Journal of Environmental Management 166 (2016) 38–44

Contents lists available at ScienceDirect

Journal of Environmental Management

journal homepage: www.elsevier.com/locate/jenvman

Research article

Pathways of nitrobenzene degradation in horizontal subsurface flow constructed wetlands: Effect of intermittent aeration and glucose addition

Wesley K. Kirui [a], Shubiao Wu [a, *], Simon Kizito [a, b], Pedro N. Carvalho [c], Renjie Dong [a]

[a] Key Laboratory of Clean Utilization Technology for Renewable Energy in Ministry of Agriculture, College of Engineering, China Agricultural University, 100083 Beijing, PR China
[b] College of Agricultural and Environmental Science, Makerere University, P.O. Box, 7062 Kampala, Uganda
[c] Department of Bioscience, Aarhus University, 8000C Aarhus, Denmark

A R T I C L E I N F O

Article history:
Received 17 July 2015
Received in revised form
29 September 2015
Accepted 2 October 2015
Available online xxx

Keywords:
Constructed wetlands
Intermittent aeration
Nitrobenzene
Nitrogen
Sulphur

A B S T R A C T

Intermittent aeration and addition of glucose were applied to horizontal subsurface flow constructed wetlands in order to investigate the effect on pathways of nitrobenzene (NB) degradation and interactions with microbial nitrogen and sulphur transformations. The experiment was carried out in three phases A, B and C consisting of different NB loading and glucose dosing. For each phase, the effect of aeration was assessed by intermittently aerating one wetland and leaving one unaerated. Regardless of whether or not the wetland was aerated, at an influent NB concentration of 140 mg/L, both wetlands significantly reduced NB to less than 2 mg/L, a reduction efficiency of 98%. However, once the influent NB concentration was increased to 280 mg/L, the aerated wetland had a higher removal performance 82% compared to that of the unaerated wetland 71%. Addition of glucose further intensified the NB removal to 95% in the aerated wetlands and 92% in the unaerated. Aeration of wetlands enhanced NB degradation, but also resulted in higher NB volatilization of 6 mg m^{-2} d^{-1}. The detected high concentration of sulphide 20–60 mg/L in the unaerated wetland gave a strong indication that NB may act as an electron donor to sulphate-reducing bacteria, but this should be further investigated. Aeration positively improved NB removal in constructed wetlands, but resulted in higher NB volatilization. Glucose addition induced co-metabolism to enhance NB degradation.

1. Introduction

Constructed wetlands (CWs) have long been recognised as an effective, low cost, and eco-friendly way to remove a wide range of wastewater pollutants (García et al., 2010; Gunes, 2011). Most rural communities and rural-based industries are not adequately served by the mainstream sewer and wastewater treatment infrastructure, and CWs may be a good alternative for wastewater management (Gustavsson et al., 2007; Mbuligwe, 2004; Solano et al., 2004). In rural areas with intensive agriculture, agro-products processing, or industrial activities, the large amount of pollutants, when discharged without proper treatment, pose an enormous threat to the environment and biodiversity (Majumder and Gupta, 2003).

Nitrobenzene (NB), a nitro aromatic compound, is one of the common pollutants from small, rural agro-processing industries. NB is a material used to produce some pesticides and herbicides. From the farm NB can be introduced to the environment through surface run-off and leaching following heavy pesticides applications. The amount of NB released into the environment form agricultural activities ranges between 35 and 250 mg/L (He et al., 2006). When released into the aquatic environment, NB has the potential to cause ecological and health problems, and therefore, its removal from wastewater prior to discharge to the open environment is crucial (He et al., 2006; Kuscu and Sponza, 2009; Majumder and Gupta, 2003). Established methods for NB removal, however, are complex and expensive. In particular, expense is the key challenge for most rural-based small industries. As an alternative, where land for construction is available, the use of CWs could serve as a cost effective option to utilise in remediation of this wastewater

* Corresponding author.
E-mail address: wushubiao@cau.edu.cn (S. Wu).

http://dx.doi.org/10.1016/j.jenvman.2015.10.001
0301-4797/

problem (Gunes, 2011).

Although CWs have been used in treating industrial wastewater (Calheiros et al., 2009; Gustavsson et al., 2007; Hadad et al., 2006; Wu et al., 2015), the use of CWs specifically for the removal of NB is not well-established. There have been some evaluations, such as (Lin et al., 2012; Lv et al., 2013), on NB removal by wetlands, but there are still many gaps to address. One such study of NB degradation observed 97% and 74% removal in a combined anaerobic baffled reactor (ABR) and CW treatment, respectively, at a loading of 89.7 mg/L (Lin et al., 2012). Another study, Lv et al. (2013), reported that three different CW configurations performed well at low influent concentrations of up to 70 mg/L, but at high NB influent loading up to 160 mg/L, NB removal decreased to less than 57%. Chinese reports have only published the presence of NB in Chinese surface waters at an NB concentration of 8.45 μg/L, but not the NB effluent concentration from their industries (Gao et al., 2008). The NB effluent concentrations from industrial processes have been reported to be greater than 100 mg/L in the USA (Jameson et al., 2002; Patil et al., 2011) and 52–250 mg/L in India (IARC, 1996). Therefore, at such high NB concentrations, the performance of CWs is expected to be ineffective. Moreover, there are still the challenges of inhibition of nitrogen removal and low efficiency performance at high influent NB concentrations. Many other considerations, such as the impact of shock loading of NB to the wetlands as well as its removal pathways, have not been addressed in detail.

According to Kulkarni and Chaudhari (2007), the process of NB removal from wastewater can occur in both oxic and anoxic conditions. Therefore, NB removal from wastewater could be optimised by enhancing existing fluctuating redox conditions in wetlands. In previous research, aeration of wetlands boosted fluctuating redox conditions in an effort to intensively remove organic matter and ammonium by promoting the growth of a complex bacterial population with higher metabolism and catabolism (Li et al., 2014; Nivala et al., 2007). However, the best way to remove NB from wetlands with fluctuating redox condition is still unclear. Significantly, if this method promotes faster NB degradation, the toxic threat of NB to wetland plants and microbial N and S transformations may be mitigated or even eliminated.

Another reported option to intensify the removal of hard biodegradable organic compounds like NB is supplementing wetlands with an easily biodegradable carbon to induce faster microbial co-metabolisation. Horvath (1972) described co-metabolism as the concomitant oxidation of a non-growth substrate during the growth of microorganisms on utilisable carbon and energy sources. Further, co-metabolism can be defined as the fortuitous biodegradation of the target chemical through reactions catalysed by non-specific microbial enzymes (Maestre et al., 2013). This process has been applied to wastewater containing 2,4,6 Trinitrotoluene(TNT) before treatment in CWs. Haberl et al. (2003) added molasses as the extra carbon source to CWs and reported an increase of 45% in TNT removal efficiency. Based on these findings, we hypothesize that the addition of an easily biodegradable carbon source will improve the wetlands' capacity to reduce NB at high concentrations. We also hypothesize that providing intermittent aeration could improve NB degradation in the wetlands. Moreover, the process of combining aeration and an extra carbon dosing to improve NB removal efficiency by CWs has yet to be reported. Therefore, this study aimed at investigating (i) the performance of CWs on removal of NB at varying influent concentrations and the potential pathways of NB degradation in horizontal subsurface flow CWs (ii) the effect of intermittent aeration and glucose addition to intensify NB removal performance (iii) the interactions with microbial nitrogen and sulphur transformations.

2. Materials and methods

2.1. Lab-scale CWs set-up

The wetland systems were made from two plastic containers of dimensions 100 cm length × 15 cm width × 50 cm depth filled with gravel of particle size 2–6 mm (density 1.67 g/cm^3). The porosity of the systems was 35% based on the gravel and size dimensions giving a pore space volume of 25 L. Wetland systems were placed indoors under controlled environmental conditions that simulated an average summer day in moderate climatic conditions. Temperature was maintained at 22 °C from 6 am to 9 pm and at 16 °C from 9 pm to 6 am to simulate daytime and nighttime, respectively. Lamps (Phillips, Master SON-PIA 400 W, Shanghai, China) were switched on at daytime as an additional artificial light source when natural illumination fell below 60 klx. The containers had two zones: a zone at the inlet section to ensure even distribution through the wetland substrate and an outlet section as a collection zone (both were 3 cm width filled with gravel, particle size of 1.6–2.9 cm). To prevent algal growth, the exterior walls of the wetlands were covered with black polythene. *Juncus effuses*, a species native to Asia and other parts of the world, was planted (150 stems per m^2) in both wetlands. The plant was selected because of previous use in wetlands. The wetlands were supplied with 10 mg/L NB synthesised wastewater for three months to acclimate microorganisms and allow a biofilm establishment. Synthesized wastewater was delivered continuously to both wetlands via peristaltic pumps at the rate of 5 L/d and a hydraulic loading rate (HLR) of 3.33 cm/d over the entire study period. To ensure subsurface conditions, the water depth of both wetland beds was maintained at 40 cm.

One of the experimental horizontal subsurface flow CWs was not aerated while the other was intermittently aerated through a perforated pipe placed at the bottom of the bed. The perforated pipe was connected to an adjustable air pump (Model ACO-6603, China). The pump was actuated via a timer switch to pump air at a flow rate of 120 L/h with intermittent periods of work (1 h) and rest (1 h). The air was applied intermittently to enhance oxygen microbial processes and to also create fluctuating redox conditions in the wetland. A layer of small stones (approximately 1.6–2.3 cm, particle size) was placed on top of the perforated pipe to prevent clogging and allow free flow of air into the wetland substrate.

To reduce potential variability within the experiment, synthetic influent wastewater was used. The properties of the influent wastewater are presented in Table 1. The influent wastewater was prepared by first dissolving analytical grade NB (95%) in deionised water by stirring using a magnetic stirrer for 2 h. The water was then transferred to a 1 L bottle to be pumped to the mixing chamber using a peristaltic pump. In the mixing chamber, the NB solution was mixed with tap water containing NH_4Cl and K_2HPO_4 H_2O. Later, in experimental phase C, glucose ($C_6H_{12}O_6$) was added at 290 mg/L (Table 1). The micro-nutrients solution was prepared according to Wu et al. (2012) and was added to the synthetic wastewater at 1 mL/L.

Table 1
Characteristics of influent artificial wastewater.

Parameter	Phases		
	A	B	C
NB (mg/L)	140	280	280
NH_4–N (mg/L)	15	15	15
PO_4–P	5	5	5
$C_6H_{12}O_6$(mg/L)	–	–	290