Prof. Juan Francisco Rodriguez Romero, ID: 05651103ªA, Full Professor of Chemical Engineering and Head of the Department of Chemical Engineering of the University of Castilla-La Mancha, building Enrique Costa, Faculty of Chemical Sciences and Technology, Campus Universitario, 13004 Ciudad Real,

INFORM,

That I have been requested for a evaluation of the PhD Thesis of MSc Claver Numviyimana entitled “Struvite precipitation from processed dairy wastes” and this is my opinion.

The general aim of the thesis is to develop a method for the phosphorous recovery from dairy wastes sludges with the focus of their transformation in struvite for its further usage as a phosphorous fertilizer.

The candidate Mr. Numviyimana has done a very complete overview of the literature in the introduction about the approaches to wastewater phosphorus recovery. The PhD candidate has done an important effort to justify the interest of the struvite precipitation for its usability as a fertilizer, with the provision of P and nitrogen in an efficiently available form for plant nutrition. The thesis collects the knowledge of existing technologies for organic biowastes treatment, their P pathway, dissolution and struvite precipitation.

The experimental work focuses on the study of process conditions for phosphorus recovery as struvite from dairy wastes through their thermochemical treatment and precipitation. The research methodology, including the characterization methods and the mathematical treatment of results, is well planned and is adequate to get the objectives of the research.

The experimental part starts describing the Struvite precipitation process from Cheese wastewater. A mineralization process based on the electrochemical hydrolyzation of the wastewater under reflux with hydrogen peroxide and hydrochloric acid to have 3% of pure H_2O_2 and 10% of concentrated HCl was applied.

A design of experiments on cheese wastewater hydrolyzation conditions is carried out to find the optimum requirements of overcoming the effect of calcium and enhance struvite precipitation at high concentration. The study concludes that for maximizing struvite precipitation, the optimum level of Ca:P mole ratio is needed to be lower than 0.25 while pH keep at 8.3. However, the conditions that maximize both P and struvite precipitation were obtained at pH 8.9.

In the published research related to this work, the in-vitro nutrient release was lower for product of precipitation with higher mole ratio Ca:P in feed reactor while it was effective under optimized lower Ca:P mole conditions.

As an alternative for improving the struvite precipitation from the hydrolyzed cheese wastewater, the addition of a natural zeolite as cliptonite for controlling the NH4+ ion coprecipitation is studied. First, the ion exchange equilibria between Mg-clinoptilolite and a model solution of NH_{4+} is investigated with batch mode experiments. The liquid-solid equilibria of the system was thermodinamically modelled with great precision and the changes in solution composition and the zeolite properties properly described based on XRD analyses and metal ion measurements.

From a practical point of view, the addition of cliptonite allows an enhancement to 97.44 percent of NH4+ by adding zeolite up to 1.5 percent of the reaction volume. The applied dose from the gradient descent precipitation supplemented with zeolite enhanced the equilibrium ammonium drop from 84.4 to 48.7 7.63 $mg.dm^{-3}$, while P remained significantly low at 4.23 $mg.dm^{-3}$, highlighting natural zeolite's ammonium sorption capacity. This is an advantage in mitigation of the environment pollution caused by excess of ammonium in struvite precipitation effluent. Furthermore, in the related published work, the clinoptilolite formulation with struvite was effective in the increase of crop yield. The in-vivo study indicated that the struvite combined with zeolite is a good formulation which improved the plant harvest dry biomass of cucumber sprout up to the double of the trials without zeolite.

The Thesis follows with an wide investigation of the phosphorus recovery from thermochemically processed sludge. In this second part, a dairy sludge is subjected to hydrothermal carbonization HTC and P recovered as struvite from the processed water.

Also, the chemically produced sludge is treated with ferric coagulants for iron recycling along with P purification to struvite.

The first step in this part of the study is a deep characterization of the sludge and the accompanying water. The first conclusion extracted from the characterization is that the concentration of P is higher in the sludge than in the wastewater. This highlights the benefits of P accumulation process used in wastewater treatment. Secondly, the use of iron coagulants, makes its concentration becoming very high in the sludge. Upon thermochemical treatment, the concentration varies in each fraction yield compared to feed sludge. The small fraction of metal ions dissolved in the liquid phase (S5) compared to sludge (S3), make that multivalent metal ions appears immobilized in hydrochar (S4). Despite the low dissolution rate, the concentration of P in HTC liquor was still high and made it a nutrient rich aqueous mixture for the recovery through precipitation process.

To facilitate the struvite precipitation from the HTC liquor and getting a better struvite product purity, the iron extraction methods are studied. Oxalic acid was demonstrated to be effective to extract P from precipitate and settle iron and calcium in as their oxalate salts. Since the ammonium effluent concentration has a regulated threshold, the natural clinoptilolite was used for ammonium sorption in the struvite precipitation effluent. The use of 0.375 $mol \cdot L^{-1}$ solution of oxalic acid was very effective decreasing 9 times the iron concentration. On the other contrary, the use of sodium sulphide was not effective for iron removal. At the same concentration of extracting agent, the iron decrease was only 23%. The main reason is the formation and evolution of hydrogen sulphide gas by hydrolysis of sodium sulphide.

To extract phosphate, decrease iron and find the proper salt dosage to mitigate the negative effect of liquor composition on product quality an extraction studio based on DOE application is performed. Up to 15 experiments were conducted for each mimic solution of the sample and the extract, due to the quality of final products in regards to fertilizer market it was found mandatory to remove iron in prior of any optimization. Calcium was also decreased along with iron while P passed in supernatant. Additionally, the effect of dilution and residence time. The growth of phosphate precipitate was found to be time and dilution (DF) dependent. An increase of 24h in residence time allows to obtain particles of half millimetre size.

Additionally, the high initial concentration enhances the precipitate growth. Particles as large as 1 mm was found when the sample was not diluted (DF1).

The final section of the Thesis is devoted to the Struvite precipitation from incinerated sludge ash. For that purpose, ash and magnesite were mixed with a Mg:P molar ratio of 1.73, a ratio that was determined experimentally. The extraction process used is the method of RecoPhos technology with some modification. *RecoPhos* proceeds with P dissolution using phosphoric acid followed by precipitation. It adopts the industrial production of triple superphosphate by use sewage sludge ash as phosphate rock substitute. In the Thesis, the addition of phosphoric acid had a double advantage including adjusting mole ratios of struvite inhibitors, i.e (Ca + Fe): P to small value, and transform mineral phosphate rock under a generalized formula of $Ca_4Mg_5(PO_4)_6$ to soluble Calcium hydrogen phosphate ($Ca(H_2PO_4)_2$) and Magnesium hydrogen phosphate ($Mg(H_2PO_4)_2$). The additional acid in intended to the efficient dissolution of iron based P rich ash.

The combination of phosphoric acid and hydrochloric acid improves the dissolution efficiencies of magnesium, calcium and iron from their matrices. The increment of hydrochloric acid solvent strength increased the dissolution efficiencies. Compared to the 2M HCl strength, the 4M HCl reached the highest magnesium dissolution of up to 80%.

Once optimised the dissolution in phosphoric acid and hydrochloric acid of the incinerated dairy sludge ash a detailed study of the struvite precipitation was performed. As a result of this study, three products were synthetized: product (a) was synthetized with magnesium chloride as Mg source, while product (b) was synthetized with magnesite acidic solution as Mg source and the third product (c) was synthetized by addition of ammonium and alkali to the ash and magnesite mixture. Compared to their original ash, the results show that the products were enriched in nitrogen and magnesium. Nevertheless, these effects are inversely proportional to the productivity where the mass of product increases with matrix effects. Thus the combination of dairy sludge ash and magnesite for struvite precipitation can yield a better primary macro nutrient profile (N,P,Mg) in the product than the ash.

To confirm the capability of the recovered products as fertilizers, kinetic measurements of nutrients release through the in-vitro assays, and nutrients use efficiencies has been

performed. The experimental results have been mathematically interpreted using a quite accurate model.

Ahead of the chemical nature of this work, the thesis contains a detailed work exploring the effect of this products as fertilizers, through *in-vivo* assay on cucumbers. The germination test showed a difference in terms of plant health and nutrient effects. After one week, the seeds were effectively germinated at 80, 32, and 88% for the control, and the soil fertilized with P products *b* and *c*, respectively. The lower germination rate observed for high iron content products (*b*) highlights the risk of phyto-toxicity. On the other hand, removing a large fraction of iron makes the product more valuable for fertilizer application. The Iron content in the product is within the accepted range and becomes a benefit to the plant for the production of a micronutrient bio-fortified diet.

Finally, the business case for producing the struvite with the use of raw materials of dairy sludge HTC process water is presented.

The author proposes a design with a system of double connected reactors with similar mechanical properties. In the first tank, the iron and calcium are precipitated by oxalic acid and the supernatant rich in P is continued to struvite precipitation reactor. The extraction time is 30-60min. In the second tank, the liquor leachate, the magnesium chloride, and sodium hydroxide are added up to pH 9 for struvite crystallization. Adopting the configuration based on the famous reactors of Pearl® Fluidized Bed Reactors Ostara type.

As conclusion of the economic feasibility study is stablished that the the struvite production cost is approximately 1.11 USD/Kg. It makes a promising and cheap technology to contribute to dairy wastes management by valorising them into a micronutrient enriched struvite fertilizer.

As a result of this part of the thesis at least on article in peer reviewed journals has been published and I am pretty sure that further publications will be released.

The quality of the scientific work performed has been also be recognized with the participation in several international congress.

I consider that the candidate has demonstrated maturity enough as researcher in the synthesis of struvites and other materials, also a deep knowledge of the materials characterization techniques and has gotten all the initial goals marked to achieve the final objective of reducing the environmental impact of sludges and take advantage of them for their us a fertilizer. Therefore, I think that not only the PhD candidate has done an excellent research work but also that the method for sludges valorisation developed have an especial importance due to the present social interest in the reduction of the environmental impact of wastewater sludges.

Taking into account all the arguments previously exposed, I state that the reviewed doctoral thesis of Claver Numviyiman, M.Sc., titled "*Struvite Precipitation from Processed Dairy Wastes"* meets the requirements for doctoral dissertations specified in Art. 187 of the Act of July 20, 2018 Law on Higher Education and Science (Journal of Laws of 2018, item 1668, as amended). Therefore, I am applying to the Chemical Engineering Discipline Council at the Wrocław University of Science and Technology for admission to the next stages of the procedure for the award of a doctoral degree in the field of engineering and technical sciences in the scientific discipline of chemical engineering."

In Ciudad Real, June 26th 2022

RODRIGUEZ ROMERO JUAN FRANCISCO - 05651103A

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