Calcium, Strontium And Barium Titanates As Photocatalysts

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Abstract. The titanates were synthesized by the sol-gel method using stearic acid as solvent and reagent. The photocatalytic activity of these materials were measured by discoloration of crystal violet in aqueous solution, irradiating with 254 nm ultraviolet light. TiO₂ anatase, frequently used as a photocatalyst, was used to compare its photocatalytic activity with respect to the titanates used here. Activity was measured through dye degradation rate constants. It was expected that strontium and barium titanates, which have reduction potentials in the conduction band more positive than that of TiO₂, would be more efficient as photocatalysts, but the experimental evidence does not confirm it.

1. Introduction

The contamination of water with organic compounds is a major problem facing today’s world. And finding processes for treatment is already a challenge. Organic pollutants must be treated by oxidation to convert their constituent elements like hydrogen, carbon, nitrogen, sulfur, and other elements into their stable oxides such as water, carbon dioxide, carbonates, nitrates, and sulfates. This treatment is called "mineralization". However, in many cases the pollutants are chemically stable and it is necessary to employ strong oxidizing processes for their degradation, often called Advanced Oxidation Processes (AOPs) that use strongly oxidant chemical species such as ozone and/or peroxides [1] or strong energy routes such as the use of electrochemical or photochemical reactions or combinations thereof [2]. Baird [3] established that advanced oxidation processes are capable of creating strongly oxidizing chemical species, mainly hydroxyl free radicals HO to degrade organic pollutants in aqueous media.

Photocatalysis is considered as an advanced oxidation process [4]. This process consists in irradiating with ultraviolet or visible light a suspension containing the organic substrate and a semiconductor (Sc) that is excited and create a hole h⁺ in the valence band and one electron e⁻ in the conduction band [5]. Both hole and electron have suitable redox potentials to drive reactions with chemicals such as water, pollutants or oxygen from air:

\[
\text{Sc} + \text{hv} \rightarrow \text{Sc}(h_\text{vb}^+) + \text{e}_{\text{cb}}^- \quad (1)
\]

\[
\text{Sc}(h_\text{vb}^+) + \text{H}_2\text{O} \rightarrow \text{Sc} + \text{H}^+ + \text{HO} \quad (2)
\]

\[
\text{e}_{\text{cb}}^- + \text{O}_2 \rightarrow \text{O}_2^- \quad (3)
\]

but:

\[
\text{O}_2^- + \text{H}_2\text{O} \rightarrow \text{HO}_2^- + \text{HO}^- \quad (4)
\]

and:

\[
\text{HO}_2^- + \text{H}_2\text{O} \rightarrow 3 \text{HO} \quad (5)
\]
The search for new photocatalysts based on semiconductors is aimed at finding materials that are cheaper, more efficient in the oxidation of substrates or that have properties such as solids that allow improving separation processes for reuse.

For the selection of a semiconductor it is necessary to consider two of its characteristics: the width of the gap energy and the reduction potentials in the limits of the valence and conduction bands. Several semiconductors have been used in photocatalysis for environmental purposes, as indicated by Batkhande in his review [5], but more frequently titanium dioxide in its anatase phase [6]. This is because the width of the gap energy corresponds to photons of 357 nm or shorter that can be provided by the sun light and several types of lamps, because the normal reduction potentials are +0.06 and 3.53 eV and because the potential of reduction of the gap in the conducting band can produce the superoxide ion $O_2^-$. Observing these characteristics in other semiconductors [7], it seems possible to use calcium, strontium and barium titanates for the degradation of organic contaminants in aqueous medium.

### Table 1. Semiconductors properties of several compounds

| Chemical                  | TiO$_2$ | CaTiO$_3$ | SrTiO$_3$ | BaTiO$_3$ |
|---------------------------|---------|-----------|-----------|-----------|
| $\varepsilon^0$, valence band, Volts* | +0.06   | -0.54     | -0.31     | +0.46     |
| $\varepsilon^0$, conducting band, Volts* | +3.53   | +2.96     | +3.68     | +3.99     |
| $E_g$, Energy Gap, Ev     | 3.47    | 3.5       | 3.99      | 3.53      |
| $\lambda_{max}$, nm      | 357.4   | 354.3     | 310.8     | 351.3     |

Photocatalysis has been applied in the degradation of several kinds of organic pollutants: pesticides, dyes, pharmaceuticals and others. These compounds are very stable and often classified as recalcitrant. In this work we chose crystal violet as a substrate because it has many double bonds and is discarded in the exhausted liquids of clinical laboratories for the classification of bacteria by means of Gram staining.

### 2. Experimental

### Table 2. Chemicals

| Chemical                  | Catalog number | MW (g/mol) | Density (g/cm$^3$) | $T_f$, °C |
|---------------------------|----------------|------------|--------------------|-----------|
| Crystal violet            | Sigma C6158    | 407.98     | - - - - - -         | 205       |
| Absolute ethanol          | Sigma-Aldrich  | 459836     | 46                 | -114      |
| Titanium(IV) tetraisopropoxide | Aldrich      | 205273     | 284.2              | 17        |
| Titanium(IV) tetrabutoxide | Sigma-Aldrich | 8690       | 340.2              | -55       |
| Ca(OH)$_2$                | Sigma C0402    | 74.02      | 2.21               | 580       |
| Sr(OH)$_2.8$H$_2$O        | Aldrich        | 433752     | 265.76             | 100       |
| Ba(OH)$_2.8$H$_2$O        | Sigma          | 82507      | 315.5              | 78        |
| Stearic acid              | Sigma          | 175366     | 284.43             | 361       |
| Titanium dioxide (anatase)| *              | 248576     | 79.87              | 1843      |
| CaTiO$_3$                 | *              | 633801     | 135.94             | 1975      |
| SrTiO$_3$                 | *              | 396141     | 183.49             | 2080      |
| BaTiO$_3$                 | *              | 208108     | 233.19             | 1625      |

*Synthesised
2.1 Synthesis of titania and calcium, strontium and barium titanates.

The titania synthesis was performed in an ice bath round bottom flask, adding 0.1 moles of titanium isopropoxide (30 mL) to 0.4 mol of absolute ethanol (23 mL). A cold mixture of 0.1 mol of deionized water (1.8 mL) and 0.08 mol of ammonium hydroxide (2.4 mL) and 0.4 mol of absolute ethanol (23 mL) is added very slowly. The final mixture was stirred for an additional 4 hours. The solvent was removed by vacuum rotoevaporation and the solid phase was collected in a porcelain dish and calcined at 450 °C [8] to optimize conversion to the anatase phase.

The synthesis of titanates was similar to that published by Lu et al [9]. Stearic acid is used as an anhydrous solvent and as a reagent in this technique. Dissolve 13 mL of titanium tetrabutoxide in 85 g of molten stearic acid and add the appropriate weight of the corresponding metal hydroxide. It is agitated for 6 or more hours to guarantee the formation of the stearate. The formation of a light brown suspension indicates that the formation of the sol phase is already finished. The temperature is increased for one or more hours to evaporate the water formed in the reaction and the dried mixture is then placed in a porcelain dish to be placed in the furnace at 985°C in order to incinerate the organic phase. The high viscosity of the stearate helps the nucleation process to occur at long times and very fine powders are obtained.

Table 3. Weights of the metallic hydroxides used in the synthesis

|       | Ca(OH)$_2$ | Sr(OH)$_2$ | Ba(OH)$_2$ |
|-------|------------|------------|------------|
| Weight | 2.96       | 10.63      | 12.62      |

The obtained powders were washed with 0.1 M HCl solution in order to remove the residual hydroxide and the carbonates formed during the incineration.

2.2 Measurement of photocatalytic activity.

Crystal violet was selected as the substrate for the measurement of the photocatalytic activity of semiconductors [10]. The degradation monitoring was easy because its solutions are highly colored with $\lambda_{\text{max}} = 590$ nm and its molar extinction is 87000 $(\text{mol} / \text{L})^{-1}\text{cm}^{-1}$. The concentration of the working solution with the dye was 8 mg/L. It was necessary to obtain the calibration curves Conc (mg/L) vs. Absorbance in 15 mL dispersions, prepared in 13x100 mm quartz test tubes (ACE glass, VWR 89063-442) of the solutions of 10, 8, 6, 4 and 2 (mg/L) of the equilibrium dye of adsorption with 10 mg of semiconductor. After centrifugation the absorbance was measured on a SHIMADZU UV 160L spectrophotometer. It was observed that the photocatalysts were impregnated with the dye, indicating the adsorption of the dye on the solid.

Dispersions of 15 mL of dye solution with 10 mg of semiconductor were irradiated with 254 nm ultraviolet light obtained from an UVL lamp of 800 milliwatts. Each sample was held in suspension with magnetic stir and bubbling with filtered air. For each solid, six or seven test tubes were prepared with the same amount of dye solution and semiconductor (15 mL, 10 mg). Each sample was irradiated for a short time, between zero and 15 hours and, after centrifugation, the absorbance of the clear liquid was measured. Absorbances were converted to concentrations and these were plotted in concentration vs. time.

3. Results

3.1 Characterization of obtained semiconductors

X-ray diffractograms were obtained from a DRX Advance D-8 diffractometer, with $0-0$ configuration with CuKα radiation source, with graphite monochromator for the secondary beam. The intensities were measured in the range of 0 to 80° in 2θ. The obtained diffractograms were compared with the standards of the Joint Committee on Powder Diffraction Standards (JCPDS), with very good coincidences. The XRD characterization is summarized in Table 4.
Table 4. Standards used in the interpretation of diffractograms

| Powder     | TiO$_2$ | CaTiO$_3$ | SrTiO$_3$ | BaTiO$_3$ |
|------------|---------|-----------|-----------|-----------|
| JCPDS Catalog | 21-1272 | 22-153    | 35-0734   | 05-0626   |
| phase      | anatase | perovskite| perovskite| cubic     |
| Reference  | [11]    | [12]      | [13]      | [14]      |

3.2 Electronic spectra

The diffuse reflectance spectra of the semiconductors synthesized from a Cary 1G Spectrophotometer with tungsten lamp for the visible region and deuterium for the ultraviolet region were obtained. For the study of the energy gap of the semiconductors, the Kubelka-Munk function was applied for permissible direct transitions [15]. Table 5 reports the results and compare them with those in the recent literature.

Table 5. Gap energies of the obtained semiconductors

| Semiconductor | TiO$_2$ | CaTiO$_3$ | SrTiO$_3$ | BaTiO$_3$ |
|---------------|---------|-----------|-----------|-----------|
| Eg, eV exptal | 3.3     | 3.02      | 3.16      | 3.10      |
| Eg, Ev, cited | 3.28    | 3.05      | 3.18      | 3.0 a 3.2 |
| References    | [16]    | [17]      | [13]      | [18]      |

3.3 Calibration Curves

The following equations Conc(mg/L) = slope*Absorbance + intercept were obtained from the calibration curves.

Table 6. Calibration equations

| System       | slope | intercept | R$^2$ |
|--------------|-------|-----------|-------|
| TiO$_2$/ dye | 7.613 | -0.319    | 0.995 |
| CaTiO$_3$/ dye | 5.157 | +0.5698   | 0.991 |
| SrTiO$_3$/ dye | 5.330 | +0.5008   | 0.992 |
| BaTiO$_3$/ dye | 6.209 | +0.4236   | 0.994 |

3.4 Kinetic of discoloration

The photocatalytic activity was measured by the discoloration kinetics. After the initial solutions were prepared, samples were taken at different irradiation times and, after centrifugation, absorbance readings were taken at 590 nm of the clear liquids and each absorbance was converted to the residual concentration by applying the corresponding equation in Table 6.

All kinetic curves follow the order 1 reaction model, as expected if the reaction mechanism is Langmuir - Hinshelwood, as described by Batkhande et al. [19]. The equation of each kinetic curve is Conc (mg/L) = C$_o$ e$^{-kt}$. Note that the values of the initial concentrations C$_o$ are very similar to 8 mg/L, which is the concentration of the working solution.

Table 7. Kinetic equations for crystal violet discoloration. Conc(mg/L) = C$_o$ e$^{-kt}$.

| Photocatalyst | TiO$_2$ | CaTiO$_3$ | SrTiO$_3$ | BaTiO$_3$ |
|---------------|---------|-----------|-----------|-----------|
| C$_o$ value, ppm | 7.509   | 7.778     | 7.294     | 8.272     |
| k value, h$^{-1}$ | 0.868   | 0.460     | 0.817     | 0.116     |
| R$^2$          | 0.997   | 0.993     | 0.987     | 0.996     |
4. Analysis of the results

It is observed that titania with a value of $e^o$ in the upper limit of the valence band (corresponding to the oxidizing capacity) is +3.53 eV and the same value for the strontium titanate is +3.68 eV and both semiconductors give very similar rate constants of 0.870 and 0.817 h\(^{-1}\). Calcium titanate CaTiO\(_3\) has a minor positive potential of 2.96 eV and also a minor kinetic constant of 0.445 h\(^{-1}\). However, barium titanate BaTiO\(_3\), with a more positive potential of +3.99 eV, shows the lower speed counter, 0.115 h\(^{-1}\). Then the rate of the degradation reaction must be attributed to other factors, including the ability of the dye to be adsorbed on the solid, as expected in heterogeneous catalysis. The four materials studied showed an acceptable capacity, judging by the coloration that the solid acquires when reaching adsorption equilibrium. In the graph $k$ vs. $C_o$ shows that a linear relationship between the initial concentrations obtained from the reaction rate curve (figure 2) and the rate constant can be noted. The value of $C_o$ is related to the adsorption capacity of the solid. A high value, similar to the concentration of the working solution, indicates that practically all the colorant is in the solution and a lower one means that the solid is better absorbent. According to Figure 2, the two best adsorbents are titania and strontium titanate, which are the ones with the best values of the rate constant. It should also be noted that TiO\(_2\) does not belong to the possible linear relationship subtended by the titanates, perhaps because it was obtained as a microcrystalline powder.

Another factor that plays a very important role is the ability of the solid to remain suspended and this is a consequence of grain size and density, since a more "opaque" suspension allows a greater
probability of interaction of the granules with the photons. We found that TiO₂, CaTiO₃ and SrTiO₃ produced very opaque and very stable suspensions, while the BaTiO₃ granules were very large, very hard and very high density, so the suspensions were very clear during irradiation despite magnetic stirring and bubbling of air. As a consequence, the reaction rate turns out to be very low.

5. Concluding remarks

It was possible to establish a method of synthesis of calcium, strontium and barium titanates. In the synthesis of titania, the use of the ammonium hydroxide and the heat treatment led to the obtaining of the anatase phase. The X-ray powder diffractograms and the gap energy values obtained by the diffuse reflectance spectrophotometry validated the nature of the compounds obtained and their crystalline phase.

The photocatalytic activity was expected to be associated with the redox potential of the hole at the top of the valence band and proved true for titania and the titanates of calcium and strontium, but not for barium titanate. Attributed to the tendency to form macrocrystals that precipitate easily, leaving a clearer dispersion than the other photocatalysts.

In the working hypothesis, it was expected that the BaTiO₃ could be a better photocatalyst due to the high value of the potential of the conduction band and due to its higher density and crystallinity, but the experimental evidence shows that its properties as a solid acted against the efficiency in the capture of photons that, finally, is the origin of the photocatalytic capacity.

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