IOP Conf. Series: Earth and Environmental Science **92** (2017) 012007 doi:10.1088/1755-1315/92/1/012007

The application of electrodialysis for the recovery of phosphorus from wastewater sludge liquid discharge

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Abstract. The paper deals with recovery of phosphorus from the liquid discharge from dewatered wastewater treatment sludge via electrodialysis. Using electrodialysis, phosphorus was transferred into concentrate, where phosphorus concentrated to673.6 mg/l (from the original value 79.87 mg/l). This enriched concentrate may be further processed, e.g. phosphorus can precipitate into the form of struvite.

1. Introduction

This paper focuses on the recovery of phosphorus from wastewater by electrodialysis to verify the efficiency of the electrodialysis process in the removal of phosphorus from the liquid discharge from dewatering the wastewater treatment sludge (further referred to as liquid discharge).The reason forphosphorus recovery from waste products of different operations is that phosphorus reserves in the form of mineral resourcesare decreasing. Extracted phosphorus is used, for example, in agriculture during the production of fertilizers or feeds, in medicine and in the production of detergents. Potential, renewable or recyclable phosphorus sources may be wastewaters, wastewater sludge, manure slurry, yellow, brown and grey waters, food waste, agricultural waste or guano [1,2,3,4].

Wastewaters and wastewater sludge contain sufficient phosphorus, and thus it is advantageous to recover it. Phosphorus is removed from wastewater most often by precipitation in the form ofstruvite, hydroxyapatite or aluminium and ferric phosphate. Other methods for phosphorus removal from wastewater are, for example, biological processes and membrane processes with subsequent precipitation of phosphorus or recycling of phosphorus in the form as fly ash from sewage sludge. Phosphorus is usually removed from wastewater in excess sludge, which can be used as fertilizer after draining, stabilization and hygienisation. The disadvantage is thatsome wastewater sludge may contain toxic elements and such sludge cannot be applied onto agricultural land [1].

2. Materials and Methods

For the recovery of phosphorus from liquid dischargewe selected an electro-membrane separation process – electrodialysis. The aim of the laboratory measurements was the verification of efficiency of this process. Phosphorus was obtained from model waters (salt solution Na_2SO_4 and $NaH_2PO_4 \cdot 2H_2O$) and real samples of liquid discharge obtained from a wastewater treatment plant. Specifically, we used liquid discharge from a wastewater treatment plant with a capacity over 100 000 EP (equivalent population).

2.1.Determined indicators

For the evaluation of experiments in the samples we determined the following indicators – pH, conductivity, turbidity and total phosphorus (P_{total}). The pH value and conductivity were determined by laboratory multimeters pH/Cond 340i, turbidity using a spectrophotometer HACH LANGE DR 2800 and total phosphorus using the method of oxidative decomposition to dissolved inorganic orthophosphates by ČSN EN ISO 6878.

2.2.Used samples

In the first series of tests of electrodialysis, the so called salt tests with 2 % Na_2SO_4 solution were carried out. It is a standard solution for checking the effectiveness and correctness of composition of an electrodialysis unit. In the next series of the tests of electrodialysis we carried out salt tests with 0.1% $NaH_2PO_4 \cdot 2H_2O$ solution. This sample was used for checking the permeability of membranes for phosphate. After salt tests we carried out electrodialysis tests with real samplesof the so called liquid discharge. Table 1 shows the analysis of the real sample.

Table 1. Input analysis of liquid discharge.

Indicator [unit]	Real sample
pH [-]	7.79
Conductivity κ [μS/cm]	5.01
Turbidity [NTU]	> 40
P_{total} [mg/l]	79.87
NH_4^+ [mg/l]	1260
COD_{Cr} [g/l]	318.60

For the correct operation of electrodialysis it is necessary to pre-treat the sample. Herein the pre-treatment method was pressure filtration. Using an ILMVAC PS20-1 vacuum pump, the aim of pre-treatment is, for example, to prevent clogging of membranes and damage in the electrodialysis unit.

2.3.Electrodialysis unit

For the tests we used a laboratory electrodialysis unit P ED(P)-Z/10-1.0 (MEGA a.s.). The unit consists of an electrodialysis module, tank for diluent (D), for concentrate (C) and for electrode solution (E), of separate pumps for D, C and E circle, of rotameters for D, C and E circle and of DC voltage source. Electrodialysis module consists of regularly alternating cation and anionic membranes RALEX which are separated by polyethylene separators. For the tests we used an electrodialysis module with 10 couples of ion exchange membranes of the total area of membranes of 1 344 cm^2 [5].

2.4.Methodology of electrodialysis tests

All the electrodialysis tests were carried out in batch mode with regulated voltage 14 V. The electrodialysis tests with real samples were carried out as below:

- pre-treatment of liquid discharge by pressure filtration;
- dosing of the relevant volumes of the test sample into the D and C circle;
- dosing 2 % Na_2SO_4solution into the E circle;
- setting the regulated voltage 14 V;
- switching on a pump and voltage;
- recording the values of pH, κ, I and U in the time interval 5 minutes;
- measuring volumes of output products at the end of the test;
- analysis of output products.

2.5.Desalination rate

In all the tests we also calculatedthe desalination rate using the equation below:

$$DR = \frac{\kappa_{input} - \kappa_{output}}{\kappa_{input}} 100,$$

where DR is the percentage of desalination [%]; κ_{input} is the input conductivity of diluent [µS/cm]; κ_{output} is the output conductivity of diluent[µS/cm].

2.6.Mass balance

Next, mass balance was carried out, which is grounded in the fact that substances entering the electrodialysis process must also leave the process – see the equation below:

$$V_{input} \cdot c_{input} = V_D \cdot c_D + V_C \cdot c_C \,,$$

where V_{input} is the volume of solution entering the electrodialysis process [l]; c_{input} is the concentration of solution entering the electrodialysis process [mg/l]; V_D is the volume of diluent leaving the electrodialysis process [l]; c_D is the concentration of diluent leaving the electrodialysis process [mg/l];V_C is the volume of concentrate leaving the electrodialysis process [l];c_C is the concentration of concentrate leaving the electrodialysis process [mg/l].

2.7.Carried out tests

As mentioned above, thetotal three series of tests were carried out – salttestwith 2 % Na_2SO_4 solution, salt test with 0.1 % $NaH_2PO_4 \cdot 2H_2O$ solution,and tests with real samples. The aim of these tests was also to reduce the volume of waste product – concentrate. Therefore, different volumes of tests samples were tested.

The first series of tests with 2% Na_2SO_4 solution was carried out to check the efficiency of electrodialysis. Input volumes of salt solution are:

- D:C = 1000 ml : 1000 ml

The second series of tests with 0.1 % $NaH_2PO_4 \cdot 2H_2O$ solution was carried out to check the permeability of the membranes for phosphates. Input volumes of the solution for the tests are:

- D:C = 1000 ml : 1000 ml
- D:C = 1000 ml : 500 ml

The third series of tests was carried out with real samples of liquid discharge. Input volumes of samples for the tests are:

- D:C = 1000 ml : 1000 ml
- D:C = 1000 ml : 500 ml
- D:C = 5000 ml : 500 ml

3. Results and discussion

As the blind test of electrodialysis unit, we selected standard salt test with 2 % Na_2SO_4 solution. Tests lasted for 65 minutes and the percentage of desalination reached 99.5% efficiency. The tests had a standard course. Salt tests with 0.1% $Na_2H_2PO_4 \cdot 2H_2O$ solution were carried out to check the efficiency of phosphate transition by ion exchange membranes. These tests were evaluated as effective.

The following tables summarize the results of electrodialysis tests of real samples of sludge water/liquid discharge. The first tests with lower volumes of input sample were terminated after 40 to 45 minutes when the current dropped to 0.04A. The percentage of desalination was 98.6 – 98.99 %. The results are summarized in tables 2 and 3.

Table 2. Selected analysis indicators V1, D1 and C1.

Indicator [unit]	V1	D1	C1	Balanceinput	Balance output	Deviation [mg/l]	Deviation [%]
V [ml]	2000	1000	1000	-	-	-	-
pH	8.245	4.854	8.382	-	-	-	-
κ [mS/cm]	6.17	0.05	10.70	12.34	10.75	1.59	12.88
COD_{Cr} [mg/l]	269.29	194.98	325.85	538.58	520.83	17.75	3.30
N_{ammon} [mg/l]	1050.00	9.80	1850.00	2100	1859.80	240.20	11.44
P_{total} [mg/l]	198.86	10.432	262.104	397.72	272.536	125.184	31.48

Table 3. Selected analysis indicators V2, D2 and C2.

Indicator [unit]	V2	D2	C2	Balance input	Balance output	Deviation [mg/l]	Deviation [%]
V [ml]	1500	1000	500	-	-	-	-
COD_{Cr} [mg/l]	268.28	128.30	348.75	402.42	302.675	99.745	24.79
N_{ammon} [mg/l]	958.30	8.26	2825.30	1437.45	1420.91	16.54	1.15
P_{total} [mg/l]	68.46	8.48	104.32	102.69	60.64	42.05	40.95

Tests with larger volumes of input sample (5500 ml) lasted for 3 hours and 55 minutes when the current dropped to 0.03 A. The average percentage of desalination was 98.67 %. The results were summarized in table 4.

Table 4. Selected analysis indicators V3, D3 a C3.

Indicator [unit]	V3	D3	C3	Balance input	Balance output	Deviation [mg/l]	Deviation [%]
V [ml]	5680	5180	500	-	-	-	-
COD_{Cr} [mg/l]	268.28	176.193	375.487	1523.83	1100.42	423.41	27.79
N_{ammon} [mg/l]	958.30	6.93	8500	5443.14	4285.90	1157.24	21.26
P_{total} [mg/l]	68.46	10.76	673.60	388.85	392.54	3.69	0.95

The results show the electrodialysis process as an effective method for phosphorus removal from liquid discharge. The phosphorus is concentrated into the concentrate stream. Based on the implementation of mass balances, we may state that higher deviations (tables 3 and 4) are most likely analysiserrors, particularly in the concentrates, where the samples had to be diluted several times. However these differences did not effect for the correct operation of electrodialysis and there were no presented features of membrane fouling. For minimum deviations in the results, it is suitable to use specific analytical methods in the future that would be more appropriate for analyses of concentrates and concentrated samples.

4. Conclusion

The aim of this paper was to verify the possibility of using electrodialysis for phosphorus recovery from liquid discharge rich in phosphorus.The condition for the reduction of phosphorus concentration from wastewater is its reduction to a minimum and its transfer into the concentrate as a product of electrodialysis. To verify electrodialysis as a suitable process for phosphorus recovery from liquid discharge we carried out several tests, with salt solutions and with real waters.

According to the measured results, electrodialysis is suitable for phosphorus recoveryfrom liquid discharge. At all the tests with real samples of liquid discharge achieved the desalination rate from 96.01 to 98.99 %. Phosphorus was transferred from pre-treated samples into the concentrate stream with output phosphorus concentration 673.6 mg/l.This concentrate can be further processed, for example, and phosphorus may precipitate into the form of struvite.

Acknowledgments
This paper was published with the support of the Ministry of Agriculture within the Project QJ1320159 “Research in processing, use and disposal of waste product from biogas stations”.

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