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# REMOVAL OF ORGANIC MATERIALS AND PLANT NUTRIENTS IN A CONSTRUCTED WETLAND FOR PETROCHEMICAL WASTEWATER TREATMENT

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**ABSTRACT.** The constructed wetland system of Bogdány Petrol Ltd. was formed in the 1970s for the post-treatment of petrochemical wastewater. Before leading to the constructed wetland, the wastewater is treated both mechanically and chemically. The constructed wetland system consists of three ponds with extended vegetation cover. Dominant macrophytes are *Phragmites australis*, *Typha latifolia* and *Typha angustifolia*, while among other plant species, *Bidens tripartitus, Carex acutiformis, Ceratophyllum demersum, Lemna minor, Potamogeton pectinatus* and *Scirpus lacustris* can be found on the area. The aim of our research was to examine the effect of the pond-system on removal of organic matters and plant nutrients from the wastewater. Organic matter removal was examined through COD and BOD values, while elimination of main plant nutrients was reflected by the data of different forms of phosphorous and nitrogen.

**Keywords:** constructed wetland, organic matters, nutrient removal, petrochemical wastewater treatment, $COD_{aCr}$, $BOD_5$

## INTRODUCTION

Natural wetlands have been used for wastewater treatment for centuries, however in the last 10 or 20 years the use of constructed wetlands has become more popular and effective around the world (Reddy and Smith, 1987, Kadlec and Knight, 1996, Cooper et al., 1996, Lakatos, 1998, Haberl et al., 2003). Constructed wetland treatment systems are engineered systems designed and constructed to utilize the natural processes involving wetland vegetation, soils and their associated microbial assemblages to assist in treating wastewater. They are designed to take advantage of many of the same processes that occur in natural wetlands, but do so within a more controlled environment. Wetland treatment systems are effective in treating organic matter, nitrogen, phosphorous, and additionally for decreasing the concentrations of heavy metals, organic chemicals, and pathogens (Haberl et al., 2003). As a consequence, constructed wetlands are an effective and low cost way to treat water polluted with organic compounds and plant nutrients.

There is several factors which affect the ability of constructed wetlands to retain nutrients including alternate dry (aerobic) and wet (anaerobic) conditions, hydraulic retention time, influent nutrient concentration, water depth, hydraulic loading rate, emergent vegetation, water chemistry, and soil type (Kadlec and Knight, 1996, Baldwin and Mitchell, 2000, Baldwin et al., 2000, Mitsch and Gosselink, 2000, Jordan et al., 2003, Dierberg et al., 2005, Chavan et al., 2008). In the wetlands, nutrient removal from wastewater occurs due to different mechanisms: (1) plant uptake; (2) microorganisms residing on the plant roots which transform nutrients (mainly N) into inorganic compounds ($NH_4^+$ and $NO_3^-$) which are directly available to plants; and (3) physical processes, such as sedimentation and filtration (Ciria et al., 2005). Vegetation plays a uniquely important role in water treatment due to the large number of functions it supports (Lakatos et al., 1997).

The aim of this paper to examine the removal of organic pollutants and plant nutrients in the constructed wetland system of Bogdány Petrol Ltd., which had been created to treat the industrial wastewater of the petrochemical company.

## MATERIALS AND METHODS

The examined constructed wetland system can be found in Nyírbogdány, in the North-Eastern part of Hungary. Area of the observed wetland is 15 500 $m^2$, the water depth is approximately 1m and the water discharge is 200-250 $m^3$/day. As it can be seen on Figure 1., after mechanical and chemical treatment, the wastewater flows into a pre-deposition pond, then it flows to the oxidation pond, the vegetation of which is dominated by reed (*Phragmites australis*) and cattail (*Typha latifolia, T. angustifolia*). Approximately 80% of the oxidation pond is covered by submerged macrophytes (*Potamogeton pectinatus* and *Chara sp.*). Beside these plant species, *Bidens tripartitus, Carex acutiformis, Ceratophyllum demersum, Lemna minor* and *Scirpus lacustris* can be found on the area in considerable quantities. Most of these plants are common species of natural wetlands as well (Grec, 2008). The last part of the system is the post-treating pond, which is recently not in operation (Lakatos et al.,

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1997). Receiver of the treated wastewater is the Lónyai Channel, which had been constructed to collect the waters of Nyírség. Near the settlement of Gávavencsellő, Lónyai Channel flows into River Tisza.

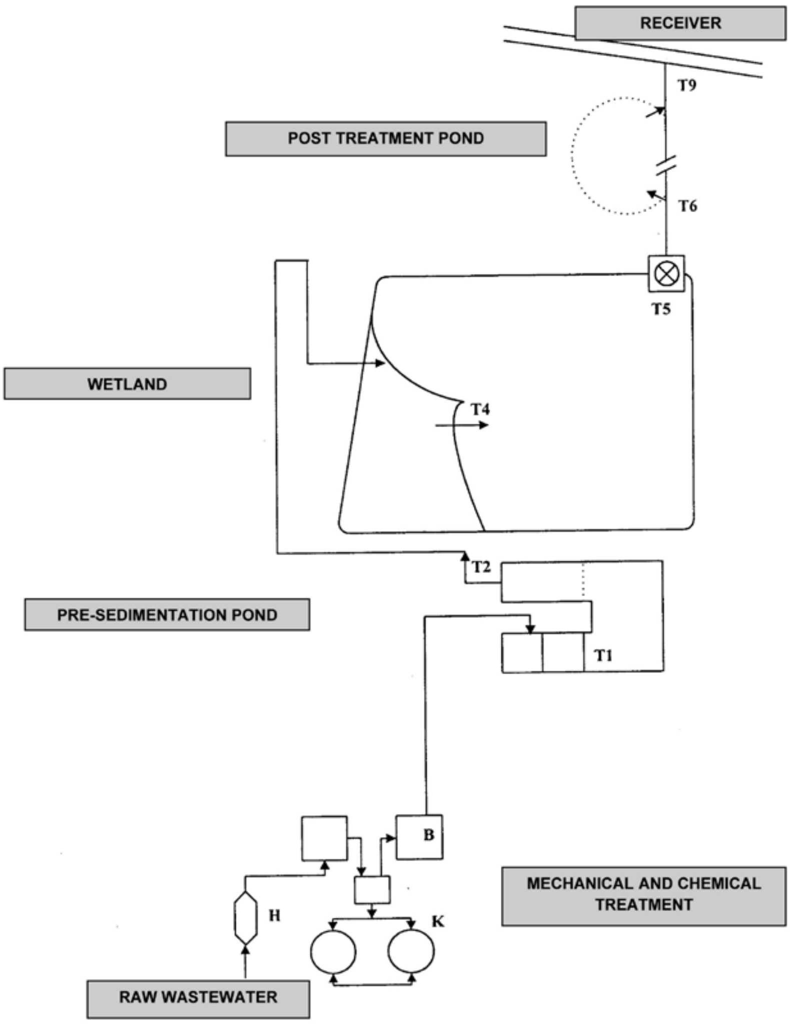


**Fig. 1** Construction of the treatment wetland system

For this survey, samples were taken three times (in spring, summer and autumn) in 2008, within a vegetation period. The water samples were taken with ladling from the surface layers of waters at depth of 15 cm. The assessment of nitrite, nitrate, ammonia, $COD_{aMn}$, $COD_{aCr}$, $BOD_5$, ortho-phosphate and total phosphorous was carried out in the laboratory of Applied Ecology, University of Debrecen, according to Felföldy (1987).

Treatment efficiency was calculated as the per cent removal (R) for each parameter and was calculated by

$$R = 100 - (C_{eff.}/C_{inf.} \times 100)$$

where $C_{inf}$ and $C_{eff}$ are the influent and effluent concentrations in mg/l.

## RESULTS AND DISCUSSIONS

The measured COD and BOD values, ortho-phosphate (o-$PO_4^{3-}$), total phosphorous (TP), nitrite ($NO_2^-$) nitrate ($NO_3^-$) ammonium ($NH_4^+$) and total nitrogen (TN) concentrations are summarized in Table 1.

### *Removal of Organic Materials*

BOD and COD (Biochemical and Chemical Oxygen Demand) are used as a sum parameter for organic matter. Major removal mechanisms of organic matters are volatilisation, photochemical oxidation, sedimentation, sorption, and microbial degradation by fermentation, aerobic and anaerobic respiration (Haberl et al., 2003).

Considering organic matter assessments, $COD_{aCr}$ is more precise method than $COD_{aMn}$ as a consequence of the higher reduction capacity of potassium-chromate.

According to our measurements, values of $COD_{aCr}$ are relatively higher than values of $COD_{aMn}$ in the inflowing wastewater which indicates the large amount of hardly degradable organic materials; however, amount of organic material is considerably decreased in the outflow (Fig. 2. and Fig. 3.).

*Table 1*

**Values of the measured parameters of water**

| | | spring | summer | autumn |
|---|---|---|---|---|
| **$COD_{aMn}$ ($O_2$ mg/l)** | **influent** | 52.47 | 43.75 | 47.06 |
| | **effluent** | 13.25 | 14.92 | 14.89 |
| **$COD_{aCr}$ ($O_2$ mg/l)** | **influent** | 131.15 | 144.35 | 101.17 |
| | **effluent** | 54.11 | 55.07 | 60.08 |
| **$BOD_5$ ($O_2$ mg/l)** | **influent** | 41.69 | 41.92 | 31.90 |
| | **effluent** | 20.75 | 13.66 | 13.04 |
| **ortho-P (mg/l)** | **influent** | 0.219 | 0.443 | 0.201 |
| | **effluent** | 0.092 | 0.135 | 0.038 |
| **TP (mg/l)** | **influent** | 0.402 | 0.854 | 0.564 |
| | **effluent** | 0.227 | 0.328 | 0.310 |
| **nitrite (mg/l)** | **influent** | 0.006 | 0.006 | 0.011 |
| | **effluent** | 0.021 | 0.003 | 0.007 |
| **nitrate (mg/l)** | **influent** | 0.180 | 0.152 | 0.098 |
| | **effluent** | 0.204 | 0.167 | 0.131 |
| **ammonium (mg/l)** | **influent** | 0.261 | 2.326 | 2.298 |
| | **effluent** | 1.683 | 1.809 | 1.896 |
| **TN (mg/l)** | **influent** | 1.168 | 3.861 | 2.776 |
| | **effluent** | 2.040 | 3.009 | 3.093 |

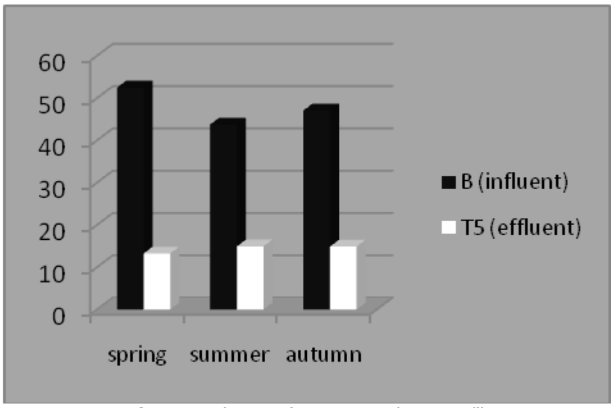


**Fig. 2** Values of $COD_{aMn}$ ($O_2$ mg/l)

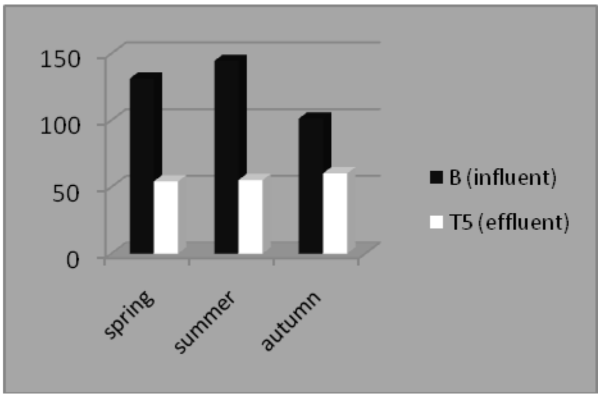


**Fig. 3** Values of $COD_{aCr}$ ($O_2$ mg/l)

*Table 2.*

**Removal rates of $COD_{aMn}$, $COD_{aCr}$ and $BOD_5$**

| R % | spring | summer | autumn |
|---|---|---|---|
| **$COD_{aMn}$** | 74.74 % | 65.89 % | 68.35 % |
| **$COD_{aCr}$** | 58.74 % | 61.84 % | 40.61 % |
| **$BOD_5$** | 50.22 % | 67.41 % | 59.12 % |

According to BOD values, removal of biodegradable materials is satisfactory in the system. In the outlet, decreased COD and BOD point to a large organic matter mineralization within the wetland. Removal rates for $COD_{aMn}$, $COD_{aCr}$ and $BOD_5$ can be seen in Table 2. Removal of COD and BOD is satisfactory; however, scientific literature mentions larger (typically between 80 % and 90 %) removal of organic substances (Ansola et al., 2003, Scholtz and Lee, 2005, Sun et al., 2005, Wand et al., 2007, Tang et al., 2008).

### *Removal of Plant Nutrients*

In constructed wetlands, the removal of inorganic nitrogen and phosphorous is frequently problematic (Brix et al., 2001, Luederitz et al., 2001, Vymazal, 2007, Tang et al., 2008).

Our values of different nitrogen forms suggest that removal of nitrogen is not always effective in the system (Table 3 and Fig. 4). According to scientific literature, percent mass removal of nitrogen can vary between 50 % and 99 % (Reddy et al., 2001, Bezbaruah and Zhang, 2003, Vymazal, 2007).

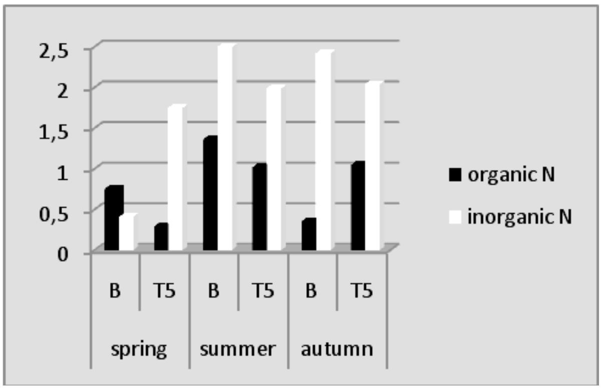


**Fig. 4** Concentrations of organic N and inorganic N

However, in Europe, a maximum of approximately 50% could be achieved after modifications to the system have been made to stimulate the transformation of nitrogen (Verhoeven and Meuleman, 1999). During our research, percent removal for total nitrogen could be determined (TN) only in the summer period. This can be explained by the higher vegetation activity in the summer, since among others, Tang et al. (2008) and Lakatos (1998) published that elimination processes of vegetation significantly enhance the removal of nitrogen in constructed wetlands. In part, insufficient nitrogen removals can be explained with some kind of inhibition in nitrification activity, which have been experienced in the system for years. In accordance, studies indicated that nitrification is the rate limiting step for nitrogen removal (Kuschk et al., 2003).

Considering nitrogen concentrations in the autumn, the amount of organic nitrogen is relatively high in the effluent, which can be explained by the large amount of organic material of the dead vegetation. As the sampling was carried out in November, when the water temperature was 6.5 $^0$C, large organic nitrogen content can be explained by the decreased intensity of degradation processes (Removal rates of $COD_{aCr}$ and BOD in the autumn samples also support this statement).

*Table 3.*

**Removal rates of nitrogen**

| R% | spring | summer | autumn |
|---|---|---|---|
| **organic N** | 61.54 % | 25.24 % | - |
| **inorganic N** | - | 20.34 % | 15.50 % |
| **TN (Total Nitrogen)** | - | 22.07 % | - |

*Table 4.*

**Removal rates of phosphorous**

| R% | spring | summer | autumn |
|---|---|---|---|
| **ortho-phosphate** | 58.00 % | 69.53 % | 81.10 % |
| **TP (Total Phosphorous)** | 43.54 % | 40,80 % | 45.04 % |

For phosphorous, researchers reported that constructed wetlands can remove between 30% and 94% of the phosphorous inputs (Braskerud, 2002, Reddy et al., 2001, Vymazal, 2007). However, the removal of phosphorous in most constructed wetlands remained close to 50 % (Verhoeven and Meuelman, 1999, Scholz and Lee, 2005), as it is supported by our results as well (see Table 4).

Figure 5 shows the concentrations of ortho-phosphate and TP (total phosphorous) in the influent and effluent waters. According to our results, values of phosphorus forms show a relatively small amount of ortho-P (which is easily available for plants) in proportion to the amount of total phosphorous. However, most of the total phosphorous is removed by the wetland.

## CONCLUSIONS

During our survey, we examined the removal of organic matters and plant nutrients in an constructed wetland, which was built for the treatment of petrochemical wastewater.

According to our results, removal of COD and BOD is satisfactory in the system; however, scientific literature mentions larger (typically between 80 % and 90 %) removal of organic substances. Decreased COD and BOD values of the effluent water indicate large organic matter mineralization within the wetland.

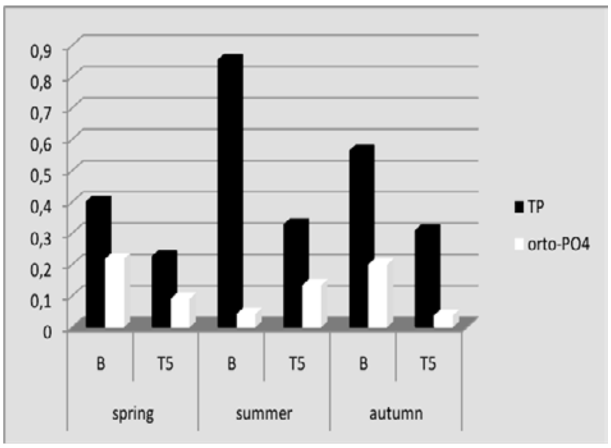


**Fig. 5** Concentrations of ortho-phosphate and TP

Considering the removal of plant nutrients, unfortunately, the nitrogen removal is not always satisfactory in the system. During our research, percent removal for total nitrogen could be determined (TN) only in the summer period, which probably can be explained by the decreased nitrification activity of microorganisms. Percent removal rate of phosphorous is in accordance with the results of scientific literature and indicates effective phosphorous removal in the system.

Despite of the aforementioned insufficiency in nitrogen removal, elimination of organic matters and plant nutrients in the examined wetland is satisfactory, however further researches are needed to maintain this favourable status.

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