High efficiency decolorization of azo dye Reactive Black 5 by Ca-Al particles

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Abstract

This work studies the degradation of azo dye Reactive Black 5 by Ca-Al metallic particles prepared by melt-spinning and ball-milling. The morphology and the phase structure of the metallic powders were characterized and the decolorization efficiency of Reactive Black 5 solutions were assessed by monitoring the dye degradation by ultraviolet-visible absorption spectrophotometry. The decolorization process using the Ca-Al powders **showed fast kinetics** and high efficiency. 40 mg L⁻¹ dye solution was successfully decolorized in 1 min using 0.1 g / 100 mL of Ca₆₅Al₃₅ powder, suggesting it as an effective, low-cost **means** for degradation of azo-compounds.

Keywords: Ball milling; Rapid solidification; Reactive Black 5; Decolorization.

1. Introduction

Wastewater from textile industry is still a major water-treatment challenge in many countries[1,2]. New dyes are designed to better resist degradation of the color; thus demanding a continuous effort in research for developing new, cheaper and more efficient processes for wastewater treatment. One of the biggest family of textile dyes used nowadays is the so-called azo-dyes, which are characterized by the presence of one or more azo-bonds ($-N=N-$) acting as chromophores of the molecule. Many different chemical and biological approaches are employed for the removal of azo dyes [3]. Decolorization by solid particles is one of such methods, in which synthetic dyes are adsorbed onto a solid surface or degraded by a reaction generated by the material. Metal oxides, polymers, zeolites and zero-valent metals (ZVM) are promising materials because of rapid decolorization reactions and convenient operation in practical applications [4–6]. The use of solid materials facilitates the confinement of the particles during the treatment and, after the process, their removal can be easily done by simple physical separation methods.

In the case of metallic particles, the specific area and chemical properties of their surface are of crucial importance. The degradation reaction involves a redox process in which surface metal atoms lose electrons to cleave the bonds of the organic molecules [7,8]. For instance, the use of zero-valent iron (ZVI) particles is a well-known strategy applied to degradation of many different compounds [7,9]. Some recent advances have been focusing on improving the particles efficiency by means of two approaches. The first approach is the increase of specific surface area that can be achieved by the production of nano-sized particles of different types of metals [10,11]. The second approach is the production of micro-sized flakes or powders of metastable amorphous or nanocrystalline metallic phases in order to increase the reaction activity of the metals. Metallic metastable phases can be produced by rapid solidification techniques [12–14] thus increasing the efficiency of the decolorization process [15–17].

Large differences depending on the powder production method have been reported, with ball milled particles showing the highest reaction activity [16]. In particular, high-energy mechanical milling process was used to prepare fine powders with high surface area. Indeed, the high density of microstrain and lattice defects and the intrinsic brittleness of these milled powders facilitates their subdivision into fine particles. However, knowledge of the effect of milling conditions on microstructural and catalytic properties of alloys remains limited. Recently, a mechanically alloyed binary Mn-Al system [18] showed the modification of the catalytic properties favoured by composition and a decolorization efficiency of about 100 %. One of the elements was found more reactive in the reduction process in aqueous media. These interesting results promoted us to explore the Ca-Al system, as a low-cost, new adsorbent for the removal of azo-dyes. As the redox potentials are -2,76 and 1,18 for Ca and Mn^{2+}/Mn respectively Ca is chosen here as a substitute for the Mn in order to observe whether this factor favors dye degradation.

The degradation of the azo dye Reactive Black 5 (RB5) has been studied by several methods [19-21], being used as a representative compound to assess the efficiency of decolorization methods of azo-dyes. In this work we report the production method of $\text{Ca}_{65}\text{Al}_{35}$ particles prepared by melt-spinning and subsequent ball-milling, and their potential as a catalyst material to degrade RB5 aqueous solutions.

2. Experimental procedure

Alloy ingots of $\text{Ca}_{65}\text{Al}_{35}$ (at%) were prepared by arc melting (MAM1 Edmund Bühler device) using pure Ca (99.9 wt%) and Al (99.99 wt%) under a Ti-gettered argon atmosphere. The ingots were melted by induction (Melt Spinner SC Edmund Bühler device) and injected through a 0.8 mm nozzle on a spinning copper wheel obtaining rapidly quenched ribbons with a thickness of 40 μm . The ribbon (flakes) samples were then put into a high energy planetary ball mill (Fritsch pulverisette 7) with a rotation speed of 600 rpm. Both the 5 balls

with 12 mm diameter and the vial are made of tempered chromium steel. The balls to ribbons weight ratio was 5:4. The ribbon flakes were introduced and milled under argon atmosphere to avoid oxidation process. A time of 5 min waiting interval was applied after each 10 min to avoid sample heating and powder agglomeration. The total milling time was 3 hours.

The morphology and structure of the Ca-Al powder were examined using a scanning electron microscope (SEM) equipped with a Vega[®] Tescan energy dispersive X-ray (EDX) analyzer and an X-ray diffraction (XRD) on a Siemens D500 using CuK_α radiation. The size distribution of the particles was obtained from the SEM images by Image J software analysis, erode and despeckle algorithms were applied to isolate the particle images from the background and the remaining touching particles were removed manually prior to the calculation of the size distribution. The crystalline structure and crystallographic parameters of the Ca-Al alloys were estimated through the Rietveld refinement of XRD patterns using the MAUD program based on the Rietveld method. The specific surface area of the Ca-Al powder was determined using the N₂ adsorption/desorption analysis according to the Brunauer-Emmett-Teller (BET) conducted at 77 K on a Nova 4200e model surface area analyzer (Quantachrome Instrument Corporation).

Aqueous solutions of RB5 with concentrations of 40 mg L⁻¹ were used to evaluate the decolorization reaction. Degradation experiments were performed with 0.01, 0.05 and 0.1 g of ball milled (BM) powders added into 100 mL of the dye solution and continuously agitated. Samples were drawn out at regular time intervals and centrifuged at 3000 rpm for 15 min in a Rotanta 460r centrifuge. The supernatants were separated and the absorbance between 200 and 800 nm was measured by spectrophotometry (Shimadzu 2600 UV-visible). The powder collected after degradation was analyzed using Fourier transform infrared spectroscopy (FTIR) spectrum to determine the presence of functional groups in the extract. The pellets were prepared in each case with the same quantity of ground sample in KBr and

the spectra were normalized for comparison between different samples. Semi quantitative elemental composition was analyzed by EDX.

The degradation process of RB5 and the qualitative analysis of the aromatic by-products were investigated by high performance liquid chromatography (HPLC) coupled with tandem mass spectrometry (LC-MS/MS). The HPLC analyses were carried out using a Beckman Gold chromatograph fitted with a Proshell 120 Phenyl Hexyl (4.6 x 150 mm x 2.7 μm) column at room temperature. The determination of the extent of dye abatement was conducted isocratically with the detector selector at $\lambda = 597\text{ nm}$ using a 90:10 (v/v) aqueous solution of ammonium acetate/methanol mixture as the mobile phase. A flow rate of 0.5 $\text{cm}^3\text{ min}^{-1}$ and injection volume of 0.2 cm^3 was always used.

3. Results and discussion

Figure 1 (a, b) shows the micrographs of the $\text{Ca}_{65}\text{Al}_{35}$ as-produced powders. The particles surface is characterized by flows and corrugations; a closer inspection reveals that larger particles are aggregations of roundish finer particles. The production method is therefore able to generate a large surface area. Figure 1c shows the size-distributions calculated from the SEM images. The mean particle size, d , and the standard deviation, σ , of the distribution of the as-produced powders are $d=16.3\text{ }\mu\text{m}$ and $\sigma=6.6\text{ }\mu\text{m}$. The EDX analysis shown in Figure 1d confirmed that the expected elemental composition of Ca and Al was approximately equals to 65:35.

Figure 2 (a, b) shows the UV-Vis spectrum evolution of dye aqueous solutions for different particle-weight/solution-volume ratios (0.01, 0.05, and 0.1 g / 100 mL) of $\text{Ca}_{65}\text{Al}_{35}$ particles. Before the treatment the maximum of absorbance located at $\lambda_{\text{max}}=597\text{ nm}$ in the visible region arises from the -N=N- azo bond. The decolorization process is extremely fast in all cases, although it saturates if the amount of added particles is less than 0.05 g / 100 mL. The UV-Vis spectrum evolution of dye aqueous solutions after the addition of 0.1 g / 100 mL

of Ca-Al particles reveals a fast and complete decolorization as shown in Figure 2c. The absorbance at 597 nm decays into nearly zero after 1 min and the solution becomes fully transparent. The other two peaks at 230 and 310 nm are ascribed to the benzene and naphthalene rings of the dye [7]. The changes in the absorbance reflect the evolution of the RB5 chromophores, the peak at $\lambda_{\max}$ becomes weaker, indicating cleavage of the azo bonds, formation of -NH₂ groups and decomposition of RB5. This is confirmed by the rapid increase of the peak at 246 nm. These results are in agreement with those observed by Zhang et al. [19] using amorphous zero-valent iron and Ben Mbarek et al. [18] using Mn-Al particles as decolorizing material for RB5 aqueous solutions. Figure 2d presents the images of RB5 solutions before and after being processed.

The evolution of the decolorization efficiency (%) during the process was calculated using Eq. 1 as follows:

$$(C_0 - C_t) / C_0 \times 100 \quad (1)$$

where C_t is the dye concentration at time t and C_0 the initial concentration. The effect of Ca₆₅Al₃₅ particles dosage on RB5 removal was investigated in the range 0.01-0.1 g / 100 mL keeping constant the temperature (25°C) and the initial dye concentration (40 mg L⁻¹). Figure 3 shows that by increasing the Ca-Al dosage from 0.01 to 0.1g / 100 mL, the dye removal percentage increased from 25 % to 100 %. In addition, more calcium content is available for oxidation and hence, more hydrogen is produced to hydrogenate the azo bonds of RB5.

A survey of the results found in literature show that the decolorization of azo dyes by ZVI is much less efficient and slower [5], even when aided by reduction of pH, increase of temperature, photo-oxidation or other complementary treatments [8]. Rahmani et al. [20] obtained a reaction time of $t = 30$ min and final decolorization 60% using 0.3 g / 150 mL of ZVI particles in 50 mg L⁻¹ RB5 aqueous solution. Chompuchan et al. [21] reported $k^{-1} > 100$ min when adding 0.25g / 100 mL of nanoscale ZVI in 100 mg L⁻¹ RB5 solution. Considering

the initial dye concentration and the quantity of powder per volume, the decolorization process observed for $\text{Ca}_{65}\text{Al}_{35}$ is more efficient and rapid than any other reported in the cited works.

Figure 4 (a,b) shows the surface morphology of the ball milled powder after the reaction. After the degradation process the surface become smooth and flower-like products cover the whole surface compactly. Similar morphologies were found covering the surface after the reaction in Fe-based [16], $\text{Mg}_{73}\text{Zn}_{21.5}\text{Ca}_{5.5}$ [17] and $\text{Mg}_{65}\text{Cu}_{25}\text{Y}_{10}$ [22] metallic glass particles or ribbons. After the reaction, the size distributions of the $\text{Ca}_{65}\text{Al}_{35}$ alloy (Figure 4c) shifted towards higher values, $d=31.9\text{ }\mu\text{m}$ and $\sigma=11.7\text{ }\mu\text{m}$, due to the effect of the precipitates growing on the particles surface. The EDX analysis shown in Figure 4d indicates the ratio of Ca to Al and O was approximately equal to 34.3:16.8:49.0. The intense peak for oxygen confirming that the needle-like products consist of crystalline oxide and hydroxide precipitates.

One important factor linked to reactivity is the specific surface area. To understand the high reaction efficiency of the Ca-Al powder, the specific surface area was measured by the Brunauer-Emmett-Teller (BET) method. The specific surface area measured was $15.16\pm 0.31\text{ m}^2\text{ g}^{-1}$. This value makes Ca-Al powder promising candidates for degradation of azo dyes by comparison with typical values ranging between 0.343 to $16.62\text{ m}^2\text{ g}^{-1}$ given in the literature [16-18, 22, 23]. Thus, mechanical alloying also improves the specific surface area of the powder mixture due to the introduction of corrugations or porous-like structures at the nanoscale. The high surface area provides abundant active sites for the adsorption and degradation of RB5 dye.

Likewise, microstructure (nanocrystalline size and density of defects) can also improve the reactivity [18]. The phase structures of all the Ca-Al samples before and after degradation reaction were evaluated by XRD technique. Figure 5a shows the XRD patterns of the melt-

spun ribbons and figure 5 (b) of the as-produced powders after the ball-milling process. The $\text{Ca}_{65}\text{Al}_{35}$ ribbons show the characteristic amorphous halo, with weak crystalline peaks that could not be attributed to any known Ca-Al intermetallic phase in equilibrium according to the phase diagram Al-Ca. Different batches of ribbons showed different degree of amorphicity, indicating that the glass-forming ability of this composition is very low. Few prominent crystalline reflections can be observed in the XRD spectrum of the as-produced powder; therefore, the energy introduced by the ball-milling process triggers the crystallization of the metallic glass. This crystalline phase is obtained through devitrification during the milling process. The XRD patterns of the ribbons milled for 3 h revealed the presence of one metastable tetragonal Ca-Al phase with $a=b=3.0929\pm0.0004$ Å, $c=8.2472\pm0.0006$ Å lattice parameters. Furthermore, the inner-particle crystalline size is nanometric, 49 ± 2 nm, and the microstrain is $1.5\pm0.1\%$. Thence, the high-energy mechanical treatment can considerably improve the reactivity of the alloy by achieving a high specific surface area coupled with a nanocrystalline structure with the consequent high level of grain boundaries, microstrain and crystallographic defects.

Figure 5c also shows the XRD patterns of the powders after the decolorization process. New crystalline reflections appear in addition to the ones associated to the metastable Ca-Al phase, which come from the hydroxides covering the particles surface as it was clearly suggested by microanalysis. These reflections can be identified as a $\text{Ca}(\text{OH})_2$ phase with space group P-3m1 and $\text{Al}(\text{OH})_3$ phase with space group P-21/a.

Figure 6a shows the FT-IR spectrum of RB5 dye powder before decolorization. In this figure we can see peaks at $3500\text{--}3700\text{ cm}^{-1}$ (--NH stretch), $2888\text{--}2968\text{ cm}^{-1}$ (CH_2), $1626\text{--}1748\text{ cm}^{-1}$ ($\text{C}=\text{C}$ stretch), $1387\text{--}1635\text{ cm}^{-1}$ (N--H bending), $1078\text{--}1256\text{ cm}^{-1}$ (O--C), the band around 1145 cm^{-1} could be sulphonic groups (--SO_3), and finally at $1011\text{--}1078\text{ cm}^{-1}$ (alkenes). The most representative peak of azo dye is about 1495 cm^{-1} which corresponds (N

=N stretch). FTIR spectrum of the residual organics products on the surface of Ca₆₅Al₃₅ powder after degradation process is shown in figure 6b. Comparatively, the peak of -NH stretch is increased and the peak at 3000–3500 cm⁻¹ is more pronounced and broad because of O—H stretch. The vibration range from 2750 to 3000 cm⁻¹ (possible C—H stretch aliphatic) disappeared. The peaks from 800 to 1500 cm⁻¹ decreased and the appearance of new peaks around 1400 cm⁻¹ (C—C Aryl) and at 850 cm⁻¹ (C—N Aryl) are observed. The peak at 1495 cm⁻¹ (N=N stretch) is gone after the degradation process. Summarizing, the peaks observed after degradation were for N—H, O—H, C—H, C—C and C—N clearly indicating the formation of primary amines as a result of the reductive cleavage of the azo bond (-N=N-) and confirming the above mentioned UV-Vis results (see Figure 2). Similar results have been obtained by Yang et al. [24] studying the decolorization ability of zero-valent iron (ZVI) as well as Ben Mbarek et al. [18] and Mendez et al. [25] studying the degradation of the RB5 solution using BM Mn-Al alloys and nickel electrodes in divided and undivided cells, respectively.

Degradation of the RB5 dye was further confirmed by HPCL. Figure 7a shows the chromatogram of the dye in solution before degradation with a broad peak eluting at 2.9 min and Figure 7b shows the mass spectrum of the same peak. The mass spectrum complexity comes from the hydrolysis of sulphated azo dye (RB5, M.W=903). The information on the structures was obtained from the detected negative ions in the spectrum: [M-2H+Na]⁻, [M-2H-SO₃+Na]⁻, [M-H-SO₃]⁻, [M-2H-SO₃]⁻, [M-H-SO₃-H₂SO₄]⁻, [M-H-2H₂SO₄]⁻, [M-H-SO₂-SO₃-H₂SO₄]⁻, [M-3H-SO₃+Na]⁻ and more monovalent ions from the hydrolysis process and divalent ions [26]. Figure 8a represents the HPLC elution profile of RB5 reacted with Ca-Al alloy for 20 min. It can be seen that instead of the peak of the parent dye a new peak was found eluting at 2.7 min, thereby suggesting the transformation of the dye. Figure 8b shows the mass spectrum of the product peak eluting at 2.7 min. The peaks could be ascribed to

aromatic amines end products as 1-2-7-triamino-8-hydroxy-3-6-naphthalenedisulphonate (MW=349), 1-sulphonic,2-(4-aminobenzenesulphonyl)-ethanol (M.W.=281) and 1-sulphonic,2-(4-hydroxibenzenesulphonyl)-ethanol (M.W.=282) and also to derivative products as a consequence of substitution or interaction reactions with the aqueous medium.

The appearance of bubbles inside the solution suggests the formation of hydrogen gas as a direct reaction product of the redox process. Based on this fact, the mechanism of the dye degradation proposed is driven by the release of H_2 from the reduction of water, the posterior cleavage of $-N=N-$ bonds and, finally, the formation of $-NH_2$ groups. The enrichment in OH^- ions as result of the reduction process of water leads to an increase of the pH value in the dye solution. According to the measurement, the pH value increases from initial 6.3 to about 9.8 after the degradation by the Ca-Al powder. In these pH conditions, precipitate of calcium hydroxide is formed and the passivation of aluminum takes place. However, the initial reactivity of calcium to form calcium ions, Ca^{2+} , leads the process of formation of hydrogen gas and the subsequent hydrogenation and rupture of the azo groups. The existence of the aluminum corrosion was assumed from oxygen detected by EDX (Fig 4) and the formation of $Al(OH)_3$ and $Ca(OH)_2$ by XRD analysis (Fig. 5).

The reduction reactions caused by zero-valent metallic particles are characterized by a reaction rate proportional to the surface area [7]. Here, a reduction of the amount of particles (less initial calcium available on the surface of the alloy) results in a decrease of the final decolorization but the kinetics remains always extremely fast. This indicates the process is related to the reactivity in water of intermetallic phases forming the Ca-Al powders, producing the degradation of the dye molecule at the same time that covers the particles surface with calcium hydroxide precipitates. The final decolorization efficiency is then limited by the surface area but the reaction rate is controlled by the high chemical activity in water.

The reactivity of metals in environmental remediation applications is attributed to the porosity of the oxide layers formed in contact with the aqueous medium. For instance, the long term activity of ZVI is basically due to the non-protective oxide scales formed during iron corrosion [27]. In other words, the remediation ability of metallic particles is favored if corrosion is persistent and can progress through the bulk material. Pure aluminum particles do not show remediation ability, as it is well-known that aluminum generates a homogeneous protective alumina layer [28]. However, in the case of Mn-Al particles Ben Mbarek et al. [18] proposed that the colorant degradation reaction was driven by the initial release of electrons by both Al and Mn atoms. In that article, the oxidation process of the Mn atoms and their subsequent dissolution in the aqueous medium caused pitting on the exposed aluminum oxide film favoring the subsequent oxidation process. A similar mechanism is expected in Ca-Al particles, the progressive dissolution of the Ca ions in the water generates pitting in the surface of aluminum oxide favoring the corrosion process. It suggests that both Al and Ca are contributing to the degradation reaction. Both hydroxide are very insoluble and precipitate in the surface of $Ca_{65}Al_{35}$ particles. The mechanism can be written as:

The reductive character of both Ca and Al and the instantaneous release of hydrogen gas bubbles justify the proposed mechanism described in equations 2, 3 and 4. The formation of hydroxyl ions from water is manifested by the increase in pH above 7 (initial pH 5.6),

although this pH could be attributed to the presence of amino groups. However, the formation of insoluble calcium and aluminum hydroxides (eq. 5 and 6) is corroborated by SEM micrographs (flower-like products on the surface), by the results of EDX (oxygen content, figure 4), as well as by the XRD results (formation of hydroxides, Figure 5) or FT-IR (with an increase of the peak between $3000\text{--}3500\text{ cm}^{-1}$) typical of the O-H bond (Figure 6).

The results obtained in this work indicate that the Ca-Al powders are efficient reducing agents like RB5, in neutral pH conditions this material is more suitable than other materials for the degradation of RB5 solution. This has a practical significance because there would be no need to add any acid into the actual industrial textile wastewater before the treatment. A schematic view of the proposed degradation mechanism of RB5 using Ca-Al system is given in figure 9.

The decolorization process using Ca-Al BM powders show, basically, the same advantages as other metallic particles; easy application and easy particle removal by simple physical separation methods. Furthermore, $\text{Ca}_{65}\text{Al}_{35}$ particles have low cost, relatively simple preparation and they are expected to be completely harmless both for health and environment.

4. Conclusions

$\text{Ca}_{65}\text{Al}_{35}$ powders were successfully fabricated by melt spinning and **ulterior** ball milling. Its efficiency to degrade organic chemicals was investigated by evaluating the decolorization process of RB5 aqueous solutions. The ball milled powder exhibited excellent degradation efficiency and high reaction rates: Dye removal of more than 90 % of 40 mg L^{-1} dye solutions in less than one minute. This high efficiency is associated to the large surface area and the particles chemical activity, which suggests these materials may be used as a low-cost, high-performance decolorizing method for textile wastewater pre-treatments. A chemical

mechanism in aqueous basic medium is proposed, the mechanism is based on the reducing power of Ca.

Acknowledgements

Work funded by MINECO grant FIS2014-54734-P and Generalitat de Catalunya grant 2014SGR00581. Financial support from MPCUdG2016/045 project is also acknowledged.

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Figure Captions

Figure 1.(a and b) Particles morphology of the of $\text{Ca}_{65}\text{Al}_{35}$ particles before the decolorization process.(c) Distribution of particle sizes of the ball milled powders.(d) The nominal compositions as examined by EDX.

Figure 2.(a-c) The changes of UV absorption spectra along with the treatment $\text{Ca}_{65}\text{Al}_{35}$ particles at 25°C for different dosage of powder.(d) Image of black 5 solutions processed by $\text{Ca}_{65}\text{Al}_{35}$ powder before and after degradation times up to 20 min.

Figure 3. Kinetics of decolorization of RB5 dyed water using different particle-weight/solution-volume ratios of BM $\text{Ca}_{65}\text{Al}_{35}$ powder: 0.01 g/100 mL, 0.05 g/mL and 0.1g/100 mL of particles in 40 mg L^{-1} RB5 aqueous solution.

Figure 4. (a and b) Particle morphologies of the of $\text{Ca}_{65}\text{Al}_{35}$ particles after the decolorization process. (c) Distribution of particle sizes of the ball milled powders. (d) Nominal compositions as examined by EDX.

Figure 5. (a) XRD patterns of the $\text{Ca}_{65}\text{Al}_{35}$ ribbons. (b) XRD patterns of the ribbon milled before and (c) after the degradation of RB5.

Figure 6. (a) FTIR spectra of RB5 powder before degradation reaction and (b) FTIR spectra of $\text{Ca}_{65}\text{Al}_{35}$ powder after degradation of RB5.

Figure 7.(a) HPLC elution profile of the native RB5 dye and (b) mass spectra of the peak from 2.9 min at $\lambda = 597$ nm.

Figure 8. (a) HPLC elution profiles after degradation of the RB5 dye and (b) mass spectra of peaks from 2.7 min.

Figure 9. A schematic view of the proposed degradation mechanism of RB5 using $\text{Ca}_{65}\text{Al}_{35}$ compound.

Figure 1. (a, b) Particles morphology of the $\text{Ca}_{65}\text{Al}_{35}$ particles before the decolorization process. (c) Distribution of particle sizes of the ball milled powders. (d) Chemical composition as examined by EDX.

Figure 2.(a-c) The changes of UV absorption spectra along the treatment with $\text{Ca}_{65}\text{Al}_{35}$ particles at 25°C for different dosages of powder. (d) Image of Reactive Black 5 solutions processed by $\text{Ca}_{65}\text{Al}_{35}$ powder before and after degradation times up to 20 min.

Figure 3. Kinetics of decolorization of RB5 dyed water using different particle-weight/solution-volume ratios of $\text{BM Ca}_{65}\text{Al}_{35}$ powder: 0.01 g/100 mL, 0.05 g/mL and 0.1g/100 mL of particles in 40 mg L^{-1} RB5 aqueous solution.

Figure 4. (a and b) Particle morphologies of the of $\text{Ca}_{65}\text{Al}_{35}$ powder after the decolorization process. (c) Distribution of particle sizes of the ball milled powders. (d) The chemical composition as examined by EDX.

Figure 5. (a) The XRD patterns of the $\text{Ca}_{65}\text{Al}_{35}$ melt-spun ribbon. The Rietveld refinements of XRD patterns of the ribbon milled before (b) and after (c) the degradation of Reactive Black 5.

Figure 6. (a) FTIR spectra of RB5 powder before degradation reaction and (b) FTIR spectra of Ca₆₅Al₃₅ powder after degradation of reactive black 5.

Figure 7. HPLC elution profile of the native black 5 dye and mass spectrums of the peak from (a) 2.9 min at (b) $\lambda = 597$ nm.

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