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Study on Struvite Precipitation in a Mechanically Stirring Fluidized Bed Reactor

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The recently developed mechanically stirring fluidized bed reactor is used with notable success in France for the precipitation of many compounds in pilot, semi-industrial and industrial scales. The aim of the work is to study the feasibility of the phosphorous recuperation in the form of struvite by precipitation in this reactor. The experiments carried out in a pilot plant with synthetic solutions show that high treatment capacity and high recuperation yield from 97 to 98% can be attained. The functioning of the reactor is very stable for weeks without sophisticated controlling systems. In addition, the precipitate is easily filterable and washable, and has a mean particle size up to 170 µm. The results are used to determine the maximum treatment capacity of the mechanically stirring fluidized bed reactor in the case of struvite in order to extrapolate it for industrial applications.

1. Introduction

Phosphorus recovery is an important area of research in the environmental engineering field. The high demographic and industrial development that has occurred in recent years has produced an increase in water pollution. Nutrient discharges to natural waters have contributed to an increase in eutrophization problems, producing serious consequences for aquatic life as well as for the water supply for industrial and domestic uses. With more stringent standards imposed regarding nutrient removal, processes have been developed to remove compounds containing phosphorus. Today, the wasted sludge has simultaneously notable concentrations of phosphorus, nitrogen and magnesium. The combination of these ions found in sludge produced from nutrient removal, specifically biological nutrient removal (BNP) processes, can result in the formation of a mineral called struvite.

Struvite is magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4{\cdot}6H_2O$). The struvite recovery technique has been applied to various wastewaters, such as swine waste, agro-industrial effluents, landfill leachate, calf manure, coke manufacturing and leather tanning. Struvite may be used as a valuable source of slow release fertilizer due to its solubility characteristics (Nelson et al., 2003). Other factors that support struvite use as a fertilizer include the low heavy metal content of the product when compared to

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phosphate fertilizers obtained from mined mineral phosphates. Therefore, since struvite is identified as a route to remove and recover phosphorus as a marketable fertilizer, the idea of its crystallization in a specific reactor is widely investigated.

In the present work, a pilot fluidized bed reactor equipped with an agitation system is used for struvite crystallization. Crystallization in a fluidized bed reactor (FBR) is used in major sectors of the chemical industry. Some examples include the production of special chemicals (where the quality of the powder is extremely important), softening of water before use, as well as anion removal like phosphate (Battistoni et al., 2000, 2001, 2002, 2006; Ohlinger et al., 2000; Iqbal et al., 2008) or fluoride (Giesen, 1998). In order to obtain good quality products, it is very important to control the precipitate specific properties of the product such as purity, crystal size distribution, shape, filterability, sedimentation rate, etc. In the precipitation industry, the use of fluidized bed reactors is becoming common, because this type of reactor allows the production of chemicals in well crystalline form and with controlled particle size distribution. In addition, they help to avoid gel production and very small particles due to the formation of agglomerates. Plasari and Muhr (2009) have theoretically proved that the fluidized beds are the best installations for precipitating compounds from diluted or very diluted solutions. This family of precipitating reactors has in the precipitation zone a high solid concentration independently to the compound concentration in the liquid phase; consequently, their treatment capacity per unit volume is tenths times higher than the capacity of classical reactors.

The hydrodynamic behavior like initial contacting and mixing of reacting fluids in fluidized bed reactors are key parameters in the control of precipitate quality, nevertheless there are few works where the problem is tackled. Working with a pilot fluidized bed without stirrers, Sellami et al. (2005) show that the reactants in the fluidized bed may follow preferential paths and the mixing is not fully developed. From this study, it is proposed a new type of fluidized bed equipped with mechanical stirring and a liquid-solid separator (thickener) on the top of the reactor. This apparatus is now used with notable success in France in pilot, semi-industrial and industrial scales for producing many compounds or protecting the environment by precipitation of harmful substances. Based on the large experience obtained during these activities, the aim of the present work is to test generally the feasibility of the struvite precipitation and to determine the maximum treatment capacity per unit sectional area, as well as the recovery yield as a function of the treatment capacity in this reactor for extrapolating purposes.

2. Experimental

The experiments are carried out in a fluidized bed reactor with a working volume of 9 l. Transparent parts in glass and Plexiglas are used to visualize the dynamics of the mixing process and the quality of liquid-solid separation in the thickener. As mentioned above, working with a fluidized bed reactor without stirrers, the mixing of the reacting fluids is really catastrophic (Sellami et al., 2005). Therefore, the experimental device in this study is equipped with a multiple impeller mechanical stirrer (impellers in the same shaft) in order to ensure accurate mixing in all precipitation zone. The stirring speed is set to a value of 30 rpm. The fluidized bed reactor scheme of the pilot plant for struvite crystallization is shown in Figure 1.

The reactor has two zones, the reacting zone which is a cylinder of 50 cm in height and 10 cm in diameter; and the liquid-solid separation zone on the top of the reactor which has a diameter of 20 cm. In the superior enlarged cylindrical part, the supernatant liquid leaves the reactor owing to an overflow system (Outlet 1). The solid accumulated in the reaction zone leaves the reactor through an outlet at the bottom of the reactor (Outlet 2). The first solution (solution A) is composed of $(NH_4)_2HPO_4$ (the phosphorus source) and $MgCl_2{\cdot}6H_2O$ (the magnesium source), pH-adjusted to 4 with hydrochloric acid 37% (struvite does not precipitate at this pH value). Solution A has a phosphorus content of 200 mg PO_4^{3-}/L and a Mg/P molar ratio of 1.3 as suggested by Nelson et al. (2003). The second (solution B) is a solution of NaOH 0.5% (for pH maintenance).

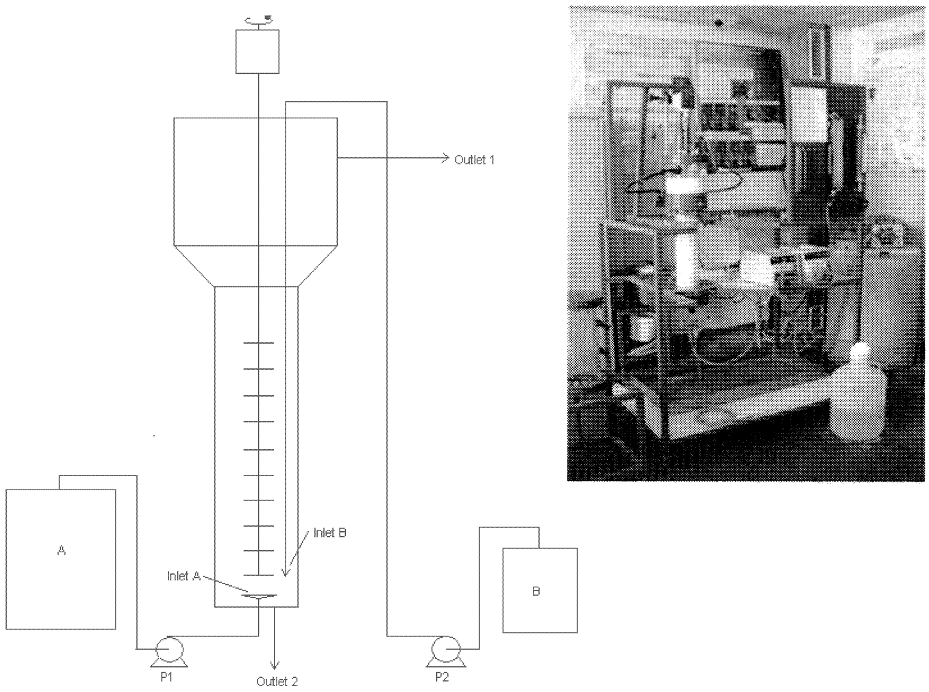

Figure 1: Fluidized bed reactor scheme and the general view of the installation.

Solution A and solution B are continuously prepared and stored in tanks A and B, respectively. Solutions coming from tanks A and B are pumped to the bottom of the fluidized bed reactor and then introduced by two inlets (inlet A and inlet B) as shown in Figure 1. Two metering peristaltic pumps continuously feed the reacting fluids in the reactor with a flow rate varying from 170 to 830 mL min^{-1} for solution A, and from 9 to 42 mL min^{-1} for solution-B. The ratio between the two flow rates is chosen so as to raise the pH solution A, initially at a value of 4, to a value between 9 and 9.3, to allow the precipitation of struvite in the reactor.

At the beginning, low feed rate solutions are injected in the reactor in order to create the solid charge. Once the charge is generated, the feed flow rates are gradually increased up to the prefixed values. After attaining the steady state, for each used feed rate, samples of fluid phase from the outlet 1 and dense suspension from outlet 2 are taken for the process characterization. A known volume of suspension is filtered and the precipitate is washed, dried and weighted in order to determine the solid concentration in the suspension. The dried crystals are observed by Scanning Electron Microscopy SEM (JEOL JSM-6490 LV). A small quantity of suspension is highly diluted with the mother liquor obtained after filtration and used to obtain the crystal size distribution by Laser Diffraction Granulometry (Malvern Mastersizer 2000). Phosphorus concentration in the influent (Inlet A) and in the effluent (Outlet 1) is determined by Plasma Emission Spectrometry (PES-ICP Thermo-ICAP) in order to obtain the phosphate recovery yield.

3. Results and Discussion

In all experiments non agglomerated and well developed struvite crystals of relatively narrow size distributions are obtained. Figure 2 illustrates the crystal size distribution and the SEM photograph of struvite crystals in one case (flow rate 60L/h). The precipitate is easily filterable and washable, and the product is rapidly dried. In addition, the liquid overflow from the top of the reactor is quite clear. The installation runs without any problem for weeks.

Table 1 gives the principal characteristics of the reactor and the produced crystals as a function of flow rate. From this table, we can first see that the mean particle size of struvite crystals increases as the flow rate increases. This is quite normal in the case of a fluidized bed; the upward flow carries away small particles toward the top of the column. When they attain by crystal growth mechanism the characteristic diameter of fluidization, the particles come down in the cylindrical zone and go out of the reactor from the bottom (Outlet 2).

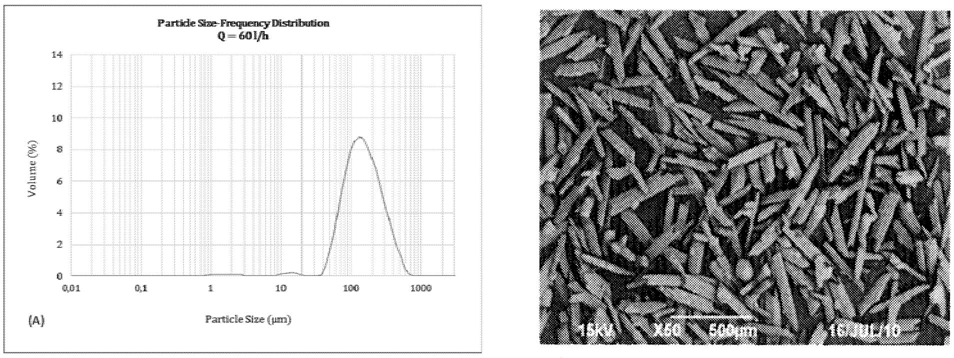

Figure 2: Crystal size distribution and SEM photograph of struvite crystals for a flow rate of 60 L/h.

We have increased the flow rate in the reactor more than 60 L/h. In these cases, the small particles are not separated in the thickener, but go out with the overflow (Outlet 1). The fluidized zone is gradually emptied and the reactor is broken-down, so the feed rate of 60 L/h is the limiting value of well-functioning of the fluidized bed which corresponds to a specific capacity of 7.6 m^3/h of feed rate per m^2 of reactor surface area. This value can be accepted for extrapolation in order to determine the diameter of the industrial reactor as a function of the feed rate.

Table 1: Mass crystal mean size, solid concentration in the suspension, recovery yield and capacity per unit of sectional area (in $m^3/h/m^2$ or m/h) as a function of flow rate in the reactor (the sum of the two flow rates A+B).

Run	Flow rate (L/h)	D[4,3] (µm)	C_{solid} (g/L)	Recovery (%)	Capacity (m/h)
1	10	70.1	220	97.9	1.3
2	20	82.9	324	97.6	1.9
3	30	104	186	98.0	2.5
4	50	110	126	96.0	6.4
5	60	171	105	96.8	7.6

The reactor used for the precipitation of struvite represents a multifunctional apparatus, which is a combination of two interconnected zones in series, one for the precipitation and one for the liquid-solid separation. In this case, the liquid-solid separation is the process limiting the treatment capacity of the precipitator. The thickener has a diameter only two times higher than the diameter of the precipitation zone. If the surface area of the thickening zone is increased, the specific capacity of this apparatus can also increase. This topic will be studied in the future.

A surprising result is the variation of the solid concentration in the reactor; with increasing the feed rate, it increases for low feed rates and decreases for high feed rates. Normally, in the case of the classical fluidized bed without precipitation, for constant particle size, it exists the phenomenon of bed expansion with increasing the fluid velocity, i.e. the concentration of the solid phase is decreased. When the precipitation takes place, the solid phase is created in the reactor, so the diameter of particles depends simultaneously on nucleation and crystal growth rates. In addition, the increase of feed rate increases the solid mass produced in the fluidized bed. For low feed rates the particle diameter increases more rapidly than the hydrodynamic diameter corresponding to bed expansion, so the bed becomes denser (the solid concentration increases). On the contrary, for high feed rates (high fluid velocity in the column), the hydrodynamic bed expansion prevails over the increase of particle diameter, the solid concentration decreases as the fluid flow increases. Nevertheless, Table 1 shows that the recovery efficiency does practically not depend on the solid concentration in the reactor.

4. Conclusion

The mechanically stirring fluidized bed precipitator equipped with a liquid-solid separation device on the top is very suitable for the recovery of phosphorous from extremely diluted solutions. Its functioning is very stable and does not need any sophisticated controlling device. The liquid overflow from the top of the reactor is quite clear. The reactor has a high treatment capacity and produces non agglomerated, but well developed struvite crystals of relatively high diameter which can be easily filtrated, washed and dried. In addition, in the interval of studied feed rate values, the recovery efficiency of phosphorous is very high of the order of 97-98 %. Based on these results, we recommend it for use in larger scale for the precipitation of struvite. A French company is now using the same type of apparatus having a diameter of 250 mm for the precipitation of struvite from a real digester solution with very good results.

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