International Journal of Engineering & Technology, 7 (4.30) (2018) 557-561

International Journal of Engineering & Technology

Website: www.sciencepubco.com/index.php/IJET

Research paper



Investigation of PO_4^{3-} Removal in Aerated and Unaerated High Fe EAF-Slag Filter System

Hamdan, R*[1], Siti Zu Nurain Ahmad[2], Nur 'Ain Nazirah Mohd Arshad[3], Wan Afnizan Wan Mohamed[4], Syahrul Nizam Maarup[5]

[1,3,4,5]*Faculty of Civil Engineering and Environmental, Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Batu Pahat, Johor, Malaysia*

[2,] *Department of Civil Engineering Technology, Faculty of Engineering Technology, Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Batu Pahat, Johor, Malaysia*

**Corresponding author E-mail: rafidahh@edu.my*

Abstract

Phosphorus in wastewater is one the main culprit which accelerates eutrophication in waterbody if it is not being treated properly. Steel slag filter emerged as one alternative treatment for wastewater. However, the variousness of metal oxides including Fe in steel slag will affect the phosphorus removal efficiency. Thus, this study was conducted to investigate the ability of a series of lab-scale high Fe electric arc furnace (EAF- slag) column filters in removing PO43- from synthetic wastewater. The systems were operated under aerated and un-aerated within acidic and alkaline conditions. Synthetic wastewater contained 25 mg/L was prepared as the feed and monitored weekly basis for the PO_4^{3-} removal efficiency and the total metals (Ca, Fe, and Mg) concentrations in the effluents. The results show that both aerated and unaerated high Fe EAF-slag filter systems have high PO_4^{3-} removal efficiency under acidic condition, which unaerated system performed slightly better. It can be observed that unaerated systems performed better in removing PO_4^{3-} at acidic and neutral pH values but not at extremely high pH. As for the PO_4^{3-} removal mechanism was achieved by adsorption and precipitation at acidic pH and the concentration of Ca, Mg and Fe in effluents was related to the PO_4^{3-} removal efficiency at different pH values.

Keywords: *Adsorption, PO43- removal; adsorption; electric arc furnace slag; pH; rock filters.*

1. Introduction

Phosphorus is a culprit nutrient in accelerating of eutrophication in natural surface waters. Eutrophication occurs when the aquatic ecosystem gets over-enrichment with a nutrient that comes from construction sites, runoff agricultural, urban areas and it is lead to algal bloom and anoxic events that exist constantly at the surface of the water. Acceleration of algae growth will eventually will cause eutrophication in aquatic ecosystem [1]. Therefore, removal of phosphorus in wastewater has become among the important issue and indicator of determining the efficiency and reliability of the treatment system of the wastewater.

Wastewater must undergo conventional and advanced treatment prior to be discharged to river. However, the need of alternative treatment is emerged due to chemical cost and complexity. Therefore, the development of low cost technology for wastewater treatment including steel slag filter is become popular. Steel slag, a by-product from steel manufacturing industry filter is amongst a high potential medium for removing phosphate from wastewater as it contains high concentrations of metal oxides including Ca, Fe, Al and Mg [2].

The removal mechanisms of PO_4^{3-} is either through adsorption or precipitation depends on the existing of metal oxides concentrations [3]. Therefore, it may due to chemical compositions of steel slag. This variousness are due to the disparity in the grade of steel products and type of furnaces used during the process of steel-making[4].

Furthermore, performance of phosphorus removal in aqueous system are affected due to several factors including pH and concentration of metallic salts [5]. The influent's pH are one of the closely related with phosphorus removal. In general, phosphorus removal using steel slag system prefers basic condition where adsorption will occur at low pH and Ca PO_4^3 will precipitate at high pH value. Insoluble phosphates in a steel slag filter system are chemically precipitated with ferric iron under aerobic conditions. For instance, Ca and Al in the form of clay particles, ferric and Al hydroxides and oxides tend to be adsorbed onto adsorbent surfaces [6]. Furthermore, some polyphosphate is hydrolysed to orthophosphate under aerobic conditions, which is a readily available nutrient and assimilates for the growth of bacteria and energy transfer. Then, orthophosphate is released as the HPO_4^{2-} ion under this condition. In Ca^{2+} concentrated system, precipitations of orthophosphate as hydroxyapatite from the solution occur and incorporated subsequently into floc particles [7].

In this study, different composition of metal oxides in steel slag has been studied. When high percentage of CaO present in the steel slag in high pH value conditions, precipitation of Ca PO_4^{3-} is expected to be formed where it dominates the removal mechanism. On the other hand, when the steel slag contains high percentage of iron, adsorption into Fe oxides will dominate the PO_4^{3-} removal mechanism at acidic and neutral pH range [8]. However, adsorption is not the only interaction which occurs between Fe oxides and ortho PO_4^{3-}. The dissolution of Fe^{3+} from Fe oxides will indicates that precipitation might occur [9]. Fe^{3+} ions are tend to dissolve in acidic condition which leads to the precipitation of Fe PO_4^{3-} meanwhile Ca^{2+} ions tend to dissolve in basic condition, which related to Ca PO_4^{3-} formation.

Copyright © 2016 Authors. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

2. Experimental

2.1. Filter medium

The EAF-slag was obtained from Antara Steel Mills Sdn. Bhd. located at Pasir Gudang, Johor, Malaysia which consist of 38.3% Fe_2O_3, 20.4% of CaO, 15.2% SiO_2, 7.0% Al_2O_3, %, 5.19% MnO and 3.22 MgO has been used as a filter medium. The EAF-slag was characterized using X-ray Fluorescence Spectroscopy (XRF) for chemical composition determination. The EAF-slag was ground using Ball Mill grinder. The EAF-slag samples sizes range from 9.5 mm to 20 mm. The samples were then washed twice and oven dried for 24 hours at drying temperature 100 ±5˚C.

2.2. Column study

Twelve sets of Lab-scale vertical high Fe EAF-slag filters was constructed to study the effectiveness of phosphorus removal system from synthetic wastewater. The filter systems were conducted in two conditions; aerated and unaerated. Column filters made from Perspex materials with the dimension of 400 mm total height, 150 mm inner diameter and 6 mm thickness. The pH values of influents were adjusted using NaOH and H_2SO_4 from acidic to alkaline and control for aerated and unaerated system as shown in Figure 1. Distilled water was used as feed for the control column filters.

The pH meter (HANNA HI-99310, UK) was used to monitor the pH value throughout the experiment to minimize the fluctuations. The synthetic wastewater was then prepared with 25 mg PO_4^{3-} /L (typical concentration of PO_4^{3-} of domestic wastewater) by dissolving into distilled water and fed via gravity to the influent of each filter. The column filters were aerated by using compressed air. The aeration was controlled to provide tiny and uniform bubbles of air to spread evenly throughout the column filters. Wastewater sample from influents and effluents of each filter have been sampled and analysed on weekly basis for the selected parameters including pH, ortho-PO_4^{3-} concentration and metals including Ca, Fe, and Mg concentration.

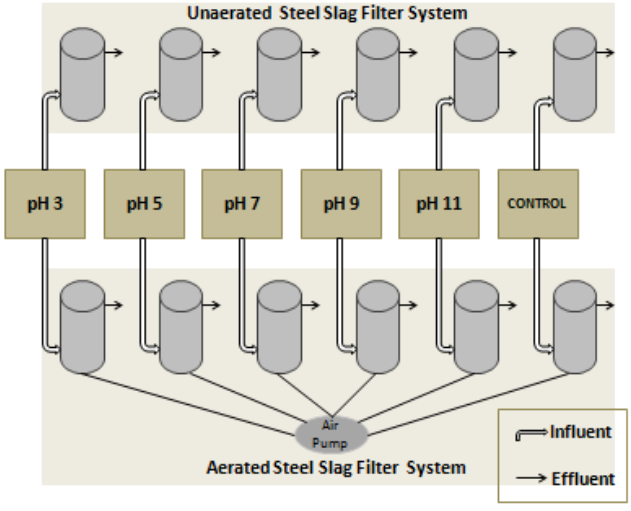


Fig. 1: Layout of the experimental setup

2.3. Analysis of PO_4^{3-}

The concentration of orthoPO_4^{3-} was measured using ascorbic acid reduction method. The removal efficiency of removal of $PO_4^{3-}$was obtained using the following equation:

$$\textbf{Removal percentage}(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

in which C_0 is the initial ortho PO_4^{3-} concentration (influent) in mg/L and C_e is the final ortho PO_4^{3-} concentration (effluent) in mg/L. Meanwhile, the metal concentration; Ca, Fe and Mg were measured using atomic absorption spectrometric (AAS), (Perkin Elmer Analyst 100, US) method.

3. Results and Discussion

3.1. High Fe EAF-slag filters Performance in removing PO_4^{3-} at different pH

Figure 2 until Figure 6 shows the PO_4^{3-} removal efficiency at different pH values EAF-slag filter systems. The PO_4^{3-} removal efficiencies for unaerated and aerated pH 3 systems were between 78-89% and 76-85% respectively. They show the best PO_4^{3-} removal efficiency for both systems. Meanwhile, the PO_4^{3-} removal efficiency for unaerated pH 5 system was 74-88% whereas for aerated system was 61-76%. Both pH 5 systems also exhibit good PO_4^{3-} removal efficiency though they have slightly less performance compared to pH 3 systems. Therefore, acidic pH EAF-slag filters have higher PO_4^{3-} removal efficiency compared to neutral and alkaline pH.

For unaerated and aerated pH 7 systems, the PO_4^{3-} removal efficiency was found to be 55-87% and 36-67% respectively. However, the first week's performance of unaerated pH 7 system was considerably slow, around 37.9% only where aerated pH 7 has shown good PO_4^{3-}removal performance, 61.7%. This contradiction at first week of the experiment compared to the rest of the weeks might be due to the vibration produced during aeration which causes reaction to proceed faster compared to without aeration (unaerated system). Eventually, the result started to follow the normal trend. On the other hand, for unaerated and aerated pH 9 systems, their PO_4^{3-}removal efficiencies were 51-71% and 25-55% respectively. It is clearly seen that unaerated system perform better at removing PO_4^{3-} compared to aerated system.

Generally, for high Fe EAF-slag filters with pH values of 3, 5, 7, and 9, they showed that the unaerated system provide higher PO_4^{3-} removal efficiency compared to the aerated system. However, significant difference can be seen in the systems with pH 11 where the PO_4^{3-} removal efficiency for aerated system is higher, 24-64% compared to the unaerated systems, around 21-41%. Only at extremely high pH (pH 11), aerated system surpass the performance of unaerated system. The PO_4^{3-} removal efficiency of EAF-slag at acidic pH influent is higher compared to the influents of neutral and alkaline pH. These results are similar and following Han *et al.*, [8] and Xue *et al.*, [10]. The difference in PO_4^{3-} removal efficiency can be related to the difference in the composition metal oxide of the EAF-slag used.

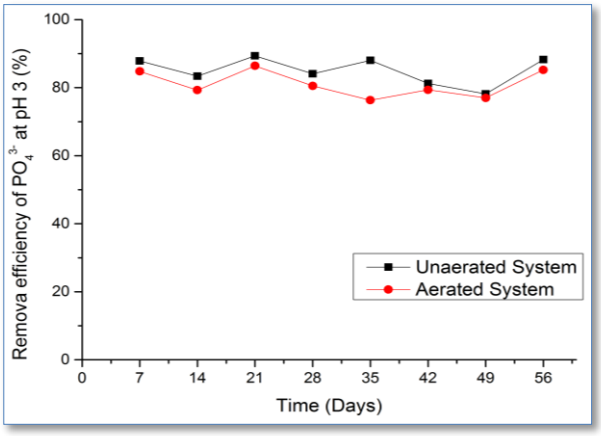


Fig. 2: Removal efficiency of PO_4^{3-} at pH 3

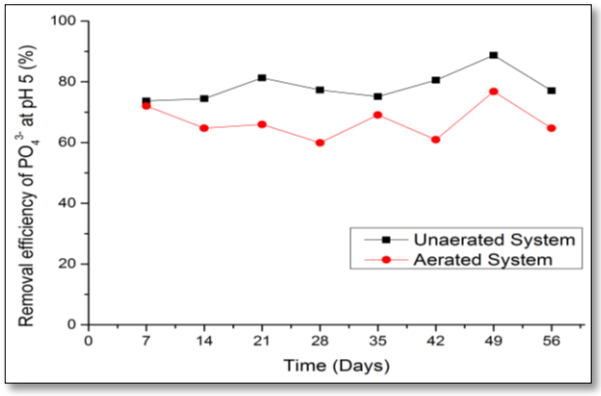


Fig. 3: Removal efficiency of PO_4^{3-} at pH 5

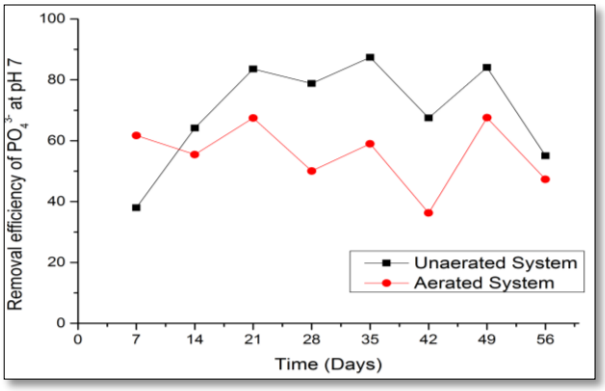


Fig. 4: Removal efficiency of PO_4^{3-} at pH 7

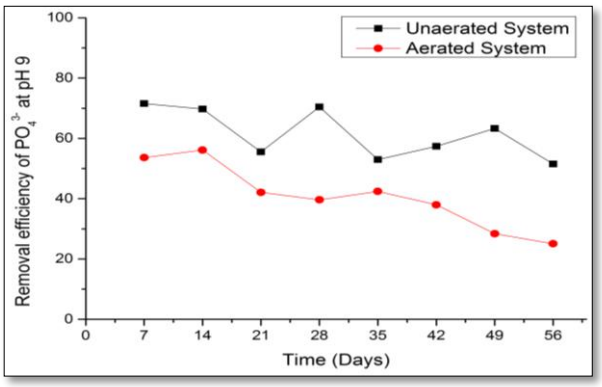


Fig. 5: Removal efficiency of PO_4^{3-} at pH 9

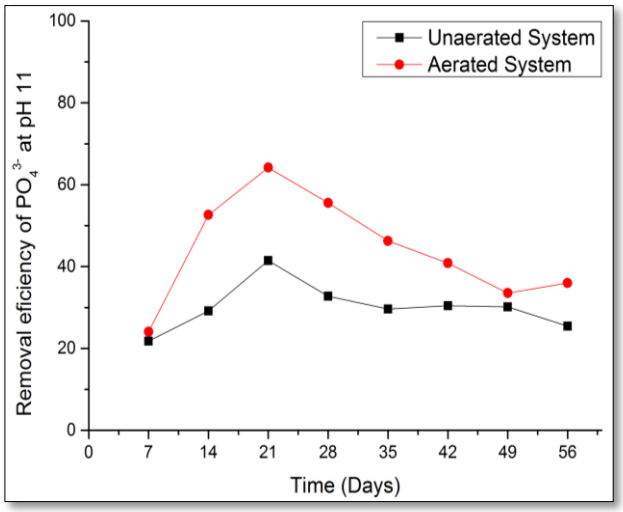


Fig. 6: Removal efficiency of PO_4^{3-} at pH 11

3.2. The concentration of Ca^{2+}, Mg^{2+} and Fe^{2+} in effluents

The Figure 7 shows the Ca^{2+} and Mg^{2+} ions concentration in effluents at the control column filters. It can be seen that both Ca^{2+} and Mg^{2+} ions concentration in aerated systems are higher compared to the unaerated systems. The concentrations of Ca^{2+} ions for aerated and unaerated Control systems are 21.7-28.9% and 12.8-23.2%. Meanwhile, the concentrations of Mg^{2+} for aerated and unaerated Control systems are 1.1-3.5% and 0.01-0.2.5 respectively. Ca^{2+} concentration is significantly high in the effluents compared to the Mg. This is match with the chemical compositions of EAF-slag which is significantly higher in Ca^{2+} compared to Mg^{2+}.

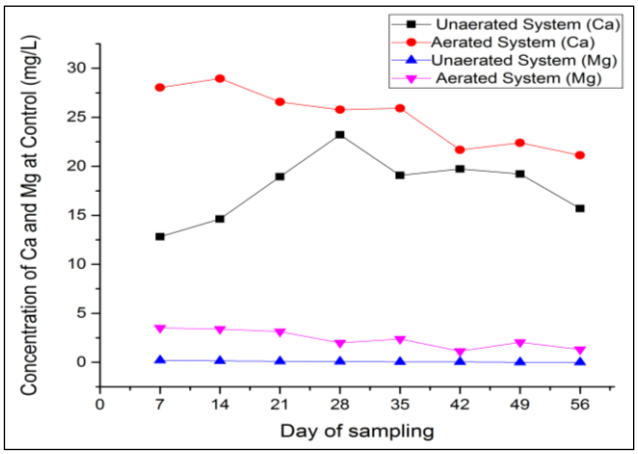


Fig. 7: Concentration of Ca and Mg at Control

Figure 8 shows the Ca^{2+} and Mg^{2+} concentrations of at pH 3 for unaerated and aerated systems. Following similar trend of Control systems, the concentrations of Ca^{2+} and Mg^{2+} at pH 3 were higher at aerated systems compared to unaerated systems. The concentrations of Ca^{2+} for aerated and unaerated at pH 3 systems were 16.5-40% and 14.6-26.2% respectively. On the other hand, the concentrations of Mg^{2+} for aerated and unaerated systems at pH 3 were 1.7-5.2%. These values are lower compared to the concentrations of Ca^{2+}. Comparing the results obtained with control systems; pH 3 systems produce higher concentrations of Ca^{2+} and Mg^{2+} in the effluents. Thus, this shows that the nature of EAF-slag filters, when in contact with aqueous solution (aqueous solution in this experiment is distilled water), then the chemical components of the EAF-slag, mainly metal oxides, might leach out from the EAF-slag itself and come in contact with the wastewater.

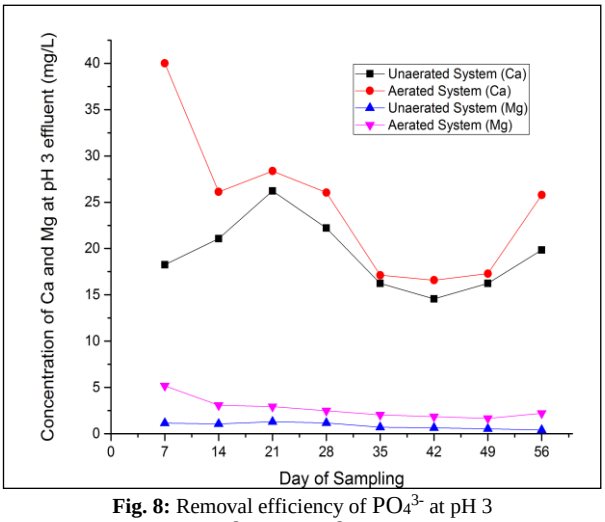


Fig. 8: Removal efficiency of PO_4^{3-} at pH 3

The concentrations of Ca^{2+} and Mg^{2+} at pH 5 for unaerated and aerated systems were plotted in Figure 9. Aerated system contains

higher Ca^{2+} and Mg^{2+} (9.9-20% and 1.6-3.1% respectively) compared to unaerated systems (3.7-8.1%).

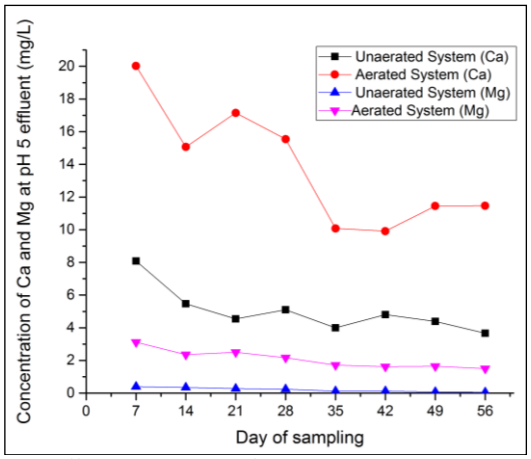


Fig. 9: Effluent concentration for both EAF-slag system at pH 5

In Figure 10, the concentrations of Ca^{2+} and Mg^{2+} at pH 7 were plotted. Similar trends as at pH 5 can be seen and shown by pH 7, 9 and 11 filters following trends shown by Control and pH 3 filters. The concentrations of Ca^{2+} for aerated systems are significantly higher compared to the concentrations of another three parameters. Figure 11 and 12 shows the concentration of Ca^{2+} and Mg^{2+} at pH 9 and pH 11 respectively. It is known that the PO_4^{3-} removal for Ca-rich materials are through the calcium PO_4^{3-} precipitation [11]. The role of Ca^{2+} released has been seen performing well in previous studies [12]. Therefore, the increase in Ca^{2+} in slag due to dissolution process can increase the concentrations of Ca^{2+} and OH^- ions [8].

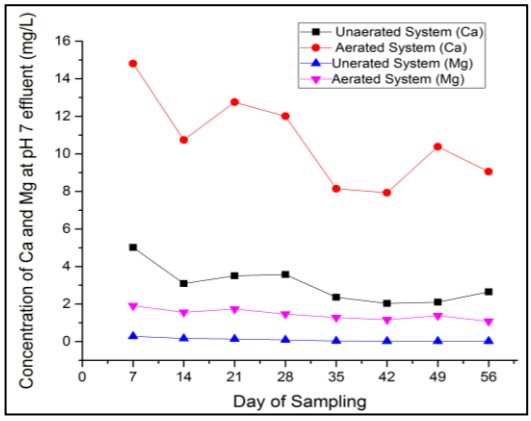


Fig. 10: Concentration of Ca and mg at pH 7 effluents

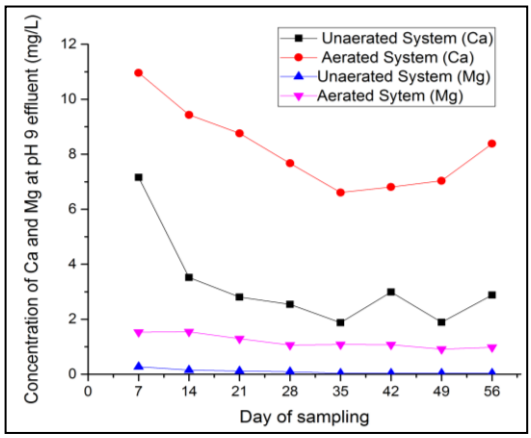


Fig. 11: Effluent concentration for both EAF-slag system at pH 9

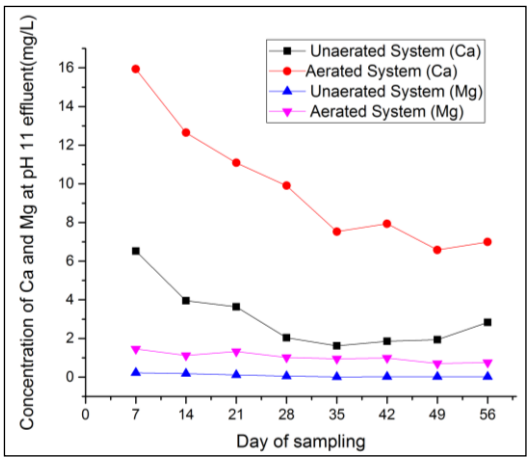


Fig. 12: Effluent concentration for both EAF-slag system at pH 11

The concentrations of Fe^{3+} in the effluents were illustrated in Figure 13. Only in a few column filters can be obtained the presence of Fe^{3+} in the effluents. Some of the unaerated systems contain Fe^{3+} which is filters of pH 3, 5, 7, and 9. Meanwhile, for aerated systems, only aerated pH 3 systems contains Fe in the effluents. Though the compositions of the EAF-slag used have highest percentage of Fe_2O_3 (38.2%), however the concentrations of Fe in the effluents did not reflects the highest percentage of Fe_2O_3. The high concentrations of Fe at pH 3 systems are the results of dissolution of Fe^{3+} at acidic pH [8]. This suggests that very small amount of Fe ions leach out of the slag thus can be related to the adsorption process for the PO_4^{3-} removal mechanism. Adsorption of PO_4^{3-} Fe oxides follows the inner-sphere ligand exchange mechanism [13] where they can react by forming bidentate or monodentate complexes depending on how they were coordinated [14][15]. However, red-brown colour sludge was also formed inside the filters which were pointed as precipitates of iron PO_4^{3-}s. This suggested that the PO_4^{3-} removal mechanism were following the precipitation process by forming precipitates with Fe ions from the steel slag apart from adsorption mechanism which happened simultaneously. Surface complexation (adsorption) tends to dominate the mechanism at low surface coverage, however, when the surface loading increase, precipitation becomes dominant [9].

Meanwhile, the concentrations of Ca^{2+},Mg^{2+} and Fe^{2+} at alkaline pH were significantly less compared to acidic pH. At higher alkaline pH, more hydroxide ions adsorbed onto slag surface which causes stronger repulsive and competitive adsorption [8] thus reduce sites for PO_4^{3-} adsorption. Therefore, PO_4^{3-} removal efficiency at higher alkaline pH decrease compared to acidic pH. Acidic system contained higher concentration of Ca and Fe ions therefore they were better at removing PO_4^{3-} compared to basic pH.

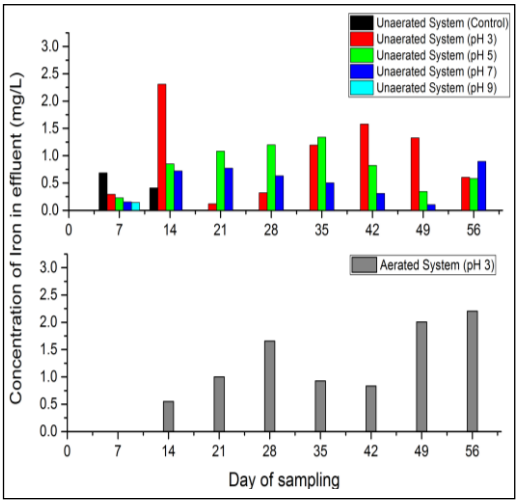


Fig. 13: Concentration of Fe in effluents

4. Conclusion

This study concluded that the high Fe unaerated EAF-slag filters system has higher PO_4^{3-} removal efficiency compared to aerated high Fe EAF-slag filters system with the exception of system at pH 11. The highest PO_4^{3-} removal efficiency can be seen at acidic pH values. Ca^{2+},Mg^{2+} and Fe^{2+} concentrations in effluents also increase with the decrease in pH values though aeration causes higher concentration of Ca^{2+},Mg^{2+} and Fe^{2+} in the effluents.

Acknowledgement

We would like to thanked our funder: Ministry of Higher Education under Fundamental Research Crant Scheme (Vot 1613) and Universiti Tun Hussein Onn Malaysia.

References

[1] Ansari, A. A., & Gill, S. S. (2014) Eutrophication: Causes, consequences and control: Volume 2. 1–262.
[2] Johansson-Westholm, L. 2006. Substrates for Phosphorus Removal–potential Benefits for On-site Wastewater Treatement?. *Water Resources*. 40: 23-36.
[3] Barca, C., Meyer, D., Liira, M., Drissen, P., Coemau, Y., Andres, Y., Chazarenc, F. 2014. Steel Slag Filters to Upgrade Phosphorus Removal in Wastewater Treatment Plants: Removal Mechanisms and Performance. *Ecological Engineering*. 68: 214-222.
[4] Barca, C., Troesch, S., Meyer, D., Drissen, P., Andres, Y., Chazarenc, F. 2013. Steel Slag Filters to Upgrade Phosphorus Removal in Constructed Wetlands: Two Years of Field Experiments. *Environmental Science Technology*. 47: 549-556.
[5] Hamdan, R., Mara, D. 2013. Study of In-filter Phosphorus Removal Mechanisms in an Aerated Blast Furnace Slag. *International Journal of Research in Engineering and Technology*. 2(8); 130-136.
[6] Scholz, M. (2006). Wetland systems to control urban runoff. Elsevier, Oxford,UK.
[7] Gerardi, M.H. (2006). Wastewater bacteria. John Wiley and Sons, Inc., New York.
[8] Han, C., Wang, Z., Yang, W., Wu, Q., Yang, H., Xue, X. 2016. Effects of pH on Phosphorus Removal Capacities of Basic Oxygen Furnace Slag. *Ecological Engineering*. 89:1-6.
[9] Wifert, P., Kumar, P. S., Korving, L., Witkamp, G., Loosdrecht, M.C.M. 2015. The Relevance of Phosphorus and Iron Chemistry to the Recovery of Phosphorus from Wastewater: A Review. *Environmental Science and Technology*. 49: 99400-9414.
[10] Xue, Y., Hou, H., Zhu, S. 2009. Characteristics and Mechanisms of Phosphate Adsorption onto Basic Oxygen Furnace Slag. *Journal of Hazardous Materials*.162: 973-980.
[11] Vohla,C., Koiv, M., Bavor, H. J., Chazarenc,F., Mander, U. 2011. Filter Materials for Phosphorus Removal from Wastewater in Treatment Wetlands- A Review. *Ecological Engineering*. 37: 70-89.
[12] Bowden, L. I., Jarvis, A. P., Younger, P. L., Johnson, K. L. 2009. Phosphorus Removal from Waste Waters Using Basic Oxygen Steel Slag. *Environmental Science Technology*. 43: 2476-2481.
[13] Zhong, B., Stanforth, R., Wu, S. Chen, J. P. 2007. Proton Interaction in Phosphate Adsorption onto Goethite. *Journal of Colloidal Interfacial Science*. 308: 40-48.
[14] Weng, L., Van Riemsdijk, W. H., Hiemstra, T. 2012. Factors Controlling Phosphate Interaction with Iron Oxides. *Journal of Environmental Quality*. 41: 628-635.
[15] Klimeski, A., Chardon, W. J., Turtola, E., Uusitola, R. 2012. Potential and Limitations of Phosphate Retention Media in Water Protection: A Process-based Review of Laboratory and Field-scale Tests. *Agricultural and Food Science*. 21: 206-223.