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Original Research Paper

Study on Treatment of Electroplating Wastewater Using Constructed Wetland

J. S. Sudarsan*, V. T. Deeptha*, Deepak Maurya*, Mukesh Goel, K. Ravi Kumar** and Ashutosh Das****
*Department of Civil Engineering, Faculty of Engineering and Technology, SRM University, Kattankulathur-603 203, T. N., India
**Centre for Environmental Engineering, PRIST University, Thanjavur-613 403, T. N., India
Corresponding Author: Ashutosh Das

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ABSTRACT

Electroplating waste with very high concentration of metals and COD has always been posing a great challenge for treatment in an environmental-friendly way. The present study attempts at use of constructed wetland in treating electroplating waste. Three types of wetland setups were used in the study, namely: single wetland cell, two-wetland cells in cascade and single wetland cell with adsorbent bed for varying hydraulic detention times (2 days, 4 days and 6 days) in batch mode. The percentage removal of all metals was found to be more than 80%. The effect of varying detention time was not found to improve the removal efficiency in all the three cells varying modes of treatment, thus indicating 2 days to be optimum detention time. The mode of set-up of the wetland cells (i.e., with cascading and with augmented adsorbents) was not found to be statistically significant compared to treatment using single-isolated wetland cell unit, based on ANOVA test for two-factors, i.e., chemical speciation and wetland cell-setup types.

INTRODUCTION

The metals of most immediate concern are chromium, zinc, iron, mercury and lead, due to their toxicity and persistence (Amiri et al. 2014). Electroplating industries are especially known for their high discharge of toxic metals in their wastewater (namely, chromium, zinc, copper, arsenic, mercury, silver, cadmium, cobalt, nickel and lead) apart from other toxic organics, primarily, tetrachloroethylene, and trichloroethylene. In fact, the chemicals used in various electroplating operations are numerous, yet the chemicals in their effluents can be classified generally as, (i) acids and alkalies for cleaning purpose, (ii) inorganic chemicals, particularly heavy metals, which take part in reactions pertaining to plating, and (iii) organic chemicals which help in achieving certain properties or to enhance the process of plating. The environmental effects of these chemicals are effected by several routes, (i) by directly reacting with air, water and soil, resulting in degeneration or disintegration, (ii) by accumulating as persistent chemicals (geo-accumulation), (iii) by entering environmental pathways and transcending from non-living to living beings, causing toxicity to living organisms, and (iv) entering into food chain and finally affecting humans and cattle, often leading to either carcinogenic and/or mutagenic effects.

Some of the conventional techniques for removal of metals from industrial wastewater include chemical precipitation, adsorption, solvent extraction, membrane separation, ion exchange, electrolytic techniques, coagulation/flotation, sedimentation, filtration, membrane process, biological process and chemical reaction (Ji et al. 2002, Christos et al. 2007). However, the high cost of treatment by these methods warrants exploration of low-cost eco-friendly techniques. In this regard, constructed wetland provides an important avenue for wastewater treatment.

Constructed wetlands are man-made wetlands that take advantage of the same principal as a natural wetland system but in a more controlled environment, resulting in what is known as, applied ecological treatment of wastewater. Nowadays, there are many constructed and natural wetland systems which have been used for wastewater treatment. Constructed wetlands have been found suitable in treatment of not only domestic wastewater and other organic pollutants including farmyard runoff, landfill leachate, dairy wastewater, seafood processing wastewater, heavy oil & refinery wastewater (Zhang et al. 2010, Ong et al. 2010(a,b), Mustafa et al. 2009, Zurita et al. 2009, Yalcuk et al. 2009), but also heavy metals and toxic inorganics (Vymazal et al. 2006, Vymazal et al. 2009, Marchand et al. 2010). Based on these studies, attempt was for treatment of electroplating wastewater using constructed wetland.

In the present study, attempt was made to use *Phragmites* sp., a local wetland species in a media consisting of a gravel bed underlain by an impermeable layer, to study the treatability of electroplating wastewater in batch mode.

MATERIALS AND METHODS

Construction of wetland unit: The wetland unit was constructed as a lab scale prototype model designed as per USEPA guidelines. Local soil was taken for experimental setup from a nearby place, unaffected by the anthropogenic activity for a long period of time, up to 1 feet depth as a grab sampling method. The soil sample was then processed by air drying for 48 hours followed by sieving to remove roots, other organic mass and nodules of soil. The pilot wetland units (wetland cells) used for the study constitute a 20-litre PVC containers (length, width and depth of 70 cm, 40 cm and 30 cm, respectively) which was provided with a continuous flow (and uniform discharge) of wastewater through the inlet, with special care was taken to ensure along the entire width in order to prevent short circuiting in the drainage. The unit was built with slight inclination of 1-2% between inlet and outlet zones. The wetland media consisted of a gravel bed underlain by an impermeable layer. The bed was filled to a height of 7 cm with gravel of diameter 10-30 mm followed by a 7 cm thick top layer sand of 2 mm diameter. The top portion of the wetland unit was filled with local sandy clay loam soil to support vegetation. The physico-chemical characteristics of soil used as wetland media are presented in Table 1. The sand used was of diameter, porosity and permeability as 0.2 mm, 45% and 0.0025 cm/sec, whereas those for gravel were 2mm, 32% and 0.04 cm/sec, respectively. The wetland vegetation used for study is *Phragmites* sp., a local wetland species, which was collected from nearby lake and planted in the wetland unit. The plants were transplanted into the wetland unit and allowed to grow for one month before the beginning of the experiment. These would increase the residence time of water by reducing velocity, and increase sedimentation of the suspended particles in addition to contributing oxygen and provide a physical site for microbial bioremediation. The outlet zone was designed to allow variations in the level of water discharge.

Wetland cell set up: Three wetland cells were constructed (Fig. 1) (i) Cell 1-single wetland cell (as per the description in preceding paragraph); (ii) Cell 2-a second wetland cell (with same dimension as the Cell-1) connected as cascading setup with Cell-1 (i.e., the outlet of Cell 1, connected to the inlet of Cell 2); (iii) Cell 3-a third wetland cell (with same dimension as Cell-1), yet with addition of another layer (7cm) of adsorbent (*Cicer arietinum* seed coat) above the sand layer.

Collection, characterization and preparation of electroplating wastewater: The electroplating wastewater (collected from an electroplating industry in Ambattur industrial area at Chennai) was tested for basic parameters so that the levels of pre-treatment required can be established. Based on initial studies, a dilution of 1:2 of the wastewater was prepared, whose characterization is presented in Table 1. The physico-chemical parameters were studied using standard methods (APHA 2005) and the metals using atomic absorption spectrophotometer (LABINDIA, model AA-7000). Since the BOD is much less in the wastewater used for study (i.e., 58 mg/L) and COD is very high (i.e., 24,610 mg/L), the contributors of oxygen depleting agents are expected to be inorganic. Thus, out of ten metals characterized in the wastewater sample, six were selected for monitoring during the present study (Pb, Ni, Co, Cu, Zn, Cr) along with COD because of their relatively higher contribution to the wastewater, compared to rest of the parameters.

Wetland study: The selected parameters (COD, BOD, TDS, heavy metals : Pb, Ni, Co, Cu, Zn, Cr) at both the inlet and outlet were tested for inlet and outlet samples, for all the three wetland cells, using batch mode for varying Hydraulic Retention Time (HRT), i.e., 2 days 4 days and 6 days for all the three cells. Efficiency of treatment was calculated as percentage difference between inlet and outlet.

Statistical study for significance: To evaluate the statistical significance of the variation of the percentage metal and COD removal between the cells and within the cells (due to cascading and due to adsorption) 2-factor ANOVA tests (without replication) were carried out between the Cell 1 and Cell 2 as well as between Cell 1 and Cell 3, using Analysis ToolPak add-in for a HRT of 2 days, because the variation between 2 days, 4 days and 6 days of HRT were found to be not significant using t-test for paired two samples for means for significant level of 0.05.

RESULTS AND DISCUSSION

Organics removal efficacy: The removal of COD is found to be significantly high (more than 80%) in all the cells. Within two days of operations, COD reduction dropped significantly from 24610 mg/L to less than 1000mg/L in all the three cells. Further reduction was nominal reaching to 405 mg/L in Cell 1 after six days and 273 mg/L in case of Cell 3. Comparable results were obtained in Cell 2 with COD depleting to 394 mg/L. It can be noted from figures that almost complete removal was accomplished in first two days in all the cells. A similar reduction pattern was found in case of BOD removal.

High COD reduction is also observed by other authors using constructed wetland for treatment of toxic wastewaters. Saeed & Sun (2013) found 90% COD removal in treating the textile wastewaters. These results are even higher than that reported by Solano et al. (2004) in treating domestic wastewater, where they have used two macrophytes, cattail (*Typha* sp.) and reed (*Phragmites* sp.). The results are espe-

Table 1: Properties of the soil used as wetland media, and the electroplating wastewater.

Sl. No.	Properties of the Soil		Properties of the Wastewater	
	Parameters	Soil (sand)	Parameters	Testing sample (1:2)
1	Diameter (mm)	0.001 (1)	pH	3.24
2	Porosity (%)	40 (42)	EC (mmhos)	14.02
3	Permeability (cm/sec)	0.000047 (0.5)	TDS (g/L)	11.57
4	Liquid limit	28%	Turbidity (NTU)	6.3
5	Plastic limit	21%	COD (mg/L)	24610
6	Flow index	13.5	BOD (mg/L)	58
7	Plasticity index	7	Pb (mg/L)	11.45
8	Toughness index	0.52	Ni (mg/L)	44.79
9	Depth (feet)	< 1	Co (mg/L)	3.56
10	pH	7.68	Cd (mg/L)	<0.002 (BDL)
11	N (mg/10g)	68.4	Ag (mg/L)	0.047
12	P (mg/10g)	5.7	Hg (mg/L)	<0.061 (BDL)
13	K (mg/10g)	59	As (mg/L)	<0.053 (BDL)
14	Type of soil & grit	Sandy clay loam	Cu (mg/L)	956
15	Type of grit	Granite	Zn (mg/L)	77.7
16	Thickness of layer	7cm	Cr (mg/L)	16760

Table 2: Comparison of BOD/COD ratio for Cell 1 and Cell 2.

Days	BOD/COD ratio	
	Cell1	Cell 2
2	0.0404	0.04357
4	0.0457	0.0533
6	0.05679	0.0625

Table 3: Metal removal comparison for Cell 1, Cell 2 and Cell 3.

Metals	% Removal		
	Cell 1	Cell 2	Cell 3
Pb (mg/L)	100.00	100.00	100.00
Ni (mg/L)	100.00	100.00	99.45077
Co (mg/L)	100.00	100.00	98.20225
Cu (mg/L)	99.48431	100.00	100.00
Zn (mg/L)	92.10167	99.98117	92.34363
Cr (mg/L)	99.46463	99.73968	100.00

cially significant since domestic wastewater is easier to mineralize using organic materials, while industrial wastewater such as electroplating wastewater is much more difficult owing to containing more toxic chemicals. BOD/COD ratio is an indication of toxicity of wastewater, lower the ratio, higher the toxicity. The ratio was evaluated for Cell 1 and Cell 2 and was compared in Table 3. As the COD removal was also similar, the ratio is also found to be similar for both the cells. Interestingly, the ratio is increasing with the period of operation. The value was 0.0406 at day 2, which increased to 0.0567 at day 6 for Cell 1. Though the difference is minimal, it speaks of importance of prolonged operation of constructed wetland so as to achieve complete mineralization. The results clearly indicate the potential of *Phragmites australis*, a local species in detoxifying the wastewater.

Metals removal efficacy: Of the six metals studied, Ni, Co, Cu and Cr have been found to be removed maximum in all the cells. Zinc was found to show relatively higher removal in Cell 2 compared to that in Cell 1 and Cell 3. Whereas, lead removal was faster in Cell 2 and all the lead was removed within 2 days of operation in case of Cell 2. Table 4 compares the different cells in their removal of metals and all of them showed similar performance for the final analysis. The results are especially significant in terms of Cr, Cu, Ni and Zn removal as these values were very high in the influent wastewater. Electroplating wastewaters are notorious for their discharge of toxic metals into aquatic streams and suitable treatment technology must be available to combat the release of these metals from the industries.

There are several other studies in the literature using wetland unit for removal of heavy metals. Apart from *Phragmites australis,* other species such as *Typha latifolia*, *Schoenoplectus lacustris*, and *Iris pseudacorus*, have also been used for heavy metal removal (Sobolewski 1999, Sjoblom 2003). Constructed wetlands are complex in their treatment process as there are undefined interactions between microbes, soils, plants and sediments. In general, the process is meditated by microbial communities, but all these pathways are dependent on each other making the process complex. Moreover, reactivity of metals also plays the role in their removal. Since the metals detected and removed in this treatment of electroplating wastewaters are cationic in nature, and hence probably precipitated at the similar rate. The main process seems to be sorption and precipitation as also observed by Singhakant et al. (2009). But our results suggested that Cell 2 (two wetlands in sequence) has higher

Table 4: Two-way ANOVA for removal efficiency (%) by various wetland cells.

Source of Variation	SS	df	F	P-value
Among composition (Cell 1 : Cell 2)	108.721289	5	0.923984881	0.53351
Among wetland cells (Cell 1 : Cell 2)	102.7470459	1	4.366059208	0.090956
Error (Cell 1: Cell 2)	117.665658	5	-	-
Among composition (Cell 1 : Cell 3)	400.6991135	5	60.43198865	0.00018
Among wetland cells (Cell 1 : Cell 3)	2.608264061	1	1.966844683	0.219717
Error (Cell 1 : Cell 3)	6.630579639	5	-	-

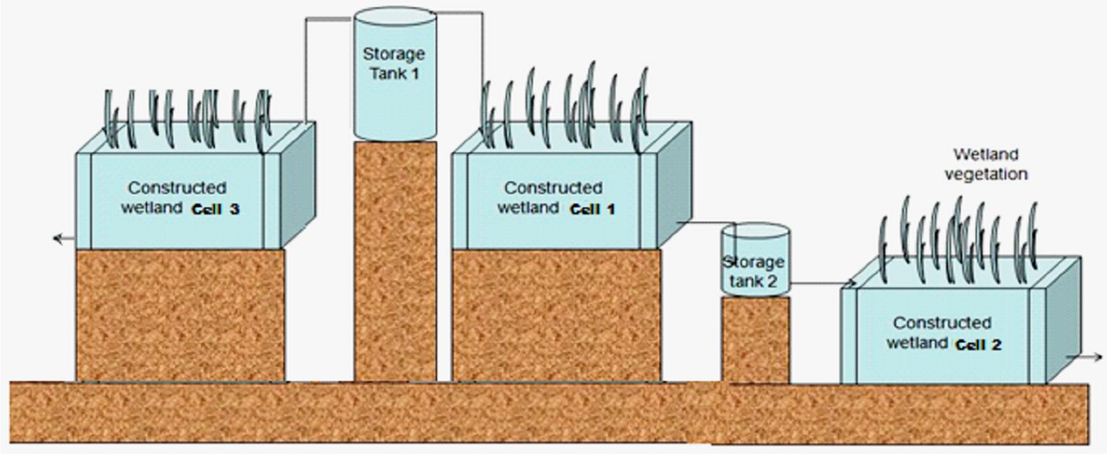

Fig. 1: Constructed wetland set-up (Cell 1, 2 and 3).

removal compared to Cell 3 (having adsorbents). Cell 2 offered longer time for precipitation and hence resulted in higher removal. Metal removal was high probably because microorganisms augment the rate by mediating redox and precipitation process. Cohen et al. (2006) observed that sulphate reducing bacteria (SRBs) reconciled the precipitation of arsenic compounds. Although plants have negligible role in metals removal (Cooper et al. 1996), they indirectly assist the process by providing organic matter as carbon source and thus promote metal oxidizing bacteria. Microbiology of constructed wetlands can provide a better understanding of metal removal from electroplating wastewater.

Significance of variation among the wetland cells: Variation of metal removal with and without cascading (which means Cell 1 and Cell 2), the cells do not show any significant change as revealed by p-value of the ANOVA (two factors without replication) as 0.09 (Table 2). This means, null hypothesis that the performance of the cells is insignificant, cannot be rejected for significant level 0.05 (alpha = 0.05%). The similar results were also observed with ANOVA test for cell with and without adsorbent with regard to effect of cells (p-value = 0.21 greater than significant level 0.05), when cells with and without adsorbents are compared (i.e., Cell 1 and Cell 3) (Table 2). This means with regard to overall metal removal, use of cascading cells or cell with augmented adsorbent bed may not be necessary; rather single constructive wetland unit would be sufficient. Interestingly, when compared among various set-ups, the variation among the metals is significantly high (p-value = 0.00018, i.e with 99.9% confidence) in case of usage of adsorbent, whereas in case of cascading the variations still remains insignificant (with p-value = 0.53 much greater than significant level 0.05%). This may be because of the fact that the variation among the metals are selective with regard to the adsorbents used, conforming to the specificity of the adsorbents.

CONCLUSIONS

The electroplating wastewater was found to be most enriched in metals and inorganics, compared to organics (as indicated by significantly high COD, compared to BOD). The use of wetland study for electroplating wastewater was found to be an efficient option, especially in dealing with COD and various metals (specifically, Pb, Ni, Co, Cu, Zn and Cr). The variation in hydraulic detention time was not found significantly to influence the removal efficiency and, thus, a two days of detention time was found to be fairly optimum for all the three types of cells used in the study. However, use of cascading setup or additional adsorbent beds, do not

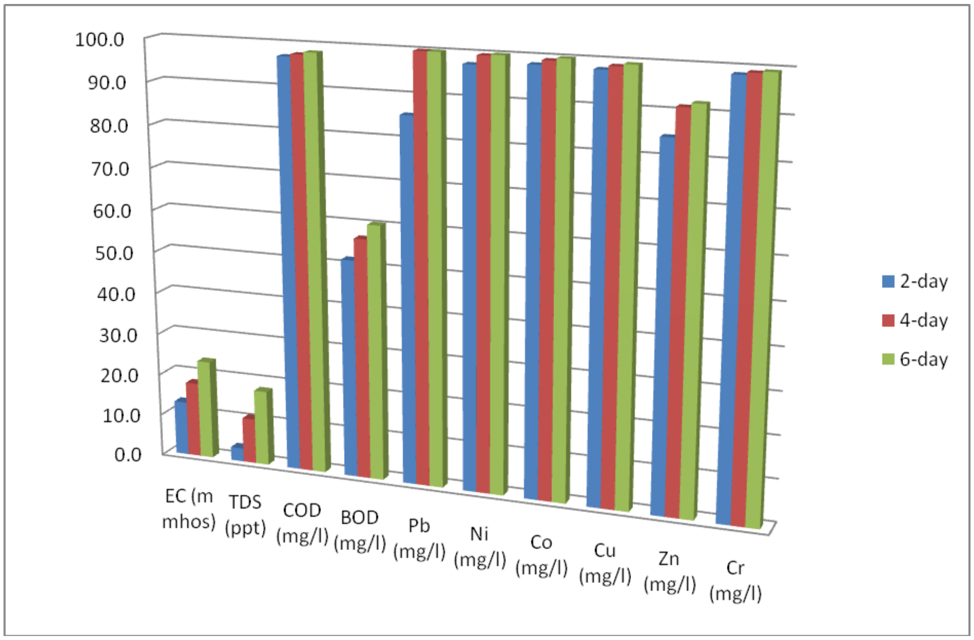

Fig. 2: Reduction in water quality parameters by wetland Cell-1 at different times.

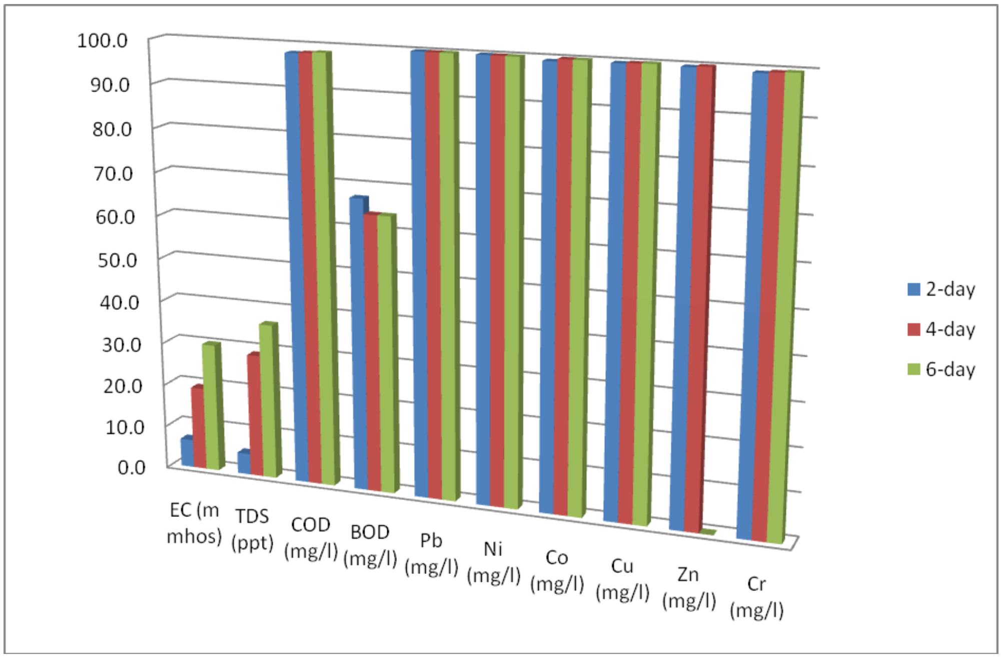

Fig. 3: Reduction in water quality parameters by wetland Cell-2 at different times.

seem to play any statistical significant improvement in overall removal of the above mentioned pollutants, in comparison to isolated wetland, although variability of metal removal is higher in case of wetland cell with adsorbent and individually Ni, Co, Cu and Cr show relatively better removal in case of cascaded setup of wetland cells.

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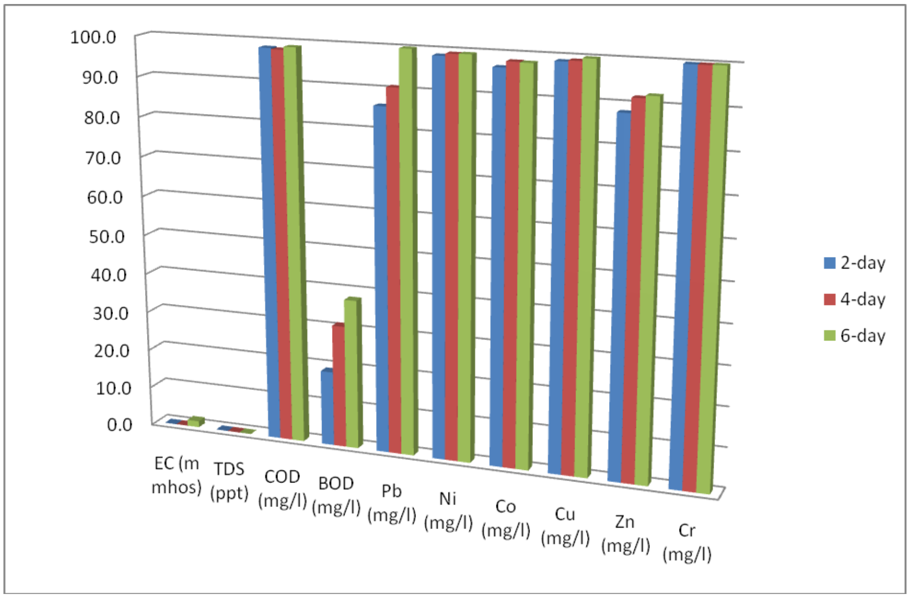

Fig. 4: Reduction in water quality parameters by wetland Cell-3 (with adsorbent) at different times.

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