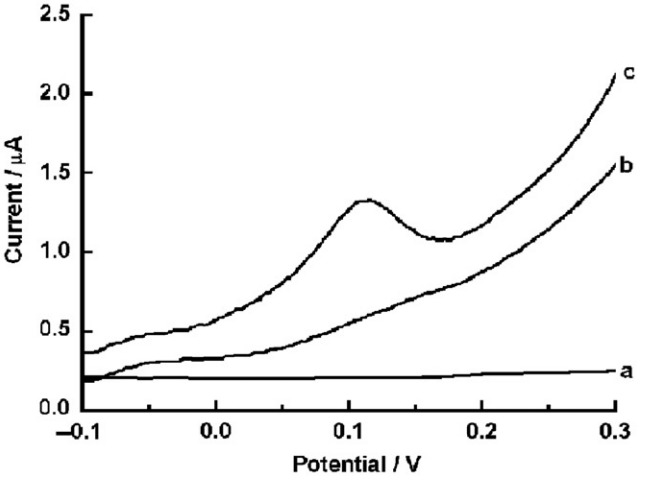
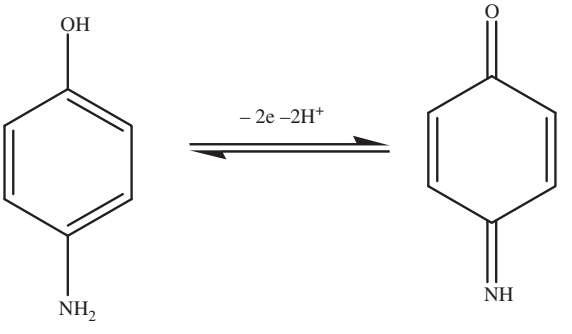


Figure 3. DPV curves of 0.2 mg L^{-1} *p*-aminophenol in pH 5.6 HAc-NaAc buffer at CPE (a) and mesoporous silica-modified CPE (c). (b): blank DPV curves of mesoporous silica-modified CPE. Pulse amplitude: 50 mV, pulse width: 40 ms, scan rate: 40 mV s^{-1}, accumulation time: 2 min.

3.3 *Optimisation of detection*

The oxidation behaviours of *p*-aminophenol in different supporting electrolytes were investigated. The supporting electrolytes include pH 3.6, 4.0, 4.6, 5.0, 5.6 HAc-NaAc buffer, pH 6.0, 6.5, 7.0, 7.5, 8.0 phosphate buffer (each 0.1 mol L^{-1}). Figure 4 describes the effect of pH value on the oxidation peak current of *p*-aminophenol at CPE (a) and mesoporous silica-modified CPE (b). When gradually increasing pH value from 3.6 to 5.6, the oxidation peak current of *p*-aminophenol gradually increases. When further improving the pH value from 5.6 to 8.0, the oxidation peak current of *p*-aminophenol gradually decreases. Therefore, the pH 5.6 buffer was employed for the determination of *p*-aminophenol since the oxidation signal is highest. Otherwise, it was found that the pH value also affects the E_{pa} of *p*-aminophenol. When increasing pH value from 3.6 to 8.0, the E_{pa} shifts linearly to more negative potential. The slope is −56.3 mV/pH, revealing that protons are involved in the oxidation of *p*-aminophenol, and the number of protons and electrons is equal. From the CV responses, we know that the ΔE_p of *p*-aminophenol is 40 mV at mesoporous silica-modified CPE, indicating that two electrons take part in the oxidation of *p*-aminophenol. Therefore, the oxidation of *p*-aminophenol involves two electrons and two protons, which can be described with following mechanism:



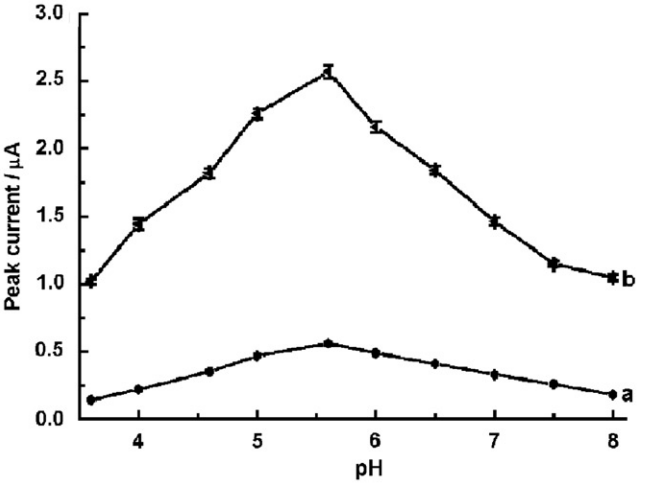


Figure 4. Effect of pH value on the oxidation peak current of 2 mg L^{-1} *p*-aminophenol at CPE (a) and mesoporous silica-modified CPE (b).

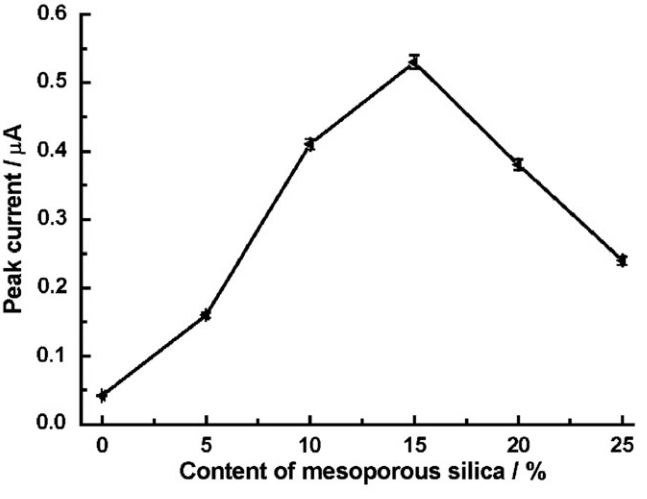


Figure 5. Influence of content of mesoporous silica on the oxidation peak current of 0.2 mg L^{-1} *p*-aminophenol. Other conditions are the same as in Figure 3.

The influence of mass content of mesoporous silica on the oxidation peak current of *p*-aminophenol was examined, which is shown in Figure 5. When the mass content of mesoporous silica gradually improves from 0 to 15%, the oxidation peak current of *p*-aminophenol remarkably increases. On increasing the amount of mesoporous silica, the effective surface area and accumulation efficiency also improve. As a result, the surface concentration of *p*-aminophenol at mesoporous silica sensor greatly increases, leading to considerable peak current enhancement. However, the oxidation peak current of *p*-aminophenol gradually decreases when further improving the mass content from 15% to 25%. Thus, the mass content of mesoporous silica is selected as 15%.

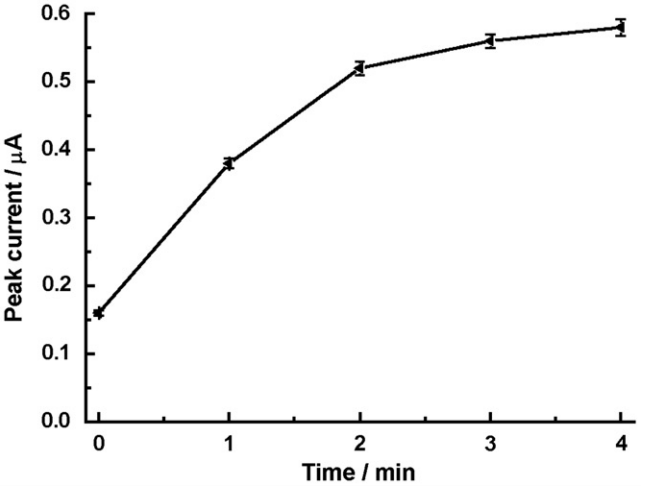


Figure 6. Effect of accumulation time on the oxidation peak current of 0.2 mg L^{-1} *p*-aminophenol. Other conditions are the same as in Figure 3.

The oxidation peak currents of 0.2 mg L^{-1} *p*-aminophenol under different accumulation potentials were measured to assess the influence of accumulation potential. It was found that the oxidation peak current changes slightly when altering accumulation potential, revealing that accumulation potential has no influence. So, the accumulation step was performed under the initial potential for the sake of convenience.

Figure 6 shows the influence of accumulation time on the oxidation peak current of *p*-aminophenol at the mesoporous silica sensor. On extending the accumulation time from 0 to 2 min, the oxidation peak current of *p*-aminophenol remarkably increases. This suggests that accumulation can obviously improve the determining sensitivity of *p*-aminophenol. When further improving the accumulation time from 2 min to 4 min, the oxidation peak current of *p*-aminophenol increases slightly. Considering sensitivity and working efficiency, 2-min accumulation was employed.

3.4 *Analytical properties of mesoporous silica sensor*

3.4.1 *Reproducibility*

The mesoporous silica sensor was used for single measurement because the surface sorption is strong. The precision between multiple mesoporous silica sensors was estimated by determining the response of 0.2 mg L^{-1} *p*-aminophenol. The relative standard deviation (RSD) is 5.6% for 10 sensors, revealing that this method has good reproducibility.

3.4.2 *Linear range and limit of detection*

Under the optimal conditions, the linear range for *p*-aminophenol was examined using DPV after 2-min accumulation. The oxidation peak current of *p*-aminophenol (i_{pa}) is proportional to its concentration (C) over the range from 0.025 mg L^{-1} to 3 mg L^{-1}, obeying the following equation: $i_{pa} = 0.0194 + 2.503\ C$ (i_{pa} in μA, C in mg L^{-1}, correlation

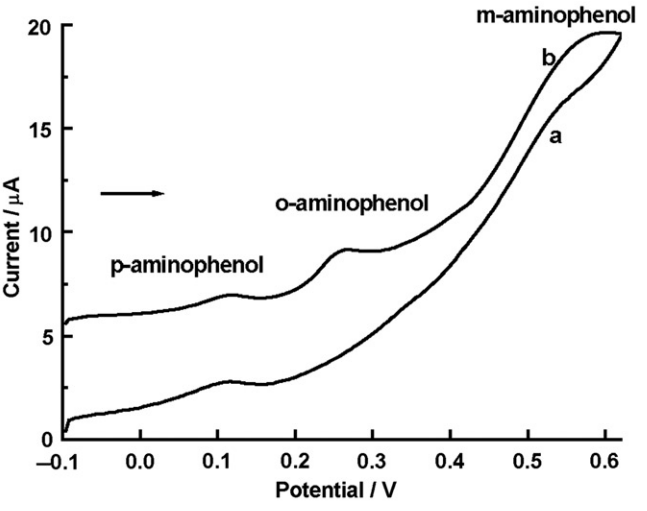


Figure 7. DPV responses of 0.1 mg L^{-1} *p*-aminophenol at mesoporous silica-modified CPE (a). (b): (a) + 5.0 mg L^{-1} *o*-aminophenol and *m*-aminophenol.

Table 1. Interferences on the determination of 0.2 mg L^{-1} *p*-aminophenol.

Interferent	Tolerance level (mg L^{-1})
Cu^{2+}, Fe^{3+}, Al^{3+}, Ni^{2+}, Pb^{2+}	200
m-Aminophenol, O_2, H_2O_2	100
o-Nitrophenol, *m*-nitrophenol, *p*-nitrophenol, ascorbic acid	50
o-Chlorophenol, *m*-chlorophenol, *p*-chlorophenol	40
Phenol	30
o-Aminophenol	20

coefficient = 0.996). Additionally, the limit of detection after 2-min accumulation was evaluated to be 0.01 mg L^{-1} based on 3 signal to noise ratio.

3.4.3 *Interferences*

The electrochemical behaviours of *o*-aminophenol, m-aminophenol and *p*-aminophenol in pH 5.6 HAc-NaAc buffer were studied using DPV. In the absence of *o*-aminophenol and *m*-aminophenol, an oxidation peak at 0.11 V is observed for *p*-aminophenol at the mesoporous silica sensor (Figure 7a). After addition of high concentration of o-aminophenol and *m*-aminophenol, another two oxidation peaks were observed at 0.26 V and 0.58 V (Figure 7b). This phenomenon suggests that the oxidation of o-aminophenol, *m*-aminophenol and *p*-aminophenol is independent at the mesoporous silica sensor.

The potential interferences of other compounds on the determination of *p*-aminophenol were estimated, which are shown in Table 1. It was found that 1000-fold concentrations of Cu^{2+}, Fe^{3+}, Al^{3+}, Ni^{2+}, Pb^{2+}; 500-fold concentrations of *m*-aminophenol, O_2, H_2O_2; 250-fold concentrations of *o*-nitrophenol, *m*-nitrophenol, *p*-nitrophenol, ascorbic acid; 200-fold

Table 2. Determination of *p*-aminophenol in water samples.

Water sample	Spiked/mg L^{-1}	Expected/mg L^{-1}	Found/mg L^{-1}	RSD ($n = 5$)	Recovery
Sample A	0.00		0.0724		
	0.100	0.1724	0.1805	4.3%	104.7%
Sample B	0.00		0.00		
	0.0750	0.0750	0.0714	3.7%	95.2%
Sample C	0.00		0.0561		
	0.0500	0.1061	0.0976	4.1%	92.0%
Sample D	0.00		0.00		
	0.100	0.1000	0.0982	4.6%	98.2%

concentrations of *o*-chlorophenol, *m*-chlorophenol, *p*-chlorophenol; 150-fold concentrations of phenol; 100-fold concentrations of *o*-aminophenol – almost have no influence on the determination of 0.2 mg L^{-1} *p*-aminophenol when the peak current change is lower than 10%.

3.5 *Analytical application*

To demonstrate its suitability and potential for sample analysis, the proposed method was used to determine *p*-aminophenol in different river water samples, which were collected from different rivers of Wenzhou City. Prior to analysis, the collected water samples were filtered under vacuum through 0.45-μm cellulose acetate membranes. Each sample solution undergoes five parallel detections with acceptable RSD. The concentration of *p*-aminophenol in water samples was obtained by the standard addition method, and the results are listed in Table 2. In addition, the accuracy was evaluated by performing a recovery test after spiking the samples. The recovery is between 92% and 104.7%, indicating that determination of *p*-aminophenol using mesoporous silica sensor is accurate and feasible.

4. Conclusion

Because of its distinctive properties such as large surface area, specific mesoporous networks and high sorption capacity, mesoporous silica exhibits highly efficient catalytic activity to the electrochemical oxidation of *p*-aminophenol. At mesoporous silica-modified CPE, the oxidation peak potential of *p*-aminophenol considerably decreases, and the oxidation signals remarkably increase. Therefore, the sensitivity of determination of p-aminophenol is greatly improved when using mesoporous silica. Compared with other published methods, this new method possesses high sensitivity, short analysis time and promising application. Moreover, mesoporous silica can be used to prepare portable and disposable electrochemical sensor for in-situ detection of *p*-aminophenol when employing screen printing technology.

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References

[1] Y.S. Cao, Y.W. Chen, J.F. Zu, J.L. Zhu, X.C. Xu, and R.M. Cheng, Spectrosc. Spectr. Anal. **23**, 751 (2003).
[2] H. Filik, M. Hayvali, and E. Kilic, Anal. Chim. Acta **535**, 177 (2005).
[3] S.D. Cekic, H. Filik, and R. Apak, J. Anal. Chem. **60**, 1019 (2005).
[4] H. Filik and A. Tavman, J. Anal. Chem. **62**, 530 (2007).
[5] M.A. Karimi, M.R. Nateghi, M. Malekzadeh, F. Banifatemeh, and O. Moradlou, Asian J. Chem. **19**, 4533 (2007).
[6] N.G. Karousos and S.M. Reddy, Analyst **127**, 368 (2002).
[7] E. Wyszecka-Kaszuba, M. Warowna-Grzeskiewicz, and Z. Fijalek, J. Pharm. Biomed. Anal. **32**, 1081 (2003).
[8] M.S. Ali, S. Rafiuddin, M. Ghori, and A.R. Kahtri, J. AOAC Int. **90**, 82 (2007).
[9] Q.C. Chu, L.M. Jiang, X.H. An, and J.N. Ye, Anal. Chim. Acta **606**, 246 (2008).
[10] H. Xu, C.F. Duan, Z.F. Zhang, J.Y. Chen, C.Z. Lai, M. Lian, L.J. Liu, and H. Cui, Water Res. **39**, 396 (2005).
[11] Y.G. Zhu, F. Gao, L. Zhang, X.J. Xie, and L. Wang, Chinese J. Anal. Chem. **33**, 743 (2005).
[12] W.S. Huang, W.B. Hu, and J.C. Song, Talanta **61**, 411 (2003).
[13] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, and J.L. Schlenker, J. Am. Chem. Soc. **114**, 10834 (1992).
[14] K. Landskron and G.A. Ozin, Science **306**, 1529 (2004).
[15] Z.X. Yang, Y.D. Xia, and R. Mokaya, J. Am. Chem. Soc. **129**, 1673 (2007).
[16] Y.H. Zeng, J.Q. Yang, and K.B. Wu, Electrochim. Acta **53**, 4615 (2008).
[17] K.M.L. Taylor, J.S. Kim, W.J. Rieter, H. An, W. Lin, and W. Lin, J. Am. Chem. Soc. **130**, 2154 (2008).
[18] H.G. Lin, T. Gan, and K.B. Wu, Food Chem. **113**, 701 (2009).
[19] A. Galarneau, M. Cangiotti, F. Renzo, F. Fajula, and M.F. Ottaviani, J. Phys. Chem. B **110**, 4058 (2006).
[20] R.S. Nicholson, Anal. Chem. **37**, 1351 (1965).