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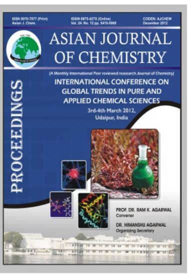

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Heterogeneous Photocatalytic Decolourization of Cobalamine in the Presence of Aqueous Titanium Dioxide Suspensions†

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The objective of this research was to investigate experimentally the decolourization of cobalamine (α-(5,6-dimethylbenzimidazolyl) cobamidcyanide with a chemical formula ($C_{63}H_{88}N_{14}O_{14}CoP$) under different conditions. The photocatalytic decolourization of cobalamine was carried out in aqueous solution of titanium dioxide (TiO_2 Degussa P25) using UVA source of irradiation. The results showed that a complete decolourization was achieved in less than 30 min, however the percent of mineralization was only 80 % after 7 h of irradiation under same conditions. It was noticed that pH of reactants was changed at the end of reaction towards 7 independent on the initial pH. The effect of various parameters, such as photocatalyst amount, cobalamine concentration, addition of H_2O_2 and flow rate of O_2 on photocatalytic oxidation were investigated. The results indicated that the photocatalytic decolourization of cobalamine was well described by pseudo first order kinetics according to the Langmuir-Hinshelwood model. The effect of temperature on the efficiency of photodecolourization of cobalamine was also studied in the range 278-298 K. The activation energy was found to be equal to 22 ± 1 kJ mol^{-1}.

Key Words: Cobalamine, Photocatalytic decolourization, TiO_2, Kinetic study.

INTRODUCTION

Porphyrins are aromatic compound have a highly conjugated system, which are composed of four smaller 5-membered heterocycles, called pyrroles, that contain one nitrogen and four carbon atoms. In porphyrins, one carbon, typically referred to as the meso-carbon, serves to connect each of the four pyrrole rings[1]. These compounds which many occur in nature, such as in green leaves and red blood cells. Porphyrins characterized by the presence of four modified pyrrole subunits interconnected at their a carbon atoms with methine bridges (=CH-)[2].

Porphyrins bind metals to form complexes. Most metals can be inserted into the metal-free porphyrins such as iron, magnesium and cobalt to form metalloporphyrins. The metalation reaction occur by substitution the metal in corrin ring in solution and lead to loss of two protons and increase the activity of ring[3].

Cobalamine contain a cyano group (-CN), hydroxyl group (-OH), methyl group ($-CH_3$) or a 5'-deoxyadenosyl group, respectively[2].

Cobalamine, also known as vitamin B_{12}, a complex organometallic compound, formed by the situated the cobalt atom in a corrin ring. Cobalamine cannot be synthesized in the human body, the main source of cobalamine is animal[4].

Cobalamine, soluble in water have the molecular formula $C_{63}H_{88}N_{14}O_{14}CoP$, mole mass 1355.37 g/mol and systematic (IUPAC) name α-(5,6-dimethylbenzimidazolyl) cobamidcyanide[5].

Semiconductor TiO_2 is the most widely used heterogeneous photocatalyst for degradation of various types of organic pollutants in wastewater. TiO_2 and irradiation source UV or visible lights can be used in photocatalysis systems[6,7].

Photolysis of cobalamine in aqueous solution produced hydroxocobalamine. The kinetics of photolysis was found to follow zero-ordar kinetics at different pH and the rate was catalyzed by both hydrogen and hydroxyl ions[8].

The idea of this research was derived from the announcement of Nine-Sigma company about decolourization of porphyrin species. The company aimed to decolourize porphyrin species to prevent staining or noticeable transfer to cloth and other absorbant surfaces.

EXPERIMENTAL

Photocatalytic reactions were carried out in a batch photoreactor with the radiation source type Philips (CLEO), Poland, mercury lamps containing 6 lamps with 15 W for each. Aqueous suspensions of titanium dioxide (TiO_2) containing cobalamine in a quartz beaker, under magnetic stirring, were

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irradiated in light of wavelength 365 nm with an irradiation intensity of 1.3 mW cm^{-2}. In all experiments, the required amount of the catalyst was suspended in 100 cm^3 of aqueous solution of cobalamine. After illumination, 2 mL was taken from the reaction suspension, centrifuged at (4,000 rpm, 15 min) in an 800B centrifuge and filtered to remove the particles. The second centrifuge was found necessary to remove fine particle of the titanium dioxide (TiO_2). After the second centrifuge, the absorbance at the maximum wavelength of the cobalamine was measured with UV-visible spectrophotometer at (298.15) K.

RESULTS AND DISCUSSION

UV-Visible spectra of dye: The calibration curve was accomplished by using standard cobalamine aqueous solutions (5, 10, 15, 20, 25, 30, 35 and 40 ppm). The absorbance of each concentration was measured at 550 nm. As shown in Fig. 1.

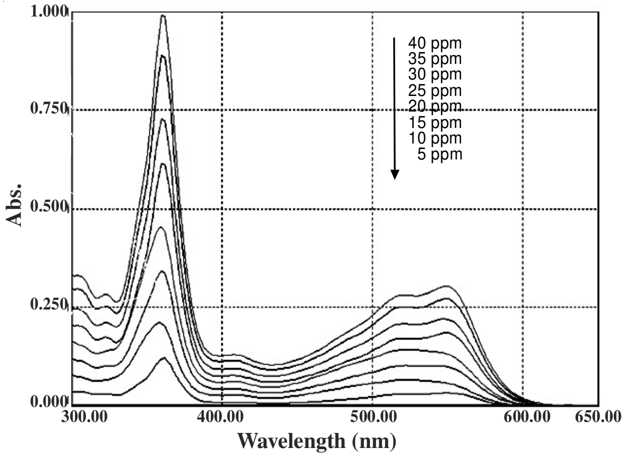

Fig. 1. UV-visible spectra of different concentration of cobalamine

Effect of TiO_2-P25 concentration: The photodegradation efficiency of cobalamine increased with the increase of the amount of catalyst up to a optimum value and then decreased slightly with the increase of the amount of catalyst as shown in Fig. 2. One possible explanation for such behaviour is that It is believed that an increase in the number of catalyst will increase the number of photons absorbed and the number of cobalamine molecules adsorbed. Therefore, the photodegradation rate can be expected to be enhanced on increasing the amount of catalyst due to the increase in total surface area available for contaminant adsorption. However, a further increase of the catalyst concentration may cause light-screening effects[9]. These screening effects reduce the specific activity of the catalyst[10].

Effect of addition of H_2O_2: The effect of addition of H_2O_2 on the degradation rate was studied for photocatalytic degradation of the cobalamine. The results as shown in Fig. 3 show that the degradation rate increases with increases in addition of H_2O_2 from 0.1 to 1.5 mmol/L, becomes maximum at 1.5 mmol/L and then. OH starts decreasing from 1.5 to 4.0 mmol/L with further increase in the concentration of H_2O_2[11].

This behaviour is due to the increasing the concentration of hydroxyl radical since it inhibits the hole-electron recombination according to the following equations.

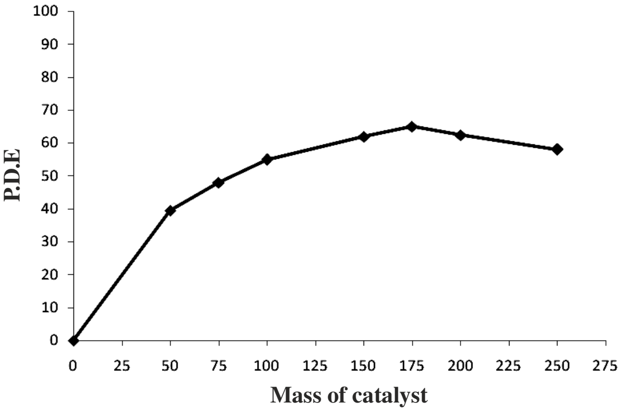

Fig. 2. Effect the masses of TiO_2 (Degussa P25) on photodecolourization efficiency of cobalamine

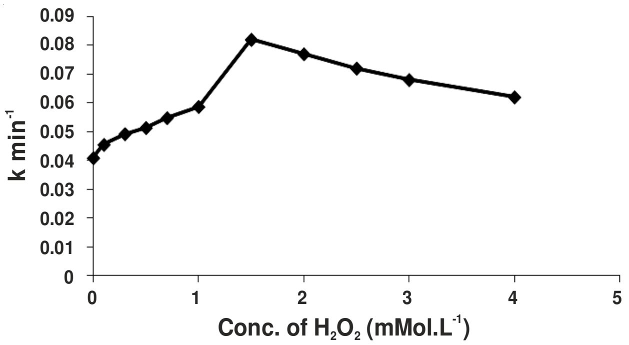

Fig. 3. Effect of addition of H_2O_2 on the apparent rate constant of photodecolourization of cobalamine

$$H_2O_2 + e^-_{cb} \longrightarrow {}^\bullet OH + OH \tag{1}$$

$$H_2O_2 + {}^\bullet O_2 \longrightarrow {}^\bullet OH + OH + O_2 \tag{2}$$

At high H_2O_2 dosage the photocatalytic processes decreases because of its hydroxyl radical scavenging effect, according to the following equations[12].

$$H_2O_2 + {}^\bullet OH \longrightarrow H_2O + HO_2^\bullet \tag{3}$$

$$HO_2^\bullet + {}^\bullet OH \longrightarrow H_2O + O_2 \tag{4}$$

Effect of temperature: The results in Fig. 5 show the photocatalytic degradation of cobalamine on TiO_2 Degussa p-25 with different temperature in the range 278.15-298.15 K and rate constant was determined from the a pseudo first order plots[13].

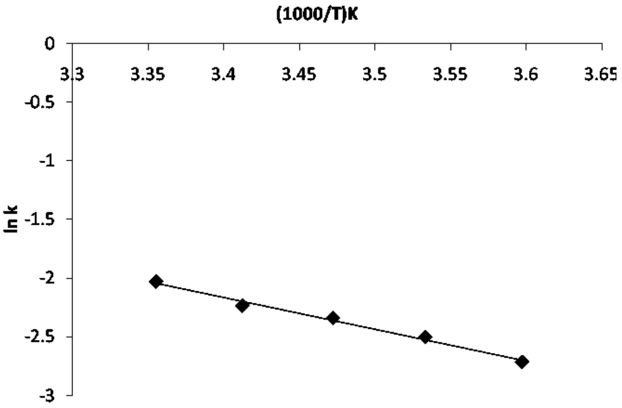

Fig. 4. Arrhenius plot for photocatalytic decolourization of cobalamine on TiO_2 Degussa P25

From Fig. 5, the results show that the degradation efficiency of cobalamine gradually increased as the temperature increased. The increase in temperature leads to the contribute the generation of free radicals[14]. Arrhenius plot shows that the activation energy for photocatalytic degradation of cobalamine is equal to 22 ± 1 kJ mol^{-1} [15].

Conclusion

Complete decolourization of cobalamine was achieved after 24 min. pH was changed at the end of reaction towards 7 (neutral). The photocatalytic process can be expressed by both, the pseudo first order reaction kinetics and the Langmuir-Hinshelwood kinetic model. The temperature is the factor that has the smallest effect on the photocatalytic decolourization of cobalamine. The acti-vation energy was found to be equal to 22 ± 1 kJ mol^{-1}. The controlled experimental indicates that the presence of UV light, oxygen and catalyst were essential for the effective destruction of cobalamine. It is important to choose optimum degradation parameters to obtain a high photocatalytic decolourization rate.

REFERENCES

1. J.L. Sessler, E. Karnas and E. Sedenberg, Porphyrins and Expanded Porphyrins as Receptors. Supramolecular Chemistry: From Molecules to Nanomaterials (2012).
2. G. Jaouen, Bioorganometallics: Biomolecules, Labeling, Medicine, Wiley-VCH, Weinheim (2006).
3. Y. Bai, Photoelectron Spectroscopic Investigations of Porphyrins and Phthalocyanines on Ag(III) and Au(III): Adsorption and Reactivity, Friedrich-Alexander-Universität Erlangen-Nürnberg (2010).
4. G. Weimin, S. Xingcan, W. Lanling, L. Hong and Z. Laijun, *Chin. J. Chem.*, **29**, 662 (2011).
5. V. Herbert, *Am. J. Clinic. Nut.*, **48**, 852 (1988).
6. C. Kormann, D.W. Bahnemann and M.R. Hoffmann, *J. Phys. Chem.*, **92**, 5196 (1988).
7. M.A. Behnajady, N. Modirshahla, M. Shokri and B. Rad, *Global Nest J.*, **10**, 1 (2008).
8. I. Ahmad, W. Hussain and A.A. Fareedi, *J. Pharmaceut. Biomed. Anal.*, **10**, 9 (1992).
9. M.A. Rahman and M. Muneer, *Desalination*, **181**, 161 (2005).
10. J. Lea and A.A. Adesina, *J. Photochem. Photobiol. A*, **118**, 111 (1998).
11. S.K. Kavitha and P.N. Palanisamy, *Int. J. Civil Environ. Eng.*, **3**, 5 (2011).
12. M.S. Mashkour, A.F. Al-Kaim, L.M. Ahmed and F.H. Hussein, *Int. J. Chem. Sci.*, **9**, 975 (2011).
13. A. Mills and S.L. Hunte, *J. Photochem. and Photobiol. A*, **108**, 1 (1977).
14. Z. He, S. Song, H. Zhou, H. Ying and J. Chen, *Ultrason. Sonochem.*, **14**, 300 (2007).
15. F.H. Hussein, A.F. Halbus, H.A.K. Hassan and W.A.K. Hussein, *E-J. Chem.*, **7**, 543 (2010).