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Kinetics of phosphorus removal and struvite formation by the utilization of by-product of magnesium oxide production

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Abstract

A byproduct of the magnesite calcination process to produce magnesium oxide (BMP) was applied for struvite production from an anaerobic digester liquor. The experiments were carried out at batch conditions. The effect of (Mg:P) molar ratio of pure MgO reagent and BMP was firstly evaluated for synthetic liquor. A first-order kinetic model was applied to the experimental results obtained and the feasibility of this model was demonstrated. Equilibrium concentrations (C_e) and the reaction rate constants (K) were determined for all the cases evaluated. Values of C_e were lower for pure MgO than for BMP while the values of K were higher for pure MgO (0.039–0.048 min^{-1}) than for BMP (0.09–0.017 min^{-1}). The experiment was also carried out with real liquor at molar ratios (Mg:P) in the range of 1.5–3.6 for BMP and 1.5 for MgO, respectively. The values of C_e decreased with the increase of molar ratio showing values for real liquor lower than those obtained with synthetic liquor. The values of K increased from 0.018 to 0.029 min^{-1} for real liquor and molar ratios in the range of 1.5–3.6, respectively and these values were higher than those obtained with the synthetic liquor (0.018–0.024 min^{-1}) at similar molar ratios. The value of K was significantly higher for MgO (0.045 min^{-1}) than that obtained for BMP (0.039 min^{-1}) for real liquor and for synthetic liquor at the same molar ratio (Mg:P) = 1.5. The higher pH and the presence of suspended particles in the real liquor probably contributed to enhance the struvite formation. It was found that particle size influenced the rate of reaction. Sieved material with particle size lower than 0.04 mm gave values of K higher than those obtained with particle sizes higher than 0.04 mm and ground material with particle size lower than 0.04 mm and raw material. The results obtained demonstrated that BMP is a good reagent for the removal of phosphorus and to produce struvite.
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Keywords: Struvite; First-order kinetics; Phosphorus removal; By-product of magnesite production (BMP); Time of reaction

1. Introduction

The formation of struvite ($MgNH_4PO_4 \cdot 6H_2O$) during wastewater treatment cause scaling on the inner surface of pumps, pipes and other equipments of wastewater treatment plants. Struvite precipitation occurs under certain environmental conditions of pH, alkalinity, temperature, phosphorus, ammonium and magnesium concentrations [1]. Whilst struvite can be a problem in wastewater treatment plants, it is a product of commercial value as it may be used as a fertiliser and soil conditioner [2–4]. Other benefits of precipitating struvite include reducing the phosphorus and nitrogen load of sidestream and sludge liquors recirculated to the head of wastewater treatment works [5–7]. Moreover, the recovery of phosphorus has been reported to reduce sludge volumes under specific conditions by up to 49% when compared to chemical phosphorus removal processes [8]. The kinetics of struvite formation was studied to determine the cause of preferential accumulation at certain locations within the anaerobic digestion and postdigestion processes in wastewater treatment [9,10]. The authors claimed that struvite precipitation followed a first-order kinetic model. Struvite nucleation was found to be reaction-controlled and strongly dependent on the struvite supersaturation level. The crystal growth rate was found to be transport-limited. Accumulation of struvite on

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selected construction materials was also studied, and experimental evidence suggested that surface roughness exerted the greatest control over preferential struvite accumulation on various materials under similar mixing and supersaturation conditions. The effect of pH at a range of 7.5–9.5 and Mg:P molar ratio at a range of between 1:1 and 1.6:1 was studied on struvite precipitation in liquids from two anaerobic swine lagoons [10]. Struvite formation reduced the PO_4-P concentration from 55 mg/l to values as low as 2 mg/l. Minimum concentrations of PO_4-P occurred at pH values in the range of 8.9–9.3 at all (Mg:P) ratios. Struvite precipitation decreased PO_4-P concentrations by 85% within 20 min at pH 9.0 for an initial Mg:P molar ratio of 1.2:1. The rate of PO_4-P decrease was described by a first-order kinetic model with rate constants of 3.7, 7.9, and 12.3 h^{-1} at pH values of 8.4, 8.7 and 9.0, respectively. The kinetics of the spontaneous precipitation of struvite was investigated in aqueous supersaturated solutions containing stoichiometric concentrations of Mg^{2+}, NH_4^+ and PO_4^{3-} ions in a batch stirred reactor at constant supersaturation [11]. A kinetic analysis demonstrated a strong dependence of the rates of PO_4-P decrease with the solution supersaturation yielding second-order dependence. An investigation into mineral precipitation in anaerobic digester liquor was carried out with the application of different kinetic models to the experimental data obtained [12,13]. From the experimental investigation and theoretical modelling analysed, it was concluded that the dominating mineral that precipitated was struvite, with small amounts of amorphous calcium phosphate and negligible newberyite, calcite and magnesite. The precipitation of struvite was controlled by the increase in pH when CO_2 was lost from the anaerobic digestion liquor. The rate and mass of struvite precipitation was controlled by the rate of pH increase and the initial Mg concentration. The reaction kinetics and design parameters of struvite production were experimentally investigated by using a basic reaction type and draft-tube type reactors [14]. Struvite production rate, which is a very important parameter in reactor design and efficiency estimation, was formulated in an equation containing a rate constant (k_2) as well as the magnesium. phosphate and ammonium concentrations. The value of k_2 increased with struvite concentration and mixing intensity in the reactor. The developed equation was applied to the results obtained from the draft-tube type reactor experiments and verified for its applicability. High struvite concentrations in the range of 10–25% were maintained in the draft-tube reactor experiments. The PO_4-P removal efficiency was 92% with effluent phosphorus concentration of 17 mg/l under the following conditions: 4 min reaction time, pH of 8.5 and (Mg/P) molar ratio of 1.1. Magnesium additions in the form of MgO were used to enhance struvite precipitation [15,16]. These authors precipitated struvite from swine waste by increasing the molar (Mg:P) ratio from 0.25:1 to 0.65:1 and 1.1:1 with MgO additions, which simultaneously increased the pH to values higher than 8. They found that PO_4-P removal increased with increasing Mg concentration. However, the further increase of the pH of the Mg adjusted wastes did not increase PO_4-P removal. Good results have recently been achieved using a low grade MgO by-product of magnesite industry (BMP) to precipitate struvite from municipal and industrial wastewaters [17,18]. With this review in mind, the aim of this work was to study the kinetics of phosphorus removal by the utilization of BMP using synthetic and real liquors derived from a municipal sewage treatment plant.

2. Materials and methods

Different experimental runs were carried out. A first initial group of assays were performed using synthetic liquor in order to compare the utilization of magnesium oxide (MgO) and the by-product of magnesium oxide production from magnesite calcination (BMP) as a source of magnesium for struvite production. Further experiments were carried out with real liquor.

2.1. Synthetic liquor

Using the analytical grade chemical reagents H_3PO_4, $MgCl_2 \cdot 6H_2O$ and NH_4Cl, a synthetic solution with a similar concentration to that real liquor used in the experiments was prepared in distilled water. This solution did not include organic carbon compounds.

2.2. Real liquor

Filtrate liquor from the dewatering process of anaerobic digested sludge was used in the experiment. The liquor samples were obtained from the “Arroyo del Soto” municipal wastewater treatment plant, Madrid (Spain). This plant uses an anaerobic/aerobic (A/O) biological phosphorus removal system. Table 1 shows the chemical composition of the real liquor used in the experiments.

2.3. Reagents for phosphorus removal

Two reagents for struvite precipitation were employed: magnesium oxide (MgO) of analytical grade and a by-product of the magnesite calcination process (BMP) that takes

Table 1
Real liquor composition used in the experiments[a]

Parameter	Average value
P (mg/l)	54
Mg (mg/l)	17
Ca (mg/l)	49
NH_4^+ (mg/l)	630
SS (mg/l)	140
Alkalinity[b] (mg/l)	2110
pH	7.8

[a] Values are average of six determinations; there was virtually no variation (less than 5%) between analyses.

[b] $CaCO_3$.

Table 2
Particle size distribution and chemical composition of BMP

Particle size	%	Component	Concentration (%)
<0.1	82.2	Mg-MgO	67.67
0.1–0.2	13.2	Ca-CaO	9.58
0.2–0.4	2.6	Al-Al_2O_3	0.37
0.4–0.5	0.7	Fe-Fe_2O_3	2.63
0.5–0.7	1.3	SO_3	3.95
		SiO_2	2.60
		LOI[a] (1100 °C)	13.20

[a] Loss of ignition.

place during magnesium oxide production. This reagent was obtained when suspended particles of the exhausted gases from the kiln were removed by cyclone separation. The settled solid particles remaining in the cyclone constituted the reagent BMP. The particle size and composition of the BMP are given in Table 2.

2.4. Experimental procedure

The first experiment was carried out to compare BMP with pure MgO using synthetic liquor. The reagents were applied at molar ratios (Mg:P) of 1.5, 2.0 and 2.5. The second experiment was performed to compare the influence of the molar ratio (Mg:P) of BMP in a range of 1.5–3.6 on the phosphorus removal using real liquor. The third experiment consisted of the evaluation of the effect of particle size. Therefore, BMP with particle size > 0.04 mm, ground BMP to particle size < 0.04 and sieved BMP with particle size < 0.04 mm were compared using real liquor. The fourth experiment consisted of the evaluation of the effect of molar ratio (Mg:P) in a range of 1.1–2.5 using sieved BMP of particle size < 0.04 mm and real liquor. All experiments were performed in 1 l glass beakers. A magnetic stirrer operating at 120 rpm was used to mix the sample and to keep the precipitate in suspension during the precipitation–crystallization process. Measurements of pH and temperature were carried out during the experiments. The reagents were added to the liquors and the samples were stirred during 240 min. Samples of 10 ml volume of the reaction mixture were taken every 30 min to determine the effect of time on the course of the reaction. During the experiments, the temperature was kept in the range of 22–25 °C by using a water bath. In the experiment with synthetic liquor, no alkali was needed to increase the pH. The initial pH of the sample was adjusted to 7.5 by the addition of NaOH in order to obtain a similar value to that observed in the real liquor. In the case of real liquor, an increase in pH of around 1 unit was achieved by 30 min of aeration before the reagent was added. The samples obtained during the experiment were filtered through a 0.45 μm filter to determine residual soluble phosphate.

2.5. Analytical techniques

Phosphorus, calcium and magnesium were determined in the solutions by plasma emission spectrometry (PES-ICP). Ammonium and alkalinity of the solutions were determined according to the recommendations of the standard methods [19]. Struvite was determined in the precipitates obtained by vacuum filtration by drying the sample at 40 °C to prevent the loss of crystallization water. Afterwards, the samples were digested by perchloric and nitric acids. The main components examined in the acid solution obtained were phosphorus, magnesium, calcium and ammonium (determined as described above).

2.6. Kinetic model

Based on the literature review, a first-order kinetic model was applied to the experimental data obtained [9–11]. The kinetic constants were determined by fitting a slightly modified first-order kinetic model to the experimental data obtained. This model relates the disappearance of a reactant ($-\mathrm{d}C/\mathrm{d}t$) to the rate constant (K) and the reactant concentration at time t (C) minus the reactant concentration at equilibrium (C_e) through Eq. (1):

$$-\mathrm{d}C/\mathrm{d}t = K(C - C_\mathrm{e}) \tag{1}$$

By integrating Eq. (1) and ordering the terms, the following linear form of the first-order rate equation was obtained (Eq. (2)):

$$-\ln[(C - C_\mathrm{e})/(C_0 - C_\mathrm{e})] = Kt \tag{2}$$

where C_0 is the initial concentration of the reactant. Assuming first-order reaction kinetics, a plot of $-\ln[(C - C_\mathrm{e})/(C_0 - C_\mathrm{e})]$ against time should give a straight line with slope K [20] and intercept equal to zero.

According to Eq. (1), the value of C_e can be obtained from the intercept with the abscissa at $-\mathrm{d}C/\mathrm{d}t$ equals zero when this parameter is plotted versus the phosphorus concentration remaining in the filtrate [21].

By integrating Eq. (2), it is possible to obtain the production of struvite as a function of the reaction time from the equation:

$$(C_0 - C_\mathrm{e}) - (C - C_\mathrm{e}) = (C_0 - C_\mathrm{e}) - (C_0 - C_\mathrm{e})\,\mathrm{e}^{-Kt} \tag{3}$$

By grouping terms, the following equation can be obtained:

$$C_0 - C = (C_0 - C_\mathrm{e})(1 - \mathrm{e}^{-Kt}) \tag{4}$$

where $(C_0 - C_\mathrm{e})$ is the amount of product of reaction per litre of wastewater.

3. Results and discussion

3.1. Comparison of MgO and BMP with synthetic liquor

Fig. 1 shows the variation of phosphorus concentration in the filtrate with time. Typical exponential curves were obtained in all cases. A rapid diminution of phosphorus concentration was achieved during the first 30 min, this effect

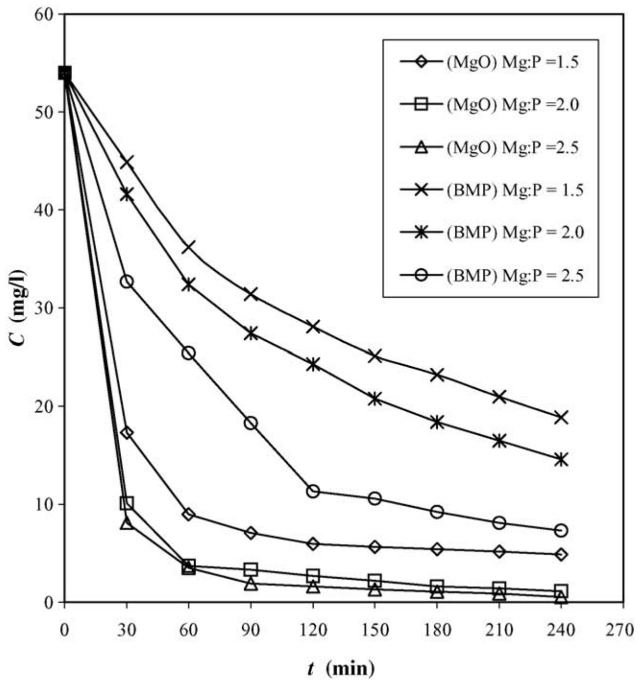

Fig. 1. Variation of the phosphorus concentration with the reaction time for pure MgO and BMP at different molar ratios in synthetic liquor.

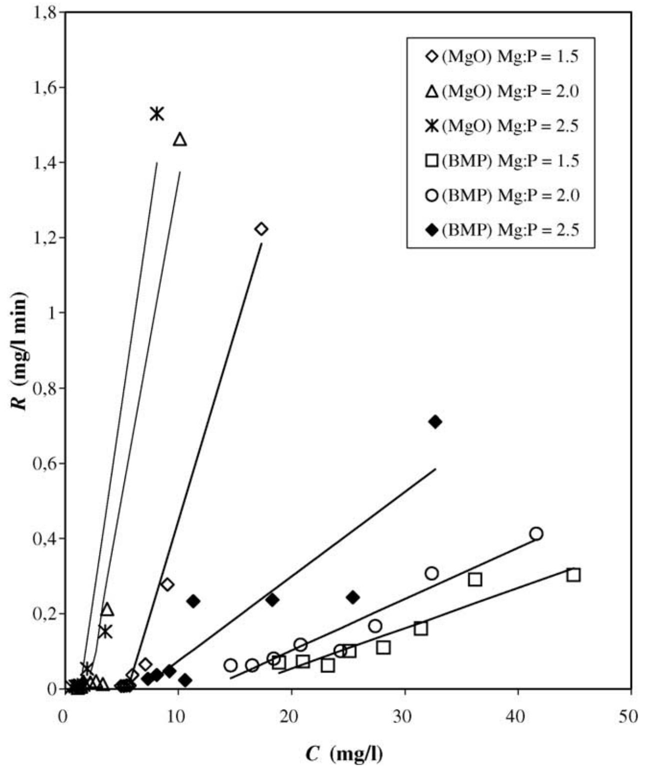

Fig. 2. Effect of the phosphorus concentration on the phosphorus removal rate for pure MgO and BMP at different molar ratios in synthetic liquor.

being more pronounced in the case of pure MgO. In the case of pure MgO, the phosphorus concentration decreased from 54 mg/l to values lower than 20 mg/l in 30 min while in the case of BMP the concentration decreased up to values higher than 30 mg/l in all cases studied. The molar ratio had a strong effect on the phosphorus removal. At times higher than 30 min, the concentration of phosphorus remained virtually constant when pure MgO was used. In the case of BMP, the reaction continued reaching the equilibrium at times higher than 210 min.

Fig. 2 shows the effect of phosphorus concentration of the filtrates on the rates of phosphorus removal (R) (equivalent to $-\mathrm{d}C/\mathrm{d}t$). As can be seen, straight lines were obtained indicating a reaction of first-order in all cases. The values of the rates of removal for MgO were higher than for BMP. Moreover, the increase of the molar ratio contributed to the increase in the removal rate. The rate of removal approached zero for certain values of phosphorus concentration. These values of concentration were the equilibrium concentrations (C_e) for the different (Mg:P) molar ratios studied and the two reagents used. Table 3 summarizes the values of the equilibrium concentrations (C_e) obtained for the two reagents studied. These values were always lower for MgO than for BMP. This behaviour is believed to be due to the fact that pure MgO contains a higher concentration of Mg^{2+} available for the reaction than raw BMP. The equilibrium concentration was also a function of the (Mg:P) molar ratio: an increase in this parameter caused a decrease in the values of C_e, showing that the reaction was more complete. However, no differences between the values of C_e were found for pure MgO when the molar ratio increased from 1.5 to 2.0. In contrast to this, in the case of BMP, the value of C_e decreased considerably when the molar ratio increased from 2.0 to 2.5. Values of the equilibrium concentration were very close for pure MgO and BMP at a molar ratio of 1.5 at 2.5, respectively. As can be seen in Fig. 3, a plot of $-\ln[(C - C_e)/(C_0 - C_e)]$ versus time gave straight lines with different slopes and intercept equal to zero. The straight lines obtained strongly suggest that the first-order kinetic model proposed fixed adequately to the experimental data. The values of the linear regression coefficients were higher than 0.92 in all cases with a probability level of 95% ($p < 0.05$).

According to Eq. (2), the values of the slopes were equivalent to the reaction constants of phosphorus removal and to the values of the kinetic constants of final product formation (struvite), as can be seen derived from Eq. (4). Table 3

Table 3
Values of the equilibrium concentrations (C_e) and first order constant (K) for pure MgO and BMP at different (Mg:P) molar ratios with synthetic liquor calculated from the data plotted in Fig. 2

Molar (Mg:P) ratio	Reagent			
	MgO		BMP	
	C_e (mg/l)	K (min^{-1})	C_e (mg/l)	K (min^{-1})
1.5	5.517	0.039	14.925	0.009
2.0	1.967	0.040	12.576	0.012
2.5	1.282	0.048	6.716	0.017

Probability level of 95% ($p < 0.05$).

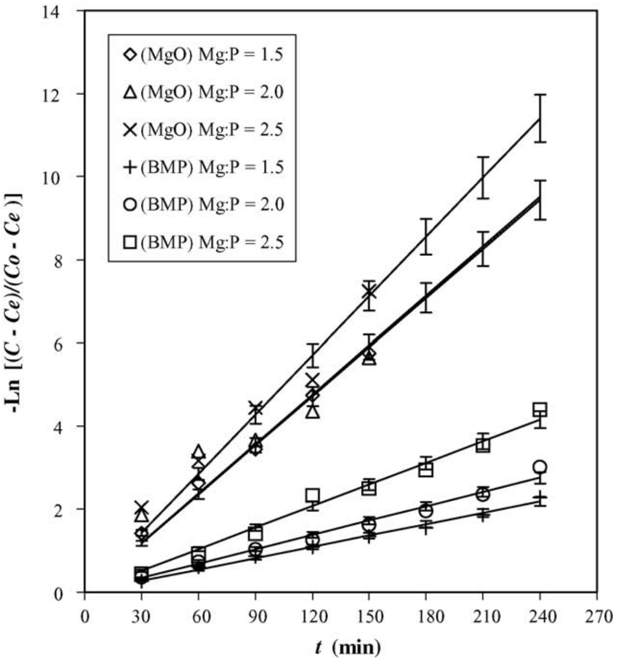

Fig. 3. Linearization of the first-order kinetic equation according to Eq. (3) for determining the kinetic constants for pure MgO and BMP at different molar ratios in synthetic liquor.

summarizes the values of the first-order rate constants (K) obtained for both pure MgO and BMP. The values of K were significantly higher for pure MgO than for BMP. Furthermore, the molar (Mg:P) ratio had a considerable influence on the values of the kinetic constant. The value of the kinetic constant increased from 0.039 to 0.048 min^{-1} when the molar ratio increased from 1.5 to 2.5 for MgO, while in the case of BMP the value increased from 0.09 to 0.017 min^{-1} for the same increase in the molar ratio. Previous works have also demonstrated that BMP contains a concentration of Mg^{2+} ions available to react lower than that contained in the pure MgO [17,18].

3.2. *Effect of the molar ratio Mg:P of BMP*

Phosphorus concentration decreased with time at different molar ratios of the reagents BMP and MgO in real liquor. A considerable decrease in concentration was observed during the first 30 min of reaction, while the phosphorus concentration decreased slowly after this time. The increase in molar ratio had a strong influence on the decrease of phosphorus concentration. The major reduction was appreciated when pure MgO was used at a molar ratio of 1.5. At molar ratios in the range of 2.0–3.6 using BMP, no variation of the phosphorus concentration was observed after 90 min of reaction time. The same behaviour was observed with pure MgO. This result indicated that the reaction was completed at 90 min and the equilibrium concentration was achieved at this time. At a molar ratio of 1.5 using BMP, the reaction continued for 210 min.

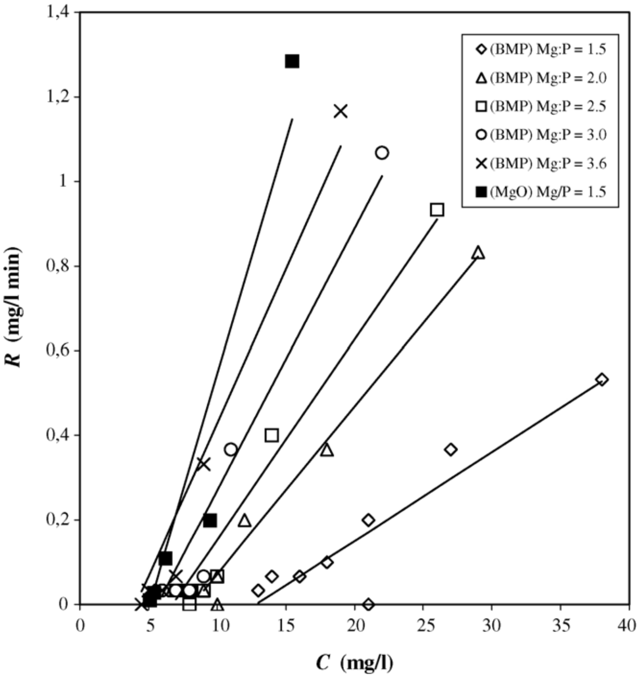

Fig. 4. Effect of the phosphorus concentration on the phosphorus removal rate for pure MgO at a molar ratio of 1.5 and BMP at different molar ratios in real liquor.

Fig. 4 shows the influence of the phosphorus concentration (C) on the phosphorus removal rate (R). Based on this figure, the value of C_e was calculated for each case studied. As can be seen, straight lines were obtained showing that a first-order kinetic model described the effect of phosphorus concentration on the rate of removal. Table 4 summarizes the values obtained for C_e from the experimental data plotted in Fig. 4. As can be observed, these values decreased with the increase of molar ratio for BMP. The value of C_e for pure MgO was lower than that obtained for BMP at ratios in the range of 1.5–3.0 and higher than that obtained for a molar ratio (Mg:P) of 3.6. The values of C_e were lower than those obtained for synthetic wastewater, probably, because the reaction in real liquor may be favoured by the presence of alkalinity which contributes to maintaining a higher value of pH during the reaction. In the case of synthetic liquor, the

Table 4
Values of C_e and K for BMP at different molar (Mg:P) ratios and for MgO at a molar ratio of 1.5, for real liquor, calculated from the data plotted in Fig. 4

Molar (Mg:P) ratio	Reagent			
	MgO		BMP	
	C_e (mg/l)	K (min^{-1})	C_e (mg/l)	K (min^{-1})
1.5	5.07	0.045	12.83	0.018
2.0	–	–	8.16	0.023
2.5	–	–	6.75	0.024
3.0	–	–	5.63	0.027
3.6	–	–	4.16	0.029

Probability level of 95% ($p < 0.05$).

Table 5
Characteristics of the real liquor after treatment with BMP and MgO at a molar ratio (Mg:P) of 1.5

Reagent	Molar ratio (Mg:P)	P (mg/l)	Mg (mg/l)	Ca (mg/l)	NH_4^+ (mg/l)	SS[a] (mg/l)	Alkalinity (mg/l)	pH
MgO	1.5	4	6	12	111	53	2450	8.81
BMP	1.5	13	15	27	234	64	2512	8.77
BMP	2.0	8	10	21	192	55	2480	8.79
BMP	2.5	5	8	16	133	58	2450	8.75
BMP	3.0	4	6	13	118	51	2430	8.66
BMP	3.6	2	4	8	68	48	2510	8.72

[a] SS: suspended solids.

pH was in the range of 8.0–8.5 for BMP and of 8.3–8.5 for pure MgO, while in the case of real liquor the pH was in the range of 8.5–9.0. Moreover, the presence of suspended solids in the real liquor may also enhance and favour the precipitation of struvite [7,11]. Based on the values of C_e and C, and taking into account Eq. (2), the values of K with a probability level of 95% ($p < 0.05$) were obtained and summarized in Table 4. As was previously mentioned, the values of K also increased with the molar ratio for synthetic liquor, the values being higher with real liquor than those obtained with synthetic liquor. These results were of the same order of magnitude than those obtained by other authors employing first-order models [10,11].

Table 5 shows the remaining concentrations of P, Mg, Ca, NH_4^+, suspended solids (SS), alkalinity and pH in the real liquor at the end of the experiment. A considerable reduction in the nutrients was achieved, mainly at molar ratios in the range of 2.0–3.6. However, additional post-treatment may be required before its final disposal due to the high concentration of ammonia that still is kept. This final liquor may be recycled to an activated sludge system or into an oxidation pond.

3.3. Comparison of different particle size of BMP

The best results were achieved for ground and sieved materials with particle size lower than 0.04 mm, confirming that the particle size is very important in the reaction performance. Fig. 5 shows the variation of the phosphorus removal rate with the phosphorus concentration. As can be seen, straight lines were obtained with intercept at the abscissa equivalent to the value of C_e. The values of C_e were found to be 13.96, 7.58 and 6.03 mg/l for a particle size higher than 0.04 mm, ground material with a particle size lower than 0.04 mm and sieved material with particle size lower than 0.04 mm, respectively. This result confirmed that a decrease in the particle size determined that the reaction is more complete. Small differences were found between ground and sieved materials with a particle size lower than 0.04 mm. However, a better quality in the final product was probably obtained when the material was sieved, increasing the crystallization sites [7,11]. According to Eq. (2), the values of K determined with a probability level of 95% ($p < 0.05$) were 0.015, 0.027 and 0.030 min^{-1} for reagent with a particle size > 0.04, ground with a particle size < 0.04 and sieved with a particle size < 0.04 mm, respectively. The lowest value of K was obtained for a particle size > 0.04 mm and the value for the sieved material was higher than that obtained for the raw material at a similar molar ratio.

3.4. Comparison of different molar (Mg:P) ratio for a particle size lower than 0.04 mm using BMP

Comparing the variation of phosphorus concentration with time for the different molar ratios studied with a particle size lower than 0.04 mm, the minimum values were observed for the highest molar ratio (Mg:P = 2.0). As was previously observed, a fast decrease occurred during the first 30 min of reaction time. In all cases after this time, the concentration decreased slowly and achieved practically a constant value at 120–150 min for molar ratios in a range of 1.3–2.0 and at 210 min for a molar ratio of 1.1. Fig. 6 shows the variation of the phosphorus removal rate versus the phosphorus con-

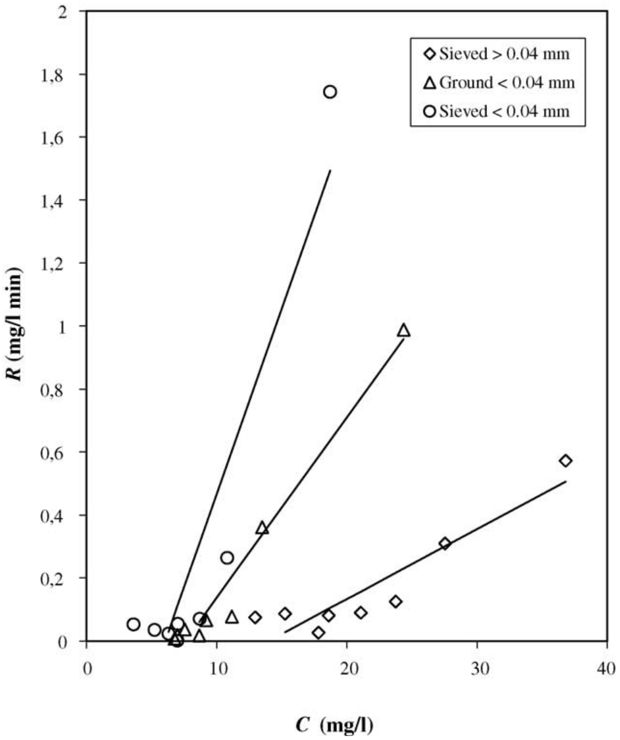

Fig. 5. Effect of the phosphorus concentration on the phosphorus removal rate for BMP at different particle sizes (sieved > 0.04 mm, ground < 0.04 mm and sieved < 0.04 mm) and a molar ratio of 2.0 in real liquor.

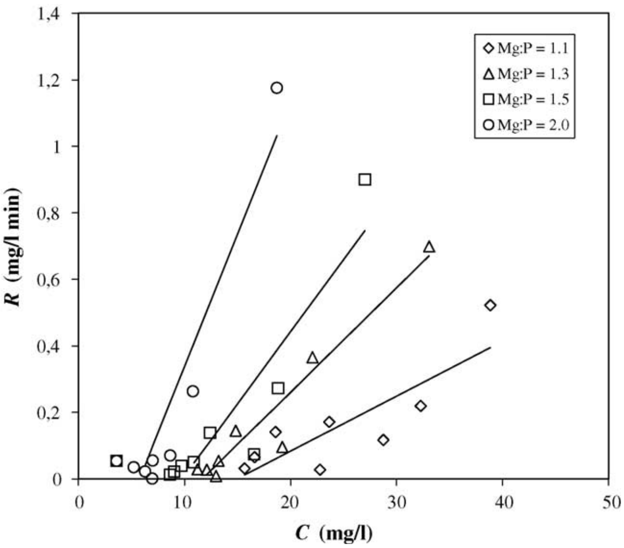

Fig. 6. Effect of the phosphorus concentration on the phosphorus removal rate for BMP at a particle size lower than 0.04 mm and different molar ratios in real liquor.

centration. Straight lines were obtained with linear regression coefficients higher than 0.90. The equilibrium concentrations were lower than those obtained for raw BMP at similar molar ratios. Moreover, the value of C_e at molar ratio of 2.0 was very close to that obtained with pure MgO at a molar ratio of 1.5. This fact is very important taking into account that the cost of BMP is considerably lower than pure MgO.

The values of K obtained for BMP at different molar ratios and particle size < 0.04 are given in Table 6. The values for K increased slightly with the molar ratio, mainly when the molar ratio increased from 1.1 to 1.3. When the values of K increased, the values of C_e were decreased. For the same molar ratio, the value of K was higher for sieved material with 0.04 mm compared with raw material. The maximum value of the kinetic constant was significantly lower compared with pure MgO (0.027 and 0.045 min^{-1}, respectively). The maximum values obtained for the constants were found to be 0.027 and 0.029 min^{-1}, for raw material at a molar (Mg:P) ratio of 3.0 and 3.6, respectively, and 0.027 min^{-1} for sieved material at a molar (Mg:P) ratio of 2.0. These values were 50% lower than those obtained by other authors with pure MgO [10,11]. Once the values of C_e and K were obtained, the struvite yield may be determined by Eq. (4), assuming that all phosphorus precipitated is in the form of struvite. This fact was corroborated by the experimental results obtained, which were summarized in Table 7 and coincided with those observed in other works reported in literature [7,17,18]. The results presented show that P, Mg and N mainly constituted the precipitates obtained in all cases, which are the components of struvite, and as was expected the ratio of Mg and P approached the unity. Comparing the characteristics of the precipitates obtained with synthetic and real liquor with those observed in pure struvite, the quality of the product obtained was better for MgO than for BMP in synthetic liquor. Moreover, the precipitates obtained with real liquor and BMP contained more impurities when compared with synthetic liquor and pure struvite. The impurities of the precipitation product obtained in the case of MgO and synthetic liquor may be attributed to the presence of calcium phosphate as was observed by other researchers [12,13]. In the case of BMP, the impurities of the precipitate increased in comparison to those observed with MgO due to the presence of certain amount of non-reactant magnesium, periclase, dolomite and magnesite [18]. This fact has been previously mentioned in preliminary experiments [18]. The use of real liquor contributed to increase the impurities of the precipitate obtained as can be observed in Table 7. Previous works carried out by the same research group have demonstrated that crystallization process certainly occurred during the experiment [18].

Table 6
Values of C_e and K for BMP at different molar ratios and particle size < 0.04 mm obtained from Fig. 6

Molar ratio (Mg:P)	C_e (mg/l)	K (min^{-1})
1.1	14.897	0.014
1.3	11.688	0.022
1.5	9.790	0.024
2.0	5.775	0.027

Probability level of 95% ($p < 0.05$).

Table 7
Chemical composition of the precipitates obtained in each case studied and comparison with pure struvite

Reagent	Liquor	Mg:P	%P	%Mg	%N	%Ca
Pure struvite	–	–	12.64	9.91	5.70	–
MgO	Synthetic	2.0	12.67	9.78	4.84	0.54
	Synthetic	2.5	10.95	8.35	4.99	0.34
BMP	Synthetic	1.5	10.04	13.25	4.10	1.95
	Synthetic	2.0	9.89	14.33	3.19	2.17
	Synthetic	2.5	9.81	12.90	3.33	1.93
	Real	2.5	9.76	14.83	3.28	2.52
	Real	3.0	8.83	13.23	3.38	0.92
BMP < 0.04 mm	Real	1.6	10.88	11.56	4.31	2.17

4. Conclusions

The experimental results obtained with synthetic liquor using pure MgO and BMP show the feasibility of BMP for phosphorous removal.

It was found that a first-order kinetic model adequately related the rate of phosphorous removal with the phosphorus concentration. It was found an increase in the value of the reaction constant (K) and a decrease in the equilibrium concentration (C_e) with the increase in the (Mg:P) molar ratio.

The values of the kinetic constant for real wastewater were higher (0.018–0.024 min^{-1}) than those obtained for synthetic liquor (0.009–0.017 min^{-1}). This behaviour could be caused by the influence of the alkalinity and presence of suspended solids in the real wastewater.

An increase in particle size caused a decrease in the value of the kinetic constant, the highest values being for particle sizes < 0.04 mm. For particle sizes < 0.04 mm, the values of the constant increased from 0.014 to 0.027 min^{-1}, when the (Mg:P) molar ratio increased from 1.1 to 1.5, decreasing the amount of BMP required in 60%.

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