Phosphorus Removal in Food Manufacturing Industry by using High Fe Steel Slag Filter System

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Abstract: Improper removal of phosphorus from industrial wastewater including from food manufacturing lead to eutrophication in water bodies and it is a global concern. This is due to the requirement of a high cost and complexity of phosphorus removal system as it is commonly removed in tertiary wastewater treatment. Therefore, it is a high time to develop an alternative low-cost wastewater treatment with high capability on removing phosphorus from industrial wastewater. Thus, the main objective of this study is to investigate the potential of a high Fe unaerated steel slag filter system in removing phosphorus from food manufacturing wastewater. Steel slag is a steel manufacturing by-product and has been kindly supplied by Antara Steel Mills Sdn,Bhd., Pasir Gudang. Treated wastewater sample from one of the local food manufacturing industry has been sampled and fed the high Fe steel slag filter system which has been set-up in the Wastewater Engineering Laboratory, FKAAS, UTHM. The system has been acclimatized for 2 weeks. Afterwards, influent and effluent of the system have been collected for analysis of selected parameters including DO, Temperature, pH, Turbidity, Total P, COD and Alkalinity to monitor the performance of the system for 2 months. Results from this study shows that the high Fe steel slag system has a potential in removing Total P from wastewater as their removal efficiency range from 46-65%. However, all the monitored parameters were not comply with the effluent standard. Therefore, the performance can be improved with a proper pretreatment and primary wastewater treatment prior to apply the polishing effluent system; high Fe steel slag system. Furthermore, as the system can be considered as an easy maintenance and low-cost, it can be adopted by the local food manufacturing industry to improve their existing wastewater treatment system. Hence, the good final effluent quality can be produced and simultaneously decreased the environmental burden due to phosphorus in industrial wastewater.

Index Terms**: *Phosphorus; Food Manufacturing Industry Wastewater; High Fe Steel Slag.***

I. INTRODUCTION

Eutrophications is known globally and have become an alarming issue. Multiple research have been done on its source of pollution, its effects on environment and water ecosystem(Mattson, Godfrey, Barletta, & Aiello, 2003),(Pinckney, Paerl, Tester, & Richardson, 2001) and methods on how to control it(Conley et al., 2009). According to Harper, 1992, eutrophication can be define as increase in plant growth concentration mainly phosphorus on aquatic ecosystem. Eutrophic water bodies are detrimental to aquatic animals since the growth of algae will used up all oxygen present in water causing oxygen deficiency and suffocating other marine life. Water quality can be further impaired when bacteria consume dead algae and dead animals, lowering the BOD of the water making it more difficult to be treated for further use. Moreover, it is confirmed that the condition of Malaysian lakes largely reflected the global situation when it is reported by National Hydraulic Research Institute of Malaysia (NAHRIM) that 90 major lakes and reservoirs had suffered from eutrophication (Sharifuddin, 2010).

Eutrophication occurred mainly due to the presence of phosphorus element in water. Under natural conditions, phosphorus is an essentials element for plant growth (Correll, 1998), however anthropogenic activities increases the phosphorus loading on water body which promotes the growth rate of aquatic plants that leads to algal bloom on the water surfaces. Phosphorus loading comes from a nonpoint sources such as runoff from pasture, croplands urban runoff, non-agricultural rural runoff and seepage from individual sewage treatment systems(Minnesota Pollution Control Agency, 2007). Effluent discharge from domestic and industrial activities without advance treatment of phosphate removal also act as a point source pollution to our water bodies(Carpenter et al., 1998). Therefore, the method to control and reduce the eutrophication from widespread is through the phosphorus removal. Several international studies have demonstrated that filtration through replaceable materials with high affinities for phosphorus binding is a viable technique to upgrade phosphorus removal in small wastewater treatment plant (Barca et al., 2013). Previously, 57 research had been done on different filter media, EAF steel slag was found to have the highest phosphorus retention capacity(Dong, Ju, Hong, & Jong, 2005). This proves that steel slag is one of the filter media that are highly promising in phosphate removal in wastewater and suitable to be used since it is low cost than any other method. However, different wastewater leads to different mechanism of removal due to different wastewater characteristic.

Multiple researches had been done in treating phosphorus using steel slag in

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synthetic wastewater and domestic wastewater to understand the removal mechanism involved (Johansson & Gustafsson, 2000),(Ugurlu & Salman, 1998),(Zu et al., 2017). However, understanding on removal mechanism of phosphorus from industrial wastewater is still lacking. Therefore, to further understand the mechanism of removal in industrial wastewater, a treatment system of high ferum steel slag filter is used without aeration in treating wastewater from food manufacturing industry.

II. LITERATURE REVIEW

A. Phosphorus in wastewater

Phosphorus is an essential nutrient required in all living organism for proper cell functioning, regulation of calcium, construction of strong bones and teeth, and for making ATP. Phosphorus is abundantly supplied in the diet through meat, grains, and dairy products (Takeda, Yamamoto, Yamanaka-Okumura, & Taketani, 2014). The phosphate amounts in wastewater are quite abundance.The presence of phosphorus in the wastewater increases the amount of natural phosphorus in the water system. Phosphorus compound cannot be found in wastewater as an element. It is predominantly found in wastewater as phosphates ion. The chemical fractions of phosphate compound consist of dissolved inorganic orthophosphate (o-PO4), polyphosphate and organically bound phosphate. The orthophosphate (PO4-3) is the main fraction available in wastewater and can be used for biological metabolism without further breakdown. The structures of polyphosphate is in a complex molecule consist of two or more atom of P (P3O10-5) and revert together with the organic phosphates through a slow-rate hydrolysis process to the soluble o-PO4 form (Rossle & Pretorius, 2001).

Each forms of phosphorus presence in wastewater reflect a different reactivity and affinity for processes of chemical precipitation, adsorption and biological removal. Therefore, the efficiency of phosphorus removal will depend on the form of phosphorus that present in the wastewater. Phosphate is a form that is readily available for chemical precipitation, adsorption, and biological removal. Therefore, the ratio of phosphate to total phosphorus of the wastewater is a parameter of great importance when evaluating the efficiency of treatment for phosphorus removal(Barca, 2013).

Table1: Classification of phosphorus in wastewater as percentage constituent of Total Phosphorus

Classification of phosphorus in wastewater		
TP:100%		
Orthophosphate Raw & settled: 70% to 90% Raw (USA): 42% to 57%	Polyphosphate Raw (USA): 29% to 33%	Organic phosphate Raw (USA): 14% to 25%

B. Food manufacturing industrial wastewater

The food processing sector is important at the national level, given the number of companies and the industrial production to complete the demand of the consumers. Therefore, this industry is known to be one of the most industries that consume large quantities of water due to the activity of washing and cleansing of food thus producing large amount of wastewater (Noukeu et al., 2016). Low wastewater management from these industries will be detrimental to our water bodies. Different activities conducted and production produced by the industries resulting different substantial composition of wastewater. Food processing in particular is very dissimilar to other types of industrial wastewater since it being readily degradable and largely free from toxicity. However, it usually has high concentrations of biological oxygen demand (BOD), suspended solid, chemical oxygen demand (COD), ammonium and total phosphorus (TP)(Ibrahim, 2014),(Noukeu et al., 2016). Chemical oxygen demand (COD) and biochemical oxygen demand (BOD5) found in untreated effluents from food processing industries are usually high (Vymazal, 2014),with levels that may be 10–100 times higher than those of domestic wastewater (Lebacq, Baret, & Stilmant, 2013).

In Malaysia, one of the most well-known food manufacturing industries is the chips manufacturing mainly tapioca chips which were produced from treated and dried cassava (manioc) root. Just like corn, potato and wheat, tapioca were among the examples of starch-rich produces that generate starch- containing wastewater during its production (Hamzah, 2015). Chips processing activities used up large amount of water and the wastewater was produced from the series of processing steps including storing, cleaning, shelling, choosing and cutting, slicing, washing, frying, salting, picking and coating and packing step-by-step of starch product(Kobya, Hiz, Senturk, Aydiner, & Demirbas, 2006).

C. Steel slag as Filter Media

Steel slag is a by-product of the steel making and steel refining process. The steelmaking industries produce million tons of steel slag per year and most of them are stockpiled in the steel plants and sent to slag disposal sites. Utilization of steel slag in civil engineering field can alleviate the need for their disposal and reduce the use of natural resources in the field. Waste utilization is one way of alternative disposal of the waste and potential pollution problems can be eliminated. Nowadays, most of steel slag has been used as an additional substrate or substitution of aggregate in concrete production. Furthermore, several researches has been done to use steel slag as filtration media in treating wastewater to remove phosphorus and the outcome shows a promising results(Johansson Westholm, 2010),(Bird & Drizo, 2010). The presence of high concentration metal (Ca, Fe, Mg and Al) oxide in steel slag provides significant contribution in phosphorus removal(Barca et al., 2013),(Zu et al., 2017).

III. METHODOLOGY/MATERIALS

A. Materials

The high Fe steel slag was collected at Antara Steel Mills in Pasir Gudang, Johor. The steel slag samples was characterized using X-ray Fluorescence Spectroscopy (XRF) to determine its chemical composition and further proving the steel slags contained high Fe ion. The steels slag samples were sieved through a 63 micrometer test sieve (British Standard sieve BS410/1986) using a shaker, Endecotts Lombard Rd. London, model Sw193BR, England and only samples with sizes 9.5mm to 20 mm were accepted and used as the filter media(Afnizan, Hamdan, & Othman, 2016). Before using the steel slags, the samples were pretreated by washing it twice using tap water followed by distilled water and dried up in the oven for 24 hours at 105˚C.

B. Sampling point of wastewater

The wastewater from food manufacturing industry that was chosen for this research is Azhar Food Manufacturing Sdn. Bhd. This manufacturing factory was chosen due to the high phosphorus reading obtained during preliminary sampling to investigate the concentration of phosphorus in the wastewater. Besides that, to further investigate the relation between pH and phosphate removal efficiency, low pH of wastewater is desirable. Based on preliminary site visit and sampling, the average of phosphate concentration presence in the wastewater is 11.23 mg/L while the pH is 3.8 which indicates that this wastewater is suitable and complying with the objective of this study.

The existing wastewater treatment installed at this factory in treating its wastewater was very basic. The treatment consists of mechanical oil separator to remove oil from the wastewater. Then the treatment continued to sedimentation tank 1, sedimentation tank 2 and to the effluent tank which are the final discharged were released to nearby river. Since the purpose of this filter system is to act as a tertiary treatment, the sampling point chosen was at the effluent tank where the standard parameters for effluent discharged such as TSS, COD, TP, DO and pH were expected to be low. The steel slag system was only for nutrient removal mainly phosphorus and also improving the quality of the effluent prior to be discharged. The location of sampling was shown at Fig 1.

Fig 1. Existing wastewater treatment and sampling point

C. Experimental set up and sampling

The laboratory scale of unaerated high Fe steel slag filter (see Fig. 2) was set up at Wastewater Engineering laboratory, FKAAS for 2 months. The 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 base of the column filters. The effluents of the samples were collected at the upper part of the column filter. The filter was design with 400mm height and diameter of 150mm with hydraulic loading rate of 0.60 m3/m3 (Johnson & Loeppert, 2006).The experimental layout is shown in Fig. 3. The wastewater which is the influent was collected twice a week at local food manufacturing industry to run the filter column. The influent was characterized by conducting in-situ tests for pH, dissolve oxygen and temperature and further analyzed with total phosphorus, alkalinity, turbidity and Chemical Oxygen Demand (COD) every time the influent were being collected. The effluent was also sampled twice a week and analyzed according to the influent. Fig. 3 shows the dimension.

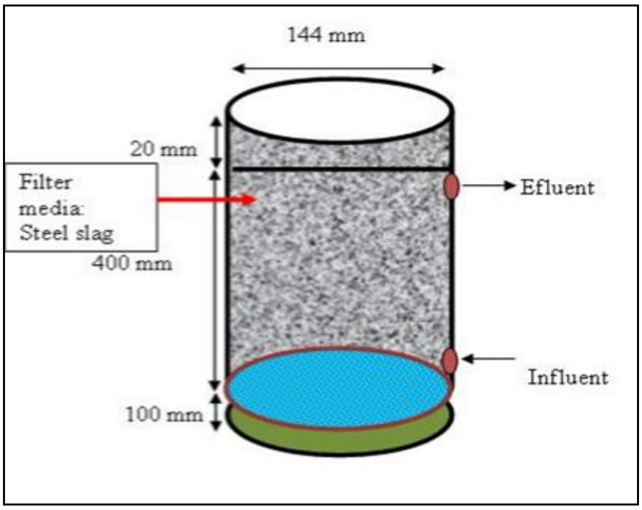

Fig 2. Schematic Diagram of filter column

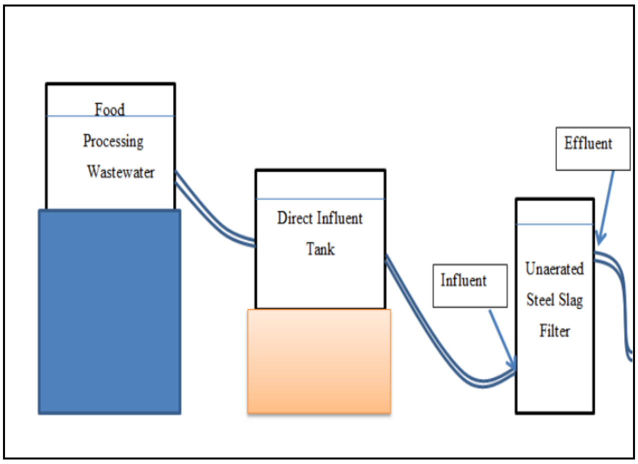

Fig 3. Experimental layout

D. Analysis of wastewater

There are several tests that are carried out to ensure the objective and the aim of the study are achieved for the unaerated high Fe steel slag filter to successfully remove phosphorus. The test and analysis on the food processing wastewater was carried out twice a week. There are several parameters were tested from the analysis on the food processing wastewater

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following the parameters in the Environmental Quality Act (Sewage) Regulation 2009 to determine the effectiveness of phosphorus removal. The parameters involved were chemical oxygen demand, total phosphorus, alkalinity, turbidity, dissolved oxygen, temperature and pH to test the effectiveness of steel slag filter to remove phosphorus. Table 2 below show analysis involved in testing the samples for each parameter in food processing wastewater.

Table2: Method for wastewater analysis

Parameter	Method of analysis
pH, Temperature	pH Meter (Hanna Instrument, USA)
DO	DO Meter (Hanna Instrument, USA)
Total P	DR6000 Spectrophotometer (method 10127
COD	DR6000 Spectrophotometer (method
Alkalinity	2320 B
Turbidity	Turbidity meter

IV. RESULTS AND FINDINGS

The wastewater from Azhar Food Manufacturing Sdn. Bhd was characterized before the experiment ware carried out to ensure the presence of phosphate and identifying other constituent present in the wastewater. The in-situ test shows the pH value for the wastewater is range between 3.80 and 4.57 which quite acidic while the temperature and the dissolve oxygen is 28.4 and 2.90 respectively. The phosphorus value of the wastewater is 34.52 mg/L PO4-3 which shows that this manufacturing factor does contribute to eutrophication. The result obtained for chemical oxygen demand is 616 mg/L while the turbidity is very high at 472 NTU.

A. Steel slag characteristic

The characterization of steel slag is needed to confirm the presence of Fe is high and further identifying the composition of the steel slag whether Ca, Mg, Al and any other ion present together with its percentage of presence. The determination of the composition of the media was done using XRF analysis and the results are presented in Table 3.

Table3: Composition of High Fe steel slag

Element	Concentration (%)
Fe_2O_3	38.2
SiO_2	15.2
MgO	3.22
C	1.0
SO_3	0.28
Al_2O_3	7.03
CaO	20.4
MnO	5.19
TiO_2	0.54

B. Removal efficiency of Total Phosphorus (TP)

Based on the result obtained from the experiment, the TP present in the influent showed high values ranging from 25.7 mg/ L PO3-4 to 42.83 mg/L PO3-4 than TP values in effluent which is range from 10.82 mg/L PO3-4 to 23.34 mg/L PO3-4. This shows that the removal of phosphate did occur even though the percentage removal is moderate. The percentage of removal efficiency for TP in the unaerated steel slag filter system is in between the range of 46% to 65%. From Fig. 4, the percentages of phosphorus removal are considerably moderate however it seems promising in removing phosphorus. The pH values for influent range in between 3.80 to 4.57 which is acidic. Under acidic condition with high Fe steel slag, the removal of P occurs through the reduction of Fe3+ where Fe were leached out from the steel slag through reduction of Fe oxide. Thus, more free Fe ions reacted with phosphate ion resulting phosphate removal with the formation of brownish precipitate formed at the bottom of the filter.

Besides that, the adsorption mechanisms are also seeming to occur since a brownish layer is observed on the surface steel slag. Phosphate ions were bind onto the oxyhydroxide (Ca2+, Mg2+, Al3+) binding site on the steel slag's surfaces. During the first week, the removal efficiency is high which at 64% and 65% respectively. However, the efficiency started to decline from week 2 at 60% to week 6 49%. The decline in phosphorus removal efficiency at the end of experiment is probably due to used up of free Fe2+/3+ in the system to be reacted with PO43- so precipitation cannot be formed anymore. Furthermore, the decline in removal efficiency was also probably due to the unavailability of binding site for phosphorus to bind anymore onto the steel slag since all binding site were used up. The result demonstrated that the unaerated steel slag filter appears to be a promising system for the wastewater treatment system due to the slag properties where the substrate is high in ferum. Based on the data tabulated, it can be seen that the phosphate removal of the effluent was not complying with the Environmental Quality Act (Sewage) Regulation 2009. The results of TP removal are higher than the allowable limit which is 10 mg/L which shows that the effluent is still not safe to be released into water body.

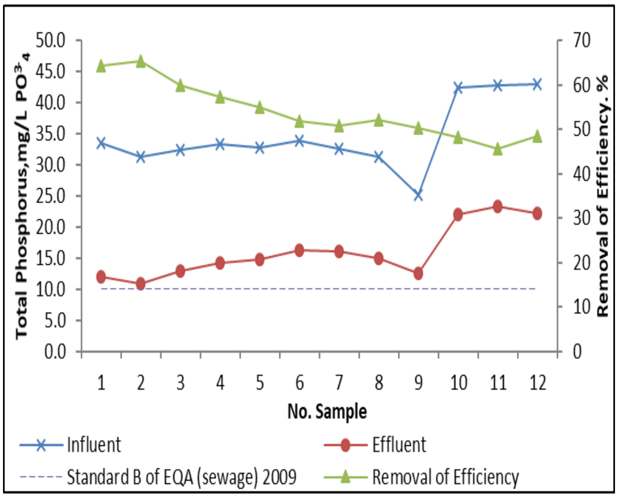


Fig 4. Removal efficiency of TP for influent and effluent

C. Effect of Alkalinity and pH

The phosphate removal mechanisms were closely related to pH and alkalinity. Total alkalinity was determined by measuring the amount of acid needed to bring the sample to a pH of 4.2. At this pH all the alkaline compounds in the sample are considered being used up. Total alkalinity for the influent was not present since there were no changes with phenolphthalein indicator because the influent was very acidic which in between the ranges of 3.80 and 4.57 starting from week 1 to week 6 respectively making it incapable to neutralize the acid added. However, after being treated in filter system, the effluent alkalinity has increased up to 2505 mg/L as CaCO3 thus increasing the pH value in the system which falls under the neutral to alkaline region which was 5.61 at the first week and 7.20 at the final week. This occurred probably due to the leaching of hydroxides ion which are abundant in the steel slags media. Since the chemical bases of slag consists mostly of lime, magnesia and other basic compounds, leaching of this material also might occurred resulting in the liberation of high concentrations of alkalinity to dissolving fluids. This indicates that the steel slag media has high alkalinity properties and capable to treat wastewater by increasing the presence of hydroxides ion resulting to pH increments from acidic to more basic pH. However, according to Environmental Quality Act (Sewage) Regulation 2009, the acceptable limit of effluent discharge for total alkalinity is 100- 200 mg/L which means the effluent is not suitable to be discharged into the drain or water bodies. Apart from that, the pH value were still fall under compliance region of Standard B in Fifth Schedule Environmental Quality (Industrial Effluent) Regulations. The results tabulated for total alkalinity and pH can be observed in Fig 5 and Fig 6 respectively.

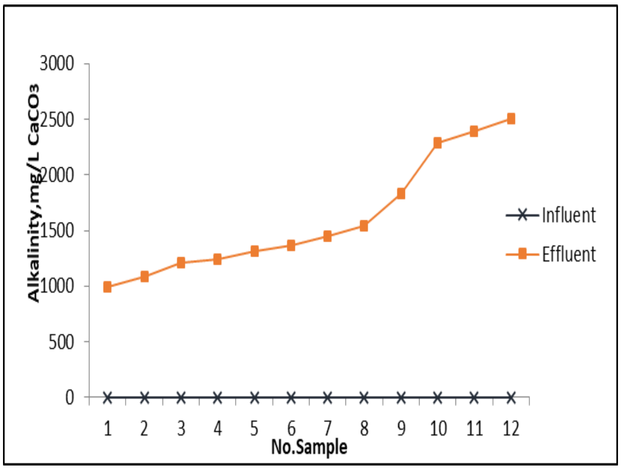
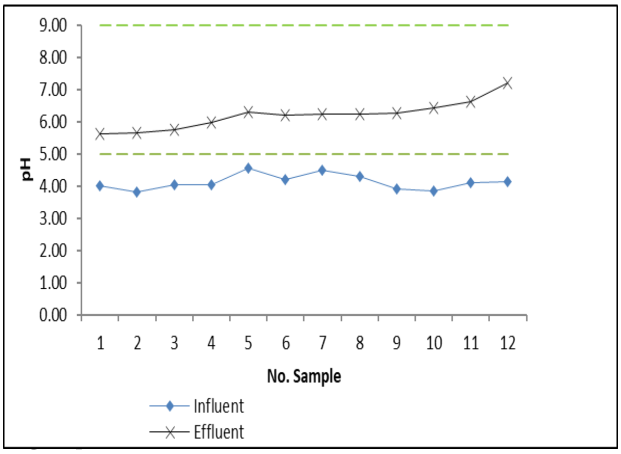


Fig 5. Alkalinity of influent and effluent



D. Effects of dissolve oxygen (DO)

Fig 7 show the dissolved oxygen graph for influent from Azhar Food Supplier and effluent of unaerated steel slag filter system. Based on the result obtained from the experiment, the DO value for influent is range between 2.57 mg/ L to 3.73 mg/L which indicated low oxygen levels and a significant level of pollution caused by the water is high. However, after 12 weeks being treated in filter system, DO value for effluents further decreased between the ranges of 1.96 mg/L to 3.44 mg/L. A low value of effluent shows that it contains less oxygen and more contaminant in it. This outcome was expected to occur since there is no source of oxygen supplied into this system since the main objective of this research was to understand the efficiency of phosphate removal without induced aeration. Furthermore, the existing oxygen present in the system were reacted with Fe ion that leached out from the steel slag forming Fe2O3 thus further undergo reduction forming Fe3O4 precipitate. Other than that, the temperature also affected the reading of DO value. The rise in the temperature will lower the dissolved oxygen value. In addition, a low DO value indicates the higher value of BOD concentrations. A high value of BOD concentrations indicates the increase of organic matter in wastewater thus may lead to high oxygen demand. Based on the data obtained, the DO values for both influent and effluent were lower than the minimum DO requirement stated in National Water Quality Standards for Malaysia which is 4.0 mg/L. This shows that the effluent is not suitable to be discharged into the drain or other water bodies.

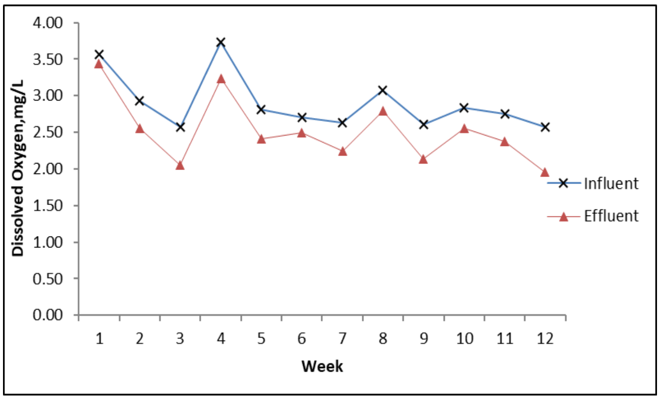


Fig. 7. Dissolve oxygen level of influent and effluent

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E. Turbidity

Turbidity is the measure of presence of suspended particles in the water. Fig. 8 shows the value of turbidity for the influent from Azhar Food Manufacturing Sdn. Bhd. and effluent of unaerated steel slag media filter. The influent turbidity values were very high since food manufacturing wastewater contains high suspended solids which ranging from 258 NTU to 718 NTU from the week 1 until week 6. After being treated with the filter, the effluent turbidity showed results ranging from 227 NTU to 491 NTU from week 1 to week 6 respectively which indicated that the concentration of effluent is lower in value compared to influent. This lower turbidity value in effluent shows that the presence of suspended particles had decreased. However, the turbidity effluent values still not complying with the acceptable limit of National Water Quality Standard for Malaysia which is 50 NTU. Therefore, the effluent is not suitable to be discharged into water bodies. Even though the turbidity value was not complying with the standard, a significant value of turbidity was reduced thus proving that steel slag media is still suitable to be used in treating wastewater with a minor modification to further enhance turbid removal in wastewater.

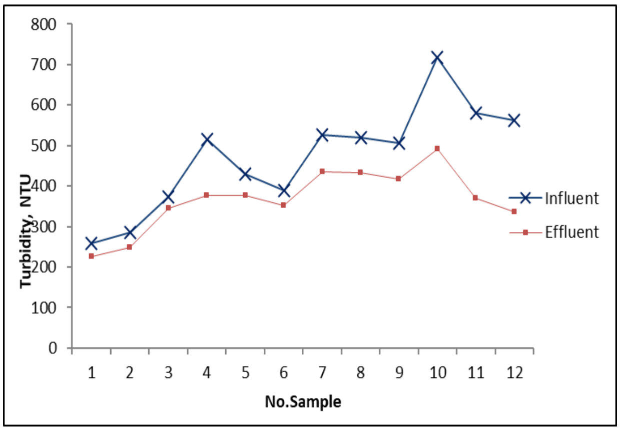

Fig 8. Turbidity of influent and effluent

F. Chemical oxygen demand (COD)

Chemical Oxygen Demand(COD) is an important indicator of organic pollution and reducing substances in surface water and is generally used as a water environmental quality parameter worldwide to describe organic pollution(Guo, Yang, Li, & Wang, 2017). Fig. 9 shows the experimental results for the chemical oxygen demand (COD) of influent collected from Azhar Food Manufacturing Sdn. Bhd. and effluent of unaerated steel slag media filter. The influent COD values range from 531 mg/L to 676 mg/L while the effluent COD values range from 521 - 619 mg/L. Based on the observation, there was no major differences between the COD concentration for the effluent and influent. There was only a small increment in oxygen content in the effluent since the COD is fluctuate decreasing from week 1 to week 6. The chemical oxygen demand of treated effluent before being discharged should be less than 200 mg/L as stated in Standard B in Seventh Schedule Environmental Quality (Industrial Effluent) Regulations 2009. However, the effluent value is still higher than the permissible limit of Industrial Effluent Standard B which was between 521 and 619 mg/L. So, it can conclude that the effluent is not complying with Standard B. The COD removal using steel slag filter are related to the design of the filter system which is the depth of the filter column (Nizam, Maarup, Hamdan, & Othman, 2013). According to the study done by Nizam et al., (2013), the highest COD removal using steel slag filter column was found to be the highest at the filter depth of 1.0m which was 64%. Hence it is understandable that the inefficiency in COD removal by this filter is due to the insufficient depth of filter column which is only at 0.52m.

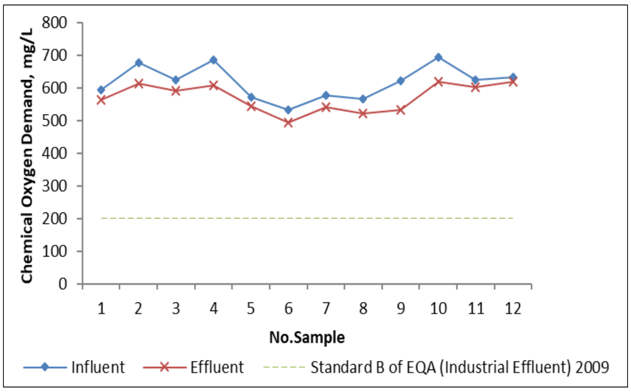

Fig 9. COD value of influent and effluent

V. CONCLUSION

Overall from this experiment, it can be concluded that high Fe unaerated steel slag filter has a potential to remove phosphorus from food processing wastewater. The phosphate removal efficiency obtained for food manufacturing wastewater is in between of 46% to 65%. The wastewater parameters monitored according to Environmental Quality (Sewage) regulations 2009 were BOD, COD, TSS, TP, Turbidity and pH and the final quality were not comply with the effluent standard. Therefore, the performance can be improved with a proper pretreatment and primary wastewater treatment prior to apply the polishing effluent system; high Fe steel slag system. Furthermore, as the system can be considered as an easy maintenance and low-cost, it can be adopted by the local food manufacturing industry to improve their existing wastewater treatment system. Hence, the good final effluent quality can be produced to comply the effluent discharge for industrial wastewater under Environmental Quality (Sewage) regulations 2009 and simultaneously decreased the environmental burden due to phosphorus in industrial wastewater

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