A STUDY TO OBSERVE THE EFFECTS OF ENHANCEMENT PO_4^{3-} REMOVAL FROM AQEOUS SOLUTION DUE TO METAL OXIDES VARIOUSNESS CONCENTRATION IN STEEL SLAG FILTER SYSTEM

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ABSTRACT

High amount of orthophosphate will accelerate the autotrophs growth and eutrophication will occur. This phenomenon will decrease the water quality and as a result from it may increase the cost of water treatment for drinking water. The overabundance of orthophosphate occurs when untreated or poor treatment of wastewater from domestic and industrial activities is released into water bodies. Conventional treatment has been developed to treat wastewater however it is not effective for phosphorus removal hence, high cost advance treatment are needed to remove phosphorus. Thus, alternative treatments are needed with low cost phosphorus removal method. Therefore this study were conducted to understand and investigate the mechanism of phosphorus removal using two different setup of steel slag filter, Set 1 for high Fe and Set 2 for high Ca. The study was operated at different pH values of 3,5,7,9 and 11 under aerated and unaerated condition. The sample of steel slag from 12 filters that has been run for 3 month for each sets were semi-quantitatively analysed using SEM-EDX to identify the adsorption of phosphate ion on the surface of the steel slag. The result of SEM-EDX studies shows that removal adsorption mechanism of phosphate removal takes place on the surface of the steel. The precipitation in the steel slag filter were collected and analysed for XRD for chemical structure identification and the precipitated were confirmed to be Fe_3O_4 which indicated that removal of phosphate did not occur.

Keywords: Eutrophication, phosphate removal mechanism, steel slag filter.

INTRODUCTION

Wastewater from domestic, industrial and agricultural contain high amount of chemical by-products and nutrients. High levels of nutrient presents will damage the water bodies thus promoting the formation of eutrophication. Eutrophication is the effect from increasing concentration of plant nutrients usually nitrogen and phosphorus. The overabundance of nutrient in water accelerates the growth of algae thus decreases the water quality resulting to the significant increase of the water treatment cost at treatment plants for surface water.

Removal systems of phosphorus are commonly installed in wastewater treatment plant (WWTP) as an advanced treatment system depending on the type of wastewater being treated. However, the cost of the system becomes the burden for the system being implemented. Therefore, research on low-cost techniques to upgrade P removal has become a priority for scientists in the last two decades. Several studies have demonstrated that filtration through replaceable materials with high affinities for phosphorus binding is a viable technique to upgrade phosphorus removal in wastewater such as using steel slag [1]. Steel slag filter system usually emerged as an alternative method in conventional treatment system. However, study of pH effect on removal mechanism of phosphorus in steel slag filter system is still lacking. Therefore, this study is necessary to prove the mechanism of phosphorus removal using steel slag did occur at certain pH to provide better information for future uses.

Wastewater or sewage originates from a variety of domestic, industrial and storm sewage sources. Domestic wastewater is defined as wastewater from household water use, wastewater that comes primarily from individuals and does not include industrial or agricultural wastewater [2]. Domestic wastewater is one of the main contributors to the formation of nutrient loading in water system. The presence of phosphorus in the wastewater increases the amount of natural phosphorus in the water system causing the excessive amount of phosphorus. An over-abundance of phosphorus can over-stimulate plant and algae growth such that they create water quality problem mainly eutrophication. Eutrophication is a term that describe the biological effects from increasing concentration of plant nutrients usually nitrogen and phosphorus on aquatic ecosystems[3].

Phosphate amount in wastewater are quite abundance. Phosphorus compound cannot be found in wastewater as an element. It is predominantly found in wastewater as phosphates ion. Therefore, advance treatment for phosphorus removal was always required for wastewater treatment plant. Hence, multiple studies have been conducted in removing phosphorus in wastewater using safe, non-toxic material as a substrate in phosphorus removal in water treatment plants. The ideal phosphorus sorbing materials for use in various practices should be free, non-toxic, industrial by-products, generated locally, widely available, and potentially useful as soil amendments once saturated with phosphorus[5]. The presence of ferum, calcium, aluminium and magnesium in material use are expected to promote the phosphate removal. Alum, gypsum and fly ash were studied as phosphorus sorbing material treating the streamside cattle loafing areas. The result shows that alum is a great material in removing phosphorus in water system. Materials such as light expended clay, crushed marble and calcite were used as a media to learned their phosphorus binding capacity [6, 7].

Phosphorus removal involved two mechanisms which are adsorption and precipitation. The effectiveness of the mechanisms depends on how the PSMs will be applied or used, physical properties, such as particle size and hydraulic conductivity of the material. Appropriate condition of pH also affects the removal mechanism of phosphorus and must be taken into consideration when predicting which PSMs is more effective. A number of researchers have interpreted adsorption onto metal oxides or oxyhydroxides on the surface of slag to be a significant phosphorus removal mechanism. Adsorption is a surface-based process where a film of adsorbate is created on the surface. The removal mechanism can be done with the presence of Fe, Ca, Mg and Al because these minerals adsorb inorganic ions, such as PO_4^{3-}, from solution. The removal of phosphorus by adsorption occurs in an alkaline pH > 9 with the amount of Fe present in the solution is high. Phosphate ions (PO_4^{3-}) in effluent are removed from solution by adsorption onto amorphous oxides or oxyhydroxides which dominate the porous matrix and surface coating of the slag. However, in the presence of high Ca, the adsorption occurs in an acidic condition.

As for precipitation mechanism, Fe and Ca salts will form in the presence of orthophosphate which describe as the formation of crystalline precipitate. Phosphate removal occurs through calcium phosphate precipitation at high pH in the presence of high calcium ion in the media. The removal process occurs is due to the precipitation of phosphate with exchangeable and dissolved Ca^{2+}. The liberated Ca^{2+} from the exchange site or from the dissolution of $CaCO_3$, CaO and Ca $(OH)_2$ are preferably precipitated by phosphate in a neutral to alkaline solution. Under neutral to acidic condition, phosphate removal probably is due to ion exchange between phosphate hydrolysis products $24(HPO,{-}HPO)^{-2}$ and the precipitation of the metallic salts of phosphate (Al^{3+}, Ca^{2+}, Fe^{3+})Ca^{2+} released by slag into solution, forms stable phosphate precipitates, such as hydroxyapatite. A few researched has been done using steel slag as filtration media in treating wastewater to remove phosphorus. Steel slag contains high amount of Fe^{2+}, Ca^{2+}, and Mg^{2+} which makes them high affinities in removing phosphorus.

METHODOLOGY

Two types of steel slag have been selected due to their chemical composition either high in Fe or Ca for variousness metal oxides study of phosphate removal in synthetic wastewater. Furthermore, samples from steel slag filter systems with different pH value (3, 5, 7, 9 and 11) were undergone surface analysis using Variable Pressure SEM (JEOL JSM-IT300LV, USA) analyser to identify the presence of phosphorus element which indicates the adsorption of phosphate ions at the surface of the steel slag. Finally, precipitates formed within the pH 3 steel slag filter was examined using XRD (SmartLab Rigaku) analysis to determine their molecular structure.

RESULTS AND DISCUSSIONS

The characterization of steel slag are needed to identify the composition of the steel slag whether Ca, Mg , Fe and any other ion present together with its percentage of presence. The determination of the composition of the media is done using XRF analysis and the results are presented below for both sets. Results on Table 4.1 shows the characterization of steel slag media with high Fe and high Ca.

Table 1: XRF Analysis of steel slag samples

Element	Concentration (%)- Set 1	Concentration (%)- Set 2
Fe_2O_3	38.2	49.50
SiO_2	15.2	18.00
MgO	3.22	0.10
C	1.0	4.32
SO_3	0.28	2.58
Al_2O_3	7.03	2.23
CaO	20.4	1.64
MnO	5.19	0.38
TiO_2	0.54	0.22

EFFECT OF pH ON PHOSPHATE REMOVAL MECHANISM IN HIGH FE AND HIGH CA STEEL SLAG

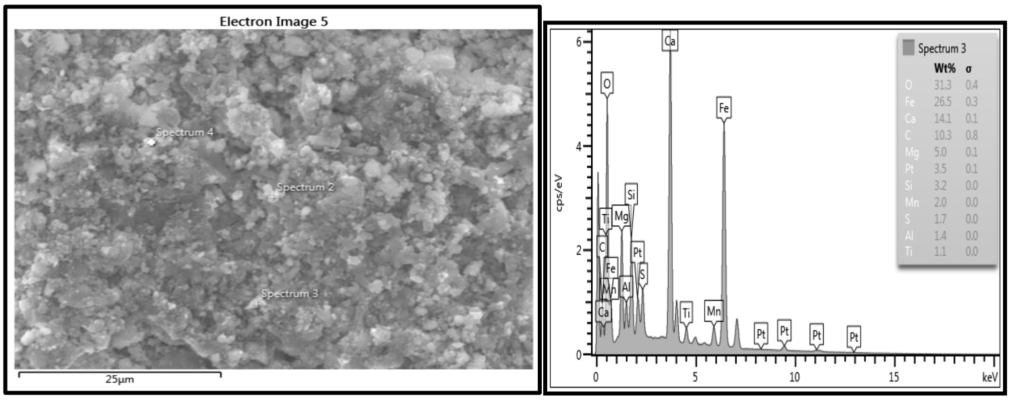
Results from this study show that the removal mechanisms of phosphate within the steel slag systems were pH dependent. As for the filter with pH neutral to alkaline, the dominant mechanisms were seen to be adsorption whereas pH neutral to acidic filter system, precipitation found to be dominant. As observed on the high Fe filter of pH 11 after 12 weeks of experiment, it can be seen clearly the formation of brownish layer on the surface of the steel slag media. The brownish layers were expected to be PO_4^{3-} ion adsorbed to the surface layer of steel slag reacting with the Fe^{2+} ion in the steel slag. This shows that the adsorption process occur at alkaline condition (see Figure. 1a).

Furthermore, in the filter with pH value neutral to acidic, precipitation were expected to occur. The Fe^{2+} ion contained in the steel slag were leached out and reacted with PO_4^{3-} forming Fe phosphate compound, $Fe_3\,(PO_4)_2$. The formation of precipitate can be observed in in filter system with pH 3 in unaerated system in after 12 weeks of experiment as provided in Figure 1b. However, the layer of PO_4^{3-} were also visible on the surface of steel slag in the filter indicates that the adsorption mechanism also takes place but not as much as precipitation. Therefore, at lower pH, both mechanisms were possible to takes place thus increasing the efficiency of phosphate removal.

To further confirmed the adsorption mechanism takes place at high pH, the surfaces of the high Fe steel slag were analysed using Variable Pressure-SEM analyser. Figure. 2 shows the SEM micrograph and spectrum of fresh steel slag before treatment without the presence of phosphate. Furthermore, Figure 3 shows the SEM micrograph and spectrum of high Fe steel slag with 9.6% of phosphate was detected on the surface which proves that some of PO_4^{3-} were adsorbed onto on the surface of the steel slag. The yellow crystalline identified by SEM were the PO_4^{3-} attached to the surface of the steel slag. In addition, the precipitates formed at pH 3 was expected to be $Fe_3\,(PO_4)_2$. However, the result shown that the precipitated compounds were Fe_3O_4 as shown in Figure 4. This might be due to the leached out Fe^{2+} from the steel slag, reacting with the O^{4-} from the dissolution of CaO, MgO and MnO. This showed that the removal of phosphate did not occur through precipitation but only adsorption in high Fe steel slag filter system.

(a) (b)

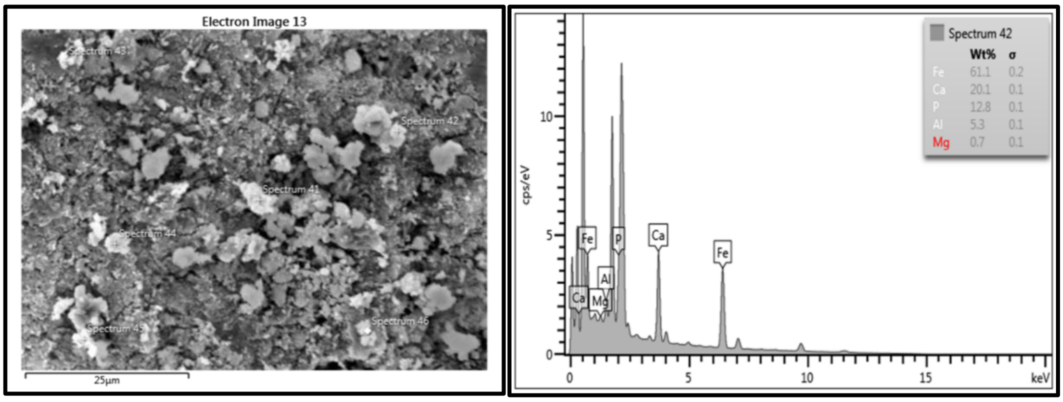
Figure 1. Adsorption mechanism on surface of steel slag in pH 11 (a) and precipitation mechanism at the bottom of the filter in pH 3, high Fe steel slag system



	Wt%	σ
O	31.3	0.4
Fe	26.5	0.3
Ca	14.1	0.1
C	10.3	0.8
Mg	5.0	0.1
Pt	3.5	0.1
Si	3.2	0.0
Mn	2.0	0.0
S	1.7	0.0
Al	1.4	0.0
Ti	1.1	0.0

(a) (b)

Figure 2. SEM micrograph of the particles of high Fe steel slag (a) before phosphate adsorption and (b) its spectrum



	Wt%	σ
Fe	61.1	0.2
Ca	20.1	0.1
P	12.8	0.1
Al	5.3	0.1
Mg	0.7	0.1

(a) (b)

Figure 3. SEM micrograph of the particles of high Fe steel slag (a) after process of adsorption occurs and (b) its spectrum at pH 9.

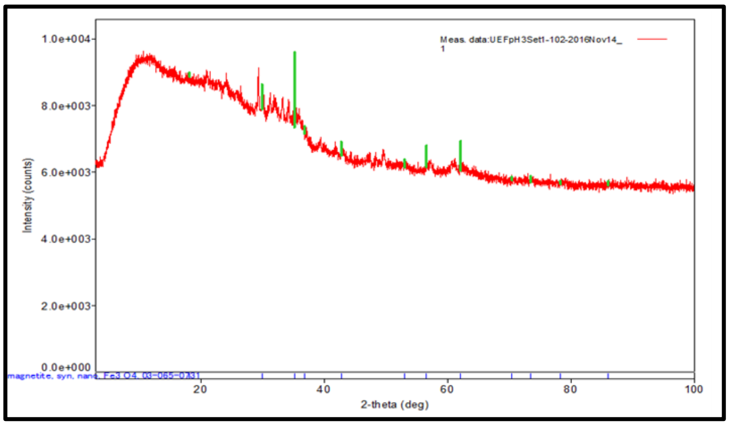
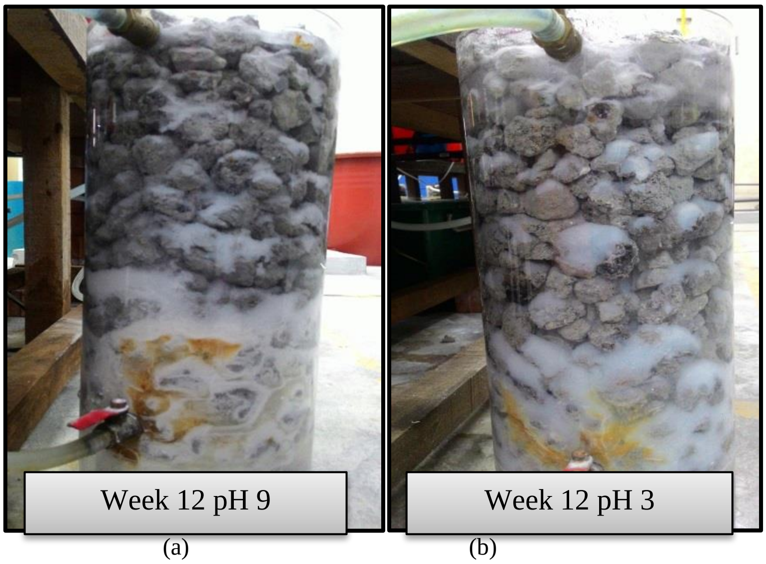


Figure 4. XRD analysis showed the peak were Fe_3O_4 for high Fe steel slag at pH 3

In steel slag with high amount of Ca, pH values of the solution also contributed in enhancing the removal of phosphate. In the solution with pH neutral to alkaline, precipitation supposed to occurred through the formation of calcium phosphate ($Ca_3(PO_4)_2$) as shown in Figure 5. The calcium were leached out from the steel slag due to the dissolution of CaO present in the steel slag and reacted with the PO_4^{3-} forming the white precipitation expected to be ($Ca_3(PO_4)_2$). As observed after 12 weeks of experiment, white precipitated were formed at the bottom of the filter with pH of 11 indicated the removal of phosphate through precipitation. However, the results obtained from XRD analysis showed the white precipitation formed were Calcite ($CaCO_3$) as shown in Figure 6. These were probably due to the reaction between dissolved Ca^{2+} with CO_3^- presence in the solution because in alkaline solution, HCO_3^- and CO_3^{2-} were the main ion constituent. The HCO_3^- was dissolute and ions exchanged occur to form the precipitated. For solution with pH neutral to acidic, adsorption mechanism were taking placed. The PO_4^{3-} was adsorbed onto the surfaces of steel slag due to the presence of oxy-hydroxide which dominated the porous matrix and surface coating of the slag. The white crystalline on the slag surfaces can be seen after 12 weeks of experiment on pH value of 3. Based on SEM analysis, the adsorptions of PO_4^{3-} were proved since its presences were detected on the slag surfaces through the formation of white crystalline (see Figure 7.).



(a) (b)

Figure 5. Precipitation mechanism at the bottom of the filter in pH 9 (a) and adsorption mechanism on surface of steel slag in pH 3, high Ca steel slag system

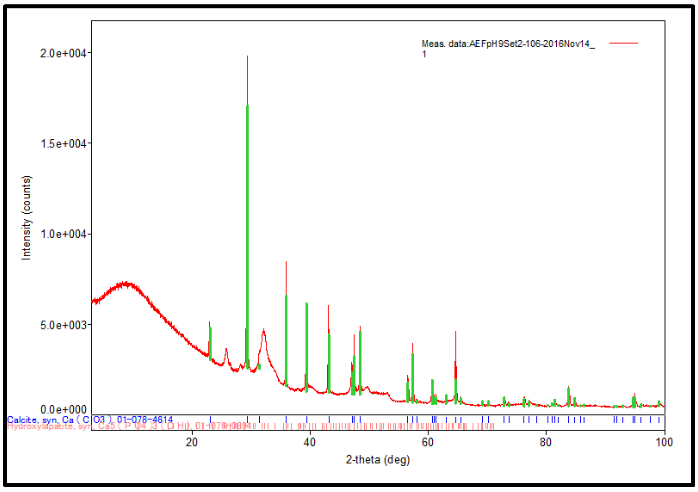
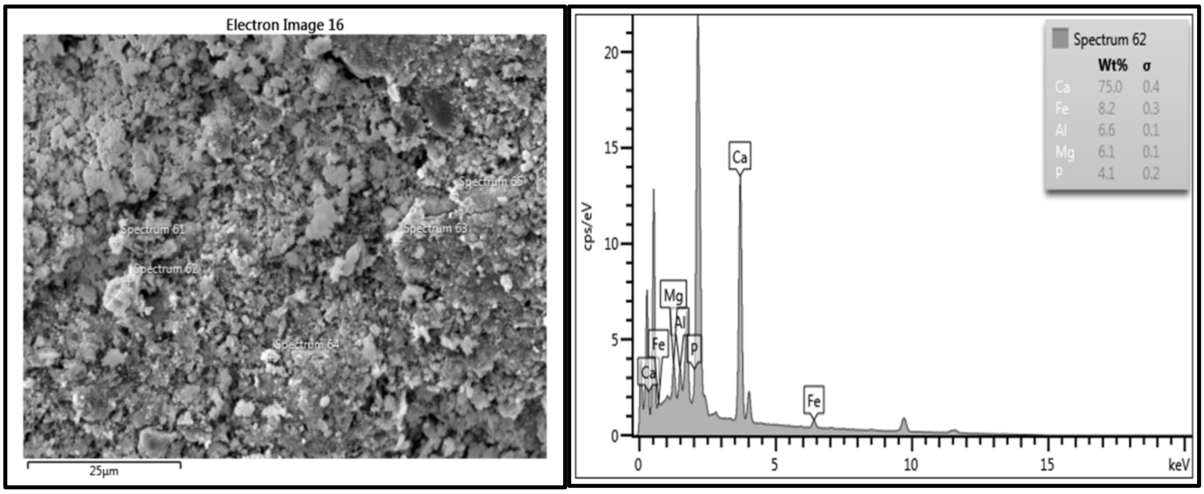


Figure 6. XRD analysis showed the Calcite peak for high calcium steel slag at pH value of 9



(a) (b)

Figure 7. SEM micrograph of the particles of high Ca steel slag (a) after process of adsorption occurs and (b) its spectrum at pH 3.

CONCLUSION

This study showed that both unaerated and aerated systems were efficient in removing phosphate from wastewater but unaerated system perform slightly better than aerated system in both high Fe and high Ca steel slag filter. However, the effects of pH were a major contributing in the types of mechanism involved in phosphate removal. The mechanism identified from these experiments for high Fe and high Ca steel slag filters were adsorption based on SEM-EDX analysis. The precipitation removal mechanisms were unable to confirm to occur in the filter system because the precipitation identified by XRD analysis were Fe_3O_4.

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