

Comparisons Study of Phosphate Removal in Un aerated and Aerated High Calcium Steel Slag Filter System of Different pH Feed

Siti Zu Nurain Ahmad¹, Hamdan R.^{1,*}, Wan Afnizan Wan Mohamed², N. Othman², Nur Shaylinda Mohd Zin², S. Musa²

¹Department of Civil Engineering Technology, Faculty of Engineering Technology, Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Batu Pahat, Johor, Malaysia

²Department of Water and Environmental Engineering, Faculty of Civil and Environmental Engineering, Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Batu Pahat, Johor, Malaysia

Abstract. Excess phosphorus in water body will lead to eutrophication. This study investigated the phosphate removal efficiencies of un aerated and aerated filter systems using high composition of Calcium (Ca) steel slag as the filter media at different pH values of the wastewater influents. Lab-scale filters were developed using 25 mg/L synthetic wastewater and weekly sampling was done to monitor the phosphate removal efficiencies together with the concentration of metals (Calcium (Ca) and Magnesium (Mg)). The results show that both un aerated and aerated systems have excellent phosphate removal efficiency at all acidic, neutral and alkaline pH feed, though un aerated systems removed slightly better compared to aerated systems; 76-98% and 69-97% respectively. The dominant phosphate removal mechanism for aerated systems was adsorption, meanwhile for un aerated systems; both adsorption and precipitation for acidic and neutral pH, while precipitation was more dominant at basic pH. The performance of un aerated systems are slightly better compared to aerated systems, however, aerated systems are recommended to be applied when simultaneous removal of nutrients (phosphorus and nitrogen) are concerned.

1 Introduction

There is a dual concern regarding nutrients, since they contribute to unfavorable health and environmental effects, thus their control is imperative, but the same nutrients are essential for the performance of the natural biological treatment systems [1]. The most significant effect of phosphorus in the environment is eutrophication or algal bloom. This process will promote a great deal of plant and animal biomass production, which eventually leads to succession in aquatic ecosystems [2]. Since 1950s, development of technologies of phosphorus removal has been studied in response to the issue of eutrophication. Since then,

*Corresponding author: rafidahh@uthm.edu.my

scientists had realized the need to reduce the amount of phosphorus allowed to enter the water body [3].

Nowadays, natural wastewater treatment process such as waste stabilization ponds (WSP), constructed wetlands (CW) and rock filters (RF) are very outstanding alternatives for phosphorus removal. The utilization of low-cost and easily available materials as the filter media has been widely demonstrated by previous studies for their reliability and contribution in the removal of phosphate including fly ash [4], limestone [5], iron oxide tailings [6], blast furnace slag [7], basic oxygen furnace slag and electric arc furnace slag [8].

Steel slag has shown great phosphate removal efficiency as filter media for RF. One of the types of steel slag is an electric arc furnace (EAF) slag which is a by-product of melting recycled scrap in an electric arc furnace during the steel-making [9]. The significant contribution of steel slag in phosphate removal is generally due to high concentration of metal (Ca, Fe, Al, Mg) oxides [10]. However, the chemical compositions of all steel slags are not the same due to the variations in the grade of steel products and type of furnaces used during the process of steel-making [10]. Nevertheless, adsorption and precipitation with metal oxides are the main phosphate removal mechanisms in rock filters [11].

Performance of phosphorus removal was affected by parameters include pH, temperature, concentration of metallic salts, HRT and many more [12]. Of all these, pH values of the influents are known to contribute significant effects on phosphorus removal. The mechanism of phosphate removal can be different due to the different chemical composition of the steel slag. Very high percentage of CaO of the steel slag provides a significant rate of dissolution of Ca, causing formation of Ca phosphate, which were formed at high pH value and the precipitation dominates the removal mechanism. On the other hand, a high percentage of Fe_2O_3 of the steel slag prefers adsorption onto Fe oxides for the phosphate removal mechanism at acidic and neutral pH ranges [13]. Besides that, precipitation might occur resulting from the dissolution of Fe from Fe oxides [14]. This is due to the fact that Fe ions tend to dissolve at acidic condition, which can be related to the precipitation of Fe phosphates meanwhile Ca ions tend to dissolve at basic condition which was related to Ca phosphate formation.

Un-aerated system and aerated system differ in the introduction of oxygen into the systems during the aeration process. Aerated system provides aerobic condition to the system during the aeration process. Under aerobic conditions, Ca and Al adsorb onto the surface of adsorbent which can be the adsorption site for phosphate removal whereas phosphate are precipitated out with Fe ions [15]. Besides that, high dissolved oxygen in aerated conditions causes much more carbon dioxide to be stripped to the atmosphere thus produce little carbonic acid. This results in the increase in pH levels in the system [12]. Therefore, this study was carried out to compare the difference performance of aerated and un-aerated high Ca steel slag systems at different pH values for its phosphate removal efficiency.

2 Experimental

2.1 Materials

The high Ca electric arc furnace (EAF) steel slag was obtained from Pasir Gudang, Johor, Malaysia. The steel slag was characterized using X-ray Fluorescence Spectroscopy (XRF) to obtain its chemical composition. The XRF results obtained were shown in Table 1. For preparation of XRF samples, the solid steel slag was crushed manually using a hammer and the crushed samples were collected and sieved through a 63 micrometer test sieve (British

Standard sieve BS410/1986) using a shaker, Endecotts Lombard Rd. London, model Sw193BR, England. Meanwhile, the steel slag samples in the range of sizes of 9.5 mm to 20 mm were accepted for use as filter media in the column study. The samples pre-treatment include washing up twice the steel slag with tap water followed by distilled water before they were dried up in the oven for 24 hours at 105°C.

Table 1. The XRF Results for Chemical Composition of Steel Slag

Compounds	Percentage (%)
CaO	49.5
SiO ₂	18
MgO	4.32
SO ₃	2.58
Al ₂ O ₃	2.23
Fe ₂ O ₃	1.64
MnO	0.38
TiO ₂	0.22

2.2 Filter Column Study

To investigate the differences between unaerated and aerated systems on the phosphate removal efficiency using high Ca steel slag as the adsorbents, lab-scale vertical column filters study was developed. Twelve column filters with different pH values of the influents (pH 3, 5, 7, 9, 11 and Control) for unaerated and aerated systems with the inner diameter of 150 mm, 6 mm thickness and total height of 400 mm made from Perspex materials were set up as shown in Fig. 1. The column filters for Control systems used distilled water as the feed. The pH values of all different pH systems were adjusted using 2N NaOH and 2N H₂SO₄.

The pH values were monitored and adjusted frequently in order to minimize its fluctuation, especially for very low and very high pH values. HANNA HI-99310 portable pH meter was used to measure the pH and temperature. The influent was set to 25 mg/L synthetic wastewater (typical concentration range of phosphorus in wastewater in Malaysia) which was prepared by dissolving KH₂PO₄ salts (as the phosphate source) into distilled water. Synthetic wastewater feed was flowed via gravity from the influent tank located at the higher level and connected to the influent point which was located at the bottom of each column filters. The effluents of the samples were collected at the upper layer valves of each column filter. The hydraulic loading rate (HLR) used for the systems was set at 0.60 m³/m³.d following Johnson [15].

Meanwhile, aerated system was developed by connecting the tube from the air pump to the base of the column filters. The column filters were continuously fed with synthetic wastewater and weekly sampling was done for the influents and the effluents of each filter to test for pH, orthophosphate concentration and metals (Ca and Mg) concentration.

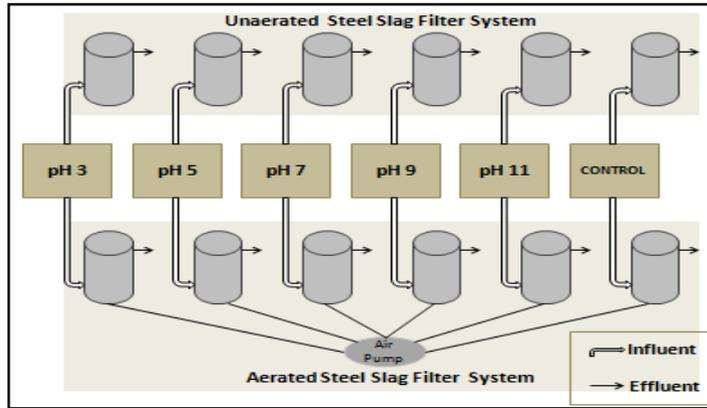


Fig. 1. Schematic diagram of lab-scale vertical steel slag column filters system

2.3 Analysis Methods

The samples were analyzed for the concentration of orthophosphate following the ammonium molybdate spectrometric method using WESTCO Discrete Analyzer, model Smartchem 200, France. The phosphate removal efficiency was obtained by determining the removal percentage of the phosphate. Meanwhile, the concentration of Ca ions and Mg ions were analyzed following 3111B Standard Methods for Examination of Water and Wastewater; atomic absorption spectrometric (AAS) method; [10] using model Perkin Elmer AAnalyst 100.

3 Results and Discussion

3.1 Phosphate removal efficiencies of unaerated and aerated high Calcium steel slag filter systems

Fig. 2 (a-e) illustrates the phosphate removal efficiencies of high Ca steel slag for unaerated and aerated filters at pH values of 3, 5, 7, 9 and 11 respectively. Generally, similar trends can be detected for all of the different pH systems; unaerated systems performances were slightly better compared to aerated systems. Nevertheless, aerated systems' performance can still be considered as efficient in removing phosphate since their percentage removal is around 69-97% while unaerated systems removed 76-98%.

Fig. 2(a) shows the removal efficiency of phosphate at pH 3 where very similar trends of phosphate removal efficiencies were shown with slightly better performance of unaerated pH 3 system compared to aerated pH 3 systems. Both systems showed excellent removal of phosphate between 77-97%. The highest percentage removal was shown during day 21 sampling at 97.9%. Meanwhile, systems at pH 5 also showed similar behaviour which can be seen in Fig. 2(b); highest removal for the first four weeks then started to decline; 77-97% and 74-97% for unaerated and aerated system respectively.

In Fig. 2(c), it can be seen that the removal efficiency of phosphate for unaerated pH 7 system was 76-98% whereas aerated pH 7 system was 71-95%. Unaerated system performed slightly better in removing phosphate compared to aerated system. Same goes to pH 9 and pH 11 systems, unaerated systems perform better; 77-97% for pH 9 and 76-97% for pH 11. The aerated systems followed closely behind; 69-96% for pH 9 and 67-91% for pH 11.

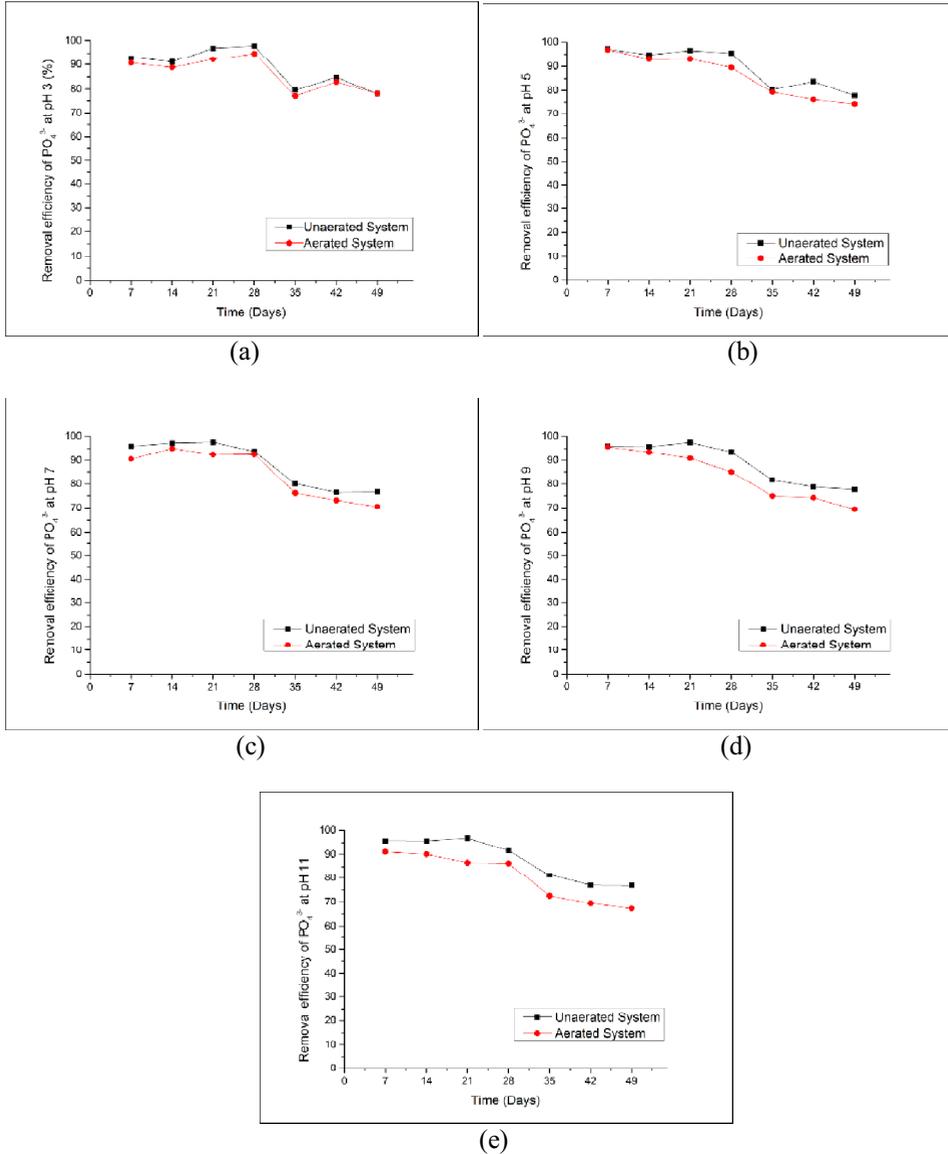


Fig. 2. (a-e) represents removal efficiency of phosphate from the filter systems of: (a) pH 3 systems; (b) pH 5 systems; (c) pH 7 systems; (d) pH 9 systems; (e) pH 11 systems.

All of the systems illustrated that the phosphate removal efficiencies are the best during the first four weeks before they started to decrease slightly and then consistent. During the first four weeks, many surface sites for removal mechanism were available. Therefore, they performed the best. However, after that, the surface sites for reaction had decreased a little due to the precipitates formed as the results of the removal causing certain surface sites to be unavailable for further reaction. This is true for unaerated systems because the systems were not disturbed; no aeration which allowed precipitates to form. On the other hand, aerated systems did not show a significant amount of precipitates inside the filters though the removal of phosphate still happened. This indicated that the removal mechanism followed adsorption mechanism rather than precipitation. However, the sampling duration should be extended some more to see the exact trends following after.

Overall, unaerated systems performed slightly better in phosphate removal compared to aerated systems. All of the different pH systems, either acidic, neutral or alkaline, has high phosphate removal efficiency and this could be very advantageous in the removal of phosphate at different pH feed for wastewater treatment technology.

3.2 The effects of pH related to the concentration of Ca, and Mg ions in effluents and the phosphate removal mechanism

Fig. 3(a-f) illustrated the concentration of Ca and Mg in effluents at pH values of 3, 5, 7, 9, 11 and Control for both unaerated and aerated systems. At pH 3 as shown in Fig. 3(a), concentrations of Ca in effluents are significantly greater in unaerated systems compared to aerated system. This showed that the significant role of Ca ions in the phosphate removal mechanism via precipitation for unaerated system.

Similar trends can be seen in pH 5, 7, 9 and Control systems as seen in Fig.3 (b), (c), (d) and (f) respectively. The concentration of Ca in unaerated systems was obviously greater compared to aerated systems. In unaerated systems, visible white precipitates formed could be seen especially at the inlet of the filters, which were thought to be Calcium-phosphate precipitates either hydroxyapatite (HAP) or its precursors. The amount of white precipitates formed was greater for basic pH systems (pH 9 and pH 11 unaerated systems). This showed that the phosphate removal mechanism for unaerated systems followed both precipitation and adsorption mechanisms, only the significance of precipitation were greater and ruled the pathway at basic pH compared to acidic pH [14].

Meanwhile, aerated systems caused less concentration of Ca in effluents. This was actually contradicted to the assumptions made that aeration causes greater rate of dissolution of the metal ions inside the steel slag due to vibration. Physically, only a small amount of cloudy sludge can be seen in the filters and no visible white precipitates were formed. Nevertheless, their performance in removing phosphate was considered as excellent, comparable to unaerated systems. Therefore, adsorption might be more significant phosphate removal mechanism in aerated systems since no white precipitates were visible in the filters. The adsorption follows inner-sphere ligand exchange mechanism [15] where they reacted by forming monodentate and bidentate complexes which were determined by how they were coordinated [16].

Meanwhile, the concentrations of Mg are very small for all of the systems, less than 1 mg/L. Little can be obtained from here since the trends are very similar for both unaerated and aerated systems, with slightly higher concentration of Mg for unaerated systems. However, this shows that Mg ions have a less significant contribution compared to Ca ions in the removal of phosphate.

The performance of unaerated systems are slightly better compared to aerated systems. Nevertheless, since the importance of aeration is very crucial when removing nitrogen from wastewater; therefore when the desired results are to remove both nutrients simultaneously, therefore aerated systems' performance can be considered as an excellent choice.

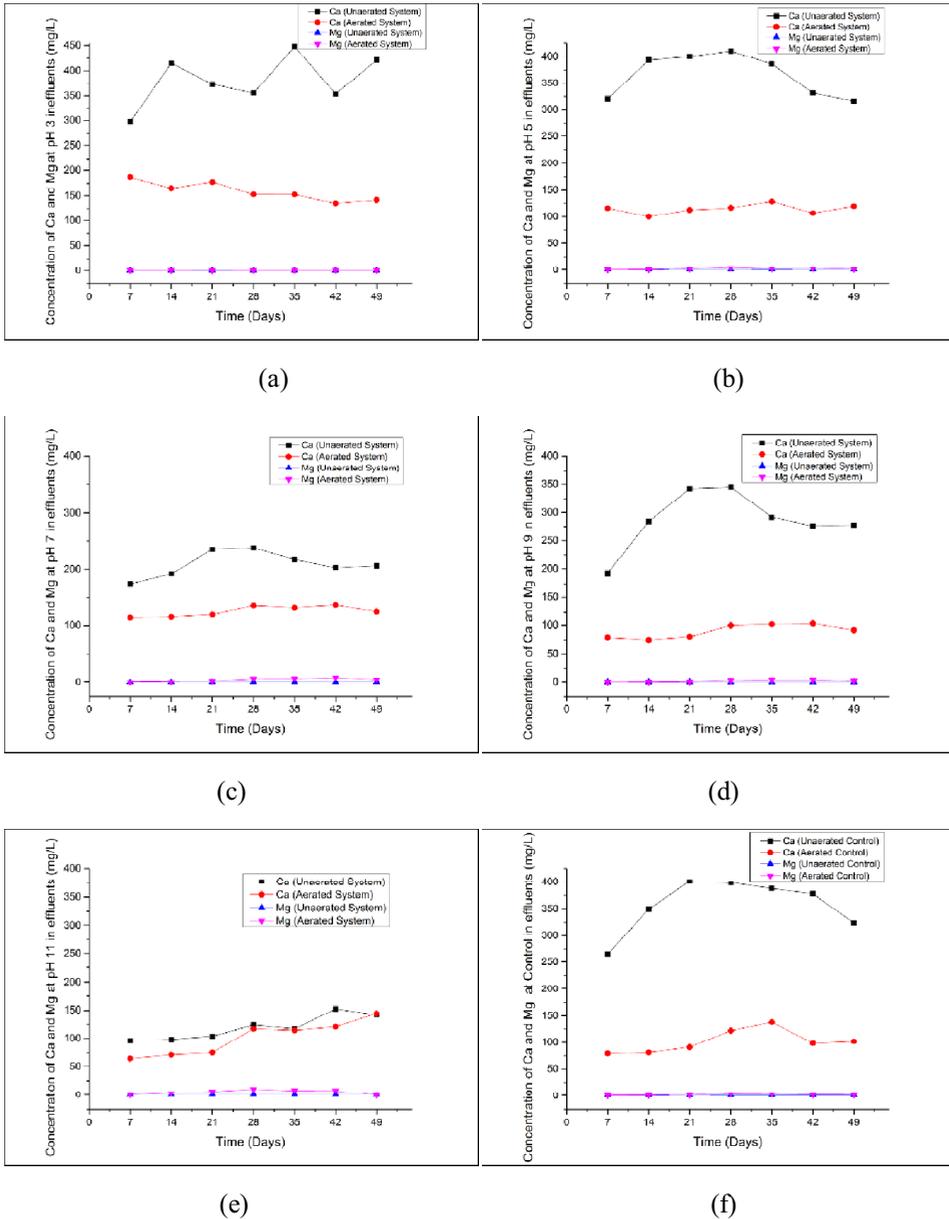


Fig. 3. (a-f) represents the concentration of Ca and Mg in effluents at systems of: (a) pH 3 systems; (b) pH 5 systems; (c) pH 7 systems; (d) pH 9 systems; (e) pH 11 systems; (f) Control systems

4 Conclusions

This study showed that both un-aerated and aerated, high Ca steel slag filter systems were very efficient in removing phosphate at all acidic, neutral and basic pH influents. The percentages of phosphate removal efficiency for un-aerated systems were found to be around 76-98%, while aerated systems removed 69-97% of phosphate. Ca concentrations in effluents are higher for un-aerated systems compared to aerated systems, meanwhile Mg concentrations are similar for all the systems. The dominant phosphate removal mechanism

followed adsorption for aerated systems and both adsorption and precipitation for unaerated systems; where at acidic and neutral pH, both adsorption and precipitation ruled the mechanism, meanwhile at basic pH, precipitation was more dominant.

We are grateful for the fundings provided by Ministry of Higher Education and University Tun Hussein Onn Malaysia; ERGS VOT.E031 and GPPS VOT U513.

References

- [1] S.C. Reed, *Nat.systems for waste management and treatment*, 2nd ed. New York:McGraw-Hill,(1995)
- [2] S. Manahan, *Fundamentals of Enviro. Chem.*, 3rd ed. Boca Raton, Florida:Taylor&Francis/CRC Press,(2009)
- [3] G.K. Morse, S.W. Brett, J.A. Guy and J.N.U. Lester, Review : Phosphorusremoval and recovery technologies. *The Sci. of the Tot. Env.*, **212**, 69–81,(1998)
- [4] Y.Z. Li, C.J. Liu, Z.K.Luan, X.J. Peng, C.L. Zhu, Z.Y. Chen, Z.G. Zhang, J.H. Fan and Z.P. Jia, Phosphate RemovalFromAqueous Solution UsingRaw and ActivatedRedMud and Fly Ash. *J. Hazard. Mater.* **137**, 374-383, (2006)
- [5] L. Johansson-Westholm, Substrates for PhosphorusRemoval–potentialBenefits for On-site WastewaterTreatment, *Water Resources.* **40**(1), 23-36. (2006)
- [6] I. Blanco, P. Molle, L. Miera, G. Ansola, Basic OxygenFurnaceSteelSlagAggregates for PhosphorusTreatment : Evaluation of ItsPotential Use as a Substrate in ConstructedWetlands, *Water Research*, **89**, 355-365 (2016)
- [7] C. Barca, C. Gerente, D. Meyer, F. Chazarenc, Y. Andres,Phosphate RemovalfromSynthetic and Real WastewaterUsingSteelSlagsProduced in Europe, *Water Resources.* **89**, 1-6 (2012)
- [8] C. Barca, S. Troesch, D. Meyer, P. Drissen, Y. Andres, F. Chazarenc, SteelSlagFilters to Upgrade PhosphorusRemoval in ConstructedWetlands: TwoYears of Field Experiments, *Env. Sci. Tech.*,**47**, 549-556 (2013)
- [9] C. Barca, D. Meyer, M. Liira, P.Drissen, Y. Coemau, Y. Andres, F. Chazarenc, SteelSlagFilters to Upgrade PhosphorusRemoval in WastewaterTreatment Plants: RemovalMechanisms and Performance, *Eco. Eng.*, **68**, 214-222 (2014)
- [10]R. Hamdan, D. Mara, Study of In-filterPhosphorusRemovalMechanisms in an Aerated Blast FurnaceSlag, *Int. J. of Research in Eng. and Tech.*, **2**(8), 130-136 (2013)
- [11]C. Han, Z. Wang, W. Yang, Q. Wu, H. Yang, X. Xue, Effects of pH on PhosphorusRemovalCapacities of Basic OxygenFurnaceSlag, *Eco. Eng.*,**89**,1-6 (2016)
- [12]P. Wifert, P.S. Kumar, L. Korving, G. Witkamp, M.C.M. Loodsrecht, The Relevance of Phosphorus and IronChemistry to the Recovery of PhosphorusfromWastewater: A Review, *Env. Sci. and Tech.*, **49**, 99400-9414 (2015)
- [13]M.Scholz, *WetlandsSystems to Control UrbanRunoff*, Elsevier, Oxford, United Kingdom, (2006)
- [14]S.E. Johnson, R.H. Loeppert, Role of OrganicAcids I Phosphate MobilizationfromIronOxides, *SoilSci. Soc. Am. J.*, **70**, 222-234 (2006)
- [15]B. Zhong, R. Stanforth, S. Wu, J.P. Chen, Proton Interaction in Phosphate Adsorption onto Goethite, *J. of ColloidalInterfacialSci.*, **308**, 40-48 (2007)

- [16] A. Klimeski, W.J. Chardon, E. Turtola, R. Uusitola, Potential and Limitations of Phosphate Retention Media in Water Protection: A Process-based Review of Laboratory and Field-scale Tests, *Agr. and Food Sci.*, **21**, 206-223 (2012)