Some Guidelines for pH Control of a P-recovery Pellet Reactor

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Abstract

Emphasis in recent years has been focused on improving processes which lead to enhanced phosphate recovery. This paper studies the precipitation features of calcium phosphate in a fluidized bed reactor in a concentration range between 4 and 50mg/L and establishes the conditions for optimum phosphate removal efficiency. A two level modeling methodology is proposed and used for the determination of a control strategy of the unit pilot.

INTRODUCTION

Phosphorus can be found under various chemical forms in urban wastewater, which represents about 30 to 50% of the total refusal of P: insoluble or dissolved organic phosphorus, orthophosphates (until 70% sometimes) and condensed inorganic phosphates. In France, the average concentration of phosphorus in domestic wastewater is within the range 15-25 mg / l, which may strongly vary from day to day, even during day. The discharge of phosphorus in the aqueous natural environment leads to an excessive development of algae and, generally to a pH increase, thus corresponding to eutrophication. Consequently, the phosphorus reduction in the rivers is considered as a key factor of the fight against pollution. The principal legislative tool in Europe for fighting against eutrophication is the EC Urban Waste Water Treatment Directive (271/91/EEC). This action came into force in 1991 and enabled waterbodies to be classified as Sensitive Areas if they display symptoms of eutrophication.

In this context, the precipitation of phosphate salts is a solution used as a P-recovery process for effluents with a low concentration in inorganic phosphorus. In the last years, several works have been devoted to calcium phosphate precipitation in the so-called pellet reactor (Hirasawa and Toya, 1990, Morse et al., 1998, Seckler et al., 1996).

In this paper, calcium phosphate precipitation is investigated in a fluidized bed reactor in a concentration range between 4 and 5 mg.L^{-1}. More precisely, the objective of this paper is to propose some guidelines for pH control of the reactor. First, the pilot unit used in this study is presented and a discussion is proposed from the observed experimental results to propose a feasible process control variable. The principles of a two modeling approach stage are presented and a possible regulation loop is finally proposed.

PROCESS DESCRIPTION

The process is based on calcium phosphate precipitation obtained by mixing a phosphate solution (orthophosphoric acid and demineralized water) with calcium ions and a base. More precisely, it involves a fluidized bed of sand continuously fed with two aqueous solutions,

$CaCl_2$ and KOH (Figure 1). Calcium phosphate precipitates upon the surface of sand grains. Simultaneously, small particles, i.e., “fines”, leave the bed with the remaining phosphate not recovered in the reactor. A layer of fines which has agglomerated is observed at the upper zone of the fluidized bed. The main experimental observations are the following ones: at high velocity, fines leave the fluidized bed while at lower values, a layer of fines is systematically observed at the upper level of the bed.

In both cases, two regimes are identified. First, a steady state regime is observed for the liquid phase leaving the bed. Measurements of the P concentration at the outlet zone show that constant values are rapidly obtained (20 min for all the runs performed). Second, a steady state regime (as measured by the fluidized bed height) is also observed in the bed after a maximum of 3 hours for all the experimental runs. More precisely, this regime is assumed to be reached when the P concentration of both the recovered sand grains and of the fine layer exhibits a constant value. These experimental observations lead to define two performance indicators of the reactor for the process.

The phosphate removal efficiency (η) of the reactor and the conversion of phosphate from the liquid to the solid phase (X) are defined respectively as:

$$\eta = \frac{w_{p,in} - w_{p,tot}}{w_{p,in}} \tag{1}$$

$$X = \frac{w_{p,in} - w_{p,sol}}{w_{p,in}} \tag{2}$$

where $\omega_{p,in}$ represents the flow rate of the phosphorus component at reactor inlet, $\omega_{p,tot}$ gives the total flow rate of phosphorus both as dissolved and as fines at reactor outlet and $\omega_{p,sol}$ is the flow rate of dissolved P at the reactor top outlet.

Both total and dissolved concentrations of phosphorus, pH and temperature are measured at the outlet stream. The temperature is kept constant during the experimental runs. In order to measure the dissolved P concentrations, the upper outlet stream is filtered immediately over a 0.45 μm filter and analyzed. Another sample is pre-treated with HCl in order to dissolve any suspended solid and total phosphorus amount is measured. If η_{agg} is the agglomeration rate, that is, the ratio between fines in the bed and in the outlet stream, the following relation can be deduced:

$$\eta = \eta_{agg} X \tag{3}$$

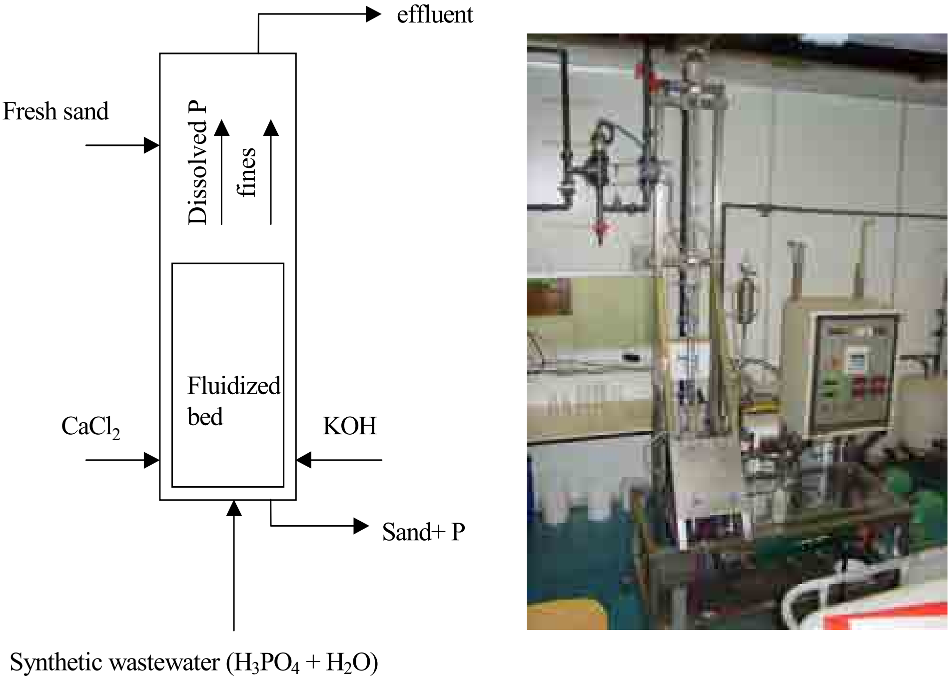

Figure 1: Schematic representation of the pellet reactor

The phosphate covered grains are removed from the bottom of the bed and replaced intermittently by fresh sand grains. In most studies reported in the literature (Morse et al., 1998), the phosphate removal efficiency of a single pass reactor, even at industrial scale, has an order of magnitude of only 50%. Let us recall that the pellet reactor efficiency depends not only on pH but also on the hydrodynamical conditions (Montastruc et al., 2002). Moreover, the conversion rate depends on calcium and phosphate ion concentrations, as well as on supersaturation, ionic strength, temperature, ion types, pH but also on time (solid-solid transformation) as noted in the literature (Baronne and Nancollas, 1977), (Van Kemenade and de Bruyn, 1987), (Boskey and Posner, 1973).

Figure 2 illustrates the evolution of both efficiency and conversion rate vs. pH.

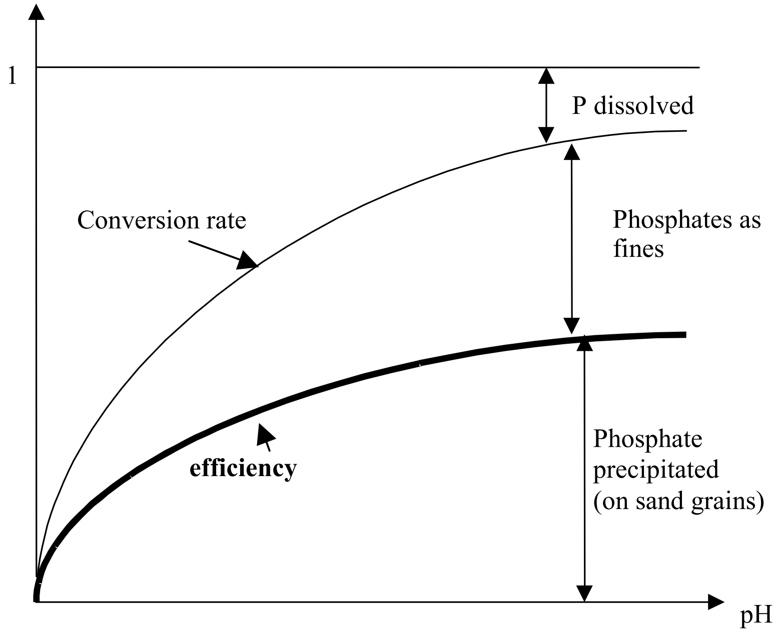

Figure 2: Conversion rate and efficiency vs. pH

The pilot reactor developed in this investigation can treat synthetic wastewater with flowrates of 0.1 m^3/h. Conductivity, pH and phosphate concentrations are measured at effluent outlet. Figure 3 gives a detailed representation of the process with its typical features (see Table 1).

Table 1: Apparatus characteristics

Equipment item	**Main features**	**Volume, geometry and flow rate**
Feed tank (solution to be treated)	Polyethylene	1 m^3
Feed tank alimentation ($CaCl_2$, KOH)	Polyethylene	60 l
Pomp P1	Volumetric with frequency variation 0-100Hz	0-130 l/h
Pomp P2	Gearing volumetric with frequency dimmer switch 0-50Hz	2,5-17 l/h
Pomp P3	Gearing volumetric with frequency dimmer switch 0-50Hz	2,5-17 l/h
Column	glass	H= 2 m, diameter = 5 cm

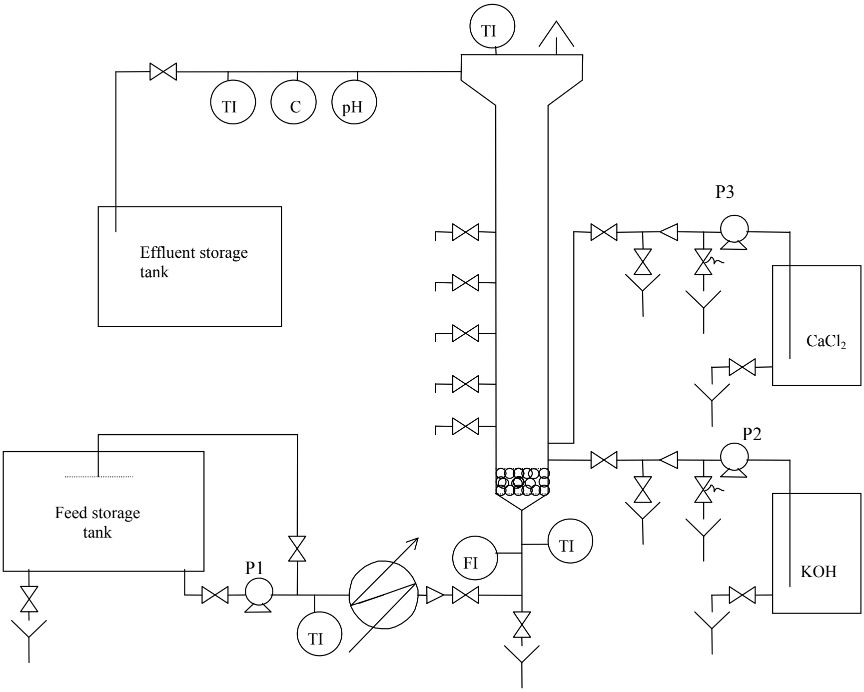

Figure 3: Detailed representation of the pilot unit

PROCESS CONTROL VARIABLES

Preliminary experiments showed pH is a key variable for process control. Another alternative is to use conductivity. To confirm this choice, experiments were performed for different values of Ca/P molar ratio and P concentrations at effluent inlet.

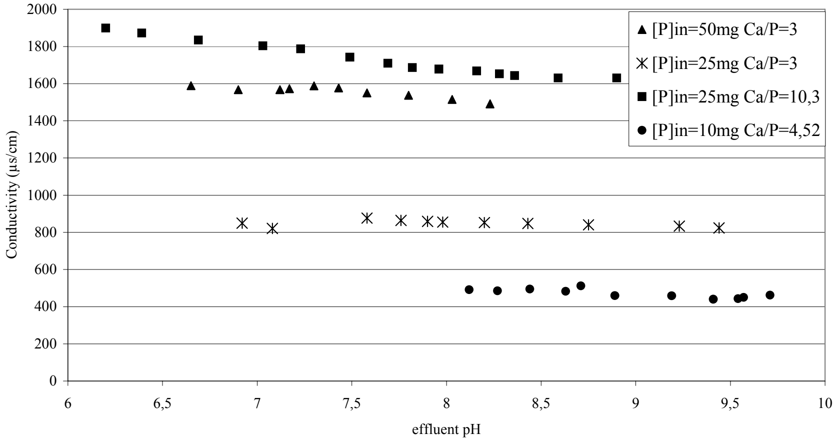

Figure 4: Conductivity vs. Effluent pH

Figure 4 presents the evolution of conductivity in function of effluent pH for different initial concentrations. For a fixed initial concentration value, the experimental conductivity decreases too slightly vs. pH value to make a systematic regulation practice. Fora fixed pH value, a decrease in the initial concentration also leads to a decrease in conductivity. Besides, the conductivity is clearly influenced by the presence of all ions or soluble salts. These reasons discard the choice of conductivity as a control process variable.

MODEL PRINCIPLES

Two important parameters to quantify the process are namely conversion rate and efficiency. A methodology was developed to compute these two indicators, as illustrated in Figure 5.

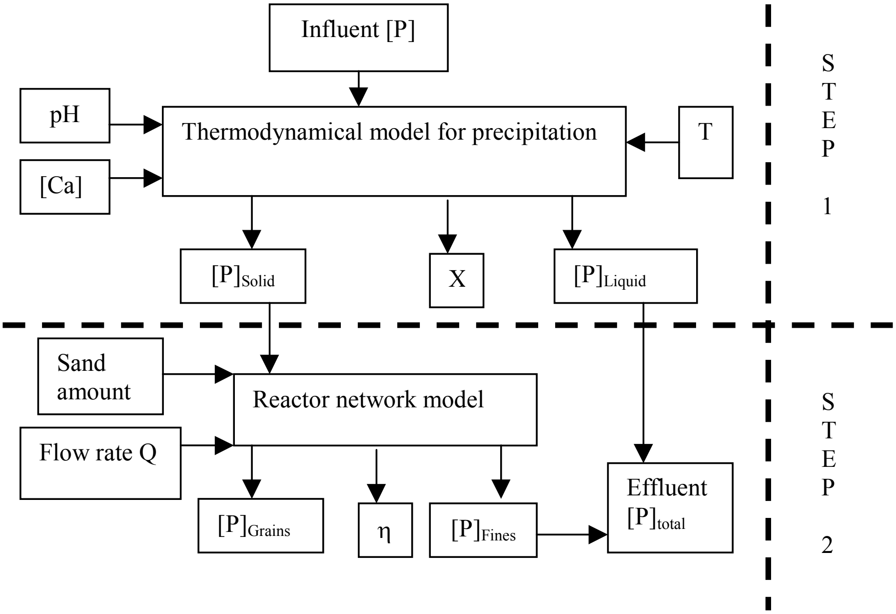

Figure 5: Principles of pellet reactor modeling

First, a thermochemical model determines the quantity of phosphate both in the liquid and solid phases vs. pH value, temperature and calcium concentration. This first model is presented in detail in a previous work (Montastruc et al., 2003a). The efficiency is computed by coupling a simple agglomeration model with a reactor network model based on the combination of elementary systems representing basic ideal flow patterns (perfect mixed flow, plug flow,…) (Montastruc et al., 2003b). More precisely, the superstructure represents the hydrodynamical conditions in the fluidized bed (volume, concentrations, type and size of each cell). The "kinetic" constant is obtained for each combination. The continuous variables are the "kinetic" constant (K), the flowrates (5) and the reactor volumes (8). In fact, the superstructure represents the hydrodynamical conditions in the fluidized bed. The "kinetic" constant is obtained for each combination generated by the Simulated Annealing algorithm. This kinetic constants depends only on the precipitation temperature and not on flowrate and sand amount.

A comparison between experimental values and result predicted by the model is proposed in Figure 6. Experimental points correspond to an initial phosphorus concentration of 50mg/L, a Ca/P molar ratio equal to 3 and a temperature of 20°C. The simulation fitting is carried out by adjusting the solubility constant values of both mineral species.

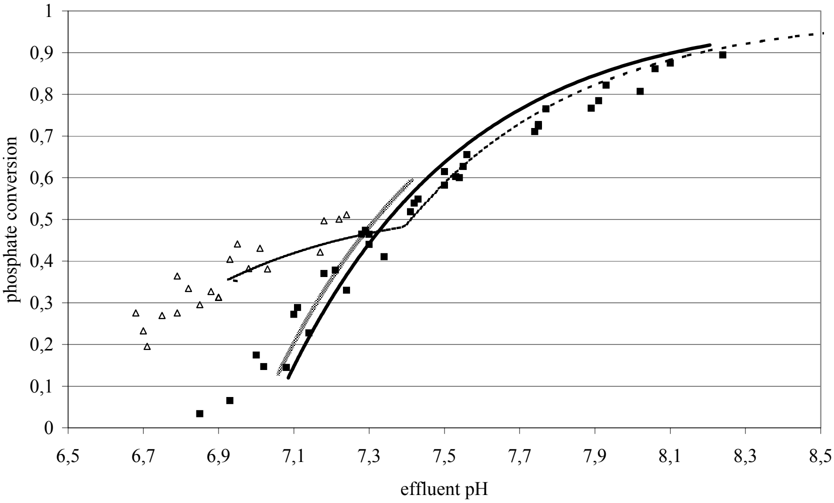

Figure 6: Phosphate conversion vs. Effluent pH

It has been demonstrated elsewhere the efficiency depends on hydrodynamical conditions (Seckler et al., 1996). Two effluent flowrates were tested (50 and 90 l/h) using the same sand size. In Figure 7, a good agreement is observed between experimental and predicted values for efficiency. An important result is that efficiency is directly linked to the conversion rate and shows that a pH work range higher than 8.5 will lead to the most interesting values for efficiency.

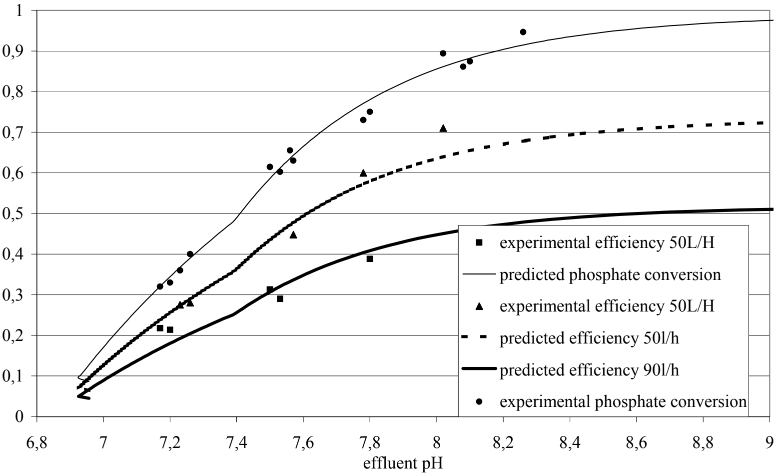

Figure 7: Phosphate efficiency vs. effluent pH

POSSIBLE REGULATION LOOP

All the previous elements have shown that:

(1) a steady state regime is reached quite rapidly for dissolved phosphorus in the liquid phase;

(2) process control efficiency and conditions for chemical equilibrium are strongly related and depend on pH. Consequently, pH seems an acceptable process control variable.

Figure 8 presents a control loop with pH as the measured variable, on which an additional constraint can be applied to limit the effluent pH (lower than 8.5 to satisfy effluent P standard) by action on temperature and on the molar ratio Ca/P. The inlet concentration $[P]_{in}$ is assumed to be known and the flowrate of the inlet solution has been determined previously from the results of the design stage.

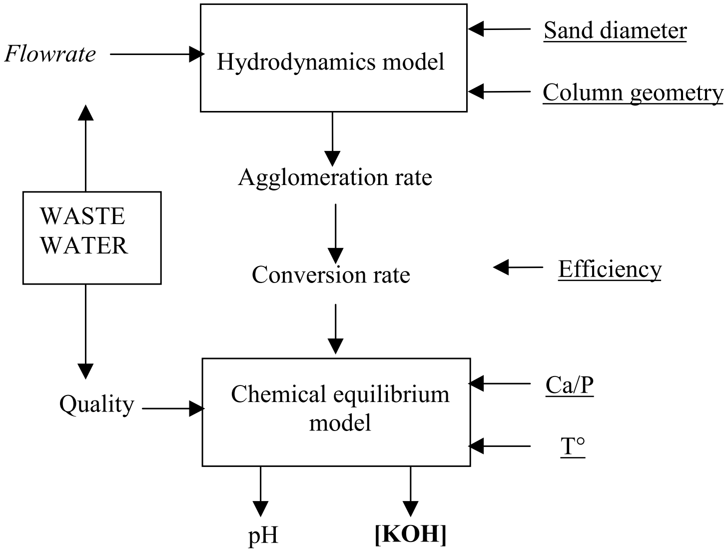

Figure 8: Process control organization chart

CONCLUSIONS

A methodology combining properly chosen experimental runs and simulations was carried out in this study to determine feasible control variable for a P-recovery pellet reactor. This study has shown that pH seems the most valuable control variable by action on KOH flowrate and a scheme for control loop has been proposed. The implementation of the control strategy is now under investigation.

Acknowledgments

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