



Determination of trace pentachlorophenol (PCP) in wastewater using solid phase extraction

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ABSTRACT

Pentachloromethane (PCP) is one of highly toxic of polychlorophenols and required to continuously monitor. This paper presenting a sensitive method using high performance liquid chromatography HPLC for trace determination of this compound. The retention time for PCP in this study was found to be 12.9 minutes and the chromatographic parameters were established through this study. The average concentration of PCP in waste water samples was 126.5 µg/L before treatment and dropped to 44 – 95 µg/L after treatment.

Keywords: Pentachlorophenol, wastewater, solid phase extraction, high performance liquid chromatography.

INTRODUCTION

Several industry of wood treatment is a very water intensive industry and the consumption can be as high as 60 m³ per tonne [1]. The wastewater from wood-recycling can be potentially polluting due to chlorinated compounds that formed during the bleaching process. Approximately 500 different chlorinated compounds have been identified in several industry effluents of resin acids, chlorinated hydrocarbons, phenols, catechols, guaiacols, furans, dioxins, etc. [2;3]. In wastewater, these compounds are measured as adsorbable organic halides (AOX). These kind of toxic compounds are recalcitrant and resist environmental decomposition also shows strong mutagenic effects due to their hydrophobicity and ability to penetrate cell membranes [4]. Upon to its toxicity effects, several countries practice tight regulation on discharge of polychlorinated phenols. Some other country has totally banned production and using chlorine containing chemicals [5 ; 6].

pentachlorophenol as representing these polychlorinated phenols as preservative chemicals was selected on this study due its widely use as wood preservative [7]. There is potential that PCP may reach to human food chain. Pentachlorophenol (PCP) is an environmentally significant chemical because of its toxic properties. Besides this, PCP has a high tendency to bioaccumulate in the aquatic food chain with bioaccumulation factors of 1000 for gold fish, 324 for mussels and 78 for oysters [8]. The objective of this study was to develop a sensitive technique via preconcentration and using high performance liquid chromatography (HPLC) method for determining low concentration of pentachlorophenol. Solid phase extraction (SPE) coupled with high performance liquid chromatography (HPLC) are used for the determination of PCP in wastewater samples. Analysis was also conducted for the wastewater samples after the aerobic treatment using granular activated carbon-sequencing batch biofilm reactor (GAC-SBBR) and percentage removal of PCP found in the influent and effluent for each batch was compared.

MATERIALS AND METHODS

2.1 Chemicals

Pentachlorophenol sodium salt (Fluka Chemical, Switzerland) was used as standard. The organic solvents were HPLC grade methanol (Fisher Scientific, UK) and acetonitrile (Merck KGaA, Germany). Other reagents were 6.0 M hydrochloric acid (Baker Analyzed, USA), deionised water adjusted to pH 2 with 6.0 M hydrochloric acid, 0.01 M phosphoric acid (Baker Analyzed, USA) and 0.01 (v/v) acetic acid (Baker Analyzed, USA) in methanol.

The sorbents used for solid-phase extraction were silica-based bonded C18 cartridges (sorbent mass: 200 mg, reservoir volume: 6mL, IST-International Sorbent Technology).

2.2 Samples

Wastewater samples were collected from (Brega Plant, Brega, Lybia) within seven day period of recycle and immediate analysis was performed. These samples were later stored at 4°C for future investigations. Samples were filtered with 0.45 µm nylon membrane filter (Whatman) using vacuum filtration processes pre solid-phase extraction.

2.3 PCP Concentration Calibration Curve

The calibration curve for PCP, 10 mg/L stock solution was firstly prepared by accurately weighing approximately 10 mg PCP-Na and transferred it to a 1 L volumetric flask, then was diluted to volume with deionised water and stirred to dissolve. The stock solution was further diluted to a required concentration of 0.05 mg/L, 0.1 mg/L, 0.5 mg/L, 2 mg/L and 5.5 mg/L. All the apparatus were washed with 0.01 M nitric acid before used.

2.4 Granular activated carbon reactor

The schematic of the reactor is shown in Figure 1. A glass reactor with a capacity of 2.0 liter was used for this experiment. It was operated in the room temperature (25°C) and packed with 200 g/l of 2-3 mm granular activated carbon as a medium.

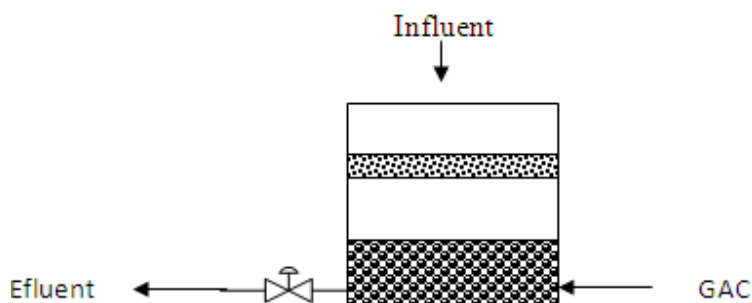


Fig.1. Schematic diagram of GAC reactor

2.5 Analytical method

2.5.1 Solid-phase extraction procedure (SPE)

Non polar media was used with Solid Phase Extraction (SPE) IST-International Sorbent Technology method for extraction of PCP from water samples using a non-polar retention mechanism. This method was used to isolate and concentrate the PCP in the samples. It was difficult to get a good chromatogram without using SPE as the determination of PCP in the samples was carried out in low concentration. Preconcentration was carried out in acidic conditions to avoid any ionization of the compounds in the sample. A 1 liter samples were adjusted to pH 2.0 with 6M hydrochloric acid. The cartridge was rinsed with 3 mL methanol and 3 mL deionised water which was adjusted to pH 2 with 6M HCl. The sample flow rate was kept within 60 mL/min. Next step is to elute interferences with 10 mL deionised water and once the retention step had been completed, the cartridge is dried for 30 seconds under vacuum. Finally, the analysts were eluted with 8 mL (2 x 4 mL) of 0.1% (v/v) formic acid (or acetic acid) in methanol.

2.5.2 High performance liquid chromatography (HPLC)

HPLC analysis was performed with Agilent binary pump instrument equipped with, multi-wavelength detector, a Zorbax SB-C18 column (4.6 mm ID x 150 mm, 5 µm), a C 18 packing. Wavelength of the detector was fixed on 254

nm where PCP has maximum absorption. A flow rate programme was developed to insure high efficiency of separation. Running time for each sample analysis was set to 20 minutes. Table 1 shows the analytical conditions of HPLC analysis.

Table 1. Analytical conditions of HPLC analysis of PCP

Parameter	Operation conditions		
Model	Agilent		
Column	ZORBAX SB-C18		
Injection volume	20 μ L		
Mobile phase	HPLC grade acetonitrile : 0.01M phosphoric acid		
Gradient	A	0.01M H ₃ PO ₄	
	B	Acetonitrile	
		<u>Time</u>	<u>B %</u>
		1	0
		2	7.5
	3	9.5	80
Flow rate	1 mL/min		
Temperature	35°C		
Wavelength	254 nm		

RESULTS AND DISCUSSION

3.1 Calibration curve

Concentrations of chlorinated phenols found in wastewater effluent following bleaching with hypochlorite were 1.4 – 4.8 mg/L [9]. Council of Europe (2002)[10] has approved a proposal that established a limit value of PCP as low as 0.15 mg/kg in wastewater. Based on these founding, five standard concentrations of PCP were selected to obtain the calibration curve. The retention time for PCP is 12.9 minutes as shown in Fig2. Calibration curve and sample result is presented in Table 2 and illustrated in Fig3.

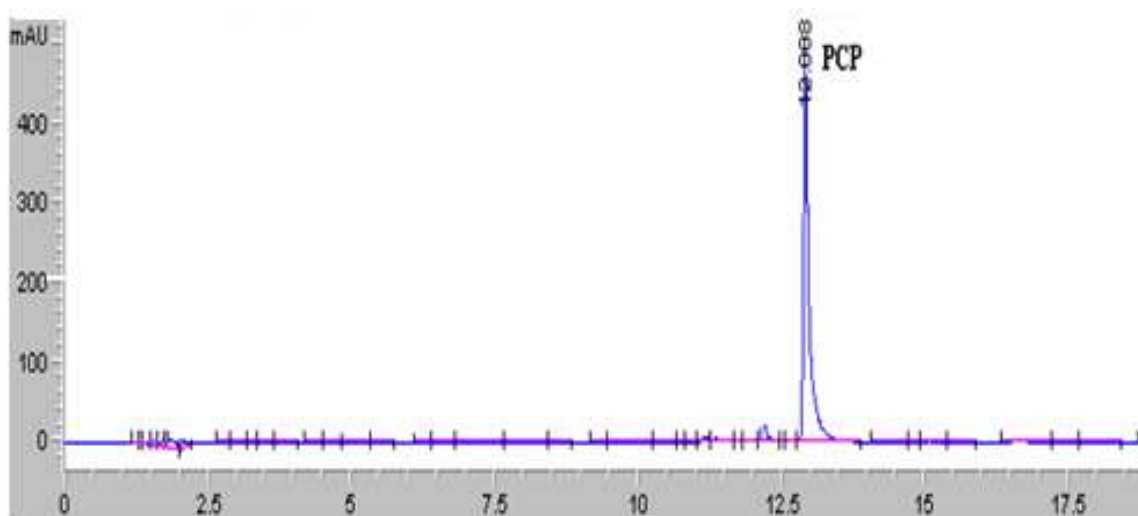


Fig 2. Chromatogram of authenticated sample of PCP at recorded at $\lambda = 254$ nm

Table 2. Typical concentration values and peak areas of PCP

Concentration (μ g/L)	Retention Time (min)	Peak Area (mAU*s)
50	12.94	23
100	12.94	38
500	12.92	192
2000	12.89	1839
5500	12.89	3625

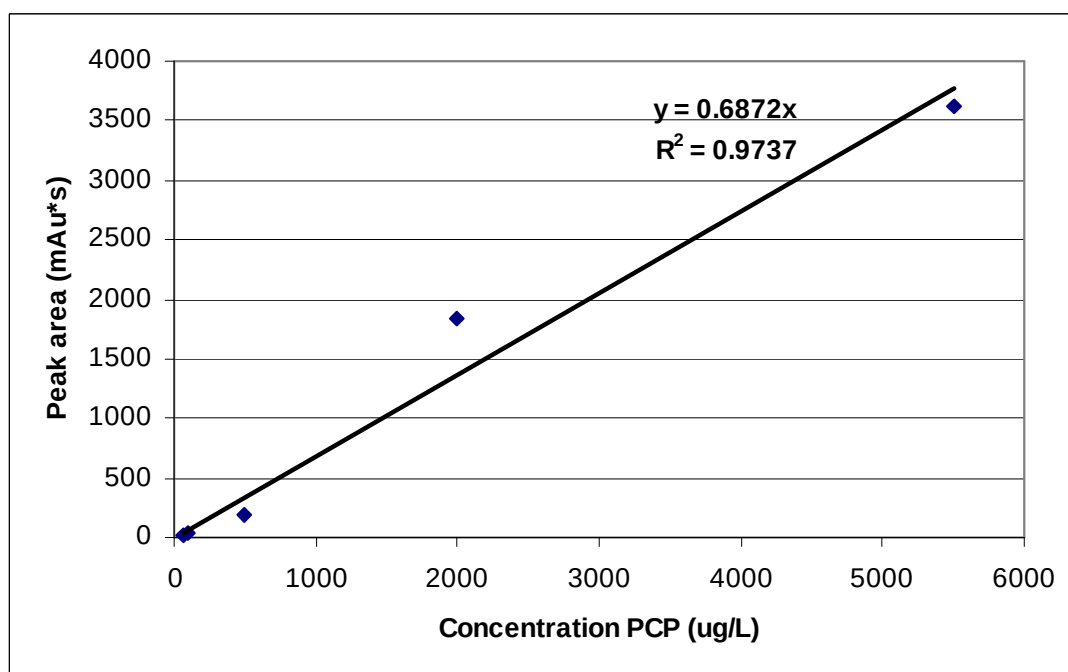


Fig 3. Calibration curve of PCP

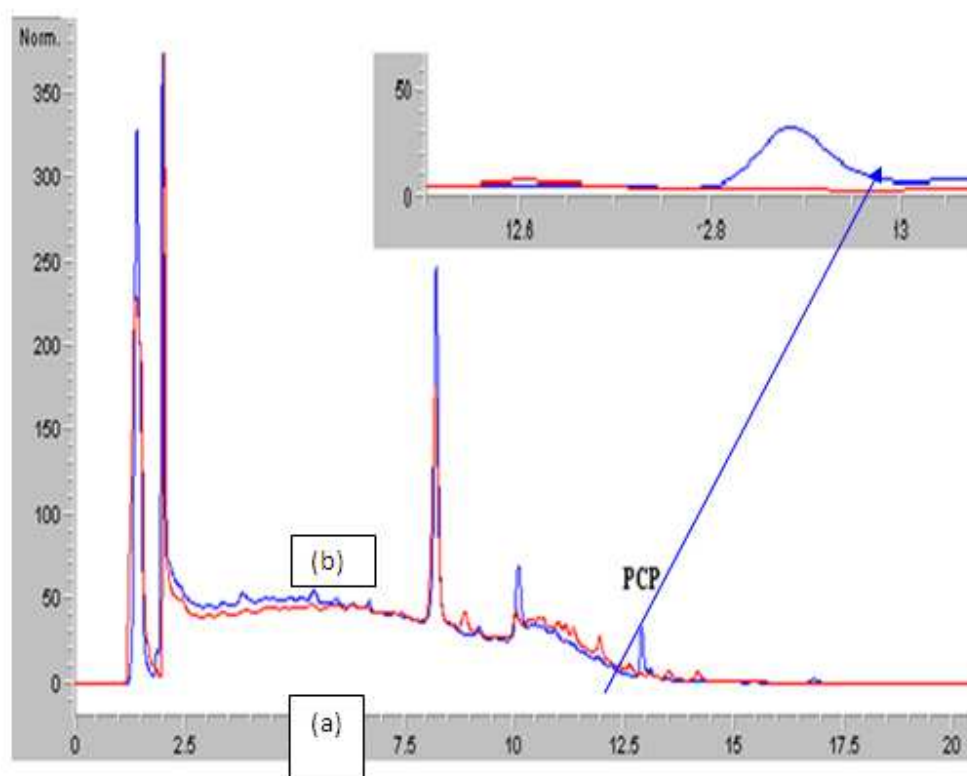


Fig 4. Spiked PCP (a) and after spike (b)

3.2 Analysis influent and effluent

Several samples of wastewater were analyzed and the average reading was considered. Analysis of the wastewater samples as indicated by chromatogram showed in **Fig 4(a)**. A low and unclear peak was found at the retention time

of 12.9 minutes and it is related to mix with peak area of another pollutant in the samples. Those pollutants produce higher peaks and overcome this lower PCP peak area. In addition to improving quantitative results, the use of standard addition methodology improved the reliability of peak identifications. Analyte peaks can be selected of a crowd of background peaks by comparison of chromatograms of spiked and unspiked extracts. A result for the samples analysis after the samples were spiked with 0.5 mg/L standard solution was showed by chromatogram in Fig 4(b).

HPLC results showed that PCP present in wastewater. The initial range for influent concentration was 41 $\mu\text{g/L}$ – 182 $\mu\text{g/L}$. For the samples after treatment, only 4 batches out of 7 batches were detected. The concentration after passing through the reactor was detected between 44 $\mu\text{g/L}$ – 94 $\mu\text{g/L}$. The results for PCP concentration that detected in influent and effluent were showed in Figure 5. From the figure, PCP concentrations were reduced after treated by GAC and these indicate that GAC can be used to remove these persistence materials from the waste water. For all data that were recorded, the average percentage of removal efficiency for PCP within 56% was achieved. Although the PCP concentrations were quite low after treatment, however this does not mean that all the PCP has been absorbed but less toxic (i.e. less concentration of PCP) to aquatic and other life.

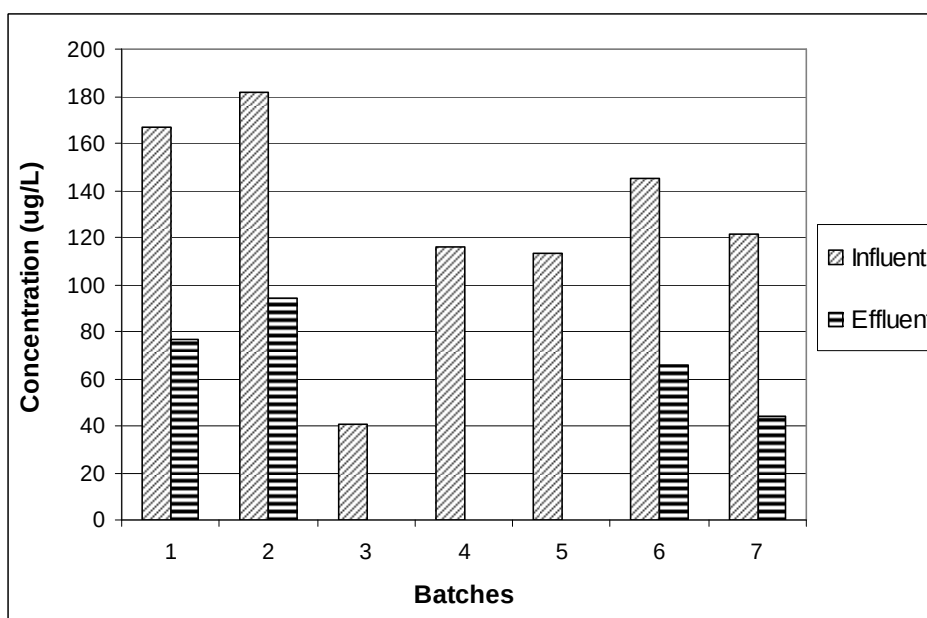


Fig 5. PCP concentration in influent and effluent

The average influent concentration for PCP in the range of 126.5 $\mu\text{g/L}$. This concentration that is present in the environment is of great concern as PCP is toxic, recalcitrant and bioaccumulation in organisms [11]. There are few factors that may contribute to this result. Removal of PCP requires chemical treatment to remove it before contaminants other material. Adsorption process however is not able to totally remove PCP, it is way of reduces such as pentachlorophenol [12]. Comparisons of detected pentachlorophenol in different wastewater samples from various sources were showed in Table 3. From the table, PCP concentration which was detected in wastewater effluent that using PCP as wood preservative was relatively higher than PCP concentration. Based on the research carried out by Domeno et al. (2005) [12] the origin of PCP is in the wood treatment.

Table 3. Detected pentachlorophenol in wastewater samples from various sources

Compounds detected	Samples	Concentration ($\mu\text{g/L}$)	References
Chlorinated phenols	Pulp mill effluent of conventional bleach process with hypochlorite.	1400 – 4800	Kookana & Rogers (1995) [9]
Pentachlorophenol	Treated waste water samples from wood treating plants located throughout USA.	290 – 4300	Ervin & McGinnis (1980) [13]
Pentachlorophenol	Waste water samples from recycle paper mill	127	This study

CONCLUSION

The analysis for PCP was carried out by using solid phase extraction (SPE) coupled with high performance liquid chromatography (HPLC). Results showed that it is possible to determine the presence of PCP using HPLC in a low region concentration. Based on the laboratory results, waste water samples from Brega Plant, Brega, Lybia contained 126.5 µg/L PCP. The removal efficiency of PCP is 56%. Although GAC can be used as a treatment option in reducing the amount of PCP that presence in wastewater.

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