PHOTOSYNTHETIC MEMBRANES IN INDUSTRIAL WASTE MINIMIZATION AND RECOVERY OF VALUABLE PRODUCTS

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An entirely innovative photochemical method, based on photographing, has been investigated and set-up technologically in recent years, for the preparation of composite polymeric membranes [1-3]. It consists in the photoinduced grafting and graft-polymerization of appropriately thin layers of multifunctional comonomers and/or their composites (with inorganic, organic or organometallic sorbents, molecular sieves, ion-exchangers, reagents, catalysts, photocatalysts, facilitated transport agents, biopolymers, cells, antigens, and the like onto macro- or microporous substrates, the porosity of which can thus be smoothly modified and controlled. These membranes have been termed "photosynthetic", that is photochemically synthesized, in order to designate that photochemistry (photochemical synthesis of membrane structures) is the new method of membrane preparation, and plays a decisive role not only during grafting and graft-polymerization of monomers and prepolymers, but also in controlling, by photocrosslinking, transport properties of photocomposites, as well as in the manufacture technology of these synthetic membranes [4-6] and in their physico-chemical behaviour [1-3].

Methods of photosynthetic membranes manufacture, as well as their characterizations and applications have been extensively reviewed [1-3].

We shall, instead, focus our attention towards applications of photosynthetic composite membranes to the problems of industrial waste minimization as well to the simultaneous recovery of valuable products or by-products in these wastes. Some examples, chosen among the most recent investigations, will be shown, in order to underline the enormous possibilities offered by photosynthetic composite membranes also in the field of environmental applications concerning recovery of products by saving energy and resources too, possibilities which can be hardly and scantily, to do not say impossibly, afforded by any other existing membrane process, with such an easiness and flexibility of operation, accompanied by extremely low, potential costs conferred by this kind of membranes.

Waste minimization in the manufacture process of membranes

The first example, which deserves to be cited, is that of waste minimization during the
manufacture process itself of the innovative membranes we are concerned with. In the usual, traditional technology of polymeric membrane manufacture, as is currently used today and as is well known, in the first step, the polymer has to be dissolved in a suitable solvent or combination of solvents. In a second step, a wet film of this polymer solution is contacted with a non-solvent for the polymer, in such a way that the desired final properties of the membrane are obtained. At a further stage in the process, this solvent is removed by exchange with (usually) water.

Enormous amounts of solvent systems and their aqueous solutions result, which have then to be recovered and separated into their components by distillation procedures, with production of corresponding, remarkably large, quantities of wastes, which often contain toxic compounds and need costly as well as energy consuming treatments.

By this way, and somewhat paradoxically, membrane processes which intend to rationalize energy consumption, product recovery and separation, make use, in the traditional and still used technology of membrane preparation itself, of methods which need abundance of energy, of solvents, and of water, and produce exceedingly large amounts of wastes to be disposed.

On the contrary, no solvent is necessary in the manufacture of photosynthetic membranes, and consequently no waste, either liquid or gaseous, is practically generated. Therefore, besides all technological advantages, which have been enumerated for this technology [3], that of being able to minimize all kinds of waste, by reducing them substantially to zero, has to be underlined, together with a fairly limited energy consumption, owing to the very rapid photochemical grafting and graft-polymerization.

Recovery of cesium cations at high concentration

Facilitated transport and extraction of metal cations by macrocyclic compounds have been an active field of study in the last fifteen years or so [7-13]. Based on fundamental studies, a process for recovery of cesium cations at high concentration from solution of nuclear waste materials has been set-up [14]. This process contemplates transport across three liquid phases. The first phase is aqueous and contains a plurality of degradation products of uranium splitting, including cesium, with an atomic weight about half respect to that of uranium. The second phase is a defined mixture of dichloromethane and carbon tetrachloride, in which calix[8]arene is dissolved. The third phase acts a "liquid membrane", allowing metallic cations to migrate from the first to the third phase, rate transfer of cesium cation by calixarene being much higher than that of the other alkaline ions. This "liquid membrane" transfer process, as far as is known appears to be the only selective "membrane" process able to separate alkali metal cations. While revealing the feature of high selectivity, which is shown by the molecule of the macrocyclic compound, this method, however, presents all known disadvantages of liquid membrane systems, from the industrial point of view.

Photosynthetic membranes have now been prepared [15] immobilizing 0.001-0.045 mol/Kg of calix[8]arene, by photografting a mixture of commercial acrylate polyester and tetraethylene glycol diacrylate (photoinitiated with a photocatalytic system [4]) onto an ultrafiltration membrane immobilizing, in its turn, 20 wt.% of active carbon in the photochemically grafted layer. Solutions containing LiOH, NaOH, KOH, RbOH, or CsOH, at