CHARACTERIZATION OF THE ORGANIC LOAD OF THE WASTE FOUNTAIN SOLUTION

Savka Adamović[1], Vladimir Rajs[1], Aleksandra Mihailović[1], Robert Lakatoš[1], Dragan Adamović[1]

[1]*University of Novi Sad, Faculty of Technical Sciences, Trg Dositeja Obradovića 6,*
21000 Novi Sad, Serbia
e-mail: adamovicsavka@uns.ac.rs

Abstract

The qualitative analysis of the organic loads of waste fountain solution (WFS) was investigated in the paper. Two liquid/liquid (L/L) extraction methods were used for WFS sample preparation: L/L extraction with methylene chloride and sequential L/L extraction with n-pentane, methylene chloride and methylene chloride at pH 2. Qualitative characterization of the organic load profile of offset effluent was performed using a gas chromatographic/mass spectrometric method.

Introduction

The sheet-fed offset printing process is based on the interaction of printing ink and fountain solution with the process materials. The fountain solution is expected to keep the printing ink off the non-printing areas of the printing plate with a liquid film, to maintain the hydrophilic nature of the non-printing areas, to promote fast spreading over the plate, to lubricate the plate and the rubber blanket, and to control the emulsification of ink and water. The fountain solution usually contains plate preservative agents, wetting agents, isopropyl alcohol or glycol-based surfactants, buffer substances, and antimicrobial additives [1]. WFS is generated as a reaction between printing plate, an initial fountain solution, printing inks and printing substrate. Therefore, the offset printing sites should apply measures that would be focused on monitoring, prevention and then on preparation for re-use of the WFS before being discharged into water and soil recipients.

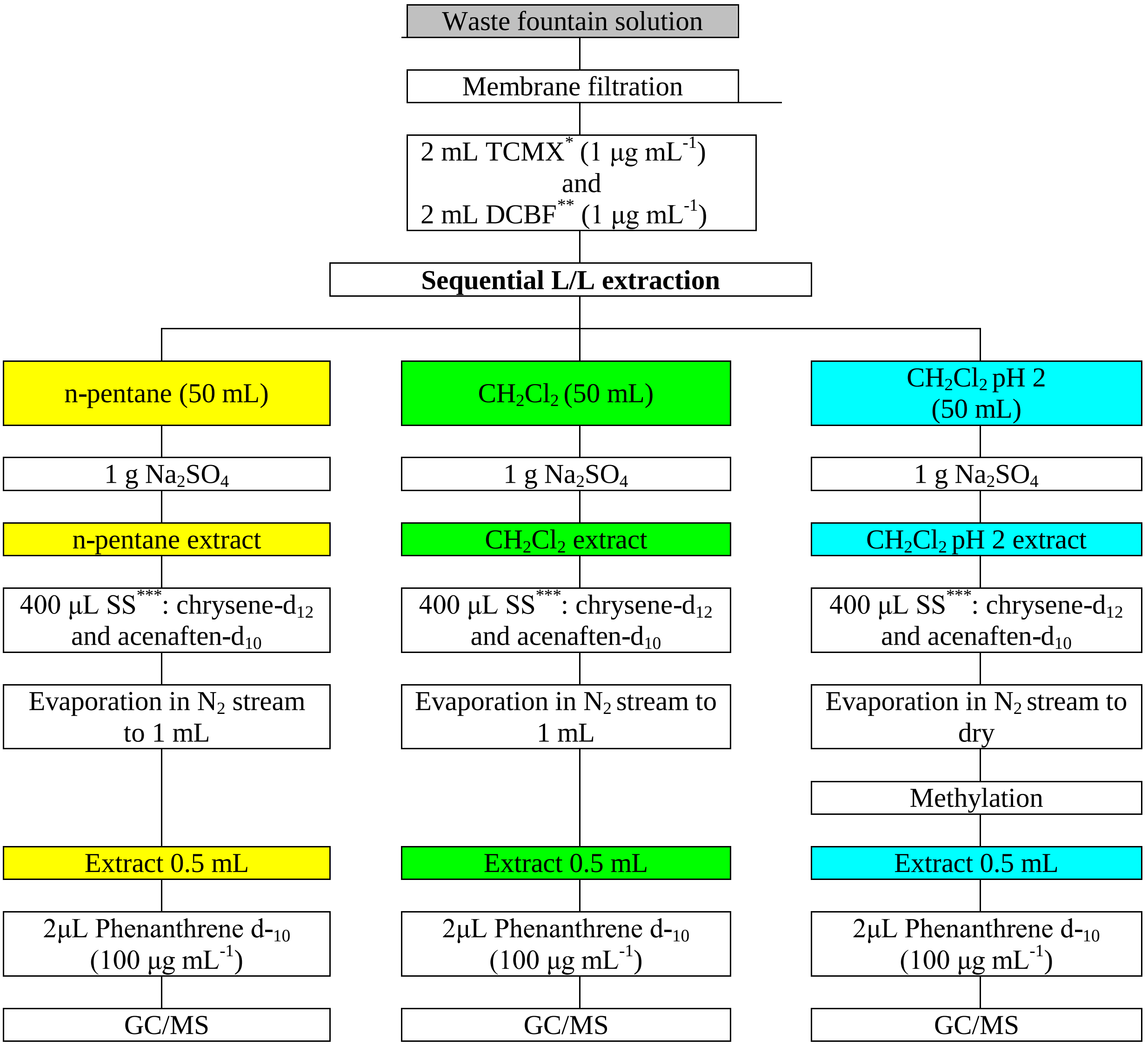
Due to the dynamic markets and the competitive forces that govern it, most manufacturers do not define the exact chemical composition of the developer [2] or other offset materials such as WFS. Unique publish information about the composition of a chemical in the printing process is available in Material Safety Data Sheet (MSDS), patent holders, or a scientific publication setting the chemical definition of analytical methods.

The paper aims are to characterize the WFS and to validate the extraction methods for the future selection of adequate effluent treatment for its safe disposal in a printing environment.

Experimental

The qualitative organic load profile of WFS was analysed by gas chromatographic/mass spectrometric (GC/MS) method. The analysis was performed using a gas chromatograph with a mass detector (Agilent 7890A GC with 5975C MSD, USA) and with an Agilent J&W Scientific DB-5MS chromatographic column of appropriate dimensions (30 m x 0.25 mm ID x 0.25 μm). Helium was used for the gas carrier. The samples were injected at an injector temperature of 270°C, while the detector temperature was 150°C. WFS sample was prepared with L/L extraction with methylene chloride and sequential L/L extraction with n-pentane, methylene chloride and methylene chloride at pH 2.

In L/L extraction with methylene chloride (I method), 1 L of WFS sample in a separation funnel was extracted with 30 ml of methylene chloride (CH_2Cl_2, J.T. Baker, USA). The extract was first collected in a laboratory beaker with three tablespoons of anhydrous sodium sulfate (Na_2SO_4, p.a., Sigma-Aldrich, Germany) due to high contamination of WFS. The extract was then transferred to a separation funnel. The extraction was repeated once more with another 30 ml of methylene chloride. The cumulative extract is evaporated to dryness and reconstituted with 2 ml of phenanthrene d10 (concentration of 0.4 µg/mL) in a mixture of hexane and methylene chloride (1:1). After L/L extraction with methylene chloride at the actual pH of WFS (pH 8.0), the pH of WFS was adjusted to 2 additions of concentrated hydrochloric acid (HCl, 35%, p.a., Merck, Germany). As the pH values of the compounds change their shape, adjust the pH of WFS to 2, the invisible ionized compounds at pH 8.0 become visible at pH 2. The L/L extraction process with methylene chloride at pH 2 was repeated according to the same procedure described above.



*TCMX = 2,4,5,6-tetrachloro-m-xylene, **DCBF = decahlorobiphenyl, ***SS = surogat standarda

Figure 1. Scheme of WFS preparation procedures by sequential L/L extraction

Sequential L/L extraction (II method) of WFS was performed according to the procedure presented in the study of Dsikowitzky et al. [3] with increasing concentrations of individual chemicals due to the multicomponent and contamination of offset effluent. Figure 1 schematically shows the WFS preparation procedures by sequential L/L extraction. To remove suspended solids from WFS, before sequential L/L extraction, 1L WFS was filtered through a membrane filtration set with a cellulose nitrate membrane filter (Sartorius Stedim Biotech GmbH, Germany) and a vacuum pump (MILIPORE, Germany). The third fraction with CH_2Cl_2 in an acidic medium was subjected to a methylation procedure. Methylation was performed according to the procedure of Santos-Delgado et al. [4] as follows: the evaporated extract was dissolved in 1 mL of methanol. 250 μL of concentrated sulfuric acid (H_2SO_4 p.a., Merck, Germany) was slowly added to the extract, after which the extract was left in the ultrasonic bath for 1 minute. The extract was then heated in a water bath for 12 minutes at 59^oC. 6 mL of 2% potassium chloride solution was added to the cooled extract. The esters were extracted with 1 mL of hexane, and then 0.5 mL of the extract was separated for GC/MS analysis.

A blank sample (1 L of distilled water) was prepared for each fraction to the same procedure as WFS. The dishes were washed with acetone: hexane in a 1: 1 ratio before use.

Deconvolution Reporting Software (DRS) was used to create the GC/MS organic profile of WFS. The Automated Mass Spectral Deconvolution and Identification System (AMDIS) software was used to identify organic substances. For more accurate identification, all mass spectra obtained with the AMDIS software were compared with the NIST (National Institute of Standards and Technology) reference spectra of the database. The presence of an organic compound in a WFS sample has been proved if the probability of presence, obtained by using AMDIS software and the NIST database, is more than 70%.

Results and discussion

To obtain profiles with more detected organic substances, a cumulative GC/MS profile of both L/L extraction methods with the probability of organic substances presence more than 70% was determined (Table 1). The cumulative qualitative GC/MS profile of organic substances in the WFS indicates that the effluent contains 73 organic substances with a probability of presence more than 70% by using AMDIS software and the NIST database.

Table 1. Cumulative GC/MS profile of organic substances in the WFS

Organic compounds	**I method**	**II method**	**AMDIS >70%**	**NIST >70%**
Hydrocarbons				
Tridecen		+	+	+
1-heksadecene		+	+	+
Eikosan		+	+	+
Heneikosane		+	+	+
Tetrakosane		+	+	+
Heksakosane		+	+	+
Heptakosane		+	+	+
Oktakosane		+	+	+
Skvalene		+	+	+
Triakontane		+	+	+
Polycyclic Aromatic Hydrocarbons (PAH)				
1-Naphthalenol	+		+	+
2-Naphthalenol	+		+	+
Phenanthrene	+		+	+
Anthracene	+		+	+
Alcohols				
Phenylmethanol		+	+	+
2-ethyl-1-hexanol	+	+	+	+

1-undecanol	+		+	+
1-dodecanol		+	+	+
1-tetradecanol	+	+	+	+
Ethers				
bis (chloromethyl) ether	+		+	+
2-Butoxy-ethanol	+	+	+	+
2-(hexyloxy)-ethanol		+	+	+
2-phenoxy-ethanol	+	+	+	+
2-(2-methoxyethoxy)-ethanol	+		+	+
2-(2-Ethoxyethoxy)-ethanol	+	+	+	+
2-(2-Butoxyethoxy)-ethanol	+	+	+	+
2-[2-(2-Butoxyethoxy) ethoxy]-ethanol	+	+	+	+
1-[2-(2-methoxy-1-methoxyethoxy)-1-methoxyethoxy]-2-propanol		+	+	+
Ketones				
1-(2,4,6-trimethylphenyl)-ethanone	+	+	+	+
1-Phenyl-1-propanone		+	+	+
4-Methyl-3-penten-2-one		+	+	+
Phenols				
Phenol		+	+	+
2-methoxy-phenol		+	+	+
2,6-Diisopropyl-phenol	+	+	+	+
m-tert-butyl-phenol		+	+	+
2,4-di-tert-butyl-phenol		+	+	+
o-phenyl-phenol	+		+	+
Substituted benzenes and benzene derivatives				
1,3,5-trimethyl-benzene		+	+	+
1,2,3,5-Tetramethyl-benzene		+	+	+
1,3-dimethyl-5-(1-methylethyl)-benzene	+	+	+	+
1,3-bis(1-methylethyl)-benzene		+	+	+
1,4-bis(1-methylethyl)-benzene		+	+	+
Benzoic acid	+		+	+
p-aminotoluene	+	+	+	+
Vanillin		+	+	+
Benzoic acid methyl ester		+	+	+
Benzoic acid 4-methyl methyl ester		+	+	+
Organic acids				
Dodecanoic acid		+	+	+
Tertradecanoic acid	+	+	+	+
Hexadecanoic acid	+	+	+	+
Octadecanoic acid	+	+	+	+
Fumaric acid	+		+	+
Terephthalic acid	+		+	+
Esters				
Octane acid methyl ester		+	+	+
Decanoic acid methyl ester		+	+	+
Tetradecanoic acid methyl ester		+	+	+
Hexadecanoic acid methyl ester		+	+	+
Linoleic acid methyl ester		+	+	+
9-(Z)-Octadecanoic acid methyl ester	+	+	+	+
Octadecanoic acid methyl ester		+	+	+
Phthalic acid dionyl ester	+		+	+

Amides				
1-methyl-1-nitrosourea	+		+	+
N-(4-ethoxyphenyl)-acetamide		+	+	+
N-butilbenzensulfonamid		+	+	+
Organic compounds with nitrogen				
Diazomethane		+	+	+
2-ethylpyridine		+	+	+
N-butylbenzenesulfonamide	+		+	+
Organic compounds with nitrogen and oxygen				
5-chloro-2-methyl-2H-isothiazol-3-one		+	+	+
1,3-benzothiazole		+	+	+
2-methylthiobenzothiazole		+	+	+
Organic compounds with phosphorus				
Tributyl phosphate		+	+	+
Amines				
Phenylamine	+		+	+
2,6-dimethyl-benzenamine		+	+	+

Comparison of GC/MS profiles obtained by L/L extraction with one solvent (I method) and with three solvents (II method) it was found that sequential L/L extraction (with 58 organic compounds) detected 48% more organic substances compared to L/L excretion with methylene chloride (with 30 organic compounds). Also, PAH compounds were detected only by L/L extraction with methylene chloride, while hydrocarbons and organic compounds with nitrogen and oxygen were detected only in sequential L/L extraction. It is concluded that the nature of the solvent determines a number and classes of extracted organic compounds.

Conclusion

The obtained GC/MS profiles show that 48% more organic substances are detected by sequential L/L extraction compared to L/L extraction with methylene chloride. Thus, the extraction solvent determines the class of organic compounds that will be extracted from the WFS.

When we have a complex effluent such as WFS to obtain a profile with more detected organic substances, it is best to determine the cumulative GC/MS profile of both L/L extraction methods**.**

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