STUDY ON PHOTOCATALITYCAL DETOXIFICATION OF WASTEWATER CONTAMINATED WITH CYANIDES

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Abstract. The presence of free and complex cyanides in industrial wastewater is a problem of major concern owing to the well-known toxicity of these species for the living organism even at low concentration values. Large volumes of wastewater contaminated with pollutants are generated by different industries including gold milling processes. The conventional processes used up today to treat these type of wastewater are mainly chemical or/and biological. A promising method for treating wastewater contaminated with cyanides consists in turnover of pollutant into less dangerous species by photooxidation in the presence of polycrystalline semiconductor oxides under UV/solar radiations. It was studied the degradation of cyanides from wastewater by heterogeneous photocatalyses with TiO_2 (anatase) suspended in solution. The experimental results show that the efficiency of cyanides degradation is affected by pH, TiO_2 dose and contact time.

Keywords: cyanides, TiO_2 (anatase), photooxidation.

AIMS AND BACKGROUND

The aims of the present study are to evaluate the possibility to apply UV/TiO_2 heterogeneous photocatalysis, in order to degrade free and complex cyanides from wastewater and to establish the operating parameters influence on process efficiency.

Hazardous waste with free and complex cyanides contain are generated in large volumes during various industrial activities such as mining. As a class, cyanides are highly toxic and must be destroyed or removed from wastewaters prior to discharge. Dissolved cyanides can be removed from water by physical, chemical and/or biological methods. The chemical methods typically involve oxidation of cyanides by reagents such as SO_2-air, chlorine, hydrogen peroxide, ozone. Photocatalytically oxidation over semiconductors is a promising method for cyanides elimination[1,2]. TiO_2 is one of the catalysts whose function can be activated by external energy (UV light). Its catalytic effect is based on photogeneration of electron-hole pairs, which in turn enable the occurrence of redox reactions at the semiconductor surface. Hence, oxidisable toxic compounds can be reduced
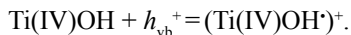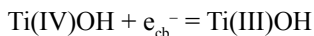
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less harmful by their photocatalytic oxidation on TiO_2 particles. The mechanism involved in semiconductor photocatalysis can be the following[3,4]:
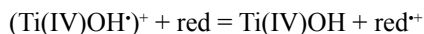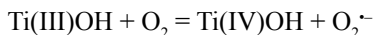
Photogeneration of electron-hole pair:

$$TiO_2 + h\nu \rightarrow e_{cb}^- + h_{vb}^+.$$
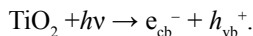
Trapping of photogenerated electron and hole:

$$Ti(IV)OH + e_{cb}^- = Ti(III)OH$$

$$Ti(IV)OH + h_{vb}^+ = (Ti(IV)OH^\cdot)^+.$$

Interfacial electron and hole trapping by adsorbed species:

$$Ti(III)OH + O_2 = Ti(IV)OH + O_2^{\cdot-}$$

$$(Ti(IV)OH^\cdot)^+ + red = Ti(IV)OH + red^{\cdot+}$$

where red are reducing species such as OH^-, CN^-.

The absorbed surface hydroxyl groups (red) on the semiconductor surface traps the hole to form the hydroxyl radical, which are very strong oxidant capable of oxidising organic or inorganic pollutants present in the wastewater.

The oxidation of cyanides is possible via the reaction of CN^- with hydroxyl radicals or holes forming cyanide radicals which subsequently dimerise to form cyanogens that undergoes dismutation to cyanide and cyanate. The cyanate produced is further oxidising to give NO_3^- and CO_2. The correspondent reactions are the following:

$$CN^- \xrightarrow{\;h^+/OH^\cdot\;} CN^\cdot$$

$$2CN^\cdot = (CN)_2$$

$$(CN)_2 + 2OH^- = CN^- + CNO^- + H_2O$$

$$CNO^- + 8OH^- + 8h^+ = NO_3^- + CO_2 + 4H_2O.$$
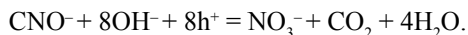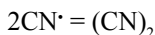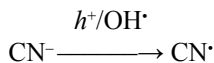
The efficiency of oxidative degradation of cyanide is affected by several parameters. In this work we studied the removal efficiency of cyanide from wastewater at different parameters such as pH, doze of semiconductor and contact time.

EXPERIMENTAL

In order to evaluate the possibilities to apply the photochemical oxidation in the field of advanced treatment of wastewater having cyanide content, there were performed experiments of heterogeneous photocatalysis, UV/TiO_2 system, on wastewater with various pollution context (different concentrations of weak dissociable cyanides, hard dissociable cyanides and sulphocyanides) and specific experimental conditions.

There were oxidised wastewater samples, CN_1, CN_2, from gold ore processing. Table 1 contains the main physicochemical characteristics of these samples.

Table 1. Physicochemical characterisation of wastewater

Indicator	Samples	
	CN_1	CN_2
pH	9.07	9.2
CN^-_t (mg/l)	9.17	7.84
CN^-_{wad} (mg/l)	6	5.88
SCN^- (mg/l)	38.54	95.87
Cl^- (mg/l)	107	167
SO_4^{2-} (mg/l)	738	858
CO_3^{2-} (mg/l)	36	36
Fe (mg/l)	< 0.004	0.072
Cu (mg/l)	6.5	6.37
Mn (mg/l)	< 0.003	< 0.003
Zn (mg/l)	< 0.001	0.037
Ni (mg/l)	< 0.004	0.12
Co (mg/l)	< 0.01	< 0.01

Photodegradation experiments were performed with a photocatalytic reactor system. This bench-scale system consisted of a cylindrical glass cell with 933 cm³ capacity (of 6 cm diameter, 33 cm height). A 150 W mercury lamp (spectral domain = 200-450 nm) was placed in a quartz cooling jacket (inside diameter 2.3 cm, 39.5 cm height) with one end tightly sealed by a Teflon stopper. The lamp and the cooling jacket were immersed in the photoreactor cell (with light path of 1 cm). To the reactor, it was added 400 cm³ of wastewater sample and different concentration of photocatalyst in suspension. Photocatalyst used was TiO_2 (anatase) produced by Merck. Compressed air was purged into the solution by bubbling compressed air from the bottom to maintain an aerobic condition, and a magnetic stirrer was used to keep the whole solution chemically uniform. The experiments were performed at specific pH values kept constant by adding NaOH solution (5%). The wastewater was radiated by UV light for given contact time and collected for the analysis. The solid TiO_2 was removed from samples by filtration and the filtrates were analysed at following indicators: CN^-_t, $CN^-_{wad.}$, SCN^-, Cu^{2+}. The CN^- and SCN^- ions concentration was colorimetrically analysed by using a UV-vis. spectrophotometer. The concentration of copper ions was analysed by atomic absorption spectrophotometry (AAS).

RESULTS AND DISCUSSION

In order to establish the pH influence on catalytical photooxidation of cyanide, the experiments were performed for two pH values: pH 9 and 10. Literature data and alkaline characteristic of the effluents were the basis of pH selection taking into account the high efficiencies for CN^- photooxidation at pH $\geq$ 9.

TiO$_2$ (Merck) powder (0.5 g/l) was used for photooxidation experiments of CN_1 sample at 1 h reaction time.

The data regarding removal efficiencies of cyanide, in different pH conditions are shown in Table 2 emphasising the followings aspects:

– the raise of operating pH from 9 to 10 leads to a slight decrease of oxidation yields (cyanide, sulphocyanides);

– in the frame of tested work conditions, maximum values of oxidation yields for CN_t^- and CN_{wad}^- are comparable, being around 93-94% for pH = 9;

– the efficiency of SCN^- oxidation is lower comparing with the recorded value for CN_t^-, the maximum yield (55%) being registered for pH = 9;

– simultaneously with the decrease of CN^-_{wad} content, the Cu^{2+} ions content decreases too, with comparable yields which means that they are present as cyanide complexes.

Table 2. pH influence on CN^- catalytical photooxidation using UV/TiO$_2$ system

pH	Characterisation of treated sample				Removal efficiencies			
	CN_t^- (mg/l)	CN^-_{wad} (mg/l)	SCN^- (mg/l)	Cu^{2+} (mg/l)	CN_t^- (%)	CN^-_{wad} (%)	SCN^- (%)	Cu^{2+} (%)
9	0.64	0.38	17.35	0.48	93.0	93.7	55.0	92.6
10	1.18	0.84	18.65	0.61	87.1	86.0	51.6	90.6

Experimental conditions: TiO$_2$ = 0.5 g/l, τ = 1 h, Vs = 400 ml, λ = 200-450 nm, light pass = 1 cm; initial sample characteristics: CN_t^- = 9.17 mg/l, CN^-_{wad} = 6 mg/l, SCN^- = 38.54 mg/l, Cu^{2+} = 6.5 mg/l, SCN^-:CN_t^- = 2:1.

As it is well known, the advanced oxidation process by the system UV/TiO$_2$, is based on the interaction between oxidisable species and OH$^\bullet$ radicals generated by semiconductor. Because its concentration is depending on the total catalyst area, as the product between external specific area (cm^3/g) and catalyst dose (g/l), it is obvious that the catalyst dose is one of the influence parameters.

In order to study the influence of photocatalyst dose on the cyanide oxidation efficiency, there were performed experiments of photocatalytical oxidation on wastewater samples CN_1 and CN_2 at pH =9 and τ = 1 h using powder of TiO$_2$ (Merck) catalyst at different doses.

The obtained results for the samples CN_1 and CN_2 are shown in Table 3 and 4, emphasising the followings aspects:

– the increasing of photocatalyst dose in the range of 0.25-0.5 g/l has a positive effect on cyanide oxidation yield for both treated samples;

– an accentuated increasing dose of catalyst (≥ 0.75 g/l) could lead to a decrease of oxidation efficiency as a results of light dispersion phenomenon generated by suspended particles (both treated samples);

– for the same dose of TiO_2, the efficiency of cyanides oxidation process is influenced by the pollution matrix; the decrease of CN^- oxidation is accentuated by the increase of SCN^-:CN^-_t molar ratio. Therefore, for a dose of 0.25 g TiO_2/l in case of CN_2 sample, having a molar ratio of SCN^-:CN^-_t = 5.5:1, the CN^-_t removal efficiency is only 43% comparing with sample CN_1 which has molar ratio SCN^-:CN^-_t = 2:1 and a CN^- removal efficiency of 93%. This system behaviour is due to the fact that the SCN^- oxidation leads to CN^- as secondary reaction product;

– the increase of photocatalyst dose leads to a similar evolution of sulphocyanides oxidation rate to CN^-_t, but the efficiencies are below 64%; for identically experimental conditions, the SCN^- removal efficiency is higher for sample CN_1 (SCN^-:CN^-_t = 2:1) comparing with sample CN_2 (SCN^-:CN^-_t = 5.5:1);

– the decrease of Cu^{2+} ions concentration is comparable with CN^-_{wad} (case of CN_1 sample) or below (case of CN_2 sample); the maximal efficiencies were recorded for 0.25-0.5 g TiO_2/l.

Table 3. Influence of TiO_2 dose on photocatalytical oxidation of CN^- using UV/TiO_2 system – sample CN_1

TiO_2 dose (g/l)	Characterisation of treated sample				Removal efficiencies			
	CN^-_t (mg/l)	CN^-_{wad} (mg/l)	SCN^- (mg/l)	Cu^{2+} (mg/l)	CN^-_t (%)	CN^-_{wad} (%)	SCN^- (%)	Cu^{2+} (%)
0	3.73	1.97	23.84	1.76	59.3	67.2	38.1	72.9
0.125	3.57	1.5	18.79	1.28	61	75	48	80.3
0.25	0.67	0.39	13.89	0.552	92.7	93.5	64	91.5
0.5	0.64	0.38	17.35	0.48	93	93.7	55	92.6
0.75	0.64	0.50	20.63	0.55	93	91.7	46.5	91.5
1	0.91	0.75	20.47	0.89	90	87.5	46.1	86.3

Experimental conditions: pH = 9, τ = 1 h, Vs = 400 ml, λ = 200-450 nm, light pass = 1cm; initial sample characteristics: CN^-_t = 9.17 mg/l, CN^-_{wad} = 6 mg/l, SCN^- = 38.54 mg/l, Cu^{2+} = 6.5 mg/l, SCN^-:CN^-_t = 2:1.

The comparative analysis of the results for the studied pollution context emphasised that the maximal oxidation yields values (η $CN^- \leq 93\%$; η $SCN^- \leq 55\%$) are recorded for 0.25-0.5 g/l photocatalyst doses.

Taking into account the negative influence of SCN^- on the advanced degradation of cyanide, the improvement of process efficiency was performed by increasing the contact time.

Therefore, it were performed photooxidation experiments on samples CN_1 and CN_2, for pH = 9 and 0.5 g/l photocatalyst doses for various reaction times.

Table 4. Influence of TiO$_2$ dose on photocatalytical oxidation of CN$^-$ using UV/TiO$_2$ system – sample CN$_2$

TiO$_2$ dose (g/l)	Characterisation of treated sample				Removal efficiencies			
	CN^-_t (mg/l)	CN$^-_{wad}$ (mg/l)	SCN$^-$ (mg/l)	Cu^{2+} (mg/l)	CN^-_t (%)	CN$^-_{wad}$ (%)	SCN$^-$ (%)	Cu^{2+} (%)
0	4.96	3.93	56.07	5.07	36.7	32.3	41.5	20.4
0.25	4.12	3.14	44.67	4.3	47.4	46.6	53.4	32.5
0.5	2.89	2.12	42.68	1.8	63.1	63.9	55.5	71.6
0.75	5.8	4.57	63.22	4.7	25	22.3	34.1	26.2

Experimental conditions: pH = 9, τ = 1 h, Vs = 400 ml, λ = 200-450 nm, light pass = 1 cm; initial sample characteristics: CN^-_t = 7.84 mg/l, CN$^-_{wad}$ = 5.88 mg/l, SCN$^-$ = 95.87 mg/l, Cu^{2+} = 6.37 mg/l, SCN$^-$:CN^-_t = 5.5:1.

Tables 5 and 6 show the recorded result for CN$_1$ and CN$_2$ samples and emphasised the following conclusions:

– the increase of reaction time has a positive effect on the photocatalytic oxidation process;

– the maximum values of oxidation yields for CN^-_t and CN$^-_{wad}$ were recorded for 0.5 g/l photocatalyst dose and τ ≥ 3 h, being in the range of 98.5-99% for sample CN$_1$ and 98.3-98.5% for CN$_2$ sample, respectively;

– high levels of SCN$^-$ concentrations lead to higher reaction times in order to reach the stipulated discharging limit for the noted indicator (CN^-_t = 0.1 mg/l));

– the removal efficiency of other pollutants from the system, respectively SCN$^-$ and Cu^{2+}, is positively influenced by increasing reaction time; for the treated samples the efficiencies recorded for 0.5 g/l TiO$_2$ dose and τ ≥ 3 h are ≥ 74% for SCN$^-$ and ≥99.2% for Cu^{2+}, respectively;

– under the tested experimental conditions, could be considered that minimum 3 h reaction time is able to assure the advanced diminishing of CN$^-$ content from wastewater.

Table 5. Influence of contact time on photocatalytical oxidation of CN$^-$ using UV/TiO$_2$ system – sample CN$_1$

Contact time (h)	Characterisation of treated sample				Removal efficiencies			
	CN^-_t (mg/l)	CN$^-_{wad}$ (mg/l)	SCN$^-$ (mg/l)	Cu^{2+} (mg/l)	CN^-_t (%)	CN$^-_{wad}$ (%)	SCN$^-$ (%)	Cu^{2+} (%)
0.5	1.36	0.78	17.22	1.08	85.2	87	62.8	83.4
1	0.64	0.38	17.35	0.48	93	93.7	62.5	92.6
2	0.4	0.16	7.71	0.29	95.6	97.3	83.3	95.5
3	0.092	0.09	<2	0.04	99	98.5	74	99.4

Experimental conditions: pH = 9, TiO$_2$ = 0.5 g/l, Vs = 400 ml, λ = 200-450 nm, light pass = 1 cm; initial sample characteristics: CN^-_t = 9.17 mg/l, CN$^-_{wad}$ = 6 mg/l, SCN$^-$ = 38.54 mg/l, Cu^{2+} = 6.5 mg/l, SCN$^-$:CN^-_t = 2:1.

Table 6. Influence of contact time on photocatalytical oxidation of CN^- using UV/TiO_2 system – sample CN_2

Contact time (h)	Characterisation of treated sample				Removal efficiencies			
	CN^-_t (mg/l)	CN^-_{wad} (mg/l)	SCN^- (mg/l)	Cu^{2+} (mg/l)	CN^-_t (%)	CN^-_{wad} (%)	SCN^- (%)	Cu^{2+} (%)
1	2.89	2.12	42.68	1.31	63.1	69.9	55.5	71.6
2	1.02	0.72	17.82	0.74	87	87.8	81.4	88.4
4	0.12	0.1	<2	0.05	98.5	98.3	88.8	99.21

Experimental conditions: pH = 9, TiO_2 = 0.5 g/l, Vs = 400 ml, λ = 200-450 nm, light pass = 1 cm; initial sample characteristics: CN^-_t = 7.84 mg/l, CN^-_{wad} = 5.88 mg/l, SCN^- = 95.87 mg/l, Cu^{2+} = 6.37 mg/l, SCN^-:CN^-_t = 5.5:1.

CONCLUSIONS

Applying the homogeneous photocatalysis in proper conditions in UV/TiO_2 system is able to assure the advanced degradation of cyanides from wastewater and the compliance of the treated effluent quality with the imposed limits.

The case study performed on wastewater sampled from the processing of gold ores revealed that the efficient degradation of cyanides (yield $\geq$ 98%) is recorded in the following conditions: pH = 9, TiO_2 dose = 0.5 g/l and τ = minimum 3 h.

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