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International Chemical Engineering Congress 2013: From fundamentals to applied chemistry and biochemistry



Foreword

This thematic issue of the *Comptes rendus Chimie* is devoted to the 1st International Chemical Engineering Congress – ICEC'13 held from 16 to 19 December 2013 in Djerba (Tunisia). Fifteen papers, covering important subjects of wastewater and exhaust gas treatments, have been selected and after peer-reviewing eleven were accepted for publication. They are focusing on recent developments of effluents management for improving performance and minimizing the impacts of pollutants on air and water. The variety of operating techniques covers adsorption, photocatalysis, electrochemical oxidation, biological treatment, chemical looping combustion, ultra-filtration, and catalytic ozonation.

With increasing concern about environmental pollution that the developing countries are facing today and the need for preventing the severe damage caused by the uncontrolled industrial effluents to the environment, the development of efficient techniques has received particular attention in recent years. Physical, chemical and biological treatments, membrane technology are related methods for pollution reduction issues, and they have attracted progressively more and more consideration from both academics and industrials.

ICEC'13 was the first international conference organized in Tunisia in the field of chemical engineering initiated by Professor Abdelmottaleb Ouederni. The main objective of the ICEC conferences is to offer opportunities for scientific connections. This scientific meeting includes presentations and discussions on the recent research findings in many chemical engineering issues such as modelling and optimisation, catalysis and reaction, process control, water treatment, and atmospheric pollution reduction. Another important activity during the ICEC'13 has been the exchange between international scientific researchers, the conception of new research projects and the implementation of collaborations between research laboratories.

The ICEC'13 conference has been hosted by the Laboratory of Process Engineering & Industrial Systems, National School of Engineers, University of Gabes, and co-organized by the Tunisian Chemical Engineering Society (TChES). The conference attracted 344 abstracts from 13 countries. Of these, 214 papers were selected by the ICEC'13 International Scientific Committee for inclusion in the final programme, which included four plenary lectures from leading scientists around the world (France, Germany, and the United Kingdom) and 88 oral presentations and 126 posters. All papers have undergone a formal peer-reviewed procedure to ensure the highest possible technical quality, with assistance from more than 80 reviewers [1].

For this thematic issue of the *Comptes rendus Chimie*, 11 manuscripts have been selected.

The first one is entitled “N₂O and NO emissions during the wastewater denitrification step: influence of temperature on the biological process” [2]. The denitrification process occurring in wastewater treatment plants (WWTPs) is responsible for emissions of nitrous (N₂O) and nitric (NO) oxides. These compounds indirectly lead to the global warming. In this study, the impact of the temperature on N₂O and NO emissions was investigated. Experiments were achieved at pH 7 in a batch reactor with acetate as the carbon source. The nitrogen source was nitrates (NO₃⁻), and the COD/N ratio was set to three. The results showed that NO and N₂O emissions increased when temperature decreased. NO emissions appeared only at 10 °C and 5 °C, with respectively 8% and 18% of the total denitrified nitrogen. N₂O emissions increased from 13 to 40, then 82% of the total denitrified nitrogen, respectively at 20, 10 and 5 °C. Several hypotheses were suggested to explain these results: a general enzymatic slow down, enzymatic inhibitions, electron donor competition between the different enzymes and metabolic pathway alterations.

The aim of the second one, “Wastewater treatment by cyclodextrin polymers and noble metal/mesoporous TiO₂

photocatalysts” [3] was to prepare cyclodextrin (CD) polymers from a cross-linking agent and β -CD, and to compare its efficiency vis-à-vis an emerging advanced oxidation process (AOP): photocatalysis for reducing the pollutant concentration in real wastewater effluents sampled in the output of two wastewater treatment plants (WWTPs) located in the North of France. Therefore, cross-linked cyclodextrin (CD) polymers were synthesized and a mesoporous TiO_2 was prepared by a templating sol-gel method, and modified with precious metals such as Ag, Au and Pd.

For both techniques, a decrease in the total organic carbon (TOC) content was observed due either to the adsorption of pollutants by CD polymers or to the mineralization of pollutants by photocatalysis. The authors clearly demonstrated the suitability of a β -CD cross-linked polymer to be used as an adsorbent for the removal of organic pollutants from wastewater. Polymers have good reusability following a simple regeneration procedure. The doped TiO_2 photocatalysts present also a good activity. The two investigated processes (adsorption and photocatalysis) could be used consecutively. Adsorption could be used to concentrate pollution and photocatalysis to mineralize the pollutant after regeneration of the adsorbent.

The third paper is entitled “Direct electrochemical oxidation of a pesticide, 2,4-dichlorophenoxyacetic acid, at the surface of a graphite-felt electrode – Biodegradability improvement” [4]. The context of the study is that pesticide biorecalcitrance is related to the presence of complex aromatic chains or to the presence of specific bonds, such as halogenated bonds, which are the most widespread. In order to treat this pollution at its source, namely in the case of highly concentrated solutions, selective processes, such as electrochemical ones, can appear especially relevant to avoid the possible generation of toxic degradation products and to improve their biodegradability in view of a subsequent biological mineralization. The authors show the feasibility of an electrochemical process for pesticide pre-treatment, since it improved significantly the mineralization rate and thus significantly shortened the length of the biological treatment if compared to non-pre-treated 2,4-dichlorophenoxyacetic acid solutions. The absence of hydroxyl radical formation was demonstrated, showing that the pre-treatment can be considered as a “direct” electrochemical process instead of an advanced electrochemical oxidation process. However, its selectivity was not as high as expected, due to the various degradation products identified and to the biorefractory degradation products remaining at the end of activated sludge culture. Nevertheless, the relevance of the proposed combined process was confirmed since the overall mineralization yield was close to 93%.

In the fourth paper, “Relevance of a combined process coupling electro-Fenton and biological treatment for the remediation of sulfamethazine solutions – Application to an industrial pharmaceutical effluent” [5], the authors implemented a combined process coupling an electro-Fenton pre-treatment and biological degradation in order to mineralize synthetic and industrial pharmaceutical

effluents, containing a veterinary antibiotic, sulfamethazine (SMT). The electro-Fenton pre-treatment of SMT synthetic solution was first examined and the obtained results showed a total SMT degradation for an initial SMT concentration of 0.2 mM after 30 min of electrolysis at pH 3, 18 °C, 500 mA, while the level of mineralization remained low (2.1 and 18.1% for 30 and 60 min electrolysis times), showing a significant residual organic content. Hence, the authors performed a subsequent biological treatment to complete the mineralization of the SMT electrolyzed solutions. They showed a significant level of mineralization after 18 days of culture, 61.4% for 30 min of pre-treatment. The same electrolysis conditions were applied to an industrial pharmaceutical effluent. This pre-treatment showed a total SMT removal in the effluent after 100 min of electrolysis, while the mineralization yield remained also low (7.5%). The mineralization yield during the subsequent biological treatment increased to an overall yield of 81.4%. Hence, the presented work proves that an integrated electro-Fenton-biological treatment process could be an efficient technology to remediate the issue of industrial pharmaceutical effluents.

The aim of the work presented in the fifth paper, entitled “Study of the performances of an oxygen carrier: experimental investigation of the binder’s contribution and characterization of its structural modifications” [6] was to investigate the binder’s (NiAl_2O_4) contribution to the performances of an oxygen carrier $\text{NiO}/\text{NiAl}_2\text{O}_4$. Indeed, experimental tests performed with this oxygen carrier showed that the reduction capacity can be higher than the amount of oxygen available on the nickel oxide. For this, oxidation/reduction cycles have been carried out with the binder in a fixed-bed reactor using CO as a fuel. The influence of the reduction parameters on the total reduction capacity of NiAl_2O_4 was studied using an experimental methodology design. The results revealed that the binder reacts significantly with the fuel to form CO_2 and its total reduction capacity increases with the operating temperature. XRD analyses performed on the binder (on the fresh one and after several cycles) showed a shift and an enlargement of the diffraction peaks corresponding to the nickel aluminate. This shift to the peaks of γ -alumina can be attributed to a progressive decomposition of the NiAl_2O_4 spinel phase into alumina and NiO. The resulting metal oxide phase formed would be responsible for the activity of the binder in the oxidation of fuel (CO). These results showed that nickel aluminate can no longer perform its binder function and could involve nickel sintering.

The sixth paper, “Stabilisation of the water permeability of mineral ultrafiltration membranes: an empirical modelling of surface and pore hydration” [7], focused on the study of the hydration phenomenon operating in Na-mordenite membranes during the conditioning step (stabilisation of filtration properties). In a first step, experimental (filtration of pure water) tests were carried out immediately after putting the membrane in its casing and until the stabilization of the membrane permeation flux. The hydraulic permeability evolution showed that there are two separate steps during membrane conditioning. A numerical approximation of the hydraulic permeability

during the conditioning step was carried out. The first part of the equation expressed a fast decrease of the membrane permeability during the beginning of the conditioning step (several hours). This behaviour was attributed to a surface hydration of the membrane and also to a modification of crystals framework. The second one was a slower phenomenon that took place until the conditioning step ended. It was attributed to the (intracrystalline) hydration of micropores.

The seventh paper is entitled “Activated carbon prepared by physical activation of olive stones for the removal of NO₂ at ambient temperature” [8]. During this investigation, the authors prepared activated carbon from olive stones by physical activation using water vapour at 750 °C. Textural, morphology and surface chemistry characterizations of the prepared materials were achieved using several analytical techniques such nitrogen adsorption, scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and temperature-programmed desorption coupled with spectrometry (TPD–MS). NO₂ adsorption tests were performed for different inlet gas compositions and temperatures. NO₂ may adsorb directly on the oxygenated surface groups, and can also be reduced into NO. Therefore, a second NO₂ molecule adsorbs on the oxygen left on the carbon surface. TPD performed after NO₂ adsorption showed the presence of various surface groups. The adsorption capacity was about 131 mg/g, which is higher than that of several activated carbons prepared from classical lignocellulosic biomass. NO₂ reduction into NO decreased with increasing the inlet oxygen concentration. In contrast, a slight decrease in the NO₂ adsorption capacity was observed with increasing temperature. The authors mention that activated carbons prepared from olive stones by steam activation could be used as efficient adsorbents for NO₂ removal.

The eighth paper, “Raw and treated marble wastes reuse as a low-cost material for phosphorus recovery from aqueous solutions: efficiencies and mechanisms” [9] deals with phosphorus removal from synthetic solutions by raw and calcined powdered marble wastes (RPMW and CPMW) in batch mode under different experimental conditions. The results showed that RPMW and CPMW have high removal efficiencies, especially in acidic media. The maximum phosphorus removal capacities were evaluated to 103.9 and 181.2 mg·g⁻¹ at an initial pH of 5 and an aqueous concentration of 350 mg·L⁻¹. The authors mention that phosphorus removal by RPMW occurred mainly through adsorption. In contrast, for CPMW, phosphorus was removed not only by adsorption, but also by precipitation as calcium phosphates complexes. Specific analyses using scanning electron microscopy, energy-dispersive spectroscopy, X-ray diffraction and Fourier transform infrared spectroscopy confirmed that this precipitate was probably hydroxyapatite. A second interesting result demonstrated in this investigation was the important ability of CPMW in removing phosphorus from highly concentrated dairy wastewater (C_{0,P} = 1000 mg·L⁻¹), since only a dosage of 10 g·L⁻¹ was enough to ensure more than 97% of phosphorus removal.

In the ninth paper, “Evaluation of an activated carbon from olive stones as an adsorbent for heavy metal removal

from aqueous phases” [10], the authors prepared a microporous activated carbon by chemical activation of olive stones and evaluated its performance for removing Cu(II), Cd(II) and Pb(II) from single and binary aqueous solutions. In the first part, the activated carbon sample was characterized using N₂ adsorption–desorption isotherm, SEM, XRD, FTIR, and Boehm titration. In the second part, the effects of the initial pH and the contact time were studied in batch techniques. Adsorption kinetic rates were found to be fast and kinetic experimental data fitted very well the pseudo-second-order equation. The adsorption isotherms fits the Redlich–Peterson model and the maximum adsorption amounts of single metal ion solutions follow the trend Pb(II) > Cd(II) > Cu(II). The adsorption behaviour of binary solution systems showed a relatively high affinity of the mixture with Cd(II) or Pb(II) for Cu(II) at the surface of the activated carbon. An antagonistic competitive adsorption phenomenon was observed. Desorption experiments indicated that about 59.5% of Cu(II) and 23% of Cd(II) were desorbed using a diluted sulphuric acid solution.

The tenth paper, “Copper supported on porous activated carbon obtained by wetness impregnation: effect of preparation conditions on the ozonation catalyst’s characteristics” [11], studies a heterogeneous catalyst copper supported on activated carbon (Cu–AC) that was developed using a wetness impregnation process. The effect of preparation conditions such as impregnation rate and calcination conditions (temperature and time) on the catalyst’s characteristics was examined. The characterization of the prepared catalyst was performed using nitrogen adsorption, Boehm and pH_{pzc} analyses. The authors showed that the catalyst’s properties and the functional surface groups were affected by the operating conditions. The highest measured surface area, 1040 m²/g, was obtained for the activated carbon (AC) impregnated with 12% of Cu loading and calcined at 550 °C for 2 hours. The performance of the prepared samples was evaluated for nitrobenzene (NB) adsorption and catalytic ozonation. The obtained results showed that copper impregnation showed an improvement of the nitrobenzene (NB) adsorption capacity of the activated carbon. Moreover, the use of Cu/AC for heterogeneous catalytic ozonation enhanced the degradation efficiency of nitrobenzene (NB) significantly compared to the ozonation with non-impregnated AC.

The last paper, “Enhancement of methylene blue removal by anodic oxidation using BDD electrode combined with adsorption onto sawdust” [12], investigates methylene blue (MB) removal from aqueous solutions by anodic oxidation (AO) using a boron-doped diamond (BDD) electrode, adsorption onto sawdust and combined treatment. The results proved that AO presents a high efficiency in removing both colour and COD for a wide pH interval. The total mineralization of the dye solution was performed in 6 hours, which corresponds to relatively high energy consumption. On the other hand, a high sawdust dosage (12 g·L⁻¹) was necessary to ensure 98% of colour and 81% of COD removal. The authors proved that combining AO and adsorption onto sawdust constitute a very interesting technology. In particular, AO for one hour

followed by sorption permits an energy consumption reduction of $80 \text{ W} \cdot \text{h} \cdot (\text{g}_{\text{COD}})^{-1}$, a reduction by more than 24 times of the adsorbent dose and an enhancement of colour and COD removal, indicating that sawdust is efficient in removing, not only the MB initial molecules, but also the electrogenerated by-products.

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