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Chlorophenols in Tigris River and Drinking Water of Baghdad, Iraq

Khalid Waleed S. Al-Janabi · Fatin Nafea Alazawi · M. Ibrahim Mohammed · Abdul Amir H. Kadhum · Abu Bakar Mohamad

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Abstract A study was conducted on a stretch of Tigris river crossing Baghdad city to determine the concentration of some chlorophenols pollutants. Aqueous samples were preliminary enriched about 500 times and the chlorophenols have determined using high performance liquid chromatography HPLC. Limits of detection LOD were (0.007–0.012 mg L^{-1}), relative standard deviations RSD% were 2.4%–5.59% and relative recoveries were 51.06%–104.07%. The existence of chlorophenols in Tigris river was in the range 0.023–4.596 mg L^{-1}. The developed method suggested in this study can be applied for routine analysis and monitoring of chlorinated phenols in environmental aqueous samples.

Keywords Chlorophenol · Tigris · HPLC · Iraq · SPE

Abbreviations

2CP	2-Chlorophenol
24DCP	2,4-Dichlorophenol
246TCP	2,4,6-Trichlorophenol
2346TeCP	2,3,4,6-Tetrachlorophenol
PCP	Pentachlorophenol
HPLC	High performance liquid chromatography
DAD	Diode-array detector
UV	Ultra violet
ALS	Autosampler
SPE	Solid phase extraction
D.I.	Deionized
RSD%	Relative standard deviation

K. W. S. Al-Janabi (✉) · F. N. Alazawi
Chemistry Department, College of Education, University of Baghdad, Baghdad, Iraq
e-mail: khalid.janabi@gmail.com

M. Ibrahim Mohammed
Chemical Engineering Department, University of Technology, Baghdad, Iraq

A. A. H. Kadhum · A. B. Mohamad
Department of Chemical and process Engineering, National University of Malaysia, Bangi, Selangor, Malaysia

The Tigris is the biggest river in Iraq and the main source of drinking water for Baghdad, which is the largest city in the country and the second largest city in the Arab world with a population estimated by 7.5 million (Burnham et al. 2006). Nevertheless there are no enough reliable studies, data or statistics available internationally about Tigris river (Kavvas et al. 2011) and its water quality while traversing Iraq, especially after the year 2003 is deteriorated. Any pollution of Tigris river may cause a direct pollution to Euphrates river and the related water sources since both rivers connected through Al Tharthar Lake (Rahi and Halihan 2010).

Water pollution is anything that degrades water quality and adversely affects living organisms or makes water unsuitable for usage (Cunningham et al. 2007). As a by-product of many industries, phenolic compounds were disposed in river water contaminating it and the environment. Chlorinated phenols are well known for their toxicity and carcinogenicity (Goodman 2001). There are many international standards as well as legal requirements and proceedings for drinking water supply (Schaefer 2008; de Vet et al. 2009). A small quantity of wastewater if in contact with groundwater may cause significant pollution to drinking water sources. Chlorophenols enter the nutrient system through contaminated drinking water and crops (DouAbul et al. 1988). The problem is more serious where

chlorine is used to disinfect drinking water. Chlorine in contact with phenols reacts to form chlorinated phenols which are even more dangerous to human health than unchlorinated phenols (Gao et al. 2008).

The main purpose of this work is to determine the pollution level by chlorophenols in Tigris river and to develop a rapid and reliable method for routine monitoring of such hazardous pollutants, which can help protecting the public health and preserving the environment of Iraq.

Materials and Methods

The standard materials of chlorinated phenols (24DCP, 246TCP, 2346TeCP, PCP) were supplied by (Supelco, USA). 2CP was supplied by Aldrich Chemie (Steinheim, Germany). Other organic solvents supplies were; Acetonitrile (HPLC-grade, Fisher Scientific), Glacial acetic acid 100% and hydrochloric acid were from (BDH Chemical Co.), methanol absolute (Tedia), Ultrapure water was prepared by a Milli-Q system (Bedford, MA, USA). DPD total chlorine reagent was from HACH (permachem reagents, USA).

Analyses of all samples were carried out using HPLC–DAD of Agilent Technologies (1200 series, USA) with separating column (Jones Chromatography SEA SDN BHD 25 cm × 4.6 mm Genesis C18 120A 4 μ). Spectrophotometric analyses were conducted using PerkinElmer (Lambda 35, UV/VIS Spectrometer). Solid phase extraction tubes (SPE) used for pre-concentration were LiChrolut EN (copolymer PS-DVB, particle size: 40–120 µm, bed weight: 500 mg, in 6 mL pp tubes) obtained from Merck KGaA. Total chlorine tests were carried out by (HACH DR/2010 Portable datalogging spectrophotometer).

Sampling points were collected from Tigris River from points close to the drainages of industrial premises suspected to discharge wastewater to the river without enough treatment (Fig. 1). Significance of each sampling point was illustrated in Table 1.

One liter from each sample was filtered through 0.45 µm Whatman filter paper, then acidified to pH 2 using HCl (6 M). The SPE tubes were conditioned by 3 mL methyl alcohol followed by 5 mL deionized water pre-adjusted to pH 2 by HCl (6 M). An exact 1 L from each aqueous sample has applied to a pre-conditioned SPE tube at a flow rate of 20 mL min^{-1} (Dionex Corporation 2009) then each tube has washed with 10 mL of deionized water acidified to pH 2 and left to dry under vacuum for 15 min. A 2,100 µL in three batches of acetonitrile acidified to 1% with glacial acetic acid was used to recover the samples from the SPE tubes. Enrichment factor of the aqueous samples was about 500 times as described in Eq. 1.

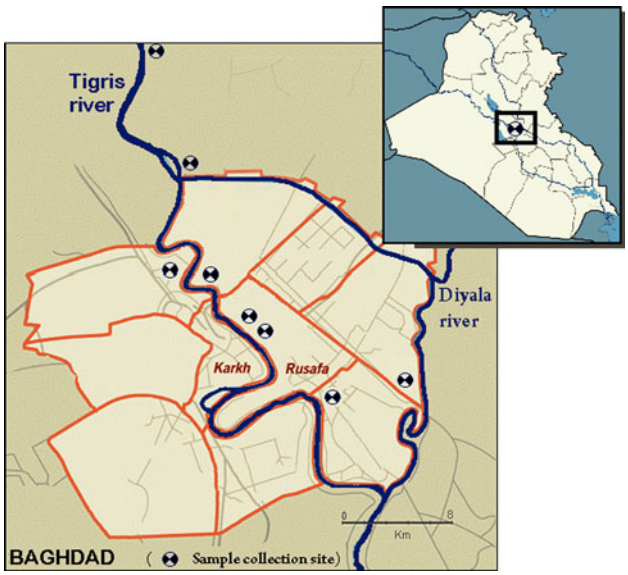


Fig. 1 Map of river Tigris indicating the collection points of the water samples

$$\text{Enrichment factor} = \frac{\text{Volume before enrichment}}{\text{Volume after enrichment}} \cong \frac{1000\ \text{mL}}{2\ \text{mL}} \cong 500\ \text{times} \quad (1)$$

By changing the proportions of the glacial acetic acid in the mobile phase it has been found that the pattern of the retention times of the chlorophenols were significantly stable in the range of 0.5%–2%, for that the acidification was chosen to be up to 1% in the mobile phases (Fig. 2). Substituting the glacial acetic acid with hydrochloric acid once and with sulfuric acid another has yielded similar results, for that there's no refer for the repeated data.

Stock solutions in concentration of 1,000 mg L^{-1} were prepared by dissolving an accurate weight of the pure standard [2CP, 24DCP, 246TCP, 2346TeCP, PCP] in acetonitrile acidified to 1% with glacial acetic acid and dilute to volume in the volumetric flask. Composite stock standard was prepared from the pre-mentioned individual stock solutions then further diluted to obtain a series of standards in the concentrations of 50, 20, 5, 4, 3, 2, 1, 0.8, 0.4, 0.2, 0.1, 0.05, 0.02, 0.01, 0.005 mg L^{-1}. One liter sample of a drinking mineral water available at the Malaysian market which is packed in polypropylene container was acidified with glacial acetic acid to pH 2 and spiked with 0.5 mL of the stock composite solution of chlorophenols earlier prepared in the concentration of 0.4 mg L^{-1} to determine the recoveries and the detection limit of the method.

Column temperature affects solute retention by enhancing the kinetic and the transport properties via decreasing the viscosity of mobile phase and increasing the analyte diffusivity at higher temperatures (Zhu et al. 2005).

Table 1 Nomination of the location of collection of water samples from Tigris river and their significance

Water samples	River Tigris—location of collection	Significance of selection
A1	Drainage1, the city of medicine	Very close to drinking water treatment plant
A2	Drainage2, the city of medicine	Very close to drinking water treatment plant
A3	Nu'aman hospital	Upstream to a water treatment plant
A4	Al-Karkh wastewater treatment plant	Close to two water treatment plants
A5	Al-Quds thermal powerplant	Upstream to DEWTP
A6	Al-Rustumiya wastewater treatment plant	Reside on Diyala river which pour its water in Tigris river
A7	Southern Baghdad powerplant	Close to water treatment plant
A8	Drinking water supplied by DEWTP	Consumed by large population in Baghdad city
A9	Raw river water from DEWTP	Water before treatment, for comparison
A11	Drinking water supplied by DEWTP	Consumed by large population in Baghdad city
A12	Raw river water from DEWTP	Water before treatment, for comparison

DEWTP Dijla East water treatment plant, capacity more than 200,000 m^3/day

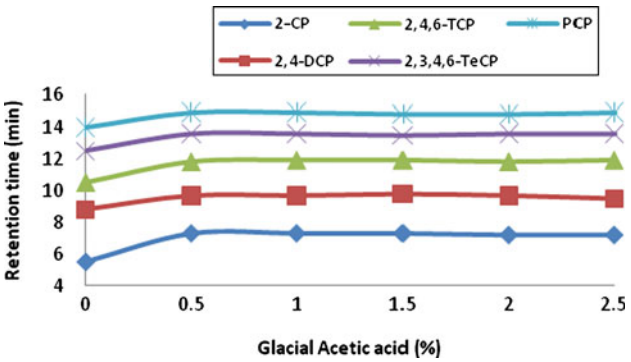


Fig. 2 Effect of changing acid proportion of the eluents on the retention time of chlorophenols

High temperature of the partition column notably improves separation efficiency through increasing the plate number of the column which is a dominant factor directly affecting chromatographic resolution (Pietrogrande et al. 2000) (Table 2). The study was carried out at two different temperatures (normally 25 and 40°C). The operating temperature of 40°C exhibited better resolution (Figs. 3, 4).

A full range scan for the chlorophenols were conducted using a PerkinElmer UV–vis spectrometer (Lambda 35) to find the best wavelength in which all of the compounds of interest can be detected (Fig. 5). The best sensitivity obtained when using λ_{max} at 280 nm, except for pentachlorophenol which exhibit very good sensitivity at λ_{max} of 254 nm.

Calibration curves with excellent linearity were obtained for each chlorophenol in the concentration range 0.005 mg L^{-1} up to 50 mg L^{-1} and the wavelength of 280 nm (Fig. 6).

Water samples have spiked with 0.5 mL standard containing 0.4 mg L^{-1} of each analyte (Fig. 7) and the relative recoveries were in the range 51.06%–104.07% (Table 3).

Table 2 Chromatographic analytical parameters obtained at two different column temperatures

Chlorophenols	t_R (min)	W (min)	k'^a	N	H	Rs	α
Values obtained when column temperature at 25 °C							
2-CP	8.46	0.41	7.46	6,812	3.670E-03		
2,4-DCP	10.65	0.37	9.65	13,256	1.886E-03	4.24	1.29
2,4,6-TCP	12.20	0.26	11.20	35,228	7.097E-04	3.66	1.16
2,3,4,6-TeCP	13.10	0.20	12.10	68,644	3.642E-04	3.22	1.08
PCP	14.05	0.18	13.05	97,483	2.565E-04	4.43	1.08
Values obtained when column temperature at 40 °C							
2-CP	7.23	0.40	6.23	5,232	4.779E-03		
2,4-DCP	9.55	0.37	8.55	10,668	2.343E-03	4.39	1.37
2,4,6-TCP	11.55	0.26	10.55	31,591	7.914E-04	4.47	1.23
2,3,4,6-TeCP	13.00	0.20	12.00	67,558	3.701E-04	4.93	1.14
PCP	14.06	0.18	13.06	97,580	2.562E-04	4.90	1.09

[a] $t_M \approx 1$ min

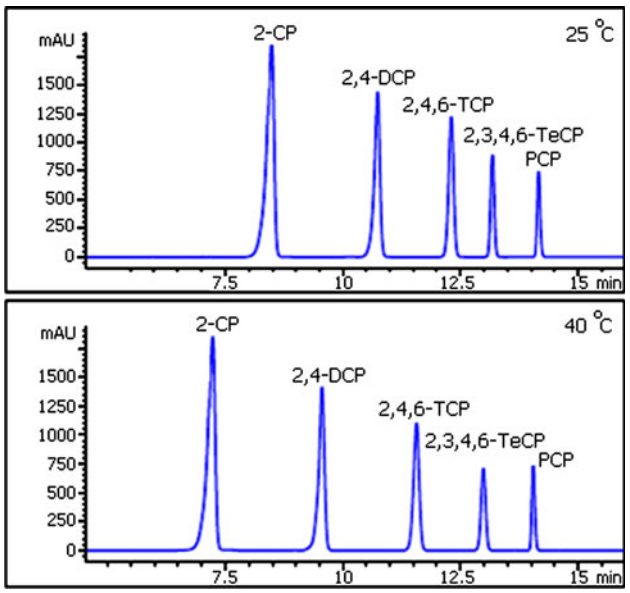


Fig. 3 Comparison of two chromatograms for the studied chlorophenols showing the effect of column temperature **a** at 25°C, **b** at 40°C, better resolution (Rs) obtained with higher column temperature

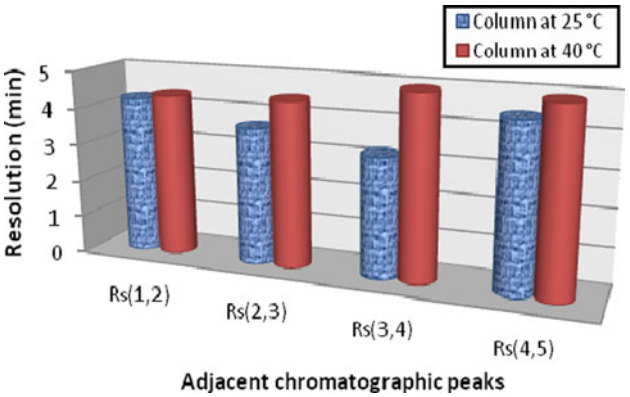


Fig. 4 Better resolution (Rs) obtained with higher column temperature

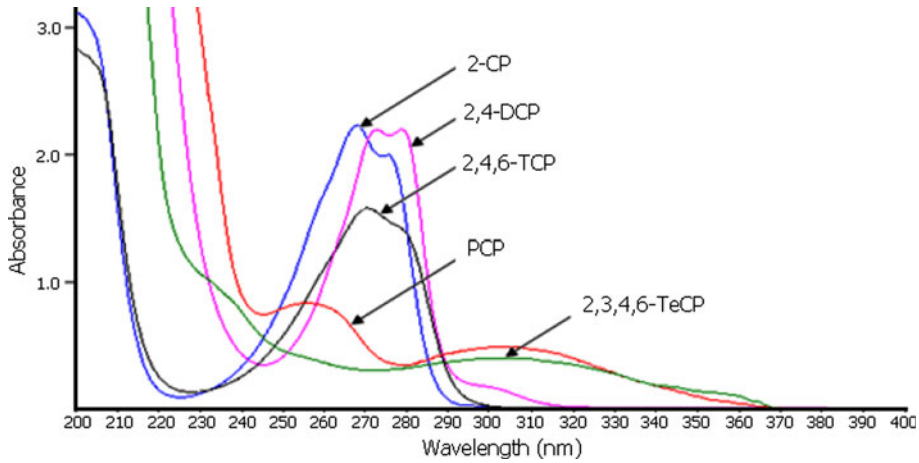
The LOD were in the range of 0.007–0.009 mg L^{-1} for most of the test compounds and 0.012 mg L^{-1} for PCP. Reproducibility expressed as RSD% were in the range 2.4%–5.59% (Table 4).

As it's obvious from Table 4 and Fig. 8, the recoveries of chlorophenols decreased with the increasing the substituted chlorine atoms on the aromatic ring of the phenol which maybe attributed to the reduction in the number of hydrogen atoms on the phenolic ring and hence the reduction in the ability of forming H-bonding. Consequently increasing the number of substituted chlorine atoms on the aromatic ring, may yield the formation of new species produced by the interactions between the analyte molecules with themselves or with other species. The resulted new species do not separate at the normal t_R and cannot be detected at the selected wavelength.

Chromatographic analyses for the samples were performed using HPLC (Agilent Technologies 1200) equipped with a diode array detector and C_{18} column at temperatures 25 and 40°C. Eluent phase at a flow rate of 1 mL min^{-1}, consisted of acetonitrile (solvent A) and D.I. water (solvent B) both acidified to 1% with glacial acetic acid. The gradient program was: 0 min, 35% solvent A; 7 min, 65% solvent A; 10 min, 65% solvent A; 11 min, 85% solvent A; 15 min, 95% solvent A; and 21 min, 95% solvent A. A post run washing for the column proceed for few minutes between individual runs using 100% solvent A until a linear baseline obtained. Detections carried out at 254 nm and 280 nm for all the samples.

Total chlorine content was determined for all the collected samples using a spectrophotometer HACH DR/2010, which has been set to the suitable program for the determination of total chlorine at a wavelength of 530 nm. DPD method 8167 was followed in the determination which is equivalent to USEPA method 330.5 for wastewater and the standard method 4500-Cl G for drinking water. A sample cell filled with 10 mL water sample was

Fig. 5 Determination of λmax for each chlorophenol by full range scan of UV–vis



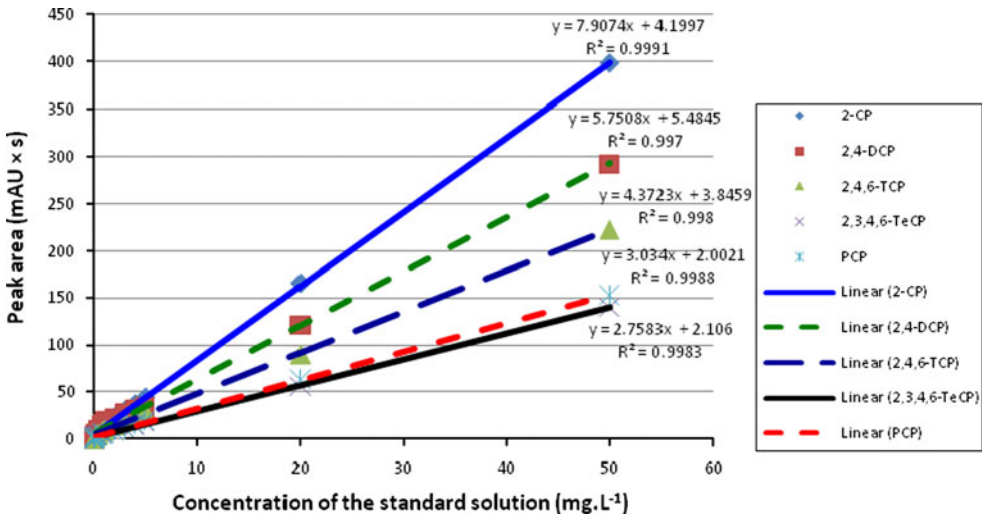


Fig. 6 Calibration curves for standard solutions of (2CP, 24DCP, 246TCP, 2346TeCP, PCP) in the concentration range of 0.005–50 mg L^{-1}

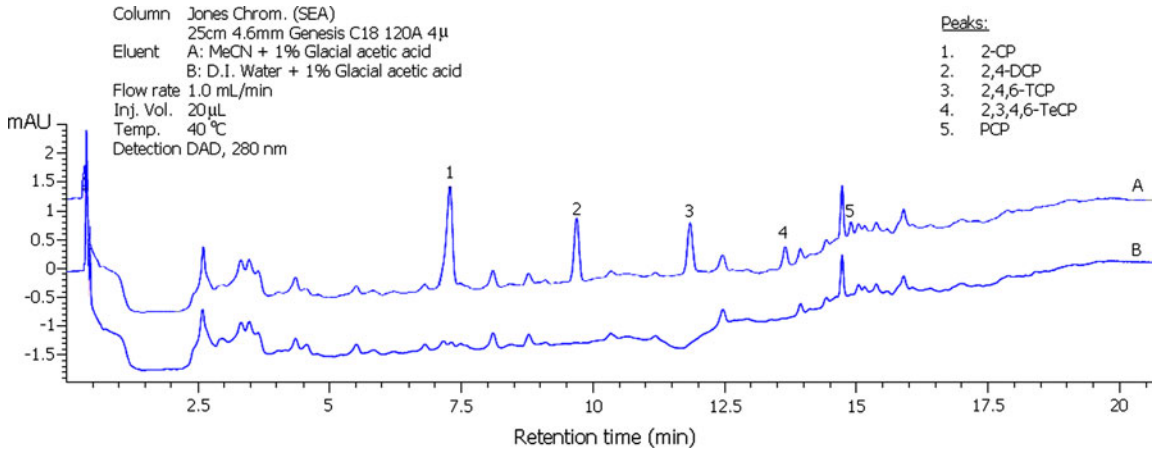


Fig. 7 Calibration curves for standard solutions of (2CP, 24DCP, 246TCP, 2346TeCP, PCP) in the concentration range of 0.005–50 mg L^{-1}

Table 3 Recoveries acquired when 1L of bottled mineral drinking water was spiked with a standard composite of chlorophenols[a]

Chlorophenol	Unspiked (mg L^{-1})	Added (mg L^{-1})	Recovery (%) of the spiked water sample
2CP	0.0098	0.133	104.07
24DCP	ND	0.133	93.10
246TCP	ND	0.133	97.96
2346TeCP	ND	0.133	75.54
PCP	ND	0.133	51.06

ND Not detected

[a] Mean value obtained from triplicate measurements

Table 4 Tabulated figures representing the linearity of the calibration curves for each chlorophenol

Analyte	Correction coefficient (r^2)	Linear regression (y-value)	Linear range (mg L^{-1})	LOD (mg L^{-1})	RSD%
2CP	0.9991	7.9074x + 4.1997	0.005–50	0.007	2.58
24DCP	0.9970	5.7508x + 5.4845	0.005–50	0.008	2.40
246TCP	0.9980	4.3723x + 3.8459	0.005–50	0.008	3.14
2346TeCP	0.9983	2.7583x + 2.1060	0.005–50	0.009	5.59
PCP	0.9988	3.034x + 2.0021	0.005–50	0.012	5.51

All the above parameters were detected at 280 nm and 40°C

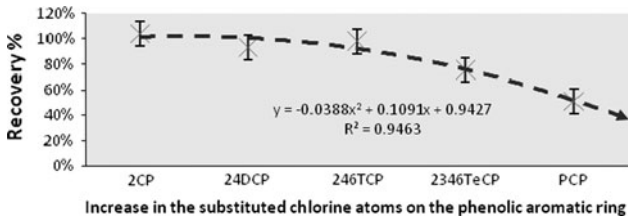


Fig. 8 Polynomial trendline indicating the decrease of recovery of chlorophenols from SPE with the increase of chlorine atoms on the aromatic ring

placed in the reading compartment as a blank and the device calibrated to zero. Then the content of one DPD total chlorine powder pillow has been added to the sample, shaked for 20 s and left for exactly 3 min to develop pink color then read by the spectrophotometer.

The presence of chlorinated phenols in the extracted samples was confirmed by FT-IR spectroscopy. The resulting chart with the positions of the peaks were compared and identified with reference to the peaks of phenolic standards measured earlier and the studies of infrared absorbance of solid chlorophenols (Pavia et al. 2001). However, the intermolecular hydrogen bonding of the polar functional groups HO···HO and OH···Cl in chlorophenols were resulting in strong shifts of FT-IR bands (Czaplicka and Kaczmarczyk 2006). Characteristic wave numbers of the bulk samples exhibit a distinguishable peaks in the positions of Ar–Cl group in the range of (1,120–1,000 cm^{-1}) and (790–680 cm^{-1}) (Nagaya, Kudoh and Nakata 2006) while C = C benzene ring stretching in the range of (1,620–1,550 cm^{-1}) and vibrational frequencies at (1,530–1,400 cm^{-1}) and (1,150–1,000 cm^{-1}) and (900–680 cm^{-1}) besides peaks of hydroxyl group of phenols in the range of (3,700–3,600 cm^{-1}) for free –OH and a broad band at (3,500–3,300 cm^{-1}) (Czaplicka and Czaplicki 2006, Photodegradation of 2,3,4,5-tetrachlorophenol in water/methanol mixture) for bonded –OH and in plane OH bending at ~1,300 cm^{-1} (Stafford et al. 1993).

The determination of total chlorine content has confirmed the existence of chlorinated organic compounds in the tested samples in the concentration of 0.05 ± 0.02 mg L^{-1}. Conversely the drinking water samples taken from water treatment plants (sterilized by chlorine) have more chlorine content than the untreated specimens.

The presence of chlorophenols in all of the collected water samples was examined via HPLC–DAD. Details about the existence and the concentration of each chlorophenol were listed in Table 5.

Results and Discussion

In this study a simple, sensitive and sufficiently selective method has been developed successfully for the simultaneous determination of some chlorophenols by gradient HPLC analysis coupled with DAD. The proposed analytical procedure can be used for routine analysis and monitoring of the phenolic pollutants in environmental water specimens.

Table 5 Results of the analyses for real water samples by high-performance liquid chromatography—diode array detection (HPLC–DAD) for chlorophenols

Water samples	Concentrations of chlorophenols in mg L^{-1}				
	2CP	24DCP	246TCP	2346TeCP	PCP
A1	0.082	0.226	N.D.	N.D.	0.652
A2	N.D.	0.502	N.D.	N.D.	N.D.
A3	N.D.	0.494	N.D.	N.D.	N.D.
A4	N.D.	0.376	N.D.	0.04	N.D.
A5	1.086	0.981	N.D.	1.55	4.596
A6	N.D.	0.031	N.D.	N.D.	N.D.
A7	0.026	0.024	N.D.	N.D.	N.D.
A8	0.033	0.094	N.D.	N.D.	N.D.
A9	N.D.	0.088	N.D.	N.D.	N.D.
A10	0.198	0.070	N.D.	N.D.	N.D.
A11	0.023	0.094	N.D.	N.D.	N.D.
A12	N.D.	0.063	N.D.	N.D.	N.D.

N.D. Not detected

The pollution of Tigris river and drinking water of Baghdad city with some chlorophenols caused by some industrial points on the banks of the river has been confirmed. 24DCP concentrations in the range of 0.024–0.981 mg L^{-1} was the dominant component contributing in the total amount of chlorophenols exist in Tigris river, while 246TCP was absent in all the examined water samples.

The study demonstrated that water treatment plants aren't being capable of riddance of chlorophenols. However, an increase in the concentration of some chlorophenols was observed after the sterilization process by chlorine during the production of tap water.

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