Research article

Nutrient management via struvite precipitation and recovery from various agroindustrial wastewaters: Process feasibility and struvite quality

Raffaele Taddeo [a, *], Mari Honkanen [b], Kari Kolppo [c], Raghida Lepistö [a]

[a] Tampere University of Technology, Laboratory of Chemistry and Bioengineering, P.O. 541, FI-33101, Tampere, Finland
[b] Tampere University of Technology, Laboratory of Materials Science, P.O. 589, FI-33101, Tampere, Finland
[c] OY Scandinavian Colloids Ltd, Tampere, Finland

ABSTRACT

Improving environmental protection and finding sustainable and renewable resources of nutrients are core issues in circular bioeconomy. Thus, this study evaluated the efficiency of recovering struvite, $MgNH_4PO_4 \cdot 6H_2O$, from different agro-industrial wastewaters (four highly loaded reject waters of anaerobically co-digested agro-industrial waste and a raw swine slurry) and assessed the quality of recovered struvite crystals and their reusability as fertilizer. The efficiency of crystallization (E_c 40–80%) and amount of struvite in the precipitate (P_p 55–94%) highly varied due to the characteristics of influent wastewaters, particularly to the content of competing elements, such as alkaline and heavy metals and total solids (TS). In particular, E_c (94, 75, 61%) and P_p (76, 66, 48%) decreased at increasing TS (0.57, 0.73, 0.99%), demonstrating the hindering effect of solid content on struvite recovery and quality. According to X-ray diffraction analysis, the structure of all isolated samples corresponded to crystalline, orthorhombic struvite, which exhibited high purity (32–48 g/kg_d N, 114–132 g/kg_d P, and 99–116 g/kg_d Mg) containing only a few foreign elements, whose amount depended on the characteristics of the influent wastewater. All struvite contained other plant macronutrients (K, Ca) and many micronutrients (Fe, Na, Cu, Mn, Co, Zn) that further enhance its agronomic value. Therefore, this study showed that struvite can be successfully recovered from a wide range of highly loaded agroindustrial wastewaters, and that the quality of the recovered struvite could be suitable for reuse in agriculture.

© 2018 Elsevier Ltd. All rights reserved.
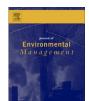
1. Introduction

The sequestration of main nutrients, nitrogen (N) and phosphorus (P), from all wastewaters is subject to increasingly strict regulations; however, in agroindustry, nutrient management remains an environmental concern. Agroindustrial wastewaters, either raw or post-treated (usually by anaerobic digestion), are commonly characterized by high N and P content, but also by a high amount of heavy metals and other contaminants, which can hinder reuse and disposal and may require further treatment. High nutrient flows originating from agricultural soil, animal husbandry, and related activities (Carpenter et al., 1998) greatly affect the wellbeing of the ecosystem, triggering water eutrophication and associated issues to marine ecosystems (Carpenter, 2005; Diaz and Rosenberg, 2008).

Moreover, farming operations contribute to air (Aneja et al., 2008) and soil pollution (Carpenter et al., 1998). For example, excessive use of chemical P fertilizer leads to heavy metals accumulating in soil (Huang and Jin, 2008; Atafar et al., 2010) and, to a large extent, to altering the biogeochemical P cycle (Steffen et al., 2015). Similarly, the manufacture of mineral N fertilizer by the Haber-Bosch process is the main source of anthropogenic reactive N, which has thoroughly changed the natural geochemical N cycle (Vitousek et al., 1997; Mackenzie et al., 2002). This anthropogenic alteration of the natural N and P cycles and the transgression of other recognized Planet Boundaries are the main drivers of the ongoing global environmental change (Rockström et al., 2009a,b). The manufacture of P fertilizer also poses a health and safety hazard due to heavy metals, such as cadmium (Cd) and lead (Pb), present in

P ores (Ju et al., 2007; Pizzol et al., 2014), which are a finite (Scholz et al., 2013) yet, like N, an essential commodity.

In this context, it is essential to secure renewable and sustainable resources to fulfil agroindustrial demands and, at the same time, to reduce the anthropogenic environmental impact of agroindustry. Various approaches are currently being studied or implemented in light of circular bioeconomy to convert wastes into renewable resources. One such approach is the precipitation and recovery of struvite, $MgNH_4PO_4 \cdot 6H_2O$. Struvite is formed from those compounds posing environmental risk, NH_4^+ and PO_4^{3-}, and is a slow-release fertilizer, though its commercial use is not yet fully regulated. Struvite is now more frequently recovered at municipal wastewater treatment plants (WWTP) (Schoumans et al., 2015; Melia et al., 2017) with the main objective to totally sequester PO_4^{3-}, so far achieved by chemical precipitation or via a biological pathway. Applying struvite precipitation to municipal wastewaters has many economic and technological advantages (Kleemann et al., 2015; Martí et al., 2017). However, in municipal wastewaters, PO_4^{3-} is usually <10 mg/L (Melia et al., 2017) and N usually between 50 and 150 mg/L (Lowe et al., 2009), whereas agroindustrial wastewaters are characterized by a far higher nutrient content. Therefore, struvite recovery from these big anthropogenic flows would be more effective both for environmental protection and for nutrient recycling.

Although some processes have been proved efficient in recovering struvite from agroindustrial wastewaters at different scales (Suzuki et al., 2007; Moerman et al., 2009), struvite precipitation is still at experimental level in treating highly loaded nutrient streams (Schoumans et al., 2015). The high N content and the unbalanced molar ratio between the struvite forming elements require addition of chemicals to reach the optimal molar ratio for struvite precipitation. Moreover, a potentially high content of competing elements can inhibit struvite crystallization. For example, K^+ could foster the formation of struvite-K, $MgKPO_4$, (Wilsenach et al., 2007), which, too, may have fertilizing properties. Struvite precipitation may also be affected by the Ca^{2+}/Mg^{2+} ratio, which could promote the co-precipitation of calcium phosphates, mainly hydroxyapatite (Le Corre et al., 2005; Song et al., 2007; Uysal et al., 2010). In addition, co-precipitation of magnesium phosphates may also occur (Doyle and Parsons, 2002; Ronteltap et al., 2007), especially in wastewaters having high concentration of carbonates (Song et al., 2007).

Heavy metals content can decrease the purity of the recovered precipitate and theoretically impede struvite reutilization as fertilizer. Heavy metals may be removed during struvite precipitation (Uysal et al., 2010) either by generating struvite analogues (Ronteltap et al., 2007; Weil, 2008) and/or by being incorporated in the forming struvite nuclei (Ronteltap et al., 2007; Ma and Rouff, 2012; Rouff et al., 2016). Furthermore, organic compounds may affect crystal nucleation by forming soluble compounds with Mg^{2+}, thus decreasing its availability for struvite precipitation (Nelson et al., 2003). Suspended matter can lower the efficiency of the crystallization process (Taddeo and Lepistö, 2015) and is expected to affect the quality of the recovered precipitate.

Accordingly, this study aimed to determine feasibility, efficiency of recovery, and quality of struvite, as well as issues affecting struvite precipitation from a wide range of highly loaded agroindustrial effluents. In particular, the study sought to evaluate the effect of the solids (Total Solids, TS, and Total Suspended Solids, TSS) and heavy metals content of influent wastewater on precipitation and quality of the recovered struvite.

2. Materials and methods

2.1. Wastewaters

Struvite was produced in a pilot reactor from five different wastewaters, mostly originating from agroindustry (Table 1). In particular, RW1 and RW2a,b were reject waters from two biogas plants, JK was reject water from the biogas facility of a solid waste management centre, and RS was raw pig slurry.

RW1 was sampled from a centralized biogas plant, co-digesting (38 °C, solids retention time, SRT, 18-23d) pig slurries with a smaller share of industrial and municipal biodegradable wastes. RW2a,b derived from another biogas plant processing in mesophilic conditions (38–42 °C, SRT 21-23d) WWTP sludge (40–50%), fat slurry (10–20%), food industry by-products (20%), and pig manure (20%). The reject water was sampled twice a few months apart and showed varying TS content, mainly caused by slightly different recipes (seasonal variation) and different polymers used in the dewatering process. The anaerobic digester (T around 52 °C, average SRT 25d) of the solid waste management centre (JK) is fed on average with 20% source-separated solid bio-waste, 50% WWTP sludge, and 30% industrial and agroindustrial sludge. The JK

Table 1
Characteristics of the wastewaters used for struvite recovery, where error limits are estimated by the standard deviation of at least three replicates.

element		RW1	RW2a	RW2b	JK	RS
pH		8.33 ± 0.07	8.20 ± 0.04	8.33 ± 0.06	8.60 ± 0.03	7.78 ± 0.03
alk[a]	(mg/L)	19969 ± 75	12714 ± 38	11300 ± 745	11825 ± 98	12900 ± 150
NH_4-N	(mg/L)	5485 ± 116	3270 ± 103	3135 ± 14	3290 ± 28	3450 ± 28
N_t	(mg/L)	6744 ± 213	4251 ± 202	3833 ± 233	4258 ± 8	4470 ± 170
TS	(g/L)	15.80 ± 0.05	14.51 ± 0.02	7.65 ± 0.05	12.42 ± 0.01	18.52 ± 0.42
TVS	(g/L)	8.26 ± 0.14	9.40 ± 0.02	4.94 ± 0.01	8.40 ± 0.02	12.45 ± 0.3
CODt	(mg/L)	15563 ± 138	15983 ± 267	7538 ± 113	18250 ± 450	32900 ± 518
CODs	(mg/L)	7870 ± 230	7130 ± 30	4105 ± 65	9230 ± 410	22663 ± 13
PO_4-P	(mg/L)	528 ± 3	33 ± 6	25 ± 2	14 ± 4	122 ± 6
Mg	(mg/L)	29 ± 7	23 ± 3	38 ± 8	19 ± 6	123 ± 8
K	(mg/L)	888 ± 13	1692 ± 27	671 ± 6	141 ± 16	2019 ± 185
Ca	(mg/L)	28 ± 1	19 ± 4	42 ± 17	28 ± 16	272 ± 22
Na	(mg/L)	498 ± 71	147 ± 10	274 ± 10	201 ± 7	634 ± 77
Ni	(µg/L)	213 ± 65	2088 ± 632	626 ± 118	252 ± 9	479 ± 61
Zn	(µg/L)	505 ± 13	1000 ± 323	375 ± 11	79 ± 7	8480 ± 825
Co	(µg/L)	452 ± 122	436 ± 33	101 ± 4	62 ± 7	145 ± 77
Cu	(µg/L)	93 ± 32	360 ± 153	55 ± 5	20 ± 0	2204 ± 48
Fe	(µg/L)	6340 ± 225	36878 ± 4648	13950 ± 925	10610 ± 310	8523 ± 739
Mn	(µg/L)	1210 ± 140	398 ± 79	110 ± 34	18 ± 7	4184 ± 892
Cr	(µg/L)	814 ± 2	757 ± 71	45 ± 12	16 ± 1	268 ± 41

[a] Alkalinity measured at pH 4.3.