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SHORT COMMUNICATION

Parabens Removal from Domestic Sewage by Free-Floating Aquatic Macrophytes

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Abstract
Parabens are substances that prevent or delay the deterioration of cosmetics, drugs and food caused by the action of microorganisms. Recent studies report their potential to affect human health. The present study reported the efficiency of two aquatic macrophytes (*Landoltia punctata* and *Lemna minor*) in parabens (methyl and propyl parabens) removal from domestic sewage. Two 3000-L tanks were used in the experiment: tank A, containing *L. punctata*; and tank B, containing *L. minor*. Samples were collected every three days for 21 days at daylight and evening times. The best methylparaben (MeP) removal results were recorded for tank A, 90.8 and 90.6% removal at daylight and at evening time, respectively. For propylparaben (PrP), the best removal were recorded for tank B, 88.0 and 90.5% removal at daylight and at evening, respectively. These results highlight the efficiency of polishing ponds containing aquatic macrophytes for parabens removal purposes.

Keywords Methylparaben · Propylparaben · Lemnaceae · Duckweeds polishing ponds · Phytoremediation

Abbreviations

MeP	Methylparaben
PrP	Propylparabens
WWTP	Wastewater treatment plants

Introduction

Parabens are chemical compounds presenting conservative properties that prevent or delay the deterioration of cosmetic, drugs and food caused by action of microorganisms. Different parabens are used as conservative in cosmetic, drug and food formulations, namely: ethylparaben (EtP), methylparaben (MeP), propylparaben (PrP), isopropylparaben (IsP), butylparaben (BuP), isobutylparaben (IbP) and benzylparaben (BeP) [1]. The mixture may often contain two or more parabens, because they have synergistic effect. MeP and PrP, which are compounds classified as emerging pollutants, are the most used parabens, since they are cheaper and present metabolic stability and resistance to biodegradation [2].

Some studies showed that emerging pollutants, even at very low concentrations, may cause adverse effects on aquatic ecosystems and humans. The adverse effects of emerging micropollutants and of their metabolites on aquatic environments include lethal and sublethal toxicity to aquatic organisms such as fish and plants, endocrine disruption, genotoxicity, and the development of resistance to pathogenic bacteria [3, 4]. It is worth highlighting the stability of these compounds in water and their potential to bioaccumulation in trophic web [4]. Frequent exposure to parabens may cause decreased hatching in birds, fish and turtles, feminization of male fish; problems in the reproductive system of fish, reptiles, birds and mammals; and changes in the immune system of marine mammals due to their bioaccumulation potential. The continuous exposure of humans to parabens can increase breast cancer incidence, interfere in male reproductive functions, and influence malignant melanoma development, which appears to be influenced by estrogenic stimulation [3].

Domestic and industrial sewage contain a wide variety of chemical compounds classified as emerging pollutants, such as pharmaceuticals, personal care products, pesticides and veterinary products. The emerging pollutants found in raw sewage are treated in wastewater treatment plants (WWTP) through conventional water and sewage treatment processes.

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However, processes associated with conventional treatment systems are unable to completely eliminate persistent compounds and require the adoption of additional treatment types [5].

Parabens are released into aquatic ecosystems mainly by sewage treatment plant discharges. MeP and PrP concentrations in Chinese rivers reach 1062 and 3142 μg L^{-1}, respectively [6]. In Japan, Yamamoto et al. reported PrP concentration of approximately 207 μg L^{-1} [7], and in European Rivers were recorded 400 μg L^{-1} of MeP and 69 μg L^{-1} of PrP [8]. It is relevant pointing out the higher expectation in Brazil about finding conservative drugs and chemical compounds in natural aquatic ecosystems due to lack of sanitary structure to treat sewage. In rivers located in Iguassu Watersheds, Curitiba metropolitan area (Brazil), Santos et al. found MeP concentrations up to 2875 μg L^{-1} [9].

Technologies focused on reducing organic pollutant concentrations have been studied (ozonation, ultrafiltration and advanced oxidation), however, these technologies remain expensive. Phytoremediation has been assessed by several authors, because it is efficient, cheap to install and ease to management [10]. Aquatic macrophytes can be applied to the polishing pond surface in order to help nutrient removal [11]. Studies performed with *Lemna* sp. showed that aquatic macrophytes are capable of removing organic pollutants through adsorption and phyto-metabolic processes [11]. Therefore, *Lemna* use as end-point technology for effluent treatment can be an important mechanism to reduce parabens rates in domestic and industrial sewage. Accordingly, the efficiency of the aquatic macrophytes *Landoltia punctata* and *L. minor* in removing MeP and PrP from domestic sewage in the Brazilian sub-tropical region was assessed.

Materials and Methods

The experiment was carried out for 21 days in Ilha Solteira County (20°25′24.4″S 51°21′13.1″W), Northwestern São Paulo State, Brazil, in order to assess the efficiency of free-floating aquatic macrophytes in removing parabens from domestic sewage. The estimated population in the area reaches 25,064 inhabitants and the climate of the region is tropical with dry and mild winter.

Equipment and Experimental Procedure

The domestic sewage used in the experiment was weekly collected from the emissary of the facultative stabilization pond of Ilha Solteira WWTP. The sewage was transported to the experimental station and deposited in two storage tanks with a capacity of 3000 L each (Fig. 1).

Each storage tank was connected to a pump with flow rate of 0.007 L s^{-1}, that continuously feeding the treatment system (tank A and tank B). There are two similar treatment systems,

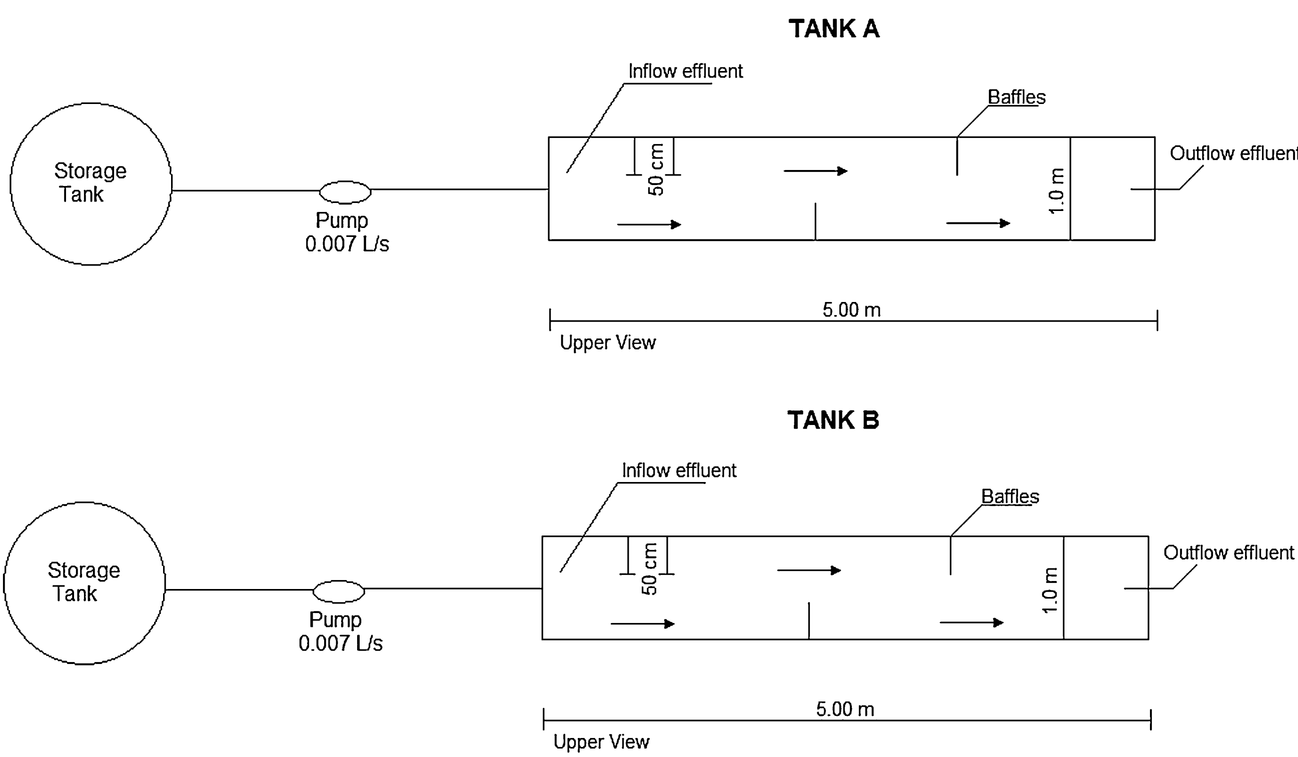

Fig. 1 Schematic diagram of the treatment system

however tank A was colonized with *L. punctata* and tank B was colonized *L. minor*. The hydraulic retention time (HRT) of tanks (A) and (B) was 21 days.

Sampling Collection

Effluent samples (5.0 mL) containing the micropollutants were collected from tanks (A) and (B) every 2 days at 08:00 am (less photodegradation interference) and at 05:00 pm (higher sunlight incidence). The samples were transferred to 5.0-mL centrifugal tubes and, then, subjected to the liquid–liquid dispersive microextraction method (DLLME). The herein used dispersing and extracting agents were 600 µL acetone (PA Synth grade), followed by 400 µL dichloromethane (HPLC JT Baker). The centrifugal tubes were stirred for 3.0 min and centrifuged at 3500 rpm for 3.0 min. The organic phase of samples containing PBs was aspirated with the aid of a 100.0-µL microsyringe; and the aspirate was then transferred to glass tubes. Eluate resuspension was performed in 200 µl acetonitrile, and injected (25.0 µL) into a high-performance liquid chromatograph (HPLC).

Analytical Methods

First, the initial parabens contents in tanks A and B were set through HPLC - Shimadzu, Chromatographic Column: LC Column Zorbax ODS C18 (150 mm X 4.6 mm ID, 5.0 µm particles). Analytes were separated through gradient elution in 90% acetonitrile and H_2O (pH 2.5–3.0) acidified with hydrochloric acid (0.01% v/v), according to the method by Baranowska and Wojciechowska [12]; flow rate was 1 mL min^{-1}. Concentrations between 1.10 and 102.0 µg L^{-1} were quantified (detection limit: 0.025 µg L^{-1} for MeP, and 0.046 µg L^{-1} for PrP; quantification limit: 0.074 µg L^{-1} for MeP, and 0.138 µg L^{-1} for PrP) in diode array detector (Model SPD-M20A, Shimadzu, Kyoto, Japan) at 254 nm. Internal parabens were used to formulate the calibration curves.

Chemical oxygen demand (COD) was determined in Digital Reactor Block 200 and HACH DR 5000 spectrophotometer, according to standard HACH TNT test tube methods.

Parabens removal efficiency was determined through the following equation:

$$R\% = (L - L_I)/100$$

wherein $R\%$ is concentration reduction rate, L_I is concentration in tank inflow (mg L^{-1} or µg L^{-1}), and L is concentration in tank outflow (mg L^{-1} or µg L^{-1}).

Results and Discussion

COD Removal

Table 1 presents the COD concentrations of the raw sewage, the WWTP effluent that was sent to the treatment in tanks A and B, and the outflow effluent of tanks A and B, as well as the removal efficiencies.

On average, COD concentration in tanks A and B, after the raw effluent at the municipal station was treated, reached 135.6 and 111.0 mg L^{-1}, respectively. The COD reduction at the end of the experiment in tanks colonized with *L. punctata* and *L. minor* was 68.2 and 47.3%, respectively. The different treatment efficiencies found for each tank can be explained due to the solar incidence received by each tank. Throughout the day, tank A was completely exposed to sunlight. Tank B, however, received shade in the afternoon.

Although COD reduction efficiency remained above 50%, on average, at the 9th experiment day, *L. punctata* and *L. minor* showed low removal efficiency. This result likely derives from lower temperatures during the experimental period (19 °C, on average).

Matamoros et al. [14] assessed the seasonal performance of four different full-scale wastewater technologies in the elimination of emerging contaminants, including methylparaben (MeP). The highest COD removal efficiency recorded by these authors was 89% during the warm season (26 °C, on average), when the waste stabilization pond technology was employed. Krishna et al. [15] observed COD removal efficiency from 50 to 95% in domestic wastewater treated with duckweed (*Lemna gibba*) at temperature ranging from 30 to 36 °C. Similar result was found by Ran et al. [16], who recorded COD reduction in domestic effluent at mean concentration 298.0 mg L^{-1}. These authors [15, 16] observed that *Lemna gibba* led to 67.5% reduction in an outdoor system exposed to mean high-summer temperatures (mean max. 35–40 °C) and to mild winter temperature (min. approximately 5 °C to max. 20 °C).

Table 1 Sewage COD concentrations and removal efficiency

Raw sewage (mg L^{-1})	607 [13]	
WWTP outflow (mg L^{-1})	Tank A	135.6 ± 44.2
	Tank B	111.0 ± 36.7
Tanks A and B outflow (mg L^{-1})	Tank A	43.0 ± 41.0
	Tank B	59.0 ± 25.9
Removal efficiency of tanks A and B (%)	Tank A	68.2
	Tank B	47.3
Total removal efficiency (WWTP + polishing) (%)	Tank A	92.9
	Tank B	90.2

Although low temperatures may negatively influence the removal efficiency of organic compounds by plants, different macrophyte species serially arranged can increase treatment system efficiency, as reported by Sims et al. [17]. They reported that the removal rates of the first and second ponds were 83 and 85%, respectively, at effluent concentration 111.0 mg L^{-1}, in the two polishing ponds containing serially disposed lemnas. The removal efficiency of organic compounds in wetlands colonized with aquatic macrophytes serially arranged is due to the nutritional requirement from different plants composing the wetland, as reported by Henares and Camargo [18] in the aquaculture effluent treatment.

MeP E PrP Removal

Table 2 presents the MeP and PrP concentrations before and after the free-floating aquatic macrophytes treatment systems, as well as the removal efficiencies achieved.

Methylparaben (MeP) inflow concentration at the beginning of the experiment in tanks colonized by *L. punctata* and *L. minor* was 157.4 µg L^{-1}, on average, and propylparaben (PrP) concentration, at the same condition, was 148.7 µg L^{-1}. The MeP output levels in *L. punctata* and *L. minor* at end of the experiment were 14.6 and 17.8 µg L^{-1}, respectively, on average. The PrP output concentrations were 57.3 and 15.9 µg L^{-1} in *L. punctata* and *L. minor*, respectively (Table 1).

Results evidenced that polishing ponds efficiency in removing parabens is different between day and evening time. The MeP removal efficiency in the tank colonized by *L. punctata* and *L. minor* during day and evening times was similar (90.7% for *L. punctata*, and 88.6% for *L. minor*, on average). On the other hand, PrP removal in the tank containing *L. punctata* was 10% higher, on average, in the evening (55.1 µg L^{-1}) than at daylight (59.5 µg L^{-1}). The PrP removal in the tank colonized by *L. minor* was also similar between the day and evening times (89.3%, on average).

Figure 2 shows the removal efficiencies achieved daily for each tank during the 21-day duration of the experiment.

Observing the Fig. 2a, The MeP removal in the tank colonized by *L. punctata* was similar between days during the experiment and it remained above 80%, regardless of the sampled period. The PrP removal efficiency, although similar between the day and evening times, was 1.5 times lower than the MeP removal efficiency, up to the 12th experiment day. The PrP removal efficiency after this period was similar to the MeP removal.

The physicochemical characteristics of the compound determine the WWTP removal mechanism in some emerging organic pollutants [19].

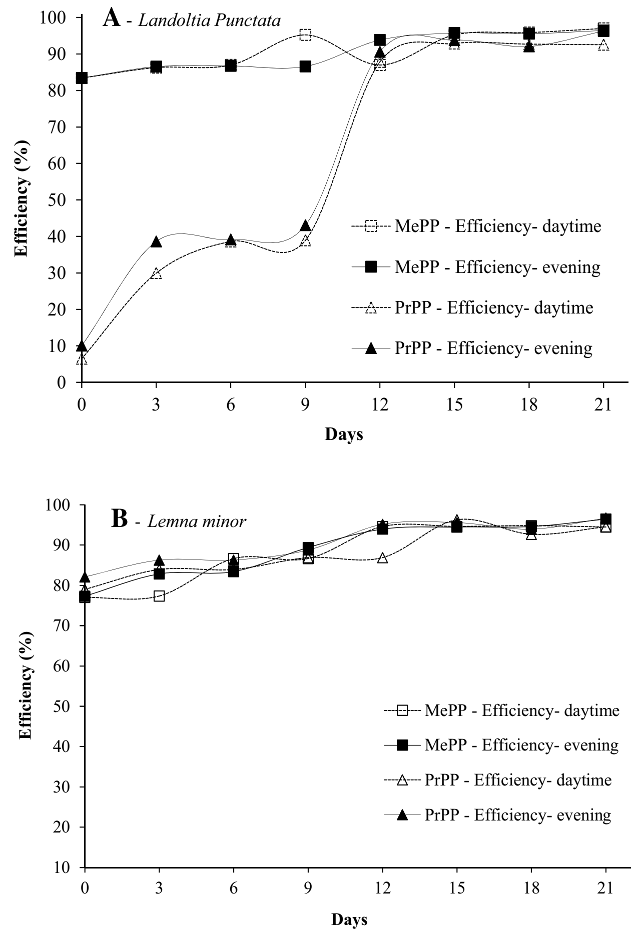

Fig. 2 Comparison between removal efficiencies in the assessed tanks. **a** Tank colonized by *Landoltia punctata;* and **b** Tank colonized by *Lemna minor*

Table 2 Parabens removal mean (n = 3) ± standard deviation

Parabens	Inflow	Aquatic macrophytes			
		L. punctata		*L. minor*	
		Daytime	Evening	Daytime	Evening
MeP (µg L^{-1})	157.4 ± 3.6	14.4 ± 8.5	14.8 ± 8.3	18.5 ± 12.7	17.2 ± 11.1
	%R	90.8	90.6	88.2	89.0
PrP (µg L^{-1})	148.7 ± 1.4	59.5 ± 3.6	55.1 ± 1.6	17.8 ± 8.8	14.0 ± 8.1
	%R	59.9	62.7	88.0	90.5

The MeP and PrP removal behavior observed in tanks colonized by *L. puncatata* and *L. minor* was similar throughout the present experiment (Fig. 2b).

The presence of plants and bacteria in the treatment effluent system may support emerging pollutants reduction through biological and physical processes such as biodegradation, adsorption and sedimentation [20]. Onuche et al. [21] isolated different bacteria species collected from aeration tanks in the sewage treatment unit of Zaria University and the isolated microorganisms were able to remove 94.4% of MePP for 13 days, by taking into consideration the initial concentration 100 µg L^{-1}. This data reinforces the idea that besides phytoremediation, the biodegradation of this paraben could have occurred in the lemna-based polishing system.

Degradation processes are often associated with the length of the parabens carbon chain [9]. According to these authors, short chain compounds, such as methylparaben and ethylparaben, can reach up to 99% degradation within 21 days. In addition to chain compound, parabens removal rates in sewage treatment plants are often high, mainly in aerobic systems [9].

In our study, although the dissolved oxygen concentrations have been low (ranged from 0 to 0.73 mg L^{-1}), the MeP removal was 90.7% in *L. punctata* and 88.6% in the *L. minor* tank, on average. Studies conducted by Gasperi et al. [22] in France, and by Albero et al. [1] in Spain, described that, besides the degradation process, there may be parabens sorption in sludge. Bittencourt et al. [19] reported that the biodegradation and solid phase sorption processes are responsible for reducing emerging organic pollutants in the aqueous phase of sewage treatments.

Kumar et al. [23] recorded 90% emergent pollutants removal efficiency in a wetland polishing system, in which surface flow presented different plant species. They also suggested that plants presenting filamentous aquatic roots provide good surface area for microbial growth, perform nutrient uptake, and may work as habitat for microorganisms that act in the mineralization process of organic compounds; inorganic compounds are uptaken by plants.

Whereas some studies suggest that biodegradation is the parabens removal mechanism [8], other research address that sorption may also help it [24]. Chen et al. [25] reported parabens sorption on magnetic nanoparticles belonging to the phenyl group that present maximum adsorption capacity 3.54 mg g^{-1}. However, there is no information about parabens sorption on the biomass found in biofilters, although parabens sorption on sludge, in WWTPs [1, 8, 24].

It is necessary understanding parabens' elimination process, as well as whether they are degraded or physically sorpted on the biomass or on the medium used in the treatment systems, due to their potential hazards. Therefore, the role played by sorption and biodegradation in parabens elimination from biological treatment systems needs to be further studied.

The diversity of physical, chemical and biological processes such as sorption, biodegradation and photodegradation are associated with pharmaceuticals' removal from biologically-based wastewater treatments [26]. These processes depend on the physicochemical properties of the compound to be eliminated and on internal plant-metabolism. Therefore, organic pollutants uptake by plants plays an important role in emergent pollutants removal. Zhang et al. [27] reported that carbamazepine was rapidly incorporated by *Scirpus. validus*; carbamazepine removal (88–97%) was also recorded by Dordio et al. [20], who used *Typha* sp.

Although order *Lemnaceae* plays an important role in the phytoremediation of emergent pollutants found in surface waters, aquatic macrophytes species such as *Typha* sp., *Eichhornia crassipes, Pistia stratiotes* and *Salvinia molesta* can be more efficient than the species belonging to order *Lemnancea* in reducing organic emergent pollutants, since they record higher shoot and root biomass rates.

Conclusions

The free-floating aquatic macrophytes *L. punctata* and *L. minor* can play an important role in parabens removal efficiency in polishing ponds. *L. punctata* rated the highest methylparaben removal rate (90.7%), whereas *L. minor* appeared to be more efficient in removing propylparaben (89.2%). Moreover, the lack of research reporting aquatic macrophytes' efficiency in removing parabens does not allow comparing the efficiency of order *Lemenacea* to that of other orders.

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