

Determination of Nitrobenzene in Wastewater Using a Hanging Mercury Drop Electrode

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Received: 24 November 2005 / Accepted: 28 June 2006 / Published online: 21 October 2006
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Abstract The determination of trace amount nitrobenzene in wastewater on a hanging mercury drop electrode was studied. The determination conditions of pH, supporting electrolyte, accumulation potential, accumulation time, and voltammetric response were optimized. The sharp peak of the nitrobenzene was appeared at 0.05 V. The peak electric current was proportional to the concentration of nitrobenzene in the range of $1.47 \times 10^{-5} \sim 1.0 \times 10^{-3}$ mol/l with relative standard deviations of 3.99 ~ 8.94%. The detection limit of the nitrobenzene in water was 5×10^{-6} mol/l. The proposed method offered low limit of determination, easy operation, the use of simple instrumentation, high sensitivity and good reproducibility. It was applied to the determination of nitrobenzene in wastewater with an average recovery of 94.0% ~ 105%. The proposed method provided fast, sensitive and sometimes real time detection of nitrobenzene.

Keywords Determination · Hanging mercury drop electrode · Linear scan voltammetry · Nitrobenzene · Wastewater

1 Introduction

Nitrobenzene (NB) is an important raw material and product in the chemical industry, which has been widely used as intermediates in the preparation of dyes, perfumes, synthetic resins, pesticides, pharmaceuticals and so on (Wang & Chen, 2002). It has been estimated that about 19 million pounds of nitrobenzene is released into the environment annually. There are several probable sources for nitrobenzene in different matrices including oil spills, industrial and municipal effluents, and atmospheric input. Because of the toxicity of nitrobenzene and its ubiquitous existence in the environment, it results in the pollution of the environment and affects the up-growth of animals and the health of man. It causes vomiting, skin and eye irritation, and headache. Its continuous exposure leads to liver damage and anemia. If the concentration in the waste exceeds 2 mg l^{-1} then the waste could be declared as hazardous waste. Because of its toxicity, nitrobenzene has been placed as one of the 129 priority pollutants (Zhao, Yang, & Gao, 2003; Majumder & Gupta, 2003).

Hitherto, many investigations have been carried out to quantify nitrobenzene. These studies show that nitrobenzene is ubiquitous in natural environment and organisms of many animals and human beings. Analyses of nitrobenzene in wastewaters have received considerable attention. Various methods have been reported for the determination of nitrobenzene by high

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performance liquid chromatography (HPLC) (Wang & Chen, 2002), gas chromatography (GC) (Nishikawa & Okumura, 1995; Patil & Lonkar, 1994) and UV–visible spectrophotometry (Chen, Liang, Xun, & Wang, 1998). However, some sample pre-treatment involving separation, extraction and/or adsorption are generally necessary, and these can be time-consuming and complex.

Different electrochemical analytical techniques, such as anodic stripping voltammetry (ASV), differential pulse voltammetry (DPV) and differential pulse polarography (DPP), have been widely applied for the determination of pharmaceuticals, dyes, insecticides and pesticides. ASV was employed for the determination of phenol at an electrochemically pretreated carbon-paste electrode (Wang, Zhang, Cui, Liu, & Liu, 1998). DPV was used for determination of trace amounts of various compounds, such as nitrobenzene (Ni, Wang, & Kokot, 2001), 2-nitrophenol (Ignacio, Juan, & Jose, 1997) and 4-nitrophenol (Hu, Xu, Wang, & Cui, 2001). Ratio DPP was applied for the quantitation of *p*-nitroaniline and *p*-nitrotoluene in their mixture (Grabaric, Grabaric, Esteban, & Casassas, 1997). Adsorptive polarography was also used for determination of phenol (Zhang, Zhang, & Deng, 2000). In this paper, linear scan voltammetry (LSV) is investigated for the determination of nitrobenzene in wastewater.

2 Experimental

2.1 Apparatus

The experiments were performed using a MEC-12B microcomputer-controlled multimode electrochemical analyzer with a MEC-12B pulsator and a three electrodes set-up (Jiangsu JiangFen Electroanalytical Instrument Company, Ltd.). The working electrode was a hanging mercury drop electrode (HMDE). An Ag/AgCl electrode with saturated KCl, and a platinum wire was used as a reference and a counter electrode, respectively. The software package (MEC-12B multi-function microcomputer electrochemical analyzer system) worked through a personal computer with data acquisition routine. Repetitions of voltammetric measurements for each nitrobenzene concentration were automatically controlled with a computer

program in order to achieve good statistics of the measurements.

2.2 Reagents and solutions

The stock solutions of $9.788 \times 10^{-2} \text{ mol l}^{-1}$ nitrobenzene solution was prepared by moving 0.1 ml nitrobenzene and dissolving it in 9.9 ml anhydrous ethanol.

A potassium hydrogen phthalate ($\text{C}_8\text{O}_4\text{HK}$)–sodium hydroxide (NaOH) buffer solution of $\text{pH} = 5.2$ was prepared by adding 29.75 ml of 0.2 mol l^{-1} sodium hydroxide solution into 25 ml of 0.4 mol l^{-1} potassium hydrogen phthalate solution. This solution was diluted to 100 ml. All reagents were of analytical reagent grade and ultra-pure water was used for dilution.

2.3 Experimental mechanism

The operation sequence of linear scan voltammetry divides into two stages. First, the electrolyte is pre-electrolyzed and concentrated in the permanent electric potential. Second, after a few moments (30 ~ 60 s), the matter concentrating on the electrode dissolves again, scanning from the negative electric potential to more positive electric potential. If the electric potential of the electrode is a linear change with time, then the electric current takes the form of peak.

2.4 Procedures

10 ml buffer solution of $\text{pH} = 5.2$ and 10 ml wastewater were transferred into an electrochemical cell. After the solution (20 ml) was prepared in an electroanalytical cell, prior to electrochemical measurements, it was deaerated by bubbling with extra pure nitrogen for about 15 min. Then, repetitive voltammetric scans started immediately after the addition NB.

The solution was stirred with the pulsator for 15 s; the LSV method was applied from -400 mV to 200 mV to the HMDE (versus Ag/AgCl reference electrode) with a scan rate of 200 mVs^{-1} . The measured data were sampled by a computer (workstation). The voltammetric measurements were carried out at room temperature ($25 \pm 2^\circ\text{C}$), and the intensity differences of replicate voltammograms were observed to be negligible as a result of these minor temperature fluctuations.

3 Results and Discussion

3.1 The choice of supporting electrolyte

Different supporting solutions of NaOH, Na₂CO₃, Na₂CO₃ + NaHCO₃, H₃BO₃ + KCl + NaOH, KH₂PO₄ + NaOH and C₈O₄HK + NaOH were applied to the determination of nitrobenzene in wastewater respectively. The experiment proved that there was a sharp oxidized peak of the nitrobenzene in C₈O₄HK + NaOH buffer solution.

3.2 Voltammetric response of nitrobenzene on HMDE

In pH = 5.2 buffer solution on HMDE, the sharp oxidized peak of the nitrobenzene was produced at 0.05 V. The linear scanning curve of this system was shown in Figure 1. Curve (a) was a volt–ampere curve in the blank solution of electrode. Curve (b) was a volt–ampere curve in 5 × 10⁻⁵ mol l⁻¹ NB. Continuing to add a certain amount of nitrobenzene, peak (b) obviously increased and it was proved that oxidized peak was produced by nitrobenzene on HMDE.

Cyclic voltammogram of NB displayed only one reduction peak, and an obvious oxidation peak was

observed (Figure 2). This confirmed the reversibility of the electrochemical reaction under investigation.

3.3 The influence of pH on peak current and peak potential

The variation of peak current and peak potential of NB was investigated in potassium hydrogen phthalate–sodium hydroxide buffer solution in the pH range of 4.2–6.2.

The voltammetric peak potential for NB became more negative with increasing pH in a roughly linear manner (Figure 3). This suggested the concentration of the hydrogen ion (proton) would affect the rate of reaction. The hydroxy group dissociated gradually and shifted the peak to more negative as pH increased.

The influence of pH on peak current was shown in Figure 4. It could be found from Figure 4 that the concentration of H⁺ affected the peak current of nitrobenzene obviously. Thus, the buffer of pH = 5.2 was selected as a suitable analytical medium in this study.

3.4 Effect of the scan rate

The peak current of nitrobenzene increased with increase of scan rate. At low scan rate (25–200 mV s⁻¹)

Figure 1 Linear scan voltammograms of NB in pH = 5.2 buffer solution. (a) blank solution (b) 5 × 10⁻⁵ mol l⁻¹ NB.

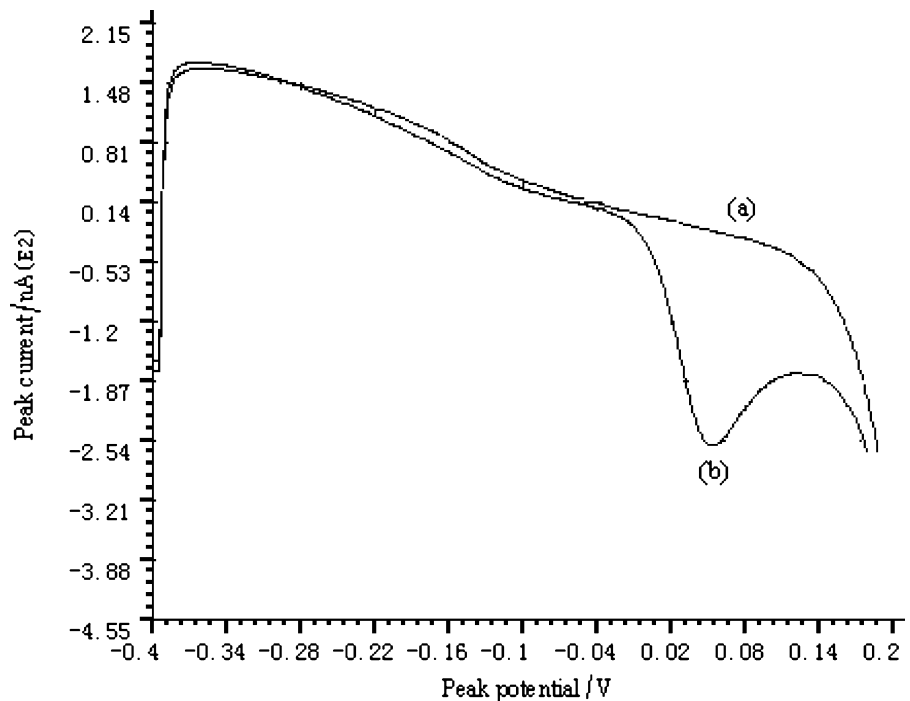
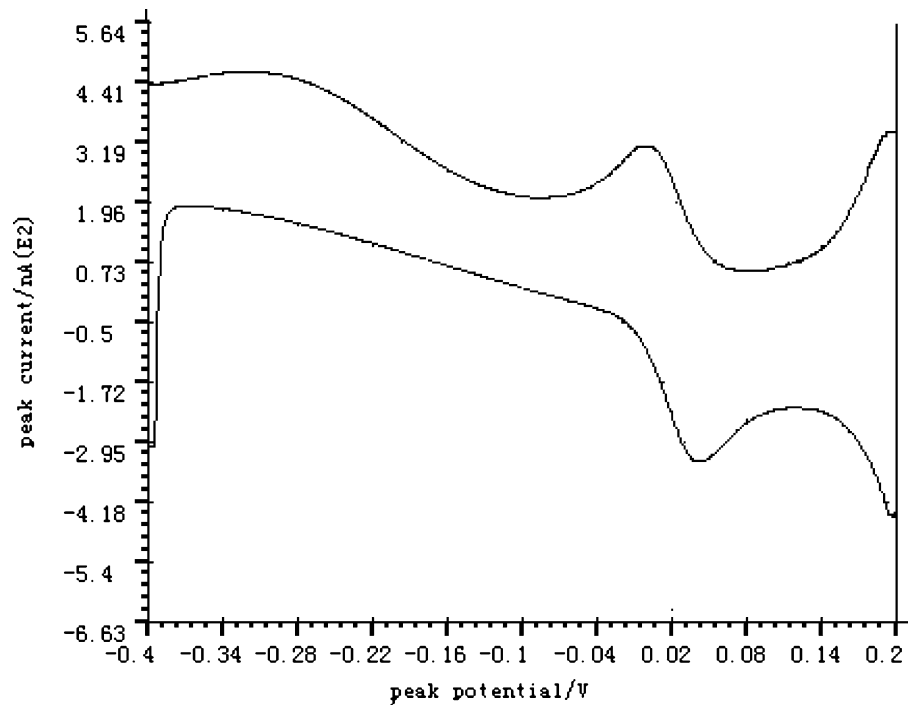


Figure 2 Cyclic voltammograms of NB in pH = 5.2 buffer solution. $5 \times 10^{-5} \text{ mol l}^{-1}$ NB.



peak current (I_p) and square root of scan rate (v) exhibited well linear relation. The pH, accumulation time and potential in $5 \times 10^{-5} \text{ mol/l}$ NB were 5.2, 60 s and -0.8 V , respectively. The linear return equation was $I_p = 4.28 + 9.33v^{1/2}$ with correlation coefficient of 0.9997, following the Ramdles–Sevick Equation: $I_p = 2.687 \times 10^5 n^{3/2} AD^{1/2} v^{1/2} c$ (A – electrode area, D – diffusion coefficient, v – scan rate, c – ion concentration).

Sensitivity could not be improved further when scan rate fasted to certain extent. Thus, scan speed 200 mV/s was chosen in this paper.

Peak potential was observed to shift to more negative potential with increasing scan rate, and the plot of peak current versus scan rate showed a linear relationship, which confirmed that the reduction current was influenced by adsorption.

Figure 3 Influence of pH of the $\text{C}_8\text{O}_4\text{HK} + \text{NaOH}$ buffer on peak potential. The scan rate, accumulation time and potential were 200 mVs^{-1} , 60 s and -0.8 V , respectively. ($5 \times 10^{-5} \text{ mol l}^{-1}$ NB).

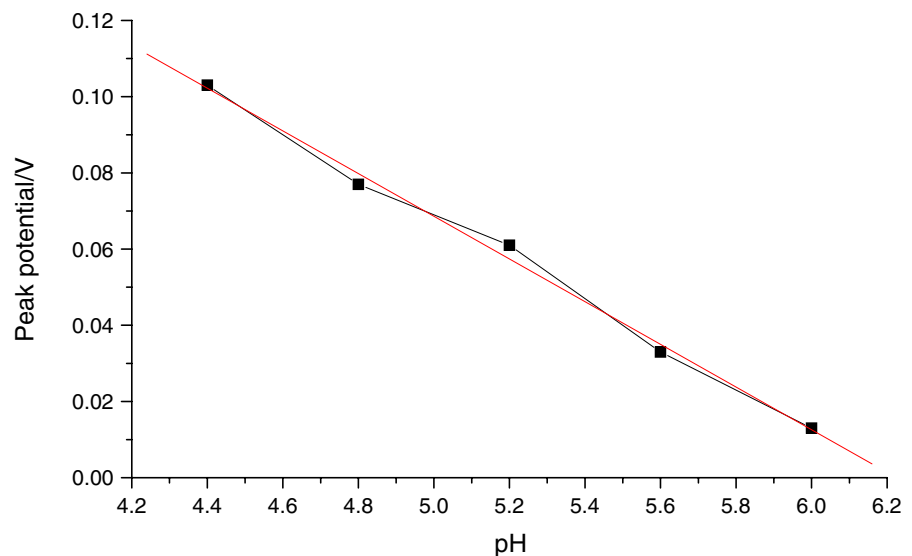
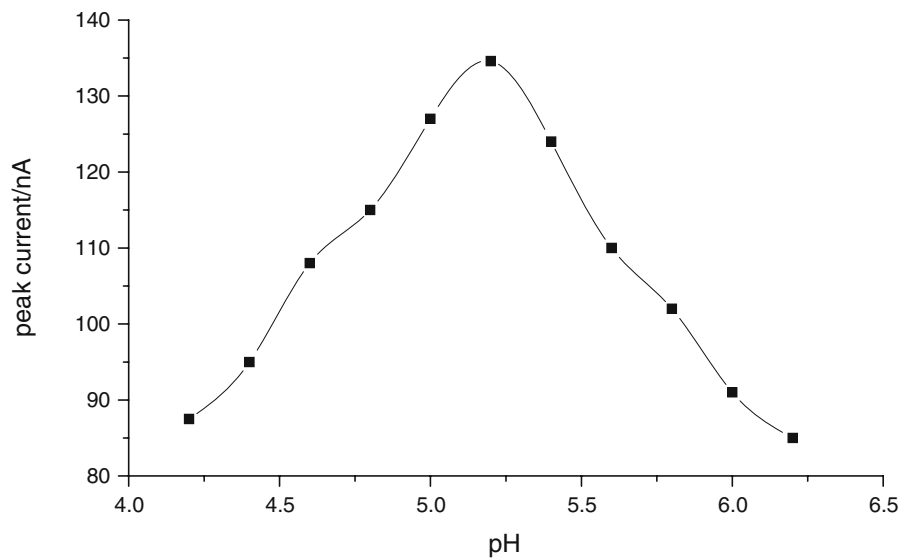


Figure 4 Influence of pH of the $C_8O_4HK + NaOH$ buffer on peak current. The scan rate, accumulation time and potential were 200 mV s^{-1} , 60 s and -0.8 V , respectively. ($5 \times 10^{-5}\text{ mol l}^{-1}\text{ NB}$).



3.5 The choice of accumulation time and potential

The effect of accumulation time for $5 \times 10^{-5}\text{ mol l}^{-1}\text{ NB}$ was investigated from 0 to 180 s. Within 60 s, the peak current of nitrobenzene increased with increase of accumulation time. Saturation coverage of the electrode occurred above 60 s. Therefore, the experimental process used 60 s as accumulation time.

The effect of accumulation potential was examined at a constant time of accumulation of 60 s over the range -1.3 to -0.5 V in buffer solution. The results were shown in Figure 5. The responses were obviously influenced by the accumulation potential.

The optimal accumulation potential was -0.8 V , which was chosen for further studies.

3.6 Reproducibility

The $1.5 \times 10^{-5} \sim 1.0 \times 10^{-3}\text{ mol l}^{-1}\text{ NB}$ was determined repeatedly with the same electrode for 11 times (Table I). The average R.S.D. was 3.99–8.94%. It indicated that the reproducibility of the electrode was remarkable. Voltammetric response of nitrobenzene ($1.5 \times 10^{-5} \sim 1.0 \times 10^{-3}\text{ mol l}^{-1}$) on HMDE was plotted in Figure 6.

Figure 5 The effect of accumulation potential ($5 \times 10^{-5}\text{ mol l}^{-1}\text{ NB}$). The pH, accumulation time and scan rate were 5.2, 60 s and 200 mV s^{-1} , respectively.

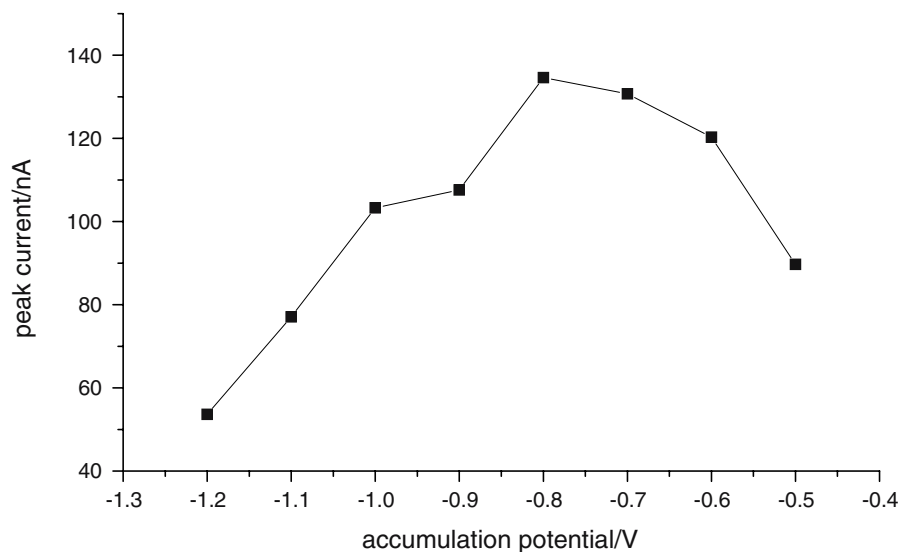


Table 1 Reproducibility of NB ($1.5 \times 10^{-5} \sim 1.0 \times 10^{-3}$ mol/l)

NB concentration ($\times 10^5$ mol/l)	Peak current (nA)	Average of peak current (nA)	CV (nA)	RSD (%)
1.5	28.88 ~ 34.32	31.22	1.70	5.43
2.5	52.93 ~ 73.07	63.60	5.69	8.94
5.0	128.5 ~ 155.1	135.3	9.39	6.94
10.0	258.2 ~ 300.4	277.9	18.9	6.83
20.0	544.9 ~ 638.3	568.1	32.8	5.78
40.0	995.2 ~ 1,223	1,127	68.0	6.03
60.0	1,533 ~ 1,807	1,705	107	6.3
75.0	1,950 ~ 2,309	2,101	103	4.91
90.0	2,295 ~ 2,707	2,457	116	4.7
100.0	2,530 ~ 2,919	2,688	107	3.99

3.7 Interferences

The potential interference of organic compounds of benzene, toluene, ethyl-benzene, aniline, picric acid, 4-nitrophenol benzene, 4-nitro-chlorobenzene, 1-chloro-2,4-dinitrobenzene and 4-nitrophenol were tested under the optimized experimental conditions. The results showed that toluene, ethyl-benzene aniline did not interfere or produced negligible contributions when their concentrations were 100 folds to NB. Picric acid, 4-nitrophenol benzene, 4-nitro-chloroben-

zene, 1-chloro-2,4-dinitrobenzene and 4-nitrophenol produced a peak potential similar to those of NB. Furthermore, if them-to-NB concentration ratio was greater than 1:1, relative errors obtained more than 10%. However, it was highly likely that in practice, the concentration of picric acid, 4-nitro-chlorobenzene, 1-chloro-2,4-dinitrobenzene would be quite low, which would result in only minor interference. 4-nitrophenol in NB could be removed by sodium hydroxide and NB could be extracted by acetone, and then proceed to measure. However, it was highly likely that in practice, the concentration of the concentration of these interferents were quite low in the investigated wastewater by standard addition.

In addition, the possible influences of anions of NO_3^- , SO_4^{2-} , CO_3^{2-} and PO_4^{3-} and several metal ions, such as Fe^{3+} , Mn^{2+} , Ni^{2+} , Al^{3+} , Zn^{2+} , Cu^{2+} , Mg^{2+} , were also investigated. The results suggested these anions did not interfere the determination when their concentrations were 100 folds to NB. It was also found that relative errors of 10% were obtained with the concentration ratios of metal ions-to-NB being 1:1 for Fe^{3+} , 5:1 for Mn^{2+} , Ni^{2+} , and 25:1 for Al^{3+} , Zn^{2+} , and 100:1 for Cu^{2+} , Mg^{2+} . However, it was anticipated that in practice EDTA should separate all the inorganic interferents.

Figure 6 Voltammetric response of NB on HMDE. The pH, scan rate, accumulation time and potential were 5.2, 200 mVs^{-1} , 60 s and -0.8 V , respectively.

- (a) blank solution
- (b) $1.5 \times 10^{-5} \text{ mol l}^{-1}$
- (c) $2.5 \times 10^{-5} \text{ mol l}^{-1}$
- (d) $5.0 \times 10^{-5} \text{ mol l}^{-1}$
- (e) $1.0 \times 10^{-4} \text{ mol l}^{-1}$
- (f) $2.0 \times 10^{-4} \text{ mol l}^{-1}$
- (g) $4.0 \times 10^{-4} \text{ mol l}^{-1}$
- (h) $6 \times 10^{-4} \text{ mol l}^{-1}$
- (i) $7.5 \times 10^{-4} \text{ mol l}^{-1}$
- (j) $9.0 \times 10^{-4} \text{ mol l}^{-1}$
- (k) $1.0 \times 10^{-3} \text{ mol l}^{-1}$.

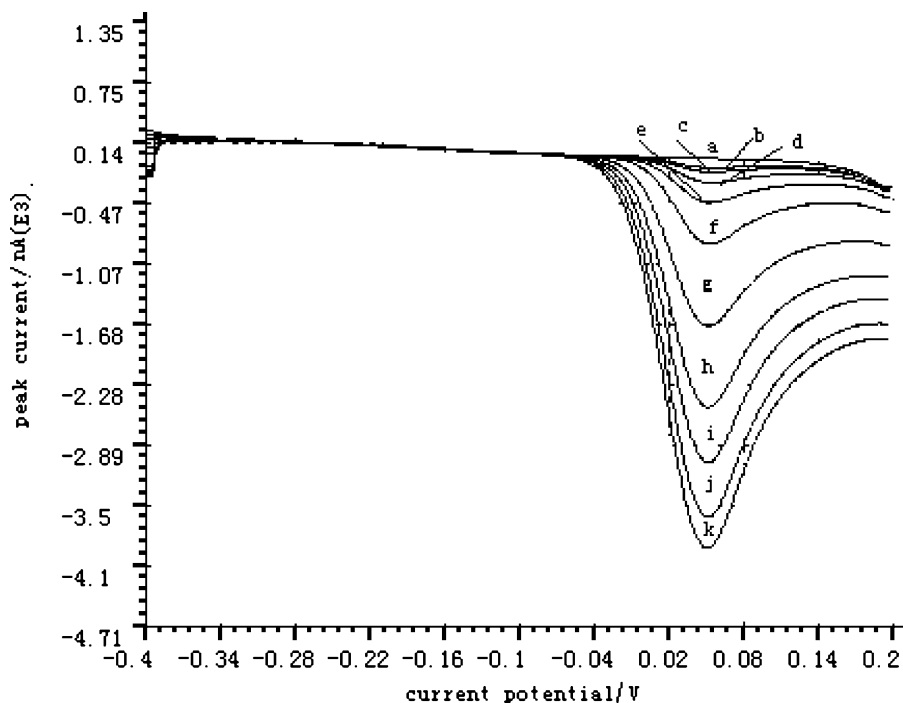


Table II Determination and recovery of samples

Sample	Found (mol/l)	Standard added (mol/l)	Found after added (mol/l)	Recovery (%)
Tap water 1	0	5.0×10^{-5}	4.7×10^{-5}	94.0
Tap water 2	0	1.0×10^{-4}	1.05×10^{-4}	105.0
Plant wastewater 1	5.2×10^{-5}	5.0×10^{-5}	9.8×10^{-5}	96.1
Plant wastewater 2	4.9×10^{-5}	1.0×10^{-4}	1.51×10^{-4}	101.3

3.8 Stability

It was found that the voltammetric response of nitrobenzene at the pH value chosen was practically stable to at least 1 h, with a maximum decrease of less than 3.0% being quite satisfactory for analytical purpose.

3.9 Linear range and detection limit

The peak electric current was proportional to the concentration of nitrobenzene in the range of $1.47 \times 10^{-5} \sim 1.0 \times 10^{-3} \text{ mol l}^{-1}$. The linear calibration equation was $I_p = 10.51 + 27.35c$, $R = 0.9995$. The detection limit of the nitrobenzene in water was $5 \times 10^{-6} \text{ mol l}^{-1}$.

3.10 Practical analysis of samples and recovery

The tap water and wastewater from chemical plants separately were determined by the proposed method. The concentration and recovery of samples was shown in (Table II.)

4 Conclusion

The work described here showed that the proposed method could be simple, accurate and precise to determine nitrobenzene in wastewater at low level at environmental administration, and it would be a

method of choice for nitrobenzene monitoring in wastewater. Its main advantages over other methods were its rapidity, no pre-treatment and low cost instrumentation.

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