# A new approach for the extraction of pollutants from wastewaters handled by the graphic industry

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## ARTICLE INFO

## ABSTRACT

It is widely recognized that the Graphic Industry handles toxic products and produces, in its various operations, toxic wastes. These wastes can cause serious environmental damages and can lead to severe health problems.

In this work we report an efficient, simple and cheap to run method for the removal of some of the most common pollutants involved in the various stages of the Graphic Industry production, using a Solid-Phase Extraction (SPE) methodology. We have determined equilibrium constants, $K_{eq}$, and adsorption ($k_{up}$) and desorption ($k_{off}$) rate constants for the extraction of benzene, xylene, toluene and ethylbenzene (BXTE) from water, using $C_{18}$ disks. The removal of these compounds was monitored by UV–vis spectroscopy, at room temperature. Average extraction efficiencies were of 60% in a mixture of BXTEs and close to 80% when pollutants were assessed separately.

Since the retention mechanism in the $C_{18}$ disk is essentially governed by hydrophobic interactions between the compounds and the alkyl chains of the disk, we have also shown that these pollutants' lipophilicity plays an important role in the rationalization of their behavior during the extraction process.

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## 1. Introduction

Due to their high toxicity, volatile organic compounds (VOCs) such as benzene, toluene, ethylbenzene and xylene (BXTEs) are considered important environmental pollutants by several national and international agencies, namely US EPA. While only some of these compounds have been considered carcinogenic (Ezquerro et al., 2004; Amzad Hossain et al., 2010), human exposure to all of them can have serious health consequences (e.g., neurological disorders). BXTEs can be emitted as combustion products of wood, gasoline and fuels, they can result from leakages from underground gasoline storage tanks and spills, and they are also extensively used as industrial solvents, paints, adhesives, degreasing agents and aerosols and as raw materials for the production of a number of different commodities (Esteve-Turrillas et al., 2009; Amzad Hossain et al., 2010; Przyjazny and Kokosa, 2002). Indoor air pollution due to BXTEs is likewise an important issue and may result from

smoking, building or furnishing materials, stored fuels, paints, adhesives and burning processes (Elke et al., 1998; Esteve-Turrillas et al., 2009).

In the facilities of graphic industries, environmental issues include wastewaters, emissions to the air, and hazardous materials management. In all these situations, BXTE compounds are among the most representative solvents present. In particular, ethylbenzene and toluene appear in aqueous solvents-based inks, as cleaning solvents, alongside with benzene and xylene, and also in blanket/roller wash, together with xylene (EHS guidelines for printing, 2007).

Most companies in the printing industry are situated in urban areas and, therefore, inappropriate treatment, storage or recycling of their wastes has a direct effect on public health. In some countries the management of these wastes is currently carried out either by hiring companies specialized in their treatment, or just by throwing them away as any other type of garbage. When the first practice is chosen, printing companies have no control upon the destination of wastes. The choice for the second option, if not properly executed, may lead to incorrect practices such as casting liquids effluents into the main sewers network which may have serious consequences (INETI, 2000; IGAOT, 2005).

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Solid phase extraction (SPE) methods (Albanis et al., 1998; Carrera et al., 1998; Green and Abraham, 2000; Marcé and Borrull, 2000; Ridal et al., 1997; Rodríguez et al., 2000) or related techniques, such as solid phase dynamic extraction (SPDE) (Sieg et al., 2008), solid phase microextraction (SPME) (Elke et al., 1998; Komatsu and Vaz, 2004), headspace solvent microextraction (HSM) (Przyjazny and Kokosa, 2002), multiple headspace solid phase microextraction (MHS-SPME) (Ezquerro et al., 2004) and semi-permeable membrane devices (SPMD) (Esteve-Turrillas et al., 2009), have been used in the determination of various pollutants, and some of them also in the extraction of benzene, xylenes, toluene, and ethylbenzene from air (Elke et al., 1998; Esteve-Turrillas et al., 2009), soil (Ezquerro et al., 2004) and water (Przyjazny and Kokosa, 2002; Sieg et al., 2008).

BXTEs, like many other VOCs, have low solubility in water and their absorption maxima are located at very low wavelengths in the UV–vis spectrum. Despite these limitations, the optimization of a solid phase extraction technique associated with UV–vis spectrometry as described in this work is a powerful method for the detection and removal of these pollutants from water. To our knowledge, this is the first time an SPE methodology using UV–vis spectrometry is proposed for the analysis of contaminants resulting from the graphic industry. The method consists in exposing the naked disks to various sample solutions and monitoring the continuous change in the analyte(s) concentration by UV–vis spectrometry, based on the well-known Beer–Lambert's law ($A = \varepsilon \cdot c \cdot l$, where $c$ is the concentration of the analyte, $A$ its absorbance, $\varepsilon$ its molar absorption coefficient and $l$, the path length of the absorbing solution). The decrease with time of the absorbance of the aqueous solution allows for the determination of the amount of analyte(s) sorbed onto the disk and thus the computation of the equilibrium constant ($K_{eq}$) and the rate of uptake ($k_{up}$) for the solid phase extraction of the pollutant from water.

This methodology using SPE disks, in our case octadecylsilica ($C_{18}$) sorbent particles embedded in a PTFE, to remove BXTE compounds from water, is not only of easy assembly and handling, but it is also cheap and efficient, and can hence be easily implemented in printing industry companies of all sizes.

## 2. Materials and methods

### 2.1. Reagents and adsorbent

Reagents were supplied by Carlo Erba, Merck and Fluka (min. 97%, except for xylene for which purity was 92%) and were used without further drying or purification. The $C_{18}$ – Silica 3M Empore – extraction disks (Empore™, 2009; ©3M), used in this work as adsorbents, were commercialized by Phenomenex (47 mm diameter, 0.5 mm thickness, 12 μm particle size) and consisted of 10% (w/w) polytetrafluoroethylene (PTFE) fibers and 90% (w/w) of silica particles containing 17% (w/w) of organic carbon. These disks, which are stable between 2 and 12 pH units, have been used for the solid phase extraction of moderately to strongly non-polar organic pollutants from aqueous solutions and are thus appropriate to extract the compounds to be analyzed in this work.

### 2.2. Apparatus

BXTE solutions were placed in a double wall glass recipient covered with a polystyrene stopper with three holes of approximately 2 cm of diameter, to allow: i- the introduction of a thermometer (precision of ±0.1 °C); ii- the fixing of a metallic stainless steel cage intended to hold the $C_{18}$ disk; iii- and the sampling of the analyte(s) at regular time intervals. Temperature inside the double wall recipient was maintained at 25.0 ± 0.1 °C by using a

Thermomix S 1400 B. Braun 18BU recirculating bath associated to a Frigomix R cooling unit. A magnetic stirring bar and a stirring apparatus Agimatic-N were used to guarantee a continuous stirring of the solutions.

The extraction experiments were monitored by UV–vis spectrometry, using a Thermo Unicam Evolution 300 UV–vis spectrometer (accuracy of ±0.001 A up to 1.0 A). The spectrometer was controlled in remote mode by the software Vision, version 1.25. Temperature in the absorption cells' compartment was also kept at 25.0 ± 0.1 °C and monitored by reading the resistance of a copper thermistor immersed in a quartz cell filled with ethanol and positioned next to the sample cell. The thermistor was connected to a Philips PM 2522A multimeter (precision ± $10^{-3}$ kΩ). The relationship between resistance and temperature was previously established through a calibration curve.

### 2.3. Extraction procedure

500 mL of sample solutions, contaminated in the laboratory with each of the BXTEs, were prepared daily in ultra-pure water (Milli-Q, Millipore). BXTEs concentrations ranged from $1 \times 10^{-4}$ to $8 \times 10^{-4}$ mol dm$^{-3}$. In order to simulate wastewaters from the graphic industry which may be contaminated simultaneously with various VOCs, we have also prepared 500 mL of an aqueous mixture, approximately equimolar in the four pollutants, with a total concentration of $4.4 \times 10^{-4}$ mol dm$^{-3}$. In both situations, 300 mL of the solutions were transferred into the double wall glass recipient and stirred at a constant rate of 700 rpm. The kinetics of the variation of BXTE concentration with time, and thus the ability of the $C_{18}$ disks to remove these pollutants from water, were measured spectrometrically between 190 and 600 nm. After allowing 15 min for temperature equilibration in the recipient, three absorbance readings, in the absence of the $C_{18}$ disk, were taken at the previously determined analytical wavelength of each compound ($\lambda_{max}$) and were used both to ensure that the initial concentration of the analytes did not vary in water and also to define the (max) absorbance at "zero" time.

The $C_{18}$ disk, pre-conditioned in methanol for 30 min, was then placed in the steel cage suspended from the stopper with a stainless steel wire, and immediately submerged in the sample solution to commence the partitioning experiment. The absorbance of the sample solution, measured in 1 cm path length quartz analytical cells, was recorded every 5 min for the first 60 min and then every 10 min until there was no change in absorbance, i.e., until equilibrium was reached. Each aliquot used was always returned to the sample solution to avoid pollutant loss and volume alterations. Each $C_{18}$ SPE disk was used only once due to analyte(s) contamination but it was analytically recovered for further applications, as described in the literature (Green and Abraham, 2000). At least three independent experiments were carried out for each compound analyzed separately.

## 3. Results and discussion

The spectrometric behavior of the aqueous solutions of all compounds was verified before the kinetic runs, to ensure that, in spite of their low solubility in water, the analytical technique could still be used in a reproducible way. Results show that all investigated compounds present a well defined and stable absorbance maximum in the wavelength range comprised between 201 and 208 nm, being the change in absorbance of benzene, ethylbenzene, toluene and xylene measured at 201, 204, 206 and 208 nm, respectively.

The equilibrium constant, $K_{eq}$, was determined from the phase ratio, $f$ ($f = V_W/V_D$, where $V_W$ and $V_D$ are the volume of water and