

Understanding Integrated Removal of Heavy Metals, Organic Matter and Nitrogen in a Constructed Wetland System Receiving Simulated Landfill Leachate

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Abstract—This study investigated the integrated removal of heavy metals, organic matter and nitrogen from landfill leachate using a novel laboratory scale constructed wetland system. The main objectives of this study were: (i) to assess the overall effectiveness of the constructed wetland system for treating landfill leachate; (ii) to examine the interactions and impact of key leachate constituents (heavy metals, organic matter and nitrogen) on the overall removal dynamics and efficiency. The constructed wetland system consisted of four stages operated in tidal flow and anoxic conditions. Results obtained from 215 days of operation have demonstrated extraordinary heavy metals removal up to 100%. Analysis of the physico-chemical data reveal that the controlling factors for metals removal were the anoxic condition and the use of the novel media (dewatered ferric sludge which is a by-product of drinking water treatment process) as the main substrate in the constructed wetland system. Results show that the use of the ferric sludge enhanced heavy metals removal and brought more flexibility to simultaneous nitrification and denitrification which occurs within the microbial flocs. Furthermore, COD and NH₄-N were effectively removed in the system and this coincided with enhanced aeration in the 2nd and 3rd stages of the constructed wetland system. Overall, the results demonstrated that the ferric dewatered sludge constructed wetland system would be an effective solution for integrated removal of pollutants from landfill leachates.

Keywords—Constructed wetlands, ferric dewatered sludge, heavy metal, landfill leachate.

I. INTRODUCTION

LANDFILL leachate is highly contaminated with organic contaminants ammonia and heavy metals. Leachate from young landfills are characterised by high chemical oxygen demand (COD), whereas leachate from old landfills are more stable, with lower COD. Ammonia, at levels as high as 5000 mg/L [1], is the major long-term pollutant in these leachates and its amount does not decrease as landfills age. These high levels, together with the enormous quantities of leachate, have posed a serious pollution threat to the water environment, so

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that the removal of ammonia has become a critical issue of leachate treatment. The presence of heavy metals and organic matter at typical concentrations in landfill leachate usually has toxic effects on microbes and further inhibits ammonia oxidation.

One economically advantageous and ecologically beneficial solution for leachate management is the constructed wetland system (CWS). This system utilises a complex variety of anaerobic and aerobic reactions to break down, immobilise or incorporate organic substances and other contaminants from polluted effluents [2]. The vertical flow constructed CWS has been widely used for purification of various types of wastewater [3]. The performance of a vertical flow CWS as a treatment can be influenced by the design of the wetland and the bed media characteristics [2]. Another significant feature is the so-called ferric dewatered sludge, which is an inevitable by-product of the drinking water treatment process when ferric sulphate is used as the primary coagulant. Conventionally, ferric dewatered sludge is regarded as a waste with unknown reuse value. However, this globally available waste has a high heavy metal retention capability, making it a useful low-cost absorbent for heavy metal immobilisation [4].

The removal of organics and nitrogen is enormously important because organic-rich wastewater such as landfill leachate often deplete the dissolved oxygen (DO) concentration in wastewater bodies, thereby inhibiting nitrification [5]. DO is a crucial environmental parameter that controls nitrification and organic matter biodegradation in CWSs, as well as the classical nitrogen removal route in CWSs, known as nitrification and denitrification. Complete total nitrogen elimination depends initially on efficient nitrification of ammonia. Intermittent aeration is an effective method that provides high DO during aeration, thereby enhancing nitrification, while the sufficient supply of carbon leads to high-efficiency denitrification when the aeration is turned off [6].

Unlike organic pollutants, heavy metals cannot be degraded through biological processes. Adsorption onto a substrate, precipitation as insoluble salts (e.g. sulphides or oxyhydroxides), filtration, sedimentation and plant uptake are the main processes for heavy metal removal in a CWS [7].

In most cases, the evaluation of the treatment potential of CWSs focuses on biodegradable organic matter and nutrients on the one hand, and toxic pollutants on the other, without

considering the effect of the presence of the latter type of pollutants on the removal of the former. Little work has been carried out to date to investigate the integrated removal of heavy metals, organic matter and ammonia in CWSs. In this study, we specifically examined the overall removal of heavy metals, organic matter and nitrogen in a CWS and assessed the impact of their relative concentrations. In addition, the effects of high pollutant loading rates and different operational conditions (anoxic condition and tidal flow) on the treatment performance were comprehensively evaluated.

II. MATERIAL AND METHODS

A. System Configuration and Operation

The CWS consisted of four stages operated with tidal flow and anoxic condition strategies. Each stage was constructed using Perspex columns 100 mm in diameter and 1000 mm in height. The columns were filled with 22±3 mm round gravel to a depth of 150 mm as the bottom layer. Air-dried ferric dewatered sludge (particle size 1-3 mm) was used as the main media layer (350 mm), followed by 7±2 mm washed gravel at a depth of 150 mm, giving an average porosity value of 0.4. Common reed, *Phragmites australis*, was planted on the top layer of each stage. Each stage experienced cyclic 'wet/dry' periods with the artificial landfill leachate, with the periods generated by peristaltic pumps. Each wet/dry cycle was completed in four hours, giving a hydraulic loading rate of 1.5 m³/m².d. Prior to loading the CWS with the landfill leachate, the system was inoculated with activated sludge obtained from a local municipal wastewater treatment plant for 3 weeks. Thereafter, the four stages (marked as 1–4) were operated based on the operating scheme summarised in Table I.

Artificial landfill leachate was synthesised in the laboratory to simulate young landfill leachates using C₂H₃NaO₂ and (NH₄)₂SO₄ for COD and ammonium (NH₄-N), respectively, and CdSO₄·8/3H₂O salt, Cr(SO₄)₂·12H₂O salt and PbCl₂ salt, respectively for Cd, Cr and Pb.

TABLE I
 OPERATING SCHEME FOR THE CWS

Stages	Input points	Distribution ratio (%)	Cycle time (h)	Wet/dry (h)
Stage 1	Influent	100	4	4.0: 0.17
Stage 2	Stage 1	100	4	1.0: 3.0
Stage 3	Stage 2, Effluent	50:50	4	1.0: 3.0
Stage 4	Stage 3	100	4	4.0: 0.17

B. Wastewater Sampling and Analysis

Wastewater samples were taken from influent, effluent and each stage once a week to analyse the transformation of heavy metals, organics and nitrogen in the four stages. DO, pH and temperature were measured with a multiparameter meter (HANNA HI9828) immediately in situ at the four different levels of the wastewater depth from the vertical column. The COD, nitrite (NO₂-N), nitrate (NO₃-N), NH₄-N and total nitrogen (TN-N) were analysed using a Hach DR/3900 spectrophotometer according to its standard operating

procedures. Heavy metals were measured with an ICP-OES instrument in the laboratory.

III. RESULTS AND DISCUSSION

The overall treatment performance during different conditions [i.e. anoxic condition (stage 1 and 4) and tidal flow (stage 2 and 3)] is summarised in Fig. 1, and the mean influent and effluent from each stage are represented in Table II. The CWS demonstrated satisfactory performance for removal of heavy metals, COD, NH₄-N and TN-N. Heavy metals were completely removed from the system effluent and the removal remained stable over an operational period of 215 days. The removal of COD was up to 84% during first 70 days at an influent concentration of 639 mg/L. However, the average removal efficiency of COD decreased to 60% after this period, perhaps due to clogging that took place after 70 days of operation. The mean removal of NH₄-N and TN-N from the system was 85% and 81%, respectively. TN-N removal mainly depended on nitrification and the availability of carbon sources for denitrification [8]. With a sufficient COD as a carbon source (Fig. 1 (a)) and effective nitrification (Fig. 1 (b)), the system achieved an effective TN-N elimination of up to 91% (Fig. 1 (c)).

A. The Rate of Heavy Metals Removal

The mean concentrations of heavy metals and heavy metal removal from the influent and the four stages are represented in Fig. 2. The figure shows that the heavy metals studied were effectively removed in the CWS; however, the removal efficiency was more pronounced in stage 1, reaching 63%, 86% and 66% for Pb, Cr and Cd, respectively. The excellent removal efficiency obtained in stage 1 for heavy metals could be attributed to the anoxic conditions in this stage, which leads to a reduction of metal oxides and results in a release of dissolved metals. These metals can still adsorb onto organic matter or form amorphous co-precipitates of (oxy)hydroxides of iron in the sludge and heavy metals [7]. In addition, previous studies have shown that the ferric dewatered sludge was mainly composed of amorphous iron, and more importantly, the ferric dewatered sludge exhibited a high heavy metal adsorption capacity [4], [9]. The Langmuir isotherms data indicated that this ferric dewatered sludge has an adsorption capacity of 40 µg/g, 130 µg/g and 30 µg/g for Pb, Cr and Cd, respectively [4]. The removal of Pb and Cd could be also occurred by precipitation of metal sulphides, which is recognised as the most important reaction for metal removal from wastewater in CWSs [10]. Mohammed et al. found 1.39 mg/g of sulphate in ferric dewatered sludge and additional sulphate was supplied by wastewater loading.

Lead forms insoluble compounds with sulphide in anaerobic zones of treatment wetlands and sulphate in aerobic zones as the condition in the first and second stages, respectively (1), (2), whereas Cd forms insoluble compounds with sulphide in the first stage (3) [7]. The formation of sulphide enables the long-term removal of heavy metals, since the metal sulphides may stay permanently in the sediment as

long as it remains anoxic, thereby limiting heavy metal bioavailability and toxicity [11].

TABLE II
 CHARACTERISTICS OF INFLUENT AND EFFLUENT FOR FOUR STAGES (MEAN \pm SD)

Parameter	Influent	Stage 1	Stage 2	Stage 3	Stage 4
DO (mg/L)	-	1.67 \pm 0.45	5.13 \pm 0.67	5.67 \pm 0.89	0.85 \pm 0.12
pH	7.88 \pm 0.23	7.81 \pm 0.23	6.52 \pm 0.38	7.14 \pm 0.26	7.42 \pm 0.24
Pb (μ g/L)	489 \pm 90.2	185 \pm 46.3	33 \pm 8.9	8 \pm 2.3	1.87 \pm 1.0
Cr (μ g/L)	484 \pm 84.2	123 \pm 43.9	11.8 \pm 5.6	1.65 \pm 0.6	0.1 \pm 0.3
Cd (μ g/L)	589 \pm 95	200 \pm 70	41 \pm 17.2	4.7 \pm 2.4	1.24 \pm 0.1
COD (mg/L)	639 \pm 64	561 \pm 62	402 \pm 93	303 \pm 92	243 \pm 84
NH ₄ -N (mg/L)	125 \pm 32	106 \pm 28	77 \pm 26	35 \pm 15	21 \pm 20
NO ₂ -N (mg/L)	0.19 \pm 0.39	0.30 \pm 0.75	0.28 \pm 0.20	0.32 \pm 0.20	0.23 \pm 0.14
NO ₃ -N (mg/L)	0.39 \pm 0.42	2.47 \pm 1.18	3.42 \pm 1.8	3.60 \pm 1.6	2.25 \pm 1.4
TN-N (mg/L)	135 \pm 36	118 \pm 33	96 \pm 27	56 \pm 24	27 \pm 2

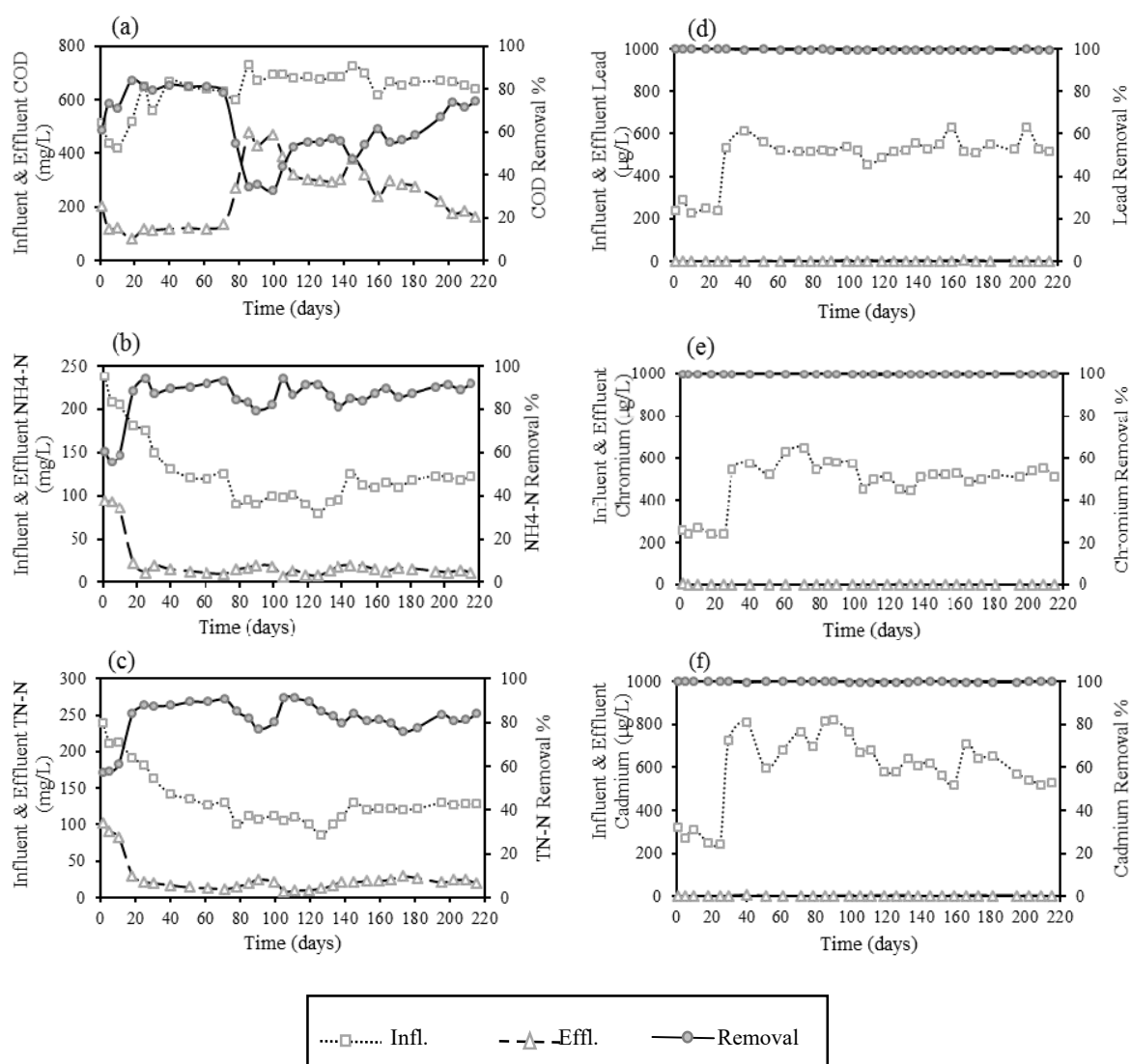


Fig. 1 Dynamics of pollutant concentration in the influent and effluent and pollutant removal in CWS

The removal of Cr can take place through co-precipitation with iron (oxy) hydroxides [7]. The pH strongly affects heavy metal removal in CWSs. Alkaline conditions are necessary to

promote co-precipitation of heavy metals [7]. In this study, the pH value ranged from 7.88 to 6.52, as shown in Table II. However, there is no sufficient carbon (CH₂O) source required

by sulphate-reducing bacteria to sulphides, so that the main process to remove heavy metals in stage 1 is adsorption and precipitation in second stage.

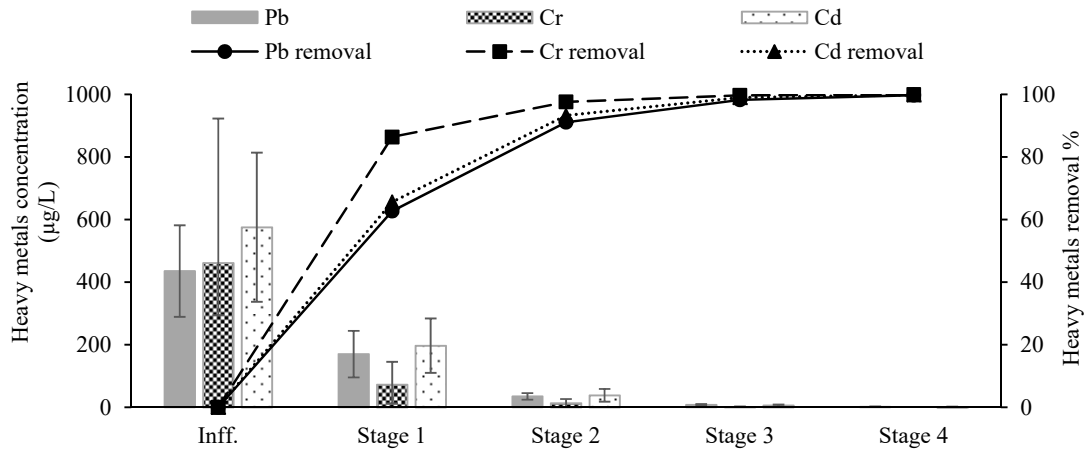


Fig. 2 Heavy metals concentration in each stage and removal efficiency

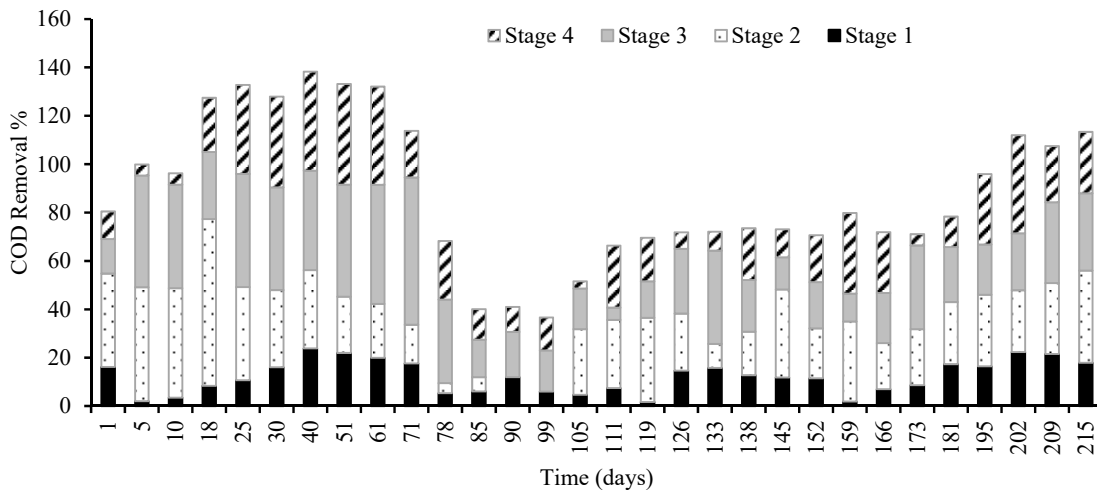


Fig. 3 Variation and removal efficiency of COD in the four stages of CWS

B. The Rate of Organic Matter Removal

The overall removal efficiency of COD across the four stages is presented in Fig. 2. Overall, results from Fig. 2 indicate that a shorter saturation time and a longer unsaturation time resulted in a greater COD removal efficiency. Note that Fig. 2 shows an enhancement of the percentage of COD removal during continuous runs under the same operation conditions. This suggests that enhanced aeration by convection and diffusion during the unsaturation phase may have played a key role in the removal of COD in stages 2 and 3. During the operation (215 days), the system achieved a COD removal efficiency of $62\% \pm 14\%$ for a COD loading rate $977 \text{ g/m}^2 \cdot \text{day}$. To our knowledge, this COD removal efficiency is lower than that used to treat domestic wastewater in vertical flow CWSs, where removal efficiencies typically range from 77% to 83% [12]. The removal of COD

reaches 84% after 20 days of operation as shown in Fig 2.

The sharp drop in COD removal, spatially, in stage 2 (Fig. 3), was identified as a serious bed clogging. A backwashing action performed on day 99 soon restored the treatment performance. The COD removal also exhibited considerable fluctuations due to the integrated removal of enhanced adsorption to ferric dewatered sludge, filtration and the biological degradation of pollutants related to COD. The removal of COD in anaerobic conditions in stage 4 occurred because the abundantly available $\text{NO}_3\text{-N}$ in this stage could directly lead to more denitrification, with simultaneous consumption of COD as a required organic source [6]. However, the first and major nitrogen transformation that occurred in stage 3 was nitrification ($\text{NH}_4\text{-N} \rightarrow \text{NO}_3\text{-N}$), which did not contribute to COD consumption. Nitrification was also the rate-limiting step for providing $\text{NO}_3\text{-N}$ for

denitrification and COD consumption.

C. The Rate of Nitrogen Removal

Fig. 3 presents the various nitrogen forms, including $\text{NH}_4\text{-N}$, $\text{NO}_2\text{-N}$, $\text{NO}_3\text{-N}$ and TN-N across the CWS. The transformation and removal of nitrogen in the CWS could be accomplished by nitrification–denitrification, plant and microbial uptake, adsorption, ammonia volatilisation, etc. [8], [13]. In this study, the classical route of nitrification, coupled with simultaneous nitrification and denitrification, is the major removal process for nitrogen retention. Nitrogen removal through plant uptake was considered as negligible due to the high nitrogen loading rate applied ($205.7 \text{ gN/m}^2\cdot\text{day}$, Table II) [7].

Fig. 3 shows clearly that a significant reduction in $\text{NH}_4\text{-N}$ was achieved during the operation of the system ($85\% \pm 9.5\%$), especially in stage 3, which employed a 1:1 recirculation and intermittent aeration. This is a result of the reduced organic loading in the system, the DO supply and the prolonged wastewater-biofilm contact due to recirculation. The essential DO concentration for the nitrification process is above 1.5 mg/L [6]. The top layer DO concentration within this stage was 5.67 mg/L and this concentration decreased gradually along the bath of wastewater from the top to bottom (Fig. 5). The $\text{NH}_4\text{-N}$ removal increase to 72% from 34% with an organic load rate reduction from $618 \text{ gCOD/m}^2\cdot\text{day}$ to $470 \text{ gCOD/m}^2\cdot\text{day}$ in this stage. The dynamics of $\text{NO}_3\text{-N}$ in the effluent indicated a significant accumulation of nitrite and nitrate in this stage throughout the experiment. However, the amounts of $\text{NO}_2\text{-N}$ were always less than 0.9 mg/L in this study. Zhi et al. [14] reported 76%–90% removal of $\text{NH}_4\text{-N}$ using a tidal flow CWS, while Fan et al. [6] showed that 99% of $\text{NH}_4\text{-N}$ had been removed in an intermittently aerated vertical flow CWS.

In all stages, the nitrification and denitrification processes may have occurred simultaneously in the CWS. This resulted

in a decrease in the $\text{NO}_2\text{-N}$ and $\text{NO}_3\text{-N}$ level—a phenomenon termed simultaneous nitrification and denitrification (SND) [2]. The intermittent aeration strategy created anaerobic and aerobic conditions in the CWS and facilitated simultaneous nitrification and denitrification [13].

Total nitrogen losses of up to 30% and 60% have been noted under aerobic conditions in stages 2 and 3, respectively. These losses may be due to denitrification occurring in the anoxic microzone inside sludge flocs. Autotrophic nitrification may occur on the surface of these flocs because of high oxygen diffusion resistance within sludge flocs [15]. According to Koch, [16] the DO gradient is controlled by several factors, such as the bulk DO level, the particle size of the floc (ferric dewatered sludge in this study), the loading of organic substrate and the aeration cycle. This phenomenon emphasises that denitrification occurs in aerobic conditions using both oxygen and nitrate as the terminal electron acceptor [15]. Several studies have shown aerobic denitrification in wastewater treatment processes and natural sediments [17], [18]. Moreover, the organic carbon level (COD/N of 5) is sufficient to provide electron donors for nitrate reduction and to serve as an energy source for denitrification microorganisms [13].

The effective TN-N removal in stage 4 (up to 91%) could be attributed to the fact that remaining carbon sources in stage 4 (Fig. 2), with an influent COD/N ratio of six, was sufficient to support the full denitrification of the nitrified nitrogen. The anoxic condition was applied in this stage, whereas the DO was less than one, as shown in Fig. 4. Chang et al. [8] demonstrated a significant improvement in TN-N removal efficiency, which increased from 25% to 70% when the COD/N ratios were increased from 2.5 to 10.

One very interesting finding is that accumulation of $\text{NO}_x\text{-N}$ in stage 1 was always negligible, which confirms that the presence of heavy metals inhibited the nitrification process.

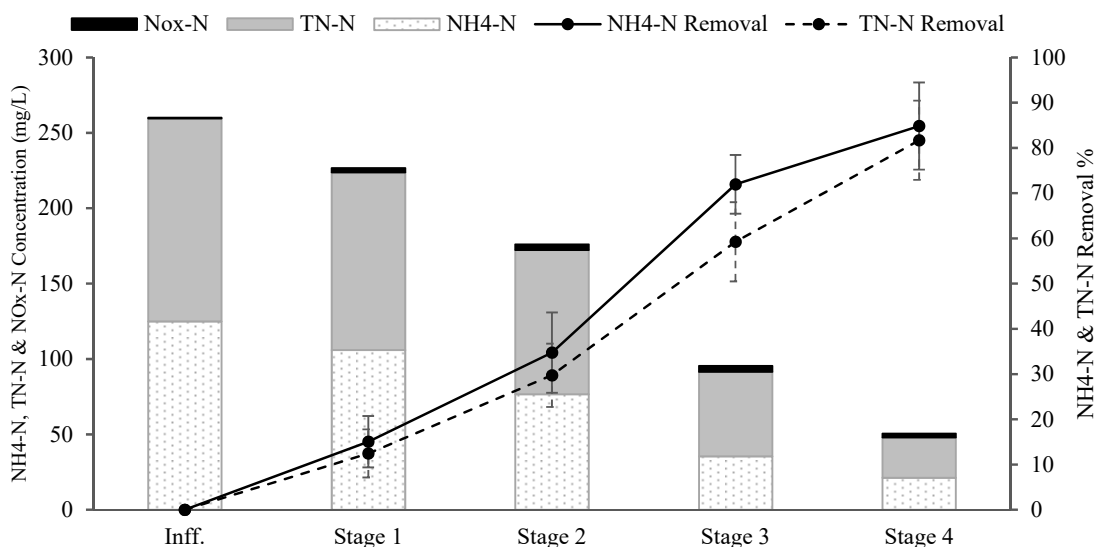


Fig. 4 $\text{NH}_4\text{-N}$, $\text{NO}_x\text{-N}$, and TN-N profile and removal efficiency of $\text{NH}_4\text{-N}$ and TN-N across four stages of CWS

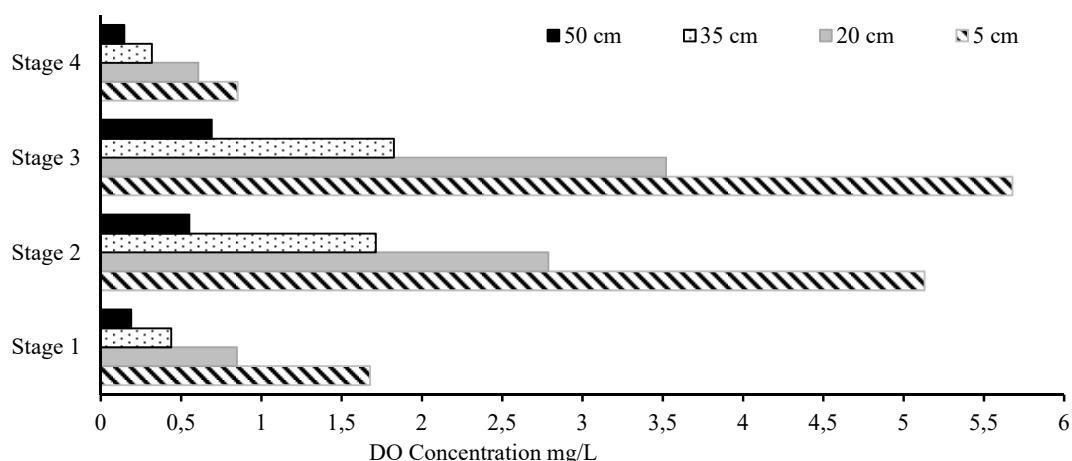


Fig. 5 Vertical initial DO distribution at different depth (from top layer to bottom) in four stages of CWS

IV. CONCLUSION

Overall, this study has demonstrated the effectiveness of combining anoxic conditions and the tidal flow strategy in a CWS to achieve enhanced pollutant removal from high-strength wastewater (landfill leachate). Sufficient bed resting time promotes COD removal and nitrification of $\text{NH}_4\text{-N}$. Anoxic conditions were the key factors for maintaining effective removal of heavy metals and total nitrogen. The main conclusions drawn are:

- i. High removal rates for heavy metals were obtained by adsorption and precipitation onto ferric dewatered sludge.
- i. The removal efficiency of COD in this study could be ascribed to aerobic microbial processes in stages 2 and 3 and anoxic microbial processes for denitrification in stage 4. However, bed clogging can be a serious problem that affects the COD removal in stage 2.
- i. An intermittent aeration strategy can effectively induce alternate aerobic and anaerobic conditions in a vertical flow CWS, so simultaneous nitrification and denitrification can occur under a sufficient COD/N ratio of 5.

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