Nanostructured  $K_x Na_{1-x} NbO_3$  hollow spheres as potential materials for the photocatalytic treatment of polluted water<!--<ForCover>Praxedes FR, Nobre MAL, Poon PS, Matos J, Lanfredi S, Nanostructured  $K_x Na_{1-x} NbO_3$  hollow spheres as potential materials for the photocatalytic treatment of polluted water, *Applied Catalysis B: Environmental*, doi: 10.1016/j.apcatb.2021.120502</ForCover>->



Fabiano R. Praxedes, Marcos A.L. Nobre, Po S. Poon, Juan Matos, Silvania Lanfredi

PII:	S0926-3373(21)00628-7
DOI:	https://doi.org/10.1016/j.apcatb.2021.120502
Reference:	APCATB 120502
To appear in:	Applied Catalysis B: Environmental
Received Date:	24 December 2020
Revised Date:	29 June 2021
Accepted Date:	30 June 2021

Please cite this article as: { doi: https://doi.org/

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2020 Published by Elsevier.

# Nanostructured K<sub>x</sub>Na<sub>1-x</sub>NbO<sub>3</sub> hollow spheres as potential materials for the photocatalytic treatment of polluted water

Fabiano R. Praxedes <sup>a,b</sup>, Marcos A.L. Nobre <sup>a,b</sup>, Po S. Poon<sup>c</sup>, Juan Matos<sup>\*d</sup>, Silvania Lanfredi<sup>\*\* a,b</sup>

<sup>a</sup>São Paulo State University (Unesp), School of Technology and Sciences, Presidente Prudente, SP, 19060-900, Brazil.

<sup>b</sup>São Paulo State University (Unesp), Institute of Biosciences, Humanities and Exact Sciences, São

José do Rio Preto, SP, 15054-000, Brazil.

<sup>c</sup>Unidad de Desarrollo Tecnológico (UDT), Universidad de Concepción, Barrio Universitario s/n, Concepción, Chile.

<sup>d</sup>Instituto de Ciencias Químicas Aplicadas, Facultad de Ingeniería, Universidad Autónoma de Chile, 8900000 Santiago, Chile.

\*Corresponding Author. E-mail: juan.matos@uautonoma.cl (J. Matos).

\*\* Corresponding Authors. E-mail: silvania.lanfredi@unesp.br (S. Lanfredi).

Phone: +56 9 9379 8340

### **GRAPHICAL ABSTRACT**



### Highlights

- Niobate-based materials with stoichiometry K<sub>x</sub>Na<sub>1-x</sub>NbO<sub>3</sub> were studied in the UV-driven photodegradation of Basic Blue 41.
- The synthesis of the niobate-based hollow spheres was performed by the spray pyrolysis method.
- The hollow spheres became as membrane-like photoreactors with an energy band-gap of 2.93 eV for K<sub>0.5</sub>Na<sub>0.5</sub>NbO<sub>3</sub>.
- The photocatalytic activity was up to 23 times more photoactive than commercial TiO<sub>2</sub>.
- The increase in photoactivity was ascribed to the formation of highly reactive apical O atoms in the niobate-based structure.

#### Abstract

Potassium-sodium niobate-based hollows spheres were studied in the photocatalytic degradation of Basic Blue 41 dye in aqueous phase under UV irradiation.  $K_xNa_{1-x}NbO_3$  materials were prepared at 700°C by the spray pyrolysis method. Photocatalysts were characterized by XRD, SEM, TEM, N<sub>2</sub> adsorption/desorption isotherms and FTIR. Different kinetic models of adsorption, direct photolysis,

and photocatalytic degradation of the azo-dye were performed as a function of the pH of solution. The increase in potassium content is responsible of the distortion and polarization of the niobate structure promoting a decrease in the energy band-gap down to 3.01 eV for  $K_{0.5}Na_{0.5}NbO_3$ . The photocatalytic activity observed on  $K_{0.5}Na_{0.5}NbO_3$  was up to 23 times higher than that on TiO<sub>2</sub> in terms of the surface concentration of the azo-dye molecules adsorbed. A mechanism for the degradation of Basic Blue 41 azo-dye based on the reactive oxygen species detected by scavenger's tests and mass-spectroscopy analysis was proposed.

Keywords. K<sub>x</sub>Na<sub>1-x</sub>NbO<sub>3</sub> photocatalysts; Ultrasonic spray pyrolysis; Hollow spheres; Basic blue 41.

### 1. Introduction

Perovskite-like structures based on niobium oxides, such as alkali niobates (LiNbO<sub>3</sub>, NaNbO<sub>3</sub>, KNbO<sub>3</sub>) have been widely investigated as main substitute for compounds based on lead [1,2] due to its ferroelectric and piezoelectric properties. These materials have also been studied in the photocatalytic degradation of organic dyes, H<sub>2</sub> and O<sub>2</sub> production, and CO<sub>2</sub> reduction reactions [3,4]. In addition, alkali niobates are characterized by a high chemical stability under irradiation, and thus, these materials are promising catalysts for environmental remediation of polluted water. Sodium niobate (NaNbO<sub>3</sub>) and potassium niobate (KNbO<sub>3</sub>) are the main niobium-based oxides studied in photocatalysis. Both are n-type semiconductors [5-13] characterized by a large band gap of ca. 3.5 eV and 3.2 eV, respectively. It is well-known, that addition of potassium cation in sodium niobate host structure result in an improvement of its ferroelectric and piezoelectric properties [14]. However, up to now, the influence of A-site cation mainly potassium, in the sodium niobate-based perovskite structure upon the photocatalytic activity have not been reported. In addition, the hydrophilic behavior is an important characteristic of potassium or sodium niobates [12,13] since the photocatalytic reactions occur mainly on adsorbed phase [15].

On the other hand, hollow nanostructured materials would promote an increase in the reactivity of semiconductor materials [16,17] due to its high surface area and tailored porosity. For instance, hollow spheres have received a great attention in several applications such as catalytic oxygen reduction [18], treatment of polluted water [19], drug delivery [20], catalytic hydrogen production [21], and lithiumion batteries [22]. This technique offers an easy and quickly way to synthesize spherical materials without templates. Thus, different photocatalysts such as graphene [25], TiO<sub>2</sub>/In<sub>2</sub>O<sub>3</sub> [26], Audecorated CdS [27], TiO<sub>2</sub>/WO<sub>3</sub> [28], Au-ZnO and Pt-ZnO [29], and Cu-based metal–organic framework's (MOF's) [30] have been prepared by spray pyrolysis and investigated as photodetectors, plasmonic materials, photocatalysts for the degradation of dyes, and photovoltaic applications. However, much of the research of Nb-based semiconductors have been investigated through the solgel, hydrothermal and ball milling route. The spray pyrolysis method [23,24] has been one of the main techniques used to prepare spherical hollow materials.

Keeping this in mind, the influence of potassium doping within a host structure based on sodium niobate was studied and the potential of these materials in the photocatalytic degradation of a commercial azo-dye was verified. To the best of our knowledge, the present work reports for the first time the synthesis of  $K_xNa_{1-x}NbO_3$  hollow spheres with stoichiometry  $K_{0.2}Na_{0.8}NbO_3$ ,  $K_{0.3}Na_{0.7}NbO_3$ , and  $K_{0.5}Na_{0.5}NbO_3$  prepared by spray pyrolysis technique. The synthesis of  $K_xNa_{1-x}NbO_3$  materials was limited for  $x \le 0.5$ , since these materials show a high sensitivity to ambient humidity which needs special consideration during synthesis procedure. However, future works could be carried out considering the  $K_xNa_{1-x}NbO_3$  materials with x > 0.5. As a first approach, the photocatalytic activity of these materials was evaluated in the UV-driven degradation of Basic Blue 41 (BB41) as target molecule. BB41 has been chosen as target molecule because the growing attention concerning about the carcinogenic and mutagenic effects of this azo-dye widely used in the textile industry [31,32].

### 2. Experimental Procedure

#### **2.1. Synthesis of materials**

Potassium-sodium niobate powders were synthesized by a modification of the spray-pyrolysis method already reported by our group for K- and Cu-doped CaTiO<sub>3</sub>-based nanostructured hollow spheres [33]. The spray pyrolysis process consists in the atomization of a precursor solution by a high frequency generated in the middle. The drops formed are transported by a gas flow into the pyrolysis zone and the physicochemical transformation of drops into particles starts with the initial evaporation of solvent at drop surface, causing an increase in the concentration of remaining solution. At this stage, salts crystallization takes place leading to the formation of a shell, and the final process consists in the solvent evaporation together with organic matter decomposition and particle sintering, yielding into a spherical and hollow nanostructured material. In the present work, materials with the following stoichiometries K<sub>0.2</sub>Na<sub>0.8</sub>NbO<sub>3</sub>, K<sub>0.3</sub>Na<sub>0.7</sub>NbO<sub>3</sub>, and K<sub>0.5</sub>Na<sub>0.5</sub>NbO<sub>3</sub>, denoted as KNN-0.2, KNN-0.3, and KNN-0.5, respectively, were synthesized. The precursor solutions of sodium-potassium niobate were prepared using niobium ammonium oxalate, (NH<sub>4</sub>)<sub>4</sub>[NbO(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub>]<sub>4</sub>·2H<sub>2</sub>O (97.0 %, CBMM-Brazil), sodium nitrate, NaNO<sub>3</sub> (99.0 %, Vetec) and potassium nitrate, KNO<sub>3</sub> (99.0 %, Vetec) as starting reagents. The final solution obtained, with a concentration of 50 mmol L<sup>-1</sup>, was placed in the spray container and atomized by a high frequency ultrasonic generator at 1.7 Mhz. The spray formed was drawn into a tubular furnace using a carrier gas (air) at 5 L min<sup>-1</sup> flow rate and the temperature of pyrolysis was set at 700 °C for the synthesis of the niobate-based materials.

### 2.2. Characterization

The morphology of the particles was verified by scanning electron microscopy (SEM) using a Carl Zeiss equipment, model EVO LS15. A small amount of sample was ultrasonically dispersed in isopropanol and a drop from the suspension was deposited on a glass coverslip. The measurements were carried out through adding a double-sided conductive carbon type. The histograms of samples were obtained from the statistical processing of images using the ImageJ software [34]. Transmission electron microscopy (TEM) was performed in a Microscope JEOL-2100F, operating at 200kV. Images

were obtained in TEM and STEM mode (HAADF-STEM). All samples were dispersed in ethanol (99.98%), using an ultrasonic cleaner for 15 min. After this time, the sample was deposited on the carbon-coated copper screen, and after drying, the samples were analyzed.

Textural properties were obtained from the N<sub>2</sub> adsorption/desorption isotherms at -196°C collected in a Nova QuantaChrome 1200 surface area analyzer. Surface area was determined by BET (Brunauer– Emmett–Teller) equation, while BJH (Barrett–Joyner–Halenda) method was used to obtain the total volume of pores, volume of micro- and mesopores and the average pore diameter.

The structure of potassium-sodium niobate materials was obtained from the analysis of the X-ray diffraction (XRD) patterns using a Shimadzu diffractometer (XRD-6000 model) with Cu-Ka radiation  $(\lambda = 1.54 \text{ Å})$  and graphite monochromator. The measurements were performed in the angular region of  $5^{\circ} \le 2\theta \le 80^{\circ}$  with 0.02° scanning step. Crystalline structures of potassium-sodium niobate samples were refined by the Rietveld method using FullProf software [35,36]. The main parameters and variables adopted during the refinement process are summarized as follows. Background coefficients using a polynomial of 5-order with a pseudo-Voigt function; scale factor; lattice parameter; atomic coordination; occupancy factors and isothermal parameters for four atoms (Na, K, Nb, O). The crystalline structures were built using Diamond software from atomic positions derived from the refinement. The influence of the texture upon the microstructure of the alkali niobate-based spheres was investigated in terms of isotropic microstrain and anisotropic crystallite size as well as crystallite shape. The apparent anisotropic crystallite size and maximum average strain were obtained from the microstructural refinement following an approach by spherical harmonic method [36,37]. This approach makes use of the Pseudo-Voigt function modified by Thompson and coworkers [38] to describe the contributions of peaks obtained by the Gaussian and Lorentzian deconvolutions. The spherical harmonic method is a phenomenological model based on Scherrer formula [36]. The anisotropic size effects are modeled from the Lorentzian contribution on the peak broadening and its linear combination with spherical harmonics. This treatment is given by Eq. 1, where  $\beta_h$  is the size

contribution on integral broadening of reflection **h**,  $a_{imp}$  and  $y_{imp}$  ( $\Theta_{\mathbf{h}}$ ,  $\Phi_{\mathbf{h}}$ ) are the spherical harmonic coefficients and the real spherical harmonic components, respectively.

$$\beta_{\mathbf{h}} = \frac{\lambda}{D_{\mathbf{h}} \cdot \cos \theta} = \frac{\lambda}{\cos \theta} \sum_{lmp} a_{lmp} \cdot y_{lmp} (\Theta_{\mathbf{h}}, \Phi_{\mathbf{h}})$$
(1)

Independently to the Laue group, this approach can be expanded to a symmetric spherical harmonic series with polar angles of vector h, with respect to crystallographic lattice in the Cartesian plane. The apparent size (D<sub>h</sub>, in Å) is calculated from the instrumental resolution (experimental parameters U, V, W) through the refinement of spherical harmonic coefficients  $a_{lmp}$ , over each reciprocal vector from crystallographic structure. In summary, the initial values in microstructural refinement were provided by the crystallographic data obtained using the previous structural refinement by Rietveld method. The structural components as cell dimension, atomic coordination, and isotropic factor were maintained fixed in the refinement. The profile parameters such as scale, zero point, and background were refined from their initial values. Other components related to Gaussian and Lorentzian contributions were refined as well as the spherical harmonic parameters (y<sub>00</sub>, y<sub>20</sub>, y<sub>22+</sub>, y<sub>40</sub>, y<sub>42+</sub>, y<sub>44+</sub>). The spherical harmonics parameters are according to the Laue group mmm from space group Pbma [35]. To obtain the crystallite apparent size, an instrumental resolution ( $U_{ins} = 0.00401$ ,  $V_{ins} = -0.00971$ ,  $W_{ins} = 0.01715$ e  $X_{inst} = 0.00752$ ) was provided from the measurement of SiO<sub>2</sub> standard. The sample parameters U, V, and W were fixed to zero. The isotropic strain was obtained by refining the U component of the sample [39]. The refinement was performed using FullProf software [35], and the anisotropic average shape was visualized in the GFourier program [40]. The crystallite apparent size and the maximum average strain were obtained with standard deviation related to anisotropy degree.

The chemical bonds of samples were analyzed by Fourier-transform infrared spectroscopy (FTIR) using a Perkin Elmer spectrophotometer (Frontier model), equipped with a diamond-crystal for the attenuated total reflection (ATR). The measurements were carried out with an instrument resolution of  $2 \text{ cm}^{-1}$  in the range of  $4000 - 250 \text{ cm}^{-1}$  for 60 scans.

The energy band gap of the samples was determined from the Kubelka-Munk theory based on the Tauc method by plotting  $(F(R)h\nu)^{1/\alpha} = B(h\nu - E_g)$ , considering  $\alpha = 2$  for indirect transition [41]. The UV-Visible analysis was carried out in the range 200 - 600 nm using a Perkin Elmer spectrophotometer (model Lambda 1050) equipped with diffuse reflectance module.

### 2.3. Adsorption and photocatalytic tests

The photocatalytic activity was evaluated following the kinetics of degradation of Basic Blue 41 (C<sub>20</sub>H<sub>26</sub>N<sub>4</sub>O<sub>6</sub>S<sub>2</sub>, Sigma-Aldrich) denoted BB41. The photocatalytic reactions were performed in a homemade continuous experimental set-up consisting of an opaque PCV photoreactor of ca. 250 mL, an immersed UV-C lamp (Osram, 15 W, 254 nm for the UV emission), a Pyrex flask for the pollutant solution, and a water pump (5 W) with a circulating rate fixed at ca. 180 L h<sup>-1</sup>. Figure S1 (Supplementary Material) shows a picture of the experimental set-up. The total volume of BB41 solution in the Pyrex flask was 1L before recirculating, while the volume of irradiated solution was ca. 250 mL. The initial concentration of BB41 was 26 µmol L<sup>-1</sup> and ca. 100 mg catalysts were used in all the adsorption and photocatalytic tests. Accordingly, the loading of samples used in the present work was constant, ca. 0.1 g  $L^{-1}$ . These values were chosen because they were optimized in a previous work of BB41 photodegradation [42]. Preliminary studies of BB41 adsorption in the dark were performed to guarantee the correct interpretation of the degradation results obtained under irradiation. The kinetics of adsorption in the dark showed that after 1h the equilibrium of adsorption was achieved. After this time, irradiation was performed by 4 h UV irradiation. Several aliquots were taken each 15 minutes for the first hour of irradiation and each 30 minutes for the next 3 hours. Aliquots were centrifuged at 3000 rpm before analysis by UV-Vis spectroscopy in a Genesis model spectrophotometer with single bean. The samples were measured at 611 nm as the wavelength of maxima absorption for BB41 dye. Since the pH of BB41 aqueous solution is ca. 5.2, the experiments were performed at neutral (7.0), acid (3.0) and basic pH (10.0). Thus, the influence of pH of solution upon adsorption and photocatalytic activity was verified. For the tests in neutral and basic pH, the

solution was adjusted to ca. 7.0, or 10.0 using KOH 0.5 M, while for the experiments in acid conditions, the pH was adjusted at ca. 3.0 using HNO<sub>3</sub> solutions at 0.5 M.

Aliquots were centrifuged at 6000 rpm before total organic carbon (TOC) analysis. The TOC was measured with a Shimadzu TOC-VCSN analyzer. In addition to neutral pH experiments, the influence of pH of solution upon the TOC evolution was also verified.

The reactive oxygen species (ROS) were evaluated by addition of benzoquinone (BQ) and isopropyl alcohol (IP) as scavengers for the capture of superoxide radical ( $\cdot$ O<sub>2</sub><sup>-</sup>) and hydroxyl radical ( $\cdot$ OH), respectively. The concentration of BQ and IP followed the same experimental conditions proposed by Chu *et al.* [43]. The scavenger's reagents were added to 1L of BB41 in the same initial concentration described before. After 1 h adsorption in the dark, the photodegradation experiments were followed as a function of irradiation time at the three pH indicated above. The aliquots were taken periodically, centrifuged at 6000 rpm for 5 min, and the changes of BB41 concentration was followed by UV-Vis spectroscopy.

The intermediates of BB41 photodegradation were investigated by gas chromatography–mass spectrometry GC-MS (QP2010 plus). The GC-MS was equipped with a low polar Rtx-5MS column (5% diphenyl and 95% dimethylpolysiloxane) 30m x 2.5mm x 0.25µm and a mass spectrometer detector with electronic ionization (70 eV). The parameters used were the following. Gas carrier was Helium injector temperature 250°C, injection volume 1.00 µL. The GC column operated in a temperature-programmed mode at 40°C for 1 min, and then raised to 280°C at 10°C min<sup>-1</sup>. The parameters for the mass spectrometer were the following. Interface temperature 250°C, temperature of the ionization chamber 280°C. Aliquots of 5 mL were taken from solution at selected irradiation times, and before the GC-MS analysis, the aliquot was centrifuged at 6000 rpm for 5 minutes. After this, 2 mL sample was taken, and 1 mL of diethyl ether was added to extract the intermediate. The extraction head was taken out, dried with magnesium sulfate and inserted into the GC-MS system. Also, the aliquot without organic solvent extraction was analyzed.

#### 3. Results and discussion

### 3.1. Characterization of K<sub>x</sub>Na<sub>1-x</sub>NbO<sub>3</sub> materials

#### **3.1.1.** Morphology and Texture

**Figure 1** shows the SEM images of  $K_xNa_{1-x}NbO_3$  samples obtained by the spray pyrolysis treatment. It can be seen the samples show a spherical shape. Digital 3D analysis using ImageJ software allowed the identification of bright and dark areas in the materials. The analysis indicates a major degree of roughness in **Figures 1d**, **1e**, **1f**, and a minor degree in **Figures 1g**, **1h**, **1i**, suggesting different porous framework of the materials. Some cracked particles exhibit the thickness of the shell which will be carefully discussed from the TEM analysis (**Figure 2**). The presence of fractures and the formation of hollow particles can be associated to the evolution of gases along the degradation of organic matter. This process leads to an increase of pressure inside of the shell/drop system formed during the pyrolysis process [24], yielding into a porous hollow structure. If this process is accelerated, the pressure inside of particle can collapse the structure, resulting in cracked particles [24,44,45]. The formation of gases such as  $NO_x$ ,  $NH_3$  and  $H_2O$  throughout the synthesis of potassium-sodium niobates can be related to the formation of hollow particles as reported for K- and Cu-doped CaTiO<sub>3</sub>-based nanostructured materials [33]. It can be seen from the **Figures 1j**, **1k**, **1l**, all samples seem to show a similar maxima value in the histograms with a mean size of particles of ca. 500 – 600 nm.



**Figure 1.** SEM images of (a) KNN-0.2, (b) KNN-0.3, and (c) KNN-0.5. Surface 3D analysis of rough particles (blue circles), for (d,g) KNN-0.2, (e,h) KNN-0.3, and (f,i) KNN-0.5. Particle size distribution histograms of (j) KNN-0.2, (k) KNN-0.3, (l) KNN-0.5 samples.

However, the particle size distributions became broader in the histograms as a function of composition with x varying from 0.2 to 0.3 and 0.5. By using the Euler's theorem, our group have reported a methodology for the accuracy estimation of the average value of different topological properties in carbon foams, a highly random material composed by carbon polygons with different number of sizes [46,47]. According to Euler's theorem, the average particle size ( $\langle P \rangle$ ) can be obtained from the particle size distribution  $\rho(n)$  in terms of the n range of the particles by Eq. (2).

$$\langle P \rangle = \Sigma n. \rho(n)$$
 (2)

The average particles size from the histograms in **Figures 1j**, **1k** and **1l**, were ca. 506 nm, 588 nm, and 619 nm for KNN-0.2, KNN-0.3, and KNN-0.5, respectively. The increase in the average particles size

can be associated with the increase of K composition within the K<sub>x</sub>Na<sub>1-x</sub>NbO<sub>3</sub> structure. In according to literature, the melting temperature of NaNbO<sub>3</sub> is equal to 1422°C [48]. This temperature decreases with the increase of the potassium concentration in the NaNbO<sub>3</sub> host structure, reaching the melting temperature at 1140°C for the K<sub>0.5</sub>Na<sub>0.5</sub>NbO<sub>3</sub> solid solution [48]. However, this temperature is much higher than the synthesis temperature (700°C) of the KNN solid solutions obtained by spray pyrolysis method. The obtention of powders at low temperature is an advantage of this method compared to the conventional method by solid state reaction, which requires high temperature of calcination of the precursor powders (1000°C), close to melting temperature [49], leading to sintering and increase of particle size. In this sense, the increase of the particle size can be explained by the physical-chemical properties of the precursor solution, which is influenced by the increase of K content. According to Li et al. [50], the particle formed via spray pyrolysis is greatly influenced by the precursor metal salts. The solubility of metal salts determines the type of particle formed: dense sphere, shrink sphere, or a hollow sphere. In the case of KNN, the solubility of potassium nitrate is much lower (38.3 g 100 mL<sup>-</sup> <sup>1</sup> water at 25°C) than that of sodium nitrate (91.2 g 100 mL<sup>-1</sup> water at 25°C). Therefore, when the potassium concentration increases according to doping, the solubility of precursor solution decrease, influencing the formation of the particle during the pyrolysis process. Accordingly, the increase of the potassium concentration favors the increase and densification of the shell of the spheres with a concomitantly decrease in the porosity. This characteristic results in an increase of the particles size, in agreement with the features observed in the SEM (Figures 1j, 1k and 1l). In other words, the higher concentration of potassium, the higher the thickness of the shell of the spherical particles, as shown the TEM images (Figure 2) discussed as follows.

**Figure 2** shows TEM images of the (a) KNN-0.2, (b) KNN-0.3, and (c) KNN-0.5 samples. It can be seen the higher concentration of potassium, the higher the thickness of the shell of the spherical particles. For the KNN-0.2 the shell thickness is ca. 17 nm, while for the KNN-0.3 and KNN-0.5 are ca. 28 nm and 42 nm, respectively. This result suggests that stoichiometry of the precursor solution

play an important role in the control of the particle. The strong contrast observed between the light center and relatively dark edge indicates the samples are composed by hollow spheres. For instance, the hollow spheres of the KNN-0.2 sample in Figure 2a are formed by an array of nanometric particles. According to the inset in Figure 2a, these particles vary between 18 - 60 nm and have cubic and pseudo-spherical shape, which is in good agreement with the features observed in the crystallite anisotropic shape for this sample discussed below in section 3.1.4. In addition, TEM images also suggest that the increase of the potassium concentration favors the densification and the size of the shell decreasing the porosity, as shown Figures 2b and 2c. Densification of the shell can be understood as solid particles assembled from numerous ultrafine primary nanoparticles, which depend on the solubility of the precursor reagents [51,52]. It means solubility plays an important role in the precipitation and formation of spherical particle. The rapid precipitation of the precursor is affected by the saturation of the solution, as shown in the schematic representation of the particle formation process in Figure 3. This feature results in hollow particle, as well as an increase in the roughness degree of the particles, in agreement with the features observed in the SEM (Figure 1). In this way, the concentration of the precursor solution has an important role in both spherical form and roughness of particle. As expected, the crystalline plane indexed in the TEM images were (101) and (141), were both associated with the NaNbO<sub>3</sub> host structure having orthorhombic symmetry. Structural features of the materials are carefully discussed below in the section 3.1.3.



Figure 2: TEM images of catalysts. (a): KNN-0.2, (b): KNN-0.3, and (c): KNN-0.5.

As expected, the increase in the average particle size affects the textural properties of the materials. **Figure S2 (supplementary Material)** shows the N<sub>2</sub> adsorption/desorption isotherms (**Figures 2Sa**, **2Sb**, and **2Sc**), the cumulative pore volume (**Figures 2Sd**, **2Se**, and **2Sf**) and the pore size distribution (**Figures 2Sg**, **2Sh**, and **2Si**). A summary of the textural results is listed in **Table 1**. All samples followed a type III isotherm characteristic of non-porous sorbents with low energy of adsorbent-adsorbate interaction [53,54] in agreement with the low values observed for BET surface area (S<sub>BET</sub>) in **Table 1**. In addition, a vertical hysteresis loop type H1 can be noticed suggesting the aggregation of nanoparticles [53,54] and a mesopore framework as can be also observed in the cumulative pore volume (**Figures 2Sd**, **2Se**, and **2Sf**). A deeper analysis from the pore size distribution (**Figures 2Sg**, **2Sh**, and **2Si**) showed all the materials are mainly characterized by small mesopores in the range from 2 to 8 nm with an almost perfect Gaussian symmetry centered at ca. 5 nm in agreement with the mean

pore diameters ( $D_{pore}$ ) of ca. 4.9 – 6.4 nm obtained from BJH method. Thus, the pore size distributions suggest all samples are mainly composed by mesopores with an almost negligible micropore volume ( $V_{micro}$ ) as reported in **Table 1**.

Sample	$\frac{S_{BET}}{(m^2 q^{-1})}$	$V_{\text{micro}}^{b}$	$V_{\text{meso}}^{c}$	$V_{Tot}^{b}$	D <sub>pore</sub> <sup>b</sup>
KNN-0.2	106 (m g )	0.004	0.164	0.168	6.4
KNN-0.3	43	0.007	0.053	0.060	4.9
KNN-0.5	40	0.002	0.056	0.058	5.9

**Table 1.** Summary of textural and porosimetry properties of the samples.

<sup>a</sup> Surface area was determined by BET (Brunauer–Emmett–Teller) equation. <sup>b</sup> Total volume of pores ( $V_{Tot}$ ), volume of micropore ( $V_{micro}$ ), volume of mesopores ( $V_{meso}$ ), and the mean pore diameter ( $D_{pore}$ ) were obtained from BJH (Barrett–Joyner–Halenda) method.

The incipient micropore framework observed from the N<sub>2</sub> adsorption/desorption isotherms can be associated with empty voids formed between these nanoparticles in the solvent evaporation stage during the spray pyrolysis, while the mesopore framework is consequence of the development of mesopores within the spheres. A schematic representation of the potassium-sodium niobate spherical hollow particles obtained from spray pyrolysis process is shown in **Figure 3**. According to the 3D analysis (**Figure 1**) and N<sub>2</sub> adsorption/desorption isotherms (**Figure S2, supplementary**), the KNN-0.2 sample exhibits particles with a more porous surface than KNN-0.3 and KNN-0.5, which can be related to a densification of the shell of hollow spheres discussed from TEM images (**Figure 2**).

There is a monotonic decrease in the specific surface area ( $S_{BET}$ ) and the total volume of pores ( $V_{Tot}$ ) with the increase in potassium concentration in the sodium niobate host structure. According to the results obtained from SEM, TEM and BET analysis, it can be suggested that the hollow spheres of KNN samples are mainly composed by a porous shell, which densification increase as a function of potassium content in the NaNbO<sub>3</sub> host structure. Therefore, the remarkable decrease in the specific surface area of KNN-0.3 and KNN-0.5 with respect to that observed in KNN-0.2 is attributed to the increase in the densification of the shells of the spheres as a function of the incorporation of higher K

content which clearly increased the shell's size from 17 nm for KNN-0.2 up to 28 nm and 42 nm for KNN-0.3 and KNN-0.5, respectively.



Figure 3. Schematic representation of the particle formation process by spray pyrolysis.

### 3.1.2. FTIR and DR/UV-Vis spectroscopy

Infrared spectra of KNN-0.2, KNN-0.3, and KNN-0.5 are shown in **Figure 4** while **Table 2** listed a summary of FTIR and UV-Vis spectroscopy results. A band around 530 cm<sup>-1</sup> is attributed to the vibrational mode in the edge-shared NbO<sub>6</sub> octahedra in the perovskite structure [55-57]. This band shifts to lower wavenumber values as a function of the increase in the concentration of potassium cation in sodium niobate host structure suggesting an increase of the ionic character of the Nb–O–Nb bond [57]. A second band at 612 cm<sup>-1</sup> is associated to vibration of Nb–O bond in the NbO<sub>6</sub> octahedron [55,56] and a third band at 830 cm<sup>-1</sup> is assigned as an asymmetric enlargement of the Nb–O bond due to formation of a more crystalline perovskite structure [56]. Two vibrational bands positioned between 1000 to 1400 cm<sup>-1</sup> can be associated to bridged nitrites (1252 cm<sup>-1</sup>) and nitro or nitrate groups (1366 cm<sup>-1</sup>) [58]. Other two bands observed at 1643 cm<sup>-1</sup> and 3414 cm<sup>-1</sup> are assigned to the bending ( $\delta$ OH) and stretching ( $\nu$ OH) of adsorbed water, respectively [59]. The presence of both OH and NO bands probably can be related to gases adsorbed on material from the niobate ammonium oxalate degraded during the pyrolysis.



Figure 4. FTIR spectra of samples.

**Table 2.** Positions and wavenumber assignments of the Nb-O vibration bands obtained from FTIR spectra, and optical properties of samples, including maxima absorption wavelength ( $\lambda_{abs-photon}$ ) and optical energy band bap (E<sub>bg</sub>) obtained from DR/UV-Vis spectra.

Samples	$\lambda_{abs-photon}$	Ebg	Wavenumber (cm <sup>-1</sup> )		
	(nm)	(eV)	Nb-O $(v)$	Nb-O (vas)	<b>Nb-O</b> (v)
KNN-0.2	385	3.21	526	612	836
KNN-0.3	387	3.20	521	612	836
KNN-0.5	411	3.01	515	612	836

On the other hand, the optical band gap for KNN-0.2, KNN-0.3, and KNN-0.5 was determined from diffuse reflectance spectroscopy in the UV-visible region (**Figure 5**). Assuming an indirect transition, the energy band gap ( $E_{bg}$ ) values were obtained from the Tauc plots (**Figure 5c**). Considering the best linear range (3.2 to 3.8 eV), the intercept of the linear regression of the Tauc plot with the energy axis determines the position of  $E_{bg}$  [41] as shown **Figure 5c**. A summary of the results is listed in **Table 2**.



**Figure 5.** (a): DR/UV-Vis spectra in terms of the Kubelka-Munk theory. (b): Tauc plot according to an indirect transition. (c) Linear regression of Tauc plot in the range (3.2 - 3.8 eV).

The band gap values of the potassium-sodium niobate showed in **Table 2** may promote controversy with some values reported in the literature for indirect transition. For instance, Zlotnik *et al.* [12] reported a band gap of 3.49 eV for NaNbO<sub>3</sub> (orthorhombic) and 3.27 eV for KNbO<sub>3</sub> (orthorhombic),

both synthesized by solid-state reaction, while Wang *et al.* [60] reported a band gap of 3.42 eV for NaNbO<sub>3</sub> nanoparticles with cubic symmetry, synthesized via low temperature crystallization method. The present results showed a range of  $E_{bg}$  between 3.01 – 3.21, which are close to those reported by Khorrami *et al.* [61] for NaNbO<sub>3</sub> and KNbO<sub>3</sub>, synthesized via sol-gel with a band gap of 3.38 eV and 3.18 eV, respectively. The present results also agree with those reported by Liu *et al.* [62] for NaNbO<sub>3</sub> nanowires with orthorhombic symmetry via hydrothermal method and with a band gap of 2.98 eV at 400°C, which increase to 3.06 eV at 600°C, being very close to band gap of NaNbO<sub>3</sub> with cube symmetry (3.09 eV) obtained at 180°C. The lower energy band gaps reported for the present K<sub>x</sub>Na<sub>1-x</sub>NbO<sub>3</sub> hollow spheres can be due to the substitution of sodium by potassium in the host structure influence this optoelectronic property. As discussed from the FTIR spectra, the increase in potassium composition influences the ionic character of the chemical bond in Nb-O-Nb. As consequence, the apical oxygen in the perovskite-based structured could be more polarized as reported elsewhere [63] for KSr<sub>2</sub>Nb<sub>5</sub>O<sub>15</sub> nanostructured materials. In other words, the polarization of the K<sub>x</sub>Na<sub>1-x</sub>NbO<sub>3</sub> structure favors the excitation by photons of lower energy promoting the charge transfer process from apical O to Nb atoms responsible for the band-gap.

SEM (**Figure 1**), TEM (**Figure 2**) and textural analysis (**Figure 2S, supplementary material**) support this inference, since histograms of particle sizes, the roughness in the surface and the changes in the pore framework of samples were remarkably affected by the increase in potassium composition. In short, it can be suggested that spray pyrolysis is an effective method to prepare nanostructured and photoactive semiconductor materials probably by an enhancement in the light harvesting efficiency as reported elsewhere [64,65] for TiO<sub>2</sub>-based nanostructured mesopore hollows spheres.

### 3.1.3. Structural analysis by X-ray diffraction

**Figure 6a** shows the XRD patterns for KNN-0.2, KNN-0.3, and KNN-0.5 powders. The patterns were identified as NaNbO<sub>3</sub> phase of perovskite structure with orthorhombic symmetry and space group

*Pbma* (n°57), according with JCPDS card 33-1270. In agree with results from Gupta and coworkers [66], the increase in the concentration of potassium cation within the NaNbO<sub>3</sub> host structure results in a lattice expansion due to the increase in the ionic radii of K<sup>+</sup>, 0.138 nm, instead of 0.102 nm for Na<sup>+</sup>. This lattice expansion can be visualized by the displacement of the diffraction lines at (101) and (141) planes as well as a decrease in their intensity as shown in **Fig. 6b**. These trends can also be observed through of (102) and (122) planes in the region between 35° and 45° in 20 (**Fig. 6c**), where diffraction line at (102) plane presents a low intensity, while the line at (122) plane has disappeared for the patterns of KNN-0.3 and KNN-0.5 [67].



**Figure 6.** (a): X-ray diffraction patterns of KNN-0.2, KNN-0.3, and KNN-0.5 powders. (b): Expansion of the region between 20° and 35°. (c): Expansion of the region between 35° and 41°.

The Rietveld plots are shown in **Figure S3** (**Supplementary Material**). The lattice parameters and unit cell volume derived from the structural refinement of potassium-sodium niobates are summarized in **Table 3.** The atomic coordinates, isotropic parameter (B<sub>iso</sub>), and relative occupancy (P) for

 $K_{0.2}Na_{0.8}NbO_3$ ,  $K_{0.3}Na_{0.7}NbO_3$ , and  $K_{0.5}Na_{0.5}NbO_3$  are listed in **Table S1** (**Supplementary material**). In addition, **Table 3** shows the parameter **b** and **c** rises proportionally to potassium concentration in the host structure. However, the difference for parameter **a** between alkali niobate compositions is unchanged or is very small. The increase in the lattice parameters is a quantitative evidence of the expansion of the unit cell, due to distortions from NbO<sub>6</sub> octahedron as a result in variation of Nb–O bond length.

Composition	Lattice parameters (Å)			Unit cell volume	D	D	D	or <sup>2</sup>
Composition	a	b c	c	$(\text{\AA}^3)$	Кр	Кwр	Nexp	X
KNN-0.2	5.57	15.61	5.54	481.31	9.68	12.3	8.69	2.10
KNN-0.3	5.56	15.70	5.62	490.55	8.38	11.3	8.64	1.79
KNN-0.5	5.61	15.80	5.64	500.38	8.05	10.8	8.52	1.67

Table 3. Lattice parameters and unit cell volume for the KNN-0.2, KNN-0.3, and KNN-0.5.

The disappearance of (122) diffraction peak at  $2\theta = 39^{\circ}$  can be associated to the oxygen-octahedra tilt. Baker and coworkers [49] reported the missing reflection in KNN in the  $35^{\circ} - 41^{\circ}$  region. This missing reflection was related with the oxygen-octahedra tilt. Although Baker investigated the tilt system as a function of temperature, the octahedra tilt can also be influenced by the potassium concentration in sodium niobate as supported by Ahtee and Glazer [68]. In our work, the increase of the concentration of K<sup>+</sup> in the sodium niobate results in the loss of octahedral tilting when the proportion of K<sup>+</sup>/Na<sup>+</sup> reaches 50%. In order to stabilize the KNN perovskite structure due to the ionic radii difference in A-site (ionic radii of K<sup>+</sup> = 0.138 nm against ionic radii of Na<sup>+</sup> = 0.102 nm), the Nb (B-site) is displaced from the central position in NbO<sub>6</sub> octahedron, occurring the oxygen-octahedron rotate [68]. As discussed below, this rotation is observed in **Figure 9**, as the octahedra from KNN-0.2 to KNN-0.5 where the Nb–O–Nb bond angle become close to 180° as the average distortion ( $\omega$ ) between [NbO<sub>6</sub>] octahedra decreases (**Table 5**) where KNN-0.2 (20.19) > KNN-0.3 (15.92) > KNN-0.5 (8.75). Thus, NbO<sub>6</sub> octahedra in the KNN structures are tilted and distorted as function of the concentration of K<sup>+</sup> cations, showing a considerable effect on the lattice parameters, in this case, promoting the lattice expansion due to the increase in the ionic radii of K<sup>+</sup>, 0.138 nm, instead of 0.102 nm for Na<sup>+</sup>. According

to this lattice expansion, the unit cell volume growth from ca. 481.31 Å<sup>3</sup> up to 500.38 Å<sup>3</sup>, as can be seen from **Table 3**.

**Figure 7** shows the graphic representation of the unit cell of KNN-0.2, KNN-0.3, and KNN-0.5 samples obtained from the data listed in **Table S1** (**Supplementary**). Niobium atoms (blue spheres) are coordinated to six oxygen atoms (red spheres), four of which are located, *a priori*, on the same plane as the niobium atoms. The other two are above and below the plane, respectively, as shown the **Figure 7**.



**Figure 7.** Graphic representation of the unit cell obtained for: (a): KNN-0.2, (b): KNN-0.3, and (c): KNN-0.5 powders.

This condition favors the formation of a M site (octahedral symmetry) in the perovskite structure. Potassium and sodium atoms, represented by green spheres, are located at the interstice among NbO<sub>6</sub> octahedra. It is interesting to note that potassium-sodium niobate structure is gradually modified by

introduction of potassium in NaNbO<sub>3</sub> host structure, presenting distortion and tilting in niobium octahedron. The bond lengths and bond angles measured from NbO<sub>6</sub> octahedra are listed in **Table 4** and **Table 5**, respectively.

Representations of NbO<sub>6</sub> octahedra from potassium-sodium niobates are shown in **Figure 8**. NbO<sub>6</sub> octahedra shows different Nb–O bond lengths at the central plane of the octahedron, represented by Nb–O3, Nb–O4, Nb–O5, and Nb–O6, which is consistent with the [NbO<sub>6</sub>] rotation over **b** axis [70]. However, Nb–O1 and Nb–O2 bond lengths, on the apical axis, do not present significant change with potassium concentration in the host structure. This fact means that the octahedron does not undergo rotation but an elongation. In this case, a slight off-center character is observed, which is related to the magnitude of displacement of Nb from the central position of [NbO<sub>6</sub>] octahedron.



Figure 8. Representation of NbO<sub>6</sub> octahedron: (a) KNN-0.2, (b) KNN-0.3 and (c) KNN-0.5.

Due to the increase in the ionic radii for K<sup>+</sup>, 0.138 nm instead of 0.102 nm for Na<sup>+</sup> discussed above, the increase of K composition within the K<sub>x</sub>Na<sub>1-x</sub>NbO<sub>3</sub> structure not only affect the particle size during condensation of crystals (**Figure 1**) but the host structure is also affected. In this sense, it is possible to quantify the relative distortion in the octahedra ( $\Delta_d$ ) by deviation of Nb–O length ( $\delta_n$ ) as a function of [Nb–O] length ( $\bar{\delta}$ ) average, derived from **Eq. 3** [71]. The results are listed in **Table 4**.

$$\Delta_d = \frac{1}{6} \sum_{n=1,\dots,6} \left( \frac{\delta_n - \bar{\delta}}{\bar{\delta}} \right)^2 \tag{3}$$

As expected, there is an increase of distortion in  $[NbO_6]$  octahedra from  $6.26 \times 10^{-4}$  to  $1.17 \times 10^{-2}$ , with the increase of potassium content in the NaNbO<sub>3</sub> host structure. It means that the host octahedra is ca. 19 times more distorted in KNN-0.3 and KNN-0.5 than in KNN-0.2. In agreement with this distortion, the angles associated to Nb–O bonds in  $[NbO_6]$  octahedra are also different.

 Table 4. Interatomic lengths of Nb–O bonds of KNN-0.2, KNN-0.3, and KNN-0.5 powders in NbO6

 octahedron.

	KNN-0.2	KNN-0.3	KNN-0.5
Bond		Length (Å)	· ·
Nb-O1	1.9756	1.9647	1.9703
Nb-O2	2.0247	1.9749	2.0216
Nb-O3	1.8991	1.9787	2.0777
Nb-O4	1.9892	2.4117	2.3553
Nb-O5	2.0604	1.9518	1.9160
Nb-O6	2.0082	1.6769	1.6265
$\overline{\mathbf{\delta}}$ (Å) <sup>a</sup>	1.9929	1.9931	1.9946
$\Delta_d^{b}$	$6.26 \cdot 10^{-4}$	0.0117	0.0117

<sup>a</sup> Average of [Nb–O] length. <sup>b</sup> Relative distortion of [Nb–O<sub>6</sub>] octahedra.

**Table 5** lists the bond angle values of NbO<sub>6</sub> octahedron. The average angle distortion in [Nb–O–Nb] can be derived from **Eq. 4** [71] where  $\omega$  is the average distortion between [NbO<sub>6</sub>] octahedra and  $\bar{\theta}$  is the average [Nb–O–Nb] bond angle.

$$\omega = 180 - \bar{\theta} \tag{4}$$

Structural order in potassium-sodium niobate would lead to [Nb–O–Nb] bond angle near to 180° in the perovskite structure. However, the set of bonds [O1–Nb–O2], [O3–Nb–O6] and [O4–Nb–O5] in **Table 5** are characterized by bond angle values lower than 180° (expected for a perfect octahedra). This result permits to conclude that the increase in potassium content is responsible for the distortion

of the host structure. Therefore, the missing (122) reflection in the KNN-0.3 and KNN-0.5 samples discussed above from **Figure 6** is an indicative of a minor structural order, as shown in **Table 5**, where the NbO<sub>6</sub> octahedra assume bond angles lower than  $180^{\circ}$  (KNN-0.2 [159.81°], KNN-0.3 [164.08°], KNN-0.5 [171.35°]).

Dand	KNN-0.2	KNN-0.3	KNN-0.5
Bond		θ (°)	
O1-Nb-O2	157.02	174.16	168.98
O1-Nb-O3	98.95	98.94	91.15
O1-Nb-O4	74.29	86.37	87.54
O1–Nb–O5	96.55	96.89	92.58
O1-Nb-O6	74.32	83.93	87.99
O2-Nb-O3	93.08	81.07	90.71
O2-Nb-O4	84.27	87.79	103.37
O2–Nb–O5	103.04	88.95	76.58
O2-Nb-O6	97.33	96.48	90.36
O3-Nb-O4	79.19	84.88	94.45
O3–Nb–O5	167.50	90.72	89.23
O3-Nb-O6	89.36	174.74	175.45
O4–Nb–O5	88.59	175.02	175.87
O4–Nb–O6	167.28	91.38	89.72
O5–Nb–O6	102.53	92.85	86.54
Nb-O1-Nb	163.79	172.42	179.87
Nb-O2-Nb	148.04	168.85	156.58
Nb-O3-Nb   Nb-O4-Nb	158.79	158.33	171.57
Nb-O5-Nb   Nb-O6-Nb	164.71	163.27	173.96
<b>θ</b> <sup>a</sup>	159.81	164.08	171.35
ω <sup>b</sup>	20.19	15.92	8.75

**Table 5.** Bond angles ( $\theta$ ) of NbO<sub>6</sub> octahedron of KNN-0.2, KNN-0.3, and KNN-0.5.

<sup>a</sup>  $\overline{\theta}$  is the average [Nb–O–Nb] bond angle. <sup>b</sup>  $\omega$  is the average distortion between [NbO<sub>6</sub>] octahedra.

In addition, the angles associated to each equatorial oxygen (O3, O4, O5 and O6) and axial oxygens (O1 and O2) are different from 90°. The distinct bond angles in [NbO<sub>6</sub>] octahedra can be associated to a second-order Jahn-Teller distortion, caused by the niobium off-center displacement [72-75].

It has been reported that the off-center displacement of Nb atom is responsible to develop the ferroelectric property in potassium-sodium niobate [72,73]. It is well-known that ferroelectric

materials [72-75] can be polarized by stress, strain, temperature, electric field, chemical substances, and by the absorption of photons promoting the so-called photovoltaic effect.

On the other hand, **Figure 9** shows the structural order in the potassium-sodium niobate materials associated to the increase of Nb-O-Nb bond angle close to  $180^{\circ}$ . The structural order of potassium-sodium niobate structure can be associated with the magnitude of the displacement of Nb from the central position in [NbO<sub>6</sub>] octahedron. The changes in bond lengths and angles have been directly related with the reactivity of apical oxygen atoms in niobate-based materials in iron-based perovskites in electrocatalytic reactions [75] and in KSr<sub>2</sub>Nb<sub>5</sub>O<sub>15</sub> nanomaterials in photocatalytic reactions [63]. Accordingly, it is expected different reactivities of the potassium-sodium niobate-based materials on the BB41 photodegradation since photocatalytic reactions occur at interfacial solid-solution phase





**Figure 9.** Structural ordering in potassium-sodium niobate associated to the increase of Nb-O-Nb bond angle close to 180°.

### 3.1.4. Microstructural refinements

The apparent crystallite size and maximum average strain of the present samples are listed in **Table 6**. The crystallite size decrease with the increase of potassium content in the perovskite structure.

This behavior is observed by a reduction in average apparent size from 207.0 Å for KNN-0.2 to 166.1 Å for KNN-0.3, and 169.8 Å for KNN-0.5. The maximum reduction is about 41 Å with the

increase of potassium concentration. As a result, from size reduction, the maximum average strain increases 1.4 times from KNN-0.2 to KNN-0.3 and 1.8 times from KNN-0.2 to KNN-0.5.

**Table 6.** Apparent anisotropic crystallite size and maximum average strain from microstructural refinement.

Sample	Crystallite size ª (Å)	Maximum Average Strain (x10 <sup>4</sup> ) <sup>a</sup>
KNN-0.2	207.0 [49.0] <sup>b</sup>	24.2 [0.0312] <sup>b</sup>
KNN-0.3	166.1 [50.3] <sup>b</sup>	34.7 [0.0331] <sup>b</sup>
KNN-0.5	169.8 [51.3] <sup>b</sup>	42.7 [0.0271] <sup>b</sup>

<sup>a</sup> The crystallite apparent size and the maximum average strain were obtained with standard deviation related to anisotropy degree. <sup>b</sup> The values in square brackets represent a measure of the degree of anisotropy

Furthermore, the anisotropic crystallite shape for potassium-sodium niobate size follows the same trend observed on the average size. This interesting result can be observed in the **Figure 10**. According to **Figure 10a**, in the crystalline plane (001) KNN-0.2 exhibits a crystallite with rectangular plate shape. The increase of potassium promotes a change to a more spherical shape in KNN-0.3 (**Figure 10b**) and KNN-0.5 (**Figure 10c**). For the crystalline plane (100), the pseudo-spherical crystallite shape of KNN-0.2 (**Figure 10d**) changed to a rhomboid shape along the **y** direction in KNN-0.3 (**Figure 10e**) and KNN-0.5, which remains in a rhomboid shape along **y** direction (**Figure 10f**). The increase in potassium introduced important changes in the anisotropic crystallite shape in the crystallite plane (010). It can be seen KNN-0.2 (**Figure 10g**) suffered an important elongation through **z** direction shape in the KNN-0.3 (**Figure 10h**) and KNN-0.5 (**Figure 10g**) suffered an important elongation through **z** direction shape in the KNN-0.3 (**Figure 10h**) and KNN-0.5 (**Figure 10i**). The size reduction and the change of shape can be due to the solvent evaporation and solute diffusion in the pyrolysis process [77]. During the solvent evaporation, several processes, such as heat transfer, mass diffusion, vapor diffusion, and droplet shrinkage occur simultaneously.



(001) crystallite plane

**Figure 10.** Crystallite anisotropic shape for potassium-sodium niobate. Crystallite displayed through (001) plane for (a): KNN-0.2, (b): KNN-0.3, and (c): KNN-0.5. Crystallite displayed through (100) plane for (d): KNN-0.2, (e): KNN-0.3, and (f): KNN-0.5. Crystallite displayed through (010) plane for (g): KNN-0.2, (h): KNN-0.3, and (i): KNN-0.5.

In the evaporation stage, the solute diffuses from the droplet surface to the droplet center. A rapid process of evaporation leads to a lower diffusion of solute [78], which can explain the change on crystallite shape from KNN-0.2 to KNN-0.5. The changes on crystallite shape may be associated with the formation of porosity in the spherical particles, observed in SEM images (**Figure 1**) and confirmed from the porosimetry analysis (**Figure 2S, Supplementary**). Thus, the crystallite anisotropic shape for potassium-sodium niobate suggests that the hollow spheres are structurally composed by sub-nanoparticles. In addition, **Figure 6** suggest the porosity of the present samples can be associated both to the mesopore framework formed through the shell walls of the spheres and the void spaces formed by the contact interface of these sub-nanoparticles.

#### **3.2. Kinetics of BB41 adsorption in the dark**

**Figure 11** shows the kinetics of adsorption in the dark of BB41 as a function of the pH of solution. The equilibrium of adsorption was achieved after 60 min for all the samples at the three pH studied. Accordingly, this time has been selected for the adsorption in the dark before irradiation in the photocatalytic tests. A summary of the kinetics results of BB41 adsorption is listed in **Table 7**.

The adsorption of BB41 is highly influenced by the K content in the niobate-based structure. The higher the potassium content the lower the BB41 adsorption for the three pH of solution. This trend agrees with the decrease both in the BET surface area and the total volume of pores discussed above (**Table 1**). Adsorption of BB41 is highly influenced by the pH of solution. Compared to neutral pH the adsorption of BB41 was remarkably inhibited at acid pH by factors of ca. 58%, 65% and 61% on KNN-02, KNN-0.3 and KNN-0.5, respectively. On the contrary, an important increase was observed up to factors of ca. 1.5 for KNN-0.2 and KNN-0.5, and 1.7 times higher for KNN-0.3 at basic pH.

The differences in adsorption trends can be explained by the changes in the pH point-zero charge  $(pH_{PZC})$  of  $K_xNa_{1-x}NbO_3$  samples [42]. The KNN-0.2 niobate-based structure is characterized by a surface pH [63] of ca. 6, which decrease down to 4 - 5 with the increase of K within the niobate-based structure. In the present study, when the pH of solution is lower than the surface pH, the surface of the

 $K_xNa_{1-x}NbO_3$  becomes positively charged. Accordingly, since BB41 is a cationic azo-dye [42], the adsorption is inhibited at very acid pH of solution due to electrostatic repulsion between the surface of the materials and BB41 molecules. On the contrary, the remarkably increase of BB41 adsorption at basic pH is promoted by the negative charge formed on the surface of  $K_xNa_{1-x}NbO_3$ .



Figure 11. Kinetics of adsorption in the dark of BB41 as a function of pH of solution. (a): KNN-0.2,(b): KNN-0.3, and (c): KNN-0.5.

Samula		n <sub>ads</sub> <sup>a</sup>	<b>k</b> 1 <sup>b</sup>		$\mathbf{k}_2^{\mathbf{d}}$	<b>D</b> <sup>2</sup> . e	k <sub>p</sub> <sup>f</sup>		C <sup>h</sup>
Sample	pН	(µmol)	( <b>min</b> <sup>-1</sup> )	$\mathbf{R}^{2}_{k1}$ <sup>c</sup>	(µmol <sup>-1</sup> min <sup>-1</sup> )	<b>K</b> k2	$(\mu mol min^{-1/2})$	$\mathbf{R}^{2}_{kp}{}^{g}$	(µmol)
KNN-0.2	Neutral	8.67	0.067	0.882	0.024	0.973	0.498	0.946	4.687
	Basic	13.0	0.044	0.927	0.007	0.980	0.956	0.996	5.434
	Acid	3.68	0.033	0.995	0.014	0.973	0.527	0.985	-0.503
KNN-0.3	Neutral	6.95	0.054	0.981	0.031	0.961	0.535	0.919	2.697
	Basic	11.5	0.070	0.962	0.019	0.915	0.869	0.945	4.239
	Acid	2.41	0.041	0.941	0.023	0.965	0.342	0.986	-0.261
KNN-0.5	Neutral	6.17	0.069	0.983	0.045	0.945	0.623	0.845	1.187
	Basic	9.54	0.061	0.884	0.011	0.985	0.840	0.965	2.621
	Acid	2.38	0.039	0.950	0.023	0.964	0.342	0.986	-0.302

**Table 7.** Summary of kinetics parameters of adsorption in the dark of BB41.

<sup>a</sup> BB41 adsorbed after 60 min. <sup>b</sup>  $k_1$  is the pseudo-first-order rate constant. <sup>c</sup>  $R^2_{k1}$  is the quadratic linear factor for  $k_1$ . <sup>d</sup>  $k_2$  is the pseudo-second-order rate constant. <sup>e</sup>  $R^2_{k2}$  is the quadratic linear factor for  $k_2$ . <sup>f</sup>  $k_p$  is the IPD rate constant. <sup>g</sup>  $R^2_{kp}$  is the quadratic linear factor for the  $k_p$ . <sup>h</sup> C is the boundary layer thickness constant for the IPD model.

The results of BB41 adsorption agree with values reported using ZnO/C composite photocatalysts [42], brick wastes [79], zeolites [80], activated carbon [81] and natural safiot clay [82]. As discussed above, the increase of K atoms within the host structure of the niobate-based perovskite is responsible of the distortion of the NbO<sub>6</sub> octahedra (**Table 4**). Accordingly, it is expected different reactivity of the axial oxygen atoms with BB41 molecules in the adsorption processes. Thus, for a deeper interpretation of the influence of pH of solution upon the adsorption process of BB41, different kinetics parameters of adsorption were obtained by comparing the pseudo-first order [83,84], the pseudo-second order [83,85], and the intraparticle diffusion [83,86,87] models. Table S2 (Supplementary) contains a summary of the kinetic expressions and parameters used for the estimation of the pseudo-first-order rate constant  $(k_1)$ , the pseudo-second-order rate constant  $(k_2)$ , the intraparticle (IPD) rate constant  $(k_p)$  and the C constant attributed to the extension of the boundary layer thickness according to the IPD model. Figures S4, S5, and S6 (supplementary material) show the results of BB41 adsorption on KNN-0.3, KNN-0.4 and KNN-0.5, respectively, using the different kinetic models as a function of the different pH conditions of the present study. A summary of the kinetics parameters obtained from these models is listed in **Table 7**. In most of cases, the values of  $k_1$  and  $k_2$  observed in basic and acid pH are lower than those observed at neutral pH. The quadratic linear factors are influenced by the pH of solution indicating that different adsorption mechanisms may take place on the present samples. For instance,

at neutral and basic pH, KNN-0.2 seems to be characterized by a chemisorption mechanism. This is inferred since the quadratic linear factors show values close to unit. ca. 0.973 and 0.980 for neutral and basic pH, respectively. On the contrary, at acid pH, this sample showed a linear factor of ca. 0.995 suggesting physisorption mechanism is favored at acid pH. In other words, for KNN-0.2 sample, the chemisorption mechanism is favored at neutral or basic pH since KNN-0.2 sample is negatively charged while physisorption is favored at acid pH since KNN-0.2 sample is positively charged. However, this trend of adsorption is not followed by the other two samples, suggesting that competition between different mechanisms may take place as a function both of the textural properties and the pH of solution affecting the surface charge. Considering the low loading of samples used in the present study (0.1 g L-1), it should be highlighted that k1 and k2 values listed in Table 7 are in the same order of magnitude than values reported for the BB41 adsorption using 0.5 g L<sup>-1</sup> of aquatic plant-derived sorbent [78] and 0.25 g L<sup>-1</sup> of olive stone-derived activated carbon [88]. This result indicates the present samples showed a high affinity for the adsorption of BB41 thought the surface area are lower than the reported for those materials [78,88].

The intraparticle diffusion model (IPD) permits a deeper explanation of the influence of pH upon the adsorption process. The values of the IPD rate-constants (k<sub>p</sub>) are clearly higher at basic pH, while k<sub>p</sub> values are lower at acid pH, with except of KNN-0.2 sample. In addition, at basic pH, the values of the C constants are clearly higher while these values remarkably decrease at acid pH, even becoming negative, which represents an irrational value for a kinetic constant. However, the remarkably decrease in C values at acid pH agrees with the electrostatic repulsion between the positively charged surface of the KNN samples and the cationic BB41 [77,88]. In other words, according to the intraparticle diffusion kinetic model, the C constant is a measurement of the quantity of molecules located at the boundary of the surface, or more precisely, C is the amount of molecules close to the adsorbent surface. Therefore, C constant is an indicative of the control of the intraparticle diffusion model suggesting the inhibition of adsorption is taking place at acid pH in the present study. On the contrary, at basic pH,

the higher values of C than those obtained at neutral pH in an indicative that the intraparticle diffusion model together with the pseudo-second order mechanism are the driven force for the adsorption of BB41. Accordingly, the results of the kinetics of adsorption indicate BB41 mass diffusion from solution to pores of materials is strongly influenced by the pH of solution.

#### **3.3. Degradation of BB41**

### 3.3.1. Preliminary analysis

**Figure 12** shows the kinetics of BB41 degradation as a function of pH of solution. **Figure 12a** shows the direct photolysis of BB41 in absence of catalysts. Direct photolysis is not negligible at the present experimental conditions. This result was expected since a UV-C lamp is used. **Figure 12a** shows that at basic pH, ca. 82% degradation of BB41 was achieved after 4 h irradiation instead of ca. 40% at neutral pH. On the other hand, a remarkably direct photolysis of BB41 is observed at acid pH with ca. 92% after only 2 h of irradiation which suggest the kinetics of direct photolysis of BB41 is highly influenced by the pH of solution. For instance, at low pH (ca. 3 in the present work), the protonated form of BB41 is the main molecular form while at basic pH (ca. 10 in the present work) the deprotonated form is dominate the molecular form. The present results of direct photolysis of BB41 agree with previous results of methylene blue degradation [83], basic blue 41 photo-Fenton-driven degradation [89] and 2-chlorophenol UV-driven degradation [90]. On the other hand, **Figures 12b**, **12c**, and **12d** show the kinetics of BB41 photocatalytic degradation under irradiated KNN-0.2, KNN-0.3 and KNN-0.5 catalysts, respectively. It can be seen the total photodegradation of BB41 is achieved at lower irradiation time when pH of solution is basic instead of neutral. In other words, an enhancement in the photocatalytic activity of the samples is observed at basic pH of solution.

**Figure S7** (**supplementary material**) shows a picture representing the decolorization of BB41 dye catalyzed by KNN-0.5 at neutral and basic pH of solution. The total photodegradation of BB41 on UV-irradiated KNN-0.2 and KNN-0.3 occurred at lower irradiation time (ca. 210-240 min) at acid or basic pH of solution than at neutral pH, which requires irradiation time higher than 240 min. On the

contrary, KNN-0.5 shows similar photoactivity at acid pH and neutral pH of solution requiring ca. 210-240 min of irradiation to total degradation of BB41.



Figure 12. Kinetics of BB41 degradation under UV-irradiation. (a): Direct photolysis. (b): KNN-0.2.(c): KNN-0.3. (d): KNN-0.5.

In addition, **Figure 12** shows that the photoactivity of KNN-0.5 at basic pH is clearly higher than the other two samples achieving a total photodegradation of BB41 after only 120 min irradiation. This activity is almost similar than that observed on direct photolysis at acid pH of solution. Thus, it can be concluded that at acid pH of solution the photocatalytic activity of the niobate-based samples is inhibited, mainly that of KNN-0.5 catalysts. This fact may be due to the high reactivity of apical O atoms in the niobate structures discussed above. The apical O atoms is characterized by a high affinity to adsorb protons in solution [63]. Accordingly, the formation of reactive oxygen species from apical O atoms is not efficient at acid pH [83], and thus, a decrease in the photoactivity is expected.

#### **3.3.2.** First-order kinetics approach

For a more precise interpretation of the kinetic data of BB41 photodegradation, some classical kinetic aspects must be considered. It is well-known [15,83,88-94] the kinetics of photocatalytic degradation of pollutants commonly follows a Langmuir-Hinshelwood mechanism, where the rate of reaction (r) is proportional to the surface coverage of pollutants ( $\theta$ ) according to **Eq. 5**:

$$r = k_r \cdot \theta = k_r \frac{K_{ads} \cdot C_{eq}}{1 + K_{ads} \cdot C_{eq}}$$
(5)

where  $k_r$  is the reaction-rate constant,  $K_{ads}$  the adsorption constant according to Langmuir model, and  $C_{eq}$  the concentration of pollutant at equilibrium conditions. For diluted solutions ( $C_{eq} < 10^{-3} \text{ mol } \text{L}^{-1}$ ), it is usually accepted [15,93,94] that  $K_{ads}$ . $C_{eq} \ll 1$ . Accordingly, **Eq. 5** can be simplified to a first-order kinetics described by **Eq. 6**:

$$r = k_r K_{ads} C_{eq} = k_{app} C_{eq}$$
(6)

where  $k_{app}$  is the first-order apparent rate-constant which can be obtained from the linear regression of the kinetic data of degradation [15,83] as a function of the irradiation time according to the **Eq. 7**:

$$\operatorname{Ln}\left(\frac{C_{eq}}{C_t}\right) = k_{app}.t \tag{7}$$

where  $C_{eq}$  is the initial concentration after achieved the equilibrium of adsorption in the dark, and  $C_t$  is the concentration at the time t of irradiation. This kinetic parameter has been widely used for the comparison of the photocatalytic activity of photocatalytic materials [15,83,88,91-94]. As discussed above, the kinetics of BB41 photodegradation (**Figure 12**) seems to follow a first-order reaction-rate mechanism. In addition, the initial concentration of BB41 is low (ca. 2.5 x 10<sup>-5</sup> mol L<sup>-1</sup>) and after the adsorption process, it became lower. Therefore, at the present experimental conditions, the first-order reaction-rate mechanism can be used as a useful kinetic approach to compare the photocatalytic activity of the present materials. **Figure 13** shows the linear regressions of the kinetic data from **Figure 12**, and a summary of the kinetic parameters obtained for the BB41 photodegradation is listed in **Table 8**.



Figure 13. Linear regression from the kinetic data of Figure 12. (a): Direct photolysis. (b): KNN-0.2.(c): KNN-0.3. (d): KNN-0.5.

Sample	рН	n <sub>ads</sub> a (umol)	$d_{BB41}^{b}$ (µmol m <sup>-2</sup> )	k <sub>app</sub> <sup>c</sup> (min <sup>-1</sup> ) x10 <sup>-3</sup>	<b>R</b> <sup>2 d</sup>	v <sub>reac</sub> x10 <sup>-3</sup> (umol m <sup>-2</sup> min <sup>-1</sup> ) <sup>e</sup>	orel f
TiO <sub>2</sub> -P25 <sup>g</sup>	Neutral	1.22	0.39	6.1	0.995	2.38	1.00
Direct	Neutral			1.9	0.963		0.31 <sup>h</sup>
Photolysis	Basic			4.5	0.993		0.74 <sup>h</sup>
	Acid			25.1	0.993		4.1 <sup>h</sup>
KNN-0.2	Neutral	8.67	0.82	9.3	0.998	7.63	3.2
	Basic	13.0	1.23	18.6	0.980	22.8	9.6
	Acid	3.68	0.35	18.7	0.992	6.49	2.7
KNN-0.3	Neutral	6.95	1.62	8.8	0.999	14.2	6.0
	Basic	11.5	2.67	15.8	0.997	42.3	17.8
	Acid	2.41	0.56	12.6	0.997	7.06	3.0
KNN-0.5	Neutral	6.17	1.54	12.2	0.996	18.8	7.9
	Basic	9.54	2.39	23.0	0.986	54.9	23.1
	Acid	2.38	0.60	16.0	0.988	9.52	4.0

Table 8. Summary of surface concentration and kinetics parameters of BB41 photodegradation.

<sup>a</sup> BB41 adsorbed after 60 min. <sup>b</sup> Surface concentration of adsorbed BB41 molecules estimated by Eq. (5). <sup>c</sup> k<sub>app</sub> estimated by Eq. (7). <sup>d</sup> R<sup>2</sup> is the linear regression factor of the first-order apparent rate-constant. <sup>e</sup> Reaction-rate estimated by Eq. (9). <sup>f</sup> Photoactivity:  $\Phi_{rel} = v_{reac-i}/v_{reac-TiO2}$ . <sup>g</sup> Values for commercial TiO<sub>2</sub>-25 taken from ref. [42]. <sup>h</sup>  $\Phi_{rel} = k_{app-i}/k_{app-TiO2}$ .

The first 120 min of irradiation were considered for the estimation of k<sub>app</sub> since in most of cases the kinetics of photodegradation observed in this range (Figure 12) showed an acceptable linearity. This inference was confirmed from the linear regression factors (R<sup>2</sup>) in Table 8 which are close to unit in all the tests (direct photolysis and photodegradations). Thus, it can be concluded that BB41 degradation in the present experimental conditions is characterized by a first-order reaction-rate mechanism. For the sake of comparative purposes, k<sub>app</sub> obtained in the BB41 photodegradation using a commercial TiO<sub>2</sub>-P25 under similar experimental conditions [42] was also included. For the direct photolysis, the comparison of photoactivity was performed in terms of the first-order apparent rate-constant. At neutral and basic pH, direct photolysis showed lower efficiency that TiO<sub>2</sub>-P25 at neutral pH. On the contrary, acid pH of solution direct photolysis is up to 4.1 times more efficient than TiO<sub>2</sub>-P25. Some interesting features can be figure out from values in Table 8. For instance, kapp observed in the direct photolysis are 2.4 and 13.2 times higher at basic and acid pH of solution, respectively, than the kapp observed at neutral pH. It means that the direct photolysis of BB41 is 5.6 times faster under acid pH than using basic pH of solution. In addition, the  $k_{app}$  value observed for the direct photolysis of BB41 at neutral pH is clearly lower than that reported [42] for TiO<sub>2</sub>-P25 at the same experimental conditions while at basic pH, the k<sub>app</sub> observed for direct photolysis is slightly lower. On the contrary, at acid pH of solution, the kapp obtained for the direct photolysis of BB41 is 4.1 times higher than the value obtained using TiO<sub>2</sub>. In presence of catalysts, the values of k<sub>app</sub> at neutral and basic pH of solution are clearly higher than values observed at direct photolysis. On the contrary, at acid pH, all catalysts showed an inhibition of the photocatalytic activity in terms of kapp in comparison of the kapp observed under direct photolysis. These results are intimately related with the trends of adsorption discussed above which are strongly influenced both by the pH of solution, and the textural and surface chemistry properties of the materials. For instance, kapp values observed for KNN-0.2, KNN-0.3 and KNN-0.5 at basic pH are ca. 2.0, 1.8, and 1.9 times higher, respectively, than values observed at neutral pH. As discussed above, the basic pH of solution promoted the deprotonated form of BB41 molecules favoring

an enhancement in both adsorption and photoactivity. KNN-0.3 and KNN-0.5 showed only 1.4 and 1.3 times higher photoactivity at acid pH compared to values at neutral pH. On the contrary, KNN-0.2 sample is characterized by a similar  $k_{app}$  value at acid and basic pH which can be due to a higher surface area of KNN-0.2 (106 m<sup>2</sup> g<sup>-1</sup> against 43 m<sup>2</sup> g<sup>-1</sup>, **Table 1**).

It is interesting to remark that in spite of KNN-05 adsorbed lower BB41 molecules than the other two catalysts in any of the pH of solution, this sample shows the highest photocatalytic activity in terms of  $k_{app}$  (23.0 x 10<sup>-3</sup> min<sup>-1</sup>, **Table 8**). This result is ascribed to the decrease in the energy band-gap discussed above (**Table 2**) with values of ca. 3.01 eV for KNN-0.5 instead of 3.21 and 3.20 for KNN-0.2 and KNN-0.3, respectively, which would permit a more efficient activation of the catalyst. In summary, the present kinetic results confirm that the mechanism of BB41 degradation by direct photolysis is strongly conditioned by the pH of solution which promotes the protonation or deprotonation form of the BB41, and thus, different mechanism of degradation. In other words, at acid pH, the degradation of BB41 by direct photolysis would follow preferentially a mechanism of reaction characterized by the unimolecular electrophilic attack of superoxide anion radical (•O<sub>2</sub><sup>-</sup>) formed under UV irradiation upon the protonated molecules of BB41. On the contrary, at basic pH, the unimolecular nucleophilic substitution would be promoted by the attack of hydroxy radical (•OH) upon deprotonated molecules of BB41. A detailed mechanism for the BB41 photodegradation under irradiated K<sub>x</sub>Na<sub>1-x</sub>NbO<sub>3</sub> hollow spheres is discussed in section 3.4.

### 3.3.3. Influence of adsorption upon the photocatalytic activity

As discussed above, the increase of K content within the niobate host is responsible both for the distortion (**Tables 4 and 5**) and polarization (**Figure 10**) of the perovskite structure (**Table 4**). In addition, keeping in mind that heterogeneous catalytic reactions occur at the interface of solid and aqueous phases [94], it is expected that the changes in the niobate structure would affect the adsorption and photodegradation processes of BB41 molecules. The influence of BB41 adsorption on the

photocatalytic activity can be readily analyzed through the surface concentration ( $d_{BB41}$ ) of BB41 adsorbed on potassium-sodium niobate. This parameter can be estimated by the **Eq. 8** [83,95]:

$$d_{BB41} = \frac{n_{ads}}{S_{BET} \cdot m} \tag{8}$$

where  $n_{ads}$  is the amount of BB41 adsorbed in the dark at equilibrium conditions (**Table 8**), S<sub>BET</sub> is the surface area from BET analysis (**Table 1**), and **m** is the mass of catalyst (i.e. 100 mg). For the sake of comparison, the data corresponding to TiO<sub>2</sub> [42] was also included in **Table 8**.

Figure 14a shows an increase of the surface concentration of adsorbed BB41 molecules as a function of pH of solution. This is a general trend for the three KNN samples. It can be seen that the values of surface concentration of BB41 molecules for the three catalysts are higher at basic pH than at neutral pH while the values became lower at acid pH. It is interesting to note that at neutral pH, all the niobate samples showed higher surface concentration of BB41 molecules than TiO<sub>2</sub>-P25 (Table 8), even for KNN-0.3 and KNN-0.5 with a surface area similar than TiO<sub>2</sub> (Table 1). For instance, the surface concentration of BB41 molecules on KNN samples sample is between 2.1 - 4.2 and 3.2 - 6.8 times higher in neutral and basic pH, respectively than on TiO<sub>2</sub>, obtained at neutral pH [42]. On the contrary, at acid pH, the surface concentration of BB41 became similar or slightly higher than that observed on TiO<sub>2</sub>. These results suggest apical atoms in the niobate structure is responsible of the high reactivity for the adsorption of BB41. This conclusion is obvious since at acid pH, the apical O atoms are protonated and thus, a decrease in adsorption capability would be expected in agreement with the very close to unit values observed in the linear regression factors for the pseudo-first and pseudo-second order adsorption rate-constants  $(k_1, k_2, Table 7)$  which is an indicative of the competition between physisorption, and chemisorption mechanisms as discussed above. It is expected the higher the surface concentration of BB41 molecules the higher the photoactivity. This inference is discussed as follows. Table 7 shows the adsorption rate-constant (k<sub>p</sub>, Table 7) and the boundary layer thickness (C constant, Table 7) for the intraparticle diffusion model (IPD) increase monotonically with the increase of pH of solution. This is an indicative that at neutral and basic pH, not only a higher amount of BB41 have

been adsorbed but also a higher quantity of molecules in solution are close to the surface of KNN samples. In other words, diffusion of molecules from the bulk of solution to the surface is favored at neutral and basic pH while the C values in **Table 7** suggest that at acid pH, some diffusional limitation can take place observed.



**Figure 14**. (a): Influence of pH of solution upon the surface concentration, and (b): Upon the global reaction-rate. (c): Correlation between the global reaction-rate and the surface concentration.

In terms of the first-order apparent rate-constants (**Table 8**), the present potassium-sodium niobate materials exhibit higher photoactivity than TiO<sub>2</sub>-P25. Addition of potassium to sodium niobate structure clearly influences the photoactivity but no monotonic relationships can be figure out. Thus, for a deeper interpretation of the photoactivity of the present materials, the global or surface reaction-rate ( $v_{reac}$ ) has been estimated from **Eq. 9** [83,95].

$$v_{reac} = k_{app} d_{BB41} \tag{9}$$

**Figure 14b** shows the relationships between the  $v_{reac}$  and pH of solution. The results are summarized in **Table 8.** It can be seen the higher the potassium content and the more basic the pH of solution, the higher the photocatalytic activity. In terms of the surface  $d_{BB41}$ , an important increase in the photocatalytic activity ( $\phi_{rel}$ , **Table 8**) was estimated at basic pH up to 9.6, 17.8, and 23.1 times higher on KNN-0.2, KNN-0.3, and KNN-0.5, respectively, than  $v_{reac}$  estimated on TiO<sub>2</sub>. At neutral and acid pH of solution, the enhancements in photoactivity were 3.2, 6.0, 7.9, and 2.7, 3.0, 4.0, on KNN-0.2, KNN-0.3, and KNN-0.5, respectively. These results suggest even at acid pH where the adsorption of BB41 molecules is limited, the present niobate-based materials are more photoactive than TiO<sub>2</sub>.

Differently from the works reported for nanoparticles as microreactor [93,94], the present potassiumsodium niobate has a highly reactive surface for catalytic reactions. In addition, due to the mesoporous framework and the hollow structure, it is expected an enhancement in the light harvesting efficiency using the present niobate-based hollow spheres as reported elsewhere using C-doped TiO<sub>2</sub> hollow spheres [64,65]. In other words, once absorbed, part of photons can be scattered and consequently reabsorbed by the inner surface, generating a higher amount of charge carriers [96-99]. In this way, the photocatalytic reaction can be proceeded also at the internal surface. The exponential correlation observed between the surface concentration and the global reaction-rate in the **Figure 14c**, indicates that the photocatalytic reaction is taking place both in the external and internal surface of the catalysts and thus, the present materials could be considered as a membrane-like photoreactors as reported elsewhere for micro/mesoporous activated carbons [95]. From the results of structural refinement for

potassium-sodium niobate samples, it is expected the niobium off-center displacement in the [NbO<sub>6</sub>] would promote a spontaneous polarization in the octahedron on perovskite structure [63,75,100]. Based on this fact, the potassium-sodium niobate photoactivity can be originated in the niobium off-center displacement [71,74,99]. Such effect can contribute to the formation of charge carriers and its migration in the structure [64,76,100]. In addition, the increase both in the distortion and polarization in host structure increasing K would favor the photocatalytic reaction at particle surface [64,76].

#### **3.4.** General Discussion

As can be seen from SEM (Figure 1) and TEM (Figure 2) characterization, the surface of the samples obtained by spray pyrolysis method are not totally uniform. However, we do believe this method has some interesting advantages in comparison of hydrothermal synthesis. First, KNN powders show the formation of spherical hollow particles in all samples. This feature has been confirmed by TEM analysis (Figure 2). In this way, the synthesis method exhibits high reproducibility in the formation of KNN particles with a controlled morphology. On the other hand, as expected, the particle size varies during the pyrolysis process, and thus, the coalescence of drops give rise to large particles. However, coalescence is not restricted only to spray pyrolysis and can also be observed on the hydrothermal method as reported elsewhere [64,65,101]. An important reason to synthesize potassium-sodium niobate by the spray pyrolysis method is because this method is particularly simple, effective, highly scalable, and suitable for on-line continuous production [102]. In addition, it is possible to obtain complex materials by spray pyrolysis than are not possible by other methods. For instance, Handoko et al. [103] reported the synthesis of potassium-sodium niobate by hydrothermal method. These authors concluded the incorporation of sodium in high concentration of potassium niobate to obtain a KNN solid solution becomes difficult via hydrothermal synthesis, since a secondary phase of sodium niobate is formed. The authors report that is necessary a heating treatment at 800°C for 2 hours to convert the mixed-phase powders in single-phase KNN powders. In other works, the hydrothermal synthesis commonly requires several steps, rigorous synthesis conditions of calcinations, longer reaction times,

and extra procedures as centrifugation and purification for the obtention of the final powder [104]. In this sense, the spray pyrolysis stands out, compared to other techniques, by the obtention of particle designing in one step, according to composition and architecture, producing hollow structures, dense spheres, yolk–shell structures, core–shell structures, nanoplates, nanorods, nanowires, thin films, among others [105]. Therefore, the spray pyrolysis method can be a promising technique to prepare advanced ceramic powders and industrially viable for mass production of functional nanostructured materials.

Additional tests including TOC, scavenger's reactive oxygen species and MS-GC were performed for the best photocatalyst observed in the present series (KNN-05) as a function of pH of solution. Figure 15 shows the TOC analysis and scavenger tests for the identification of the reactive oxygen species (ROS) detected along the photocatalytic degradation of BB41. The UV-Vis spectra of the scavenger experiments are shown in the Figure S8 (supplementary). It can be seen from Figure 15a that the higher the pH of solution the higher the fraction of TOC mineralized under irradiation. It can be concluded that KNN-05 is an efficient photocatalysts for the photomineralization of BB41 showing TOC values of ca. 69%, 79%, and 95% after 360 min irradiation at pH of solution of 3, 7, and 10, respectively. TOC analysis is in agreement with the kinetics of BB41 photodegradation observed on irradiated KNN-0.5 (Figure 12d) where after 240 min irradiation, BB41 was totally photodegraded, but as expected, a higher reaction time is required to achieve the photomineralization of the TOC. For a better understanding of the photocatalytic mechanisms of BB41 degradation, the reactive oxygen species were in situ evaluated along the photocatalytic degradation of BB41 under irradiated KNN-0.5 catalyst. The experiments were conducted by addition of benzoquinone (BQ) and isopropyl alcohol (IP) as scavengers for the capture of superoxide radical ( $\bullet O_2^-$ ) and hydroxyl radical ( $\bullet OH$ ), respectively. It can be seen from Figure 15b, 15c, and 15d that pH of solution has a remarkably influence upon the scavenger of ROS, mainly •O<sub>2</sub><sup>-</sup>. It is clear that the formation of superoxide radical is favored in the present KNN-05 photocatalyst in the three pH studied. This is inferred since the kinetics of BB41

photodegradation is remarkably inhibited in presence of benzoquinone which is the specific molecule for the scavenger of  $\cdot O_2^-$ .



**Figure 15.** (a): Kinetics of TOC analysis on irradiated KNN-0.5; (b-d): Scavenger tests detected along reaction as a function of pH of solution.

It is interesting to remark that this scavenger effect is higher at acid pH than at neutral pH. However, at pH 10, there is a remarkable scavenger effect in presence of BQ and a light effect of IP, suggesting that at basic pH the main mechanism of BB41 photodegradation follows is the unimolecular electrophilic addition (E1) and in much lower proportion the unimolecular nucleophilic substation (SN1) as reported by our group for the degradation of methylene blue [83]. In summary, the present scavenger results permit to conclude that the main path of reaction for the photocatalytic degradation of BB41 is the E1 by the attack of  $\cdot O_2^-$  upon the aromatic fragments of the azo-dye. This is an important observation since the preferential formation of  $\cdot O_2^-$  radical may be correlated with the highly reactive apical oxygen atoms that characterize the structure of the present K<sub>x</sub>Na<sub>1-x</sub>NbO<sub>3</sub> hollow spheres. From

the analysis in sections 3.1.3 and 3.1.4 it was concluded that the increase in potassium is responsible for the distortion of the NaNbO<sub>3</sub> host structure. The off-center displacement of Nb atom is responsible to develop the ferroelectric property in potassium-sodium niobate [72-75], and thus, these type of materials can be polarized by stress, temperature, electric field, chemical substances, and of course, by the absorption of photons promoting the so-called photovoltaic effect. In the present case, it can be concluded the high photoactivity of KNN-0.5 photocatalyst at basic pH is due to the selective formation of  $\cdot$ O<sub>2</sub><sup>-</sup> radical on the apical oxygen of the niobate material as suggest the scavenger tests.

Finally, Figure 16 shows a mechanism proposed for the photodegradation of BB41 under irradiated K<sub>x</sub>Na<sub>1-x</sub>NbO<sub>3</sub> hollow spheres. This mechanism is based on the ROS analysis and MS-GC spectra (Figure S9, supplementary) obtained at selected times of irradiated KNN-0.5 photocatalyst at basic pH. Before irradiation, the parent m/z ion 371 of BB41 is predominant but under irradiation, the MS-GC spectra shows the appearance of different ions of smaller mass indicating the degradation of the azo-dye. For instance, after 60 min irradiation, Figure 16 shows the following parent m/z ions 344, 343, 332, 330, and 316 detected from MS-GC indicating that cleavage of N-N bond and intramolecular rearrangements have taken place during the degradation of the azo-dye according to the unimolecular electrophilic attack of •O<sub>2</sub><sup>-</sup>. After 120 min irradiation, the parent m/z ions 181, 167, and 165 detected by MS-GC suggested the cleavage of benzene rings takes place as can be seen in the Figure 16. The benzene cleavage is mainly promoted by the attack of  $\cdot O_2^-$  radical. However, after 180 min irradiation, the cleavage of the aniline-based groups was also detected. The formation of the parent m/z ions 151 and 152 suggest that aniline-based groups were converted by the attack of both  $\cdot$ OH and  $\cdot$ O<sub>2</sub><sup>-</sup> radicals, respectively in agreement with the mechanism reported by Al Agad and Basheer using a Zn/graphene oxide photocatalysts [106]. After 240 min irradiation, several products with single ring structure were only observed. After 360 minutes organic fragments were not detected, indicating total mineralization as suggested the TOC analysis discussed above.



Figure. 16. Proposed mechanism for the photodegradation of BB41 under irradiated  $K_x Na_{1-x} NbO_3$  hollow spheres.

#### Conclusions

In spite of the direct photolysis in acidic medium exhibits the highest degradation efficacy (**Table 8**), it is important to highlight the meaning of the present work. Firstly, it must be pointed out that since BB41 is a cationic azo-dye, the pH in aqueous solution is ca. 5.2, which is close to neutral pH. Accordingly, after adjusting the pH at neutral or basic pH, the direct photolysis is almost negligible, and thus, in absence of acidic chemical additives, the photodegradation of BB41 is slow. On the contrary, both in neutral and basic conditions, the catalysts remarkably increase the degradation of the azo-dye. Secondly, it is important to highlight that to the best of our knowledge, the present work reports for the first time the production of with stoichiometry  $K_{0.2}Na_{0.8}NbO_3$ ,  $K_{0.3}Na_{0.7}NbO_3$ , and  $K_{0.5}Na_{0.5}NbO_3$  synthesized by the spray pyrolysis method and thus, the present works has an important meaning for the state-of-art of photoactive semiconductors for the treatment of polluted water.

The present results suggest the high photocatalytic activity of potassium-sodium niobate is due to several contributions, including structural, morphological, and surface chemistry. The spray pyrolysis method showed to be a promising technique for obtention of alkali niobates materials with representative surface area. The changes in the structural and crystallite anisotropic shape suggested the hollow spheres are structurally composed by sub-nanoparticles. The incipient micropore framework observed from the N<sub>2</sub> adsorption/desorption isotherms can be associated with empty voids formed between these nanoparticles in the solvent evaporation stage during the spray pyrolysis, while the mesopore framework is consequence of the development of mesopores within the spheres. Adding potassium to sodium niobate increased its acid surface pH, resulting in a decrease in the amount of BB41 adsorbed molecules in the three pH of solutions studied. The structure modification caused by the substitution of sodium by potassium promote the formation of highly reactive apical O atoms on potassium-sodium niobate increasing the photoactivity. From the analysis of kinetics models of adsorption can be concluded that the present materials behave as membrane-like materials where mass diffusion from the bulk of solution and adsorption processes can simultaneously coexist or compete as

a function of the pH of solution. In addition, the hollow and spherical shape of the niobate-based materials played an important role on adsorption of BB41. Contrary to the direct photolysis results where acid pH of solution promoted the total degradation of BB41 in only 2 h irradiation, it can be concluded that acid pH of solution inhibits the photocatalytic activity of the niobate-based samples, mainly that of KNN-0.5. This can be due to the protonation of the apical O atoms in the niobate structure. An important increase in the photocatalytic activity was found up to 23.1 times higher at basic pH on KNN-0.5 than that observed on TiO<sub>2</sub>. At neutral and acid pH of solution, the enhancements in photoactivity were up to 7.9, and 4.0 on KNN-0.5, respectively. These results indicate that even at acid pH where, the adsorption of BB41 molecules is limited, the present niobate-based nanostructured materials are more photoactive than TiO<sub>2</sub>. On basis to the adsorption study by different kinetic models, and photocatalytic results, it can be proposed the present materials can be considered as a membrane-like photoreactors. Since the present niobate-based nanostructured hollow spheres are characterized by an energy band-gap within the visible range of the electromagnetic spectra, these materials have a high potential for the solar-driven remediation of polluted water. Accordingly, further experiments are being conducted under real solar experimental conditions.

### **Conflicts of interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### **Ethical Approval**

All the authors have read and approved to publish the paper in the Applied Catalysis B: Environmental journal. Authors declare the paper has not been published previously nor is it being considered by any other peer-reviewed journal.

#### **Credit Authorship Contribution Statement**

S. Lanfredi and M.A.L Nobre contributes with the conceptualization, investigation, writing, and review. F. R. Praxedes contributes with investigation, preparation of powders and methodology, data curation and writing. P.S. Poon contributes with the analysis of results and revision. J. Matos contributes with the conceptualization, writing, review, and analysis and interpretation of the kinetic data of adsorption and degradation of the pollutant.

### Availability of data and materials

Not applicable.

### **Acknowledgments and Funding**

F.R. Praxedes thanks "Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) -Finance Code 001. S. Lanfredi acknowledges the Brazilian projects: Grant# 2007/03510-9, 2014/11189-0, 2019/06623-6, 2020/00781-6 from São Paulo Research Foundation (FAPESP) and CNPq for financial support; Brazilian Nanotechnology National Laboratory (LNNano/CNPEM) for the use of TEM facilities (proposal # TEM-C1 27802), E.R.P. González and S.R. da Silva for GC-MS measurements, A.B. Moreira for Total Organic Carbon (TOC) measurements (Grant# 2005/51242-8 from São Paulo Research Foundation (FAPESP). V.P. Carvalho-Jr for DR/UV-Vis measurements.

P.S. Poon thanks ANID-PIA/APOYO CCTE AFB170007. J. Matos acknowledges the Chilean projects: ANID-FONDECYT 1190591 and the Millennium Science Initiative Program-NCN17-040.

### References

 E. Ringgaard, T. Wurlitzer, Lead-free piezoceramics based on alkali niobates, J. Euro. Ceram. Soc. 25 (2005) 2701–2706.

[2] J. Wu, D. Xiao, J. Zhu, Potassium-sodium niobate lead-free piezoelectric materials: Past, present, and future of phase boundaries, Chem. Reviews 115 (2015) 2559–2595

[3] T. Ahmad, U. Farooq, R. Phul, Fabrication and photocatalytic applications of perovskite materials with special emphasis on alkali-metal-based niobates and tantalates, Ind. Eng. Chem. Res. 57 (2018) 18–41.

[4] Q. Gu, K. Zhu, N. Zhang, Q. Sun, P. Liu, J. Liu, J. Wang, Z. Li, Modified solvothermal strategy for straightforward synthesis of cubic NaNbO<sub>3</sub> nanowires with enhanced photocatalytic H<sub>2</sub> evolution, J. Phys. Chem. C 119 (2015) 25956–25964.

[5] G. Li, T. Kako, D. Wang, Z. Zou, J. Ye, Synthesis and enhanced photocatalytic activity of NaNbO<sub>3</sub> prepared by hydrothermal and polymerized complex methods, J. Phys. Chem. Solids 69 (2008) 2487–2491.

[6] J.W. Liu, G. Chen, Z. Li, Z.G. Zhang, Hydrothermal synthesis and photocatalytic properties of  $ATaO_3$  and  $ANbO_3$  (A = Na and K), Inter. J. Hyd. Energy 32 (2007) 2269–2272.

[7] X. Li, Z. Zhuang, W. Li, Q. Li, Hard template synthesis of nanocrystalline NaNbO<sub>3</sub> with enhanced photocatalytic performance, Catal. Letters 142 (2012) 901–906.

[8] H. Shi, X. Li, D. Wang, Y. Yuan, Z. Zou, J. Ye, NaNbO<sub>3</sub> nanostructures: Facile synthesis, characterization, and their photocatalytic properties, Catal. Letters 132 (2009) 205–212.

[9] H. Shi, T. Wang, J. Chen, C. Zhu, J. Ye, Z. Zou, Photoreduction of carbon dioxide over NaNbO<sub>3</sub> nanostructured photocatalysts, Catal. Letters 141 (2011) 525–530.

[10] H. Hayashi, Y. Hakuta, Y. Kurata, Hydrothermal synthesis of potassium niobate photocatalysts under subcritical and supercritical water conditions, J. Mater. Chemistry 14 (2004) 2046–2051.

[11] H. Shi, Z. Zou, Photophysical and photocatalytic properties of ANbO<sub>3</sub> (A = Na, K) photocatalysts,
J. Phys. Chem. Solids 73 (2012) 788–792.

[12] S. Zlotnik, D.M. Tobaldi, P. Seabra, J.A. Labrincha, P.M. Vilarinho, Alkali niobate and tantalate perovskites as alternative photocatalysts, ChemPhysChem 17 (2016) 3570–3575.

[13] K.I. Katsumata, C.E.J. Cordonier, T. Shichi, A. Fujishima, Photocatalytic activity of NaNbO<sub>3</sub> thin films, J. Amer. Chem. Society 131 (2009) 3856–3857.

[14] X. Meng, W. Wang, H. Ke, J. Rao, D. Jia, Y. Zhou, Synthesis, piezoelectric property and domain behavior of the vertically aligned  $K_{1-x}Na_xNbO_3$  nanowire with a morphotropic phase boundary, J. Mater. Chem. C. 5 (2017) 747–753.

[15] J.-M. Herrmann, Photocatalysis fundamentals revisited to avoid several misconceptions, Appl. Catal. B: Environ. 99 (2010) 461–468.

[16] C. Takai, H. Watanabe, T. Asai, M. Fuji, Determine apparent shell density for evaluation of hollow silica nanoparticle, Coll. Surf. A: Physicochem. Eng. Aspects 404 (2012) 101–105.

[17] M. Xiao, C. Zhao, H. Chen, B. Yang, J. Wang, Ship-in-a-bottle growth of noble metal nanostructures, Adv. Functional Mater. 22 (2012) 4526–4532.

[18] K.M. Yeo, S. Choi, R.M. Anisur, J. Kim, I.S. Lee, Surfactant-free platinum-on-gold nanodendrites with enhanced catalytic performance for oxygen reduction, Angew. Chem. Inter. Ed. 50 (2011) 745–748.

[19] J. Matos, S. Miralles-Cuevas, A. Ruíz-Delgado, I. Oller, S. Malato, Development of TiO<sub>2</sub>-C photocatalysts for solar treatment of polluted water, Carbon 122 (2017) 361-373.

[20] J. Liu, S.Z. Qiao, S.B. Hartono, G.Q. Lu, Monodisperse yolk-shell nanoparticles with a hierarchical porous structure for delivery vehicles and nanoreactors, Angew. Chem. Inter. Ed. 49 (2010) 4981–4985.

[21] T. Arai, S.I. Senda, Y. Sato, H. Takahashi, K. Shinoda, B. Jeyadevan, K. Tohji, Cu-doped ZnS hollow particle with high activity for hydrogen generation from alkaline sulfide solution under visible light, Chem. Materials 20 (2008) 1997–2000.

[22] Z. Wang, L. Zhou, X.W. Lou, Metal oxide hollow nanostructures for lithium-ion batteries, Advanced Materials 24 (2012) 1903–1911.

[23] H. Choi, D. Kim, S.P. Yoon, J. Han, S. Ha, J. Kim, Production of molybdenum oxide particles with high yield by ultrasonic spray pyrolysis and their catalytic activity toward partial oxidation of n-dodecane, J. Anal. Appl. Pyrolysis 112 (2015) 276–283.

[24] J.S. Cho, J.C. Lee, S.H. Chung, J.K. Seo, S.H. Rhee, Effect of grain size and density of spraypyrolyzed hydroxyapatite particles on the sinterability of hydroxyapatite disk, Ceram. International 40 (2014) 6691–6697.

[25] Z. Gao, Z. Jin, Q. Ji, Y. Tanga, J. Kong, L. Zhang, Y. Li, Crumpled graphene prepared by a simple ultrasonic pyrolysis method for fast photodetection, Carbon 128 (2018) 117–124.

[26] C. Li, T. Ming, J. Wang, J. Wang, J.C. Yu, S.H. Yu, Ultrasonic aerosol spray-assisted preparation of TiO<sub>2</sub>/In<sub>2</sub>O<sub>3</sub> composite for visible-light-driven photocatalysis, J. Catalysis 310 (2014) 84–90.

[27] N. Kumar, V.K. Komarala, V. Dutta, In-situ synthesis of Au-CdS plasmonic photocatalyst by continuous spray pyrolysis and its visible light photocatalysis, Chem. Eng. J. 236 (2014) 66–74.

[28] J. Yang, X. Zhang, H. Liu, C. Wang, S. Liu, P. Sun, L. Wang, Y. Liu, Heterostructured TiO<sub>2</sub>/WO<sub>3</sub> porous microspheres: Preparation, characterization, and photocatalytic properties, Catal. Today 201 (2013) 195–202.

[29] P. Pawinrat, O. Mekasuwandumrong, J. Panpranot, Synthesis of Au-ZnO and Pt-ZnO nanocomposites by one-step flame spray pyrolysis and its application for photocatalytic degradation of dyes, Catal. Comm. 10 (2009) 1380–1385.

[30] X. He, Z. Gan, S. Fisenko, D. Wang, H.M. El-Kader, W.N. Wang, Rapid formation of metalorganic frameworks (MOFs) based nanocomposites in microdroplets and their applications for CO<sub>2</sub> photoreduction, ACS Appl. Mater. Interfaces 9 (2017) 9688–9698.

[31] J. Benvenuti, A. Fisch, J.H.Z. dos Santos, M. Gutterres, Silica-based adsorbent material with grape bagasse encapsulated by the sol-gel method for the adsorption of basic blue 41 dye, J. Environ. Chem. Eng. 7 (2019) 103342.

[32] N.M. Mahmoodi, J. Abdi, Nanoporous metal-organic framework (MOF-199): Synthesis, characterization, and photocatalytic degradation of basic blue 41, Microchem. J. 144 (2019) 436–442.

[33] S. Lanfredi, J. Matos, S.R. da Silva, E. Djurado, A.S. Sadouki, A. Chouaih, P.S. Poon, E.R.P. González, M.A.L. Nobre, K- and Cu-doped CaTiO<sub>3</sub>-based nanostructured hollow spheres as alternative catalysts to produce fatty acid ethyl esters as potential biodiesel, Appl. Catal. B: Environ. 272 (2020) 118986.

[34] C.A. Schneider, W.S. Rasband, K.W. Eliceiri, NIH image to ImageJ: 25 years of image analysis, Nature methods 9 (2012) 671-675.

[35] J. Rodríguez-Carvajal, Recent advances in magnetic structure determination by neutron powder diffraction, Phys. B: Phy. Cond. Matter 192 (1993) 55–69.

[36] J. R. Carvajal, An introduction to the Program FullProff 2000 (Laboratorie Léon Brillouin, CEACNRS, Saclay), France (2001).

[37] N.C. Popa, The (hkl) Dependence of diffraction-line broadening caused by strain and size for all Laue groups in Rietveld refinement, J. Appl. Crystallography 31 (1998) 176–180.

[38] P. Thompson, D.E. Cox, J.B. Hastings, Rietveld refinement of Debye–Scherrer synchrotron X-ray data from Al<sub>2</sub>O<sub>3</sub>, J. Appl. Crystallography 20 (1987) 79–83.

[39] M. Casas-Cabanas, M.R. Palacín, J. Rodríguez-Carvajal, Microstructural analysis of nickel hydroxide: Anisotropic size versus stacking faults, Powder Diffraction 20 (2005) 334–344.

[40] J. González-Platas, J. Rodríguez-Carvajal, Graphic Fourier program GFOURIER, Version 4.02,Universidad La Laguna, Tenerife, Spain (2002).

[41] P. Makuła, M. Pacia, W. Macyk, How to correctly determine the band gap energy of modified semiconductor photocatalysts based on UV-Vis spectra, J. Phy. Chem. Lett. 9 (2018) 6814–6817.

[42] S. Lanfredi, M.A.L. Nobre, P.S. Poon, J. Matos, Hybrid material based on an amorphous-carbon matrix and ZnO/Zn for the solar photocatalytic degradation of basic blue 41, Molecules 25 (2020) 96.

[43] C.Y. Chu, M.H. Huang, Facet-dependent photocatalytic properties of Cu<sub>2</sub>O crystals probed by using electron, hole and radical scavengers, J. Mater. Chem. A 5 (2017) 15116–15123.

[44] L.S. Gomez-Villalba, E. Sourty, B. Freitag, O. Milosevic, M.E. Rabanal, TEM-STEM study of europium doped gadolinium oxide nanoparticles synthesized by spray pyrolysis, Adv. Powder Technol. 24 (2013) 864–870.

[45] P. Majerič, D. Jenko, B. Friedrich, R. Rudolf, Formation mechanisms for gold nanoparticles in a redesigned ultrasonic spray pyrolysis, Adv. Powder Technol. 28 (2017) 876–883.

[46] J. Matos, M. Labady, A. Albornoz, J. Laine, J.L. Brito, Topological organization and textural changes of carbon macro-networks submitted to activation with N<sub>2</sub> and CO<sub>2</sub>, J. Mater. Sci. 39 (2004) 3705-3716.

[47] J. Matos, M. Labady, A. Albornoz, J. Laine, J.L. Brito, Catalytic effect of KOH on textural changes of carbon macronetworks by physical activation, J. Molec. Catal. A: Chem. 228 (2005) 189-194.

[48] B. Jaffe; W.R. Cook; H. Jaffe, Piezoelectric Ceramics, Academic Press: London, UK, 1971.

[49] D.W. Baker, P.A. Thomas, N. Zhang, A.M. Glazer, A comprehensive study of the phase diagram of K<sub>x</sub>Na<sub>1-x</sub>NbO<sub>3</sub>, Applied Physics Letters 95 (2009) 091903.

[50] Y. Li, X. Li, Z. Wang, H. Guo, T. Li, Distinct impact of cobalt salt type on the morphology, microstructure, and electrochemical properties of  $Co_3O_4$  synthesized by ultrasonic spray pyrolysis, J. Alloys and Compounds 696 (2017) 836–843.

[51] J. Leng, Z. Wang, X. Li, H. Guo, H. Li, K. Shih, G. Yan, J. Wang, Accurate construction of a hierarchical nickel–cobalt oxide multishell yolk–shell structure with large and ultrafast lithium storage capability, J. Mater. Chem. A 5 (2017) 14996–15001.

[52] K. M. Yang, C. K. Yun, M. J. Sang, J. C. Yun and S. K. Yang, Electrochemical properties of spherical hollow composite powders with various Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>/SnO<sub>2</sub> ratios prepared by spray pyrolysis, Int. J. Electrochem. Science 8 (2013) 11972–11983.

[53] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou (Netherlands), R.A. Pierotti, J. Rouquerol, T. Siemieniewska, Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity, Pure Appl. Chem. 57 (1985) 603–619.

[54] M. Thommes, K. Kaneko, A.V. Neimark, J.P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K.S.W. Sing, Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report), Pure Appl. Chem. 87 (2015) 1051–1069.

[55] M. Feizpour, H.B. Bafrooei, R. Hayati, T. Ebadzadeh, Microwave-assisted synthesis and sintering of potassium sodium niobate lead-free piezoelectric ceramics, Ceram. Inter. 40 (2014) 871–877.

[56] C. Leal-Marchena, C. Saux, R. Dinamarca, G. Pecchi, L. Pierella, Alkaline niobates ANbO<sub>3</sub> (A = Li, Na, K) as heterogeneous catalysts for dipropyl sulfide oxidation, RSC Advances 6 (2016) 102015–102022.

[57] S. Lanfredi, M.A.L. Nobre, M.R. Besse, A.R.F. Lima, G. Palacio, Spectral deconvolution as a tool to understanding Curie-temperature shifting and niobium off-centering phenomenon in ferroelectrics of type niobates, Appl. Math. Sciences 9 (2015) 5839–5869.

[58] F.E. López-Suárez, M.J. Illán-Gómez, A. Bueno-López, J.A. Anderson, NOx storage and reduction on a SrTiCuO<sub>3</sub> perovskite catalyst studied by operando DRIFTS, Appl. Catal. B: Environ. 104 (2011) 261–267.

[59] D. Liu, P. Yuan, H. Liu, J. Cai, D. Tan, H. He, J. Zhu, T. Chen, Quantitative characterization of the solid acidity of montmorillonite using combined FTIR and TPD based on the NH<sub>3</sub> adsorption system, Appl. Clay Science 80–81 (2013) 407–412.

[60] L. Wang, H. Gu, J. He, T. Zhao, X. Zhang, C. Xiao, H. Liu, X. Zhang, Y. Li, Scale synthesized cubic NaNbO<sub>3</sub> nanoparticles with recoverable adsorption and photodegradation for prompt removal of methylene blue, J. Alloys and Compounds 695 (2017) 599–606.

[61] G.H. Khorrami, A. Kompany, A. Khorsand Zak, Structural and optical properties of (K,Na)NbO<sub>3</sub> nanoparticles synthesized by a modified sol-gel method using starch media, Adv. Powder Technol. 26 (2015) 113–118.

[62] Q. Liu, L. Zhang, Y. Chai, D.L. Dai, Facile fabrication and mechanism of single-crystal sodium niobate photocatalyst: Insight into the structure features influence on photocatalytic performance for H<sub>2</sub> evolution, J. Phys. Chem. C. 121 (2017) 25898–25907.

[63] J. Matos, S. Lanfredi, R. Montaña, M.A.L. Nobre, M.C. Fernández de Córdoba, C.O. Ania, Photochemical reactivity of apical oxygen in KSr<sub>2</sub>Nb<sub>5</sub>O<sub>15</sub> materials for environmental remediation under UV irradiation, J. Coll. Inter. Science 496 (2017) 211-221.

[64] J. Matos, P. Atienzar, H. García, J.C. Hernández-Garrido, Nanocrystalline carbon-TiO<sub>2</sub> hybrid hollow spheres as possible electrodes for solar cells, Carbon 53 (2013) 169-181.

[65] J.R. Rangel-Mendez, J. Matos, L.F. Cházaro-Ruiz, A.C. González-Castillo, G.Barrios-Yáñez, Microwave-assisted synthesis of C-doped TiO<sub>2</sub> and ZnO hybrid nanostructured materials as quantumdots sensitized solar cells, Appl. Surf. Science 434 (2018) 744-755.

[66] S. Gupta, V. Petkov, S. Priya, Local atomic structure of K<sub>x</sub>Na<sub>(1-x)</sub>NbO<sub>3</sub> by total x-ray diffraction,
 Appl. Phys. Letters 105 (2014) 232902.

[67] J. Koruza, J. Tellier, B. Malič, V. Bobnar, M. Kosec, Phase transitions of sodium niobate powder and ceramics prepared by solid state synthesis, J. Appl. Phys. 108 (2010) 113509.

[68] M. Ahtee, A. M. Glazer, Lattice parameters and tilted octahedra in sodium-potassium niobate solid solutions, Acta Cryst. A32, (1976) 434.

[69] S. Kobayashi, Y. Ikuhara, T. Mizoguchi, Lattice expansion and local lattice distortion in Nb- and La-doped SrTiO<sub>3</sub> single crystals investigated by x-ray diffraction and first-principles calculations, Phys. Review B 98 (2018) 134114.

[70] P. Vousden, The structure of ferroelectric sodium niobate at room temperature, Acta Cryst. 4 (1951) 545-551.

[71] J.A. Alonso, M.J. Martínez-Lope, M.T. Casais, M.T. Fernández-Díaz, Evolution of the Jahn-Teller distortion of  $MnO_6$  octahedra in RMnO<sub>3</sub> perovskites (R = Pr, Nd, Dy, Tb, Ho, Er, Y): A neutron diffraction study, Inorganic Chem. 39 (2000) 917–923.

[72] H. Ge, Y. Huang, Y. Hou, H. Xiao, M. Zhu, Size dependence of the polarization and dielectric properties of KNbO<sub>3</sub> nanoparticles, RSC Advances 4 (2014) 23344–23350.

[73] S. Lanfredi, I.A.O. Brito, C. Polini, M.A.L. Nobre, Deriving the magnitude of niobium off-center displacement in ferroelectric niobates from infrared spectroscopy, J. Appl. Spectroscopy 79 (2012) 254–260.

[74] D. Damjanovic, Ferroelectric, dielectric and piezoelectric properties of ferroelectric thin films and ceramics, Rep. Prog. Physics 61 (1998) 1267–1324.

[75] S. Yagi, I. Yamada, H. Tsukasaki, A. Seno, M. Murakami, H. Fujii, H. Chen, N. Umezawa, H. Abe, N. Nishiyama, S. Mori, Covalency-reinforced oxygen evolution reaction catalyst, Nature Comm. 6 (2015) 8249.

[76] G.L. Messing, S.C. Zhang, G.V. Jayanthi, Ceramic powder synthesis by spray pyrolysis, J. Amer.Ceram. Society 76 (1993) 2707–2726.

[77] S.H. Ju, H.C. Jang, Y.C. Kang, Al-doped Ni-rich cathode powders prepared from the precursor powders with fine size and spherical shape, Electrochim. Acta 52 (2007) 7286–7292.

[78] A. Chadlia, M.M. Farouk, Removal of basic blue 41 from aqueous solution by carboxymethylated posidonia oceanica, J. Appl. Polymer Sci. 103 (2007) 1215–1225.

[79] F. Kooli, L. Yan, R. Al-Faze, A. Al-Sehimi, Removal enhancement of basic blue 41 by brick waste from an aqueous solution, Arab. J. Chem. 8 (2015) 333–342.

[80] I. Humelnicu, A. Băiceanu, M.-E. Ignat, V. Dulman, The removal of basic blue 41 textile dye from aqueous solution by adsorption onto natural zeolitic tuff: Kinetics and thermodynamics, Process Saf. Environ. Prot. 105 (2017) 274–287.

[81] S. Afshin, S.A. Mokhtari, M. Vosoughi, H. Sadeghi, Y. Rashtbari, Data of adsorption of basic blue 41 dye from aqueous solutions by activated carbon prepared from filamentous algae, Data Brief 21 (2018) 1008–1013.

[82] A. El Kassimi, A. Boutouil, M. El Himri, M.R. Laamari, M, El Haddad, Selective and competitive removal of three basic dyes from single, binary and ternary systems in aqueous solutions: A combined experimental and theoretical study, J. Saudi. Chem. Society 24 (2020) 527-544.

[83] J. Matos, J. Arcibar-Orozco, P.S. Poon, G. Pecchi, J.R. Rangel-Mendez, Influence of phosphorous upon the formation of DMPO-•OH and POBN-• $O_2^-$  spin-trapping adducts in carbon-supported P-promoted Fe-based photocatalysts, J. Photochem. Photobiol. A: Chem. 391 (2020) 112362.

[84] Y.S. Ho, G. McKay, A Comparison of chemisorption kinetic models applied to pollutant removal on various sorbents, Process Saf. Environ. Prot. 76 (1998) 332-340.

[85] F.-C. Wu, R.-L. Tseng, R.-S. Juang, Kinetic modeling of liquid-phase adsorption of reactive dyes and metal ions on chitosan, Water Res. 35 (2001) 613-618.

[86] F.-C. Wu, R.-L. Tseng, R.-S. Juang, Initial behavior of intraparticle diffusion model used in the description of adsorption kinetics, Chem. Eng. J. 153 (2009) 1-8.

[87] G. McKay, M.S. Otterburn, A.G. Sweeney, The removal of color from effluent using various adsorbents—III. Silica: Rate processes, Water Res. 14 (1980) 15-20.

[88] S. Boumaza, F. Kaouah, S. Omeiri, M. Trari, Z. Bendjama, Removal of dyes by an integrated process coupling adsorption and photocatalysis in batch mode, Res. Chem. Intermed. 41 (2015) 2353-2375.

[89] P. Bouras, P. Lianos, Synergy effect in the combined photodegradation of an azo dye by titanium dioxide photocatalysis and photo-Fenton oxidation, Catal. Lett. 123 (2008) 220-225.

[90] X. He, H. Chi, B. Zhang, J. Zhang, D. Wang, J. Ma, Efficient removal of halogenated phenols by vacuum-UV system through combined photolysis and OH oxidation: Efficiency, mechanism and economic analysis, J. Hazard. Mater. 403 (2021) 123286.

[91] A. Giwa, P.O. Nkeonye, K.A. Bello, K.A. Kolawole, Photocatalytic decolorization and degradation of C. I. basic blue 41 using TiO<sub>2</sub> nanoparticles, J. Environ. Protection 3 (2012) 1063–1069.

[92] M.K.E. Bouchareb, M. Bouhelassa, M. Berkani, Optimization of photocatalytic decolorization of C.I. basic blue 41 in semi-pilot scale prototype solar photoreactor, J. Chem. Technol. Biotechnol. 89 (2014) 1211–1218.

[93] C.S. Turchi, D.F. Ollis, Photocatalytic degradation of organic water contaminants: Mechanisms involving hydroxyl radical attack, J. Catalysis 122 (1990) 178–192.

[94] A. Houas, H. Lachheb, M. Ksibi, E. Elaloui, C. Guillard, J.-M. Herrmann, Photocatalytic degradation pathway of methylene blue in water, Appl. Catal. B: Environ. 31 (2001) 145–157.

59

[95] J. Matos, V. Fierro, R. Montaña, E. Rivero, A. Martínez de Yuso, W. Zhao, A. Celzard, High surface area microporous carbons as photoreactors for the catalytic photodegradation of methylene blue under UV-vis irradiation, Appl. Catal. A: Gen. 517 (2016) 1-11.

[96] Z. Wang, J. Hou, C. Yang, S. Jiao, K. Huang, H. Zhu, Hierarchical metastable gamma-TaON hollow structures for efficient visible-light water splitting, Energy Environ. Sci. 6 (2013) 2134–2144.

[97] J. Qi, K. Zhao, G.D. Li, Y. Gao, H.J. Zhao, R.B. Yu, Z.Y. Tang, Multi-shelled CeO<sub>2</sub> hollow microspheres as superior photocatalysts for water oxidation, Nanoscale 6 (2014) 4072–4077.

[98] K.V. Kumar, K. Porkodi, F. Rocha, Langmuir-Hinshelwood kinetics - A theoretical study, Catal. Comm. 9 (2008) 82–84.

[99] A.W. Hewat, Cubic-tetragonal-orthorhombic-rhombohedral ferroelectric transitions in perovskite potassium niobate: neutron powder profile refinement of the structures, J. Phys. C: Solid State Phys. 6 (1973) 2559.

[100] M. Stock, S. Dunn, Influence of the ferroelectric nature of lithium niobate to drive photocatalytic dye decolorization under artificial solar light, J. Phys. Chem. C. 116 (2012) 20854–20859.

[101] L. Xu, Y. S. Ding, C. H. Chen, L. Zhao, C. Rimkus, R. Joesten, S. L. Suib, 3D flowerlike  $\alpha$ -nickel hydroxide with enhanced electrochemical activity synthesized by microwave-assisted hydrothermal method, Chemistry of Materials 20 (2008) 308–316.

[102] J. Leng, Z. Wang, J.Wang, H.H. Wu, G.Yan, X. Li, H. Guo, Y. Liu, Q. Zhang, Z. Guo, Advances in nanostructures fabricated: Via spray pyrolysis and their applications in energy storage and conversion, Chemical Society Reviews 48 (2019) 3015–3072.

[103] A. D. Handoko, G. K. L. Goh, Hydrothermal synthesis of sodium potassium niobate solid solutions at 200 °C, Green Chemistry 12 (2010) 680–68.

[104] X. Meng, W. Wang, H. Ke, J. Rao, Y. Zhou, Synthesis of potassium sodium niobate nanostructures by hydrothermal combining with the sol-gel method, Materials Sci. Eng. B: Solid-State Mater. Adv. Technology 212 (2016)1–6.

[105] K. Kanie, H. Mizutani, A.Terabe, Y. Numamoto, S. Tsukamoto, H.Takahashi, M. Nakaya, J.Tani, A. Muramatsu, Precursor effect on hydrothermal synthesis of sodium potassium niobate fine particles and their piezoelectric properties, Jap. J. Appl. Physics 50 (2011) 09ND09.

[106] K.M. Al Aqad, C. Basheer, Photocatalytic degradation of basic blue dye using zinc nanoparticles decorated graphene oxide nanosheet, J. Phys. Org. Chem. 34 (2021) e4117.

### **Captions of Tables**

Table 1. Summary of textural and porosimetry properties of the samples.

**Table 2.** Positions and wavenumber assignments of the Nb-O vibration bands obtained from FTIR spectra, and optical properties of samples, including maxima absorption wavelength ( $\lambda_{abs-photon}$ ) and optical energy band bap ( $E_{bg}$ ) obtained from DR/UV-Vis spectra.

Table 3. Lattice parameters and unit cell volume for the KNN-0.2, KNN-0.3, and KNN-0.5.

**Table 4.** Interatomic lengths of Nb–O bonds of KNN-0.2, KNN-0.3, and KNN-0.5 powders in NbO<sub>6</sub> octahedron.

**Table 5.** Bond angles ( $\theta$ ) of NbO<sub>6</sub> octahedron of KNN-0.2, KNN-0.3, and KNN-0.5.

 Table 6. Apparent anisotropic crystallite size and maximum average strain from microstructural refinement.

Table 7. Summary of kinetics parameters of adsorption in the dark of BB41.

**Table 8.** Summary of surface concentration and kinetics parameters of BB41 photodegradation.

### **Captions of Figures**

**Figure 1.** SEM images of (a) KNN-0.2, (b) KNN-0.3, and (c) KNN-0.5. Surface 3D analysis of rough particles (blue circles), for (d,g) KNN-0.2, (e,h) KNN-0.3, and (f,i) KNN-0.5. Particle size distribution histograms of (j) KNN-0.2, (k) KNN-0.3, (l) KNN-0.5 samples.

Figure 2: TEM images of catalysts. (a): KNN-0.2, (b): KNN-0.3, and (c): KNN-0.5.

Figure 3. Schematic representation of the particle formation process by spray pyrolysis.

Figure 4. FTIR spectra of samples.

**Figure 5.** (a): DR/UV-Vis spectra in terms of the Kubelka-Munk theory. (b): Tauc plot according to an indirect transition. (c) Linear regression of Tauc plot in the range (3.2 - 3.8 eV).

**Figure 6.** (a): X-ray diffraction patterns of KNN-0.2, KNN-0.3, and KNN-0.5 powders. (b): Expansion of the region between 20° and 35°. (c): Expansion of the region between 35° and 41°.

**Figure 7.** Graphic representation of the unit cell obtained for: (a): KNN-0.2, (b): KNN-0.3, and (c): KNN-0.5 powders.

Figure 8. Representation of NbO<sub>6</sub> octahedron: (a) KNN-0.2, (b) KNN-0.3 and (c) KNN-0.5.

**Figure 9.** Structural ordering in potassium-sodium niobate associated to the increase of Nb-O-Nb bond angle close to 180°.

**Figure 10.** Crystallite anisotropic shape for potassium-sodium niobate. Crystallite displayed through (001) plane for (a): KNN-0.2, (b): KNN-0.3, and (c): KNN-0.5. Crystallite displayed through (100) plane for (d): KNN-0.2, (e): KNN-0.3, and (f): KNN-0.5. Crystallite displayed through (010) plane for (g): KNN-0.2, (h): KNN-0.3, and (i): KNN-0.5.

Figure 11. Kinetics of adsorption in the dark of BB41 as a function of pH of solution. (a): KNN-0.2,(b): KNN-0.3, and (c): KNN-0.5.

Figure 12. Kinetics of BB41 degradation under UV-irradiation. (a): Direct photolysis. (b): KNN-0.2. (c): KNN-0.3. (d): KNN-0.5.

Figure 13. Linear regression from the kinetic data of Figure 12. (a): Direct photolysis. (b): KNN-0.2. (c): KNN-0.3. (d): KNN-0.5.

**Figure 14**. (a): Influence of pH of solution upon the surface concentration, and (b): Upon the global reaction-rate. (c): Correlation between the global reaction-rate and the surface concentration.

**Figure 15.** (a): Kinetics of TOC analysis on irradiated KNN-0.5; (b-d): Scavenger tests detected along reaction as a function of pH of solution.

**Figure. 16**. Proposed mechanism for the photodegradation of BB41 under irradiated  $K_xNa_{1-x}NbO_3$  hollow spheres.