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Fattima Al-Zahra Gabar Gassim, Ali Jj MakkawiAsmaa, Makkawi, et al.

Synthesis and Characterization of ZnO-AgCl Nanocomposites and Applications in the Removal of Reactive Black 5H from Wastewater

Fattima Al-Zahra Gabar Gassim[1, a)], Ali Jj Makkawi[2], Asmaa and H. Hammadi[1]

[1]*College of Pharmacy, University of Babylon. Hilla, Iraq*
[2] *Directorate of Education in Babylon, Ministry of Education, Hilla, Iraq*
[a)] Corresponding author: alzahraafatema6@gmail.com

Abstract. The nanocomposites of AgCl–ZnO were synthesized in water using a one-pot refluxing technique at a temperature of 90 °C. The structural properties of nanocrystal were studied through X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). The photocatalytic activity of the nanocomposites was investigated by the degradation of reactive black 5H (RB5H) which indicates an improved interaction regarding the ZnO and AgCl nanostructures. The removal of the percentage of RB5H on the nanocomposite using solar light is about 97.7% . The mechanism of ZnO-AgCl nanocomposite illumination was suggested for the production of oxidizing species and their influence on degrading RB5H dye in an aqueous solution.

Keywords: ZnO nanoparticles, environmental treatment, photodegradation

INTRODUCTION

Nanostructures can be defined as the scope of particles and structure of dimension ranging between (1-100 nm.) and considered the basic structure unites of a nanoparticle. Nanomaterials have different chemical and physical properties better than bulk materials because of their size and structure [1]. Nanometric ZnO has shown remarkable properties due to its high surface area to volume ratio and unique chemical and physical features [2]. Zinc oxide used in the elimination of organic dyes and toxic pollutants [3] is the semiconductor photocatalyst, such as Zinc Oxide (ZnO). This heterogeneous catalyst has a relatively higher catalytic interactivity and seems to be feasible and f, not toxicity or solubility [4]. Zinc oxide represents a significant n-type [5] semiconductor, as its bandgap energy of 3.3 eV at room temperature is a huge binging energy suitable for diverse applications, including UV light with wavelength 387 nm [6].

The properties of ZnO nanostructures suggest it to be a promising photocatalyst, such as its higher quantum efficiency, non-toxicity, low cost, chemical superiority, physical stability, and high redox potential [7]. However, the photocatalytic activity of ZnO remains limited by the photo-generated electron-hole pairs that are recombined rapidly [8]. Additionally, ZnO can only absorb UV. Meanwhile, several attempts have been made to extend the adsorbing rate of ZnO, yet only less than 5% [9] of solar light energy can be used for photocatalytic reactions.

A useful technique for adjusting the energy rate surface state of ZnO is the transition metal-doped nanostructure [10], as it contributes to its further improvement through alterations in the doping concentration of the material, eventually improving their physical and optical characteristics in terms of mechanisms and optics [11], as well as the electric and thermal forms of transport which vary in particle size, shape, orientation, and aspect ratio [12]. This causes controlling the size and morphological growth of ZnO to be a rather tough issue in terms of designing new, functional devices when modifying ZnO with noble metal nanoparticles [13]. For example, the Ag loading on ZnO nanostructures improves its photostability, enhances its efficiency in the separation of photo-generation electron and hole pairs, and eventually extends the light absorption to visible light [14].

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Preparing AgCl–ZnO nanocomposites and investigating their photocatalytic activities are not studied yet. Ji et al. [15] prepared Ag–TiO2 and AgCl–TiO2 nanoparticles and demonstrated how the photocatalytic interaction of AgCl–TiO2 in degrading Rhodamine B under visible light irradiation was noticeably larger than for Ag–TiO2. Liu et al. [16] examined how the Ag loading on ZnO affects the photocatalytic degrading of Rhodamine B (RhB), indicating that its degrading process over pure Ag nanowires was comparatively nihil, as its degrading efficiency rose when decorated with Ag nanoparticles.

AgCl–ZnO nanocomposites were initially prepared through a one-pot refluxing technique in water at about 90 °C, followed by examinations using XRD, SEM, and UV-visible (DRS). The photocatalytic interactions of nanocomposites were studied by degrading a model organic pollutant, namely reactive black 5H, under dark visible light irradiation, as well as the influence of AgCl loadings.

EXPERIMENTAL

Materials

As for the materials, zinc nitrate tetrahydrate (Zn (NO3)2_4H2O), silver nitrate (AgNO3), sodium chloride, sodium hydroxide, and absolute ethanol of high quality have been purchased from Merck, whereas the azo dye, Reactive Black 5H was supplied from Shanghai, neither of which were used with any purifying processes.

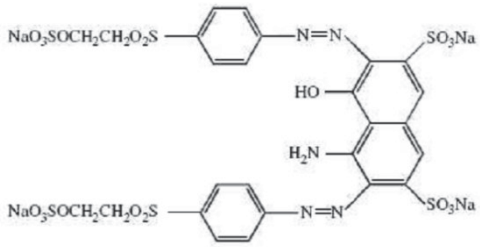

FIGURE 1. Chemical structure of Reactive Black 5H

Preparation of the nanocomposites

ZnO-AgCl nanocomposites with 0.383 moles of silver chloride can be prepared by dissolving 5.220 g zinc nitrate tetrahydrate and 2.110 g silver nitrate into 50 ml of distilled water while being stirred at room temperature. Next, an aqueous solution of NaOH (5 M) is added dropwise while stirring at 1250 rpm at room temperature, until the pH value of the solution reaches 10. Then, an aqueous solution of sodium chloride (1.450 g dissolved in 20 ml of water) was slowly added to the formed suspension. The suspension was refluxed at about 90 C0 for 3 h. The precipitate was separated and washed two times with deionized water and ethanol to remove the unreacted reagents and dried in an oven at 60C0 for 24 h. Then gray powder was crushed by using a ceramic mortar. The final product was obtained by calcination of the precipitate at 2000C for 1 h [18]. The reactions for obtaining ZnO NPs are written as the following:

$$Zn(NO_3)_2.4H_2O + AgNO_3 + 3NaOH \rightarrow Zn(OH)_2 + AgOH + 3NaNO_3 + 4H_2O$$

$$AgOH + NaCl \rightarrow AgCl + NaOH$$

$$Zn(OH)_2AgCl \xrightarrow{reflexing} AgCl - ZnO + H_2O$$

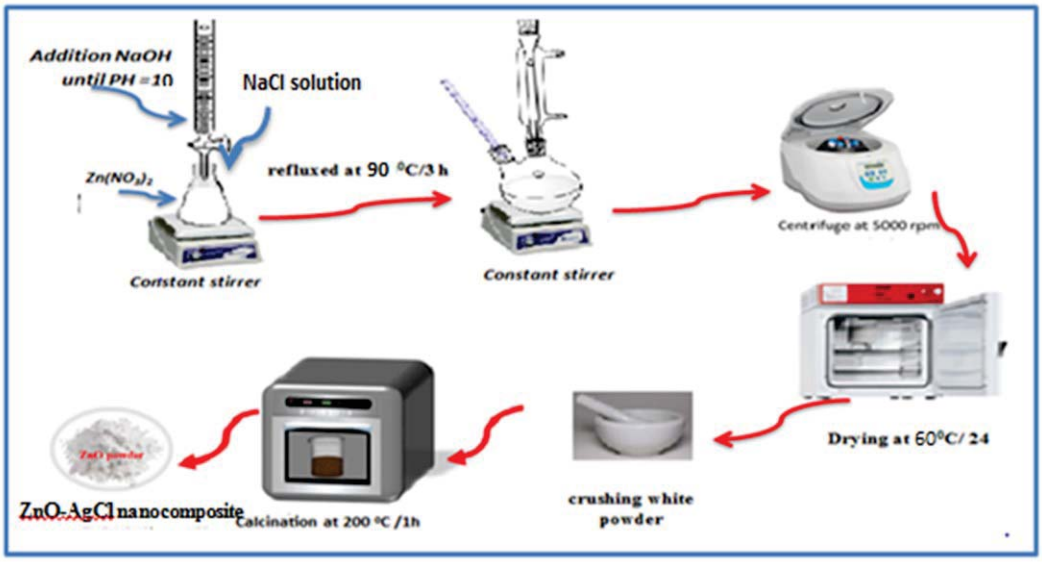

FIGURE 2. Schematic diagram of the steps used for synthesizing ZnO nanocomposites.

Characterizations

X-ray diffraction patterns were obtained from 20° to 80° in 2θ by an XRD with Cu Kα radiation (D8-Advanced, Bruker, Germany). An analysis of the morphological properties of the sample surfaces was performed using SEM (Quanta 450 FEI USA), whereas the optical adsorbing process was examined through UV–vis diffuse reflectance spectrophotometer (U-41000, HITACHI, Tokyo, Japan) and UV-vis spectroscopy (UV-1800 SHIMADZU).

Photocatalysis experiments

An aqueous reactive black 5H dye solution (50 ppm) was prepared by adding 40 mg of the prepared sample to 50 ml of Reactive Black 5H (RB5H). The reaction mixture was put in a 250 ml Pyrex glass beaker reservoir under laboratory temperature (25 °C). The stirring process done on a magmatic stirrer ensures keeping the mixture homogeneous. The Pyrex glass beaker is covered in cellophane for keeping solar light inside the vessel, providing this cover with a hole to enable atmospheric air to pass.

Analytical methods

A UV-vis spectroscopy (UV-1800 SHIMADZU) with a spectrometric quartz cell has been used in studying the process of optical adsorbing. The highest adsorbing wavelength of RB5H was at 597.6 nm. Throughout the reaction process, it has been observed that no interference occurred between the concentration of RB5H and the decoloring products. The concentration rate of RB5H within the reaction mixture at more than one moment was measured using determining how intensive the solution adsorption is at 597.6 nm, using a calibration curve.

RESULTS AND DISCUSSION

SEM has been applied for observing the morphological characteristics and size particles of the synthesized samples [19]. Figure 3 displays the SEM images of ZnO–AgCl nanocomposites. ZnO particles formed in the ZnO-AgCl hybrid show an individual rod structure whenever the diameters of the nano-rods ranged from 80 to 96 nm, and a length of about 1.0μm. Moreover, the AgCl particles were also observed in the hybrid with a spherical shape, having length diameters of 43 nm.

X-ray diffraction techniques can be used to understand the crystalline nature and quality of pure and metaled ZnO NPs. Figure 4 shows The diffraction peak of pure ZnO appeared at 2θ values 31.83°, 34.48°, 36.30°, 47.80°, 56.66°,63.38o and 68.48o are related to zinc oxide respectively, which can be indexed to hexagonal wurtzite structure of bulk crystalline ZnO[20] (JCPDS 36-1451). Seven additional peaks at 2θ of 27.6, 46.32, 54.95, 57.55, 66.92, 74.51, and 76.71 indicated the formation of Ag2Cl nanoparticles on the surface of ZnO nanorod [21]. The average crystallite sizes (D) were estimated to be about 31.077 nm which was calculated by using Scherrer's Equation 22.

$$D = \frac{K\,\lambda}{\beta \cos\theta}$$

Where D represents the average crystal size, k=0.94 stands for the constant crystal lattice, λ=0.154 nm is the x-ray wavelength of Cu kα, β is the total width of the peak measured at half its maximum intensity.

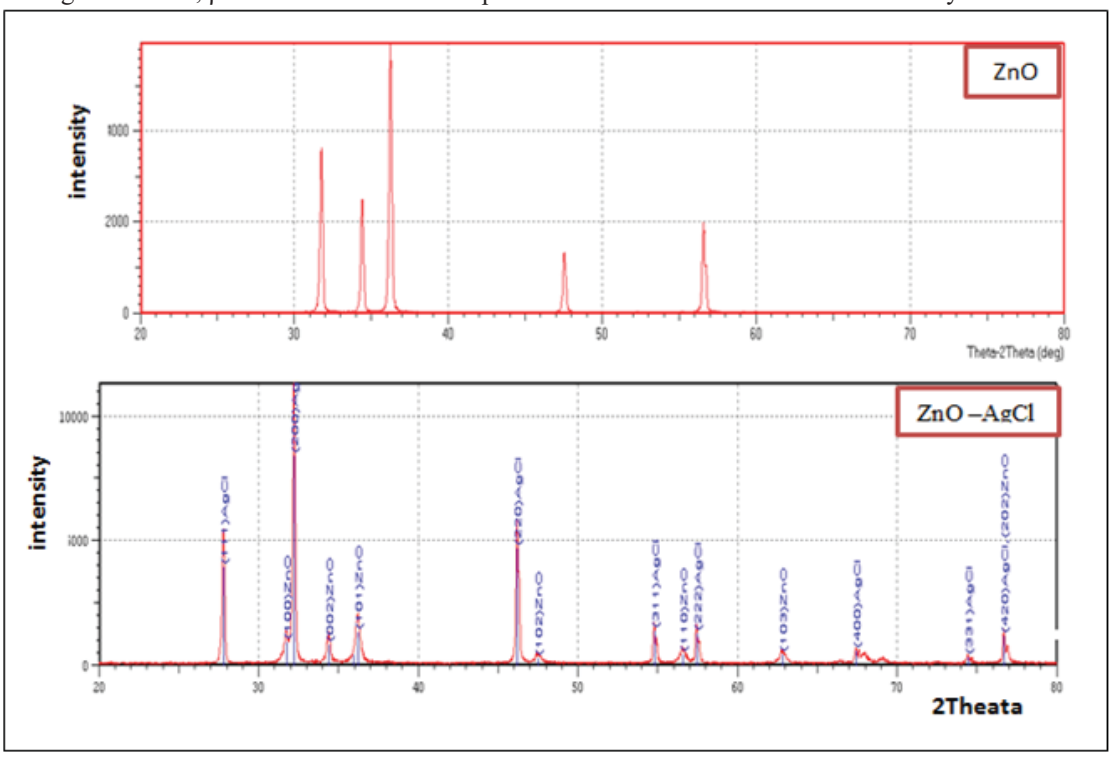

FIGURE 3. XRD patterns for AgCl–ZnO nanocomposites

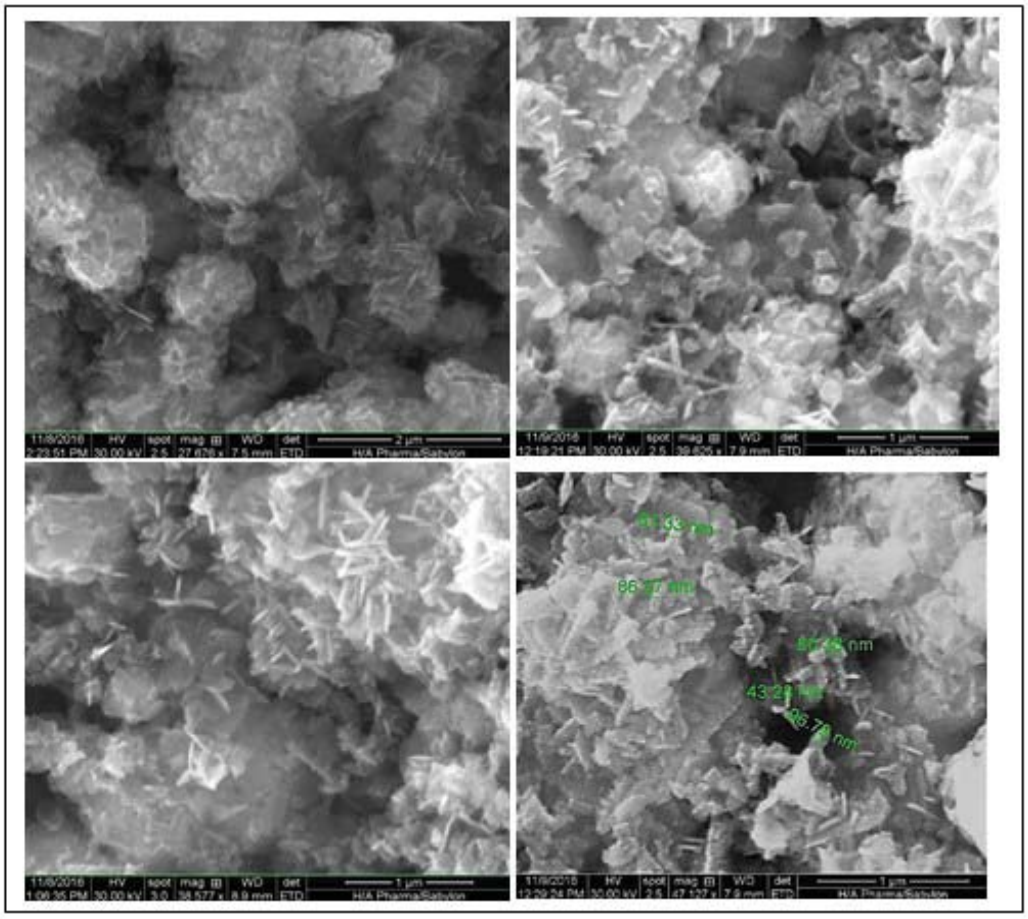

FIGURE 4. SEM images of ZnO-AgCl nanocomposites with various scales.

To test the photocatalytic degradation of RB5H over ZnO-AgCl nanocomposites catalysts, several primary experiments were performed under three conditions. reaction without ZnO-AgCl nanocomposites under visible light irradiation. Figure 5 shows that no decolonization or photodegradation occurred to the dye because of the high stability of RB5H towards the light.

The results of the dark experiment show that the removal percentage of dye is about 52% when using 0.8 mg/ml nano-composites catalysts. The marginal degradation may be traced back to adsorbing the RB5H over ZnO-AgCl nanocomposites [23].

As illustrated in Figure 6, the maximum removing rate for RBH5 was achieved at 0.8 mg/ml of ZnO-AgCl nanocomposites in presence of solar light and atmospheric O2 equal to 97%. A possible mechanical pathway of the catalysts for photocatalytic degradation is suggested as follows: under light irradiation, photo-generated electron-hole pairs ($e_{cb}-$–h^{+}_{vb}) are created in ZnO rods [24], after which the hvb+ and AgCl might witness a reaction forming Ag+ and Cl0. Some of the hvb+ are formed by ZnO reacting with OH− to generate OH. The Cl0 and OH might then react with the RB5H pollutant [25]. Therefore, despite the ZnO-AgCl showing a comparatively better electron-hole pairs recombination suppressing performance, yet the low rate of ZnO for producing hvb+ eventually restricts its photocatalytic interaction for evaluating the improvement of nanocomposites [26].

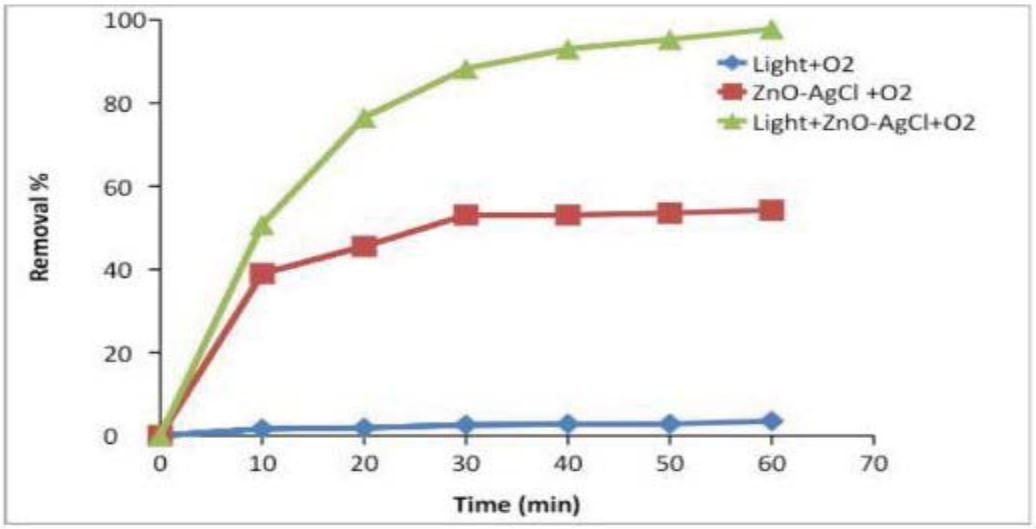

FIGURE 5. removal percentage of RB5H dye in aqueous solution with the various condition at 250C.

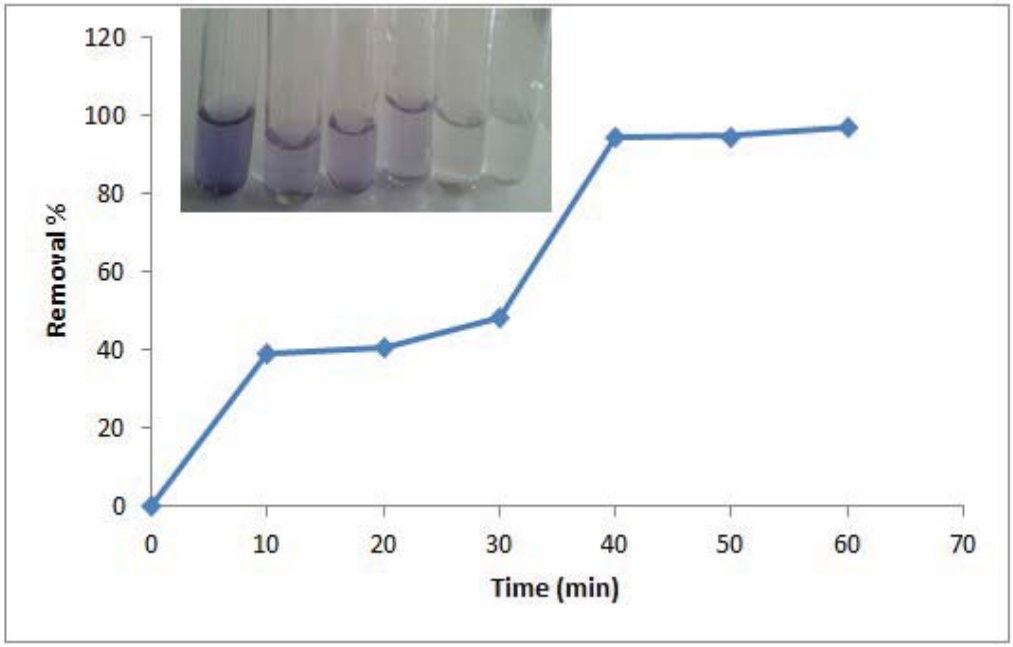

FIGURE 6. removal percentage of RB5H dye in aqueous solution with the various condition at 250C.

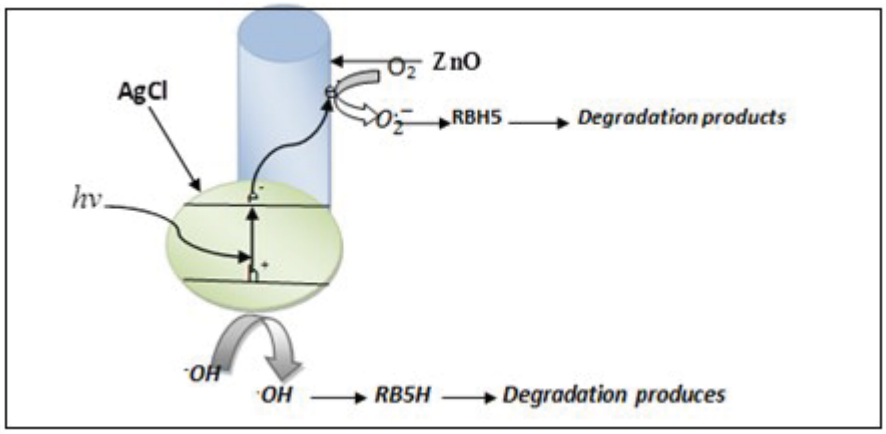

FIGURE 7. Schematic band diagram of ZnO-AgCl Hybrid Nanostructure.

Figure 7 presents a Schematic band diagram of ZnO-AgCl Hybrid nanostructure in an aqueous solution. The diagram shows the generation process of reactive oxidation species ($Ó^{-}_{2}$, ÓH, H_2O_2)which causes photocatalytic degrading of the RBH5 dye. The reaction processes could be illustrated using the following Equations 27:

$$ZnO + hv \rightarrow e^{-}_{(cb)} + h^{+}_{(vb)}$$

$$e^{-} + O_2 \rightarrow \dot{O}_2^{-}$$

$$Ag^{+} + e^{-}_{(cb)} \rightarrow Ag$$

$$h^{+} + OH^{-} \rightarrow \dot{O}H$$

$$\dot{O}H + RB5H\ dye \rightarrow degradation\ products$$

$$\dot{O}_2^{-} + RB5H\ dye \rightarrow degradation\ products$$

CONCLUSIONS

The nanocomposites of ZnO-AgCl were synthesized using the one-pot refluxing technique in water at about 90 °C. Characterization of the nanocomposites took place using XRD, SEM, and UV-visible (DRS). The photocatalytic activity of the resulting functional nanocomposite was examined through sunlight photo-degradation of RB5H in an aqueous solution as an illustrating example. The results demonstrated high photocatalytic activity under direct sunlight and a nanocomposite of (97%). However, the dye was decolorized in presence of ZnO-AgCl nanocomposites under dark conditions (52%) due to the dye adsorbed onto the surface of the nanocomposite. It can therefore be concluded that pairs of excited electrons and holes represent the major active species for the degradation processes.

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