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PERFORMANCE INVESTIGATION OF FURNACE BOTTOM ASH AS A FILTER MEDIA FOR PHOSPHATE REMOVAL

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Abstract

This study investigates the capability of furnace bottom ash (FBA) as a filter media for phosphorus removal from wastewater effluents. Lab-scale studies were conducted, in which a mass of FBA was brought into contact with the phosphate solution (a predominant form of phosphorus in wastewater) in batch experiments and lab-scale filter. Intraparticle Diffusion Model (IPD) was applied and revealed that the mechanism of phosphate adsorption onto FBA consist of three phases; film phase occurred in the external surface and intraparticle diffusion phases take place in the wide pores and microspores. A Point Zero Charge (PZC) study was conducted and indicated that the FBA acts as anion exchanger and develops negative charge when the pH more than 9. Based on the PZC outcomes the FBA efficiency was regenerated by two washing methods (continuous and intermittent) with deionized water solution at pH 9.5 and 10. The intermittent washing method gave better results as the FBA regenerate 95% of its efficiency. FBA was achieved the phosphate permissible limit (0.1 mg/L) in synthetic solution at 150 min. While, in real wastewater sample was achieved it in 180 min. The FBA washing method based on PZC can be adopted as a strategy for absorbents efficiency regeneration and phosphorus recovery.

Key words: filter media, furnace bottom ash; phosphate sorption, wastewater treatment

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1. Introduction

1.1. Survey on phosphorus removal from the environment

Industrial countries generate a significant quantities of domestic and industrial wastewater. The effluents must be treated before being dumped into the rivers, lakes or the sea so as to reduce the amount of contaminants and protect the aquatic environment. Particular attention should be given towards the inorganic substances in wastewater such as phosphate (a predominant form of phosphorus in wastewater) because it encourage abnormal vegetal growth in aquatic systems. These substances contribute in eutrophication of the water bodies (Martinez et al., 2000). Using fertilizers in agriculture and the wastewater from domestic and industrial activates are considered as the most significant sources contribute the increasing of phosphate concentration in the effluents (Daneshgar et al., 2018).

Many methods developed for phosphorus removal such as chemical precipitation, constructed wetland, enhanced biological phosphorus removal method and sequencing batch reactor (Alattabi et al., 2017; Jianbo et al., 2009; Kartashevsky et al., 2015; Selvaratnam et al., 2015;). However, seeking for new phosphorus removal methods in-line with economic and environmental requirements still standing. Recently, the tendency to utilize the phosphate sorption materials (PSMs) for treating municipal wastewater offered a solution that consistents with the approach of sustainability (Klimeski et al., 2012). In

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addition, using materials that characterized as low cost, highly available, and require no additional pretreatment have served wastewater treatment as an attractive and efficient technique (Crini, 2006; Leechart et al., 2009; Robinson et al., 2012).

The common denominator of all phosphate sorption technologies is PSM, which is capable of retaining the phosphate chemically (Johansson Westholm, 2006; Li et al., 2006; Renman, and Renman, 2010). The most efficient PSMs tend to be those that include Fe/Al hydroxides or easily soluble Ca/Mg compounds (Lyngsie, 2013). Different PSMs have been examined, but most of these PSMs were investigated at high phosphate concentrations in wastewaters (Cucarella and Renman, 2009; Ragheb, 2013; Ugurlu and Salman, 1998;). This work has focused on the efficiency evaluation of furnace bottom ash (FBA) as a PSM without pre-treatment.

Coal ash is not a simple chemical compound and it is produced as a consequence of coal burning, especially, in the power generation plants. After burning, a portion of the coal ash caught in the chimneys; this part is referred to as fly ash. Another portion, which is the non-combustible inorganic residue, is recovered from the bottom grates of the furnaces and it is known as bottom ash (Kirk et al., 2003). FBA is a coarse ash predominantly consist of oxides of iron, aluminum, and silica. Since plenty of bottom ashes are produced as waste from thermal power treatment, they are considered the most dumped solid residues (Hjelmar et al., 2010). According to Kirk et al. (2003) the bottom ash is available for free and it is categorized as a waste material.

Recently, efforts have been made to reuse bottom ash for different purposes. Sobik-Szoltysek et al. (2016) pointed that the interaction of wastewater containing heavy metals with ashes can help them to reduce their concentration in effluents. Hai et al. (2012) illustrated that several solids have been investigated as a sorption material for removing organic pollutants and heavy metals from wastewater, but their high costs have limited their large scale use for removal. Although, ashes which have been proven to be a suitable sorption material for different pollutants, the majority of the FBAs were disposed in landfills (Papandreou et al., 2007). Ashes which generated from power plants contain several heavy metals such as Pb, Zn, Cd and Cu. However, bottom ash releases fewer heavy metals than fly ash (Mangialardi et al., 1998). Nevertheless, fly ash and bottom ash are utilized for the adsorption of heavy metal contaminants in water and wastewaters (Gupta and Torres, 1998). Daneshgar et al. (2018) stated that the wastewater treatment plants around the world are exerting enormous efforts to control the phosphate concentration and he added that phosphorus reserves might be depleted around 2300. Therefore, applying the phosphate recovery process in line with elimination process became a necessity to maintain the phosphorus resources.

It would be beneficial to investigate the performance of suggested filter material to remove the

contaminants from real wastewater influent. This study has been conducted by testing the removal capacity of FBA for phosphate from real wastewater and comparing the results with the findings that were obtained from phosphate removal from synthetic phosphate solution. The real wastewater contains various types of contaminants that may be have an influence on FBA efficiency to remove the phosphate. While, during this research a synthetic phosphate solution has been used to test the efficiency of selected material as phosphate sorption material. Therefore, the final findings of this experiment will help to give an insight into the performance of FBA about phosphate removal from wastewater. This work aim to introduce a method of regenerate the filter media to increase it is lifetime as phosphate sorption material.

1.2. Background about adsorption kinetic

Recently, several adsorption kinetic models were investigated to describe the mechanism and fate of the adsorbent material (Karthikeyan et al., 2010). Weber and Morris proposed the intraparticle diffusion model (IPD) as a tool to describe the adsorption kinetics, and it has been widely adopted by the researchers for adsorption applications (Wu et al., 2009).

Intraparticle diffusion model is a transport process between two phases; it includes the species movement from the solution into the solid phase. Moreover, the species diffusion from the solute into the solid phase take place by external or internal diffusion or by both kinds of diffusions. The external diffusion involved the transportation of the species from the solution to the boundary layer of the liquid phase. While, the internal diffusion included the migration of species between the surface of the adsorbent and their internal pores (Karthikeyan et al., 2010).

Description of solute species transport into the adsorbent by intraparticle diffusion model is performed according to Eq. (1) (Karthikeyan et al., 2010).

$$q_t = Ki t^{1/2} + Ci \tag{1}$$

where: q_t is the adsorption amount at time t (mg/g), K_i is diffusion coefficient which is referee to the rate of the intraparticle diffusion (mg/(g min^{1/2})), and *Ci* is a constant or any experiment (mg/g). It is proportional to the boundary layer thickness. The slope that obtain from plotting the amount of adsorption at any time against the square root of time is represent the diffusion rate. While, the plot interception is represent the extent of the boundary layer thickness.

In this section, an overview on the PZC will be introduced such as its hypothesis, work mechanism and the methods of measurement to understand the significance of measuring the PZC in the process of determining the pH of FBA washing solution. 'The point of zero charge PZC is the pH of the suspension at which the net charge on the surface of an insoluble oxide/ hydroxide is zero' (Mahmood et al., 2011a). This means the sum of all the surface positive charges balance the sum of all the surface negative charges. PZC has made a significant contribution regarding to characterization the surface of metal oxides/hydroxides (Bourikas et al., 2005). In the aqueous environment the PZC is considered one of the factors that plays a vital role in locating how potentially harmful ions can be adsorbed by metal oxide/hydroxides.

Insoluble metal oxides/hydroxides are an important category of inorganic ion exchangers because they act as sorbents for soluble impurities. Most of the metal oxides are amphoteric (Anderson and Rubin, 1981); and their surface dissociation may be represented schematically as Eq. (2) and (3):

$$MOH_{2^+} \leftrightarrow MOH + H^+$$
 (2)

$$MOH \leftrightarrow MO^- + H^+$$
 (3)

Where *M* represent the solid surface. The amphoteric behaviour of the surface of metal oxides allows the surface to develop either a positive or a negative overall electrical charge. In case the pH of a solution at lower values than the desired PZC the surface of the metal oxides will develop a positive charge (the oxide behaves as an anion exchanger). In contrast, the solution at pH values higher than PZC, a negative charge will develop over the surfaces of the metal oxides (the oxide behaves as a cation exchanger) (Cardenas-Peña et al., 2012). Mixed oxides can have both exchange types, depending on the relative pKa values of the different surface sites (Ibanez et al., 2007).

Several studies have determined the value of PZC for different metal oxides/ hydroxides (Kosmulski, 2006; Mahmood et al., 2011b; Naeem et al., 2007;). The findings of these studies revealed different PZC values for the same oxide. Moreover, the findings showed that a particular sample of a metal oxide/ hydroxide never has a constant PZC value (Kosmulski, 2006). The values of PZC are often divergent; for example, the PZC of aluminium oxide was varied from 6.5 to 10 based on the sort of aluminium oxide. This variation was attributed to the differences in the origin of samples and PZC measurement methods. Many methods are applied to determine the PZC such as fast titration, salt addition, mass titration, and ζ potentiometry.

2. Materials and method

2.1. Materials

The FBA sample was collected from the Fiddlers Ferry Power Station. It is a coal-fired power station situated in the North-West England between the towns of Widnes and Warrington on the north bank of the River Mersey. Sieve analysis was conducted to determine the FBA particles size which is utilized in

this investigation. The shape of the surface for FBA was identified by using scanning electron microscopy (SEM). While, X-ray fluorescence (XRF) analysis was performed to identify the chemical composition of the FBA. According to Chandler et al. (1997), the bottom ashes have a surface area ranging from 3 to 46 m²/g; they were measured by using Brunauer-Emmett-Teller (BET) adsorption isotherms. Nova 2000 was used as an instrument to measure the surface area of FBA; the method of this technique includes gas sorption (nitrogen) by the samples which are placed in heated jacket at 150 °C. Raw FBA samples are used to investigate its capability as adsorbent for phosphate. This investigation included washing the FBA samples to eliminate the impurities that might have negative effects on adsorption mechanism. The FBA samples were washed by deionized water for several times until obtain a clear run off. Then the samples dried in oven at temperature 110 °C, finally stored in capped bottles.

A phosphate solution was used as a source of phosphorus in these experiments. Aqueous solutions contain phosphate ions at a concentration of 10 mg/L; they were prepared by dissolving potassium dihydrogen orthophosphate (KH₂PO₄) in deionized water. Phosphorus concentration in municipal wastewaters is varied. It has an average concentration between 6 and 8 mg/L. While, in other sources have concentrations between 4 and 11 mg/L (Cornel and Schaum 2009; Parsons and Smith, 2008; Tchobanoglous et al., 2014). Jenkins et al. (1971) reported that the concentration of total phosphorus (organic and inorganic) in municipal wastewater was 10 mg/L because most of the phosphorus decomposed to orthophosphate according to bacterial action. Thus, the aqueous solution was prepared at a concentration of 10 mg/L to simulate one of the highest expected concentrations.

The phosphate concentration was measured by HACH LANGE DR 2800 spectrophotometer, according to the Amino Acid method. This method measure the concentration range 0.1 to 30 mg P/L. The pH of the solutions was adjusted by adding either hydrochloric acid (HCl) or sodium hydroxide (NaOH).

2.2 Method

2.2.1 Leaching study

During utilize FBA as filter media for phosphate removal a leaching of heavy metals expected. Therefore, investigation of the safety of the effluent from the heavy metals was performed by atomic absorption spectrometry (AAS). AAS is analytical tool for determine the elements' concentration. At first, the expected heavy metals determine based on the findings of the XRF analysis and the previous literature review about the chemical composition of ashes. Afterward, 23 g of FBA will be soaked in 40 ml of phosphate solution with concentration 10 mg/L in 1 liter flask for 24 hr. Final step includes samples collection and measure the concentrations of the heavy metals by AAS. This test is conducted at the same conditions and steps of batch experiment which is described in next section. The amount of metal leached per unit mass of sample at any time q_t was calculated according to Eq. (4):

$$q_t = \frac{C V}{m} \tag{4}$$

where: C concentration of the metal in the suspension (mg/L); V volume of the suspension (l) and m dry mass of the FBA (kg).

2.2.2 Phosphate removal experiments

Batch experiments were conducted to obtain an initial understanding of how the FBA can be used as a PSM. Afterward, upflow filter test was performed to simulate the actual filtration process.

Batch experiments were performed by take a volume of 40 ml from the phosphate solution and brought into contact with 23g from FBA in one-liter capacity flask to determine the contact time of optimal removal efficiency. The experiments were performed at room temperature. The material soaked in the solution did not show any upward buoyancy at material/solution ratio of 1/1.74 (23 g / 40 ml). The suspension was shook at a constant speed (100 rpm) for 2 min to allow all the surface area to come in contact with solution ions. Then it was allowed to stagnate over the course of the experiment to prevent the effect of mixing on the sorption results. In the beginning, the samples were collected at minor intervals; then the collection time was increased with the progress of the experiment time.

Therefore, the samples collection times were 5 min, 15 min, 30 min, 1 h, 2 h, 4 h, 8 h, 16 h, and 24 h. All samples were filtered through a 0.45 µm filter paper to exclude the suspension particles that may cause light scattering during measure the phosphate concentration in spectrophotometer. All experiments were carried out in triplicate, and the average value was used. An additional flask contains 40 ml of phosphate solution was used as a blank over all experiments. During the upflow filter test a several runs were operated by pumping aqueous solution with volume 7 l and concentration 10 mg P/L over a mass of 1220 g from the FBA. The FBA mass was packed in upflow filter (100 mm diameter and 350 mm height). Each run was ended when the effluent concentration was reached the desired effluent limit of 0.1 mg P /l and then a new run started with influent concentration 10 mg P/L. All experiments in this study were utilized the aqueous solution as a source of phosphate to simulate the real phosphate concentration in the wastewater and achieve the conditions of safety and health in the lab. However, in the final stage a real wastewater sample was used to give more realistic insight about the capability of the FBA to remove the phosphate.

2.2.3. Method of FBA washing

The FBA washing method should be taken into consideration because it is increased the lifetime of the

FBA to remove the phosphate from wastewater. The washing solution characteristic determined according to the PZC method. According to the chemical composition analysis, these materials contain Fe/Al oxides, and they are responsible of capturing the phosphate ions from the influent. Based on the literature review, the PZC of Fe/Al oxide should be obtained at alkaline pH value. However, measuring the pH variation of FBA samples at acidic pH was performed to follow the standard methods in measuring PZC, and avoid any misleading outcomes. The salt addition method was applied to determine the PZC of FBA because it is simple, accurate and required a small quantity of material as compared to other techniques (Mahmood et al., 2011b).

According to this method, the PZC value of any material is determined by mixing this material with a solution able to set off an ionic exchange with this material. Therefore, the FBA sample was mixed with KH₂PO₄. The ratio of each FBA sample to the solution was 1:1.74; utilizing the same ratio in batch experiments to present more realistic results. Based on these considerations, 23 g of FBA sample and 40 ml of KH₂PO₄ (concentration 10 mg P/L) were mixed in different reaction flasks. 10 samples were prepared at an initial pH value of 2, 3, 4, 5, 6, 7, 8, 9, 10, or 11. The pH of the solutions were adjusted by adding either hydrochloric acid HCl or sodium hydroxide NaOH. Each flask was agitated in a shaker bath for 24 h. After settling, the final pH of each suspension was measured by pH-meter model HI 2210.

In order to give better characterization for ion exchange between the FBA and the solution, the solution was investigated at three different temperatures 10, 20, 30 °C. An additional flask contain 40 ml of phosphate solution was used as a blank over all experiments to monitor any adverse effects on the quality of the experiment's performance. The initial pH values of the solutions were plotted against ΔpH (the difference between initial and final pH after settling). The initial pH value at which ΔpH equal zero was considered the PZC of FBA. Finally, the washing solutions are salt such as NaOH added to deionized water; salt quantities are control the pH of the solution.

Continuous and intermittent washing were suggested as washing methods to achieve the regeneration process. The configurations of the proposed method was same upflow filter test characteristics (7 l washing solution, 1220 g semi saturated FBA, washing flow rate 1 L/min and filter dimensions 100 mm diameter; 350 mm height). The continuous washing method includes pumping the solution into the filter at constant flow rate.

The same washing quantity in continuous washing has been utilized in the intermittent washing method; but the washing solution is pumped intermittently. The washing solution is pumped into the filter in doses over time; each quantity being in contact with the FBA for a specific period. The washing solution quantity and washing time for both methods was the same to avoid any changes which could influence the results.

3. Results and discussion

3.1. FBA characteristics

The shape of the FBA surface was identified by using scanning electron microscopy (SEM). Images with a magnification of 300 μ m and 500 μ m were took, as shown in (Fig. 1) a and b, respectively. It was revealed that the presence of numerous bends and protrusions on the FBA surface offered more surface area for contact with the influents. The surface area of FBA was measured and the outcome was consistent with the findings of (Chandler et al. (1997), the FBA had surface area 31.33±0.45 m²/g.

The chemical composition of the FBA plays a crucial role in phosphate sorption. Thus, analyzing its chemical composition is important for understanding the phosphate removal mechanism. Its chemical composition was determined using an energy dispersive X-ray fluorescence, Shimadzu EDX 720 analyzer, and the findings are shown in Table 1.

Table 1. X-ray fluorescence analy	ysis of the composition of
furnace botton	m ash

Composition	Weight %
СНО	61.89074
SiO2	21.29694
A12O3	10.00113
Fe2O3	3.28503
K2O	1.33200
CaO	1.26386
MgO	0.65530
Fine	0.26739
ZnO	0.00324
NiO	0.00307
Cr ₂ O ₃	0.00130

The X-ray fluorescence analysis revealed that the chemical composition of FBA contained oxides of Fe, Al and Mg that might be an essential factor that supporting the adsorption of phosphate. The finer fractions from FBA give a higher phosphate sorption capacity because they offer a large surface area. Large surface area is increased the chances of contact between the material and influent.

Consequently, lead to increase the removal efficiency. In this present study, sieve analysis was conducted to remove coarser fractions; the finer particles' size was ranged 1-4 mm. They are collected from sieves number (6, 10 and 16).

3.2. FBA safety examination

According to the XRF analysis for FBA as shown in (Table 1), it was contained ZnO, Cr2O3 and NiO. All these oxides are available with minor weight percentages. However, before embarking on the study of the validity of FBA for phosphate removal from wastewater treatment an inspection for materials' safety was conducted. According to the literature review the heavy metals such as Pb, Cd and Cu it's expected to present in ashes. Therefore, these elements were measured as well. Atomic absorption spectroscopy (AAS) was utilized to determine the concentration of heavy metals which were expected to leach from FBA. The results revealed that the concentrations of leached samples for heavy metals such as Pb, Cd and Cu are very low and approaching to zero as showed in (Table 2).

While the Zn, Cr and Ni concentrations were 0.015, 0.008 and 0.006 mg/L, respectively. The permissible limit of the concentrations of the measured elements in water was showed in (Table 2) according to Hassan et al. (2012). The AAS results revealed that all measured elements concentrations were below the permissible limit. In addition, the amount of the metal leached which is calculated by using Eq. (3) presented in (Table 2). Consequently, FBA is safe to introduce as filter media for phosphate removal.



Fig. 1. Scanning electron micrographs of furnace bottom ash surface at: (a) magnification 300 μ m; (b) magnification 500 μ m.

Composition	Permissible limit mg/L	Mean conc. mg/L ± S.D	amount of metal leached mg/kg
Pb	0.05		
Zn	5	0.015±0.001	0.026
Cr	0.1	0.008 ± 0.002	0.014
Ni	0.2	0.006 ± 0.002	0.010
Cd	0.01		
Cu	2		

Table 2. Concentration of leaching samples

3.3. Influence of contact time on adsorption process

The experiment was performed at a phosphate solution concentration of 10 mg/L and room temperature. The normal pH of the solution was 6.4. The experiment was operated for 24 hours, and 10 duplicate samples were collected according to samples collection times as mentioned in the previous section. As shown in (Fig. 2), the phosphate removal reached the maximum level (76%) after approximately 8 hours. The phosphate removal for contact time longer than 8 hours was very low in comparison with the removal before this stage. Therefore, the contact time for the rest of the batch experiments was set at 8 hours.



Fig. 2. Influence of contact time on P sorption by furnace bottom ash (Solution concentration = 10 mg P/L, pH = 6.4, contact time = 24 hr)

According to Klimeski et al. (2012), most previous studies have focused on the study of the phosphate sorption at extremely high phosphate concentrations. In this study, the phosphate concentration was 10 mg/L. In spite of the difference in the phosphate levels, the phosphate removal via ashes presented the same removal pattern. For example, Pengthamkeerati et al. (2008) investigated the feasibility of phosphate sorption via fly ash at an initial phosphate concentration of 1000 mg P/L and contact time of 24 hours; the phosphate removal reached the maximum level after 8 hours then became very low for the remaining of the time.

3.4. Phosphate adsorption kinetics onto FBA

A straight line was plotted as a q_t against $t^{1/2}$ as showed in (Fig. 3.b); it is noticeable that the straight line did not pass through all points and the intercept was positive. According to Wu et al. (2009) if the

model of the Intraparticle diffusion is represented as a straight line with no need to pass through the origin, and the intercept is positive; this is an indication that a rapid adsorption occurred within a short time. However, he stated this behavior of adsorption has never been reported before. Therefore, the outcomes of IPD revealed a nonlinear relationship for phosphate adsorption onto FBA.

It is noteworthy that the adsorption kinetics is multiline; it was consisted of three phases as shown in (Fig. 3.a). The steep line in first phase indicates a high and Instantaneous phosphate uptake was occur by FBA. In this initial phase film diffusion process is dominated instead of intraparticle diffusion because the line dose not pass through the origin (Biyan et al., 2009). In the second phase, phosphate adsorption slowdown in comparison with the first phase as a results of diffusion of the phosphate molecules into the pores. While, in the third phase, the adsorption become slower as a results of diffusion that take place from the wide pores into the microspores. Second and third phases are controlled by intraparticle diffusion as Biyan et al (2009) reported the intraparticle diffusion is the preferable model to describe the diffusion in pores of the adsorbents.

The coefficient of determination R^2 in (Table 3) revealed that the absorption data are close to fit the plotted regression line; which is increased the confidence in the outcomes. The value of the K_i decreased drastically when the adsorption process moves from the film diffusion (first phase) into the intraparticle diffusion (second and third phases); indicating that the most phosphate uptake was occurred in the external surface of the FBA.

3.5. Lab-scale filter results

Same experimental conditions in Batch experiments were kept in upflow filter test to avoid any possible interference. The number of runs were determined depending on the outcomes after each run. The experimental work was stopped after five runs because the required time to reach the desirable phosphate removal became long. The capability of phosphate removal over all runs is shown in (Fig. 4).

The results revealed that the first run required less than 160 min for total phosphate removal. In the following runs, the time of the phosphate removal increased as a result of saturation some positions of the FBA surface. In comparison between the first and final run there is a noticeable difference in treatment period; the difference is up to 140 min.



Fig. 3. Intraparticle diffusion model analysis of adsorption kinetics for FBA: (a) IPD as multiline (b) IPD as line

The outcomes indicates that the method of contact of FBA with the aqueous solution of phosphate give better insight on the FBA efficiency for phosphate removal. It is noteworthy the large difference in removal time between the Batch experiment and pumping the phosphate solution into upflow filter. This indicated that the influent contact method has a significant influence on phosphate

removal efficiency.

 Table 3. Intraparticle diffusion model constants for Phosphate adsorption by FBA

Phase	$K_i(mg/(g min^{1/2}))$	Ci mg/g	R ²
One	0.0419	0.030	0.9637
Two	0.0171	0.281	0.9834
Three	0.0037	0.576	0.9044

However, better attention is required for the flow rate value because the variation in flow rate wasn't take in an account in this study. Hashim et al. (2019) and Hashim et al. (2018) revealed that using electrocoagulation technique to reduce the phosphate concentration achieved many advantages such as no chemical additives required, short treatment time and produces less sludge than traditional chemical and biological treatment methods. Phosphate removal by FBA has the same positive aspects for phosphate removal by electrocoagulation technique; moreover, FBA as an active filter media isn't required energy to achieve the phosphate reduction.

3.6. Measuring the PZC of FBA

As shown in (Fig. 5), the initial pH at range from 2 to 8 indicate positive values of ΔpH with a maximum value at pH 3. While, the values of ΔpH at initial pH 10 and 11 indicate negative values. It is noticeable that ΔpH was zero when the initial pH was around 9 for all investigated temperatures. It can be concluded from the findings of the PZC test, the FBA has an amphoteric behaviour (develops positive charge when pH values less than 9 and acts as anion exchanger and develops negative charge over pH over than 9 and acts as cation exchanger).

Therefore, the decision to regenerate the FBA has been implemented by washing the FBA with solution at pH over 9 for desorption of the captured phosphate ions. Determination of the PZC for FBA helps to avoid the random selection of the pH of the washing solution. Consequently, reducing the experiment time, material consumption and providing a scientific basis in regard to the pH selection of the washing solution.



Fig. 4. Phosphate removal via FBA packed in the upflow filter over several operating sessions



Fig. 5. ΔpH versus initial pH of FBA at different temperatures

3.7. Regeneration the efficiency of FBA

According to the results of the PZC, the phosphate desorption from FBA occurred when the pH solution become over 9. Therefore, two solutions were prepared with adjusted pH values at 9.5 and 10 by adding NaOH to deionized water. The decision was taken to test the phosphate desorption efficiency by utilizing washing solutions at these pH values, to avoid any adverse effects which can be happen because of high alkalinity. Therefore, there is no tendency to increase the pH of the washing solution over 10.

At the beginning, the time of washing FBA was determined. Firstly, FBA samples from the fifth run (mass of FBA which was packed in upflow filter) was soaked in washing solution pH 9.5 and another samples in pH 10. The ratio and method of contact between the FBA samples and washing solutions is the same in batch experiment. Each FBA sample was soaked in one of the washing solutions for specific time. The first FBA sample soaked for 5 min, second sample for 10 min and continue until the last sample soaked for 2 hours. Secondly, batch experiments (at previous experimental conditions) same were conducted to investigate the samples' performance for phosphate removal after regenerating them via washing solutions by bringing them in contact with phosphate solution at concentration 10 mg P/L for 24 hours. (Fig. 6) illustrates the phosphate removal efficiency via FBA samples versus washing time of these samples by solutions at pH 9.5 and 10.

It is obvious the removal efficiency is increased with increasing contact time with both solutions. Specifically, the samples are regenerated in the first 30 and 40 min for washing solution pH 10 and 9.5, respectively. Then they are slowed down; for 90 and 80 min the removal efficiency only increased 3.6% and 2.3% for solution pH 10 and 9.5, respectively. Based on these results, washing FBA for around 30 min has been adopted. Therefore, in the continuous washing method the washing solutions were pumped continuously for 30 min at flow rate 1 l/min. While, in the intermittent method the washing solutions were pumped in 7 doses; each dose has a quantity of 1 l and submerges the FBA for 4 min.

After washing the FBA with solution at pH 9.5 and 10, influent at concentration 10 mg P/L was pumped for one run to detect if the FBA is activated again to remove the phosphate effectively. The run time was 160 min to simulate the first run in upflow filter test before regeneration process. The results have been compared with the FBA removal efficiency for the first run before performing the washing process. According to (Hashim et al., 2017) the regeneration efficiency RE% was calculated by using Eq. (5):

$$RE\% = \left(\frac{Co-Creg}{Co}\right) \times 100 \tag{5}$$

where: C_o is initial phosphate concentration 10 mg P/L, and C_{reg} phosphate concentration in the effluent after they treated by the regenerated FBA at the time when complete removal occurred in first run before regeneration process. (Table 4) shows the outcomes of the regeneration efficiency of FBA in comparison to the efficiency of the first run before the regeneration process according to the pH values of solutions and the washing method.

 Table 4. Regeneration efficiency of FBA according to pH and method of washing

pH of washing solution	Washing method	RE%
0.5	Intermittent	90
9.5	Continuous	85
10	Intermittent	95.5
	Continuous	89.7

Washing solution at pH 10 and intermittent washing method has achieved the highest FBA regeneration efficiency. While, the lowest regeneration occurred at pH 9.5 and continuous washing method. It might be the FBA has reached the highest regeneration efficiency at intermittent washing method because this method provides solution stagnation for a period, which allows better contact between solid and liquid phase. The washing solution will contain the eliminated phosphate by FBA. Therefore, study of extract the phosphorus from washing solution is recommended. In addition, the total quantity of washing solution until the efficiency of FBA can't be regenerated is also important to identify.

3.8. Phosphate removal from wastewater sample

The wastewater sample was collected from the secondary treatment of Liverpool wastewater treatment works (LWTW), Sandon Docks, Liverpool, United Kingdom; the concentration of phosphate was 8 mg P/L. The concentration of synthetic phosphate solution was altered to 8 mg P/L to resemble the wastewater concentration. Both solutions were pumped into the lab-scale upflow filter at the same conditions of the previous experiment of upflow filter. The experimental results for both solutions was through the represented plotting phosphate concentration, versus contact time as shown in (Fig. 7). It is noticeable that the FBA removed the phosphate faster from the treated P solution in comparison with wastewater.

The interference of pollutants with the removal mechanism might have an influence on the FBA's

efficiency in removing phosphate from wastewater. While FBA has exhibited better phosphate removal from P solution because the solution is empty from ions except phosphate. The difference between wastewater and P solution in terms of the time needed for phosphate to reach the required limit. The phosphate has reached the concentration of 0.1 mg P/L when the influent is wastewater after 180 min. While, when the P solution is the influent the concentration became 0.1 mg P/L after 150 min. It is observed that the removal pattern for both solutions is approximately the same, at the beginning a large amount of phosphate was removed then a decrease in influent concentration. This is might be due to that the concentration decrease with the passage of time reduces the chance of contact with captured ions onto the FBA surface.

4. Conclusions

FBA presented robust performance to remove the phosphate from the wastewater. Specifically, when the contact between the filter material and influent increased. The low amount of the metal leached from FBA is significant aspect introduce it as a safe and valid phosphate sorbent material.



Fig. 6. Phosphate removal efficiency via FBA samples versus washing time



Fig. 7. Adsorption of phosphate onto FBA for wastewater and synthetic phosphate solutions

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Used a real wastewater sample made the findings more realistic. Especially, the phosphate removal pattern for aqueous solution is approximately same the wastewater sample. However, the interference and effects from wastewater components should be take into consideration. The capability of FBA for phosphate removal investigated according to the time instead of the saturation point as long-term incompatible with economic treatment is considerations. Regeneration the efficiency of FBA based on the suggested washing method gave better insight to increase the lifetime of the filter material.

The main contribution of this work was in the reuse of wastes for phosphate removal so as to enhance the treatment approach of wastes by wastes.

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