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STUDIES ON THE REMOVAL OF HEAVY METAL IONS FROM INDUSTRIAL WASTE WATER BY USING TITANIUM ELECTRODES

RAUNAK KUNDRA, RISHBHA SACHDEVA, SALIM ATTAR and
MADAN PARANDE*

Department of Chemical Engineering, Bharati Vidyapeeth College of Engineering, PUNE – 411043 (M.S.) INDIA

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ABSTRACT

Water pollution caused by heavy metals is a global problem and has received worldwide attention. Water containing heavy metals used for drinking purpose, if not treated properly can cause serious health problem to human being and severe damage to the environment. The present work focuses on treatment of waste water from Indian chemical process industries containing primarily heavy metal ions. The process makes use of titanium as a working electrode, which is stable, energy efficient and can treat variety of effluents.

Key words: Heavy metal ions, Industrial waste water, Titanium electrodes.

INTRODUCTION

Water is one of the essential materials required to sustain life and unfortunately has long been suspected of being the source of much human illness. Source waters (surface water and ground water) have been increasingly contaminated due to increased industrial and agricultural activities. The public has been more enhancing in its demands as time has passed, and today water engineers are expected to produce finished waters that are free of colour, turbidity, tastes, odour, nitrate, harmful metal ions and a wide variety of organic chemicals such as pesticides and chlorinated solvents. Expanding population with resultant increased industrial operations, power production, and use of motor driven vehicles, plus new industries based upon new technology have intensified old problems and created new ones in the field of water supply. There is a need to understand contaminant fate and effects, as well as to acquire expertise in pollution control strategies beyond the conventional handling of effluent waste streams. The wide variety of heavy metals and organic chemicals produced and used by industry has also been shown to contaminate surface waters and groundwater. These compounds are of public health concerns, and they also may have an adverse effect on the desirable aquatic life. Water pollution caused by heavy metals has received worldwide attention due to their potentially toxic effects on human beings, flora and fauna. Heavy metal containing waters- both potable and waste, if not properly managed, could lead to severe damage to the environment and result in long term adverse effect on the health of the people. Heavy metal containing waters- both potable and waste, if not properly managed, could lead to severe damage to the environment and result in long term adverse effect on the health of the people. Health problems associated with some of these chemicals include cancer, birth defects, central nervous systems disorders, disruption of endocrine system and heart disease.

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*Authors for correspondence; E-mail: parandemadan2007@yahoo.co.in

The present work originated from the problem of hazardous heavy metal pollution. Heavy metal pollution is extremely pernicious because these metals are environmentally persistent and toxic. It is well perceived that there is a permissible limit each metal, above, which they are generally toxic and some are even hazardous. Metals are the only constituents that cannot be destroyed or altered by chemical or thermal methods. They must be either treated or converted into the most stabilized form to prevent their leaching back in to the environment though the conventional methods of treatment are widely accepted at industrial scale, they pose threat to environment even after the treatment process. These processes not only lack versatility to treat variety of contaminants but also are not environmentally compatible due to the use of specific chemicals and reagents. Regular discharge of wastewaters purified by methods like chemical precipitation into sources of domestic water supplies or other large water bodies may first lead to suppression of self purification process and subsequently to gradual poisoning of water and aquatic organisms. To combat this hazard electrochemical removal of mercury using carbon aerogel electrodes has been proposed for raising the overall efficiency of metal removal process.

Various electrochemical treatments are available[1] for effluent treatment however; these processes were basically developed for the treatment of either organic impurities or desalination of waters for human consumption. Moreover the cost of these electrochemical treatments was a major factor of concern due to degeneration and non reusability of the electrodes used. The present technique focuses primarily on the treatment of heavy metal ions containing wastewaters from various defence and industrial establishments. This process utilises titanium as a working electrode, which is stable, energy efficient and can effectively treat variety of effluents.

Objectives of the present work

This study involves control and minimization of environmental pollution through remediation of toxic metal ions from aqueous solutions using titanium electrodes. This technique can be up-scaled for the treatment of metal containing effluent from various industrial establishments thus, preventing the release of hazardous metal ions to water-bodies, which can otherwise lead to poisoning of aquatic as well as human life.

EXPERIMENTAL

For all experimental studies, waste water from local chemical and process industries (industrial sector in and around Pune, Maharashtra) was used.

(A). On the basis of batch mode studies, electrochemical reactor was designed. The reactor is operated as Continuous Stirred Tank Reactor (CSTR) with a batch recycles capacity of 10 Litres. The experimental set up is shown schematically in Fig. 1. The samples were drawn at regular intervals for monitoring of metal ion concentration. The setup on which experimentation was carried out is shown in Fig. 2.

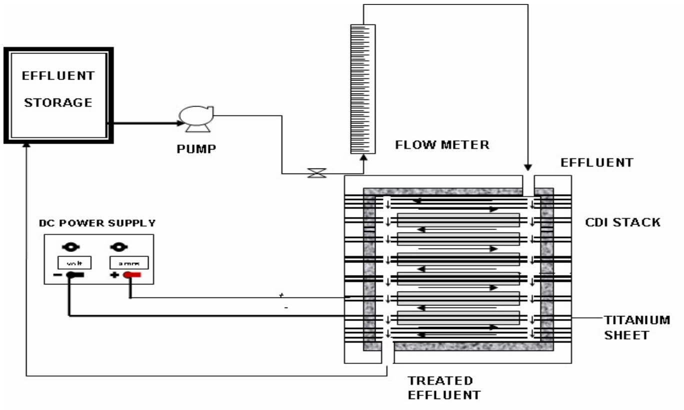

Fig. 1: Schematic Diagram of the Flow-Scale Set Up

Fig. 2: Experimental Setup for Flow Scale Process

RESULTS AND DISCUSSION

(B). Electrochemical removal of lead

Mechanism

Lead nitrate $Pb(NO_3)_2$ solutions is used as an electrolyte and after passage of current the following reaction takes place:

$$Pb(NO_3)_2 \xrightarrow{\quad} Pb^{2+} + 2(NO_3)$$

The reaction at anode is:

$$Pb^{2+} \xrightarrow{\quad} Pb^{4+} + 2e^{-} \quad E = -1.6 \text{ volts}$$

Then Pb^{4+} ion is further oxidized to hydrated lead dioxide ($PbO_2.\ xH_2O$).

Reaction at cathode:

$$NO_3^{-} + 2e^{-} \xrightarrow{\quad} NO_2^{-}$$

Nitrate ions are reduced more easily than Pb^{2+} ions and thus function as cathodic depolarisers to maintain the cathode potential below the value required for the reduction of lead ions. So, as the result of this experiment lead gets deposited on anode in the form of hydrated lead oxide.

B(1). To study the effect of concentration on lead removal (2, 10) the next experiments was conducted at fixed initial pH 1.45, lead concentration 5.697 mg/L and charge 0.2375 Ah. The maximum removal of lead was obtained at low concentrations as at a fixed charge as shown in Table 1. Table 1 is graphically represented in Fig. 3. Samples collected for analyzing drop of concentration in lead is shown in Table 1.

B(2). To study the effect of concentration on lead removal (4, 5, 10) the experiments were conducted at fixed initial pH 2.01 and lead concentrations 9.4 mg/L and charge 2.5 Ah. The maximum removal of lead was obtained at low concentrations as at a fixed charge as shown in Table 2 and Fig. 5.

Table 1: Electrochemical removal of lead using titanium electrodes

Sample No.	Time (min.) for withdrawl of sample	Current (A)	Voltage (V)	Concentration (ppm)
L0	0	-	-	5.7578
L1	5	0.07	1.6	5.6956
L2	10	0.07	1.6	5.5897
L3	15	0.07	1.6	5.4892
L4	25	0.07	1.6	5.3364
L5	35	0.07	1.6	5.1917
L6	45	0.07	1.6	4.7966
L7	55	0.07	1.6	4.3695

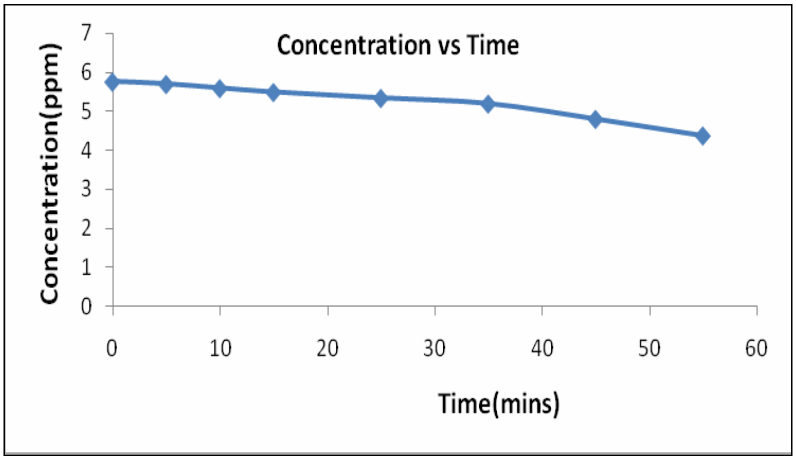

Fig. 3: Graphical representation for removal of lead with time

Fig. 4: Samples collected for analysing concentration drop of lead

Table 2: Electrochemical removal of lead using titanium electrodes

Sample No.	Time (min.) for withdrawl of samples	Current (A)	Voltage (V)	Concentration (ppm)
G0	0	-	-	9.413
G1	10	1	0.2	9.045
G2	20	1	0.2	8.996
G3	30	1	0.2	8.586
G4	45	1	0.2	8.300
G5	60	1	0.2	7.856
G6	75	1	0.2	7.023
G7	100	1	0.2	6.956
G8	125	1	0.2	6.233
G9	150	1	0.2	5.216
G10	175	1	0.2	4.864

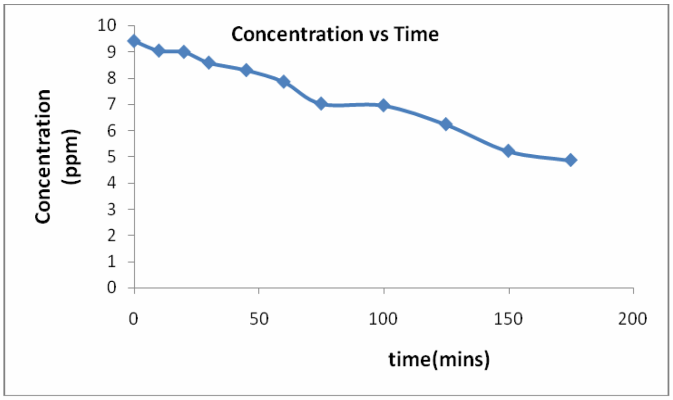

Fig. 5: Graphical representation for removal of lead with time

B(3). To study the effect of concentration on lead removal, further experimentation was conducted at fixed initial pH 2.7, lead concentration 5.697 mg/L and charges 0.2375 Ah. The maximum removal of lead was obtained at low concentrations as at a fixed charge as shown in Table 3. The data obtained (Table 3) is graphically represented in Fig. 6, Fig. 7 exhibits the samples collected for analysing drop of concentration in lead.

Table 3: Electrochemical removal of lead using titanium electrodes

Sample No.	Time (min.) for withdrawl of samples	Current (A)	Voltage (V)	Concentration (ppm)
T0	0	-	-	5.6974
T1	5	0.07	10.6	5.9124
T2	10	0.07	10.6	5.6727
T3	15	0.06	10.6	5.5663
T4	20	0.06	10.6	5.2681

Cont…

Sample No.	Time (min.) for withdrawl of samples	Current (A)	Voltage (V)	Concentration (ppm)
T5	30	0.06	10.6	5.2138
T6	40	0.06	10.6	5.1616
T7	60	0.06	10.6	4.9661
T8	80	0.06	10.6	4.5130
T9	105	0.06	10.6	4.2002
T10	135	0.06	10.6	4.1961
T11	165	0.06	10.6	4.1439
T12	195	0.05	10.6	4.0337
T13	225	0.05	10.6	3.7845
T14	255	0.05	10.6	4.4387
T15	285	0.05	10.6	3.287
T16	315	0.05	10.6	2.8796
T17	345	0.05	10.6	2.6489

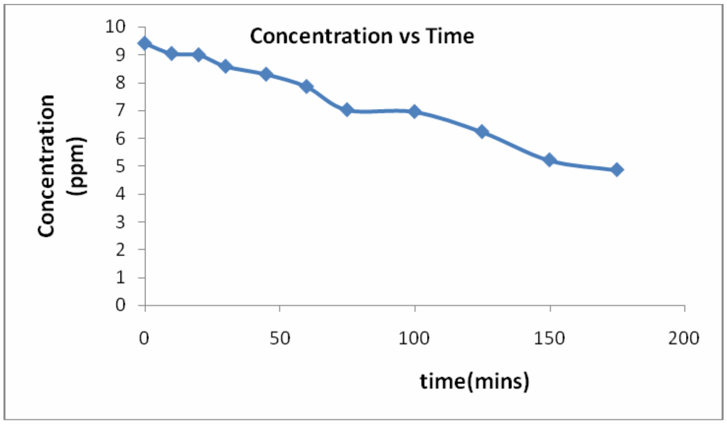

Fig. 6: Graphical representation for removal of lead with time

Fig. 7: Samples collected for analysing drop of concentration in lead

C. Effect of pH on lead removal

Increasing the pH of initial solution from 2 to 6, it was found that there is increase in the percentage removal of lead ions (Table 4). It is very clear from the results that titanium is effective for the quantitative removal of lead over the pH range 2-6. Between pH 2 and 6, the percentage of lead removal increases sharply and almost attains quantitative significance. This may be attributed mainly to the ionisable surface charge of the titanium.

Table 4: Removal efficiency of lead using titanium electrodes

Exp. No.	pH	Reduced conc. (ppm)	% Removal
B(1)	1.45	1.6	24.11
B(2)	2.01	4.5	48.32
B(3)	2.7	3	53.5

D. Electrochemical removal of chromium

Mechanism

Since all Cr (VI) species (3) are anionic, they would be drawn to the anode. In contrast, Cr (III) species could be either cationic or anionic. Since cationic species are already in the low oxidation state, complexation at the cathode without any cathodic reduction is expected, though reduction to metallic chromium is possible in some circumstances. However, trivalent anionic species such as Cr $(OH)_4^-$ and CrO_2^- would be forced to the anode where anodic oxidation to $HCrO_4^-$, CrO_4^{2-} or $Cr_2O_7^{2-}$ would be possible.

Parts of Cr (VI) also get reduced to Cr (III) on the cathode. This cathodically reduced Cr (III) can be electrodeposited on cathode or held in the cathodic layer, while a fraction can also be transported back into the electrolyte.

$$Cr^{6+} \xrightarrow{+e-} Cr^{3+} \qquad E = + 1.33\ V$$

$$Cr^{3+} \xrightarrow{+e-} Cr \qquad E = - 1.32\ V$$

For the above experimental studies, synthetic waste water sample prepared from $k_2Cr_2O_7$ was used and in this initial sample the total chromium exists in the form of Cr (VI). However, after the experiment, the final sample also consist some amount of Cr (III) validating the above supposition.

Effect of concentration on chromium removal

To study the effect of concentration on chromium removal experimentation were carried out at fixed pH 3 and chromium concentrations of 7.7 mg/L and charge of 2.025 Ah. As observed during the experimentation there was conversion of Cr^{6+} to Cr^{3+} resulting in the colour change from orange to greenish tinge after 3-4 hours of treatment. The results are tabulated in Table 5 and graphically in Fig. 8. HACH spectrophotometer was used for analysing samples of Cr^{3+}. Typical samples collected are shown in Fig. 9 and Fig. 10 shows the titanium electrode on which chromium is deposited.

Table 5: Electrochemical removal of chromium using titanium electrode

Sample No.	Time (min.)	Current (A)	Voltage (V)	Total concentration (ppm)	Cr^{6+}	Cr^{3+}
L0	0	-	-	7.702	7.2	0.502
L1	20	0.54	19.7	6.972	6.6	0.372
L2	40	0.54	19.7	7.053	6.4	0.653
L3	60	0.54	19.7	7.119	3.8	3.319
L4	80	0.54	19.7	7.254	3.4	3.854
L5	110	0.54	19.7	7.177	3.1	4.077
L6	140	0.54	19.7	7.092	2.8	4.292
L7	170	0.54	19.7	7.111	1.6	5.511
L8	200	0.54	19.7	7.191	1.4	5.791
L9	230	0.54	19.7	7.091	1.2	5.891

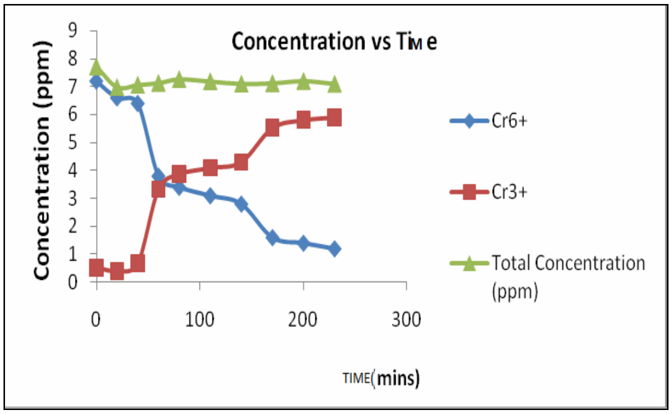

Fig. 8: Graphical representation for removal of chromium with time

Fig. 9: Samples collected for analysis of removal of chromium

Fig. 10: Chromium deposited on titanium electrode

(E). Electrochemical removal of nickel

Effect of concentration on nickel removal

To study the effect of concentration (5) experiments were conducted at fixed pH, charge and concentration. It was found that the percentage removal was infinitesimal. This is because there was a reaction between titanium and nickel sulphate resulting in the formation of titanium sulphate and resulting in corroding the surface of electrode. The results are tabulated in Table 6. Graphical representation of Table 6 is shown in Fig. 11. Corroded titanium electrode is shown in Fig. 12.

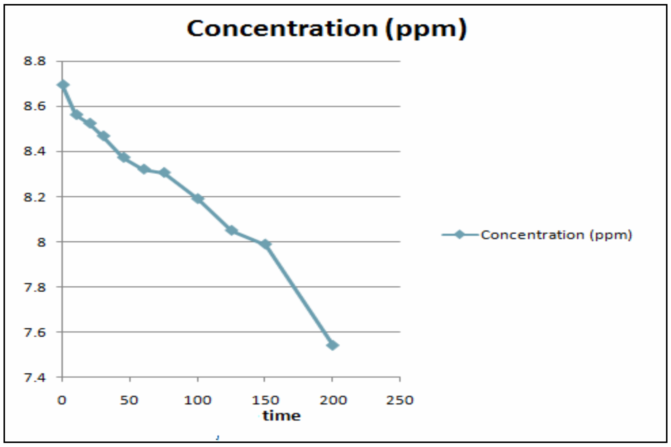

Fig. 11: Graphical representation of removal of nickel with time

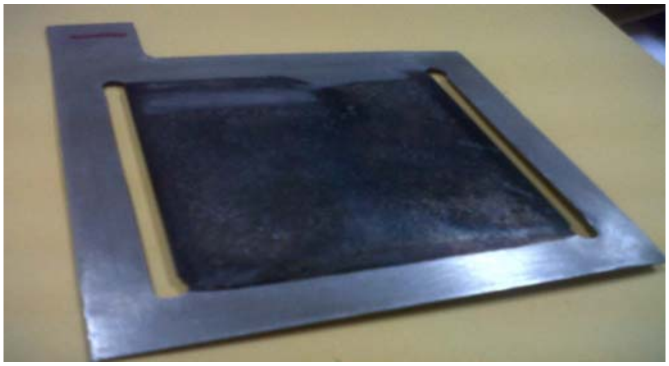

Fig. 12: Corroded titanium electrode

Table 6: Electrochemical removal of nickel using titanium electrodes

Sample No.	Time (min.) for withdrawl of the samples	Current (A)	Voltage (V)	Concentration (ppm)
S0	0	-	-	8.694
S1	10	0.14	29.1	8.562
S2	20	0.14	29.1	8.524
S3	30	0.14	29.1	8.468
S4	45	0.14	29.1	8.373
S5	60	0.14	29.1	8.321
S6	75	0.13	27.8	8.306
S7	100	0.13	27.8	8.301
S8	125	0.13	27.8	8.289
S9	150	0.13	27.8	7.989

CONCLUSION

In this study importance is given to the removal of toxic heavy metal ions from waste water. In the present work, we have made an attempt to present a detailed view of the widely adopted treatment methods and possible clean alternative to the conventional removal processes. This technique can also be employed for other heavy metal ions, viz; Cr, Cd, Hg, etc. Although, there are few reports (6, 7, 8, 9) in the literature stating that the efficiency of the electrode can be improved by using carbon aerogel on the titanium electrode, but detailed experimentation, mechanism and economics is not incorporated extensively.

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