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EVALUATION OF ECO-COMPATIBLE METHODOLOGIES TO CLEAN STONE SURFACES POLLUTED BY OIL SPILL

Manuela SGOBBI, Laura FALCHI*, Francesca C. IZZO,
Martina ZUENA, Elisabetta ZENDRI

Ca‘ Foscari University of Venice Department of Environmental Sciences, Informatics and Statistics, ‚Scientific Campus, Via Torino 155, 30172 Mestre Venice (Italy)

Abstract

This research concerns the structuring of a suitable method for the removal of oil (Fuel Oil 120 cSt) from traditional bricks and Istrian Stone, materials commonly found amongst embankments and buildings of North Adriatic coastal cities. A cleaning protocol, based upon non-toxic products, was developed in consideration of its compatibility with historical, architectural surfaces. The contamination effects of oil on Istrian stone and fired clay bricks was studied, followed by a range of cleaning treatments using bulk sorbents, surfactant solutions and N,N-dimethyl-octanamide. The application was executed using the products singularly, combined or in succession. The succession of sorbent, solvent and surfactant solution demonstrated good capability of removal and was then applied on macrosamples of brick masonry showing good results.

Keywords: *Oil spill; Historic materials; Bio-degradable; Compatible; Environment safeguard*

Introduction

Petroleum can be considered one of the most detrimental threats for marine ecosystems with its evident toxicological impact upon the natural environment and wildlife.

Without considering the illegal washing of ship tanks, the annual quantity of oil spills due to ship collision and oil transportation is nonetheless difficult to estimate as a result of misreports. 2003 statistics estimated the amount of oil spill to be around 3.2 million in tonnes [1, 2], while the total recorded amount of oil lost to the environment in 2014 was approximately 4,000 tonnes [3]; another 40% of which petroleum, deriving from natural infiltrations and production processes, must be added too [4].

Fortunately, in the face of a continuous increase in seaborne oil trade (around 10’000 billion tonnes/Miles in 2014) such might imply an increase of accidental oil spills, given the number of tanker spills has significantly decreased from around 60 per year in 1980 to less than 10 in 2014, according to the International Tanker Owners Pollution Federation Limited [3].

Oil spills are hazardous not only for marine environments and natural shorelines, but also for historical and architectural assets that reside in close proximity to the sea and therefore have contact with polluted water. The case of Venice is emblematic: the city is in continuous contact with lagoon water and its cruise ship harbor faces the historical city centre. Throughout

* Corresponding author: laura.falchi@stud.unive.it

2014, 3553 transits (including cruise ships, jetfoils, and ferryboats) were registered to the Port of Venice, those of which were involved in the transportation of 8’713’339 tonnes of crude oil and refined product [5].

The self-depuration power of the sea, otherwise known as natural bioremediation, is not sufficient to rapidly absorb large amounts of petroleum [6-10]. Consequently, within the last 40 years, international corresponding conventions and protocols were developed in order to confront accidental oil spills [11-14]. The protocols’ main focus is upon the cleanup of shorelines, natural environments, ecological sensitive sites [15, 16], giving little attention to the oiled historical masonry and built heritage. Current systems for the removal of oil or other petroleum derivatives from stone surfaces often involve the use of organic solvents (e.g. Orange) [17], which are not compatible with marine ecosystems and human health [18, 19].

This paper will present the results of an investigation into the development of a specific protocol to intervene in the case of oil spills coming into contact with masonry surfaces through the use of non-toxic products for both men and the environment.

Two substrates, Istrian stone and fired clay bricks, were chosen as the most representative materials used in Venetian masonries and embankment walls [20]. The differences in porosity, surface roughness and stone nature of these two substrates allow us to observe the different behaviour of oil on stone matrices and its possible interactions.

Based on characteristics of low human and aquatic toxicity, eco-compatibility, and high biodegradability, five products, predominantly used to tackle marine oil spills, were chosen: two bulk sorbents, a N,N-dimethyl-octanamide and two surfactants.

Materials and Methods

In order to define an intervention protocol involving the most suitable products and methods, the research followed a step-by-step methodology involving:

- the individuation and description of oil, substrates and cleaning products;
- the study of the contamination dynamic of the substrates in contact with a mixture of Lagoon water and oil;
- the effectiveness of single products in removing oil: study of interactions and behaviour in contact with pure oil;
- the setting up of the removal methodology : the evaluation of oil-removal effectiveness from substrates of different porosity and surface roughness by application of pure products, product poultice and different products in succession;
- The evaluation of the procedures involving the use of different products on brick masonry macro-samples.

The instrumental methods used to evaluate the effectiveness of the different treatments included: naked eye observation, optical and electron microscopy observation (including SEM-EDX analysis), colour measurements, and FT-IR spectroscopy, as described later.

Description of oil, substrates and cleaning products

The Intermediate Fuel Oil 120cSt, a bunker oil commonly used for marine diesel engines or steam-generating boilers, was nominated for the simulation of oil spill.

As reported in the technical data sheet, it is composed of a mixture of long chain hydrocarbons (12-70 C), with a sulphur content < 3.5%, max. viscosity 120cSt at 50ºC and density 0.97kg/l.0 at 15°C [21].

As previously remarked upon, Istrian stone and fired clay bricks were selected as representative of the traditional Venetian masonries and embankment walls [22, 23]. These stones are characterized by different porosity, surface roughness and composition. Istrian stone is a compact microcrystalline limestone utilised by Venetians because of its durability within marine environments. In actual fact, it has low open porosity (around 1.-2.0%) and low surface roughness [24, 25]. Fired Clay Bricks, having an open porosity of around 40%, were used to simulate the traditional Venetian full bricks, generally characterised by an open porosity between 30 and 45% (often higher in the presence of decay due to salt water and salt crystallization) [26]. Bricks from local clays were supplied by San Marco Laterizi Spa (Venice).

Five products typically used to deal with marine oil spills were chosen for their characteristics of low human and aquatic toxicity, eco-compatibility, and high biodegradability [15, 16]. Liquid solvent, cleaning agents and solid adsorbents were taken into account; their description is reported in Table 1.

. Bulk sorbents (solid adsorbents) and surfactants of Table 1 are generally used in oil spill disasters, in oiled shoreline cleanups [27] and for the removal of fuel from streets in road accidents.

The products were either applied directly on the surfaces or with cellulose pulps or Methocel 311 (Table 1) as described in the following paragraph.

Table 1. Characteristics of the used cleaning products [28-33]

Material type	Commercial name	Composition/ description	Appearance	Applications and Precautions
Bulk sorbent	Cansorb	Oil-absorbent from the fibers of Sphagnum Peat Moss. It absorbs up to 40-60% w/w	Brown fibers	To be handled with gloves
Bulk sorbent	Ecosorboil	Highly porous, cellular, oil-absorbent grains. Composed of silicates, carbonates, calcium hydroxide	White round grains. Size Fractions 0.80/1.20 mm	To be handled with gloves
Surfactant	HCS Biologic Remover	Non ionic surfactants, pH7, biodegradable at 90%	Yellowish liquid	No need of particular care for use and manipulation
Surfactant	ECO83	Non ionic surfactants, pH7, biodegradable at 90%	Bluish liquid	No need of particular care for use and manipulation
Solvent	Agnique AMD8	C8 Fatty acid Dimethylamide	Yellowish liquid	To be handled with gloves. Wear respiratory protection if ventilation is inadequate.
Poultice agent	Cellulose pulp	A polysaccharide consisting of a linear chain of several hundred to over ten thousand β(1→4) linked D-glucose units	White flakes similar to cotton	No need of particular care for use and manipulation. Non toxic, biodegradable.
Poultice agent	Methocel 311	Cellulose derivative. Hydroxypropyl cellulose. $-CH_2CH(OH)CH_3$.	White fine powder	No need of particular care for use and manipulation. Non-toxic, biodegradable

Contamination dynamic of Brick and Istrian stone in contact with Fuel Oil 120cSt

In order to observe the absorption process of oil in Istrian stone and bricks and their ensuing interactions, the substrate specimens were isolated with plastic tape on all sides, leaving one face uncovered, and then dipped vertically in a mixture of Fuel Oil 120cSt and lagoon water at 17%. In this way, just one surface was put in contact with the pollutants simulating a real case of oil in contact with an embankment wall.

Different immersion periods were tested: 20 minutes; 24 hours; 8 days. The contamination was evaluated by optical microscopy, SEM-EDX observation on the exposed surfaces and on sections (obtained by scalpel) in order to evaluate the penetration depth.

Behaviour of products in contact with pure Fuel Oil 120cSt

The effectiveness of selected products was tested by putting them in direct contact with Fuel Oil 120cSt. For the solvents and cleaning agents, 10mL of product were stirred with 5.0g of Fuel Oil 120cSt for 20 minutes; then the mixture was separated with a separating funnel and the quantity of residual oil (not emulsified or dissolved) was measured. The bulk sorbents were put in contact with oil in proportion 1.0g oil to 5.0g sorbent for 20 minutes, then the residual oil, not retained by the sorbent, was weighted. The percentage proportion of remaining oil to starting oil was calculated to express the products effectiveness.

Oil removal from substrates of different porosity and surface roughness

A removal test from substrates of different porosity provides an observation of product effectiveness and the individuation of the most suitable cleaning protocol. Two types of removal tests were developed based upon different application methodologies, as described below. Table 2 summarizes the different treatments executed.

Table 2. Removal methods: application of different products on polluted substrates

Application type		Products	Mixing ratio	Application time (min)	Substrate
Application by poulticing	Mixture of product and poultice agent applied by poulticing	HCS Biologic Remover + Methocel 311	1/14.5	20	Istrian Stone; Brick
		HCS Biologic Remover + Cellulose Pulp	1/10		
		ECO83+ Methocel 311	1/3.5		
		Agnique AMD8 + Methocel 311	1/8.8		
		Agnique AMD8 + Cellulose Pulp	1/8.8		
	Layer of pure product covered by poultice agent + water	Cansorb; Methocel 311 + H_2O	1/10		
		Cansorb; Cellulose Pulp + H_2O	1/10		
		Ecosorboil; Methocel 311 + H_2O	1/10		
		Ecosorboil; Cellulose Pulp + H_2O	1/10		
Direct application	Pure product applied by brush	HCS Biologic Remover ECO83 Agnique AMD8	pure	5	
	Products mixture applied by brush	ECO 83 + AMD8 HCS Biologic remover + AMD8	1/1	5	
	Sequence of products applied by brush	AMD8; ECO83 AMD8; HCS Biologic remover	pure	5+5	
	Sequence of products scrubbed and applied by brush	Cansorb; ECO 83 Cansorb; HCS Biologic remover Cansorb; AMD8 Ecosorboil; ECO 83 Ecosorboil; HCS Biologic remover Ecosorboil; AMD8 Cansorb; AMD8; ECO 83 Cansorb; AMD8; HCS Biologic remover Ecosorboil; AMD8; ECO 83 Ecosorboil; AMD8; HCS Biologic remover	pure	5+5+5	

Application by poulticing

The use of poultice for the removal of oil from substrates at different porosity was investigated as follows. Owing to its advantageous approval within the restoration field, poulticing is a practice widely employed as for the following; it allows an extended contact of the cleaning products with the polluted substrates; it slows down the evaporation of the solvents; it limits the diffusion of the solvent and possible pollutants dissolved within the substrate pores; it allows the application of powders on vertical surfaces and it limits the product dispersion in the environment during the cleaning operations [34].

Poultices were obtained by mixing each liquid solvent and cleaning agents with Methocel 311 and/or Cellulose pulp in appropriate proportions in order to obtain a poultice consistence suitable for its application on vertical surfaces (Table 2). The obtained poultices were applied on Istrian stone and brick surfaces soiled by oil slicks for 20 minutes.

The bulk sorbents were applied as a pure layer of absorbent on the substrate surface, then they were covered by a poultice of Methocel 311 or Cellulose pulp mixed with water in 1/10 w/w to keep the powder in place and finally were covered with transparent film for 20 minutes

(Fig.1a). The suitable contact time of 20 minutes was individuated owing to preliminary tests (ranging contact time from10 to 20min). In order to avoid further penetration of the mixed product within the porous substrate and to simulate the real situation of brick masonries along the canals, the brick specimens were saturated with distilled water before the application of poultices. After the treatment the surface was rinsed with deionised water and cleaned with cotton wool.

Direct application

As reported in Table 2, the products were also applied directly on the polluted substrates individually, combined and in succession.

The liquid products were brushed directly on the stone surfaces, while the bulk sorbents were scrubbed on the surfaces for five minutes. After every product applications, the surfaces were rinsed with distilled water.

Oil removal from Brick Masonry macro-samples

A simulation of a factual case is necessary to highlight the effectiveness and critical points of a cleaning protocol. According to international recommendation [15, 16] the first instructions in the case of accidental oil spills are to constrain the oil spill and to use solid adsorbents to absorb the exceeding oil, followed by the use of further products to clean polluted substrates and to emulsify the remaining oil.

A masonry wall ($50\times75\times25cm^3$) made of fired clay bricks and a cement-lime grout was casted over a plastic reservoir. The reservoir was filled with lagoon water for one week, then an excess of fuel oil was poured in the water simulating an accidental oil spill. The Cansorb bulk sorbent was used to absorb the exceeding oil (Fig.1b), then the wall surface was isolated from water.

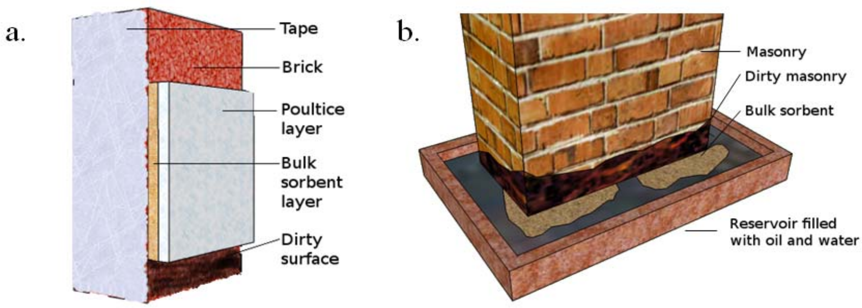


Fig. 1. a. Scheme of the application of packs containing bulk sorbents;
b. Scheme of the masonry macrosample used for real case simulation

As a results of the preliminary tests, two cleaning methods were used on two different sides of the wall: Cansorb scrubbed on the surfaces, application of Agnique AMD 8 by brush and of the cleaning agents HCSBiologic remover or ECO83. After the application of each liquid, the surface were rinsed down with distilled water.

Instrumental methods and instrument set-up

The observation of the specimens was performed by naked eye helped by optical microscopy observations, with a DINO-lite Premier AM4113T digital portable microscopy with adjustable magnification (10-200X), 1.3MPx.

The individuation of oil distribution and residues, the effects on the substrate morphology on the micro scale, the elemental composition before and after the treatments were recorded by SEM-EDX analysis with a JEOL JSM 5600 LV instrument with a OXFORD-Link series 300 microanalysis system on sample collected by scalpel from the substrate surfaces and sections. The samples were not metalized prior to the observation, therefore low vacuum mode was set in sample chamber to avoid local charge accumulation.

The specimens composition and the individuation of oil residues were detected also by FT-IR spectroscopy by using a Nicolet Nexus 670/870 spectrometer in the mid-infrared region (4000-400cm^{-1}), with 4cm^{-1} resolution; 32 scans each on KBr pellets (sample: KBr = 1:100 – wt%).

Colorimetric measurements were performed using a CM2600d Konica Minolta portable spectrophotometer with aD65 illuminant and 10° standard observer was used to measure the colour of the surfaces according to UNI EN 15886:2010 [35]. In order to consider the surface inhomogeneities and obtain a reliable measure, a medium averaged spot size of 8 mm Ø, an average of 9 scans was considered for each observation point. The data were registered in SCI (Specular component included) modality and processed by Spectra Magic software. According to the CIE Lab (L*, a*, b*) colorimetric space, the total colour variation (ΔE**) was calculated as $[(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)]^{1/2}$, where L* indicates the lightness of the colour, a* its position between red/magenta and green and b* stands for the colour position between yellow and blue [36-42].

Results and discussion

Oil absorption on porous substrates: study of the interaction between oil and Istrian stone and fired clay bricks

Istrian stone and brick specimens dipped in the oil/lagoon mixture for 20 minutes showed black and shiny surfaces immediately after the extraction. For bricks, the surfaces became black and matte after 6 hours of drying due to oil absorption within the pores, whilst Istrian stone surfaces were characterized by a bulk oily layer (Fig.2). The oil rose up by capillary forces from the oil/water level to a maximum of 16.9mm in the bricks case and 8.5mm in Istrian stone case; the penetration depth measured on the broken section was limited to 2mm in brick and for few microns in Istrian stone (mean of 10 specimens). In all probability a selective absorption took place within the bricks, with the low-weight hydrocarbon fractions more prone to diffusion and in-depth penetration, but also with loss of the more volatile part.

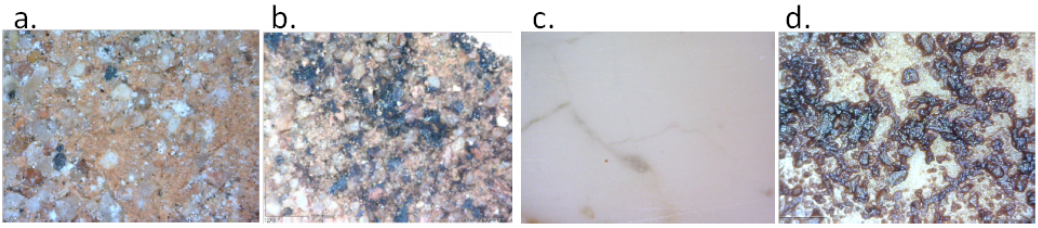


Fig. 2. a. and b. - Surface of brick before and after dipping for 20 minutes in the mixture water of lagoon-oil, 65X; c. and d - Surface of Istrian stone before and after dipping for 20 minutes in the mixture water of lagoon-oil, 65X

Immersion times of 24 hours and 8 days highlighted that the oil penetration and capillary diffusion was limited by its high density. In fact, with longer immersion times the penetration front did not move forward neither in bricks nor in Istrian stone. The first oil layer constituted a barrier for further penetration or diffusion within the substrates and the equilibrium was reached rapidly.

SEM observation evidenced a regular, homogeneous and continuous morphology of the oil layer on Istrian stone surfaces, thinner than the one observed on bricks (Fig. 3). The exact penetration depth of oil within bricks was difficult to assess since it was difficult to establish a clear border; nevertheless, a gradual reduction of carbon percentages to the level of the bulk brick was recorded. This confirms the selective absorption and the chromatographic effect of the pore structure of the brick.

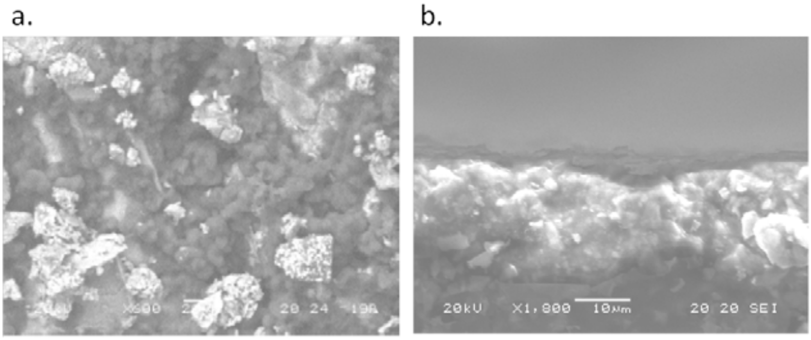


Fig. 3. SEM observation: a. Oiled brick surface 600X; b. Cross section of oiled Istrian stone 1000X

Behaviour of products in contact with pure Fuel Oil 120cSt

Table 3 reports the results obtained by mixing each product with oil. The indicated percentage is calculated from the ratio between remaining/residual oil to the primary/original amount of oil, concluding a higher percentage that corresponds with a lower product miscibility capability.

The products which showed the highest quality of effectiveness were Agnique AMD8 (with no phase separation after 20 minutes) and Cansorb (able to absorb almost fivefold its weight in oil).

Table 3. Products miscibility/absorption with/of oil

Product	Product amount	Oil amount (g)	Interaction time (min)	Amount of residual oil (%)
ECO 83	10 mL	5	20	3.8 %
HCS Biologic remover	10 mL	5	20	11.8 %
Agnique AMD8	10 mL	5	20	~1%
Cansorb	1 g	5	20	5 %
Ecosorboil	1 g	5	20	78.8 %

Oil removal from substrates of different porosity and surface roughness

Application by poulticing

Table 4 summarizes the effectiveness of the different cleaning treatments applied by poulticing. The evaluations were attained by comparison of the different specimens and of the original substrates, aided by OM observation and FT-IR analysis. An excellent results correspond to cleaned surfaces similar to the original ones, very poor corresponds to no-removal and to surfaces similar to oiled substrate.

The adhesiveness of the obtained poultices proved competent in all the case studies and equally for the application upon vertical surfaces, allowing an accurate and prolonged contact between the cleaning product and oil. Furthermore, the removal of the poultices was straightforward for the non-porous substrates Istrian Stone. Due to their roughness, poultice residuals and whitish residues were observed upon the bricks' surfaces.

Only when liquid cleaning products were directly mixed with the poulticing agent, did the treatments demonstrate a sufficient effectiveness, particularly on smooth and non-porous substrates.

The solvent Agnique AMD8 demonstrated particular efficacy owing to its high affinity with oil, not to mention good swelling and dissolution capability on the oil/poultice interface and an effective retention of the dissolved oil within the poultice. On the contrary, the bulk sorbents presented extremely poor effectiveness. This could be due to a partial absorption of water from the wet poultice layer instead of that of the oil, or, most probably, to a limited interaction oil-sorbent, i.e. the sorbent touches and absorbs only the external oil surface and is not able to penetrate the deeper layers. A similar mechanism might explain the limited action of the emulsifier agents HCS Biologic Remover and ECO83. In this case a mechanical action (e.g. by brushing or scrubbing) could be necessary in order to increase the contact surface between the oil and products to obtain greater effectiveness.

Table 4. Removal effectiveness of the different poultices

Application type	Products	Ease of poultice removal		Effectiveness of oil removal	
		Istrian Stone	Brick	Istrian Stone	Brick
Mixture of product and poultice agent applied by poulticing	HCS Biologic Remover + Methocel 311	3	1	**1**	**2**
	HCS Biologic Remover + Cellulose Pulp	3	1	**1**	**2**
	ECO83+ Methocel 311	3	1	**4**	**3**
	Agnique AMD8+ Methocel 311	3	1	**4**	**3**
	Agnique AMD8 + Cellulose Pulp	3	1	**4**	**3**
Layer of bulk sorbent covered by poultice agent + water	Cansorb; Methocel 311+ H_2O	3	4	**2**	**1**
	Cansorb; Cellulose Pulp + H_2O	3	4	**2**	**2**
	Ecosorboil; Methocel 311 + H_2O	3	4	**1**	**1**
	Ecosorboil; Cellulose Pulp + H_2O	3	4	**1**	**1**

6 - Excellent; 5 - Very good; 4 - Good; 3 - Fair; 2 - Poor; 1 =- Very poor

Direct application

Table 5 summarizes the effectiveness of the different cleaning treatments applied by brush. The evaluation was carried out according to naked eye observation, aided by OM observation and FT-IR analysis.

A general observation, regarding the direct application, indicates that the higher porosity and surface roughness of the bricks led to an incomplete removal of the oil impregnating the substrate. However, the removal of oil, from the smooth and compact surfaces of the Istrian stone, was more straightforward, yet oil residues caused a general yellowing of the surface and were found to be retained particularly within clay swirls and veins.

The singular use of cleaning agents, brushed on the stone's surface, had led to an incomplete removal of oil (Fig. 4), with traces visible by OM and detectable by FT-IR. The typical peaks of hydrocarbon chains related to oil residuals were present in FT-IR spectra (e.g. C-H aliphatic stretching ν at 2920 and 2850cm^{-1} and bending δ at 1400-1500cm^{-1}), beside the IR absorptions of silicates present in brick samples (ν Si-O-Si 1000-1100cm^{-1}) and carbonates in Istrian stones (ν -C=O 1420cm^{-1}, δ –CO_3 875cm^{-1}) (Fig. 4). The use of the solvent Agnique AMD8, alone or combined with cleaning agents, demonstrated greater effectiveness.

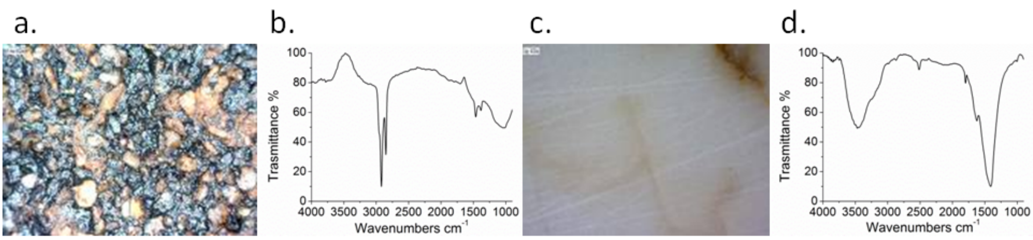


Fig. 4. OM observation and FT-IR spectra after the cleaning treatment. a., b. Brick surface after cleaning with ECO83 by brush; c., d. Istrian stone surface after cleaning with Agnique AMD8 by brush

The combination of additional products, either mixed or in succession, produced better results; in particular, using a solvent primarily, and then a cleaning agent. However, the consecutive use of a bulk sorbent, a solvent and a surfactant demonstrated the greatest effectiveness and homogenous results amongst the performed treatments.

Table 5. Removal effectiveness of the different cleaning treatments by direct application.

Application type	Products	Effectiveness of the treatment	
		Istrian Stone	Brick
Pure product applied by brush	HCS Biologic Remover	4	2
	ECO83	4	2
	Agnique AMD8	5	3
Products mixture applied by brush	ECO 83 + AMD8	5	2
	HCS Biologic remover + AMD8	5	2
Sequence of products applied by brush	AMD8; ECO83	5	2
	AMD8; HCS Biologic remover	5	2
Sequence of products scrubbed and applied by brush	Cansorb; ECO 83	3	1
	Cansorb; HCS Biologic remover	3	1
	Cansorb; AMD8	5	2
	Ecosorboil; ECO 83	3	2
	Ecosorboil; HCS Biologic remover	5	2
	Ecosorboil; AMD8	5	2
	Cansorb; AMD8; ECO 83	6	3
	Cansorb; AMD8; HCS Biologic remover	6	3
	Ecosorboil; AMD8; ECO 83	6	3
	Ecosorboil; AMD8; HCS Biologic remover	6	3

6 - Excellent; 5 - Very good; 4 - Good; 3 - Fair; 2 - Poor; 1 - Very poor.

Use of bulk sorbent, solvent, surfactant, in succession

The cleaning treatments, based on the consecutive application of bulk sorbents, solvents, surfactants, were further investigated as possible means for use in real-life situations.

Fig. 5 demonstrates OM and SEM observations of dirty and cleaned surfaces: one can acknowledge the greater effectiveness of removal when treating the Istrian stone, but also the permanence of oil residual on the bricks. Very few cases saw the somewhat difficult removal of the Ecosorboil bulk sorbent from the bricks, due to the finer particles, which caused a partial occlusion of the surface porosity. Owing to its fiber-shape, Cansorb was easily removed with the mere use of a brush. Furthermore, a partial abrasive action (presence of small scratches) was noticed when using Ecosorboil.

Colour measurements were carried out in order to compare the original surfaces with the dirty and cleaned ones. L*, a* and b* mean parameters for original Istrian Stone and bricks and the overall colorimetric variation expressed as ΔE* are reported in Table 6. A standard deviation of two points was calculated within each substrate, due to intrinsic scarce homogeneity of the surfaces, thus ΔE* lower than 2 were not considered as significant.

Comparing the substrates between original conditions and after the cleaning treatments, values of ΔL* till 10, Δa* and Δb* till 5 were observed within each specimen. None of the surfaces cleaned revert back to a state similar to the original, since ΔE* variations above three are noticeable by naked eye observation [43]; however, the use of Cansorb; AMD8; HCS Biological remover showed the lowest ΔE* amongst the tested treatments.

This colour measurement was particularly significant for Istrian stone, where the pollutant was almost completely removed, whereas for bricks, a change in colour surface was obvious, due to the oil residue.

The scarce homogeneity between cleaning actions, deriving from the application method repeated just once and a similar contact time given for each treatment, allowed for comparison. In a real-life situation, further cleaning could be envisaged. In this sense, the colour measurement could aid the cleaning in situ, by pointing out quantitatively and in a non-invasive way the most critical areas, in order to achieve good homogeneity.

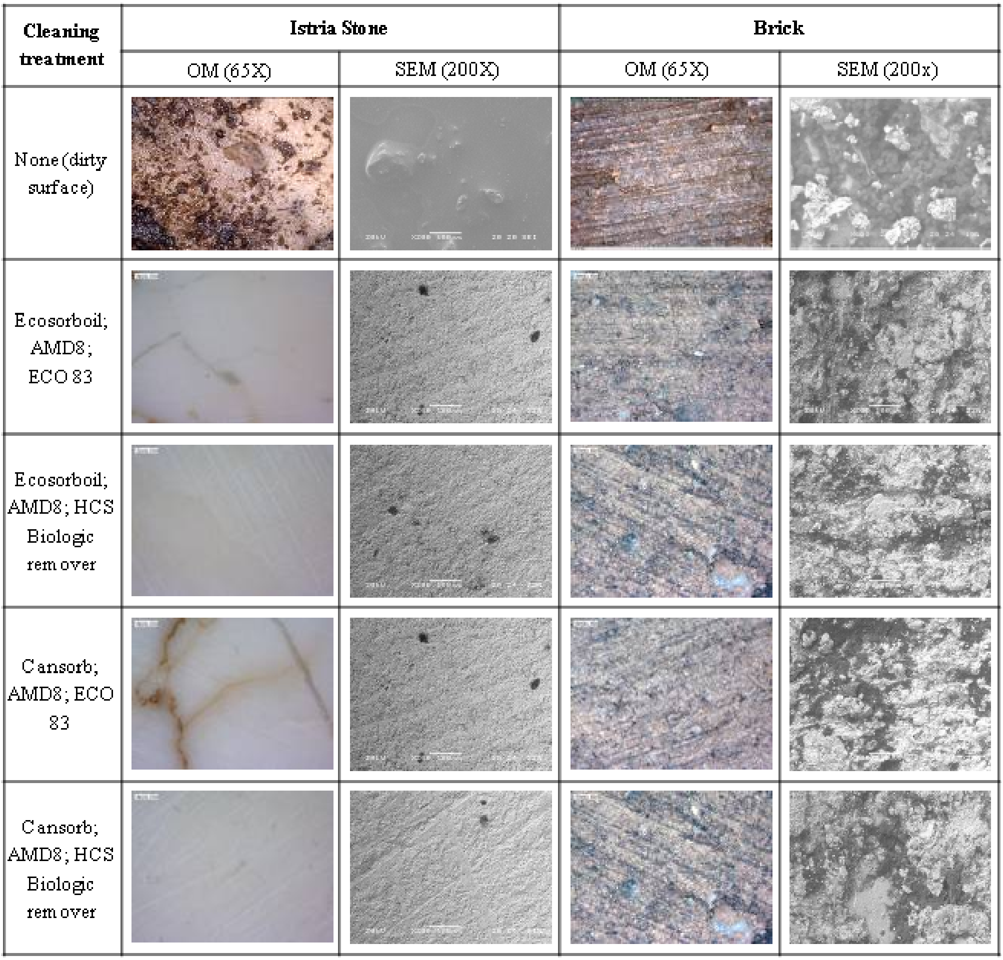


Fig. 5. OM and SEM images of the surfaces after the cleaning treatments by direct application of the indicated products in succession

Table 6. Colour coordinates L*, a* and b* of the specimens surface; total colour variation ΔE* between the original surfaces and the treated ones

Specimen	Istrian stone				Brick			
	L*	**a***	**b***	**ΔE***	**L***	**a***	**b***	**ΔE***
Original surfaces	78,98	0,89	7,18	-	58,55	15,92	24,35	-
Dirty surfaces	31,4	9,59	33,43	54.00	9,76	2,37	6,34	53.19
Surfaces cleaned with Ecosorboil, AMD8, ECO83	71,26	1,91	15,13	8.06	23,11	15,75	36,5	38.69
Surfaces cleaned with Cansorb, AMD8, ECO83	72,23	1,55	13,98	9.80	20,12	15,75	32,71	41.68
Surfaces cleaned with Ecosorboil, AMD8, HCS Biologic remover	76,3	1,41	11,81	4.90	23,24	19,54	38,12	36.73
Surfaces cleaned with Cansorb, AMD8, HCS Biologic remover	74,62	1,59	12,58	7.76	23,11	18,71	37,52	36.38

With regards to the application of the cleaning treatments upon masonry embankment walls in Venice, the penetration depth of the oil residual, before and after the treatment, was measured by SEM observations on brick cross sections (the mean of 30 measured points is reported in Table 7). FT-IR spectra of the brick surface after cleaning were compared with measurements performed on the original brick and on the dirty surface. Moreover, the percentage of carbon was evaluated by EDX on the surfaces, while the ratio between the intensity of the stretching absorption ν_{C-H} at 2920cm^{-1} due to $–CH_2$ aliphatic groups (revealing the presence of oil) and $\nu_{Silicate}$ 1050cm^{-1} due to Si-O-Si groups (typical and stable absorption for bricks) was calculated from FT-IR data. Both these method constitute semi-quantitative evaluations of the residual oil.

Even if the morphology of brick influenced the results obtained, the investigation of the penetration depth reached by the oil showed that:

- oil residues were present on the external parts of the specimens cleaned with Cansorb; AMD8; ECO83 or HCSBio: the dissolved/emulsified oil was not carried further inside the specimens by the cleaning treatment.
- The penetration depth increased when using Ecosorboil; AMD8; ECO83or HCS Biological remover. In all probability, this cleaning method had caused further penetration of dissolved oil within the brick.
- Higher C% and higher ratio of ν_{C-H} 2920cm^{-1}/ $\nu_{Silicate}$ 1050cm^{-1} found for Ecosorboil; AMD8; ECO83or HCS Biological remover indicates a greater permanence of oil traces upon the surfaces.

Table 7. Depth of polluted/dirty area; C% - Semi-quantitative carbon amount detected by EDX on surfaces; ratio between the intensity of the FT-IR peaks ν_{C-H} 2920cm^{-1}/ $\nu_{Silicate}$ 1050cm^{-1}

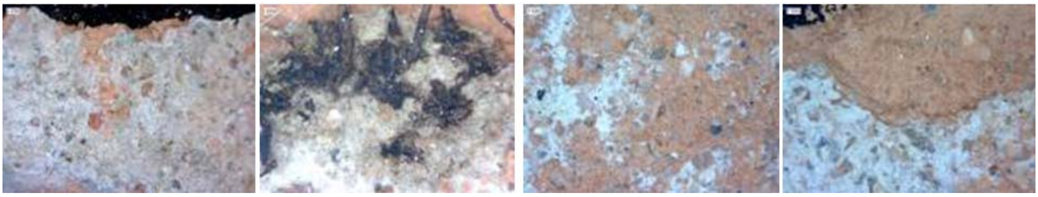
Specimens	**Oil depth (mm)**			**C% on bricks surfaces (%)**	**ν_{C-H} 2920cm^{-1}/ $\nu_{Silicate}$ 1050cm^{-1} (%)**
	min	mean	max		
Original surfaces	-	-	-	13,43	0
Dirty surfaces	1,25	1,48	1,86	69,69	99
Surfaces cleaned with Ecosorboil; AMD8; ECO83	1,80	2,19	2,62	48,98	48
Surfaces cleaned with Ecosorboil; AMD8; HCSBiologic remover	1,40	1,99	2,72	49,62	41
Surfaces cleaned with Cansorb; AMD8; ECO83	1,07	1,48	1,87	40,87	25
Surfaces cleaned with Cansorb; AMD8; HCSBiologic remover	1,26	1,52	1,87	42,52	41

Simulation of a real case

According to the results obtained from previous tests, a cleaning protocol for a real-life case simulation was developed considering the sequential use of Cansorb, Agnique AMD 8 and a cleaning agent (HCS Biologic remover/ECO83). After the application of each product, the surface was rinsed with distilled water. The effectiveness of each cleaning treatment was predominately evaluated by naked eye observations, aided by OM observation, in order to obtain an extensive evaluation of each method.

Punctual SEM observations and FT-IR measurements were also carried out to support what observed macroscopically regarding the overall situation in the non-homogeneous surfaces of masonries. An accurate choice of the sampling areas guaranteed the representativeness of the analysis.

OM observations of the surfaces subsequent to cleaning treatments are shown in figure 6.



a. b. c. d.

Fig. 6. OM images of masonry surfaces (60X): a. original masonry; b. oiled masonry; c. surface after cleaning by direct application of Cansorb; AMD8; ECO 83 in succession; d. after direct application of Cansorb; AMD8; HCS Biologic remover ECO 83 in succession

The methodologies used were more effective on real-life case simulations, than on brick samples. For the duration of the simulation case study, the masonry was completely soaked by brackish water from capillary rise, preventing a deep penetration of oil within the masonry. Furthermore, the oil floated on the water's surface, having not been mixed, and just few centimetres were in direct contact with the masonry. The presence of salt efflorescence on the masonry surface, due to the evaporation of salty water, may have also acted as a protective layer.

Images in Figure 6 show that the deposit was almost completely removed, just few traces remained.

SEM-EDX analyses on few point of the C% confirmed that the final C% after cleaning was similar to that starting situation; the FT-IR spectra do not show the typical absorption due to –CH stretching of organic compounds at 2920 and 2850cm^{-1}. Additionally, colour measurements, suggested for the non-invasive and more extensive monitoring of the surface, indicate that no noticeable changes were recorded (Table 8).

Table 8. C% - Semi-quantitative carbon amount detected by EDX on surfaces; colour coordinates L*, a* and b* of the specimens surface; total colour variation ΔE* between the original surfaces and the treated ones

Specimens	C (%)	L*	a*	b*	ΔE*
Original surfaces	12.11	56.72	11.93	22.12	-
Dirty surfaces	84.74	39.10	13.05	32.18	20.32
Surfaces cleaned with Cansorb; AMD8; ECO83	23.96	61.51	9.65	18.90	6.02
Surfaces cleaned with Cansorb; AMD8; HCSBiologic remover	17.16	59.84	10.68	20.71	3.64

Conclusions

Corresponding to the case of Venice, cultural assets, in the vicinity of marine or river environments, may well be under threat of pollution by oil spill. Existing intervention protocols focus predominantly on the cleanup of shorelines, natural environments, ecological sensitive sites [14] and little attention is therefore given to the cleanup of historical masonry and built heritage.

This study of pollution dynamics demonstrates that a mixture of 17% water and Fuel Oil 120cst could penetrate a few millimetres in bricks, whilst sound Istrian stone cannot be penetrated. However in all likelihood, with historic brick specimens of higher porosity and surface roughness, the oil could perhaps penetrate more in depth. It is notable that the distribution of the oil failed to change with long contact times of 8 or 24 hours. However, even if longer contact times did not exhibit dramatic consequences, a fast intervention is nonetheless suggested; given that prompt intervention would prevent ageing of the oil, which left untreated could cause an increase of density and accordingly would prove more difficult to remove. No chemical interaction was evidenced in the polluted substrates, yet merely a physical retention of the oil into the stones porosity and clay veins.

The development of a cleanup protocol involved testing several sustainable, atoxic products and treatments. The parameters considered (e.g. oil penetration/diffusion depth, colour changes and carbon amount) gave adequate information to evaluate the effectiveness of the cleaning.

The results evidenced that:

- the application by poulticing was not so effective; a mechanical action was required to increase the contact area of the cleaning agent/oil and to promote their interaction;
- the application of single products had limited effectiveness, whilst better results, in terms of removal, were obtained by using different products in sequence. In particular, the combined usage of Cansorb bulk sorbent, Agnique AMD8 and a cleaning agent (both ECO 83 or HCS Biologic remover), demonstrated good removal capability;
- When products were used in succession, it was observed that even if the removal of oil was not complete, the residue of hydrocarbons were most likely reduced (to smaller chains), due to the intensive treatment, small chains that are easily removed by microorganism.

Following the simulation upon brick masonry, the results obtained proved very promising. This is also comparable with the same treatments tested upon bricks alone: where lagoon water soaked the masonry and created a salty patina on the surface diminishing the affinity between oil and bricks. In reality, embankment walls are most likely even more protected, thanks to the bio fouling and algae present in correspondence to the water level.

These tested methods may well be proposed for the cleaning of embankment walls, but also for floor clean-ups, in the case of flooding due to high tide.

The use of the developed procedure in question guarantees compatibility with the substrate, avoiding substrate scratches and generating a good oil removal overall. It should also guarantee environmental compatibility, given that all the products utilised are biodegradable and therefore produce residues that are safe for the environment.

Further testing regarding the bio-compatibility of said method, are envisaged in particular by testing the released substances with eco toxicological tests on paracentrotus lividus [44], tests on microorganisms (e.g. MICROTOX test). Its application within real-life cases, in particular within the harbor area, will follow.

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