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A sensitive and selective spectrophotometric method for 2-chlorophenol based on solid phase extraction with mixed hemimicelle magnetic nanoparticles



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Abstract The first study of a sensitive and selective spectrophotometric detection of 2-chlorophenol (2-CP) was reported. The method is based on derivatization of 2-CP with 4-aminoantipyrine (4-AAP) and subsequent preconcentration by solid phase extraction (SPE) using mixed hemimicelles adsorbent of cetyltrimethylammonium bromide coated magnetic nanoparticles (CTAB coated Fe₃O₄ NPs) before its detection by spectrophotometry at 510 nm. The adsorption capacity was evaluated using the Langmuir adsorption isotherm model, with high correlation coefficients ($R^2 = 0.9983$). The optimum conditions for SPE were CTAB coated Fe₃O₄ NPs 20 mg under vortex 60 s and methanol as the desorption solvent under sonication for 7 min. The linearity of the method was in the range of 0.05–1.0 mg L⁻¹ with correlation coefficient (0.9970). The limit of detection (LOD) and limit of quantitation (LOQ) were 0.01 mg L⁻¹ and 0.05 mg L⁻¹, respectively. Good precision with relative standard deviation (%RSD, $n = 5$) less than 3.7% was obtained. The method was successfully applied for the determination of 2-CP in soil samples with satisfactory recoveries (81.7–95.2%).

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1. Introduction

2-Chlorophenol (2-CP) is one of the priority pollutants classified by both the EU (European Union) and US EPA (United State Environmental Protection Agency) (Ruzgas et al., 1995). Like the other CPs, it has been widely used in various fields such as the pesticides, phenolic resins, plastics and other

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chemicals industries (Agboola et al., 2005 and Khanikar and Bhattacharyya, 2013). The regulations have been established by various organizations such as EU and EPA to control the emission of the discharges from chlorophenol used industries. For example, the maximum concentration allowance of 2-CP in aquatic environments is established at low $\mu\text{g L}^{-1}$ level by the EU (European Environment Agency, 2007 and European Commission, 2006). Several analytical methods have been used for the determination of CPs, and are those sensitive and selective instrumental methods such as HPLC and GC. The EPA official method for the determination of 2-CP in aquatic environments is liquid-liquid extraction coupled with GC-MS (EPA method 625) which provided LOD in $\mu\text{g L}^{-1}$ range (<http://www.epa.gov>, 2006).

However, spectrophotometer can be used as an alternative technique to the sophisticated instruments for the detection of 2-CP and the other CPs. Although, CPs can be easily detected via their aromatic moiety by spectrophotometry in UV region, the sensitivity and selectivity for the spectrophotometric detection can be enhanced by derivatization of CPs with various reagents. Among the derivatizing agents used, 4-aminoantipyrine (4-AAP) has been widely used because of its highly sensitive and stable colored derivative (Ettinger et al., 1951 and Venkateswarlu and Seshaiiah, 1995). In addition, the sensitivity of spectrophotometric detection can be increased further by the preconcentration techniques such as liquid-liquid extraction (Ettinger et al., 1951).

Solid phase extraction (SPE) is nowadays accepted as an alternative method to classical liquid-liquid extraction. Besides its environmental friendly from low consumption of organic solvent, SPE is simple and fast (Thuman and Mills, 1998; Solid phase extraction, in: Principles and Practice, Wiley, New York; Sadeghi and Sheikhzadeh, 2009; Aydin and Soylak, 2007 and Amjadi and Samadi, 2013). In SPE, adsorbent plays an important role in selectivity and capacity of the extraction. A number of researches have been focused on the synthesis of specific adsorbents or modification of the commercial available adsorbents. The modification of adsorbents can be performed by either chemical or physical approach.

Recently, mixed hemimicelles adsorbents were synthesized and applied in SPE of various compounds including metal ions (Karatapanis et al., 2011; Pouraberi et al., 2012 and Ezoddin et al., 2010), inorganic compounds (Hrenovic et al., 2008 and Janoš and Šmídová, 2005) and organic compounds (Li et al., 2007 and López-Jiménez et al., 2005). These adsorbents were the mineral oxides supports such as alumina (Ezoddin et al., 2010; Saitoh et al., 2011 and Moral et al., 2006), silica (Zhu et al., 2010), clay mineral (Özdemir et al., 2007 and Gürses et al., 2010) and titanium dioxide (Pouraberi et al., 2012) which were modified with ionic surfactants such as sodium dodecyl sulfate (SDS) (Özdemir et al., 2007; Shariati et al., 2011; Faraji et al., 2010; Bagheri et al., 2011 and Moral et al., 2006) or cetyltrimethylammonium bromide (CTAB) (Zhu et al., 2010; Liu et al., 2012; Gürses et al., 2010; Niu et al., 2007 and Koniari and Avranas, 2011). The existence of mixed micelles of ionic surfactants on the mineral oxides supports was explained by the electrostatic interaction between the head group of ionic surfactants and oppositely charged groups on the supports (Henglein, 1989). The use of mixed hemimicelle sorbents in SPE has many advantages such as easy preparation of the adsorbent, easy elution of analytes and high extraction efficiency. However, a relative small surface area of the

micro-particles sorbents may lead to a relatively low extraction capability, resulted in long time consuming for large volume sample. To overcome this limitation, nanosized materials have been used as adsorbent in SPE.

Magnetic nanoparticles (Fe_3O_4 NPs) have attracted particular interest in the scientific public due to their superparamagnetic nature as well as their unique physical and chemical properties especially for SPE as follows: (i) good stability, (ii) easy synthesis which can be conveniently modified with functional groups because of the abundant hydroxyls on the surface of Fe_3O_4 NPs, (iii) high surface area, thus providing high extraction efficiency and (iv) easy to separate by magnetic field due to its strong magnetism (Ngomsik et al., 2005; Faraji et al., 2010; Zheng et al., 2006; Gardimalla et al., 2005 and Gao and Chen, 2013). According to low toxicity and low cost, Fe_3O_4 NPs has been used in various applications such as environmental, material science and analytical chemistry (Gao and Chen, 2013).

The aim of this work was to develop a simple and sensitive spectrophotometric method for the determination of 2-CP. 2-CP was firstly derivatized with 4-AAP before being extracted by mixed hemimicelles CTAB coated Fe_3O_4 NPs as the adsorbent for SPE method. The derivatization of 2-CP facilitates the detection in the visible wavelength. The parameters affecting SPE were investigated and optimized. In addition, some physico-chemical properties and the adsorption behavior of the adsorbent were studied insightfully and discussed in detail.

2. Experimental

2.1. Chemicals and reagents

All chemicals were analytical reagent grade and all solutions were prepared in deionized water with a resistivity of $18.2 \text{ M}\Omega \text{ cm}$ (RiO₃™ Type I Simplicity 185, Millipore, USA). Phenol, 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol, 2,4,5-trichlorophenol and 2,4,6-trichlorophenol were purchased from Aldrich (Germany). The stock solution of $1000 \mu\text{g mL}^{-1}$ 2-CP was prepared by dissolving in methanol. Acetonitrile (RCI Lab scan, Thailand), methanol (QRéc, New Zealand) and acetone (Lab scan, Ireland) were used as desorption solvent. HCl (37%, v/v) and NaOH were obtained from Carlo Erba (France). Sodium tetraborate decahydrate ($\text{B}_4\text{Na}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$) was purchased from Sigma-Aldrich (France). 4-Aminoantipyrine (98%) was purchased from Acros organics (Belgium). Potassium hexacyanoferrate(III), $\text{K}_3\text{Fe}(\text{CN})_6$, was obtained from Sigma (Spain). Hexadecyltrimethylammonium bromide (CTAB, $\text{C}_{19}\text{H}_{42}\text{BrN}$) was purchased from Fluka (Denmark).

2.2. Instrumentation

Absorbance measurements and spectra recording were performed on a UV-Vis spectrophotometer (Agilent 8453) with a 1-cm quartz cell.

Fourier transform infrared spectroscopy (FT-IR, Perkin Elmer Spectrum one) was used to confirm the chemical bonding between Fe_3O_4 NPs and CTAB. The existence of CTAB on the surface of Fe_3O_4 NPs was confirmed by conductometry (PHM 210, Standard pH meter). The magnetic properties of Fe_3O_4 NPs both before and after coating with CTAB were

measured at room temperature by a vibrating sample magnetometer (VSM 7403; Lake Shore).

The HPLC system (Waters, Massachusetts, USA) consisted of an in-line degasser, a 600E quaternary pump, and a Waters 2996 photodiode array detector (PDA). Empower software was used to control the system and for the acquisition and analysis of data. The separation was performed on a Waters Atlantis T3 column (150 mm \times 4.6 mm i.d., 5 μ m) (Dublin, Ireland) at room temperature. Chromatographic analysis was carried out at room temperature using isocratic elution with methanol:water (60:40%, v/v) as the mobile phase. The flow rate was set at 1.0 mL min⁻¹ and the eluate was monitored using UV detection at 250 nm.

The synthesis and characterization of the Fe₃O₄ NPs have been mentioned in our previous work (Mukdasai et al., 2013).

2.3. Preparation of CTAB coated Fe₃O₄ NPs

0.1 mol L⁻¹ borate buffer solution pH 9.5 (1000 μ L) was added into dried Fe₃O₄ NPs (3.0 g) and then 1.2 mmol L⁻¹ CTAB (3 mL) was added into solution and mixed thoroughly. After stirring for 1 h, the suspension was washed with water and finally dried overnight at room temperature. The proposed structure of the adsorbent is shown in Fig. 1a.

2.4. Extraction of 2-CP by SPE

2-CP (0.5 mg L⁻¹) was mixed with 20 mmol L⁻¹ borate buffer (pH 9.5) 2000 μ L, 2.0 mmol L⁻¹ 4-aminoantipyrine (204 μ L), 1.5 mmol L⁻¹ K₃Fe(CN)₆ (60 μ L) and adjusted with water to a final volume of 10 mL. The solution was left for 10 min for

derivatization of 2-CP as the chemical reaction shown in Fig. 1b (Fiamegos et al., 2002). After that CTAB coated Fe₃O₄ NPs (10 mg) were added into a vial containing the derivative. The vial was vortexed for 60 s. The adsorbent was separated from the solution by magnet. The aqueous solution was withdrawn by a syringe. Methanol (1000 μ L) was then added into the vial and was sonicated for 7 min. The solution was separated from the adsorbent by a syringe with the aid of magnet. The solution was subsequently subjected to spectrophotometer for the absorbance measurement at 510 nm. A blank reagent was prepared in the same manner without the addition of 2-CP. All the experiments were consecutively performed in triplicate.

2.5. Determination of 2-CP in soil samples

Three soil samples were collected from Sugar factory in Kalasin province (Thailand). The soil samples were air-dried at room temperature, then ground and passed through 250 μ m sieve. Soil sample was accurately weighted (5.0 g) and put into a 50 mL centrifuge tube and then 10.0 mL water was added. The mixtures were first vigorously shaken on a vibrator for 30 min at 250 rpm and then centrifuged at 3500 rpm for 5 min. Next, the supernatant was filtered through a 0.45 μ m membrane and a 5.00 mL aliquot of the supernatant was transferred to a vial and finally extracted by the extraction method (see Section 2.4).

For spiked samples, three different concentrations of standard 2-CP were added into soil samples (providing concentration of 0.3, 0.6 and 0.9 μ g g⁻¹) before the extraction by this method.

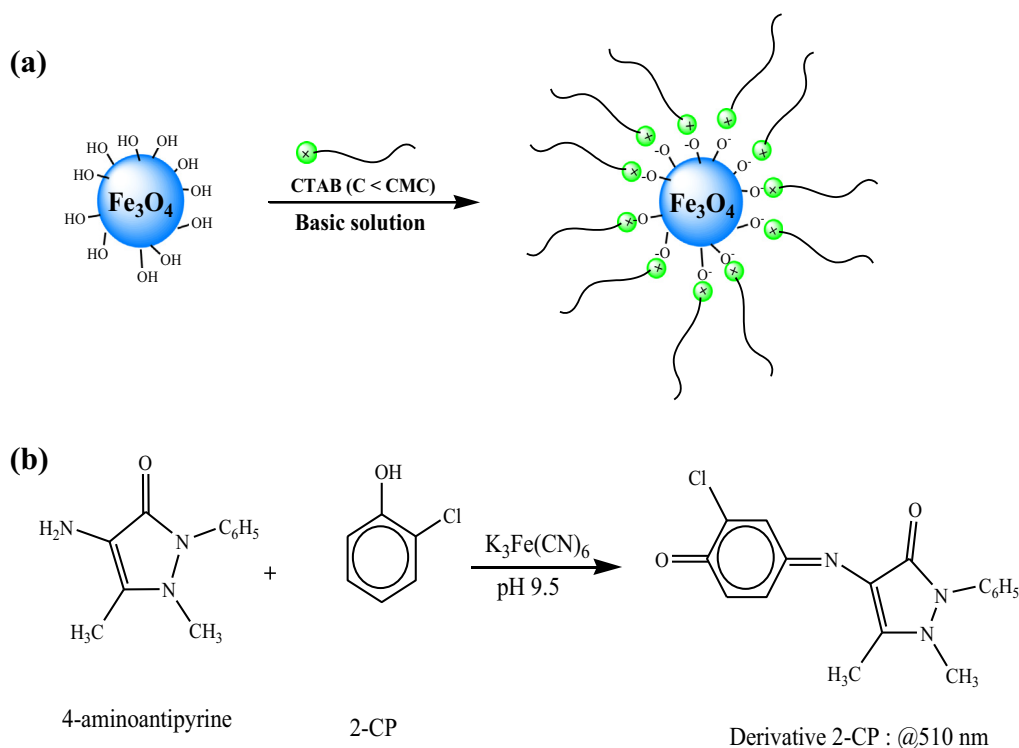


Figure 1 Schematic diagram of (a) the preparation of the cetyltrimethylammonium bromide coated magnetic nanoparticles (CTAB coated Fe₃O₄ NPs) as the adsorbent and (b) the chemical reaction for 2-CP derivative.

3. Results and discussion

3.1. Characterization and behavior of CTAB on Fe_3O_4 NPs

Fourier transform infrared spectroscopy (FT-IR) has been employed to qualitatively determine the adsorption of CTAB on surface of Fe_3O_4 NPs. The FT-IR spectrum of CTAB coated Fe_3O_4 NPs showed the extra bands at 2918 and 2852 cm^{-1} compared to the FT-IR spectrum of Fe_3O_4 NPs (data not shown, [Supplementary data Fig. S1](#)), which are assigned to be stretching vibration of C–H ([Farahani and Shemirani, 2012](#)). All of these bands successfully confirmed the presence of CTAB on Fe_3O_4 NPs.

Modification of the Fe_3O_4 NPs with appropriate functional groups not only provides the selectivity for extraction but also facilitates the extraction since it can prevent the agglomeration of Fe_3O_4 NPs. To investigate the effect of CTAB on the magnetic properties of Fe_3O_4 NPs, the magnetic properties of the Fe_3O_4 NPs both before and after coating with CTAB were investigated. The maximum saturation magnetizations (data not shown, [Supplementary data Fig. S2](#)) are 44.92 and 72.70 emu g^{-1} for CTAB coated Fe_3O_4 NPs and Fe_3O_4 NPs, respectively. The decrease in the magnetic strength resulted from the non-magnetic shell of CTAB. Although, the magnetic strength decreased after modification, it remains superparamagnetic, thus it can be easily separated by magnet ([Zhang et al., 2010](#)).

The existence of CTAB on the surface of Fe_3O_4 NPs was also confirmed using conductometric method. The dependence of specific conductivity (κ) on the concentration of CTAB is shown in [Fig. 2](#). It can be seen that the specific conductivity decreased with increasing of the CTAB concentration and reached a minimum at 2.1 mmol L^{-1} of CTAB. The breaking point ([Fig. 2](#)) at 2.1 mmol L^{-1} CTAB indicates the formation of micelle. Before the critical micelles concentrations (cmc i.e. 2.1 mmol L^{-1} CTAB), the adsorbed surfactant molecules may spread themselves on the oxides surface of Fe_3O_4 NPs to form a single-layer coverage (hemimicelles), probably through the electrostatic interaction between charged oxide surface and

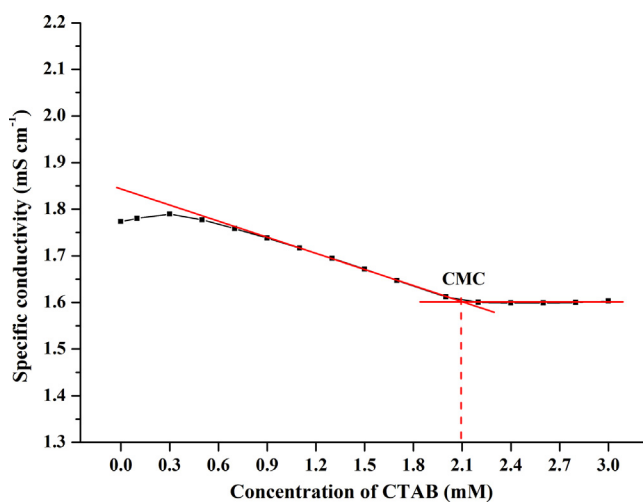


Figure 2 The relationship of specific conductivity (κ) and concentration of CTAB on the surface of Fe_3O_4 NPs.

the oppositely charged surfactant head group. Thus, the conductivity decreased from the balance charge of negative charge on Fe_3O_4 NPs and positive charge of CTAB. The second region involved the hydrophobic and electrostatic interactions which resulted in the formation of bilayers (admicelles) of CTAB ([Nagashima and Blim, 1999](#) and [Fan et al., 1997](#)). Above this point (2.1 mmol L^{-1} of CTAB) the specific conductivity started to keep constant indicating that the overall surface of Fe_3O_4 NPs was saturated by surfactants and micelles in the solution. Thus, 1.2 mmol L^{-1} of CTAB was chosen to modify surface of Fe_3O_4 NPs.

3.2. Adsorption isotherm on surface of CTAB coated Fe_3O_4 NPs

The adsorption isotherm of 2-CP on the surface of CTAB coated Fe_3O_4 NPs was studied. Adsorption isotherm provides not only the qualitative information on the capacity of adsorbent but also the nature of the solute surface interaction. Two common isotherm models namely, Langmuir and Freundlich models ([Gao and Chen, 2013](#) and [Zhou et al., 2013](#)) were

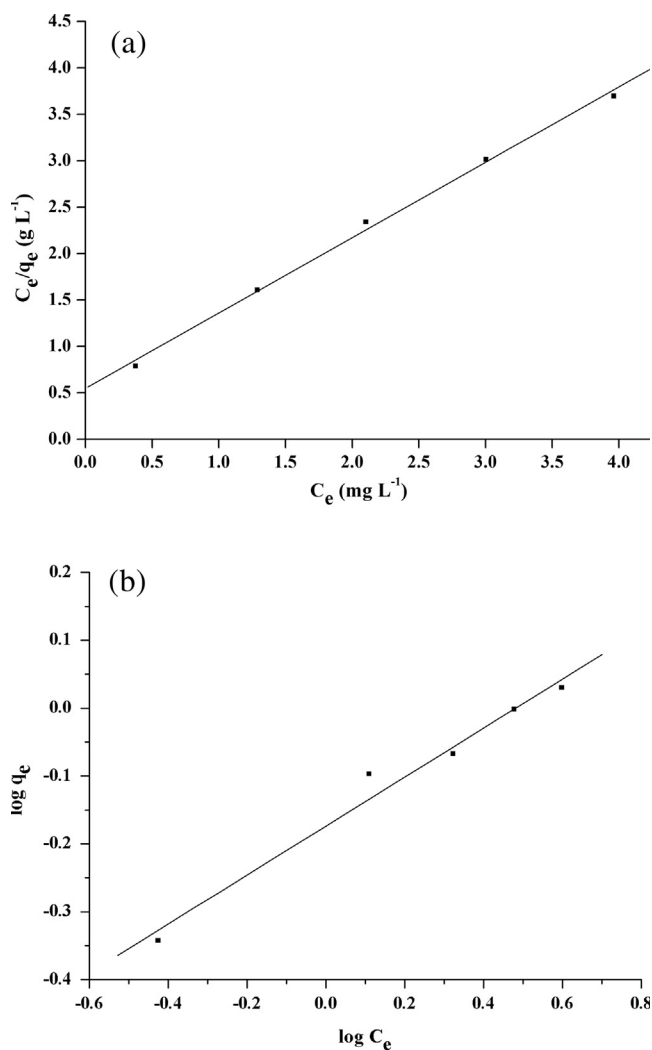


Figure 3 Linearization of adsorption isotherms of 2-CP derivative on surface of CTAB coated Fe_3O_4 NPs in accordance with (a) Langmuir-type model (C_e/q_e vs. C_e) and (b) Freundlich-type model ($\log q_e$ vs. $\log C_e$).

Table 1 Parameters deduced from Langmuir-type model and Freundlich-type model for the adsorption of 2-CP derivative on CTAB coated Fe_3O_4 NPs.

Langmuir				Freundlich		
^a q_m (mg/g)	^b K_L (L/mg)	^c R^2	^d R_L	^e K_F (L/mg)	^f $1/n$	^c R^2
12.32	1.4774	0.9983	0.4036	0.6701	0.3611	0.9863

^a q_m is the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg g^{-1}).

^b K_L is the Langmuir constant (L mg^{-1}).

^c R^2 is correlation coefficient.

^d R_L is separation factor that is the essential characteristic of Langmuir isotherm within the range $0 < R_L < 1$, indicated favorable adsorption (Foo and Hameed, 2010).

^e K_F is the Freundlich constant (L mg^{-1}).

^f n is adsorption intensity, $1/n$, ranging between 0 and 1, presented favorable adsorption.

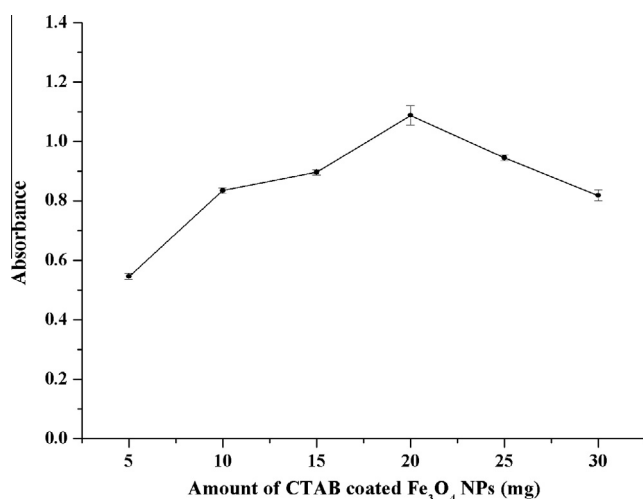


Figure 4 The dependence of the absorbance of 2-CP derivative on the amount of the adsorbent (CTAB coated Fe_3O_4 NPs); *Extraction conditions:* vortex time 60 s, MeOH 1000 μL as desorption solvent and desorption time 7 min.

investigated. For Langmuir model, relation of the concentration of 2-CP at equilibrium, C_e (mg L^{-1}) and the maximum adsorption capacity corresponding to complete monolayer coverage on the surface, q_e (mg g^{-1}) was plotted as C_e/q_e versus C_e (Fig. 3a), while, the plot of $\log q_e$ versus $\log C_e$ was constructed for Freundlich model (Fig. 3b). All isotherm parameters (q_m , K_L , K_F , R_L , $1/n$) corresponding to Langmuir and Freundlich models together with regression coefficient (R^2) are summarized in Table 1. The results indicated that the adsorption of 2-CP on the adsorbent (CTAB coated Fe_3O_4 NPs) was fit well with the Langmuir isotherm model with high correlation coefficients ($R^2 = 0.9983$) compared to the Freundlich isotherm model ($R^2 = 0.9863$). It can be assumed that 2-CP was adsorbed on surface of the adsorbent to achieve the complete monolayer coverage as indicated by Langmuir model.

3.3. Optimization of the extraction conditions

In this study, 2-CP was derivatized with 4-AAP to facilitate the detection by spectrophotometry in visible region at 510 nm. The derivatization of 2-CP was studied whether it should be

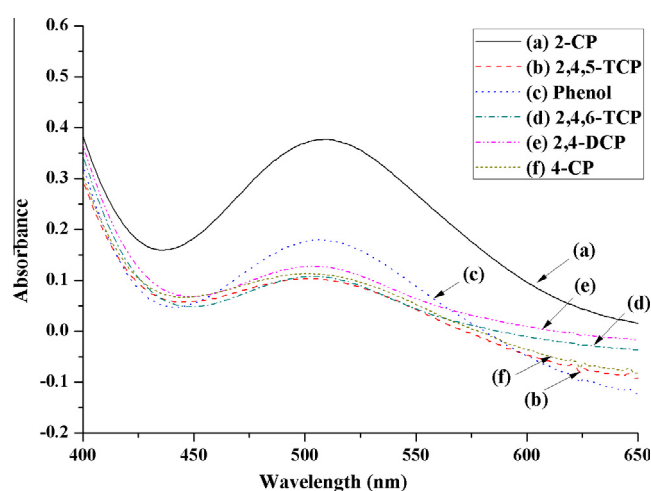


Figure 5 The absorption spectra of phenol and chlorophenols obtained using the proposed method.

performed before SPE or after SPE. The results showed that the derivatization of 2-CP before SPE provided more sensitivity with the molar absorptivity (ϵ) of $8.7 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ which is ten times higher than that of the extraction of 2-CP before derivatization. Therefore, 2-CP was derivatized with 4-AAP before extraction by SPE. Parameters affecting the SPE were then studied and optimized.

3.3.1. Effect of the amount of CTAB coated Fe_3O_4 NPs

The adsorbent amount is the key parameter affecting the extraction efficiency. To optimize the amount of adsorbent for the extraction, the amounts of CTAB coated Fe_3O_4 NPs ranging from 5 to 30 mg were studied. Fig. 4 shows that the absorbance increased with increasing amount of the adsorbent, and reached a maximum at 20 mg, then decreased with the following increase of the adsorbent amount. Therefore, 20 mg of the adsorbent was the optimum amount to achieve highest extraction efficiency of 2-CP.

3.3.2. Effect of type and volume of the desorption solvent and desorption time

A complete desorption of analytes from the sorbent is highly related to the hydrophobicity of the desorption solvent. Therefore, the different organic solvents were studied including

Table 2 Analytical performance of the proposed method.

Linear equation	Linear range (mg L ⁻¹)	Correlation coefficient (<i>R</i> ²)	Precision (%RSD)		LOQ (mg L ⁻¹)	EF	LOD (mg L ⁻¹)
			Intra-day (<i>n</i> = 5)	Inter-day (<i>n</i> = 5 × 3)			
<i>Y</i> = 1.9823 <i>X</i> + 0.6072 (<i>Y</i> = 0.1415 <i>X</i> + 0.3292) ^a	0.05–1.0 (0.3–15.0) ^a	0.9970 (0.9950) ^a	3.7	6.6	0.05	14.0	0.01 (0.11) ^a

^a Values obtained from 2-CP derivative without SPE using CTAB coated Fe₃O₄ NPs are reported in parentheses.

Table 3 The molar absorptivity (ϵ) of the phenol and the other chlorophenols using the proposed method.

Analyte	The molar absorptivity (ϵ) at 510 nm (L mol ⁻¹ cm ⁻¹)
Phenol	1.6×10^4
2-CP	8.7×10^4
4-CP	9.2×10^3
2,4-DCP	1.2×10^4
2,4,5-TCP	1.15×10^4
2,4,6-TCP	1.35×10^4

acetone, acetonitrile and methanol. According to the absorbance signals, methanol gave the highest absorbance for the derivative 2-CP, followed by acetonitrile and acetone, respectively (data not shown, [Supplementary data Fig. S3a](#)). Therefore, methanol was selected as the desorption solvent for the subsequent studies.

The volume of methanol was then investigated by varying from 500 to 1500 μ L. The absorbance increased with increasing of methanol volume until 1000 μ L, and then it decreased slightly due to effect of dilution (data not shown, [Supplementary data Fig. S3b](#)). Therefore, 1000 μ L of methanol was selected as the optimum desorption volume.

The desorption time was studied in the range of 1–10 min. The absorbance signal increased up to 7 min and then decreased slightly (data not shown, [Supplementary data Fig. S3c](#)). This may be due to longer sonication time providing heat inside the vial and causing desorption of the analyte from the adsorbent into the aqueous phase, and thus loss of extraction efficiency. As a result, 7 min was selected as the optimum desorption time.

3.4. Analytical performance

A series of experiments for evaluation of the analytical performance including linearity, limit of detection (LOD), limit of quantitation (LOQ), repeatability and recoveries were investigated under the optimum conditions. The results are listed in [Table 2](#).

The linearity of the method was verified in the range of 0.05–1.0 mg L⁻¹ with high correlation coefficients (0.9970). The calibration curve was obtained by plotting the absorbance signal versus concentrations of 2-CP, fitted to the equation $Y = 1.9823X + 0.6072$.

The LOD and LOQ are calculated as the concentrations of the 2-CP at 3SD/*m* and 10SD/*m* (SD is the standard deviation of five replicates of blank and *m* is the slope of calibration curve), respectively. The results showed that the LOD and LOQ values were 0.01 mg L⁻¹ and 0.05 mg L⁻¹, respectively.

The relative standard deviations (%RSDs) for the 2-CP were 3.7% RSD for intra-day precision (*n* = 5) and 6.6% RSD for inter-day precision (5 × 3), illustrating good precision.

The performance of the proposed method was compared by HPLC method (data not shown) based on *t*-test performed at a 95% confidence level. The results indicated that there is no significant difference between the proposed spectrophotometry and HPLC.

3.5. Interferences

4-AAP is a well known chromogenic reagent for phenolic compounds and their derivatives ([Ettinger et al., 1951](#) and [Venkateswarlu and Seshiah, 1995](#)). Therefore, the selectivity

Table 4 Results of the determination and recoveries of the 2-CP in soil samples.

Samples	Spiked (μ g g ⁻¹)	2-CP (<i>n</i> = 3)	
		Found (μ g g ⁻¹)	Recovery (%)
Soil I	–	nd	–
	0.3	0.26	85.1 ± 5.0
	0.6	0.51	84.4 ± 8.3
	0.9	0.79	87.8 ± 3.3
Soil II	–	nd	–
	0.3	0.26	88.3 ± 9.1
	0.6	0.49	81.7 ± 8.1
	0.9	0.81	90.1 ± 4.7
Soil III	–	nd	–
	0.3	0.26	86.7 ± 7.5
	0.6	0.56	93.4 ± 6.6
	0.9	0.86	95.2 ± 7.3

nd, not detected.

of the proposed method on the detection of 2-CP was investigated for the phenol and the other chlorophenols. Using the optimum condition for the detection of 2-CP, Fig. 5 shows the absorption spectra of phenol and chlorophenols. The molar absorptivities (ϵ) at 510 nm of the studied compounds were evaluated and the values are summarized in Table 3. It can be seen that 2-CP has the highest molar absorptivity ($\epsilon = 8.7 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$), which is five to ten times higher than the other compounds studied. In addition, the equilibrium parameter (R_L) from Langmuir isotherm was adopted to illustrate the favorable of the adsorption of the analyte onto the surface of adsorbent. The R_L of 2-CP (0.4036) is higher than (for example) 2,4,5-TCP (0.2124). It can be concluded that under the studied conditions, the proposed method is selective and sensitive to 2-CP.

3.6. Analysis of real samples

The applicability of the method was demonstrated for the determination of 2-CP in soil samples. The influence of matrix was investigated by comparing the slopes of calibration curve from standard aqueous solution and from matrix match calibration. The slopes of the calibration curve and the matrix match curve were not significantly different ($p = 0.05$), suggesting that no matrix effects from the studied samples. 2-CP was not detected in any of the studied samples. The accuracy of method was also evaluated by measuring the average recoveries of the 2-CP at three concentrations (0.3, 0.6 and $0.9 \mu\text{g g}^{-1}$). The results (Table 4) show that recoveries were between 81.7% and 95.2% suggesting that the method has the great potential to be used as a reliable method for monitoring 2-CP in soil sample.

4. Conclusions

A simple and sensitive method for detection of 2-CP by spectrophotometry was successfully developed. An adsorbent based on CTAB coated Fe_3O_4 NPs mixed hemimicelles was used for extraction and preconcentration of 2-CP in the form of 4-AAP derivative. The extraction mechanism may be due to hydrophobic interaction between CTAB on surface of Fe_3O_4 NPs and 2-CP. Solid phase extraction using CTAB coated Fe_3O_4 NPs could greatly improve sensitivity of spectrophotometry. The benefits of the proposed method are the use of less toxic solvent (methanol) and the ability to use an unsophisticated instrument i.e. vis spectrophotometer. Good recoveries suggest that this method has high potential for the detection of trace organic pollutants from soil samples.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.arabjc.2014.12.023>.

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