



Effect of Fe–Zn–Mg–Al hydrotalcites on the methane potential of synthetic sulfate-containing wastewater



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ABSTRACT

Three hydrotalcites of M^{2+} -Mg–Al were synthesized using the co-precipitation method, where M^{2+} was Fe^{2+} , Zn^{2+} and $Fe^{2+} + Zn^{2+}$. The hydrotalcites and their calcined form of mixed oxides obtained by their thermal decomposition were characterized by FTIR, XRD and SEM. Subsequently their effect on the methane potential of synthetic wastewater comprised of sucrose and sulfur was evaluated in a multiple batch system at $37 \pm 0.5^\circ C$. The best methane potential was observed from the Fe–Zn–Mg–Al hydrotalcite at 500 mg/L yielding 372 mL CH_4/gVS which corresponds to an 8.1% increment against the control. The better performance of the Fe–Zn–Mg–Al hydrotalcite can be attributed to the Zn^{2+} ions. These react with S^{2-} in the substrate to yield zinc sulfide and therefore prevent it from forming H_2S by sulfate reducing bacteria, meanwhile reducing competition for methanogens to form methane. Calcined hydrotalcites neither stimulated nor inhibited the methane production which suggests that the enhancement of methane produced by the Fe–Zn–Mg–Al hydrotalcite was related to the presence of Fe^{2+} and Zn^{2+} cations incorporated and immobilized in the layered sheet structure of the hydrotalcite.

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1. Introduction

The ongoing need to promote the production and use of renewable energy has opened way to research for improving the mature technologies found nowadays. Upgrading and optimization of industrial process design has led to increased energy efficiencies where a main focus is also energy recovery. Anaerobic digestion of organic waste and wastewater is a well-established treatment technology, it not only destroys pathogenic organisms and reduces problems associated with management and disposal of waste, but it also allows potential energy recovery in the form of methane-rich biogas. Methane derived via anaerobic digestion is often described as an ideal fuel [1,2]. It requires low energy to be produced, generates limited atmospheric pollutants and less carbon dioxide per unit energy. It will produce roughly 47% less carbon dioxide than coal and 24–27% less carbon dioxide than gasoline and diesel [3]. Methane can be easily distributed with existing pipelines making it available for domestic, municipal and industrial use and depending

on its purity; it can be used for appliances, vehicle fuel, industrial applications and power generation.

Anaerobic digestion is widely applied as wastewater treatment in various types of industries and commonly in agriculture and the municipal sector. However for the pulp and paper industry it has received attention only in the recent past years. The pulp and paper industry is one of the most water consuming industries and although much effort has and is been implemented in reducing their water footprint it still generates high volumes of wastewaters, from 13 to 30 m³ of water per ton of produced paper, with very particular characteristics [4]. One of the common characteristic is the presence of sulfur compounds due to the chemicals used in kraft pulping; which is the most widely used type of chemical pulping. Kraft pulping uses hydrogen sulfite (HSO_3^-) as the main chemical, resulting in sodium sulfide (Na_2S), sodium sulfate (Na_2SO_4), sodium sulfite (Na_2SO_3) and sodium thiosulfate ($Na_2S_2O_3$) present in the process effluent [4]. Wastewaters are also characterized by high biochemical oxygen demand (BOD), high chemical oxygen demand (COD), chlorinated compounds (measured as adsorbable organic halides AOX), suspended solids (mainly fibers), fatty acids, tannins, resin acids, lignin and other wood extractives [5,6].

Usually pulp and paper mills treat their wastewaters in aerobic activated sludge plants, which consequently create large production of waste sludge. This led to an increase of studies on various pretreatment methods in order to enhance the methane

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Table 1
Methane potential of different wastes from the pulp and paper industry.

Substrate	Methane yield (NmL/gVS)	Reference
Poplar biomass waste	230–320	[1]
Willow biomass waste	130–300	[1]
Pulp and paper mill biosludge	40–200	[2]
Bleached kraft secondary sludge	50	[7]
Thermomechanical secondary sludge	89–197	[7]
Sulphite secondary sludge	159	[7]
Kraft secondary sludge	145	[7]
Chemithermomechanical secondary sludge	97–199	[7]
Bleached kraft and paper secondary sludge	108	[7]
Microcrystalline cellulose wastewater	333	[1,27]

potential of pulp and paper sludge [2,7,8]. Buyukkamaci and Koken [9] explain the economic and effective alternative of combining anaerobic wastewater treatment with aerobic post treatment. This is due to the fact that in most cases the application of only anaerobic treatment does not deliver treated effluent of sufficient quality. However by implementing anaerobic treatment first, it reduces the organic load to the aerobic treatment; which in many cases is overloaded; and causes less sludge production. Moreover there is the potential of energy recovery which gives the economic incentive. Nonetheless, few literature is found on the anaerobic digestion and methane enhancement of pulp and paper wastewater.

Meyer and Edwards [2] reviewed the anaerobic digestion and methane potential of different effluents coming from pulp and paper mills. Depending of the type of pulping and the chemical used during the pulping process the COD removal and methane productions vary greatly (Table 1). They found that condensate streams from chemical pulping have the highest COD removal rates (75–90%). The lowest rates correspond to chemical sulfite pulping effluents (29–38%) and debarking effluents (44–70%) from the mechanical pulping; mostly due to sulfur inhibition and concentration of lignin and resins respectively. Methane production followed the same pattern. Bleaching effluents in general were found to have inhibitory compounds for anaerobic digestion having the lowest methane production (0–380 mL kg⁻¹ COD removed). Effluents with the highest methane potential were from the neutral sulfite chemical pulping (NSSC) condensate (380–400 mL kg⁻¹ COD removed), where there is high acetic acid concentrations contributing to the direct formation of methane. They concluded that the numerous studies conducted show that, contrary to common perception, most mill effluents were to some extent anaerobically treated even the difficult to digest streams. This suggests the possible enhancement of methane production of these effluents by means of pretreatment, co-digestion or catalysis.

Hydrotalcites (HTs) or layered double hydroxides are anionic clays that have a broad spectrum of applications such as catalysts, pharmaceuticals, absorbents, ion exchangers and many more applications arising due to the possibility of designing them tailored to specific reactions and/or substrates [10,11]. HTs and their calcined products have also gained attention in wastewater treatment and purification for its high ion-exchange capacities for adsorption of various anionic pollutants which include bromide, arsenic, lead, fluorine, chromate and other toxic anions [12–16]. Douglas et al. [17] studied the formation and effect of HTs in the treatment of mining wastewater and acidic wastewaters. They report results of optimal removal of a broad spectrum of contaminants from the wastewaters, including uranium. HTs have also been employed to increase hydrogen production in fermentation processes [11,18].

HTs compounds have a brucite-like structure with stacked layers of metal cations following the general formula of $[M_1-xM_2^2+M_3^3+(OH)_2]_n[A_{x/m}]^{m-} \cdot nH_2O$, where M_1^{2+} is a divalent cation, M_3^{3+} is a trivalent cation, A an interlamellar anion with charge m^- and x is the

ratio of $M^{3+}/(M^{2+} + M^{3+})$ [15]. For this study two anions (Fe^{2+} and Zn^{2+}) were chosen to be incorporated into the HT structure by co-precipitation; in order to assess their influence on the improvement of anaerobic digestion and methane potential of the substrate. The functionality of iron in the anaerobic process is well known [19]. Iron is essential for microbial growth and is an important component of many of the enzymes involved in the metabolic pathways of bacteria; it also enhances the granulation process. Methanogens have a specific growth requirement for iron, and concentrations of 2.6 g L⁻¹ of $FeCl_2$ have increased conversion of acetic acid to methane. However if present in high concentrations (5.6 g L⁻¹) it becomes toxic [19,20]. Though iron is one of the most abundant elements, its bioavailability is limited since the majority is in the insoluble 3+ state. Casals et al. [21] studied iron oxide nanoparticles in anaerobic digesters and found an increase in biogas production of up to 40% when 0.15 mg/mL iron sulfate was added, concentrations higher than resulted in a dramatic decrease in biogas production. Zinc was chosen for its ability to remove sulfur components [22,23]. Another key characteristics is the nano-scale particle size of HTs, this provides large surface areas (20–120 m²/g) that may possibly boost bacterial anchoring in the anaerobic process [24]. Nanoparticles have the advantage of reacting rapidly with the electron donors leading to kinetic improvements and also act as biocatalysts enhancing the activity of microorganisms [25]. This study addresses the importance of evaluating a new pretreatment for pulp and paper effluents. The idea of boosting methane production from these waste streams and generating energy is becoming more widespread through the pulping industry and the need for different pretreatment options is clearly noticeable. In this study, M^{2+} -Mg-Al HTs with combinations of Fe and/or Zn metal ions, were synthesized with the co-precipitation method and characterized. Most importantly, their effect on the methane potential of synthetic sulfate-containing wastewater was evaluated.

2. Materials and methods

2.1. Hydrotalcite preparation

Hydrotalcites of M^{2+} -Mg-Al were synthesized using the co-precipitation method as described in the literature [26], where M^{2+} was Fe^{2+} , Zn^{2+} and $Fe^{2+} + Zn^{2+}$. The ratio between the molar fraction of divalent and trivalent cations (M^{2+}/M^{3+}) was 3:1. In this method two solutions were prepared. The first aqueous solution consisted of a 300 mL mixture of metal nitrates of $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ and/or $FeSO_4 \cdot 7H_2O$, and $Zn(NO_3)_2 \cdot 6H_2O$ in the desired molar ratios. The second solution was prepared by dissolving NaOH (2.25 M) and Na_2CO_3 (0.45 M) in 300 mL of distilled water. The second solution was added to the first solution dropwise at a rate of 50 mL/h under vigorous stirring until the pH reached around 9–10. The thick slurry formed was aged in a thermostatic bath for 18 h at 60 °C. Afterward, the slurry was filtered and washed thoroughly with deionized water in order to remove the alkaline metals and nitrate ions until the filtrate effluent reached a neutral pH. Finally, the filter cake was dried at 110 °C for 24 h and ground in a mortar. Calcined HTs were obtained by placing ground HTs in a muffle furnace at 500 °C for 4 h.

2.2. Hydrotalcite characterization techniques

The structures of HTs as prepared and after calcination were analyzed by X-ray diffraction (XRD) technique using a Bruker D8 instrument equipped with a Cu target and a graphite monochromator. XRD patterns were recorded at 40 kV and 40 mA by using Cu radiation ($\lambda = 0.15406$ nm) at a rate of 0.02°/s from $2\theta = 5-75^\circ$. The average crystals sizes (Dc) were estimated from full width at

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