Photo-catalytic reduction of hexavalent chromium (Cr(VI)) under visible light with Bi-Zn co-doped TiO_2

B.Benalioua[1], Kada.Manseri[1], I.Benyamina[1], M.Mansour[1], A.Bentouami[1] & B.Boury[2] 1. Laboratoire de Valorisation des Matériaux, Université Abdelhamid Ibn Badis – Mostaganem ; BP 227 – Mostaganem, Algérie.

2. Laboratoire de Chimie Moléculaire et Organisation du Solide, Université Montpellier II. France.

Abstract

The aim of this study is based on the synthesis of a new photo catalystby co-doping $TiO_2$with bismuth and zinc and its application on the photo-reduction of hexavalentchromiumunder visible light. The material obtained was characterized by XRD, BET and UV-vis DRS. The XRD characterization results of the obtained material Bi-Zn-TiO_2revealed the presence of the anatase phase and the absence of the rutile phase compared tothe TiO_2 P25 diffractogram. Otherwise, the UV- visible diffuse reflection spectroscopy (UV-vis DRS) characterization showed that the Bi-Zn-TiO_2 exhibits redshift relative to commercial TiO_2-P25, this property promises a photo catalytic activity of Zn-Bi-TiO_2 under visible light. Indeed, the efficiency of photo catalyticBi-Zn-TiO_2under visible light is has been proved by a complete reduction ofhexavalent chromiumsolution of 10 mg/L after 120 minutes, whereas with the P25-$TiO_2$the photo-reduction is achieved after 240 minutes.

Keywords: *POA, heterogeneous photocatalysis, TiO_2, doping*

1. Introduction

Chromium is widely used in many industrial activities, such as leather tanning, metal finishing, dyeing, textiles, fertilizing, etc. [1-3].

Chromium hexa valent Cr (VI) is the most toxic of all chrome species because it is a very strong oxidant, it can attack the respiratory system, kidneys, liver, skin and eyes, [4-7], it is toxic to most organisms when its concentration is above 0.05 mg / L and can cause irritation and damage to human skin [8-10], because of its toxicity it is classified as a human carcinogen by the International Agency for Research on Cancer (IARC) [11, 12].

In most cases, the chromium can be in two common oxidation states Cr (III) and Cr (VI). Chromium hexa valent is carcinogenic and poisonous. Cr (III) is less toxic and can be easily precipitated or adsorbed on a variety of organic and inorganic substances at an alkaline or neutral pH.

Industrial sources such as chromium plating, electronics, metallurgy, wood processing and leather tanning industries release Cr (VI) into the effluent. These effluents must be treated before they are discharged into surface waters. The methods generally used to treat waste water containing hexa valent chromium are adsorption, ion exchange and reduction by chemical methods followed by coagulation-precipitation [13], It appears that even after treatment, the water leaves the treatment plants with low Cr (VI) concentrations and is generally slightly higher than the CMA.

The heterogeneous catalysis photo appears as one of the least expensive POAs to be put in place to lead to the degradation of organic compounds [14, 15], reduction of metal cations [16-18] or the mixture of the two [19-21]. This method is based on the excitation of a semiconductor by a radiation most often ultraviolet. Among the photocatalysts, titanium oxide, a very coveted and highly used semiconductor, gives good catalytic photo-yields by its anatase phase. However, it has two major problems: its relatively large band gap (3.2 eV), which makes its spectral range limited in the UV region (it does not absorb in visible light), a high rate of charge recombination (electron / hole).

In the present work, we have been interested in the photo reduction of hexavalent chromium by Bi-Zn co-doped TiO_2 which has already been used in the degradation of an organic pollutant indigo carmine [22], the material was characterized by ATG, DRX, MEB, BET, UV-DRS, XPS and published in my first article [22], this material exhibits a high photocatalytic activity under visible light in the reduction of hexavalent chromium in comparing with TiO_2-P25.

2. Experimental

2.1. Adsorption study in the absence of light

2. 1.1. In the presence of oxalic acid

In order to study the chromium hexavenlent adsorption kinetics by Bi-Zn-TiO_2 and TiO_2-P25, 100mL of a 10 mg / L chromate solution and 0.1 g of material were placed under stirring away from light with a 10 mg / L oxalate solution at pH 3.2 and at room temperature. Samples were taken at regular time intervals for 2 hours and then centrifuged. The equilibrium concentrations of Cr (VI) in the supernatant, after complexing with diphenylcarbazide, are analyzed at 540 nm using a HACH DR4000 UV-vis spectrophotometer.

2. 1.1. In the absence of oxalic acid

Under the same conditions as above, 100 mL of a solution of Cr (VI) 10 mg / L at natural pH and 0.1 g of material (Bi-Zn-TiO_2, TiO_2-P25) were suspended under agitation away from light. Samples were taken at regular time intervals for 180 minutes and then centrifuged. The residual Cr (VI) concentration in the supernatant was analyzed as above.

2.2. Kinetics of photo-reduction of chromium VI

The photocatalytic activity of Bi-Zn-TiO_2 was studied in comparison with the commercial TiO_2-P25 Degussa. The photo-reduction kinetics studies were undertaken with initial concentration ranging from 10 et 20mg/L of hexavalent chromium at pH 3,2 and a room temperature, and with 1g/L of solid/solution ratio, and with a ratio of Cr(VI)/oxalate was equal to one ($R_{(Eq\text{-}g.\ Oxa/Eq\text{-}g.Cr(VI))}$=1). A 250mL open Pyrex cylindrical beaker was used as photo-reactor to provide photocatalytic reduction experiments of 100mL of hexavalent chromium solution under visible light irradiation. The pH was measured at the beginning but not adjusted during the test. No oxygenation was introduced in the solution. The photo-reactor was placed in cooled bath with circulating water in order to keep the room temperature stable. Aliquots were taken, centrifuged and the residual concentrations of Cr (VI) in the supernatants were determined as above.

The light source used for the reduction of hexavalent chromium is the same source used for carmine indigo degradation and under the same operating conditions [22], the emission spectrum of the lamp is represented in my work which has already been published [22].

2.2. In the absence of the catalyst: direct photolysis

The effect of the absence of photocatalyst was carried out in the presence of oxalate under visible light. This study was carried out in a 250 mL beaker containing 100 mL of Cr (VI) and oxalate solution (R (Eq-g, Oxa / Eq-g, Cr (VI) L in the absence of the catalyst at acidic pH and at ambient temperature. The irradiation is ensured by a visible lamp of 500 W at a distance of 17 cm from the solution. The samples of about 5 ml are carried out at regular, centrifuged times and the residual Cr (VI) concentrations in the supernatant were analyzed as above.

2.3. In the presence of the catalyst

The study of the photo-reduction kinetics of Cr (VI) in the presence of the Bi-Zn-TiO_2 and TiO_2-P25 catalyst with a solid / solution ratio of 1 g / L was carried out in the same way as photolysis at a different Cr (VI) concentration of between 10 and 20 mg / L at a pH of 3.2 and at room temperature.

A sample is first taken from each concentration to confirm the value of its initial concentration (t = -30 min), then the solution is allowed to stir in the absence of light, in contact with material, for minutes until reaching the adsorption equilibrium. After this contact period, a sample is taken to be analyzed (t = 0min), then the lamp is switched on. The photocatalytic reduction of Cr (VI) is monitored by sampling at regular times. After centrifugation of the samples taken, the residual Cr (VI) concentrations in the supernatant were analyzed as above.

2.4. Effect of the concentration of oxalic acid on the reduction of Cr (VI)

The effect of the concentration of oxalic acid on the photo-reduction kinetics of Cr (VI) was carried out with different gram-equivalence ratios of oxalic acid to Cr (VI), this ratio varies between 0 and 2 for a Cr (VI) concentration of 10 mg / L while maintaining the solid / solution ratio of 1 g / L and the natural pH of the solution of 3.2.

2.5. Effect of the pH of the solution on the reduction of Cr (VI)

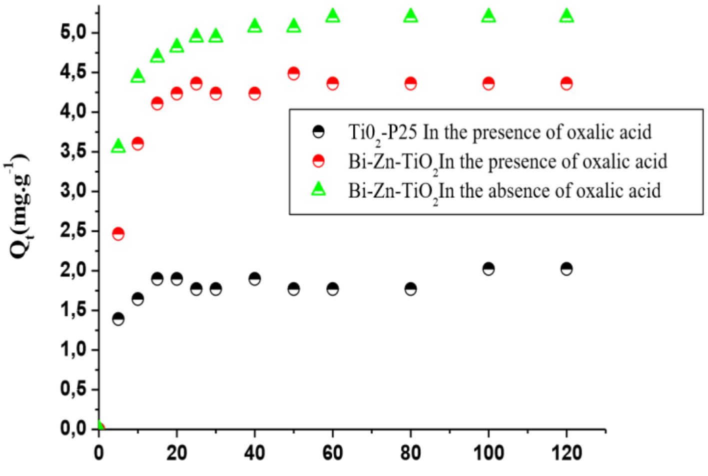
The pH effect of the solution on the photo-reduction kinetics of Cr (VI) was carried out with different pH values (3.2, 6.2, 7.2) for a Cr (VI) of 10mg/L, maintaining the solid/solution ratio of 1 g/L and with a ratio of oxalic acid to Cr (VI) equal to one (R (Eq-g, Oxa/)=1).

3. Results and discussion

3.1. Adsorption study in the absence of light

The study of the adsorption kinetics was carried out with the two materials TiO_2-P25 and BiZn-TiO_2. The variation of the quantities of Cr (VI) adsorbed as a function of the contact time is plotted in the form of a graph in Fig. 1. The phenomenon of adsorption of chromium (VI) by the two materials is rapid, after twenty minutes, in many works concerning the fixation of electrolytes such as cadmium, zinc, lead, copper by clays, takes place in 10 to 15 minutes [23, 24], this speed can probably be explained by the fact that it is an ion exchange process.

The maximum amount of chromium (VI) adsorbed in the presence of oxalate by the two materials is 2.0 and 4.2 mg / g for TiO_2-P25 and Bi-Zn-TiO_2 respectively. These values are very low, however, the Bi-Zn-TiO_2 material displays a high equilibrium adsorption vis-à-vis Cr (VI) compared to that of TiO_2-P25, and this may be due to surface characteristics (volume and pore diameter) of Bi-Zn-TiO_2 different from those of TiO_2-P25 [22].



Contact time (min)

Fig. 1. Chromium (VI) adsorption kinetics by TiO_2-P25 and Bi-Zn-TiO_2 in the presence and absence of oxalic acid.

Moreover, the amount of equilibrium adsorption of chromium (VI) adsorbed by Bi-Zn-TiO_2 in the absence of oxalate is slightly greater than that adsorbed in its presence. Indeed, equilibrium adsorption amounts of Cr (VI) of 4.4 and 4.2 mg / g were obtained in the absence and in the presence of oxalate respectively. The adsorption of Cr (VI) by this material was slightly competed by the presence of oxalate anion ($C_2O_4^{2-}$), so that a slight oxalate adsorption probably took place on the surface of the material instead of chromate anions (CrO_4^{2-}).

3.2. Photocatalytic reduction study

a) - Study of the effect of the absence of the material

The photo-reduction kinetics of Cr (VI) by direct photolysis for 180 minutes (in the absence of material and in the presence of oxalic acid) is presented in Fig 2. It appears from the graph that the Cr (VI) is resistant to the irradiations of the visible light. Indeed, a photo-reduction rate of 14% was obtained after 15 minutes of irradiation under the visible lamp despite the presence of oxalic acid and at pH = 3.2. This low level of reduction remained unchanged even after 120 minutes, this result may be due to an oxidation-reduction reaction between oxalates and Cr (VI). However, and even if this reaction can take place, it is very slow.

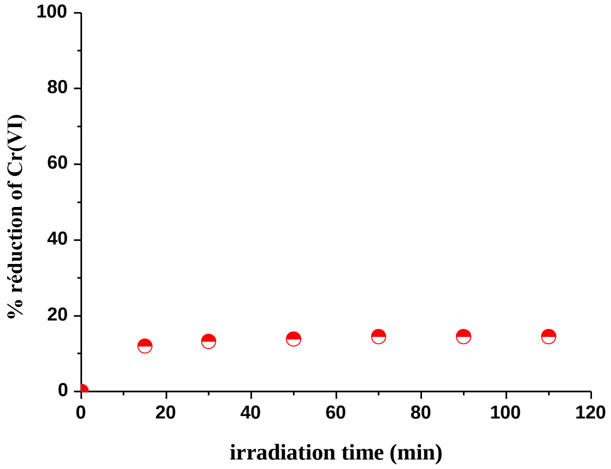


Fig. 2. Kinetics of photo-reduction of chromium (VI) in the absence of material: (Ci (Cr (IV) = 10 mg / L, Ci (A, Ox) = 10 mg/L).

b) - Study of the effect of presence of the material

The kinetic study of photo-reduction of Cr (VI) as a function of the initial concentration was carried out by varying the initial Cr (VI) concentrations from 10 to 20 mg / L with a ratio of oxalic acid and Cr (VI) is equal to one. Fig 3 reports the monitoring of the residual Cr (VI) concentration of its photo-reduction by the two materials Bi-Zn-TiO_2 and TiO_2-P25 as a function of time. The curves show that chromium (VI) under irradiation of visible light and in the presence of the material disappears with time, this elimination is probably a reduction in chromium (III) or even more. The time required for its reduction varies according to the initial concentration. Note that chromium (VI) photo-reduction by Bi-Zn-TiO_2 is faster than that observed for TiO_2-P25.

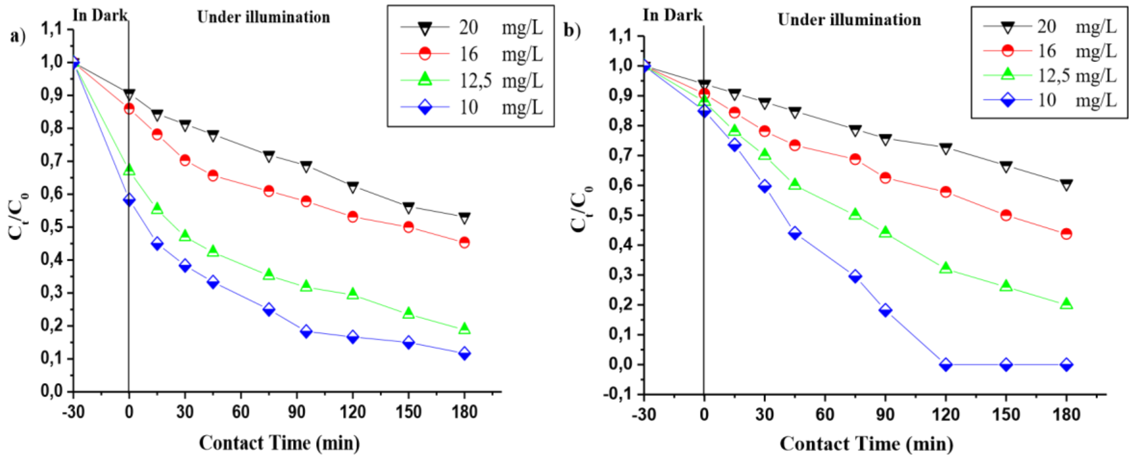


Fig. 3. (a and b) photo-discoloration under visible light at different concentrations of chromium (VI) with TiO_2–P25 and Bi–Zn–TiO_2 respectively.

The plots of the graphs in Figure 3 reveal a difference in the efficiency between the two materials in the photo-reduction of Cr (VI). Indeed, Bi-Zn-TiO_2 showed better photo-catalytic reduction rates than those obtained with TiO_2-P25. In addition, the photo-reduction time is shorter with Bi-Zn-TiO_2 than with TiO_2-P25. By way of example, for an initial Cr (VI) concentration of 10 mg / L, the photo-reduction is 100% in 120 minutes whereas it is 60.2% during the same period, the results of the UV-visible DRS characterization shows that the material Bi-Zn-TiO_2 absorbs in the visible region in relation to that of TiO_2-P25 [22].

3.3. Effect of oxalic acid concentration on Cr (VI) reduction

The effect of the concentration of oxalic acid on the kinetics of photo-reduction of Cr (VI) was carried out with different ratio of gram equivalent of oxalic acid to Cr (VI), this ratio varies between 0 and 2 for a concentration of Cr (VI) of 10 mg / L maintaining the solid / solution ratio of 1 g / L and at the natural pH of the solution of 3.2. The results show that the rate of photo-reduction increases as the ratio of gram equivalent of the oxalic acid / Cr (VI) ratio increases to a ratio of 1 (Table 1). Indeed, after 120 min of irradiation, a total (100%) degradation is obtained, beyond ratio 1, the photo-reduction rate during the same contact time decreases and becomes equal to 60% for a ratio of 2. This drop in efficiency can probably be explained by competitive adsorption between the oxalate and chromate anions at the photocatalyst surface. This also confirms that photo-reduction of Cr (VI) is at the surface and depends on the surface properties of photo-catalysts [22].

The improvement in the photo-reduction rate of Cr (VI) with the increase in the ratio confirms, on the one hand, the importance of the presence of a reducing agent such as oxalate and on the other side, allows to fix the necessary and sufficient dose to ensure the reaction of the photo-reduction and to avoid the excess of the products. The main possible reactions that we can suggest during the process of Cr (VI) reduction on the surface of Bi-Zn-TiO_2 can be described as follows: ○ Photo-excitation of TiO_2:

$$Bi - Zn - TiO_2 \xrightarrow{h\nu\ (visible)} Bi - Zn - TiO_2(e^- + h^+)$$ **Eq.-1**

○ Reaction of additives with positive holes:

$h_{BV}^{+} + C_2O_4^{2-} \rightarrow C_2O_4^{\bullet -}$

Eq.-2 $2H_2O + 4h^+ \rightarrow 2O_2 + 4H^+$

Eq.-3 ○ Reduction of Cr (VI) by the radicals of the additives:

$CrO_4^{2-} + C_2O_4^{\bullet -} \rightarrow Cr^{3+} + photo\ products$ **Eq.-4**

- Reduction of Cr (VI) by electrons:

$$CrO_4^{2-} + 14H^+ + 6e_{BC}^- \rightarrow 2Cr^{3+} + 7H_2O \qquad \textbf{Eq.-5}$$

$$Cr^{3+} + 3e_{BC}^- \rightarrow Cr^0 \qquad \textbf{Eq.-6}$$

Table 1.
Reduction rates and apparent rate constants as a function of the equivalent g-ratio of oxalic acid.

	% photo-reduction			
	Equivalent-g ratio (Oxalic Acid / Cr (VI))			
Time 15	**0**	**0,5**	**1**	**2**
	50,6	47,5	26,4	25,0
45	52,9	52,5	55,9	33,75
95	54,1	52,5	75,47	52,5
120	54,1	52,5	100,0	60,0
180	54,1	55,0	100,0	67,5
K_{app} (min$_{-1}$)	0,0013	0,0015	0,0135	0,0058

Fig. 4 illustrates the variation of the speed constant Kapp as a function of the equivalent gram ratio between oxalic acid and Cr (VI) for the photo-reduction of the latter in the presence of Bi-Zn-TiO_2.

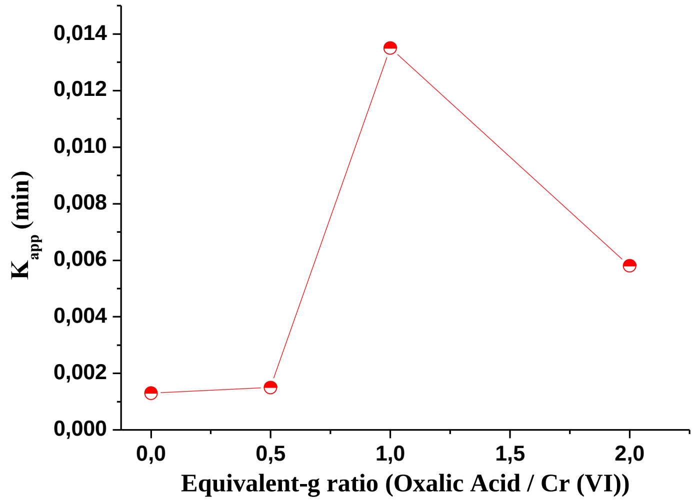


Fig. 4. The effect of the equivalent ratio -gram of oxalic acid and Cr (VI) on the kinetic constant of photo-reduction of Cr (VI) by Bi-Zn-TiO_2 in a solid ratio / solution of 1 g / L and at pH = 3.2.

3.4. Effect of pH of the solution on Cr (VI) reduction

The results of photo-reduction of Cr (VI) under irradiation of visible light at different pH are shown in Figure 5. From this figure, it is obvious that the pH of the solution is a key parameter in the reaction. The reduction rate of Cr (VI) is maximum (100%) for a weakly acidic pH (pH = 3.2), after 120 min of irradiation, however, this rate decreases during the same period at pH = 6.2 (38.82%), and further decreased at neutral pH (pH = 7.2) (17.65%). This result can be explained probably for two reasons:

1. The standard Cr (VI) Cr (III) reduction potential ranges from 1.32 V at pH 0 to 0.38 V at pH 7 [25].
2. The surface charge of the photocatalyst changes as a function of pH, it is probably positively charged at acidic pH, which may explain the electrostatic attraction between chromate ions and the surface of Bi-Zn-TiO_2.

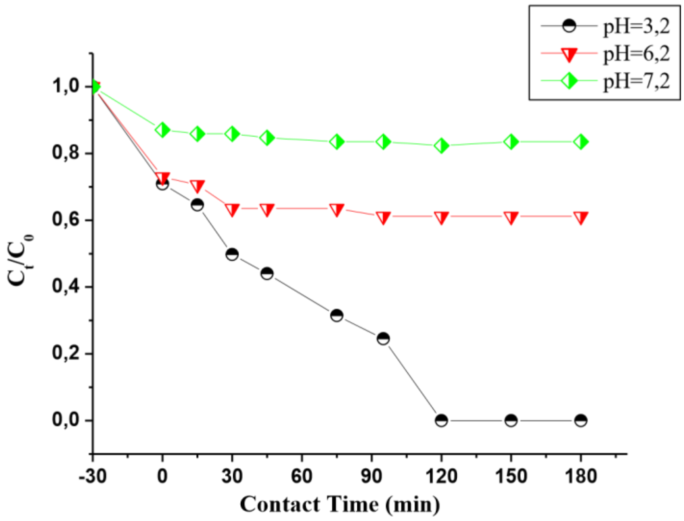


Fig. 5. Effect of the pH of the solution on photo-reduction of Cr (VI) by Bi-Zn-TiO_2, Conditions: [Cr (VI)] = 10 mg / L, [A OX] / [Cr (VI)] = 1.

In order to calculate the apparent rate constants, we have plotted ln (Cicorr / Ct) of Cr (VI) reduction as a function of irradiation time, obtained at different pH values. Fig. 6 representing these curves, shows that it correlates perfectly with the appearance of a line of equation Ln (Cicorr / Ct) as a function of the irradiation time with high correlation coefficients, which makes it possible to deduce that the Cr (VI) reduction follows the reaction of pseudo first order. The results of the reduction rates and the apparent speed constants are reported in Table 2.

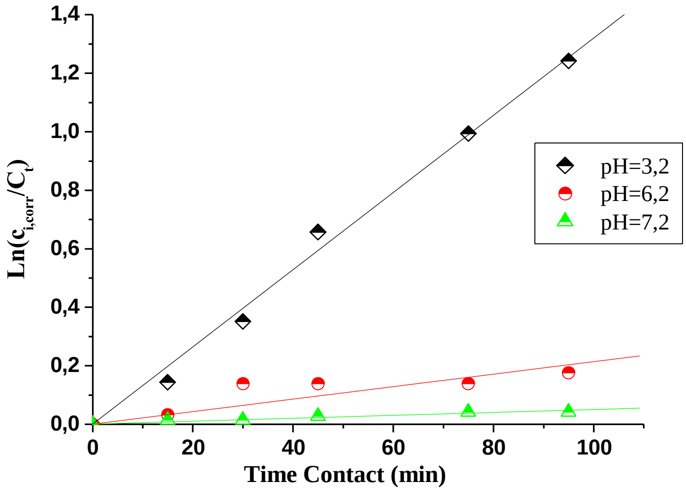


Fig. 6. Kinetics of reduction of Cr (VI) as a function of the pH of the solution according to the pseudo first-order reaction.

Table 2
Reduction rates and apparent rate constants as a function of the pH of the solution.

pH	3,2	6,2	7,2
photoreduction (%)	100	38,82	16,47
K_{app} (min^{-1}) $*10^4$	135,4	22,0	5,1

Fig.7 illustrates the variation of the Kapp speed constant as a function of the pH of the solution for chromium (VI) photo-reduction in the presence of Bi-Zn-TiO_2. It is known that the chromate oxidation reactions (Cr (VI)) are carried out in a strongly acidic medium at theoretically negative pH values, the results presented in the table show that it is possible to reduce by photo-catalytic Cr (VI) even at slightly acidic pH as 3.2. This photo-reduction can take place even at neutral pH but with slow kinetics. This efficiency is due to the interaction between the chromates and the electrons of the conduction band after irradiation of the material with light. Indeed, it has been shown that chromates play a role of electron scavengers in the determination of the species responsible for degradation of organic compounds [22, 26, 25].

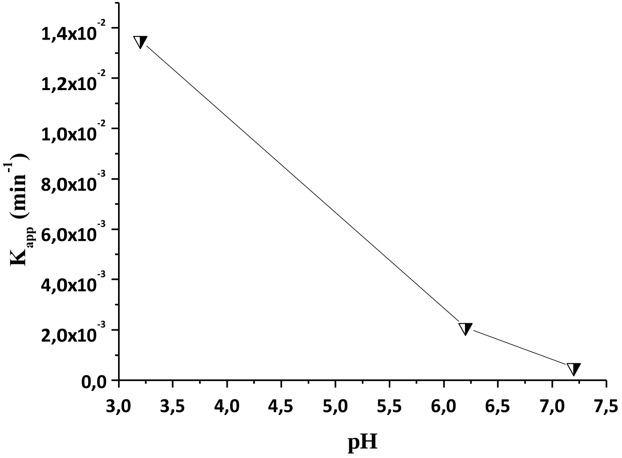


Fig. 7. Variation of the rate constant as a function of the pH of the solution for chromium (VI) photo-reduction by BiZn-TiO_2.

Conclusion

In the present work, Bi–Zn–TiO_2 was prepared by layered double hydroxide synthesis route and characterized by TGA, SEM, XRD, N2 Adsorption/desorption, UV–vis DRS, and XPS. The obtained material was investigated for the photocatalytic discoloration of indigo carmine and photo reduction of chromium hexavalent under visible light irradiation in comparison of commercial TiO_2–P25. The results of the kinetics of the photocatalytic reduction of Cr (VI) in the presence of oxalic acid showed a total photo-reduction of Cr (VI) after 120 and 240 min in the presence of Bi-Zn-TiO_2 and TiO_2-P25, respectively, for a Cr (VI) concentration of 10 mg/L with a weakly acidic pH (3.2). In the study of the effect of the absence and presence at different concentrations of oxalic acid on the reduction of Cr (VI) at low acid pH by Bi-ZnTiO_2, the results expressed in terms of reduction rate in Gram-equivalent ratio oxalic acid/Cr(VI) function (R = 0, 0.5, 1 and 2) have shown that a 54% Cr (VI) of reduction rate was obtained in the absence of oxalic acid, however, this rate increases with increasing oxalic acid concentration to a maximum for a ratio of 1 gram equivalent acid/Cr(VI) of 1, beyond this ratio, the efficiency probably decreases due to a competitive adsorption between chromate and oxalate anions. The results of the pH effect (3.2, 6.2 and 7.2) on the photo-reduction of Cr (VI) show that a better photocatalytic reduction was obtained in weakly acidic medium.

References

[1] J. K. Yang, S. M. Lee, Removal of Cr(VI) and humic acid by using TiO_2 photocatalysis, Chemosphere, 63 (2006) 1677-1684.

[2] G. S. Khorramabadi, R. D. C. Soltani, A. Rezaee, A. R. Khataee, A. J. Jafari, Utilisation of immobilised activated sludge for the biosorption of chromium (VI), Can. J. Chem. Eng. 90 (2012) 1539-1546.

[3] V. K. Gupta, B. Gupta, A. Rastogi, S. Agarwal, A. Nayak, A comparative investigation on adsorption performances of mesoporous activated carbon prepared from waste rubber tire and activated carbon for a hazardous azo dye—Acid Blue 113, J. Hazard. Mater. 186 (2011) 891-901.

[4] S. A. Katz, H. Salem, The Toxicology of Chromium with Respect to its Chemical Speciation: a Review, J. Appl. Toxicol. 13 (1993) 217-224.

[5] M. Shirzad-Siboni, S. Azizian, S. M. Lee, The Removal of Hexavalent Chromium from Aqueous Solutions Using Modified Holly Sawdust: Equilibrium and Kinetics Studies, Environ. Eng. Res. 16 (2011) 55-60.

[6] A. K. Jain, V. K. Gupta, S. Jain, Suhas, Removal of Chlorophenols Using Industrial Wastes, Environ. Sci. Technol. 38 (2004) 1195-1200.

[7] S. Karthikeyan, V. K. Gupta, R. Boopathy, A. Titus, G. Sekaran, A new approach for the degradation of aniline by mesoporous activated carbon as a heterogeneous catalyst: kinetic and spectroscopic studies, J. Molecul. Liq. 173 (2012) 153-163.

[8] J. R. Memon, S. Q. Memon, M. I. Bhanger, M. Y. Khuhawar, Banana Peel: A Green and Economical Sorbent for Cr(III) Removal, Anal. Environ. Chem. 9 (2008) 20-25.

[9] A. Mittal, D. Kaur, A. Malviya, J. Mittal, V.K. Gupta, Adsorption studies on the removal of coloring agent phenol red from wastewater using waste materials as adsorbents, J. Colloid Interface Sci. 337 (2009) 345-354.

[10] A. Mittal, J. Mittal, A. Malviya, D. Kaur, V. K. Gupta, Adsorption of hazardous dye crystal violet from wastewater by waste materials, J. Colloid Interface Sci. 344 (2010) 497-507.

[11] S. X. Liu, Bull, Removal of Copper (VI) from Aqueous Solution by Ag/TiO_2 Photocatalysis, Environ. Contam. Toxicol. 74 (2005) 706-714.

[12] M. Shirzad Siboni, M. T. Samadi, J. K. Yang, S. M. Lee, Photocatalytic reduction of Cr(VI) and Ni(II) in aqueous solution by synthesized nanoparticle ZnO under ultraviolet light irradiation: a kinetic study, Environ. Technol. 32 (2011) 1573-1579.

[13] Q. W. Wang, A. T. Lemley, Oxidation of diazinon by anodic Fenton treatment, Water Res. 36 (2002) 3237-3244.

[14] C. S. Turchi, D. F. Ollis, Photocatalytic degradation of organic water contaminants: mechanisms involving hydroxyl radical attack. J. Catal., 122 (1990)178-192.

[15] J.M. Herrmann, J. Disdier, P. Pichat, S. Malato, J. Blanco, TiO_2-based solar photocatalytic detoxification of water containing organic pollutants, Case studies of 2,4dichlorophenoxyacetic acid (2,4-D) and of benzofurane. Appl. Catal., B 17 (1998)15-23.

[16] T. Iwata, M. Ishikawab, R. Ichino, M. Okido, Photocatalytic reduction of Cr(VI) on TiO_2

film formed by anodizing. Surf. Coat. Technol., 169 -170 (2003) 703-706. **[17]** S. Chakrabarti, B. Chaudhuria, S. Bhattacharjeea, A. K. Rayb, B. K. Dutta,
Photoreduction of hexavalent chromium in aqueous solution in the presence of zinc oxide as semiconductor catalyst. Chem. Eng. J., 153 (2009) 86-93.

[18] W. Ketir, A. Bouguelia, M. Trari. Photocatalytic removal of M_{2+} (Ni_{2+}, Cu_{2+}, Zn_{2+}, Cd^{2+},Hg^{2+} and Ag^{+}) over new catalyst $CuCrO_2$, J. Hazard. Mater., 158 (2008) 257-263. **[19]** M.R. Prairie, L.R. Evans, B.M. Stange, S.L. Martinez, An investigation of TiO_2 photocatalysis for the treatment of water contaminated with metals and organic chemicals, Environ. Sci. Technol., 27(1993) 1776-1782.

[20] X.R. Xu, H.B. Li, J.D. Gu, Simultaneous decontamination of hexavalent chromium and methyl tert-butyl ether by UV/TiO_2 process. Chem., 63 (2006) 254-260.

[21] S.G. Schrank, H.J. José and R.F.P.M. Moreira, Simultaneous photocatalytic Cr(VI) reduction and dye oxidation in a TiO_2 slurry reactor. J. Photochem. Photobiol., A 147 (2002) 71-76.

[22] B. Benalioua, M. Mansoura, A. Bentouamia, B. Boury,E. H. Elandaloussia, The layered double hydroxide route to Bi–Zn co-doped TiO_2 with highphotocatalytic activity under visible light. J. Hazard. Mat. 288 (2015) 158–167.

[23] S. Chiron, A. Fernandez-Alba, A. Rodriguerz, E. Garcia- Calvo (2000) «Pesticide chimical oxidation : state of- the-art » Water. Res. Vol. 34, PP: 366-377.

[24] A. B. C. Alvares, C. Diaper, S. A. Parsona (2001) "Partial oxidation by ozone to remove recalcitrance from wastewaters-a review". Environ. Technol. Vol. 22, P: 409-427.

[25] T. Aarthi, G. Madras, Photocatalytic reduction of metals in presence of combustion synthesized nano-TiO_2. Catal. Commun., 9 (2008) 630-634.

[26] F.-T. Li, X.-J. Wang, Y. Zhao, J.-X. Liu, Y.-J. Hao, R.-H. Liu, D.-S. Zhao, Ionic-liquidassisted synthesis of high-visible-light-activated, N–B–F-tri-doped mesoporous TiO_2 via a microwave route, J. Appl. Catal. B 144(2014) 442-453.

[27] L. M. Pastrana-Martinez, S. Morales-Torres, A.G. Kontos, N.G. Moustakas, J.L. Faria, J.M. Dona-Rodriguez, P. Falaras, A.M.T. Silva, TiO_2, surface modified TiO_2 and graphene oxide-TiO_2 photocatalysts for degradation of water pollutants under near-UV/Vis and visible light, Chem. Eng. J. 224 (2013) 17–23.