

Separation of motor oils, oily wastes and hydrocarbons from contaminated water by sorption on chrome shavings

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Abstract

In this paper, the ability of chrome shavings to remove motor oils, oily wastes and hydrocarbons from water has been studied. To determine amount of hydrocarbons sorbed on tanned wastes, a FT-NIR methodology was used and a multivariate calibration based on partial least squares (PLS) was employed for data treatment. The light density, porous tanned waste granules float on the surface of water and remove hydrocarbons and oil films. Wastes fibers from tannery industry have high sorption capacity. These tanned solid wastes are capable of absorbing many times their weight in oil or hydrocarbons (6.5–7.6 g of oil and 6.3 g of hydrocarbons per gram of chrome shavings). The removal efficiency of the pollutants from water is complete. The sorption of pollutants is a quasi-instantaneous process.

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1. Introduction

Water preservation implies recovering oils and hydrocarbon oils from water, among other pollutants. When an oil spill occurs on water, it is critical to contain the spill as quickly as possible in order to minimize danger and potential damage to persons, property, and natural resources. Containment equipment is used to restrict the spread of oil and to allow for its recovery, removal, or dispersal. The use of floating barriers is the most commonly used technique to control the spread of oil, whereas sorbents are most often used to remove final traces of oil, or in areas that cannot be reached by skimmers. Natural organic substrates (wood, cotton fibers, bark, wool, milkweed, etc.), inorganic materials (activated carbon, charcoal, exfoliated graphite, fly-ash, etc.) or synthetic fibers (acetylated cellulose, polypropylene, polyethylene terephthalate, polyhexamethylene adipamide, etc.) may be used as sorbents [1–11]. The retention capacity of dif-

ferent materials is referred to as the amount of oil retained by 1g of dry substrate. Once sorbents have been used to recover oil, they must be removed from the water and properly disposed of on land or cleaned for re-use. Any oil that is removed from sorbent materials must also be properly disposed of or recycled. According to Gregg [12], the sorption capacity in a vast range of solids depends on the surface area, pore size and connectivity.

The production of chromium-containing solid waste (including chrome shavings, trimmings and tanned splits) in a tannery has been recognized as a problem for many years, but recently pressure from environmental authorities has given the problem increasing urgency. High amount of solid wastes is produced by leather industry. The U.S. leather industry generates more than 50,000 metric tonnes of shavings and trimmings each year; the world-wide total is about 10 times as much [13]. Historically, shavings, trimmings and splits from the chrome tanning of hides and skins have been disposed of in landfills. Increased local restrictions on land disposal, recent increases in the costs of land disposal and decreases in the number of disposal sites have combined to spur research into alternative treatments. Many

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scientific groups have oriented their research to find a process to recycle and treat these wastes [13–19].

The motivation of this research is to aid the leather industry in the development of alternatives to dispose of solid tannery waste and to find effective methods for the treatment and cleaning of water polluted by oils and hydrocarbons. The objective of this work is to study the ability of wet-blue shavings to remove motor oils, oily wastes and a mixture of three hydrocarbons (*n*-hexane, isooctane and toluene) from polluted water. A FT-NIR methodology previously developed by our group was used to analyse hydrocarbons in water and to determine the amount of these polluting products removed by sorbents.

2. Materials and methods

2.1. Materials

2.1.1. Chrome shavings

Chrome shavings are small pieces of leather shaved off when the thickness of wet blues is rendered uniform by a bladed cylinder. The wet blue is the wet chrome tanned leather, without dressing. Chrome shavings have a highly organized structure in the form of fibers ($\Phi = 100$ nm) which are parallel and very tight to each other [16].

Tanned wastes products assayed in the present study were collected from Moroccan tannery appointed in Mohammedia (Morocco).

2.1.2. Oils and hydrocarbons mixture

Three oils were used to study their sorption on wastes: diesel motor oil, premium motor oil and used oil (oily wastes). Their determined characteristics are shown in Table 1. The hydrocarbons mixture used for the experiments have the following composition: 37.5% of *n*-hexane (GC analysis, 96%), 37.5% of isooctane (2,2,4-trimethylpentane, GC analysis) and 25% of toluene.

2.2. Tanned wastes characteristics

Bulk density and specific surface area of chrome shavings were determined. The tested wastes were also analysed for: ash, chromium oxide, fat, dermal substance and pH of soluble matter. The physicochemical characteristics of wastes were analysed using standard methods [20].

2.3. Determination of the sorption capacity of tanned wastes

Tanned wastes were used for sorption of oils in their pure form. Oil (70 g) was placed in a 100 mL beaker and 1 g of sorbent was immersed in the bath. After 4 h, the amount of oil sorbed by the material was determined by subtracting the initial sorbent weight from the total weight of the wetted sorbent. Retention capacity was determined for raw chrome shavings and ground wastes (2–5 mm) before and after drying. All sorption experiments were carried out at room temperature (around 20 ± 2 °C).

Tanned solid wastes were also used for hydrocarbons sorption. Chrome shavings (0.5 g) were immersed in a 100 mL beaker containing 6 g of hydrocarbons mixture. The experiment was carried out at room temperature. After 10 min, the solid was separated and was introduced in tube containing CCl_4 ($20 \times$ weight of tanned wastes). Total hydrocarbons were then extracted from the sorbent using ultrason method (Bransonic Ultrasonic Cleaner). The variable parameters are the following: sonication amplitude, 50–60 Hz; sonication time, 30 min; power HF, 10 W (42 kHz).

The analytical methods to determine hydrocarbons as a whole are quite numerous and their results can be very different [21]. Numerous parameters are important: the solvent, extraction conditions, IR absorption and calculation of IR absorbance levels (method of calibration, wavelengths used). To determine the amount of hydrocarbons sorbed by tanned wastes, a FT-NIR spectrometer from Bruker MPA (Bremen, Germany), equipped with a quartz beamsplitter, an air cooled NIR source and an InGaAs detector was employed. For measurement control and data acquisition it was employed the OPUS program (version 4.1) from Bruker. However, spectra treatment and data handling was made using the Omnic 2.1 software from Nicolet (Madison, WI, USA). PLS calibration models were established using TurboQuant Analyst 6.0 package from Thermo Nicolet Inc. Transmission absorbance spectra were obtained in the wavenumber range from 14,000 to 3500 cm^{-1} , from sample extracts in CCl_4 in a 9.5 mm internal diameter glass cylindrical cell using a nominal resolution of 8 cm^{-1} and cumulating 32 scans per spectrum.

2.4. Sorption study in a water bath

2.4.1. Motor oils sorption

For each oil and waste used, a mass of oil (5.5 g of commercial oils and 7.5 g of oily wastes) was added to 1000 mL beaker containing 500 mL of water. To this mixture sorbent material was then added. The sorbent weigh effect on oil removal efficiency was studied using different amounts of waste ranging from 1 to 3 g. Tests were carried out with and without stirring. In the case of stirring, the beakers were placed on a shaker operating at 60 rpm for 10 min. At the end of the experiments, the solid–liquid phases were separated and the amount of residual oil in water and that retained by the tanned wastes was determined. Residual oil in water was extracted with petroleum ether. The solvent extractor was evaporated and the residual oil was weighed. The amount of oil sorbed on wastes was determined by subtracting the amount of residual oil in water from the initial mass of oil added to beakers containing water. Water content was determined by subtracting the weight of sorbed oil and the initial weight of the material from the weight of the wet sorbent recovered after drainage.

2.4.2. Hydrocarbons mixture sorption

In this case, a beaker containing 50 mL of water and 6.2 g of hydrocarbons mixture was used. The effect of the sorbent weigh on removal efficiency was studied using different amounts of weight ranging from 0.1 to 3 g. After ultrasonic extraction with

Table 1
Characteristics of studied oils

Oil	Density	Viscosity at 20 °C (Pa s)	Weight loss (%)		
			After 24 h	After 48 h	After 72 h
Diesel motor oil	0.885	0.337	NL	NL	NL
Premium motor oil	0.881	0.294	NL	NL	NL
Used oil	0.894	0.281	0.001	0.002	0.002

NL, no loss.

Table 2
Characteristics of chrome shavings

Parameter	Values
Average moisture (%)	22.3
Ash (%) ^a	12.9
Chromium oxide Cr ₂ O ₃ (%) ^a	4.4
Fat (%) ^a	1.6
Dermal substance (%) ^a	78.6
pH of soluble matters ^b	3.6
Bulk density (g cm ⁻³)	0.1
Specific surface (m ² /g)	1.12

^a Based on dry weight.

^b 5 g of waste was stirred in 100 mL of distilled water.

CCl₄, the amount of total hydrocarbons sorbed was measured and removal efficiency was then calculated.

3. Results and discussion

3.1. Physicochemical characteristics of wastes

The chrome shavings used as raw materials in this study, were analysed for pH, ash, fat, proteins and chromium oxide and the results are presented in Table 2. As can be seen, these wastes are formed mainly by proteins (78.6%) which are high molecular weight substances formed by amino acids. The amount of chromium oxide is about 4.4% and the amount of fat is around 1.6%. The bulk density of chrome shavings (0.1 g cm⁻³) indi-

cates that this waste occupy a large volume as compared to other solid wastes. This causes problems in the handling of high amount of chrome shavings generated in leather industry. The specific surface area of chrome shavings is 1.12 m²/g.

3.2. FT-NIR analysis of hydrocarbons analysis

In our previous works, we have developed a new procedure for the determination of hydrocarbons retained in solid tanned wastes from polluted waters. The method uses the near infrared (NIR) transmission spectra obtained from leachates of the hydrocarbons with CCl₄ being employed a partial least squares (PLS) calibration model based on the use of mixtures of *n*-hexane, isooctane and toluene diluted with CCl₄ [22].

The IR results grouped in Table 3 show that near infrared spectroscopy is a good method for determining the concentration of each hydrocarbon. For example, when *n*-hexane is alone in sample, the apparatus indicates that the concentration calculated with FT-NIR spectrometry is similar to the percentage prepared for experiments. Toluene and isooctane were not detected (~0%) in this case. The calculated percentage values of each hydrocarbon in CCl₄ are relatively similar to the actual percentage. In the case of the mixture of hydrocarbons, FT-NIR spectrometry is also a good method for determining the concentration of each compound in CCl₄ and consequently the amount of total hydrocarbons sorbed by the tanned wastes. Therefore, the total percentage of hydrocarbons in CCl₄ could be determined by adding the percentage of each compound present in

Table 3
FT-NIR analysis of hydrocarbons

	<i>n</i> -Hexane		Toluene		Isooctane	
	Actual percentage (%)	% IR	Actual percentage (%)	% IR	Actual percentage (%)	% IR
CCl ₄	0.00	0.07	0.00	0.27	0.00	-0.13
<i>n</i> -Hexane 2%	2.01	2.13	0.00	-0.01	0.00	-0.12
<i>n</i> -Hexane 5%	5.21	4.97	0.00	-0.12	0.00	-0.04
<i>n</i> -Hexane 10%	10.49	10.70	0.00	-0.12	0.00	0.03
<i>n</i> -Hexane 20%	20.02	19.94	0.00	0.12	0.00	0.01
Toluene 2%	0.00	-0.35	2.00	2.13	0.00	-0.06
Toluene 5%	0.00	0.11	5.06	4.88	0.00	0.20
Toluene 10%	0.00	0.11	10.60	10.73	0.00	-0.10
Toluene 20%	0.00	-0.05	19.72	19.67	0.00	0.05
Isooctane 2%	0.00	0.19	0.00	-0.04	2.15	2.29
Isooctane 5%	0.00	-0.06	0.00	-0.14	4.93	5.18
Isooctane 10%	0.00	-0.06	0.00	-0.12	10.05	13.20
Isooctane 20%	0.00	0.02	0.00	0.15	19.99	19.99

Table 4
FT-NIR determination of total hydrocarbons

	Percentage (%)							
	Actual	FT-NIR	Actual	FT-NIR	Actual	FT-NIR	Actual	FT-NIR
<i>n</i> -Hexane	0.00	0.00	1.51	1.49	2.26	2.27	3.05	3.09
Isooctane	0.00	0.00	1.51	1.49	2.26	2.27	3.05	3.09
Toluene	0.00	-0.01	1.00	0.99	1.51	1.51	2.03	2.07
Total	0.00	-0.01	4.02	3.97	6.03	6.05	8.13	8.25

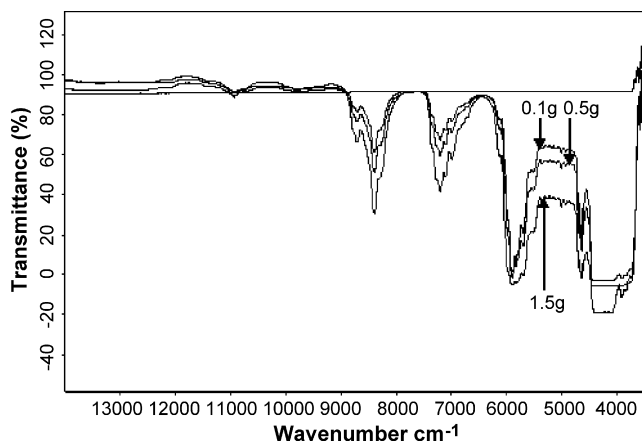


Fig. 1. Infrared spectra of hydrocarbons extracted with CCl_4 from 0.1, 0.5 and 1.5 of chrome shavings.

the solvent (Table 4). The percentage calculated using FT-NIR spectrometry concurs very well with the actual percentage and the total concentrations are relatively similar. Fig. 1 shows the transmittance spectra obtained for the mixture of hydrocarbons extracted with CCl_4 from different masses of chrome shavings (0.1, 0.5 and 1.5 g). As can be seen, transmittance spectra vary according to the amount of sorbent used. Intensity of bands and consequently concentration of hydrocarbons in extract increase with the sorbent mass.

3.3. Determination of oil sorption capacity

Table 5 groups the retention capacity (RC) of raw chrome shavings (RCS) and ground chrome shavings (GCS) before and

Table 5
Oils sorption capacities of tanned wastes for pure oils

Oil type	Waste type	Oil/waste (g/g)	
		Before drying	Dry waste
Diesel motor oil	Ground chrome shavings (2–5 mm)	5.7	7.0
	Raw chrome shavings	4.1	3.7
Premium motor oil	Ground chrome shavings (2–5 mm)	6.5	6.5
	Raw chrome shavings	2.6	3.8
Used oil	Ground chrome shavings (2–5 mm)	5.3	7.6
	Raw chrome shavings	3.4	3.8

after drying of wastes. The RC of these wastes is very high, about 6.5–7.6 and 3.7–3.8 g/g dry substrate for GCS and RCS, respectively. The presence of moisture decreased the RC of the waste. For chrome shavings, variation of particle size changed sorption capacity. When the wastes are ground (2–5 mm) the retention capacity increases. The high oil affinity of chrome shavings is mainly due to the diffusion phenomenon. The pollutant penetrates into sorbent by capillary action and then fibers form aggregates which can be removed easily from water surface.

3.4. Sorption study in a water bath

3.4.1. Sorption of oils from water surface

Table 6 shows the variation of removal efficiency (RE) value of the tanned solid assayed in water using 1, 2 and 3 g of sorbent/500 mL. Results show that the removal efficiency value is very significant. The removal efficiency of the oils from a synthetic oil–water mixture exceeds 90% (ranging from 90 to 100%). Observation shows that oils are removed only in the zones that are in contact with the sorbent. Thus, the removal efficiency (RE) of oil is directly dependent on the surface exposed to the oil–water interface.

The water sorption is negligible and clearly lower than the oil sorption. The water sorption depends on the amount of solid wastes on the surface. Results showed that an excess of sorbent can cause the retention of water on the sites not impregnated by oil. To avoid this problem, the oil retention capacity must be taken into consideration and only the necessary amount of waste sorbent must be used and dispersed on the water surface.

To determine the effect of time on the retention capacity, oil–water mixtures were treated with sorbents for a period of time from 5 s to 1 h. The evolution of sorption as a function of time shows that the sorption kinetics is quasi-instantaneous (Fig. 2).

Observations show also that oil-saturated wastes float and this occurs because the wastes fibers become more hydrophobic than the raw wastes. The removal of saturated wastes from water is easy and rapid.

The removal efficiency (RE) of oils is not affected by stirring velocity of 60 rpm. Consequently, the tanned wastes could be efficiently used in case of contamination of coastal areas with oil spills.

3.4.2. Sorption of hydrocarbons from water surface

Table 7 groups the retention capacity (RC) of ground chrome shavings regarding the solution of hydrocarbons. The solution treated contains 37.5% of *n*-hexane, 37.5% of isooctane and

Table 6
Oils sorption of wastes in water baths containing various amount of oil

Oil type	Weight of oil (g)	Weight of waste (g)	Oil in waste (%)	Oil in water (%)	Water in waste (g)
Diesel motor oil	5.5 ^a	1.0	96.6	3.4	0.2
	5.5 ^b	1.1	99.5	0.5	0.2
	5.6	2.0	100	0.0	2.6
	5.5	2.1	100	0.0	2.6
	5.6	3.0	100	0.0	5.9
	5.6	3.1	100	0.0	6.4
Premium motor oil	5.6	1.0	98.6	1.4	0.6
	5.6	1.1	98.5	1.5	0.4
	5.5	2.1	100	0.0	2.8
	5.5	2.1	100	0.0	3.1
	5.6	3.1	100	0.0	9.2
	5.5	3.1	100	0.0	9.7
Used oil	7.5	1.0	99.1	0.9	0.0
	7.5	1.0	92.1	7.9	0.0
	7.5	2.1	100	0.0	2.3
	7.6	2.1	100	0.0	3.3
	7.6	3.0	100	0.0	5.1
	7.6	3.0	100	0.0	5.8

^a Without stirring.

^b With stirring 60 rpm.

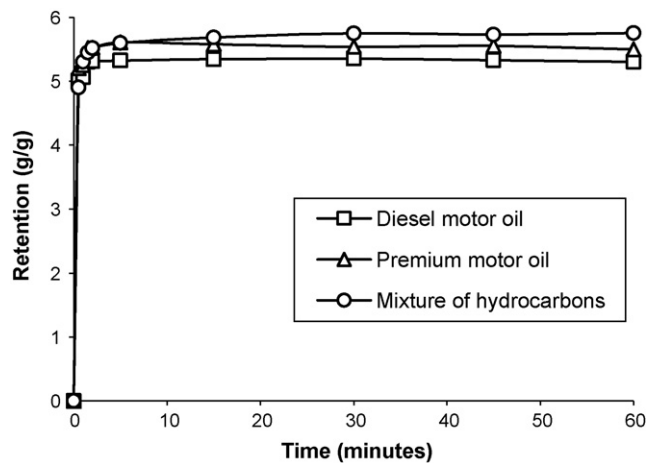


Fig. 2. Sorption vs. time for diesel motor oil, premium motor oil and hydrocarbons.

25% of toluene. As can be seen, chrome shavings have a significant capacity to sorb hydrocarbons. The sorption capacity is about 6.3 g/g. The effect of the sorbent weight on the removal of hydrocarbons from contaminated water surface was also studied. Fig. 3 shows that 1.2 g of chrome shavings is very sufficient to remove all hydrocarbons (6.2 g) floating on the water surface. Therefore, the tanned wastes have a higher affinity for hydropho-

Table 7
Hydrocarbon retention capacity of wet-blue shavings

	Sorbed hydrocarbons (g/g) ^a
<i>n</i> -Hexane	3.42
Toluene	1.04
Isooctane	1.82
Total	6.28

^a Hydrocarbons are in mixture.

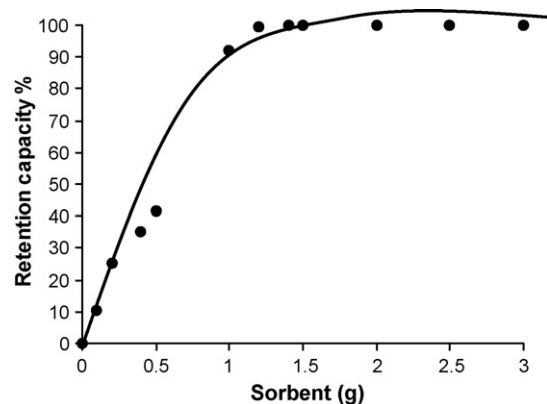


Fig. 3. Retention of hydrocarbons vs. weight of sorbent (quantity of hydrocarbons added on water surface: 6.2 g).

bic compounds than for water. The sorption of hydrocarbons is also a quasi-instantaneous process.

4. Conclusion

This work shows that FT-NIR spectrometry is suitable for determining the concentration of hydrocarbons in water. This analytic method can be used efficiently to determine the percentage of each hydrocarbon and therefore it was used to evaluate the amount of total hydrocarbons sorbed by the tanned wastes. It has also been demonstrated that wet-blue shavings can be used to control the spread of oil and hydrocarbons. Solid tanned wastes are capable of absorbing many times their weight in oil or hydrocarbons (7.6 g of oil or 6.3 g of hydrocarbons per gram of chrome shavings). The main advantages of using these tanned solid wastes as sorbent are the following: low density and high buoyancy of fibers, porosity and non-toxicity of the wastes, significant

and quasi-instantaneous sorption of oils and hydrocarbons, and easy and efficient removal of saturated sorbents.

The results look fairly promising as to possibilities of using tanned wastes for removing oils and hydrocarbons from industrial effluents or contaminated coastal areas. The use of natural waste materials for the removal of pollutants from effluents prior to their treatment could decrease the cost of upgrading the quality of treated effluents. The manufacture of a sorption filter using wet-blue shavings for industrial wastewater and the determination of the sorbent performance when other pollutants are present in the effluents are the current objectives of this research group.

Tanned wastes have a higher inferior heat value [23]. Sorption of oils and hydrocarbons by tanned solid wastes can increase the calorific value of these materials. Consequently, these wastes can be easily treated by incineration. The combustion of wastes containing chromium implies some precaution [24] in order to avoid a pollution transfer resulting in atmospheric pollution (fumes) or soil pollution (disposal of ashes). The ashes obtained have a significant amount of chromium oxide and may be used in several industries such as cementry.

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