Optimization of the acid hydrolysis process of dairy waste for the production of organic-mineral fertilizer

Rafał Taf[1], Filip Gil[1], Małgorzata Mironiuk[1], Katarzyna Chojnacka[1]

[1]Department of Advanced Material Technologies, Faculty of Chemistry, Wroclaw University of Science and Technology, Wroclaw, Lower Silesia, 50-370, Poland
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Presenting author email: rafal.taf@pwr.edu.pl

The dairy industry constitutes a major segment of the food sector, particularly in Europe. Milk and dairy products are consumed worldwide, with the most popular being butter, cheese, powdered, skimmed and condensed milk, yoghurt, and cream. In the European Union countries, 160.8 million tons of milk are produced annually, of which 149.3 million tons are used at processing sites, yielding 106.6 million tons of dairy products (Eurostat, 2024). It was estimated that about 192.5 mln m^3 of wastewater is generated during processing only in European Union (Stasinakis et al., 2022). By comparison, worldwide, milk processing produces about 4-11 million tons of solid and liquid wastes (Usmani et al., 2022). In accordance with EU law (Regulation (EC) No 1069/2009), waste from milk processing is classified in Category III, characterized by low environmental risk, but not intended for human consumption. Waste from this class can, after appropriate processing, be successfully used in the production of fertilizers and soil-improvers (EUR-Lex, 2009).

Fertilizers play a critical role in ensuring sufficient crop yields in modern agriculture and make it possible to obtain large enough yields, to provide the food needs of the population. Previous studies indicate that dairy wastes contain appreciable levels of inorganic salts, fatty acids, proteins and macroelements (N, P and K), among others (Ahmad et al., 2019). For this reason, there is a very high potential for their processing toward obtaining fertilizer formulations. This represents a practical application of circular economy principles in waste valorization, during which the resulting waste is neutralized and becomes a raw material for the production of valuable agricultural products. For this reason, work has begun on developing a fertilizer based on dairy waste from the SM Gostyń dairy cooperative, aiming to apply chemical and biological methods to obtain fertilizer formulations rich in amino acids, which are excellent biostimulants. An overview of the research methodology is presented in Figure 1.

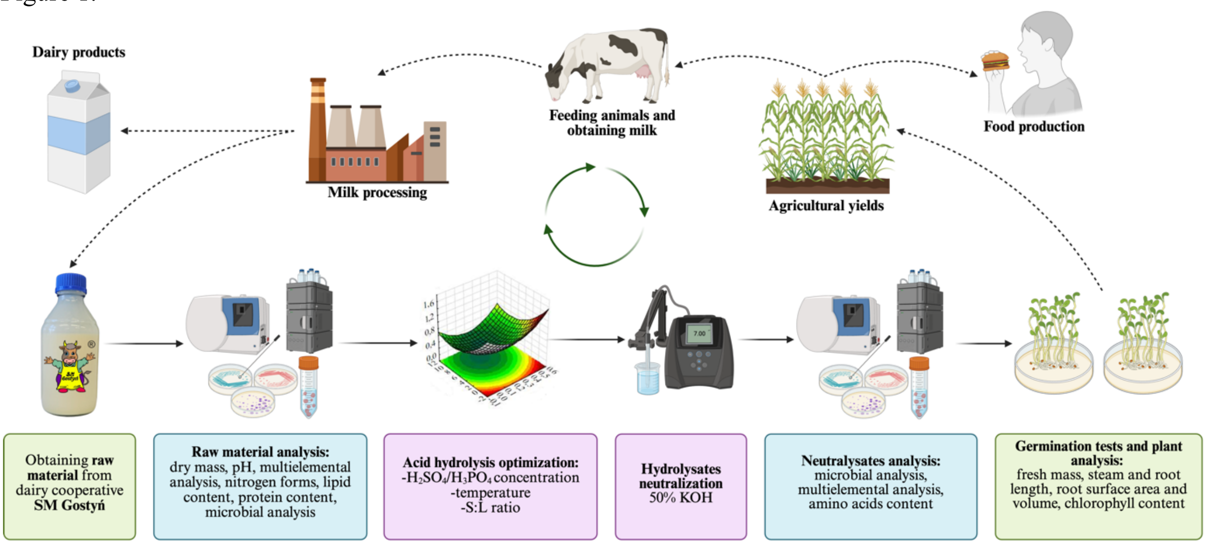

Figure 1. Research scheme and the idea of implementation according to the circular economy

In the first stage of the research conducted, a detailed analysis of the raw material obtained from the dairy industry was carried out. Using a moisture analyzer, the dry mass was determined, which was 63.1%. The pH was also determined, the value of which was 6.18. The Bligh-Dyer method was used to determine the lipid content and a value of 3.14±0.30% was obtained. Protein content was determined using the Bradford method and an average of about 6.50% protein was obtained, but the value varied from 3.57±0.50% to 10.5±0.9%, depending on the sampling, which indicated the need for thorough homogenization of the material. In addition, the total microbial count was determined in accordance with PN-EN ISO 4833-1: 2013-12 using the pour plate method, which was $2.85 \cdot 10^6$ cfu/g. Multi-elemental analysis (ICP-OES) and C/N determination (thermal conductivity) were performed, while Hg was analyzed by AAS. It was found that the material contained 29.8±3.0% C, the total N content was 1.20±0.12%, and the sum of nitrate and ammonium N was at 0.14±0.01%. Considering micronutrient content, the highest contents were observed for Fe (6.02±0.90 mg/kg) and Zn (28.2±4.2 mg/kg). Toxic elements such as As, Cd, Cr total, Cr(VI), Pb and Hg were below the detection level of the apparatus, which is advantageous because no additional process is required for their removal.

In the next step, the optimization of the chemical hydrolysis process was carried out. For this purpose, the design of experiments (DoE) methodology and Box–Behnken plan were used. Groups labeled Treated Dairy Waste (TDW) from 1 to 15 (TDW1–TDW15) were formed. The variables analyzed were the ratio of hydrolyzing medium to raw material (10, 20, 30%), the acid mixture concentration (10, 55, 100%) and temperature (20, 60, 100°C). The initial hydrolyzing medium (100% value for the concentration of the acid mixture) was a 2:1 mixture of 96% H_2SO_4 and 85% H_3PO_4. After hydrolysis, the hydrolysates were neutralized with 50% KOH to pH 5.0, optimal for soil application. The neutralizates were then subjected to detailed compositional and microbiological analyses. Taking into account the greatest preservation of N in the neutralizates, the best hydrolysis conditions were determined to be 20% of the acid mixture, 55% of the concentration of the acid mixture and a temperature of 60°C. Temperature had the greatest impact on the decontamination of the material. It was found that above 60°C, in most cases, the total number of microorganisms dropped below $4.00 \cdot 10^1$. For the best groups of treated dairy waste (TDW), N content above 0.96% and C content above 22.97% were shown. In addition, elevated S and K contents were found due to the media used in the process. All neutralizates contained >50.0 mg/kg of total amino acids.

In the final stage, germination tests with cucumber seeds (*Cornichon de Paris*) were performed to check the neutralizates' usefulness and exclude any phytotoxicity. None of the 15 neutralizates exhibited phytotoxic effects. Considering stem length, a value above 2.01 cm was shown for most of the neutralizate-fertilized groups, and the best results were 2.39±0.37, 2.45±0.24 and 2.54±0.32 cm, compared to 1.55±0.20 cm for the irrigated-only group and 1.87±0.23 cm for the group treated with the reference fertilizer. The highest fresh mass was recorded in the neutralizate-treated group (6.80 g), compared to 4.63 g in the irrigated-only group and 5.37 g in the group treated with reference fertilizer (Table 1).

As a result of the study, the utility of the obtained dairy waste in the production of plant growth promoters was confirmed. The acid hydrolysis of the waste was successfully optimized, followed by detailed chemical and microbiological analysis confirming the absence of toxicity and presence of biostimulant activity. These results support the feasibility of implementing a technology for processing large quantities of dairy waste into fertilizers, providing a solution in line with the idea of circular economy. In the next stages of the research, experiments will be conducted on such topics as alkaline hydrolysis, enzymatic hydrolysis and process upscaling.

Table 1. Selected results of germination tests

Sample	**Stem length** *cm*	**Root length** *cm*	**Fresh mass** *g*
Only irrigated	1.55±0.20	57.1±11.8	4.63
Reference fertilizer	1.87±0.23	60.2±12.7	5.37
TDW5	**2.45±0.24**	51.9±10.9	5.36
TDW9	**2.54±0.32**	56.4±12.3	**6.80**
TDW12	**2.39±0.37**	39.9±8.1	4.49

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