Industrial symbiosis and green chemistry: one's waste is another's resource!

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ABSTRACT

Industrial symbiosis, the sharing of industrial by-products to add value, reduce costs and improve the environment, will become increasingly important for the sustainable future of our planet. By employing this philosophy alongside green chemical technologies it is possible to develop new materials that will open doors to a variety of applications. Herein, three case studies demonstrate how "wastes" from food, agriculture and consumer electronics may be transformed into valuable materials for water treatment, construction and medical applications, respectively.

Case study 1: Worldwide, more than 1000 tons of dyes are discharged into water courses annually. This poses a significant hazard to flora and fauna. Waste polysaccharides (starch and alginic acid) can be expanded and pyrolysed to produce mesoporous carbonaceous materials (Starbon®).[1] Starbons® have demonstrated great promise as adsorbents for the removal of cationic and anionic dyes from aqueous waste streams. Manipulation of pyrolysis temperature provides full tuneability of chemical and textural properties, allowing control over adsorption characteristics. Polysaccharides are inexpensive, non-toxic, biodegradable and are found in nearly every geographical location on the planet.[2] Making Starbons® ideal candidates for water treatment.

Case study 2: Many countries are combusting large volumes of biomass in order to meet renewable energy targets, resulting in significant quantities of new waste: biomass fly ash and slag. The valorization of these wastes is vital to ensure recovery and reuse of the inorganic species.[3] Current and ongoing research is demonstrating the use of silicates from ash as an effective replacement for traditional formaldehyde binders in construction boards.

Case study 3: Liquid crystal displays (LCD) are the fastest growing electronic waste stream in the EU and contain many valuable chemicals, including indium (reserves of which are dwindling).[4,5] Emphasizing the necessity for industrial symbiosis and "elemental sustainability" for all elements, not just carbon! By adopting a holistic approach to LCD utilization we have demonstrated that liquid carbon dioxide can efficiently extract liquid crystals, indium can be recovered and low value polymers can be transformed into porous materials that may find use as tissue scaffolds.

Keywords: Waste, carbon, silicate, supercritical, adsorption

1 CASE STUDY: WATER PURIFICATION

Clean potable drinking water is one of the most precious resources on the planet. Worldwide industrial effluents are subjected to costly treatment prior discharge into water courses.[6] Physical adsorption using activated carbons as an adsorption matrix is efficient at removing dyes and pigments from water courses.[7] These dyes can be toxic, persist in the environment, non-biodegradable and consume vast quantities of water in their use. The disadvantages of using activated are that they can be expensive and are frequently required in large volumes to improve rates of extraction. The impact of releasing dye or pigment wastes into water courses can poses a significant hazard to our environment.[8]

Polysaccharides including starch are non-toxic, biodegradable, possess polyfunctionality and are found in nearly every geographical location on the planet.[2] The development of tuneable, nano-structured, graphitizable and mesoporous carbon (Starbons®) derived from waste polysaccharides from the food industry will open new doors to absorbents. The surface chemistry, functionality and surface polarity of these materials can be controlled through varying the temperature of preparation and selection of polysaccharide precursor.[1] Carbonaceous materials from starch and alginic acid were prepared at 300^{o}C and 800^{o}C, are known as Starbon® (S300 and S800) and Algibon (A300 and A800) respectively. These materials were compared to commercially available activated carbon Norit to examine the effect of: adsorbent type, adsorbent preparation temperature and adsorption time.

^{13}C-MAS NMR spectra of a range of Starbon® and Algibon demonstrate at 300 ^{o}C aliphatic carbons are present in the materials, on pyrolysis to higher temperatures an increased aromatic and graphitic like structures are observed. Textural properties of Starbons® significantly differ to those of Algibon (Figure 1).

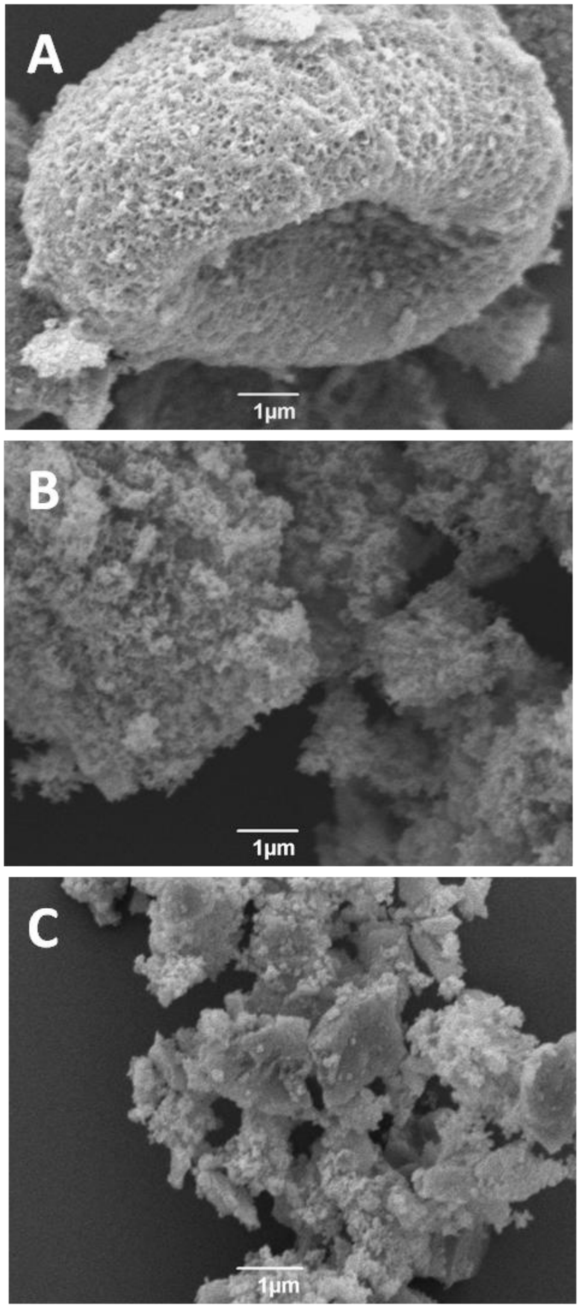

Figure 1. SEM images (A) S800, (B) A800, (C) Norit

Norit exhibited almost complete microporous structure (Fig. 2) compared to Algibon and Starbon® which are highly mesoporous. Algibon have a significant advantage over Norit in that they have a large total pore volume and significant mesoporosity (Table 1), making the adsorption less likely to be diffusion limited and allows better access to available surface area.

Table 1 Porosimetry characteristics of Starbons®, Algibons & Norit

	S300	**S800**	**A300**	**A800**	**Norit**
S_{BET} ($m^2\ g^{-1}$)	332	535	280	265	798
Total pore volume ($cm^3\ g^{-1}$)	0.82	0.75	1.41	1.08	0.57
Microporous volume ($cm^3\ g^{-1}$)[a]	0.165	0.215	0.112	0.043	0.42
% Microporosity	20.12	28.67	7.94	3.98	79

[a] Calculated through the Dubinin-Radushkevich method

For the application of Starbon® and Algibon as absorbents in water treatment of dye effluent obtaining information about their kinetic activity is vital. Typical kinetic traces of adsorptions are shown in figure 2. For both dyes A800 showed the fastest rate of adsorption and Norit the slowest. Samples prepared from waste polysaccharides demonstrate reversible adsorption, this may lead to the recovery and reuse of the material or dyes. The first order kinetic constants (k) for all materials demonstrate a clear trend to that of degree of mesoporosity. Larger rate constants are observed for Algibon samples with lower degrees of microporosity, thus the signifying the importance of large pores for adsorption to allow diffusion through the porous network.

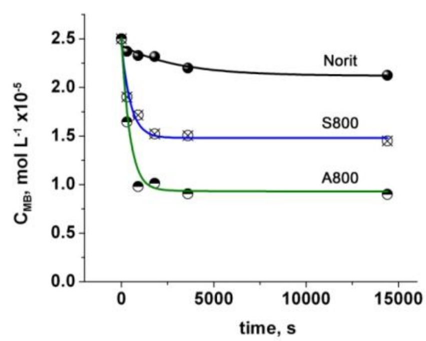

Figure 2. Kinetic data for the adsorption of methylene blue

Carbonaceous polysaccharide derived mesoporous materials from starch and alginic acid were found to be effective for treatment of dye effluent and outperformed commercially activated carbons. Analysis demonstrated that variation of the preparation temperature alters the surface and textural properties of the Starbon® and Algibon, with materials becoming graphitic like at high preparation temperatures. The speed of adsorption of small dyes is directly linked to the level of mesoporosity, suggesting that pore size is important to prevent limited diffusion.

2 CASE STUDY: VALUE OF ASH

Agricultural residues are at the heart of sustainable chemistry in offering greener routes to chemicals, materials and energy.[3] Little work has looked at the utilization of the inorganic components of biomass and its ash. This is vital to recycle valuable nutrients, create new materials and improve the economics of energy technologies.

We have studied the effect of temperature and time on the mineralogical, chemical and textural properties of ashes and chars from the combustion and pyrolysis of wheat straw. We have discovered that a valuable product, bio-silicate solution, can be formed without the need for additional chemicals and with lower energy intensity than the current process. A high surface area, microporous material can be formed as a co-product. We are utilizing the bio-silicate solution to form new, entirely bio-derived, fire resistant, moisture resistant composite boards. These results and the methods used should be applicable to a wide-range of agricultural feedstocks in different countries. We have discovered, for the first time, that the inherent alkali in unleached wheat straw is sufficient to solubilize up to 30% of the silica in ash and char at room temperature. Lower temperatures and generally shorter times increase the concentrations of silicon, potassium, magnesium, phosphorous, sodium and sulfur in solution, whilst calcium levels increase with higher temperature. We have correlated these observations to the changes in the inorganic components within the ash during thermochemical conversions. Variations between the impacts of pyrolysis and combustion are observed.

This research enables new valuable products to be made entirely from ash and char under benign conditions. In addition, the understanding gained should enable more efficient recycling of all elements in ash. The high silica and alkali content of wheat straw ashes indicates that they could be directly applicable for the formation of alkali silicate solutions. These are widely used with applications including the formation of zeolites, used as binders, in water treatment and pulp bleaching. This is a novel approach eliminating the need for additional chemicals and creating a higher value application for biomass ashes. We have demonstrated that wheat straw ash could be used to produce potassium silicate solution as a new valuable by-product of its combustion. It was also found that incomplete combustion at high temperatures, following leaching of ashes can lead to the formation of porous activated carbons and inorganic materials, demonstrating yet another valuable use for this waste material.

3 CASE STUDY: LCD WASTE TO VALUABLE CHEMICALS

The influence of Liquid Crystal Displays (LCDs) on modern society has been dramatic. LCDs are now almost all electronic goods including large area high definition televisions. The success of LCDs has also led to significant amounts of LCDs in waste streams. Approximately 2.5 billion LCDs are approaching their end of life and LCD waste electrical and electronic equipment (WEEE) is the fastest growing waste stream in the European Union.[4] The WEEE Directive 2002/96/EC of the European Parliament and of the Council on Waste Electrical and Electronic Equipment now requires the disassembly of all LCDs with an area greater than 100 cm^2 and those containing mercury backlights.[9]

In the UK alone it is predicted that over 10, 000 metric tons of LCD were available for recycling in 2010. Which equating to 9 tons of liquid crystals; 900 kg of indium and 8,000 tons of optical quality glass, which are currently lost in landfill or incineration.[10] This project investigated the recovery and reuse of valuable components from LCD waste including liquid crystal recovery, high value material development and indium recovery.

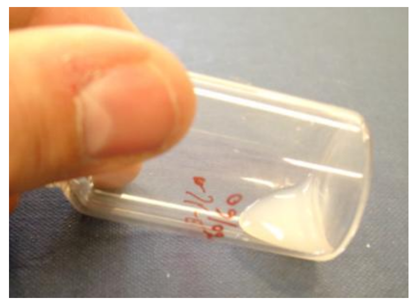

Figure 3. Extracted liquid crystal

Extraction of liquid crystals with volatile organic solvents such as dichloromethane offers a short term solution for the recovery of liquid crystals; these highly toxic and potentially carcinogenic solvents are not viewed as a “sustainable” long term solution to the problem. The development of a holistic and environmentally acceptable strategy for the recovery of liquid crystals and the reuse of other materials from LCD panels is key to the successful utilization of this valuable waste stream.[4] It was demonstrated that both liquid and supercritical carbon dioxide are effective and environmentally benign solvents for extraction of liquid crystals from display devices. Typically, the recovery with liquid carbon dioxide was in excess of 96% after 15 minutes (figure 3). Extractions with carbon dioxide demonstrate numerous advantages over traditional solvents such as dichloromethane; toxicity is reduced, no solvent residues remain after release of pressure and in many cases secondary purification processes are not required. Pilot scale extractions demonstrated high extraction yields consistent with those achieved on a laboratory scale. Variation of both temperature and pressure (and therefore density) has shown that a degree of fractionation is achievable at the point of extraction and/or collection.

As well as demonstrating that liquid carbon dioxide is efficient at extracting high purity liquid crystals from defunct LCDs, low value polymers such as polyvinyl alcohol (PVA) from polarizers can also be obtained. By heating the recovered PVA in water (gelatinization), cooling (retrogradation) and dehydration with ethanol, it is possible to produce a high surface area structured mesoporous material. Addition of iodine to virgin PVA is essential in changing the micro-structure of PVA and thereby allowing expansion to take place. Use of recovered PVA required no additional iodine, producing expanded materials with high surface areas (95.0 m^2 g^{-1}) and total pore volumes (0.56 cm^3 g^{-1}). These materials may find use in many applications including tissue scaffolds, due to the high surface area and compatibility with the human body.[4] The antimicrobial properties of these materials were enhanced by the simple reaction of silver nitrate with the PVA/iodine complex to form silver nanoparticles encapsulated within the polymer matrix. These materials demonstrated excellent antimicrobial properties against both *Staphylococcus aureus* and *Escherichia coli* (figure 4).

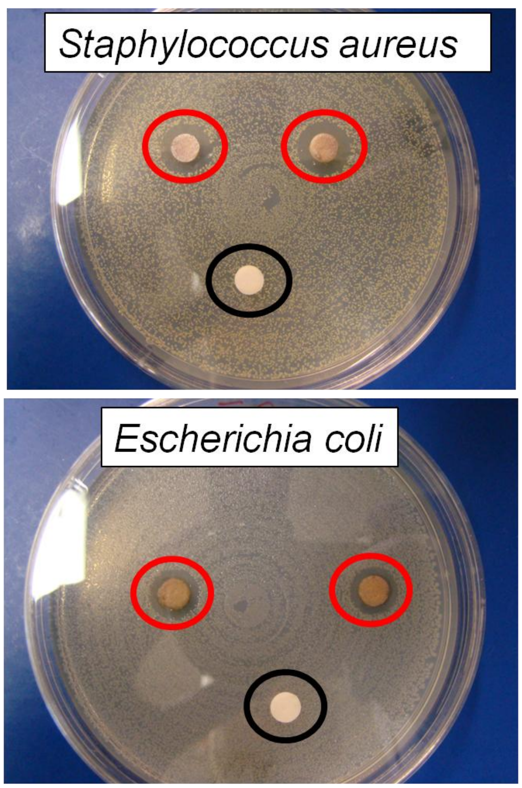

Figure 4. Inhibition of bacteria growth by PVA-Ag coated disks

Traditional supplies of elements such as indium are running out. Reserves of indium, vital for consumer electronics including LCD screens, solar cells and semiconductors, may be used up in 13 years.[5] These are unique and finite elements and we are quickly dispersing them throughout our environment, making it more costly and difficult to recover them. This emphasises the necessity for a new approach to waste utilisation, especially waste electrical and electronic equipment (WEEE). We must attempt to recover all elements and reuse them in close-looped systems, limiting the demand for new supplies and increasing the lifetime of our reserves infinitesimally. This project has successfully extracted and concentrated indium from LCD waste through acid leaching. It is vital for the future of this technology and others that full recovery of indium and other valuable elements is achieved.

CONCLUSIONS

Through the use of green chemical case studies it has been demonstrated that materials that would traditionally be regarded as a waste problem can be converted into high value chemicals or materials.

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