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The effect of magnesium as activator and inhibitor of anaerobic digestion

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A B S T R A C T

Anaerobic digestion stands as a key technology in the emerging green energy economy. Mg^{2+} has been identified as an important element to improve digesters methane production; however the inhibition risk that high Mg^{2+} concentrations can cause to the AD process must also be considered when dosing Mg reagents and wastes containing Mg^{2+}. Despite its importance, Mg^{2+} stimulation and inhibition mechanisms as well as threshold values are scarce in the literature. This research paper investigates the impact (stimulation and inhibition) of Mg^{2+} on pig manure anaerobic digestion. Mathematical modelling was used to better understand the interaction between substrate, inoculum and magnesium, where Mg^{2+} inhibition was modelled by a n-component non-competitive inhibition function. Modelling was done on absolute curves rather than specific methane productions curves (new approach) to account for the lower background methane production of the inoculum as the Mg^{2+} concentration increased. Results showed that no stimulation or inhibition occurred between 40 (native concentration) and 400 mg Mg^{2+} L^{-1}, while minor and major inhibition were observed at 750 and 1000 mg Mg^{2+} L^{-1}, and at 2000 and 4000 mg Mg^{2+} L^{-1}, respectively. Mg^{2+} half maximal inhibition concentration was estimated at 2140 mg Mg^{2+} L^{-1} with an inhibition order of 2. The latter indicates that Mg^{2+} inhibition is a progressive rather than a steep inhibition mechanism.

1. Introduction

Anaerobic digestion (AD) stands as an important technology in the emerging green energy economy (Batstone and Virdis, 2014). AD implementation has been steadily increasing over the last years worldwide (De Baere and Mattheeuws, 2010; Lettinga, 2014; Li et al., 2011); however, there is still a great need to: (i) improve the economic feasibility of AD plants, and (ii) apply AD to a range of new substrates (Mata-Alvarez et al., 2014). For both scenarios, magnesium ion (Mg^{2+}) has been identified as a key element, since it can stimulate and inhibit anaerobic microbial activity. On the one hand, the addition of magnesium reagents and compounds containing magnesium (e.g. magnesium-rich zeolites and newberyite) have shown good results at enhancing digesters methane yields (Azman et al., 2015; Lee et al., 2007; Milán et al., 2010a; Romero-Güiza et al., 2014). On the other hand, high magnesium concentrations can be found in potential substrates for anaerobic (co-)digestion such as seaweed (e.g. *U. lactuca*; 4–14 g Mg^{2+} L^{-1}) (Allen et al., 2014; Nkemka and Murto, 2012; Peu et al., 2011; Rybak et al., 2012; Yaich et al., 2015, 2011), micro-algae (6–9 g Mg^{2+} L^{-1}) (Roberts et al., 2016) and plants (e.g. *Spartina alterniflora*; 0.1–0.5 g Mg^{2+} L^{-1}) grown in brackish and saline environments (Cai et al., 2013; Chen et al., 2014; Yang et al., 2009), olive oil mill wastewater (0.5–3.1 g Mg^{2+} L^{-1}) (Magdich et al., 2013; Raposo et al., 2003; Ureña et al., 2013) and molasses (0.1–0.4 g Mg^{2+} L^{-1}) (Jiménez et al., 2004; Kuroda et al., 2015; Onodera et al., 2013).

Mg^{2+} is an indispensable macronutrient to maintain proper function of biomass, as it plays vital functions in ribosome, cell membranes and nucleic acids (Ma et al., 2009). Nonetheless, Mg^{2+} can become inhibitory at high concentrations (Ahring et al., 1991; Yang et al., 2009). Some studies have addressed the effect of Mg^{2+} on AD performance. First studies analysed the impact of Mg^{2+} on methanogenic microorganisms' morphology. Ahring et al. (1991), who evaluated the effect of several cations on the morphology and growth of Methanosarcina thermophila TM-1, reported an optimum Mg^{2+} concentration of 730 mg Mg^{2+} L^{-1}. The authors also adapted M. thermophila up to 7290 mg Mg^{2+} L^{-1} without a change in growth rate; nonetheless, no growth was observed at 9720 mg Mg^{2+} L^{-1}. Schmidt and Ahring (1993) studied the influence of Mg^{2+} on thermophilic acetate-degrading granules

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in up-flow anaerobic sludge blanket (UASB) reactors fed with acetate. Results showed that acetate-degrading granules were affected by Mg^{2+} concentration, with concentrations between 12 and 245 mg Mg^{2+} L^{-1} giving the best performance of the UASB reactors. Recent studies regarding Mg^{2+} stimulation/inhibition have been carried out by researchers trying to combine AD and nutrient recovery (i.e. struvite precipitation) in the same reactor (Demirer et al., 2013; Romero-Güiza et al., 2015). In this matter, Othman et al. (2010) showed that Mg^{2+} concentration between 279 and 812 mg Mg^{2+} L^{-1} on waste activated sludge had no significant impact on biogas production when compared to control at 12 mg Mg^{2+} L^{-1}. Uludag-Demirer et al. (2008) observed no impact on biogas production when adding 209 mg Mg^{2+} L^{-1} to cattle manure, but partial inhibition when the addition was increased to 837 mg Mg^{2+} L^{-1}. In a following study, Demirer et al. (2013) did not find any impact on methane production when digesting sewage sludge at a 923 and 1847 mg Mg^{2+} L^{-1}. Contrariwise, Romero-Güiza et al. (2014) reported that increasing the Mg^{2+} concentration through a newberyite reagent from <20 to 50 and 700 mg Mg^{2+} L^{-1} was one of the possible reasons why the specific methane production of pig manure anaerobic digesters increased 25% and 40%, respectively. Finally, Milán et al. (2010b, 2003) observed that magnesium-modified zeolites were able to increase the specific methanogenic activity of archaea as well as stimulate their abundance. Table 1 summarises the impact of Mg^{2+} on different anaerobic digestion studies.

The aim of the present study was to investigate the impact of Mg^{2+} on AD performance regarding biomass stimulation and inhibition. Two sets of biomethane potential (BMP) tests under different Mg^{2+} concentrations were carried out to determine Mg^{2+} impact on manure biodegradability (extent and kinetics). Mathematical modelling was used to quantify the impact of the targeted inhibition on process performance.

2. Materials and methods

2.1. Pig manure, inoculum and chemicals origin

Pig manure and anaerobically digested pig manure were collected from a centralised AD plant located in Lleida (Spain). Both were stored at 4 °C prior to use; the inoculum was degassed at 37 °C for 3 days prior utilisation. Pig manure and the inoculum characterisation are given in Table 2. Analytical grade $MgCl_2{\cdot}6H_2O$ (Panreac Quimica, Spain) was used as Mg^{2+} source. $MgCl_2{\cdot}6H_2O$ was selected over other Mg sources (e.g. $Mg(CO_3)_2$, MgO, Mg

Table 1
Effect of magnesium on anaerobic digestion.

Waste	Inoculum	Reactor	OLR	T (°C)	Mg^{2+}		AD yield			Ref.
					Source	mg L^{-1}	Control	Sample	Units	
Synthetic	SS digestate	UASB	3gCOD L^{-1} (HRT = 9 h)	55	$MgCl_2{\cdot}6H_2O$	12–240[*]	0.57	0.85	$VS_{end}\ VS_{start}^{-1}$	Schmidt and Ahring (1993)
						730[*]		1.03		
						243[*]		0.81		
S. alterniflora	Leaching landfill UASB digestate	BMP		35	*S. alterniflora*	430[*]		0.36	LBiogas gVS^{-1}	Yang et al. (2009)
Synthetic	Winery WW sludge digestate	BMP		35	Magnesic zeolite	0.5[**]	0.26	0.43	$LCH_4\ gVSS^{-1}\ d^{-1}$	Milán et al. (2010a)
SS	SS digestate	Bench scale batch		35	$MgCl_2$	181[**]	0.22	0.21	LBiogas	Othman et al. (2010)
						336[**]		0.22		
CM	CM digestate	BMP		35	$Mg(OH)_2$	417[*]	0.10	−0.075	Net biogas (L)	Uludag-Demirer et al. (2008)
					$MgCl_2{\cdot}6H_2O$	447[*]		0.088		
Synthetic (acetate)	SS digestate	BMP		35	$MgCl_2{\cdot}6H_2O$	923[*]	0.14	0.14	LCH_4	Demirer et al. (2013)
						1847[*]		0.14		
SS	SS digestate	CSTR	50 gCOD L^{-1}	35	$MgCl_2{\cdot}6H_2O$	3281[*,a] 2066[*,b]	3.3–4.5	1.0–4.4 2.6–4.3	$LCH_4\ d^{-1}$	
PM	PM digestate	CSTR	1.1 gVS $L^{-1}\ d^{-1}$	37	$MgHPO_4{\cdot}3H_2O$	50[**]	0.13	0.17	$LCH_4\ gVS^{-1}\ d^{-1}$	Romero-Güiza et al. (2014)
						700[**]		0.19		
PM	PM digestate	BMP		37	$Mg(OH)_2$	288[**]	0.15	0.02	$LCH_4\ gVS^{-1}$	Romero-Güiza et al. (2015)
					$MgCl_2.6H_2O$	1086[**]		0.06		
					LG-MgO	770[**]		0.02		
					HG-MgO	831[**]		0.04		
					$MgHPO_4{\cdot}3H_2O$	715[**]		0.15		
Paper industry WW	SS digestate	BMP		30	$MgCl_2$	122[*]	0.31[c]	0.27	$LCH_4\ gVS^{-1}$	Azman et al. (2015)
							0.11[d]			

SS: Sewage sludge; WW: Waste water; PM: Pig manure; CM: Cattle manure; BMP: Biomethane potential test; CSTR: Continuous stirred tank reactor.
[*] $[Mg^{2+}]_{in}$.
[**] $[Mg^{2+}]_{end}$.
[a] Shock dose.
[b] Daily dose.
[c] Positive control.
[d] Inhibition control.