HEAVY METALS AND CYANIDE REMOVAL USING PHOTO-CATALYTIC OXIDATION IN GALVANIZATION WORKSHOPS

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Abstract

Industrial wastewater from galvanization workshops located in meet Ghamer city at Dakahlya governorate in Egypt contains high concentrations of copper, chromium, nickel, zinc and cyanide which violating the Egyptian environmental standard. Three commercial TiO_2 specimens were tested in this work namely: TiO_2 Degussa P25 (80% anatase, 20% rutile), TiO_2 Aldrich (100% anatase) and TiO_2 Aldrich (100% rutile) and added with 0.3 ml/l hydrogen peroxide. At optimum operating conditions: TiO_2 Degussa P25 photo catalyst (0.25 g l^{-1}), 0.3 ml/l H_2O_2, PH =11 and temp = 298°C and time photolysis of 30 min., The results confirmed that TiO_2 Degussa P25 shows the best photo catalytic activity in the removal of cyanides. The removal efficiency reaches 80%. By increasing time and dose of catalyst give no effect in quality of effluent. So, addition of 1 ml/l hydrogen peroxide to the photo catalytic reaction increases the removal efficiency to 99.8%. Also, 80% of (Cr^{6+}), 70% (Ni^{2+}) and 94.5% (Zn^{2+}) metal ions have been photo catalytically removed from cyanide solution.

Keywords: wastewater, metal galvanization, photo-catalytic oxidation

Introduction

Wastewater from galvanization work shops located in Meet Ghamer city, Dakahlya Government provides the material of the study. The work shops discharges its wastewater into the sewerage network without any treatment. Wastewater discharged from the workshops during the two working shifts; is about 5.5m^3/week. The Production operation includes metal finishing and shaping, surface preparation (dry cleaning / acid cleaning), surface finishing and drying. Surface finishing is performed by either galvanization or electroplating.

The liquid wastes discharged from industries such as metal finishing are not voluminous, but are extremely dangerous because their toxic contents Abdel Wahaab (2000). From these industries and process wastewater may contain a varity of hazardous materials such as heavy metals like chromium, zinc, and nickel (El-Gohary, et al, 2002; Van and Pols, 2005).

In the metal finishing process, metal pieces are dipped into bathes containing chemical solution which will give the appropriate coating. The pieces are then rinsed in several containers of flowing water, to remove residual plating or processing solutions. The solution often comprise acids, alkalis, cyanides as well as various base metals such as chromium, nickel, zinc, iron and copper. The industry is a major source of hazardous waste and generates tones of hazardous industrial waste in the country annually.

A number of methods are currently available for cyanide remediation with varying degrees of effectiveness , namely biological treatment ((Kuns, et, al., (2001)), (Wang et, al., (1996)) and (Gupta et, al., (2010)) chemical oxidation (Futakawa, et, al., (1994)) and (Costarramone, et, al., (2004)), electrochemical decomposition (Fugivara, et, al., (1996)) and (Lu, et, al., (2002)), photo catalytic (Chiang, et, al., (2002) and Auguliaro, et, al., (1999)) and catalytic oxidation (Alicilar, et, al., (2002)), (Basu, et, al.,(1993)), (Christoskova, and St. Stoyanova M. (2009)) and (Yeddou, et, al., (2010).

Photo-catalytic degradation of cyanides using several powdered semiconductors- TiO_2, ZnO, Fe_2O_3, ZnS and CdS have been studied lasting recent years. It was extensively found that these metal oxide worked best because of their chemical stability; however, anatase, a polymorph of TiO_2 was preferred due to its high quantum efficiency for photoconversation, and its stable formation of an electron-hole pair.

Also heterogeneous photocatalysis has shown a high efficincy in the removal not only of free cyanides ((Futakawa, et, al., (1994) and Costarramone, et, al., (2004)), but also of iron (Fugivara et, al., (1996) and Stavart and Lierde (2001)), copper (Lanza and Bertazzoli (2002)), copper(II) and cyanide (Mohamed, R.M and Mohamed, M. M.(2008)) and gold cyanocomplexes (Lu, et, al., (2002)).

The present work is focused on the study of photo- catalytic performance of different type of TiO_2 for achieving the simultaneous reduction of oxidation of cyanide from true industrial-wastewater solutions. The treated wastewater can be recycled in the industrial processes or disposed safely either into the sewerage network or any surface water.

The aim of the present study is to evaluate existing situation and environmental problems for one the largest cluster of metal galvanization workshops in Egypt and the treatment options of industrial wastewater to comply with law 44/2000 which regulate the discharge of wastewater to sewage network and segregate as well as removal of heavy metal and oxidize cyanide ions to carbon dioxide and nitrogen

Materials and Methods

Industrial wastewater from galvanization workshops located in meet Ghamer city at Dakahlya governorate in Egypt contains high concentration of heavy metals and cyanide which violating the Egyptian environmental standard. Composite sample of wastewater from end of pip collected to study. The analysis results showed that the wastewater contains high concentration of copper, chromium, nickel, zinc and cyanide at pH 11.7. Table (1)

Table (1) Physico-chemical characteristics of mixed wastewater sample collected according to discharged ratio

Parameter	Concentration mg/l
T.S.S	510
O&G	65
CN	350
Cr	60
Cu	6.5
Ni	283
Zn	63.5
COD	1200

Three commercial TiO_2 specimens were tested in this work. TiO_2 Degussa P25 (80% anatase, 20% rutile), TiO_2 Aldrich (100% anatase) and TiO_2 Aldrich (100% rutile) were tested without any preliminary treatment. Hydrogen peroxide ($0.25gl^{-1}$) used as a catalyst in this process. The reactivity experiments were performed in Pyrex batch photoreactor, of cylindrical shape, containing 400 ml of the reaction mixture. For all the runs, the amount of catalyst suspended in the cyanide solution was the same and equal to $0.25gl^{-1}$. The invariance catalyst content among the various runs guaranteed that the irradiation conditions of suspension didn't change; this condition depended only on the catalyst content as the aqueous solution behaves a non-participating medium. A medium pressure Hg lamp (Heraeus-nobleligh 150 W/cm^2), immersed within the suspension was used UV-radiation source. It was surrounded by a Pyrex jacket that allowed to the both refrigeration by circulating cool water to cut-off any radiation with wavelength blow 300 nm. The lamp emission spectrum in the near-UV region had large emission band centered at 365 nm. In order to increase the efficiency of the illumination, the whole reactor was lined with aluminum foil. Some ports of the photoreactor s upper section allowed sampling and flowing gases. A magnetic stirrer guaranteed satisfactory powder suspension and uniformity the reaction. The suspension temperature was 298 K for all the runs. Figure (1) shows the schematic experimental setup. Photocatalytic runs were carried out by the following procedure. The catalyst (0.25gl^{-1}) was added in the always 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 outset of irradiation time was taken at the moment the lamp was switched on. Samples for analysis were withdrawn at fixed intervals of time. Physico-chemical analysis, unless specified, were carried out according to American standard method devised by **APHA (2005)**. Heavy metals were determined using **Atomic Absorption Spectrometer Varian Specter AA (220)** with graphite furnace accessory and equipped with the deuterium arc background corrector.

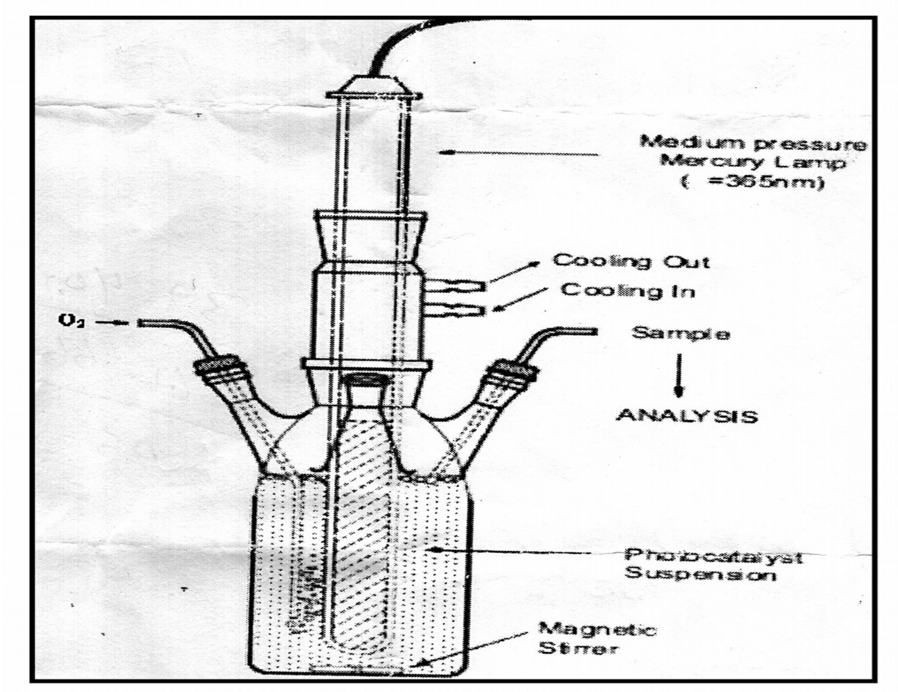

Figure (1) Schematic diagram of the photo catalytic unit

Results and discussion

Photo-catalytic degradation

Composite final effluent samples of the galvanization workshops were subjected to multistage treatment train. The final effluent was treated by primary settling followed by advanced catalytic oxidation and chemical treatment.

Treatment train

TiO_2 Degussa P25 (80% anatase, 20% rutile), TiO_2 Aldrich (100% anatase) and TiO_2 Aldrich (100% rutile) were tested as photo catalyst for removal of total cyanides. No oxidation of total cyanides was observed in the absence of light and / or of catalyst and/ or of oxygen. It was also checked that the bubbling of gas into reacting mixture didn't decrease the cyanide concentration due to a (unlikely) stripping effect. The total cyanide removal (%) was plotted against the time of photolysis to evaluate the efficiency of the photo catalytic activity, Table (2) and Figure (2). It was found that the cyanide was photo catalytically removed and the removal efficiency increased with time maximum values at 30 min. of photolysis.

However, increasing time to 2 hours doesn't give any effect. Addition of hydrogen peroxide to aide efficiency of photo catalytic reaction was examined; by adding various doses of hydrogen peroxide to determine the optimum does (dose ranged from 0.1 ml/l to 1ml/l). TiO_2 Degussa P25 shows the best photo catalytic activity in the removal of cyanides when added with 0.3 ml/l hydrogen peroxide. At optimum operating conditions: TiO_2 Degussa P25 photo catalyst (0.25 g l^{-1}), 0.3 ml/l H_2O_2, PH =11 and temp = 298°C and time photolysis of 30 min., the removal efficiency reaches 80%. By increasing the time and dose of catalyst give no effect in quality of effluent. So addition of 1 ml/l hydrogen peroxide to the photo catalytic reaction increases the removal efficiency to 99.8%.

Also, 80% of (Cr^{6+}), 70% (Ni^{2+}) and 94.5% (Zn^{2+}) metal ions have been photo catalytically removed from cyanide solution. Table (3) shows that efficiency of industrial wastewater from galvanization workshops.

In photo catalytic process, electron-hole pairs generated which may be trapped in order to avoid recombination. The hydroxyl ions (OH) 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 super oxide species (O_2) which are unstable, reactive and may evolve in several ways (Chiang, et, al., (2002)).

$$TiO_2 + hv = TiO_2 + e_{cB} + h^+_{VB}$$

$$TiO_{2\ (substrate)} - OH^-_s + h^+ = TiO_{2(substrate)} - OH_{(ads)}$$

$$O_2 + e^- = O_{2\ (ads)}$$

Table (2) Relation ship between of photolysis and the percentage of the total cyanide removal using different photo catalysis

Time (min)	Cyanide removal %		
	Degussa P25	Aldrich 100(%) Anatase	Aldrich 100(%) (%) Rutile
0	350	350	350
5	40	25	20
10	55	40	25
15	70	50	40
20	85	63	55

25	87.7	75	66
30	88	78	72.5
45	88.8	82	79.5
60	90	84	81.5

Table (3) Treatment efficiency of industrial wastewater from galvanization workshops

Parameters mg/l	Raw wastewater	Photo Catalytic only	Photo catalytic $+H_2O_2$	Law 93/62
pH-value	11.7	10	8	6-9.5
COD	1200	131	126	1100
TSS	510	116	98	800
Cyanide	350	35	N.D	<0.1
Copper	6.5	3.66	0.6	1.5
Nickel	283	70.9	4	1.0
Chromium	60	9	0.2	<10
Zinc	63.5	3.5	<0.05	1.0

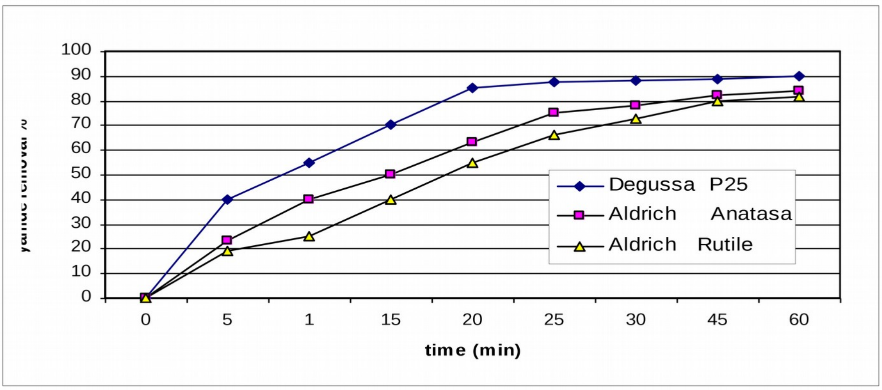

Figure (2) Effect of exposure time of photolysis on cyanide removal using different photo-catalysis (0.25 g l^{-1}, PH 11, Temp of 298˚C)

The results obtained in Table (2) and illustrated inFigure (2) confirmed that TiO2 Degussa P25 gave the best photocatalytic activity in the removal of cyanides. Degussa P25 consists of anatase and rutile phases and good inter particle contacts are formed between anatase and rutile particles in water [13]. Band bending 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 (electron volt) and 3.0 eV, respectively. The positions of their valence bands mainly consisting of O_{2p} orbital's are situated at 3.0 eV (vs SHE). 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_2 Degussa P25 at its optimum operating pH 11, Temp. of 298°C and exposure time of 30 min). High percentage removal values of COD, TSS, and Cyanide and heavy metals concentrations were obtained.

Conclusions

From the obtained results TiO_2 Degussa P25 shows the best photo catalytic activity in the removal of cyanides when added with 0.3 ml/l hydrogen peroxide. At optimum operating conditions: TiO_2 Degussa P25 photo catalyst (0.25 g l^{-1}), 0.3 ml/l H_2O_2, PH =11, temp = 298°C and time photolysis of 30 min., the removal efficiency reaches 80%. By increasing time and dose of catalyst give no effect in quality of effluent. So, addition of 1 ml/l hydrogen peroxide to the photo catalytic reaction increases the removal efficiency to 99.8%. Also, 80% of (Cr^{6+}), 70% (Ni^{2+}) and 94.5% (Zn^{2+}) metal ions have been photo catalytically removed from cyanide solution**.**

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