Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.22218

112 (2018) 310–318
April

Mixed hemimicelles silica-coated magnetic nanoparticles for solid-phase extraction of chlorophenols from different water samples

Jasmin Shah*, Muhammad Rasul Jan, Mehwish Iqbal, Muhammad Zeeshan

Institute of Chemical Sciences, University of Peshawar, Peshawar 25120, Khyber Pakhtunkhwa, Pakistan, Tel./Fax: +92-91-9216652; emails: jasminshah2001@yahoo.com (J. Shah), rasuljan@yahoo.com (M.R. Jan), imehwish90@yahoo.com (M. Iqbal), zeeshan_ics11@yahoo.com (M. Zeeshan)

Received 9 September 2017; Accepted 16 March 2018

ABSTRACT

In this study, silica-coated magnetic nanoparticles with mixed hemimicelles were used for the solid-phase extraction of chlorophenols such as 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol from aqueous samples. Magnetic nanoparticles (Fe_3O_4) were prepared by coprecipitation method, modified with silica (SiO_2) and characterized using different techniques. The effect of various parameters including solution pH, contact time, amount of adsorbent and volume of surfactant (cetyltrimethylammonium bromide [CTAB]) was evaluated in batch experiments for the maximum adsorption of chlorophenols. The results showed that the percentage removal of 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol was 85%, 87%, 95% and 96%, respectively, achieved by using Fe_3O_4@SiO_2 at neutral pH 7 with 150 mg/g of CTAB amount in 60 min. For the extraction of chlorophenols, type of eluent, volume of eluent and extraction time were optimized. The limit of detections of chlorophenols ranged from 0.02 to 0.07 μg/L using high-pressure liquid chromatograph with UV detector. The proposed method was applied for the determination of chlorophenols in real water samples including groundwater, river water, wastewater and tap water. The percentage recovery of 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol and 2,4,6-trichlorophenol was in the range of 95%–99%, respectively.

Keywords: Mixed hemimicelles; Solid-phase extraction; Magnetic nanoparticles; Chlorophenols

1. Introduction

The ingestion of hazardous chemicals in water can cause serious health problems for the exposed population. The quality control of drinking water is an important health issue to insure safe water for consumers [1,2]. Chlorophenols (CPs) are highly toxic chemicals, including estrogenic, mutagenic and carcinogenic effects. They have acute toxicity, interfering with oxidative phosphorylation and inhibiting adenosine triphosphate synthesis. There is also evidence that CPs are precursors of extremely toxic dioxins and furans either upon incineration or after metabolism in humans. The anti-microbiological properties of CPs have led to their use as disinfectants in agriculture such as herbicides, insecticides and fungicides, and also as wood preservative [3–5]. European Union (EU) in 1982 issued the pollutant list that includes many CPs. According to EU, the acceptable concentration of CPs in drinking water is 0.5 g/L [1,6].

For the determination of CPs, many analytical methods have been reported including gas chromatography (GC) [2] in combination with mass spectrometry detection [7–9] or with electron capture detection [5]. Derivatization is required for the analysis of CPs by GC due to low vapor pressure and high polarity of CPs, which is a time consuming and tedious process. The new trend for determination of CPs is toward the analyses of CPs with high-pressure liquid chromatograph (HPLC) [10]. Common detection techniques with HPLC for CPs

---

* Corresponding author.

1944-3994/1944-3986

determination reported are ultraviolet [11], mass spectrometry [12] and fluorimetry [13]. Whatever, the method selected for separation and determination, cleaning and preconcentration of environmental samples required to attain acceptable selectivity and sensitivity before analysis. Diverse methods of extraction using solid phase have been developed for the extraction of organic compounds. Among them, nanosize materials have been preferred due to their size and properties [14].

Modified solid-phase extractions using magnetic nanoparticles (MNPs, Fe_3O_4) have been developed as a fast, convenient and environment-friendly method for the separation and extraction of different types of organic compounds and inorganic metal ions. MNPs have attracted particular interest as a sorbent and catalyst in the separation science due to their super-paramagnetic nature as well as their unique physical and chemical properties. MNPs provide high surface area and high extraction efficiency are easy to separate due to their magnetic properties [14–16]. MNPs are easy to prepare and less toxic, but bare MNPs are unstable as their surface area and super-paramagnetic properties change due to coagulation, therefore, surface-modified MNPs were prepared [17,18].

Mixed hemimicelles, which are formed due to the adsorption of ionic surfactants on silica, alumina, titanium dioxide and iron oxides, have been used as good adsorbents for the solid-phase extraction of organic compounds [19]. Some of the advantages acquired using mixed hemimicelle adsorbents are easy adsorbent preparation, high extraction efficiency and simple analyte elution. However, the applications of mixed hemimicelles-based solid-phase extraction reported in literatures were mostly based on ionic surfactants adsorbed onto micro-size particles but these particles have relatively small surface areas, which may lead to somewhat low extraction efficiency and preconcentration factor. If the advantages of mixed hemimicelles combine with magnetic silica nanoparticles to produce nanosized solid-phase extraction adsorbents with high surface area and chemical stability along with good magnetic separation, then a new type of mixed hemimicelles nanosized solid-phase extraction adsorbent can be attained.

The aim of this work was to evaluate the use of mixed hemimicelles adsorbed on prepared silica-coated MNPs (Fe_3O_4@SiO_2) for the extraction of CPs from water samples. Therefore, the possibility of mixed hemimicelles silica-coated MNPs as an adsorbent was studied using 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP) and 2,4,6-trichlorophenol (2,4,6-TCP) as model CPs. The factors affecting the extraction efficiency of CPs and the analytical application of the proposed hemimicelles solid-phase extraction were studied. To the best of our knowledge, according to the literature, no data are available for the simultaneous extraction of four CPs using magnetic mixed hemimicelles adsorbent. This will be the first report of using silica-coated MNPs mixed hemimicelles-based solid-phase extraction for the preconcentration of CPs from water samples.

2. Experimental

2.1. Materials and methods

All chemicals were of analytical grade purity or similar and used as received. Ferric chlorides ($FeCl_3.6H_2O$) and ferrous sulfate ($FeSO_4.7H_2O$) were obtained from Merck (Darmstadt, Germany). Cetyltrimethylammonium bromide (CTAB) was purchased from Avon Chem (United Kingdom). Different CPs (2-CP, 4-CP, 2,4-DCP and 2,4,6-TCP) were supplied by Sigma-Aldrich, Laborchemikallen GmbH, Germany. Standard stock solutions of the four types of CPs were prepared in methanol. Working standards were prepared fresh daily from stock solution with deionized water. Structures of studied CPs are given in Fig. 1.

2.2. Instruments

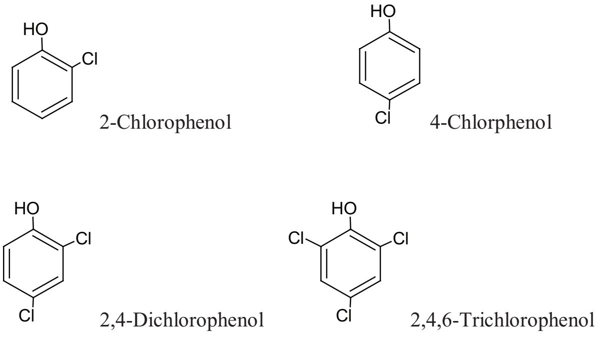
An Acme 9000 series HPLC equipped with SP930D isocratic pump, UV730D detector (Younglin, Anyang, Korea) was used. Analog pH meter (Model-7020 Kent Industrial Measurement Limited Electronic Instrument Ltd., Chertsey Survey England) was used for pH measurement. Thermostatically controlled water bath (Yu Jia, China), orbital shaker (Model OS-340C, Digisystem Laboratory Instrument Inc., Taiwan ROC) and ultrasonic bath (model ks 300, Kum Sung Ultrasonic, Korea) were used for adsorption and extraction study and as mobile phase degasser, respectively.

2.3. Synthesis of silica-coated MNPs

MNPs (Fe_3O_4) were synthesized using chemical coprecipitation method reported in our previous work [20,21]. Silica-coated MNPs (Fe_3O_4@SiO_2) were synthesized according to the reported method [16] with modification. Briefly, sodium silicate (5.0 M) solution was added into 10 g of Fe_3O_4 nanoparticles, and the suspension pH was adjusted to 6.0 using 0.2 M HCl solution. The mixture was sonicated for 3 h, and the temperature was maintained at 60°C under nitrogen atmosphere. The obtained nanoparticles were then washed thoroughly with deionized water, dried and stored for extraction process. The magnetic properties were also determined with magnet (Fig. S1).

2.4. Characterization of nanoparticles

The morphology of silica-coated MNPs (Fe_3O_4@SiO_2) was studied by scanning electron microscope (SEM) model JSM-5910 (JOEL, Japan). The successful coating of silica on Fe_3O_4 nanoparticles was confirmed by elemental analysis with energy dispersive X-ray (EDX, JSM5910, JEOL, Japan). The attachment of SiO_2 to Fe_3O_4 was also confirmed by Fourier-transformed infrared (FTIR) spectroscopy using IR



2-Chlorophenol 4-Chlorphenol 2,4-Dichlorophenol 2,4,6-Trichlorophenol

Fig. 1. Chemical structure of studied chlorophenols.

Prestigue-21 (Shimadzu, Japan) in the spectral range of 400–4,000 cm^{-1}. Surface area was determined by N_2 adsorption/desorption method at 77.4 K using a surface area analyzer (NOVA2200e, Quantachrome, USA). The adsorbents were outgassed before analysis for 2 h at 100°C using high vacuum line in order to remove all the adsorbed gases and moisture from the adsorbent pores and surface. Surface area of the adsorbent was calculated using Brunauer, Emmett and Teller (BET) and Barrett, Joyner and Halenda (BJH) methods, after complete pore condensation (P/PO = 0.995) of the adsorbed nitrogen, pore volume was calculated using ratio of the densities of liquid and gaseous nitrogen. The pore size and pore volume were calculated using the BJH method.

The point of zero charge (pzc) of the Fe_3O_4 nanoparticles and Fe_3O_4@SiO_2 nanoparticles was determined by potentiometric method reported previously in our work [20].

2.5. HPLC analysis

Four CPs (2-CP, 4-CP, 2,4-DCP and 2,4,6-TCP) were separated and quantified using reverse-phase HPLC system. The column was maintained at room temperature, and 20 µL sample injection volume was used. Isocratic separation of four CPs was investigated using acetonitrile, methanol and water (40:35:25, v/v) as a mobile phase. The flow rate was kept at 0.7 mL/min. For separation of CPs, HiQ C_{18} column (Teknokroma, S. Coop. Ltd., Barcelona, Spain) 250 mm × 0.46 mm with 5 µm particle size was used. The signals were measured at wavelength 254 nm and processed on Autochrom-3000 for quantification of CPs.

2.6. Procedure

Extraction of CPs using mixed hemimicelles Fe_3O_4@SiO_2 was performed in two steps: first, adsorption and second, extraction of CPs. For adsorption study, 0.2 g of Fe_3O_4@SiO_2 nanoparticles as adsorbent was added in series of 100 mL conical flasks containing known concentration of CPs. Followed by the addition of 150 mg/g of CTAB and Britton–Robinson buffer solution [22] of pH 7 to each flask. Then, the total volume was adjusted to 25 mL with a final concentration of 200 µg of each CP. The flasks were agitated on an orbital shaker for 60 min at 150 rpm at room temperature. After required contact time, the Fe_3O_4@SiO_2 nanoparticles were separated with external magnet, and the solutions were analyzed for unabsorbed CPs using HPLC at optimum conditions of separation.

For extraction, acidic methanol solution was added to the CPs loaded Fe_3O_4@SiO_2 and vortexed for 30 s to desorb CPs from the sorbent. The desorbed CPs were analyzed by HPLC.

2.7. Sample preparation

The proposed mixed hemimicelle solid-phase extraction method was applied to water samples collected from different areas of Peshawar such as industrial effluents from Hayat Abad Industrial Estate, Peshawar, groundwater from old city of Peshawar and tap water from laboratory in the Institute of Chemical Sciences, University of Peshawar. Random sampling method was used for sample collection. The suspended particles from all water samples were removed by filtration through 0.45 µm pore size nylon membrane filter. The samples were stored at 4°C for analysis. For validation of the method, samples were spiked with standard CPs of different concentrations.

3. Results and discussion

3.1. Characterization of adsorbent

The surface morphology of Fe_3O_4 and Fe_3O_4@SiO_2 was studied by SEM and shown in Figs. 2(a) and (b), respectively. As compared with Fe_3O_4, more spherical and dispersed nature of Fe_3O_4@SiO_2 nanoparticles shows that core shell of SiO_2 avoids the agglomeration of Fe_3O_4 nanoparticles. Therefore, the problem of aggregation of Fe_3O_4 nanoparticle in aqueous solution can be resolved by coating Fe_3O_4 nanoparticles with Si–OH functional group on the surface. The average diameter of the Fe_3O_4 and Fe_3O_4@SiO_2 was calculated and found to be 46.44 and 50.17 nm, respectively. It can be observed from the figures that the particle size increased with silica coating. The thickness of the silica shell is about 3–4 nm. The micrographs depicted in Figs. 2(c) and (d) show that 2,4-DCP and 2,4,6-TCP have been successfully adsorbed on Fe_3O_4@SiO_2 nanoparticles after adsorption in aqueous solution.

The elemental analysis using EDX of Fe_3O_4 and Fe_3O_4@SiO_2 nanoparticles in Figs. 3(a) and (b), respectively, shows Si concentration in the spectra of Fe_3O_4@SiO_2 along with Fe, while the spectra of Fe_3O_4 show only Fe concentration which confirmed the coating with silica.

The FTIR spectra in Fig. 4(a) show the absorption bands in Fe_3O_4, and Fig. 4(b) shows the absorption bands in Fe_3O_4@SiO_2 nanoparticle. The absorption band at 540 cm^{-1} in Fe_3O_4 is due to the Fe–O stretching vibrations and belongs to the magnetite in bulk form, while band at 460 cm^{-1} is assigned to the O–Si–O bending vibration. Strong absorption peaks at 1,109.07 and 1,404.18 cm^{-1} correspond to Si–OH and Si–O–Si vibrations in Fe_3O_4@SiO_2 that confirms the surface coating of Fe_3O_4 with functional group of Si–OH. A broad peak at 3,300–3,400 cm^{-1} is attributed to the OH groups stretching vibration.

Surface area, pore volume and pore size of Fe_3O_4 and Fe_3O_4@SiO_2 were calculated by BET and BJH methods. The cumulative surface area of the Fe_3O_4 and Fe_3O_4@SiO_2 determined by BET method was found to be 81.35 and 80.18 m^2/g, while the cumulative surface area using BJH method was found as 106.43 and 103.8 m^2/g, respectively. The values of average pore volume and pore size of Fe_3O_4 were found as 0.27 ccg^{-1} and 46.41 Å and of Fe_3O_4@SiO_2 are 0.21 ccg^{-1} and 44.23 Å, respectively.

3.2. Effect of pH

The charge on the surface of mineral oxide changes greatly with pH of solution. The Fe_3O_4 nanoparticles become soluble in acidic solution (pH ≤ 3), therefore, Fe_3O_4 nanoparticles were coated with thin layer of silica to prevent solubilization in acidic solution for extraction. The application of Fe_3O_4 nanoparticles extended with silica coating and can be used in a wide range of solution pH from acidic to basic. The effect of pH on adsorption of CPs was studied in the range of 2–10. Fig. 5 shows the percentage adsorption against the change in pH. It is clear from the figure that the %

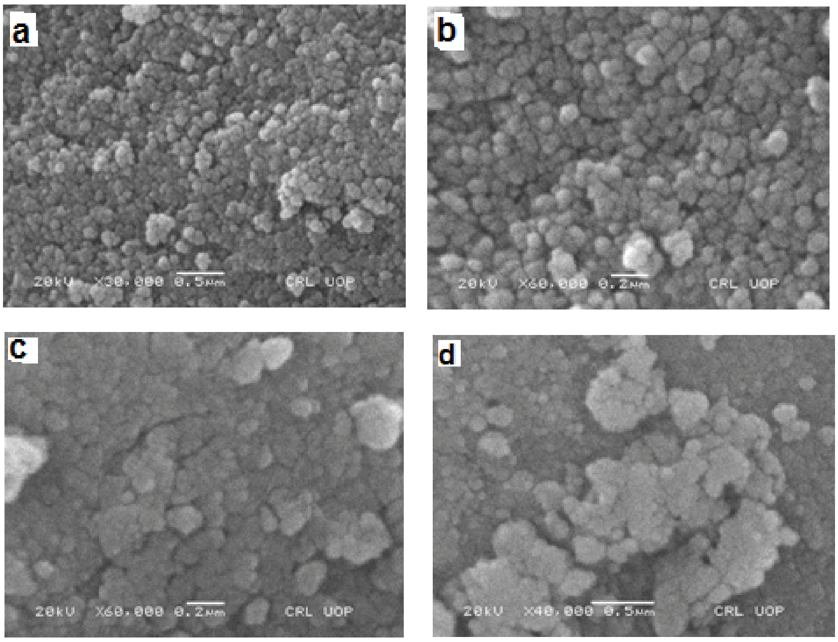


Fig. 2. SEM micrograph of (a) Fe_3O_4 nanoparticles, (b) Fe_3O_4@SiO_2 nanoparticles, (c) Fe_3O_4@SiO_2 nanoparticles after adsorption of 2,4-DCP and (d) Fe_3O_4@SiO_2 nanoparticles after adsorption of 2,4,6-TCP.

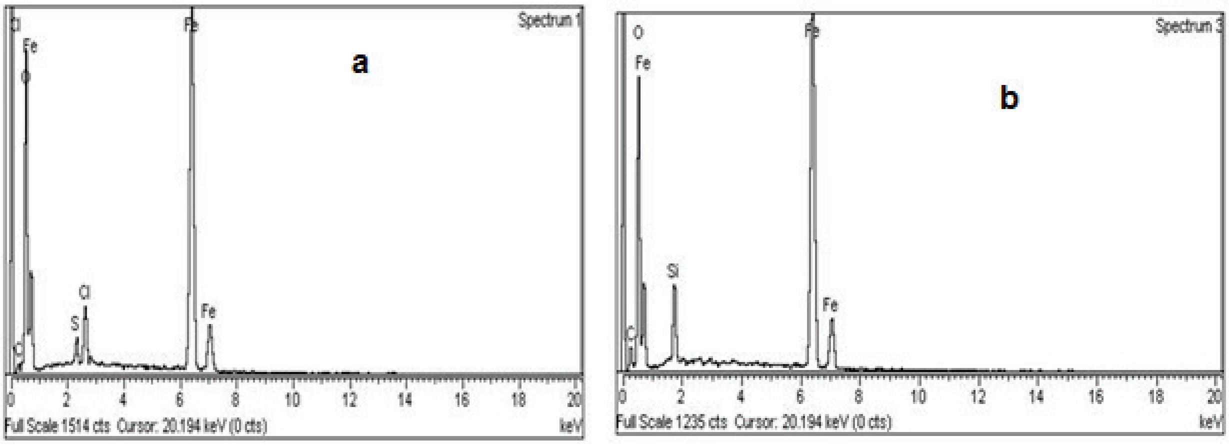


Fig. 3. EDX spectra of (a) Fe_3O_4 nanoparticles and (b) Fe_3O_4@SiO_2 nanoparticles.

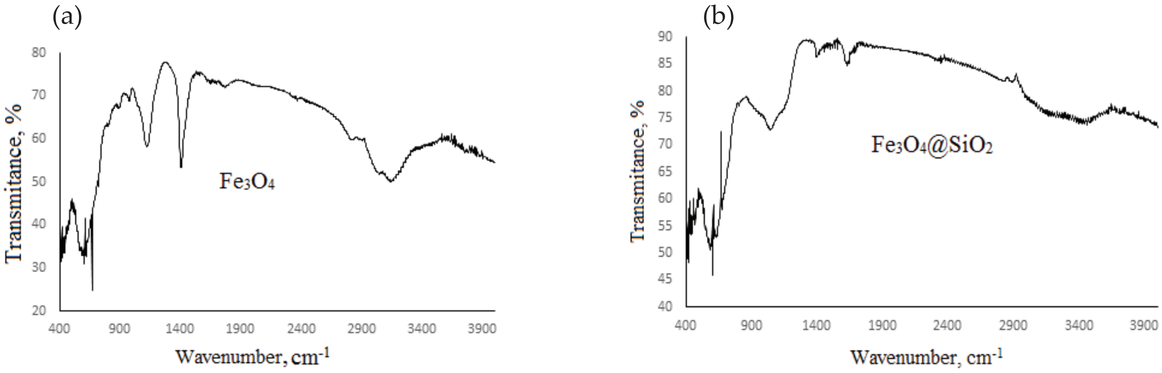


Fig. 4. FTIR spectra of (a) Fe_3O_4 and (b) Fe_3O_4@SiO_2.

adsorption increases as the pH increases and maximum % adsorption of all studied CPs were found at pH 7.

The pzc was found at pH 5.6 for Fe_3O_4 nanoparticles and pH 6.6 for $Fe_3O_4@SiO_2$ nanoparticles. When the pH value of solution increased beyond pzc, the surface became negatively charged, therefore, electrostatic attraction between the negatively charged surface of $Fe_3O_4@SiO_2$ nanoparticles and positively charged CTAB occurred. At pH 7, there is hydrophilic and hydrophobic interaction between the mixed hemimicelle and CPs, which resulted in maximum adsorption of CPs. Therefore, for further studies, pH 7 was selected as an optimum value.

3.3. Effect of adsorbent mass

Nanoparticles have large surface area as compared with ordinary adsorbents such as agricultural and forestry wastes or some carbonaceous materials. The amount of $Fe_3O_4@SiO_2$ nanoparticles was optimized with mixed hemimicelles in the range of 0.05–0.3 g (50–300 mg). Results in Fig. 6 shows that with increase in weight of adsorbent, there is increase in % adsorption of CPs. The increase in % adsorption is due to increase in number of sites that are available for CPs. The adsorption increased rapidly by increasing weight of adsorbent but with further increase the % adsorption remained constant. The mass of 0.2 g was selected for CPs adsorption and extraction study.

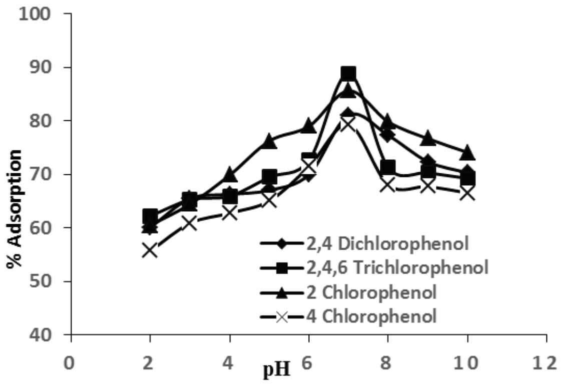


Fig. 5. Effect of pH on % adsorption of chlorophenols.

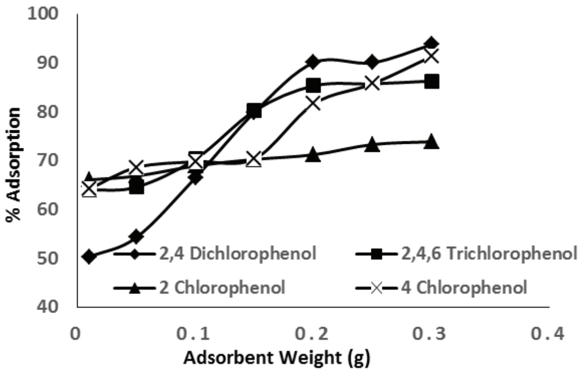


Fig. 6. Effect of adsorbent weight on % adsorption of chlorophenols.

3.4. Effect of CTAB

The type of surfactant aggregates (hemimicelles, mixed hemimicelles with admicelles and admicelles) on $Fe_3O_4@SiO_2$ nanoparticles depends on the surfactant and nanoparticle weight ratio. The effect of CPs % adsorption was explored in the range of 50–250 mg/g (CTAB/NP) to obtain hemimicelles, mixed hemimicelles and admicelles regions. The results are shown in Fig. 7 where hemimicelles were formed at CTAB concentration of 50–150 mg/g and mixed hemimicelles with admicelles between 150 and 250 mg/g. The maximum adsorption of studied four CPs was acquired with 150–250 mg/g of CTAB/NP. Therefore, 150 mg/g of CTAB/NP system was further used for adsorption and extraction process.

3.5. Effect of time

The effect of time for the adsorption of CPs on $Fe_3O_4@SiO_2$ nanoparticles was also studied. It was observed that % adsorption of 2,4-DCP and 2,4,6-TCP increased to 90%, while the % adsorption of 2-CP and 4-CP constantly increased with the increase in time (Fig. 8). Therefore, 60 min time was selected as an optimum time for the adsorption study.

3.6. Desorption study

Mixed hemimicelles system can be easily broken with organic solvents, and the CPs can be removed from the

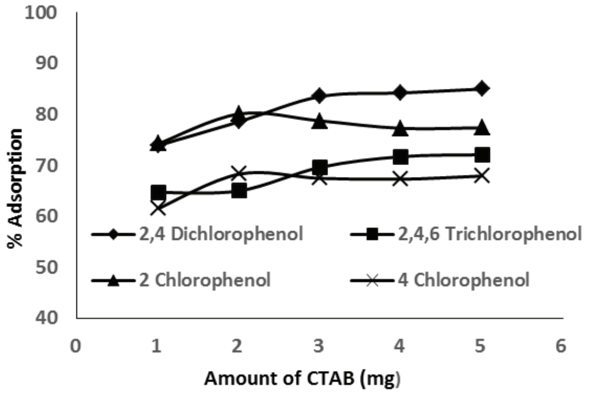


Fig. 7. Effect of CTAB on % adsorption of chlorophenols.

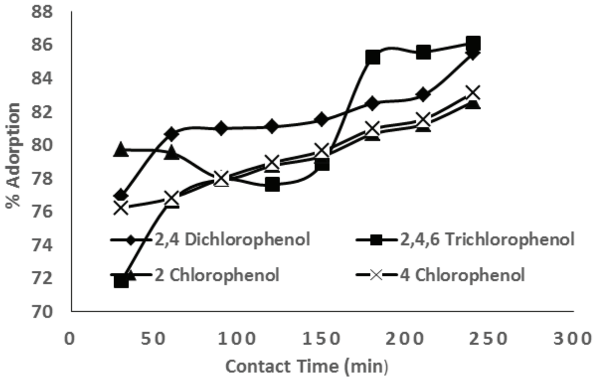


Fig. 8. Effect of contact time on % extraction of chlorophenols.

adsorbent surface. The effect of desorption solvent type and volume was examined on the extraction efficiency of four CPs (2-CP, 4-CP, 2,4-DCP and 2,4,6-TCP). The results in Fig. 9 show the extraction efficiency of CPs using different solvents such as methanol, ethanol, acetone, acidic methanol (contained equal volumes of methanol and 0.05 mol/L HCl, v/v) and alkaline methanol (contained equal volume of methanol and 0.05 mol/L NaOH, v/v). The extraction efficiency was high with acidic methanol such as 2-CP (95%), 4-CP (96%), 2,4-DCP (98%) and 2,4,6-TCP (99%). This may be due to the fact that when the pH of solution was below the pzc, the surface becomes positively charged and the mixed hemimicelles disrupted from the surface of $Fe_3O_4@SiO_2$ nanoparticles. Therefore, 2 mL of acidic methanol was preferred for the extraction of CPs from CTAB covered $Fe_3O_4@SiO_2$ nanoparticles.

3.7. Reusability of adsorbent

Reusability of the adsorbent was checked by adsorption and desorption of CPs. The used adsorbent was washed first with water and then with ethanol repeatedly and dried for further reuse. There was no significant decrease in the extraction of CPs after seven times using the same adsorbent. The results indicated that the adsorbent is stable as well as durable during the extraction of CPs.

3.8. Analytical performance

The analytical characteristics of the method at optimized conditions in terms of linear range, limit of detection (LOD), limit of quantification (LOQ), repeatability and recoveries were determined (Table 1). The results show that good linearity was obtained in the concentration range of 0.5–20 μg/L with coefficient of determination value of 0.9996 for 2-CP, 0.9993 for 4-CP, 0.9986 for 2,4-DCP and 0.9983 for 2,4,6-TCP. The LOD values for four CPs were calculated from five to six determinations of analyte concentration in tap water using a three ratio of signal to noise (the ratio between the peak areas for each CP and peak areas of noise, S/N = 3). The LOD values were 0.07, 0.02, 0.03 and 0.02 μg/L for 2-CP, 4-CP, 2,4-DCP and 2,4,6-TCP, respectively. Precision of the proposed method was obtained by analysis of spiked water samples in triplicate, and values of relative standard deviation (RSD) were calculated from each sample peak area. The RSD values were found from 0.27% to 2.2%.

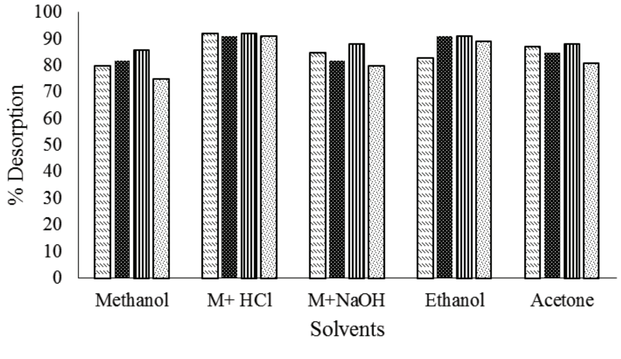


Fig. 9. Desorption studies of chlorophenols.

3.9. Method validation

The proposed mixed hemimicelles extraction method was applied to different environmental samples including tap water, groundwater and industrial wastewater to determine CPs. Water samples were analyzed for the presence of CPs before spiking and confirmed that no concentration of CPs were present. For recovery determination, the samples were spiked with 4 and 8 μg/mL concentration of each CP and extracted with the proposed extraction method. Determinations were based on extraction of each concentration in triplicate, and the recoveries for all CPs were in the range of 95.0%–99.0% (Table 2). The method showed good precision and accuracy.

3.10. Comparison with literature methods

To evaluate the performance of the proposed method, a comparison of the linearity, LODs and RSDs obtained with different microextraction methods coupled with HPLC. Table 3 summarizes the analytical methods developed for the determination of CPs in water. All of these results indicated that the proposed method is simple, accurate and reproducible.

4. Conclusion

In this research, a mixed hemimicelles silica-coated MNPs solid-phase extraction method has been developed for the extraction of CPs from water samples. CPs were entrapped with mixed hemimicelles on the surface of silica-coated MNPs and released back with the use of acidic methanol solvent. Silica-coated MNPs are chemically more stable due to inert coating of silica without change in magnetic property as well as improved the extraction of CPs. Additionally, the proposed mixed hemimicelles solid-phase extraction method extended the advantages such as use of small amount of adsorbent (high surface area), no filtration (time consuming), high extraction efficiency, simplicity and economical eluents.

Table 1
Analytical parameters of the proposed method

Analytes	Linearity range (μg/L)	Calibration equation	Correlation coefficient	RSD (%)	LOD (μg/L)	LOQ (μg/L)
2-CP	0.5–20	$y = 0.0171x + 0.0039$	0.9996	2.2	0.07	0.24
4-CP	0.5–20	$y = 0.0136x - 0.0107$	0.9993	0.72	0.02	0.07
2,4-DCP	0.5–20	$y = 0.0122x - 0.0036$	0.9986	0.56	0.03	0.09
2,4,5-TCP	0.5–20	$y = 0.0101x + 0.0039$	0.9983	0.27	0.02	0.05

Table 2
The extraction recoveries obtained for the studied chlorophenols from different spiked water samples

Type of chlorophenols	Spiked (μg/mL)	% Recovery		
		Tap water	Groundwater	Wastewater
2-CP	0.0	0.0	0.0	0.0
	4.0	97.0 ± 4.0	96.0 ± 3.5	95.0 ± 2.5
	8.0	96.0 ± 5.0	96.5 ± 2.0	96.0 ± 4.0
4-CP	0.0	0.0	0.0	BDL
	4.0	98.0 ± 3.5	96.0 ± 4.0	96.0 ± 3.0
	8.0	96.6	97.4 ± 1.8	96.0 ± 4.0
2,4-DCP	0.0	0.0	0.0	BDL
	4.0	98.0 ± 1.0	97.0 ± 2.8	98.0 ± 4.0
	8.0	98.0 ± 2.6	98.0 ± 4.0	99.0 ± 3.0
2,4,6-TCP	0.0	0.0	0.0	BDL
	4.0	99.0 ± 3.5	98.0 ± 3.0	99.0 ± 5.0
	8.0	98.0 ± 2.8	97.0 ± 2.0	97.0 ± 5.0

BDL, Below detection limit.

Table 3
Comparison of the proposed solid-phase extraction method for CPs with reported methods

Analyte	Linear range (μg/L)	Recovery (%)	RSD (%)	LOD (μg/L)	Sorbent material	Methods	Reference
4-CP	5–400	91	5.1	0.5	Hollow fiber supported ionic liquid membrane	HPLC-UV/vis	[6]
2,4-DCP	5–400	90	4.3	0.5			
2,4,6-TCP	10–200	88	5.9	1.0			
3-CP	0.1–1.0	99.4	2.0	–	Graphene nanoplates	UV-visible Spectrophotometer	[23]
4-CP	0.1–1.0	95.2	3.8	–			
2,4-DCP	0.1–1.0	96.9	3.1	–			
2-CP	0.1–100	96.4	3.2	0.1	3D graphene magnetic nanocomposite	HPLC-UV/vis	[24]
3-CP	0.1–100	95.8	3.5	0.1			
2,3-DCP	0.1–100	96.2	3.5	0.1			
3,4-DCP	0.1–100	99.1	3.3	0.1			
2-CP	5.2–104.5	84.5	6.2	0.22	Magnetic polysulfone microcapsules	HPLC-UV	[25]
4-CP	1.0–101.2	85.5	5.8	0.17			
2-CP	1.0–200	95.4	3.1	0.12	Magnetic porous carbon	HPLC-UV/vis	[26]
3-CP	1.0–200	90.8	4.39	0.12			
2,3-DCP	1.0–200	93.6	5.1	0.1			
3,4-DCP	1.0–200	94.1	2.6	0.1			
3-CP	2–100	77.9	4.1	0.35	Ionic liquid functionalized magnetic microsphere	HPLC-DAD	[27]
2,4-DCP	2–100	79.8	2.4	0.35			
PCP	2–100	86.2	9.6	0.20			
4-CP	0.5–50	95.9	1.7	0.05	Magnetic ionic liquid molecularly imprinted polymer	HPLC-UV/vis	[28]
2,4-DCP	0.5–50	91.8	1.9	0.05			
2,4,6-TCP	0.5–50	89.9	3.0	0.05			
2,3,5,6-TCP	0.5–50	86.8	2.4	0.05			
PCP	0.5–50	88.7	2.6	0.05			
2-CP	0.5–20	95.0	2.2	0.07	Mixed hemimicelles silica-coated magnetic nanoparticles	HPLC-UV/vis	Present work
4-CP	0.5–20	96.0	0.72	0.02			
2,4-DCP	0.5–20	98.0	0.56	0.03			
2,4,6-TCP	0.5–20	99.0	0.27	0.02			

PCP, Pentachlorophenol.

References

[1] D. Puyol, V.M. Monsalvo, S. Sanchis, J.L. Sanz, A.F. Mohedano, J.J. Rodriguez, Comparison of bioaugmented EGSB and GAC–FBB reactors and their combination with aerobic SBR for the abatement of chlorophenols, Chem. Eng. J., 259 (2015) 277–285.

[2] R.M. González Paredes, C. García Pinto, J.L. Pérez Pavón, B. Moreno Cordero, In situ derivatization combined to automated microextraction by packed sorbents for the determination of chlorophenols in soil samples by gas chromatography mass spectrometry, J. Chromatogr. A, 1359 (2014) 52–59.

[3] C. Fan, N. Li, X. Cao, Determination of chlorophenols in honey samples using in-situ ionic liquid-dispersive liquid–liquid microextraction as a pretreatment method followed by high-performance liquid chromatography, Food Chem., 174 (2015) 446–451.

[4] R. Alizadeh, Chlorophenols ultra-trace analysis in environmental samples by chitosan-zinc oxide nanorod composite as a novel coating for solid phase microextraction combined with high performance liquid chromatography, Talanta, 146 (2016) 831–838.

[5] N. Fattahi, Y. Assadi, M.R.M. Hosseini, E.Z. Jahromi, Determination of chlorophenols in water samples using simultaneous dispersive liquid-liquid microextraction and derivatization followed by gas chromatography-electron-capture detection, J. Chromatogr. A, 1157 (2007) 23–29.

[6] J. Peng, J. Liu, X. Hu, G. Jiang, Direct determination of chlorophenols in environmental water samples by hollow fiber supported ionic liquid membrane extraction coupled with high-performance liquid chromatography, J. Chromatogr. A, 1139 (2007) 165–170.

[7] J.I. Cacho, N. Campillo, P. Vinas, M. Hernandez-Cordoba, Stir bar sorptive extraction polar coatings for the determination of chlorophenols and chloroanisoles in wines using gas chromatography and mass spectrometry, Talanta, 118 (2014) 30–36.

[8] R. Morales, L.A. Sarabia, M.S. Sánchez, M.C. Ortiz, Experimental design for the optimization of the derivatization reaction in determining chlorophenols and chloroanisoles by headspace-solid-phase microextraction gas chromatography/mass spectrometry, J. Chromatogr. A, 1296 (2013) 179–195.

[9] A. Ribeiro, M.H. Neves, M.F. Almeida, A. Alves, L. Santos, Direct determination of chlorophenols in landfill leachates by solid-phase microextraction gas chromatography-mass spectrometry, J. Chromatogr. A, 975 (2002) 267–274.

[10] Y. Chao, Y. Tu, Z. Jian, H. Wang, Y. Huang, Direct determination of chlorophenols in water samples through ultrasound-assisted hollow fiber liquid–liquid–liquid microextraction on-line coupled with high performance liquid chromatography, J. Chromatogr. A, 1271 (2013) 41–49.

[11] X. Li, A. Xue, H. Chen, S. Li, Low-density solvent-based dispersive liquid–liquid microextraction combined with single-drop microextraction for the fast determination of chlorophenols in environmental water samples by high performance liquid chromatography-ultraviolet detection, J. Chromatogr. A, 1280 (2013) 9–15.

[12] S. Pan, L. Zhou, Y. Zhao, X. Chen, H. Shen, Amine-functional magnetic polymer modified graphene oxide as magnetic solid-phase extraction materials combined with liquid chromatography–tandem mass spectrometry for chlorophenols analysis in environmental water, J. Chromatogr. A, 1362 (2014) 34–42.

[13] Y. Li, S. Zhang, C. Song, J. You, Determination of bisphenol A and alkylphenols in soft drinks by high performance liquid chromatography with fluorescence detection, Food Anal. Methods, 6 (2013) 1284–1290.

[14] H. Heidari, H. Razmi, Multi-response optimization of magnetic solid phase extraction based on carbon coated Fe_3O_4 nanoparticles using desirability function approach for the determination of the organophosphorus pesticides in aquatic samples by HPLC–UV, Talanta, 99 (2012) 13–21.

[15] D. Barreca, W.J. Blau, G.M. Croke, F.A. Deeney, F.C. Dillon, J.D. Holmes, C. Kufazvinei, M.A. Morris, T.R. Spalding, E. Tondello, Iron oxide nanoparticle impregnated mesoporous silica as platforms for the growth of carbon nanotubes, Microporous Mesoporous Mater., 103 (2007) 142–149.

[16] P. Wang, X. Wang, S. Yu, Y. Zou, J. Wang, Z. Chen, N.S. Alharbi, A. Alsaedi, T. Hayat, Y. Chen, X. Wang, Silica coated Fe_3O_4 magnetic nanospheres for high removal of organic pollutants from wastewater, Chem. Eng. J., 306 (2016) 280–288.

[17] D. Maity, D.C. Agrawal, Synthesis of iron oxide nanoparticles under oxidizing environment and their stabilization in aqueous and non-aqueous media, J. Magn. Magn. Mater., 308 (2007) 46–55.

[18] M.M. Rahman, S.B. Khan, A. Jamal, M. Faisal, A.M. Aisiri, Iron oxide nanoparticles, Nanomaterials, 3 (2011) 43–67.

[19] X. Zhao, Y. Shi, T. Wang, Y. Cai, G. Jiang, Preparation of silica-magnetite nanoparticle mixed hemimicelles sorbents for extraction of several typical phenolic compounds from environmental water samples, J. Chromatogr. A, 1188 (2008) 140–147.

[20] J. Shah, M.R. Jan, A.U. Haq, S. Jamil, Magnetic nanoparticles impregnated low cost agriculture waste for removal of methyl blue from aqueous solution, Toxicol. Environ. Chem., 96 (2014) 218–226.

[21] J. Shah, M.R. Jan, M. Zeeshan, M. Iqbal, Solid phase extraction of 2,4-dichlorophenol from aqueous samples using magnetic graphene nanocomposite, Sep. Sci. Technol., 51 (2016) 1480–1489.

[22] H.T.S. Britton, Hydrogen Ions, Monographs on Applied Chemistry, John Wiley & Sons, Inc., New York, 1943, p. 313.

[23] K.C. Sadanala, B.C. Chung, Graphene nanoplates as a solid phase extraction sorbent for analysis of chlorophenols in water, J. Korean Soc. Appl. Biol. Chem., 56 (2013) 673–678.

[24] X.-L. Liu, C. Wang, Q.-H. Wu, Z. Wang, Preconcentration of chlorophenols in water samples using three dimensional graphene-based magnetic nanocomposite as absorbent, Chin. Chem. Lett., 25 (2014) 1185–1189.

[25] X. Liu, J. Yin, L. Zhu, G. Zhao, H. Zhang, Evaluation of a magnetic polysulfone microcapsule containing organic modified montmorillonite as a novel solid-phase extraction sorbent with chlorophenols as model compounds, Talanta, 85 (2011) 2451–2457.

[26] C. Wang, R. Ma, Q. Wu, M. Sun, Z. Wang, Magnetic porous carbon as an adsorbent for the enrichment of chlorophenols from water and peach juice samples, J. Chromatogr. A, 1361 (2014) 60–66.

[27] F. Yang, R. Shen, Y. Long, X. Sun, F. Tang, Q. Cai, S. Yao, Magnetic microsphere confined ionic liquid as a novel sorbent for the determination of chlorophenols in environmental water samples by liquid chromatography, J. Environ. Monit., 13 (2012) 440–445.

[28] W. Ma, K.H. Row, Solid-phase extraction of chlorophenols in sea water using a magnetic ionic liquid molecularly imprinted polymer with incorporated silicon dioxide as a sorbent, J. Chromatogr. A, (2018) 1–8. doi: doi.org/10.1016/j.chroma.2018.01.013.

Supplementary data

Fig. S1. Checking the magnetic property of Fe_3O_4 and $Fe_3O_4@SiO_2$ particles with magnet.