

How Feasible is Packing Oxidants for Their Use in Treatment of Contaminated Sites

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Protection of different active ingredients is recognized as quite an old practice (in 1931 gelatine microspheres were obtained by coacervation process) and it quickly developed, with applications in pharmaceutical, textile and food industries, and lately for products applied in agriculture. Coating or encapsulating different chemicals implies placing an external "shell", with protective role, on a core of active ingredient. The final product is a micro-particle, under the form of individual core-shell micro-capsule or a matrix, with more active particulates embodied in. Many physical and chemical techniques have been used for packing ingredients, which were, in most of the cases, chemical substances amenable to be consumed / self-depleted before being active for a specific role. For application in environmental technologies a major challenge is raised by the high chemical reactivity of reagents, especially oxidants, often used for the synthesis or chemical transformation of the potential shell materials. Still, some oxidants were reported to have been packed (Sodium Persulfate or Percarbonate, Potassium Permanganate, too), and the final products were particles in the range of hundreds μm - cm , which released the oxidant in interval of hours - days. Obtaining microcapsules in the range of micrometric size ($< 100 \mu\text{m}$), with slow reagent release is an additional challenge. More preparation methods were experimentally developed (e.g. in-situ polymerization, coacervation or double layer coating) for Potassium Permanganate coating. Better results are obtained when using physical methods, although the economical feasibility is questionable even when using the most cost-efficient methods.

Key words: *packing oxidants, Potassium Permanganate, in-situ polymerization, coacervation, slow release*

Microencapsulation is the application of a thin coating to individual core materials that have an arbitrary particle size range from 1-1000 μm , according Lachman et al., 1986 [1]. Since 1931 when the first microencapsulation procedure was published by Bungenburg de Jong and Kaas (dealing with preparation of gelatin microspheres by coacervation process) [2], this technology has developed rapidly, owing to its advantages:

- separation of incompatible components;
- conversion of liquids to free flowing solids;
- increased stability (protection of the encapsulated materials against oxidation or deactivation due to reaction in the environment);
- masking of odour, taste and activity of encapsulated materials;
- protection of the immediate environment;
- controlled release of active compounds (sustained or delayed release);
- targeted release of encapsulated materials.

The microcapsule, as a controlled release product (CRP), has been widely used in various fields, including printing, cosmetics and drug delivery at the beginning, food, petroleum, textile and chemical industries, and agrochemicals in last 2 decades [3].

Encapsulating reagents for soil remediation and water treatment are quite recent concerns (10 – 15 years). The first application of microencapsulation for in situ soil remediation was made by Vesper et al (in 1994), who created a slow release oxygen source for bioremediation, by encapsulating percarbonate in polyvinylidene chloride [4].

In situ chemical oxidation (ISCO) is one of the newest and most promising technologies for soil and water decontamination, especially when chlorinated hydrocarbons are the contaminants (these are heavy products that tend to settle at the bottom of the aquifer). In this technology highly reactive liquids or gases are injected into a contaminated zone, where the oxidants are expected to rapidly react, oxidize and breakdown subsurface contaminants to less toxic by-products. But there are serious drawbacks in the field application of these technologies, from the high reagent consumption for non-targeted oxidation of soil valuable organic matter to risk for human health [5].

A way to improve ISCO technologies for soil remediation is to develop slow release or control release systems for chemical oxidants delivery.

Literature provides limited data regarding packing the oxidants for reaching CRPs. The most intensively studied oxidant is Potassium Permanganate (KMnO_4), and paraffin wax or paraffin-based blends have been proposed as packing materials [6 – 9].

According to these methods, the melted mixture is dispersed using different equipment or techniques (e.g. the rotating disk, mill-grinding, spray congealing device). A recent reference [10] recommends potassium permanganate encapsulation in stearic acid, using coacervation method to obtain stable particles, appropriate to be used as permeable reactive barriers.

One common drawback of the previous research is that particles bigger than 300 μm , or macro-capsules, were obtained, and, as known, the dispersion of such capsules

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from the injection point is poor, in case they can be injected. This is why obtaining microcapsules $<100\ \mu\text{m}$ is of particular interest. Only a limited number of techniques can be applied for encapsulation of solid, hydrophilic substances as microparticles [11]. Such methods are physico-mechanical techniques (spray drying or spray congealing, rotating disk, spray coating), physico-chemical methods (coacervation, solvent evaporation) and the chemical method (polymerization)

Additionally, the encapsulating polymer has to be biodegradable (1), not soluble in and impermeable to water (2), chemically resistant to the oxidant attack (3), soluble in organic solvents (4), to release the oxidant only when the contaminants are encountered (5) and if release is controlled by diffusion this should be slow (up to 30 days) and very limited ($<10\%$) in the first interval (when the so-called "burst" takes place) (6).

The polymers selected to be used for encapsulation, in the present work, were those recommended by literature as suitable for packing oxidants: Ethyl Cellulose (EC), Polycaprolactone (PCL) and Polyurethane (PU) [12 – 13].

On the other hand, for selecting the encapsulating technique, in relation with the polymer selected, a thorough study of conditions practiced for other hydrophilic compounds were studied (fertilizers, pesticides, herbicides, dyes, scents, perfumes, detergents, antioxidants) [14 – 16].

The use of (micro)capsules in aqueous media, without significant release of the active ingredient, was the request for all these cases.

This work presents¹ the preliminary, laboratory research results for obtaining microcapsules of KMnO_4 , using biodegradable polymers and examining the feasibility of preparation techniques, other than spray congealing/drying or spray coating.

Experimental part

The experiment setting had a three fold objective:

- preparation of Potassium Permanganate micro-particles (average size $100\ \mu\text{m}$);
- reaching higher particle load compared with those obtained in spray congealing method (5 – 10%) and
- reaching enough long oxidant release to allow suspension preparation and injection.

Materials and methods

Methylene Chloride (Sigma Aldrich, Germany), Ethyl Acetate, HPLC grade (ACROS ORGANICS), Ethanol, abs. (CHIMOPAR, Romania), N-Hexane (Merck, Germany), Cyclohexane (Merck, Germany), Toluene (Merck, Germany), Poly Ethylene Glycol - PEG 300 (Loba Feinchemie), PEG 400 (Sigma Aldrich, Germany), Stearic Acid (Sigma Aldrich, Germany), 1,4-Diazabicyclo[2,2,2]-octane (Merck, Germany), Sorbitanmonooleat purum - Span 80 (Schuchardt, Germany), DESMODUR N75, DESMODUR L75, DESMODUR VL (Bayer, Germany, via BRIDGEXIM, Romania), Polycaprolactone (Aldrich, Germany), Ethyl Cellulose (Sigma Aldrich, Germany), Polyethylene, medium density (Aldrich, Germany), Sodium Persulfate (Merck, Germany), Potassium Permanganate (Merck, Germany).

The oxidants used for packing were grinded (FRITSCH pulverisette grinding mill) and sieved (MATEST Sieving machine), and the $45 - 63\ \mu\text{m}$ fraction was used, when other is not specified.

a. In situ polymerization

Potassium permanganate was microencapsulated in polyurethane by in situ dispersion polymerization, in accordance with the methods described in literature for sodium persulfate encapsulation [12]: in a three necks reaction glass flask (fig. 1) Potassium permanganate was dispersed in an organic medium containing toluene, ethyl acetate, and soybean oil, under 1100 rpm stirring, at room temperature.

In step one (1), under continuous stirring, a solution of Desmodur 75 L (a toluene diisocyanate adduct of trimethylolpropane) dissolved in ethyl acetate is added to the dispersion by dripping; additional solution of Desmodur CB-75N in ethyl acetate was added gradually, by dripping over a longer period.

In the second stage (2), a solution of ethylene glycol in ethyl acetate, containing also the catalyst (1,4-diazabicyclo [2.2.2] octane) was gradually added to the dispersion. The dispersion is further stirred, as the polyurethane begins to coat the particles with a capsule wall.

Steps (1) and (2) can be repeated to increase the wall thickness.

Then the dispersion is heated ($35 - 55^\circ\text{C}$) and held at this temperature for 2 to 3 h for polymerization to complete. Finally, the microcapsules are collected by filtration and washed with toluene.

Three iso-cyanates and three polyols were tested: Insitu 1, Insitu 2, Insitu 3, Insitu 7, Insitu 8, Insitu 9, Insitu 10 microencapsulated formulation were prepared with different polyols and iso-cyanates.

b. Encapsulation by coacervation

b.1. Coacervation - thermal change

Potassium permanganate was microencapsulated in ethyl cellulose by organic coacervation-thermal change method.

Weighed quantity of ethyl cellulose (EC) is dissolved in cyclohexane (at about 80°C), under vigorous stirring, in the three neck reaction glass flask. In this solution, and in this order are added: Span 85, as stabilizer and potassium permanganate ($45 - 63\ \mu\text{m}$), at 700 rpm. For a good dispersion vigorous stirring was continued through the process, for 1-2 hours. The temperature was then reduced to induce phase separation, using a water-ice bath. The obtained microcapsules were separated by filtration, washed (n-hexane), and air-dried at room temperature.

b.2. Melt encapsulation

Potassium permanganate is added to molten polycaprolactone (PCL, MW 14000), at $75 - 80^\circ\text{C}$ and thoroughly mixed with a spatula. Then it is poured into hot sunflower oil containing Span 85, maintaining heating (hot plate, 75°C) and stirring (1000 rpm). To ensure good polymer dispersion through the oil, this was sonicated (Ultrasonic bath, Grant, Germany) for 5 min. Next, the polymer-in-oil emulsion was cooled rapidly (ice bath) while stirring, to allow microparticles to solidify. The resultant microparticles were collected by filtration, washed with hexane and dried over night at room temperature.

b.3. Solvent evaporation

Potassium permanganate particles were dispersed in dichloromethane solution containing Polycaprolactone (PCL) under stirring. Then, the dispersion was added in sunflower oil, containing Span 85 as stabilizer, under stirring (2000 rpm), to form an o/o emulsion. Dichloromethane was removed by evaporation at room temperature ($25 -$

¹ Permanganate encapsulation in paraffin wax and paraffin-based blends is approached in a separate paper

30°C) under continuous stirring (1000 rpm, 3 h). The microparticles were collected by filtration, washed with hexane, and dried at room temperature.

c. Double layer coating

Permanganate microcapsules prepared by methods a.2-3) and b) were encapsulated in a second layer of stearic acid by organic coacervation, thermal change method.

Weighed stearic acid was dissolved in ethanol (absolute grd.) by heating (60°C) with vigorous stirring (in the 3 neck reaction flask). PEG 4000 is added as stabilizer, then the permanganate microcapsules, under stirring at 700 rpm and vigorous stirring was still continued for 15-30 min. The temperature was then reduced slowly, also stirring (to 300-400 rpm), to induce stearic acid crystallization and phase separation. The obtained microcapsules were separated by filtration, washed with ethanol and air-dried at room temperature.

Microcapsule formation, their aspect and consistency

Samples of the obtained microcapsules were microscopically observed using a Trinocular optical microscope (Optech), with attached Canon PowerShot G6 digital camera. Microscope slides for observations were prepared by adding the microcapsule samples directly on a standard glass slides, no cover slips added. Selected samples were microscopically observed with a 200 x magnification Stereomicroscope (Motic DM143), with built in 2.0 Megapixel Live Imaging Device. The observations were made on 40 x magnification; a scale bar was added and pictures were captured using Motic Images Plus 2.0ML software, live imaging module.

Permanganate quick release tests

Weighed amounts of KMnO_4 -containing microcapsules were dispersed into 100 mL distilled water, in 250 mL amber glass bottles and stirred (orbital shaker), at 75 rpm, room temperature. The concentration of KMnO_4 in solution was measured periodically using the spectrophotometric method (SPEKORD 205, 525 nm wavelength).

Stability of coating materials in presence of permanganate solution

Tests for checking different polymer stability were conducted in similar conditions as release tests. The polymers which were tested were Ethyl Cellulose (grinded), Polycaprolactone (grinded) and Polyurethane (obtained in identical conditions as the encapsulated oxidants, but replacing the oxidant with volcanic tuff). The polymers were contacted with dissolved KMnO_4 at a mass ratio of 1:1. Periodic control on the KMnO_4 concentration was made.

Results and discussions

The three encapsulation methods, with variants, were developed with variations of working parameters and conditions. From the results only part is presented and these were organized in relation with the objectives of the experimental work: particle size and consistency, particle load and oxidant release (burst).

In-situ polymerization/poly-condensation had a strong driver in the successful sodium persulfate micro-encapsulation, described in one US patent [12].

Oxidant release from the microcapsules was quantified by periodically measuring the oxidant concentration in the aqueous phase, after continuous contacting (shaking at

Sample	Isocyanate/Glycol	Oxidant : Isocyanate ratio / Oxidant	Oxidant concentration (%) in microcapsules (theoretical)	MnO_4^- released, %		Remarks
				Burst	24 h	
InSitu1	Desmodur 75L / Ethylene Glycol	2 : 1 / Permanganate	64.9%	58% (1 h)	47%	Polymerization continued for 24 h
InSitu2	Desmodur 75L / Propylene Glycol	1 : 1 / Permanganate	46.3%	67% (1 h)	52%	Polymerization stopped in 5-6 h
InSitu3	Desmodur 75L / Polyethylene Glycol 300	1 : 1 / Permanganate	41.7%	76% (30 min)	57.5%	Polymerization stopped in 5-6 h
InSitu7	Desmodur 75N / Polyethylene Glycol 300	2 : 1 / Persulfate	Apparently no encapsulation (microscopic observations)			
InSitu8	Desmodur 75L / Polyethylene Glycol 300	1 : 1 Persulfate	41.7%	56% (1 h)	86.4%	Quick burst, gradual $\text{S}_2\text{O}_8^{2-}$ concentration. increase
InSitu9	Desmodur 75N / Polyethylene Glycol 300	2 : 1 / Permanganate (20 – 45 μm)	Permanganate of this size can't be encapsulated, using this method			
InSitu10	Desmodur VL / Polyethylene Glycol 300	2 : 1 Permanganate	52.6%	41.4% (30 min)	40%	Brownish particles and filtrate after 2 days

Table 1
MAIN CHARACTERISTICS FOR
RELEASE ON SHORT TERM
FROM POLYURETHANE
ENCAPSULATED OXIDANT
PARTICLES

Sample/ Polymer	Method	MnO_4^- , initial		MnO_4^- released, %						
		%, capsules	mg/l, soln.	30'	1 h	3h	6h	24h	2 d	3d
EC1	Fast cooling	21.51%	571	45%	48.6%	-	-	-	-	-
PCL1	Solvent evaporation	3.59%	72.09	39.6%	47.8%	54.4%	53.3%	37.4%	No colour – no release	
PCL2	Solvent evaporation	20.00%	400.40	10.3%	10.7%	12.4%	9.2%	9.5%	39.7%	34.3%
PCL3	Melt, no sonication	25.10%	505.01	100%	MnO_4^- constant concentration					
PCL-m1	Melt	7.53%	152.11	4.4%	7.3%	9.8%	17.5%	BROWNISH		
PCL-m2	Melt + sonication	21.54%	373.93	7.6%	9.2%	10.4%	10.3%	7.21%	3.94%	3.14%

Table 2
SHORT TERM RELEASE OF
POTASSIUM PERMANGANATE
WHEN ENCAPSULATING BY
COACERVATION

Oxidant, initial concentration	Encapsulating polymer	Oxidant concentration, mg/l					
		1 h	3 h	2 days	3 days	7 days	2 weeks
Permanganate, 1573 mg/l	PU	1369	1205	936	415	Brownish	
Persulfate, 1977 mg/l	PU	1621.5	1759	1921	1962	1914	1926
Permanganate, 880 mg/l	EC	731	710	703	-	589	No specific colour
Permanganate, 815 mg/l	PCL	876	881	759	-	870	800*

* the same after 3 weeks

Table 3 OXIDANT STABILITY WHEN STAYING IN CONTACT WITH THE ENCAPSULATING POLYMER

Table 4
COMPARATIVE PERMANGANATE RELEASE FROM PCL MONO-LAYER AND DOUBLE-LAYER (PCL + SA) MICROCAPSULES

Sample	MnO ₄ ⁻ , initial (calculated)		MnO ₄ ⁻ release, %								
	% in capsules	mg/l in soln.	15'	30'	1h	3h	6h	24h	2 d	3 d	7 d
PCL _{m2}	21.54%	373.93	6.78%	7.64%	9.23%	10.48%	10.27%	7.41%	3.94%	3.14%	Brownish*
PCL _{m2} +AS	10.77%**	216.48	20.72%	22.52%	22.64%	23.97%	24.90%	24.97%	26.15%	31.7%	23.2%

* sonication practised

**this is the maximum possible value, but definitely lower factually, as much SA crystallizes individually



Fig. 1. Potassium Permanganate in Ethyl Cellulose - immediate settling



Fig. 3. Sodium Persulfate in PU + water + KJ

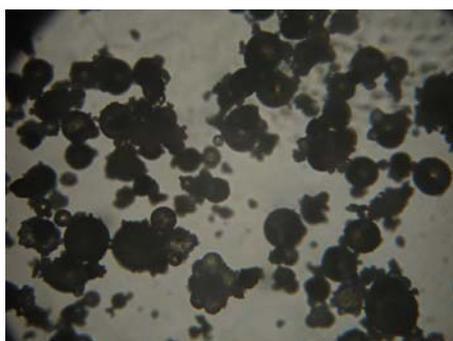


Fig. 2. Potassium Permanganate in PolyUrethane (PU), EtOH



Fig. 4. Potassium Permanganate in PU, Sunflower oil

75 rpm) of the microcapsules with distilled water, at room temperature.

Microcapsules with quite fast release were produced for different oxidant : PU ratios, different iso-cyanates or glycols.

In figure 2 dry microparticles of Permanganate, of different shapes and sizes, are presented and figure 3 shows how the encapsulated Persulfate releases S₂O₈²⁻ once water is added (oxidizing J⁺ to J₂). Additional protection and surface smoothing can be ensured dispersing the microcapsules in oil (fig. 4).

It was established that "high burst" (high percentage of the encapsulated oxidant released on short term) is

between 40 – 50%. When burst was at times below 1 h, release for 24 h is also measured. Some of the experimental results are presented in table 1.

Although the recommendations are strong in favour of Desmodur 75L, oxidant burst is almost similarly fast for all three isocyanates tested. As the oxidant concentration was too high in the aqueous phase in 24 h, measurements for longer periods were not followed.

Direct coacervation was conducted either with solvent evaporation or precipitation/crystallization of the encapsulant polymer around Permanganate particles by temperature reduction. The selected polymers used in this method were Ethyl Cellulose (EC) and Polycaprolactone

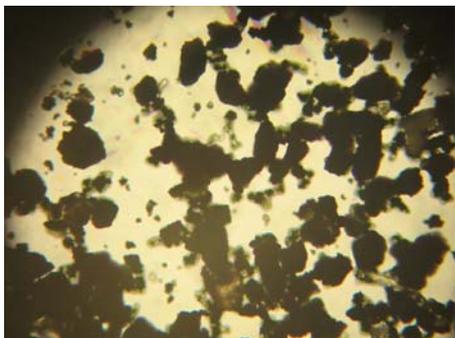


Fig. 5. Potassium Permanganate in Polycaprolactone (PCL)-solvent



Fig. 6. Potassium Permanganate in PCL-melt 1



Fig. 7. Potassium Permanganate in PCL-melt 2

(PCL). When working with dissolved polymer, the equipment (tree neck-flask) and bulk of microcapsules settling is shown in figure 1.

Microcapsule of different size and rough surface are obtained when PCL was added as solution (fig. 5), but round and neat microspheres resulted when working with PCL melt (fig.6). Good encapsulation is still maintained when the oxidant : PCL ratio was increased in favour of Permanganate (fig. 7), but oxidant-free microcapsules are also formed. Also, the oxidant seems to quickly diffuse through the PCL membrane when water is added (fig. 8).

For the two polymers tested, the short-term behaviour of the microcapsules is presented in table 3.

The results in the tables, and also the microscopic images demonstrate a good encapsulation of Permanganate in PCL, although at lower particle load than that in the in-situ polymerization method. Comparing between the two techniques, it seems that a slower release was obtained working with PCL melt, but the oxidant : PCL ratio is drastically limited by fire risk when bulk permanganate gets in contact with over-heated PCL. Encapsulation conditions and results for PCL2 deserve more investigation.

Even the burst is very fast (30' or less) for all cases, it happens at low percentage release and no significant further release happens for days: the oxidant remains encapsulated.

This finding, that Permanganate can be safely encapsulated in PCL, was a very positive result.



Fig. 8. Potassium Permanganate in PCL-melt, Water

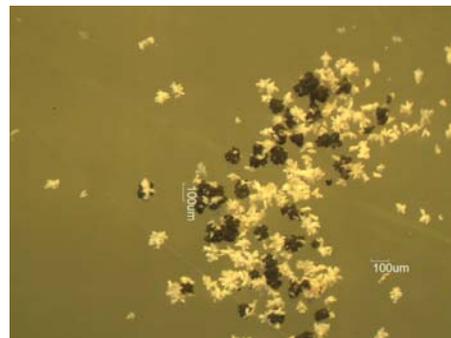


Fig. 9. Potassium Permanganate in PU+Stearic Acid (SA)

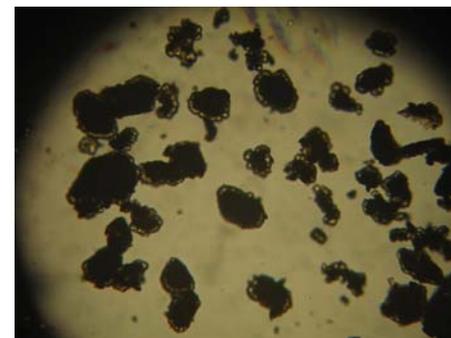


Fig. 10. Potassium Permanganate in PU + SA (2)

Some visual and microscopic observations, also the oxidant concentration decrease in time, raised the suspicion that the shell (PU, EC and PCL) are not stable in time to the oxidant attack.

For checking PU stability, the inert material encapsulated (InSitu3 conditions) was a volcanic tuff and the resulting particles were similarly shaken, in KMnO_4 solution (polymer : oxidant ratio = 1:1). Similarly, grinded EC and PCL were kept in contact with the oxidant.

The oxidant concentration was periodically measured (table 3).

The measured oxidant concentrations in the two cases of Persulfate – PU and Permanganate - PCL systems are within the method error limit and the results indicate that PU is stable for persulfate packing and PCL is stable for permanganate, while PU and EC are not appropriate packers for Permanganate.

Double layer packing using Stearic Acid (SA) was thought a good option for delaying burst and ensuring chemical stability to microcapsules. As the SA deposition is a crystallization process, there are chances that crystallization germs are not necessarily formed on the oxidant microcapsule surface (fig. 9). In these conditions, the right ratio and adjusting the processing conditions are decisive factors. Addition of the second SA layer on the PU-packed permanganate succeeded, although not complete surface coverage seems to have been obtained (figs. 10 - 11). Using sonication instead of ultrahigh speed stirring (>

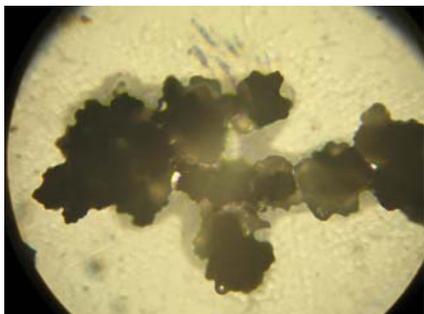


Fig. 11. Potassium Permanganate in PU+SA (3)



Fig. 12. Permanganate release form PU-packed particles (layer 1) + SA (layer 2)

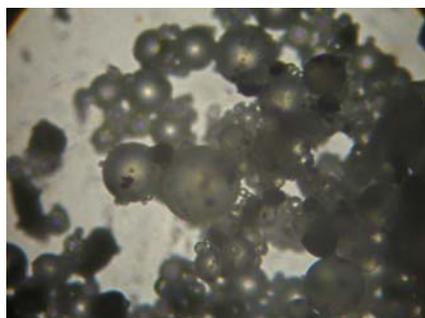


Fig. 13. Potassium Permanganate in Paraffin Wax (PW)

20,000 rpm recommended) seems to have a role (fig. 12): IS2AS1 – higher AS : particles ratio than IS2AS2, both with sonication, IS2AS3 – no sonication. Although burst could be delayed (from minutes to hours), this was not satisfactorily long (desired from hours to days), and Permanganate attack on the PU- first- layer could not be stopped, but just delayed with 4 – 5 days, and only in case of no sonication.

The sonication role is still not clear; while ensuring a very good dispersion is desired, there are signs that it induces some free radicals formation, causing undesired oxidant depletion.

Micrometric permanganate microcapsules that were successfully packed in waxes Paraffin (PW) and Carnauba (CW) using spray-congealing method, although within the required size range ($<100\ \mu\text{m}$) and with limited surface defects, had two major drawbacks: the active load was limited to about 10% and burst took place within hours. Based on the fact that waxes and SA seem chemically compatible, the second layer applied to PW-Permanganate (fig. 14 versus fig. 13), or to CW-Permanganate (fig. 16 vs. fig. 15) shows poor SA adherence, if any, to the either first layer. This was also supported by the release values (1 h): 12.5% for PW-Permanganate vs. 10.4% PW-Permanganate + SA, and almost no change for CW-packed permanganate.

The second SA layer applied on the PCL coated Permanganate led to interesting results. As seen in figure 17, it is not clear how much SA covers the mother capsules (which are not translucent any more), and how much is separately crystallized. Permanganate release was not

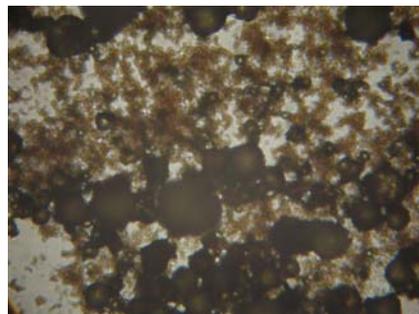


Fig. 14. Potassium Permanganate in PW+SA

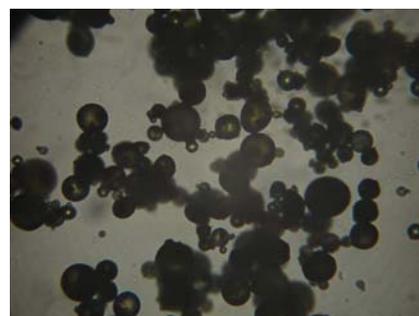


Fig. Fig. 15. Potassium Permanganate in Carnauba Wax (CW)

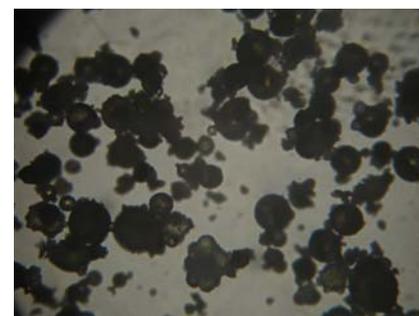


Fig. 16. Potassium Permanganate inCW+SA

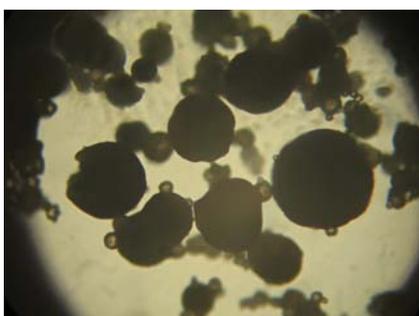


Fig. 17. Potassium Permanganate in PCLmelt+SA

adversely influenced, but on the contrary, it was speeded up. As no further release was noticed for PCL melt-Permanganate after day 1 – 2 (table 2), the suspicion that sonication might have induced depletion of the encapsulated Permanganate still persisted.

Comparative Permanganate release results from PCL mono-layer and PCL+SA double layer microparticles are presented in table 4.

So, it seems that the addition of the SA second coating layer did not have a significantly positive role in slowing release (which is valid for all first-coating materials tested), and is also expected to decrease the oxidant load. This is crucially important from the point of view of applicability. Preliminary assumptions and calculation show that for 1 t of heavily contaminated site (e.g. 10 g TCE/kg) 1.200 kg 20% suspension of packed - permanganate (10% load)

should be injected to satisfy stoichiometry. Taking into account the relationship between the particle size and coverage (spacing between capsules), according to which the theoretical spacing between the (desirable) particle size range of 20 – 100 μm is from 0.2 – 2 mm [17], it is quite clear that practical aspects bring certain limits to filed applications. Still, this second layer could have a role on the long-term release potential: its presence (and possibly of other hydrophobic chemicals) could favour interaction with the encapsulating shell and also the encapsulated oxidants' release.

Conclusions

Encapsulation of oxidants as microparticles (microcapsules or microspheres), with a medium diameter of about 100 μm still remains a target hard to reach. The first milestone is the selection of encapsulation material. Polymers known as compatible with oxidants (e.g. ethyl-cellulose with potassium dichromate, polyurethane with persulfates) seem to be oxidized in time by permanganate solution, and the oxidation seems to be influenced by different preparation conditions. In these conditions, when studying the reactivity of different encapsulated oxidants, for different contaminants, the influence / possible competitiveness of encapsulating material has to be thoroughly defined.

Based on the literature data review and the experimental work, obtaining KMnO_4 microcapsules that simultaneously meet the requirements:

- size within $100 \pm 50 \mu\text{m}$,
- oxidant release/diffusivity to happen in days – weeks, or
- oxidant release only in contact with contaminants,
- high load of microcapsules and
- reduced production costs

do not presently seem easily feasible. To all these some practical considerations should be added when filed application is intended: for a contaminated site (e.g. 10 g/kg TCE) the quantity of 20% packed permanganate suspension may exceed the amount of soil to be remediated.

Some specific facts that have adverse effects on permanganate encapsulation are:

- due to the permanganate good solubility, the osmotic pressure increase inside the capsule cannot be avoided, and thus quite a high burst effect. This could be avoided if the microparticles dispersion is made in a salty solution, but permanganate microcapsules can not be worked in aqueous media;
- due to the small particle size, the burst effect leads to quick "loss" of the active compound when the microcapsule load is in the range 10 – 20%, even less. In these conditions it is questionable if the remained encapsulated active has enough oxidizing power for a heavily contaminated site.

Although the application of the second encapsulating layer (with stearic acid) did not lead to visible release improvement, more research is worth to be done, as:

- the technique is relatively simple, safe and not expensive
- higher dosage of stearic acid could be tried, possibly diminishing the dosage of the first layer material.

Encouraging results were obtained for permanganate encapsulation in PCL. Still more research is needed in the following directions:

- increase the load as much as possible;
- establish the release profile for the entire particle load and
- check on the reactivity for different contaminants.

Whatever the micro-encapsulation method, the encapsulating material is in all cases more expensive than the oxidant. If the environmental sustainability is obvious (considerably less oxidant consumed, less soil organic matter oxidized) for the economic sustainability to be acceptable, not only the cost of microcapsules should not be 8 – 10 times higher than that of the oxidant², but the entire quantity of the encapsulated reagent should fulfil the targeted role.

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² as the oxidant consumption when used as aqueous solution is reported to be within 80 – 100% higher than stoichiometry