This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 691911

Technology Description (TD) for

Anaerobic Digestion Technologies

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Technology Description:

NAME OF TECHNOLOGY	Sewage sludge co-digestion under biosulfidogenic conditions
ASSIGNMENT OF TECHNOLOGY	Enhanced production of biogas and organic fertilizer based on sewage sludge with phosphogypsum additive at municipal WWTP

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TECHNICAL READINESS LEVEL		
TRL 1 - basic principles observed **TRL 2** - technology concept formulated **TRL 3** - experimental proof of concept **TRL 4** - technology validated in lab **TRL 5** - technology validated in relevant environment (industrially relevant environment in case of key enabling technologies) **TRL 6** - technology demonstrated in relevant environment (industrially relevant environment in case of key enabling technologies) **TRL 7** - system prototype demonstration in an operational environment **TRL 8** - system completed and qualified **TRL 9** - actual system proven in operational environment (competitive manufacturing in the case of key enabling technologies; or in space)		1 2 3 **4** 5 6 7 8 9
TECHNOLOGY/EQUIPMENT AVAILABILITY		
PATENT RIGHTS		YES, patented in Ukraine
METHOD OF MAKING THE TECHNOLOGY AVAILABLE	*Licence selling*	NO
	Licence granting	NO
POSSIBLE END USERS OF TECHNOLOGY	*Please name end users/ contacts that should be invited to project workshops*	Wastewater treatment plant utilities, urban waste or livestock treatment facilities, SME with biologically degradable waste

Description of the technology/equipment:

The system of anaerobic digestion with the heavy metals (HM) precipitation by biogenic hydrogen sulfide is the promising way of sewage sludge detoxification with biogas production. The process for the production of biogas and organic fertilizer based on sewage sludge with phosphogypsum additive in laboratory scale was developed at the Sumy State University [L. Plyatsuk, Y. Chernysh etc. 2013-2016] The basic stages of co-processing of sewage sludge and gypsum waste were studied. Biochemical equations of wastes detoxification on the final stage of anaerobic digestion under bio-sulfidogenic conditions were developed. After biosulfidogenic treatment, organic complexes with heavy metals were destroyed and formed insoluble compounds of metal sulfides. Thus, heavy metals were transformed into the unavailable form for plants. The technological applications efficiency of such system

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was formed [Plyatsuk / Chernysh, 2013, 2016, Patent of Ukraine for invention 103087, Patent of Ukraine for utility model 87422].

Anaerobic digestion under bio-sulfidogenic conditions

The SRT is a fundamental design and operating parameter for all anaerobic processes. The influence of SRT on the efficiency of COD reducing indicates that (I) the retention times 6 days are insufficient for a stable fermentation: removal of COD is slowed due to acclimatization of microorganisms and a washout of SRB, (II) COD values are still relatively high for SRT of 6–12 days: there is an incomplete breakdown of organic compounds, (III) stable fermentation is obtained after 12–20 days: low COD values, the active breakdown of organic compounds started, and (IV) the breakdown curve stabilizes at SRT 30 days; all sludge organic compounds are significantly reduced (efficient removing of COD_t and COD_s) (Figure 1).

Noted that the two-step hydrolysis may be a reflection of two classes of organic matter within the sludge, i.e. readily and slowly degradable material. Furthermore, the results suggest that while the readily degradable fraction is removed under both electron-acceptor conditions, a larger proportion of the less readily available material is only available under pretreatment conditions.

Solid liquid separation in system was good yielding average particulate. Total COD removal of 85% (decreased from 2435 mg COD /l to 365 mg COD/l) was recorded for the sulfidogenic system respectively over a period of 20 days. The concentration of sulfide (as hydrogen sulfide) increased in the sulphidogenic system to reach a maximum concentration of 778 mg/l on day 20, indicating that the SRB population was active. After day 20, the H_2S decreased from 778 mg/l to 97 mg/l (day 30). These data is confirmed by inhibition activity of SRB.

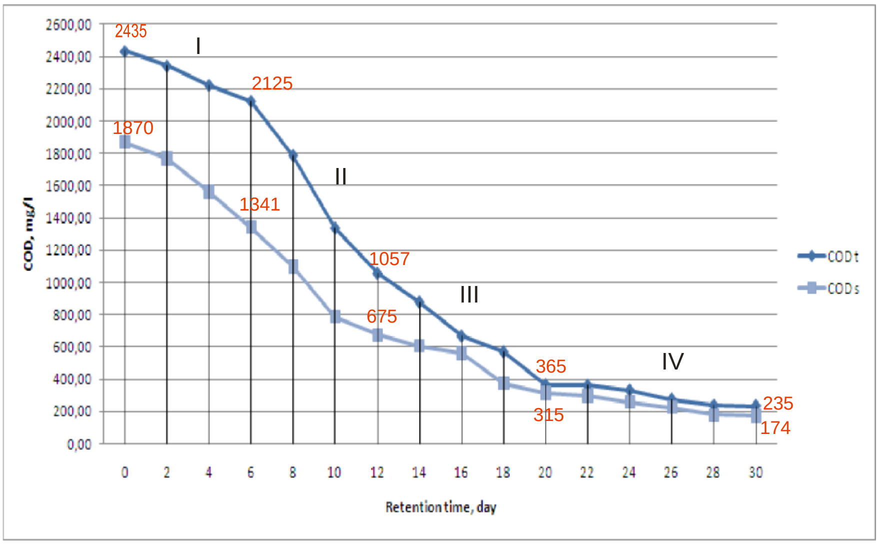

Fig. 1: COD profiles for process digestion under bio-sulfidogenic condition

The activity of sulfate reduction bacteria (SRB) was measured, or rather assessed by decrease in sulfates concentration and simultaneous increase in sulfide concentration.
Note that investigation of the hydrogen sulfide production is very important for developed technology of wastes detoxification.
SRB is used organic and mineral substrate (mixture of sludge and phosphogypsum) for biomass growth that is accompanied by the formation of hydrogen sulfide. Thus, the active SRB multiplication in the space bioreactor was shown by results of the investigation that is consistent with previous works [Chernish/Plyatsuk, 2012-2014].
Sulfate reduction should cause the pH of the medium to increase as the reduction of sulfate results in the formation of sulfide ions. A portion of these ions dissolve in the liquid phase and is involved in chemical reactions with the ions of heavy metals. The remainder escapes as hydrogen sulfide gas.
When determining the optimum combinations of factors such as retention time and the pH was constructed three-dimensional surface chart (fig. 2). While digestion highest biogas yield of 5.8 dm^3 / day was observed on day 10. With an increase in the retention time is stabilized biogas yield at 3.50 dm^3 / day. pH of 7.2 units. 20 th day.

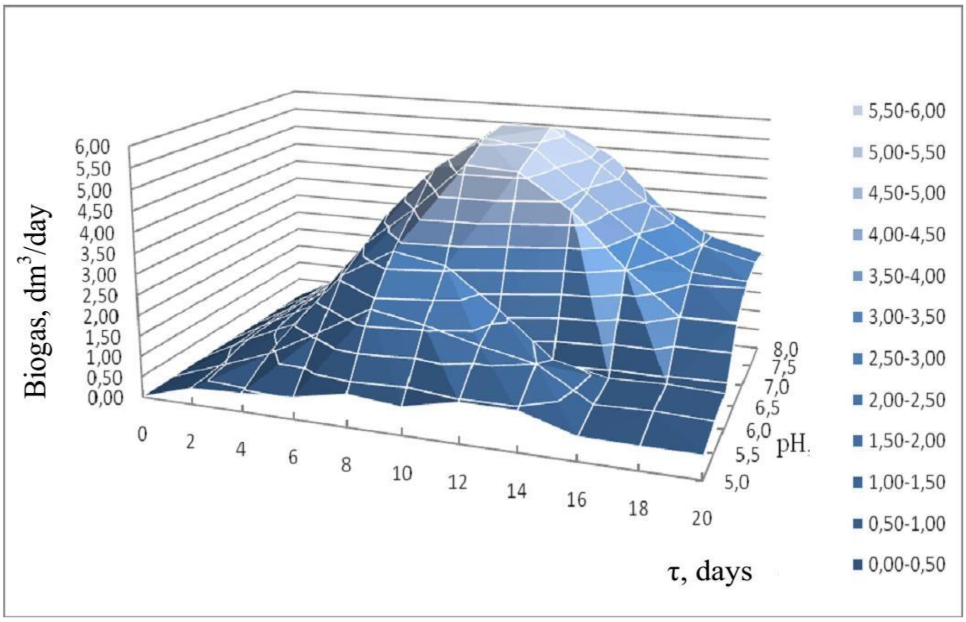

Fig. 2: Biogas production

The significant presence of SRB is indicated by the low effluent sulfate concentrations and good sulfate removal achieved (~ 94.5% on day 20). The most important that sulfate contained in the phoshpogypusm can be freely used by SRB as a mineral substrate for their growth. Phoshpogypusm is a class IV of hazard (low hazard). Waste of this class of hazard does not contain toxic substances that can damage the normal functioning of the microorganisms groups in the anaerobic bioreactor. In addition, after fermentation the concentration of sulfide ions in the liquid fraction of digested waste mixture was 0.10 mg/l under effluent standard is 1 mg/l. Therefore, the liquid phase of treated wastes was pure environmental product. The solid fraction of digested mixture of wastes consisted heavy metals (HM) in the insoluble sulfides form.

Transformation compounds of HM to insoluble form and phosphorus recovery

In the mineral composition of the raw sewage sludge were found such compounds: iron phosphate hydroxide - $Fe_4(PO_4)_3(HO)_3$, compounds of aluminum and silicon as a double layer of hydrated complex of potazium illite-montmorillonite - $KCu_4(Si,Al)_8P_2O_7$ 5H_2O (primary sewage sludge) and anorzite - $(Ca,Cr)Al_2Si_2O_8$ (activated sludge), the structure of the crystal lattice which includes atoms HM (impurities).

Reactions oxidation of organic matter during anaerobic digestion provoked output HM to liquid phase, after that metals ions reacted with *H_2S*. After biosulfidogenic treatment sewage sludge purchased black color and characteristic odor of decomposed organic matter. By separating the liquid fraction from the solid product was obtained, which in dried form acquired grayish brown

Among the major mineral components of the final product of the biosulfidogenic treatment are: quartz, or amorphous silica - SiO_2, potassium hydroxide (potazium hydroxide) - KOH and potazium hydrogen phosphate hydrate - $K_2H_2P_2O_7$ 1/2H_2O, brushite - Ca PO_3(O H)2H_2O, phosphorus oxide - P_2O_5, calcite - $CaCO_3$, ammonium sulfate (mascagnite), sulfides of HM such as iron sulfide (marcasite), zinc sulfide (sphalerite), copper sulfide (covellite), nickel sulfide etc.

The results of diffractometry of raw sewage sludge and final product of anaerobic digestion under biosulfidogenic condition were compared. Thus several of waste biochemical transformations became such as:

- Biological recovery of phosphates; a significant portion of the liberated phosphate ions chemically bind with calcium and partially into the liquid phase;
- Due to the evolution of carbon dioxide in the system was formed of calcium carbonate;
- Ammonia, which is released during the decomposition of protein compounds, interacted with sulfate ions to form ammonium sulfate;
- Complex compound with HM destroyed and HM ions passed reacted with biogenic sulfide and came to stable form of metal sulfides.

Thus, HM mobility was limited by the formation of metal sulfides and caused their minimum flow into soil pore. So, HM did not migrate to the system “soil-plant”. The schematic process is shown in Figure 3.

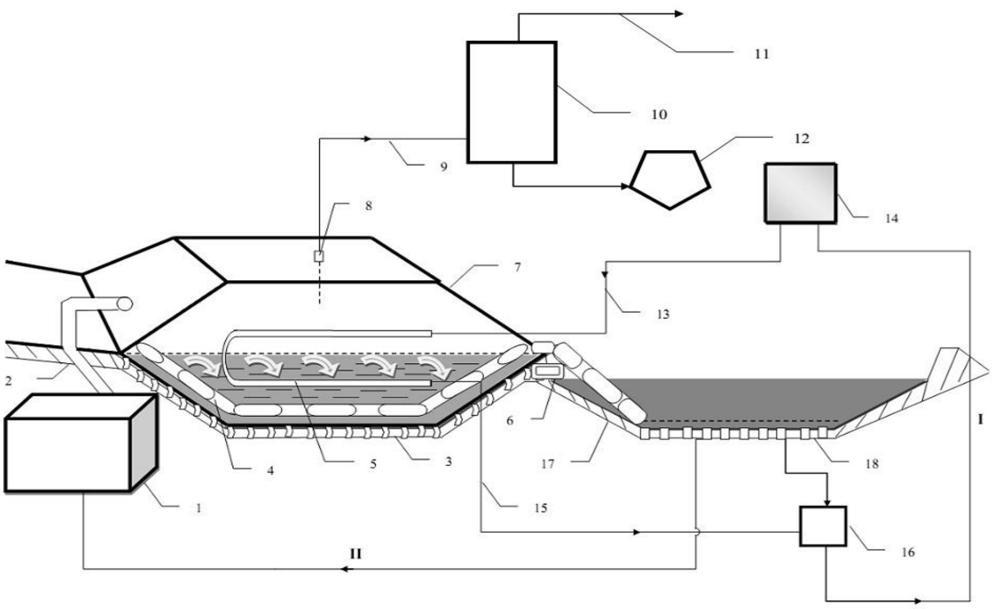

Fig. 3: Complex biotechnology application: accumulation capacity (1); pipeline (2); anaerobic bioreactor (3); a scraper-conveyor (4); tubular heat exchanger (5); electric drive (6); opaque coated-dome (7); a nozzle (8); gas inflow (9); biofilter (10); biomethane outflow (11); settling tank (12); the line (13); a hot water boiler (14); the pipeline (15); a node (16); silt sites (17); drainage system (18)

The technological scheme works as follows. Sewage sludge with phosphogypsum from accumulation capacity (1) is fed by pipeline (2) to the anaerobic bioreactor (3). It is designed as a trench with insulated walls and bottom, on which is a scraper mounted (4). Above the conveyor (4) tubular heat exchanger (5) is mounted. The bioreactor (3) is equipped with electric drive (6) and topped with sealed opaque coated-dome (7), in which biogas is accumulated and then diverted through a nozzle (8). Gas in pipeline (9) is transported to the biofilter (10), containing immobilized biomass of *Thiobacillus sp.*, where hydrogen sulfide is transformed to bio-sulfur form. The purified biogas exits the system (11).Sulfur flotation occurs in a settling tank (12). The liquid fraction of fermented waste enters the heat exchanger (5) as a coolant through the line (13). This fraction is purified to a level suitable for reuse and heated in a hot water boiler (14). The liquid fraction, which is cooled in a heat exchanger (5), of the pipeline (15) returns through the node (16), used for mixing the liquid fraction flows and through line is transferred to the hot water boiler (14). Separation of fermented waste in solid and liquid fractions is implemented in silt sites (17) with insulated bottom and drainage system (18). Solids are environmentally friendly organic fertilizer. The part of solids is fed along the line II to the input of the bioreactor (3) accumulation capacity (1) as an inoculum containing sulfate reduction bacteria (SRB).

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List of the main published articles using this biotechnology by research group:

E. Chernish (Y. Chernysh): ***The sulfide fraction impact on heavy metals behaviour in the system "sewage sludge – solid – plants"***, Scientific statements of Belgorod State University. Science Series, No 2, pp. 159–162, 2013. (in Russian)

L. Plyatsuk, E. Chernish (Y. Chernysh): ***Intensification of the anaerobic microbiological degradation of sewage sludge and gypsum waste under bio-sulfidogenic conditions***, Journal of Solid Waste Technology and Management, vol. 40, No 1, pp. 10 – 23, 2014. (in English)

Y. Chernysh: ***Ecobiotechnology of sewage sludge treatment: phosphorus compounds removal***, Chemical engineering, ecology and resource conservation, No 1, pp. 131–140, 2015. (in Russian)

Y. Chernish (Y. Chernysh), L. D. Plyatsuk: ***Opportunity of biochemical process for phosphogypsum utilization***, Journal of Solid Waste Technology and Management, vol.42, no 2, pp.108-115, 2016. (in English)

- **Patent of Ukraine for invention 103087**

Process for the treatment of organic wastes with removal of heavy metals Published on 10.09.2013, bul. № 17/2013

- **Patent of Ukraine for utility model 87422**

Installing anaerobic processing of organic waste
Published on 10.02.2014, bul. № 3