

M. NIAOUNAKIS and C. P. HALVADAKIS

Olive-Mill Waste Management: Literature Review and Patent Survey

430 pp. (17×24 cm.)

Publication Number 297

Copyright © Michael NIAOUNAKIS and Constantinos P. HALVADAKIS

First published: February 2004

Executive Editor: Christos STAVROPOULOS

Compositor - Pagemaker, Films: Maria-Nelli KARELOU

Montage: Rania AMOLOCHITOU

Cover Designer: Kyriakos ATHANASIADES

Corrector: Efthimia EXARCHOU

TYPOTHITO - GEORGE DARDANOS Publications GEORGE DARDANOS

37, Didotou St., 106 80 Athens

Tel. 210.3642003

Fax: 210.3611374, 210.3642030 www.dardanosnet.gr

e-mail: info@dardanosnet.gr

Waste Management Laboratory, Department of Environmental Studies, University of the Aegean

khalv@aegean.gr

Statement

The views and opinions expressed in this book are those of the individual authors and do not represent the views of the European Patent Office (EPO)

No part of this publication may be reproduced in any form or by any means, electronic or mechanical, including photocopy, recording or any information storage or retrieval system, without permission in writing from the authors.

Printed in Greece

All Rights Reserved

ISBN 960-402-123-0

CONTENTS

Foreword	xi	
PART I: BACKGROUND INFORMATION	1	
Chapter 1 INTRODUCTION	3	
Chapter 2	1.0	
CHARACTERIZATION OF OLIVE-MILL WASTE	13	
Olive by-products	14	
Pruning and harvest residues	14	
Olive-mill extraction by-products	17	
Olive cake	17	
Olive-mill wastewater (OMWW)	18	
Organic compounds	22	
Inorganic compounds	31	
Microbial content of OMWW	34	
Two-phase olive-mill waste (2POMW)	35	
Microbial content of 2POMW	37	
Experimental techniques	38	
Chapter 3		
ENVIRONMENTAL EFFECTS	45	
Antimicrobial behavior	45	
Phytotoxicity	46	
Effect on water	47	
Effect on soil	50	
Effect on atmosphere	56	vi

CHAPTER 4	
THE EFFECT OF OLIVE-MILL TECHNOLOGY	57
Evolution of production methods	57
Olive oil production systems	60
Pressing process (traditional or classical system)	62
Centrifugation	63
i) Three-phase centrifugation	63
ii) Two-phase centrifugation	63
Electrophoresis	68
Chemical separation	68
Stone-removing process	68
Percolation (Selective filtering)	71
recording (Selective intering)	/ 1
PART II: TREATMENT PROCESSES	73
Chapter 5	
PHYSICAL PROCESSES	75
Dilution	75
Sedimentation/Settling	76
Filtration	77
Flotation	78
Centrifugation	80
Membrane technology	80
(microfiltration, ultrafiltration and reverse osmosis)	81
(interoritiation, diffaritiation and reverse osmosis)	81
Chapter 6	
THERMAL PROCESSES	89
Physico-thermal processes	89
Irreversible chemico-thermal processes	97
Combustion	98
Pyrolysis	101
Lagooning	103
	100
Chapter 7	
PHYSICO-CHEMICAL PROCESSES	105
Neutralization	105
Precipitation/Flocculation	106

T	
Inorganic flocculants	107
Ferric chloride	107
Ferric sulfate and aluminum sulfate	108
Sodium silicate	108
Lime	109
Miscellaneous inorganic flocculants	111
Organic flocculants	114
Adsorption	116
Chemical oxidation process	119
Advanced oxidation processes (AOPs)	122
Photolysis of O_3	123
Photolysis of H_2O_2	123
Photocatalysis	124
Fenton reaction	127
Wet oxidation	130
Electrochemical oxidation	133
Ion exchange	136
CHAPTER 8 BIOLOGICAL PROCESSES	
BIOLOGICAL PROCESSES	137
Anaerobic processes	137
Landfills	149
Aerobic processes	150
Biofilm (trickling filter or biofilter or fixed-bed)	151
Activated-sludge	152
Rotating Biological Contactor	154
Oxidation ditch	155
Sequencing Batch Reactors	155
Use of specific aerobic microorganisms	157
Fungi	157
Bacteria	165
Aerobic-anaerobic processes	168
Composting Biotechnological processes	170
Biotechnological processes Phytoremediation (Watlanda)	176
Phytoremediation (Wetlands) Irrigation of agricultural land/Land.	176
Irrigation of agricultural land/Land spreading	181
Chapter 9	
COMBINED AND MISCELLANEOUS PROCESSES	187

PART III: UTILIZATION	199
Chapter 10	
USES	201
Use as fertilizer	201
Use as pesticide.	203
Use in animal feeding.	
Recovery of residual oil	215
Recovery of organic compounds	220
Pectins	222
Antioxidants	222
Enzymes	223
Production of various products	235
Alcohols	236
Biosurfactants	236
Biopolymers	238
Activated carbons	240
Biogas	242
Generation of energy	243
Miscellaneous	244
	245
Appendix Bibliography	249
Bibliography	253
Literature Patents	253
Patents	321
Glossary	353
Index	271
List of authors	371
List of patents	387
	403
SUPPLEMENT	
OLIVE-MILLS IN THE NORTH AEGEAN REGION	407
	107

Foreword

live milling like every human activity and industrial process results in a low-entropy desired product and a high-entropy unwanted by-product or waste termed olive mill waste. The production of olive oil, viewed in a holistic perspective, begins with the picking of olives and ends after their processing in olive mills. Olive mill technology at present generates a variety of waste in both energy and mass forms. In addition to solid waste generated in the olive groves by annual pruning of olive trees, a considerable amount of solid waste is generated during milling in the form of leaves and small twigs brought to the mill with the olives and in the form of crushed olive stones and sizable remnants of olive pulp (flesh) following olive oil extraction. Leaves and twigs can be used as animal feed (mainly for goats) or in the production of compost after mixing with other appropriate materials. Liquid waste is known as olive mill wastewater (OMWW) since during olive milling and olive oil extraction substantial amounts of added water as well as olive juice (or olive vegetation water) combine with small amounts of unrecoverable oil and fine olive pulp particles to constitute this type of waste. Gaseous waste consists of fumes produced during malaxation of crushed olives and exhaust gases from burners providing thermal energy to the mill. Finally, energy waste consists of thermal energy losses and acoustic energy (noise) of utilized machinery.

From an environmental point of view OMWW is the most critical waste emitted by olive mills in terms of both quantity and quality. There is archeological evidence that this effluent has been damaging delicate shoreline environments for thousands of years around the Mediterranean. Pollution from olive oil production is often a problem in poor communities in southern Eu-xi

rope and North Africa where sophisticated solutions to the problem are too expensive. The problems created in managing this waste have been extensively investigated during the last 50 years without finding a solution, which is technically feasible, economically viable and socially acceptable. The prevalent waste management strategy up to date has been traditional wastewater treatment processes aimed at reducing pollution loads to legally accepted levels for disposal into environmental media (mainly land and water bodies). Recently, Spain has adapted a manufacturing process for olive oil production, which minimizes the utilization of water and, therefore, of generated wastewater, the so-called two-phase olive mill extraction technique. The pollution load is, however, the same since it originates from the olives and not from the water utilized during olive processing. In view of the above, it is apparent that a new strategy for olive waste management must be adopted. Up to now the emphasis has been on detoxifying OMWW prior to disposal. However, the present trend is towards further utilization of OMWW by recovering useful byproducts.

OMWW contains most of the water-soluble chemical species of the olive fruit. Critical chemical species like water-soluble phenols and polyphenols appear to be an obstacle during treatment -being recalcitrant- but can be industrially beneficial if isolated. If one considers that the pollution load is merely the remnants of olives (a natural product), it is preferable to adopt a waste utilization management strategy. It is not surprising that during recent years a number of patents have appeared following such strategy. OMWW management is presently approached by both in-house process modification combined with waste minimization and end-of-pipe waste utilization.

The focus of the present study is to evaluate the existing technologies and to develop environmental criteria for disposing and/or reusing olive mill wastes in general, and wastewater in particular. The prior art is critically reviewed by both discussing the extensive literature coverage -more than 1000 references are cited and commented upon, including journals, patents, conference proceedings, dissertations, theses, technical notes, reports of projects-and by recording the traditional techniques still being used by smaller olive mills, which have been passed down from generation to generation. It is a fact that most of the literature or know-how comes from countries around the Mediterranean. A substantial part of the literature collection consists of patents. Despite their technological importance, up until now patents appear to have been cited rarely in scientific journals or books.

More emphasis has been given to OMWW and to the new by-product, known as "alpeorujo" in Spain, generated by the two-phase extraction pro-

xiii

cess (2POMW). OMWW represents the still unsolved problem of the olive mill industry, both for its extent and significance. 2POMW represents a new type of problem due to its consistency (thick sludge that contains pieces of stone and pulp of the olive fruit as well as vegetation water) and its steadily increasing production, especially in Spain. The rest of the olive wastes, such as olive cake, leaves and twigs, do not represent a serious environmental problem and have only been commented upon briefly. The various olive oil extraction systems have been described shortly together with the effects each one of them has on the environment.

The wastewater (brines) arising from the table olive industry has also not been reviewed. It was considered that brines constitute a different type of wastewater.

It is not the intention of the present study to propose any solution. Instead, it defines the problems faced by the olive mill industry, makes proposals for discharge/reuse of olive mill wastes on the basis of each treatment technique and shows the current trends in the olive waste management.

Some of the conclusions of the present study are:

 Most of the technologies reviewed in this study have been tested on a small scale only. In depth assessment of these results and subsequent full-scale applications has yet to be carried out.

• The olive mill waste management can be viewed as: i) extracting valuable materials (e.g. irrigation water, compost, fodder, fuel, antioxidants etc.); and ii) in lowering pollution load for final disposal to natural receiving bodies (surface water, land and sea). The double nature of olive mill waste (as a pollutant of streams or a resource to be recycled) causes antagonism between agriculture and environmental groups, because of their different

point of view on this topic.

• Most of the treatment processes are focused on both bioremediation, as a means of reducing the polluting effect of OMWW and transformation into valuable products, together with modification of the technology used in oil extraction. The presence of large amounts of phenolic compounds constitutes one of the major obstacles in the detoxification of OMWW. These recalcitrant compounds decelerate the process, hinder removal of part of COD and detract from its economic viability. Nowadays, the trend is towards turning this problem to a benefit by extracting these compounds. Recent studies have shown that the abundant phenolic antioxidant fractions of olive oil have a potent inhibitory ability on reactive oxygen species. There is an increasing body of evidence indicating the involvement of oxygen-derived free radicals in several pathologic processes, such as cancer

and atherosclerosis. OMWW has a powerful antioxidant activity, and thus might be a cheap source of natural antioxidants. Up to now the antioxidant compounds of OMWW have not been effectively exploited, due to the impracticality of extracting usable amounts of antioxidant compounds using conventional technology.

• The problem of olive mill waste is further aggravated by the lack of a common policy among the olive oil producing countries. Every country has its own legislation/regulations that often vary greatly among them with a consequent non-uniform application of generally accepted guidelines. For this reason there is a need for a unified strategy behavior among the EU member states.

To the best of our knowledge this is the first extensive and all-encompassing review to appear on the subject of olive mill wastewater. A few earlier reviews can be found in the literature, but these are mostly partial in scope and outdated. This is quite surprising given the environmental impact of this waste. It is hoped that this review will increase public awareness and will further provide a valuable information resource for olive oil producers, researchers and policy makers dealing with the problem of olive mill wastes.

The present publication has been finance by EU Regional Directorate-General (ERDF Innovative Actions 2000-2006, Programme 2001 GR 16 0 PP 209. The project title was "North Aegean Innovative Actions and Support (NAIAS)", while this work was a deliverable of Action 7.6 "Innovative Olive Mill Waste Management Systems".

The authors would like to acknowledge the help of various individuals who contributed in certain aspects of the present work. Specifically, thanks are due to D. Schaelicke and M. Karatzas for aiding in management issues and compiling supplement information; C. Tzoutzoumitros and M. Hadjimanolakis for perfecting certain figures and chemical formulae; W. Bolger for helpful comments regarding the text; and to the editorial board of Dardanos Publications for their efforts into materializing the book form of this work.

Dr. M. Niaounakis Prof. C. P. Halvadakis Mytilene, January 2004