Environmental engineering: From laboratory data to industrial applications.

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INTRODUCTION AND OBJECTIVES

The high rates of global development produce enormous anthropogenic changes that added to natural ones give rise to a decrease of life quality, ecosystems equilibria and natural resources and excessive land use and waste generation. A way of overcoming environmental issues found in this research group is the transformation of residues into value added substances and materials, aiming to close an industrial cycle, and at the same time solutions for environmental problems are reached. Materials prepared from agricultural residues may be considered as Renewable Raw Materials (RRM) (1,2), with the added bonus of avoiding other that are often non-renewable, under the so-called “cradle to grave” philosophy.

Agriculture is one of the pillars of society, given the increasing world population and countries which have large agricultural resources, such as Spain, also produce vast amounts of residues, that can produce environmental hazards on the environment. However, these agri wastes can also be considered as a source of low cost RRM with interesting applications like energy production, advanced materials or platform chemicals inside a Biorefinery concept, with the added bonus of not competing with food resources (3-5). The work presented is based in some examples of our research on the valorisation of agroindustrial wastes useful in:

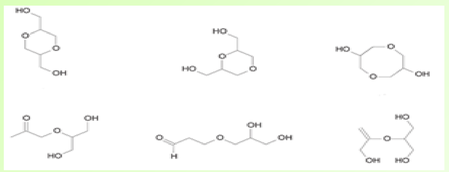
1. Preparation of adsorbents capable of competing with commercial ones for effluent cleaning
2. Catalysts developed from own company`s wastes transform biodiesel waste into value added substances
3. Multivalorization of fruit juice processing wastes into valuable chemicals, pectin and biomaterials for tissue engineering of hard and soft tissues.

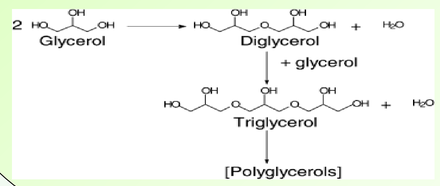
Etherification of waste glycerol from biodiesel production with company´s own residues

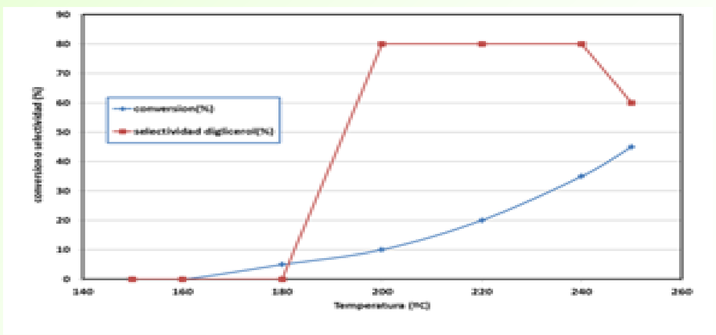
Renewable energies are considered as one possible solution to world energy crisis, being biodiesel one of the most studied. Biodiesel production generates ca. 10% glycerol as a sub product, this leading to a fall in glycerol prices, making the search for its industrial applications a necessity. Etherification is a promising alternative, since glycerol ethers can be used as such or with slight modification as platform chemicals for cosmetics, food additives, lubricants, monomers for polymerisation processes, fuel additives, etc.

A biodiesel producing company contacted our group with the aim to valorise glycerol. The residues of this industry were transformed into catalysts to produce glycerol ethers. The catalysts prepared in this way are in fact Ecomaterials and their origin makes them competitive with commercial ones. Production of ethers with more than three glycerol molecules competes with di-ethers and thus control of the selectivity is important. Etherification of glycerol with acid catalysts was found to be difficult to control, however, the catalytic transformation of glycerol into ethers, carried out with basic catalysts allows more controllable results. A bibliographic search showed alkaline and alkaline earth oxide catalysts that achieved interesting conversions with selectivities to di- and tri-glycerols, at 220 ºC (20 h) giving rise to higher glycerol conversions on the more basic catalysts: 5 % (MgO), 58 % (CaO), 80 % (SrO) and 80 % (BaO). Furthermore, the use of heterogeneous catalysts derived from the agriresidues, compared to homogeneous bases has the added bonus of being easily separated from the reactants and products for reuse with the corresponding economic benefits and by carrying out the reaction in the absence of solvent, in this work only filtering the catalyst was needed, with evident economic and environmental advantages.

The conditions used for glycerol etherification were chosen with catalysts from sunflower oil production agriresidues (RP45), given their composition of alkaline (26 % K) and alkaline-earth cations (5 % Mg, 7 % Ca) make them of basic nature. Adsorbed acetic acid indicated that RP45 contained basic centres of low (100-200 ºC), medium (200-500 ºC) and high basicity (550-650 ºC) and can catalyse Knoevenagel condensation reactions.







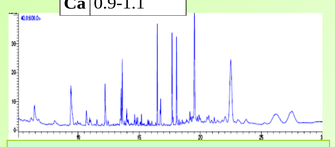
Cleaning of industrial effluents with agroindustrial waste derived adsorbents

Industrial effluents often have variable concentrations of toxic substances and adsorbents are ideal for their decontamination, with good economic turnover. The sorbates diffuse to the adsorbent surface and are stored inside the pore structure, being of utmost importance its surface area and porosity.

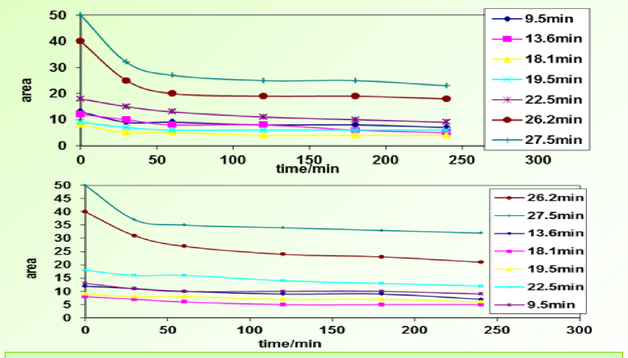
The research group was contacted to treat wastewaters containing terpenoids from industrial preparation of fine chemicals, in order to reduce water consumption, economic expenditure and environmental hazards.

Adsorbents were prepared from cereal agriresidues (of difficult storage and transport due to their high volume to weight ratio) and compared to commercial ones. The results indicated better adsorption and therefore cleaning capacities in the residue derived materials than in the commercial ones. The chemical oxygen demands (COD) after wastewater treatment with agri residue derived adsorbents allowed the treated water to be reused, being the performance of the reside derived adsorbents much better than that of the commercial ones.

%	Adsorbents
C	1.0-7.0
Si	42.1-55.6
P	0.4-0.5
K	2.3-3.6
Ca	0.9-1.1



Upper: Analysis of adsorbent (ICP)
Lower: Waste water analysis (GCMS).

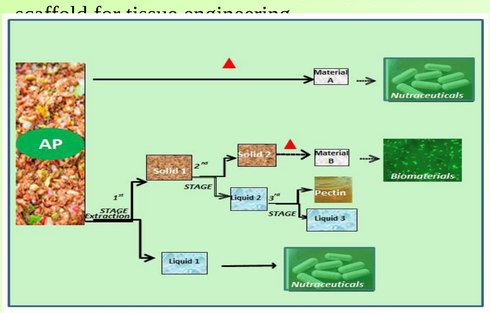


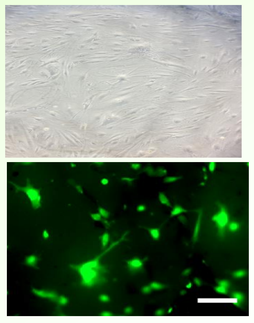
Adsorbent performance (Retention times (min)). Upper: Residue derived adsorbent.
Lower: Commercial adsorbent

Multivalorization of fruit wastes

This research used an industrial waste from juice production as RRM to develop materials that can be utilized as biocompatible scaffolds for osteoblasts and chondrocytes growth, employed in tissue engineering, valuable extracts that can be used as nutraceuticals and pectin. All of these have much higher value than the original raw material, pectin can be priced up to 1 euro/g, chlorogenic acid is *ca.* 120 euros/g, caffeic acid 3-5 euros/g and especially the scaffolds that are usually made by synthetic methods using non RRM materials with high fabrication costs and sold at prices higher than 100 euros/g, while the residues used here have prices lower than 100 euros per ton. Therefore there are clear environmental and financial incentives in transforming this wastes into valuable substances and materials.

The procedure consists in sequential extractions of antioxidants, pectin and finally the preparation of a biocompatible material, giving priority to the latter due to its importance as a renewable scaffold for tissue engineering





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5. Recent Publications: M. Yates, M.A. Martin-Luengo, M. Ramos, et al. Synthesis of p-cymene from limonene, a renewable feedstock (App. Cat. B:Env. 81 (2008)218-224). Biomaterials from beer manufacture waste for bone growth scaffolds (Green Chemistry Letters and Reviews 4 (2011) 229-233). Renewable Fine Chemicals from rice and citric sub products (Ecomaterials) (Applied Catalysis B: Env. 106 (2011) 488-493). Multivalorisation of apple pomace towards materials and chemicals. Waste to wealth (J. Cleaner Production 143 (2017) 847-853). Beverage waste derived biomaterials for tissue engineering (Green Chemistry (accepted 2017))