



Sol-gel preparation and characterisation of SnO_2 powders employed as catalyst for phenol photodegradation

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Received 18 August 2011; received in revised form 13 April 2012; accepted 21 January 2013

KEYWORDS

Tin dioxide;
 Sol-gel;
 Photocatalysis;
 Phenol degradation.

Abstract. Crystallized pure SnO_2 powders were prepared by the sol-gel process, and were used as photocatalyst for the degradation of phenol under UV light at pH 6.5 and a temperature of 20°C. The physical properties of photocatalyst were characterized by X-ray diffraction, Scanning Electron Microscopy, nitrogen adsorption-desorption and Ultraviolet-visible diffuse reflectance spectroscopy. The influences of different operating variables, such as the pH, the photocatalyst loading, and the initial concentration of phenol, were studied to improve the efficiency of phenol degradation.

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1. Introduction

Heterogeneous photocatalysis is nowadays recognized as a strategic area of growing importance in what concerns the development of sustainable technologies for energy production and storage [1], green chemical synthesis [2], and water [3] and air [4] treatments. Indeed, upon band gap excitation of the photocatalyst (semi-conductor), the photoinduced electrons and positively charged holes can reduce and oxidize the species adsorbed on the semiconductor particles [5-7].

Phenol and its derivatives are toxic hazardous compounds, because they are suspected to be carcinogens and are known as precursors of dioxins. They often appear in wastewaters from many heavy chemical, petrochemical, and oil refining industries. Because of their toxicity and poor biodegradability, phenolic wastewaters must be specially treated before disposing off. Various treatment techniques have been

applied to remove or eliminate phenolic compounds from wastewaters, including chemical oxidation [8], solvent extraction [9], membrane techniques [10], adsorption [11], coagulation-flocculation [12], biological processes [13], and photodegradation [14]. So, heterogeneous photocatalysis with semiconductor particles represents an attractive solution for the degradation of phenol at room temperature [15,16].

SnO_2 , semi-conductor with a band gap equal to 3.6 eV [17], is used in several applications, such as gas sensors, photocaptors, antistatic films, and oxidation catalysts because of its interesting optical properties, its transparency in visible range and its very high chemical stability [18]. Furthermore, the dual valency of SnO_2 facilitates a reversible transformation of the surface composition from stoichiometric surfaces with Sn^{4+} surface cations into a reduced surface with Sn^{2+} surface cations, depending on the oxygen chemical potential of the system and on the size of SnO_2 particles [19]. These redox phenomena present at the surface of SnO_2 are particularly attractive for photocatalytic applications, such as the phenol photodegradation.

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It is particularly interesting to synthesize SnO_2 by the sol-gel process, because sol-gel chemistry is an efficient tool for controlling morphology and reactivity of solids. In recent decades, it has permitted the development of new highly dispersed materials, presenting both good homogeneity and purity [20–22].

The first aim of this work is to synthesize a crystallized pure SnO_2 powder by the sol-gel process. SnO_2 powder is characterized by using techniques, such as nitrogen adsorption isotherms, X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and UV-Vis spectroscopy. The second aim of this work is to study the degradation of phenol on SnO_2 photocatalyst and to establish the relationships between operating variables, such as the pH, the photocatalyst loading, the initial concentration of phenol, and the efficiency of phenol degradation.

2. Experimental section

2.1. Photocatalyst preparation

37 mmol of SnCl_2 (Aldrich, Purity: 99.99%) was mixed in 100 mL of absolute ethanol (Merck, Purity: 99.9%) under stirring, and refluxed at 80°C under nitrogen ambient in a closed vessel for 2 h. A white tin alkoxide powder was obtained after heating of solution at 80°C under vacuum condition [23] to which 50 mL of absolute ethanol and 50 mL of distilled water were added. This solution was then stirred and heated for 2 h at 50°C . The stirring was stopped, and gelation underwent in about 5 days. Afterwards, the gel was dried at 110°C for 2h. Finally, the powder was calcined under flowing air (0.1 mmols^{-1}) at 700°C for 4h.

2.2. Photocatalyst characterization

Nitrogen adsorption-desorption isotherms were measured at -196°C on a Fisons Sorptomatic 1990, after outgassing for 24 h at ambient temperature.

SnO_2 particles sizes were examined by SEM on a Jeol JSM-840 under high vacuum at an acceleration voltage of 20 kV. The samples were deposited onto carbon tape and coated with gold in a Balzers plasma sputterer (30 s at 30 mA).

XRD was used to determine the nature and the size of crystalline phases of SnO_2 . Patterns were obtained with hand-pressed samples mounted on a Philips PW 1830 goniometer, using the $\text{Cu-K}\alpha$ line ($\lambda = 0.15458 \text{ nm}$).

Diffuse reflectance measurements in the UV/Vis region (250–800 nm) were performed on a Varian Cary 5000 UV/Vis/NIR spectrophotometer, equipped with a Varian External DRA-2500 integrating sphere, using BaSO_4 as the reference. Spectra were recorded in diffuse reflectance mode (R = reflection intensity), and were transformed into the absorbance coefficient ($F(R)$) by the Kubelka-Munk function, $F(R) = (1 -$

$R)^2/2R$ [24]. SnO_2 band gap energy value, E_g , was obtained by extrapolating the straight line portion of the plot to zero absorption coefficient.

The PZC (point of zero charge) of SnO_2 , that is the pH value, at which the electrical charge density on the support surface is zero, was determined by the method of Park and Regalbuto (Equilibrium pH at High Loading, EpHL) [25]: the solid material is soaked in water solutions of various starting pHs, and after stabilization, the pH is measured again. The PZC of the solid corresponds to a plateau in a plot of the final pH vs. the initial pH. Using a spear-tip semi-solid electrode (electrode accumet), the equilibrium pH of SnO_2 was measured over a wide range of initial pH values (from pH = 1 to pH = 13) adjusted using either HCl or NaOH solutions.

2.3. Photocatalytic experiments

To determine the photocatalytic activity of the synthesized material, the study of the degradation of phenol (Riedel-de Haën, Purity: 99.5%) under UV irradiation was realized.

The phenol degradation was carried out at 20°C , using a water-cooled cylindrical 200 mL glass reactor with external lamp (125 W UV lamps, Black light Mercury HgV). In a first time, the amount of catalyst powder, $[\text{SnO}_2]$, was kept at 1.0 g L^{-1} , the initial concentration of phenol, C_0 , was 0.2 g L^{-1} , and the pH of the solution was fixed to 6.5. In a second time, photocatalytic experiments were realized with varying operating variables: three different pH values (2.5, 6.5 and 12.5) adjusted with aqueous solutions of HCl and NaOH (2 mol.L^{-1}), ten photocatalyst concentrations $[\text{SnO}_2]$ (from 0.2 to 2.0 g L^{-1}) and five initial concentrations of phenol, C_0 (from 0.05 to 0.25 g L^{-1}).

Before each photocatalytic test, the mixture was kept in the dark for 1h to ensure that the adsorption-desorption equilibrium was reached before illumination. The sample was then taken out at the end of the dark adsorption period, just before the light was turned on, in order to determine the phenol concentration in solution, C_0' . In all cases, the difference between C_0 and C_0' were found to be negligible when compared to the error of the method.

When the lamp was turned on, the experiment started. After a given irradiation time, the sample was taken out from reactor, then the catalyst $[\text{SnO}_2]$ was removed by centrifugation, and the remaining phenol concentration in the solution was measured with the photocoulometric method of 4-amino-antipyrine [26], analyzed with a 1201 Shimadzu spectrophotometer.

Repetition tests were made to ensure the reproducibility of results. So all the photocatalytic results presented in this work are the mean of three replicates.

3. Results and discussion

3.1. Synthesis of crystallized pure SnO_2 by the sol-gel process

The crystallization of the calcined SnO_2 powder was checked by X-ray diffraction. In Figure 1, all the peaks [JCPDS Powder Diffraction File Card 5-0467] corresponding to tetragonal SnO_2 ($a = b = 0.4731$ nm and $c = 0.3173$ nm) are observed. The mean size of SnO_2 crystallites is calculated from Scherrer's formula, based on line broadening analysis [27], and is equal to around 36 nm.

By SEM analysis, it is observed in Figure 2(a) that the calcined SnO_2 powder is composed of aggregates of SnO_2 particles. The mean size of SnO_2 particles is equal to 50 nm (Figure 2(b)) and is in agreement with the SnO_2 particle size calculated from XRD measurements.

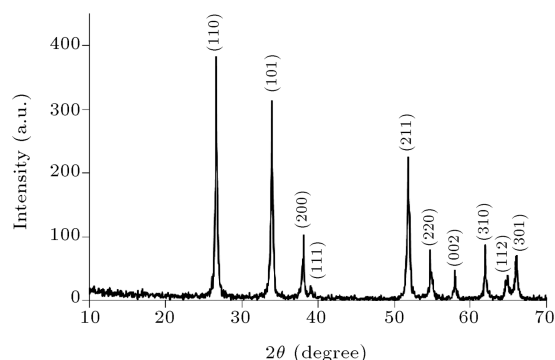
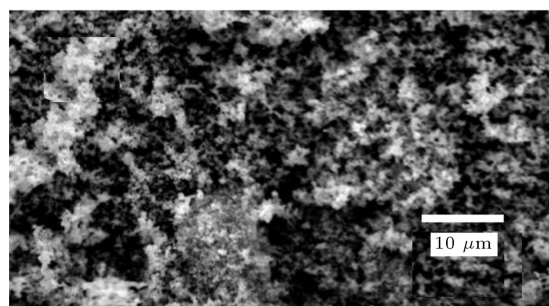
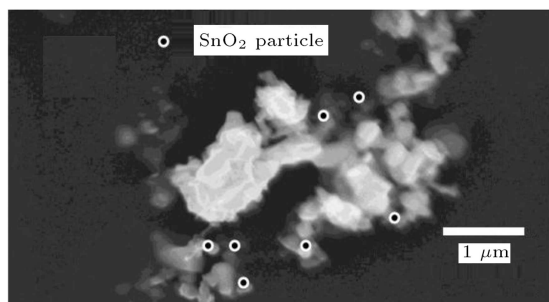


Figure 1. XRD pattern of the calcined SnO_2 powder.



(a)



(b)

Figure 2. SEM micrograph of the calcined SnO_2 powder: (a) 2000 $\times$; and (b) 10,000 $\times$.

A nitrogen adsorption-desorption isotherm was carried out to analyze the textural properties of the calcined SnO_2 powder shown in Figure 3. This isotherm displays a slight increase of the adsorbed volume at very small p/p_0 values, which is the characteristic of the presence of micropores (< 2 nm) inside SnO_2 particles [28]. Furthermore, the isotherm shows a hysteresis at p/p_0 from 0.4 to 1, due to capillary condensation in mesopores (2–50 nm) corresponding in the voids between the 30–50 nm SnO_2 powder particles [28]. Finally, the specific surface area obtained by the BET method [28] of the calcined SnO_2 powder is equal to $25 \text{ m}^2 \text{ g}^{-1}$; characteristic of a material with low porosity or a crystallized material [6,7].

Calculated from UV/Vis measurements, the Kubelka-Munk function $(F(R)E)^{1/2}$ as a function of energy level, E , for the calcined SnO_2 powder is shown in Figure 4. The sample displays a band-gap value, $E_g = 3.6$ eV, which is the band gap of a crystallized pure SnO_2 semi-conductor [17]. This sample is also the characteristic of a photoactive material in UV region ($\lambda < 380$ nm) [7].

Because one of the aims of this work is to determine the relationships between the initial pH of phenolic solution and the degradation of phenol, it is very important to know the PZC of the calcined SnO_2 powder. The PZC of the calcined SnO_2 powder is

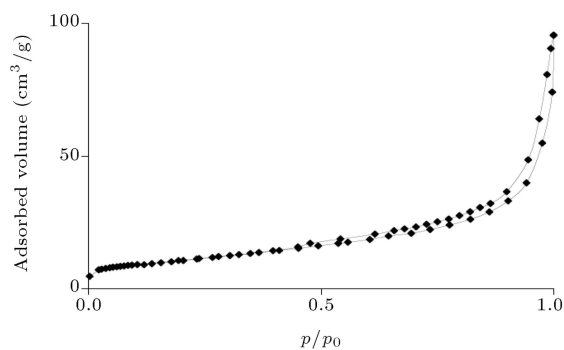


Figure 3. Nitrogen adsorption-desorption isotherm of the calcined SnO_2 powder.

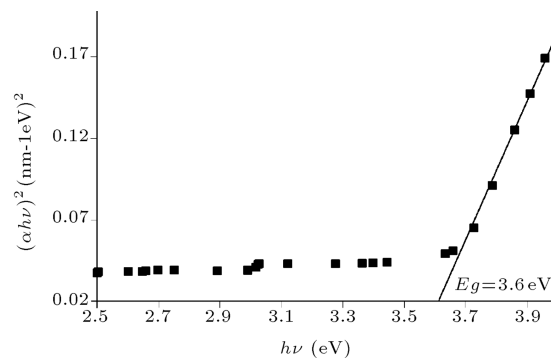


Figure 4. Determination of E_g of the calcined SnO_2 powder.

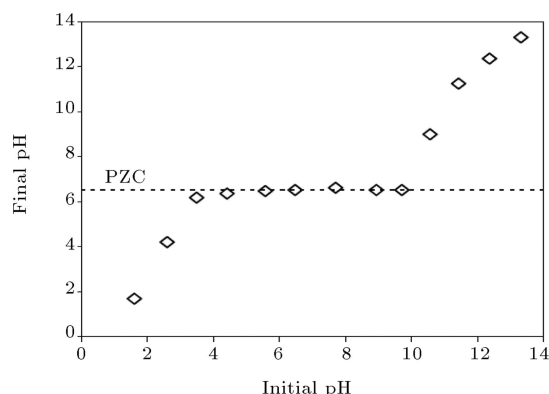


Figure 5. PZC determination of the calcined SnO_2 powder.

shown in Figure 5. This curve clearly shows a plateau at 6.52. The hydroxyl ($-\text{OH}$) groups that populate SnO_2 surface become protonated and so positively charged below 6.52, while the same hydroxyl groups become deprotonated and negatively charged above this characteristic pH value. So a SnO_2 powder placed in solutions at pH values below 6.52 adsorbs anions, while at pH values above 6.52, the same support adsorbs cations.

3.2. Photocatalytic activity of the calcined SnO_2 powder

3.2.1. Kinetic study

The photodegradation of phenol in contact with the calcined SnO_2 powder as a function of time is shown in Figure 6, with the following operating variables: three different pH values for the phenolic solution (2.5; 6.5 and 12.5), $[\text{SnO}_2] = 1.0 \text{ g L}^{-1}$ and $C_0 = 0.2 \text{ g L}^{-1}$. For pH = 6.5, which is the PZC of the calcined SnO_2 powder, for the first 40 min, the phenol photodegradation is fast: about 40% of phenol was degraded. Afterwards, the phenol photodegradation

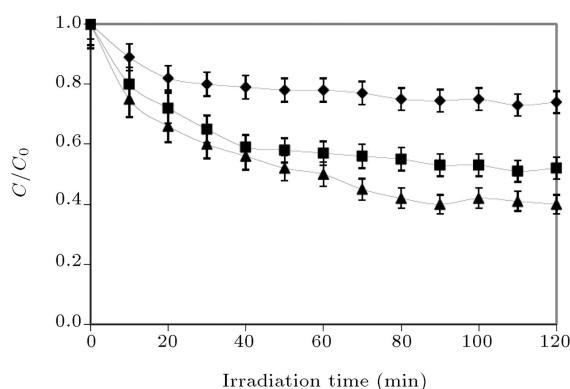


Figure 6. Degradation of phenol as a function of time where C_0 is the initial phenol concentration (g L^{-1}) and C is the phenol concentration at the time t . $C_0 = 0.2 \text{ g L}^{-1}$, $[\text{SnO}_2] = 1.0 \text{ g L}^{-1}$. pH = 2.5 ($\blacktriangle$), pH = 6.5 ($\blacksquare$) and pH = 12.5 ($\blacklozenge$).

rate decreases: about 10% of phenol was degraded for the following 80 min.

This decrease of the phenol degradation rate could be the consequence of the formation of by-products of phenol, such as hydroquinone and catechol, strongly adsorbed at the surface of the photocatalyst, as explained in [29]. So these by-products compete with phenol for adsorption sites on the surface of SnO_2 , and the phenol degradation is slowed down.

3.2.2. pH effect

At the time of phenol photodegradation, the decomposition targets are organic compounds that are usually anionic electron donors or neutral. At low pH ($\text{pH} < 6.52$), the positively charged tin hydroxide provides suitable surface for chemisorption of organic compounds. The organic compounds are adsorbed on the surface and are attacked directly by positive holes of valence band: the direct charge transfer is predominant with an increase of the degradation photoactivity [29]. Indeed, in Figure 6, at pH = 2.5, a slightly increase of the rate of phenol degradation is observed: after 120 min, about 60% of phenol is eliminated from the wasted water. At high pH ($\text{pH} > 6.52$), on the contrary, the organic compounds are mainly attacked by free activated oxidant species. The free activated oxidant species are supposed to exist in the aqueous phase adjacent to the surface of SnO_2 , because they cannot disperse far into the water due to short lifetime [29]: mass transfer limitations of phenol appear early at the surface of the photocatalyst, and the photocatalytic activity decreases. Furthermore, in a basic medium, phenol becomes the anion phenolate ($\text{C}_6\text{H}_5\text{O}^-$) for which it is nearly impossible to be adsorbed on the negatively charged surface of SnO_2 . Therefore, the photocatalytic efficiency decreases. This trend is observed in Figure 6, because at pH = 12.5, only about 25% of phenol is degraded after 120 min. From these results, the pH of the initial phenolic solution was adjusted to 2.5 for the following degradation measurements presented below.

3.2.3. Effect of catalyst concentration

In order to avoid an ineffective excess of catalyst and to ensure a total absorption of efficient photons, the optimum mass of the SnO_2 photocatalyst needs to be found. In this work, $[\text{SnO}_2]$ was varied from 0.2 to 2.0 g L^{-1} at pH = 2.5 and $C_0 = 0.1 \text{ g L}^{-1}$.

As shown in Figure 7, the residual phenol fraction after 120 min in the solution, $(C/C_0)_{120}$, decreases with an increase of the mass of catalyst up to an amount of 1.0 g L^{-1} . This behaviour can be associated to an increment of the active sites available for phenol degradation [30]. However, an increase in the catalyst loading to 2.0 g L^{-1} results in a slight increase of $(C/C_0)_{120}$, which can be attributed to

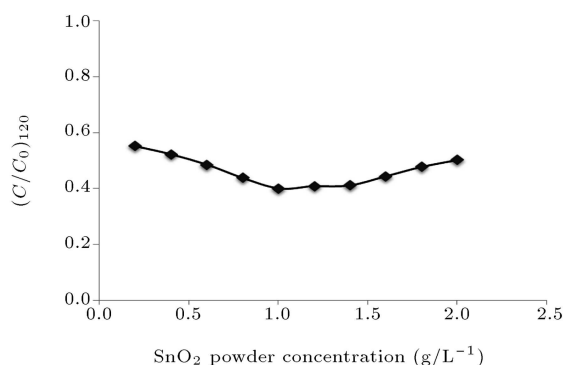


Figure 7. Residual fraction of phenol after 120 min, $(C/C_0)_{120}$, as a function of the SnO_2 powder concentration in the suspension. $C_0 = 0.2 \text{ g L}^{-1}$.

a screening effect due to the redundant dispersion of UV radiation caused by the substantial amount of suspended photocatalyst. Furthermore, in these conditions, particles of SnO_2 tend to agglomerate, making a significant fraction of the catalyst to be inaccessible to absorbing the radiation, with consequent decrease in the active sites available to the catalytic reaction [30].

3.2.4. Effect of phenol concentration

The initial phenol concentration, C_0 , was varied from 0.05 to 0.25 g L^{-1} at $\text{pH} = 2.5$ and with $[\text{SnO}_2] = 1.0 \text{ g L}^{-1}$. Results are presented in Figure 8. It is observed that $(C/C_0)_{120}$ slightly decreases when C_0 increases from 0.05 to 0.20 g L^{-1} . This behaviour can be associated to an increment of adsorbed phenol on the photocatalyst surface, which is followed by the degradation of phenol. We note $(C/C_0)_{120}$ begins to increase when C_0 is increased to 0.25 g L^{-1} . This observation is in agreement with previous studies [29,30]: as phenol concentration increases, more reaction intermediates (catechol, hydroquinone) are adsorbed on the surface of the photocatalyst. Therefore, these by-products compete with phenol for adsorption sites on the surface of SnO_2 , and the phenol degradation is slowed down.

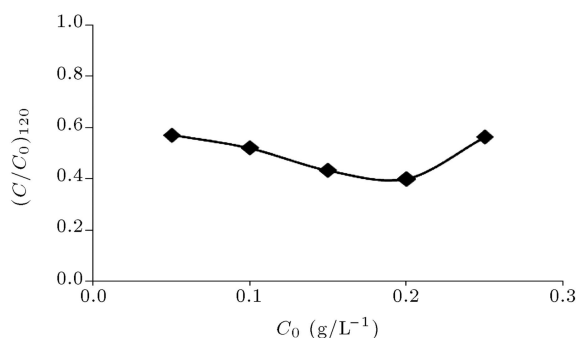


Figure 8. Residual fraction of phenol after 120 min, $(C/C_0)_{120}$, as a function of the initial phenol concentration; C_0 . $[\text{SnO}_2] = 1.0 \text{ g L}^{-1}$.

4. Conclusions

The sol-gel process used in this work allowed producing a crystallized pure SnO_2 powder after a calcination step. This calcined SnO_2 powder was very active for the degradation of phenol under UV irradiation.

The photocatalytic process was influenced by several operating variables such as pH of the solution, catalyst loading and initial phenol concentration. In this work, it was established that the use of a $\text{pH} = 2.5$ for the medium, a SnO_2 concentration = 1.0 g L^{-1} and initial phenol concentration = 0.20 g L^{-1} allowed the degradation of about 60% of phenol after 120 min.

These first results being interesting, the degradation of phenol by-products, such as catechol and hydroquinone, is actually studied on SnO_2 photocatalyst synthesized by the sol-gel process.

Acknowledgments

C.A.P. and S.D.L. are grateful to F.R.S.-F.N.R.S for his postdoctoral research position and her research associate position respectively. L.T. is grateful to the Belgian Fonds pour la Formation la Recherche dans l'Industrie et dans l'Agriculture, F.R.I.A., for a PhD grant. The authors would like to thank Ms. Martine Dejeneffe (CERM, University of Liege) for SEM micrographs. They also acknowledge the Fonds de Recherche Fondamentale Collective, the Ministère de la Région Wallonne, FWO-Vlaanderen and the Interuniversity Attraction Pole (IAP-P6/17) for financial supports.

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Thierry Salmon received his MSc in Industrial Chemistry in 1983 from the Institut Supérieur Industriel of Bruxelles (ISIB). He manages the entire organisation of the laboratory, the building of the pilot plants, and supervises the technical part of the work of the MS and the PhD students. He also assists in the realisation of the analysis and the interpretation of the results.

Dirk Poelman studied physics and obtained his PhD in solid state physics at Ghent University (Belgium). Since 2001, he has had a permanent appointment at Ghent University, where he is leading the research group Lumilab. He has been a full professor since

2012. Dirk Poelman has experiences in different fields of solid state physics research, including thin film deposition and optical characterization, photo-, electro- and cathodoluminescent materials, structural and electrical defects in semiconductors, photocatalysis for air purification, x-ray analytical techniques and human vision. He has published about 125 papers in peer reviewed international journals.

Michel Crine received his MSc in Chemical Engineering from the University of Liege (Belgium) in 1972 and his PhD in Applied Sciences in the same university in 1978. Between 1981 and 1994, he became permanent in the Department of Chemical Engineering of the University of Liege as a FRS-FNRS Research Associate (1981-1989), a FRS-FNRS Senior Research Associate (1989-1993) and a FRS-FNRS Research Director (1993-1994) respectively. In 1994, he was nominated as Professor in the same department. His fundamental research activities have been focused, for a long time, on the study of multiphase unit operations (catalytic trickle-bed reactors, biological trickling filters, and so on). He has paid a special attention to the experimental investigation of fluid flow hydrodynamics, and developed advanced experimental techniques to visualize the non intrusively local flow hydrodynamics, e.g. X-ray tomographic techniques and particle image velocimetry. Since 1994, Dr Crine's research activities have been re-oriented towards gas-liquid absorption packed columns, distillation packed columns, as well as dewatering and drying techniques. More recently, his research interests have been extended to the hydrodynamics in multiphase rheologically complex fluids (non newtonian fluids, pasty materials), such as those used in biotechnology, processing of agro-foods and drying of sludges.

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