Atmospheric Emissions of Volatile Organic Compounds From a Solvent Paint Sludge - Chemical Identification and Quantification

A. METALI^{a*}, M. ZIATI^{a,b}, C. CAMSELLE^c, S. GOUVEIA^c

^aLaboratory of Soft Technologies, Physicochemical, Valorization of Biological Materials and Biodiversity, Chemistry Department, Faculty of Sciences, M'hamed Bougara University, Boumerdes 35000 (Algeria). a.metali<u>@univ-boumerdes.dz</u>

^bLaboratory of Applied Chemistry and Materials, Chemistry Department, Faculty of Sciences, M'hamed Bougara University, Boumerdes 35000 (Algeria)

^cDepartment of Chemical Engineering, BiotecnIA Group, University of Vigo, Vigo36310, (Spain)

*Corresponding author: a.metali@univ-boumerdes.dz; Tel: +213 657 390 987

Abstract

Solvent based paint sludge contains volatile organic compounds (VOCs) that negatively impact both ecosystems and human health. These VOCs contribute to ground-level ozone formation and are key precursors in the creation of secondary organic pollutants in the atmosphere. There are limited studies that quantify the gaseous compounds released from solvent based paint sludge. In this context, we conducted our experimental study on detection of gaseous emission from paint sludge samples taken from an Algerian paint industry, in both short and long period of storage. Results revealed that paint sludge samples emitted a wide range of VOCs; over 36 compounds were identified, quantified and classified into different chemical groups. Among the compounds identified, aliphatic hydrocarbons, aromatic hydrocarbons, esters, ketones and alkanes. The collected sample from the waste storage area(PS2)contains a higher concentration of oxygenated compounds than those collected in the regeneration station (PS1) and in the waste storage chamber (PS3). Therefore, the gas emitted from paint sludge increased depending on the type and duration of storage. Given that many of the identified VOCs are carcinogenic, toxic, or harmful by inhalation, it is essential to regulate gas emissions during waste management and treatment.

Keywords: volatile organic compounds, paint sludge, solvent-based paint, gas chromatography, environment

1. Introduction

The paint manufacturing industry generates toxic and environmentally hazardous wastes from different paint production processes. According to Salihoglu et Salihoglu [1] the main waste fraction is paint sludge. This sludge can be water-based or solvent-based depending on the type of production [1]. Solvent-based paint sludge has a significant amount of organic solvent and inorganic materials, heavy metals and other hazardous materials, compared to those from water-based paint production [2].

The most of hazardous materials presents in the solvent paint sludge are organic solvents which contains VOC emissions species in level I and level II such as naphthalene, 2-chlorotoluene, benzene,

ethylbenzene, acrolein, styrene, and chloroform, considered as extremely important priority control species. Furthermore, naphtha and xylene were common chemical compositions in automotive paint [1, 3]. This gaseous emissions present high toxicity, persistent environmental risks, mutagenicity and potential carcinogenicity [4, 5].

On the other hand, the disposal of the solvent paint sludge in area generates a lot of gaseous emission into the atmosphere such as sulfide (H_2S), ammonia (NH_3) and volatile organic compounds (VOCs), this atmospheric emission is generally associated with odorous nuisance and health risks [6, 7, 8]. The main health diseases are cardiovascular risks and chronic diseases for human like leukemia and cancer, furthermore, the exposure to styrene and ethylbenzene causes type 2 diabetes mellitus [9, 10].

Furthermore, in the troposphere VOC react photo chemically with NO_x and favor ozone formation [8, 12] and a photochemical smog which cause air pollution and increasing air humidity by evaporation of sweated water [11, 12, 13, 14].

In addition, in the presence of organic solvents and heating system, the uncured paint form a film which make a cure resin and the sludge will be very sticky and difficult to manage during disposal. Therefore, this sludge must be properly process before landfill in order to minimize its environmental effect [15].

Currently Several studies were investigated in detection of VOC emission from paint sludge such as Tian et al. [16], experimentally quantified the pyrolysis kinetic reaction mechanism of waste solvent-based automotive paint sludge (OAPS) and water-based automotive paint sludge (WAPS) at four different heating rates using thermogravimetric-Fourier transform infrared (TG-FTIR) spectrometry and pyrolysis-gas chromatography-mass (Py-GC/MS) spectrometry analyses.

Liu et al. [17] did a comparison between the emission characteristics and kinetics of VOCs from automotive waste paint sludge in an environmental test chamber.

Liang, et al. [18], studied the differentiated emissions and secondary organic aerosol formation potential of organic vapor from industrial coatings in China. Where a solvent- and water-based industrial paints were evaporated, sampled and tested using online and offline instruments.

Moura et al. [19] characterized the main sources of volatile organic compounds (VOCs) and identified the main analytes emitted by the coatings used in a car factory painting line. In order to define the list of potential VOCs existent in the indoor air of the factory.

However, few studies focus on quantification of gaseous emission from solvent paint sludge during storage time and method in the plant.

Our study focus on characterization and evaluation of VOCs emission degree from solvent paint sludge taken from paint industry plant, in order to quantify VOC's emitted by this sludge during the storage in the plant and their effect on climate change. Three samples were taken: the first one from solvent regeneration system (PS1), the second one waste storage area (PS2) and third one waste storage chamber (PS3). The emission of VOC from all samples was analyzed using gas chromatography, while the elemental composition and the functional groups present in the sludge were examined through elemental analyzer and FTIR analysis respectively.

2. Materials and methods

2.1. Presentation of the paint manufacturing plant

Fig. 1 shows Paint manufacturing plant diagram. The paint manufacturing plant subdivided in several sections, the first one about aerial and underground storage of raw materials (such as acetate vinyl monomer stored in underground, which used in production of polyvinyl acetate for water based paint production). The second section focus on production of solvent and water based paint, the third one about maintenance workshop for different equipment used in the plant. The fourth section contains laboratory for quality control of final and semi-finished products, the fifth section contains machines to clean equipment used in production.

The diagram in the Fig.2 explain the different steps of equipment cleaning and regeneration of cleaning solvents and waste paint sludge (PS1), these sludge are stored in sixth section containing waste storage area (PS2) and waste storage chamber (PS3). The cleaning solvent is stored in underground solvent stock.

The last section contains the canteen and administration service.

The paint sludge are generated from solvent regeneration station, after cleaning production equipment process, this sludge is a mixture of all solvent paint products in the plant.

2.2. Sampling of paint sludge

Samples of solvent-based paint sludge were collected from a paint production plant in Algeria. This industrial plant generates approximately 25000 t/year of solid waste. Three samples were collected from different points in the industrial facility and they were included in this study:

- Solvent based paint sludge 1(PS1): it was collected from the solvent regeneration station and transported to the laboratory where it was stored in a dark glass vial at 4 °C for 4months before analysis.
- Solvent based paint sludge 2 (PS2): it was collected from the waste storage area. It was stored for 42months in the industrial plant and then transported to the laboratory in dark glass vial at 4 °C.
- Solvent based paint sludge 3 (PS3): it was collected from the waste storage chamber and stored for 42 months in the industrial plant, and then transported to the laboratory in a dark glass vial at 4 °C.

The three samples were a mixture of different components used in the manufacturing of paints and varnishes. Samples showed a pasty appearance, with a variety of colors and intense smell due to the volatile raw materials used in the formulation of paints and varnishes, such as oil-based solvents, binders, thickeners, resins, additives, polymers and pigments.

2.4. Characterization and analysis of paint sludge

The three sludge samples were characterized by FTIR analysis, elemental analysis and VOCs content. For FTIR analysis, samples were oven-dried at 70°C for 36 h, and then crushed by rapid crushing, and sieved by a standard sieve (CB/T6003.1-2012, 200 mesh) at less than 0.2mm particle size. The prepared samples were stored in desiccators before the FTIR analysis, using a Nicolet 6700 spectrometer with wave numbers ranging from 400 to 4000cm⁻¹.

The elemental composition (C, H, N, and S) was determined directly in the samples as they were collected (with no drying), using an elemental analyzer "Vario EL Cube" from Elementar (Germany).

2.5. VOC's analysis

VOCs were determined in the three samples by gas chromatography. The analysis procedure consisted of two steps. In the first step, 5 g of waste sample were introduced in a cylindrical tube and connected to an adsorption

tube. The VOCs volatilized from the sample were absorbed in the absorption tube. To accelerate the process, a pump was connected to the cylindrical tube-absorption tube system to force the flow of VOCs from the sample to the absorption tube. The pump operated at 20 mL/min for 240 min so that the total volume extracted from the sample in the cylinder was 4,8 L (Fig.3), as recommended by the norm ENISO 16017-1 [20] that recommend a volume between 1 L and 10 L.

The VOCs retained in the adsorption tube were analyzed according to the norm NF EN ISO 16017-12003[20]by gas chromatography–mass spectrometry using the Gas Chromatograph model Clarus680 from Perkin Elmer. For the analysis, the adsorption tubes were inserted in a compatible thermal desorption apparatus. The air and oxygen was purged to avoid undesirable reactions with the VOCs and stationary phase. Then, the tube is heated to favor the desorption of VOCs with the simultaneous injection of a vector gas stream. The vector gas stream flowed in the opposite direction than that in the absorption step. For optimum desorption, the flow of the vector gas should be in the range 30-50 mL/min. Desorption conditions are summarized in table 1.

3. Results and discussion

3.1. Description of raw materials used for generation of waste paint sludge

In paint manufacturing plant, solvent-based paint is produced, in general, by mixing chemicals (primarily resins, dry pigment, and pigment extenders). In the course of the mixing, solvents and drying oils are also added. After mixing, additional grinding and mixing may occur. Next, tints, thinner (regularly a volatile naphtha or blend of solvents), and the remaining resin are added and mixed to the paint base or concentrate. The paint is filtered in order to remove non-dispersed pigment, to reach the proper consistency [21].

The minor and major products used as raw materials consumed in paint production plant and the consummated quantity per year shows in the table 2. The raw materials consumed in paint production plant pigments extenders (186709 tons/year) such as silicone dioxide(SiO₂); Calcium carbonate (CaCO₃); Barium sulfate (BaSO₄); dolomite (CaMg(CO₃)₂) and talc (Mg₃Si₄O₁₀(OH)₂).

Pigments (87588 tons/year) like: zinc phosphate ($Zn_3(PO_4)_2$), titanium dioxide (TiO_2), lead chromate(PbCrO_4), molybdate orange ($C_{26}H_{12}N_4O_2$), iron oxide (Fe_2O_3), dioxazine, phtalocyanine ($C_{32}H_{16}CuN_8$), lead molybdate (PbMoO_4), organic red ($C_{22}H_8Br_2O_2$), methyl violet ($C_{25}H_{30}ClN_3$), blue pigment ($C_{37}H_{34}N_2Na_2O_9S_3$), black iron oxide, carbon black, N-methyl-N,2,4,6-tetranitraniline.

Resin (10440 tons/year) such as alkyd resin and resins based on cobalt (6%); on calcium (4%) and lead (24%).

Binders (18559 tons/year) like aluminosilicate, polymers (polyamide and polycarboxilic acid) and nitrates cellulose ($C_6H_7N_3O_{11}$).

Thinners or solvents (43513 tons/year) such as ethyl acetate, n-butyl acetate, propylene glycol methyl ethyl ether, methyl ethyl ketone, Propylene glycol monomethyl ether acetate, white spirit, isoparl, xylene, isopropanol. Additives (10207 tones/year) like montmorillonite, plasticizer (di octyle phtalate and di butyl phtalate), zinc stearate ($C_{36}H_{70}$ O₄ Zn), ammonium polyphosphate, pigment dispersing agent, Alcohol ethoxylate and ethylene oxide, methyl ethyl ketoxine, Polypropylene (C3H6)n, Fumed silica(form of SiO₂), dispersing agent, 4-n-buthyl acetate. These input products in paint manufacturing plant produce 354 440 tons per year of solvent based paint products such as building paint, marking paint on roadways and curbs paint and car body paint. After cleaning products equipments using cleaning solvent 2500 tons/ yeas of wastes are generated. (Fig. 4)

3.2. Characterization of the paint sludge

Table 3 shows the elemental analysis of the three samples PS1, PS2, and PS3. Results reveal a higher carbon content (ranging from 10% to 13,93%) than to other elements such as hydrogen (0,55% to 0,75%), nitrogen (0,24% to 0,27%) and sulfur, which concentration is below 0,30%. Based on the elemental analysis, the chemical composition of the three samples can be described as $C_{13,93}H_{0,75}N_{0,26}S_{0,3}$ for PS1; $C_{10,70}H_{0,55}N_{0,27}S_{0,3}$ for PS2; and $C_{13,31}H_{0,69}N_{0,24}S_{0,3}$ for PS3. It is important to note that PS2 contains less carbon (10,70%) than PS1 and PS3, likely due to the origin of the sample collection and the volatilization of compounds in this sludge, particularly n-butyl acetate, which was identified in high weight percentage (50,02 wt. %) in the VOCs analysis.

On the other hand, after drying the three samples PS1, PS2 and PS3, FTIR spectra in Fig. 5 shows distinctive bands for the three dried paint sludge analyzed. Similar peaks (functional groups) are found for the three samples, with the differences lying in their intensity. The most intense peaks are characterized by stretching vibrations v3 (1409 cm⁻¹), v2 (872 cm⁻¹) and v4 (709,9 cm⁻¹; 611 cm⁻¹) corresponding to calcium carbonate. Therefore, a part of the carbon present in these samples may originate from calcium carbonate as an inorganic compound. This explains that most of the organic carbon in this sample exists as a solvent, which volatilizes during storage.

As we see in Fig. 6 the major constituent in production of the paint are extenders pigments(52,29%), and the high consumption level of calcium carbonate(178288,25 tones/year), therefore the most carbon exists as inorganic carbon. The source of organic carbon may be from pigments (24%), solvents (12%), binders (5,2%), resin(2,9%), or additives (2,86%). On the author hand, the elemental analysis shows the less quantity of hydrogen, nitrogen and sulfur compared to carbon, these atoms form with carbon a organic compounds as result we suggest that the most carbon in these solid waste exists as inorganic carbons. In addition, the PS2 which is stored in open area , it has less carbon than PS1 and PS3, therefore, the most carbon of this sample lost in storage time, and it presents as solvent.

In addition, there are some peaks with low intensity corresponding to free OH and C-H stretching between 2000 and 3000 cm⁻¹. The vibration frequencies v_3 (1183 cm⁻¹), and v_4 (666; 611,3 and 607 cm⁻¹) are attributed to calcium sulfate present in anhydrous form (anhydrite). The peak at 1071 cm⁻¹ is related to the C-N< elongation of the amide group and the Si-O-Si stretching vibrations of silica(silicon dioxide). Some bands in the range 423-875 cm⁻¹ can be attributed to vibrations of TiO₂, N-H deformation for secondary amides and PbCrO₄.[22]

3.4. Characterization of VOCs emission from paint sludge

The identified peaks and the composition obtained from the analysis of gas emissions from the three paint sludge samples are detailed in table 4. Significant differences in composition can be observed between the sludge recovered from the solvent regeneration station (PS1) and that from the storage area (PS2) or chamber (PS3).

It was possible to identify 36 different compounds in the sludge samples; 12 compounds were detected in gas emitted by PS1, whereas 14 compounds were detected in gas emitted in PS2 and PS3. The detected compounds showed different chemical functional groups, such as esters, ketones and alkanes. Hydrocarbons (solvents) and

oxygenated compounds were the main compounds in the gas emitted by the oil-based paint sludge [16].Butyl acetate was the typical chemical component found in the gas emitted by PS1 and PS2. Ethanol, decane, tetradecane and xylene were common chemicals in PS2 and PS3.

The sample PS2, from the waste storage area, contains higher concentration of oxygenated compounds thanPS1 and PS3.n-butylacetate (50,02 wt.%) was the most abundant oxygenated compound present in PS2. Other components were ethanol (28,20 wt.%), 2-propanol (6,18 wt.%), acetone (1,96 wt.%), and hydrocarbons such as decane (3,22 wt.%), 1,2,3-trimethylbenzene (2,94 wt.%), p-ethyltoluene (2,52 wt.%), 2,2- dimethylheptane (1,28 wt.%), and4-ethylheptane (1,21 wt.%). Additionally, compounds such as 4-propyl heptane, 3-methyldecane, tetradecane, o-cymene and p-xylene were detected at concentrations slightly below 1%.

Hydrocarbon solvents were also detected in the sludge samples from the solvent regeneration station and the storage chamber. Thus, PS1 contains ethylacetate (51,52wt.%), 2-butanone(21,59wt.%) and 3-methylheptane(10,97wt.%). In PS3, the detected components were ethanol (64,37wt.%) as oxygenated compound, along with hydrocarbons such as isopropylbenzene (7,68wt.%), decane(11,44wt.%), and 4-methylnonane(3,78wt.%).

According to the legal framework of Catalonia Law[23] the maximum allowed percentage of toxic volatile organic solvents in industrial waste must not exceed 3 wt.% for landfilling. However, most of the compounds identified in the three samples of our study: ethylacetate, 2-butanone, 3-methylheptane, octane and styrene in PS1; n-butylacetate, ethanol, 2-propanol, decane in PS2; and ethanol, decane, isopropylbenzene, 4-methylnonane, 1,2,4-trimethyl benzene, m-ethyltoluene in PS3; showed percentages exceeding that limit. Consequently, the dumping of those wastes in open areas or landfills is not allowed. In addition, hydrocarbon compounds emitted in both storage area (PS2) and storage chamber (PS3) can be associated with the cracking, cyclization and aromatization of styrene, toluene and xylene detected in the samples of our study[24].Styrene was used as a diluent and cross-linking agent in the paint production process and largely volatilized during curing and storage.

Those results confirm the potential toxicological effects associated with exposure to VOCs emitted by the paint waste sludge in short and long term of storage[24]. As reported in the literature, high concentration of alkanes such as 3-methylheptanes and octane in PS1, and decane in PS2 and PS3,lead to anesthetic and narcotic effects, although other compounds, e.g. lower molecular weight hydrocarbons, cause particularly potent effects, primarily due to their high volatility and solubility and hence, bioavailability[25, 26]. Furthermore, the emission of VOCs provokes environmental and health problems. Exposure to VOCs causes adverse health impacts such as renal, hematological, neurological, hepatic alterations and mucosal irritation. The environmental problems are related to the contribution of VOCs to the depletion of stratospheric ozone, and the formation of photochemical smog (ozone generation at ground level)[27]. Additionally, these VOCs contribute to global warming by absorbing infrared energy radiated by Earth, thereby increasing their concentration in the Earth atmosphere [28,-29]. In this regard, the United States Environmental Protection Agency (USEPA) and the European Commission (EC) have classified these VOCs as priority pollutants.

3.5. Comparative study with literature

The table 5 shows different VOC's emissions from automotive and paint manufacturing plant wastes ,the solvent based waste sludge from paint manufacturing plant presents the following order of gaseous emission esters (51,52 %) > ketones (21,59 %) > hydrocarbons(25,88%).

According to Liu et al. [17], the order of VOC's emission from automotive waste oil-based paint sludge is hydrocarbons (51,4%) > alocohol (39,6%) > ester (5,7%).

According to **Tian et al. [16]** the order of VOC's emission from pyrolysis waste solvent-based automotive paint sludge is hydrocarbon (64,7%) >Acid (13%) > alocohol(10,4%) > ester (8,2%) > ketones (3,9%) > aldehyde (3,3%) > phenol (1,6%) > ether (0,5%).

In this study, Gaseous emission from paint manufacturing plant present important quantity of esters such as Ethylacetate (51,52%), because, the most solvent consumed in paint production plant is Ethylacetate with 10987,2 tones per year.

4. Conclusion

Paint industries are major sources of hazardous waste. The most problematic waste is the solvent-based paint sludge that generates significant amounts of volatile organic compounds (VOCs) that cause air pollution. This study provides detailed qualitative and quantitative data on VOCs emitted from three types of paint sludge: PS1 (collected from a solvent regeneration station), PS2 (collected from a waste storage area where it has been stored for 42 months), and PS3 (collected from a waste storage chamber where it has been stored for 42 months). The results indicated that all paint sludge samples emitted a broad spectrum of VOCs. The identified VOCs were classified into three groups: hydrocarbons, oxygenated compounds, and other compounds. A total of 36 compounds were detected and quantified. Butyl acetate was detected in the emissions of PS1 and PS2, while ethanol, decane, tetradecane, and xylene were found in PS2 and PS3. Samples PS2 and PS3 were stored for 42 months in the industrial facility. In PS2 and PS3 samples numerous hydrocarbon solvents were detected in the emissions, confirming the negative impact of the sludge for health and environment even after long storage. Therefore, exposure to paint waste sludge in short and long term poses serious toxicological risks, underscoring the need to control emissions during storage and final treatment and disposal.

Declaration of Competing Interest

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of the article.

Acknowledgements

The authors gratefully acknowledge support from University M'hamed Bougara of Boumerdes, Laboratory of Soft Technologies, Physico-chemical Valorization of Biological Materials and Biodiversity and Laboratory of Industrial Biotechnology and Environmental Engineering- BiotecnIA, Department of Chemical Engineering, University of Vigo (Spain).

Funding

This work did not receive any funding.

References

- Salihoglu, G. and Salihoglu, N. K. "A review on paint sludge from automotive industries: Generation, characteristics and management ", J. Environ. Manage. (JEM), 169, pp. 223-235 (2016). https://doi.org/10.1016/j.jenvman.2015.12.039
- Huang, S. L. Yin, C.Y. and Yap, S. Y. "Particle size and metals concentrations of dust from a paint manufacturing plant ", J. Hazard. Mater. (JHM), **174**(1-3), pp. 839-842 (2010). https://doi.org/10.1016/j.jhazmat.2009.09.129
- Wang, X. and Xu, Y. "Recent Advances in Catalytic Conversion of C5/C6 Alkanes to Olefins: A Review. ", Catal. Surv. Asia (CSA), 26(4), pp. 245-260 (2022). https://doi.org/10.1007/s10563-022-09367-7
- Ruffino, B. Farina, A. Dalmazzo, D. et al. "Cost analysis and environmental assessment of recycling paint sludge in asphalt pavements", Environ. Sc. Pollut. Res. (ESPR), 28(19), pp. 24628-24638 (2021). https://doi.org/10.1007/s11356-020-10037-2.
- 5. Li, L. Zhang, D. Hu, W. et al." Improving VOC control strategies in industrial parks based on emission behavior, environmental effects, and health risks: A case study through atmospheric measurement and emission inventory ", Sci. Total Environ. (STE), 865, pp. 161235 (2023). https://doi.org/10.1016/j.scitotenv.2022.161235.
- Kim, B. Zinbo, M. Adams, J. et al. "Nonbiodegradable organic compounds found in automotive spraybooth scrubber water", Water Environ. Res . (WER), 72(4), pp. 405-412 (2000). https://doi.org/10.2175/106143000X137932
- Mustafa, M. F. Liu, Y., Duan, Z. et al. "Volatile organic compounds emission and health risk assessment during composting of fraction of municipal solid waste ", J. Hazard. Mater. (JHM), 327, pp. 35-43 (2017). https://doi.org/10.1016/j.jhazmat.2016.11.046
- Nie, E. Zheng, G. Gao, D. et al. "Emission characteristics of VOCs and potential ozone formation from a fullscale sewage sludge composting plant", Sci. Total Environ. (STE), 659, pp. 664-672 (2019). https://doi.org/10.1016/j.scitotenv.2018.12.404
- Banerjee, S. Xie, M. Cheng, S. et al. "Associations between specific volatile organic chemical exposures and cardiovascular disease risks: insights from NHANES", Front. Pub. Health. (FPH), 12, pp. 1378444 (2024). https://doi.org/10.3389/fpubh.2024.1378444
- Yu, L. Liu, W. Zhang, Y. et al. "Styrene and ethylbenzene exposure and type 2 diabetes mellitus: A longitudinal gene–environment interaction study", Eco. Environ. Health (EEH), 3(4), pp. 452-457 (2024). https://doi.org/10.1016/j.eehl.2024.07.001.
- Hu, R. Liu, G. Zhang, H. et al. "Levels, characteristics and health risk assessment of VOCs in different functional zones of Hefei", Ecotoxicol. Environ. Saf. (EES), 160, pp. 301-307 (2018). https://doi.org/10.1016/j.ecoenv.2018.05.056.
- KIM, B. R., "VOC emissions from automotive painting and their control: A review. ", Environ. Eng. Res. (EER), 16(1), pp. 1-9 (2011). https://doi.org/10.4491/eer.2011.16.1.001

- Zhao, J. Uhde, E. Salthammer, T. et al. "Long-term prediction of the effects of climate change on indoor climate and air quality", Environ. Res. (ER), 243, pp. 117804 (2024). https://doi.org/10.1016/j.envres.2023.117804
- Mansor, A. Abdullah, S. Ahmad, A. et al. "Indoor air quality and sick building syndrome symptoms in administrative office at public university", Dialogues. Health. (DH), 4, pp. 100178 (2024). https://doi.org/10.1016/j.dialog.2024.100178.
- Iticescu, C. Georgescu, L.P. Murariu, G. et al. "The Characteristics of Sewage Sludge Used on Agricultural Lands. ", Aip Conf. Proc. (ACP), 2022(1), pp. 020001 (2018). https://doi.org/10.1063/1.5060681
- Tian, L. Liu, T. Yang, J. et al. "Pyrolytic kinetics, reaction mechanisms and gas emissions of waste automotive paint sludge via TG-FTIR and Py-GC/MS", J. Environ. Manage. (JEM), **328**, pp. 116962 (2023). https://doi.org/10.1016/j.jenvman.2022.116962
- Liu, Z. Yan, Y. Lv, T. et al. "Comprehensive understanding the emission characteristics and kinetics of VOCs from automotive waste paint sludge in a environmental test chamber ", J. Hazard. Mater.(JHM), 429, pp. 128387 (2022). https://doi.org/10.1016/j.jhazmat.2022.128387
- Liang, C. Feng, B. Wang, S. et al." Differentiated emissions and secondary organic aerosol formation potential of organic vapor from industrial coatings in China ", J. Hazard. Mater. (JHM), 466, pp. 133668 (2024). https://doi.org/10.1016/j.jhazmat.2024.133668
- Moura, P. C. Santos, F. Fujão, C. et al. "Towards the identification of the volatile organic compounds emitted by the coatings used in a car factory painting line ", J. Coat. Technol. Res. (JCTR), 21, pp. 665-682 (2024). https://doi.org/10.1007/s11998-023-00847-7
- DIN, ENISO. 16017-1, Indoor, ambiant and workplace air-Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography-Part 1: Pumped sampling, (2000). https://www.iso.org/standard/29194.html
- Dursun, D. and Fusun, S. "Waste minimization study in a solvent-based paint manufacturing plant", Resour. Conserv. Recycl. (RCR), 47(4), pp. 316-31 (2006). https://doi.org/10.1016/j.resconrec.2005.12.004.
- 22. M. Pavlič, M. Petrič, and J. Žigon, «Interactions of Coating and Wood Flooring Surface System ProInteractions perties », *Coatings*, vol. 11, nº 1, 2021, doi: 10.3390/coatings11010091.
- 23. Catalonia Law. "Management on the industrial wastes", Off. J. Catalonia (OJC), Generalitat of Catalonia (1997). https://residus.gencat.cat/web/.content/home/ambits_dactuacio/planificacio/precat20_en.pdf
- 24. Mangotra, A. et Singh, S. K." Volatile organic compounds: A threat to the environment and health hazards to Living Organisms–A Review ", J. Biotech. (JB), 382, pp.51-69 (2024). https://doi.org/10.1016/j.jbiotec.2023.12.013
- Domingo, J. L. and Nadal, M. "Domestic waste composting facilities: A review of human health risks", Environ. Inter. (EI), 35(2), pp. 382-389 (2009). https://doi.org/10.1016/j.envint.2008.07.004
- 26. Khadhar, S. Higashi, T. Hamdi, H. et al." Distribution of 16 EPA-priority polycyclic aromatic hydrocarbons (PAHs) in sludges collected from nine Tunisian wastewater treatment plants.", J. Hazard. Mater. (JHM), 183, pp.98-102 (2010). https://doi.org/10.1016/j.jhazmat.2010

- 27. Hau, K. M. Connell, D. W. and Richardson, B. J. "A study of the biological partitioning behavior of n-alkanes and n-alkanols in causing anesthetic effects", Regul. Toxicol. Pharm. (RTP), **35**(2 Pt 1), pp. 273-279 (2002). https://doi.org/10.1006/rtph.2001.1531
- Hester, R. E. and Harrison, R. M. "Volatile organic compounds in the atmosphere", issues in environmental science and technology, R. Soc. Chem. (RSC), 4thEdn., pp.109-121, UK (1995).
- Derwent, R. G. and Murrells, T. P. " Impact of policy-relevant scenarios on ozone in southern England: Influence of chemical mechanism choice", Atmos. Environ. (AE), 72, pp. 89-96 (2013). https://doi.org/10.1016/j.atmosenv.2013.02.038

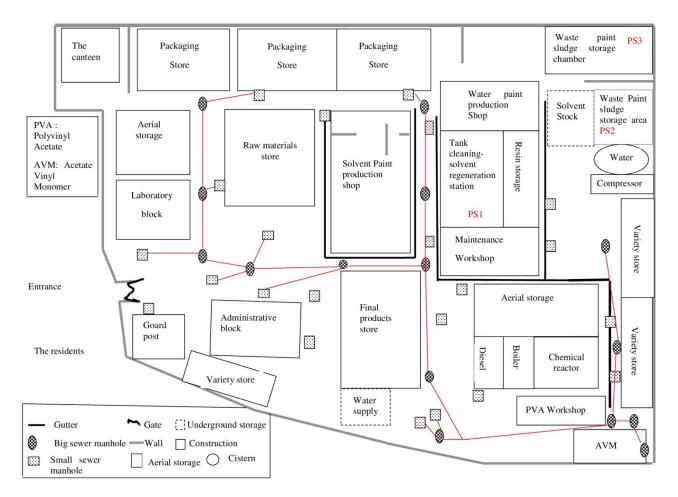
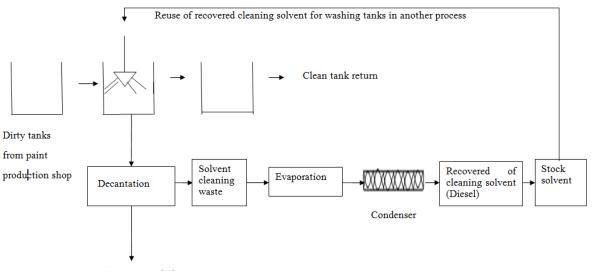


Fig. 1. Paint manufacturing plant diagram



Waste paint sludge

Fig. 2. Process of generation of waste paint sludge in solvent regeneration station

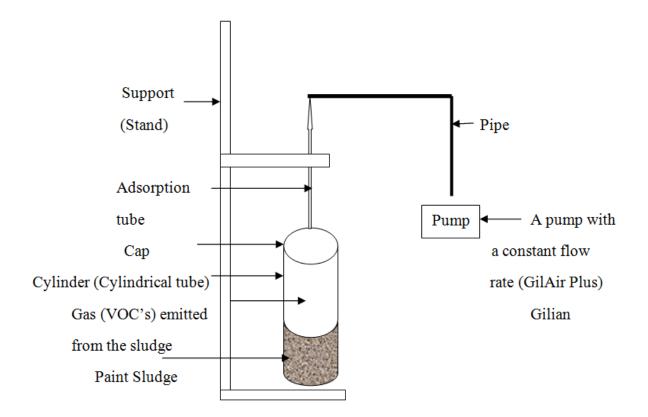


Fig. 3. Extraction and adsorption of VOCs emitted from the solvent paint sludge using the pumping method according to NF EN ISO 16017-12003

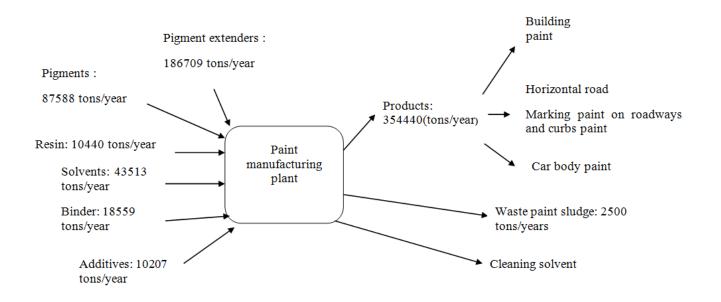


Fig. 4. Inputs and outputs products of a paint manufacturing plant

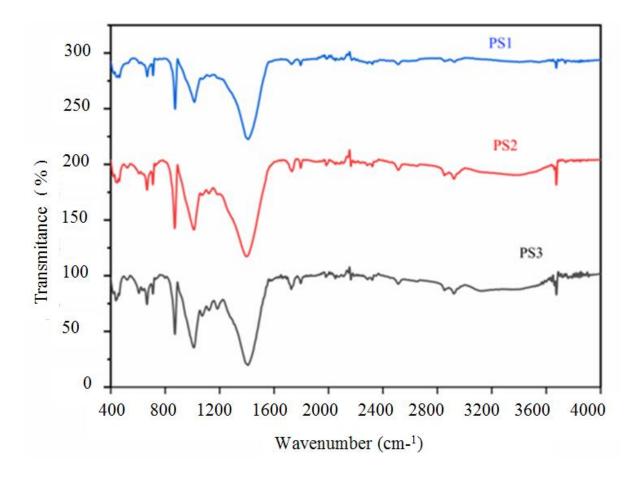


Fig. 5. FTIR spectra of raw solvent based paint sludge samples

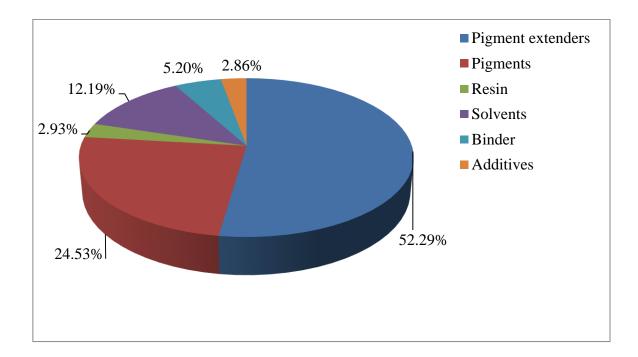


Fig. 6. Principal constituent of the paint products

Table 1.VOCs desorption conditions

Parameter	Value
Desorption temperature	250 - 325 °C
Desorption time	5 - 15 min
Desorption flow	30 - 50 mL/min
Condensation trap, low temperature	+20 -180 °C
Condensation trap, high temperature	250 - 350 °C
Condensation trap adsorbent	40 - 100 mg
Column	Length: 60 m, Inner diameter: 0,25 mm, and Film thickness 1,4 µm
Stationary phase	Rtx®-VMS
Vector gas	Helium

	Raw materials	Composition (scientific designation)	Consumption (tones per
			year)
Pigment	Calcium carbonate	CaCO ₃ (Calcium carbonate)	178288.25
extenders	Baryte Sulfate	BaSO ₄ (Barium sulfate)	3380.17
	Talc	$Mg_3Si_4O_{10}(OH)_2$	2045.89
	Medium grain sand	SiO ₂ (Silicon dioxide)	1675.15
	Dolomite	CaMg(CO ₃) ₂	1320.00
	Titanium	TiO ₂ (Titanim dioxide)	80148.91
	Solid Helios Red BBN	Fe ₂ O ₃ (Iron oxide)	3874.57
	Phtalo blue	C32H16CuN8 (Phtalocyanine blue)	1428.01
	Zinc phosphate	Zn ₃ (PO ₄) ₂ (Zinc phosphate)	1093.80
D!	Molybdate orange	$C_{26}H_{12}N_4O_2$	446.31
Pigment	Molybdenum red	PbMoO ₄ (Lead molybdate)	412.23
	Chrome yellow	PbCrO ₄ (Lead Chromate)	131.08
	Black iron oxide	Magnetite(Fe ₃ O ₄); quartz SiO ₂ and	16.46
		aluminium oxide (Al ₂ O ₃)	
	Melafor MR 6212	N-methyl-N,2,4,6-tetranitraniline	14.46

Table 2. Description of minor and major products used as raw materials consumed in paint production plant

	Violet hostaperm RL SPEC	Dioxazine	9.97
	Carbon black	Carbon black (carbon)	8.39
	Organic red	$C_{22}H8Br_2O_2$	8. <i>39</i> 3.84
	Blue pigment	$C_{37}H_{34}N_2Na_2O_9S_3$	0.26
	Violet pigment	Methyl violet ($C_{25}H_{30}ClN_3$)	0.13
	Ethyl acetate	C ₄ H ₈ O ₂	10987.20
	Normal buthyl acetate	n- Buthyl acetate $C_6H_{12}O_2$	9768.00
	-	$C_4H_{10}O$	7680.00
	Normal buthyl alcohol or n- Butyl Alcohol	C4H10O	/080.00
	-	СЧ	5121.00
	Xylene	C_8H_{10}	
	White spirit	mixture of hydrocrbons derived from	3168.00
		petrolium includes : cycloalkanes; aliphatic	
		and aromatic hydrocarbons	
	Dowanol PM	Dowanol Propylene glycol Methyl ether	2434.80
Solvent	MEK	Methyl Ethyl Ketone(C ₄ H ₆ O)	2138.40
	Dowanol PMA	Propylene glycol Monomethyl ether	864.00
		Acetate)	
	Isoparl	Mixture of paraffin, naphtalene and	711.36
		aromatic hydrocarbons -light Naphta	
		(petroleum) hydrotreated (aliphatic solvent	
		C ₅ -C ₉)	
	Isopropyl alcohol	Isopropanol or 2-propanol (C ₃ H ₈ O)	633.60
	Sol Bitum oxide /xylene	Mixture of oxidized bitumen and	7.31
		xylene(C ₈ H ₁₀)	
	Epoxy EE780 HYBRIDE	Epoxy prepolymer resin, graphite powder,	11559.36
		nano-zinc oxide, nanotitania, organic	
		bentonite, butyl alcohol, dimethyl benzene,	
		butanone, defoaming agen tand curing	
Binder		agent	
	Nitrocellulose	Nitrates cellulose(C ₆ H ₇ N ₃ O ₁₁)	4257.00
	Alkyd thixo	Alkyd resin, polyamide and	2682.70
		polycarboxilic acid	
	Bitumen 85/25	Aluminosilicate	60.00
	Alkyd resin CH2 132	Alkyd resin, polyamide and polycarboxilic	9066.72
		acid	
Resin	(6%) Cobalt octoate	Cobalt based resin Co ₃ O ₄	408.00
	(4%) Calcium octoate	Calcium based resin	510.00
	(24%) Lead octoate	Lead based resin	456.00
	Plasticizer (DOP and DBP)	Di Octyle phtalate ($C_6H_4(C_8H_{17}COO)_2$;Di	5687.67
Additives		Butyl Phtalate	

Bentone	Montmorillonite	1371.90
	$(Na,Ca)_{0,3}(Al,Mg)_2Si_4O_{10}.nH_2O$	
Aflammit INS	Ammonium polyphosphate in powder	1219.20
Tergitol 15-S-40	Alcholol ethoxylate and ethylene oxide	590.40
Nuosperse 657 RD	Pigment dispersing agent	561.60
Anti- cratering agent	Antiskinning agent (methylethyl ketoxine)	203.58
BYK 300	Polyether modified polydimethylsiloxane	188.40
Thixotropic silica agent	Fumed silica (form of SiO ₂)	169.61
PP- Degassing agent	Polypropylene (C ₃ H ₆)n	125.17
Zinc stearate CS	$C_{36}H_{70} O_4 Zn$	79.20
Dispersing agent	Solvent and surfactant	8.02
LORAMA LDA 100	Hydroxy functional unsaturated modified	2.64
	carboxylic acid	
Non- Silicone defoamers	4-n-Buthyl acetate	0.36

Table 3. Elemental composition (CHNS) of paint sludge samples.

Samples	N (%)	C (%)	H (%)	S (%)
PS 1	0.26	13.93	0.75	<0.30
PS 2	0.27	10.70	0.55	<0.30
PS 3	0.24	13.31	0.69	<0.30

Table 4.VOC determined in the paint sludge

PS	1	PS 2		PS 3	
Composition	Gas Weight	Composition	Gas	Composition	Gas Weight
	emission		Weight		emission
	(%)		emission		(%)
			(%)		
Ethylacetate	51.52	n-Butylacetate	50.02	Ethanol	64.37
2-Butanone	21.59	Ethanol	28.20	Decane	11.44
3-	10.97	2-Propanol	6.18	Isopropylbenzene	7.69
Methylheptane					
Octane	6.22	Decane	3.22	4-Methylnonane	3.78

Styrene	3.46	1,2,3-	2.94	1,2,4-Trimethyl	3.54
		Trimethylbenzene		benzene	
4-Methyloctane	2.69	p-Ethyltoluene	2.52	m-Ethyltoluene	3.45
3-Ethylheptane	1.40	Acetone	1.96	Propylbenzene	1.84
2,4- Dimethyl	1.14	2,2- Dimethylheptane	1.28	4-Methyldecane	1.38
heptanes					
Butylacetate	9.95×10 ⁻¹	4-Ethylheptanes	1.21	Tetradecane	1.04
m-Xylene	5.48×10 ⁻³	4-Propyl heptanes	9.54 ×10 ⁻¹	2,3,5-Trimethyl	4.92×10 ⁻¹
				hexane	
Toluene	1.13×10^{-4}	3-Methyldecane	8.26 ×10 ⁻¹	m-Propyltoluene	4.42×10 ⁻¹
Ethylbenzene	2×10 ⁻⁶	Tetradecane	4.40×10^{-1}	2,3- Dimethyldecane	3.85× 10 ⁻¹
		o-Cymene	2.5×10^{-1}	3-Ethyl-o-xylene	1.25×10-1
		p-Xylene	2.81×10-3	p-Xylene	3.02×10 ⁻²

Table 5. Comparison of VOC's emission from solvent paint sludge with author studies

Composition	Gas Weight	Gas Weight	Gas Weight
	emission (%)	emission(%) [17]	emission(%) [16]
Ethylacetate	51.52	/	/
2-Butanone	21.59	/	/
3-Methylheptane	10.97	/	/
Octane	6.22	/	/
Styrene	3.46	/	17.7
4-Methyloctane	2.69	/	/
3-Ethylheptane	1.40	/	/
2,4- Dimethyl heptanes	1.14	/	/
Butylacetate	9.95×10 ⁻¹	/	/
m-Xylene	5.48×10 ⁻³	4.2	/
Toluene	1.13× 10 ⁻⁴		/
Ethylbenzene	2×10 ⁻⁶	0.5	/
Hydrocarbons	/	/	47.00
Acid	/	/	13.00
Alcohols	/	/	10.40
Ester	/	/	8.20
Ketones	/	/	3.90
Aldehydes	/	/	3.30

Phenols	/	/	1.60
Ether	/	/	0.50
1-butanol	/	39.60	/
1,2,3-trimethylebenzene	/	5.40	/
1-ethyl-4-methylbenzene	/	9.40	/
1,2,4-trimethylbenzene	/	23.80	/
1-methylethylbenzene	/	0.50	/
Acetic acid butyl ester	/	5.70	/
Undecane	/	1.00	/
1,3 diethylbenzene	/	2.70	/
1-ethyl-2-methylbenzene	/	3.90	/

Biographies

Aicha METALI

Aicha METALI is currently member of laboratory of Soft Technologies, Physicochemical, Valorization of Biological Materials and Biodiversity of the University of Boumerdes (Algeria), **preparing her research work as part of her doctoral thesis**.

She received herMaster in Chemistry fromHouariBoumedienne University of Sciencesand Technologyof Algiers-Algeria.

Metali participated in several national and international conferences. She is presently workings on decontamination of industrial sludge by the electrokinetic process.

Mounir ZIATI

Mounir ZIATI is currently a Professor in the department of Chemistry, faculty of Sciences at M'hamedBougara University of Boumerdes in Algeria. Member of laboratory of Soft Technologies, Physicochemical, Valorization of Biological Materials and Biodiversity, and Laboratory of Applied Chemistry and Materials of the University of Boumerdes (Algeria).

Pr. ZIATI received his undergraduate degrees as well as his PhD degree from BadjiMokhtar University of Annaba-Algeria.

Pr ZIATI published a number of papers in proven Journals, and participated in several national and international conferences. His main interests included environmental decontamination particularly water and soil, by eliminating pollutants using various physicochemical, electrochemical or biological processes.

Claudio Camselle :

Dr. Claudio Cameselle is Professor in the Department of Chemical Engineering at the University of Vigo, Spain. He received his Ph.D. in chemical engineering from the University of Santiago de Compostela (Spain) in June 1995. Then, he joined the University of Vigo where he developed his teaching and research career in chemical engineering and environmental technology. He was the coordinator of the master program in Industrial Pollution: Assessment, Prevention and Control (2012-2017). He published several book chapters and conference proceedings about teaching and teaching innovation. His research activity focuses on (a) the development of processes for environmental pollution abatement, (b) the valorization of wastes, and (c) the treatment and recycling of industrial effluents with chemical, photochemical and electrochemical processes. He is the author of over 95 research papers and 2 books/textbooks on soil remediation and sustainable engineering. His research is leading to practical solutions to the real-world problems.

Susana Gouveia :

Dr. Susana Gouveia is a postdoctoral researcher at the BiotecnIA group, University of Vigo. She holds a degree in Chemical Engineering from Instituto Superior Técnico, Lisbon, Portugal. After 7 years in the chemical industry and the private sector, she joined the PhD program in the department of Chemical Engineering at the University of Vigo. Her dissertation thesis developed lignin enzymatic modification processes for the valorization of lignin in wood-composite industry. Her research interests include soil remediation, industrial waste valorization, and wastewater treatment. She has published over 30 articles and 4 book chapters.