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Removal of phthalates and other contaminants from municipal wastewater during cultivation of *Wolffia arrhiza*

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ABSTRACT

The usefulness of *Wolffia arrhiza* for decontamination of waters from phthalates and other organic compounds was studied using artificial growing medium and real municipal wastewater samples. The eight most frequently detected phthalates were considered: dimethyl (DMP), diethyl (DEP), dipropyl (D*n*PP), dibutyl (D*n*BP), diisobutyl (DIBP), bis(2-ethylhexyl) (DEHP), diizoheptyl (DIHP) and diizononyl (DINP). The reduction of phthalates concentration observed during seven days of *W. arrhiza* cultivation on artificial growing medium was between 78.9 and 99.7%. Kinetics of phthalates degradation by *W. arrhiza* in real effluent wastewater was similar to those with laboratory-made solutions. The significant removal of nutrients (75–78%) and reduction of oxygen demand (93–97%) was achieved during cultivation of *W. arrhiza*. Purification efficiency of non-treated municipal wastewater with *W. arrhiza* was better than obtained with the use of *Lemna minor*, which is wide used in constructed wetlands, and not much worse than those obtained in conventional Wastewater Treatment Plant (WWTP). Analysis of biochemical components, stress markers and antioxidant activity in *W. arrhiza* shows its good acclimation to high pollution of aquatic environment.

1. Introduction

The use of plant organisms in constructed wetlands for wastewater treatment meets all requirements of ğreenpurification processes. Due to its high removal efficiency, simple operation, low cost and great potential for water reuse this method of purification have become a popular option for wastewater treatment (Kadlec and Wallace, 2009). The use of plants for wastewater purification is most useful in countries with warm climates, and in view of its advantages seems to be an ideal solution for developing countries (Zhang et al., 2014). Additional benefits of phytoremediation is biomass which can be used for the energy, paper or charcoal production, reduction of CO_2 emission, erosion control and improving of an attractiveness of a landscape. Plants used for phytoremediation are characterized by a rapid increase in biomass and tolerance to a variability in a composition of treated water or soil as well as a high content of salt, phosphates and nitrogen (Justin et al., 2010). For this purpose are used higher terrestrial plants (*Salix viminalis L.*, *Populus deltoides*), wetland plants (*Phragmites australis*, *Typha latifolia*, *Schoenplectus lacustris*, *Sparganium ramusom*, *Glyceria aquatica*, *Iris pseudoacorus* and species of the *Carex* family, as well as *Myriophyllum spicatum*, *Apium nodiflorum* (L) and aquatic plants of the genus Lemnaceae (Adhikari et al., 2015; Appenroth et al., 2015; Obarska-Pempkowiak et al., 2010). The use of duckweeds, including *Lemna* and *Spirodela* spp. for pollutants removing from different kinds of wastewater is well known for many years (Sutton and Ornes, 1977; Vermaat and Khalid Hanif, 1998), but an applicability of *W. arrhiza* to water purification has received only a little attention. *W. arrhiza* is the smallest flowering plant. Under conditions conducive to photosynthesis it behaves like a typical plant. In the case of limited access to a light it changes the mode of feeding and begins collecting nutrients from the environment (Fujita et al., 1999). It has been observed that intense biomass growth of *W. arrhiza* is possible only in an environment rich in biogenic compounds and therefore it can be considered as an indicator of eutrophication (Czerpak and Piotrowska, 2005). In experiments conducted with the mineral medium it was found that *W. arrhiza* culture significantly removes nutrients, heavy met-

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als and reduces oxygen deficit in growth medium (Fujita et al., 1999; Piotrowska et al., 2010; Soda et al., 2013; Vermaat and Khalid Hanif, 1998). Only few works were devoted to growing *W. arrhiza* on real wastewater. Most of them describe the growth rates and changing of nutrient content in the plant during cultivation on wastewater as growing medium as well as the use of plant tissues after the completion of the treatment process as a source of biomass energy or for ethanol production (Fujita et al., 1999; Soda et al., 2015; Verma and Suthar, 2015). Mishra et al. (2000) evaluated nutrient removal from dairy wastewater while Suppadit (2011) and Suppadit et al. (2008) studied changes in biological oxygen demand (BOD) and some other physicochemical parameters of shrimp and quail farm wastewaters through *W. arrhiza* cultivation. Some research on the assessment of the changes in municipal wastewater during cultivation of *W. arrhiza* were also conducted about 20 years ago by Mical et al. (1997). It should be taken into account that the constitution of municipal wastewater during last years has changed significantly since society consumption of detergents and personal care products has been constantly growing. The high consumption of cosmetics, common use of packaging made of plastics as well as the fact that phthalates are not chemically bond with polymers so they can freely migrate from them, cause significant pollution of urban wastewater by this group of compounds (Wittassek et al., 2011; Zota et al., 2014). Inadequate treatment of wastewater prior to their introduction into natural waters is a major cause of presence of phthalates in different compartments of environment (Gavrilescu et al., 2015; Vandermeersch et al., 2015). The concentration of phthalic acid esters in natural water reservoirs varied between few nanograms per liter and few hundreds micrograms per liter, while in sediments and soils reaches several dozen milligrams per kilogram (Gao and Wen, 2016). Their widespread occurrence in natural water reservoirs has adverse effect to water organisms and to humans (Wittassek et al., 2011; Zota et al., 2014). They are considered as endocrine active compounds as phthalates can mimic the hormone activity by binding to specific receptors, elicit a similar response as natural hormones or block the receptors (Palanza et al., 2016; Rouiller-Fabre et al., 2014). It is believed that the long-term exposition to phthalates is partially responsible for some humans disorders like cryptorchidism, hypospadias and testicular cancer. The epidemiological studies have shown a link between a level of absorption of phthalates and increased numbers of obesity, insulin resistance and attention-deficit hyperactivity disorders (Latini, 2005; Wittassek et al., 2011). Children are particularly sensitive to phthalates (Sathyanarayana, 2008). In order to protect them, the European Union banned the use of di(2-ethylhexyl (DEHP) and di-isononyl (DINP) phthalates in toys. Moreover, the EU recommends that the concentration of phthalates in toys and other products has to be not greater than 0.1%.

The occurrence of phthalates in wastewater varies in a wide range of concentration depending on chemical nature of compounds, a season of the year, temperature and intensity of the light (Gani and Kazmi, 2016). The accomplished studies shown that in WWTPs phthalates mainly undergo biotransformation in an activated sludge processes (ASP) and in a small extend photodegradation (Barreca et al., 2014). The efficiency of their removal is influenced by the molecular structure of phthalates, construction of WWTP and the nature of applied processes. The literature survey shows that the application of conventional ASP's, a sequencing bath reactor (SBR) and a combined up flow anaerobic sludge blanket (UASB) with post treatment by polishing pond, have allowed removal of phthalates at 74%, 80% 83%, respectively (Gani and Kazmi, 2016). The use of the flat sheet membrane bioreactor has eliminate only 29% of diethyl phthalate from synthetic wastewater (Gao and Wen, 2016). The literature also describes attempts to use four plants with a root system to remove phthalates from contaminated waters. Zavoda et al., 2001 investigated the possibility of hydroponic purification of model solutions containing D*n*BP, benzylbutyl phthalate (BBP) and dioctylphthalate (DOP) in the presence of heavy metals and radionuclides using *Helianthus annuus* and *Brassica juncea*. Xiaoyan et al., 2015 conducted experiments using *Thalia dealbata* and *Arundo donax* var. *versicolor* for removing DMP, DEP, D*n*BP, BBP, DEHP, DOP from municipal wastewater. The conducted research has shown that in constructed wetlands with root plants the effectiveness of removing phthalates ranges from 19 to 83%. Considering above data, it could be stated that the search for a new, environment friendly and more efficient method for removing phthalates still remains a valid concern. For this reason in presented paper the effectiveness of the use of *W. arrhiza* for removing phthalates and other pollutants from artificial growing medium and real municipal wastewater samples was studied. Additionally the purification experiments were done also with the use of L. *minor*, the organism from duckweeds family which is most often employed for wastewater purification. To the best of our knowledge, studies on the removal of phthalates from contaminated waters using floating plants are being presented for the first time. At the same time, the removal of four phthalic acid esters: D*n*PP, DIBP, DIHP and DINP detected in the environment was investigated for the first time in any hydroponic systems.

2. Materials and methods

2.1. Chemicals and reagents

Methanol of analytical grade was purchased from Chempur, Poland. Diethyl ether and acetone of analytical grade were supplied by POCH, Poland. *n*-Hexane (98%) was produced by Meck, Germany. Standards of n-alkanes (C_8-C_{40}) and phthalates: DMP, DEP, D*n*PP, D*n*BP, DIBP, DEHP, DIHP, DINP were supplied by Sigma-Aldrich, Germany. Standard solutions of studied phthalates were prepared by dissolving of about 10 mg of each in 100 mL of methanol. The obtained mixture was stored at temperature −20°C not longer than two weeks. Other reagents were of analytical grade. They were purchased from POCH, Poland.

2.2. Apparatus

All spectrophotometric determinations were done using a Hitachi U-2800 A spectrophotometer (Japan). The following working settings of the apparatus were applied: scan speed 1200 nm/min and spectral bandwidth (1.5 nm). Gas chromatographic – mass spectrometric (GC–MS) analysis was carried out using an HP 6890 gas chromatograph with an electronic pressure control device connected to a mass detector MSD 5973 (electron impact source and quadrupole analyzer, Agilent Technologies, USA) equipped with a HP-5MS column (5% phenylmethylsiloxane) with length of 30 m and i.d. of 0.25 mm coated with a 0.25 μm thick film and using a split/splitless injector. Helium of 99.999% purity was used as a carrier gas. The electron impact source temperature was 230°C with electron energy of 70 eV. The quadrupole temperature was 150°C and the interface between GC and MS temperature was 280°C.

2.3. Wastewater collection

Non-treated wastewaters were collected from the local WWTP in Lomza, the city in the west area of Podlasie region (north-east Poland). The facility collects sewage from the city and two neighboring municipalities with the total population 84,300. The average flow of wastewater is 25 000 m^3/24 h. The purifying process is based on mechanical-biological treatment. The samples of sewage were collected to glass containers and carried immediately to laboratory and analyzed for various physicochemical parameters such as pH,