Effect of Precursor Ions on the Removal of Phosphate from Low Strength Wastewater by Precipitation

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Abstract: Phosphate removal from wastewater by precipitation isbecoming alternative method to prevent eutrophication in the receiving water bodies and thus recover phosphorus sources. This study aims to understand the effect of precursor ions on phosphate removal from the actual domestic wastewater as well as the characteristic of theprecipitated product. The precipitation of phosphate was observed on actual and synthetic wastewater, and evaluated based on initial pH variation, mixing duration, and the use of quartz sand as seed material. All experiments were conducted in a batch system, at room temperature, and initial pH value ranging from 7.0 to 9.0. It is found that phosphate removal efficiency and its precipitation process were significantly influenced by pH and precursor ions. At the initial pH value of 7.0 to 8.5, phosphate removal was increased during process and reached its removal peak after 150 minutes of reaction on actual and synthetic wastewater, i.e., ranging from 31% to 53% and 28% to 89%, respectively. Meanwhile, at initial pH of 9.0, fast precipitation was achieved after 10 minutes with around 77% and 84% of phosphate removal, then increased slowly to 78% and 92% on actual and synthetic wastewater, respectively, at the end of reaction. An X-ray Diffraction (XRD) analysis indicates that the precipitates were full of amorphous matter. However, Energy-Dispersive X-ray (EDX) test confirms that the dominant species of precipitates were in the form of calcium phosphate.

Keywords: Chemical Precipitation; Mixing;pH; Phosphate removal; Precursor ions.

Introduction

Phosphates are generally contained in domestic wastewater, which can be measured between 10-15 mg/L[1]. This requires further attention, sincewithoutproper treatment, wastewater containing phosphate would createenvironmental issues in water bodies (rivers, lakes, combined drainage and sewerage systems, and ponds), i.e., eutrophication, alga bloom, and thus decreasing water quality. Several phosphate treatment methods have been developed and implemented around the world since 1950s[2], i.e., chemical precipitation with alum or ferric chloride as coagulants[3, 4], enhanced biological phosphorus removal[5], ion exchange[6], and adsorption[7, 8]. The otheralternativemethod is chemical precipitation with initial crystallisation. This process is able to remove phosphate from wastewater and produce some precipitates that can be further recoveredto support resources in phosphate-based industries. Phosphate minerals have been used largely in the production of fertilisers, detergents, animal feeds, fire retardants, pesticides, etc[9]. Therefore, it is considered that phosphate is treated as a resource which can be recovered by applying chemical precipitation.

Crystallisation process consists of three stages, i.e., supersaturation, nucleation, and crystal growth. The performance of every stages are affected by some factors i.e., pH, supersaturation rate, ion composition and

concentration, temperature, precursor ion, mixing intensity, and duration[10-12]. Supersaturation and nucleation stages usually occur within minutes or seconds. Conversely, transformation phase of precipitate towards equilibrium (crystal growth) sometimes goes on a low rate and can only be reached on a long period, sometimes in months[13]. Crystallisation has been successfully used to remove and recover phosphate from municipal wastewater and pure human urine, with around 70 % to 90% removal efficiencies[14-16].

Although chemical precipitation of phosphate has been studied for decades, however, to the authors' best knowledge, the extent of phosphate removal from the actual low strength domestic wastewater, particularly with the presence of precursor ions has not been reported extensively.Therefore,this paper discusses the effect of precursor ions on phosphate removal efficiency from domestic wastewateras well as the characteristic of the recovered phosphate products. The effects of pH, mixing duration, and natural quart sand as seed materialon the precipitation rate were also studied. In addition, a synthetic wastewater was also used to mimic actual wastewater in order to clearly understand the effect of precursor ions.

Experimental

Sample preparation

Actual wastewater samples were obtained from the influent of the activated sludge unit atlocal community Wastewater Treatment Plant (WWTP) in Surabaya, Indonesia. This WWTP collects wastewater from domestic activities that close to hospital service area. Prior to the experiments, it was analysed and characterised as shown in Table 1.

Table 1. Characteristic of the Actual Low Strength Wastewater

Parameter	Concentration (mg/L)	Parameter	Concentration (mg/L)
pH[a]	7.7	Mg^{2+}	100.00
PO_4-P	13.90	HCO_3^-	250.00
NH_4^+	71.64	Cl^-	124.00
Ca^{2+}	121.40	SO_4^{2-}	39.20

[a] Dimensionless.

Synthetic wastewater was prepared by adding 250 ml of 15.92 mmol/L NH_4Cl; 250 mL of 12.42 mmol/L $CaCl_2.2H_2O$; and 250 ml of 16.67 mmol/L $MgCl_2$ to 250 mLof 1.79 mmol/L KH_2PO_4. The solution was thenstirredfor 30 seconds.

Preparation of Seed Material

Seed material was applied to prevent spontaneous nucleation, control crystal size distribution, and obtain enhanced precipitation process as well as phosphate removal[17]. In this study, natural quartz sand was applied as seed material to simulate actual condition of wastewater. The seed material was then crushed into small particles and sieved into 300 – 600 µm standard sieves. This size was selected based on a previous research performed by Kubota, et al.[18], suggesting an ideal crystal growth with the addition of 327.5 - 550 µm seed material into the reactor. The quartz sand was acid washed using 50% hydrochloric acid and rinsed using demineralised water several times, which was then followed by oven dried at 105°C for 24 hours.

Batch Experiments

The experimental set-up is shown in Figure1. In each experiment, 1 L of the each type of wastewater and 15 mg of seed material (quartz sand) were placed in a beaker glass, and stirred in a jar test apparatus for approximately 2.5 hours at 150 rpm. All experiments were accomplished at room temperature and in five different initial pH variants (i.e., 7.0; 7.5; 8.0; 8.5, and 9.0). Samples were prepared on the same day of experiment. Sodium hydroxide (NaOH) 1 M or hydrochloric acid (HCl) 1 M was used for adjustment of initialpH. An amount of 10 mL sample was taken at 10, 30, 60, 90, 120, and 150 minutes of experiment and filtered through a 0.22 µm membrane filter (Millipore). The pH of solution was measured continuously using

pH meter (Lutron YK-2005WA). Since the process is pH sensitive, few amounts of NaOH 1 M or HCl 1 M were added to maintain the desired pH level. At the end of the experiments, the solutions were allowed to settle down for at least 3 hours before precipitate separation. The precipitate samples were then drained from the solution and filtered by a 0.45 µm membrane filter (Sartorius Stedim). Finally, it was dried in room temperature for approximately 4-6 hours before further analysis.
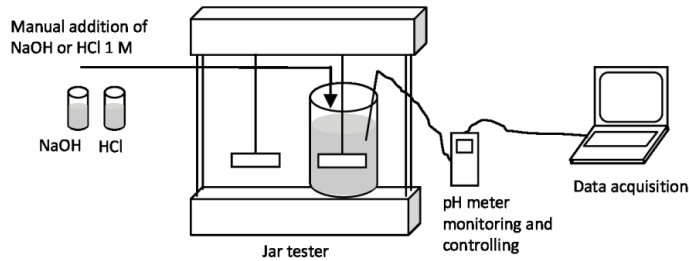
Figure1. Experimental set-up

Analytical method

Phosphate concentration was determined based on Stannous Chloride ($SnCl_2$) method and measured by a spectrophotometer (Genesys 20, Thermo Scientific) at particular 690 nm wavelength. The efficiency of phosphate was calculated by means of:

$$\alpha\ (t) = (C_o - C_t)/C_t \text{ x } 100 \hspace{3cm} (1)$$

where C_t = phosphate concentration on t period, and C_o = the initial phosphate concentration in the reactor. The concentration of Ca^{2+} and Mg^{2+} were carried out using EDTA titrimetric method (3500-Ca and 3500-Mg)[19]. To understand the possibility character of recovered crystal, the precipitate sample was analysed using X-ray Diffraction (XRD, Phillips) and scanning electron microscopy (SEM, Zeiss EVO MA10) equipped with Energy-Dispersive X-ray Analysis (EDX, Bruker).

Results & Discussion

**Table 2. Overall results of phosphate removal from Actual and Synthetic Wastewater**

| Type of Wastewater	Duration (minute)	Phosphate Removal Efficiency (%)				
		pH				
		7,0	7,5	8,0	8,5	9,0
Actual	0	0,00	0,00	0,00	0,00	0,00
	10	28,70	26,80	24,17	45,14	77,38
	30	30,01	36,18	30,09	50,41	78,37
	60	28,78	31,49	32,07	51,81	77,63
	90	27,54	27,63	34,21	55,42	76,97
	120	30,34	26,23	41,85	53,37	77,79
	150	31,57	28,61	45,47	53,70	78,70
Synthetic	0	0,00	0,00	0,00	0,00	0,00
	10	12,46	16,72	65,61	85,26	84,85
	30	17,37	35,72	76,74	86,82	87,96
	60	20,08	37,11	78,22	88,29	90,42
	90	23,84	41,78	80,18	88,70	91,40
	120	28,02	45,54	82,07	89,60	92,79
	150	28,18	47,67	82,31	89,76	92,88

The experiment was started by adjusting the pH of each sample to 7.0; 7.5; 8.0; 8.5; and 9.0. During mixing, the supersaturation in the solution was increased, and nuclei of precipitates started to form. This formation of precipitates can be detected based on visual colour changes of the solution (i.e, from clear to murky). Each growth of precipitates leads to the release of proton (H^+) so that dropping the pH solution. Thus, the addition of NaOH or HCl was necessary to maintain at particular pH level. Overall results of phosphate removal are illustrated in Table 2.

Effect of pH on phosphate removal

Figure2 shows the effect of pH value on phosphate removal from actual and synthetic wastewater. It is noted that pH significantly affects the removal efficiency of phosphate. In the case of actual wastewater, it can be seen that at pH 7.0, the percentage of phosphate removal was around 31%. However, when the pH levels were adjusted to 7.5, 8.0, 8.5, and 9.0, the removal efficiency wasincreasedto 28%; 45%; 53%, and 78%, respectively. Similarly, the phosphate removal efficiency on synthetic wastewater were rose significantly to 28%, 47%, 82%, 89%, and 92% as pH level increases from 7.0 to 9.0 at interval of 0.5.

Moreover, the pH level also influences the phosphate removal inside the solution. It was also recorded that phosphate removal at pH 8.5 and 9.0 were higher than at pH 7.0, 7.5, and 8.0. Within the first 10 minutes of reaction, the phosphate removal on actual wastewater was up to 45% and 77%, at pH 8.5 and 9.0, respectively. Meanwhile, the removal of phosphate on synthetic wastewater at pH 8.5 and 9.0 was around 85% and 84%, respectively.
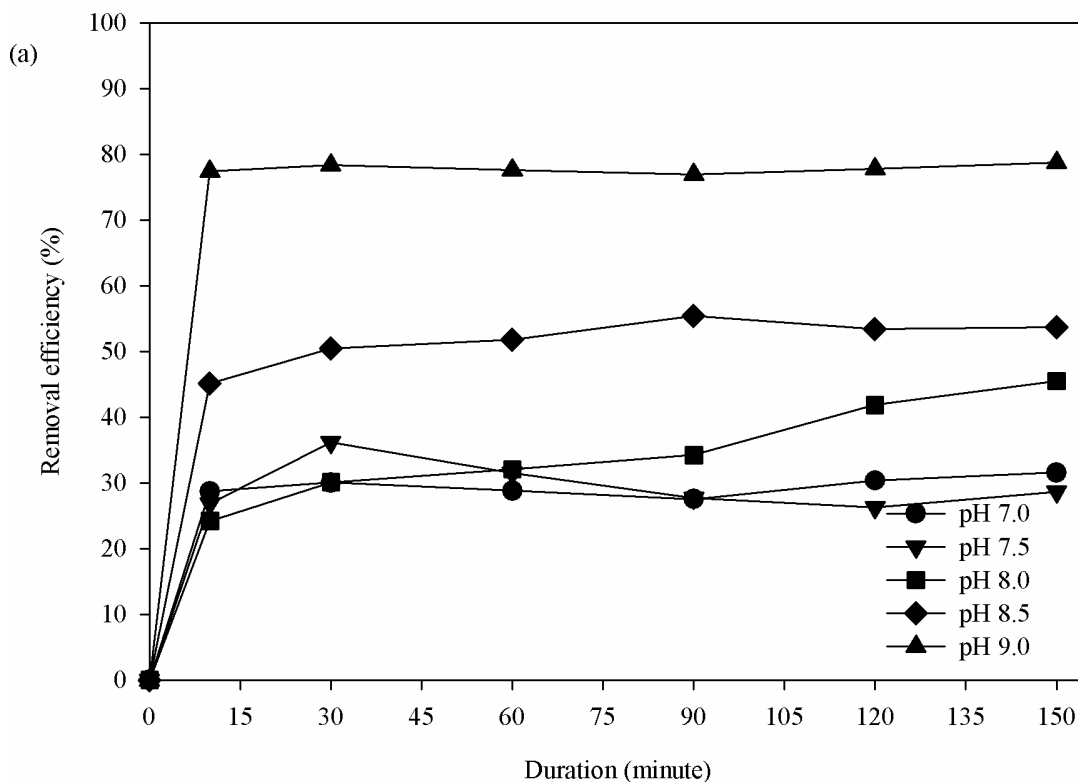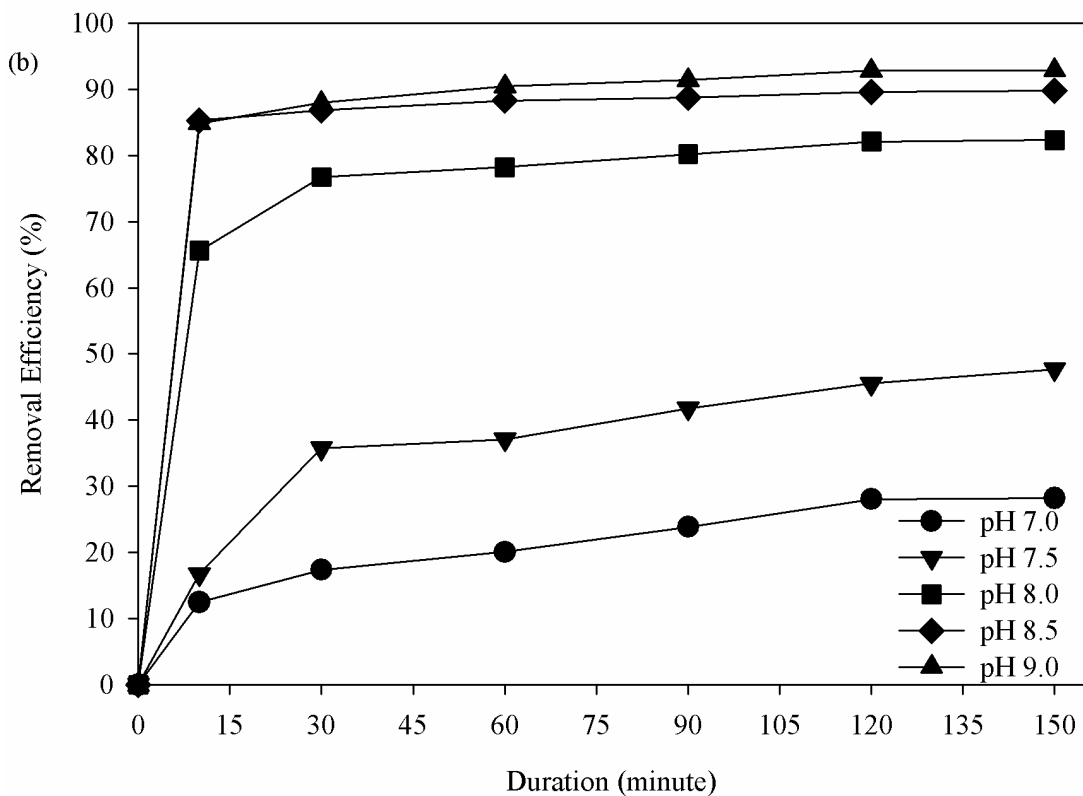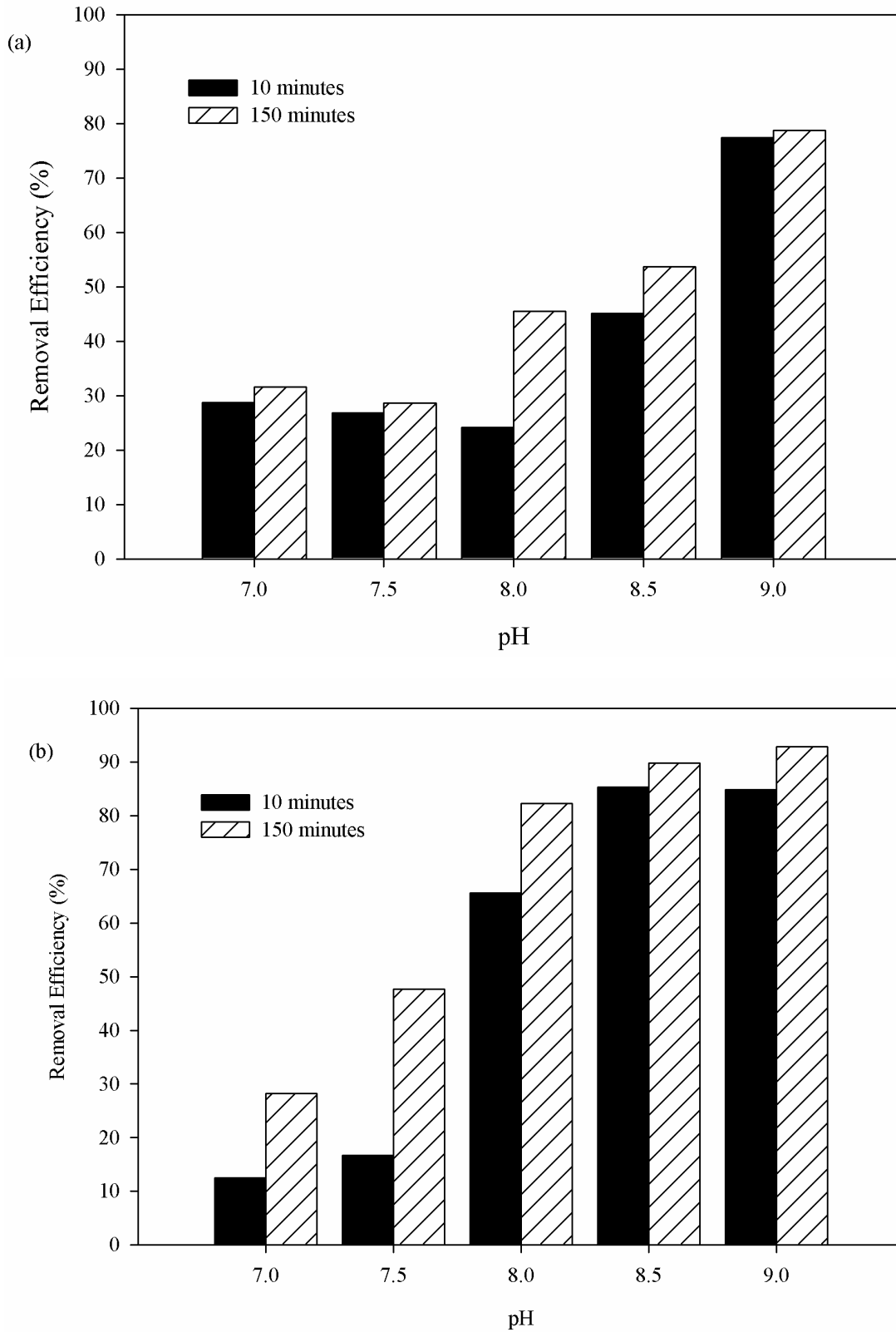
Figure2. Effect of pH value on phosphate removal (a) Actual Wastewater; (b) Synthetic Wastewater

It implies that phosphate precipitation more likely occurs on higher pH level. As stated on the previous research, pH is the key aspect in chemical precipitation, which control the rate and the time of precipitation[12]. The change of pH level correlates with solubility and supersaturation of the solution. When pH within solution increased, it promotes the supersaturation process and enhanced the growth of precipitates.

Effect of mixing duration on phosphate removal

The effect of mixing duration on phosphate removal can be seen in Figure 3. At pH 7.0, 7.5, 8.0, 8.5, and 9.0, the phosphate removal efficiency on actual wastewater were increased gradually from 28% to 31%, 26% to 38%, 24% to 45%, 45% to 53%, and 77% to 78%, respectively, in the first 10 minutes to 150 minutes of experiments. Likewise, the increasing trends were also reported on synthetic wastewater. It can be implied that by prolonging mixing duration from 10 to 150 minutes, the compounds will have more time to react, bond, form nuclei of precipitates, and thus enhance the removal of phosphate. The effect of mixing duration hasalso been reported on a previous research. It was suggested that the removal phosphate were profusely greater when mixing intensity (G) and mixing duration (td) were increased[20].

Figure3. Effect of mixing duration on phosphate removal (a) Actual Wastewater; (b) Synthetic Wastewater

Effect of Precursor Ions on Phosphate Removal

According to previous researchers, precursor ions may lengthen induction time and inhibit the nucleation of specific precipitate[21, 22]. These precursor ions may include calcium, magnesium, carbonate, or bicarbonate ions. Some previous studies have concluded thatthe presence of precursor ions could hinder the growth of specific precipitates,i.e., calcium ions influenced the formation and purity of struvite[23, 24], magnesium ions inhibit precipitation and the purity of calcium phosphate, carbonate or bicarbonate ions reduced the precipitation of phosphate[25].

In this study, the effect of precursor ions can be observed from phosphate removal efficiency on actual and synthetic wastewater (Figure4). Compared to synthetic wastewater, the presence of high concentration of precursor ions, i.e., bicarbonate, on actual wastewater have reduced the phosphate removal by 14 to 37%. The interference of bicarbonate ions on actual wastewater were detected on pH 7.0 and 7.5. At this particular pH levels, supersaturationstage was very slow. In addition, the changing of solution visual colour during mixing, which indicates the growth of precipitates, were almost none. Precipitation of phosphate was hindered as bicarbonate and phosphate compete for calcium or magnesium ions. By the end of experiments, the removal of phosphate at pH 7.0 and 7.5 were just around 31% and 28%, respectively. According to previous studies, the effect of bicarbonate ions can be minimised by applying degassifier upon experiment[14, 26].
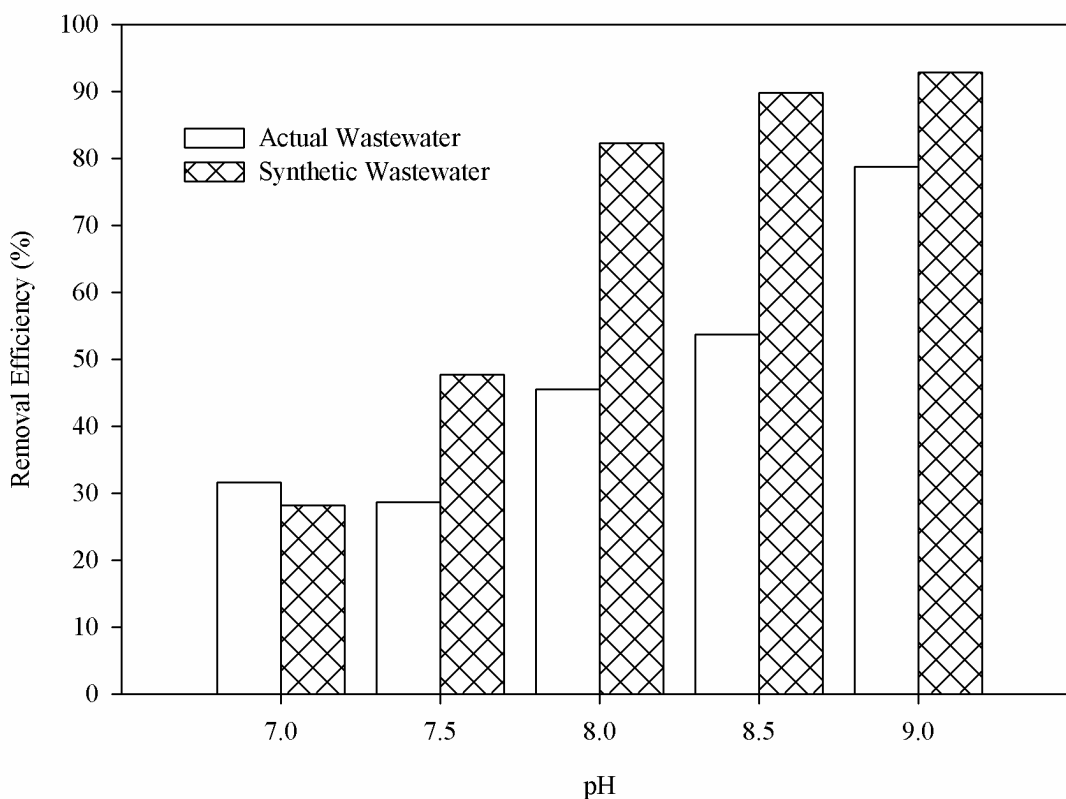
Figure4. Effect of Precursor Ions on Phosphate Removal

Recovered precipitates

To determine the species of recovered precipitates and investigate the effect of Ca^{2+} and Mg^{2+}, dried precipitates from pH 9.0 were analysedusing XRD and SEM-EDX. As presented in Figure5, XRD pattern generated on both samples shows noisy background with some slightly equal peak size. It was difficult to distinguish between noise and specific species of precipitates, which may indicate potential forming of surface on the newly formed precipitate[22].
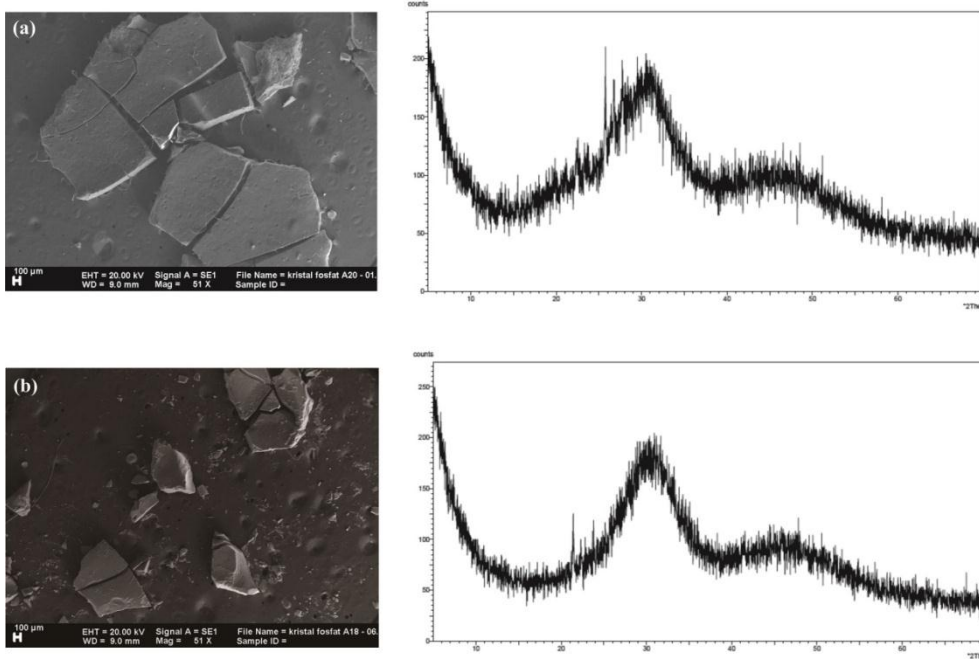
Figure5.SEM and XRD pattern of precipitate (a) Actual wastewater, (b) Synthetic wastewater

In order to clarify the composition of amorphous matter, SEM-EDX analysis was conducted. It was noticed that both EDX test on the local specific area of SEM images showed prominent peaks of phosphorus, calcium, and oxygen (Figure6), which confirming the calcium phosphate compound. These results clarifies that nucleation of calcium phosphate were easier than magnesium phosphate. Moreover, some traces of magnesium which were found in the precipitates also indicates that the purity of calcium phosphate is disrupted. A previous study by Abbona and Franchini-Angela[13],confirms that the presence of magnesium could block or delay the hydroxyapatite (HAP) formation and thus increase the nucleation of more unstable calcium phosphate phase such as whitlockite (Mg-TCP) and amorphous calcium phosphate (ACP).
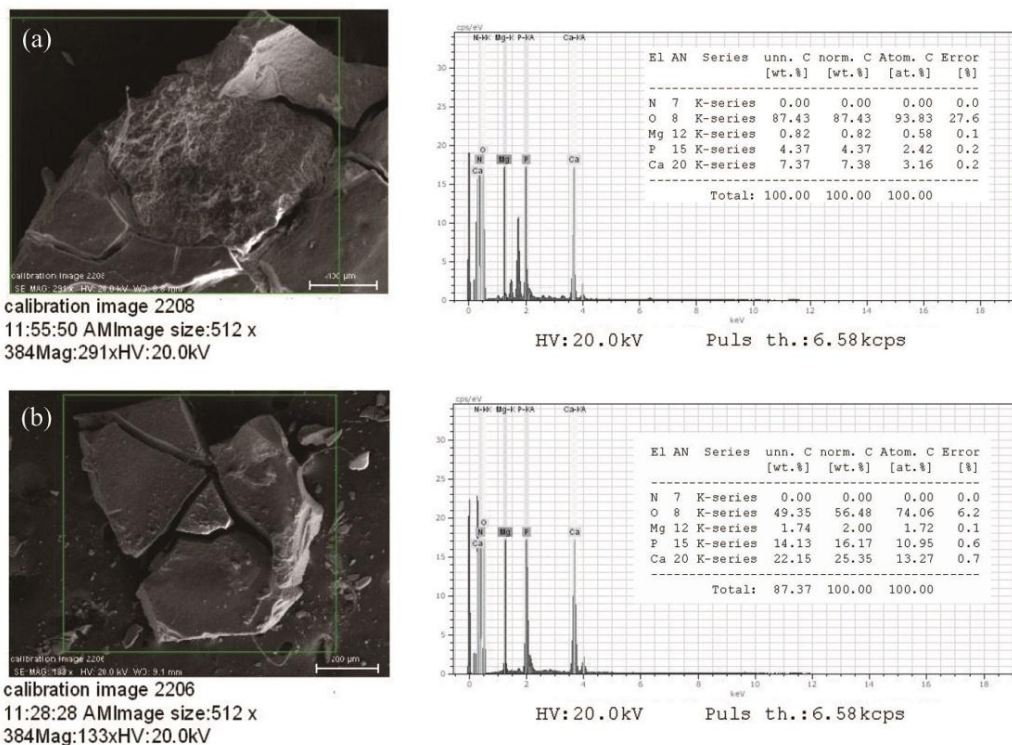

Figure6. SEM and EDX image of precipitates (a) Actual wastewater, (b) Synthetic wastewater

Conclusions

The removal of phosphate highly depends on pH, wastewater characteristic and the presence of precursor ions. It is apparent that phosphateremoval was highly achieved at higher pH level. Up to 78% and 92% of phosphate removal were achieved at pH 9.0 on actual and synthetic wastewater, respectively. Meanwhile, it is also noted that at higher pH, i.e., pH 8.5 to 9.0, fast precipitation were likely to occur in the first 10 minutes of reaction. As the pH within solution is increased, it induces supersaturation process and promotes the growth of precipitates. While the nuclei of precipitates is being formed, hydrogen ions are released, lowering pH level. At this point, the addition of NaOH is necessary to maintain pH to the desired level, enhance supersaturation rate, precipitation process, and thus improve the removal percentages of phosphate.

Although the effect of mixing duration was less significant on the removal of phosphate,it was still needed to enhance the transfer mass of ions within solution and increase phosphate removal efficiency. On the other hand, precursor ions contained in the wastewater may reduce the precipitation of phosphate by hinder formation of calcium phosphate or magnesium phosphate and create impurities within the specific spesies of precipitates.

Acknowledgements

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