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Research paper



Comparative Study of High Calcium and High Iron Filter Media of Unaerated and Aerated Steel Slag Filter Systems in Removing Phosphorus

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Abstract

Improper wastewater treatment will accelerate eutrophication in waterbody due to phosphorus content in wastewater. However, to remove wastewater from requires a high and complex processes. This study was conducted to explore an alternative treatment of phosphorus removal using steel slag filter system in particular of affinity different chemical composition of steel slag. Therefore, this study has been designed for comparisons between steel slag of high composition of iron (Filter HFe) and steel slag of high composition of calcium (Filter HCa) when used as the filter media of unaerated (UEF) and aerated (AEF) lab-scale column filters in removing phosphorus. Both Filter HFe and Filter HCa were continuously running for three months using 25 mg/L synthetic phosphorus wastewater of different pH systems (pH 3, pH 5, pH 7, pH 9, pH 11 and control using distilled water) as the influents. Sampling was done weekly for analysis of pH values, phosphorus (in the form of orthophosphate) removal efficiency, and concentration of Ca, Mg and Fe in the effluents. The results showed that Filter HFe has excellent (>59%) orthophosphate removal efficiency at acidic systems (pH 3 and pH 5 systems) and average removal efficiency (21-87%) at pH 7, pH 9, pH 11 systems. Also, unaerated systems performed better compared to aerated systems. Meanwhile, for Filter HCa, orthophosphate removal efficiencies for all pH systems were better (80-100%) compared to Filter HFe.

Keywords: *Adsorption, aerated filter, electric arc furnace, phosphate removal, precipitation*

1. Introduction

Steel slag, as the filter media for rock filters has shown great phosphate removal efficiency due to high concentration of metal (Ca, Fe, Mg, and Al) oxides. However, the chemical compositions of all steel slag vary due to the influence of variation of steel products and types of furnaces used (Han et al., 2016). Different chemical compositions of steel slag primarily affect the mechanism of orthophosphate removal. Higher composition of calcium oxide (CaO) will follow different mechanism as compared to a higher composition of ferric oxide (Fe_2O_3). When the percentage of CaO of the steel slag is very high, the rate of dissolution of Ca is very significant. This causes formation of Ca phosphate related compounds thus removes orthophosphate. This usually happened at high pH value and the removal mechanism followed the precipitation pathway.

On the other hand, when the percentage of Fe_2O_3 of the steel slag is very high, orthophosphate removal mechanism prefers adsorption on the surface of the steel slag. This occurs at acidic and neutral pH ranges. On top of that, precipitation due to dissolution of Fe ions will occur since Fe has a high rate of dissolution in acidic condition. However, when comparing between many researches, the removal mechanisms of phosphorus are still unclear and conflicting due to the complexity of reaction[1].

Aerated system differs with unaerated system due to the introduction of oxygen into the systems during the aeration process. Under aerobic conditions, adsorption of Ca and Al onto the surface of adsorbent can be expected besides phosphates are precipitated out with Fe ions. Also, during aeration, more carbon dioxide is stripped to the atmosphere, thus produce less carbonic acid. Thus, this results in the increase in pH levels in the system[2]. Therefore, this study was carried out to compare the difference performance of aerated and unaerated high Ca steel slag systems with aerated and unaerated high Fe steel slag systems at different pH values for its phosphate removal efficiency.

2. Materials and Methods

Two sets of continuous electric arc furnace (EAF) slag filter systems of different filter media were developed for duration of three months for each set. The first set (Filter HFe) was using EAF slag of high Fe; low Ca, Mg and Al (38.2% Fe2O3, 20.4% CaO) as the filter media, whereas the second set (Filter HCa) was made of EAF slag of high Ca; low Fe, Mg and Al (49.5% CaO, 1.64% Fe2O3).

Figure 1 illustrates the schematic diagram of the set-up of the continuous filter system. For each set, a total of twelve filters were developed with six filters each for UEF filters of different pH of the influents; pH 3, pH 5, pH 7, pH 9, pH 11 and Control (using distilled water) and another six different filters as for AEF systems. The influents were synthetic wastewater of 25 mg/L phosphorus solution (typical range concentration of phosphorus in domestic wastewater). The influents were flowed into the bottom of the column filters via gravity and the effluents were collected at the upper level of the column filters. Direct influent tank was used to ensure uniform flow rate. Each overflow tank had a small air pump which would pump the excessive influents back into the

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main influent tank. The hydraulic loading rate (HLR) of the system was 0.6 m3.m3/day following Johnson, 2006.

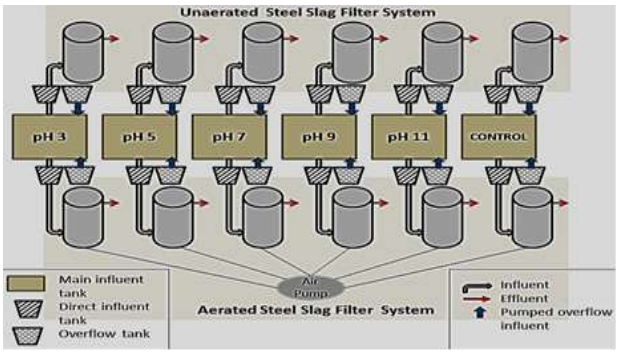


Figure 1: Schematic diagram of slag filter

Meanwhile, aeration was introduced by connecting the air tubes at the bottom of the column filters with the air pump. The air pump was adjusted to ensure a uniform distribution of tiny bubbles to all six column filters of AEF system. Sampling was done weekly for the influents and effluents and tested for pH, concentration of orthophosphate following standard method 4500-P F (Automated ascorbic acid reduction method) using Smartchem 200 WESTCO Discrete Analyzer, and metals such as Ca, Fe, Mg following 3111 B using AAS Perkin Elmer model AAnalyst 800. All experiments performed were conducted in triplicate

3. Results and Discussion

The orthophosphate removal efficiencies for both Filter HFe and Filter HCa systems were tabulated in Table 1. For Filter HFe, pH 3 systems were the most efficient in removing orthophosphate; in the range of 78.17-92.73% for UEF pH 3 system and 76.32-87.96% for aerated AEF pH 3 system. Following the increasing pH systems (pH 5, pH 7, pH 9 and pH 11 systems), the orthophosphate removal efficiencies for UEF and AEF Filter HFe systems decreased. When the pH in the systems increased, the solubility of the Fe ions decreased and the stability of Fe oxides increased (Wilfert et al., 2015). Therefore, less Fe ions were dissolved, thus less reacting with orthophosphate to remove them. Eventually, less magnetite (Fe2O3) precipitates were formed and the orthophosphate removal mechanism followed adsorption only instead of precipitation. In addition, at higher pH values, more OH- ions were found in the system. Thus, the negative species PO43- and OH- would repel each other and caused lower adsorption of phosphate which resulted in lower orthophosphate removal efficiency[3].

For all pH systems Filter HFe except pH 11, UEF systems performed better compared to the AEF systems due to more possible formation of magnetite (Fe3O4) which were formed by the reduction of hematite (Fe2O3). Hematite is originally found in the steel slag and especially in a higher concentration for Filter HFe systems. Magnetites have high orthophosphate binding capacities. Since UEF systems have less dissolved oxygen, therefore, formation of magnetite was more stable due to less possibility of hematite oxidation in UEF systems.

Table 1: Orthophosphate removal efficiency for Filter HFe and Filter HCa.

Feed	UEF Filter HFe (%)	AEF Filter HFe (%)	UEF Filter HCa (%)	AEF Filter HCa (%)
Ph 3	78.17-92.73	76.32-87.96	91.17-100.0	88.79-100.0
Ph 5	73.68-84.75	59.91-73.82	95.39-100.0	88.16-96.08
Ph 7	37.99-87.37	36.26-67.54	93.85-99.06	90.52-98.65
Ph 9	42.80-71.56	25.04-56.15	93.59-99.24	90.06-97.02
Ph 11	21.81-52.28	24.06-64.19	91.63-99.03	81.08-94.38

Meanwhile, for Filter HCa, all systems showed excellent orthophosphate removal efficiencies regardless of the pH of the influents. However, to pick one, the best removal would be for UEF and AEF pH 3 systems; almost 100%. Other pH systems Filter HCa (pH 3, pH 5, pH 7 and pH 11) removed more than 80% phosphate. Though the removal efficiencies of same pH of UEF and AEF systems were comparable, however, slightly better orthophosphate removal efficiencies were shown by UEF systems, similar case with Filter HFe.

Comparing the phosphate removal efficiencies between Filter HFe and Filter HCa, Filter HCa generally performed better in removing orthophosphate as compared to Filter HFe. One of the main reasons was due to the high percentage of CaO (49.5%) in steel slag of Filter HCa compared to Filter HFe (20.4%). Most of the great filter media studied for phosphorus removal were high in CaO content [4]. On the other hand, Filter HFe have higher Fe2O3 and less CaO compared to Filter HCa and they removed phosphate via adsorption only (except both adsorption and precipitation for pH 3 Filter HFe). Eventually, the sites for adsorption would be occupied and not available for removal reaction anymore. Compared to Filter HCa, high Ca contents allowed high Ca ions available which could react with orthophosphate either via adsorption or precipitation. They could form many precipitates thus more available surface sites for orthophosphate removal.

3.1 Concentrations of Ca and Mg ions in effluents

Table 2 and Table 3 show the concentration of Ca and Mg ions in the effluents for Filter HFe and Filter HCa systems. The concentration of Ca ions in the AEF Filter HFe was higher compared to UEF systems of the same pH. Vibration caused by aeration helped in the leaching out of Ca ions into the effluents[5]. Also, amount of Ca ions in UEF and AEF Control systems was quite high relative to other pH systems; similar amount to pH 3 systems but more than pH 5, pH 7, pH 9 and pH 11 systems. This showed that Ca ions voluntarily leached out of the filter media, though no phosphate present in Control systems. Also, even less Ca ions were found in the effluents of pH 5, pH 7, pH 9 and pH 11 systems. Less hydrolysis and ionization reaction occurred since it occurred more significantly at more acidic.

However, UEF Filter HCa has a higher amount of Ca ions in the effluents compared to the same pH AEF systems. This might be due to the very high composition of Ca ions in the steel slag which leached out voluntarily. Also, this was directly associated with the very high initial percentage of CaO compounds (49.5%) in the filter media of Filter HCa. The highest Ca ions were found in pH 3 systems. Higher amount of Ca ions in the effluents for Filter HCa caused higher orthophosphate removal. When increasing the pH systems (pH 5, pH 7, pH 9 and pH 11), the concentration of Ca ions decreased. Filter HCa still has high possibility of more soluble Ca ions in the effluents form phosphate precipitates. In the Filter HCa column filters of higher pH, tremendous amount of white precipitates (calcite; CaCO3) formed compared to lower pH Filter HCa and other Filter HFe systems. Since Filter HFe contained a higher percentage of Fe ions in the filter media compared to Ca ions, therefore Fe ions ruled the systems of Filter HFe meanwhile Ca ions ruled the system of Filter HCa.

Meanwhile, for the concentration of Mg ions were 0.009 – 5.166 mg/L and 0.000 – 10.847 mg/L for Filter HFe and Filter HCa respectively. Table 3 shows the concentration of Mg ions in effluents for both Filter HFe and Filter HCa. More Mg ions were found in the effluents of Filter HCa; similar behaviour to Ca ions since Filter HFe mainly involved Fe ions only, and less contribution of Ca and Mg ions. Since there were very few differences in concentration of Mg ions leached out for all systems, parallel with the initial chemical composition of the filter media, therefore Mg ions have little influence in orthophosphate removal efficiency for each different pH systems.

Table 2: Concentration of Mg ions in effluents for Filter HFe and Filter HCa systems

	Conc. of Ca ions in effluents (mg/L)			
pH Feed	UEF HFe	AEF HFe	UEF HCa	AEF HCa
Control	12.826-	20.602-	264.441-	36.183-

	23.223	28.954	401.021	138.056
pH 3	14.573-26.221	16.580-39.996	296.842-448.458	97.850-187.140
pH 5	3.057-8.090	9.91-20.02	250.532-410.681	70.680-128.552
pH 7	1.541-5.227	7.93-14.809	172.858-253.280	57.984-135.642
pH 9	1.835-7.162	6.608-12.247	192.74-344.950	42.121-103.051
pH 11	1.622-6.515	6.581-15.937	38.665-152.360	52.226-144.463

Table 3: Concentration of Mg ions in effluents for Filter HFe and Filter HCa systems

	Conc. of Mg ions in effluents (mg/L)			
pH Feed	**UEF HFe**	**AEF HFe**	**UEF HCa**	**AEF HCa**
Control	0.01-0.193	0.805-3.504	0.000-0.076	0.291-3.850
pH 3	0.114-1.308	1.271-5.166	0.020-0.090	0.000-0.090
pH 5	0.05-0.399	0.786-3.116	0.000-0.063	0.392-4.368
pH 7	0.019-0.285	0.571-1.912	0.000-0.071	0.104-8.874
pH 9	0.020-0.272	0.464-1.546	0.000-0.060	0.166-4.223
pH 11	0.009-0.221	0.370-1.458	0.000-0.061	0.000-10.847

3.2 Concentration of Fe ions in Effluents

Figure 2 illustrates the graph of the concentration of Fe ions in the effluents of Filter HFe. Fe ions were present in nearly all UEF systems (pH 3, pH 5, pH 7, and pH 9) except in pH 11. The ranges of Fe ion were 0 – 2.636 mg/L. Since Fe ions have greater solubility at acidic pH, therefore, they could be leached out at acidic pH and difficult to leach out at basic pH thus no Fe ions leached out at UEF pH 11 systems. The Fe ions were in the form of stable oxides which locked phosphorus on it through adsorption[6].

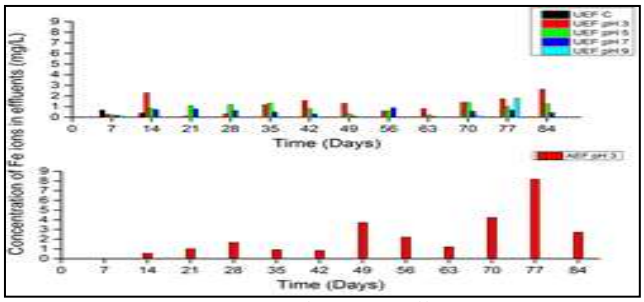


Figure 2: Concentration of Fe ions in effluents Filter HFe

However, in UEF systems, more dissolved carbon dioxide were obtained, which keep Fe ions in solution, thus Fe related compounds were more difficult to precipitate causing more Fe ions dissolved in the effluents. Nevertheless, the vibration from aeration causing the Fe ions to leach out in pH 3 system; acidic pH. At acidic pH, Fe ions underwent reductive dissolution, however aeration provides a more oxidizing environment which favored formation of Fe oxides precipitates[7]. Therefore, no leaching out of Fe ions were obtained in aerated systems except for very acidic AEF pH 3 system.

For Filter HCa systems, only UEF pH 3 showed the presence of Fe ions as shown in Figure 3. The range of concentration was in between 0-1.3023 mg/L. In addition, Fe ions adsorption was negatively affected by Ca ions (Teunissen et al., 2008). Since very little amount of Fe ions were originally found in the filter media (1.64%) and very high amount of CaO (49.5%), therefore very little Fe ions leached out in Filter HCa as well. Fe ions could only be noticed at a very acidic pH (pH 3 systems) and at UEF system. Lack of aeration provides reduction state for the hydrolysis of Fe ions and Fe ions to stay in the solution.

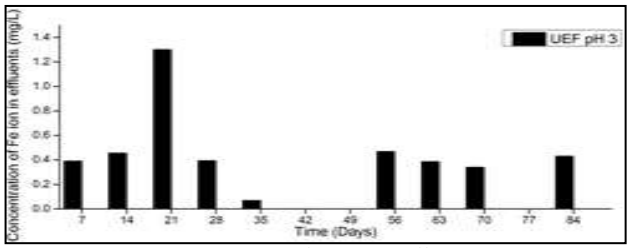


Figure 3: Concentration of Fe ions in effluents Filter HCa

4. Conclusion

Filter HCa showed excellent orthophosphate removal efficiency for all pH systems, whereas Filter HFe showed good orthophosphate removal at acidic (pH 3 and pH 5 systems) and average removal efficiency at neutral and basic systems (pH 7, pH 9, pH 11 systems). The concentration of Ca and Mg ions were higher in effluents of AEF systems compared to UEF systems for Filter HFe but vice versa in Filter HCa. For Fe ions, Filter HFe have more systems in which Fe ions are present. UEF systems have slightly better orthophosphate removal compared to aerated systems.

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References

[1] R. Hamdan and D. Mara, "Aerated Blast-Furnace-Slag Filters for the Simultaneous Removal of Nitrogen and Phosphorus from Primary Facultative Pond Effluents," *Int. J. Integr. Eng.*, vol. 5, no. 1, pp. 17–22, 2013.

[2] M. C. Wilfert, P., Kumar, P. S., Korving, L., Witkamp, G. J., & van Loosdrecht, "The relevance of phosphorus and iron chemistry to the recovery of phosphorus from wastewater: a review.No Title," *Environ. Sci. Technol.*, vol. 49, no. 16, p. 9400–9414., 2015.

[3] S. Xue, Y., Hou, H., & Zhu, "Characteristics and mechanisms of phosphate adsorption onto basic oxygen furnace slag.," *J. Hazard. Mater.*, vol. 162, no. 2–3, pp. 973–980, 2009.

[4] Ü. Vohla, C., Kõiv, M., Bavor, H. J., Chazarenc, F., & Mander, "Filter materials for phosphorus removal from wastewater in treatment wetlands—A review.," *Ecol. Eng. 37(1)*, vol. 37, no. 1, pp. 70–89, 2011.

[5] L. Zhu, X. Li, C. Zhang, and Z. Duan, "Pollutants' release, redistribution and remediation of black smelly river sediment based on re-suspension and deep aeration of sediment," *Int. J. Environ. Res. Public Health*, vol. 14, no. 4, 2017.

[6] X. Han, C., Wang, Z., Yang, W., Wu, Q., Yang, H., & Xue, "Effects of pH on phosphorus removal capacities of basic oxygen furnace slag," *Ecol. Eng.*, no. 89, pp. 1–6, 2016.

[7] K. Teunissen, a. Abrahamse, H. Leijssen, L. Rietveld, and H. van Dijk, "Removal of both dissolved and particulate iron from groundwater," *Drink. Water Eng. Sci. Discuss.*, vol. 1, no. 1, pp. 87–115, 2008.

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