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Simultaneous spectroscopic determination of trace mixed organic acids in aqueous samples using magnetic solid phase extraction coupled with chemometrics method

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The polyaniline-coated magnetite/silica nanomaterials (Fe_3O_4@SiO_2/PANI) have been synthesized and successfully applied as an effective sorbent for preconcentration of several typical organic acids from environmental water samples. The properties of Fe_3O_4@SiO_2/PANI are characterized by FT-IR and XPS. These magnetic materials can enrich trace organic acids effectively by solid-phase extraction. Three kinds of organic acids, including benzoic acids, phthalic acids, and *p*-toluene sulfonic acids, are selected as target analytes for magnetic solid phase extraction (MSPE). Various experimental parameters of the MSPE were investigated and optimized. After the desorption process, the elution is detected by the UV-visible spectrophotometer. The spectroscopic data are analyzed through the partial least squares (PLS) method, which facilitate quantitation of mixture from complex data. The enrichment factor of benzoic acids, phthalic acids and *p*-toluene sulfonic acids reached 19.53, 20.31, and 16.89, respectively. A wide measurement range of 10 μg L^{-1} to 50 mg L^{-1} is obtained. The LOD is 0.8 μg L^{-1}. The spiked recoveries in the range of 94%-101% with RSD (n=8) lower than 4%. The results illustrated that the combined approach of MSPE and PLS has great applied potential for a mixture of trace compounds in different fields because of its high efficiency, easy to operate conditions, speediness, and simplicity.

Keywords: Polyaniline; Magnetic material, Solid phase extraction, Organic acid, Simultaneous spectroscopic determination

Solid-phase extraction (SPE)[1-4] is an effective approach available for the rapid and selective sample pretreatment in many field[5-7]. In order to satisfy the various needs of different applications, cartridge[8], column[9], and membrane disk-based SPE[10], direct immersion solid-phase microextraction[11-13], microextraction by packed sorbent[14,15], stir-bar sorptive extraction[16,17] and magnetic solid phase extraction (MSPE)[18,19] rose in response to the proper time and conditions. Thereinto, MSPE[20,21] has a number of advantages, including high recovery, outstanding adsorption efficiency, and an excellent ability to disperse in solution. Naturally, MPSE has attracted increasing attention as a powerful sample preparation technique prior to qualitative and quantitative analysis. As a result, many researchers prepared different magnetic nanomaterials in order to achieve favorable extraction effect.

Because there are lots of π bonds in the polyaniline (PANI) materials, PANI has a great adsorption capacity. As a result, Fe_3O_4@SiO_2 polyaniline-graphene oxide composite, which was synthesized by Su et al.[22], was applied to determine trace/ultratrace rare earth elements in environmental samples. Relatively good experimental results were acquired. After that, Liu et al.[19] prepared an extraction agent of magnetic zeolite imidazolium skeleton-8 microspheres and obtained good extraction results in extracting several typical phthalate compounds from water samples. In 2017, Zhou et al.[23] synthesized similar magnetic materials with core-shell structure as high-performance adsorbents to extract effectively endocrine disrupting compounds from water samples.

As for environmental water analysis, acidic organic wastewater is a kind of environmental pollutant to be hardly treated. Traditional instruments occasionally cannot determine the mixture with ultralow concentration and composition complexity. UV-visible measurement is a widespread analytical technique due to its reliability and accessibility. In addition, the chemometrics method can be introduced into the analysis process of the spectroscopic data in order to quantify multi-component mixtures simultaneously[24]. Therefore, a joint approach of MSPE, UV-visible detection, and partial least squares (PLS) regression can be used to quantify trace organic acid mixture.

Based on this background, we firstly coated a layer of silicon on Fe_3O_4 to prepare magnetic silicon-coated nanomaterials (Fe_3O_4@SiO_2). By grafting polyaniline into Fe_3O_4@SiO_2, polyaniline-coated magnetite/silica nanomaterials (Fe_3O_4@SiO_2/PANI) were synthesized. The factors that might affect MSPE are optimized. The combined method of MSPE, UV-visible detection, and PLS was performed in order to analyze quantitatively trace-level organic acids in the water sample.

Materials and Methods

Reagents and chemicals

In the experiments, benzoic acids, phthalic acids, *p*-toluene sulfonic acids, Fe_3O_4, ethyl orthosilicate (TEOS), aniline, polyvinylpyrrolidone (PVP), ammonium persulfate ($(NH_4)_2S_2O_8$), sodium dodecyl benzene sulfonate (SDBS), HCl, citric acid, ammonia water, and ethanol were all purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., China. The water used in the experiments was ultrapure water.

Apparatus

An EVOLUTION 300 UV-visible spectrometer (a range of spectra from 190 to 800 nm) purchased from Thermo Fisher Scientific Co., Ltd., USA, was used for the detection of all the samples. An ultrasonic cleaner (Shanghai Crown Ultrasonic Instrument Co., Ltd., China) was used for desorption. A constant temperature magnetic stirrer DF 101S (Gongyi Yuhua Instrument Co., Ltd., China) was used during the process of preparing magnetic particles. The pH values of different solutions were measured using a pH-meter with a glass electrode of model PHS-W bought from Shanghai Bout Instrument Co., Ltd., China. The valence bond structure of Fe_3O_4@SiO_2/PANI was characterized by FTIR-7600 Fourier transform infrared spectrophotometer (FT-IR) manufactured by Tianjin Gangdong Sci.&Tech. Development Co., Ltd. K-alpha 20082390 X-ray photoelectron spectrophotometer (XPS) produced by Thermo Fisher Scientific Co., Ltd., USA was used to analyze the elementary composition of the Fe_3O_4@SiO_2/PANI.

Synthesis of Fe_3O_4@SiO_2 nanoparticles

Firstly, 1.5 g of Fe_3O_4 was weighed and dispersed in 50 mL ethanol solutions completely with the aid of an ultrasonic cleaner. Secondly, 6 mL of 25% $NH_3 \cdot H_2O$, 8 mL of H_2O, and 0.4 mL of TEOS were added to the solution. After the ultrasonically promoted reaction for 60 min, the products were magnetically collected and washed several times alternately with water and ethanol. Finally, the obtained Fe_3O_4@SiO_2 nanoparticles were dried in a vacuum oven at 50 °C for 12 h.

Preparation of Fe_3O_4@SiO_2/PANI nanoparticles

At first, 40 mg of Fe_3O_4@SiO_2nanoparticles were dispersed into 150 mL of ultrapure water. Next, 0.15 g of PVP were dissolved in 200 mL water. Then, the solution of PVP, 50 µL of aniline, and 250 µL of HCl were added into the Fe_3O_4@SiO_2 nanoparticles emulsion in sequence under stirring for further reaction. 50 mL of 0.01 g mL^{-1} ammonium persulfate solution, which could initiate oxidative polymerization, was injected into the reaction system in one portion when the reaction last for 1 h. In order to obtain qualified Fe_3O_4@SiO_2/PANI nanoparticles, the mixture should be stirred mechanically for 7 h. The next step is to wash the target products several times with water and ethanol and collect them by an applied magnetic field. Finally, Fe_3O_4@SiO_2/PANI was dried in a vacuum oven at 50 °C for 12 h. The preparation process can be illustrated in Fig. 1.

Procedure for magnetic solid phase extraction

The entire magnetic solid phase extraction process was shown in Fig. 2. Initially, Fe_3O_4@SiO_2/PANI nanoparticles were dispersed into 50 mL organic acid mixed solution. Then, a magnet was attached to the bottom of the beaker when adsorption equilibrium reached with the action of ultrasonic dissolution. Subsequently, the Fe_3O_4@SiO_2/PANI nanoparticles adsorbing the analyte were drawn to the bottom of the beaker magnetic force. Consequently, the solution can be poured out from the top of the beaker while the Fe_3O_4@SiO_2/PANI magnetic adsorbents were left at the bottom. In order to elute the analytes from the magnetic adsorbents, 2 mL of deasorbent was added into the beaker for ultrasonic enhanced desorption. The desorption solution, which was collected based on the means of magnetic separation, was detected by the UV-visible spectrometer. Finally, the PLS method

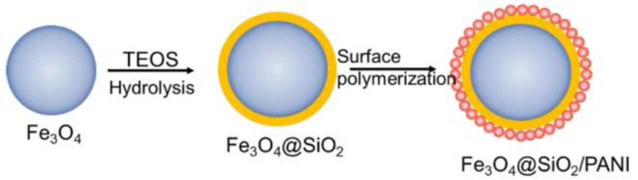

Fig. 1 — Schematic structure of the nanocomposite

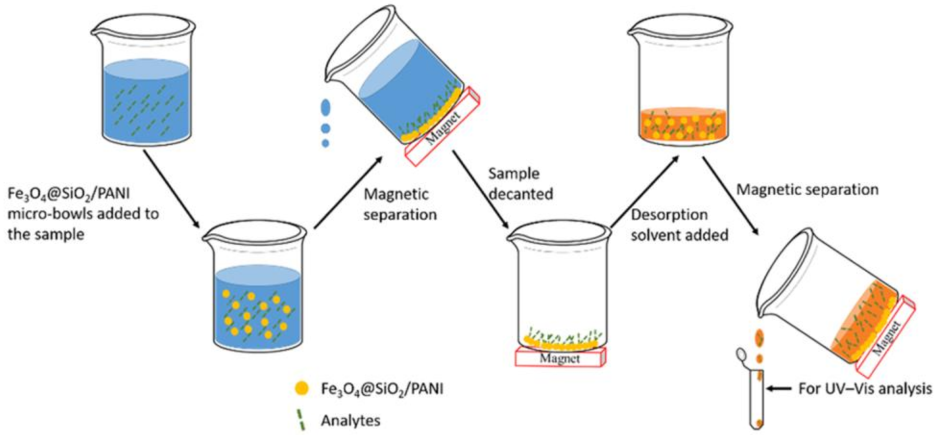

Fig. 2 — Schematic diagram of the extraction procedure

can be introduced into the data analysis process to obtain the concentrations of the different analytes.

PLS modelling analysis

In order to establish an ideal calculation model, the modelling samples were selected according to the actual experimental conditions. Fifty random groups of the mixed solutions produced by MATLAB® software automatically, including benzoic acids, phthalic acids, and p-toluene sulfonic acids with concentration from 5 to 250 mg·L^{-1}, were prepared and then the UV absorption spectra of various samples were thoroughly collected. Standard curves were established according to the UV spectra of 50 groups mixed organic acid solutions (in Supplementary Data, Fig. S1).

PLS model was established by using chemometrics with the assistence of MATLAB® software. In the process, two thirds of the UV spectra of 50 groups mixed organic acid solutions were used as the training set and the others as the prediction set for model self-correction and regression verification. The establishment of the best model of PLS by optimizing the number of factors to achieve the smallest error. The calculate the relative errors of calibration and prediction set were shown in Supplementary Data, Fig. S2.

Results and Discussion

Characterization of $Fe_3O_4@SiO_2$/PANI

Fe_3O_4, $Fe_3O_4@SiO_2$, and $Fe_3O_4@SiO_2$/PANI were characterized by FT-IR shown in Fig. 3. The absorption peak at 585 cm^{-1} is attributed to the Fe-O stretching vibration. After the coating of silica with TEOS on the pure Fe_3O_4 surface, the absorption peak at 1090 cm^{-1} appears in the FT-IR spectra, attributed to the stretching vibration of Si-O, which indicated that $Fe_3O_4$was successfully modified by SiO_2. In the FT-IR spectra of $Fe_3O_4@SiO_2$/PANI, the characteristic peaks at 1600 and 1520 cm^{-1} are attributed to the stretching vibration of C=C in the quinonoid and benzenoid ring, respectively, which shows the existence of polyaniline. Simultaneously, the XPS spectrum is shown in Fig. 4 reveal the peaks of 285, 532, 400, and 1000 eV corresponding to C1s, O1s, N1s, and Si2p, respectively. These data illustrate some elements, including carbon, oxygen, nitrogen, and silicon in $Fe_3O_4@SiO_2$/PANI. In N1s spectra (Fig. 4b), the peaks at 400.7 eV, 399.5 eV, and 398.2 eV could be ascribable to -N$^+$ groups, NH-, and -N=, respectively, which were come from the

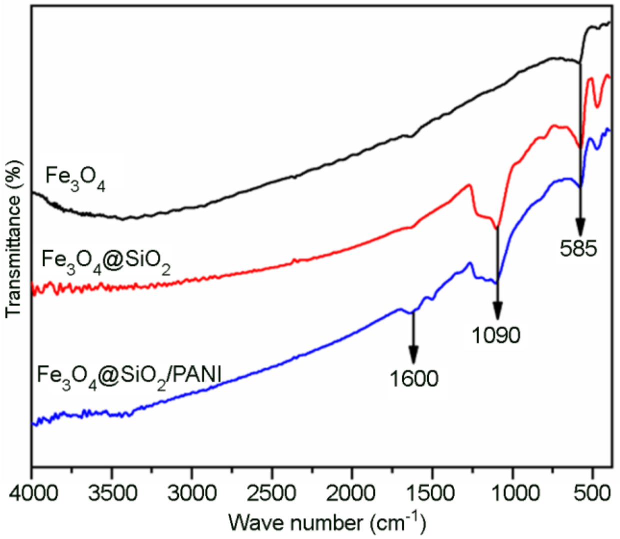

Fig. 3 — The FT-IR spectra of Fe_3O_4, $Fe_3O_4@SiO_2$ and $Fe_3O_4@SiO_2$/PANI

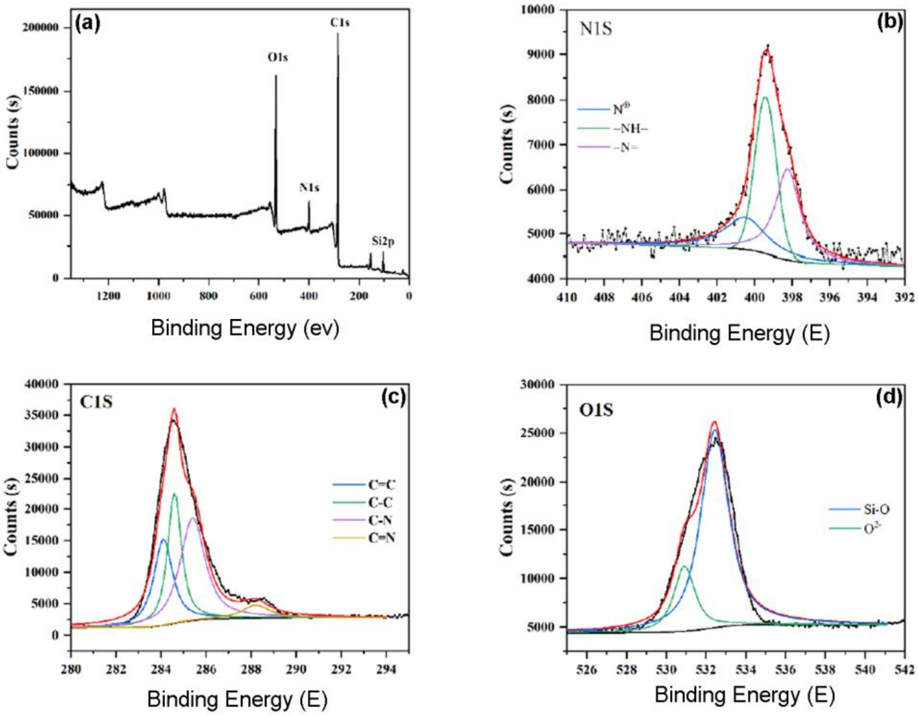

Fig. 4 — XPS spectra of Fe_3O_4@SiO_2/PANI

different states of PANI. It is observed from the peak of C 1s spectra (Fig. 4c) that three peaks at 284.1, 284.6, 285.4, and 288.2 eV are consistent with the bonds of C-C, C=C, C-N, and C=N, respectively. The presence of the C and N species were found on the Fe_3O_4@SiO_2 surface, which indicated that the Fe_3O_4@SiO_2 was successfully modified by PANI. Two prominent peaks are shown in the O1s spectra (Fig. 4d). One peak located at 530.8 eV comes from Fe_3O_4, and the other peak at 532.4 eV, which can be arising from SiO_2.

Optimization of the MSPE conditions

There are many factors in the process of MSPE that affect the extraction effect. Therefore, optimizing the extraction experimental conditions are very important for obtaining the preferred extraction results. As a result, the effects of the amount of adsorbent, adsorption time, pH value of the sample solution, the choice of desorbent, desorption time, and pH value of the desorbent were investigated.

Optimization of the adsorption process

In the process of step by step optimization, only one parameter was set as a variable to be optimized while the others were kept constant. As a first step toward understanding the adsorption process, by increasing the amount of Fe_3O_4@SiO_2/PANI from 5 to 25 mg, the exact effect of dosage of the adsorbent were shown in Fig. 5a. The absorbance data illustrate that the adsorption quantity almost becomes a constant when the amount of Fe_3O_4@SiO_2/PANI was equal to or higher than 20 mg. Therefore, 20 mg of Fe_3O_4@SiO_2/PANI was selected as the optimum dosage adsorbent for the following experiments.

In the next place, the absorbance data of different adsorption time were acquired. It can be seen from Fig. 5b that the time profile of MSPE becomes very stable when the adsorption time was longer than 5 min. There are no more organic acids adsorbing onto Fe_3O_4@SiO_2/PANI even if the operation time was prolonged deliberately because the adsorption equilibrium achieved at that time. As a result, 5 min was chosen as the optimal adsorption time for all the experiments.

At the same time, in order to the effect of sample pH on the adsorption efficiency, the sample pH ranging from 3 to 7 was investigated. The experimental data shown in Fig. 5c indicate that Fe_3O_4@SiO_2/PANI performed high performance of adsorptive property when the pH value is lower than 4. Consequently, Fe_3O_4@SiO_2/PANI dosage of 20 mg, adsorption time of 5 min, and the sample pH of 4 was selected as the optimum adsorption conditions for mixing organic acids in water samples.

Optimization of the desorption process

The desorption experiment optimization process can be described as follows. For one thing, the choice of eluent was critical in the desorption process. These experiments investigated the desorption effect of ethanol, methanol, and acetonitrile as eluents on the desorption of organic acids. The results in Fig. 6a show that ethanol was a preferred eluent because it can elute the mixing organic acids effectively.

For another, desorption time is also an important parameter for the desorption process. As a result, the time profile for the desorption process was drawn in Fig. 6b. The experimental data reveal that the extraction efficiency was significantly improved from 2 min to 8 min and became almost a platform when the desorption time was longer than 8 min because that the desorption equilibrium had been reached.

Meanwhile, the pH values of the desorption solution also have great effects on the desorption of organic acids. The effects of desorption with different pH were illustrated in Fig. 6c. From the spectroscopic data of the eluents, it can be seen that the desorption quantity increased when the pH in the range of 4-6 was adopted and decreases when the pH values were higher than 6. In conclusion, the optimum desorption conditions were as follows: the eluent was ethanol, the desorption time was 8 min, and the pH of the eluent was set at 6.

Comparison of extraction efficiency of Fe_3O_4@SiO_2 and Fe_3O_4@SiO_2/PANI

Under optimum conditions, the comparison of the extraction efficiency of Fe_3O_4@SiO_2 and Fe_3O_4@SiO_2/PANI was performed. The experimental data shown in Fig. 7 demonstrated that the extraction efficiency of Fe_3O_4@SiO_2/PANI was much higher than that of Fe_3O_4@SiO_2. In the magnetic solid phase extraction, Fe_3O_4@SiO_2/PANI reveals a strong adsorption capacity in that the polyaniline structure has a large number of π bonds. The conjugated system of the benzene ring, which the polyaniline modified magnetic material itself can offer help to the adsorption of the organic acidic pollutants in aqueous solution. It is clearly indicated that the modification method for Fe_3O_4@SiO_2 can produce the desired results for the MSPE process.

Analytical performance

In order to further quantify the concentration of the mixing organic acids, the PLS method was introduced into the data processing of different ultraviolet spectrogram[24]. The linearly dependent coefficient of the final standard model is higher than 0.99 after optimizing. The calculation results confirmed that the PLS model could be used for the prediction of unknown samples with high reliability and negligible deviation. The prediction concentrations and the enrichment factors (EF) of different analytes in

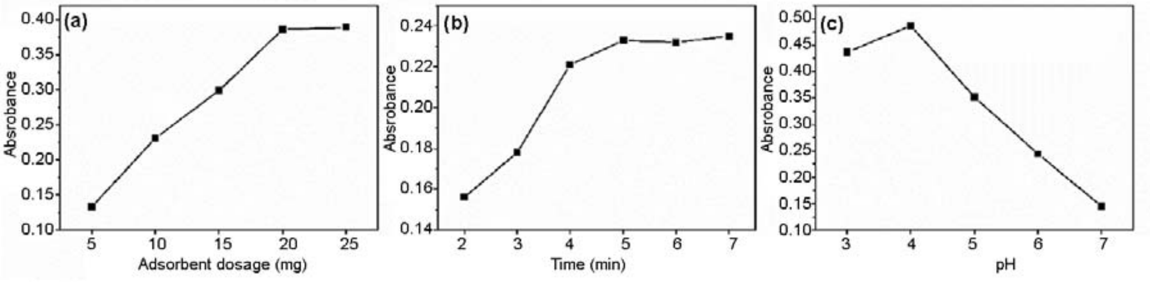

Fig. 5 — Optimization of the adsorption process, (a) Effect of the sorbent amount, (b) Effect of adsorption time and (c) Effect of sample pH values

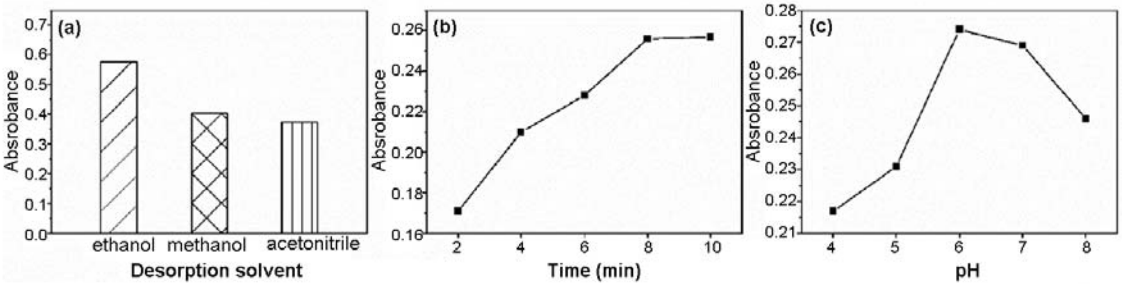

Fig. 6 — Optimization of the desorption process, (a) Effect of eluent type, (b) Effect of desorption time and (c) Effect of desorption solution pH

unknown samples are shown in Table 1. Therefore, EF can be defined as the ratio of the final concentration (C_{final}) of elution and the initial concentration ($C_{initial}$) of the sample solution. For the sake of intuitively revealing the analytical performance of MSPE based on Fe_3O_4@SiO_2/PANI, the experimental data of Fe_3O_4@SiO_2/PANI and Fe_3O_4@SiO_2 were all listed in Table 1.

It can be clearly seen from Table 1 that Fe_3O_4@SiO_2/PANI used as the extraction materials to extract the mixed organic acids in the water had a better extraction effect. The EFs of benzoic acids, phthalic acids, and *p*-toluene sulfonic acids also reached 19.53, 20.31, and 16.89, respectively. As Compared with Fe_3O_4@SiO_2, the EFs of Fe_3O_4@SiO_2/PANI was increased by many times. These results show that the Fe_3O_4@SiO_2/PANI are more beneficial to the extraction process.

In order to determine the applicability of the combined method and the Fe_3O_4@SiO_2/PANI material, the measurement range, the limit of detection (LOD), recovery, relative standard deviation (RSD), and other factors were evaluated. Under optimal experiment conditions coupled with the suitable PLS method, a wide measurement range of 10 µg L^{-1} to 50 mg L^{-1} was obtained. The LOD based on 3 times of signal-to-noise ratios was 0.8 µg L^{-1}. Furthermore, the spiked recoveries were between 94%-101% with RSD (*n*=8) lower than 4%.

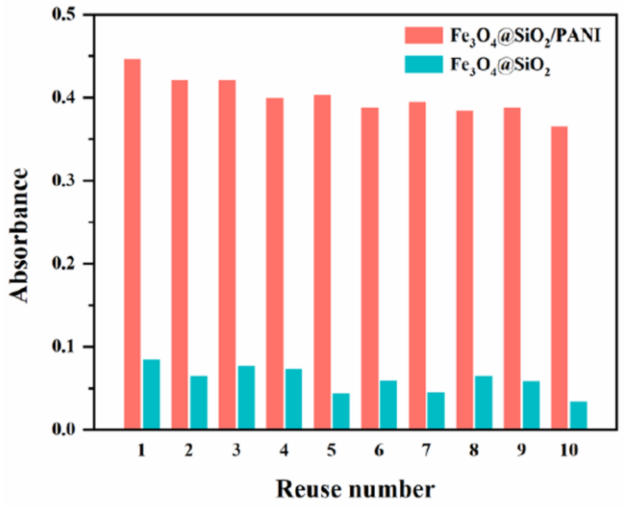

Fig. 7 — Comparison of extraction efficiency of Fe_3O_4@SiO_2/PANI and Fe_3O_4@SiO_2

Table 1 — Comparison of extraction effects

Sample	benzoic acid	phthalic acid	*p*-toluene sulfonic acid
Fe_3O_4@SiO_2/PANI magnetic nanoparticles			
C_{fianl}(mg L^{-1})	97.64	101.55	84.46
EF	19.53	20.31	16.89
Fe_3O_4@SiO_2 magnetic nanoparticles			
C_{fianl}(mg L^{-1})	57.29	12.78	1.59
EF	11.47	2.56	0.32

As real samples, surface water samples from the Pan Lake of Tiangong University, Jing Lake of Tiangong University, Qingnian Lake of Tianjin University and Haihe River (Tianjin), were collected in 500 mL plastic container. After sampling, all water samples were altered pH of solutions, and immediately analyzed by the above-mentioned determination method. The test results indicate that no organic acid was detected at least three repetitions of the samples collected at the four sampling points.

Conclusions

In the present study, Fe_3O_4@SiO_2/PANI materials were synthesized as potential adsorbents for MSPE. After the characterization by FT-IR and XPS to verify the existence of polyaniline, Fe_3O_4@SiO_2/PANI materials were successfully applied to the extraction of mixing organic acids in water samples. The magnetic property of the Fe_3O_4 core allowed the adsorbent to be easily separated from the water samples and the eluents that reduced the time-consuming compared with traditional SPE methods. Under optimum conditions, the comparison of the extraction efficiency of Fe_3O_4@SiO_2 and Fe_3O_4@SiO_2/PANI was performed. Fe_3O_4@SiO_2/PANI materials show preferred extraction efficiency. With the assistance of the combined method of MSPE and PLS, the concentration of each compound was calculated. A wide measurement range of 10 µg L^{-1} to 50 mg L^{-1} was obtained. The LOD was 0.8 µg L^{-1}. The spiked recoveries in the range of 94%-101% with RSD (*n*=8) lower than 4%. These experimental results show the applicability in the aspect of high efficiency, easy to operate conditions, speediness and simplicity for the determination of trace organic acid mixture in water samples. The proposed combined method has great applied potential for a mixture of trace compounds in a different field.

Supplementary Data

Supplementary Data associated with this article are available in the electronic form at http://nopr.niscair.res.in/jinfo/ijca/IJCA_60A(02)245-249_SupplData.pdf.

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