Mixed hemimicelles solid-phase extraction based on cetyltrimethylammonium bromide-coated nano-magnets Fe_3O_4 for the determination of chlorophenols in environmental water samples coupled with liquid chromatography/spectrophotometry detection

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Abstract

Mixed hemimicelles solid-phase extraction (SPE) based on cetyltrimethylammonium bromide (CTAB)-coated nano-magnets Fe_3O_4 was investigated for the preconcentration of four chlorophenols (CPs) in environmental water samples prior to HPLC–spectrophotometry determination in this paper. By the rapid isolating (about 5 min) of Fe_3O_4 nanoparticles (NPs) through placing a Nd–Fe–B strong magnet on the bottom of beaker, the time-consuming preconcentration process of loading large volume sample in conversational SPE method with a column can be avoided. The unique properties of Fe_3O_4 NPs such as high surface area and strong magnetism were utilized adequately in the SPE process. This novel separation method produced a high preconcentration rate and factor. A comprehensive study of the adsorption conditions such as the Fe_3O_4 NPs zeta-potential, CTAB added amounts, pH value, standing time and maximal extraction volume was also presented. Under optimized conditions, four analytes of 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (TCP) and pentachlorophenol (PCP) were quantitatively extracted. The method was then used to determine four CPs in five real environmental water samples. High concentration factors (700) were achieved for each of the analytes, with observed detection limits ranging between 0.11 and $0.15 \mu\text{g L}^{-1}$. The accuracy of method was evaluated by recovery measurements on spiked samples. Good recovery results (83–98%) with satisfactory relative standard deviation (RSD) were achieved. It is important to note that satisfactory preconcentration factors and extraction recoveries for the four CPs were obtained with only a little amount of Fe_3O_4 NPs (0.1 g) and CTAB (60 mg). To the best of our knowledge, this was the first time a mixed hemimicelles SPE method based on Fe_3O_4 NPs magnetic separation had been used for the pretreatment of environmental water samples.

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1. Introduction

Recently, a new solid-phase extraction (SPE) method based on mixed hemimicelles assemblies (hemimicelles/admicelles) has been proposed for the preconcentration of a variety of

inorganic and organic compounds from complex environmental matrices [1–6]. In these SPE methods, the used sorbents were produced by the adsorption of ionic surfactants such as sodium dodecyl sulfate (SDS) or cetyltrimethylammonium bromide (CTAB) on the surface of mineral oxides (such as alumina, silica and titanium dioxide). Electrostatic attractive interactions between the head group of ionic surfactants and oppositely charged groups on the oxide result in the formation of mixed hemimicelles assemblies. The outer surface of the mixed hemimicelles is hydrophobic and ionic, respectively, providing a two-fold mechanism for retention of analytes. The

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use of mixed hemimicelles assemblies in SPE has a number of advantages, such as high extraction yields, high breakthrough volumes, easy elution of analytes and high flow rate for sample loading. Furthermore, this SPE technique requires no clean-up steps and is easy to regenerate, and is thus able to meet the needs of rapid analysis. However, because of a relatively small surface area of the micro-particle sorbents used, the reported mixed hemimicelles assembly SPE method may lead to a relatively low extraction capability in addition to being time-consuming when large volume samples are loaded.

To overcome these limitations, a number of research groups have explored the possibility of applying nanosized SPE sorbents for the pretreatment of environmental water samples [7–20]. Findings from these efforts indicate that the nanosized SPE sorbents have very high extraction capacities with rapid extraction dynamics performance. However, the NPs packed SPE column also has a high backpressure, which makes it difficult to adapt high flow rates in the column dynamic extraction mode and very high filtration rates in the static batch mode.

How can we keep the advantages of nanosized SPE sorbents while overcome their disadvantages? Maybe adopting the magnetic NPs sorbents is one of the best ways. Nanoscale ferrite materials have attracted increased interests in recent years [21]. The use of magnetic NPs for biological and clinical applications has undoubtedly been one of the most challenging and attractive research areas in the field of nanomagnetism [22–25]. Generally, Fe_3O_4 NPs possess a high surface area and strong magnetism, and it can be assumed that its use in analytical chemistry can improve the adsorption capacity of analytes and avoid the time-consuming enrichment process of loading large volume samples through the rapid isolation of Fe_3O_4 with an adsorptive magnet. Therefore, compared with the traditional SPE method, the novel SPE method based Fe_3O_4 NPs would have higher extraction efficiency and enrichment factor. Chlorophenols (CPs), used extensively as preservative agents, fungicides, pesticides, disinfectants, and intermediates in many industries, are some of the most important contaminants present in the natural waters and soils [26–28]. In addition, CPs are generated during the chlorine treatment of drinking water [29]. High-performance liquid chromatography (HPLC), one of the many analytical methods available for the determination of CPs in water, has been widely used for the separation and determination of CPs [30–33], and is often coupled with various detectors such as ultraviolet (UV) [31,34], fluorescence [35], electrochemical [36], and mass spectroscopy [37]. However, because of the relatively low concentrations of most CPs and the inherent complexity in environmental water samples, a preconcentration step usually becomes necessary, prior to their analysis.

In the present study, we established a novel SPE method where four CPs, 2-chlorophenol (2-CP), 2,4-dichlorophenol (2,4-DCP), 2,4,6-trichlorophenol (TCP) and pentachlorophenol (PCP), were adsorbed onto mixed hemimicelles sorbents in which positively charged CTAB ions were adsorbed onto negatively charged magnetic Fe_3O_4 NPs in weak basic media. The properties of the CTAB-coated Fe_3O_4 NPs were then evaluated and the predominant experimental factors affecting the recovery

were examined. The results of analyzing four CPs in real environmental samples were proven to be dependable.

2. Experimental

2.1. Chemicals and materials

All reagents were analytical grade and used as supplied. 2-CP, 2,4-DCP, 2,4,6-TCP and PCP standards (1.00 mg mL^{-1}) were obtained from the National Research Center for Reference Material (Beijing, China). A standard stock solution was prepared by dissolving 1 mL of each standard in 10 mL methanol and stored in dark at 4°C . Working solutions were obtained daily by appropriately diluting the stock solutions with deionized water. $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were purchased from Beijing Chemicals Corporation (Beijing, China). CTAB was obtained from Shanghai Reagent Corporation (Shanghai, China). HPLC-grade acetonitrile and methanol were supplied by Merck (Darmstadt, Germany). Water ($18.3 \text{ M}\Omega$) used in all experiments was prepared using a compact ultrapure water system from Barnstead (Dubuque in IA, USA).

An effluent wastewater sample was collected from Gaobeidian sewage treatment plant (Chaoyang District, Beijing). River water samples were taken from Xiaoqing River and Jingmi Canal (Haidian District, Beijing) in January 2007. The groundwater sample was collected from a deep well in a western suburb of Beijing. The tap water sample was taken from our laboratory. All water samples were collected randomly. Samples were filtered through $0.22 \mu\text{m}$ nylon membranes and stored at 4°C .

2.2. Preparation of magnetic Fe_3O_4 nanoparticles

Fe_3O_4 NPs were prepared by mixing $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (2.0 g), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (5.2 g) and 0.85 mL hydrochloric acid into 25 mL deionized water degassed with nitrogen beforehand. The mixture was added to a stirred 250 mL NaOH solution (1.5 M) with nitrogen gas passing continuously through the solution during the reaction. The produced magnetic NPs were rinsed with deionized water ($5 \times 50 \text{ mL}$) and then resuspended in deionized water (200 mL). The generated NPs concentration was estimated to be about 10 mg mL^{-1} . The magnetic property of Fe_3O_4 NPs and CTAB-coated Fe_3O_4 NPs was analyzed using a vibrating sample magnetometer (VSM, LDJ9600) at room temperature.

2.3. SPE procedures

The SPE procedure was carried out as follows: a 700 mL filtered water sample was placed in a 1 L beaker and the pH was adjusted to about 9.0 with 1 M NaOH. To prepare the CTAB-coated magnets mixed hemimicelles assemblies, 10 mL Fe_3O_4 NPs solution and 6 mL 10 mg mL^{-1} CTAB solution were added into the sample solution. To trap the target CPs, the mixture was sonically agitated for 5 min to thoroughly suspend the NPs, then allowed to stand for 10 min. The Fe_3O_4 NPs were isolated by placing a Nd–Fe–B strong magnet at the bottom of the beaker and the solution was poured away. The isolated NPs were washed with methanol ($3 \times 1.5 \text{ mL}$) to desorb the target analytes

Fig. 1. Procedures for the analysis of CPs by using CTAB/ Fe_3O_4 NPs mixed hemimicelles SPE.

and the methanol solution was collected into a 10 mL test tube. The methanol solution was then dried with a stream of nitrogen at 60°C and re-dissolved in 1.0 mL methanol. A $20\ \mu\text{L}$ of this methanol solution was injected into the HPLC system for analysis (Fig. 1).

2.4. Adsorption study and HPLC analysis

The adsorption experiments were carried out in batch mode as follows: 10 mL nano-magnets Fe_3O_4 solution (containing 0.1 g Fe_3O_4 nanoparticle) was added to a series of 500 mL aqueous solutions containing variable amounts of CTAB (the added CTAB amount kept 60 mg when the pH effect experiments were carried out) in the presence of CPs ($2\ \mu\text{g L}^{-1}$); then the pH was adjusted to 9 (the pH value was varied among 5 and 10 when the pH effect experiments were carried out). For the CPs extraction experiments, the Fe_3O_4 nanoparticles were isolated by a magnet and the adsorbed CPs was determined using HPLC-UV analysis. For zeta-potential experiments, the suspension was added into $1.0 \times 10^{-3}\ \text{mol/L}$ NaCl background electrolyte solution, then Fe_3O_4 nanoparticles were isolated by centrifuge and the zeta-potential were determined using zetasizer 2000 apparatus (Malvern, UK). For the measurement of the Fe_3O_4 nanoparticles isoelectric point, the pH value of solution was adjusted between 4.5 and 11 by 1 M NaOH or HCl solution in the absence of CTAB; following the same SPE procedure, the zeta-potential were determined under different pH value. According the zeta-potential variations, the isoelectric point can be obtained from Fig. 3.

The four CPs were separated and quantified using a liquid chromatography–spectrophotometry system (P680 HPLC gradient pump with a PDA100 photodiode array detector, Dionex, USA) with an automatic sample injector (ASI-100, Dionex, USA). The analytical column was a 250 mm Diamonsil- C_{18} column ($4\ \mu\text{m}$ particle diameter and 4.6 mm I.D.) supplied by Dikma Technologies (Beijing, China). A $20\ \mu\text{L}$ of prepared sample solution was injected into the HPLC system for analysis. The mobile phase consisted of acetonitrile–water containing 1% acetic acid (acetonitrile–water, 20:80, v/v, solvent A) and acetonitrile containing 1% acetic acid (solvent B). The

gradient elution program was as follows: started at 10% B, increased B to 55% in 15 min, increased B to 100% in 5 min and kept for 5 min, then decreased B to 10% in 1 min and kept for 2 min to equilibrate the column. The flow rate was set at $1\ \text{mL min}^{-1}$. Spectrophotometry detection of analytes was performed at 285 nm.

3. Results and discussion

3.1. Characterization of Fe_3O_4 nanoparticles

The particle size was determined with a laser particle size analyzer (Malvern, UK) and the diameter was in the range of 5–60 nm. The percentage of the main particle size (10–20 nm) was about 80%. The samples morphology was determined by transmission electronic microscopy (TEM) with JEM-200CX operating at 200 kV. Representative TEM image of Fe_3O_4 NPs was shown in Fig. 2, from which it can be seen that most of the particles were quasi-spherical with an average diameter of 10–20 nm.

The isoelectric point (iep) is an important characteristic of metal oxides. The charge density is a main factor affecting the

Fig. 2. A TEM image of Fe_3O_4 nanoparticles.

Fig. 3. Variation of the Fe_3O_4 nanoparticles zeta-potential under different pH value.

surfactant loading on the oxide surface, and it varies strongly with pH. The mineral oxides surface is negatively charged when the pH value is above iep and is positively charged when the pH value is below iep. The iep can help us control the charge density of mineral oxides through selecting appropriate pH. Therefore, the Fe_3O_4 nanoparticles iep was measured in our experiment, and it was found to be 6.5 from Fig. 3, which is consistent with the data reported [38].

It was known that particles sizes less than 40 nm offer a large surface area and superparamagnetic properties [39]. Fig. 4 shows the magnetization curve of Fe_3O_4 NPs and CTAB-coated Fe_3O_4 NPs, and it shows both Fe_3O_4 NPs and CTAB-coated Fe_3O_4 NPs exhibit typical superparamagnetic behavior due to no hysteresis. There is no remanence and coercivity, suggesting that such NPs are superparamagnetic. Another key parameter is the large saturation magnetization, which is a measurement for the maximum magnetic strength [40]. The saturation magnetization is 63.2 emu/g for Fe_3O_4 NPs and 58.7 emu/g for CTAB-coated Fe_3O_4 NPs. This large saturation magnetization makes them

Fig. 4. Magnetization curves of Fe_3O_4 NPs and CTAB-coated Fe_3O_4 NPs obtained by VSM at room temperature.

Fig. 5. Effect of the CTAB added amount for zeta-potential of the Fe_3O_4 NPs suspensions at pH 9.0.

very susceptible to magnetic fields and causes solid and liquid phases to separate easily. Therefore, the superparamagnetic properties have no significant changes when the surfactants form mixed hemimicelles on Fe_3O_4 NPs.

3.2. Effect of surfactant on the zeta-potential of the Fe_3O_4 NPs

The zeta-potential curve of Fe_3O_4 NPs was useful for understanding the theory of extraction process and optimizing the conditions of SPE method. Generally, ionic surfactant adsorption isotherms on mineral oxides can be divided into three regions [41,42]. In the first region, the adsorbed surfactant molecules spread themselves on the oxides surface to form a single-layer coverage (hemimicelles), probably through coulombic attraction between charged oxide surface and the oppositely charged surfactant head group. The second region involves hydrophobic and electrostatic interactions, which result in the formation of bilayers (admicelles). The process of extracting analytes in hemimicelles and admicelles is termed as “adsolubilization”. Both the above-mentioned regions are suitable for SPE method. At the end of isotherm region, the overall surface of mineral oxide is saturated by surfactants and surfactants begin to form micelles in solution (above the critical micelles concentrations). However, this may cause the analytes to be absorbed into micelles in bulk solution again, which makes the isotherm span unsuitable for SPE application. Fig. 5 shows the zeta-potential change of Fe_3O_4 NPs suspension by adsorption of CTAB. As seen in Fig. 5, the zeta-potential increased from negative to zero to positive with increases in cationic surfactant concentration.

The zeta-potential change could be interpreted as follows. At first, the suspension had a negative zeta-potential in a weakly basic media for the reason that the point of zero charge (PZC) of Fe_3O_4 (about 6.5) [43] was lower than the pH of solution. Then, with increases in cationic surfactant concentration, the surfactant adsorbed on negatively charged Fe_3O_4 NPs through

electrostatic attraction. With the self-assembled surface micelles formed gradually, it may have screened the negative charge of Fe_3O_4 NPs and made the zeta-potential increase positively. The maximal change in zeta-potential occurred at low surfactant concentrations, which suggested that with almost adsorbing every surfactant ion, a H^+ was desorbed and almost all adsorbed surfactant ions had their head groups close to the Fe_3O_4 surface in this region. After compensation for the surface charge by surfactants, the surface charge became independent of the surfactant concentration even though the adsorption of surfactants continued to increase. This suggests that the adsorption of surfactants started in second layer and the effect of surfactants adsorption on zeta-potential became small.

3.3. Influence of CTAB concentration on the adsorption of CPs

Fig. 6 depicts the percentage of adsorbed CPs as a function of the amount of CTAB added. In the absence of CTAB, the CPs hardly adsorbed onto the surface of Fe_3O_4 NPs. In contrast, with increases in CTAB, the sorption amount of CPs increased remarkably. The increase in sorption can be explained by the gradual formation of hydrophobic mixed hemimicelles (hemimicelles and admicelles) on the surface of Fe_3O_4 NPs and CPs are extracted gradually. Maximum sorption was obtained when CTAB amounts were between 40 and 80 mg. The main difference was in the maximal adsorption percentage of CPs, which was about 85% for 2-CP, 90% for 2,4-DCP and above 90% for other two CPs. These experimental results suggest that the adsorption behaviors of CPs are related to the number of chlorine groups, the hydrophobic properties of the CPs increasing with increases in the number of chloro-substitutes. The water–octanol distribution constants, $\log K_{\text{ow}}$, were 2.15, 3.17, 3.45 and 5.18 for 2-CP, 2,4-DCP, 2,3,4-TCP and PCP, respectively [37]. Results of the present study indicated clearly that the hydrophobic interactions played an important role in the adsorption process. The adsorption amount decreased when the amount of CTAB added exceeded 80 mg, after which the

Fig. 6. Effect of the amount of CTAB added for the extraction of CPs at pH 9.0.

Fig. 7. Effect of pH on the adsorption of CPs into mixed hemimicelles consisting of 60 mg CTAB and 0.1 g Fe_3O_4 NPs.

CTAB molecules began to form micelles in the bulk aqueous solution with more surfactant added. Furthermore, the micelles caused the CPs to redistribute into the solution again. When the added amount of CTAB was more than 120 mg, the CTAB-coated Fe_3O_4 NPs became difficult to be isolated with the same magnet. Given these findings, 60 mg CTAB was adopted as the final addition amount of surfactant in the next studies.

3.4. Effect of pH

pH is one of the prime factors influencing the adsorption behavior of mixed hemimicelles system. In the present study, the pH effect was examined by varying pH between 5.2 and 10. As shown in Fig. 7, the Fe_3O_4 NPs exhibited no obvious adsorption for CPs when pH was between 5.2 and 6.3. With increases in pH, the sorption amount increased dramatically before reaching a maximum above pH 8.5. This can be attributed to the fact that the surface of Fe_3O_4 NPs was positively charged when the pH level was below its PZC (6.5) and the CTAB molecules were hardly adsorbed to the surface of Fe_3O_4 NPs. With increases in pH value, the Fe_3O_4 surface became negatively charged so that the strong electrostatic attraction between the CTAB molecules and the negatively charged Fe_3O_4 NPs surface is high enough to produce a great adsorption affinity for CPs. Therefore, pH 9.0 was selected for the next studies.

3.5. Standing and magnetic separating time

In the SPE process, we found that the standing time had obvious effect on the target analyte extraction. When the Fe_3O_4 NPs were isolated immediately without a standing process, the recovery of 2-CP, 2,4-DCP, 2,4,6-TCP and PCP was only 23, 36, 58 and 57%, respectively. However, when the standing time was adjusted to 5 min, recovery of the four CPs improved to 67, 78, 87 and 90%; when the standing time was increased to 20 min, the recovery increased to 85% for 2-CP and 90% or more for

Table 1
Analytical parameters of the proposed method

Analytes	Linearity range ($\mu\text{g L}^{-1}$)	Correlation coefficient (r^2)	LOD ($\mu\text{g L}^{-1}$)	RSD (%) ($n=6$)
2-CP	0.5–50	0.9912	0.15	5.9
2,4-DCP	0.5–50	0.9930	0.13	4.8
2,4,6-TCP	0.5–50	0.9925	0.11	5.2
PCP	0.5–50	0.9910	0.14	4.9

other CPs. Better recovery of each CPs cannot be obtained if increasing the standing time further.

After a 20 min standing process, the CTAB–Fe₃O₄ NPs in suspension solution can be completely isolated in 5 min with the adsorptive Nd–Fe–B magnet. In contrast, the same suspension solution needed almost 3 h to precipitate to the bottom of the beaker without the adsorptive magnet.

3.6. Desorption conditions

Desorption of CPs from the CTAB-coated Fe₃O₄ NPs mixed hemimicelles was studied with different organic solvents (acetonitrile, methanol) and 0.01 M HNO₃. Quantitative recoveries (above 90%) of CPs were obtained using 4.5 mL (3×1.5 mL) methanol. When using 4.5 mL (3×1.5 mL) acetonitrile, the recoveries were 87, 86, 82 and 75% for 2-CP, 2,4-DCP, 2,4,6-TCP and PCP, respectively, and a higher volume acetonitrile (8 mL) was required for desorbing the CPs completely. When using 0.01 M HNO₃, we found Fe₃O₄ NPs were oxidized quickly and lost magnetism. Furthermore, some NPs were dissolved. Thus, 4.5 mL (3×1.5 mL) methanol is recommended for desorption. Under this optimized desorption conditions, no carryover was observed in the next analysis.

3.7. Maximal extraction volume

The maximal extraction volume for CPs was determined using a series of different volume aqueous solutions (100–1000 mL) spiked with fixed 0.5 μg of each the CPs at pH 9. The amount of Fe₃O₄ NPs used was 0.1 g and CTAB added

was kept 60 mg. Insufficient recovery was considered to occur when recovery was below 90%. Insufficient recoveries occurred when aqueous solution volume was above 700 mL for 2,4-DCP, 2,4,6-TCP and PCP. In the process of increasing solution volume, the maximal recovery for 2-CP was just about 85% and it began to decrease above 700 mL. For the four CPs, complete desorption was obtained with 4.5 mL methanol. By drying the desorption solution with a nitrogen flow and re-dissolving the analytes in 1.0 mL methanol, a preconcentration factor value (700) for each CP was achieved. It is important to note that satisfactory preconcentration factors and extraction recoveries for the four CPs were obtained with only a little amount of Fe₃O₄ NPs and CTAB.

3.8. Analytical performance and application

Quantitative parameters of the proposed method, such as linear range, correlation coefficients, limits of detection (LODs) and precision, were evaluated by enriching 700 mL standard solutions (Table 1). Each analyte exhibited good linearity with correlation coefficient (r^2) > 0.99 in the studied range. The limits of detection, calculated on the basis of signal-to-noise ratio of 3 ($S/N=3$) [38] ranged between 0.11 and 0.15 $\mu\text{g L}^{-1}$. The precision of the analytical method was studied using six replicate experiments with 700 mL standard solution containing each CPs 1.0 $\mu\text{g L}^{-1}$, and the relative standard deviations (RSD) below 6.0% were obtained.

In order to validate the method, the method was applied to five real environmental water samples, the results shown in Table 2. No CPs were found in the tap water, groundwater and Jinmi

Table 2
Determination and recoveries of CPs in real water samples

Samples	Added ($\mu\text{g L}^{-1}$)				Founded ^a ($\mu\text{g L}^{-1}$)				Recovery ^b (%)			
	2-CP	2,4-DCP	2,4,6-TCP	PCP	2-CP	2,4-DCP	2,4,6-TCP	PCP	2-CP	2,4-DCP	2,4,6-TCP	PCP
Tap water	0	0	0	0	n.d. ^c	n.d. ^c	n.d. ^c	n.d. ^c				
	0.6	0.6	0.6	0.6	0.52	0.55	0.59	0.57	87 $\pm$ 3	92 $\pm$ 3	98 $\pm$ 4	95 $\pm$ 4
Groundwater	0	0	0	0	n.d. ^c	n.d. ^c	n.d. ^c	n.d. ^c				
	0.6	0.6	0.6	0.6	0.51	0.54	0.58	0.55	85 $\pm$ 2	90 $\pm$ 3	97 $\pm$ 3	92 $\pm$ 5
Jingmi canal river	0	0	0	0	n.d. ^c	n.d. ^c	n.d. ^c	n.d. ^c				
	0.6	0.6	0.6	0.6	0.50	0.57	0.53	0.56	83 $\pm$ 3	95 $\pm$ 3	88 $\pm$ 2	93 $\pm$ 3
Xiaoqing river	0	0	0	0	n.d. ^c	0.49	0.72	0.56				
	0.6	0.6	0.6	0.6	0.53	1.04	1.26	1.08	88 $\pm$ 2	92 $\pm$ 4	90 $\pm$ 3	87 $\pm$ 3
Gaobeidian effluent	0	0	0	0	n.d. ^c	0.52	0.65	n.d. ^c				
	0.6	0.6	0.6	0.6	0.51	1.08	1.17	0.53	85 $\pm$ 3	93 $\pm$ 5	87 $\pm$ 4	88 $\pm$ 3

^a Mean of three determinations.

^b Standard deviation for three determinations.

^c Not detected.

Fig. 8. Solid-phase extraction/LC–spectrophotometry chromatograms. (a) Standard solution containing 2 mg L^{-1} of each compound (b) Xiaoqing river water sample, and (c) Xiaoqing river water spiked with $0.6 \mu\text{g L}^{-1}$ standard solution. 1, 2-CP; 2, 2,4-DCP; 3, 2,4,6-TCP; 4.PCP.

Canal River samples. For the other two water samples, different CP contents were found. The accuracy of the method was evaluated by the recovery test carried out with spiked water samples. Recoveries ranged between 82 and 98% for four CPs. The chromatograms of Xiaoqing River water sample are shown in Fig. 8.

4. Conclusion

A novel SPE method based on CTAB-coated Fe_3O_4 NPs mixed hemimicelles was developed for the preconcentration of four CPs in five environmental water samples. The use of NPs endowed the SPE method with high extraction capacity and preconcentration factors. The magnetic separation greatly improved the separation rate while avoided the time-consuming column passing or filtration operation. The strong hydrophobic interactions between the mixed hemimicelles and CPs made this new developed SPE method possess high extraction efficiency and capacity. The adsorbed analytes were easily desorbed with methanol and no carryover was observed in the next analysis. The established SPE method proved to be effective for concentrating trace CPs in water prior to HPLC analysis. Good recoveries and precision of this method were obtained, which indicates that CTAB-coated Fe_3O_4 NPs mixed hemimicelles SPE method has high analytical potential for the preconcentration of other trace organic pollutants from water samples.

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