PHOSPHATE REMOVAL AND RECOVERY AS BRUSHITE BY UNSEEDED GRANULATION IN A FLUIDIZED-BED REACTOR

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ABSTRACT

The effects of influent phosphate pH, Ca^{+2}:PO_4^{-3} molar ratio, and additions of commonly encountered ions in a thin film transistor-liquid crystal display (TFT-LCD) manufacturing plants such as fluoride (F^-), sulfate (SO_4^{-2}), and nitrate (NO_3^-) in the synthetic wastewater were investigated to maximize phosphate granulations and phosphate removal in an unseeded granulation in a fluidized-bed reactor. The solid phosphate granules (~1.00mm) collected after the 60 h reaction time were identified as brushite ($CaHPO_4 \cdot 2H_2O$) by XRD. Experimental results showed that the highest phosphate removal of 97.58% was obtained at influent phosphate pH of 9 and Ca^{+2}:PO_4^{-3} molar ratio of 1.4:1.0. The addition of inorganic ions resulted in a slight decrease in phosphate removal of up to 5.33%. Effective granulation and high removal rates show that unseeded granulation of calcium phosphate using Fluidized-Bed Reactor (FBR) could provide a foundation for phosphate removal and regeneration.

Keywords: Fluidized-bed reactor, brushite, calcium phosphate, phosphate removal, granulation, crystallization, TFT-LCD

1. Introduction

Nutrient enrichment of surface waters caused by phosphorus and nitrogen brought about by human activity and commonly referred to as cultural eutrophication has become the primary water quality issue in most parts of the world. Excessive discharge of phosphorus into water bodies leads to a series of undesirable effects including oxygen depletion, fish kills, algal blooms, decrease in water transparency, filter clogging in water treatment plants, reduction in the aesthetic value of the water body and an increase in macrophyte vegetation (Smith & Schindler, 2009; Kuo et. al., 2006).

One of the major anthropogenic sources of phosphorus is the manufacturing industry for thin film transistor-liquid crystal display panels (TFT-LCD) which generates millions of tons of wastewater annually (Veriansyah et. al., 2005). In the past decade, Taiwan was the largest manufacturer of TFT-LCD displays used in notebooks, mobile phones, desktop monitors and other consumer electronics (Hung et. al., 2012). According to the 2007 EPA-96-G104-02-222 report, the concentration of phosphorus as phosphate (PO_4^{-3}) in the wastewater of the photonics industries in Taiwan range from 0.33 to 1505.44 mg/L phosphate (Gunawan et. al., 2010). This level of phosphate concentration is high and poses a serious threat to environmental health and sustainability.

Phosphorus is a non-renewable resource and the demand for phosphorus is predicted to increase by 50-100% by 2050 due to the increase of global demand for food and changing diets. Studies claim that at current rates of extraction, phosphate rocks will be depleted in the next 50 to 100 years (Cordell et. al, 2009), underlining the importance of phosphate recovery technologies. Current phosphate removal technologies include chemical precipitation, biological phosphorus removal, adsorption, tertiary filtration, and crystallization (Morse et. al, 1998). Among these, the most promising is crystallization by fluidized-bed reactor (FBR). Compared to conventional precipitation, FBR crystallization reduces sludge volume, eliminates dewatering cost, produces more marketable end-products, and reduces the operating and maintenance costs (Morse et. al, 1998; Tai et. al, 2006).

In this study, phosphate granulation and removal as brushite ($CaHPO_4 \cdot 2H_2O$) through unseeded granulation in a fluidized-bed reactor was investigated to determine its applicability in treating TFT-LCD wastewater.

2. Fluidized-bed reactor and operating conditions

Conventional processes for the treatment of phosphorus through precipitation include coagulation, flocculation, sludge and water separation, and sludge dewatering. These processes generate huge amounts of water-rich sludge that need to be treated and dewatered prior to disposal. The waste sludge produced still contains a large amount of water and reuse of phosphate is not economically attractive (Piekema et. al., 2001). An alternative method is to apply crystallization in a fluidized-bed reactor (FBR) as shown in Figure 1. In the FBR, the coagulation, flocculation, separation, and dewatering processes are combined into one by the crystallization/ granulation process. The granulation in the FBR process involves three main steps: formation of supersaturation, nucleation, and crystal growth.

In this study, the concentration of PO_4^{-3} used was 1500 ppm. For the effect of adding commonly encountered ions in TFT-LCD plants, 7 ppm F^-, 550 ppm SO_4^{-2}, and 70 ppm NO_3^- were used. These assigned values were based on the typical maximum concentration range of TFT-LCD / photonics industry wastewater (Gunawan et. al., 2010).

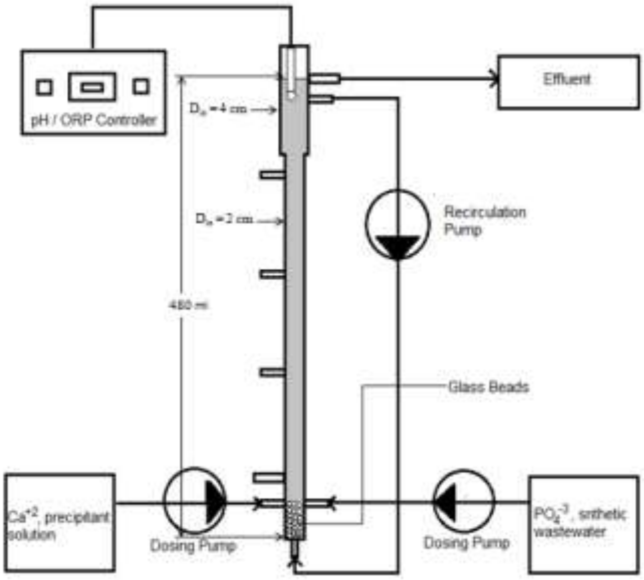

Figure 1: Fluidized-bed reactor set-up

The Ca^{+2} concentrations in the precipitant solution were 317, 380 and 443 ppm for $Ca^{+2}:PO_4^{-3}$ Molar ratio of 1.0:1.0, 1.2:1.0 and 1.4:1.0, respectively. The influent feed flow rates were fixed at 20 mL/min while the recirculation rate was adjusted from 40 – 120 mL/min. On the other hand, the concentrations of Fluoride, Sulfate and Nitrate ions in the effluent were not monitored because this study was focused mainly in the phosphate concentration. Hence, measurement of other ions in the effluent is highly recommended to the future researchers.

3. Calculations performed

The percent granulation, η, gives the ratio of the amount of phosphates converted into solid granules to the influent phosphate concentration, P_{in}. The effluent phosphate concentration, P_{out}, is the orthophosphate concentration in the unfiltered samples and is the sum of the fines (suspended) and dissolved phosphates. Phosphate removal and phosphate granulation were computed using the equations found in Figure 2.

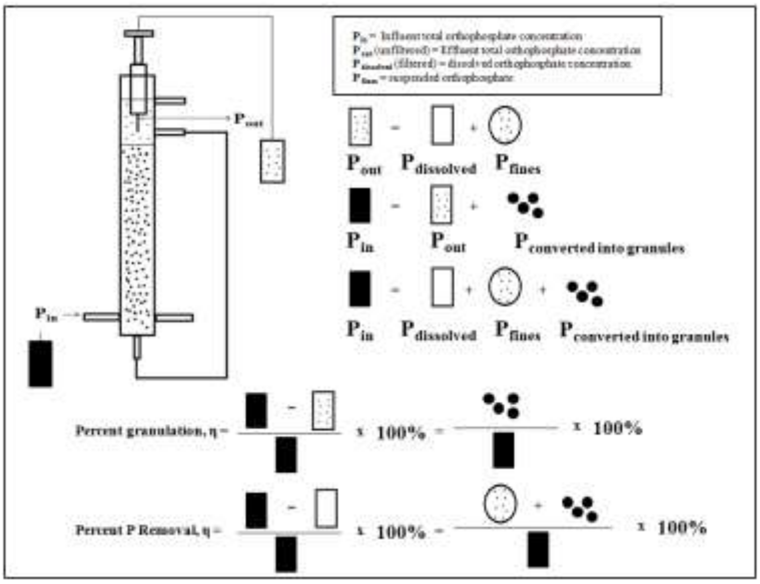

Figure 2: Fluidized-Bed Reactor Set-up with representation of phosphate granulation and phosphate removal

4. Results

4.1. Effect of Influent pH

The effect of influent phosphate pH of 6, 7, and 9 to phosphate granulation and phosphate removal are shown in Fig. 3. During the 60-h run, phosphate granulation and removal at pH 6, 7, and 9 was increased showing that as the liquid phosphates underwent granulation, the amount of phosphates exiting the reactor was lessened. Since the source of phosphate in the prepared synthetic wastewater was sodium dihydrogen phosphate (NaH_2PO_4), increasing the pH added hydroxide ions into the solution and shifted the equilibrium to the left of Equation 1, thereby increasing percent removal because more HPO_4^{-2} and PO_4^{-3} became available to react with Ca^{+2} ions

$$PO_4^{-3} \overset{H^+}{\leftrightarrow} HPO_4^{-2} \overset{H^+}{\leftrightarrow} H_2PO_4^{-} \overset{H^+}{\leftrightarrow} H_3PO_4 \qquad (1)$$

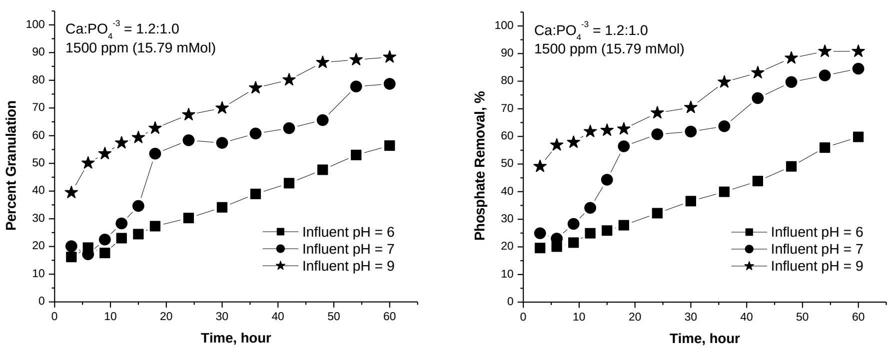

Figure 3: Effect of Varying Influent pH on Phosphate Granulation and Removal

4.2. Effect of Ca:PO_4^{-3} Molar Ratio

Fig. 4 shows the effect of Ca:PO_4^{-3} molar ratio on phosphate granulation and removal. The lowest phosphate granulation and removal was attained at Ca:PO_4^{-3} = 1.0:1.0 while the highest value was attained at Ca:PO_4^{-3} = 1.4:1.0. These values showed that increasing the Ca:PO_4^{-3}

molar ratio increased both phosphate granulation and removal because more Ca^{+2} ions are available to react with phosphate ions.

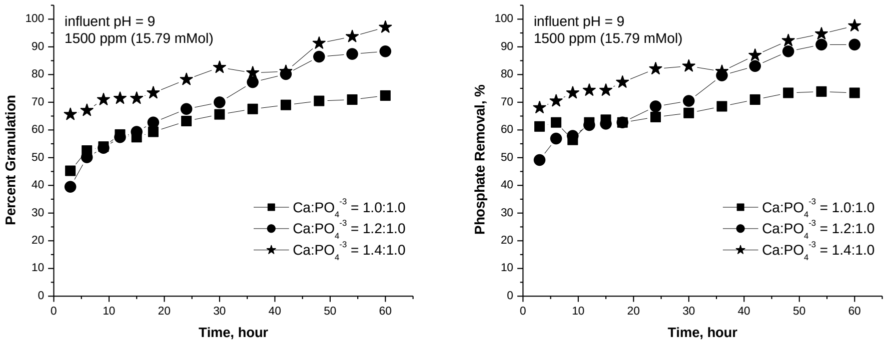

Figure 4: Effect of Varying Molar Ratio on Phosphate Granulation and Removal

4.3. Effect of Adding Fluoride (F^-), Sulfate (SO_4^{-2}) and nitrate (NO_3^-) ions

Six runs (see Figure 5) were conducted to observe the effect of adding F^-, NO_3^-, and SO_4^{-2} ions into the system. Adding these commonly encountered ions found in the TFT-LCD / photonics industry would approximate the effectivity of using Ca^{+2} as precipitant on actual wastewater to granulate calcium phosphates. The presence of ions slightly decreased phosphate granulations of the systems from 0 to 7.75% and also phosphate removals from 2.42% to 5.33% with respect to the runs with phosphate ions only. The slight decrease in phosphate granulation and removal are attributed to the increase of supersaturation due to the presence of F^-, NO_3^-, and SO_4^{-2} and the subsequent increase in the bulk density inside the reactor. The solid phosphate granules were identified as brushite ($CaHPO_4 \cdot 2H_2O$) by XRD and SEM.

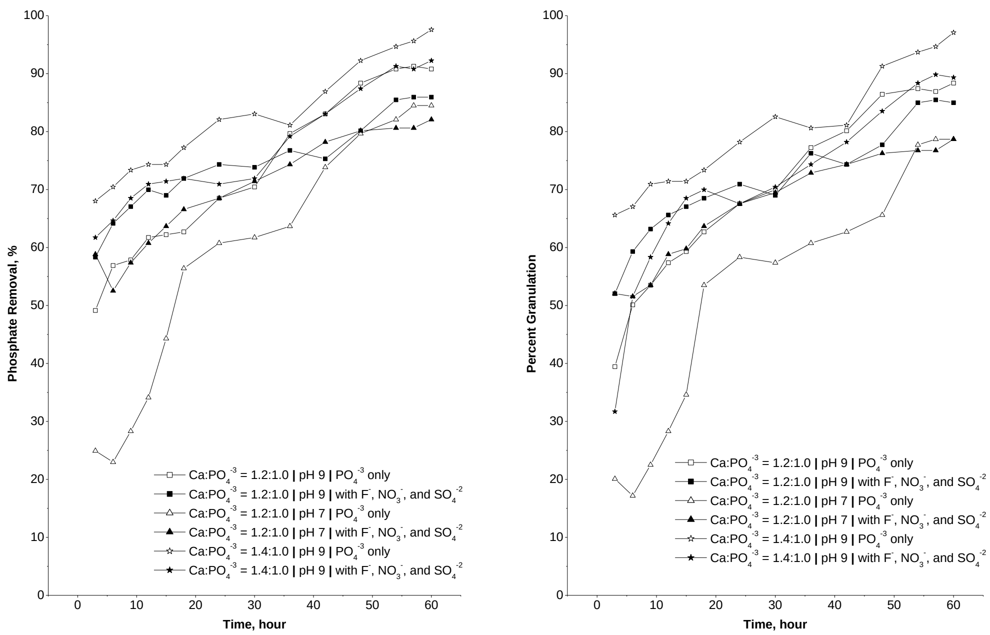

Figure 5: Effect of Varying Molar Ratio on Phosphate Granulation and Removal

5. Conclusions

This study has shown that phosphate could be removed and recovered as brushite via unseeded crystallization in a fluidized-bed reactor. Phosphate granulation and removal increases as the pH of the synthetic PO_4^{-3} wastewater increases from pH 6 to 9 as well as Ca^{+2}:PO_4^{-3} molar ratio from 1.0:1.0 to 1.4:1.0. Maximum phosphate granulation of 97.09% and phosphate removal of 97.58 was attained using an influent phosphate pH of 9, and $Ca:PO_4^{-3}$ molar ratio of 1.4:1.0. XRD data proved that the collected granules from the best experimental run with the addition of F^-, NO_3^-, and SO_4^{-2} ions are of plate-like dicalcium phosphate dihydrate (DCPD) or brushite.

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