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Review

Comparison of biosorption and phytoremediation of cadmium and methyl parathion, a case-study with live *Lemna gibba* and *Lemna gibba* powder

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ABSTRACT

Heavy metals and pesticides can be adsorbed by several biomasses such as living or non-living aquatic plants. In this study adsorption properties of live *Lemna gibba* and *Lemna gibba* powder were investigated with regard to cadmium and methyl parathion (MP). Toxicity data (IC50) on live *L. gibba* indicated that the period of four days was adequate for phytoremediation. Initial adsorption studies showed that both adsorbents were capable of removing cadmium and methyl parathion. Cadmium and methyl parathion adsorption onto *L. gibba* powder was fast and equilibrium was attained within 120 min. The adsorption data could be well interpreted by the Freundlich model. The K_F were: 7.8963 (Cd^{2+}/ live *Lemna*); 0.7300 (MP/live *Lemna*); 11.5813 (Cd^{2+}/*Lemna* powder); 1.1852 (MP/*Lemna* powder) indicating that Cd^{2+} was more efficiently removed by both biosorbents than MP. Adsorption kinetics for cadmium and methyl parathion in both systems and rate constants were determined for each contaminant. It was found that the overall adsorption process was best described by pseudo-second-order kinetics. Boyd model and external mass-transfer expression were tested. It was concluded that cadmium and methyl parathion sorption onto *Lemna* powder is governed by film diffusion.

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1. Introduction

Elimination of toxic pollutants from contaminated water using biomass can take place by phytoremediation and bioaccumulation or biosorption (Pilon-Smits, 2005; Vijayaraghavan and Yun, 2008; Chojnacka, 2010). In this respect biosorption is considered a method or process effective to remove toxic pollutants from water through ion exchange, precipitation, solvent extraction, reverse osmosis, evaporation, membrane technology, electrochemical treatment, etc. (Arslan and Pehlivan, 2007; Hashim et al., 2011).

The definition of biosorption is somewhat controversial in the literature; for some authors it is a passive process limited to dead biomass that can be opposed to bioaccumulation (Vijayaraghavan and Yun, 2008; Chojnacka, 2010), in contrast for other authors it can take place both with living or dead biomass and it includes adsorption to the biomass and absorption by the biomass (Gadd, 2009). In any case, removal of metals involves extracellular accumulation/precipitation, cell surface sorption/precipitation, and intracellular accumulation and can occur by complexation, co-ordination, chelation of metals, ion exchange, adsorption and microprecipitation (Gadd, 2009; Chojnacka, 2010). Biosorption appears to offer satisfactory prospects for wastewater treatment especially for effluents with low concentration of contaminants (Li et al., 2011; Guendouz et al., 2013).

Activated carbon and polymer adsorbents have been the most commonly used sorbents but require energy for their synthesis and are therefore seen as expensive processes. Therefore, phytotechnologies have been proposed for alternative or tertiary treatment for industrial effluents and agricultural effluents (Lesage et al., 2007; Dosnon-Olette et al., 2009). Biosorption of heavy metals, organic pollutants, and pesticides from wastewater has been investigated using several plants species including macrophytes (Schröder and Collins, 2002; Keskinkan et al., 2004; Pilon-Smits, 2005; Li et al., 2009, 2011; Mukherji et al., 2011; Megateli et al., 2013).

Among the aquatic floating macrophytes, duckweed (*Lemna* sp.) presents a high growth rate and was found particularly efficient to remove metals and pesticides from water as no long toxicity was observed (Miretzky et al., 2006; Dirilgen, 2011). Nevertheless, the use of powders obtained from plants, such as *Lemna minor* (Li et al., 2011) for metal or pesticide removal could be more advantageous than the use of live plants. Indeed, since there is no requirement of growth media or nutrients and no toxicity, it allows higher contaminant concentrations. Several additional advantages may be cited as for example (1) contaminant desorption could regenerate the adsorbent, (2) minimization of the volume of chemicals and/or biological sludge to be disposed of, (3) low cost, (4) long storage capacity, and (5) possibility of transport.

The present study compares biosorption of an organic and an inorganic pollutant and provides evidence for biosorption (or adsorption) of cadmium and the pesticide methyl parathion by live *Lemna gibba* and *Lemna gibba* powder. Cadmium and methyl parathion were chosen for this study because they were found to occur simultaneously in a polluted site located in the South East of Algiers.

2. Materials and methods

2.1. Plant material

2.1.1. Live Lemna gibba

L. gibba stock cultures were established from plants collected from a pond of El Hamma botanical park (Algiers). The plants were washed with sterile distilled water, ethanol and sodium hypochlorite diluted solutions (0.5 percent), followed by sterile distilled water and maintained in culture medium (Semsari et al., 2009).

The composition of the culture medium was adapted from that proposed by Hoagland and Arnon (1938) and presented earlier (Megateli et al., 2009). Toxicity and live *Lemna* sorption tests were conducted with colonies from the culture stock. Plants were rinsed with sterile distilled water and placed in sterile cultured medium. The pH was adjusted to 5.6 with 0.1 M NaOH when necessary. Whether for stock or experiments, cultures were placed in a thermostated room (24 ± 2 °C) at photoperiod of 16 h of light and 8 h of darkness. Cultures were illuminated using fluorescent tubes (36 W/54) providing an intensity of 400 $\mu E\ m^{-2}\ s^{-1}$ at plant level.

2.1.2. Lemna gibba powder

Plant samples were washed thoroughly several times using sterile distilled water and dried at 65 °C for three days. The dried samples were ground using blender and sieved to obtain uniform particle size of 0.5–0.8 mm. The biomass powder was then prepared as described by Gardea-Torresdey et al. (1998). Briefly, 500 mg sample of biomass was washed twice with 0.01 M HCl to remove any soluble biomolecules that might cause interference, and then cleaned with sterile distilled water. The sample was filtered and dried at 65 °C for 48 h.

2.2. Chemicals

All chemicals used were of analytical-reagent grade (purity ≥ 99 percent). All the glassware used for dilution, storage and experiments was cleaned with liquid detergent, strongly rinsed with water, soaked overnight in 30 percent of NHO_3, rinsed and autoclaved (20 min) before use.

2.3. Cadmium and methyl parathion toxicity

Since phytoremediation requires functional plants, cadmium and methyl parathion toxicity was assessed using growth rate inhibition as a marker of toxicity.

The plants (twenty fronds) were incubated in 250 mL Erlenmeyer's flask containing 100 mL of culture medium contaminated by various cadmium concentrations (10^{-3}, 10^{-2}, 10^{-1} and 1 mg L^{-1}) or methyl parathion (8, 16, 32 and 48 mg L^{-1}), for 1–6 days period.

Growth inhibition rates I (percent) was calculated as presented in Megateli et al. (2013) and IC50 were determined.

2.4. Cadmium and methyl parathion removal by live plant

Removal was determined by quantifying the residual concentrations of cadmium or methyl parathion in the medium after incubation. After incubation plants were harvested, oven-dried at 80 °C for 24 h and weighed. The amount of cadmium or methyl parathion removed q_t (expressed as mg g^{-1}) at time t, was calculated using the following Eq. (1):

$$q_t = \frac{(c_0 - c_t)V}{W} \quad (1)$$

where C_0 and C_t (mg L^{-1}) are the initial aqueous phase contaminant concentration and the value at time t, respectively, V is the volume of solution, and W is the dry weight of biomass (g).

All samples were triplicated and three independent experiments were run. The results presented are the arithmetic means with their corresponding standard errors.

2.5. Sorption experiments with Lemna powder

Batch biosorption experiments were carried out at room temperature (24 ± 2 °C), which represented the same conditions as for the live plant experiments. In 250-mL conical flasks 0.5 g of biomass powder was suspended in 100 mL of contaminated solutions and placed under magnetic agitation at 250 rpm. All sorption experiments were carried out at pH 4.2 adjusted with 0.01 M HCl solution. The contact times were 30, 60, 90, 120, 180, 240, and 300 min and initial concentrations of cadmium were 10^{-3}, 10^{-2}, 10^{-1}, and 1 mg L^{-1} while those of methyl parathion were 8, 16, 32, and

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