THE EVALUATION OF THE ORGANIC LOAD OF THE WASTE OFFSET DEVELOPER WITH EXTRACTION METHODS

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Abstract: The validation of the extraction method is significant for the characterization of the offset effluent and the selection of an adequate effluent treatment for its safe disposal in a printing environment. For the aforementioned reasons, the qualitative characterization of the organic load profile of the waste offset developer was evaluated based on the application of two liquid/liquid (L/L) extraction methods. The gas chromatographic/mass spectrometric (GC/MS) method was used for the qualitative detection of the organic compounds present in the offset effluent. The cumulative qualitative GC/MS profile of organic substances in the waste offset developer indicates that the effluent contains 69 organic compounds with a probability of presence higher than 70% according to the AMDIS software and the NIST database.

Key words: offset developer, effluent, extraction, organic compounds

1. INTRODUCTION

An offset developer and a printing plate are in a close interdependent relationship. On one hand, the composition of the offset developer and the parameters according to which the developer is applied, like temperature, time of exposure, pH value, and age, affect the characteristics of the printing plate. On the other hand, the developer has to be adjusted in its composition to the type of the copy layer of the printing plate, the developing of which it is being used for (Mahovic Poljacek et al, 2012). Unfortunately, most manufacturers in Material Safety Data Sheet (MSDS) do not define the exact chemical composition of the offset developer or other offset printing liquid materials such as fountain solutions, cleaning agents, etc. Information about the chemical composition of offset printing materials are available partially in MSDS, in patent holders, or in scientific publications (Adamović, 2016; Adamović et al, 2019).

In literature data, a small number of authors have dealt with the problem of analysis of the initial and waste offset developers as well as their possible treatments. Thus, Vengris et al. (2007) state that in the starting developers under the commercial names of Polychrome 4003, Polychrome 2000 K and HD-P1 are the following chemical substances: potassium silicate, sodium silicate, potassium hydroxide, and D-sorbitol. After the process of developing, these waste offset developers are enriched by matters from the surface of the printing plate, such as: novolac, organic polymeric binders, photosensitive compounds, and pigments. Via the treatment by the Fenton's advanced oxidation process, almost all organic substances are removed (Vengris et al, 2007). In the paper by Lin et al. (2002), it is stated that the average waste offset developer consists of: p-phenylenediamine, hydroquinone, phenidone, benzyl alcohol, diethylene glycol, triethylene glycol, hydroxylamine, triethanolamine, formalin (consisting of 40% formaldehyde, 8% methanol and 52% water), dialdehyde glutamic acid, organic heterocyclic compounds (sodium sulfite, potassium sulfite, potassium carbonate, sodium hydrogen carbonate, boric acid, potassium hydroxide, sodium hydroxide, ammonium bromide and potassium bromide).

The waste offset developer as a byproduct of the developing of the offset printing plate is most commonly toxic by its characteristics and potentially harmful to the environment. For this purpose, this paper deals with the qualitative characterization of the organic load profile of the waste offset developer and with the validation of the two L/L extraction methods for the future selection of an adequate effluent treatment for its safe disposal in a printing environment.

2. METHODS

GC/MS method was used for the qualitative detection of the organic compounds present in the waste offset printing developer. 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 μ m) was used. The mass detector temperature was 150°C, while the samples were

injected at an injector with the temperature of 270°C. Helium was used as the carrier gas (Adamović, 2016; Adamović et al, 2019).

Two L/L extraction methods were used for the preparation of the waste offset printing developer samples: L/L extraction with methylene chloride (I method) and sequential L/L extraction with n-pentane, methylene chloride and methylene chloride at pH 2 (II method).

In the I method, the extraction was performed in the following order: 1 L of waste printing developer was extracted with 30 ml of methylene chloride (CH₂Cl₂, J.T. Baker, USA) in a separation funnel. The extract was first collected in a laboratory beaker with three tablespoons of anhydrous sodium sulfate (Na₂SO₄, p.a., Sigma-Aldrich, Germany) due to high contamination of the offset effluent. 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 was evaporated to dryness and reconstituted with 2 ml of phenanthrene d10 (0.4 µg/mL) in a mixture of hexane and methylene chloride (1:1). After the L/L extraction with methylene chloride at the actual pH of the waste printing developer (pH 12.0), the pH of effluent 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, adjusting the pH of effluent to 2, the invisible ionized compounds at pH 12.0 become visible at pH 2. The L/L extraction process with methylene chloride to the same procedure as described above (Adamović, 2016; Adamović et al, 2019).

In the II method, the extraction was performed according to the procedure: 1L of offset effluent was filtered through a membrane filtration set with a cellulose nitrate membrane filter (Sartorius Stedim Biotech GmbH, Germany) and a vacuum pump (MILIPORE, Germany) to remove suspended solids from the waste offset developer. Then, 2 mL of 2,4,5,6-tetrachloro-m-xylene (1 μ g/mL) and 2 mL of decachlorobiphenyl (1 μ g/mL) were added to the filtered effluent. By the extraction with 50 ml of n-pentane, the first n-pentane fraction was obtained. The n-pentane fraction was filtered through anhydrous sodium sulfate. Following the same procedure with methylene chloride (50 mL) and methylene chloride at pH 2 (50 mL), the second and third fractions were obtained, respectively. Then, 400 μ L surrogate standards (chrysene-d12 and acenaften-d10) were added to all three fractions. Then the n-pentane and methylene chloride fractions were evaporated in a stream of nitrogen to 1 mL. The third fraction with methylene chloride in an acidic medium was subjected to a methylation procedure.

Methylation was performed according to the procedure of Santos-Delgado et al. (2000) as follows: the evaporated extract was dissolved in 1 mL of methanol. 250 μ L of concentrated sulfuric acid (H₂SO₄ 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°C. 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. After the evaporation of the first and second extracts and methylation and evaporation of the third extract, 2 μ L of phenanthrene d-10 (100 μ g/mL) was added to each extract (0.5 mL). The prepared samples were analyzed by GC/MS (Adamović, 2016; Adamović et al, 2019). 1 L of distilled water as a blank sample was prepared for each fraction according to the same procedure as for the waste offset developer. The dishes were washed with the mixture of acetone: hexane in a 1: 1 ratio before use.

The Deconvolution Reporting Software was used to create the qualitative GC/MS organic profile of the offset effluent. The Automated Mass Spectral Deconvolution and Identification System (AMDIS) software was used to identify organic substances. Also, 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 waste offset developer sample has been proved if the probability of presence (match), obtained by using AMDIS software and the NIST database, is higher than 70% (Adamović, 2016).

3. RESULTS AND DISCUSSION

By using the L/L extraction with methylene chloride (I method) and the sequential extraction (II method), 45 and 24 organic substances were detected in the waste offset developer, respectively. In order to obtain a qualitative profile with the maximum number of detected organic substances, a cumulative GC/MS profile was determined for both extraction methods. The cumulative and qualitative GC/MS profiles of organic substances in the waste offset developer indicate that the effluent contains 69 organic substances with a probability of presence (match) higher than 70% by using the AMDIS software and the NIST database (Table 1).

Class of organic compounds	Organic compounds	l method	ll method	AMDIS Match	NIST Match
Hydrocarbons	Pentadecane		+	79	84
	Undecane		+	85	86
	Tetradecane		+	71	78
Bicyclic	5-Ethyl-bicyclo [2.2.1] hept-2-ene	+		76	81
hydrocarbons	Indane	+		88	79
Polycyclic Aromatic Hydrocarbons (PAH)	Biphenyl		+	71	79
	Naphthalene	+		97	93
	1-Naphthalenol	+		98	92
	2-Naphthalenol		+	91	86
	Fluoranthene	+		90	84
	Pyrene	+		85	84
	2-ethyl-1-Hexanol		+	99	92
Alashala	1-Undecanol	+		75	81
	1-Dodecanol	+		96	92
AICOHOIS	1-Tetradecanol	+		78	88
	Phenylmethanol or Benzyl Alcohol		+	100	94
	α , α 4-trimethyl-3-cyclohexene-1-Methanol	+		92	84
Ethors	2-(2-butoxyethoxy)-Ethanol	+		84	89
cuters	2-phenoxy-Ethanol	+		89	79
	Benzaldehyde	+		97	94
Aldehydes	2-chloro-1-phenyl-ethanone		+	87	90
and	2,3-dihydro-1H-Inden-1-one	+		78	77
Ketones	1,2,3,4-tetrahydronaphthalen-1-one	+		72	76
	Diphenylmethanone	+		78	82
	Phenol	+		87	82
	3-methyl-Phenol	+		99	98
	4-methyl-Phenol	+		100	94
	2-ethyl-Phenol	+		72	74
Phenols	3,5-dimethyl-Phenol		+	77	79
	4-(1-methylethyl)-Phenol		+	73	70
	m-tert-butyl-Phenol	+		73	70
	p-tert-butyl-Phenol		+	87	85
	2,4-di-tert-butyl-Phenol	+		96	89
	o-phenyl-Phenol		+	96	89
	Bis-4,4'-(1-methylethylidene)-Phenol	+		90	83
Substituted benzenes and benzene derivatives	Methylbenzene		+	73	83
	1-methyl-3-(1-methylethyl)-Benzene		+	83	87
	1-methyl-3-propyl-Benzene	+		77	77
	1-methoxy-4-(2-propenyl)-Benzene		+	91	85
	4-methyl-1,2-diamino-Benzene		+	79	76
	Vanillin	+		86	80
	Benzoic acid	+		86	76
	2,5-dimethyl-Benzoic acid	+		77	81
	3,5-dimethyl-Benzoic acid	+		93	88
	p-tert-butyl-Benzoic acid	+		86	74
	Benzoic acid methyl ester		+	100	96
	Benzoic acid 4-methyl methyl ester		+	95	94
	Benzonitrile	+		73	73
Organic acids, Esters and Salts of organic acids	3-Phenylpropanoic acid	+		90	86
	Pentanoic acid	+		74	76
	Heptanoic acid	+		88	88
	Octanoic acid	+		88	86
	Nonanoic acid	+		92	88
	Decanoic acid	+		93	89
	Dodecanoic acid	+		97	94

Table 1 (part 1): Cumulative and qualitative GC/MS profile of organic substances in the waste offset developer

Table 1 (part 2): Cumulative and qualitative GC/MS profile of organic substances in the waste offset developer

	Tertradecanoic acid	+		78	88
	Hexadecanoic acid	+		92	88
	Octanoic methyl ester		+	95	92
	Decanoic acid methyl ester		+	92	92
	Dodecanoic acid methyl ester		+	96	93
	Tetradecanoic acid methyl ester		+	98	94
	Hexadecanoic acid methyl ester		+	98	91
	1-naphthyl methylcarbamate	+		71	70
	1 (3H)-Isobenzofuranone (lactone)	+		91	89
	Phthalic anhydride	+		99	96
Amines	N-butyl-1-Butanamine		+	93	88
	Aniline	+		100	98
	Diphenylamine	+		96	91
Terpenes	Camphor	+		75	75

By comparing the GC/MS profiles obtained by the I and II methods, it was found that the L/L extraction with methylene chloride (with 45 organic compounds) detected 47% more organic substances compared to the sequential L/L extraction (with 24 organic compounds). Also, bicyclic hydrocarbons, ethers, organic acids, some salts of organic acids, and terpene (camphor) were detected only by the L/L extraction with methylene chloride, while hydrocarbons and esters of organic acids were detected only in sequential L/L extraction. It is concluded that the nature of the solvent determines the number and class of extracted organic compounds.

4. CONCLUSIONS

In case of a complex effluent such as the waste offset developer, in order to obtain a profile with a higher number of detected organic substances it is best to determine the cumulative GC/MS profile of both L/L extraction methods. The obtained cumulative GC/MS profiles show that almost 2 times more of the organic substances are detected by the L/L extraction with methylene chloride compared to the sequential L/L extraction. Thus, the extraction solvent determines the class of organic compounds that will be extracted from the offset effluent.

5. ACKNOWLEDGMENTS

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