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Phosphorus removal by electric arc furnace steel slag adsorption

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Abstract. As to overcome the eutrophication in lakes and reservoirs which is resulted from excessive input of phosphorus due to rapid urbanization or uncontrolled agricultural activities, Electric Arc Furnace steel slag (EAFS), a steelmaking by-product, in which the disposal of this industrial waste considered economically unfavourable yet it's physical and chemical properties exhibits high potential to be great P adsorbent. The objective of this study was to identify most suitable mathematical model in description of adsorption by using traditional batch experiment and to investigate the effect on Phosphorus removal efficiency and Phosphorus removal capacity by EAFS adsorption through variation of parameters such as pH, size of slag and initial concentration of Phosphorus. Result demonstrated that, Langmuir is suitable in describing Phosphorus removal mechanisms with the Maximum Adsorption Capacity, Q_m of 0.166 mg/g and Langmuir Constant, K_L of 0.03519 L/mg. As for effect studies, smaller size of adsorbent shows higher percentage (up to 37.8%) of Phosphorus removal compared to the larger size. Besides that, the experiment indicated a more acidic environment is favourable for Phosphorus removal and the amount of Phosphorus adsorbed at pH 3.0 was the highest. In addition, the adsorption capacity increases steadily as the initial Phosphorus concentration increases but it remained steady at 100mg P/L. Eventually, this study serves as better understanding on preliminary studies of P removal mechanisms by EAFS.
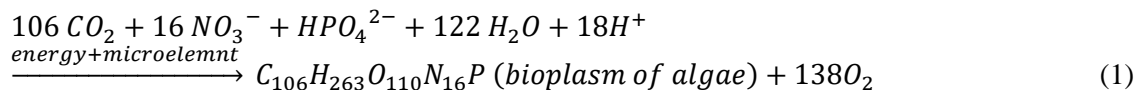
1. Introduction

Based on United Nations Environment Programme (UNEP), lakes could be defined as "natural, standing, freshwater or saline enclosed water body surrounded by land found on the Earth's continental land masses." It is playing an important role to the aquatic ecosystem by providing habitat for aquatic livings, serving as huge storage basins for municipal and industrial water supply, flood mitigation or power generation station. Furthermore, it could be one of the tourisms spot or water based recreational sites by implementation commercial or sports activities accordingly [1]. However, based on a recent research with regards to water quality of lakes in Malaysia, although most of the lakes studies classified under Class II which is appropriate for water supply with treatment system and served for recreational purposes but the studies indicated that most of the lakes and reservoirs studied consist of high total phosphorus (TP) concentration which exceeding 0.1 mg/L or could be classified as hypereutrophic that lead to algae bloom such as Aman and Ayer Keloh lakes. Eventually, this will affect human uses for drinking, aesthetic and recreation values [2]. Besides that, another research

indicated 62% of lakes were eutrophic out of 90 lakes and reservoir evaluated in Malaysia by using Carlson's Trophic State Index (TSI), which is developed from TP and chlorophyll relationship [3]. Hence, it reflected the severity of eutrophication phenomenon in Malaysia, constant follow-up, enforcement of laws and regulations or any appropriate solutions should be implement as soon as possible to prevent status of lakes gone severely.

Eutrophication can be defined as the summation of the impacts of the uncontrolled growth of planktons causing imbalanced primary and secondary productivity as well as faster rate of succession from existence to higher serial stage as resulted from excessive of nutrient (phosphorus & nitrogen) in water bodies through runoffs, leaching and sewage disposal. In fact, it is a slow natural process but contribution of human activities such as rapid industrialization, discharge of wastewater, wetland drainage, deforestation or heavy development agricultural activities on nutrient input will greatly altered the process [4]. As for the process eutrophication, it started with a body of water contained excess amount of phosphorus from sewage and watershed runoff that exceed the limiting factors of growth, eventually it accelerated the growth of plant biomass under photosynthesis which called algal bloom based on equation (1) below. It showed nitrogen and Phosphorus are the dominant control factors for the propagation of algae, particularly Phosphorus [5, 6].

$$106\ CO_2 + 16\ NO_3^- + HPO_4{}^{2-} + 122\ H_2O + 18H^+$$
$$\xrightarrow{energy+microelemnt} C_{106}H_{263}O_{110}N_{16}P\ (bioplasm\ of\ algae) + 138O_2 \tag{1}$$

Consequently, aquatic plants that live underneath of algae bloom unable to conduct photosynthesis due to blockage of sunlight. Then, decomposition by bacteria take into place once bottom of the lake accumulated by dead biomass plant. As the decomposition required oxygen, the concentration of dissolved oxygen in lake decreased which affected the lake aquatic ecosystem. Then, body of water filled with plant through formation of marsh, these phenomenon is called eutrophication. Eutrophication creates negative impacts to environment and community, either physically, chemically or biologically. The general negative impacts of eutrophication on lakes and reservoirs are listed in table 1 below. The most significant effects of eutrophication as it can interrupt the natural equilibrium of aquatic ecosystem by declining functions of water ecosystem. Furthermore, eutrophication will decrease transparency of water and deteriorate the water quality. In addition, decomposition of dead plants underneath of algae bloom will lead to lack of dissolved oxygen level in water which endanger the species or aquatic animals. Toxins could be release from algae which is poisonous to seashell and fish causing shortage of drinking water supply since the toxin is poisonous to human as well [6].

In order to tackle and combat this global phenomenon, various approaches either in biological, chemical or physical technologies such as development of constructed wetlands (CW) were implemented for phosphorus or nitrogen removal but these methods had several drawbacks and disadvantages particularly. Since 1980s, different researches have been conducted to investigate the potential of steel slag in Phosphorus removal from wastewater [7]. Therefore, the utilization of steel slag (an industrial by-product in the steelmaking process) in phosphorus adsorption seems to be a potential alternative in tackling eutrophication. Various researches indicated that Phosphorus removal efficiency was highly depended on initial P concentration, pH, size of adsorbent, dosage of adsorbent, agitation mode and temperature. In addition, different combinations of these variables will affect P removal efficiency in their own ways [8-10]. However, only several parameters will be selected to be investigated while others remained as controlled variables in this paper.

2. Materials and methods

2.1. Materials
The samples of EAFS tested in this study were collected from Southern Steel Berhad, a steel manufacturing company located in Penang, Malaysia. The samples were crushed and sieved into different size stated on table 2 below. Sieved EAFS were washed with distilled water to remove

impurities. The, EAFS were dried in oven at 110°C for 24 hrs and stored in heavy duty plastic bags until used [11].

Table 1. Classifications on size of EAFS.

Classification of size	Size (mm)
A	1.18 – 2.36
B	2.36 – 3.35
C	3.35 – 4.75
D	4.75 – 5.00
E	5.00 – 9.50

2.2. Phosphorus batch adsorption experiments

Table 2. List of controlled parameters in batch experiment [10].

Controlled parameters	Value
Mass of EAFS (g)	5
Volume of P Solution (mL)	100
Slag to Solution Ratio (g/mL)	0.05
Speed of Agitation (rpm)	175
Time of contact – on shaker (min)	90
Time of contact – after shaking (h)	168
pH (Original)	5.02-6.05
Temperature (°C)	22-25 (Room Temp.)

Based on Table 2 above, 100 mL of 6 different initial concentrations which ranged between 5 – 100 mg KH_2PO_4/L of Phosphorus solution with its original pH was mixed with 5 g of EAFS in size C in order to achieve ration of slag to solution of 0.05 g/mL. Then, the adsorption studies were conducted on an orbital shaker at 175 rpm for 90 minutes under room temperature between 22 – 25°C. All flasks were tightly covered to avoid contamination. Mixture was let to rest for 168 hours after agitation to achieve equilibrium. Then, 50 mL of mixture was then filtered with 0.45µm membrane filter with their pH adjusted to 2 and stored in 4°C chiller until used. This experiment was conducted in duplicate. Based on Table 3 above, the effects on variation of initial Phosphorus concentration (5 – 100 mg KH_2PO_4/L) on efficiency of P removal by EAFS was investigated. The series of phosphorus solution will be sent absorbance test using spectrophotometer. With similar conditions and procedures above, mixture of ration 0.05 g/mL which consist of Phosphorus solution with initial concentration of 30 mg KH_2PO_4/L and 5g of EAFS in size C, the effects of pH value on P removal efficiency is investigated. The pH value was moderated by using 1M Sodium Hydroxide (NaOH) and 1M Hydrochloric Acid (HCl). The pH values of P solution were adjusted from 3.0 – 12.0 in this experiment. This experiment was conducted in duplicate. With similar conditions and procedures above, mixture of ratio 0.05 g/mL which consists of Phosphorus solution with initial concentration of 30 mg KH_2PO_4/L and 5g of different size EAFS, the impact of different sizes of EAFS was investigated. This experiment was conducted in duplicate.

2.3. Removal efficiency and adsorption capacity
Removal efficiency or removal percentage (RP) of P by EAFS adsorbent can be calculated by using equation (2) below,

$$RP = \frac{c_o - c_e}{c_0} \ x \ 100\% \tag{2}$$

where C_o and C_e are initial and final concentration of phosphorus (mg/L), respectively; the amount of Phosphorus adsorbed by EAFS during equilibrium (q_e) can be obtained by using equation (3) below,

$$q_e = \frac{C_o - C_e}{m} \, x \, V \tag{3}$$

where q_e represents amount of Phosphorus adsorbed by EAFS during equilibrium (mg P/g) , m indicates the mass of EAFS used (g) and V represents as volume of solution (L).

2.4. Langmuir adsorption isotherm

It assumed single layer adsorption on the outer surface of adsorbent with adsorption can only occur at a fixed number of definite localized sites which all the sites are equivalent and identical. Furthermore, lateral interaction and steric hindrance between adsorbed molecules and adjacent sites were not existed [12, 13].

$$\frac{C_e}{q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \tag{4}$$

where Q_m, C_e and K_L represents maximum adsorption capacity (mg/g), equilibrium concentration (mg/L) and Langmuir constant (L/mg) respectively. The Langmuir constant can be obtained by slope and intercept from linear graph of $\frac{C_e}{q_e}$ versus C_e.

In order to determine the favourability of Langmuir isotherm on adsorption, R_L, a dimensionless constant known as separation factor or equilibrium parameter shown as equation (5) can be used.

$$R_L = \frac{1}{1 + K_L C_0} \tag{5}$$

where C_0 indicated as initial concentration of Phosphorus.

2.5. Freundlich adsorption isotherm

It is a well-known model that used to describe non-ideal adsorption of multilayer adsorption over heterogeneous surface with assumption of stronger binding sites will be occupied first. It also stated the degree of site occupation increased, the binding strength decreased [13].

$$ln \, q_e = ln \, K_F + \frac{1}{n} ln \, C_e \tag{6}$$

where K_F represents Freundlich constant (mg/g), n indicates adsorption intensity and C_e defined as the equilibrium concentration of adsorbate (mg/L). Value of K_F and n can be determined through linear graph of $ln \, q_e$ versus $ln \, C_e$.

3. Results and discussion

3.1. Characterization of adsorbent
The specific surface area and pore size distribution of steel slag were determined from BET analysis method by using using N_2 adsorption/desorption at 77.3 K. The data were tabulated in Table 3 below.

Table 3. Surface data of EAFS samples.

Parameters	Value
BET surface area, m^2/g	5.5264
Pore Volume, cm^3/g	0.09610
Average Pore Diameter, Å	713.7362

As for the surface images of the EAFS (before & after Phosphorus adsorption), it was captured by SEM test as shown in Figure 1 and 2 below. Since size particle, diameter of pore and specific surface area of adsorbent are the main parameters that affecting the adsorption capacity of adsorbent [14]. Figure 1 showed that existence of pore on the surface of steel slag hence confirmed the porosity of the steel slag. Based on the observation obtained from SEM shown in Figure 2, a fine distributed crystalline layer was identified on the surface of EAFS which believed the crystal is Hydroxylapatite (HAP) [15].
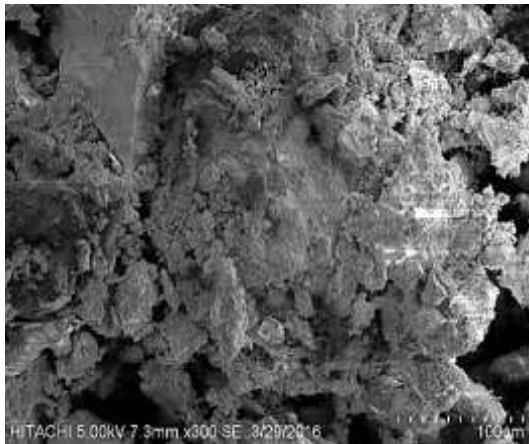

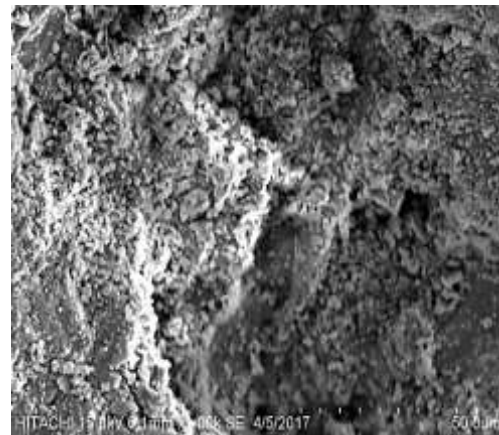**Figure 1.** Surface image of EAFS before phosphorus adsorption (7.3mm x 300)

Figure 2. Surface image of EAFS after phosphorus adsorption (6.1mm x 1.00k)

EDX analyses revealed the difference of chemical components of EAFS (before and after Phosphorus adsorption) as shown in table 4 below. Before Phosphorus adsorption, the main elements existed on surface of EAFS are Ca & Fe (Metals) followed by Si (Metalloids) in their oxides form which is CaO, Fe_2O_3 and SiO_2 and these results agreed with the findings of other study [16]. However, due to inconsistency and high variation of the chemical composition in EAFS, the proportion of certain elements might be different, but the main highlight of this comparison is on the existence of the phosphorus, it confirmed the adsorption of Phosphorus by EAFS.
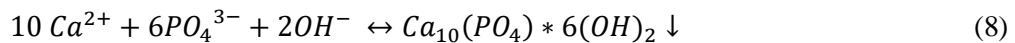
Table 4. Weight proportion of element in EAFS before and after adsorption.

Element	Before adsorption			After adsorption		
	Weight (%)	Formula	Compound (%)	Weight (%)	Formula	Compound (%)
C	6.00	C	6.00	6.56	*C*	6.56
O	37.77S			30.72S		
F	4.64	F	4.64	3.18	F	3.18
Mg	2.95	MgO	4.89	1.91	MgO	3.16
Al	5.08	Al_2O_3	9.60	4.14	Al_2O_3	7.82
Si	10.01	SiO_2	21.41	6.57	SiO_2	16.22
P	0		0	*2.80*	**P**	*2.80*
Ca	16.64	CaO	29.93	16.37	CaO	22.90
Fe	15.39	Fe_2O_3	22.01	*24.69*	*Fe_2O_3*	*35.30*
Co	1.51	Co	1.51	*2.05*	*Co*	*2.05*
Total	100		100	100		100

Based on Figure 3 below, XRD test revealed the EAFS was made up by several constituents including Ca_3O_5Si, Periclase (MgO), Gehlenite ($Al_{1.91}Ca\ Fe_{0.02}Mg_{0.05}O_7Si_{1.02}$), Tricalcium Oxynitride Silicate ($Ca_{2.894}N_{1.76}O_{4.24}Si_2$) and Franklinite ($Fe_{1.96}\ Mn_{0.36}O_4Zn_{0.68}$). Therefore, it concludes Ca is the dominant element in the EAFS, by ignoring the variation of Fe proportion in table 5, the decrement of certain element was noticeable. For instance, the decrease in weight of CaO might due to its dissolution throughout the adsorption mechanisms. Eventually this finding is support the proposed Phosphorus removal mechanisms by one of the research [15]. The dissolution process can be explained in the equations 7 and 8 below.

$$CaO + H_2O \rightarrow Ca^{2+} + 2OH^- \tag{7}$$

Then Ca^{2+} will react with $PO_4{}^{3-}$ to form HAP, [22]

$$10\ Ca^{2+} + 6PO_4{}^{3-} + 2OH^- \leftrightarrow Ca_{10}(PO_4)*6(OH)_2 \downarrow \tag{8}$$

In addition, the decrement of weight in Al_2O_3 also can be identified in table 5. Therefore, the available Al^{3+} ions might react with $PO_4{}^{3-}$ to form $AlPO_4$ shown as equation (9) below [17].

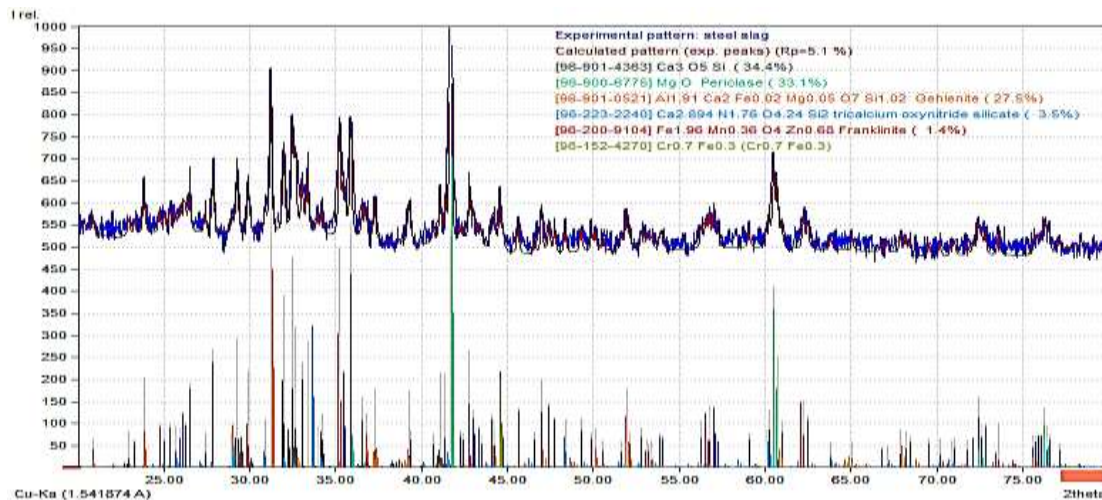$$Al^{3+} + H_nPO_4{}^{3-n} \leftrightarrow Al(PO_4) + nH^+ \tag{9}$$

Figure 3. X-ray diffraction pattern of EAFS (before phosphorus adsorption).

3.2. Adsorption isotherm

In this paper, the equilibrium data were analysed with 2 well-established isotherm mathematical models; Langmuir and Freundlich. The adsorption data have been fitted to liner form of these mathematical model as shown as Figures 4 and 5 below. As for the Langmuir and Freundlich constant, it showed as Table 5 below.

Table 5. Parameters obtained from Langmuir and Fruendlich Isotherm Plot.

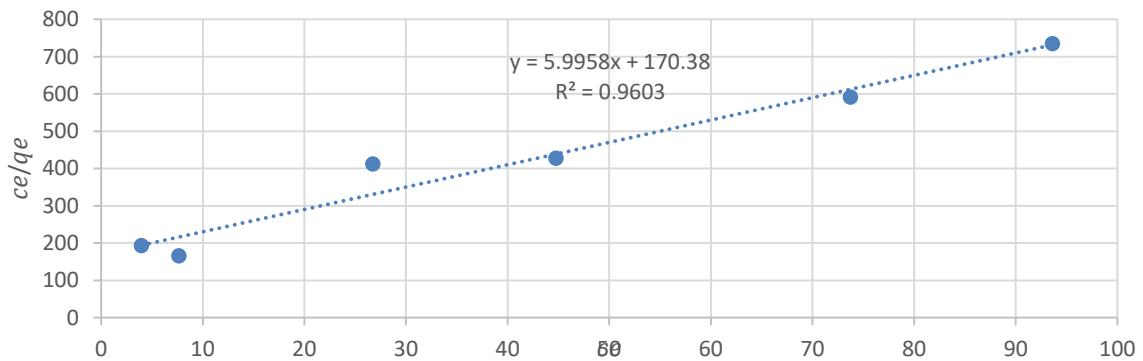| Langmuir		Freundlich	
Q_m, mg/g	0.166	K_F, mg/g	0.0118
K_L, L/mg	0.03519	N	1.8311
R^2	0.9603	R^2	0.9469

Figure 4. Langmuir plot for phosphorus adsorption onto EAFS.
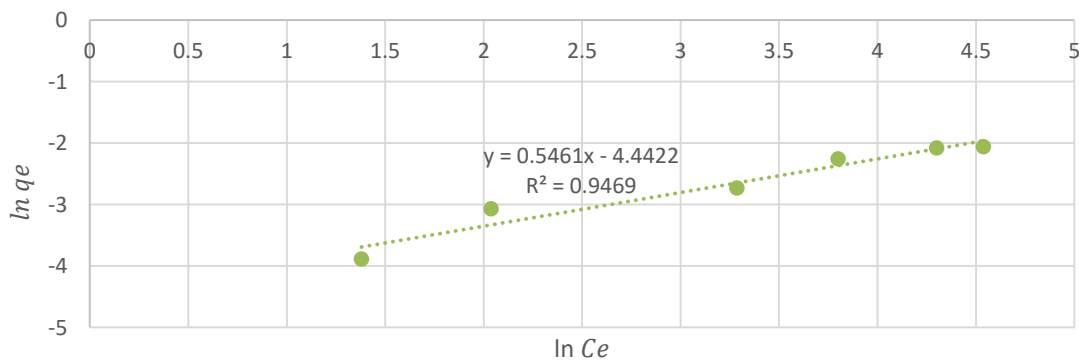

Figure 5. Freundlich plot for phosphorus adsorption onto EAFS.

Based on the coefficient of determination (R^2), the values for Langmuir model and Freundlich are 0.9603 and 0.9469 respectively which showed Langmuir model is more suitable in description of adsorption process compared to Freundlich model. As mention on previous section, R_L value will identify the favourable level of isotherm for adsorbent. Based on Figure 6 below, it showed the relationship between R_L value and initial Phosphorus concentration. By referring to Table 6 below, it indicated the range of R_L with respective favourability, as the R_L value ranged between 0.85 – 0.22 (fall under $0 < R_L < 1$ category), it further affirmed the suitability of Langmuir model in description of P removal by EAFS.

Table 6. R_L value and level of favourability.

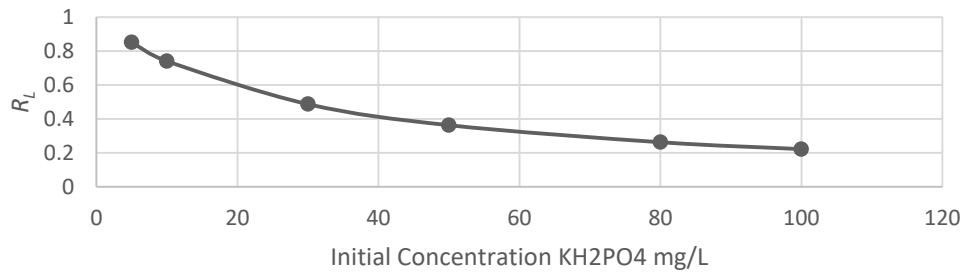| Value	Indicator
$0 < R_L < 1$	Favourable
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$R_L = 0$	Irreversible

Figure 6. R_L Value versus initial concentration of KH_2PO_4.

3.3. Effect of various conditions on phosphorus removal efficiency

3.3.1. Effect of slag size. Figure 7 below showed the effect of size of slag with the phosphorus removal efficiency of EAFS. It indicated the P-removal percentage increased as the size of slag decreased with a fixed mass of slag (5g) in the experiment despite the rebound on Phosphorus removal percentage on the size between 4.75- 5.00 mm. The rebound result might be caused by large range of difference between size D and E, 4.75-5.00 and 5.00-9.50 respectively due to limited availability of sieve.
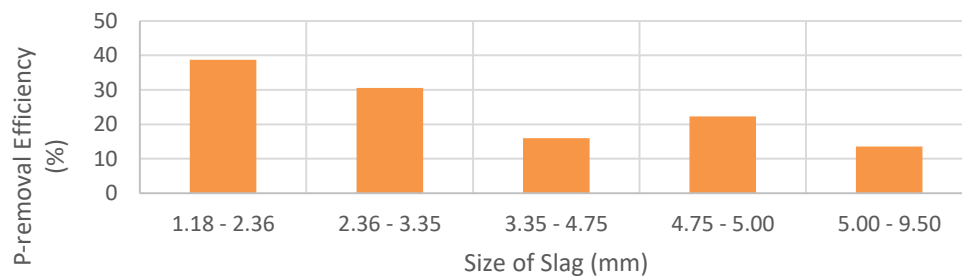

Figure 7. Effect of slag size on phosphorus removal (Experimental conditions: Initial phosphorus concentration=30mg P/L; solid to solution ratio=0.05 mg/ml; agitation speed = 175rpm; original pH=5.02-6.05; temperature = 22-25°C)

According to the BET results on pore size and pore area earlier which confirm the porosity of the EAFS. Hence, smaller size of slag has a larger surface area resulting higher adsorption on phosphorus and its removal percentage. These results agreed with the finding in other study [9]. Since the diffusion path decreased as the size of slag decreased, eventually it increased the effectiveness of the penetration of adsorbate as well as then depth of penetration in adsorbent particle resulting higher rate of adsorption. In addition, mass transfer limitation and internal diffusional resistance will decrease as the size of slag decrease which further increased the rate of adsorption of P [18].

3.3.2 Effects of pH. The effect of pH of solution (Initial pH) on phosphorus removal efficiency has been demonstrated in Figure 8 below. As the initial pH increase by becoming a higher basicity solution, the P removal efficiency decreased exponentially. Besides that, the results demonstrated the amount of P adsorbed at pH 3.0 was the greatest which indicated the adsorption of P by EAFS is effective under acidic environment. Although these findings are likely support with several studies but in terms of the optimum value of pH, the value is not similar where their studies indicated pH 5 - 5.5 consisted of highest P-removal efficiency [8, 9]. Due to the variation of chemical composition in the EAFS hence the optimum pH for highest P-removal efficiency is subjected to the chemical composition.
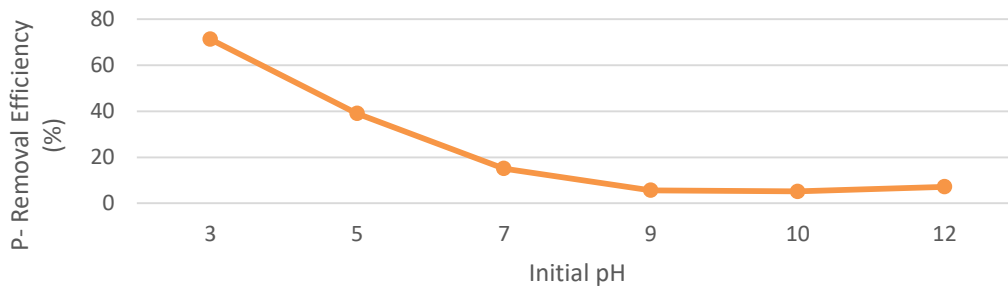
Figure 8. Effect of initial pH on P-removal (Experimental conditions: Initial P-concentration=30mg P/L; solid to solution ratio=0.05 mg/ml; size of slag: 3.35-4.75mm; agitation speed = 175rpm; temperature = 22-25°C)

Based on the result on chemical composition of EAFS through EDX, most of the metal existed in their respective oxides such as CaO, Fe_2O_3 and SiO_2 which indicated the large existence of oxygen atoms and hydroxyl groups on the surface of slag. According to a recent research, the acid or basic properties and the reactivity of these surface is highly depending on the hydroxyl group on the surface [19]. In a higher pH or a more basic condition, negative charges (OH^-) may generated on the surface of slag thus would repulse the negative charged phosphate ion (PO_4^{3-}) from being adsorbed.

3.3.3. Effect of Initial Phosphate Concentration. Based on Figure 9 below, it showed the relationship between the initial phosphate concentration with the Adsorption capacity of the EAFS, the adsorption capacity is increased steadily as the P-concentration increase because there was more P existed and available for sorption in solution per unit mass of slag. However, it was tending to be flatten at 100 mg P/L because for a fixed mass of adsorbent (5g in this study), the total available adsorption sites is constant hence it will only absorb same amount of phosphate. Therefore, it led constant amount of percentage removal at 100 mg P/L [20].
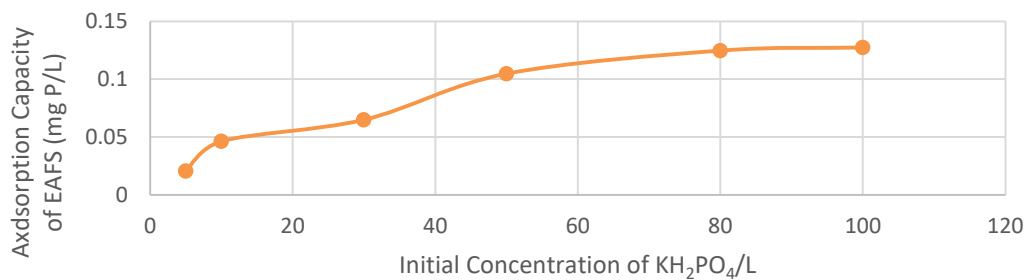

Figure 9. Effect of initial phosphate concentration on P-removal (Experimental conditions: solid to solution ratio=0.05 mg/ml; size of slag: 3.35-4.75mm; agitation speed = 175rpm; original pH=5.02-6.05; temperature = 22-25°C)

4. Conclusions

This paper serves as the purpose of preliminary studies on phosphorus removal by EAFS. It showed the Langmuir model is more suitable in description of phosphorus removal by EAFS in compared to Freundlich model with the maximum adsorption capacity, Q_m of 0.166 mg/g and Langmuir constant, K_L of 0.03519 L/mg. Furthermore, this study clearly indicated the importance of size of slag, pH and initial concentration of phosphorus on effectiveness of its removal by EAFS. Based on the experiment, small size of adsorbent shows higher percentage (up to 37.8 %) of Phosphorus removal compared to the larger size. Besides that, the experiment showed a more acidic environment is favourable for phosphorus removal and the amount of Phosphorus adsorbed at pH 3.0 was the highest. In addition, the adsorption capacity increases steadily as the initial Phosphorus concentration increase but it

remains nearly constant at 100mg P/L due to fixed adsorption site at given mass throughout experiment.

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