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Effect of Modification of Zirconium Phosphate by Silver on Photodegradation of Methylene Blue

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Abstract:

The results of the photocatalytic degradation of Methylene Blue in aqueous solution indicated that the Ag-ZrP photocatalyst prepared by refluxing amorphous zirconium phosphate in silver nitrate method exhibited better photocatalytic performance than α-Zirconium Phosphate (α-ZrP). The best photodegradation efficiency was obtained in basic solution at pH 8 and saturation was attained from 70 and 100 min for Ag-Zrp and α-ZrP respectively. These results indicate that materials could be used as alternative in waste water treatment for the removal of dyes

Keywords: Methylene Blue; Zirconium phosphate; Silver nitrate; Photocatalytic degradation

1. Introduction

Waste waters generated by the textile industries, are known to contain considerable amounts of non fixed dyes and especially of azo-dyes. It is well known that some azo-dyes and degradation products such as aromatic amines are highly carcinogenic. A total of 15% of the total world production of dyes is lost during the dyeing process and is released in textile effluents [1-2]. The release of those colored waste waters in the ecosystem is a dramatic source of esthetic pollution, of eutrophication and of perturbations in the aquatic life [3]. As international environmental standards are becoming more stringent (ISO 14001, October 1996), technological systems for the removal of organic pollutants, such as dyes have been recently developed [4-5]. Among them, physical methods, such as adsorption [6], biological methods (biodegradation) [3] and chemical methods [7] are the most frequently used. The traditional processes for treatment of these effluents prove to be insufficient to purify the important quantity of waste waters after the different operations of textile dyeing and washing. Some methods such as combined coagulation, electrochemical oxidation, active sludge have recently been investigated and proved to be adequate. Other methods such as flocculation [3], membrane process [4] and adsorption have also been tested [6]. The drawbacks of these methods are mainly the creation of a more concentrated pollutant-containing phase. The processes by bacterial beds are less adapted because of the fluctuations of the wastewater composition

Currently, the photocatalytic treatment is a more attractive alternative for the removal of soluble organic compounds. It does not require expensive oxidants and can be carried out at mild temperature and pressure. Among various catalysts such as metal oxide semiconductors, were used as photocatalysts under UV irradiation because of their physical and chemical stability, low cost, ease of availability, non-toxicity, and electronic and optical properties [11,12]. It was shown that silver has a beneficial influence on the photoactivity of nanocrystalline semiconductor photocatalysts [13].

Zirconium phosphate is an important class of inorganic material that is widely studied in different chemical fields including ion exchange, high temperature stability, ion conduct, catalysis and photodegradation, and has received considerable attention [13,15]. Photodegradation activity of synthetic zirconium phosphates is related to their relatively no negligible surface area, swelling properties and high cation exchange capacity. The chemical treatment of synthetic zirconium phosphates has long been studied with the intention of modifying their texture, acidity and photochemical property in order to make them useful as adsorbents or catalysts supports [12-14]. Different metals such as Ag, Cu and Zn were used in the modification of Zirconium phosphate [15,16]. The silver loaded zirconium phosphate was recently emerging as various commercial products due to its high antibacterial activity [17], its catalytic activity [18] and its good photochemical property [14,19].

The aim of this study is to analyze the feasibility of discoloration of Methylene Blue dye using α-ZrP and amorphous zirconium phosphate activated by nitrate silver. The factors that influence the dye photocatalytic removal such as pH, time and silver effects were investigated.

2. Experimental

2.1. Preparation and characterization of Zirconium phosphates

Followed Clearfield method [20], amorphous zirconium phosphate a-ZrP was prepared by adding gradually zirconyl chloride ($ZrOCl_2$, $8H_2O$) into a flask containing 500 cm^3 of phosphoric acid H_3PO_4 within 60 min and shaken overnight at 400 rpm to yield a gelatinous precipitate which was separated by centrifugation and washed with 2% H_3PO_4(aq) and then with deionised water. Finally, the a-ZrP particles were dried at 353K for 24 h for further use.
α- Zirconium phosphate was prepared by refluxing amorphous zirconium phosphate a-ZrP in 200 cm^3 of phosphoric acid H_3PO_4 for 24h. The resulting crystalline α- ZrP was centrifuged, washed with deionised water and dried at 80°C for 2 days.

For silver activation, 5g of amorphous a-ZrP was added to solution of silver nitrate $AgNO_3$ (400 mg; 200 cm^3) and agitated for 1h. Then, 18 cm^3 of phosphoric acid H_3PO_4 was added and the mixture was refluxed for 2 days to yield precipitate denoted Ag-ZrP for the simplicity. The samples were centrifuged, washed with deionised water and dried at 80°C for 2 days.

For all samples, the phases X-ray powder diffraction (XRD) patterns were obtained by Philips X'Pert PRO with Cu Kα radiation and the FTIR measurements were performed with 4 cm^{-1} resolution by VERTEX 70 spectrometer.

2.2. Photocatalytic evaluation

Methylene Blue (MB) was selected, as a model for the photocatalytic degradation experiments because it is a non-volatile and common contaminant in the industrial wastewaters. The setup used for photocatalytic degradation experiment consists of a 250mL beaker and 20 cm above it, a low-pressure mercury lamp UV (15 W, Philips) was used as an artificial sunlight source. Moreover, the content of the beaker was stirred by a magnetic stirrer during irradiation. UV-VIS spectrophotometer (Standard UNICAM) was used to measure the UV–vis absorption spectra of IC as function of irradiation time.

The experiments were performed by suspending calculated amount of the catalyst into MB solution (100 ppm). The reaction was carried out isothermally at 25 ◦C and samples of the reaction mixture were taken at time intervals for a total reaction time 2 h. The decolourisation was determined at the maximum 608 nm. Removal efficiency (%) of IC was measured by applying the following equation:

$$\text{removal efficiency (\%)} = \frac{Co - C}{Co} x100$$

where Co is the original Methylene Blue (MB) content and C is the retained IC in solution.

3. Results and discussion:

3.1. Characterization

Both α –ZrP and Ag-ZrP were obtained as white powders and the comparison between their XRD patterns is reported in Fig 1. The spectra of both materials exhibit the same main reflections with different intensity and resolution. On the other hand, the interlayer spacing for all materials was retained at around 0.75 nm. The X-ray diffraction patterns of α-ZrP indicated that a well crystallized material was obtained, in agreement with published data [21] whereas Ag-ZrP presents broad ill-defined reflections indicating its low cristallinity. The different degrees of crystallinity can be also associated with the modification of sample morphology [22]. Clearfield and co-workers have shown that the unit cell dimensions of α –ZrP vary with the degree of crystallinity [23]. The ratio of intensities of the 002 and 204 is known to vary; samples exhibiting preferred orientation of the particles have an intense reflection corresponding to hkl = 002, where with as low crystallinity materials such as Ag-ZrP have the 204 reflection as the more intense [21]. This low crystallinity for Ag-ZrP can be due to the exchange of Hydrogen ions by silver ions.

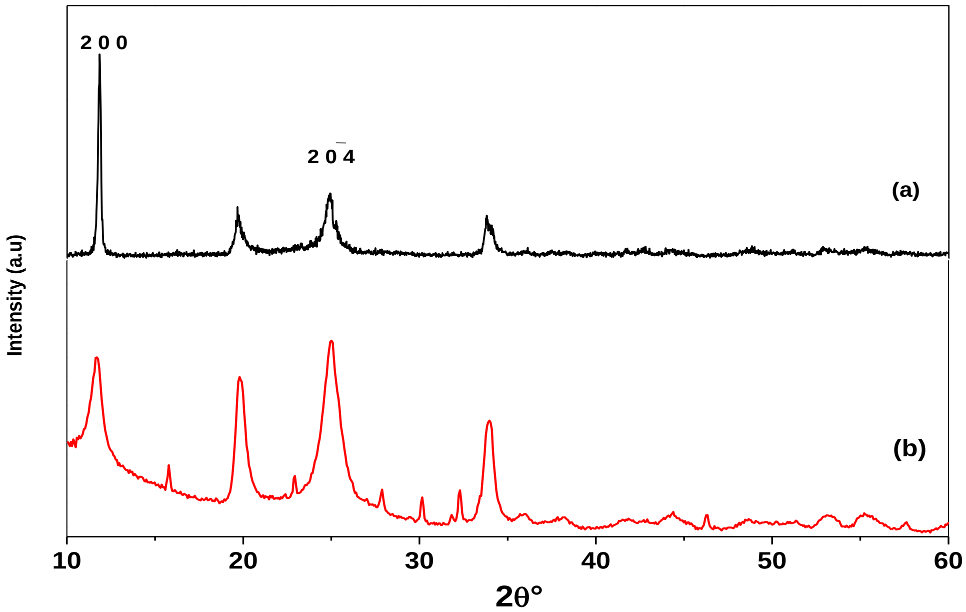

Fig. 1. X-ray powder diffraction of (a) α-ZrP, and (b) Ag-ZrP

These results were assessed by FTIR data (Fig. 2) from which it was shown that there is no drastic change observed in band position in the FTIR spectrum of Ag-ZrP as compared to α-ZrP.

However, the intensities of some peaks concerning the OH bands were slightly reduced after activation of Zirconium phosphate by silver nitrate confirming probably the substitution of hydrogen by silver ions. The peaks can be assigned as follows: The typical symmetrical mode characterising the P–O–P bridge at around 970 cm^{-1}. The band at 1619 cm^{-1} is due to the bending vibrations of –OH of water associated PO_4^{3-} group which supports the presence of water of crystallisation in the lamellar solid [24]. The stretching vibration of –OH group and of physically adsorbed water found at around 3170 cm^{-1} [25]. The band at 3509 cm^{-1} may be due to the stretching vibration of P–OH. The antisymmetric stretches of the crystal/interlayer water present at 3598 cm^{-1}.

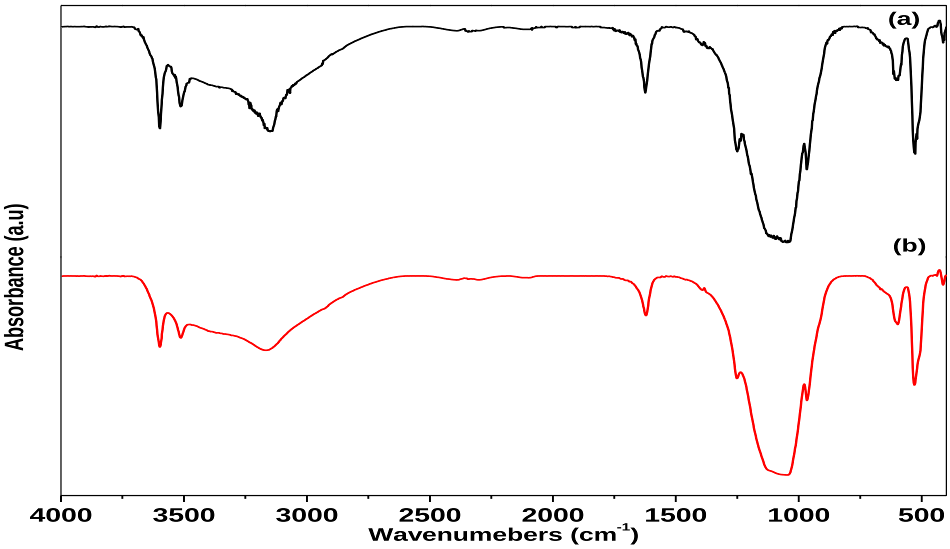

Fig 2. Infrared spectra of (a) α-ZrP, and (b) Ag-ZrP

3.2. Catalytic activity

3.2.1 Effect of pH

The photocatalytic efficiency of MB on Ag-ZrP and α-ZrP at different pH values was shown in Fig. 3. The pH of the solution was adjusted with diluted NaOH and HCl. It was found that the photocatalytic efficiency of the dye over Ag-ZrP and α-ZrP was highly pH dependent.

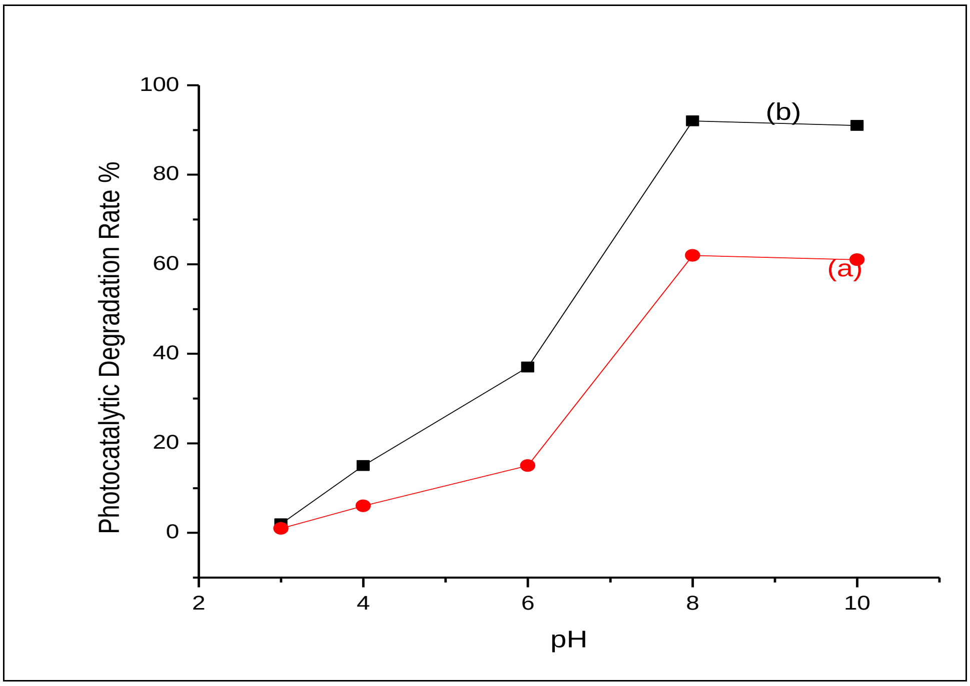

Fig. 3. Effect of pH on the photocatalytic efficiency of MB on (a) α-ZrP, and (b) Ag-ZrP.
V= 200 ml, m_{cat} = 100 mg, t = 2 h, [MB] = 100 ppm**.**

The photocatalytic efficiencies increased with increasing pH values. In strong acidic condition, the decolourization of the dye was negligible. The photocatalytic efficiency dramatically increased at the pH 8.

The photocatalytic oxidation of organic compounds on Ag-ZrP and α-ZrP may be carried out in two processes:
(1) The diffusion of organic compound to the particle surface to forming a complex.
(2) Exchange of electrons with the reactive surface of samples [26].
Both of α-ZrP and Ag-ZrP surfaces are positively charged below pH 4. Methylene Blue is a cationic dye in aqueous solution and it can keep its cationic configuration in the pH range 3–11. At pH basic, electrostatic interactions between the negative catalyst surface and cationic dye lead to strong adsorption of the latter on the metal oxide support [26]. The photocatalytic efficiency decreases with decreasing pH due to the electrostatic repulsion between the dye species and the surface of the catalyst as a result of which the photocatalytic degradation percentage was found to be minimum at strong acidic condition. All further experiments were carried out at pH 8.

3.2.2.. Effect of silver activation and time on photocatalytic efficiency of MB

The refluxing of amorphous zirconium phosphate in silver salt lead to an increase of the degree of photocatalytic efficiency of Methylene Blue solution compared to α-ZrP. Thus, enhanced degradation under UV irradiation maybe ascribed to the effects of Ag deposits acting as electron traps leading to better electron excitation. In addition, the rate-determining step in photocatalytic oxidations is believed to be the electron transfer from Ag–ZrP surface to the adsorbed oxygen [27].

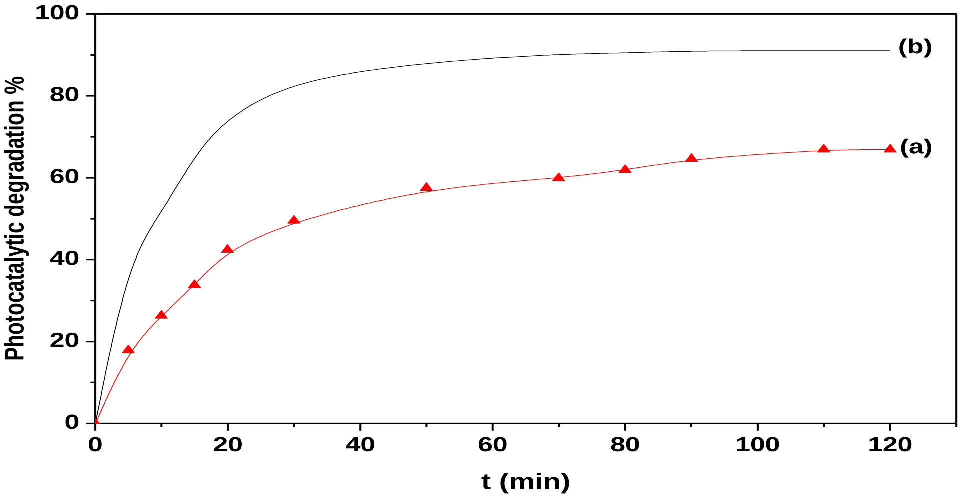

Fig. 4. Kinetics of photocatalytic degradation of MB on (a) α-ZrP, and (b) Ag-ZrP.
pH 3, V= 200 ml, m_{cat} = 100 mg, [MB] = 100 ppm

It can be seen that the dye uptake process was found to proceed through two stages:
(1) An initial rapid uptake for the first 10 min was found that 50 % and 29 % for Ag-ZrP and α-ZrP respectively of IC decolorized as shown in Fig. 4.
(2) The dye uptake attains saturation from 70 min and 100 min for Ag-ZrP and α-ZrP respectively. The high removal efficiency at the initial period (10 min) may be due to increasing the number of vacant sites available at the initial stage and as a result an expected variation in the concentration of adsorbate in solution and on adsorbent surface (concentration gradient) tends to enhance the dye sorption rate [27]. As time proceeds, this concentration gradient decreases due to accumulation of dye molecules on vacant sites and thus saturation stage was almost perceived [27].

Conclusion

The results of our study have shown that the degradation of Methylene Blue dye was successfully carried out using α-ZrP and Ag-ZrP. The photocatalytic degradation reaches ca. 90% with Ag-Zrp and ca. 60% with α-ZrP. The presence of silver enhanced the photocatalytic degradation due to its effect, which acts as electron traps leading to better electron excitation. High photocatalytic activity was found at pH 8 due an electrostatic interaction between the negative catalysts surface and cationic dye.

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