Current Trends in Natural Sciences Vol. 7, Issue 14, pp. 69-75, 2018

Current Trends in Natural Sciences (on-line)
ISSN: 2284-953X
ISSN-L: 2284-9521

Current Trends in Natural Sciences (CD-Rom)
ISSN: 2284-9521
ISSN-L: 2284-9521

DIFFERENT SUBSTRATE MATERIALS FOR PHOSPHORUS REMOVAL FROM WASTEWATERS IN CONSTRUCTED WETLANDS

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Abstract
Phosphorus (P) is commonly considered as the limiting nutrient with respect to the eutrophication of water bodies. Therefore, wastewater treatment plants, either conventional or natural, must meet maximum P discharge limits. While various chemicals are used in conventional wastewater treatment plants, substrate materials play significant roles in phosphorus removal in natural treatment systems, also called constructed wetlands. Constructed wetland technology is commonly used for domestic wastewater treatment especially in rural sections. Emergent aquatic plants are grown in specially designed basins filled with substrate material to filter pollutants from wastewaters. Phosphorus removal is largely dependent on surface characteristics and pore structure of the substrate materials used in constructed wetland basins. Pumice and zeolite-like volcanic originated natural materials and fly ask like waste materials are commonly used to enhance phosphorus removal efficiency of substrate materials. These materials mostly used in certain mixture ratios with sand and gravel filter material. In this study, information was provided about general phosphorus removal mechanisms, surface characteristics of different substrate materials and their phosphorus removal efficiencies.

Keywords: constructed wetland, phosphorus, substrate, zeolite.

1. INTRODUCTION

Natural treatment systems, so called as constructed wetlands, are engineered treatment systems that have been designed and constructed to imitate and utilize the natural process of physical, chemical and biological synergistic action among substrates, plants and microorganisms, but do so within a more controlled environment (Vymazal, 2006). Today, these systems are well-recognized as a reliable wastewater treatment technology with several advantages such as low construction cost, easy operation, no-energy requirement, convenient maintenance and management, as well as remarkable ecological benefits. Therefore, they represent a suitable solution for the treatment of various wastewater around the world, such as domestic sewage, industrial wastewater, non-point source agricultural pollution, polluted surface water (Wu, 2008).

The substrate occupies almost the whole volume in constructed wetland basin, which is the important distinguishing item between constructed and natural wetlands. Substrates provide physical and chemical support for wetland plants, surface areas and nutrients for microbial attachment and hydraulic condition for sewage flow (Gokalp, 2011) and they also remove kinds of pollutants directly by the action of filtration, adsorption and precipitation and so on. So substrate is the crucial item for purification capacity and stable operation of constructed wetlands.

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In general, substrate material accounts for majority of construction cost of constructed wetlands, thus, selection of appropriate substrate material is an important step when designing and constructing constructed wetlands. Traditionally, constructed wetlands are constructed with local soil as substrate. However, this had caused problems with overland flow and short-circuiting of the wastewater between inlet and outlet because of the low hydraulic conductivity of soils. Therefore, present adopted design guidelines are based on sand or gravel and in some cases intermittently loaded vertical-flow beds instead of horizontal-flow beds (Brix et al., 2001).
Despite suitable hydraulic conductivity, sand or gravel are quite poor in phosphorus removal. Then the selection of the material with a high phosphorus binding capacity, used either alone or mixed with sand or gravel as substrate, plays a crucial role in constructed wetland design (Gokalp et al., 2014). Several studies have been conducted to investigate the potential use of various other substrate materials for phosphorus removal from wastewaters. In this study, initially brief information was provided about the pollutant removal mechanisms and especially phosphorus removal from domestic wastewater influents. Then substrate materials were presented for phosphorus removal in constructed wetlands.

2. POLLUTANT REMOVAL MECHANISMS IN CONSTRUCTED WETLANDS

Constructed wetlands are basically designed either as surface-flow wetlands or sub-surface flow wetlands. Surface flow constructed wetlands encompass shallow water flowing over plant media and water depths that vary through the wetland. They are quite similar with the natural wetlands and include mineral or organic soil underneath vegetation. Vegetation in these systems includes reeds and cattails but can also include floating plants which are also known as macrophytes. On the other hand, sub-surface constructed wetlands contain coarse substrate media such as sand or gravel which the water travels through. Water level is below the media surface in these systems and plant roots are allowed to grow in the coarse media. These wetlands remove contaminants by different means but the basic processes and mechanisms are the same for both (Figure 1).
Constructed wetlands encompass many processes and mechanisms in the removal of contaminants. The basic three are physical, biological, and chemical removal processes. Physical processes are often used in primary treatment of traditional wastewater treatment systems. The processes are similar with the ones going on in natural wetlands. Water flows through substrate materials of the constructed wetlands rather slowly. Vegetation of the constructed wetlands then helps in trapping sediments. Such a flow also allows particles to settle out (DeBusk, 1999a).
Another pollutant removal mechanism in constructed wetlands includes biological processes. Plant uptake is the main and primary means of biological removal of the pollutants. Constructed wetland microorganisms uptake and store nutrients but the metabolic functions are more crucial in organic pollutant removal. The bacteria, mostly in the form of soil bacteria, use the carbon found in organic matter as an energy source and convert to carbon dioxide in aerobic conditions and methane in anaerobic conditions. The microbial metabolism is also very important in the removal of inorganic nitrogen.
Chemical processes are the last mechanisms used in pollutant removal in constructed wetlands. These processes include sorption, photo oxidation and volatilization. Sorption is the most important chemical process and involves the movement of charges from aqueous phases to solid phases. Sorption includes the processes of adsorption and precipitation. Adsorption is to transfer ions into substrate particles and precipitation is to convert metals into insoluble forms. These physical, chemical, and biological processes make up the foundation from which constructed wetlands remove pollutants (DeBusk, 1999b).

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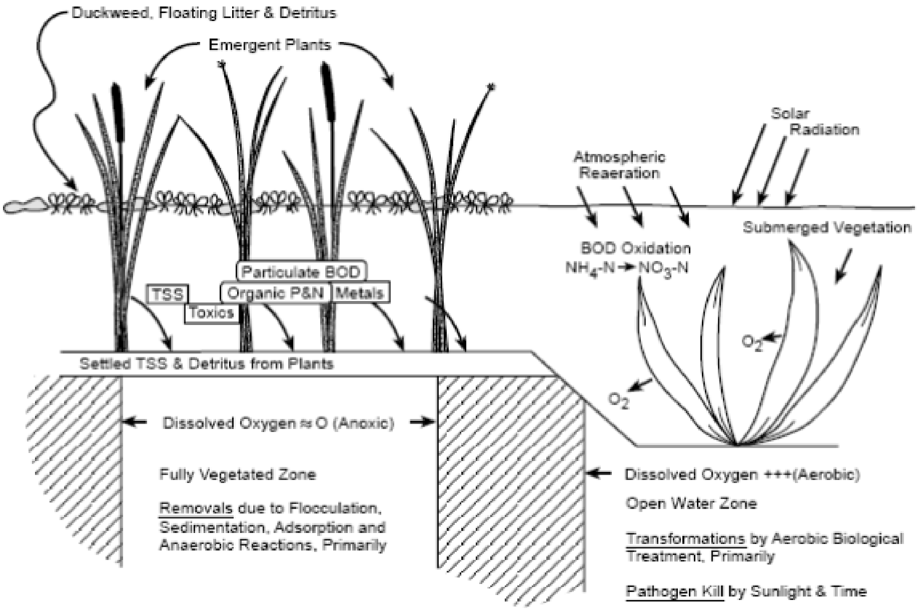

Figure 1. Pollutant removal mechanisms in constructed wetlands (EPA, 1999)

3. PHOSPHORUS REMOVAL IN CONSTRUCTED WETLANDS

Plant uptake, substrate adsorption, precipitation and complexation are the primary phosphorus removal mechanism in constructed wetlands. Adsorption over substrate surfaces is the primary phosphorus removal mechanism in vegetated beds. Physical and chemical conditions, wastewater characteristics, plant roots, characteristics of substrate materials and wetland microorganisms greatly influence adsorption process of pollutants.

Phosphorus is an essential nutrient for plants. However, even the trace quantities of phosphorus may have significant impacts on aquatic environments. Therefore, sufficient phosphorus removal rates should be achieved in treatment systems. Wetlands use physical, chemical and biological means to reduce or remove phosphorus. Phosphorus exists as phosphates in inorganic and organic forms. The predominant form is in the form of orthophosphate which can be used by algae and macrophytes. Inorganic phosphorus can also be found as polyphosphates. Organic forms include phospholipids, nucleic acids, nucleoproteins, and phosphorylated sugars. These forms are primarily known as easily decomposable phosphorus and there other forms called slowly decomposable organic phosphorus which contains phytin (Figure 2).

Adsorption of phosphorus through substrate media is mostly used in sub-surface flow constructed wetlands. Type of media dominates the phosphorus removal rates. Generally, three groups of substrate materials are used in constructed wetlands: Natural materials (soil, peat, sand, gravel, pumice, zeolite), processed minerals (amended zeolite) and waste materials (flay ash, slugs). Typical phosphorus removal of different substrate materials were reported as between 40-60% (Vymazal, 2011).

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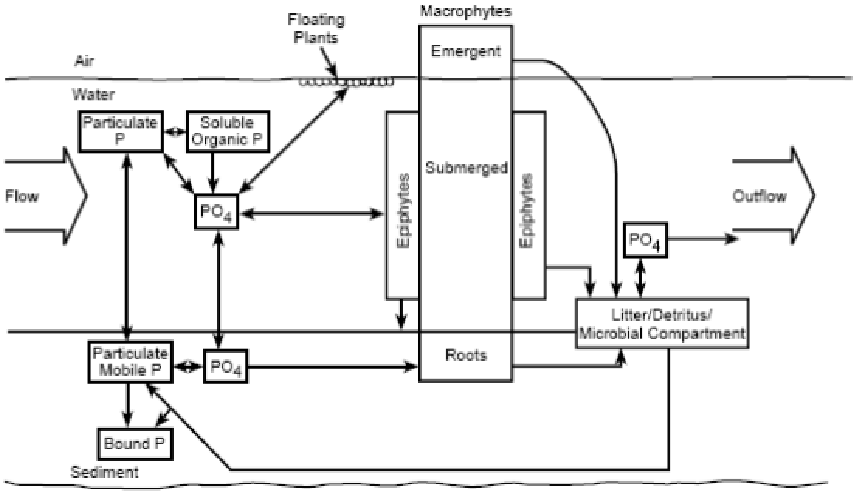

Figure 2. Phosphorus transformation in constructed wetlands (EPA, 1999)

4. SUBSTRATE MATERIALS FOR PHOSPHORUS REMOVAL

Substrate materials constitute almost all volume of wetland basin and they are the most distinctive component of constructed wetlands distinguishing them from the natural ones. While substrate materials support emergent vegetation in one hand, they provide microbial attachment surfaces and play significant roles in regulation of hydraulic conditions in a wetland basin on the other hand. They can also provide direct removal of pollutants through filtration, adsorption and precipitation. Therefore, selection of proper substrate material is the key issue for reliable and sustainable operation of constructed wetlands. Some common substrate materials used in sub-surface flow constructed wetlands and their functions especially in phosphorus removal from wastewater influents are provided below.

Sand-Gravel

Sand-gravel like natural aggregates, abundant in various parts of the country, are used for phosphorus adsorption from wastewaters (Figure 3). Sand and gravel have quite low adsorption capacity and such a capacity vary greatly with the physical attributes of sand and gravel. However, they play significant role in arrangement of hydraulic conditions within a wetland basin. P-adsorption capacity of sand or gravel grains may be improved through coating them with certain materials (calcite or crushed marble) (Brix et al., 2001). It was observed in a previous study that iron aluminum hydroxide-coated sand provided about 70% phosphorus removal from wastewaters (Ayoub et al., 2001).

Figure 3. Sand-gravel substrate materials

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Similarly, Arias et al. (2006) reported that aluminum hydroxide-coated sand grains provided a phosphorus removal of 0.94–0.99 g P kg^{-1} in 24 hours period. Boujelben et al. (2008) carried out study in Tunisia and reported a P-adsorption capacity of 1.5 g P kg^{-1} for iron oxide-coated sand grains.

Pumice

Pumice is quite similar with sand in size (Figure 4). It has sand-like particle sizes. Pumice is form through physical and chemical disintegration of volcanic-originated rock. It is a quite porous material with several micro and macro continuous and intermittent pores. Such a porous nature of the material makes it quite advantageous over the sand. Pumice provides quite available sorption surfaces for the pollutants, especially phosphorus, which are removed through sorption over the material surfaces.

Figure 4. Pumice substrate material (Source: http://www.gardenpomza.com/)

Zeolite

Natural zeolites are aqueous alumina silicate minerals containing abundant quantities of aluminum, silicon and oxygen. They are formed through the reactions in nature between volcanic tufa and saline water. Zeolites are able to hold positively changed atoms, ions and other compounds and they act as a filter tool removing all these substances from the wastewaters (Figure 5).

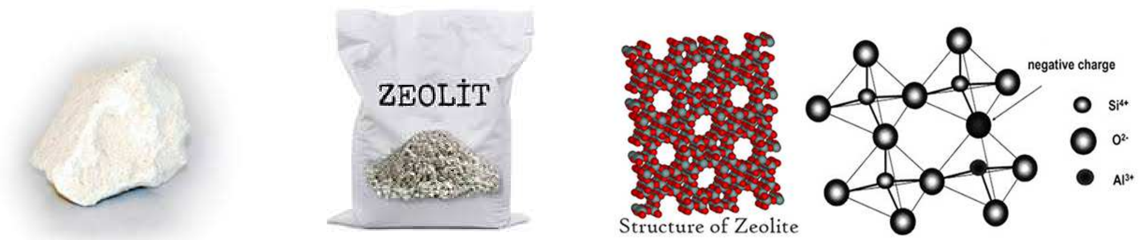

Figure 5. Zeolite substrate material (Source: http://www.gordeszeolite.com/)

Zeolites are alumina-silicates that can either occur as a natural mineral or can be synthesized artificially. They are fine-grained with open meshes of crystals; this results in low bulk densities and high porosities, giving high liquid adsorption capacities. Zeolites have an affinity for ammonium and a remarkably high cation exchange capacity (Pansini, 1996), which far exceeds that of, for example, smectite clays like bentonite, and which permits an efficient removal of heavy metal cations. Some zeolites have also been found to remove phosphate from wastewater (Liberti et al., 1979).

Fly Ash

They are the waste material of thermal power plants (Figure 6). The materials are quite rich in Si, Al and Fe and offer large absorption and precipitation surfaces for pollutants in wastewaters. They

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are especially used for phosphorus removal. Fly ashes have low permeability coefficients and therefore they are mixed with sand-gravel (15–30%).

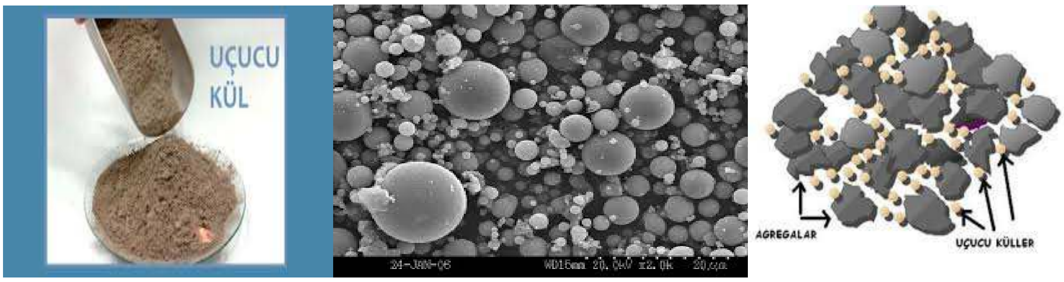

Figure 6. Fly ash substrate material (Source: https://kutahyacimento.com/tr/pulverize-ucucu-kul)

Cheung and Venkitachalam (2000) found that unweathered fly ashes were very efficient at removing P from septic tank effluent. Oguz (2005) and Xu et al. (2006) carried out studies with fly ashes and reported phosphate removals of 71.87 and 8.81 g P kg^{-1}, respectively. Cheung and Venkitachalam (2000) reasoned that fly ash would be most effective when added to coarse sand (15–30%) and used as a filter bed, as higher proportions of fly ash would lead to clogging due to its low permeability. The P-retention characteristics and heavy metal contents of fly ashes are likely to vary widely, depending on the coal source and combustion process. The main chemical components of the fly ashes were reported as SiO_2 (50.6%), Al_2O_3 (25.3%), CaO (11.6%) and FeO (7.7%) (Oguz, 2005).

5. CONCLUSION AND RECOMMENDATIONS

When the treated effluents were reached to aquatic environments, they may result in eutrophication if they were not sufficiently treated for phosphorus removal. Therefore, required discharge criteria should definitely be met both in conventional and natural treatment systems. For phosphorus removal, while various chemicals are used in conventional treatment systems, mainly substrate materials are employed in constructed wetlands. Surface characteristics, porous nature and chemical composition of substrate materials greatly influence their phosphorus removal capacities. Generally sand, gravel, pumice and zeolite-like natural aggregates, amended zeolite-like processed minerals and fly ash and slug-like industrial waste materials are used as the common substrate materials in constructed wetlands. These substrate materials used either alone or in mixtures with sand-gravel. Further research is recommended about different mixture ratios, other waste materials and their surface characteristics for phosphorus removal.

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