

## Combined Photocatalytic Oxidation and Chemical Coagulation for Cyanide and Heavy Metals Removal from Electroplating Wastewater

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**Abstract:** Industrial wastewater from galvanization workshops contains high concentrations of copper ( $6.5 \text{ mg l}^{-1}$ ), chromium ( $60 \text{ mg l}^{-1}$ ), nickel ( $283 \text{ mg l}^{-1}$ ), zinc ( $63.5 \text{ mg l}^{-1}$ ) and cyanide ( $350 \text{ mg l}^{-1}$ ) which are violating the Egyptian environmental standards. The wastewater is highly alkaline. The pH value is around 11.7. Photocatalytic Oxidation using three commercial  $\text{TiO}_2$  specimens was investigated in the present study namely,  $\text{TiO}_2$  Degussa P25 (80% anatase, 20% rutile),  $\text{TiO}_2$  Aldrich (100% anatase) and  $\text{TiO}_2$  Aldrich (100% rutile). The obtained results indicated that  $\text{TiO}_2$  Degussa P25 gave the best photocatalytic activity for the removal of cyanide at the following operating conditions:  $0.25 \text{ g l}^{-1}$   $\text{TiO}_2$  Degussa P25 photocatalyst, pH 11, Temp. of  $298^\circ\text{C}$  and exposure time of 30 min. The efficiency of photocatalytic removal of cyanide was enhanced by the addition of  $\text{H}_2\text{O}_2$  as electron acceptor.  $0.3 \text{ ml/l}$   $\text{H}_2\text{O}_2$  was added to the photocatalytic reaction. The results indicated that cyanide was not detected and residual heavy metals concentrations were  $< 0.05$  in the treated effluent. The treated wastewater can be recycled in the industrial processes or disposed safely into the sewer network.

**Key words:** Metal electroplating • Wastewater • Photocatalytic oxidation

### INTRODUCTION

Egypt has been engaged in a rapidly progressing economic-related industrial development program. The industrial base in the country accommodates a variety of chemical industries that have created several environmental and health problems, the most important of which are those discharging hazardous wastes. A great number of industries such as textile, pulp and paper, printing, iron-steel, petroleum, pesticides, pharmaceuticals and metal finishing, consume large volumes of water and organic-based chemicals. Among the above-mentioned wastes, the most worrying ones from an environmental point of view are those containing non-biodegradable or persistent compounds. Since these compounds remain unaffected in the food chain, they cause a series of diverse and irreversible damage to the environment and the health of the people [1]. Industrial effluents generated from metallic industries, electroplating, steel hardening,

synthetic rubber production, organic synthesis usually contain free and metal/cyanide complexes. Considering the hazardous and acute toxicity of this type of wastewater for living organisms, the treatment of cyanide wastewaters prior to discharge into the waterways is attracting the attention of the public and regulatory authorities [2,3]. A number of methods are currently available for cyanide remediation with varying degrees of effectiveness, namely biological treatment [4,5], chemical oxidation [5-7], electrochemical decomposition [8-11], photocatalytic [12-16] and catalytic oxidation [17,18]. The most common method for treating cyanides is the alkaline chlorination which results in the formation of a highly toxic intermediate, the cyanogen chloride and chlorinated VOC's in case of organic material presence. These compounds and residual chlorine create additional environmental problems. Consequently, there is a growing need for alternative non-chlorine methods, for destroying cyanides. The use of biological treatment is limited to

very low concentrations of cyanides [19] and therefore is not applicable for wastewater discharged from most industries. Recently, photocatalytic degradation of cyanides using several powdered semiconductors; TiO<sub>2</sub>, ZnO, Fe<sub>2</sub>O<sub>3</sub>, ZnS and CdS have been extensively studied. It has been found that these metal oxides are very effective because of their chemical stability. However, anatase, a polymorph of TiO<sub>2</sub> was preferred due to its high quantum efficiency for photoconversion and its stable formation of an electron-hole pair. Also, heterogeneous photocatalysis has shown a high efficiency for the removal, not only of free cyanides [6,7] but also of iron [8,9], copper [10] and gold cyanocomplexes [11]. The present work is focused on the study of the photocatalytic performance of different types of TiO<sub>2</sub> for achieving the simultaneous reduction-oxidation of cyanide from real industrial-wastewater solutions. The objective of the present study is to develop an appropriate technique to segregate and oxidize the cyanide ions to carbon dioxide and nitrogen; and suggest an integrated treatment option for the wastewater to comply with environmental laws in Egypt.

## EXPERIMENTAL WORK

**Description of Production Processes:** Wastewater discharged from a cluster of galvanization workshops as small size enterprise located at Dakhlyia Governorate provided the material of this study. The workshops discharge their wastewater into the sewerage network without any treatment. Wastewater discharged from the workshops during the two working shifts; is about 25.5m<sup>3</sup>/day. The production processes includes metal forming and shaping, surface preparation (dry cleaning/acid cleaning), rinsing and surface finishing by galvanization in both acidic and cyanide alkaline bath and electroplating (nickel/ chrome). Manufacturing operation processes in the workshops under investigation are shown in Figures [1,2].

**Photocatalytic Oxidation:** Three commercial TiO<sub>2</sub> specimens were tested in this study. TiO<sub>2</sub> Degussa P25 (80% anatase, 20% rutile), TiO<sub>2</sub> Aldrich (100% anatase) and TiO<sub>2</sub> Aldrich (100% rutile) were tested without any preliminary treatment. The experiments were performed in Pyrex batch photoreactor, of cylindrical shape, containing 400 ml of the reaction mixture. For all runs, the amount of catalyst suspended in the cyanide solution was kept

constant at 0.25 g l<sup>-1</sup>. The constant catalyst content among the various runs guaranteed that the irradiation conditions of suspension did not change. A medium pressure Hg lamp (Heraeus-Noblelight 150 W/cm<sup>2</sup>), immersed within the suspension was used as UV-radiation source. It was surrounded by a Pyrex jacket that allowed both refrigeration by circulating cool water and to cut-off any radiation with wavelength below 300 nm. The lamp emission spectrum in the near-UV region had a large emission band centered at 365 nm. In order to increase the efficiency of the illumination, the whole reactor was lined with aluminum foil. Ports at the photoreactor's upper section allowed sampling and the flow of gases. A magnetic stirrer guaranteed satisfactory powder suspension and the uniformity of the reacting mixture. The suspension temperature was 298°C for all the runs. Figure (3) shows the schematic diagram of the experimental setup of the photocatalytic oxidation. Photocatalytic runs were operated according to the following procedure: the catalyst (0.25 gl<sup>-1</sup>) was added in the dark to the cyanide solution and allowed to equilibrate for about 30 min. Oxygen was bubbled during this stage in order to ensure the availability of oxidant gas in the solution. The irradiation time was taken at the moment when the lamp was switched on. Samples for analyses were withdrawn at fixed intervals of time. For recovery of the catalyst, the residual was filtered through 0.45 μm membrane (HA, Millipore) for separation and regeneration. The cyanide concentration was analyzed according to APHA [20]. The removal efficiency of CN<sup>-</sup> was estimated by applying the following equation.

$$\text{Removal Efficiency (\%)} = \left( \frac{C_0 - C}{C_0} \right) \times 100$$

Where C<sub>0</sub> is the original cyanide content and C is the residual cyanide in solution.

**Physico-Chemical Treatment:** In order to precipitate residual heavy metals; chemical coagulation- flocculation-precipitation was carried out after photocatalytic oxidation using suspension solution of calcium oxide (CaO). The optimum coagulant dose and pH were determined using the jar test procedure. All heavy metal analysis was performed using an Atomic Absorption Spectrometer Varian Specter AA (220) with graphite furnace accessory and equipped with the deuterium arc background corrector before and after treatment according to APHA [20].

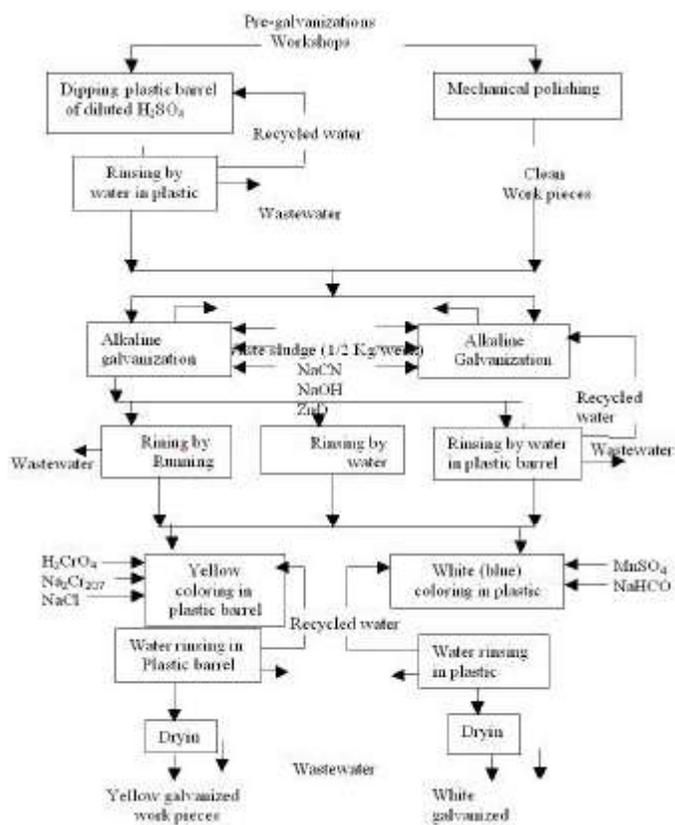


Fig. 1: Block diagram for alkaline cyanide baths

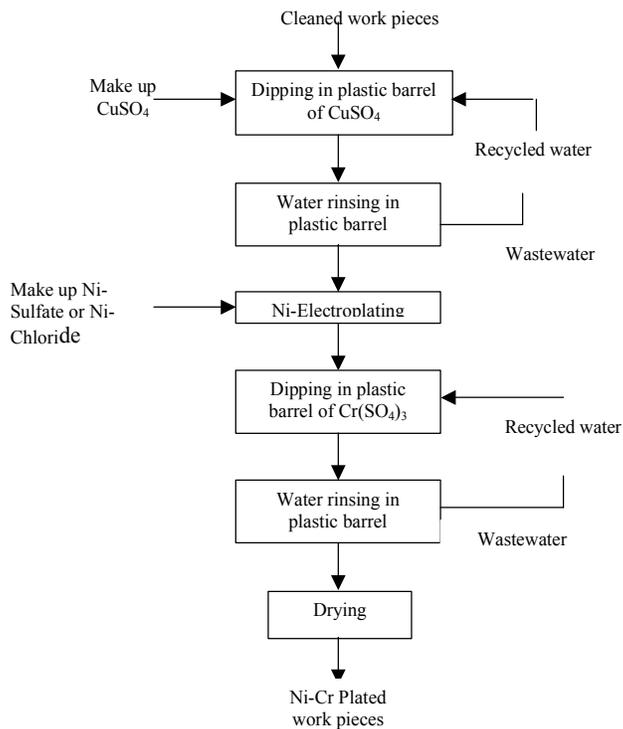


Fig. 2: Block diagram for Ni-Cr Electroplating

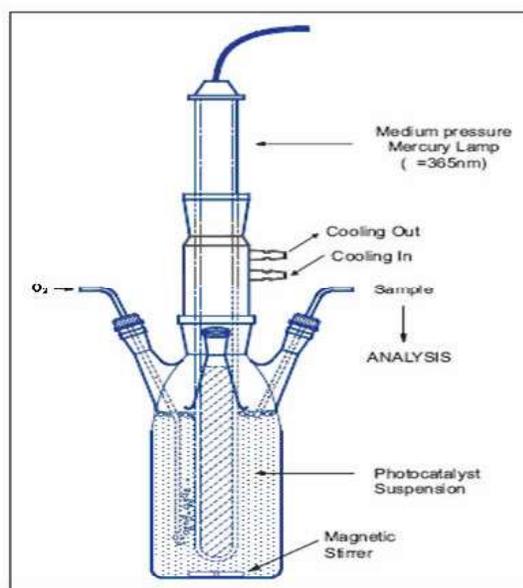
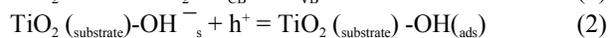
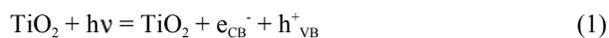


Fig. 3: Schematic Diagram of the Photo Catalytic Unit

## RESULTS AND DISCUSSION

**Wastewater Characteristics:** Wastewater discharged from the company under investigation originates mainly from rinse tank's overflow and fresh water wash. Results of the physiochemical analysis of the wastewater are presented in Table 1. Available data indicates that the wastewater contains high concentrations of copper (6.5 mg l<sup>-1</sup>), chromium (60 mg l<sup>-1</sup>), nickel (283 mg l<sup>-1</sup>), zinc (63.5 mg l<sup>-1</sup>) and cyanide (350 mg l<sup>-1</sup>). These values exceed the standards set by the Egyptian laws regulating discharge of wastewater into public sewerage system.

**Photocatalytic Removal of Cyanide:** Composite end of pipe effluent was subjected to using TiO<sub>2</sub> Aldrich (100% anatase), TiO<sub>2</sub> Degussa P25 (80% anatase, 20% rutile) and TiO<sub>2</sub> Aldrich (100% rutile). The results presented in Table (2) and illustrated graphically in Figure (4) show the relationship between exposure time of photolysis and cyanide removal using different photo-catalysts. The interpretation of the photocatalysis processes is shown in Figure (6). The hydroxyl ions (OH<sup>•</sup>) are the likely traps for holes, leading to the formation of hydroxyl radicals which are strong oxidant agents, while the traps for electrons are adsorbed oxygen species, leading to the formation of superoxide species (O<sub>2</sub><sup>•-</sup>) which are unstable, reactive and may evolve in several ways [11].



As indicated in Figure (4), it is seen that the holes generated at the valence band will oxidize the metal-cyano complexes (MCN) to CO<sub>2</sub>, NO<sub>3</sub><sup>-</sup> and M<sup>n+</sup> and the free CN<sup>-</sup> species to CO<sub>2</sub> and NO<sub>3</sub><sup>-</sup>. At the conduction band, the electrons will reduce the metal ions M<sup>n+</sup> to M(0). A model for such process can be assumed in two-step reaction as follows: adsorption of metal cyanide complexes on TiO<sub>2</sub> surface, followed by oxidation of CN<sup>-</sup> with removal and reduction of metal ion. It is worth mentioning that the cyanide was photocatalytically removed and the removal efficiency increased with time, reaching maximum values at 30 min. of photolysis. However, increasing time to 2 hour doesn't give any significant effect.

Table 1: Raw Industrial wastewater characteristics as comparing to the Egyptian Environmental Standards

Parameters	Unit	Raw Wastewater	Law (93/62)/ and Decree (44/2000)
pH-value	-	11.7	6-9.5
COD	(mg l <sup>-1</sup> )	1200.0	<1100.0
TSS	(mg l <sup>-1</sup> )	510.0	<800.0
Cyanide	(mg l <sup>-1</sup> )	350.0	< 0.1
Copper	(mg l <sup>-1</sup> )	6.5	1.5
Nickel	(mg l <sup>-1</sup> )	283.0	1.0
Chromium	(mg l <sup>-1</sup> )	60.0	0.5
Zinc	(mg l <sup>-1</sup> )	63.5	< 10.0
Lead	(mg l <sup>-1</sup> )	0.1	1.0
Cadmium	(mg l <sup>-1</sup> )	<0.01	0.2

Table 2: Relationship between exposure time of photolysis and the percentage removal of total cyanide using different photo-catalysts

Time (Min)	Percentage Removal of Cyanide		
	Aldrich (100% anatase)	Degussa P25 (80% anatase, 20% rutile)	Aldrich (100% rutile)
0	0.0	0.0	0.0
5	25.0	40.0	20.0
10	40.0	55.0	25.0
15	50.0	70.0	40.0
20	63.0	85.0	53.0
25	75.0	87.7	65.0
30	77.0	88.0	73.0
45	82.0	88.7	80.0
60	84.0	90.0	81.0

Table 3: Treatment efficiency of industrial wastewater from galvanization workshops

Parameters (mg l <sup>-1</sup> )	Raw Wastewater	Photo catalytic only	Photo catalytic + H <sub>2</sub> O <sub>2</sub>	Lime	Law (93/62)/ and Decree (44/2000)
pH-value	11.7	10.00	8.0	9.5	6-9.5
COD	1200.0	131.00	126.0	117.0	<1100.0
TSS	510.0	116.00	98.0	4.0	<800.0
Cyanide	350.0	35.00	N.D	N.D	< 0.1
Copper	6.5	3.66	0.5	< 0.05	1.5
Nickel	283.0	70.90	4.0	< 0.05	1.0
Chromium	60.0	9.00	0.1	< 0.05	0.5
Zinc	63.5	3.50	< 0.05	< 0.05	< 10.0
Lead	0.1	< 0.01	< 0.01	< 0.01	1.0
Cadmium	< 0.01	< 0.01	< 0.01	< 0.01	0.2

The results obtained in Table (2) and illustrated in Figure (4) confirmed that TiO<sub>2</sub> Degussa P25 gave the best photocatalytic activity in the removal of cyanides. Degussa P25 consists of anatase and rutile phases [12] and good inter particle contacts are formed between anatase and rutile particles in water [13]. Band bending [14,15] happens in both anatase and rutile through Fermi level lineup when they contact each other. The band gaps of anatase and rutile are 3.2 eV and 3.0 eV, respectively [16, 17]. The positions of their valence bands mainly consisting of O<sub>2p</sub> orbital's are situated at 3.0 eV (vs SHE) [17,18]. It could be concluded that the conduction band energy increase in the space charge layer of anatase stops the electrons going from anatase to rutile, but the holes in anatase particles can be transferred to rutile particles through the valence band bending. These concepts can explain P25's intrinsic charge separation and high photoactivity in liquid reaction. Therefore, it was decided to use TiO<sub>2</sub> Degussa P25 at its optimum operating conditions (0.25 g l<sup>-1</sup> TiO<sub>2</sub> Degussa P25 photo catalyst, pH 11, Temp. of 298°C and exposure time of 30 min). High percentage removal values of COD, TSS, Cyanide

and heavy metals concentrations were obtained. However, the residual values of both cyanide and heavy metals are still high and not complying with the regulatory standards (Table 3).

**The Effect of H<sub>2</sub>O<sub>2</sub> Dose on Photocatalytic Removal of Cyanide:** In this run, photocatalytic removal of cyanide was enhanced by the addition of hydrogen peroxide. To determine the optimum H<sub>2</sub>O<sub>2</sub> dose, the use of different doses ranging from 0.1 ml/l to 1.0 ml/l was investigated. The results obtained are presented in Figure (5). As shown in Figure (5). The results show that by increasing the H<sub>2</sub>O<sub>2</sub> the removal of cyanide increased. When a H<sub>2</sub>O<sub>2</sub> dose higher than 0.3 g/L was used complete removal of cyanide, in shorter time has been recorded. However, for economic reason the use of a dose equivalent to is recommended.

In addition, all heavy metals concentrations (except nickel) were < 0.05 mg l<sup>-1</sup>, each. The use of lime at pH 9.5 improved the quality of treated effluent. Residual values for all heavy metals < 0.05 mg l<sup>-1</sup> were achieved. TSS concentration reached 4.0 mg l<sup>-1</sup>.

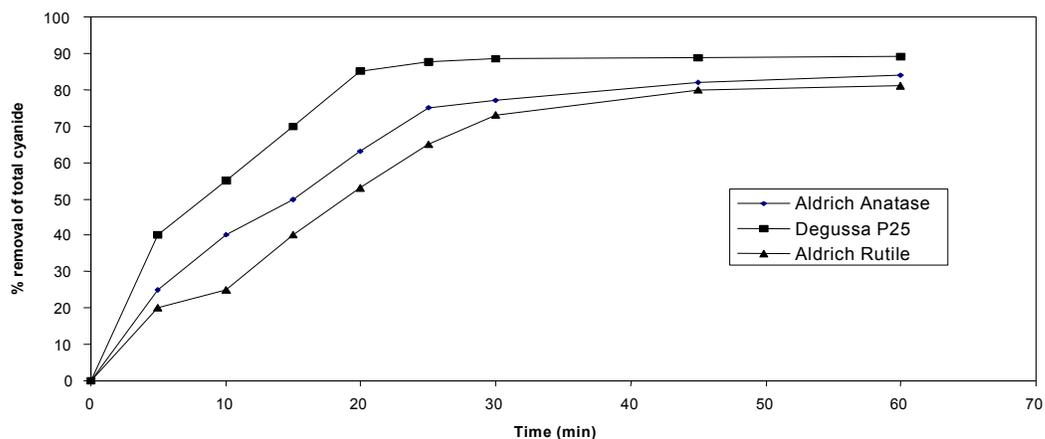


Fig. 4: Effect of exposure time of photolysis on cyanide removal using different photo-catalysts (0.25 g l<sup>-1</sup>, pH 11, Temp. of 298°C )

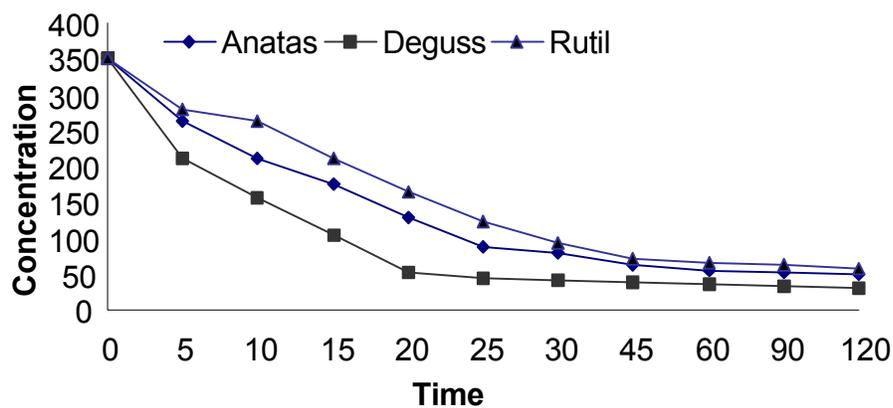


Fig. 5: Kinetics study of photocatalytic removal of Cyanide using different photocatalysts

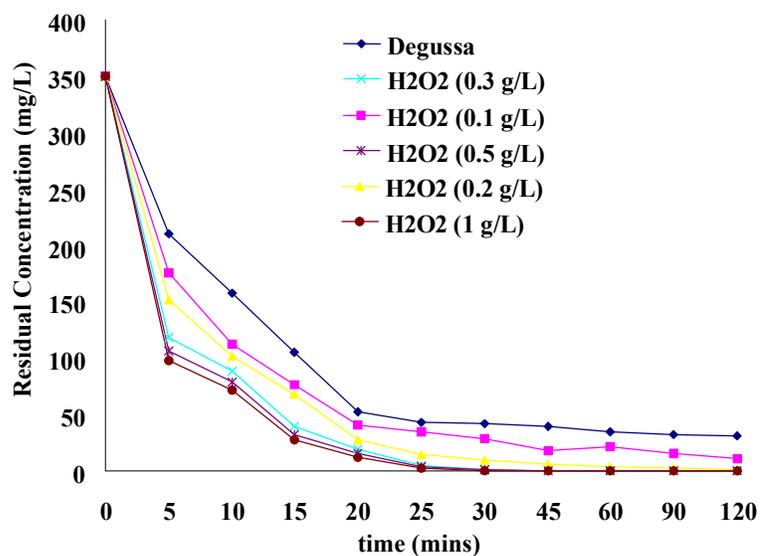


Fig. 6: The Effect of H<sub>2</sub>O<sub>2</sub> dose on photocatalytic Removal of Cyanide with UV/TiO<sub>2</sub> at pH of 11.6, TiO<sub>2</sub> dose of 0.25 g/L

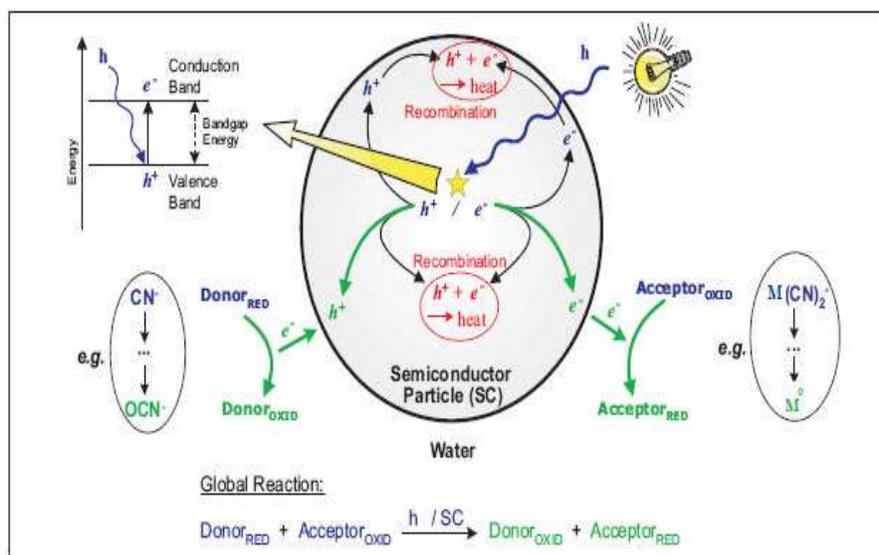


Fig. 7: Charge transfer during the photo-catalytic process.

### CONCLUSIONS

Available results indicate that the use of TiO<sub>2</sub> Degussa P25 at its optimum operating conditions (0.25 gl<sup>-1</sup> TiO<sub>2</sub> Degussa P25 photocatalyst, pH 11, Temp. of 298°C and exposure time of 30 min.) gave the best photocatalytic activity for the removal of cyanide. The addition of 0.3ml/l of H<sub>2</sub>O<sub>2</sub> enhanced and accelerated the photocatalytic activity. In order to completely remove residual heavy metals, the use of lime at a pH of 9.5 is recommended.

### REFERENCES

1. Abdel Wahaab, R., 2000. Up-grading of industrial wastewater treatment units at automobile industry. *Inter. J. Biomedical and Environmental Sci.*, 30: 219-241.
2. Grosse, D.W., 1986. Treatment technologies for hazardous wastes. 4. A review of alternative treatment processes for metal bearing hazardous-waste streams. *J. Air Pollut. Control Assoc.*, 36: 603-614.
3. Hassan, S.Q., M.P. Vitello, M.J. Kupferle and D.W. Grosse, 2007. Treatment technology evaluation for aqueous metal and cyanide bearing hazardous wastes. *J. Air Waste Manage. Assoc.*, 41: 710-715.
4. Kunz, D.A., R.F. Fernandez and P. Parab, 2001. Evidence that bacterial cyanide oxygenase is a pterin-dependent hydroxylase, *Biochem. Bioph. Res. Co.*, 287: 514-518.
5. Wang, C.S., D.A. Kunz and B.J. Venables, 1996. Incorporation of molecular oxygen and water during enzymatic oxidation of cyanide by *Pseudomonas fluorescens* NCIMB 11764, *Appl. Environ. Microb.*, 6: 2195-2197.
6. Futakawa, M.H., G. Takahashi and G. Inoue, 1994. Treatment of concentrated cyanide waste-water, *Desal.*, 98: 345-352.
7. Costarramone, N., A. Kneip and A. Castetbon, 2004. Ferrate (VI) oxidation of cyanide in water. *Environ. Technol.*, 25: 945-955.
8. Fugivara, C.S., P.T.A. Sumodjo and A.A. Cardoso, 1996. Electrochemical decomposition of cyanides on tin dioxide electrodes in alkaline media. *Analyst.*, 121: 541-545.
9. Stavart, A. and A.V. Lierde, 2001. Electrooxidation of cyanide on cobalt oxide anodes. *J. Appl. Electrochem.*, 31: 469-474.
10. Lanza, M.R.V. and R. Bertazzoli, 2002. Cyanide oxidation from wastewater in a flow electrochemical reactor. *Ind. & Eng. Chem. Res.*, 41: 22-26.
11. Lu, J., D.B. Dreisinger and W.C. Cooper, 2002. Anodic oxidation of copper cyanide on graphite anodes in alkaline solution. *J. Appl. Electrochem.*, 32: 1119-1129.
12. Chiang, K., R. Amal and T. Tran, 2002. Photocatalytic degradation of cyanide using titanium dioxide modified with copper oxide, *Adv. Environ. Res.*, 6: 471-485.

13. Dabrowski, B., A. Zaleska, M. Janczarek, J. Hupka and J. Miller, 2002. Photo-oxidation of dissolved cyanide using TiO<sub>2</sub> catalyst. *J. Photochem. Photobiol. A: Chem.*, 151: 201-205.
14. Bozzi, A.I., J. Guasaquillo and J. Kiwi, 2004. Accelerated removal of cyanides from industrial effluents by supported TiO<sub>2</sub> photo-catalysts, *Appl. Catal. B: Environ.*, 51: 203-211.
15. Augugliaro, V., V. Loddo, G. Marci, L. Palmisano and M. Lopez-Munoz, 1997. Photocatalytic oxidation of cyanides in aqueous titanium dioxide suspensions. *J. Catal.*, 166: 272-283.
16. Augugliaro, V., J. Blanco Galvez, J. Caceres Vazquez, E. Garcia Lopez, V. Loddo, M. Lopez Munoz, S. Rodrigez, S. Malato Rodrigez, G. Marci, L. Palmisano, M. Schiavello and J. Soria Ruiz, 1999. Photocatalytic oxidation of cyanide in aqueous TiO<sub>2</sub> suspensions irradiated by sunlight in mild and strong oxidant conditions. *Catal. Today.*, 54: 245-253.
17. Alicilar, A., M. Komurcu and M. Guru, 2002. The removal of cyanides from water by catalytic air oxidation in a fixed bed reactor. *Chem. Eng. and Processing*, 41: 525-529.
18. Basu, B., S. Satapathy and A.K. Bhatnagar, 1993. Merox and related metal phtalocyanine catalyzed oxidation processes, *Catal. Rev. Sci. Eng.*, 35: 571-609.
19. Barakat, M.A., Y.T. Chen and C.P. Huang, 2004. Removal of toxic cyanide and Cu(II) Ions from water by illuminated TiO<sub>2</sub> catalyst. *Applied Catalysis B: Environmental.*, 53: 13-20.
20. Botz, M.M., 2001. Cyanide treatment methods. *The Cyanide Guide* (Mudder T I, ed.). A Special Edition of the Mining Environmental Management, 9: 28-30.
21. Kitis, M., A. Ackil, E.N.O. Karakaya and N.O. Yigit, 2005. Destruction of cyanide by hydrogen peroxide in tailings slurries from low bearing sulphidic gold ores. *Mineral Engineering*, 18: 353-362.