Kinetics of the reversible reaction of struvite crystallisation

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H I G H L I G H T S

- Struvite crystallisation may be represented by a reversible kinetic model.
- Struvite crystallisation follows a first-order kinetics regarding the supersaturation.
- The struvite solubility product increases as the temperature increases.
- The estimated enthalpy confirms that struvite formation is an endothermic reaction.

## A R T I C L E   I N F O

A B S T R A C T

The crystallisation of struvite could be a sustainable and economical alternative for recovering phosphorus from wastewater streams with high phosphate concentrations. Knowledge regarding the kinetics and thermodynamics that are involved in the crystallisation of struvite is the key to determine the optimal conditions for obtaining an efficient process. This study was conducted in a continuous stirred batch reactor. Different sets of experiments were performed in which struvite was either dissolved (undersaturated) or precipitated (oversaturated). These experiments were conducted at different temperatures (25, 30 and 35 °C) and pH values (8.2, 8.5 and 8.8) to determine the kinetics of struvite precipitation and dissolution. Struvite crystallisation was modelled as a reversible reaction. The kinetic rate parameters of struvite precipitation were $1.03 \cdot 10^{-4}$, $1.25 \cdot 10^{-4}$ and $1.54 \cdot 10^{-4}$ mol m^{-2} min^{-1} at 25, 30 and 35 °C, respectively. Similar kinetic rate parameters were determined for struvite dissolution. Struvite heterogeneous crystallisation can be represented by a first-order kinetic model that fitted well the experimental data.

1. Introduction

Struvite crystallisation could be a sustainable and economical alternative for recovering phosphorus from wastewater streams with high phosphate concentrations. Struvite is a magnesium ammonium phosphate salt ($MgNH_4PO_4 \cdot 6H_2O$) that usually crystallises in a reversible reaction and produces orthorhombic crystals with a Mg^{2+}:NH_4^+:PO_4^{3-} molar ratio of 1.0:1.0:1.0 (Equation (1)). Struvite crystallisation occurs when magnesium, ammonium and phosphate concentrations exceeds the struvite solubility product (Ksp) (Doyle and Parsons, 2002). The crystallisation of struvite is a complex process that depends on supersaturation, pH, temperature and the presence of foreign ions, such as calcium. Calcium ions could interfere in the struvite crystallisation process by promoting the formation of calcium phosphates (Bouropoulos and Koutsoukos, 2000).

$$Mg^{2+} + NH_4^+ + H_nPO_4^{n-3} + 6H_2O \leftrightarrow MgNH_4PO_4 \cdot 6H_2O + nH^+$$

(1)
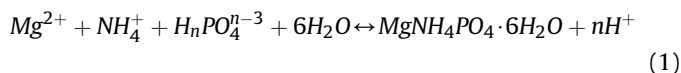
Struvite crystallisation could be accomplished using diverse wastewater types with different ions concentrations and by using different reactor configurations that could be operated under a wide range of operational conditions, especially the temperature, pH or hydraulic residence time. Thus, knowledge about the kinetics and thermodynamics of struvite crystallisation could be useful for predicting the soluble ion concentrations in the effluents of any crystallisation reactor. The kinetic study provides information about the rate of struvite crystallisation (or dissolution), while properties such as struvite solubility are related to the thermodynamics of the process.

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Struvite crystallisation can occur via two different mechanisms, homogeneous precipitation or heterogeneous precipitation. Homogeneous precipitation occurs in supersaturated solutions in the absence of crystals or other solid phases (e.g. other solid impurities in suspension or sites on the pipe walls). During this precipitation process, the spontaneous formation of nuclei occurs. The nuclei grow beyond a critical size that represents the minimum size of a stable nucleus. The particles that are smaller than the critical size will dissolve. Similarly, particles that are larger than the critical size will continue to grow under supersaturation conditions (Kashchiev and van Rosmalen, 2003; Mersmann, 2001). Heterogeneous precipitation is associated with the presence of struvite crystals or other solid phases, which induce precipitation at lower supersaturation levels. The rate of heterogeneous precipitation is affected by the struvite specific surface area, which is the surface area that is available for deposition. In practice, the heterogeneous precipitation of struvite generally occurs (Mersmann, 2001).

Struvite crystallisation is considered a reversible reaction (Koutsoukos et al., 2007; Loewenthal et al., 1994), as suggested by Equation (1). If the process is a reversible reaction, the reaction can be controlled by the thermodynamics of the process. In reversible reactions, the concentrations of the reacting species at equilibrium are related to the equilibrium constant, which is known as the solubility product (Levine, 2002). For reversible reactions, the maximum attainable conversion is the equilibrium conversion, which is affected, among other factors, by temperature. Even when considering that struvite crystallisation is a reversible process, most of the available kinetics studies have considered struvite crystallisation as a first order irreversible reaction (Jordaan et al., 2010; Le Corre et al., 2007; Nelson et al., 2003; Quintana et al., 2005; Rahaman et al., 2008; Türker and Çelen, 2007). Table 1 shows the conditions under which these experiments were conducted and the reported values for the kinetics parameters. Jordaan et al. (2010), Nelson et al. (2003) and Quintana et al. (2005) determined the kinetics of struvite crystallisation relative to phosphate concentration and found a first-order kinetic rate parameter for a wide range of values (Table 1). In contrast, Le Corre et al. (2007) and Türker and Çelen (2007) investigated struvite crystallisation kinetics relative to magnesium concentration. Le Corre et al. (2007) determined first-order kinetic rate parameters of between 9.4 and 15.7 h^{-1}, depending on the experimental conditions. Furthermore, Türker and Çelen (2007) determined a second-order kinetic rate parameter of $17.76 \cdot 10^{-3}$ L mol^{-1} h^{-1}. Nevertheless, most of the aforementioned results are restricted to the experimental conditions in which they were specifically determined.

Relatively few studies have investigated the kinetics of struvite crystallisation by considering the reversibility of the process. In addition, most of the authors who have considered struvite crystallisation as a reversible reaction have focused on modelling the process by using a population balance equation in which crystal growth and aggregation are considered (Ali and Schneider, 2008; Galbraith et al., 2014; Hanhoun et al., 2013; Harrison et al., 2011; Triger et al., 2012). In these studies, the evolution of crystal size is

determined with time by using the following equation:

$$G(t) = dL/dt = k \cdot S(t)^n \qquad (2)$$

where L is the crystal sized, t is the elapsed time, S is the supersaturation ratio, n is the order of the reaction, and k is the kinetics rate coefficient. Ali and Schneider (2008) estimated values of 1.5 and 0.17 μm min^{-1} for the reaction order and the kinetic rate coefficient, respectively. In contrast, Hanhoun et al. (2013) determined values of 1.34 and 280.8 μm min^{-1} for the reaction order and kinetic rate coefficient, respectively.

A more classical perspective that is rarely analysed is to determine the kinetic parameters of the struvite crystallisation process by considering a typical model for reversible heterogeneous reactions, which is described by the following equation (adapted from Koutsoukos et al., 2007):

$$r = k \cdot a \cdot \left(S^{1/v} - 1 \right)^n \qquad (3)$$

where k and n are the kinetics parameters, kinetic rate coefficient and order of the reaction, respectively, a is the specific surface area of the suspended crystals, S is the supersaturation ratio and v is the total number of cationic and anionic species ($v = x + y + z$). This equation could be useful for determining the kinetics of struvite crystallisation/dissolution in water under different operational conditions.

Therefore, the objectives of this research were to study the struvite crystallisation from a thermodynamic and kinetic point of view and to obtain a struvite precipitation/dissolution model.

2. Materials and methods

2.1. Experimental set-up and operating strategy

Two different type of experiments were conducted, dissolution and precipitation experiments. These experiments were performed in a continuous stirred batch reactor (1 L). Precipitation and dissolution experiments were conducted to study the effects of temperature and pH on the struvite formation process. Thus, the first set of experiments was performed at three different temperatures (25, 30 and 35 °C) with the pH fixed at 8.5. The temperature was controlled by using a thermostatic bath. Subsequently, an additional series of experiments was conducted at different pH values (8.2, 8.5 and 8.8) and the temperature was fixed at 30 °C. In all experiments, a fixed amount of synthetic struvite (3 g) was added. A summary of the experimental conditions for struvite precipitation and dissolution is showed in Table S1 in the Supporting Information.

For the dissolution experiments, struvite was added to 1 L of KH_2PO_4 solution (0.8 mmol PO_4^{3-} L^{-1}). Prior to adding struvite, the pH of the KH_2PO_4 solution was adjusted to 8.2, 8.5 or 8.8 (depending on the experiment). The KH_2PO_4 solution was used as a

Table 1
An overview of previous kinetics studies of struvite crystallisation.

Study	Kinetics with regard to:	Order of reaction	Kinetic parameter	Temperature	pH range	Initial concentration of P
			h^{-1}	°C		mg P L^{-1}
Nelson et al. (2003)	Phosphate concentration	1	3.7–12.3	22–24	8.4–9.0	50.5
Quintana et al. (2005)	Phosphate concentration	1	2.34–2.88	22–25	8.7–8.8	54.0
Jordaan et al. (2010)	Phosphate concentration	1	1.55	21	8.4	32.4 ± 5.5
Rahaman et al. (2008)	Phosphate concentration	1	0.69–2.71	20	7.6–8.5	30.5
Le Corre et al. (2007)	Magnesium concentration	1	9.4–15.7	20	7.7–9.0	74.0
Türker and Çelen (2007)	Magnesium concentration	2	$17.76 \cdot 10^{-3}$ (L mol^{-1} h^{-1})	37	8.5	24.0 ± 5.0