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The biofiltration process by the bivalve *D. polymorpha* for the removal of some pharmaceuticals and drugs of abuse from civil wastewaters

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ABSTRACT

This study shows the evaluation of the possible use of the freshwater bivalve *Dreissena polymorpha* for the removal of some recalcitrant contaminants, namely many pharmaceuticals and drugs of abuse that are not sufficiently removed from civil wastewaters. This mollusk has an enormous filtering capability and is highly resistant to natural and anthropogenic stresses and to a significant bioaccumulation of lipophilic contaminants. All these characteristics may be particularly useful for the removal of compounds not easily eliminated by conventional wastewater treatment processes. To verify this hypothesis an experimental study was conducted at the pilot scale using a pilot plant installed in the largest wastewater treatment plant of Milan (Milano-Nosedo, Italy). First, we presented results obtained in several preliminary tests in order to evaluate the capability of zebra mussel specimens to survive in different wastewater mixtures, its filtering capacity and the possible influence of bio- and photo-degradation in the abatement of the molecules of interest. Finally, data obtained in the final tests demonstrated a capacity of this filter-feeder to reduce the concentrations of several pharmaceuticals and drugs of abuse higher than that obtained by the simple natural sedimentation, suggesting a possible implementation of the bio-filtration process in wastewater management.

1. Introduction

Today, the main challenge in the wastewater treatment of Western countries is the abatement of several environmental pollutants recalcitrant to removal, such as pharmaceuticals and personal care products (PPCPs), drugs of abuse and related metabolites. These compounds have been detected in sewage flows, surface and groundwater with levels generally ranging from traces to pbb values (Fatta-Kassinos et al., 2011). Despite it is known that these chemicals are to be associated with adverse effects in aquatic organisms at environmental relevant concentrations, it is now well accepted that conventional WWTPs are not designed to quantitatively remove micropollutants, because they are basically designed for the elimination of macropollutants (suspended solids, organic matter and nutrients). Thus, in the last decade, intense efforts have been made to improve the performances of WWTPs in respect to micropollutants' removal by introducing new steps designed to remove such contaminants more efficiently (Batt et al., 2007; Clara et al., 2005a; Nakada et al., 2007). Thus, a plethora of several different new and pioneering methods have been developed and tested as final wastewater treatment to remove these pollutants, such as activated carbon adsorption (Yu et al., 2008), ozonation and advanced oxidation processes (Kim et al., 2008), membrane filtration (Snyder et al., 2007), reverse osmosis (Lee et al., 2012; Dolar et al., 2012) and bio-filtration (Reungoat et al., 2011). Unfortunately, each of them possesses several drawbacks and/or most of them are able to eliminate only specific contaminants. In fact, the current consensus on treatment in the research community is that no single technology can completely remove pharmaceuticals because of their very particular physical–chemical characteristics and that integration of removal technology may prove essential to handling of today's mixtures of compounds in wastewater (Fatta-Kassinos et al., 2011). Moreover, their efficiency of removal is significantly affected by several factors: the physicochemical properties of pharmaceuticals, the treatment processes employed, the age of the activated sludge, the hydraulic retention time (HRT) and

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environmental parameters such as temperature and light intensity (Clara et al., 2005b; Andreozzi et al., 2003).

In this context, we tried for the first time worldwide a natural, not expensive and energy-free treatment for the abatement of some recalcitrant environmental pollutants from wastewaters exploiting the physiological characteristic of the freshwater bivalve zebra mussel (*Dreissena polymorpha*), which is well known for its huge filtering capacity. This filter feeder can filter a wide range of suspended particles of greater than 0.7 μm from the water (Sprung and Rose, 1988), whose a percentage is assimilated (typically in the range of 15–40 μm; Ten Winkel and Davids, 1982) and the rest deposited to the benthic zone as faeces and pseudofaeces. Furthermore, zebra mussel has an enormous filtering capacity, ranging from 5 to 400 mL/bivalve/h (Ackerman, 1999; Baldwin et al., 2002) and the capability to reach a high population density, with more than 700,000 specimens/m^2 (Pathy, 1994). Its possible use in the wastewater treatments is also promoted by the great resistance to physical and chemical changes (e.g. temperature, pH, hardness and salinity) and the ability to attach itself to hard substrates by the byssus. McLaughlan and Aldridge (2013) consider the freshwater filter feeders as "keystone organisms" or "ecosystem engineers" because they are characterized by a system that processes large volumes of water in order to trap and concentrate food from their surrounding. On the other hand, there are several evidences in the use of zebra mussel for environmental management as biofilter. Piesik (1983) examined almost thirty years ago the possible application of *D. polymorpha* in eutrophication control in a canal of Poland, concluding that these mussels succeeded in removing dissolved nutrients from the water. Richter (1986) gave preliminary results of a study in Lake Tjeukemeer (The Netherlands), which suggested zebra mussels could be effective tool for reducing algal density in Dutch lakes. Antsulevich (1994) proposed the construction of artificial reefs in the Neva Bay (Finland), which could be periodically removed and cleaned from uncrusting zebra mussels to improve the water quality. More recently, Elliott et al. (2008) tested the influence of different ecological factors, such as the density of the mollusks, the current speed and the amount of food, on the zebra mussel filtration capacity. These authors also suggested that zebra mussels could be used as an on-site industrial bio-filter for water treatment. Finally, Schernewski et al., 2012 considered the opportunities of using zebra mussel cultivation in the Szczecin Lagoon (Germany) in order to improve water quality. Although these evidences based on the capability of zebra mussel to be exploited in the environmental management, no data are available until now on the possible use of this filter feeder as complementary treatment in WWTPs. Thus, this study is a novelty in the wastewater management overview and could represent a possible starting point to take advantage on the natural characteristics of an aquatic organism that can be enforced in the prevailing engineering and chemical approaches. Our idea started from the consideration that many environmental chemicals are bound to suspended particulate matter (SPM) in different ways, depending not only on lipophilic properties, such as persistent organic pollutants (POPs), but also on specific other characteristics (cation exchange, complexation and hydrogen bonding), typical of some relatively polar or ionic chemical classes, such as pharmaceuticals and drugs of abuse (Lahti and Oikari, 2011; Baker and Kasprzyk-Hordern, 2011; Petrie et al., 2013; Darwano et al., 2014). Thus, we hypothesize that the very high filtration rate due to hundreds of thousands of zebra mussel specimens can decrease the concentration of several pollutants in wastewater by the increase of SPM deposition on the bottom of the plant. Moreover, the high filtration rate allows a fast intake of environmental pollutants in the mussel soft tissues, increasing their elimination from the wastewater. To verify this hypothesis, we carried out this research at the pilot scale at the largest WWTP of Milan (Milano-Nosedo; Northern Italy) by the construction of a pilot-plant that was implemented with other facilities during the entire study. In detail, we investigated the possible use of zebra mussel to decrease the concentrations of 13 pharmaceuticals (atenolol, carbamazepine, ciprofloxacin, clarithromycin, dehydroerythromycin, diclofenac, furosemide, ibuprofen, hydrochlorothiazide, ketoprofen, naproxen, ofloxacin, paracetamol) and 4 drugs of abuse (cocaine, benzoylecgonine, methamphetamines and methadone) still present in the outflow of the largest WWTP of Milan. Moreover, we showed also the results obtained in the needful preliminary tests carried out to verify the capacity of this mussel to live in different wastewater mixtures, the better conditions to maintain higher the filtration rate and data from tests conducted to evaluate the percentage of decrease of the chemical oxygen demand (COD), chosen as starting marker of the filtration capability of the zebra mussel specimens.

2. Materials and methods

2.1. The pilot-plant

Fig. 1 shows the pilot-plant and other equipment used for this project. In detail, the pilot-plant was a stainless steel tank with a volume of 1000 L (l = 154 cm, h = 102 cm, w = 80.5 cm) with 20 removable Plexiglas® panels (size of 70 × 40 cm; Fig. 2) to which the zebra mussel specimens attached themselves. The particular arrangement of panels forced the wastewater into a zigzag pathway to increase its residence time (Fig. 2). More than 2000 zebra mussel specimens were attached to each panel, for a total of approximately 40,000 individuals in the pilot-plant. The tank had a hopper bottom with five outflow valves to allow the collection and elimination of the sediments, faeces and pseudo-faeces (Fig. 1). A submerged pump collected the treated effluent directly from the canal between the sedimentation tanks and the sand filters of the WWTP. This position also guaranteed the lack of the possible accidental release of *D. polymorpha* specimens into the WWTP outflow because the sand filters and the following disinfection process (by peracetic acid) should stop and kill any leaked organism. Moreover, we added several plastic grids with a narrow mesh to all valves and outputs from the pilot-plant to prevent any mussel outflow. In the canal from which the effluent was pumped to the pilot-plant, the temperature ranged between 14 and 24 °C, the optimal survival temperature for zebra mussels (McMahon, 1996). We also added a 200 L re-circulation tank (Fig. 1) to feed the plant by re-circulation to investigate various hydraulic retention times (30, 60, 90, 120, 15, 180, 210, 240 min). The re-circulation pump allowed a maximum waste flow of 3500 L/h. Finally, two "attachment tanks", in which the zebra mussels can attach themselves to panels by the byssus, completed the entire facility, in addition to a "nursery" (Fig. 1) in which the panels with the attached mussels can be stored before their placement into the pilot-plant. The pilot-plant and other facilities were completely cleaned cyclically by tap water and before each test to guarantee the best conditions and the elimination of the possible "memory effect" from the previous assay.

The mussels were collected by scuba divers at different times from Lake Maggiore and Lake Lugano, located at the Italy-Switzerland border. We gently detached the mussels from the submerged substrates (rocks, branches, anthropic wastes) and rapidly transferred them to the WWTP of Milano-Nosedo by refrigerated bags to decrease any stress factors.

First, we conducted the following preliminary tests: (1) evaluation of the time and method required for the mussels' adhesion to the panels; (2) adaptation of the individuals to the fed effluent; (3) control of the possible concentration decrease of pharmaceuticals