



## Barium removal by photocatalytic process: An alternative for water treatment



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### ABSTRACT

This study describes the application of TiO<sub>2</sub> in different forms (anatase, P25, TiO<sub>2</sub> commercial), ZnO and Nb<sub>2</sub>O<sub>5</sub> for barium ions (Ba(II)) reduction by photocatalysis process. Specific surface area (B.E.T method), X-ray diffraction and photo-acoustic spectroscopy techniques were applied for the catalysts characterization. The parameters studied in the reaction were: presence of additives, pH, amount of catalyst, effect of inorganic compounds, adsorption, photolysis, type of catalyst, additives and the time of contact of the additive/catalyst. No significant reduction in the Ba(II) concentration was observed in absence of additive, however a reduction higher than 50% was observed in the presence of additive after 120 min of reaction time. Moreover, the effect of Cl<sup>-</sup> ions, generally present in natural waters, indicated an increase in the Ba(II) reduction time. The adsorption and photolysis tests were not efficient in the Ba(II) removal. However, the contact time between the additive (formic acid) and the catalyst, before the photocatalytic process, showed an improvement in the catalytic activity for all catalysts studied. Therefore, the photocatalysis tests indicated that the catalysts that showed the highest efficiency in the Ba(II) removal were anatase, P25 and ZnO, respectively. The maximum percentage of Ba(II) removal was obtained using anatase as catalyst and at optimized conditions Ba(II) removal was higher than 99% were obtained a reaction time of 90 min.

### 1. Introduction

Barium (Ba) is an element that presents high solubility in water, characteristic that results in a great mobility in the environment [1,2]. This element is potentially toxic and human exposure to Ba may cause various health problems, such as heart and/or kidney failure, pulmonary edema, respiratory paralysis, and gastric and intestinal excessive bleeding [3]. Barium is also present in industrial waste from chemical, petrochemical, automotive, metallurgical and industrial processes, among others. However, there are few studies in the literature concerning the pollutant potential of Ba, but due to new and increasing applications of Ba in industrial processes, and therefore an increase in the potential of human exposure to this element, there is a need to develop effective processes for Ba removal from the environment [3,4]. The United States Environmental Protection Agency (US EPA) has set the maximum limit concentration for 2.0 mg L<sup>-1</sup> (ppm) in water samples [5], and in Brazil, the Brazilian Ministry of Health (Portaria n° 2.914I, 12/2011) has established a limit of 0.7 mg L<sup>-1</sup> of Ba in drinking water [6]. In this context, the heterogeneous photocatalysis has aroused great interest due to its potential application in the removal

of organic and inorganic pollutants in different matrices [7–11].

Titanium dioxide (TiO<sub>2</sub>) is one of the most widely semiconductors used as catalysts in photocatalytic processes, due to its non-corrosive, nontoxic, high photo-activity, high photo-stability and economical nature. Titanium dioxide occurs in three distinct polymorphs: rutile, anatase and brookite. However, anatase and rutile crystal structures are commonly used as photocatalyst, although for most reactions, anatase form showing greater photocatalytic activity [12–15]. In anatase form, TiO<sub>2</sub> has band gap energy of 3.2 eV and thus needs light below 388 nm to be capable of producing electron-hole pairs. However, other semiconductors such as zinc oxide (ZnO) and niobium pentoxide (Nb<sub>2</sub>O<sub>5</sub>) have been used as catalysts in photocatalytic processes for the removal of several compounds [16–18]

Zinc dioxide crystallizes in three forms: hexagonal wurtzite, cubic “zincblende” and the rock salt, rarely observed [19]. The wurtzite structure is more stable at ambient conditions [20] and therefore the most common form of ZnO. This oxide is a suitable semiconductor due to its high photocatalytic activity, approximate band gap energy (3.4 eV) [19] and similar photocatalytic mechanism of reaction as compared to TiO<sub>2</sub>. Zinc oxide and TiO<sub>2</sub> possessed different redox energy

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levels for their corresponding conduction and valance bands. Zinc oxide is also one of the most extensively investigated photocatalysts and has relatively high catalyst efficiency, low cost, non-toxic and chemical stability [7]. Some studies demonstrate the use of ZnO as a photocatalyst for dye photodegradation [21,22]. Niobium pentoxide, as an n-type transition metal oxide semiconductor, has been largely studied in sensors, electrochromics and bioelectrochemistry. This catalyst, has been applied for dye photodegradation in the textile industry [7].

Thus, this work proposes the use of photocatalytic processes for reduction and subsequent removal of Ba(II) in aqueous solutions. The experimental conditions of pH, type effect and concentration of additives, concentration of catalyst (TiO<sub>2</sub> (anatase)) and presence of interfering ions will be optimized. In addition, the influence of different catalysts and the effect of the catalyst/additive interaction on the Ba(II) removal percentage were evaluated.

## 2. Experimental procedure

### 2.1. Chemical

The following chemicals were used for the experiments: (i) Isopropyl alcohol UV/Spectroscopic HPLC (Vetec with over 99.7% degree of purity); (ii) Methanol (ProQuímios with over 99.5% degree of purity); (iii) Formic acid (Synth with over 85.0% degree of purity); (iv) Barium standard solution 1000 mg L<sup>-1</sup> (SpecSol); (v) Sodium hydroxide (Dynamics with over 98% degree of purity); (vi) Barium Nitrate (Perquim with over 99.9% degree of purity); (vii) HNO<sub>3</sub> (Biotec with over 65% degree of purity); (viii) Potassium chloride (Dynamics with over 99% degree of purity); (ix) Sodium chloride (Neon with over 99% degree of purity).

The following oxides were evaluated as catalysts: i) Titanium dioxide (TiO<sub>2</sub>) in anatase form (Sigma-Aldrich with over 99.9% degree of purity); ii) Degussa P-25 (Sigma-Aldrich with over 99% degree of purity); iii) TiO<sub>2</sub> commercial (Perquim); iv) Zinc oxide (Dynamics with over 99.0% degree of purity) and v) Niobium pentoxide Nb<sub>2</sub>O<sub>5</sub> (Brazilian Mining and Metallurgy Company (CBMM) Brazil).

### 2.2. Pore properties (B.E.T method)

Pore volumes were established using a QUANTACHROME Analyzer – Model Nova-1200 with N<sub>2</sub> adsorption at 77 K. Both calcined (at 623.15 K during 4 h under static air atmosphere) and non-calcined samples were submitted to these analyses. The samples had been previously submitted to a thermal treatment at 573 K, under 2-h vacuum to eliminate any existing water within the pores of the solids.

### 2.3. Characterization of photocatalyst

The techniques used to characterize the catalysts were: photoacoustic spectroscopy (PAS), X-ray diffraction (XRD).

#### 2.3.1. Photo-acoustic spectroscopy

Band gaps of the catalysts were determined by photoacoustic spectroscopy. All the measurements in the ultraviolet and visible spectral regions were performed using a lab-made experimental setup. We obtained the monochromatic light through a 1000-W xenon arc lamp (Oriel Corporation 68820) and a monochromator model 77250 (Oriel). The light beam was modulated by a mechanical chopper – Stanford Research Systems SR540. A lab-made photoacoustic cell was made of aluminum block, machined to hold samples with dimensions up to 5 mm diameter and 1 mm thickness, which allows light to enter through a high transparent quartz window of 6 mm diameter and 2 mm thickness. The distance of the microphone chamber was 15 mm; it was connected to the sample holder room through a 1-mm diameter duct. The capacitive microphone used was the 12-mm diameter Bruel & Kjaer model 2639 – very sensitive, presenting a gain of 50 mV/Pa, and a

frequency response between 1 Hz and 10 kHz. We used a lock-in amplifier by EG & G Instruments, model 5110. All the photoacoustic spectra were obtained at a 20 Hz modulation frequency and recorded between 220 and 720 nm. Data were acquired using a personal computer and the PAS spectra were normalized with respect to the carbon black signal.

The band gap energies were established through Eq. (1):

$$\lambda = \frac{hc}{E_{gap}} = \frac{1240}{E_{gap}} \quad (1)$$

Where  $E_{gap}$  is the band gap energy in eV units,  $h$  is Planck constant and  $c$  speed of light. The direct method was applied to obtain the values, ie,  $m = 2$ . [23].

### 2.3.2. X-Ray diffraction

The samples were measured in a Rigaku-Denki Diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at a voltage of 140 V and current of 40 mA. The patterns obtained were then compared with the diffraction dataset from the Joint Committee of Powder Diffraction Standards.

### 2.4. Photocatalytic experiments

All the photocatalytic experiments were performed in a closed system in absence of natural light. In the system, the photocatalytic reactions were conducted in a 1000 mL borosilicate reactor, under magnetic agitation, using a speed of agitation sufficiently high to guarantee the homogeneous catalyst dispersion on the analytical solution, and an air flow of 13 L h<sup>-1</sup>. The temperature of the system was kept constant at 293 K, by an ultra-thermostatic bath, Model SP-152/10, ultraviolet radiation was provided by a 250 W mercury vapor lamp without the external glass bulb. The samples were collected in regular intervals, centrifuged and the remaining concentration of Ba(II) in solution was determined by atomic absorption spectrometry (Perkin Elmer AAnalyst 700). Adsorption tests were performed applying the same procedure, but without presence of light. Photolysis tests were also performed without catalyst.

## 3. Results and discussion

The results of the specific surface area, mean pore diameter and pore volume, are presented in Table 1.

As observed, the different forms of TiO<sub>2</sub> analyzed (P-25, Anatase, commercial and commercial calcined at 623.15 K) showed significant differences in the surface areas. The highest surface area was obtained for TiO<sub>2</sub> P-25 (33.95 m<sup>2</sup>/g), approaching the literature data in which the surface area varies around 40–50 m<sup>2</sup>/g [24,25]. However, when comparing the specific surface area of non-calcined commercial TiO<sub>2</sub> (19.78 m<sup>2</sup>/g) and the calcined at 623.15 K (12.74 m<sup>2</sup>/g), it is possible to observe that there is a decrease in the specific surface area, which is possibly due to particles agglomeration during the calcinations [26]. In addition, Teh et al. also found that high calcination temperature of 600 °C reduced the specific surface area up to eight times as compared to the catalyst which was calcined at 200 °C [27].

**Table 1**  
Specific surface area, mean pore diameter and pore volume of the catalysts.

| Catalysts                      | Specific surface area (m <sup>2</sup> /g) | Pore volume (cm <sup>3</sup> /g) | Average pore diameter (Å) |
|--------------------------------|---|----------------------------------|---------------------------|
| Commercial                     | 19.78                                     | 0.028                            | 28.36                     |
| Commercial (calcined 623.15 K) | 12.74                                     | 0.190                            | 29.89                     |
| Anatase                        | 6.12                                      | 0.086                            | 27.97                     |
| P-25                           | 33.95                                     | 0.389                            | 22.95                     |
| ZnO                            | 7.89                                      | 0.012                            | 29.23                     |
| Nb <sub>2</sub> O <sub>5</sub> | 11.50                                     | 0.049                            | 15.60                     |

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