Journal of Chemical Technology and Metallurgy, 53, 5, 2018, 816-824

DEVELOPMENTS IN NUTRIENT REMOVAL AND RECOVERY

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Received 12 February 2018
Accepted 21 May 2018

ABSTRACT

Global fertilizers use based mainly on nitrogen (N) and phosphorus (P) is steadily growing. Nitrogen is a renewable source present vastly in the atmosphere. However, the air molecular nitrogen converted to ammonia and nitrates through nitrogenase and lightening is of a limited amount. The intensive agriculture requires huge quantities of chemical nitrogen fertilizers for food grains production. Currently, the industrial production of ammonia nitrates is quite energy demanding and has a negative impact on the environment. Yet, nitrogen is abundantly present in nature. Unlike nitrogen, P can be obtained primarily from mineral deposits available only in few geographic locations. The residual sludge from the purification of domestic and some industrial waste waters is a very promising alternative to phosphate rocks source. The present communication discusses a promising way to use a P rich solution from spent algae growing media (of a P concentration higher than 100 mg dm^{-3}). It is characterized by a low organic matter content which is highly advantageous for struvite crystallization. It is also demonstrated that the electrochemical/bio-electrochemical treatment of the waste water enables the increase of P/ammonia content in the cathodic chamber at an extent allowing efficient struvite precipitation.

Keywords: nutrient removal and recovery, bioelectrochemical cell, struvite.

INTRODUCTION

Phosphorus (P) is an essential element of all living organisms involved in several biological processes. It plays an important role in plants nutrition. Plants and other photosynthetic organisms convert inorganic phosphates into organic phosphorus needed for all living organisms. Inorganic phosphates used in agriculture and industry are mined from the world limited rock deposits. Since phosphates are available only in limited geographic locations, phosphorus recovery is crucial to improve food security [1]. In 2007 the supply of phosphorus is estimated to run out at the current rate of consumption in 345 years [2]. As a consequence of the above mentioned facts there is a trend towards phosphorus recycling. A very promising alternative refers to phosphate rocks residual sludge streams from the purification of domestic and some animal waste. Furthermore, it will also affect positively the environmental issues related to the nutrient load of surface and ground waters due to waste and wastewater pollution.

P can be recovered through extraction of inorganic phosphorus from sewage sludge or from animal manure and following precipitation as magnesium ammonium phosphate - $MgNH_4PO_4 \cdot 6H_2O$. It can be easily synthesized and further applied as a direct slow release fertilizer. The latter use provides to overcome [3,4] the disadvantages of direct sludge application in the agriculture (high organic content, potential presence of heavy metals and pathogenic microorganisms).

The struvite formation process is a function of pH and the molar ratio between magnesium, ammonium and phosphate ions. Mg^{2+} precipitation occurs under alkaline conditions, while an optimal crystal formation is observed at pH above 9 and equimolarity of the constituent ions [5]. However, several studies show that struvite can be synthesized in a wide pH range. It is reported that experiments carried out in neutral solutions show positive results, but the formation and the precipitation rates are very slow when they do not proceed in the optimal pH range [6]. Furthermore, the effective struvite precipitation depends strongly on the organic content [5]. The high organic content in the substrate liquors can affect the struvite production, sedimentation and end product quality in a negative way [7]. The application of waste as a source of ammonia and phosphates for struvite production requires effective and ecologically clean methods connected with organic matter separation and P dissolution from the solid phase. The latter is of great importance in case of animal manures.

The aim of this study is to evaluate the effectiveness of UF in membrane separation of the organic matter contained in sludge dewatering liquor stream of a MWWTP, acidic P dissolution in treating animal manure and the potential of bio-electrochemical concentration of nutrients in a desalination cell.

EXPERIMENTAL

Membrane separation

For the purposes of this study, a lab-scale UF unit was designed and used to reduce the organic content measured as COD. The experiments for reduction the colloidal and suspended matter were carried out in a cross-flow operating unit equipped with a ceramic tubular membrane of CMF19033 type (made of 99 % α-Al_2O_3/ZrO_2) with two different pore sizes - 50 nm and 200 nm. The principal scheme of the UF system is shown in Fig. 1. The operation parameters included an external pressure of 4 bars. The filtration system was fed with sewage sludge treated in an anaerobic digester with total suspended solids concentration (TSS) of 26 g dm^{-3}. The obtained permeate was analysed in respect to COD and phosphate concentration.

Fig. 1. Principle scheme of the cross-flow UF system used.

Acidic P dissolution

Two types of manure containing high phosphate and ammonia levels were used in this study. The digested sludge was taken from a buffalo farm (Lozenets, Yambol region, South-East Bulgaria) and a cow farm (Dobrinovo, Burgas region, South-Eastern Bulgaria). Initially, the sludge was centrifuged at 4000 rpm. The fugate was analyzed in respect to inorganic phosphorus (IP), ammonia and COD (Table 1).

In order to evaluate the acid-extractable P content, the livestock sludge was treated with nitric acid (5 % HNO_3) aiming to reach pH = 3 and pH = 4. Such treatment released IP through the organic matter oxidation [8]. The experiments were carried out in the following

Table 1. Fugate characteristics.

Wastewater	Ammonia, mg dm^{-3}	IP, mg dm^{-3}	COD, gO_2 dm^{-3}
Buffalo manure	1297.2	316.3	60.1
Cow manure	1753.5	377.6	21.6

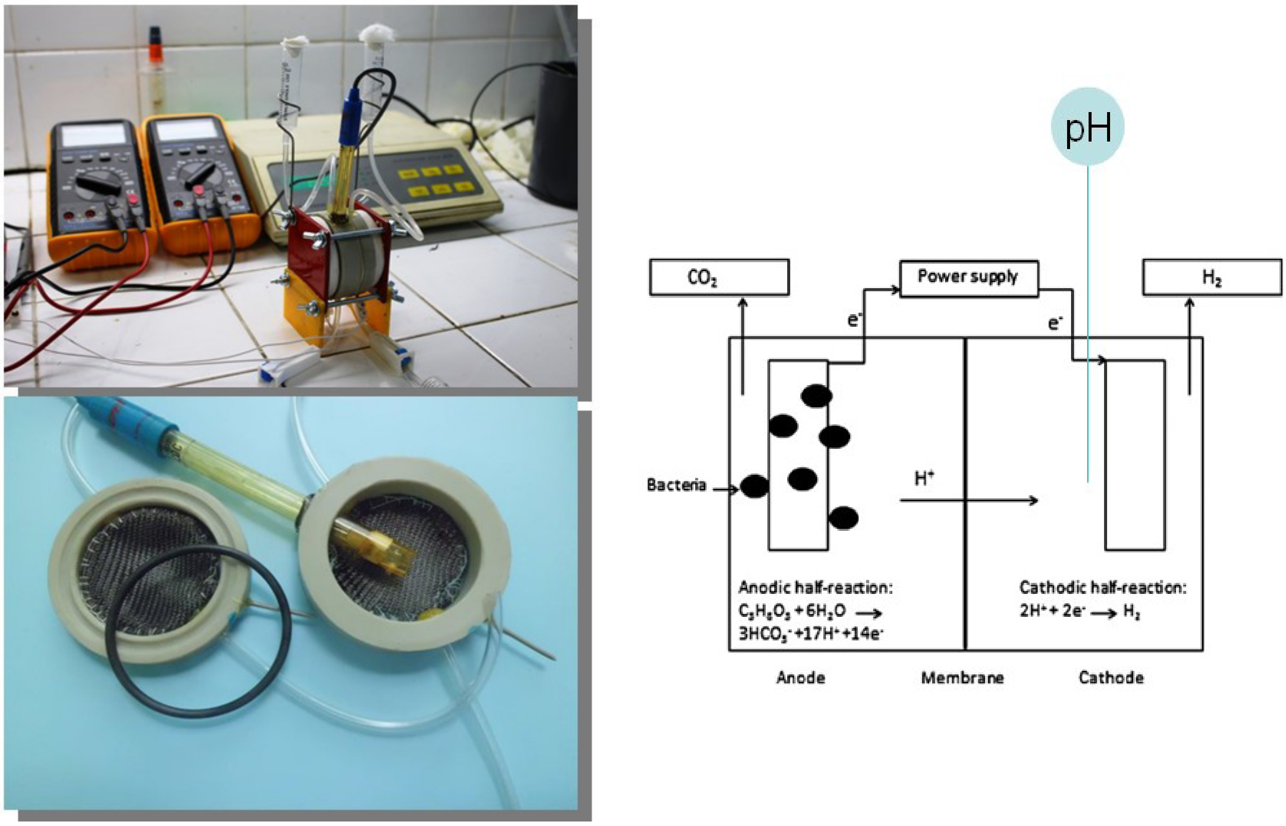

Fig. 2. Schematic presentation of the experimental setup using a microbial electrolysis cell used for electrochemical pH elevation.

manner: nitric acid (5 %) was added to 50 cm^3 manure sludge followed by stirring and filtration through a paper filter. The obtained filtrate was analyzed to determine IP and ammonia content. The analyzes were carried out by HACH LANGE DR 3900 spectrophotometer using Cuvette test - LCK 303, LCK 350 and LCK 514 for determination of ammonia, phosphates and COD, respectively.

Non-reagent pH elevation by Bio-Electrochemical Process (MEC)

In order to elevate pH to values suitable for struvite precipitation (above pH 8), specifically after the process of acidic P dissolution, a non-reagent alkalization by a microbial electrolysis cell (MEC) was applied. For this study a MEC reactor was designed. The schematic representation of the cell and the actual reactor used in the investigation are presented on Fig. 2.

The MEC was a cylindrical reactor with two sections separated by an ion exchange membrane. The electrodes were made of carbon cloth. They were connected to an external power source (in this particular case a 1.5 V battery). A potentiometer controlling the voltage applied to the cell was included. A pH electrode was placed into the cathodic chamber of the cell for direct pH measurement and recording. The preparation of the microbial culture and growth medium was performed according to the above mentioned procedure. The experiments were performed in two parallel reactors equipped with two different types of membranes – Nafion® Proton Exchange Membrane and Ralex® Cathion Exchange Membrane.

Bio-electrochemical N&P removal and recovery

The constructed lab-scale bio-electrochemical cell (Fig. 3) consisted of two anode compartments connected in series with each other and a cathodic compartment located between them. An anion-exchange membrane

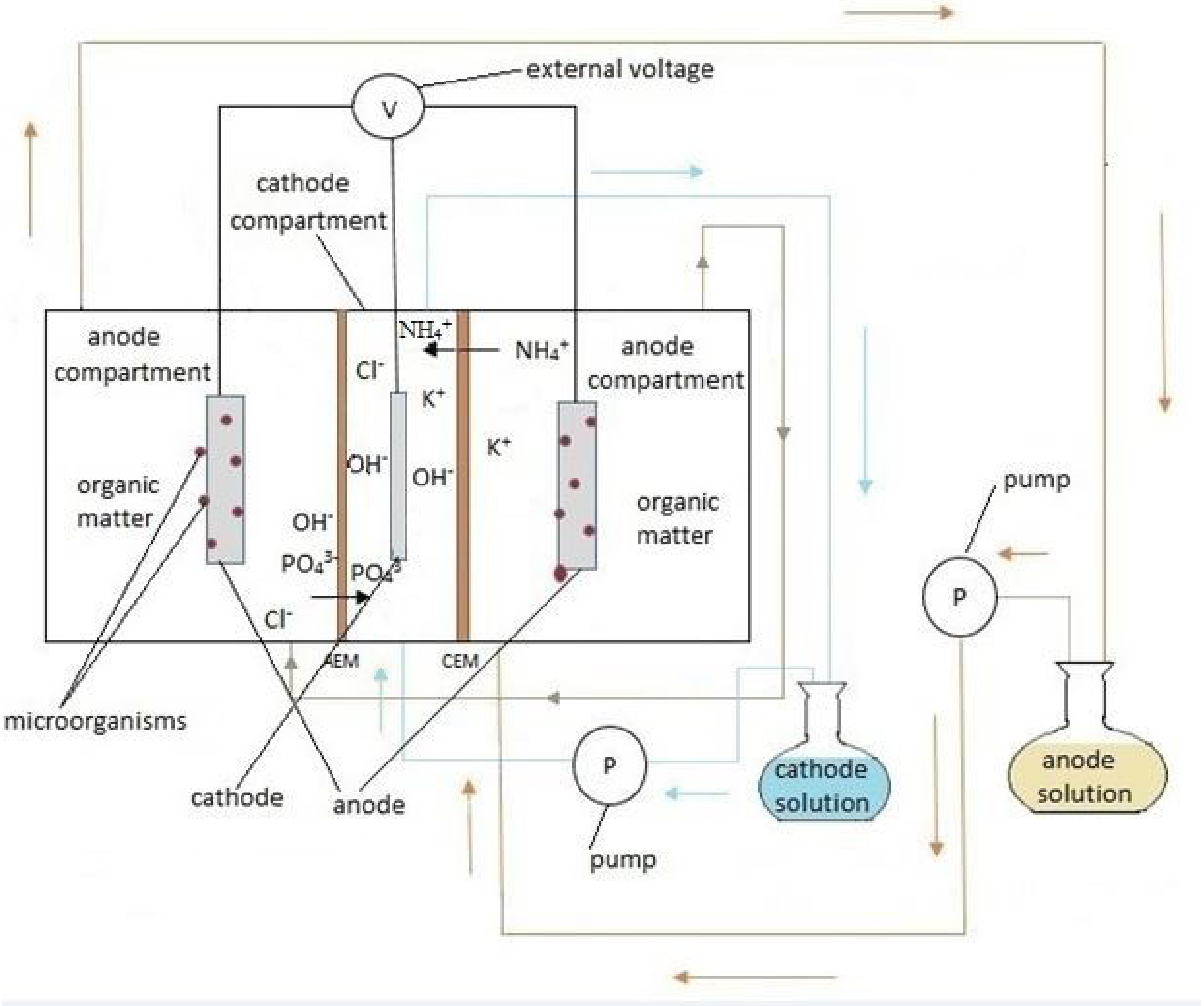

Fig. 3. Lab BES cell.

(AEM, polymeric membrane, Ralex) and a cation-exchange membrane (CEM, polymeric membrane, Ralex) separated the anodic and the cathodic compartments. The cathode was made of carbon cloth while graphite brushes acted as anodes. The internal volumes of the cathode and each of anode compartments were 20 cm^3 and 30 cm^3, respectively. The electrodes were connected to an external power source of 0.8V. In case of the biotic experiments the anode solution contained 0.35 g dm^{-3} $(NH_4)_2HPO_4$ and electrogenic microorganism provided from the bottom sediment of Yasna Polyana dam. The bacteria enrichment was done as follows: a sample of the sediment was transferred to a rich liquid culture medium containing casein tryptone (10 g dm^{-3}), yeast extract (5 g dm^{-3}), NaCl (5 g dm^{-3}), and glucose (20 g dm^{-3}). After 72 h of culturing at 14 ºC-18ºC, the biomass was separated, washed and re-suspended in a fresh medium of a composition similar to that above but excluding glucose. The final cell concentration referred to ca 107 CoE/cm^3. The cathode chamber was filled with distilled water. During the experiment the anode and cathode solution were continuously circulating using a peristaltic pump (BPPI, Biobase Biodustry Co. Ltd, Shandong) at 5 ml/min (HRT 1.2 h) and 7 ml/min (HRT 17 min (0.29 h) for the anode and cathode solution, respectively. External tanks of volumes of 100 cm^3 and 300 cm^3 were connected to the cathode and anode compartments, respectively. The anode solution was circulated between the closed at the top side external tank (300 cm^3) and the sequentially connected anode compartment. The cathode solution was circulated between the open from the top side external tank (100 cm^3) and the cathode compartment. The process was carried out under anoxic conditions and each run took

Table 2. Effect of UF membrane pore size on COD removal and P content in the permeate. The cross flow process design in combination with tube shaped ceramic membranes applied in this study show a significant effect in respect to organic matter/phosphorus separation.

Membrane pore size (nm)	Initial COD (mg O_2 dm^{-3})	Initial PO_4 (mg dm^{-3})	Residual COD in permeate (mg O_2 dm^{-3})	COD removal (%)	Residual PO_4 in permeate, (mg dm^{-3})
50	78100	225	414	99.47	118
200	78100	225	642	99.18	195

240 h. The operating temperature during the experiment was in the range of 28 °C - 30°C.

During the experiments, the anode and cathode media of the bio-electrochemical cell were analyzed for ammonium nitrogen (NH4-N, mg.dm^{-3}), orthophosphates (o-PO4, mg dm^{-3}) and chemical oxygen demand (COD, mgO_2 dm^{-3}). The analyzes were carried out spectrophotometrically by HACH LANGE DR 3900 using Cuvette test - LCK 303, LCK 350 and LCK 514 for determination of ammonia, phosphates and COD, respectively. Ammonium nitrogen and phosphate were measured once in 24 h while COD was registered over a period of 120 h. Because of the limited catholyte volume, NH_4-N and o-PO_4 were measured at the beginning and at the end of the experiment. Every 24 h, the conductivity and pH of the anode and cathode solution were measured with Lange HQ 40d apparatus. Experiments were carried out in an abiotic mode (the anodic chamber contained an organic matter without seeds of electrogens) and a biotic mode (the anodic chamber contained an organic matter plus electrogens).

RESULTS AND DISCUSSION

Membrane separation

The preliminary studies with dead-end filtration technique (Fig. 4) applying flat MF membranes of 0.45 μm porosity show that more than of 83 % (from 210 mg dm^{-3} to 35 mg dm^{-3}) of phosphorus is reduced [9] besides the organic matter removal. Such a low level of phosphates is not appropriate for eventual struvite precipitation.

The results obtained with the cross flow UF system, presented in Table 2, show that the UF technique has a promising effect on COD removal while keeping P content high enough. The application of a membrane with pore size of 50 nm provides a phosphate concentration in the permeate of about 50% lower compared to the initial one. The filtration experiments with larger pore

Fig. 4. Dead-end filtration unit.

Table 3. Characterization of the non-acidified manure filtrate.

Wastewater	IP, mg dm^{-3}	NH4, mg dm^{-3}	COD, g dm^{-3}
Buffalo manure	3.9	859.8	27.6
Cow manure	8.2	953.1	11.3

size (200 nm) show almost 90 % phosphate recovery rates and high effectiveness in respect to COD content in the product. It has to be pointed out, that high organics removal (99.18 %) is achieved under these conditions. This is compatible with the results obtained with the lower membrane pore size (50 nm).

Acidic P dissolution

Two types of manure of high phosphate and ammonia levels are used in this study. Based on the results obtained it is found out that organic matter content is high in both cases. Trying to separate the organic matter particulates the fugate is filtered by filter paper (medium retention 3 µm). The obtained filtrates are analyzed for IP, ammonia and COD (Table 3). Unlike the centrifugation process, it is shown that the filter paper retains considerable amount of IP. For both manure studied the IP concentration is found to be is below 10 mg/L. This is an indication of the high adsorptive capacity towards solid phase IP.

In order to evaluate the acid-extractable P content, the livestock sludge is treated with nitric acid. The results obtained (Table 4) show that the acidification of the livestock manure leads to release of IP. Evidently, the o-phosphate level following the acidification is suitable for struvite precipitation.

Non-reagent pH elevation by Bio-Electrochemical Process (MEC)

Non-reagent alkalization using a microbial electrolysis cell (MEC) is applied aiming pH elevation. The test is applied to digested sludge filtrate at initial pH of 7.7. The results obtained are given in Fig. 5.

The results show a slower pH elevation rate probably due to the complex composition of the reagent mixture and presence of alternative (to H^+) electron acceptors which affects the efficiency of process. However, MEC is still able to elevate the fluid pH to above 9 within 24 h.

In order to overcome the complications related to the organic matter separation from fluids containing phosphates (membrane separation of the organic matter or acidic P dissolution), a source of waste stream of low organic matter content is identified. Namely, it is the spent growth media of Spirulina, edible micro-algae. It is toxic-free, rich in proteins and vitamins and has a high nutritional and even medicinal value [10]. Over the past 30 years, the spirulina industry has been supplied by many small to large-scale farms around the world. Most current commercial farms are designed as shallow raceway ponds circulated by paddlewheels. Ponds vary in size up to 5000 square meters (about 1.25 acres) or larger, while the water depth is typically 15 cm to 25 cm. Photo-bioreactors, tube, plate and tank systems have been developed to grow algae in closed systems in colder climates, to prevent contamination, or grow higher value algae that require a greater cultivation control.

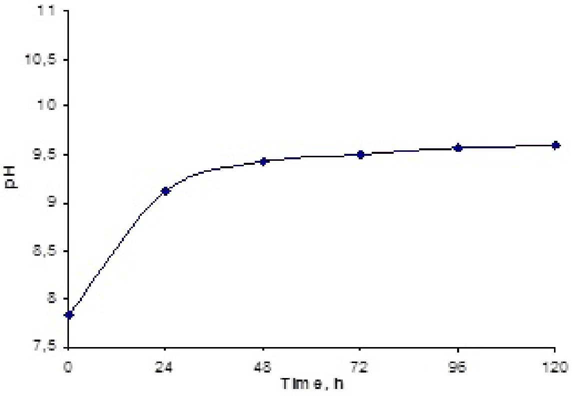

Fig. 5. pH values vs. time in MEC treatment of the digested sludge filtrate.

Table 4. Characteristics of the filtrate obtained through consecutive acidification/filtration.

Manure	pH value	PO_4, mg dm^{-3}	NH_4, mg dm^{-3}
Buffalo manure	3	169.9	836.8
	4	170.8	851.9
Cow manure	3	201.3	565.1
	4	150.1	541.2

Usually, the yield of dry Spirulina biomass is up to 1 g per liter nutrient medium, which contains variety of mineral sources of nitrogen and phosphorus. In addition, Spirulina has the natural tendency to grow in an alkaline environment [11]. These nutrients may remain as pollutants in the residual water after the biomass separation and that is why this waste flow is considered as a wastewater and needs to be managed and treated. The amounts of this waste are huge. For example, the annual spirulina production only in Inner Mongolia region of China is estimated to be around 18000 tons causing of discharge of 18 million m^3 wastewater [12]. Our preliminary studies show that the spent nutrient media contains phosphates in the range of 102 mg dm^{-3} -112 mg dm^{-3} and COD below 50 mgO$_2$ dm^{-3}. The media pH is 11.1. These conditions are favorable for efficient struvite precipitation [9]. The product of the precipitation, white crystals is proved to be predominantly struvite by ICP-OES and X-ray diffraction technique.

Bio-electrochemical N&P removal and recovery

Recently some innovations related to the abilities of bio-electrochemical systems (BES) for removal of ammonium and phosphate from wastewater have been published. Zhang et.al. [13] succeed to remove 83.4 % of ammonia and 52.4 % of phosphates from a BES anode solution, and to reduce up to 95 % of the organic matter within 144 h by applying 0.8 V as an external voltage. At the same time, the initial cathode solution (tap water) was concentrated in respect to ammonium nitrogen and phosphate. In another study [14], artificial human urine is used as a source of nutrients. The application of 0.9 V within 47 h results in increase of the cathode solution concentration to 45 % and 30 % in respect to ammonia and phosphate respectively. By using a microbial nutrient recovery cell [15], a reduction of over 96 % of ammonium nitrogen is achieved, while the phosphates concentration is decreased by 64 %. The experiments described above verify the principal possibilities of nitrogen and phosphorus removal by BES.

Through the experiment reported herein the possibilities of a lab-scale BES for simultaneous ammonium nitrogen and phosphate removal from synthetic wastewater is studied. The aim is to show the extent of ammonium and phosphate separation in biotic/abiotic mode at applying external voltage to the bioelectrochemical cell electrodes.

The difference between BES used in this study and the system cited above [13] refers to the ratio between the anolyte and catholyte volumes, the operating conditions regarding the presence of oxygen in the cathode chamber, the anode solution content, the hydraulic retention time and the cathode solution type.

The results obtained for the transition of ammonia and phosphate from the anodic into the cathodic chamber are given in Figs. 6 and 7. It is found that during the abiotic run the extent of ammonia decrease in the anodic compartment is negligible. On the contrary, the ammonia concentration drops significantly through the biotic mode of operation. It changes from 147.3 mg/L to 42.8 mg/L for a period of 240 h (Fig. 6). Similar is the trend of P concentration change.

It is found that the phosphate concentration in the anodic chamber decreases from 61.64 mg dm^{-3} to 6.11 mg dm^{-3} in case of a biotic mode, while this effect is considerably smaller (it changes from 58.8 mg dm^{-3} to 26.6 mg dm^{-3}) in an abiotic mode application, Fig.7.

Regarding the COD changes during the runs, it is found that during the biotic 240 h run COD in the anodic chamber decreases considerably. The data obtained listed in Table 5 shows that COD reduction in a biotic mode is over 95 %, while it amounts to 34 % in course of the abiotic one. The COD change during the biotic run can be attributed to the bio-electrochemical processes carried in the cell. The measured DO in the cathodic chamber (in the range of 7 mg dm^{-3} O$_2$ - 8 mg dm^{-3} O$_2$) obviously plays the role of an electron acceptor at the cathode improving the ion transfer through the membranes based on the bio-electrochemical process of electron generation and an additional potential created between the electrodes. Another proof of this assumption is that during the biotic

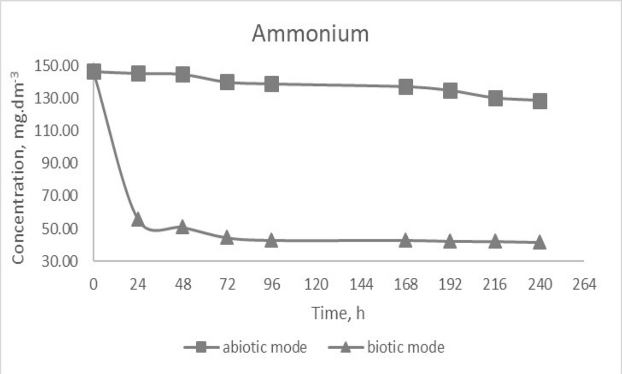

Fig. 6. Change of ammonia concentration in the anodic chamber.

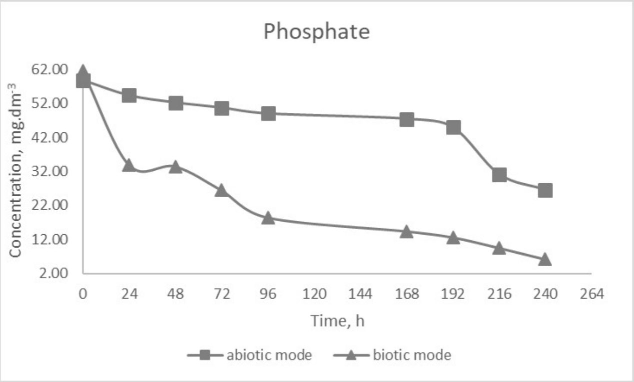

Fig. 7. Change of phosphates concentration in the cathodic chamber.

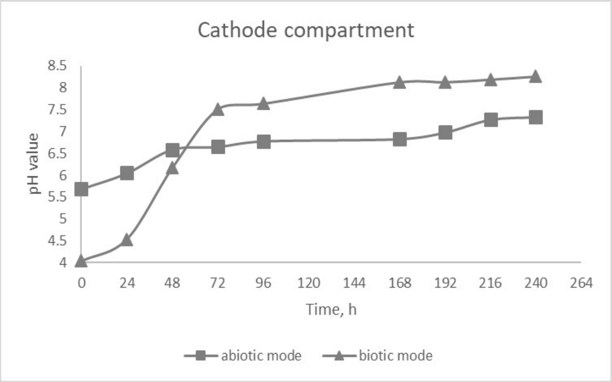

Fig. 8. Change of pH in BES cathode compartment.

mode the voltage between the electrodes has increased from the basic voltage applied (0.8 V) to 1.1V.

More intensive bio-oxidation is also evidenced by the observed higher rate of organic matter oxidation in the anodic chamber. The organic content in the cathodic compartment in case of both modes application does not change (44 mg O_2 dm^{-3} within 240 h run).

The results obtained are compared with those of a previous study in which a similar bio-electrochemical system (R2-BES) [14] is used. The latter reference reports 85.3 % ammonium and 52.4 % phosphate ions removal, while the effectiveness of removal obtained in this study is 71 % and 90.1 %, respectively. It should be noted that the initial ion concentration in using R2-BES is much lower (28.5 mg dm^{-3} of NH_4^+ and 5.3 mg dm^{-3} of PO_4^{3-}) than in the work reported herein (147.3 mg dm^{-3} of NH_4^+ and 61.64 mg dm^{-3} of PO_4^{3-}). Another difference refers to the higher membrane surface area of R2-BES anode and cathode compartment volume [13]. However, regardless the more "intensive" conditions related to the membrane surface of R2-BES experiment, better results concerning phosphorus removal are obtained in the experiment described in this communication.

pH change in the cathode compartment is shown in Fig. 8. Under biotic conditions pH reaches a value of 8.1. In a standard BES, the increase of cathode pH is typical, attributed to consumption of protons there.

The conditions of the cathodic chamber in case of a biotic mode application (pH 8.1, concentrations of phosphates of 89.1 mg dm^{-3} and of ammonia higher than 219.5 mg dm^{-3}) seem to favor struvite precipitation.

CONCLUSIONS

The results obtained show a considerable effect of organic matter separation by UF depending on membrane porosity in a cross flow mode of filtration. It provides preservation of a high P content which favors struvite precipitation. The acidification applied to animal manure results in almost double increase of P content in the liquid phase. In respect to the neutralization of the solute required, bio-electrochemical alkalization is applied. pH values higher than 9 are achieved within 24 h by BES non-reagent alkalization. The work discusses the promising way to use a P rich solution from spent algae growing media (higher than 100 mg dm^{-3} P) characterized by a low organic matter content and high pH (above 11) for struvite crystallization. It is also demonstrated that the electrochemical/bio-electrochemical treatment of waste water containing ammonia and inorganic phosphorus enables increase of phosphorus and nitrogen content in the cathodic chamber in an extent allowing efficient struvite precipitation.

Table 5. Changes of anodic chamber COD.

time, h	COD (abiotic mode), mgO_2 dm^{-3}	COD (biotic mode), mgO_2 dm^{-3}
0	2224	2230
120	1500	146
240	1472	102

Acknowledgements

The authors thank the National Science Fund of Bulgaria (BNSF) for the financial support of these investigations through Grant DN 17/14.

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