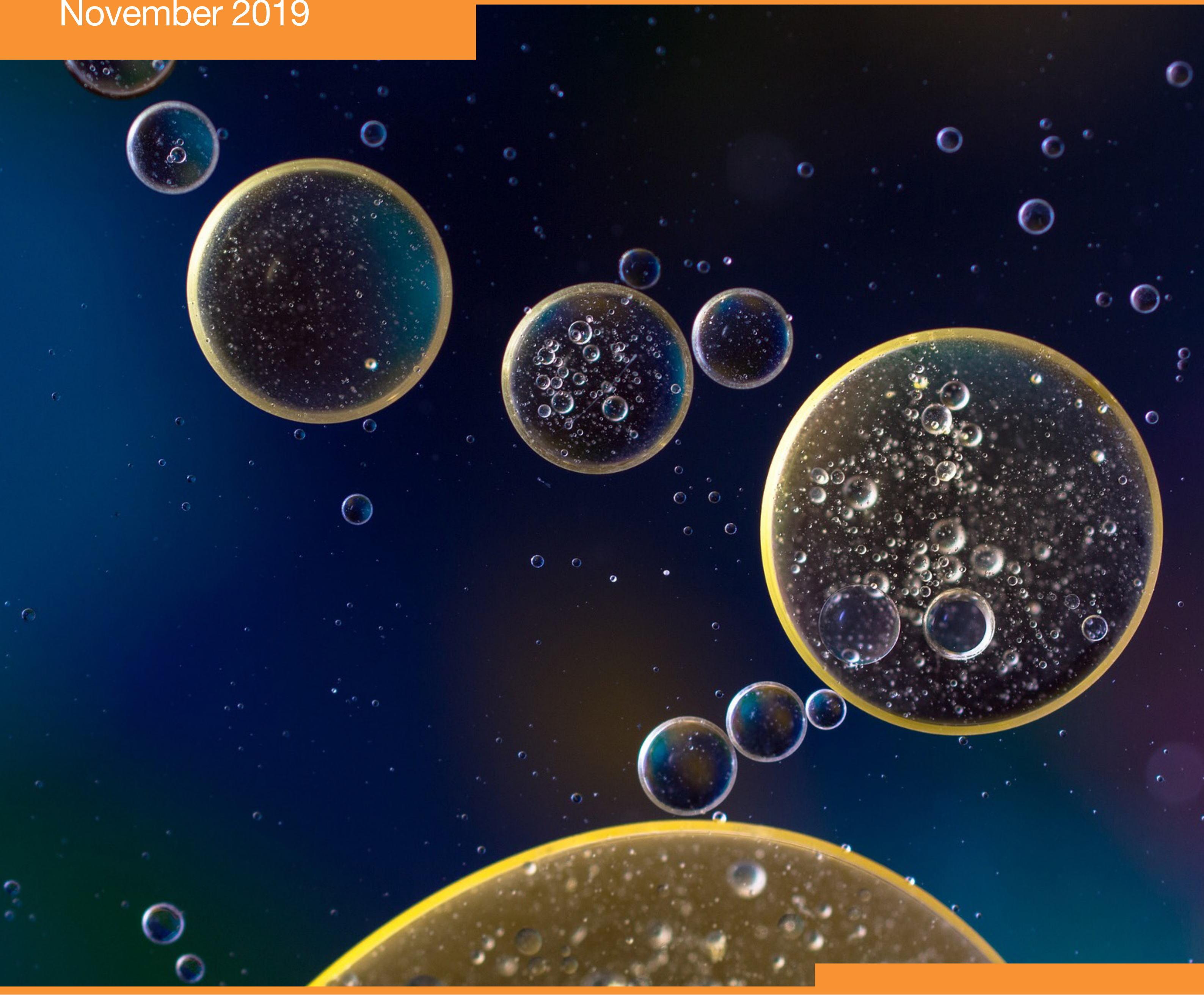
Development of a Carbon-Based Polymer Composite Product for Efficient Recovery of Crude Oil in Oil Spill Environments

Report of Researcher Exchange March 2019

November 2019



INDIA-UK
Water Centre
भारत-यूके
जल केन्द्र

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Ministry of Earth Sciences
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The India-UK Water Centre promotes cooperation and collaboration between the complementary priorities of NERC-MoES water security research.

भारत-ब्रिटेन जल केंद्र एमओईएस-एनईसीआरसी(यूके) जल सुरक्षा अनुसंधान के पूरक प्राथमिकताओ के बीच सहयोग और सहयोग को बढ़ावा देने के लिए करना है

Front cover image: Pixabay

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Executive Summary

This document reports on the Junior Researcher Exchange program conducted at the Indian Institute of Science (IISc) in Bangalore, India, during the month of March 2019. The theme of the Research Exchange; transforming science into management catchment solutions, brought into sharp focus the issues surrounding laboratory based results and scaled up solutions to catchment management. Awareness of this unfortunate reality inspired this exchange to attempt to produce output that works on simple, scalable principles for removing crude oil from water. The lead researcher Mr Jonathan Bloor from the University of Plymouth in the UK worked with host researcher, Dr Sai Siva Gorthi and his lead postdoctoral researcher Dr Vikram S. to develop polymer based composite products for the recovery of crude oil. The outcome of the exchange resulted in a prototype Graphene Oxide (GO) Aerogel foam that can separate crude oil and water via simple gravity method. Additional output also involved the rapid prototyping of electrospinning nanofibre membranes to enhance the selectivity and mechanical strength of the foam.

This report is intended for members of the IUKWC Open Network and water security stakeholders.

1. Activity Leads

The Junior Researcher Exchange was convened by the India-UK Water Centre (IUKWC) and led by Activity Leads:

Mr Jonathan Bloor

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The exchange was held at the Indian Institute of Science (IISc) Bangalore, India.

2. Aims

The India-UK Water Centre is based around five key cross-sectoral themes and aims to deliver a portfolio of activities across these themes. This exchange focused on the theme: Transforming science into catchment management solutions. One of major issues in India right now is the ability to transform scientific endeavour in the laboratory and put it into practice in the ‘real world’ to help clean-up polluted water. Many laboratory-based research papers have shown efficacy in water remediation, but few are brought to market due to the problems faced when scaling up. Awareness of this unfortunate reality inspired this exchange to attempt to produce output that works on simple, scalable principles for removing crude oil from water.

In addition to the development of a water quality remediation technology, other activities were also undertaken. Firstly, the capabilities and facilities of the partner institution, what is available, and the local cost of the each technique and speciality was assessed. Capabilities also extended to the contacts with local industries and small start-ups, Small Medium Enterprises (SMEs), which are already focusing on scaling up the outputs from research that are ready for manufacturing. The value in this is in the improved planning and efficiencies of future collaborative projects.

Human resources was also a consideration. Many projects here in the UK lack funding to take development of a technology further, making recruiting and retention of man-power a huge problem; this can stifle innovation and research output. Assessing this issue for both institutions will yield greater insight into the allocation of resources in the future.

The exchange aimed to:

- Develop a proof of concept Aerogel to separate crude oil from water
- Improve structure and selectivity of the Aerogel by electro spinning a complimentary nanofibre membrane
- Develop and test nanofibre membrane in aqueous environment
- Assess capabilties of both institutions, including start-up potential

3. Participants

The research at IISc was conducted by Mr Jonathan Bloor and Professor Sai Siva Gorthi’s lead postdoctoral researcher Dr Vikram S. Initial meetings between the exchange team members, led to the decision that the exchange would build on the work that had already been completed in the University of Plymouth on the development of aa prototype for oil/water separation as part of Mr Bloor’s PhD thesis research. The emphasis to further this work entailed a new technique of membrane construction, electrospinning. Dr Vikram is an expert in electrospinning at IISc and has even built his own electrospinning apparatus. Mr Bloor worked long hours with Dr Vikram to develop complementary membranes for the Aerogel structures. The other members of Dr Gorthi’s research group, Optics and Microfluidicis instrumentation (OMI), provided much needed support throughout this process.

4. Structure and Results

4.1. Aerogels

The Research Exchange started on the 4th of March and continued through to the 25th of March, 2019. Following introductions to Dr Vikram and the OMI team, as well as a health and safety induction, a work plan was outlined. The development of the aerogel structures required a little adaptation to the use in crude oil separation and this became the first main focus.

Aerogels are extremely low-density solids consisting of an open cell porous network similar to open cell polyurethane foam. The weight to volume ratio of a typical aerogel is approximately 0.1 - 0.5g/cm3, and these can be made from a variety of materials, including, silica, metal oxides and graphene/polymer based materials (Zuo *et al*., 2015). The use of aerogels as a super-adsorbent and intercalating structure has generated some high profile attention in recent years, harking back to its use as a detector for radiation, plus a diverse repertoire of other applications, from energy storage in batteries, ultralight translucent building materials and aerospace heat shield applications (Bheekhun *et al*., 2013, Kabiri *et al*., 2014).

Potable and wastewater treatment is of particular interest for aerogel research as the material has an extremely large specific surface area to volume ratio, potentially yielding a maximum number of binding sites per unit weight to adsorb and remove contaminants; the efficacy of this principle has already been demonstrated in a deconstructed Graphene foam for wastewater treatment (Tabish *et al*., 2018). Graphene oxide and cellulose nanofibril hybrid aerogels have also been shown to remove 21 antibiotics simultaneously through the adsorptive process (Yao *et al*., 2017). Further studies have revealed the ability to produce robust aerogels with a high fatigue resistance of over a million cycles, whilst being stretched up to 200% (Guo *et al*., 2018). The ability for aerogel composites to separate oil and water often requires hydrophilic properties, but these same hydrophilic properties must not compromise the integrity of the structure. The composite addition which is usually a polymer, acts as a cross linking agent that binds the Graphene oxide (GO) platelets together and maintains this structure in an aqueous environment and hence, this was the first step of the Exchange.

The prototype developed for testing included, two adapted syringe tubes with the graphene oxide aerogel sandwiched in between them using two bulldog clips. A mixture of crude oil and water was then poured into the top syringe (Figure 1) and a video was taken of the process. Images shown in figure 1 have been extracted from this video to illustrate the efficacy of the prototype.

Immediately, as the oil /water mixture comes in contact with the aerogel, the water is facilitated through the aerogel due to the hydrophilic properties of the functionalised surface. The top right image in figure 1 shows a column of oil and water mixed, note here crude oil does not form a typical uniform oil water column due to the complexity of the hydrocarbons present. Nevertheless the aerogel is still able to allow the water to pass through with a relatively high flux rate, and a total time of the separation of less than 40 seconds. As is evident from the bottom right picture in figure 1, the oil does not pass into the beaker below, admittedly it is a little difficult to see the water pooling in the beaker, but the video format illustrates this principle without ambiguity; the aerogel separated the crude oil from the water.

Having achieved a prototype for oil-water separation and following further meetings with Dr Vikram and Professor Sai, the focus shifted towards improving the mechanical strength of the aerogel. A novel technique currently used by the OMI lab at IISc is electrospinning of nanofibres. Nanofibres have similar characteristics to aerogel structures, they both have the ability to be surface functionalised and exhibit a high Brunauer Emmett Teller (BET) specific surface area to volume ratio. The next task was to coat the aerogel in an electrospun nanofibre membrane.

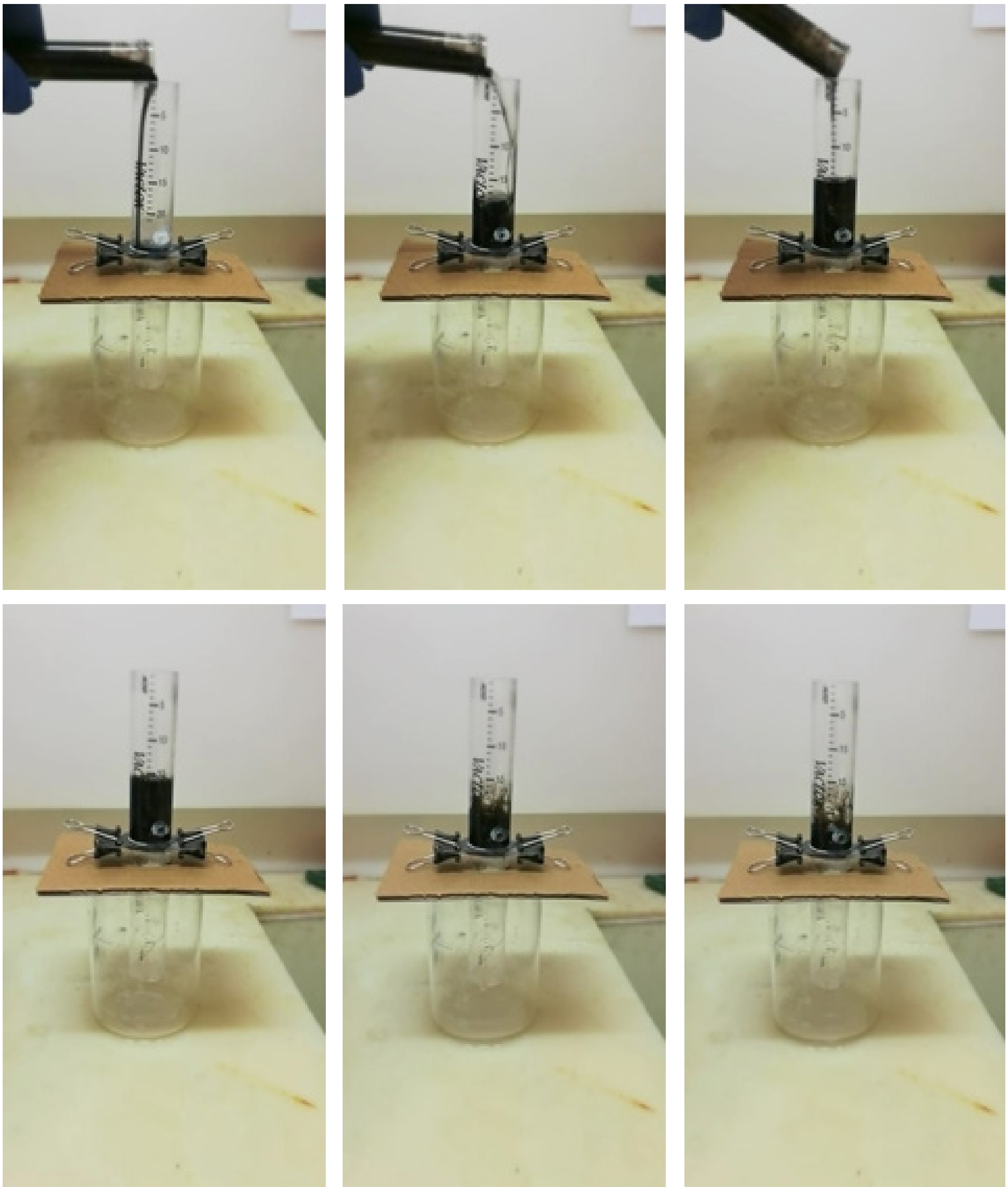

Figure 1: Time-lapse (top left to bottom right) of crude oil and water separation using a prototype Graphene oxide aerogel

4.2. Electrospinning

Electrospinning nanofibres derives from traditional ideas of yarn spinning for fabric production but using an electric field potential as the separator of the fibre from the bulk material. This relatively simple technique can be achieved with a simple, low-cost set of apparatus found in most laboratories around the world. The applications of electrospinning are numerous and far reaching, from controlled drug release, microfluidic medical diagnostics, air purification, wound dressing to smart fabrics, prosthetic autoimmune prevention coating, and membrane filtration. There are three basic components to an electrospinning set up;

- Syringe pump
- High voltage power supply
- Collector plate

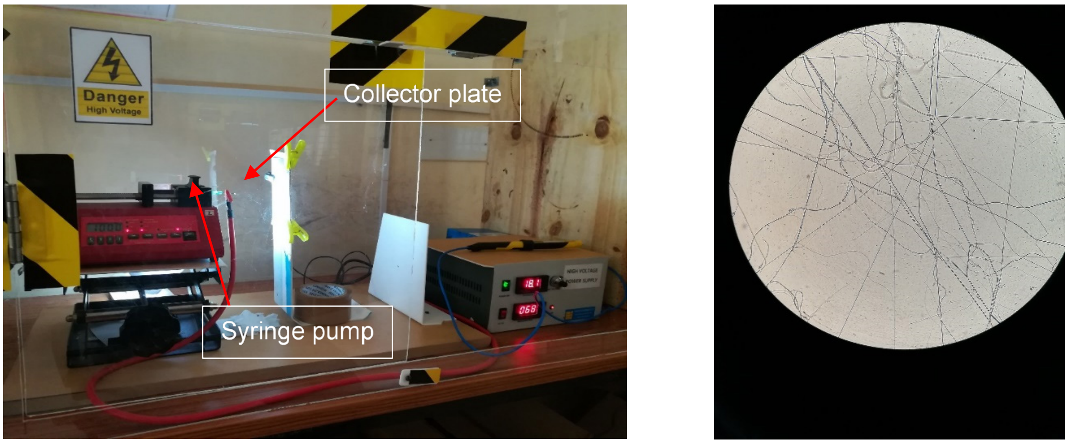

Figure 2: Electrospinning equipment used at IISc Bangalore (left), Optical image of the nanofibres produced (right)

The productivity of the nanofibres is largely dependent on the collector plate, seen here in Figure 2 (left), illuminated and clipped to the Perspex support. In our set-up, the collector was made of a single sheet of aluminium foil grounded to the negative terminal of the high voltage supply. The syringe pump is insulated using a Teflon sheet and the positive electrode is clamped to the syringe needle directly. As the flow rate is determined in conjunction with the other critical parameters, for example, conductivity and viscosity of the polymer solution, temperature and humidity, the optimal voltage can be selected to provide a continuous nanofiber (Figure 3, right). The deposition of the nanofibre upon the collector is potential-based and will be directed randomly to the area with the highest potential difference. Thickness of the nanofibre membrane is time dependant and can range from a 0.5 – 1000 micrometres.

Figure 3: Graphene Oxide electrospun nanofibre membranes

In Figure 3, we have two examples of the nanofibre membrane, on the left is Graphene oxide at 0.05%wt and the right hand image is at 0.0025%wt of Graphene oxide both in a polymer matrix. This introduction to electrospinning was a steep but beneficial learning curve that ensured competency to operate the system independently; this was critical as it takes at least 4-6 hrs to spin a membrane shown in figure 3. Due to the requirements for mechanical strength in crude oil recovery, the aerogels need to be robust enough. The next stage of this project was to incorporate the aerogels within an electrospun nanofibre membrane, improving mechanical strength and adding selectivity.

Characterisation of the nanofibre membranes using a Scanning Electron Microscope (SEM) gave some useful information regarding the morphology of the nanofibres and the relative pore size of the membrane. Due to the extremely low concentrations of conducting materials, the ability to get high resolution images was limited - the higher the kilo voltage (Kv) of the SEM the more damage is done the membrane surface. However, we were able to get some insightful mages (Figure 4).

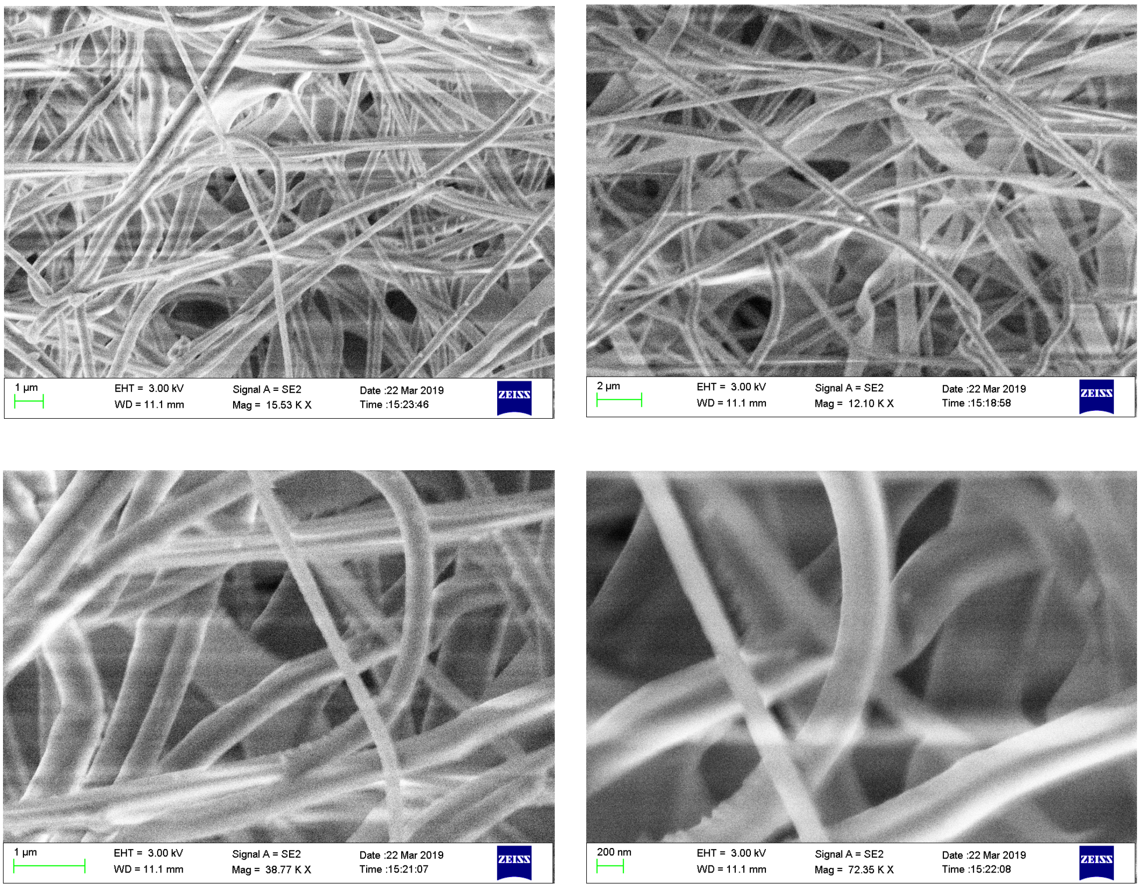

Figure 4: SEM images of the electrospun nanofibre membranes

The images from figure 4 are of GO nanofibre membranes spun at 0.05%wt. The morphology of the fibres were relatively uniform and produced an overall homogeneous surface from a macroscopic perspective. In some areas of the membrane, especially in the top right image in figure 4, a ribboning effect can be seen. This is due to the tuning of the parameter before a stable whipping jet of nanofibre was established.

Post processing of the nanofibres to improve their stability in an aqueous environment proved to be quite a challenge. Issues were encountered using a glutaraldehyde vapour technique, which is a crosslinking agent that would improve the structure, but this exposure could only maintain the fibres in an aqueous solution for 24 - 48 hrs. As a result of the nanofibre membranes instability in water, the incorporation of the structure within the aerogel did not occur within the time and resources available during this exchange. Hence, the production of a multifunctional member was not possible.

Despite this, the technology is ideally situated for water quality management. By using the scientific ideas behind aerogels and electrospinning it is possible that we can clean-up oil contamination in fresh water in the short term with a low cost effective point of use solution until a more robust infrastructure is put into place.

4.3. Assessing start-up potential

The IISc has a number of excellent aspects for future start-ups. For one, IISc has a state of the art clean room facilities and a democratic access to that equipment. Although most of this work was not based there, this meant that world class innovation can be achieved. Secondly, bringing products to market from research outputs is made possible at IISc with the help of the Society for Innovation and Development (SID). SID provides support, workspace and business advice for start-up companies that have outputs from research within the institution. This service provides the missing link for the development of research to a market ready product.

The competencies and capabilities of the team were also assessed both dynamically during team meetings, but also on the basis of previous work carried out by each team member. The current team has the capacity to undertake future work and commercialisation with the guidance of the team leader Prof. Sai Siva, as it has a capable producer of Graphene Oxide and subsequent aerogel structures who is currently a PhD Student (Mr Bloor) and an electrospinning expert in Dr Vikram, who has also previously worked with the Indian military providing electrospun material for ballistic protection.

5. Activity Conclusions

5.1. Key outcomes

- Fabrication of Aerogel for crude oil and water separation
- Experience of developing electrospun nanofibre membranes
- Initiation of collaborative partnerships and relationships
- Increased understanding of facilites and capabilities of each institution
- Insight into efficiencies for a future working relationship

This productive and successful IUKWC Junior Researcher Exchange highlighted some potentially useful applications of science and how it can be translated into catchment management solutions.

The effective crude oil and water separation mechanism using an aerogel structure has been demonstrated as a proof of concept. The scaling up and testing of this material in a real-time environment will be the next challenge and this ideally would be achieved by incorporating an electrospun nanofibre membrane.

Collaborative partnerships have been fostered and reliable routes for the transfer of knowledge and ideas have also been established. Greater insight into the facilities available within each institution makes a huge impact on the planning of future collaboration, as without this insight the correct allocation of resources would not be possible.

5.2. Conclusions and recommendations from the exchange experience

This Exchange provided an invaluable experience for myself as the lead researcher. Firstly, my experiences were very positive, not least due to the host and the host institutional set-up. An impressive unexpected aspect of my exchange, and a credit to Professor Sai and Vikram, was the openness and collaborative nature of the researchers at the OMI lab in IISc. I found the environment open, friendly and most importantly without the usual closed ranks of some research groups. This enabled a free flow of ideas and ultimately, what I see as an efficient hive mind working together. I would have no hesitation in working again with the team, thus strengthening the potential for future collaborations.

Secondly, I have some key recommendations for future junior researchers interested in exchanges.

Prior to the exchange, I had a number of illusions regarding the way research is conducted elsewhere in the world, and India is not just ‘anywhere’. Hence, I would recommend a buffer period at the start of the exchange to acclimatise to the change in climate and culture. This could lead to improved productivity..

Time is of the essence when working on an ambitious, but time-limited exchange program especially in a new environment. It is so surprising how just navigating yourself around takes more time than you think. So with this in mind, to achieve the high expectations of the proposal, planning of time would have to be more conservative in order to fully realize your goals. Another aspect to this is the ability to logistically get to places on time, Bangalore traffic makes a big difference, as we found out on a trip to a start-up company on the outskirts of the city. We also have to bear in mind the power outages, booking of equipment and also using local equipment required by other team members. I think contingency plans should also be written up in advance to mitigate unexpected delays or logistical restrictions.

Finally, greater efficiencies for future collaborations can be developed with knowledge obtained about the infrastructure and facilities available at the both the host and visiting institutions. With this in mind, IUKWC could potentially consider a two part collaboration Exchange program, giving both parties the opportunity to build on good foundations.

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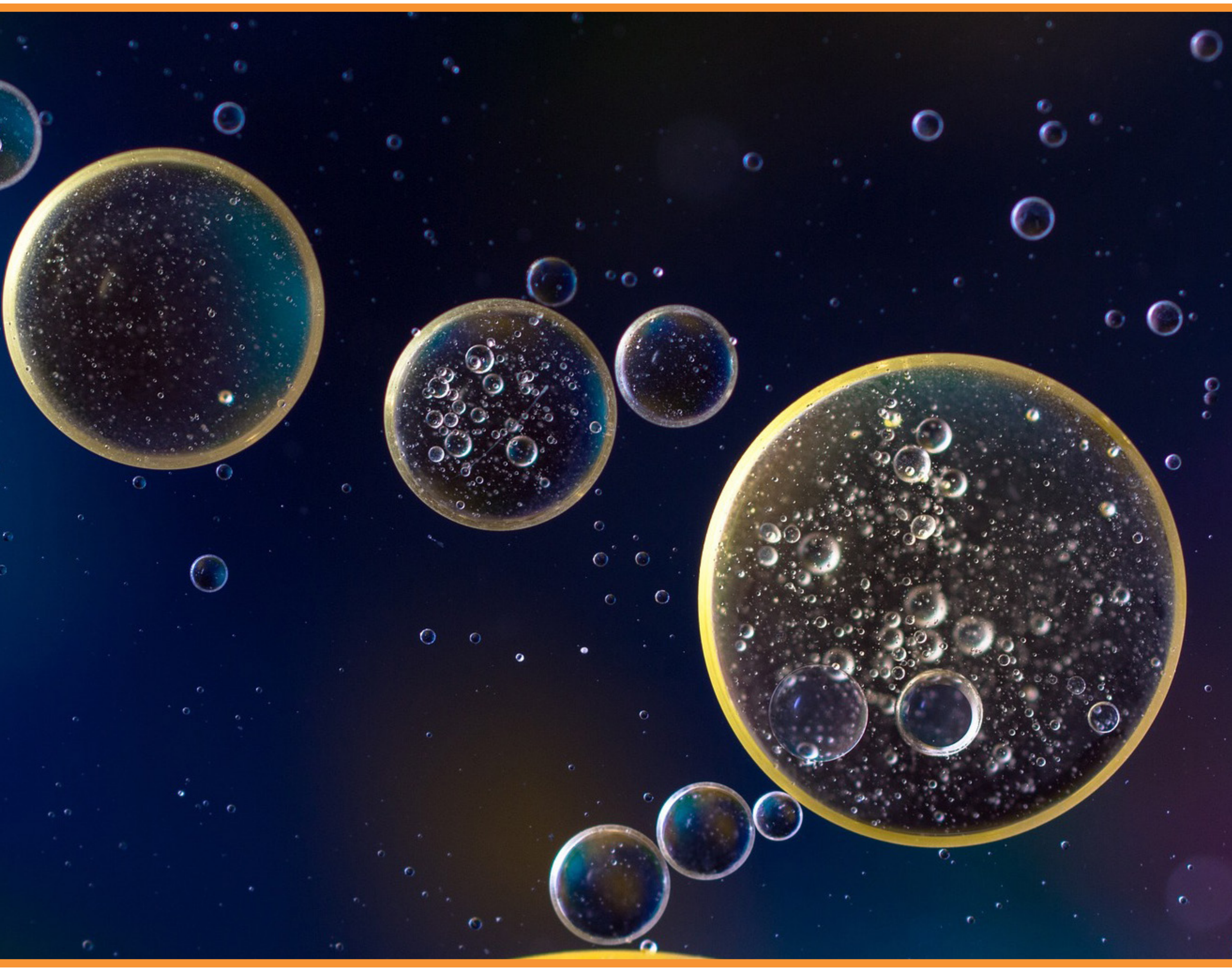

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