Innovative eco-friendly activated carbon filters for harmful vapors & gases VOC purification

Project number 315250

PUBLISHABLE SUMMARY

FINAL REPORT

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1. FINAL PUBLISHABLE SUMMARY

Executive summary

The main objective of the project is to obtain an innovative activated carbon filter with improved structural and functional features, which will be used for the removal of Volatile Organic Compounds (VOCs).

Volatile Organic Compounds (VOCs) include thousands of chemical compounds that are toxic for health. They also include precursor compounds of the photochemical oxidants responsible of the photochemical smog that contributes to the greenhouse effects and to the degradation of the atmospheric ozone layer. These VOCs are mainly industrially produced by organic solvents used to produce inks, paints, varnishes and refinishing products for vehicles.

According to the above facts, the reduction of VOC emissions is of vital importance to the EU (various Directives to control VOC emissions have been produced).

The existing activated carbons for this purpose are generally made from wood or coal materials. CARVOC activated carbons are based on materials out of hemp, an environmentally friendly and sustainable crop.

One of the targets of the project consisted in the revalorization of a waste product from the hemp industry by using it as the starting material for the production of activated carbons suited to act as the adsorbent in activated carbon filters (ACF) system for VOC/TIC removal. UA has conducted a systematic study about the preparation of ACs using this biomass residue as the carbon precursor. With the collaboration of ENSCR, an optimum AC with tailored textural and surface chemistry properties for enhanced removal of these gaseous pollutants has been prepared. This AC reaches the performance of commercial activated carbons, and we have been able to agglomerate it (a requirement for their use in ACF) using a cellulose binder without compromising its performance. As another outcome, tailoring of the pore size distribution of the resulting ACs is now possible, which allows the preparation of a wide catalogue of ACs that could be used in different applications. We have been able to scale-up the production protocol from lab scale to kilogram scale, and ENV partner is now ready to start the production at industrial level. The preparation procedure involves the use of an activating agent that can be recycled in the process and low carbonization temperatures, and it renders a high production yield. These features makes possible the commercial exploitation of the process at industrial scale by ENV partner.

The other project target is the development of light weight, easily portable devices that can be used in case of exposure to toxic gases, either by accidental discharges in the work place or by deliberate release of TICs (Toxic Industrial Gases) through terrorist action. MAST’s main role in the project has been to demonstrate the viability of monolithic carbon structures in low burden personal protection devices for use by the emergency services and the general population and ways of producing these. Phenolic resin derived monolithic carbons have given excellent performance, sufficient to underpin further commercial development. Extension of this result to lower cost lignocellulosic precursors, such as hemp, was less successful. However, new production routes have been developed and patented and applications in for instance carbon dioxide capture look promising.

Summary description of project objectives and the main objectives

Scientific objectives

The overall scientific objective of project CARVOC consists in obtaining a pre-industrial filtering system where the material used as the adsorbent is an activated carbon produced from hemp fiber residues that have been specially designed for optimal adsorption of the VOC and TICs that have previously been identified as pollutants that can be emitted by industries or that might be released by accident or purposely in a terrorist attack. This goal has been achieved during the course of the project. The degree of fulfilment of specific scientific objectives that were drafted in the project proposal within this goal is resented below:

- Impact of the different activation conditions on the porosity of the prepared samples.

Depending on the conditions used, activating agent and/or activation conditions (temperatures, gas nature and flow, impregnation conditions…), ACs with different properties have been obtained. The comprehensive study carried out by UA partner resulted in a catalogue of activated carbons of different surfaces areas (from 500 to 2000 m^2/g) with a broad variety of pore size distributions. In consequence, ACs of tailored pore size and volumes can be prepared by choosing between the different experimental conditions that have been tested and compiled by UA.

- Understanding of the effect of scaling up the preparation procedures of the activated carbon.

UA and ENV have worked together for scaling-up the preparation protocol for the optimum AC following a step-by-step approach in order to have a deeper understanding of the effect of up-scaling in each step. It has been demonstrated that the mixing stage at kilogram scale delivers a slightly larger porosity development, while the up-scaled carbonization stage rendered a larger mesoporosity development. The amount of water used in the washing stage is critical to enable the recovery and recycling of the activated agent, H_3PO_4, which is mandatory for achieving an economically viable industrial implementation of the process. The porosity released using a minimized amount of water is around 90% of the targeted value. Consequently, up-scale of the preparation protocol for the AC production in the kilogram scale has been proven to be feasible.

- Optimum agglomeration conditions. How they affect the porous texture and mechanical properties of the prepared activated carbons.

The optimization of the agglomeration set-up and the conformation of the optimized powdered activated carbon into activated carbon monoliths have been successfully accomplished. A preparation protocol has been developed were the amount and concentration of cellulose binder, pre-drying process, applied pressure and calcination temperature were identified as the most relevant variables. Once the optimum conditions were selected, ACMs with good mechanical properties and showing a porosity blockage lower than 20% can be obtained.

- Potential for producing activated carbon fibers and monoliths from lignin and cellulose derived from hemp.

The results of the study have shown that the hemp derived materials are unlikely to be usable in personal protection devices, because the pore structure is not suited to the monolithic structures required. The phenolic resin derived monolithic structures have better performance in this application. However, the production methodology that has been developed potentially provides a basis for a reduced cost monolithic material based on other forms of activated carbon precursors where the pore structure constraint is less demanding.

- Establish a global approach of the anthropogenic sources of volatile organic compounds by screening the industrial emissions of VOC in Europe.

ENSCR has explored an important bibliographical database concerning the Volatile Organic Compounds (VOCs) emissions issues in Europe (public reports, scientific reports or articles, public websites, etc.). An inventory of the various sources of VOCs in Europe was carried out, and then, the emissions by sector of activities were detailed. Thus, a list of ten VOCs was determined. These compounds belong to different chemical families and can be considered under the scope of the CARVOC project.

- Increase the understanding of the adsorption process and the relationship between the properties of the activated carbons and their abilities to remove the VOC.

The kinetics of adsorption were evaluated and it was shown that the nature of the VOC had only a slight influence on the rates of adsorption. This result is interesting since no kinetic limitation could be expected when complex mixtures of VOC would be treated in industrial applications. The isotherms of adsorption at ambient temperature (25 °C) were measured for all materials and one activated carbon sample was selected as the as the most effective adsorbent with the highest adsorption capacities. The efficiency of this sample was compared to the performances of commercial AC and to the adsorption capacities of the AC from partner TCPLAS. A significant interest of this new material from partner UA was demonstrated with adsorption capacities at least equal to commercial AC, and, most often, higher than the other AC.

- Get a better comprehension of the competitive adsorption between the VOCs.

The kinetics of adsorption was measured by ENSCR in the AC samples from UA, to determine the time required reaching the equilibrium and then the isotherm of adsorption is assessed using the bottle-point method. In addition, some tests of multicomponent adsorption were carried out. These experiments demonstrated competitive effects between VOC.

- Enhance knowledge in the field of air treatment by combining the adsorption with the absorption process in order to remove poorly adsorbed VOCs.

A short list of VOCs (ethylmercaptan, butyric acid, isopropanol, dichloromethane and acetone) were poorly removed by the activated carbons from hemp obtained in the project, mainly because of their polarity (except for di-chloromethane which is hydrophobic). For these compounds, absorption (wet scrubbing) in either aqueous or organic solvents was proposed as an alternative. The results demonstrate a high selectivity of the water whereas the two organic solvents (PDMS and DEHA), especially DEHA, exhibit rather good affinity with all the VOCs even if the order of magnitude of the Henry's law constant between the most soluble and the less soluble compounds for those solvents can vary from 1 to 2 orders of magnitude.

- Demonstrate that efficient regeneration of the newly developed carbons is feasible.

The project the AC obtained from hemp residues was evaluated for usage in temperature-swing adsorption processes. Steam was used as the external heat fluid and the temperature of the fixed bed rose up to 120 °C for the thermal desorption of the volatile organic compounds that were previously adsorbed.

Technological objectives

The technological aim of the project with respect to the activated carbon and filtering systems sectors is the development of a new activated carbon (from hemp) for VOC/TIC abatement with new and better adsorption properties and acceptable regeneration properties compared to the commercial activated carbons that are currently used in this application. A series of specific goals were set in the proposal of the project, and the advances reached in every one of them are as follows:

- Prepare optimum activated carbons (grams scale).

The preparation of ACs at gram scale has been optimized in accordance to feed-back from ENSCR partner. Using as model adsorbents ACs developed by UA of different textural properties that covered most ranges of pore sizes, it has been found that phosphoric acid activation of hemp residue under certain conditions produces an AC with enhanced VOC removal capability that matches the performance on VOC abatement of commercial ACs.

- Upgrade to kg. Understand commercial potential of the materials.

Starting from the preparation conditions covered in the protocol for the preparation of optimized ACs at lab scale, the production process at kilogram scale of optimum ACs with textural properties that match those of the AC prepared at lab scale, have been studied and accomplished. The optimized AC can be agglomerated and conformed as required by partner TCPLAS for their filter systems. The production process of optimum AC seems to be economically viable if the process for recovery and reuse of wasted phosphoric acid is adequately designed.

- Develop activated carbon based on hemp wastes to be used in a filtering system. Adsorb harmful VOC.

An optimum AC with tuned textural properties for enhancing the VOC removal has been developed and conformed in monoliths and pellets for being used in filtering systems.

- Required experimental activation conditions: desired porosity, pore size distribution.

The desired porosity and pore size distribution can be customized depending on the desired final properties of the filter that will depend on the adsorbates and/or mixtures to be adsorbed and on the adsorption experimental conditions (concentration, temperature…).

- Develop optimum experimental conditions to prepare agglomerated activated carbons.

The optimization of the agglomeration set-up, as well as the agglomeration experiments, has been concluded satisfactorily in terms of both textural and mechanical properties.

- To help the other partners about optimum activation and agglomeration conditions.

The preparation protocols of optimum powdered and monolith-shaped activated carbons designed by academia partners have been successfully transferred from them to SME partners. Productive collaboration between partners allowed to adapt these protocols for their implementation in the large scale manufacture of the optimum materials.

- To trigger the design of an industrial filtering system using a numerical model especially developed for the adsorption of VOC onto activated carbons.

Modelling the adsorption process enables further investigations on the performances of the new activated carbons made from hemp wastes. Numerical simulations were developed accounting for mass and heat balances. Then, this model was adjusted and verified on experimental breakthrough curves. Finally, the performances of industrial treatments were assessed for two practical applications: the removal of trace concentrations of VOC and the recovery of solvents.

- The design of new and more cost effective personal protection devices.

Hemp residue derived carbon was successfully produced in monolithic form using a lignin binder phase. However, the tests carried out have shown that working either directly from the hemp residues or from active carbon from phosphoric acid activated hemp, the performance was poor, with significantly better results with the phenolic resin derived monoliths.

Description of main S&T results/foregrounds

One of the main goals of CARVOC project is the revalorization of a biomass residue from the hemp industry by using it as the starting material for the production of activated carbons that could be implemented as adsorbents in VOC/TIC filter systems like those found in the portfolio of TCPLAS and KOU. Research on activated carbons (ACs) has been a topic of great interest over the last decades because of their wide number of applications, especially in gas and liquid phase adsorption. Porosity is the most determining feature of ACs. Thus, surface area, pore volume and the pore size distribution (i.e., the amount of micro, meso and macropores) are very important for the final application of ACs. Together with porosity, surface chemistry of the ACs strongly influences their performance in applications for gas and liquid phase adsorption. Thus, the characterisation of an activated carbon from the point of view of porosity and surface chemistry is crucial for determining if it is suitable for an application or not.

Regarding their production, the selection of a suitable precursor and an appropriate method of preparation are required. These two factors (precursor and the activation conditions) have great importance since they determine the final porous structure of the activated carbon. The precursor must present a high amount of carbon in its chemical composition, and it must be compatible with the activating agent in terms of developed porosity and yield of the process. In this sense, the hemp precursor has been characterized in terms of elemental composition (C, N, H, O and S) and proximate analysis (to obtain the moisture, volatile matter, fixed carbon and ash content). From the analyses performed it can be stated that the hemp precursor is mainly formed by volatile mater (75.6 %), typical of lignocellulosic materials with very low ash content (1.5% wt.). In the case of elemental analysis, it can be concluded that the precursor is rich in carbon (45.6 ± 2.0 wt.%) and specially rich in oxygen (47.8 wt.%), the percentages of nitrogen and sulphur being very low (<1 wt.%). The ash content of the hemp precursor was determined by burning in air the sample, being relatively low (1.5 ± 0.1 wt. %). The high carbon content eases achieving a high process yield, while the low ash content is useful for producing an AC with a low amount of inorganic matter, which is beneficial considering that it is a non-adsorbent material.

About the selection of the activating agent, UA partner has screened four possible activating agents, the first one being the physical activation of hemp using CO_2 as the activating agent. The reactivity of the hemp precursor in CO_2 was determined by its pyrolysis and subsequent complete oxidation in CO_2 atmosphere at different temperatures. The results obtained in this kind of experiments have allowed us an accurate designing of the preparation of activated carbons in CO_2 atmosphere. Using this physical activation methodology ACs with interesting porosities and surface chemistry contents have been prepared. However, the main shortcoming is the low final yield obtained.

Chemical activation of the hemp waste precursor has been carried out using different activating agents, sodium hydroxide (NaOH), potassium hydroxide (KOH) and phosphoric acid (H_3PO_4). Regarding NaOH or KOH activation, different hemp/activating agent ratios have been studied and the activation has been done in N_2 atmosphere using a large flow rate and a carbonization temperature of 750ºC and a carbonization time of 1h, these conditions being selected due to previous experience of the UA research group in chemical activation using hydroxides. As a conclusion it can be remarked that use of either NaOH or KOH as activating agents produces ACs with different porosities (specific surface areas between 1150 and 1350 m^2/g for NaOH and up to 2000 m^2/g for KOH) and different surface chemistry (main surface functionalities are carboxylic acids, anhydrides and lactones with KOH activation producing larger degree of functionalization than NaOH activation). However, the obtained yields in all the activations are very low (below 15%), and, therefore, these activation methods are not suitable to produce ACs at large scale.

Regarding the activation with H_3PO_4, the studies conducted by partner UA have revealed that this is the most interesting activating agent for the preparation of ACs from the hemp waste precursor, especially in terms of yield. For the preparation of ACs by phosphoric acid activation, different phosphoric/hemp waste ratios, drying times, activation temperatures, gas flowing during the treatment (N_2 or air) or gas flow rate during the activation process, have been selected and studied. The specific surface area of the prepared ACs varies between 700-1800m^2/g. Furthermore, the micropore and mesopore volume of the ACs can be tailored to obtain either mainly microporous ACs or materials with a combination of micro and mesoporosity. Finally, from the surface chemistry of the prepared ACs, it has been concluded that the hemp/gas flow ratio and the atmosphere used during activation (N_2 or air) have a great influence on the concentration of surface oxygen groups in the ACs. The obtained results show that depending on the activation conditions selected, the final properties of the ACs can be tuned to obtain ACs with different porosities and surface chemistry with high yields (40-50%).

In summary, more than 50 ACs have been prepared and characterized as result of this study. Activated carbons with a wide range of textural properties and surface areas from 500 to 2000 m^2/g have been obtained from the hemp residue. This large collection of diverse porosity developments achieved using different preparation conditions is highly valuable, since it allows tailoring the pore size distribution and porosity development of ACs prepared from hemp residue for specific applications. This availability of textural properties is especially wide in the case of H_3PO_4 activation, and therefore brings the opportunity to ENV to have a flexible production of ACs with tailored properties for targeted applications using the same production facility built for the preparation of the optimum AC of this project by simply adjusting one or two experimental variables.

From the results obtained in this section, a selection of the suitable experimental preparation conditions has been done to obtain the "optimum" ACs to be used for the VOC adsorption study.

The availability of an extensive collection of activated carbons of different surface properties have allowed partner UA to prepare five ACs with different porosities (S_{BET} from 650 to 1700 m^2/g, micropore volumes from 0.30 to 0.65 cm^3/g, mesopore volumes from 0.05 to 0.55 cm^3/g) and different amount and nature of surface oxygen groups, that have been used as model adsorbents for a large battery of VOC adsorption tests conducted by ENSCR. The results of the VOC removal tests on these samples have allowed ENSCR to stablish the most relevant surface properties for achieving an enhanced abatement of VOCs. Consequently, a protocol for the preparation of an activated carbon with an optimum performance in the removal of VOCs has been developed at laboratory scale.

The agglomeration of the activated carbons is also of paramount importance. Activated carbons produced following the activation protocols developed in this project are obtained in form of small particles (powdered activated carbon) that fall apart when submitted to pressure or attrition. Powder activated carbon cannot be properly handled, and, when used in large industrial filters, they originate a large pressure drop in the fixed bed that increases the pumping power required by the system. In the other hand, the textural properties of powdered activated carbon can be severely affected (and, in our particular case, their adsorption capacity for VOCs greatly hindered) when they are agglomerated if the amount of binder and the thermal treatments are not properly set.

UA partner has studied the agglomeration of the optimum ACs for the production of activated carbon monoliths (ACMs). Thus, a variety of activated carbon monoliths (ACMs) have been successfully prepared from the powered ACs. These monoliths show good mechanical properties, and they are able to preserve their structural integrity after the impact tests (Figure 1). The effect of several variables in the agglomeration and conformation of ACs and their relevance in the obtained textural and mechanical properties of ACMs have been studied. The protocol developed by UA includes (i) the use of a cellulose binder solution, (ii) mixing the binder solution with powdered AC, (iii) drying the mixture at slow rate until the paste acquires a suitable viscosity, (iv) the pre-dried mixture is pressed in a cylindrical mold and (v) the molded mixture is dried and calcined at 200ºC for achieving an ACM. Following this protocol, optimum conditions for the preparation of ACMs have been studied and established. It has been demonstrated that the use of 10 wt. % of cellulose binder is not enough for obtaining good mechanical properties; on the other hand, the use of more than 20 wt. % of binder in the formulation of the paste hinders the accessible porosity of the parent AC. Using an intermediate amount of binder in the formulation, ACMs with good mechanical properties and BET surface areas between 1200-1400 m^2/g have been prepared.

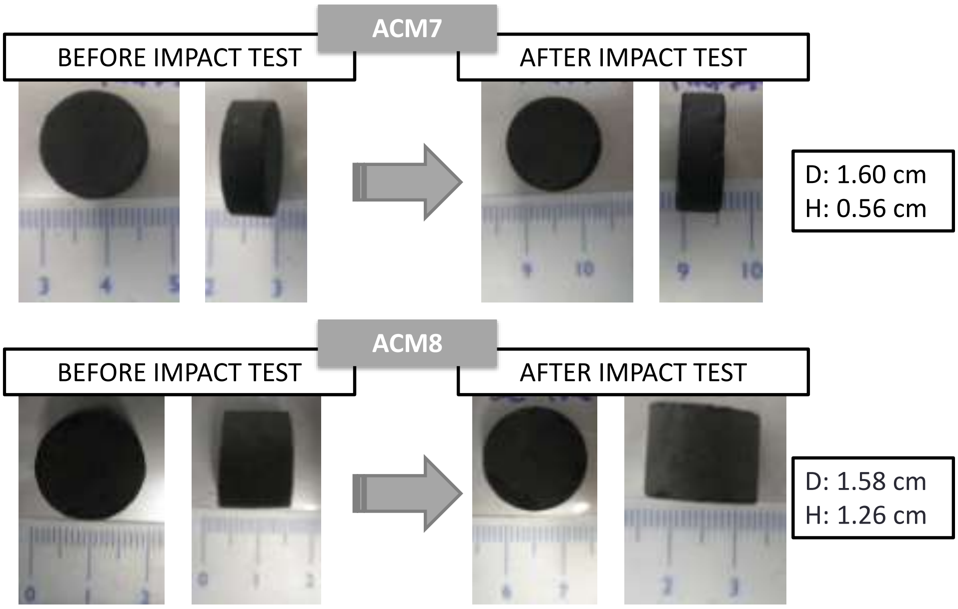
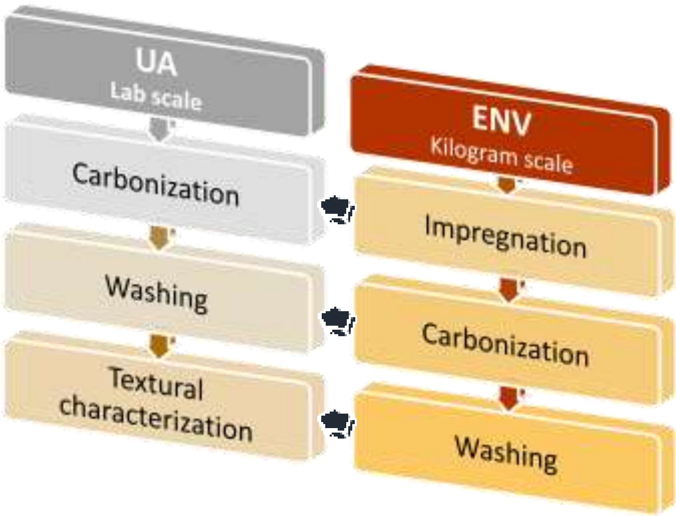


Figure 1. Images of the carbon monoliths ACM7, ACM8 before and after the impact test.

The validity of the protocols developed for obtaining optimum ACs and ACMs have been checked at lab scale by using as the raw material a new batch of hemp residue that has been supplied by ENV. ACs and ACMs obtained using this new batch have been characterized, showing fairly similar properties to those measured the original batch of hemp residue.

Another major objective of the project is the development of ACF in amounts of kilograms, which is necessary for studying the performance of the optimum AC in similar conditions to those employed in the adsorption filter systems of TCPLAS. In order to do so, both the preparation protocol of the optimum AC and the agglomeration process designed by UA for the production of ACMs must be convincingly adapted and up-scaled for the production of several kilograms of ACF sample by ENV partner. In consequence, these protocols have been adapted by close collaboration between the project partners (UA, ENV). For a deeper understanding of the effect of scaling up in the surface properties of ACs, each step of the process must be up-scaled and certified as valid separately. In order to do so, partner ENV has carried out the synthesis of the optimum AC at kg scale stopping at the end of each preparation step. Then, samples from these unfinished products have been delivered to partner UA, which completed the preparation procedure in their facilities in the same equipment and conditions previously used for the production of the optimum AC. This step-by-step approach for scaling-up the production process ensures that each step works adequately before moving to the next level of the preparation protocol. Scheme 1 summarizes the workflow that has been followed for the production and characterization of these ACs.



Scheme 1. Workflow followed for the validation of the scaling up of the production process.

Each preparation step has been certified as suitable for AC kilogram scale production by UA partner by measuring the textural properties of samples obtained after each up-scaled step. When they match those of the optimum AC developed at lab scale, the step was considered to be up-scaled properly.

For conducting this study, ENV hired and adapted external equipment, which have allowed the production of several kg of optimum AC, consisting in:

- 80L horizontal stirrer for the mixing step
- rotating drum furnace equipped with a stainless steel drum for the activation step
- a filter-press equipment with a solid suspension pump for the washing step
- a blender with a screw extruder and a conventional electric furnace for the conformation step

The only modification introduced in the preparation protocol of optimized AC has been made in the washing step. Given the mandatory requirement of closing the cycle of phosphoric acid inside the activation plant that ENV partner is building for ensuring a cost-effective manufacturing process, the H_3PO_4 concentration in the washing waters obtained in the laboratory scale, was lower than required for their reuse. Thus, a new washing procedure, where several washing steps are carried out using a much lower water to AC ratio, has been developed and implemented.

As a result of the tests and the characterization work carried out by UA, it has been concluded that the optimum ACs and ACFs prepared at kilogram scale by ENV have reached a 90% of the porosity development reported for the optimized AC. These properties are closer to the service conditions of TCPLAS adsorption systems. In more detail, it has been determined that the mixing stage at kg scale provides a slightly larger microporosity development, while the carbonization stage rendered a larger mesoporosity development. Specific surface areas are within 1350-1650 $m^2\ g^{-1}$, values that are close to the targeted 1500 $m^2\ g^{-1}$ of the optimum AC.

Concerning the amount of water used in the washing stage, the porosity released after four washing cycles with a minimum amount of water is around 80% of the targeted value. It renders a higher H_3PO_4 concentration that enables an economically viable large scale production of optimum AC and ACFs. Three additional washing steps are required for obtaining 90% surface are of the optimum value, while producing waste waters that can be economically handled. As a conclusion, the partners have been able to produce of several kilograms of an AC with textural properties that resembles those of the optimum AC prepared at lab scale and that can be used in service conditions required by TCPLAS.

Finally, an additional effort was made in providing ENV with the capacity to produce the optimum ACs in industrial scale, from which the engineering design specifications and industrial equipment necessary for large scale and economically-viable production were drawn and selected by two external specialist. More specifically, they provided the specifications for an efficient recovery of H_3PO_4 and for setting the furnace for the feed rates required by the process, which have helped ENV in the construction of a pilot plant for the production of AC in powder and agglomerated forms.

At the same time of the tasks described above, and in coordination with them, ENCR has carried out a list of 12 Volatile Organic Compounds (VOC), which was approved by all partners. These molecules were representative of industrial emissions and were representing all chemical species of interest. The isotherms and kinetics of adsorption for this panel of VOC onto five activated carbons (AC) prepared by partner UA were determined. Besides, these results were compared with the adsorption onto a commercial AC supplied by partner TCPLAS, which is used in their industrial applications. This experimental task was carried out for the adsorption of VOC, pure or in mixtures. Two procedures were used using either gas chromatography coupled with a flame ionization detector or thermo-gravimetric analysis coupled with a mass spectrometer. The kinetics of adsorption were evaluated and it was shown that the nature of the VOC had only a slight influence on the rates of adsorption, regardless of the AC. This result is interesting since no kinetic limitation could be expected when complex mixtures of VOC would be treated in industrial applications. Furthermore, the isotherms of adsorption at ambient temperature (25 °C) demonstrated that one of the samples from UA was the most effective adsorbent with the highest adsorption capacities. Finally, the efficiency of this sample was compared to the performances of commercial AC and to the adsorption capacities of the AC from partner TCPLAS. A significant interest of this new material from partner UA was demonstrated with adsorption capacities at least equal to commercial AC, and, most often, higher than the other AC.

A statistical treatment of the experimental data was carried out. The best relationship was obtained by multi-linear regression for the description of the linearized form of the Freundlich equation. This relationship might be of interest if we want to consider the adsorption of other VOC and if there is a lack of experimental data. Approximations of the performances of the AC produced from hemp residues are thus predicted with an accuracy of around 20 %.

A lab-scale prototype was then designed for gas-phase filtration with operating conditions representative of the industrial units for air treatment. The adsorption of acetone and ethyl acetate was studied for the activated made from hemp residues. A comparison was done with a commercial activated carbon made from coal. The results showed that the pressure drops were negligible as well as showing narrow mass transfer zones within the bed. The main drawback of the material for gas filtration would be its very low density which would result in too large unit for practical and industrial use.

Furthemore, temperature-swing adsorption was studied and the thermal desorption of acetone and ethyl acetate was achieved using steam as the heat fluid. The pellets of activated carbon obtained with the best sample from UA were shown to have high regeneration efficiencies for both organic compounds (above 85 %). A moderate impact of the regeneration steps was observed on the breakthrough curves. Therefore, this adsorbent was shown to be a promising material for this type of adsorption process. Moreover, its performances were higher than a commercial activated carbon (with regeneration efficiencies around 45 %).

Modelling the adsorption process enabled further investigations on the performances of the new activated carbons made from hemp wastes. Numerical simulations were developed accounting for mass and heat balances. This model was adjusted and verified on experimental breakthrough curves. Finally, the performances of industrial treatments were assessed for two practical applications: the removal of trace concentrations of VOC and the recovery of solvents which are fully detailed in the draft user manual.

For recalcitrant VOC, absorption was considered as an alternative to adsorption. Dynamic absorption of 3 poorly adsorbed VOCs (dichloromethane, propanol and acetone) and of the toluene as a model compound has been carried out batch wise in 3 solvents (water, DEHA and PDMS). The Henry's law constant and the overall volume liquid-side mass transfer coefficients have been deduced for each VOC/solvent couple from this experiment. The results demonstrated a high selectivity of the water whereas the two organic solvents, especially DEHA, exhibited rather good affinity with all the VOCs even if the order of magnitude of the Henry's law constant between the most soluble and the less soluble compounds for those solvents can vary from 1 to 2 orders of magnitude. Simulations of VOC absorption in packed column in these 3 solvents have been performed. It highlighted that the removal of the some VOCs (acetone, isopropanol and dichloromethane using the PDMS) can be hardly achieved, even using the organic solvents.

Regarding the personal protection devices (PPD), MAST has carried out a preliminary study into the phenolic resin derived monoliths for use in PPD's, which has demonstrated their exceptional adsorption behavior. Then, the work was concentrated on the direct use of the lignocellulosic wastes using lignin as a binder. The lignocellulosic precursors used were rice husk waste and flax waste, in addition to hemp waste, along with a commercially available Oxosolve lignin. The use of these materials demonstrated that monoliths could be produced. The performance of the lignocellulosics was however inferior to that of the phenolic resin derived materials. The process route was however patented and the further work is justified.

A more detailed investigation into the performance of the phenolic derived materials demonstrated the critical dependence of the performance on the kinetic of the monoliths. Below a threshold activation level of ~25% burn off relatively poor performance was observed with poor breakthrough characteristics. Comparison of the phenolic monoliths with those produced from lignocellulosics also demonstrated that performance was even more dependent on the presence of a narrow micro pore structure. This precluded the use of phosphoric acid activated carbons which had a broad and more mesoporous structure. Based on the phenolic monoliths a method has also been developed for impregnating the Cu/Mo/Ag/Zn –TEDA package required for chemical protection and these have been successfully tested against ammonia and sulphur dioxide.

The work in project period 2 has further demonstrated the critical impact of the carbon microstructure and diffusive characteristics on performance for PPD's and that hemp derived carbons are unlikely to meet these stringent demands. This arises from the more mesoporous structure which could however be beneficial in for instance gasoline vapour recovery. The breakthrough time for the hemp monolith was 8 minutes compared to 150 minutes for the phenolic monolith despite relatively similar surface areas. This work did however lead to the discovery of a new production method for extrudates based on the lignin binders where a patent is being prepared. This could prove relevant in the production of more conventional adsorbents for use in industrial vapour recovery.

For the validation of the performance of the activated carbon filter media under realistic flow conditions, the testing has been extended from single monoliths to clusters of monoliths mounted in a canister. Despite the extremely low pressure drop at a full canister flow of 15L/minute the loss in efficiency was only 15% compared to a single monolith. We believe that this can be further improved through the use a flow distributor with minimal impact on the dP fully meeting our goal of a low burden protection device. Whilst complete hood systems have been produced these could not be tested against a chemical challenge due to some residual leakage paths around the half mask used to mount the monoliths canisters. Improvements have now been and further tests are planned.

These results have confirmed the commercial potential of the monolithic systems in PPD's and further development in conjunction with KOU is planned.

Description of potential impact and main dissemination activities and the exploitation results

The study conducted by UA about the activation of hemp residue has resulted in the development of a wide catalogue of products with very different porosity specifications. As an example, Figure 2 illustrates the surface area offered by the products in this catalogue, while Figure 3 contains the mesopore and micropore volumes in these products. This huge availability of pore size distributions and porosity developments is a valuable resource for the SME partners, since they can now either produce tailored ACs for the adsorption of specific target molecules or more general adsorption-related applications, adding advanced products to their current portfolio; or in the user side, they can now demand engineered adsorption products with a deeper knowledge about the real possibilities in tailoring the textural properties of ACs, and also about the cost-structure of their production and the economic margin and prices they can expect from the manufactures.

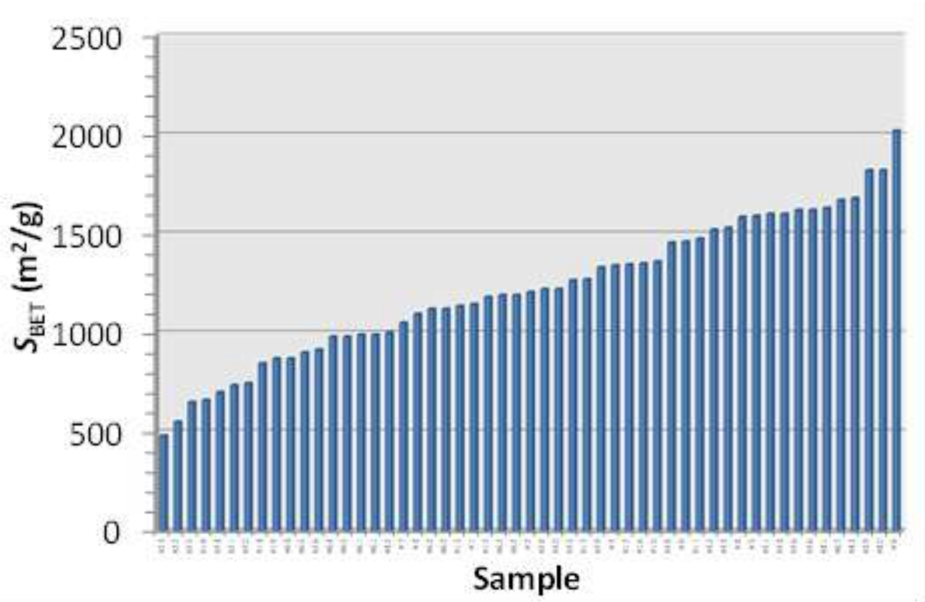


Figure 2. Summary of all the achieved BET surface areas of ACs prepared in this project using hemp residue as the raw material.

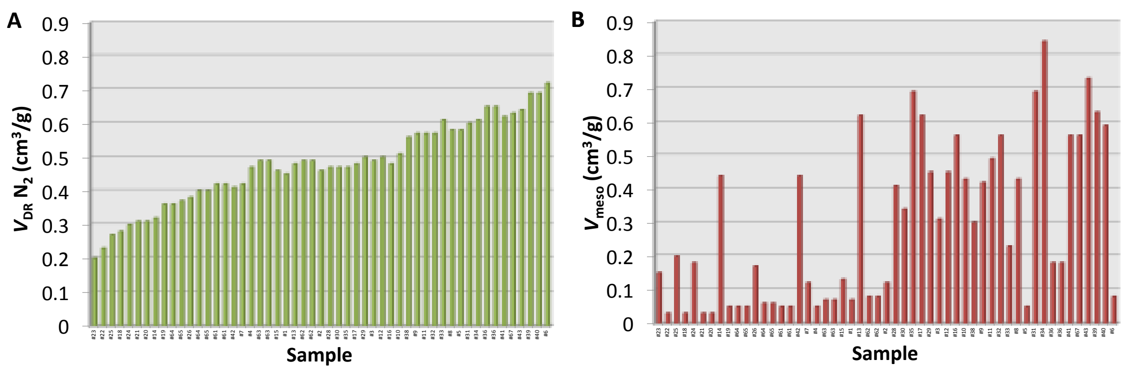


Figure 3. (A) Micropore volume (VDRN$_2$) and (B) mesopore volume (Vmeso) for ACs prepared in this project using hemp residue as the raw material.

Although there exist in the market a wide number of general-purpose ACs, it is not so easy to find ACs specifically designed for VOC's purification. The development of a new product portfolio by UA in conjunction with the model developed by ENSCR for relating the ACs properties with their expected performance in VOC removal helps to satisfy the explicit market, environmental and social needs for more effective VOC abatement systems. Yet this is not the only potential application of these materials. Since most of these materials have been prepared via H_3PO_4 activation, which is able to deliver most of the pore size ranges and amounts, the same production plant could be used for achieving the majority of the product specifications covered in this catalogue. Since SMEs are now equipped with a number of adsorbents with pore sizes covering from less than 0.7 to more than 10 nm, they can screen the market needs for adsorbents that could specifically adsorb targeted molecules. This is possible attending to the molecular size of the target molecule and matching it with an AC of pore size distribution that is centred on that size, thanks to the pore size distributions available in the catalogue. Furthermore, and attending to their pore size distributions, some of them can be potentially used as molecular sieve adsorbents for separation process. Those showing a high mesoporosity development or a wide pore size distribution could serve in general-purpose waste water treatment and purification. ACs with tuned surface chemistry could be prepared for adsorption of metal species in contaminated waters. Similarly, they could be used for dye adsorption and recovery from industrial waters. Those predominantly mesoporous can be used in the food industry for separation and recovery of large biomolecules. As seen here, the list of possible applications of this product portfolio is vast, pointing out the huge impact the work carried out in this project can potentially reach.

Another major breakthrough has been reached in the large scale production of ACs. Precise knowledge has been gained by the members of the project consortium about identifying the most relevant variables for scaling up an AC production protocol developed in the lab while being cost-effective, developing decision making skills for a proper selection of the values of these variables in the basis of engineering and economic concepts, and selecting the most adequate equipment available in the market for each specific production step and adapting them to match the necessities of the protocol. As a result, now it is possible to revalorize waste products from the hemp industry by deriving part of the production of this by-product to the preparation of highly-valued carbon materials. Furthermore, the large scale production of AC can be entirely achieved based on European-based products and by European companies, cutting the large dependence of European industries of low cost, yet low quality, activated carbons imported from abroad. Since AC demand is continuously increasing, the availability of this knowledge and its transfer to European SME can be considered of huge impact in strategic terms (as it reduces the dependence of Europe from importing AC or AC precursors currently not available in the EU).

Following this pathway, another major milestone achieved in this task is the construction of an industrial pilot plant that provides ENV partner with the capacity for large scale production of optimum ACs for VOC abatement. This enables ENV for the production of Tons of tailor-made ACs within few weeks of operation. As a result, ENV could potentially supply TCPLAS with enough AC to refill an industrial filter system and perform a full-scale demonstration of the material.

The global market for respirators reached in excess of €33.6 million and €37.2 million in 2013 and 2014, respectively. This market is expected to grow at compound annual growth rate (CAGR) of 8.9% to reach $19.0 billion in 2019. Whilst it is assessed that the KOU FRESP and LifeHood respirators will only reach a small percentage of this market (circa. 10%) there will be additional opportunities to provide activated carbon developed under CARVOC to other respirator manufactures for use in their respirator canisters.

Traditional full-face respirators can typically cost in excess of €150 and hood solutions such as FRESP and LifeHood in excess of €100. Although a pricing strategy is still to be completed early indications are that price of FRESP and LifeHood could be €75. Furthermore, the cost of traditional full-face respirators which incorporate in their canisters activated carbon developed under CARVOC could be reduced.

The main competitors to the KOU products are primarily in Europe and the USA although many of those work with partner companies throughout the world. These include Avon (UK and USA), Draeger (Germany), Scott Health & Safety (UK), MSA (USA), IlC Dover (USA), Honeywell (USA), Western Safety Products (USA), Safe Home Products Inc (USA). Although these companies are competitors for the Koukoula products they are equally partners for activated carbon developed under CARVOC for use in their respirator canisters

The canister systems were presented at the CBRN Symposium, Royal Military College Shrivenham in November 2014. This created considerable interest and since then meetings have been held with three of the major protection device manufacturers as well as an invitation to present the work to the US Military in Washington in January 2015.

As for the dissemination actions and transfer and share of knowledge with the society, thanks to the collaboration between UA and ENSCR partners for selecting the optimum AC for enhanced VOC removal, part of the results obtained when assessing the relationship between the textural and surface chemistry properties of ACs and their performance as VOC adsorbents, will be presented as a contribution in a chemical engineering conference in France during the course of 2015 year. Furthermore, a scientific contribution about the statistical correlation found between the properties of ACs and their adsorption capacities for VOCs is currently being written, and will be submitted to a peer-reviewed journal.

The results achieved by partner MAST lead to an invitation to present the technology at the XVIIth International CBRN Symposium, Royal Military College, Shrivenham, November 2014. Several contacts have been established by partners MAST and KOU with the major protection device manufacturers, as well as different tasks were also been held with CBRN groups in the US Military.

Partners ENV and CTA were presenting CARVOC at Expocañamo 2015, where a stand was rented for promoting project CARVOC results to hemp sector, and giving a lecture in an industrial roundtable. Partner CTA organized together with ENV an International Conference on project CARVOC results. It was held on 26th May 2015 in Noain (Navarra, Spain). Moreover, ENV attended a regional event oriented to enhance the networking among SMEs active in innovation related to the agro food sector in Pamplona (Navarra, Spain) on 12th May 2015.

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Attached documents

Project logo, diagrams or photographs illustrating and promoting the work of the project (including videos, etc...), as well as the list of all beneficiaries with the corresponding contact names have been submitted.