

REVIEW

Университет
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by Assoc. Prof. PhD Lubka Georgieva Atanasova, Department of "Chemical technology", University "Prof. Dr. Asen Zlatarov" – Burgas, member of the Scientific jury according to Order № УД-28/26.02.2023 of the Rector of the University "Prof. Dr. Asen Zlatarov" – Burgas

for the PhD thesis for acquiring the educational and scientific degree "Doctor" in professional field 5.10 *Chemical technology, scientific specialty "Technology of water purification"*.

Author: Eng. Maya Bogdanova Stancheva, full-time PhD student at the Department of "Chemical technology", Faculty of technical sciences, University "Prof. Dr. Asen Zlatarov" – Burgas

Topic: „Technological opportunities for recovery of resources from waste flows”

Supervisors: Prof. Dr. Valentin Nenov and Assoc. Prof. PhD Hussein Yemendjiev

1. Brief information about the professional development of the PhD applicant Maya Stancheva

Eng. Maya Bogdanova Stancheva graduated the University of Food technology – Plovdiv with bachelor degree. In 2009, she graduated the same University with Master’s degree in specialty "Analysis and control of food products". She has worked consecutively as technologist at "Zaharni izdelia" Ltd, later as laboratory assistant and then specialist on food quality at the Food testing Laboratory "Buljak" of the "Buljak" company, Burgas. of food testing She speaks and writes in German and English.

2. Relevance of the topic of the dissertation

The topic of the dissertation work is related to the estimation of the **opportunities for recovery of resources from waste flows**. With the development on industry, the amount of wastes increases. At the same time, the availability of natural resources gradually decreasing while the environmental pollution is increasing. Therefore, the solution of the problems connected with the preservation and recovery of the resources present in the waste flows, as well as their proper management in environmentally safe way is of exceptional importance. *The waste flows should be regarded as resource which can be used.* One of the main roads to the achievement of this goal is the **recovery of resources from waste flows**. In recent years, we have witnessed the efforts of the researchers focused on the development of new technologies allowing recovering the resources during the whole cycle of waste flow purification, including waste waters from various origins.

The task set for the dissertation work is to study waste flows rich in biogenic components, from stock breeding (manure and waste waters from the activity) and from production of cheese

(whey) and show the possibilities for their processing to extract the biogenic components and energy from them so they could be reused (recovery).

This provides grounds to me to state that the dissertation work is relevant and it is *certainly a contribution for the joint efforts of the researchers in the search for opportunities for effective extraction, recovery and reusing of resources of different types of waste flows.*

3. Survey and analysis of the dissertation work

The PhD thesis traditionally includes the following **sections**: introduction, literary survey, experimental, results and discussion, conclusions and contributions. The thesis is presented on 143 pages and includes 29 tables and 50 figures which illustrate the experimental and the research work the reference list contains 243 citations which are mainly publications after year 2000 which indicates that the information is relevant.

In Section *Literary survey*, the author presents a review of the literature related to the topic of the PhD thesis. Special attention is paid to the element phosphorus as nutritious component for the plants and its *contents in the manure* which is waste flow and object of analysis in the dissertation work from which certain resources can be recovered. The possibility to produce biogas from manure by anaerobic digestion (basic biological process) is considered. Special attention is paid to the possibilities to *obtain struvite from the waste flows* considered and analyzed in the dissertation work. *Struvite is magnesium ammonium phosphate which can be used as fertilizer* as it contains the main nutritious element required by the plants like nitrogen and phosphorus and the microelement magnesium necessary for the plants' metabolism. Its chemical and physical properties are considered, the structure of its crystals and the influence of different factors on its crystallization aiming to obtain high quality crystals for the consequent process of filtration and use as fertilizer. The operation of various struvite production reactors is described.

A review is made on the performance of *microbiological fuel cells and microbiological electrolysis cells* in regard to the obtainment of struvite by electrochemical processes. Literary sources are cited where the preparation of struvite by ion-exchange and membrane technologies is discussed and its use as fertilizer. The literature review ends with the description of the technologies for preparation of struvite by recovering from waste flows which have been realized on *industrial scale*.

On the basis of the literature review, the aim and the main research tasks of the dissertation work are formulated: *Choice and characterization of waste flows with high potential for the recovery of biogenic components; study of the anaerobic degradation as an approach to the primary processing of the waste flows and increase the concentration of the chemically available forms of nitrogen and phosphorus and, simultaneously, production of biogas as source of energy; treatment of waste flows to facilitate the subsequent stage of extraction of the biogenic*

components from them; analysis of the processes of precipitation and recovery of the biogenic components.

The **extensive literature review** on the topic of the dissertation made by the PhD supplicant indicates that she has thoroughly investigated the problem and the achievements in this scientific field, made correct conclusions and formulated the aim and tasks of the dissertation work.

Section Experimental

For the fulfillment of the first task set for the elaboration of the dissertation work – choice and characterization of waste flows with high potential with respect to their biogenic components contents the PhD candidate selected and studied samples and substrates taken from the following waste flows: from stock breeding, (cow and buffalo manure), waste water from swine-breeding farm and whey – waste flow from milk processing factories. For the characterization of the waste flows, **lots of analyses necessary for the determination of the compositions of the above mentioned waste flows** studied were made to characterize the waste flows mentioned above. The *chemical substances and reagents* used for the analyses are clearly and comprehensively described.

I would like here to make a note to the PhD applicant that when we discuss a scientific work like PhD thesis, it is correct to cite the names of the chemical compounds in accordance with the nomenclature defined by the International union for pure and applied chemistry (IUPAC). For instance, according to IUPAC, monopotassium hydrogen phosphate is potassium dihydrogen phosphate, tetra hydrate with 4 molecules of water, rather than with 1 molecule, etc.

Further, detailed description and presentation of the **methods of analysis** used to determine a great number of indicators are given, namely: fecal coliforms in waste precipitates, phosphorus, orthophosphates, hydrolysable phosphates and orthophosphates, total phosphorus content in the samples analyzed, an universal method for of testing was used to determine the content of water-extractable phosphorus, phosphorus desorbing from biological wastes. The Kjeldal method for determination of total nitrogen content in precipitates from waste water purification stations is described. The methods of determination of water hardness, chemical demand of oxygen (CDO) biochemical demand of oxygen (BDO), dry substance, inorganic dry substance, volatile dry substance, solid substances available for precipitation, volatile acids and alkalinity, total content of suspended substances are discussed. The determination of traces of elements and ones with ultralow concentration was carried out by mass-spectrometry with inductively connected plasma. The method of preliminary treatment of dry sample is described. Software was used to determine the index of saturation – identification of the tendency of the solid state substances to precipitate or dissolve in aqueous solution.

All the analyses were carried out at least twice and the results were calculated as the average value obtained by the measurements.

The experimental equipment and installations used by the PhD applicant during her work are described and presented. These are:

- Anaerobic fermenter where the process of anaerobic degradation was carried out (the process in periodical and for one of the experiments it was semi-continuous). The biogas released by the anaerobic reactor is measured.
- Laboratory system for ultrafiltration.

In my opinion, the PhD applicant has used the correct methods of analysis for the determination of the characteristics of the samples studied which allow to fulfill the tasks set and to achieve the goal of the dissertation work.

Section three. Results and discussion

For the completion of the first task, the following studies were carried out using the methods of analysis described earlier:

1. An analysis of the phosphorus fraction present in buffalo farm manure was made after separation and of the waste water from pig-breeding farm before the separator. The results obtained showed that these sources provide possibilities to recover the phosphorus contained in them and that they are suitable for direct precipitation of struvite.
2. The characteristics of waste waters from pig-breeding farm before and after the separation process were compared under two regimes. One regime was at 4°C and the other – at room temperature.
3. The elemental composition of waste flows from cow, buffalo and pig breeding farms were determined.
4. Analyses were carried out to determine the physicochemical properties of whey. The latter was found to contain organic compounds with high concentrations. Furthermore, the concentrations of orthophosphate and ammonium ions were high enough to allow obtaining struvite from this waste flow.

The second task is related to studies of the anaerobic degradation as an approach to the primary treatment of the waste flows aimed at increase the concentrations of the chemically available forms of nitrogen and phosphorus and, simultaneously, produce biogas as source of energy. The waste flows subjected to anaerobic degradation are: manure from cow-breeding farm, manure from buffalo-breeding farm, fresh manure form buffalo-breeding farm, mixed substrate of buffalo manure and waste water from pig-breeding farm in ratio 1:1 and buffalo manure treated by semi-continuous process. Comparison is made between the properties of all the batches described above.

The third task is related to the treatment of waste flows aiming to enhance the following stage of extraction of the biogenic components from them. For this purpose, the following experiments were carried out: waste water from pig-breeding farm taken from the collector and

after the separation was titrated with 0,4 n H₂SO₄ and 1n NaOH. Acidification and ultrafiltration of waste water from pig-breeding farm and ultrafiltration of whey.

The fourth task set is to study the processes of precipitation and recovery of biogenic components from waste flows. The processes of precipitation of struvite from waste waters from pig-breeding farm and from whey were analyzed and studied.

All the results obtained from the analyses and experiments are intelligibly presented in tables. The relationships studied fin the basis of which the main conclusions were made are presented as graphs.

4. Contributions of the dissertation work

The contributions outlined by the PhD applicant correspond to the work done by her to fulfill the aim set and the tasks set in the dissertation work connected with it. They are:

1. For the first time and in details, **the potential of waste flows from stock-breeding and dairy processing farms as source of recovery of phosphorus was studied.**

2. The **anaerobic degradation** was studied and analyzed as process of treatment and stabilization of the waste flows which must improve their properties as substrates for **precipitation of struvite**, as well as to **recover part of the energy by methanation and obtaining biogas from organic substances.**

3. The behavior of the different initial substrates in the process of anaerobic degradation was clarified and the **dynamics of the targeted ammonium and phosphate ions was investigated.**

4. It was found that the waste flows from **pig-breeding farms are not suitable for carrying out full-scale methanation process and are not subject of effective anaerobic stabilization.**

5. An approach for mobilization of additional potential with respect to the phosphates available for precipitation by **treatment of the substrates with acids was applied and high efficiency was achieved.**

6. It was found that **ultrafiltration is an effective method for additional purification of the working fluids from organic impurities** with simultaneous preservation of part of the phosphate, ammonium and magnesium ions.

7. Data were obtained from experiments with real waste flows which is a solid base for development of hybrid technologies for **simultaneous treatment of waste waters from stock-breeding and recovery of resources from them.**

5. Estimation of the correspondence of Author's summary with the dissertation work

The Author's summary submitted by the PhD applicant fully corresponds to the dissertation work and represents its contents.

6. Estimation of the participation of the PhD applicant in the elaboration of the dissertation work and the publication of the Thesis

The knowledge of the candidate about the different analytic methods and their proper use to obtain objective results from the analyses makes good impression. For the studies of the anaerobic processes, she successfully used the available laboratory equipment. The candidate has enough skills to use software products. The sequence of the analysis and the aims to be achieved by them are logically described. She correctly interprets the results obtained and makes the corresponding conclusions. Eng. Maya Stancheva has carried out great amount of experimental work with the necessary preciseness.

So far as the publication activity is concerned, the candidate has fulfilled the criteria formulated in the *Regulations for the terms and conditions for the acquirement of scientific degrees and occupying academic positions at the University "Prof.Dr. Asen Zlatarov"- Burgas*. The total number of publications is 6, among which 1 manuscript has Impact Factor and three papers have SJR. The candidate has taken part with reports at three conferences with international participation which were held in Bulgaria. She is member of the team in **two projects**. One is financed by the Ministry of education and science and the other by the Fund "Scientific research and artistic activity".

7. Critical remarks on the PhD thesis

I have no critical remarks. I have a question to Maya Stancheva. Among the great number of studies she has carried out and reported for in her dissertation work, can she point out which of all these processes aimed at recovery of resources from waste flows can be developed as a technology which could be realized on industrial scale?

8. Conclusion

Taking into account the scientific research results and contributions I give **positive estimation** of the dissertation work produced by Eng. Maya Bogdanova Stancheva in my full conviction and I consider it well-grounded to propose the scientific jury to **vote for granting the educational and scientific degree "Philosophy doctor" in professional field 5.10. Chemical technology, scientific specialty "Technology of water purification"**.

6.02.2023 год.

Burgas

Reviewer :..

/Assoc. Prof. PhD Lubka Atanasova /

Подпис заличен
Чл.2 от ЗЗЛД