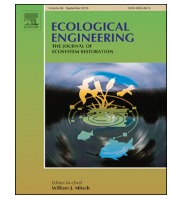
Ecological Engineering 117 (2018) 18–27

Contents lists available at ScienceDirect

Ecological Engineering

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



Phosphate removal using zeolite in treatment wetlands under different oxidation-reduction potentials

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A R T I C L E I N F O

Keywords:
Langmuir adsorption kinetic
Oxidation-reduction potential
Phosphate
Sewage
Subsurface flow treatment wetland
Zeolite

A B S T R A C T

The aim of this study was a comparison between PO_4^{-3}-P removal from sewage using zeolite as support medium in subsurface flow treatment wetlands (SSF TWs) operated with different oxidation-reduction potentials (ORPs). In addition, the zeolite's phosphate adsorption characteristics were evaluated. For this, Two mesocosm SSF TWs were installed and operated during 504 d for the PO_4^{-3}-P adsorption from sewage: a) mesocosm SSF TW with natural zeolite (MTW-Z1) and b) mesocosm SSF TW with gravel (MTW-G1). Two ORPs was used in MTW-Z1 and MTW-G1: a) ORP-A, ORP $> +50$ mV, b) ORP-B, ORP < -50 mV. Furthermore, the adsorption characteristics were evaluated in batch assays (zeolite amount and particle size were studied) with different PO_4^{-3}-P initial concentrations. Regarding the mesocosm SSF TWs evaluation, the PO_4^{-3}-P removed from sewage by MTW-Z1 is between 20% and 50% significantly ($p < 0.05$) higher than the MTW-G1. At the same time, ORP-A, above $+50$ mV, significantly improves ($p < 0.05$), by 10% more, the PO_4^{-3}-P removal capacity from sewage. Regarding adsorption characteristics, maximum adsorption capacity determined by Langmuir kinetic was 0.03 mg PO_4^{-3}-P g^{-1} for initial concentrations of 10–15 mg PO_4^{-3}-P L^{-1}. In the case of MTW-Z1 with ORPs A ($> +50$ mV) and B (< -50 mV), the zeolite maximum adsorption capacity was 0.3 mg PO_4^{-3}-P g^{-1}. Therefore, the potential maximum adsorption capacity of natural zeolite used as a medium in SSF TWs with ORP conditions below -50 mV and above $+50$ mV can be increased until 10-fold regarding Langmuir adsorption kinetic.

1. Introduction

Subsurface flow treatment wetlands (SSF TWs) are an alternative technology to traditional activated sludge systems to treat sewage in rural areas (Vera et al., 2011; Vera et al., 2013). Sewage is composed principally by solids (total suspended solids (TSS)), organic matter (5-day biological oxygen demand (BOD_5)), chemical oxygen demand (COD), nitrogen (60–65% as ammonium nitrogen (NH_4^+-N), phosphorus (60–80% as phosphate (PO_4^{-3}-P)), and pathogens (fecal coliform, total coliform) (Jácome et al., 2016; López et al., 2015; Stefanakis et al., 2009). When SSF TWs are used for sewage treatment, removal efficiency of TSS, BOD_5, and COD is above 80%, and Fecal Coliforms (FC) removal units is between 1 and 4 Log10 MPN/100 ml (Burgos et al., 2017; García et al., 2013). For nitrogen, the removal can be intensified in SSF TWs by different operational strategies and innovative designs, thus improving removal efficiencies to levels of 50–90% (Wu et al., 2014). However, phosphorus removal from sewage by SSF TWs is more complicated, and typical removal efficiencies are below 50% (Rojas et al., 2013; Vera et al., 2013).

Phosphorus removal from sewage by SSF TWs is carried out by two pathways: a) biological, principally by assimilation/accumulation into plants tissues (if plants are harvested), and b) physical-chemical, by precipitation and adsorption onto a medium (Vymazal, 2004). The biological pathway removes P because PO_4^{-3}-P is the P form employed directly by plants (Vymazal, 2007). Typical plants used in SSF TWs, such as *Typha* spp., *Phragmites* spp., and *Schoenoplectus* spp., uptake only between 5% and 10% of P from sewage (Tanner, 2001). Therefore, the physical-chemical pathway is the most important for the PO_4^{-3}-P removal mechanism.

In the physical-chemical pathway, between different factors for the precipitation and adsorption process, oxidation-reduction potential (ORP) and support medium are the most important especially for horizontal SSF TWs (Vymazal, 2004). ORP values in horizontal SSF TWs are below -100 mV, affecting PO_4^{-3}-P removal capacity (García et al., 2004; Rojas et al., 2013; López et al., 2015). For solving this, modification in ORP through artificial aeration has been proposed (Nivala

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https://doi.org/10.1016/j.ecoleng.2018.03.008
Received 9 October 2017; Received in revised form 10 March 2018; Accepted 14 March 2018
0925-8574/

et al., 2013). With this, the ORP can be increased in +100 mV, and the PO_4^{-3}-P removal efficiency can be increased by > 30% in SSF TWs (Tang et al., 2009; Vera et al., 2014).

In the case of support medium, the selection is very important. Gravel is widely used in SSF TWs as a support medium for plants. Since gravel has low P adsorption capacity, between 0.03 and 0.05 mg P g^{-1} (Cucarella and Renman, 2009), adsorbent materials such as Alunite, Bauxite, Blast Furnace Slag, Calcite, Dolomite, Filtralite ®, Fly Ash, HeloFIR ®, LECA, Limestone, Maerl, Marble, Norlite, Ochre, Opoka, Peat, Polonite, Sands, Seashells, Vermiculite, Zeolite and Wollastonite have been proposed as support mediums for the plants in SSF CWs (Vera et al., 2014; Vohla et al., 2011). These alternative mediums have been shown to increase the removal of P from sewage by 10–80% (Arias and Brix, 2005; Vohla et al., 2011).

Among the different potential mediums for SSF TWs with adsorption capacities, natural zeolites are promising because they are abundant, relatively inexpensive (0.6–1.6 USD kg^{-1}) and have regenerative capacities (Dai and Hu, 2017; Wendling et al., 2013). Natural zeolites are minerals of a porous structure with valuable physicochemical properties, such as cation exchange (sodium, potassium or calcium), molecular sieving, catalysis and sorption (Wang and Peng, 2010). The cation exchange properties of natural zeolite are important for PO_4^{-3}-P precipitation and adsorption and thus for phosphate removal from sewage (Dai and Hu, 2017).

Traditionally, the Langmuir and Freundlich adsorption kinetic have been used to determinate the PO_4^{-3}-P adsorption capacities for natural zeolite and other materials with sorption potential (Dai and Hu, 2017; Del Bubba et al., 2003; Moharami and Jalali, 2013; Wang and Peng, 2010). However, Langmuir adsorption kinetic fits better to the P adsorption onto different materials (Del Bubba et al., 2003; Dionisiou et al., 2012). In this way, maximum adsorption capacities between 0.3 and 6.8 mg P g^{-1} have been determined for natural zeolites (Cucarella and Renman, 2009; Dai and Hu, 2017; Drizo et al., 1999). These values are useful for estimating the operational parameters of SSF TWs when natural zeolite is employed as a support medium and SSF TWs are used in continuous operation, but is not clear if these values are useful in SSF TWs with different ORPs during operation.

Additionally, the performance of continually operating SSF TWs using natural zeolite as a support medium and the resultant PO_4^{-3}-P maximum adsorption capacity has not yet been studied and even less when different ORPs has been used during operation. Previous studies of natural zeolites and other materials with PO_4^{-3}-P adsorption capacity have focused on two topics, column experiments and water quality effects (Arias et al., 2001; Drizo et al., 2002; Seo et al., 2005). However, the accumulation effects on performance and in addition, its relationship with adsorption capacities determinate in batch assays fitted to Langmuir adsorption kinetic have not researched (Moharami and Jalali, 2013; Navia et al., 2003; Stefanakis et al., 2009; Vera et al., 2014).

Therefore, taking the above into account, the aim of this study was a comparison between PO_4^{-3}-P removal from sewage using zeolite as support medium in subsurface flow treatment wetlands (SSF TWs) operated with different oxidation-reduction potentials (ORPs). In addition, the zeolite's phosphate adsorption characteristics were evaluated.

2. Materials and methods

2.1. Influent

Sewage was used as the influent for feeding the experimental SSF TWs. Sewage was obtained with instantaneous sampling after passing through a 40-mm screen from a full-scale sewage treatment plant (STP), which serves a community of 20,000 inhabitants. Subsequently, the influent was stored in 20-L plastic cans, in the dark, at 4 °C for a maximum of three weeks (Araya et al., 2016; Vera et al., 2014). Table 1 shows influent characteristics.

The concentrations in Table 1 indicate that the influent can be considered "concentrated sewage" (Henze et al., 2002). However, the PO_4^{-3}-P and NH_4^+-N average concentrations in Table 1 exceeds up to 70%, the concentration of 10 mg PO_4^{-3}-P L^{-1} and 50 mg NH_4^+-N L^{-1}, respectively, this classification (Henze et al., 2002). This high PO_4^{-3}-P and NH_4^+-N concentrations can be explained by the water use and the rural behavior of the population discharging to the STP (Vera et al., 2014). Another explanation could be the instantaneous sampling, because in a full-scale STP, PO_4^{-3}-P and NH_4^+-N concentrations can change significantly during the day (Araya et al., 2016).

Table 1
Physicochemical characterization of the sewage.

Parameter	Units	Average ± standard deviation	Range (min–max)
BOD_5	mg O_2 L^{-1}	138 ± 70	24–276
COD	mg O_2 L^{-1}	336.1 ± 116.5	80.8–769.7
TSS	mg TSS L^{-1}	245.1 ± 150.3	40.0–696.6
PO_4^{-3}-P	mg PO_4^{-3}-P L^{-1}	12.9 ± 2.7	4.8–20.3
NH_4^+-N	mg NH_4^+-N L^{-1}	85.1 ± 41.2	25.3–163.1
NO_3^--N	mg NO_3^--N L^{-1}	0.4 ± 0.1	0.1–1.3
TP	mg TP L^{-1}	15.2 ± 2.4	12.2–19.4
TN	mg TN L^{-1}	90.6 ± 32.1	30.0–125.0

n = 72 for COD, NH_4^+-N, NO_3^--N and PO_4^{-3}-P; n = 36 for TSS and BOD_5; n = 9 for TP and TN.

2.2. Adsorbent and support medium

2.2.1. Zeolite

Natural zeolite was used as the adsorbent and support medium in the experimental SSF TW. Yacimiento Serrin, located in Parral (Chile), provided natural zeolite. The mineralogical composition of the natural zeolite was 27.93% of Clinoptilolite ($(Na,K,Ca)_{2.5}Al_3(Al,Si)_2Si_{13}O_{36}\cdot 12(H_2O)$), 40.23% Calcium Mordenite ($(Ca_{3.4}(Al_{7.4}Si_{40.6}O_{96})(H_2O)_{31})$), and 23.76% of Mordenite ($Na_{7.79}(Al_{7.87}Si_{40.13}O_{96})(H_2O)_{10.16}$). The Zeolite also contained minor elements represented by quartz (SiO2) (5.45%) and magnetite ($Fe_{21.34}O_{32}$) (2.63%). Fig. 1 shows the X-ray Diffraction of the natural zeolite.

In addition, the chemical composition was determined by X-ray fluorescence and showed the following main elements: a) Silicium (SiO_2) = 68.6%, b) Aluminum (Al_2O_3) = 13.9%, c) Calcium (CaO) = 2.5%, d) Sodium (Na_2O) = 1.7%, e) Potassium (K_2O) = 0.3%, f) Iron (Fe_2O_3) = 0.2%, g) Magnesium (MgO) = 0.2%, and h) Phosphorus (P_2O_5) = < 0.005.

Regarding physical characteristics, natural zeolites have a BET (Brunauer-Emmett-Teller) surface area of 243 m^2 g^{-1} and an average

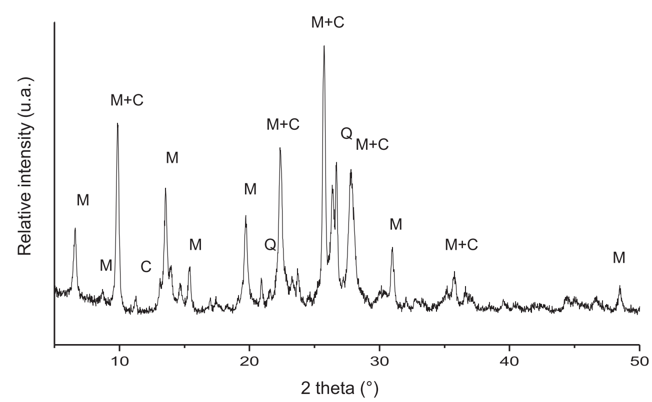

Fig. 1. Zeolite mineralogical composition by X-ray Diffraction. M: Mordenite (63.99%); C: Clipnotilolite (27.93%); Q: Quartz (5.45%).