Determination of Phosphorus Removal Mechanism in Aerated and Unaerated Steel Slag Filter System as Secondary Treatment System for Textile Industrial Wastewater

Nur Ain Nazirah Mohd Arshad[1], R. Hamdan[2*]

[1]Faculty of Civil Engineering and Built Environment,
 Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Johor, MALAYSIA

[2]Micropollutant Research Centre,
 Universiti Tun Hussein Onn Malaysia, 86400 Parit Raja, Johor, MALAYSIA

*Corresponding Author

Abstract: Phosphorus is the element that promotes growth in plant. However, over loading of phosphorus into surfaces water leads to severe environmental problems known as eutrophication. Improper treatments of phosphorus removal prior discharges from industrial effluent are one of the contributions to eutrophication. Textile effluent is one of the sources of phosphorus loading in surface water with concentration of 1-9 mg/L P. Since attentions are given in removing the color from the effluent, phosphorus is commonly ignored in wastewater treatment system. Thus, the study of phosphorus removal in textile wastewater is conducted using steel slag system filter under aerated (ASSF) and unaerated (USSF) condition. The system was set up for influent pH range of 5.30-7.00 at primary treated wastewater for textile wastewater under aerated and unaerated condition. Sampling was done twice a week for 12 weeks and analyzed for Total phosphorus concentration. The Activated Carbon (ACF) filter in the existing treatment system is also sampled to compare the removal efficiency The USSF filter shows better removal than ASSF filter with 46% to 70% of efficiency removal. Meanwhile, the removal efficiency of ASSF is 37% to 66%. The adsorbate formed in ASSF is analyzed using SEM-EDX and the precipitation formed in USSF is analyzed using XRD. This shows that steel slag filter provides promising result in phosphorus removal.

Keywords: Eutrophication, removal of phosphorus, steel slag, textile wastewater

1. Introduction

Phosphorus (P) is a non-metallic chemical element that is commonly found in nature and a part of natural nutrient present in aquatic systems. The growth of aquatic plant and algae are supported by phosphorus however; excessive phosphorus concentrations lead to severe impact on water system which is eutrophication. Eutrophication is a global enemy when numerous reports on the occurrence all around the world such as United Kingdom, China, and Australia [1]-[3]. Recently, research conducted by National Hydraulic Research Institute of Malaysia (NAHRIM) stated that 60% of 90 major lakes in Malaysia reported are nutrient rich which reflects that eutrophication have become one of the major environmental concerns in Malaysia [4].

Industrial activities are one of the main contributors to P loading in surface water. Malaysia has become as one of the countries in Southeast Asia with increasing growth rate in population and economy resulting in rapid industrialization is inevitable. Massive production of industrial activities such as food manufacturing, poultry and textile industry consumes huge amount of wastewater and produced contaminated water two times greater [5].

Furthermore, it is the common industries in Malaysia that contribute to phosphorus loading [6]-[8]. Incomplete treatments of wastewater from these industries prior discharged due to the lack of proper wastewater treatment management are one of the problems faced by the industries. However, phosphorus loading from textile industry is commonly neglected as attentions are given more in colour and dye removal. Previous multiple studies have reported the presence of phosphorus in textile water was too high to be ignored. Studies found that phosphorus presence in textile wastewater streams are from the range of 1-9.7 mg/L P [9]. Another recent study also mentioned quite similar range which is from 5.30- 10.33 mg/L. This indicates that textile wastewater, aside from its aesthetically unpleasant due the color, it also degrading the ecosystem as the contributors of eutrophication.

One of the possible abatement measures in catering eutrophication are at source by preventing phosphorus loading in surface water. Even 0.1 mg/L of phosphorus can accelerate the algae growth in water bodies thus strengthen the reasoning need of law enforcement on the allowable discharge limit of phosphorus from industrial effluent in Malaysia [10]. Realizing the effect of eutrophication toward Malaysia's water system, phosphorus discharges limit are introduced in EQA 1974, Environmental Quality (Sewage Discharge) Regulations 2009 in the second schedule. The regulation requires the wastewater treatment plants to meet the effluent P limit of 5.0 mg/l in Standard A and 10.0 mg/l in Standard B. However, this limit is not applicable for industrial effluent and the limit value is relatively high compared to other country. In China, India, and USA, only 1 mg/L of phosphorus are allowed to be discharged from industrial effluent while for Europe and Hong Kong have 2 mg/L of phosphorus discharge limit [11], [12]. Other well-developed country such as Europe have stricter discharge limit which are 0.1 mg/L of P [13].

In the last decade, researchers are focusing more on treating wastewater from municipal and domestic effluent that industrial effluent are often being neglected. Industrial wastewater differs than domestic wastewater which it has stronger and concentrated phosphorus content depending on the manufacturing processes involve. Therefore, the treatments are often complicated and high-end technologies are needed for a complete phosphorus removal since conventional treatments are no longer sufficient. Natural treatment such as waste stabilization pond (WSP), constructed wetland and rock filter emerged as alternative solutions for phosphorus removal as the treatments shows a promising result in phosphorus removal [14]-[17]. Among these 3 methods, rock filter is preferable to be used with combination of natural material as filter substrate to promote high phosphorus removal efficiency. The past research has demonstrated that material such as fly ash [18], coconut coir pith [19], limestone [20], iron oxide tailing [21] and electric arc furnace slag [22] have high affinities in phosphorus binding.

Among all of the material available, steel slag showed an outstanding result in phosphorus removal. The presence of calcium, iron, magnesium and aluminum in the steel slag promotes the removal of phosphorus by adsorption or precipitation mechanism, or both [23]. The removals of phosphorus are likely to occur from the formation of calcium phosphate (Ca-P) owing to the high calcium content in steel slag. Other than that, the precipitation of hydroxyapatite $(Ca_5(PO_4)3OH; HAP)$ and octacalcium phosphate $(Ca_8H_2(PO_4)6·5H_2O; OCP)$ also contributed to phosphorus removal in steel slag filter system by the formation of white crystalline at the bottom of the filter [24]. Besides that, the removal of phosphorus by adsorption also plays and important role. The adsorption of phosphorus occurs due to the presence of amorphous oxides or oxyhydroxides which dominate the porous matrix and surface coating of the slag. The ion exchanges between the hydroxyl group in the wastewater and the oxyhydroxides on the surfaces of the slag are formed through the formation of monodentate and bidentate complexes as visualized in Fig. 1. However, pH values have an absolute effect on which mechanism takes place as the presence of hydroxyl group determine whether ion exchange would occur.
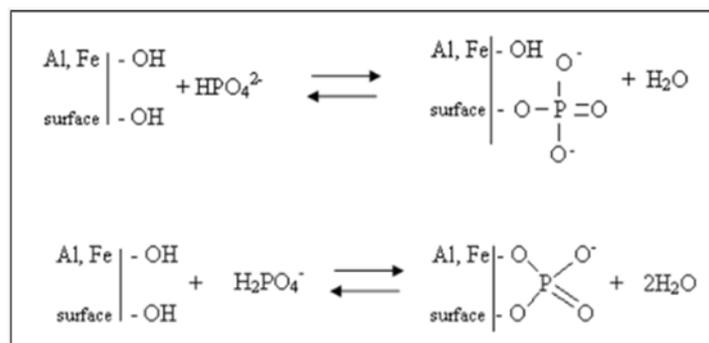

Fig 1 - Formation of bidentate and monodentate for adsorption mechanisms [25]

Aside from that, the study using steel slag for rock filter methods in textile wastewater are still insufficient and require in depth understanding. Other than a piece of information that the pH of solution plays an important role in determining the mechanism involved, the effect of pH towards the mechanism of removal to improves the ability of the steel slag in removing phosphorus remains unclear. Therefore, this study is conducted to understand the removal mechanism of phosphorus in textile wastewater, high alkaline wastewater, and its efficiency. Then, to compares the

mechanism and efficiency of studied treatment with common tertiary treatment system in a treatment plant. Lastly, to determine the effects of pH towards the mechanism of removal involved. The study of material conditions and behavior in actual industrial wastewater is important for the full-scale application level so that it will be readily applied or act as a benchmark for modification. Lack of available solutions leave the industry out of choice other than to implement high-cost tertiary treatment in removing phosphorus from their wastewater.

2. Methodology

Two units of vertical lab-scale column filters were developed to function as secondary treatment and with the aim of studying the removal mechanism of phosphorus that occurs in slightly acidic to neutral pH range of actual wastewater (5.30-7.00) under aerated and unaerated conditions. The filter was installed in an existing wastewater treatment plant of the chosen textile manufacturing factory located in Parit Sulong, Batu Pahat. The existing treatment plant consists of pH adjustment in the equalizing tank, the flocculation tank and the primary clarifier as the primary treatment system. The wastewater enters the secondary treatment stage of the aeration pond and secondary clarifier and moves to the tertiary treatment of the activated carbon filter (ACF). Both aerated and unaerated filters were installed simultaneously and fed with wastewater after the primary clarifier to function as secondary treatment system at the existing treatment plant to measure its ability to remove phosphorus. The point of filter installed is shown in the Fig. 2. The column filter with inner diameter of 150 mm, 6 mm thickness and total height of 400 mm were made from Perspex materials and installed at the textile wastewater treatment plant as shown in Fig. 3. The high concentration of Ca steel slag with the optimum sizes of 9.5 to 20 mm was used as filter media [26]. The influent of the filter is the primary treated wastewater that already undergo the pH equalization and flocculation stages of the existing treatment plant with slightly acidic to neutral pH ranges from 4.89 -7.00. In order to supply the filter with the best flow, the filter was constructed with hydraulic loading rates (HRT) of 1.04 m^3/m^3d [26]. For the effluent and sampling point, the influent was supplied upward from the bottom of the filter to the top of the filter. Figure 4 provides an illustration of the filter system layout. For the aerated system, a 0.25 L/min air flow was created by connecting the air pump to the tube that was inserted at the base of the filter. For 16 weeks, both systems were continuously used. The influent and effluent sampling was performed weekly for each filter for total phosphorus concentration analysis (PO_4^{3-}) using the WESTCO Discrete Analyzer, Smartchem 200, France. The steel slag sample was analyzed using a variable pressure scanning electron microscope (VP-SEM), model Jeol, South Korea, for the determination of the material bind onto the steel slag surfaces. Then, the precipitation formed are also analysed using X-ray Diffractometer (XRD), Smartlab Rigaku, Japan to determine the material formed. All analysis was following the Standard Method for the Examination of Water and Wastewater. Besides that, the effluent from the existing treatment system as tertiary treatment which is Activated Carbon Filter (ACF) in the water treatment plant are also collected just to compare the ability of removing phosphorus with the column filter.
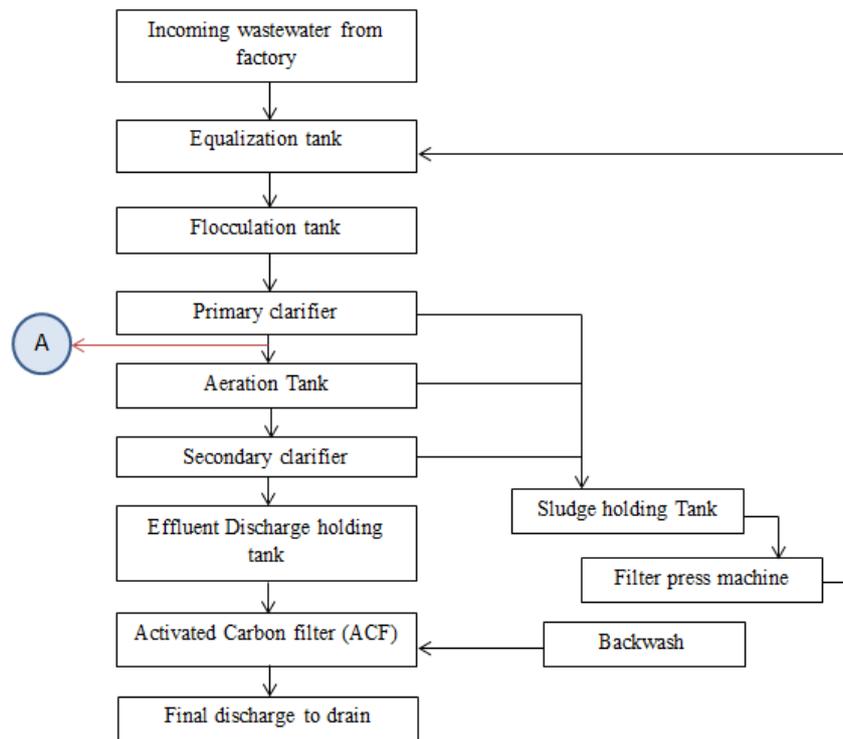

Fig. 2 - Existing wastewater treatment system and point of ASSF and USSF installed
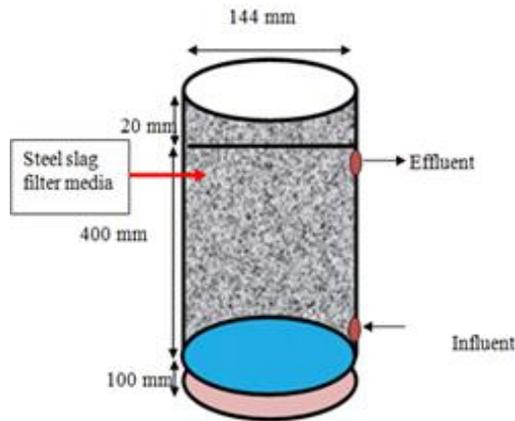
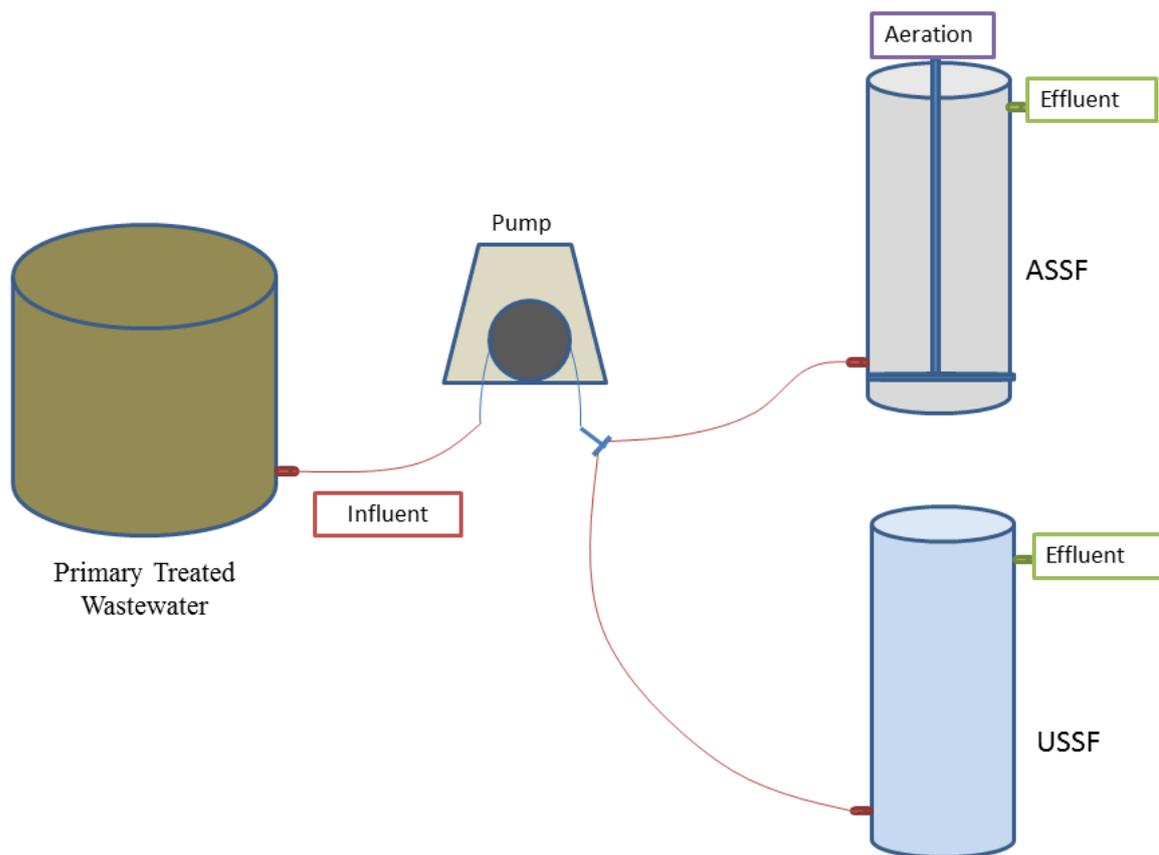**Fig. 3 - Filter column sizes and dimension**

Fig. 4 - Layout of experimental setup of Steel slag filters system

3. Results and Discussion

The removal of phosphate ion closely related to the pH condition and the alkalinity of the wastewater. High alkalinity of wastewater provides more hydroxides ion for ion exchange for phosphorus removal through adsorption while precipitation of Ca-P related materials such as $Ca(PO_4)_2$ are likely to occur at lower alkalinity and pH of wastewater [27]. The influents have pH value ranging from slightly acidic to neutral which is 5.30 to 7.00. On the other hand, the effluent pH value of ASSF, USSF and ACF are alkaline which are 7.91 to 9.12, 7.17 to 9.60 and 6.2 to 7.78 respectively. Since the influent pH lies in the slightly acidic to neutral range, this indicates that the steel slag in ASSF and USSF does increase the pH of the solution since steel slag was a high alkaline material. The ASSF and USSF have higher effluent pH range compared to the ACF since ACF effluent have undergo complete treatment from the existing treatment plant while the ASSF and USSF are only undergo primary treatment. Based on the efficiency graph illustrated on Fig. 5, both USSF and ASSF showed fluctuation in removal efficiency mainly due to the used of actual wastewater as influent. Actual wastewater used are closely related to the production of the materials in the textile

manufacturing factory which change once a week depending on the factory's production schedule which researchers have no control in this study. However, the range of phosphorus presence in the wastewater (influent) never exceeding 11mg/L which ranging from 5.2 mg/L to 10.4 mg/L. Since both filters were run simultaneously, this confirms that every wastewater fed is similar in both filters. USSF shows fluctuation on the removal efficiency from week 1 to 8 and increasing until week 10. Starting from here, the efficiency decreases until week 16. On the other hand, filter ASSF shows better removal trend as the removal efficiency increases from week 2 until week 10 which the highest removal efficiency. Starting from here the efficiency decreases until week 16. Excellent removals of phosphorus shown in ASSF however USSF performs slightly better as the removal efficiency is higher than ASSF. The removal efficiency of ASSF was in the range of 37% to 66% while USSF is in the range of 46% to 70%. The USSF was able to remove phosphorus better than ASSF due to undisturbed condition from aeration. The aeration bubble provide disturbance to the adsorption where the vibration making the matter released from its attached surface [28]. Aside from that, the efficiency removal for both ASSF and USSF filters are compared with ACF that installed in the existing treatment as illustrated in Fig. 6. The comparisons made are only to obtain initial information on upscaling the column filter system for future studies and also to show that even tertiary treatment is unable to completely remove phosphorus from wastewater. The ACF removes phosphorus only at efficiency of 36% to 54% which shows that the USSF removes phosphorus better than ASSF and ACF. Meanwhile, ASSF and ACF have similar fluctuation trend, however ACF performs slightly better than ASSF.
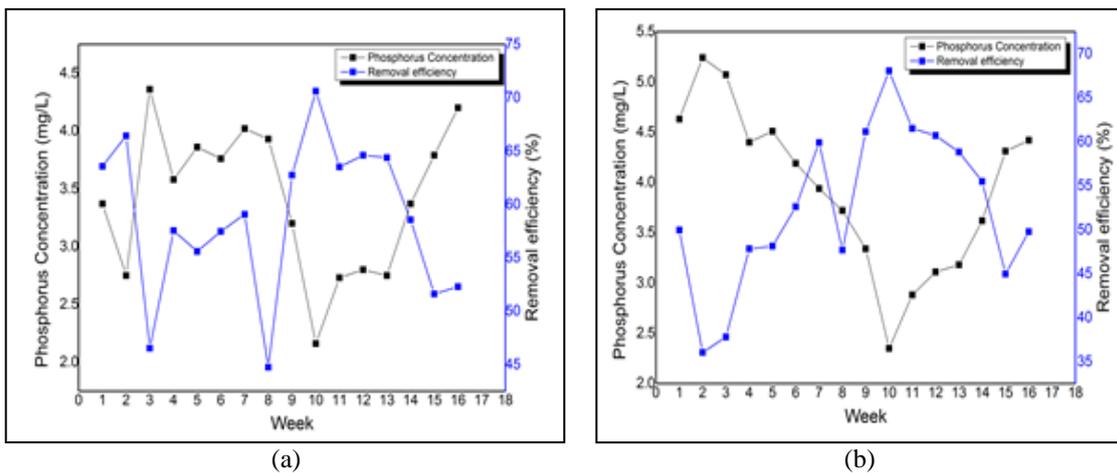

(a)   (b)

Fig. 5 - Phosphorus removal efficiency in (a) USSF, and; (b) ASSF
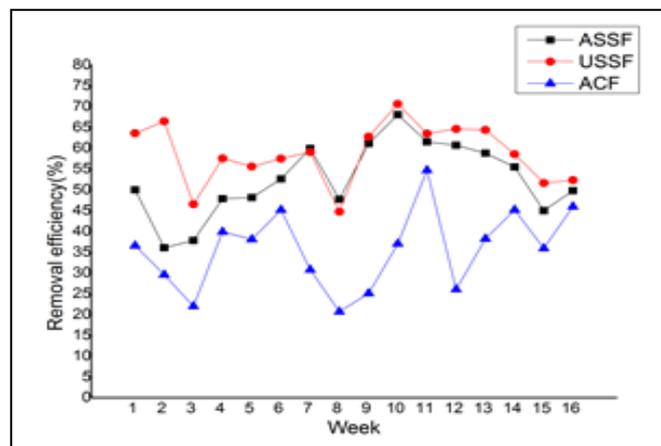

Fig. 6 - Comparison of removal efficiency in USSF, ASSF and ACF

The mechanism of removal is likely to be through precipitation mechanism at alkaline pH for USSF. According to Barca et al. [29], precipitation mechanism occurs when the liberated Ca^{2+} from the exchange site or from the dissolution of $CaCO_3$, CaO and $Ca(OH)_2$ were precipitated by phosphate in a neutral to alkaline solution producing white precipitated in the filter. Furthermore, findings from Hamdan et al. [30] also similar to Barca et al. [29] when using synthetic wastewater as feed [16]. This result was also similar with both studies where the precipitation was dominant at alkaline pH for USSF due to the formation precipitated at the bottom of the filter. However, the precipitates were brown which contradicting with Hamdan et al. [30] and Barca et al. [29] since both of the research

have white crystalline precipitate. The brown precipitate were probably due to the reaction between Feric oxide present in the slag which indicates the reaction between the liberated Fe^{2+} or the dissolution of Fe_2O_2 and $Fe(OH)_2$ from the steel slag and phosphorus in the wastewater [30]. On the other hand, brown layer of adsorbate was also found on the surface of the slag formed in ASSF most likely due to the binding of Fe^{2+} presence in the steel slag surfaces with PO_4^{3-} in the wastewater. Nonetheless, both filters showed promising result in removing phosphorus even though at higher pH. The adsorbate and precipitation formed are shown in Fig. 7 in ASSF and USSF. In effluent pH range of 7.91 to 9.12, the adsorption likely to occur under aerated condition while precipitations occur in unaerated conditioned with pH of 7.17 to 9.60. Besides that, the precipitations are brown in colour which shows that the formation of calcium phosphate did not occur for precipitation mechanism. Furthermore, the layer of adsorbate formed on the steel slag surface was also in brown colour. The removals of phosphorus are further identified by SEM-EDX analysis done on the steel slag collected at ASSF. The SEM-EDX detected the phosphorus embedded on the steel slag surface which confirmed the removal through adsorption on aerated filter system as shown in Fig. 8. On the other hand, the removal of phosphorus in USSF is determined by XRD analysis on the brown precipitate collected at the bottom of the filter as shown in Fig. 9. As mentioned above, removal through the formation of Ca-P compound on the steel slag are unlikely to occur due to the brown color of the precipitate formed on filter. The removal of phosphorus occurs through the formation of Iron Oxide phosphate, $Fe_2(PO_4)$ O as visualized in Fig. 9.
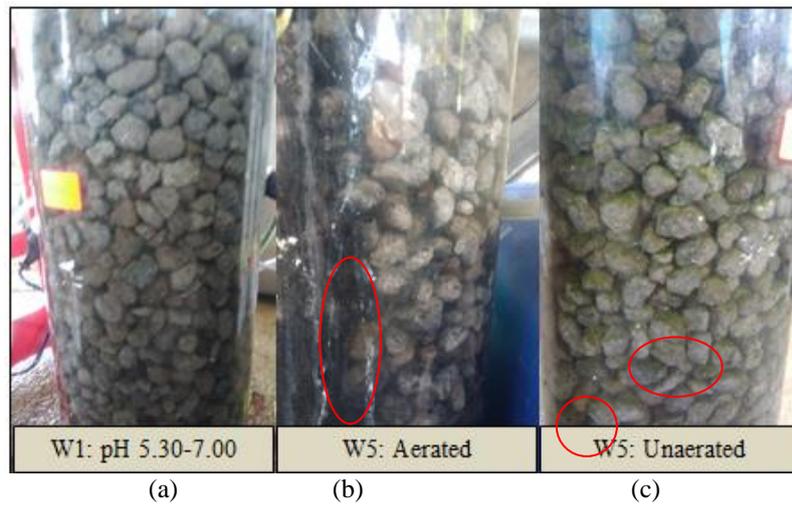

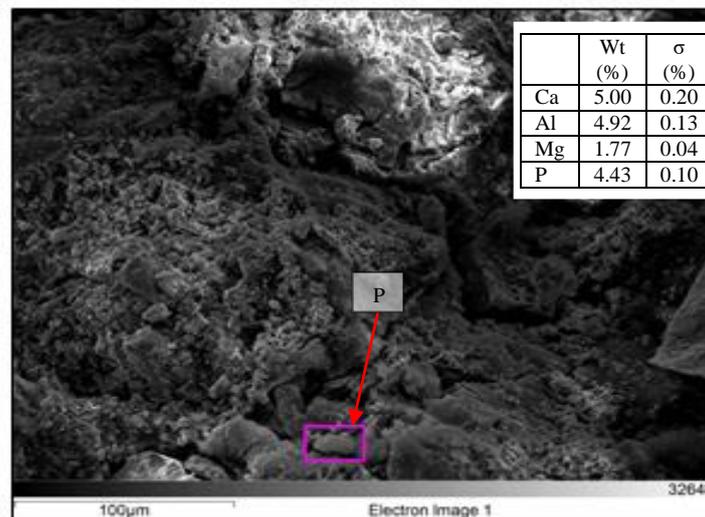**Fig. 7 - Filter condition at (a) initial and after 10 weeks for; (b) ASSF and; (c) USSF**

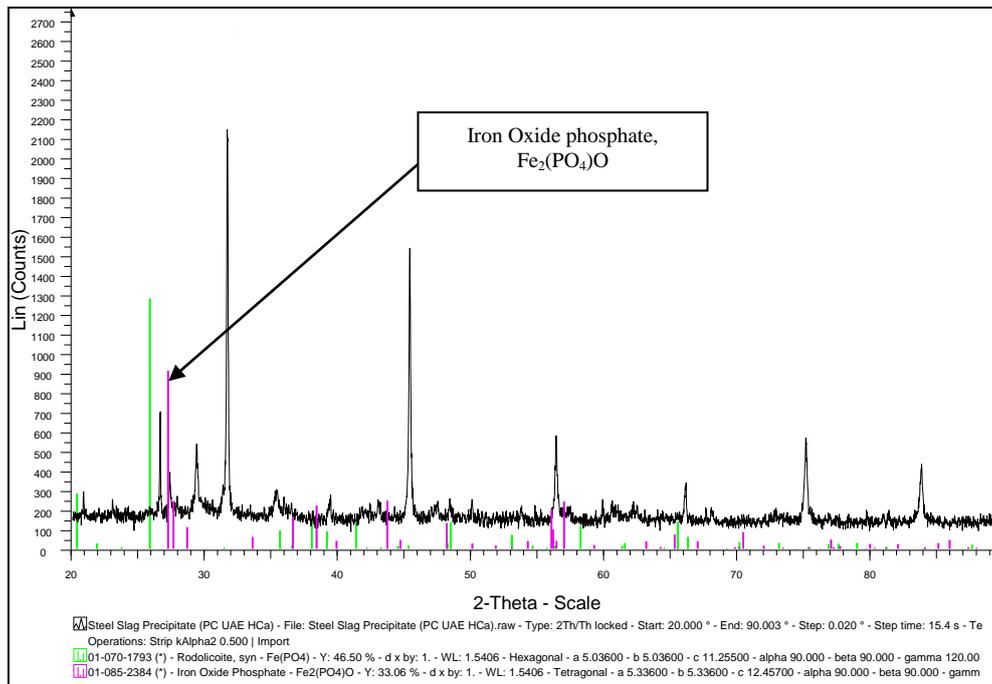**Fig. 8 - SEM-EDX imaging of adsorbate on the steel slag in ASSF**

Fig. 9 - XRD analysis on precipitation formed in USSF

4. Conclusion

The overall performance of all filters is efficient in removing phosphorus however USSF performs a lot better than ASSF. USSF also able to increases the pH to provide better phosphorus removal condition. The USSF have higher removal efficiency compared to ASSF with range of 46% to 70%. The removal mechanism takes place for both filter ASSF and USSF is adsorption and precipitation mechanism respectively. However, USSF performed better than ASSF and ACF. The SEM-EDX analysis strengthens the finding that removal occurs through adsorption in ASSF with P found to be bound on steel slag surfaces. The XRD analysis shows that the removal occurs in USSF through the formation of iron oxide phosphate. Thus, the use of steel slag in removing phosphorus from textile wastewater is possible. This provides new insight on the application of steel slag filter system in industrial sector as well as new effort in waste utilizations.

Acknowledgement

References

[1] Huang X., Liao X. Liao& Shi B. (2009). Adsorption removal of phosphate in industrial wastewater by using metal-loaded skin split waste. Journal of Hazardous Materials, 166 (2-3), 1261-1265. https://doi.org/10.1016/j.jhazmat.2008.12.045

[2] Minnesota Pollution Control Agency (2007). Phosphorus: Sources, forms, impact on water quality - A general overview. Minnesota Pollution Control Agency, pp. 1-2.

[3] Dai Y., Griffiths P.& Morgan S. (2012). State of art Australian wastewater treatment design and operation. https://www.semanticscholar.org/paper/State-of-Art-Australian-Wastewater-Treatment-Design-DaiGriffiths/fdab1 62ae 2246b32379ae13591373b2895f6d747.

[4] Sharip Z., Suratman S. & Shaaban A. J. (2016). Development of national lake water quality standards for sustainable management of lakes and reservoirs in Malaysia. Proceeding of the UNESCO International Scientific Symposium, Kyoto, Japan.

[5] Mokhtar N. M., Lau W. J. & Goh P. S. (2013). Effect of hydrophobicity degree on pvdf hollow fiber membranes for textile wastewater treatment using direct contact membrane distillation. Jurnal Teknologi, 4, 77-81. https://doi.org/10.11113/jt.v65.2334

[6] Ibrahim M. S. S. (2014). Treatment of food processing industrial wastewater using two stages anaerobic system.

Master Thesis, Universiti Tun Hussein Onn Malaysia.

[7]   Abdeshahian P., Shiun, Shin,J. W. & Hashim H. (2016). Potential of biogas production from farm animal waste in Malaysia. Renewable and Sustainable Energy Review, 60, 714-723. https://doi.org/10.1016/j.rser.2016.01.117

[8]   Gmurek M., Ledakowicz S. & Bilin, L.(2016). Comparison between industrial and simulated textile wastewater treatment by AOPs - Biodegradability , toxicity and cost assessment. Chemical Engineering Journal, 306, 550-559. https://doi.org/10.1016/j.cej.2016.07.100

[9]   Cai T., Park S. & Li Y. (2013). Nutrient recovery from wastewater streams by microalgae: Status and prospects. Renewable and Sustainable Energy Review, 19, 360-369. https://doi.org/10.1016/j.rser.2012.11.030

[10]   Alamdari A. & Rohani S. (2007). Phosphate recovery from municipal wastewater through crystallization of Calcium Phosphate. The Pacific Journal of Science and Technology, 8(1), 27-31.

[11]   Li W., Sheng G. Zeng R. & Yu H. (2012). China's wastewater discharge standards in urbanization.Environmental Science and Pollution Research, 19, 1422-1431.

[12]   Ghaly A. E., Ananthashankar, Alhattab R. M. & Ramakrishnan V. V. (2014). Chemical engineering and process technology production, characterization and treatment of textile effluents: A Critical Review. Chemical Engineering and Process Technology, 5(1), 1-18. http://dx.doi.org/10.4172/2157-7048.1000182

[13]   Bloch H. (2005). European Union legislation on wastewater treatment and nutrients removal. https://wtp-operators.thewaternetwork.com/document-XAs/european-union-legislation-on-wastewater-treatment-andnutrients-removal-xcIQziBZNCFa_6tquupXVA

[14]   Vymazal J. (2014). Constructed wetlands for treatment of industrial wastewaters: A review. Ecology Engineering, 73,724-751. https://doi.org/10.1016/j.ecoleng.2014.09.034

[15]   Schmidt J. J., Ragush C. M., Krkosek W. H., Gagnon G. A. & Jamieson R. C. (2016). Characterizing phosphorus removal in passive waste stabilization ponds in Arctic communities. Arctic Science, 2, 1-14. https://doi.org/10.1139/as-2015-000

[16]   Ahmad S. Z. N., Hamdan R., Wan Mohamed W. A., Othman N., Zin S. & Musa S.(2017). Comparisons study of phosphate removal in unaerated and aerated high calcium steel slag filter system of different pH feed. Matec Web of Conferences, 103, 06018. https://doi.org/10.1051/matecconf/201710306018

[17]   Dong C. S., Ju S. C., Hong J. L. & Jong S. H. (2005). Phosphorus retention capacity of filter media for estimating the longevity of constructed wetland. Water Research, 39 (11), 2445-2457.   https://doi.org/10.1016/j.watres.2005.04.032

[18]   Ugurlu A. & Salman B. (1998). Phosphorus removal by fly ash. Environment International, 24 (8), 911-918.

[19]   Krishnan K. A. & Haridas A. (2008). Removal of phosphate from aqueous solutions and sewage using natural and surface modified coir pith. Journal of Hazardous Materials, 152 (2), 527-535.

[20]   Westholm L. J. (2006). Substrates for phosphorus removal - Potential benefits for on-site wastewater treatment? Water Research, 40(1), 23-36. https://doi.org/10.1016/j.watres.2005.11.006

[21]   Blanco I., Molle P., Sáenz de Miera L. E. & Ansola G. (2016). Basic oxygen furnace steel slag aggregates for phosphorus treatment: Evaluation of its potential use as a substrate in constructed wetlands. Water Research, 89, 355-365. https://doi.org/10.1016/j.watres.2015.11.064

[22]   Penn C. J. & McGrath J. M. (2011). Predicting phosphorus sorption onto steel slag using a flow-through approach with application to a pilot scale system. Journal of Water Resources and Protection, 3(4), 235-244.

[23]   Penn C. J., Bryant R. B., Kleinman P. J. & Allen A. L. (2007). Removing dissolved phosphorus from drainage ditch water with phosphorus sorbing materials. Journal of Soil and Water Conservation, 62(4), 269-276.

[24]   Zuo M., Renman G., Gustafsson J. P. & Klysubun W. (2018). Dual slag filters for enhanced phosphorus removal from domestic waste water: Performance and mechanisms. Environmental Science and Pollution Researc., 25(8), 7391-7400.

[25]   Ahmad S. Z. N. (2018). Phosphate removal efficiencies and mechanisms of different chemical compositions of steel slag column filter system. Universiti Tun Hussein Onn Malaysia.

[26]   Afnizan W. M. W., Hamdan R. & Othman N. (206). Study of the maximum uptake capacity on various sizes of electric arc furnace slag in phosphorus aqueous solutions. IOP Confeerence Series: Materials Science and Engineering, 136, 012060.

[27]   Hamdan R. & Mara D. D. (2013). Aerated blast-furnace-slag filters for the simultaneous removal of nitrogen and phosphorus from primary facultative pond effluents. International Journal Integrated Engineering, 5(1), 17-22.

[28]   Zhu Z., Li L., Zhang X. & Duan C. (2017). Pollutants' release, redistribution and remediation of black smelly river sediment based on re-suspension and deep aeration of sediment. International Journal of Environmental Research and Public Health, 4(14), 374.

[29]   Barca C., Meyer D., Liira M., Drissen P., Cameau Y., Andres Y. & Chazarenc F. (2014). Steel slag filters to upgrade phosphorus removal in small wastewater treatment plants: Removal mechanisms and performance. Ecological Engineering, 68, 214-222. https://doi.org/10.1016/j.ecoleng.2014.03.065

[30]   Hamdan R., Arshad N. A. N. M. & Ahmad S. Z. N. (2018). The effects of PO_4^{3-} removal from aqueous solution with varied concentrations of metal oxides in steel slag filter system. Journal of Physic Science, 29, 71-80. https://doi.org/10.21315/jps2018.29.s3.9

114