Photocatalytic degradation of methyl orange, methylene blue and rhodamine B with AgCl nanocatalyst synthesised from its bulk material in the ionic liquid [P_6 6 14]Cl

Borja Rodríguez-Cabo, Iago Rodríguez-Palmeiro, Raquel Corchero, Rosario Rodil, Eva Rodil, Alberto Arce and Ana Soto

**ABSTRACT**

The photocatalytic degradation of wastewater containing three industrial dyes belonging to different families, methyl orange (MO), methylene blue (MB) and Rhodamine B (RhB), was studied under UV-Vis irradiation using synthesised silver chloride nanoparticles. The nanocatalyst was prepared by a dissolution/reprecipitation method starting from the bulk powder and the ionic liquid trihexyl(tetradecyl)phosphonium chloride, [P_6 6 14]Cl, without addition of other solvents. The obtained catalyst was characterised by UV-Vis absorbance, X-ray powder diffraction, transmission electron microscopy and scanning electron microscopy. The decolourisation of the samples was studied by UV-Vis absorbance at the corresponding wavelength. Starting from 10 ppm dye solutions and 1 g L\(^{-1}\) of the synthesised AgCl nanoparticles, degradation efficiencies of 98.4% for MO, 98.6% for MB and 99.9% for RhB, were achieved in 1 h. The degradation mechanisms for the different dyes were studied. Comparison with other frequently used nanocatalysts, namely P-25 Degussa, TiO\(_2\) anatase, Ag and ZnO, highlights the strong catalytic activity of AgCl nanoparticles. Under the same experimental conditions, these nanoparticles led to higher (more than 10%) and faster degradations.

*Key words* | dyes, industrial wastewater, ionic liquid, nanocatalyst, photodegradation

**ABBREVIATIONS**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>LC</td>
<td>Liquid chromatography</td>
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<tr>
<td>MB</td>
<td>Methylene blue</td>
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<td>MO</td>
<td>Methyl orange</td>
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<td>MS</td>
<td>Mass spectrometry</td>
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<td>Q</td>
<td>Quadrupole</td>
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<td>RHB</td>
<td>Rhodamine B</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
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<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
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<tr>
<td>TOF</td>
<td>Time-of-flight</td>
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<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<tr>
<td>Vis</td>
<td>Visible</td>
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<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
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<tr>
<td>XRD</td>
<td>X-ray powder diffraction</td>
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**INTRODUCTION**

Synthetic dyes are being used in many different industries nowadays, mainly textiles, paper, plastics, leather tanneries, food technology and cosmetic industries. This sector produces large amounts of liquid waste that contain organic and inorganic compounds. Annually, more than 10,000 tons of dyes are utilised and approximately 100 tons of dyes are released into water streams (Ashrafi et al. 2017). Synthetic dyes can cause serious environmental and health problems, and the large-scale production and extensive application aggravates this complex situation (Shore 1996; Robinson et al. 2001). This scenario of pollution implies the necessity of finding technological solutions to solve the problem.

Thus, different techniques have been studied to degrade or eliminate these synthetic compounds, such as adsorption, photocatalytic degradation, biological treatments, sedimentation, coagulation/flocculation, Fenton systems (Utset et al. 2000; Moghaddam et al. 2010; Apostol et al. 2012; Zavastin et al. 2012; Madhusudan et al. 2013), etc. Degradation of dyes by using UV or sunlight and a catalyst for...
their oxidation has been gaining attention in recent years (Kansal et al. 2007; Poureetal et al. 2009; Safavi et al. 2012; Chen et al. 2013; Kumar et al. 2013; Jiang et al. 2014; Peng et al. 2014; Allaedini et al. 2015; Huang et al. 2015). A wide variety of nanocatalysts have been used for that purpose. For instance, Kansal et al. (2007) tested, under different conditions, the use of TiO2, ZnO, SnO2, ZnS and CdS combined with UV or solar light for the degradation of methyl orange (MO) and Rhodamine 6G. Meanwhile, Kumar et al. (2015) used silver nanoparticles obtained from a biological source to degrade the azo dye MO, and Chen et al. (2013) investigated the influence of the morphology of TiO2 nanomaterials in the degradation of Rhodamine B (RhB) (a xanthene dye). Although there are lots of works presenting different types of nanocatalysts, the use of pure silver halides is not deeply explored, and, as far as we know, only a few research works use the sole silver halide (Jiang et al. 2014; Cui et al. 2015; Rodríguez-Cabo et al. 2015). Most of the papers refer to composites and/or a combination of silver halide with silver (Kim et al. 2010; Wang et al. 2011a; Sohrabnezhad & Pourahmad 2012; Daupor & Wongnawa 2014; Sohrabnezhad et al. 2014). For instance, Shu et al. (2014) worked with an AgCl@Ag hybrid photocatalyst for the degradation of MO, methylene blue (MB), RhB and 4-Nitrophenol. Wang et al. (Wang et al. 2008; Wang et al. 2009a; Wang et al. 2011b) used different silver/silver halide composites (Ag@AgCl,Br and Ag@AgCl-AgI) as catalysts to study the photodegradation of MO, isopropyl alcohol and the photoreduction of CrVI.

Nanocatalysts are numerous and the methods used for their synthesis are very different. In recent years, ionic liquids (ILs) are acquiring an important role as solvents which can be used to obtain materials at the nanoscale (Antonietti et al. 2004; Scholten et al. 2012; Duan et al. 2014). As it is well known, ILs are salts that have melting points or glass-transition temperatures below 100 °C. They typically exhibit properties such as extremely low vapour pressures, wide liquid ranges, ability to dissolve a broad variety of compounds, and considerably good thermal and chemical stabilities. Moreover, a judicious selection of cation and anion allows the obtaining of ILs for a specific task. Thus, some studies can also be found in literature related to the synthesis of photocatalysts by using ILs (Xu et al. 2011; Rodríguez-Cabo et al. 2015). Xu et al. (2011) studied the ability of the common Ag/AgCl composite structure to photodegrade a MO solution. For the synthesis of the catalysts, the authors used the IL 1-octyl-3-methylimidazolium chloride not only as a Cl source but as the reducing reagent of AgO.

In our previous work (Rodríguez-Cabo et al. 2015), a silver chloride nanocatalyst was synthesised using a phosphonium-based IL, and tested for the degradation of Orange II with UV light. AgCl was selected as photocatalyst to benefit from the synergy of the use of a simple, green and effective method for the synthesis of the nanocatalyst and its high photocatalytic activity for dye degradation. In that preceding paper (Rodríguez-Cabo et al. 2015), it was shown that the catalyst is maintained as AgCl after the photocatalytic degradation and no conversion to Ag0 occurred due to the absence of reducing agents, and this was verified by X-ray photoelectron spectroscopy (XPS) measurements after the end of the photodegradation cycles. It was found that, in optimal conditions, a total degradation of the dye can be reached. However, there is a huge diversity of dyes with different structures and they have higher or lower tolerance to different degradation systems. Dyes are normally classified according to their chromophores. The most common dyes are those containing an azo group (like Orange II or MO, amongst others). Nevertheless, the most studied dyes are the thiazine-based ones (mostly represented by MB), and xanthenes (with a dominance of RhB in publications) (Rochkind et al. 2015). Moreover, in many real industrial effluents, different dyes are mixed and dispose of together.

With the aim of ensuring the efficacy of the proposed photodegradation system not only for a specific dye (Orange II) but also for other industrial dyes of very different families, the degradation of MO azo dye, MB thiazine dye and RhB xanthene dye was carried out. The nanoparticles were obtained according to a previously published method (Rodríguez-Cabo et al. 2022a, 2022b) using only the bulk powder and an IL, trihexyl(tetradecyl)phosphonium chloride [P6 6 6 14]Cl. This quick and easy method, used for the synthesis of the catalyst, avoids air pollution issues, since no volatile solvents are required. To compare the photocatalytic activity of AgCl nanoparticles with other commercial nanoparticles commonly used, the degradation of the three different dyes was evaluated at room temperature by studying the evolution of the UV-Vis absorbance spectra of the degraded samples over time. Synthesised AgCl and commercial AgCl, Ag, ZnO, TiO2 and P-25 Degussa nanoparticles were tested as catalysts. In the case of AgCl nanoparticles, the different decomposition mechanisms are studied and the kinetics of the processes was also obtained. Finally, the photodegradation of a mixture of dyes is performed, comparing the results with the ones obtained for each of the individual dyes.
EXPERIMENTAL

Materials and equipment

Silver chloride (99%), toluene (≥99.5%), acetone (≥99.5%), titanium (IV) oxide (99.7% anatase, nanopowder), zinc oxide (≥97%, nanopowder), silver (99.5%, nanopowder) and %), titanium (IV) oxide (>99.5% P25 degussa, nanopowder), MO (85%), MB (>97%) and RhB (95%) were acquired from Sigma-Aldrich. Figure 1 shows the structure of the studied dyes. Ethanol was purchased from Panreac with a purity of 99.8%. The IL trihexyl(tetradecyl)phosphonium chloride, [P6661 4 ]Cl, was obtained from CYTEC under the commercial name CYPHOS IL 101 (97.7%). 1H and 13C NMR analysis were used to check its purity. The IL was dried under high vacuum (10⁻⁵ atm) at 70°C for 24 h prior to use. Its water content was measured (<2,000 ppm) by a titration method (Metrohm 737 Karl-Fischer coulometer) and then stored under inert atmosphere.

With the aim of characterising the formed catalyst, to confirm the structure of the as-prepared nanomaterial and to ensure that no transformation took place during the synthesis and precipitation processes, a Philips X-ray powder diffractometer with Cu anode radiation (XRD) was used. The size and shape of the nanoparticles were studied by means of a Philips CM-12 transmission electron microscope (TEM). A Zeiss Fesem Ultra Plus scanning electron microscope (SEM) was also used to analyse the solid agglomerates with the aim of characterising the surface of the nanoparticles. For the determination of possible compositional changes in the catalyst after usage, an X-ray photoelectron spectroscope was used, specifically a Thermo Scientific K-Alpha ESCA instrument equipped with aluminium Kα monochromatised radiation at 1486.6 eV X-ray source. Surface elemental composition was determined using the standard Scofield photoemission cross sections.

The ultraviolet-visible (UV-Vis) absorbance characterisation of the nanocatalyst and the measurement of the decrease in absorbancy of the dye solutions were performed in an Agilent 8543 UV-Vis absorption spectrophotometer. The UV source used for the photodegradation was a RZB lamp (UV-A, λ = 320–400 nm, 8 W), with length 590 mm and diameter 26 mm. Final degradation products were analysed by liquid chromatography-quadrupole-time-of-flight-mass spectrometry (LC-Q-TOF-MS). The LC system was an Agilent 1,200 Series liquid chromatographic system (Agilent Technologies) consisting of a membrane degasser, a binary high-pressure gradient pump, a thermostated LC column compartment and an autosampler. Separation was carried out on an Ascentis express C18 column (5 cm × 2.1 mm; 2.7 μm particle size) (Supelco). This system is interfaced to a Q-TOF mass spectrometry instrument (Agilent 6520 Series, Agilent Technologies) equipped with a Dual electrospray ion source.

Figure 1 | Structure of the studied dyes. From left to right: methyl orange (MO), methylene blue (MB) and Rhodamine B (RhB).
Experimental procedure

Silver chloride nanoparticles were prepared by a very quick and promising method previously developed by our group (Rodríguez-Cabo et al. 2022a, 2022b). Bulk silver chloride (1 g) was added into 9 g of the IL [P6,6,6,14]Cl to achieve a concentration of 10% w/w. The mixture was stirred in a round-bottom flask and heated up at 120 °C for 2 h, until complete dissolution of the solid. UV-Vis absorbance study was carried out to confirm the existence of the silver chloride nanoparticles in the IL and to study their optical properties. An aliquot (25 μL) taken from the nanodispersion was dissolved in toluene (1 mL). The blank consisted in the same volume of pure IL (25 μL) also dispersed in toluene (1 mL). The band gap (Eg) of the nanodispersions of AgCl was computed by means of the visible spectral results and the equation of Tauc (Tauc & Menth 1972; Chakraborty et al. 2005),

\[(ehv)^2 = C(hv - E_g)^m \]  

(1)

where \(e\), \(h\), \(v\), \(C\), and \(E_g\) are: the molar extinction coefficient, Planck’s constant, frequency of light, an arbitrary constant, and band gap of the size quantised particle, respectively. When \(m = 1/2\), \(E_g\) in Equation (1) denotes the allowed direct band gap; for higher multiples of \(1/2\) it leads to forbidden and indirect band gaps. The linear parts of the plots of \((ehv)^2\) against \(hν\) were considered for the evaluation of \(E_g\). Nonlinearity in the higher wavelength region arose from indirect transitions and polydispersity in particle dimension (Ghobadi 2013; Majumder et al. 2014).

TEM was used to investigate the size and shape of the nanoparticles in the dispersion. With this aim, another aliquot (25 μL) of the solution dissolved in toluene (5 mL) was added on a copper grid covered with Formvar, manually shaken and left to evaporate overnight, and several micrographs from different parts of the grid were collected.

Then, the nanoparticles were precipitated from the IL phase following the procedure explained in our previous work (Rodríguez-Cabo et al. 2023). Ethanol was added to cause the precipitation of the nanoparticles, keeping the sample in the dark. Thus, the liquid phase (containing the IL) was removed by centrifugation and the large amount of precipitated AgCl nanoparticles were washed three times with acetone. Finally, they were left to dry in an oven overnight at a moderate temperature. XRD and SEM were used to corroborate the structure, size and morphology, respectively, of the precipitated nanoparticles.

In order to be able to quantify the decolouration of the samples with dyes, concentration calibrations were obtained for each dye by studying the UV-Vis absorbance spectra of the solutions. 10 ppm dye solutions were prepared in distilled water. The tested nanoparticles (synthesised AgCl and commercial Ag, ZnO, TiO2 and P-25 Degussa) were added to 5 mL of these solutions to obtain a concentration of 1 g L\(^{-1}\). The samples were stirred at room temperature for 30 min in the dark, in order to reach the adsorption-desorption equilibrium, and for 60 min under UV radiation using a UV-A lamp. Afterwards, with the aim of separating the catalyst, the samples were centrifuged in the dark for 10 min at 4,000 rpm (in the case of P-25 Degussa 20 minutes at 14,000 rpm were required) and the supernatant was collected and analysed by UV-Vis absorbance. The operational parameters (catalyst amount, 1 g L\(^{-1}\); concentration of dyes, 10 ppm; reaction time, 60 min; and natural pH, 5.85) were defined according to a previous study (Rodríguez-Cabo et al. 2025), where the AgCl nanoparticles were used to photodegrade Orange II. With the aim of ensuring repeatable results, all the experiments carried out in this section were performed at least twice, recording the average value. The wavelengths used were 464, 664 and 552 nm for MO, MB and RhB, respectively (Tayade et al. 2009; Ramakrishnan et al. 2012).

The concentration of the samples at different photodegradation times was analysed. The absorbance of both the initial and the treated samples was measured, and the percentage of degradation was calculated according to Equation (2):

\[\% \text{ degradation} = \left(1 - \frac{C_1}{C_0}\right) \cdot 100\]  

(2)

where \(C_0\) and \(C_1\) are the initial and the final concentration of the dye, respectively.

To check the recyclability of the AgCl nanocatalyst, five cycles of degradation of each dye were carried out. The nanoparticles were separated by centrifuge after each cycle and collected to be reused. At the end of the cycles, nanoparticles were analysed by XPS to verify their structure. Kinetics studies were also carried out by determining concentration data versus time for each dye.

Finally, each dye solution (10 ppm), with a concentration of the nano-AgCl catalyst of 1 g L\(^{-1}\), was stirred at room temperature for 60 min under natural light. The aim was analysing the influence of the radiation source on the degradation efficiency.
The ability of the photocatalytic system was further tested. With the aim of knowing its capacity for degrading mixtures of dyes (as in many real wastewater effluents), a mixture consisting in equal volumes of the three studied dyes was treated with the silver chloride and UV radiation for 60 min.

RESULTS AND DISCUSSION

Characterisation of the nanoparticles

The characteristic absorbance peak below 300 nm (Husein et al. 2005) in the UV-Vis absorption spectrum of the dispersed nanomaterials (10 mM) points out the presence of silver chloride (Figure 2(a)). Moreover, the absence of absorbance in the visible region indicated that the silver chloride did not convert into silver (whose absorbance peak should appear at 400 nm (Petit et al. 1993)). The absorption edge around 300 nm corresponds to a band gap energy of 3.85 eV calculated by using Equation (1) (Figure 2(b)). Values between 3.20 and 4.37 eV are found in the literature (Wang et al. 2008; Daupor & Wongnawa 2014; Majumder et al. 2014) for the band gap of AgCl nanoparticles depending on their size. The value here obtained is consistent with those data. The band gap of the bulk AgCl is 5.6 eV (Glaus et al. 2002; Majumder et al. 2014). This is in agreement with the fact that band gaps decrease with the size of nanomaterials (Wang et al. 2008; Daupor & Wongnawa 2014; Majumder et al. 2014). This large band gap energy

Figure 2 | AgCl nanoparticles characterisation: (a) UV-Vis-absorbance, (b) Tauc plot for determination of the band gap, (c) PXRD pattern, (d) TEM micrograph, (e) SEM micrograph of the synthesised AgCl nanoparticles.
also means that UV irradiation for photocatalytic processes is necessary, and photocatalytic activity in the visible region with this nanocatalyst is not possible.

The structure of the nanoparticles was analysed by means of XRD. The corresponding pattern (Figure 2(c)) shows only the presence of chlorargyrite, the cubic structure of silver chloride, with the peaks matching a standard JCPD card 31–1238. The pattern of 2θ peaks are: 27.82°, 32.24°, 46.24°, 54.83°, 57.49°, 67.46°, 74.47°, 76.75° and 85.70° corresponding to the crystal planes of face centre cubic crystal of AgCl (111), (200), (220), (311), (222), (400), (331), (420), (422) (Wang et al. 2009; Choi et al. 2010). Moreover, any characteristic peak of Ag0 was found in the structure of the nanomaterial, confirming once more the total absence of elementary silver. The characteristic strong diffraction peak 32.24° (2θ) which is commonly assigned to the basal d(200) reflection of AgCl remained virtually unchanged (Wang et al. 2009; Choi et al. 2010). Figure 2(d) shows the TEM micrograph of the nanoparticles separated and dispersed in toluene, before the agglomeration process. As it can be seen, they are spherical and homogeneous, with a narrow size distribution of 5–20 nm. Figure 2(e) shows the SEM image of the precipitated nanoparticles, the solid was formed by large cubic agglomerates. This agglomerating behaviour of the AgCl nanostructures was previously found by ourselves as well as by other authors (Kim et al. 2010; Song et al. 2013; Rodriguez-Cabo et al. 2015).

Degradation experiments

The photodegradation of MO, MB and RhB, was performed under UV light by using the synthesised AgCl and other commercial nanoparticles (Ag, ZnO, TiO2 and P-25 Degussa) frequently used as catalysts (Tayade et al. 2007; Wang et al. 2012; Mohmood et al. 2013). The final UV-Vis absorbance spectra led to the degradations shown in Table 1.

As it is shown in Table 1, the prepared silver chloride nanomaterial is highly effective with final degradations of 98.4%, 98.6% and 99.9% for MO, MB and RhB, respectively. For all of the studied dyes, the best level of degradation was found with our synthesised nanoparticles. Results found with the P-25 Degussa nanocatalyst were clearly lower, and the performances of the rest of the nanomaterials were much worse.

To check the recyclability of the AgCl nanocatalyst, five cycles of degradation were carried out of each dye in which the nanoparticles were easily and almost completely separated from aqueous solutions by centrifugation (10 min, 4,000 rpm) after each cycle. According to XPS measurements, Figure 3(a) shows the Ag3d spectrum, which consist of two peaks at 373.91 and 367.92 eV, which correspond to the binding energies of Ag 3d5/2 and Ag 3d3/2 of AgCl, respectively. Figure 3(b) shows two peaks at 198.36 eV and 200.0 eV, belonging to the Cl 2p1/2 and Cl 2p3/2 spectra of AgCl, respectively. Therefore, silver is present as Ag+, with a total absence of silver in the elemental form. The binding energy values, along with the obtained Ag/Cl ratio of 0.99, evidence that the catalyst is maintained as AgCl after the photocatalytic degradation, and no conversion to Ag0 was observed (Zhang et al. 2008). This behaviour was also found in a previous paper (Rodriguez-Cabo et al. 2015) where the degradation of Orange II with these nanoparticles was tested.

Moreover, in the case of P25-Degussa nanocatalyst, its suspension in water showed a hydrocolloid with high stability, making the separation of this catalyst from water more difficult. Consequently, recovery and re-utilisation of this catalyst in next photodegradation reactions becomes more complicated and implies lower efficiency (Torres et al. 2006; Prado et al. 2008). At least 20 min of centrifugation at 14,000 rpm were required for a good separation.

Thus, AgCl nanocatalyst shows two advantages in comparison with P-25 Degussa: a higher degradation performance and an easier recoverability (according to the time and rpm required for the separation). However, it must be highlighted that the differences in the shape and size of the nanomaterial can be highly relevant to the degradation efficiencies, as previously stated (Wang et al. 2007).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Size (nm)</th>
<th>MO degradation (%)</th>
<th>MB degradation (%)</th>
<th>RhB degradation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgCl (synthesised)</td>
<td>&lt;20</td>
<td>98.4 ± 0.8</td>
<td>98.6 ± 0.9</td>
<td>99.9 ± 0.7</td>
</tr>
<tr>
<td>Ag</td>
<td>&lt;100</td>
<td>10.1 ± 0.6</td>
<td>62.4 ± 0.4</td>
<td>32.1 ± 0.5</td>
</tr>
<tr>
<td>ZnO</td>
<td>&lt;50</td>
<td>68.1 ± 0.5</td>
<td>75.5 ± 0.8</td>
<td>65.7 ± 0.6</td>
</tr>
<tr>
<td>TiO2 (anatase)</td>
<td>&lt;25</td>
<td>42.8 ± 0.4</td>
<td>40.8 ± 0.6</td>
<td>52.3 ± 0.7</td>
</tr>
<tr>
<td>P-25 Degussa</td>
<td>&lt;21</td>
<td>87.9 ± 0.8</td>
<td>87.9 ± 0.9</td>
<td>81.3 ± 0.8</td>
</tr>
</tbody>
</table>

Table 1 Degradation performances (%) obtained with classical nanocatalyst: dye concentration 10 ppm, 1 g L⁻¹ of nanoparticles, and 60 min of UV irradiation.
Figure 4(a) shows, for the MO solution, the evolution of the degradation with time. It can be observed that the initial orangish-yellow sample gradually becomes completely colourless. Figure 4(b) shows the decrease in the absorbance peak at 464 nm, corresponding to the azo bond. It can be seen that in only 10 min of UV radiation the concentration of MO is reduced to less than 10% of the initial concentration, and the orange colouration has almost disappeared in one hour (98.4%). These results are very similar to those found for Orange II dye (Rodríguez-Cabo et al. 2015).

With regard to the decolouration of the MB sample, and referring to Figure 5(a), it can be observed that almost all the samples keep a certain colouration, changing from intense blue to pale blue, and finally to a transparent solution.
Figure 5(b) shows that the UV absorbance peaks decrease more slowly than in the previous case, pointing out that this thiazine-based dye is more difficult to degrade than MO (in this case only 54.6% of decolouration is achieved in 10 min). Nevertheless, the photodegradation is over 90% after 30 min, and very similar values to those of MO are found after one hour (98.6%).

In the case of RhB, Figure 6(a) shows the total decolouration of the pink sample. The decrease in the absorbance peak at 552 nm shown in Figure 6(b), the colouration of the sample is reduced to 36.6% in 10 min, 1.5% in 30 min and finally, an almost completely decoloured sample (99.9% of degradation) is obtained in 1 h.

The radiation of UV on the catalyst surface generates holes and electrons, as reported in similar works (Wang et al. 2014; Divya et al. 2013). These electrons are able to produce super-oxide anionic free radicals, O$_2^-$, and then H$_2$O$_2$, that can attack the dye. Although all the three samples are satisfactorily decoloured in a short time, the ease breaking of the azo bond of the MO dye in comparison with the cyclic structures of MB and RhB, explains the faster degradation of the MO sample. Moreover, the products formed after certain degradation times were identified by LC-Q-TOF–MS in both positive and negative mode. A summary of the detected compounds is shown in Table 2. The concordance between the measured exact mass and the isotopic profile ions with the theoretical one (score) (Rodil et al. 2015) was higher than 90% for the identified products. Moreover, the structure of the degradation products was tentatively identified by interpretation of their MS/MS (tandem spectrometry) fragmentation pattern in the product ion scan mode. In MO photodegradation experiments only benzenesulfonic acid could be identified. This suggests a degradation mechanism through the cleavage of azo group connecting the two aromatic rings (Gomathi Devi et al. 2009), with subsequent oxidation of the intermediates that are further converted into small molecules such as carbon dioxide, sulfate, H$_2$O, etc. For MB, neither products previously reported for the degradation of this dye nor even new degradation products were found. This suggests a fast
mineralisation, according to the literature (Houas et al. 2001; Wang et al. 2014). A mechanism is proposed via a cleavage of the central aromatic ring followed by the formation of single structures before mineralisation. In RhB photodegradation experiments, N-deethylated derivatives, phthalic acid and benzoic acid were identified. As reported in the literature (He et al. 2009), RhB degradation mechanism occurs through N-deethylations, further destruction of the conjugated structure and formation of benzene intermediates such as phthalic acid and benzoic acid and final mineralisation. The identified photodegradation products represent less than a 5% in molar base of the initial dye concentration. In agreement with previously published mechanisms (Houas et al. 2001; Gomathi Devi et al. 2009; He et al.

**Table 2** LC-Q-TOF-MS scan data on degradation products identification

<table>
<thead>
<tr>
<th>Precursor dye</th>
<th>Chromatographic retention time (min)</th>
<th>Ionisation mode</th>
<th>Experimental m/z</th>
<th>Proposed formula</th>
<th>Theoretical m/z</th>
<th>Score</th>
<th>Products identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>MO</td>
<td>1.5</td>
<td>Negative</td>
<td>156.9962</td>
<td>C₆H₆O₃S</td>
<td>156.9965</td>
<td>99.7</td>
<td>Benzencesulfonic acid</td>
</tr>
<tr>
<td>RhB</td>
<td>1.6</td>
<td>Negative</td>
<td>165.0195</td>
<td>C₇H₆O₄</td>
<td>165.0193</td>
<td>91.2</td>
<td>Phthalic acid</td>
</tr>
<tr>
<td>RhB</td>
<td>1.6</td>
<td>Negative</td>
<td>121.0298</td>
<td>C₇H₆O₂</td>
<td>121.0295</td>
<td>90.2</td>
<td>Benzoic acid</td>
</tr>
<tr>
<td>RhB</td>
<td>13.7</td>
<td>Positive</td>
<td>415.2101</td>
<td>C₁₀H₁₂N₂O₅</td>
<td>415.2016</td>
<td>90.1</td>
<td>Xanthylium, 9-(2-carboxyphenyl)-3-(diethylamino)-6-(ethylamino)-</td>
</tr>
<tr>
<td>RhB</td>
<td>13.3</td>
<td>Positive</td>
<td>387.1701</td>
<td>C₂₆H₂₇N₂O₃</td>
<td>387.1703</td>
<td>97.9</td>
<td>Xanthylium, 3-amino-9-(2-carboxyphenyl)-6-(diethylamino)-</td>
</tr>
</tbody>
</table>

**Figure 6** Evolution in time of the system [RhB + nano AgCl + UV light] at room temperature: (a) decolouration of the samples, (b) UV-Vis absorbances, (c) kinetics of the degradation processes.
MB and RhB can be attributed to the irradiation, the good degradation results obtained for MO, account the low decolouration of the samples without UV to adsorption rather than photodegradation. Taking into account the low decolouration of the samples without UV irradiation, the good degradation results obtained for MO, MB and RhB can be attributed to the efficiency of this photocatalytic system. This is in agreement with the large band gap energy previously found for the nanocatalyst.

Kinetics

With the values of the concentration, in time, the kinetics of the photodegradation process was obtained for each dye (Figures 4(c), 5(c) and 6(c)). According to standard deviations obtained, a second-order kinetics equation was selected for MO, but MB and RhB follow a first-order kinetics equation. Both equations are expressed as follows:

\[ \ln \left( \frac{C_0}{C_t} \right) = k_{app} \cdot t \]  (3)

\[ \frac{1}{C_t} - \frac{1}{C_0} = k_{app} \cdot t \]  (4)

where \( k_{app} \) is the pseudo-first-order constant (min\(^{-1}\)) in Equation (3) and the pseudo-second-order constant (g·μg\(^{-1}\)·min\(^{-1}\)) in Equation (4), and \( t \) the reaction time (min). In Figure 4(d) \((C_t - C_0)\) is plotted versus time for MO, and in Figure 5(d) \(\ln(C_0/C_t)\) versus time for MB and in Figure 6(d) for RhB. In all cases linear fits with very high values of \( R^2 \) are obtained. The value of the pseudo-second order rate constant for the photocatalytic degradation of MO is 0.0980 g·μg·min\(^{-1}\). For the MB and RhB the value of the pseudo-order rate constants is 0.0743 and 0.1279 min\(^{-1}\), respectively. The higher order of reaction in the case of MO may be due to the easy breaking of the azo bond of the MO dye in comparison with the cyclic structures of MB and RhB.

Degradation of mixtures of dyes

The effect of the interaction between different dyes was also analysed. The UV-Vis absorbance of a three-dye mixture before and after the photocatalytic degradation (60 min) was studied. The decrease in the absorbance of the treated sample for all the dyes led to final degradation performances of 83.1%, 93.0%, and 93.2% for MO, MB and RhB, respectively. When comparing this result with the ones obtained for each dye separately, it is observed that the efficiency of the degradation is slightly lower for the mixture (around 5–6% for MB and RhB, and 15% for MO). Despite this small reduction in the performance, the degradation results are very good, obtaining an average diminution of dye concentration of 89.8%.

CONCLUSIONS

A photocatalytic system consisting in AgCl nanoparticles and UV radiation was tested for the degradation of three common industrial dyes with different chemical structures, MO, MB and RhB. The nanoparticles were prepared inside an IL without the addition of any other surfactants or co-solvents. They are spherical, with sizes between 5 and 20 nm.

The degradation was performed starting from 10 ppm dye solutions, using 1 g L\(^{-1}\) of nanocatalyst and irradiating the samples for 60 min. Under these conditions the obtained degradation efficiencies were 98.4%, 98.6% and 99.9% for MO, MB and RhB, respectively, pointing out that the studied photocatalytic system is a very suitable option for the treatment of textile wastewaters. Moreover, it was observed that the degradation of MO occurred faster than in the case of the other two non-azo dyes, probably due to the easy breakup of the chromaphore. Furthermore, it was confirmed that the effect of the degradation due to sunlight is almost negligible. The elemental analysis performed by XPS showed that after five cycles the catalyst remains as silver chloride. The kinetics of the processes was obtained too. MO was degraded following a second order reaction, with a rate constant of 0.0980 g·μg·min\(^{-1}\). The behaviour of MB and RhB was depicted by first-order kinetics, with constants of 0.0743 and 0.1279 min\(^{-1}\), respectively. The degradation of a mixture of dyes also showed very good performances, although slightly lower than for the separate dyes.

A comparison established with the currently used photocatalyst P-25 Degussa showed that AgCl nanoparticles led to better degradations with an easier recovery process. Further studies beyond this work, considering economic evaluation and the life cycle analysis of the whole process, are required to draw a conclusion about the best nanocatalyst.
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