GRID 2020
10 . INTERNATIONAL SYMPOSIUM
GRAPHIC ENGINEERING AND DESIGN
12-14. NOVEMBER 2020
10th JUBILEE

The evaluation of the organic load of the waste offset developer with extraction methods

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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.

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.

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.

Problem Description

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

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 μm) was used. The mass detector temperature was 150oC, while the samples were injected at an injector with the temperature of 270oC. Helium was used as the carrier gas.

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).

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%.

Results

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).

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

Class of organic compounds	Organic compounds	I method	II method	AMDIS Match	NIST Match
Hydrocarbons	Pentadecane		+	79	84
	Undecane		+	85	86
	Tetradecane		+	71	78
Bicyclic hydrocarbons	5-Ethyl-bicyclo [2.2.1] hept-2-ene	+		76	81
	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
Alcohols	2-ethyl-1-Hexanol		+	99	92
	1-Undecanol	+		75	81
	1-Dodecanol	+		96	92
	1-Tetradecanol	+		78	88
	Phenylmethanol or Benzyl Alcohol		+	100	94
	α, α4-trimethyl-3-cyclohexene-1-Methanol	+		92	84
Ethers	2-(2-butoxyethoxy)-Ethanol	+		84	89
	2-phenoxy-Ethanol	+		89	79
Aldehydes and Ketones	Benzaldehyde	+		97	94
	2-chloro-1-phenyl-ethanone		+	87	90
	2,3-dihydro-1H-Inden-1-one	+		78	77
	1,2,3,4-tetrahydronaphthalen-1-one	+		72	76
	Diphenylmethanone	+		78	82
Phenols	Phenol	+		87	82
	3-methyl-Phenol	+		99	98
	4-methyl-Phenol	+		100	94
	2-ethyl-Phenol	+		72	74
	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
Substitued 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

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

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
	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.

Conclusion

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.

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ACKNOWLEDGMENTS

The authors acknowledge the financial support of the Ministry of Education, Science and Technological Development, Republic of Serbia through the project no. 451-03-68/2020-14/200156: "Innovative scientific and artistic research from the FTS (activity) domain".