

# SCIENTIFIC REPORT - SUMMARY

*Stage-2: January– December 2016*

Project title: “**Polymer-based materials as sorbents for the enhanced removal of oil spills and dyes from the contaminated waters**”

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***OBJECTIVE – I : Preparation and characterization of polymer-based sorbent materials and their application for the enhanced removal of oil spills from contaminated waters***

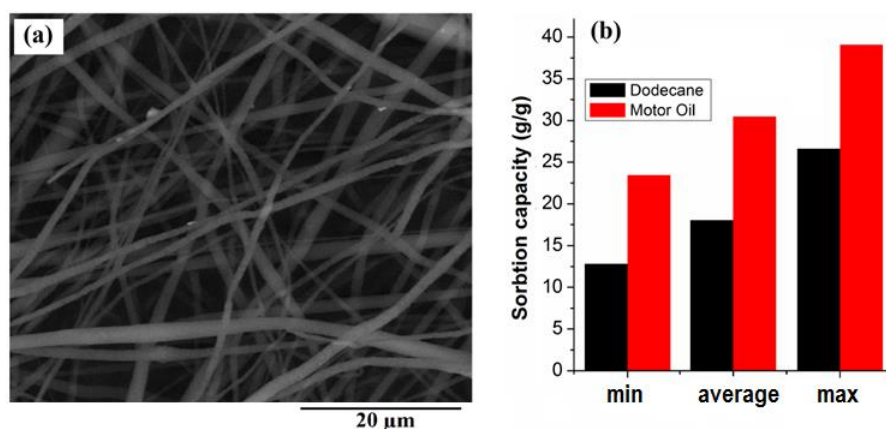
## **Activity I.1 *Preparation of electrospun fibrous nonwovens and their application for sorption of oils***

In this study we were able to produce high-porous sorbents consisting of polymeric nanofibers by means of the electrospinning method. The polymeric solutions for spinning were prepared based on hydrophobic polymers such polysulfone (PSf) or polyvinylidene fluoride (PVDF).

By varying the electrospinning conditions (i.e. voltage, needle-collector distance, polymer solution flow rate) we produced about 15 types of sorbents with various fiber diameters and different porous morphologies. Based on full factorial design and multiple regression modeling method we have determined the optimal conditions of electrospinning that provided efficient fibrous sorbents with maximal sorption capacities for oil spill cleanup. The electrospun fibrous sorbents were characterized by *scanning electron microscopy* (SEM) and water-contact angle measurements. SEM images were analyzed statistically and the histograms were build to reveal fiber diameters and pores distributions. Some details related to this activity are presented in the following.

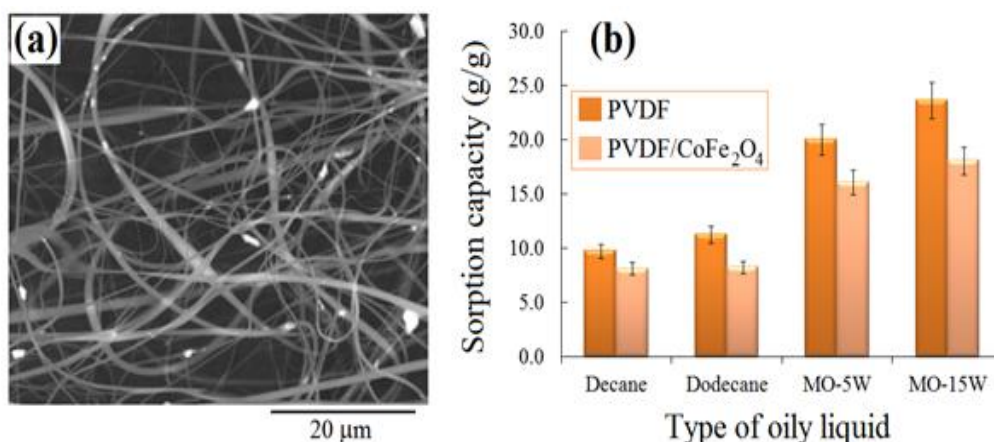
The hydrophobic properties of polysulfone sorbents were confirmed by water contact angles greater than 126° (degree). On the basis of experimental design and response surface methodology, two multivariate regression models were developed and statistically validated by ANOVA (analysis of variance) test. These models enabled to predict the material sorption performances (for dodecane and motor oil) depending on electrospinning variables involved to control sorbent fabrication. Good match was observed between models and experimental data. The model-based optimization was carried out

by desirability function approach and Monte-Carlo simulation method. The optimal electrospinning conditions determined by desirability function approach involved an applied voltage of 25 kV; a tip-to-collector distance of 15 cm and a low flow-rate for the feed (dope) solution. The polysulfone sorbents produced by electrospinning method revealed a fibrous-porous structure (**Fig.I.1a**) with high porosity (> 90%). Moreover, these materials indicated relevant performances for sorption of oily liquids such as dodecane and motor oil (**Fig.I.1b**). The efficient recovery of oil from spent sorbents was achieved by centrifugation technique.



**Fig.I.1.** Plots showing the morphology and sorption performance of the PSf sorbent fibers; (a): SEM image illustrating the morphology of the electrospun polysulfone sorbent fibrous; (b): Sorption capacity of the produced fibrous sorbents PSf depending on the type of tested oily liquid (dodecane and motor oil): minimum, average and maximum levels of sorption.

In recent years, one of the most important topics of research has been devoted to polymeric-inorganic fibrous composites because of their promising abilities for environmental engineering applications. Therefore, in this study, we developed a polymeric fibrous nanocomposite based on polyvinylidene fluoride (PVDF) and cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ) magnetic nano-particles. This kind of fibrous composite was successfully prepared by electrospinning method. The pure spinel phase of  $\text{CoFe}_2\text{O}_4$  and PVDF/ $\text{CoFe}_2\text{O}_4$  composites were confirmed by X-ray diffraction analysis (XRD). Likewise, the composite sorbent (PVDF/ $\text{CoFe}_2\text{O}_4$ ) was characterized by magnetic measurements. It revealed good magnetic properties that are of real interest to facilitate the separation of oil-loaded sorbent under the external magnetic field. Finally, the produced PVDF-based electrospun sorbents with fibrous-porous morphology (**Fig.I.2.a**) were tested for sorption of oily liquids, i.e. decane, dodecane and commercial motor oils (**Fig.I.2b**). The results revealed that the produced composite PVDF/ $\text{CoFe}_2\text{O}_4$  is an interesting material with magnetic property and relevant sorption performances for real applications.



**Fig.I.2.** Plots showing the morphology and sorption performance of the PVDF-based electrospun fibers; (a): SEM image illustrating the morphology of the electrospun fibrous composite PVDF/CoFe<sub>2</sub>O<sub>4</sub>; (b): Sorption capacity of the produced fibrous sorbents PVDF and PVDF/CoFe<sub>2</sub>O<sub>4</sub> depending on the type of tested oily liquid.

### Activity I.2 Hydrophobization of polymeric nonwovens by polysiloxanes

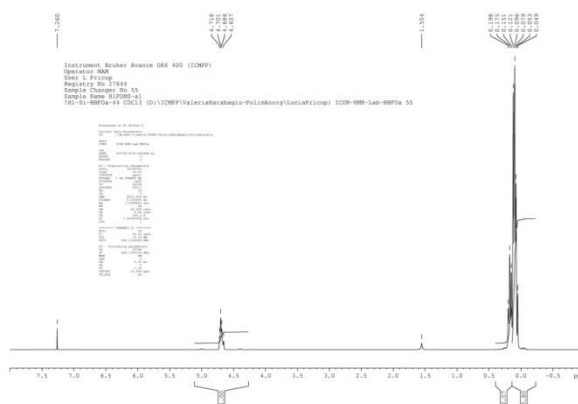
In this application, the polysiloxane copolymers with Si-H reactive groups were aimed at hydrophobization of commercial nonwoven materials made of polyester fibers.

Therefore, poly(methylhydro-dimethyl)siloxane copolymers (PHS) of various molecular weights and different dimethylsiloxy / methylhydrosiloxy molar ratios were synthesized using a bulk heterogeneous polymerization-equilibration reaction between octamethylcyclotetrasiloxane (1), linear hydromethylsiloxane (2) and hexamethyldisiloxane (3). The reaction was carried out in the presence of VIONIT CS 34C acidic catalyst according to the method presented elsewhere [1].

The synthesized polysiloxanes were characterized by infrared (FTIR) spectra, nuclear magnetic resonance (<sup>1</sup>H-NMR) and gel permeation chromatography (GPC). The typical infrared (FTIR) spectrum for poly(methylhydro-dimethyl)siloxane copolymer revealed the following peculiar wavenumbers for the peaks, FTIR (cm<sup>-1</sup>): 2962 cm<sup>-1</sup> (C-H stretching in -CH<sub>3</sub> groups); 2158 cm<sup>-1</sup> (Si-H); 1259 and 791 cm<sup>-1</sup> (Si-CH<sub>3</sub>); 1076-1016 cm<sup>-1</sup> (Si-O-Si). The typical <sup>1</sup>H-NMR spectrum for a poly(methylhydro-dimethyl)siloxane copolymer is given **Fig.I.3**.

By imposing target values for the molecular weight of the copolymer ( $M$ , from 1000 to 4000 g/mol) and the ratio between dimethylsiloxy and methylhydrosiloxy structural units ( $r=m/n$ , from 1 to 7), nine PHS copolymers (denoted PSH1 to PSH9) were designed and synthesized. The amount of active hydrogen was determined from <sup>1</sup>H-NMR spectra and modified Zerewitinoff method, ranging from 0.1% to 0.6%. The characterization of PHS copolymers by gel permeation chromatography (GPC) indicated a reasonable agreement between the target molecular weight ( $M$ ) and the observed number-average molecular weight ( $M_n$ ). The polydispersity index ( $M_w/M_n$ ) ranged from 1.5 to 1.8.

Afterwards, the hydrophobization of polytetser nonwovens was done by the immersion-evaporation technique from the organic solution containing polysiloxanes and following the cross-linking reaction. The produced hydrophobic nonwoven materials were characterized by infrared spectroscopy (FTIR), SEM images and water-contact angle measurements.

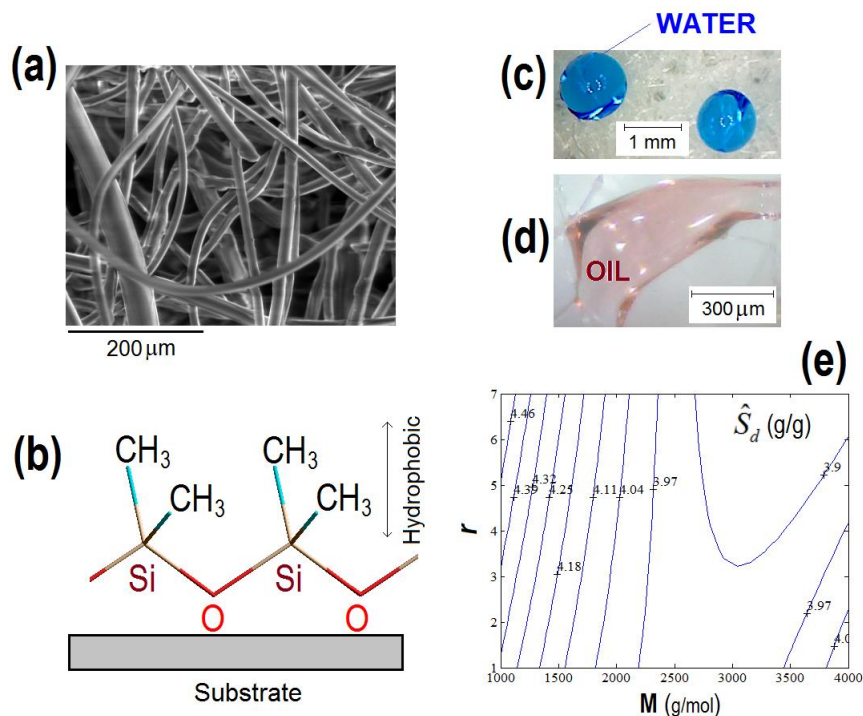


**Fig.I.3.** Typical  $H^1$ -NMR spectrum for a poly(methylhydro-dimethyl)siloxane copolymer;  $^1H$ -RMN ( $CDCl_3$ ),  $\delta$ , ppm: 0.1-0.2 (Si- $CH_3$ ); 4.7 (Si-H).

### **Activity I.3** *Application of hydrophobic nonwovens for the sorption of oil products*

The hydrophobic polyester nonwovens were produced according to an experimental design of the type Box-Behnken. Herein, the most significant factor was the concentration of poly(methylhydro-dimethyl)siloxane copolymer in the hydrophobization bath. Resulted hydrophobic nonwoven sorbents were tested for the sorption of oily liquids, following the indications of the existing standards (ASTM F 726-12 and CAN/CGSB-183.2-94).

Based on Box-Behnken experimental design we investigated the coupling effects of the experimental factors on the sorption efficiency of the produced materials. Thus, we developed mathematical models able to predict the sorption capacities of the obtained materials. The models were used for the process optimization that revealed the most efficient hydrophobized nonwoven material yielding the maximum sorption of oils and diminished collection of water. The mechanism of oil attachment to polymeric fibers was investigated by digital imaging microscopy. Furthermore, the advanced recovery of oils from spent sorbents was done by centrifugation method. **Figure I.4** shows a summary of the results related to hydrophobized polyester nonwovens and their application for oil spill cleanup.



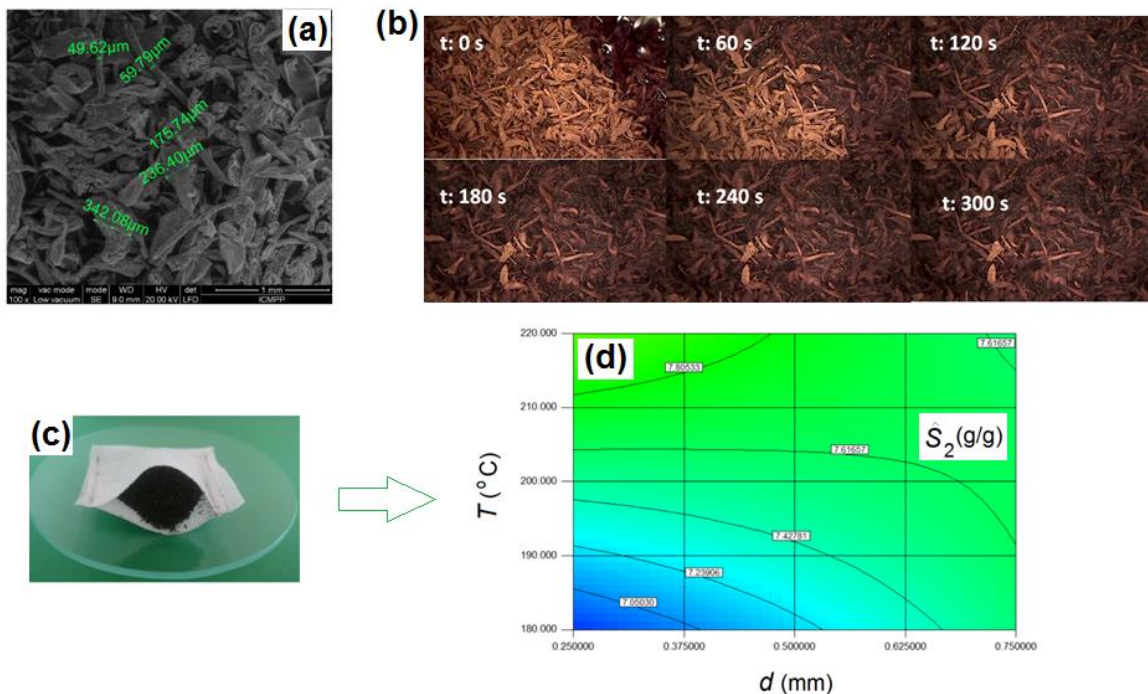
**Fig.I.4.** Summary of results related hydrophobized polyester nonwovens and their application for oil spill cleanup: (a) SEM images of polyester fibers hydrophobized with thin films of poly(methylhydrodimethyl)siloxane copolymer; (b) molecular representation of polysiloxane film on fiber (substrate); (c) hydrophobic properties of treated polyester fibers: water droplets with high contact angle; (d) oleophilic properties of treated polyester fibers: oil droplet spread between polyester fibers forming capillary bridges; (e) sorption capacity of hydrophobic nonwoven depending on  $r$  and  $M$  factors.

**Activity I.4** *Preparation of the enclosed sorbents based on thermally activated peat and polymeric nonwoven fabrics and their application for the sorption of oil products*

In this phase of the project, we have investigated the thermal activation process of the peat (*i.e.* lingo-cellulosic material). First, the peat samples were milled and sieved to obtain different fractions of particle size (*i.e.* in the range 0.1-2 mm). Second, the peat was thermally treated at 180-220 °C to improve its hydrophobic and oleophilic properties by degradation of oxygen-containing substances. Third, the peat samples before and after thermal activation were characterized by FTIR, SEM and thermal-gravimetric analysis (TG/DTG). Forth, the sorption mechanism of peat for the uptake of hydrophobic liquids was examined by digital imaging microscopy and desorption isotherms. These results revealed that the mechanism of sorption was based on capillary and adsorption phenomena. The former one (capillarity) was the most predominant. Fifth, we were able to develop pillow-type sorbents (or enclosed sorbents) by using activated peat as padding material and thermally-pressed polypropylene nonwoven net as hydrophobic containment barrier (envelope). The sorption capacity of the pillow-type sorbents was determined in pure oil bath and in the presence of water. Finally, the



recovery of retained oils from spent sorbents was done by the centrifugation method with an efficiency of about 77%. **Figure I.5** depicts a summary of the results regarding the peat-based sorbents.



**Fig.I.5.** Summary of the results regarding the peat-based material and pillow-type sorbents: (a) SEM image of the peat particles/granules; (b) microscopic images showing the uptake of oily liquid by capillary phenomena; (c) pillow-type sorbent made of peat particles surrounded by a polypropylene nonwoven net; (d) sorption capacity of the pillow-type sorbent (for the uptake of motor oil) depending on two factors: activation temperature ( $T$ , °C) and particle size ( $d$ , mm) of peat.

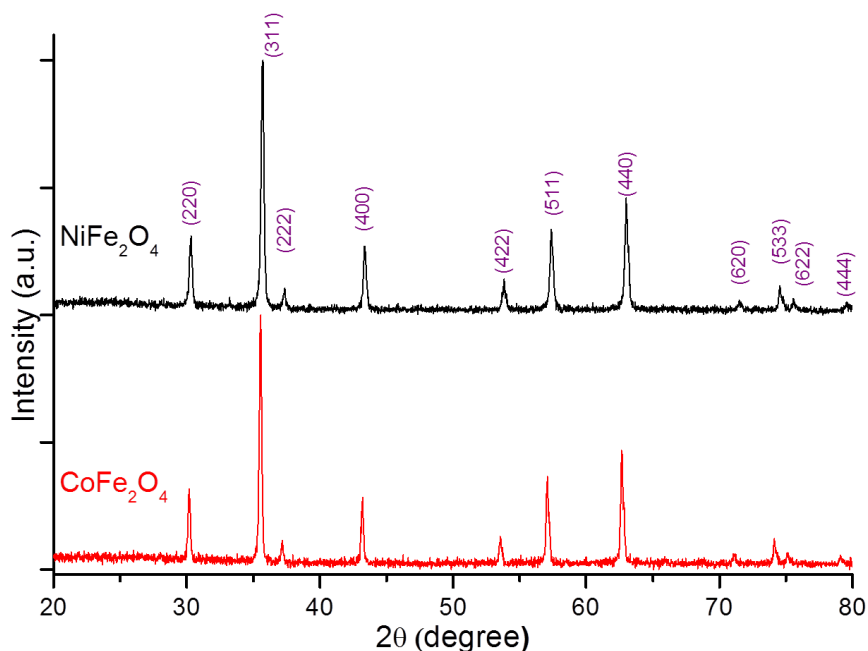
**OBJECTIVE – II : Preparation and characterization of polymer-based composite materials and their application for the removal of dyes from synthetic wastewaters**

**Activity II.1** *Preparation of magnetic nanoparticles (MNPs) by sol-gel auto-combustion method*

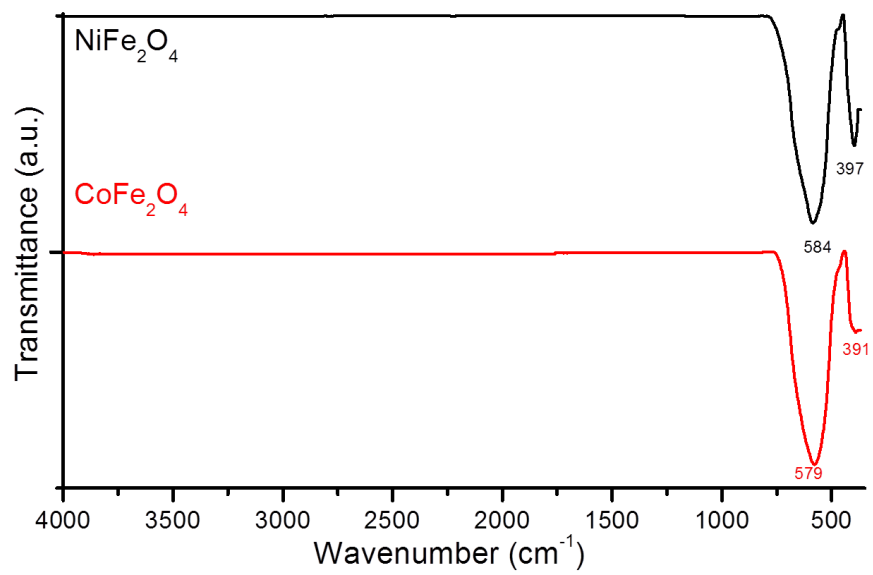
In this study,  $\text{NiFe}_2\text{O}_4$  and  $\text{CoFe}_2\text{O}_4$  spinel ferrites were selected as magnetic components for developing polymeric composites. These inorganic compounds were prepared by sol-gel autocombustion method [2] from high-purity starting materials: nickel nitrate  $[\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ , cobalt nitrate  $[\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}]$ , iron nitrate  $[\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ , and citric acid monohydrate  $[\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}]$ . The invoked sol-gel auto-combustion method enabled to obtain nano-sized spinel ferrites with narrow

size distribution and relevant magnetic properties. These magnetic nanoparticles (MNPs) were designed for using as magnetic component in the developing of polysaccharide/ferrite composites. The spinel ferrites were subjected to several characterization techniques in order to study their: structural (XRD and FTIR), morphological (TEM) and magnetic (VSM) properties.

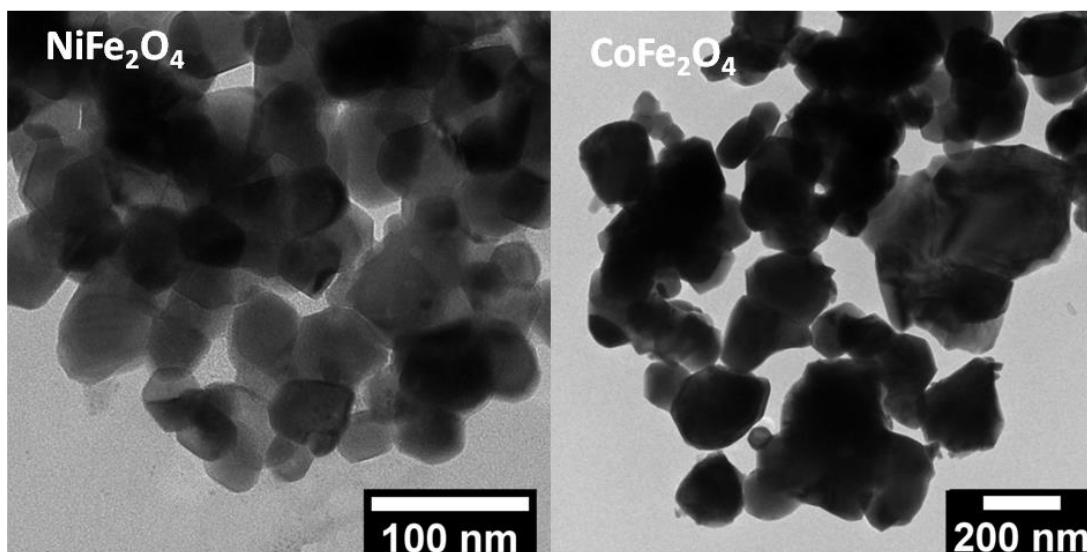
All the peaks observed in the XRD profiles (**Fig.II.1**), proved the formation of pure face-centered cubic spinel structures. In addition, the IR spectra (**Fig.II.2**) revealed only the specific bands for metal-oxygen stretching vibration from the tetrahedral site in the range  $584\text{-}579\text{ cm}^{-1}$  and octahedral site in the range  $397\text{-}391\text{ cm}^{-1}$ , typical for spinel ferrites. TEM micrographs (**Fig.II.3**) suggested the formation of soft aggregates from nano-sized grains with nano-polyhedral shapes. Additionally, we explored the capability of the rare-earth doped spinel ferrites as catalyst for the chemical degradation of dyes. Results revealed that doped spinel ferrites can act as efficient catalyst for dyes degradation from wastewaters by wet oxidation process.



**Fig.II.1.** XRD patterns of NiFe<sub>2</sub>O<sub>4</sub> and CoFe<sub>2</sub>O<sub>4</sub> spinel ferrites.



**Fig.II.2.** FTIR spectra of  $\text{NiFe}_2\text{O}_4$  and  $\text{CoFe}_2\text{O}_4$  spinel ferrites.



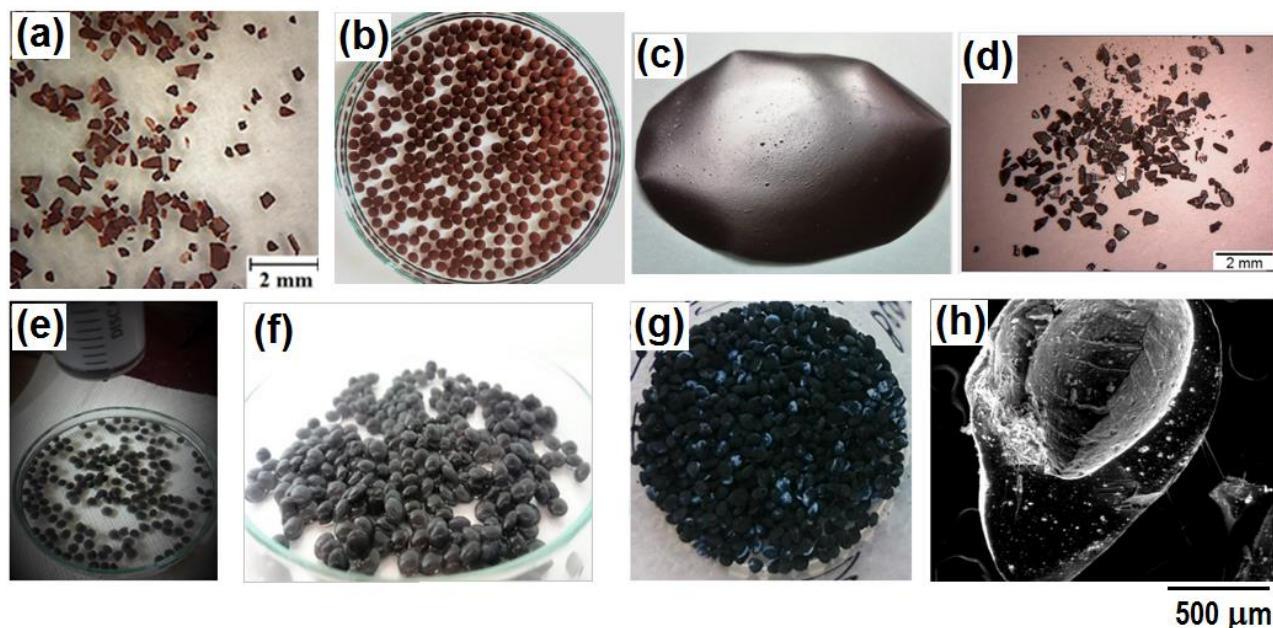
**Fig.II.3.** Representative TEM images of  $\text{NiFe}_2\text{O}_4$  and  $\text{CoFe}_2\text{O}_4$  spinel ferrites.



## Activity II.2 Preparation of novel polymer-MNPs composites as magnetic adsorbents

In this phase of the project, we have developed novel magnetic responsive composites (of type polysaccharide/ferrite) such as alginate-MNPs and chitosan-MNPs. For this purpose, two synthesis methods were employed: 1) solvent evaporation technique and 2) coacervation/precipitation method. The solvent evaporation method enabled to prepare composite membranes that were crashed and sieved to obtain asymmetric particles (<1 mm) in the form of powder sorbent. The coacervation / precipitation method yield to the formation of polysaccharide-composite beads (1-3 mm).

All polymeric composites were chemically cross-linked. For example, the alginate-based materials (polyanions) were ionically cross-linked by calcium ( $\text{Ca}^{2+}$ ) cations [3]. In turn, the chitosan-based composites were cross-linked with epichlorohydrin (ECH) [4] to obtain the polymeric composites with polycationic properties. Thus, we have developed the following composite sorbents of type polysaccharide/ferrite, *i.e.* ALG-Ca@NiFe<sub>2</sub>O<sub>4</sub> and CHI-ECH@CoFe<sub>1.98</sub>Sm<sub>0.02</sub>O<sub>4</sub> both types of materials were produced as powder and beads (see **Fig.II.4**). The obtained composite materials were characterized by FTIR, VSM, SEM and DVS (BET/GAB) methods. Note that, in this phase we adopted two methods of preparation of composites in order to avoid the potential risk for obtaining the sorbents with low sorption performances and moderate magnetic properties.



**Fig.II.4.** Micrographs showing the morphology of the produced polysaccharide/ferrite composites:  
(a) ALG-Ca@NiFe<sub>2</sub>O<sub>4</sub> (particles/powder); (b) ALG-Ca@NiFe<sub>2</sub>O<sub>4</sub> (beads);  
(c) CHI-ECH@CoFe<sub>1.98</sub>Sm<sub>0.02</sub>O<sub>4</sub>; (membrane/film); (d) CHI-ECH@CoFe<sub>1.98</sub>Sm<sub>0.02</sub>O<sub>4</sub>; (particles/powder);  
(e-g) CHI-ECHb@CoFe<sub>1.98</sub>Sm<sub>0.02</sub>O<sub>4</sub> (beads); (h) SEM image of CHI-ECHb@CoFe<sub>1.98</sub>Sm<sub>0.02</sub>O<sub>4</sub> bead.

### Activity II.3 Application of polymer-MNPs composites for the adsorption of dyes from the synthetic wastewaters

The aim of this activity was to evaluate the performance of composite sorbents for the removal of dyes from aqueous solutions according to screening tests as well as kinetics and equilibrium (isotherm) studies. Screening tests were done in order to reveal the most efficient composite materials from adsorption performance and magnetic properties standpoints. Herein, we mainly compared the powder adsorbents versus beads adsorbents. Note that, powder composites were better than beads ones in terms of magnetic properties (VSM measurements).

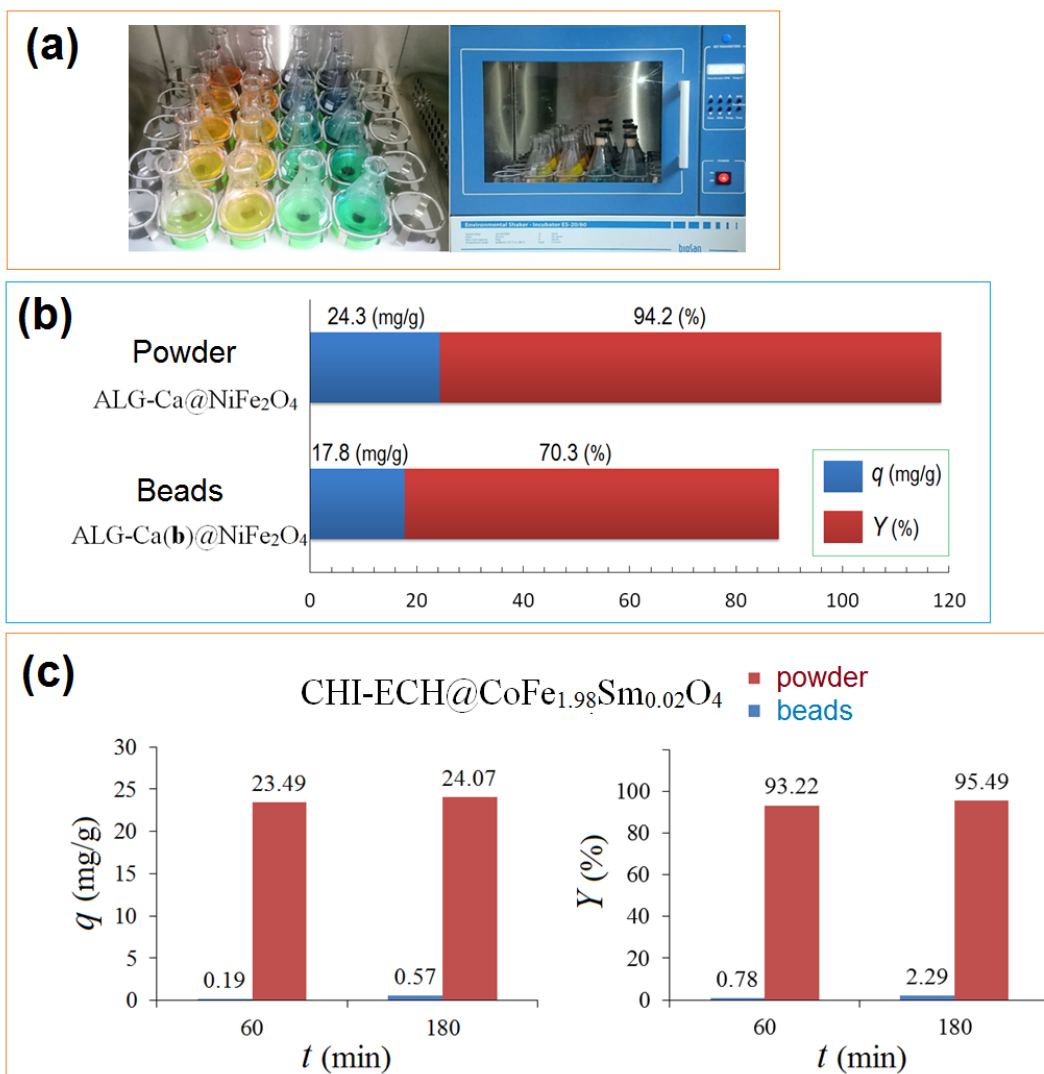
Composite adsorbents were tested for the removal of dyes from aqueous solutions (50 mg/L) in batch mode. The separation of the solids from liquid phase was done by a permanent magnet. Dyes concentrations in water were determined by UV-Vis spectrometry using SPECORD 200 Analytik JENA equipment. Alginate-MNPs adsorbents were tested for the adsorption of cationic dyes (*Methylene Blue* was selected as the representative one). In contrast, chitosan-MNPs adsorbents were applied for the adsorption of the anionic azo dyes (*Orange-II* was selected as the representative one).

**Figure II.5** presents in summary the preliminary results for screening polysaccharide/ferrite composites as adsorbents for the removal of dyes from aqueous solutions. Results revealed better sorption performances for the powder type composites comparing with beads adsorbents. Therefore, the kinetics and equilibrium studies were performed for the powder type composite adsorbents.

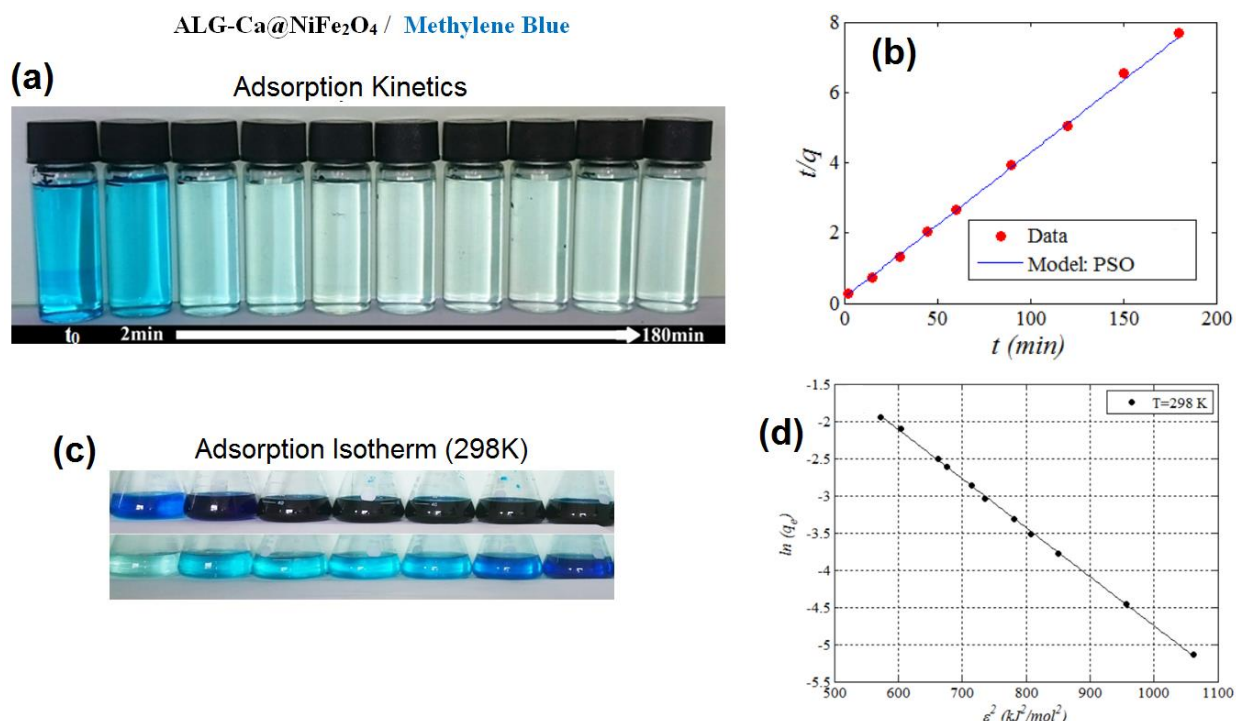
The collected kinetic experimental data were analyzed by linear and non-linear regression methods to construct kinetic models, such as [5-6]: pseudo-first-order (PFO), pseudo-second-order (PSO), pseudo-n-order (PnO), mixed 1,2-order (MOE) and intraparticle diffusion (ID) equations. Equilibrium data were fitted by a number of isotherm adsorption models [5-7] like Freundlich (F), Langmuir (L), Sips (SP), Redlich-Peterson (R-P) and Dubinin-Radushkevich (D-R). Based on D-R isotherm analysis, the mean free energy was calculated to figure out the type of the adsorption process.

**Figure II.6** shows a summary of outcomes related to kinetics and equilibrium (isotherm) studies for the adsorption system ALG-Ca@NiFe<sub>2</sub>O<sub>4</sub> (powder) / *Methylene Blue*. The kinetics data suggested a fast adsorption of *Methylene Blue* dye onto the solid surface of the composite ALG-Ca@NiFe<sub>2</sub>O<sub>4</sub>. The mean free energy calculated according to Dubinin-Radushkevich (D-R) isotherm [6] was in the range of 8-16 (kJ mol<sup>-1</sup>) indicating an ion-exchange mechanism for sorption.

The adsorption kinetics and isotherms studies for other systems (polysaccharide/ferrite composites) will be investigated in the next stage of the present project (*i.e.* stage-3/2017).



**Fig.II.5.** Summary of preliminary results for screening polysaccharide/ferrite composites as adsorbents for the removal of dyes from synthetic wastewaters (screening tests): **(a)** snapshots taken during adsorption experiments (BIOSAN ES-20/60 orbital shaker/incubator purchased in the frame of PN-II-RU-TE-2014-4-1266 project); **(b)** performances of alginate based composites (ALG-Ca@NiFe<sub>2</sub>O<sub>4</sub>) for the adsorption of cationic *Methylene Blue* dye: comparison between composite particles (powder) and composite beads; **(c)** performances of chitosan based composites (CHI-ECH@CoFe<sub>1.98</sub>Sm<sub>0.02</sub>O<sub>4</sub>) for the adsorption of anionic *Orange-II* dye: comparison between composite particles (powder) and composite beads;



**Fig.II.6.** Results related to ALG-Ca@NiFe<sub>2</sub>O<sub>4</sub> (powder) composite applied as sorbent for the removal Methylene Blue dye: (a) snapshot showing the outcomes of adsorption kinetics; (b) adsorption kinetics data and PSO fitted model (linear form); (c) snapshot showing the outcomes of adsorption isotherm; (b) adsorption isotherm data and D-R fitted model (linear form).

## Conclusions

In the frame of the present project, we were able to develop polymeric-based materials with porous morphology suitable for oil spill sorption. Such materials referred to PSf and PVDF electrospun nanostructured fibers, hydrophobized polyester microfibers (nonwovens) and pillow-type sorbents made of peat and polypropylene nonwovens. All developed materials were efficient, showing excellent hydrophobic and oleophilic properties as well as relevant sorption capacities for oil spill cleanup.

Likewise, we were able to develop novel magnetic responsive composites (i.e. polysaccharide / ferrite: alginate-MNPs and chitosan-MNPs) that were used for the removal of dyes from aqueous solutions. Our findings revealed a better efficiency of the powder type composites comparing with beads ones in terms of both adsorption capacity and magnetic properties.

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