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Investigation of the surface properties and microstructure of TiO₂ sorbents prepared in supercritical CO₂ for the treatment of Sr²⁺ contaminated effluents

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ABSTRACT

Nuclear facilities generate contaminated effluents containing radionuclides (such as Cs, Sr, Co...) that need to be removed for human health and environment protection reasons. Inorganic sorbents are attractive candidate materials because of their high thermochemical and radiation stability. Furthermore, their microstructural and surface properties can be adjusted to increase the radionuclide extraction efficiency. In this study, nanostructured sorbents consisting of aggregated TiO₂ **nanocrystals** with different surface properties and microstructures were prepared in supercritical CO₂ by varying the synthesis temperature. The Sr²⁺ sorption process was characterized by measuring the surface properties and extraction capacity of the samples as a function of pH. In basic effluents, the Sr sorption capacity of these materials is directly linked to their specific surface area and sorption site density

1 through a classic physisorption mechanism. Sr^{2+} diffusion into the mesopores leads to rapid
2 initial sorption, which is followed by a slower process driven by a proposed multistep
3 mechanism. This mechanism involves the initial adsorption of partially hydrated Sr^{2+} ions up
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5 to complete TiO_2 surface coverage, which implies slower Sr ion diffusion due to steric
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7 hindrance in small mesopores thus limiting access to additional secondary sites with lower
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9 adsorption energies.
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16 **Keywords:** Supercritical CO_2 , mesoporous TiO_2 , physisorption, ion diffusion, effluent
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1. Introduction

An attractive approach to reduce the volume of waste produced in nuclear effluent treatment is to transfer the radioelements (Cs, Sr, Co, Ag, U, Pu, Am...) to a solid substrate (IAEA 2002a). The high resistance to radiation and thermochemical stability of inorganic sorbents make them well suited for these applications (IAEA 2002b). The inorganic compound investigated here, titanium dioxide (TiO_2), has a wide range of applications, notably as a pigment dye, sunscreen agent, photocatalyst, and sorbent. Its attractiveness for radionuclide extraction stems from the fact that on its surface, water sorption leads to the formation of hydroxyl (-OH) groups, which are preferential complexation sites for ions in the aqueous phase (Kim et al. 1995; Kasap et al. 2001; Zhijun et al. 2005; Schmidt & Vogelsberger 2009; Zhang et al. 2009). Studies of the sorption properties of TiO_2 materials have shown that their extraction performance can be optimized by carefully controlling their physicochemical characteristics (Klabunde & Mulukutla 2002; Gao et al. 2004; Gülsen & Tel 2005): a large specific surface area is favorable for metal ion extraction and good sorption site accessibility is essential for fast sorption kinetics. Mesoporous powders with a high surface to volume ratio are beneficial because the active sites are easily accessible. Adsorption performance also seems to depend on the organization of the active sites and therefore on the crystalline structure of the sorbent (Ma & Tu 2011). Synthesizing nanostructured anatase TiO_2 with a high surface area and a well-defined mesoporous network would thus be a key advance for sorption-based decontamination processes.

The TiO_2 sorbents investigated here were synthesized using supercritical carbon dioxide (SC- CO_2) as the reaction solvent, which has been shown to offer several advantages for the preparation and processing of inorganic nanostructured materials (nanopowders, thin films, impregnation of catalysts...) (Sanli et al. 2012; Bozbag et al. 2012). The unique diffusion properties and solvent power of SC- CO_2 allow mesoporous anatase powders with a

1 high specific area to be prepared at low temperatures without any surfactant (Hertz et al.
2 2017). The density of the CO₂ is known to be a crucial parameter in controlling the particle
3 size and morphology of metal oxides synthesized in SC-CO₂ (Lane & Zimmerman 2019). In
4 this study, TiO₂ particles were synthesized at a fixed pressure (~300 bar) and the effect of the
5 SC-CO₂ temperature was investigated on their size, morphology, microstructure, surface
6 properties, and the nature and density of the sorption sites. The adsorption mechanism and
7 Sr²⁺ extraction efficiency of these materials were then investigated at different pHs and
8 correlated with their microstructure and surface properties. Finally, the Sr sorption properties
9 of the particles (kinetics, isotherms, maximum capacity, distribution coefficient, and
10 thermodynamic sorption constants) were measured under batch conditions at pH 11.
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27 **2. Experimental**

28 **2.1. Chemicals**

29 The CO₂ was used as received from Air Liquide (99.998% purity; residual water
30 concentration, 3 ppmv). Titanium (IV) isopropoxide (TIP) (Sigma-Aldrich, 97%) was used as
31 the ceramic precursor, with nitric acid (HNO₃) (Sigma-Aldrich, 69 %) as the sol stabilizer and
32 isopropanol (Sigma-Aldrich, 99.9%) as co-solvent. The sorption experiments were performed
33 using deionized water, NaNO₃ (Sigma-Aldrich, 99.5%) and Sr(NO₃)₂ (Sigma-Aldrich, 99%).
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44 **Commercial P25 TiO₂ powder (Degussa, Evonik), composed of 80% anatase and 20% rutile,**
45 **was used as TiO₂ reference for comparison of Sr²⁺ sorption kinetics (SEM photograph in Fig.**
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54 **2.2. TiO₂ synthesis in supercritical CO₂**

55 TiO₂ powders were synthesized in SC-CO₂ using a batch reactor (described in (Hertz
56 et al. 2017)), consisting of a 0.5 L vessel which can be heated up to 350°C and can withstand
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operating pressures up to ~30 MPa. The TIP sol-gel precursor (50 ml of isopropanol + 10 ml of TIP + 5 ml of nitric acid) was poured into the reactor, the reactor was closed and CO₂ was injected up to a pressure of ~5 MPa. The device was then heated (thus increasing the pressure) up to the target temperature (150°C, 250°C, or 350°C) and pressure (30 MPa), which were maintained for 1 h. The TiO₂ powders (#P150 #P250 #P350, prepared at 150°C, 250°C or 350°C, respectively) formed by thermal decomposition of the precursor and were recovered after the reactor was depressurized and returned to room temperature.

2.3. Structural, microstructural and **chemical** characterizations

The crystalline structure of the TiO₂ powders was investigated by X-ray diffraction (XRD, X'Pert PRO-PANalytical) using Cu K α radiation. X-ray induced photoelectron spectroscopy (XPS, Thermo Electron ESCALAB 250) was performed under ultra-vacuum (10⁻¹⁰ mbar) using a monochromatic aluminum source to identify chemical elements and their bonds at the extreme surface of the particles. Fourier-transform infrared (FTIR) spectra were measured in absorption mode using a Perkin-Elmer Spectrum 100 spectrometer, the thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed using a Setaram Setsys Evolution 16 device associated with Hiden QGA 300 mass spectrometer. The powders were observed by field-emission scanning electron microscopy (FESEM, Hitachi S4800) and the size, structure and shape of **primary particles** were evaluated by transmission electron microscopy (TEM, JEOL 2010F). Particle size distributions were determined by SEM image analysis (FEI Inspect S50). Nitrogen adsorption–desorption isotherms were measured using a Micromeritics ASAP 2020 device and specific surface areas, pore volumes and pore sizes were determined using the Brunauer–Emmett–Teller and Barrett–Joyner–Halenda methods. Surface acidity constants (K_a), points of zero charge (PZC) and sorption site densities were determined using potentiometric acid-base titrations, and zeta

1 potentials were measured by electrophoretic light scattering (Malvern Zetasizer) to determine
2 the isoelectric point (IEP) of the particles. The pKa values associated with the acid constants
3 Ka1 (pKa1, Ti-OH site protonation) and Ka2 (pKa2, Ti-OH site deprotonation) were
4 determined from titration tests with a strong acid (0.1 M HNO₃) under N₂ flow.
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10 **2.4. Batch sorption experiments**

11 **2.4.1. Sr²⁺ sorption efficiency**

12 Sorption experiments with Sr²⁺ ions were performed in batch mode at ambient
13 temperature (25°C). Samples (10 mg) of TiO₂ powder were suspended in closed flasks
14 containing aqueous Sr²⁺ solutions with N₂ bubbling to avoid any precipitation of strontium
15 through the formation of carbonate species with CO₂. The suspensions were stirred, collected
16 at fixed times and filtered. The filtrates were analyzed by inductively coupled plasma atomic
17 emission spectrometry (ICP-AES, Thermo Scientific iCAP 6000) to quantify the Sr²⁺
18 concentration. The concentration data were then used to calculate Sr²⁺ sorption capacities:
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34 $Q(\text{mg/g}) = \frac{(C_0 - C_f) \times V}{C_f \times m}$, and distribution coefficients: $K_d (\text{mL/g}) = \frac{Q}{C_{\text{eq}}}$ where C_0 , C_f and C_{eq}

35 (mg/L) are the initial, final and equilibrium Sr²⁺ concentrations, and m (g) and V (L) are the
36 TiO₂ mass and the volume of the suspension, respectively.
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43 **2.4.2. Sorption kinetics**

44 Kinetic experiments were conducted using 1 L of a 50 mg/L Sr²⁺ solution whose pH was
45 adjusted to ~11 by adding KOH and containing 0.5 g/L sorbent. The Sr²⁺ sorption capacity
46 (Q_t) was plotted versus time to determine the equilibrium time (stabilization of the sorption
47 capacity) and the corresponding value of the sorption capacity (Q_{eq}).
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2.4.3. pH isotherms

The effect of pH on the sorption process was evaluated by measuring the Sr^{2+} sorption capacity of suspensions of 0.2 g/L sorbent in 10 mg/L Sr^{2+} solutions whose pH was adjusted to between 2 and 12 by adding either NaOH or HNO_3 . Sorption capacities were measured after a contact time of 2 h.

2.4.4. Concentration isotherms

The effect of the Sr^{2+} concentration was assessed by measuring sorption isotherms in 50 mL suspensions of 0.2 g/L of sorbent in solutions, containing up to 120 mg/L of Sr^{2+} . The pH was adjusted to ~11 with KOH and the contact time was 40 h.

3. Results and discussion

3.1. Characteristics of the TiO_2 powders

3.1.1. Morphology and microstructure

The morphology and characteristic parameters of the TiO_2 powders synthesized at 150, 250 and 350°C in SC- CO_2 , are compared in Fig. 1 and Table 1. The powders are all composed of spherical micrometric particles (microspheres) containing small aggregates (secondary particles) of nanocrystals (primary particles). The sizes distributions of TiO_2 nanocrystal (determined by TEM), microsphere diameters (SEM) and BJH pore diameters (N_2 physisorption) are shown in Fig. 2.

The microsphere size distributions in Fig. 2a show that there are two distinct populations of particles in the powders. The first is centered at 1.5 μm in all the samples and predominates in #P350, while the second is a broader distribution of larger particles with a maximum at ~5 μm for #P150, ~3 μm for #P250 and ~4 μm for #P350 and is weaker in the latter. The mean diameter of the microspheres is inversely related to the synthesis temperature (3 μm , 2.2 μm and 2 μm for #P150, #P250 and #P350 respectively). Within the microspheres, the secondary

1 particles (15 to 50 nm) are composed of nanocrystals whose mean size ($d(\text{TEM}) = 5\text{--}18$ nm)
2 and size distribution (Fig. 2b) also depend on the synthesis temperature.
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4 As detailed in a previous article (Hertz et al. 2017) the decrease of SC-CO₂ density when
5 temperature increases, and the associated increase of self-diffusion coefficients for
6 nanoparticles and/or reacting species, favor reaction kinetics and crystallite growth.
7 Crystallite growth seems to be heterogeneous at 350°C, certainly due to multi-step
8 precipitation during the temperature rise step in the reactor (Hertz et al. 2010), yielding a wide
9 (bimodal) particle size distribution for #P350 with maxima at ~15 and 35 nm.
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19 The size distributions in the #P250 and #P150 powders are narrower and centered at 7
20 and 5 nm, respectively. The largest microspheres (~5 μm) and smallest primary particles (~5
21 nm) were obtained at the lowest reaction temperature (150°C). This indicates that the primary
22 particles have a strong tendency to aggregate, probably because of both small primary particle
23 size (to minimize surface energy) and presence of species on the surface of the particles that
24 are not all decomposed at this temperature. At 350°C, heterogeneous nanocrystal growth leads
25 to a broader distribution of microsphere sizes. The larger TiO₂ crystals (formed by
26 coalescence of small crystallite stacks) yield the smallest (most compact) microspheres.
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38 Figure 3a show that all three powders consist of anatase TiO₂ (JCPDS card 21-1272).
39 The average size of crystalline mono-domains ($d(\text{XRD})$; Table 1) were estimated by applying
40 the Scherrer formula to the (101) peak, with a shape factor of 0.96 (Oskam et al. 2003). The
41 results are in good agreement with the TEM observations of nanocrystals, with the average
42 size of crystalline mono-domains increasing with the synthesis temperature from 6 to 13 nm.
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51 As expected, the specific surface area, pore volume and pore size distribution of the
52 microspheres also depend on the synthesis temperature (Table 1). The specific surface area of
53 the microspheres is inversely correlated with the synthesis temperature, in keeping with the
54 growth of larger TiO₂ crystallites at higher temperatures. The N₂ physisorption isotherms
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(Fig. S2) were of type IV, which is typical of mesoporous materials. The pore size distributions derived from the desorption branch (Fig. 2c) are monomodal for all three samples but the pore size and size distribution increase with the synthesis temperature.

As shown in table 1, the XRD, TEM and N₂ physisorption analysis revealed that the measured crystallite sizes (domains) correspond to the primary particles composing the TiO₂ microspheres. The whole surface of these primary particles is accessible to N₂ molecules. As expected, when the temperature increases, the growth of crystallite causes a drop in the specific surface area.

3.1.2. Functional groups (sorption sites) and adsorbed species

The presence of functional groups (correlated to the density of sorption sites) on the particles has been evidenced by XPS, FTIR and TGA. The main results are presented in Fig. 3 and Tables 2 and 3.

The FTIR spectra (Fig. 3c) of the powders show a band at 426 cm⁻¹ from the Ti-O bond in anatase (Vuk et al. 2005) and a broad band in the range 2700–3600 cm⁻¹, typical of adsorbed water and hydroxyl groups (Morterra 1988). Part of the broad band ranging from 2700 to 3600 cm⁻¹ can also be assigned to O-H bonds in carboxylic acid (inseparable from those of Ti-OH and H-O-H) as well as the wide band at 1379 cm⁻¹. In the #P150 spectrum, the bands at 1712 and 1687 cm⁻¹ correspond to C=O stretching vibrations in saturated and unsaturated carboxylic acid. The band at 1300 cm⁻¹ is characteristic for the single C-O bond in carboxylic acids. This functional group is not observed in the powders synthesized at higher temperatures. In addition, the bands observed at 2970, 2930 and 2880 cm⁻¹ for #P150 correspond to -CH₂ and -CH₃ groups from residual isopropanol or TTIP. The intensity of these bands decreases for #P250 and they completely disappear for #P350 sample. The bands observed at 1160, 1128 and 1106 cm⁻¹ for #P150 also correspond to isopropanol. We can thus

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conclude that an increase of the synthesis temperature facilitates the elimination of both unreacted precursor and isopropanol during reactor depressurization at the end of the synthesis.

The XPS data (Fig. 3b, Table 2) show that all three powders have a high surface carbon content, partly in the form of carboxylic acid groups. The intensity of the C=O band from carbonyl and carboxylic acid groups is inversely related to the synthesis temperature. The small number of C-O (Ti-C-O) bonds observed in all the samples may come from the partial degradation of organic reagents (uncomplete oxidation (Hertz et al. 2017)) during synthesis in SC-CO₂. There is also evidence of surface defects: the O/Ti atomic ratio (Table 2) is slightly higher than 2 (the value expected for anatase TiO₂) in the TiO₂ lattice (indicating the presence of Ti³⁺ instead of Ti²⁺), while increasing the synthesis temperature leads to a decrease in the proportion of stoichiometric defects such as oxygen vacancies ([TiO_{2-x}] / [TiO₂]).

Finally, the TGA curves (Fig. 3d-g, Table 3) show a first thermal event for all samples at $T < 150^{\circ}\text{C}$, which corresponds to the evaporation of physisorbed water. The higher water content of the powders produced at low temperatures is directly related to their higher specific surface area. A second weight loss event, corresponding to the dehydration and dehydrogenation of carboxylic acid, is observed for the #P150 and #P250 samples between 150 and 280°C. The final weight loss between 280°C and 400°C was attributed to the removal of chemically bonded hydroxyl groups and to the complete degradation of carbon species (formed by uncomplete oxidation of isopropanol and TTIP during SC-CO₂ synthesis (Hertz et al. 2017)).

3.1.3. Assessment on TiO₂ microsphere formation

The thermal decomposition of TTIP in CO₂-SC medium leads to the formation of nanostructured TiO₂ anatase microspheres. These spheres are made up of an assembly of

1 secondary particles, themselves made up of aggregated primary particles (nanocrystals).
2 These primary particles form a mesoporous network developing large specific surface areas.
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4 The preparation temperature has no impact on the crystalline structure and morphology of the
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6 TiO₂ microspheres, although the size of mesopores decreases when the synthesis temperature
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8 decreases. At low temperature, a high specific surface area is measured, due to the small size
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10 of primary nanocrystals. These nanocrystals have a large number of defects (vacancies, Ti³⁺
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12 and Ti²⁺ species), and provide high density of surface sorption sites (-OH and -COOH). The
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14 powders produced at 150°C contain carboxylic acid groups (-COOH) in addition to the Ti-OH
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16 sites. The degradation of -COOH groups for synthesis temperatures beyond 250°C yields
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18 residual carbon species (uncompleted oxidation in SC-CO₂) on powder surface.
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24 These different phenomena are mainly related to the evolution vs. synthesis temperature
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26 in SC-CO₂ of the diffusion and integration rates of the growing units. Microspheres are
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28 formed by aggregation/agglomeration of nanocrystals. Small crystal sizes accelerate the
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30 aggregation kinetics by promoting attractive colloidal interactions. Thereby, the specific
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32 properties of SC-CO₂ (viscosity, diffusion coefficients) which can be modulated by
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34 temperature, play a key role in nanocrystals mobility. Indeed, a decrease in temperature
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36 lowers the viscosity of SC-CO₂, thus potentially favoring the aggregation kinetics of
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38 crystallites and secondary particles. In addition, the carboxylic acid groups on #P150 powder
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40 surface might promote the formation of hydrogen bonds through their -OH groups and further
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42 accelerate aggregation.
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51 **3.2. Surface properties in aqueous media – influence of pH on sorption**

52 The surface properties of the TiO₂ sorbent in aqueous media are important for
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54 understanding the ion extraction mechanism in solution. The surface charge resulting from the
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56 acid-base equilibrium between water and Ti-OH sites determines whether anions or cations
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1 are adsorbed, while the number of Ti-OH sorption sites can affect the sorption efficiency. The
2 measurements performed of the acid-base properties of the powders (surface charge, PZC,
3 IEP and pKa) and the number of surface sites (pH titration, zeta potential) are presented in
4 Table 4. Figure S3 shows the concentrations of protonated [Ti-OH₂⁺] and deprotonated [Ti-
5 O⁻] species and the surface charge (σ_0) estimated from titration experiments and Fig. 5a
6 shows the evolution of the surface charge as a function of pH and the PZC of the three
7 samples. The absolute surface charge (in C/g) is inversely related to the synthesis temperature,
8 which can be explained by the decrease in hydroxyl site density and specific surface area as
9 the synthesis temperature is increased. The PZC values of the #P250 and #P350 powders are
10 similar (pH 5.7 ± 0.3 and 6.2 ± 0.3 , respectively) while the PZC of the #P150 sample is more
11 acidic because of the presence of carboxylic acid groups (-COOH).
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27 The fact that the IEPs measured for suspensions of the samples in 10^{-2} M NaNO₃
28 solutions (Fig. 4b) are close to the PZC values shows that there is no specific adsorption of
29 Na⁺ or NO₃⁻ ions on the TiO₂ hydroxyl sites. The surface charge of the powders (Fig. 4a) is
30 therefore representative of the density of deprotonated -OH sites (nm⁻²), which is much
31 higher in the #P150 sample than in the #P250 and #P350 powders, probably because of the
32 additional carboxylic acid groups (-COOH) and greater number of defects (oxygen vacancies,
33 Ti³⁺), which promote the formation of -OH sites.
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44 Finally, Fig. 4c shows that at pHs < pKa1, the surface sites (predominantly Ti-OH₂⁺)
45 are positively charged and tend to repel Sr²⁺ ions. The carboxylic acid groups on the surface
46 of the #P150 particles, which dissociate at a lower pH than the hydroxyl sites, allow a small
47 amount of Sr²⁺ sorption at acidic pHs. At pHs between the PZC and pKa2, the particles are
48 negatively charged overall, but the surface sites are mainly neutral (Ti-OH). At pHs above
49 pKa2, the negatively charged Ti-O⁻ sites attract Sr²⁺ ions and the extraction capacity is
50 highest at pHs above 10. Since the interactions between the hydroxyl groups (Ti-OH) and Sr²⁺
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ions seem to be purely electrostatic, the adsorption mechanism appears to be outer-sphere complexation.

3.3. Sr²⁺ ion sorption in solutions at pH 11

3.3.1. Sorption kinetics

Figure 5a compares the time evolution of the sorption capacity of the three TiO₂ powders. The corresponding equilibrium capacities and kinetic coefficients were estimated using pseudo-second order modeling (Table 5) (Ho & McKay 1999; Simonin 2016; Inyinbor et al. 2016):

$$\frac{t}{Q_t} = \frac{1}{k \times Q_{eq}^2} + \frac{1}{Q_{eq}} t \quad (1)$$

where Q_t (mg/g) is the sorption capacity at time t , Q_{eq} (mg/g) is the equilibrium sorption capacity, t is the time in hours and k is the kinetic constant (mg/g/h).

Table 5 also shows the diffusion rate constants K_{diff} (mg/g/h^{1/2}) determined by fitting the square-root time evolution of the sorption capacities (Fig. 5b), with a Weber-Morris intraparticulate diffusion model (Weber & Morris 1963; Inyinbor et al. 2016):

$$Q(t) = K_{diff} \times \sqrt{t} + \text{constant} \quad (2)$$

The kinetic curves all show two stages (Fig. 5a,b) with the sorption capacity increasing sharply at first and then more gradually. The data in the second (plateau) stage are well fitted by Eq. (1) but the fits are less accurate for the initial phase. The amounts of Sr retained by the #P350, #P250 and #P150 powders after 5 min contact are respectively 10, 40 and 65 mg/g, which corresponds to ~100% coverage of the adsorption sites (one Sr²⁺ ion adsorbed on two -O⁻ sites for surface charge compensation). This fast process ($K_{diff1} \approx 400 \text{ mg/g/h}^{1/2}$) corresponds to a physisorption mechanism without Nernst layer restrictions at the TiO₂ surface. The high specific surface area and sorption site density of the #P150 powder explain why it shows the best Sr²⁺ sorption performance (the highest equilibrium capacity, Q_{eq}

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~ 77 mg/g, with fast kinetics: 84% of Q_{eq} in less than 5 min). The diffusion constant for the second, slower process (K_{diff2} , Table 5) increases with the size of the mesopores in the samples, which is indicative of intra-particulate/inter-crystallite diffusion limitations. Furthermore, this slower process seems to correspond to the adsorption of more than one Sr^{2+} ion per pair of O^- sites. For #P350 indeed, the slope of the diffusion curve changes twice, once at a capacity corresponding to each Sr^{2+} ion interacting with two $-O^-$ sites and a second time at a capacity corresponding to 1:1 interactions. This suggests that the adsorbed Sr^{2+} ions become hydrated in basic media, leading to the formation of $Sr-O^-$ sites with a lower adsorption energy than the $Ti-O^-$ sites. A surface layer of hydrated Sr^{2+} ions would limit access to additional internal sorption sites and slow down the adsorption kinetics, particularly in the powders with smaller mesopores. These results are therefore consistent with an outer-sphere sorption mechanism.

For comparison, the equilibrium capacity measured for the #P25 commercial TiO_2 powder ($S_{BET} \sim 60 m^2/g$) is around 26 mg/g (Fig. 5a). This capacity is slightly lower than the value measured for #P350 sample (~ 32 mg/g), in good agreement with its higher specific surface area ($90 m^2/g$). However, the initial sorption kinetic is faster for #P25 (Fig. 5b) due to a better dispersion of its nanocrystals in the suspension (less aggregated particles). This shows that the sorption mechanism for #P25 is not limited by the diffusion of Sr^{2+} ions in the particle mesoporosity, as in the case of TiO_2 microspheres. However, the interest of handling TiO_2 microsphere instead of isolated nanoparticles (health hazard) is still motivating our research activity in this area.

3.3.2. Sr²⁺sorption isotherms

Figure 6a shows the Sr²⁺ sorption isotherms measured for the three TiO₂ powders. As expected, the #P150 powder has the highest sorption capacity, with a distribution coefficient of ~10⁶ mL/g at low Sr²⁺ concentrations (Fig. 6b). This high sorption capacity is explained by the large specific surface area of the #P150 powder. The isotherm profiles do not level out, which is consistent with the proposed multistep adsorption mechanism. The experimental data were fitted using three thermodynamic models (Langmuir, Freundlich and Temkin; Fig. S4), to estimate the maximum sorption capacity (Q_{\max}) and the thermodynamic parameters in the models (Table 5) (Dada et al. 2012; Inyinbor et al. 2016; Ajawei et al. 2017).

The Langmuir model describes adsorption in a monolayer with a uniform adsorption site energy and no interactions between vicinal sites. The linearized equation for the Langmuir model is:

$$\frac{1}{Q_{eq}} = \frac{1}{Q_{\max}} + \frac{1}{K_L \times Q_{\max} \times C_{eq}} \quad (3)$$

$$\text{with} \quad \Delta G = -RT \ln Q_{\max} K_L \quad (4)$$

where Q_{\max} (mg/g) is the maximum monolayer coverage capacity, Q_{eq} (mg/g) is the equilibrium sorption capacity, C_{eq} (mg/L) is the equilibrium solution concentration, K_L is the Langmuir isotherm constant (L/mg), and ΔG (KJ/mol) is the sorption free energy, with R , the gas constant and T (K) the temperature.

The Freundlich model describes multilayer adsorption on a heterogeneous surface assuming exponential distributions of active sites and site energies. The linearized equation for the Freundlich model is:

$$\log Q_{eq} = \log K_F + \frac{1}{n} \log C_{eq} \quad (5)$$

where $1/n$ is the adsorption intensity and K_F is the Freundlich constant (mg/g). When $n = 1$, the partition between the two phases is independent of concentration and the adsorption

1 isotherm is linear; $n > 1$ corresponds to normal sorption with values from 1 to 10 yielding a
2 favorable isotherm, while $n < 1$ corresponds to cooperative adsorption.
3

4 The Temkin model takes into account indirect adsorbate interactions and assumes that
5 the heat of adsorption decreases linearly as surface coverage increases. The linearized
6 equation for the Temkin model is:
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$$9 \quad Q_{\text{eq}} = B \ln A + B \ln C_{\text{eq}} \quad (6)$$

10 where B is a constant related to the heat of adsorption (ΔH , J/mol) and A is the Temkin
11 isotherm equilibrium binding constant (L/g).
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14 The fitting parameters in all three models provide useful information on the adsorption
15 mechanism. The fact that ΔG in the Langmuir model is negative is consistent with a
16 spontaneous physisorption mechanism, and the inverse relationship between the absolute
17 value of ΔG and the synthesis temperature confirms that #P150 has the most favorable
18 adsorption properties. The values of $1/n$ (~ 0.2) in the Freundlich model show moreover that
19 the adsorption process is favorable for all the samples. The positive values of the Temkin
20 constant (B) indicate that the adsorption process is endothermic.
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23 In keeping with the proposed complex multi-step physisorption mechanism, the
24 Langmuir model (monolayer adsorption) does not accurately fit the experimental data, and
25 while the fit is improved with the Freundlich equation, these results indicate that adsorption of
26 Sr^{2+} on the TiO_2 sorbents is best described by the Temkin model. This supports the suggested
27 adsorption of several Sr^{2+} ions per active site and the variation of the energy of the adsorption
28 sites with the multi-layered surface coverage. The maximum sorption capacity in the
29 Langmuir model indicates that 1.1–1.6 Sr^{2+} ions per active site on the TiO_2 particles (Table
30 5), which is higher than expected for a simple electrostatic mechanism (0.5 Sr^{2+} per $-\text{O}^-$ or
31 COO^- sorption site). The powder with the lowest adsorption site coverage (1.1) is #P150,
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probably because of its smaller pores (~4 nm). Since the hydrated diameter of Sr²⁺ ions is ~0.82 nm, steric effects limit the number that can be accommodated in such small pores.

4. Conclusions and prospects

This study shows that TiO₂ powders prepared in SC-CO₂ crystallize as anatase at temperatures as low as 150°C, and that their microstructure and surface properties are favorable for effluent treatment by adsorption. These TiO₂ sorbents are composed of mesoporous micrometric spherical particles formed by the successive agglomeration of primary nanometric TiO₂ particles and particle agglomerates. The mean size of the mesopores increases with the synthesis temperature and this was attributed to the way the primary particles growth and agglomerate. High specific surface areas, up to 275 m²/g, are obtained at low synthesis temperatures, because of the small crystallites and mesoporous structure (pore diameter ~4 nm) of the particles. Surface hydroxyl and carboxylic acid groups become active adsorption sites in basic media.

The Sr²⁺ extraction properties of these materials depend on the pH of the solution, which affects their surface properties and the overall adsorption mechanism. The specific surface area and number of sorption sites (-OH and -COOH) are the main parameters that affect the adsorption capacity in basic media. Here, the powder prepared at the lowest temperature (150°C) was found to have best adsorption performance, with the mesoporous network providing rapid access (< 5 min) to all surface sorption sites. However, the small size of the mesopores limits further diffusion by steric hindrance due to TiO₂ surface coverage of hydrated Sr²⁺ ions in basic media. This multi-step adsorption mechanism is much more complex than the expected homogeneous physisorption on TiO₂ surface sites and further investigations with complementary experiments such as microcalorimetry are warranted.

1 Overall though, this study shows that the microstructure and active site density of
2 mesoporous TiO₂ microspheres prepared at 150°C in SC-CO₂ are attractive for adsorption
3 processes, with a high Sr²⁺ sorption capacity in basic media. In addition, the synthesis
4 protocol could be adapted to deposit nanostructured mesoporous films on relevant supports.
5
6 Work is ongoing on the preparation in SC-CO₂ of hierarchical sorbents with a highly
7 interconnected porous structure by coating mesoporous films on macroporous substrates. The
8 idea is to combine the favorable diffusion properties of the macroporous network with the
9 large active surface area of the nanostructured mesoporous TiO₂. These sorbents could thus be
10 implemented in either column or filtration processes for effective effluent treatment.
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23 **Conflict of Interest:**

24 The authors declare that they have no conflict of interest.
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Captions

Table 1 Morphological and microstructural characteristics of TiO₂ microspheres prepared in supercritical CO₂ at 150, 250 and 350°C, in comparison with a P25 commercial TiO₂ powder provided by Degussa-Evonik (literature data (Rui et al. 2014, Han et al. 2018))

Table 2 Semi-quantitative XPS analyzes of C/Ti and O/Ti atomic ratios and the proportion of bonds (at. %) involving oxygen (O1s) in TiO₂ microspheres prepared in supercritical CO₂ at 150, 250 and 350°C

Table 3 Thermogravimetric analysis of TiO₂ microspheres prepared in supercritical CO₂ at 150, 250 and 350°C

Table 4 Surface properties of TiO₂ microspheres prepared in supercritical CO₂ at 150, 250 and 350°C estimated by acid-base titration and zeta-potentiometry

Table 5 Kinetic and isotherm modeling data for suspensions of TiO₂ microspheres prepared in supercritical CO₂ at 150, 250 and 350°C

Table 1 Morphological and microstructural characteristics of TiO₂ microspheres prepared in supercritical CO₂ at 150, 250 and 350°C, in comparison with a P25 commercial TiO₂ powder provided by Degussa-Evonik (literature data (Rui et al. 2014, Han et al. 2018))

Powder	Size of crystalline mono-domains / nanocrystals ^a (nm)	Microsphere diameters (μm)		S _{BET} ^b (m ² /g)	Pore volume (cm ³ /g)	d _{BJH} ^c (nm)
		Average	Max of the distribution			
#P150	6, 6, 5	3	1.5 & 5	275	0.37	4
#P250	8, 7, 8	2.5	1.5 & 3	190	0.55	7
#P350	16, 13, 18	2	1.5 & 4	95	0.45	14
#P25 (Rui et al. 2014, Han et al. 2018)	21	15-40nm slightly agglomerated (SEM/TEM primary particles)		55-65	0.17-0.22	12-18

^aThe three values correspond to measurements by N₂ adsorption, X-ray diffraction and transmission electron microscopy

^bSpecific surface area determined using the BET method

^cAverage pore size determined using the BJH method

Table 2 Semi-quantitative XPS analyzes of C/Ti and O/Ti atomic ratios and the proportion of bonds (at. %) involving oxygen (O1s) in TiO₂ microspheres prepared in supercritical CO₂ at 150, 250 and 350°C

Powder	C1s	O1s	Ti2p3	O/Ti	C/Ti	TiO _{2-x}	TiO ₂	O=C/O-H	O-C
#P150	38	45	17	2.7	2.2	11	60	21	7
#P250	39	43	17.1	2.5	2.3	9	69	15	7
#P350	40	42	18	2.3	2.2	3	77	11	8

All values in atomic percent

Table 3 Thermogravimetric analysis of TiO₂ microspheres prepared in supercritical CO₂ at 150, 250 and 350°C

Temperature range	< 150 °C	150–280 °C	> 280 °C	25–500 °C
Powder	Δm_1 (%)	Δm_2 (%)	Δm_3 (%)	Total Δm (%)
#P150	4.8	4.1	7.1	16.0
#P250	2.5	1	5.1	8.6
#P350	1.4	-	2.3	3.7
Volatilized species ^a	Physisorbed water	Degradation of unreacted precursors and -COOH dehydration and dehydrogenation	Degradation of structural water -OH and residual -COOH	

^aIdentified by mass spectrometry

Table 4 Surface properties of TiO₂ microspheres prepared in supercritical CO₂ at 150, 250 and 350°C estimated by acid-base titration and zeta-potentiometry

Powder	pKa1	pKa2	PZC	IEP	Deprotonated sites (nm ⁻²)
#P150	4.7	8	4.2	4.7	3.4
#P250	5.0	7.8	5.7	5.9	2
#P350	5.1	7.8	6.2	6.1	1.9

PZC, point of zero charge; IEP, isoelectric point

Table 5 Kinetic and isotherm modeling data for suspensions of TiO₂ microspheres prepared in supercritical CO₂ at 150, 250 and 350°C

	#P150	#P250	#P350	
Kinetic data				
Q_{eq} (mg/g) - Pseudo 2nd order	77.5	47.4	32.4	
Kreaction 2nd order (mg/g/h)	0.083	0.065	0.053	
Kdiff 1 (mg/g/h ^{1/2})	~400	~400	~400	
Kdiff 2 (mg/g/h ^{1/2})	6.7	8.0	16.4	
Kdiff 3 (mg/g/h ^{1/2})	1.7	1.2	4.6	
Q (mg/g) at the end of first sorption step (5min)	65	40	10	
Sr adsorbed in 5 min (% of Q_{eq})	84%	86%	30%	
Number of Sr atom /site at the end of first sorption step (5min)	0.5	0.7	0.4	
Number of Sr atom /site at the end of second sorption step	0.5	0.8	1	
Isotherm data				
Langmuir model Equation (3)	slope = $1 / Q_{max}$	0.0068	0.0111	0.0283
	intercept = $1 / (Q_{max} * L)$	0.0062	0.017	0.0325
	Q_{max} (mg/g)	147	90	35
	K_L (L/mg)	1.1	0.7	0.9
	ΔG (KJ/mol)	-12.6	-10.1	-8.5
	Correlation coefficient	0.982	0.961	0.951
Freundlich model Equation (5)	slope = $1 / n$	0.2115	0.1484	0.2066
	intercept = $\log K$	1.8641	1.6952	1.1967
	n	4.7	6.7	4.8
	K_F (mg/g)	73	50	16
	Correlation coefficient	0.982	0.980	0.985
Temkin model Equation (6)	slope = B	15.525	8.2042	3.6155
	intercept = $B \ln A$	84.546	53.463	19.127
	B (J/mol)	15.5	8.2	3.6
	A (L/g)	232	676	198
	Correlation coefficient	0.993	0.994	0.981
Density of Sr atoms at Q_{max} (nm ⁻²)	3.7	3.2	2.6	
Number of Sr atoms per adsorption site at Q_{max}	1.1	1.6	1.4	

Captions

Figure 1 (a–j) Scanning and transmission electron micrographs of TiO₂ microspheres prepared in supercritical CO₂ at (a, b, c, d) 150°C, (e, f, g) 250°C and (h, i, j) 350°C. (k) Schematic representation of the microstructure of the TiO₂ particles

Figure 2 Distributions of (a) crystallite sizes determined by transmission electron microscopy, (b) microsphere diameters determined by scanning electron microscopy and (c) pore sizes determined using the Barrett–Joyner–Halenda method for TiO₂ microspheres prepared in supercritical CO₂ at 150, 250 and 350°C

Figure 3 (a) X-ray diffraction patterns of TiO₂ microspheres prepared in supercritical CO₂ at 150, 250 and 350°C; (b) O1s X-ray photoelectron spectrum of the powder prepared at 250°C; (c) FTIR spectra with expanded view in the ranges 900–1800 cm⁻¹ and 2400–3600 cm⁻¹ for #P150, #P250 and #P350 powders; (d) heat flow and amounts of H₂O and CO₂ released as a function of temperature for #P150 sample; and (e–g) thermogravimetric curves for the powders prepared at (e) 150°C, (f) 250°C and (g) 350°C.

Figure 4 Evolution of (a) the surface charge, (b) the zeta potential (0.3 g/l TiO₂; 10⁻² M NaNO₃) and (c) Sr²⁺ sorption capacity after 3 h contact time as a function of the pH of the solution, for suspensions of TiO₂ microspheres prepared in supercritical CO₂ at 150, 250 and 350°C

Figure 5 (a) Kinetic curves measured for suspensions of TiO₂ microspheres prepared in supercritical CO₂ at 150, 250 and 350°C and commercial P25 TiO₂ (1 L, 50ppm Sr²⁺, 0.5g/L

sorbent, pH 11) with second order kinetic fittings, and (b) Weber-Morris intra-particulate diffusion modeling of the same data

Figure 6 (a) Concentration adsorption isotherms fitted with the Temkin equation, (b) distribution (K_d) isotherms for TiO₂ microspheres prepared in supercritical CO₂ at 150, 250 and 350°C in suspensions at pH 11

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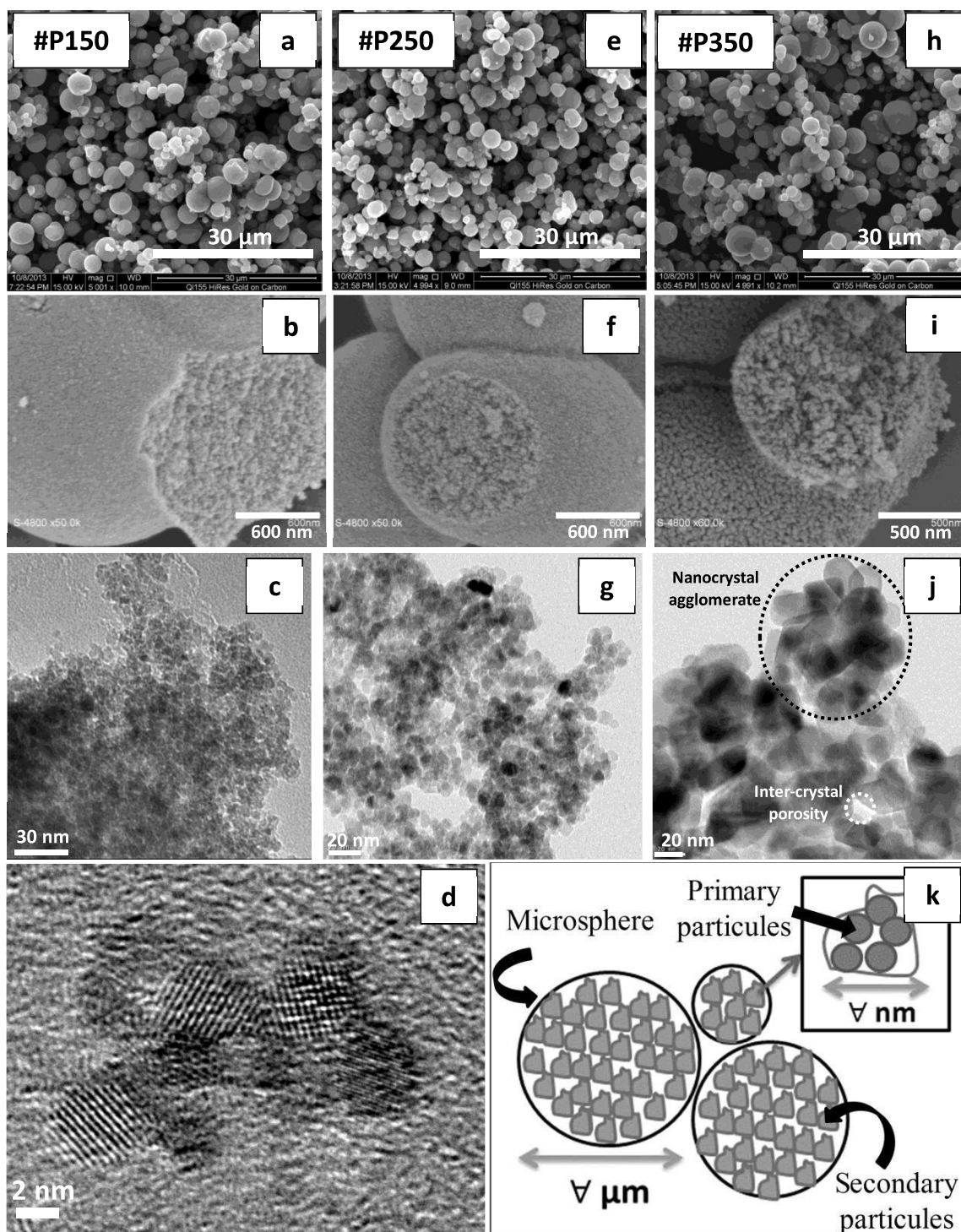


Figure 2 Distributions of (a) **nanocrystals diameter** determined by transmission electron microscopy, (b) microsphere diameters determined by scanning electron microscopy and (c) pore sizes determined using the Barrett–Joyner–Halenda method for TiO₂ microspheres prepared in supercritical CO₂ at 150, 250 and 350°C

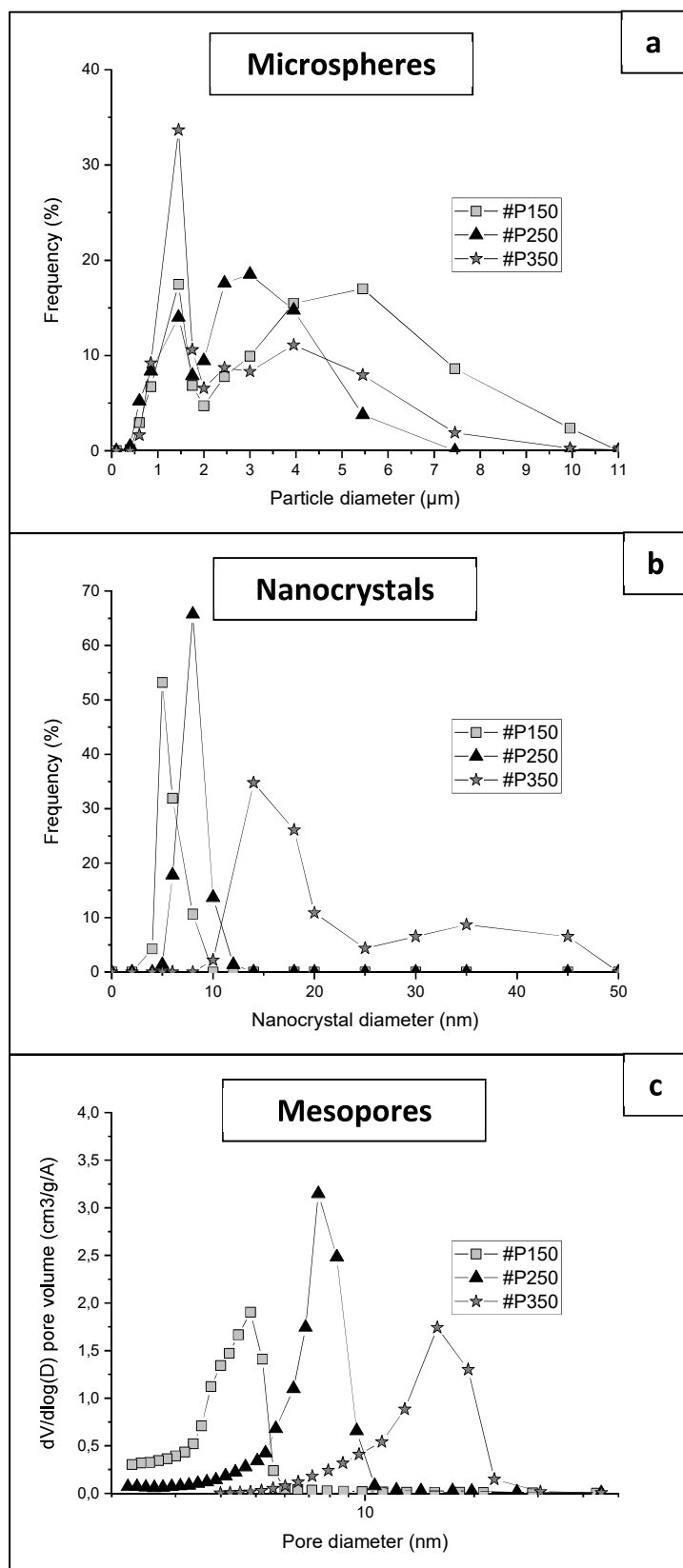


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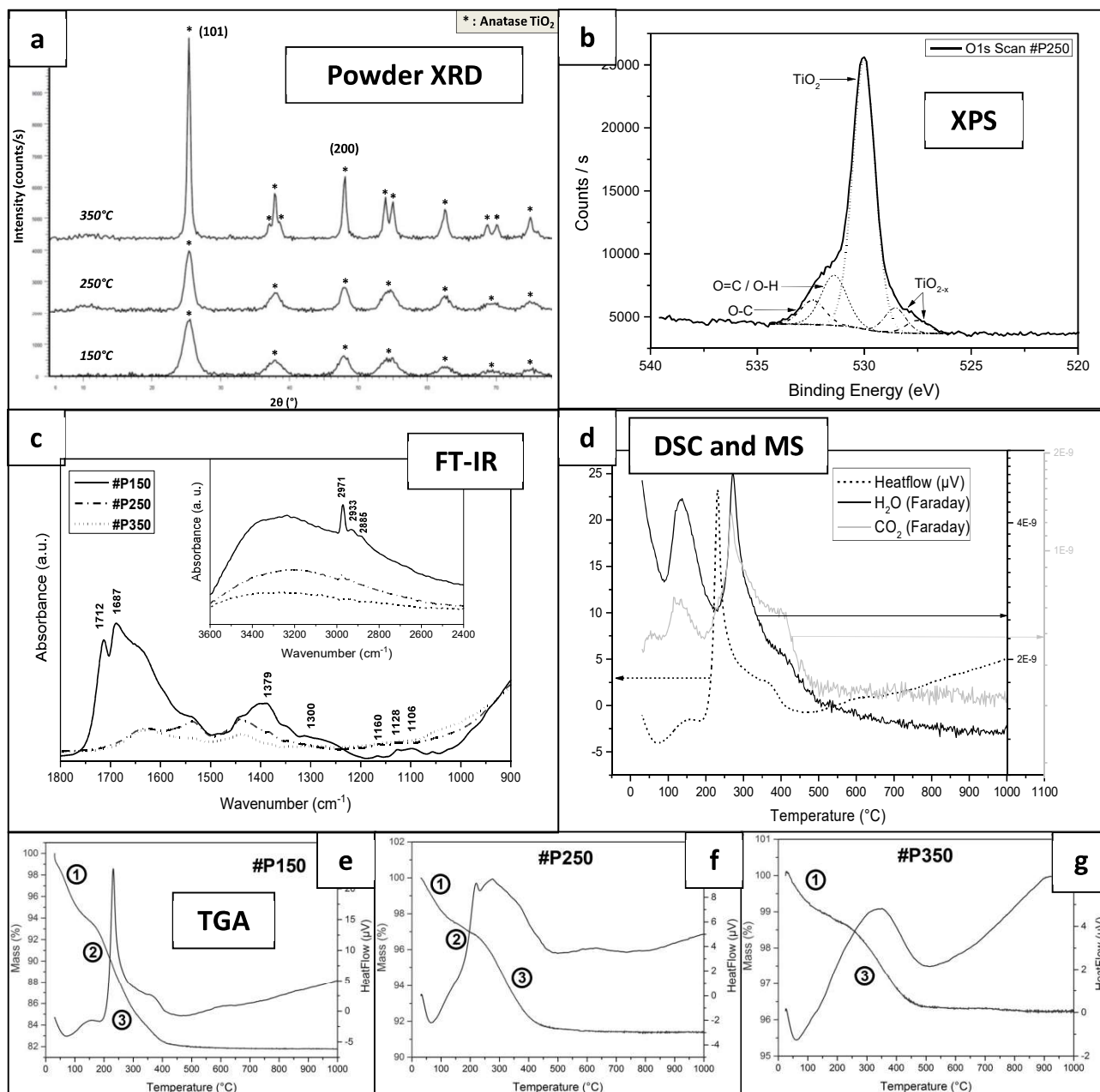


Figure 4 Evolution of (a) the surface charge, (b) the zeta potential (0.3 g/l TiO₂; 10⁻² M NaNO₃) and (c) Sr²⁺ sorption capacity after 3 h contact time as a function of the pH of the solution, for suspensions of TiO₂ microspheres prepared in supercritical CO₂ at 150, 250 and 350°C

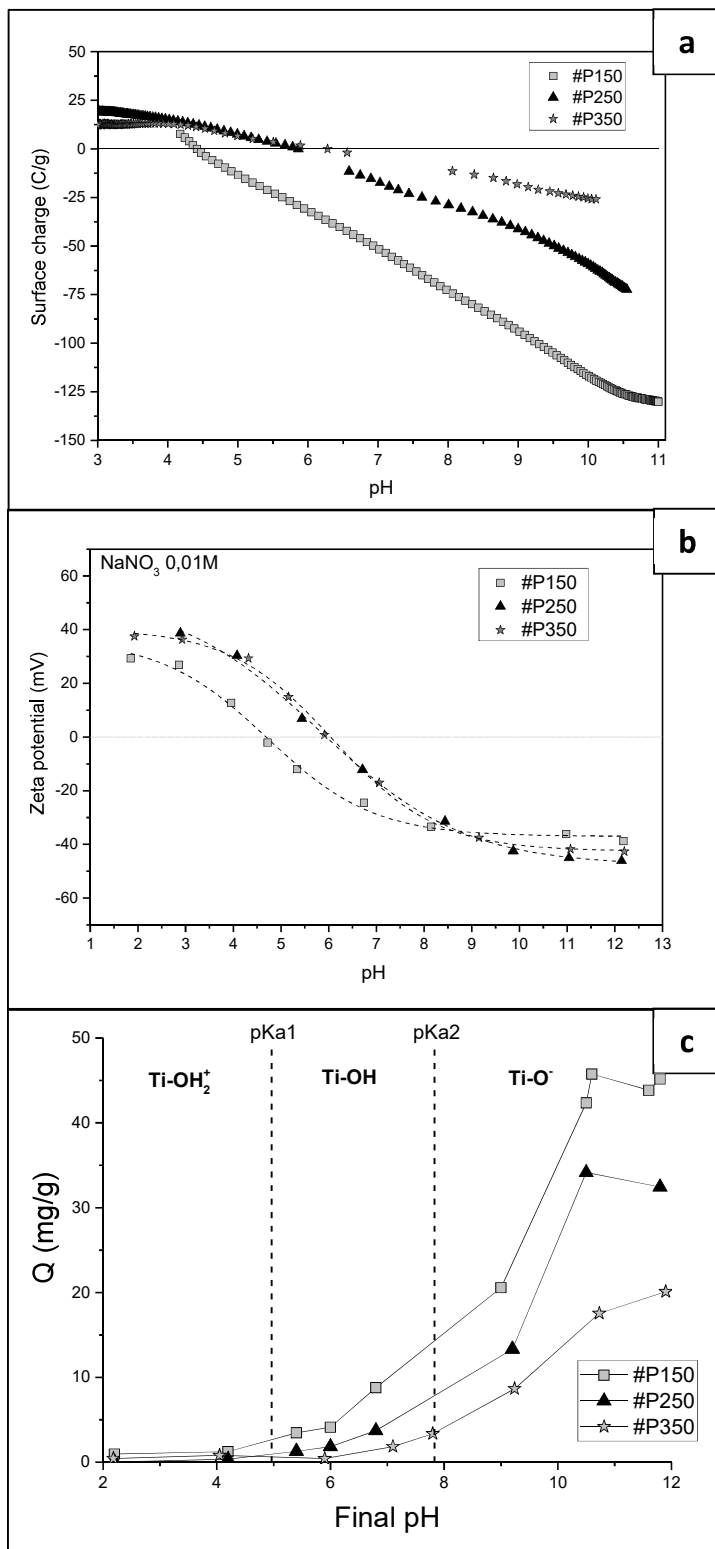


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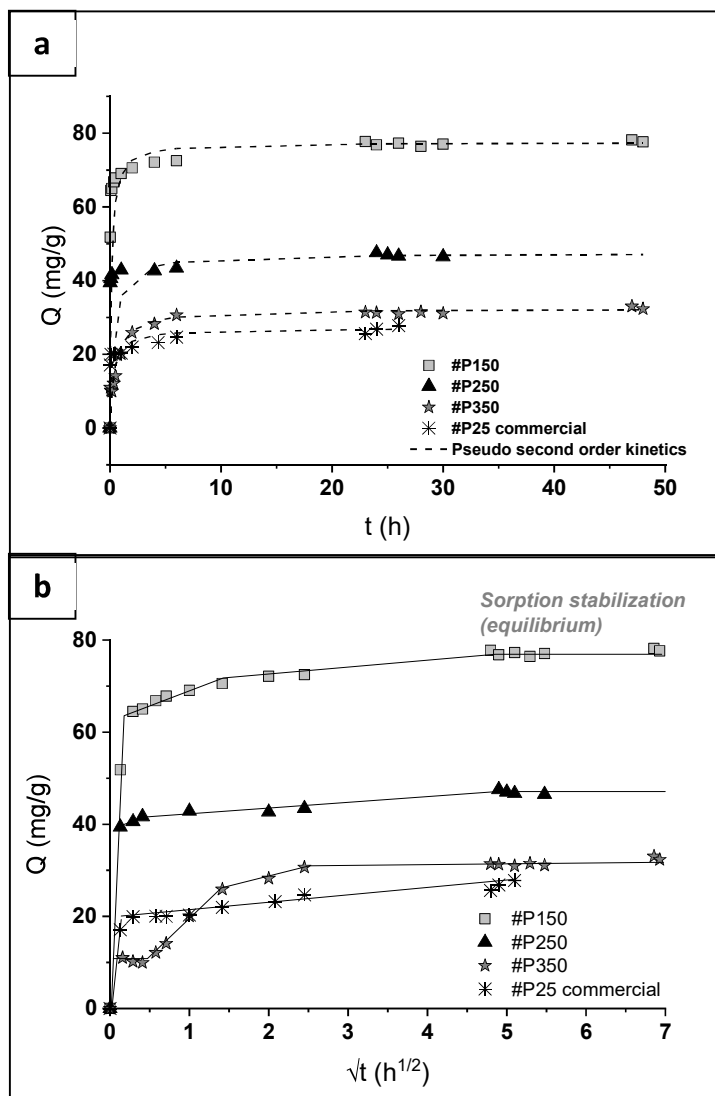
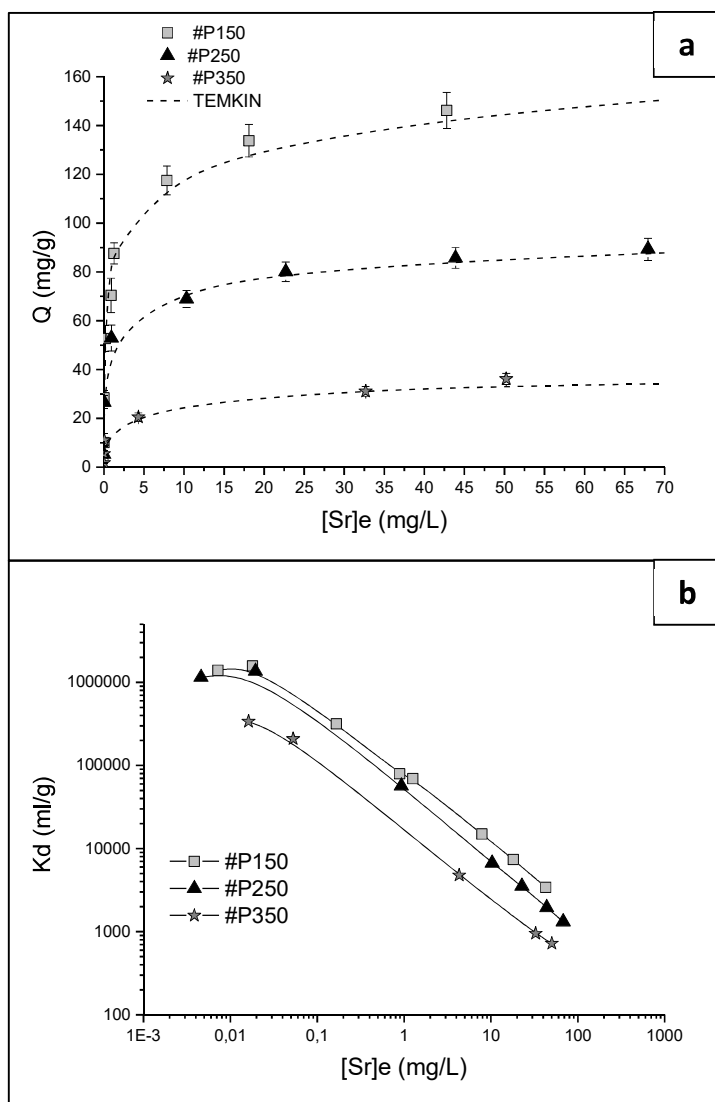


Figure 6 (a) Concentration adsorption isotherms fitted with the Temkin equation, (b) distribution (Kd) isotherms for TiO₂ microspheres prepared in supercritical CO₂ at 150, 250 and 350°C in suspensions at pH 11





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