Phenols and Manganese Removal from Landfill Leachate and Municipal Wastewater Using the Constructed Wetland

Amin Mojiri, Lou Ziyang

Abstract**—**Constructed Wetland (CW) is a reasonable method to treat wastewater. Current study was carried out to co-treat landfill leachate and domestic wastewater using a CW system. *Typha domingensis* was transplanted to CW, which encloses two substrate layers of adsorbents named ZELIAC and zeolite. Response surface methodology and central composite design were employed to evaluate experimental data. Contact time (h) and leachate-to-wastewater mixing ratio (%; v/v) were selected as independent factors. Phenols and manganese removal were selected as dependent responses. At optimum contact time (48.7 h) and leachate-to-wastewater mixing ratio (20.0%), removal efficiencies of phenols and manganese removal efficiencies were 90.5%, and 89.4%, respectively.

Keywords**—**Constructed wetland, manganese, phenols, *Thypha domingensis*.

I. INTRODUCTION

MUNICIPAL SOLID WASTE (MSW) has continued to be a major problem in many nations of the world. Solid waste has gradually become a threat to the environment of developing countries as they progressively move towards industrialization. Sanitary landfills are the most prevalent manner of solid waste treatment in most countries. Although this type of solid waste treatment provides some benefits, it has a disadvantage, namely, the production of leachate [1]. Leachate is created when water penetrates into landfill waste, carrying with it certain forms of pollutants, such as ammoniacal nitrogen (NH_3–N), chemical oxygen demand (COD), color, phenols, and metals. Leachate composition depends on deposited waste, landfill age, site hydrology, landfill operation, and landfill type [2]. One of the most pollutants in landfill leachate is metals. The main sources of heavy metals in landfills are fluorescent tubes, pharmaceuticals, photographic chemicals, detergent, waste oil, batteries, paint, and electronic waste [3]. When water sources are polluted by leachate containing heavy metals, the mechanism leading to health hazards is bioaccumulation. Heavy metal toxicity can result in damaged or reduced mental, central nervous function, etc. [3]. Another contaminant in the landfill leachate is phenols. Phenol is the priority pollutant since it is toxic and harmful to organisms even at low concentrations [4]. Typically, combinations of physical, chemical, biological and remediation techniques are applied for landfill leachate treatment because of difficulty in obtaining satisfactory treatment efficiencies by a single method [5].

The use of plants for remediation of wastewater, has gained acceptance in the past two decades as a cost effective and non-invasive method [6]. A constructed wetland (CW) system includes permeable substrata, such as gravel, which is commonly planted with emergent wetland plants, such as *Typha*, *Schoenoplectus*, *Phragmites*, and *Cyperus* [7]. *Typha* is often found close to water, in lakes, lagoons and riverine areas of numerous regions of the world, in America, Europe and Asia [8]. Southern cattail (*Typha domingensis*) is highly salt-tolerant and considered as the potential source of pulp and fiber [9]. Mojiri [6] studied on metals removal from municipal wastewater using *Typha*. This result showed that *Thypha* is an effective plant to removal metals from wastewater.

Current study aimed to (1) co-treat urban landfill leachate and municipal wastewater by using CW and (2) use a new composite adsorbent, namely ZELIAC, and zeolite in CWs.

II. MATERIALS AND METHODS

A. Landfill Leachate and Domestic Wastewater Sampling

Urban landfill leachate samples were selected from Isfahan Landfill (geographical coordinates 32° 45′ 36″ N and 51° 46′ 31″ E). The total landfill area is approximately 56 ha.

Domestic wastewater samples were taken from Isfahan East Wastewater Treatment Plant. Isfahan is a large city located at the center of Iran.

B. Constructed Wetland System

T. domingensis were transplanted to the constructed wetland (CW), which contained two substrate layers of adsorbents (named ZELIAC and zeolite, respectively) whose widths were both 2 mm (Fig. 1). The volume of the wetland was approximately 43 L. An air pump was used to supply air to the wetland.

C. ZELIAC and Zeolite Preparation

To prepare the ZELIAC, zeolite, activated carbon, lime stone, rice husk ash, and Portland cement were ground, passed through a 300 mm mesh sieve, and then mixed. The mixture was then evenly poured in the mold after the addition of water. After 24 h, the materials were removed from the mold and soaked in water for three days for the curing process. After allowing the materials to dry within two days, they were

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crushed and passed through a sieve. The diameters of ZELIAC and zeolite were both 1 mm [10].

TABLE I
CHARACTERISTICS OF LANDFILL LEACHATE, DOMESTIC WASTEWATER AND SLUDGE

Parameters	Leachate	Wastewater	Standard discharge limit [a]
pH	7.95	6.74	6.5 – 8.5
EC (ms/cm)	3.87	1.53	-
TSS (mg/L)	607	-	60
COD (mg/L)	2301	123	100
BOD_5/COD	0.20	-	-
Total iron (mg/L)	8.13	1.11	3
Total manganese (mg/L)	2.08	0.50	1
Phenols	1.01	0.11	0.01

a. Effluent Limitations for Non-Hazardous MSW Landfills in the Iran

D.Analytical Methods and Statistical Analysis

Colour, chemical oxygen demand (COD), phenols, and manganese contents in leachate and wastewater, and manganese contents in the roots and shoots were monitored through spectrophotometry in accordance with Standard DR/2500 HATCH [11].

The removal efficiencies of phenols, and manganese were determined by evaluating the target parameters before and after treatment were performed. Removal efficiency was calculated using (1):

$$\text{Removal (\%)} = \frac{(C_i - C_f)\times 100}{Ci} \tag{1}$$

where Ci and Cf are the initial and final concentrations of the parameters, respectively.

Response surface methodology and central composite design were utilized to analyze experimental data. Contact time (h) and leachate-to-wastewater mixing ratio (%; v/v) were considered as independent factors. Phenols and manganese contents were used as responses. The total number of experiments for two factors was 13. Each factor is composed of three levels; thus, a quadratic model is an appropriate model, as shown in (2):

$$Y = \beta \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_i X_{i2} + \sum_{i<j}^{k} \sum_{j}^{k} \beta_{ij} X_i X_j + \cdots + e \tag{2}$$

where Y is the response; Xi and Xj are the variables; β0 is a stable coefficient; βj, βjj, and βij represent the interaction coefficients of linear-, quadratic-, and second-order terms, respectively; k is the number of analyzed parameters; and e is the error. The results were investigated through ANOVA in Design Expert Software Version 6.0.7.

III. RESULTS AND DISCUSSIONS

Table I shows that leachate contains high levels of phenols (1.01 mg/L), and manganese (2.08 mg/L). The 3D surface plots for the pollutant removal (color, COD, ammonia, and phenols) in normal SBR and PZ-SBR are shown in Figs 2, 3. The ANOVA results for response parameters and response value under optimum conditions are shown in Tables II, III, respectively.

TABLE II
EXPERIMENTAL VARIABLES AND RESULTS

Run	Contact Time (h)	L/W Ratio (%)	Phenols rem. (%)	Mn rem. (%)
1	42.0	50.00	86.87	81.69
2	12.0	50.00	85.18	78.46
3	42.0	50.00	86.82	78.56
4	72.0	20.00	90.01	86.21
5	42.0	50.00	87.69	82.38
6	42.0	50.00	89.11	85.13
7	72.0	50.00	86.64	79.23
8	12.0	20.00	86.71	83.24
9	42.0	50.00	88.69	83.93
10	42.0	80.00	85.84	72.00
11	12.0	80.00	83.62	72.47
12	42.0	20.00	90.35	91.09
13	72.0	80.00	84.19	70.05

TABLE III
ANOVA RESULTS FOR RESPONSE PARAMETERS

Responses	R^2	Adj. R^2	Adec. P.	SD	CV	PRESS
Phenols	0.9155	0.8552	12.27	0.79	0.91	7.12
Mn	0.9200	0.8628	13.03	2.26	2.81	144.7

R^2: Coefficient of determination; Adj. R^2: Adjusted R^2; Adec. P.: Adequate precision; SD: Standard deviation; CV: Coefficient of variance; PRESS: Predicted residual error sum of square

A. Phenols Removal

Landfill leachate contains a large number of dangerous compounds, such as aromatics, halogenated compounds, heavy metals, phenols, pesticides, and ammonium, which are considered dangerous even in small amounts. The harmful effects of these compounds are often caused by multiple and synergistic effects. Phenolic compounds released into the environment are particularly of high concern because of their potential toxicity. These compounds detected in the leachate include cresols, phenol, and substituted as well as chlorinated phenols. Cresols and phenol, which are short-chain phenols previously reported by [12] in leachates of urban and industrial landfills, originate from various types of wastes. Phenol and its substitutes are commonly produced by the transformation of several pesticides [13]. Kurata et al. [14] measured 41 kinds of phenols in three landfill sites in Japan.

The removal efficiencies varied from 83.62% (contact time = 2 h, and leachate-to-wastewater ratio = 80%) to 90.35% (contact time = 42 h, and leachate-to-wastewater ratio = 20%). An optimal phenols removal efficiency of 90.36% was obtained at 53.82 h contact times, and 22.75% leachate-to-wastewater ratio.

Yalcuk [15] investigated the removal of phenol from olive mill wastewater in constructed wetlands. This result showed that the constructed wetland was an affective system in removing phenols. Bubba et al. [16] obtained 83.4% of phenol removal from Olive Mill Wastewater (OMW) by using a grain layer constructed wetland system in their study.

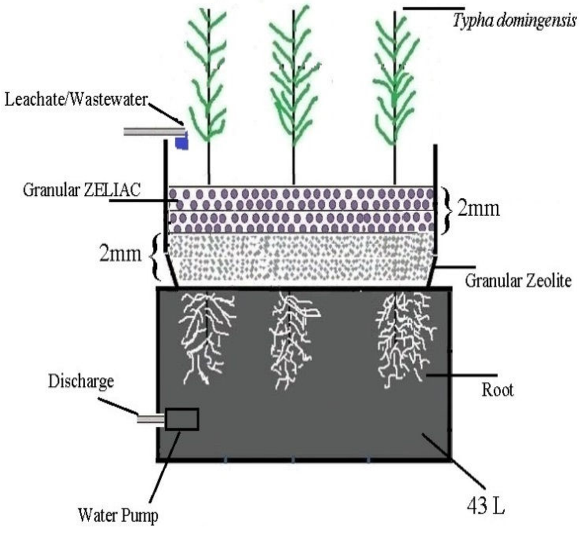

Fig. 1 Constructed Wetland in Current Study

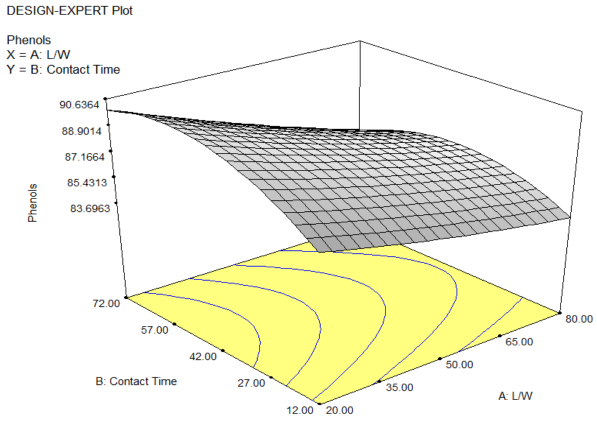

Fig. 2 The 3D surface plots of phenols removal

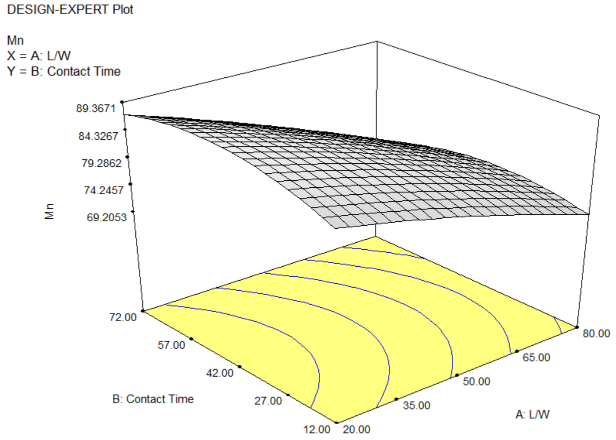

Fig. 3 The 3D surface plots of Mn removal

B. Manganese Removal

Manganese (Mn) ions are released in wastewaters by numerous industries, such as pyrolusite (MnO_2) treatment, ink and dyes, glass and ceramics, paint and varnish, steel alloy dry cell batteries, fireworks and match manufacturing, and galvanized metal waste processing plants [17].

The removal efficiencies varied from 70.05% (contact time = 72 h, and leachate-to-wastewater ratio = 80%) to 91.09% (contact time = 20 h, and leachate-to-wastewater ratio = 20%). An optimal Mn removal efficiency of 89.37% was obtained at 48.65 h contact times, and 20.00% leachate-to-wastewater ratio.

In wetlands, plants can uptake metals. Moreover, media and substrates can help facilitate metal removal. Wojciechowska and Waara [18] reported metal removal rates of 90.9% to 99.9% by using CW.

C. Accumulation Mn in Shoots and Roots of Typha

Table IV shows the concentrations of Mn in the roots and shoots of *Typha* in each run the equation. The efficiency of phytoremediation can be quantified by calculating translocation factor. The translocation factor indicates the efficiency of the plant in translocating the accumulated metal from its roots to shoots. It is calculated as [19]:

$$TF = \frac{C_{shoot}}{C_{root}} \tag{3}$$

where C_{shoot} is concentration of the metal in plant shoots and C_{root} is concentration of the metal in plant roots.

Based on Table IV, translocation factors (TF) were more than 1 in all treatments.

TABLE IV
ACCUMULATION OF MN IN ROOTS AND SHOOTS OF *THYPA*

Run	Root	Shoot	TF
1	0.159	0.164	1.03
2	0.011	0.012	1.09
3	0.191	0.198	1.03
4	0.101	0.105	1.04
5	0.148	0.152	1.02
6	0.168	0.179	1.06
7	0.194	0.185	0.95
8	0.019	0.018	0.94
9	0.227	0.218	0.96
10	0.183	0.148	0.80
11	0.116	0.095	0.81
12	0.015	0.015	1.00
13	0.205	0.221	1.07

Soluble metals can enter into the root symplast by crossing the plasma membrane of the root endodermal cells, or they can enter the root apoplast through the space between cells. While it is possible for solutes to travel up through the plant by apoplastic flow, the more efficient method of moving up the plant is through the vasculature of the plant, called the xylem. To enter the xylem, solutes must cross the Casparian strip, a waxy coating, which is impermeable to solutes, unless they pass through the cells of the endodermis. Therefore, to enter the xylem, metals must cross a membrane, probably through the action of a membrane pump or channel. Once loaded into the xylem, the flow of the xylem sap will transport the metal to the leaves, where it must be loaded into the cells of the leaf, again crossing a membrane. The cell types where the metals are deposited vary between hyper-accumulator species [20].

Metal accumulating plant species can concentrate heavy metals like Cd, Zn, Co, Mn, Ni, and Pb up to 100 or 1000 times more than those taken up by non-accumulator (excluder) plants. The uptake performance by plant can be greatly improved [21].

IV. CONCLUSION

Normally, combinations of physical, chemical, biological and remediation methods are employed for landfill leachate treatment due to difficulty in obtaining satisfactory treatment efficiencies using a single technique. Current study was carried out to co-treat landfill leachate and domestic wastewater using a constructed wetland (CW) system. CCD and RSM were employed to optimize parameters. The main conclusions of this study are presented below:

1. At the optimum condition, the designed CW could eliminate 90.5%, and 89.4% of phenols and Mn, respectively.
2. The accumulation of Mn in the roots and shoots of plant was observed. The results displayed that TF was >1 in several runs. So *Typha* is a hyper-accumulator plant.

ACKNOWLEDGMENT

The authors would like to acknowledge the Sganghai Jiao Tong University for their supports to present this work in the international conference.

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