



## Research article

# Determination of trace potassium permanganate in tap water by solid phase extraction combined with spectrophotometry

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## ABSTRACT

A simple solid phase extraction (SPE) coupled with spectrophotometric method was developed for determination of trace permanganate ( $\text{MnO}_4^-$ ) in water. Commercial reagent polyamined-6 powder was used as SPE stationary phase to retain  $\text{MnO}_4^-$  which is based on the fact that  $\text{MnO}_4^-$  can be adsorbed on polyamide 6 (PA-6) sorbent as water samples flow through the SPE cartridge. 3,3',5,5'-tetramethylbenzidine (TMB) were used both as eluent solution and chromogenic agent to convert the adsorbed  $\text{MnO}_4^-$  into  $\text{Mn}^{2+}$  and generate blue oxidized product with high molar absorptivity. Quantification of  $\text{MnO}_4^-$  could be obtained by spectrophotometric detection of the resulting solution flow out of the SPE cartridge. The extraction and detection variables was optimized to maximize the absorbance of the TMB oxidized product. Under optimized conditions, this method provided linear dynamic ranges of 0.01–1  $\mu\text{mol L}^{-1}$  for  $\text{MnO}_4^-$  with preconcentration of 100 mL water sample. The limits of detection ( $3S_b/m$ ) of this method in deionized water were calculated to be 5.1 nM, and the relative standard deviations were determined to be 3.2% ( $C = 0.1 \mu\text{mol L}^{-1}$ ,  $n = 5$ ). This method has been applied to the determination of  $\text{MnO}_4^-$  in spiked tap waters and satisfactory recovery was obtained.

## 1. Introduction

As a strong oxidant, potassium permanganate ( $\text{KMnO}_4$ ) has been used extensively in the treatment of wastewater and tap water [1–4] to remove reductive substances [5], odorous and phenolic compounds, degrade organic and inorganic pollutants, inhibit bacterial growth [6,7], and so on. Although the amount of  $\text{KMnO}_4$  used in water treatment can be artificially controlled, there are still some safety risks due to the negative effects of residual  $\text{KMnO}_4$  on the human body and the long-term effects of drinking it on a number of illnesses [8,9]. Therefore, the determination of residual  $\text{KMnO}_4$  concentration in treated water is an important step in  $\text{KMnO}_4$  water treatment technology and it's of great significance to the safety of drinking water.

Several laboratory-based techniques for quantifying trace permanganate concentrations in water have been reported, including photo thermal lens spectrometry [10], colorimetric detection by dark-field optical microscopy [11] and fluorescence sensors [12–15] with organic compounds or carbon quantum dots as fluorescence probe. However, these techniques are usually complex for fabricating of nanoparticle or fluorescence probe and have to be performed by skilled manpower and rely upon sophisticated instruments. For the low-cost and rapid detection of  $\text{MnO}_4^-$ , spectrophotometric methods are more practical. Several spectrophotometric methods [16–18] have been developed for determination of  $\text{MnO}_4^-$  in water. Despite their outstanding advantages such as fast, low cost, simplicity and

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suitable for field detection, there still the request for improving the selectivity and sensitivity due to the low concentration and matrix interferences of real water sample. In general, appropriate sample treatment techniques could improve detection methods' selectivity and sensitivity by removing interferences and increasing analyte concentration. As a result, combining photometric analysis with appropriate sample pretreatment techniques may provide a more suitable field detection method for actual sample analysis.

Solid phase extraction (SPE) is the most commonly used sample pretreatment technique in environmental water sample analysis. The selection of suitable adsorbent is critical in solid phase extraction. During the past several decades, however, only three adsorbents have been reported for SPE of trace  $\text{MnO}_4^-$  in water samples. Xue et al. preconcentration of  $\text{MnO}_4^-$  on cross-linked chitosan [19], Zadeh synthesized nickel–aluminum layered double hydroxide (Ni–Al LDH) as a nano-sorbent for SPE of chromium and manganese [20]. Kenawy et al. [21] use an ion-exchanger pre-concentration of trace permanganate. Despite advancements, those methods suffered from long preconcentration times, complex operations (permanganate must be reduced and eluted after preconcentration), and detection method limitations (atomic absorption spectrometry (AAS) was the only method available).

Polyamide 6 (PA-6), which are also called nylon 6, are widespread used adsorbents in thin layer chromatography. The basic structural units of nylon 6 contain a  $-\text{NHCO}-$  groups, which can strongly bond permanganate groups to each other through hydrogen bonds [22]. Our preliminary study found that  $\text{MnO}_4^-$  can be rapidly enriched with PA-6. However, as with other SPE methods for  $\text{MnO}_4^-$ , it's difficult to directly elute the adsorbed  $\text{MnO}_4^-$  in its original form. In other reported SPE methods for  $\text{MnO}_4^-$ , reductants such as hydroxylamine hydrochloride, hydrazine, and ascorbic acid were used to reduce permanganate to manganese ions and elute them from SPE column.

Recently, the high efficiency redox reaction between  $\text{KMnO}_4$  and 3,3',5,5'-Tetramethylbenzidine (TMB) has been reported [23]. In this reaction,  $\text{MnO}_4^-$  is reduced to  $\text{Mn}^{2+}$ , while TMB is oxidized to produce a blue oxidation products ( $\text{TMB}_{\text{OX}}$ ). Therefore, this reaction can be used to elute the permanganate adsorbed on the SPE column, and it will generate a blue product with a high molar absorptivity.

In this work, we use a low cost commercial reagent PA-6 powder as SPE adsorbent for preconcentration of trace  $\text{MnO}_4^-$  in water. After extraction, 3,3',5,5'-Tetramethylbenzidine (TMB) was used as a chromogenic substance to react with  $\text{MnO}_4^-$  adsorbed on adsorbent to produce blue oxidation product of TMB (ox-TMB) for absorbance measure. By combining SPE with TMB chromogenic assay, we developed a highly sensitive and selective method for detection of  $\text{MnO}_4^-$  in water sample.

## 2. Experimental

### 2.1. Materials and apparatus

200–400 mesh polyamide 6 powder was purchased from Aladdin Reagent Co. Ltd. (China), 60–80 mesh and 100–200 mesh Polyamide 6 powder were purchased from macklin Reagent Co. Ltd. (China). Polytetrafluoroethylene (PTFE) micropore membrane (47 mm in diameter, 0.15  $\mu\text{m}$  pore size) purchased from Weichuang Water Treatment Material Co., Ltd (Zhejiang, China) were used to filter particulate matter in actual water samples. Vacuum pump with pressure regulating valve (Jinteng Instrument Co., Tianjin, China) was used to adjust the SPE filtering speed. The absorption spectra were recorded by a DAD-3000 photodiode array detector (Thermo Fisher Scientific, US) equipped with a 1 cm optical path flow cell). A 722G spectrophotometer (Shanghai Analytical Instrument Factory, Shanghai, china) with a 1 cm optical path micro quartz absorption cell (700  $\mu\text{L}$  in volume) was used for measurement absorbance value.

### 2.2. Reagents and standard solutions

$\text{KMnO}_4$  was purchased from Yaohua Industry Co., Ltd. (Tianjing, China). TMB was purchased from Aladdin Reagent Co. Ltd. (China). Chemicals such as hydrochloric acid (HCl, AR), dipotassium hydrogen phosphate trihydrate ( $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$ , AR), potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ , AR) were purchased from kemiu chemical Reagent Co., Ltd. (Tianjing, China),  $10^{-2}$  mol.  $\text{L}^{-1}$  stock solution of  $\text{KMnO}_4$  was prepared by dissolving proper amount of  $\text{KMnO}_4$  in deionized water. Working standard solutions of  $\text{KMnO}_4$  were obtained by diluting the stock solution step by step with deionized water just before to use. The solution of TMB ( $0.10$  mol  $\text{L}^{-1}$ ) was prepared by dissolving TMB in dimethyl sulfoxide (DMSO), further dilution was completed by using DMSO.

### 2.3. Adsorption experiment

To evaluate the adsorption rate and adsorption capacity of  $\text{MnO}_4^-$  on PA-6 adsorbent, adsorption kinetics and isotherms studies were performed. For adsorption kinetics study, 30 mg of PA-6 powder were added to 10 mL of  $10^{-4}$  mol.  $\text{L}^{-1}$   $\text{KMnO}_4$  solution. The mixture is oscillated by a vortex oscillator at 500 rpm for different times and then separated by centrifugation. For adsorption isotherms studies, 30 mg of PA-6 powder were added to 10 mL of  $\text{KMnO}_4$  solution with different concentration in the range of  $1 \times 10^{-5}$ – $1 \times 10^{-3}$  mol.  $\text{L}^{-1}$ . The mixture is oscillated by a vortex oscillator at 500 rpm for 4 h and then separated by centrifugation. The concentration of initial and unadsorbed  $\text{KMnO}_4$  in the solution was determined by measuring the absorbance of the upper solution at 525 nm after centrifugation, and calculated with equation (1).

$$C = A / 3340 \quad (1)$$

Where  $C$  (mol. $\text{L}^{-1}$ ) is the concentration of  $\text{KMnO}_4$  in solution,  $A$  is the absorbance of solution at 525 nm, 3340 (mol $^{-1}$ .cm $^{-1}$ ) is the

molar absorptivity [16] of  $\text{KMnO}_4$  at 525 nm.

The adsorption capacity of  $\text{KMnO}_4$  on PA-6 were calculated according to equation (2):

$$Q = (C_i - C_t) * V/m \quad (2)$$

Where  $Q$  ( $\text{mol} \cdot \text{g}^{-1}$ ) is the amount of  $\text{KMnO}_4$  adsorbed on per unit of PA-6 adsorbent,  $C_i$  ( $\text{mol} \cdot \text{L}^{-1}$ ) is the initial concentration of  $\text{KMnO}_4$  solution,  $C_t$  ( $\text{mol} \cdot \text{L}^{-1}$ ) is the concentration of unadsorbed  $\text{KMnO}_4$  in the solution with different adsorption time,  $V$  (L) is the volume of the  $\text{KMnO}_4$  solution, and  $m$  (g) is the weight of the PA-6 adsorbent.

#### 2.4. Column preparation

The SPE column were prepared by dry packing 50 mg PA-6 powder into a 2 mL empty polypropylene cartridge (i.d. = 9 mm), two polyethylene sieve plate were placed at both ends of the adsorbent to prevent loss and make the upper and lower surfaces of the adsorbent flush and dense. Before loading the sample, the SPE column was cleaned and conditioned by passing 1 mL of DMSO and 2 mL of deionized water, respectively.

#### 2.5. General procedure

100 mL of water sample was used for vacuum filtration through the polyamide 6 sorbent packed column at a flow rate of  $30 \text{ mL min}^{-1}$ . After loading, 2 mL deionized water was filtered through SPE column to remove all unadsorbed material and to allow the sample to enter all available adsorption sites on the SPE column. Then, 1 mL  $10 \text{ mmol} \cdot \text{L}^{-1}$  TMB mixed with  $0.001 \text{ M}$  HCl solution was added. A plunger rod fitted with the cartridge were used to push the solution into contact with the adsorbent and incubate for 3 min. Then, the colorized solution was push out and its absorbance at 370 nm was determined.

#### 2.6. Prepare of $\text{MnO}_4^-$ solution in tap water

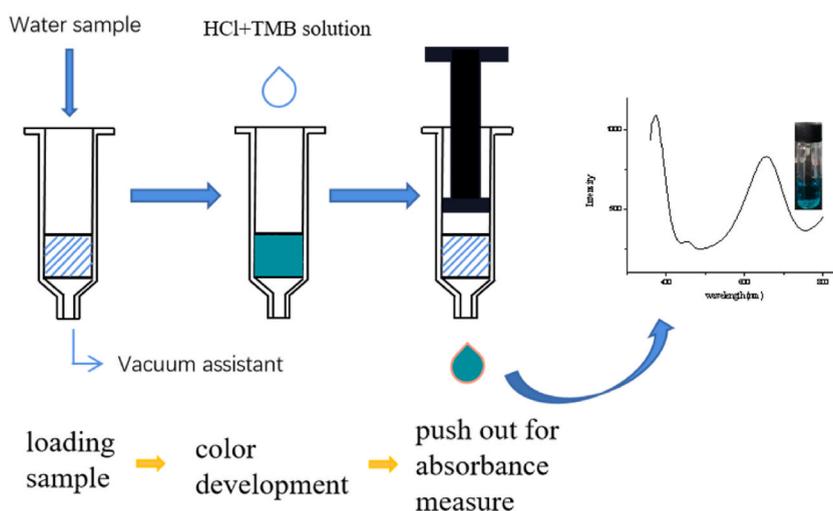
Spiked tap water was used as real water sample to evaluate the analytical performance of the proposed method. Tap water collected from our laboratory is used to prepare potassium permanganate solutions with concentrations of approximately  $1 \times 10^{-5} \text{ mol L}^{-1}$ . This solution was then vacuum filtered through  $0.15 \mu\text{m}$  polytetrafluoroethylene (PTFE) micropore membrane to remove particulate matter and its exact concentration were determined using direct spectrophotometric by measure the absorbance of the solution at 525 nm. Subsequent standard solution in tap water were prepared by diluting this solution with tap water which filtered through  $0.15 \mu\text{m}$  polytetrafluoroethylene (PTFE) micropore membrane.

#### 2.7. Limit of detection and limit of quantification

The limit of detection (LOD) and limit of quantification (LOQ) were calculated according to equations (3) and (4) respectively.

$$\text{LOD} = 3S_b/m \quad (3)$$

$$\text{LOQ} = 10S_b/m \quad (4)$$



**Scheme 1.** The principle of preconcentration and detection of  $\text{MnO}_4^-$

Where  $S_b$  is the standard deviation of the blank and  $m$  is the slope of the calibration graph.

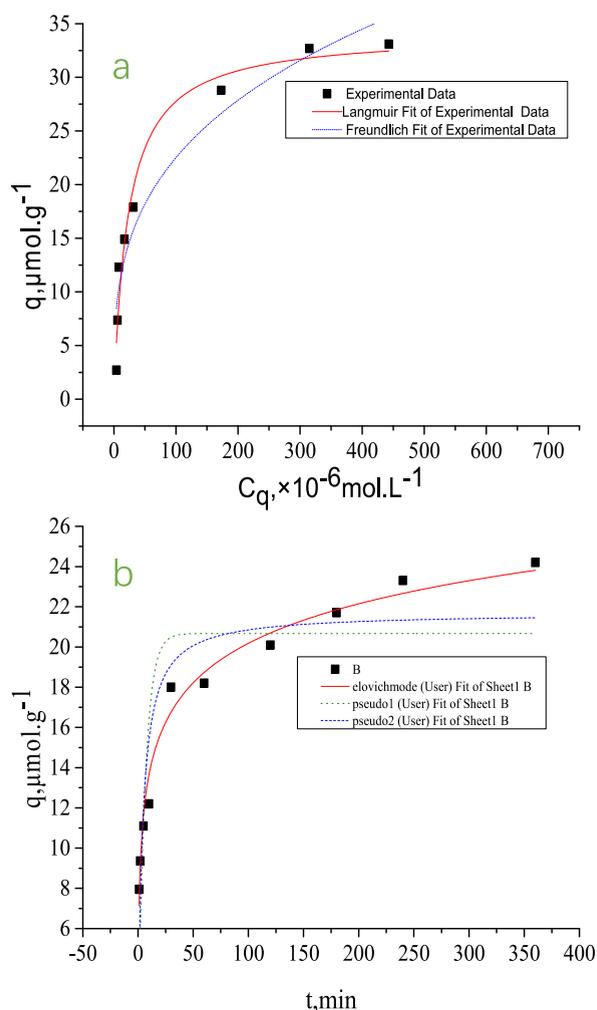
### 3. Results and discussion

#### 3.1. Strategy for preconcentration and detection

**Scheme 1** outlines the SPE and detection principle employed in this study. In the SPE process, water sample passing through the packed PA-6 column by vacuum filtration and  $MnO_4^-$  ions were selectively adsorbed on the PA-6 adsorbent through the hydrogen bond interaction [22]. After SPE, TMB solution mixed with 0.001 M HCl solution is immediately added to the SPE column to react with the potassium permanganate adsorbed on the PA-6 sorbent, an obvious color change from colorless to blue of added mixture solution was immediately observed (**Scheme 1**). The blue reaction solution was pushed out of the SPE cartridge and its absorption spectrum was measured. The absorption spectrum of reaction solution showed two UV-vis absorption peaks located at 370 and 650 nm, which coincided with the absorption spectra of the oxidation products of TMB [24–26], indicating that TMB was oxidized by adsorbed  $MnO_4^-$ . In this way, the concentration of potassium permanganate was quantified based on the absorbance increase of the TMB oxidation product.

#### 3.2. Sorption capacity and adsorption rate of adsorbent

Adsorption capacity and adsorption rate are important parameters of adsorbent. To estimate the adsorption rate and capacity of  $MnO_4^-$  on PA-6 sorbent, adsorption kinetics experiment and adsorption isotherm experiment were conducted follow the procedure



**Fig. 1.** (a) Sorption isotherm of  $MnO_4^-$  adsorbed on the PA-6 powder and fitted with different model. Conditions: volume = 10 mL,  $t = 180\text{min}$ , temperature = 25 °C. (b) Sorption kinetic profile of  $MnO_4^-$  adsorbed on PA-6 powder and fitted with different model. Conditions: volume = 10 mL 0.1 mM  $KMnO_4$  in pure water, temperature = 25 °C.

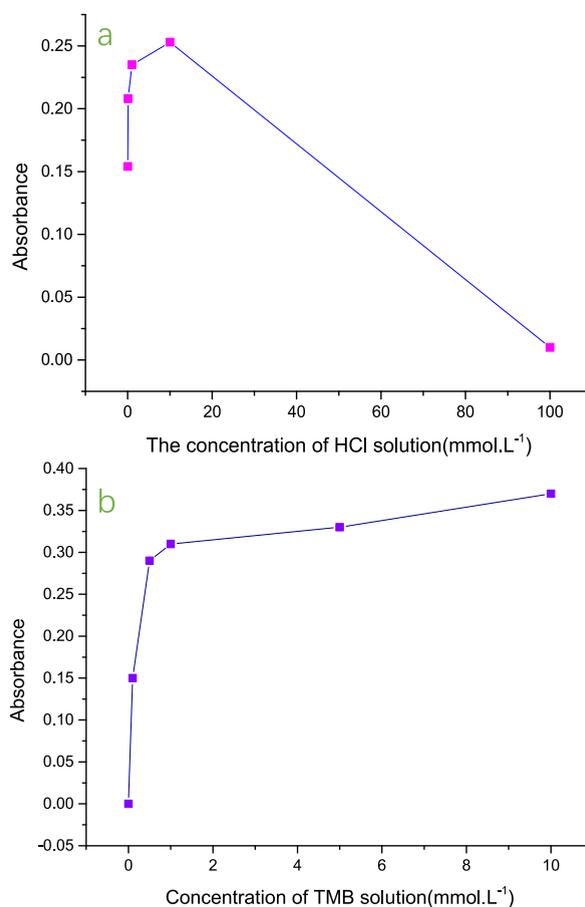
described in sec 2.3. As shown in Fig. 1a the sorption capacity increased with the concentration of  $\text{MnO}_4^-$ . Freundlich and Langmuir models were used to fit the isotherm experimental data. The fitted equation and related parameter values are supplied in Tables S-2. The results show that Langmuir model gives a higher fitting correlation coefficient, which indicates that the adsorption of permanganate on PA-6 adsorbent is mainly monolayer adsorption. According to the fitting result of Langmuir model, the maximum sorption capacity  $q_{\text{max}}$  of the PA-6 sorbent was  $0.025 \text{ mmol g}^{-1}$ , and  $K_L = 0.11 \text{ L. M}^{-1}$  ( $R^2 = 0.984$ , see Tables S-2). The adsorption kinetics curve of  $\text{MnO}_4^-$  adsorbed on PA-6 sorbent is shown in Fig. 1b, which shows a very fast adsorption rate at the beginning, and then it slows down. Three adsorption kinetic models, namely quasi-first order equation, quasi-second order equation and Elovich equation, were used to fit the experimental data of adsorption kinetics. The fitted equation and related parameter values are supplied in Tables S-2, and the fitted curve is shown in Fig. 1b. Of the three fitting models used, Elovich mode described the experiment points best and give a relatively high correlation coefficient ( $r = 0.98$ , see Tables S-2), which indicated that the adsorption of  $\text{MnO}_4^-$  on PA-6 sorbent was predominantly chemical interaction.

### 3.3. Optimization of detection variables

In this study,  $\text{MnO}_4^-$  retained on the adsorbent was reduced and quantified based on the redox reaction between  $\text{MnO}_4^-$  and TMB. To obtain the optimal reaction condition between TMB and adsorbed  $\text{MnO}_4^-$ ,  $20 \text{ mL } 1 \times 10^{-6} \text{ mol.L}^{-1} \text{ KMnO}_4$  solution were first loaded on a column packed with  $100 \text{ mg}$  of nylon powder with a loading speed of  $30 \text{ mL min}^{-1}$ , then the detection variables were optimized following the procedure described in section 2.5.

#### 3.3.1. Concentration of HCl solution

HCl solution is the reaction medium for the reaction between  $\text{MnO}_4^-$  and TMB in this work. To investigate the influence of the concentration of HCl solution on the absorbance, HCl solution in the concentration range of  $0\text{--}100 \text{ mmol.L}^{-1}$  were prepared and used as reaction medium between adsorbed  $\text{MnO}_4^-$  and TMB. As shown in Fig. 2a, in the case of  $0 \text{ mol. L}^{-1}$  HCl solution, TMB will be precipitated out of solution and no color change will be observed. As the concentration of HCl solution increased in the range of



**Fig. 2.** Influence of (a) concentration of HCl solution, (b) concentration of TMB solution upon absorbance of the resulting solution. The initial concentration of  $\text{MnO}_4^-$  was  $1000 \text{ nM}$ ; sample volume was  $20 \text{ mL}$ ; sample solution pH was  $7.0$ ; volume of HCl solution was  $900 \text{ }\mu\text{L}$ ; Volume of TMB solution was  $100 \text{ }\mu\text{L}$ .

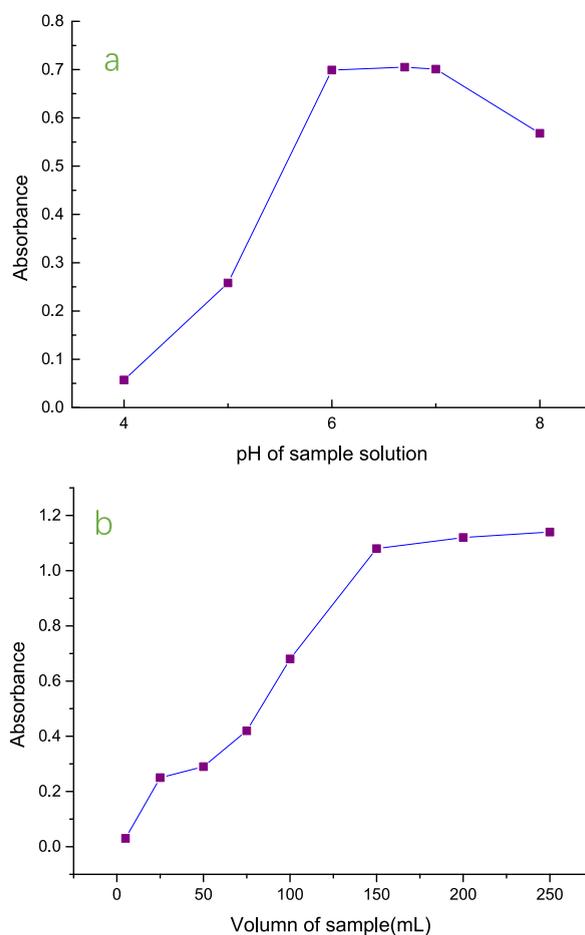
0.01–10 mmol.L<sup>-1</sup>, the absorbance increased rapidly. The highest absorbance was obtained when the concentration of HCl was at 10 mmol.L<sup>-1</sup>. In a more concentrated HCl solution, the color of reaction mixture changes to yellow resulting in a rapid drop of absorbance. So 10 mmol.L<sup>-1</sup> HCl solution was selected as reaction medium due to its best absorbance signal.

### 3.3.2. Concentration of TMB solution

TMB was used both as chromogenic agent and reduce agent in this study. To optimize the amount of TMB, the volume of TMB solution is fixed at 100 μL, and the influence of TMB concentration in the range of 0.01–10 mM on absorbance at 370 nm were investigated. As shown in Fig. 2b, as the concentration of TMB increase from 0.1 to 1 mmol.L<sup>-1</sup>, the absorbance increased rapidly. In the concentration range of 1~5 mmol.L<sup>-1</sup>, the absorbance increases slowly with the increase of TMB concentration. While further increase the concentration of TMB to 10 mmol.L<sup>-1</sup>, the absorbance signal has no significant change. So, 5 mmol.L<sup>-1</sup> TMB solution was used for further experiments.

### 3.3.3. Incubating time

When the mixture of TMB and reaction medium flowed through PA-6 column, they reacted with MnO<sub>4</sub><sup>-</sup> adsorbed on adsorbent to form TMB oxidation product. To ensure that all the adsorbed permanganate can react completely, the mixture of TMB and reaction medium were pushed into contact with adsorbent and incubated with different time. The results show that the absorbance reach maximum after incubate 3 min. The stability of the colorized solution was also investigated by measuring the absorbance value of this solution at different time. The results showed that the absorbance signals of the solution did not change significantly within 30 min. This results indicated that the reaction rate between adsorbed MnO<sub>4</sub><sup>-</sup> and TMB is very fast, and the product can be stably existed for a long period, which is very beneficial for spectrophotometric determination.



**Fig. 3.** Influence of (a) pH of sample solution, (b) volume of sample on absorbance of the resulting solution. The concentration of MnO<sub>4</sub><sup>-</sup> was 1000 nM; sample volume was 20 mL for a; volume of 10 mmol.L<sup>-1</sup> HCl solution was 900 μL; Volume of 5 mmol.L<sup>-1</sup> TMB solution was 100 μL.

### 3.4. Optimization of extraction variables

#### 3.4.1. Sample pH

The sample pH affects the retention of permanganate ions on PA-6 adsorbent, thus affecting the absorbance. To evaluate the influence of sample pH on absorbance value,  $\text{KMnO}_4$  aqueous standard solutions ( $1 \times 10^{-6}$  M, 100 mL) at different pHs (4–8, adjusted using 0.2 M PBS buffer solution), were analyzed follow the procedure described in section 2.5. The effects of pH value on the absorbance are shown in Fig. 3a. It can be seen that the absorbance was higher and changes slowly at the sample pH range of 6–8, absorbance tend to decline at other sample pH. The reason was suggested as that with an acidic pH, the protonated nitrogen of  $-\text{NHCO}-$  group ( $>\text{N}-\text{H}$  bond in  $>\text{NH}_2^+$  group exist out of symmetry) cannot directly interact with  $\text{MnO}_4^-$ . With a basic pH, the NH group became more hydrophobic, which is not conducive to the formation of intermolecular interaction between  $\text{MnO}_4^-$  and adsorbent [27,28]. To further evaluate the effect of buffer on adsorption,  $\text{KMnO}_4$  aqueous standard solutions without buffer was analyzed for comparison. The results showed that the addition of buffer solution can reduce the absorbance to a certain extent. Since the pH of tap water sample are usually in the range of 6–8, so no buffer solution was used for pH adjusting.

#### 3.4.2. Loading volume

The loading volume affects the sensitivity and linear range of SPE method. To select an appropriate loading volume, different volumes of  $1 \mu\text{mol L}^{-1}$   $\text{KMnO}_4$  solution were loaded on SPE column packed with 50 mg PA-6 adsorbent. The relationship between absorbance and loading volume in the range of 5–250 mL was shown in Fig. 3b. As shown in Fig. 3b, the absorbance was linear increased with the loading volume up to 150 mL. Considering the potential influence of the real sample matrix on the adsorption capacity, loading volume of 100 mL was selected.

#### 3.4.3. Flow rate

The sample flow rate affects the extraction efficiency and extraction time of SPE. In our experimental study, the sample flow rate was controlled by adjusting the vacuum pressure in the range of 5–30  $\text{mL min}^{-1}$ . The results show that the absorbance has no obvious change with the sample flow rate in the investigated range. The influence of  $\text{MnO}_4^-$  retention on PA-6 sorbent was investigated by varying the flow rate of the sample solution in the range of 5–30  $\text{mL min}^{-1}$ . Based on the obtained results, the retention of the  $\text{MnO}_4^-$  was practically not changed up to 30  $\text{mL min}^{-1}$  of flow rate. Hence, the maximum flow rate of 30  $\text{mL min}^{-1}$  was selected. At this flow rate, SPE of 100 mL water sample can be completed within 4 min.

#### 3.4.4. Particle size of PA-6 and the packing parameters of SPE column

Adsorbent particle size and the packing parameters of SPE column play an important role on the adsorption rate. Three different sizes of PA-6 powder were used to test the effect of particle size on absorbance. As shown in Table 1, the absorbance increases significantly as the particle size of adsorbent decreases. This result is consistent with the expectation, because the specific surface area of the adsorbent increases significantly with the decrease of the particle size, and a large specific surface area can increase the adsorption rate and thus the absorbance. Using 200–400 mesh PA-6 powder, we investigated the effect of packing parameters on absorbance. As shown in Table 1, absorbance increases with the increase of the ratio of the height to the diameter of the SPE column. Although a large ratio of height to diameter can be obtained by packing a small diameter cartridge or increasing the amount of the adsorbent, the filtration resistance will also increase rapidly, thus increasing the extraction time. Considering the influence on absorbance and extraction time, the ratio of height to diameter 0.33 was selected.

### 3.5. Interference of potential ions

The influences of some potential ions that may presented in tap water and can coexist with  $\text{MnO}_4^-$  on the determination of  $\text{MnO}_4^-$  was examined in this study. The solutions of 100 nM of  $\text{MnO}_4^-$  containing the potential interfering ions were tested to compare absorbance with  $\text{MnO}_4^-$  at the same concentration. If the absorbance change is less than 5%, it is considered that the external ions do not interfere. As the results showed that 1000 fold of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ; 500 fold of  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ; and 100 fold of  $\text{CO}_3^{2-}$  all did not interfere with the determination.

**Table 1**  
Effect of adsorbent particle size and filling parameters on absorbance.

Particle size (mesh)	Amount of adsorbent (g)	Cartridge diameter (mm)	Packing height (mm)	the ratio of the height to the diameter of the SPE column	absorbance
60–80	0.0515	9	2	0.22	0.277
100–200	0.0523	9	2.3	0.26	0.468
200–400	0.0494	9	3	0.33	0.826
200–400	0.1022	9	6	0.67	0.943
200–400	0.0512	4.5	16	3.6	1.193

### 3.6. Analytical performance and sample analyses

To evaluate the analytical performance of this method,  $\text{KMnO}_4$  standard solutions of different concentrations were prepared with deionized water. Under the selected conditions described above, the concentration of  $\text{MnO}_4^-$  is linear related with absorbance in the range of 10–1000  $\text{nmol.L}^{-1}$  (Fig. 4). The calibration equation is fitted as  $A = 0.0007C + 0.0135$  ( $R^2 = 0.9961$ ,  $n = 9$ ), where A is the absorbance of the reaction solution at 370 nm and C is the concentration of  $\text{KMnO}_4$  in the sample solution in  $\text{nmol.L}^{-1}$ . The limit of detection (LOD) and limit of quantification (LOQ) were calculated as 5.1  $\text{nmol.L}^{-1}$  and 17.1  $\text{nmol.L}^{-1}$  respectively according to equations (3) and (4).

The relative standard deviation (RSD) for 100  $\text{nmol.L}^{-1}$  of  $\text{KMnO}_4$  was 3.60% ( $n = 5$ ). As the amount of  $\text{KMnO}_4$  in 100.0 mL of the solution was concentrated to 1 mL, a preconcentration factor of 100 was achieved in this method.

In consideration that this method is mainly applied to the monitoring of  $\text{KMnO}_4$  residue in the treatment of tap water. In order to evaluate the analytical applicability of the proposed method, potassium permanganate solution prepared from tap water was used to construct the working curve. Several spiked tap water sample were analyzed following the procedure described in sec. 2.6. The fitting results of working curves and the analysis results of spiked water samples are shown in Tables 2 and 3, respectively. The obtained RSD values were  $\leq 5.6\%$  and the obtained recoveries were in the ranges of 85–117%.

### 3.7. Comparison of the current method with reported methods

A comparison of the current method with the recently reported spectrophotometric methods is shown in Table 4. Compared with other spectrophotometric methods, the current method has lower linear range and detection limit. Although comparable detection range can be obtained by using a 10 cm cuvette. The cost will increase and is not suitable for all spectrophotometers. In the current method, the detection range can be easily adjusted by changing the loading volume.

One of the application scenarios of potassium permanganate quantification methods is the detection of residual potassium permanganate in tap water treatment. However, the performance of the reported spectrophotometric methods in tap water is little known. In this work, potassium permanganate solution prepared from tap water was used to construct standard curves, good linear correlation coefficient ( $R^2 > 0.99$ ) was obtained in the linear range investigated. The results show that this method is suitable for the determination of trace potassium permanganate in tap water.

## 4. Conclusion

In this study, we developed a simple, rapid and high sensitive method for quantification of trace  $\text{MnO}_4^-$  in tap water by combining SPE with TMB chromogenic assay. SPE of  $\text{MnO}_4^-$  is based on the fact that  $\text{MnO}_4^-$  can be adsorbed on PA-6 sorbent. We have characterized the adsorption kinetics and isotherms of  $\text{MnO}_4^-$  adsorbed on PA-6 powder, and a fast adsorption rate and good adsorption capacity were observed. Quantification of  $\text{MnO}_4^-$  is based on the redox reaction of  $\text{MnO}_4^-$  and TMB to produce a product with high molar absorbance coefficient. We optimized the detection variables and the SPE variables. Under the optimized condition, the proposed method showed excellent sensitivity towards  $\text{MnO}_4^-$ . Using the developed method spiked tap water were analyzed with accurate results.

### Author contribution statement

Liang Hao: Conceived and designed the experiments; Wrote the paper.

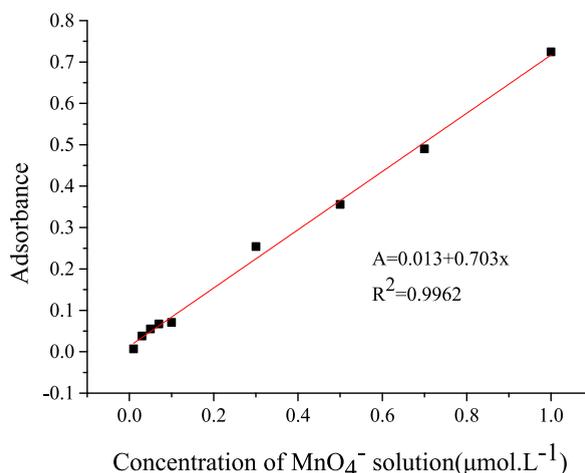


Fig. 4. Calibration curve for determination of  $\text{MnO}_4^-$  in deionized water.

**Table 2**  
Working curves for determination of  $\text{MnO}_4^-$  in tap water.

Linear ranges ( $\mu\text{mol.L}^{-1}$ )	Regression equations	Correlation coefficient ( $R^2$ )
0.01–0.10	$A = 0.013 + 1.14C$	0.9932
0.10–1.0	$A = 0.098 + 0.22C$	0.9946

**Table 3**  
Determination of  $\text{MnO}_4^-$  in deionized water and tap water.

samples	Added ( $\mu\text{mol.L}^{-1}$ )	found ( $\mu\text{mol.L}^{-1}$ )	Recovery (%)	RSD (%)
deionized water	0.00			
	0.02	0.022	110	3.2
	0.08	0.076	95	2.4
	0.60	0.68	113	2.6
tap water	0.00			
	0.02	0.019	95	5.6
	0.08	0.068	85	2.6
	0.60	0.75	117	4.3

**Table 4**  
Comparison of this method with the recently reported spectrophotometric methods.

Method	Investigated linear range ( $\mu\text{mol.L}^{-1}$ )	LOD ( $\mu\text{mol.L}^{-1}$ )	Sample matrix	Ref.
ABTS spectrophotometric	0.60–25	0.01	Pure water	[16]
Nal spectrophotometric	0.63–48	0.02	Pure water	[16]
DPD spectrophotometric	0.02–0.2 (10 cm cuvette)	0.01	Ultrapure water	[17]
	0.2–2 (10 cm cuvette)		Reservoir water	
	1–10 (2 cm cuvette)		River water	
SPE-TMB spectrophotometric	0.01–1	0.005	Deionized water	This work
			Tap water	

ABTS: 2,2'-azino-bis(3-ethylbenzothiazoline-6-sul)onic acid; DPD: N,N-diethyl-p-phenylenediamine.

Yaxin Qi: Performed the experiments.

Yingchun Wu: Analyzed and interpreted the data.

Donghui Xia: Contributed reagents, materials, analysis tools or data.

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### Data availability statement

Data included in article/supplementary material/referenced in article.

### Declaration of interest's statement

The authors declare no conflict of interest.

### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.heliyon.2023.e13587>.

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