



# Ultrasound-assisted solid phase extraction of nitro- and chloro-(phenols) using magnetic iron oxide nanoparticles and Aliquat 336 ionic liquid



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## ABSTRACT

A novel and sensitive ultrasound-assisted solid phase extraction (UASPE) method for pre-concentration and determination of ultra-trace amounts of nitrophenols and chlorophenols in water samples was demonstrated. Four hazardous phenolic compounds in water samples were extracted and monitored by high performance liquid chromatography. The results demonstrated that in the presence of Aliquat 336 (ALQ), magnetic iron oxide nanoparticles (MIONPs) were quite efficient in the adsorption and pre-concentration of traces of analytes. MIONPs were synthesized and characterized by transmission electron microscopy (TEM) and X-ray diffraction (XRD). The important parameters influencing the extraction efficiency were studied and optimized. The separation and pre-concentration steps were fast and completed in 10 min. Acetonitrile was used for the desorption of target analytes. Under optimum adsorption conditions, a linear range between 0.015 and 100  $\mu\text{g L}^{-1}$  ( $R^2 \geq 0.997$ ), and limits of detections (LODs) ranging from 0.005 to 0.041  $\mu\text{g L}^{-1}$  were obtained. Enrichment factors in the range of 76–195 were achieved and relative standard deviations (%RSDs) were less than 10.0 ( $n=3$ ) for the target analytes. The analytical method was successfully applied for environmental water samples such as tap water and river water. The recoveries varied within the range of 70–119% confirming the good performance of the method in various water samples. The results showed that the proposed method is a rapid, convenient and feasible technique for the determination of nitrophenols and chlorophenols in aqueous samples.

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## 1. Introduction

Phenols are common by products of large-scale production and the use of man-made organics such as phenolic resins, drugs, dyes, antioxidants, paper pulp and pesticides that cause ecologically undesirable effects. Repeated or prolonged exposure to phenolic compounds or their vapors may cause headache, nausea, dizziness, difficulty in swallowing, diarrhea, vomiting, shock, convulsions, or death. Phenols can affect the central nervous system, liver, and kidneys [1–3]. These compounds are harmful to organisms at low concentrations and many of them have been classified as hazardous pollutants [4]. Most phenols exhibit different toxicities, and some chlorophenols and nitrophenols are even known to possess carcinogenic and immunosuppressive properties. Due to their potential harm to human health, phenol derivatives and

related compounds are considered as priority pollutants. As a consequence, both the US Environmental Protection Agency (EPA) and the European Union (EU) have included some phenols in their lists of priority pollutants. The maximum amount of phenols in wastewater allowed by the European Community is lower than 1  $\text{mg L}^{-1}$  [5,6]. The European Union sets a maximum concentration of 0.5  $\mu\text{g L}^{-1}$  for total phenols and 0.1  $\mu\text{g L}^{-1}$  for their individual concentration in drinking water [7,8]. The major sources of phenol pollution in aquatic environment are wastewaters from paint, pesticide, coal conversion, polymeric resin, gasoline, rubber proofing, steel, petroleum and petrochemical industries [9,10].

New SPE techniques based on the use of magnetic or magnetizable adsorbents called magnetic solid-phase extraction (MSPE) have been used for the separation and pre-concentration of an analyte from large volumes of water solution by using a permanent external magnet [11–15]. Generally, most of the dissolved environmental pollutants are nonmagnetic, and thus do not respond to the magnetic field. The surface modification of magnetic nanoparticles is a challenge for different applications and can be accomplished by the physical/chemical adsorption of organic compounds using

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four major methods: organic vapor condensation, polymer coating, surfactant adsorption and direct silanation [16]. Removal of hazardous compounds from industrial effluents and also monitoring their concentrations are growing needs at the present time.

Aliquat 336 (tricaprylmethylammonium chloride) is a water insoluble quaternary ammonium salt made by the methylation of mixed tri octyl/decyl amine, which is capable of forming oil soluble salts of anionic species at acidic or slightly alkaline pH. Aliquat 336 is composed of a large organic cation associated with chloride ion,  $[R_3NCH_3]^+Cl^-$  and exists as a stable cation–anion pair over a wide range of pH. Because the ammonium structure has a permanent positive charge, it can form salts with anions over a wider pH range than primary, secondary or tertiary amines. For this reason, Aliquat 336 finds application in environments ranging from acidic to slightly alkaline pH. In spite of several studies on the solid phase extraction of phenolic compounds with Cethyltrimethylammonium chloride (CTAB) [17,18], no procedure has been reported for the systematic solid phase extraction and separation of such compounds using Aliquat 336.

Ultrasonic (US) radiation has been proven to be a very useful tool in intensifying the mass transfer process of the target analytes to the surface of an adsorbent [19,20]. This leads to an increment in the extraction efficiency of the pre-concentration technique in a short time. The effects of US are primarily related with the cavitation phenomenon, which involves the implosion of bubbles formed in the liquid medium during US application. The enhanced adsorption rate by sonication may be attributed to the extreme conditions generated during the violent collapse of the cavitation bubbles. When the bubble is collapsing near the solid surface, symmetric cavitation is hindered and the collapse occurs asymmetrically. The asymmetric collapse of bubbles in a heterogeneous system produces micro-jets with high velocity. Additionally, symmetric and asymmetric collapses generate shockwaves, which cause extremely turbulent flow at the liquid–solid interface, increasing the rate of mass transfer near the solid surface. An important effect of US is the dispersion of aggregated nanoparticles which produces more surfaces and increases more active sites. The mentioned factors results in an increment in the mass-transfer of the analytes onto the adsorbent surface [19–22].

Several diverse methods were applied for the determination of nitrophenols and chlorophenols in environmental samples. These include ultraviolet spectrophotometry (UV) [23,24], chemiluminescence [25–27], high performance liquid chromatography (HPLC) [12,28–34], gas chromatography [35,36] and electrochemical methods [5,37,38]. Some of these techniques suffer from interferences and matrices. On the other hand, the low level of these constituents makes their determination a difficult task.

It is well known that the analysis of polar compounds such as nitrophenols and chlorophenols is a challenge due to the strong interactions of these compounds with water molecules in aqueous solutions. Establishing simple, fast, low-cost, sensitive, and selective analytical methods for the extraction and determination of pollutants in the environment is one of the main areas of research in environmental chemistry [11–16,32–38].

In this work, we developed a facile method to synthesize Aliquat 336 coated magnetic iron oxide nanoparticles (ALQ@MIONPs) for the adsorption of phenols. The ALQ@MIONPs demonstrated high potential ability for solid phase extraction (SPE) and pre-concentration of phenolic compounds from environmental water samples with high efficiencies. Hence, 2,4,6-trinitrophenol (picric acid, PIC), paranitrophenol (PNP), 2-chlorophenol (2-CP) and 2,4-dichlorophenol (2,4-DCP) were selected as the model analytes. Ultra-trace amounts of 2,4,6-trinitrophenol (picric acid, PIC), paranitrophenol (PNP), 2-chlorophenol (2-CP) and 2,4-dichlorophenol (2,4-DCP) were determined in water samples. The target analytes

(PIC, PNP, 2-CP and 2,4-DCP) were successfully evaluated by HPLC analysis.

## 2. Experimental

### 2.1. Chemicals and reagents

All chemicals and reagents were of analytical grade. Acetone (99.5%, w/w), acetonitrile (HPLC grade), water (HPLC grade), 2,4,6-trinitrophenol (picric acid, PIC), paranitrophenol (PNP), 2-chlorophenol (2-CP) and 2,4-dichlorophenol (2,4-DCP), hydrochloric acid (37% w/w), methanol (99.9% w/w), ammonia solution (25% w/w),  $FeCl_3$  (96% w/w),  $FeCl_2 \cdot 4H_2O$  (99.9% w/w), and Aliquat 336 were purchased from Merck (Darmstadt, Germany) and used without further purification. The stock standard solutions of the analytes were prepared in water–acetonitrile (70:30) solution mixture at a concentration of  $100\text{ mg L}^{-1}$  and stored at  $4^\circ\text{C}$ , protected from light. The standard working solutions were prepared daily by appropriate dilution of the stock standard solutions with water–acetonitrile (70:30) solution to the required concentrations. ALQ stock solution (2% v/v, equivalent to  $1760\text{ mg L}^{-1}$ ) was prepared in pure EtOH. Tap water was collected from our laboratory. River water samples were gathered from the Karron River at Ahvaz, Iran.

### 2.2. Apparatus

Chromatographic measurements were carried out using a Knauer HPLC system (Germany) consisting of a K-1001 pump and a k-2501 UV detector. Two KQ-100DE ultrasonic cleaner were purchased from Kunshan Ultrasonic Instrument Co., Ltd. (Kunshan, China). The frequency and output power of the ultrasonic cleaner were 21 kHz for both and 30, 60 W for the first and 45 W for the second, respectively. A pH-meter (827 pH lab, Metrohm1, Herisau, Switzerland) was also used for pH adjustment. Transmission electron microscopy (906E, LEO, Germany) and scanning electron microscopy (SEM) (XL-30 electron microscope, Philips, Eindhoven, The Netherlands) were used to study the morphology of the magnetic nano-particles. Structural analysis of the MIONPs was done using an X-ray diffractometer (XRD, Bruker D8 Discover, Germany). Infrared spectra were obtained using a Fourier Transform-Infrared Spectrometer (FT-IR spectrum 100, Perkin Elmer, Australia) to identify the functional groups and chemical bonding of the adsorbent, modifier and target analytes.

### 2.3. Preparation of magnetic iron oxide nanoparticles

MIONPs were synthesized by the co-precipitation of a mixture of chloride salts of ferrous and ferric ions (molar ratio 1:2) in an ammonium hydroxide solution at  $80^\circ\text{C}$  under vigorous stirring and a  $N_2$  atmosphere was prepared based on our previous work [39]. In order to stabilize the nanoparticles they were stored in ultra-pure water.

### 2.4. Preparation of ALQ modified magnetic iron oxide nanoparticles

A separate experiment was carried out to ensure the coating of MIONPs by ALQ ionic liquid. A 2 mL portion of MIONPs solution mixture (equivalent to 40 mg of dried MIONPs) and also 2 mL of 2% ALQ in EtOH were added to 50 mL deionized water at pH 8 and then sonicated (21 kHz, 60 W) for 5 min. Subsequently, the resultant ALQ@MIONPs were collected by a magnet (10 cm  $\times$  5 cm  $\times$  4 cm, 1.2 T) and washed with deionized water several times to remove the unreacted materials, and dried at  $40^\circ\text{C}$  under nitrogen gas for

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