



**HAL**  
open science

## Efficient removal of persistent and emerging organic pollutants by biosorption using abundant biomass wastes

Pierre-Alexandre Deyris, Franck Pelissier, Claire Grison, Peter Hesemann,  
Eddy Petit, Claude Grison

### ► To cite this version:

Pierre-Alexandre Deyris, Franck Pelissier, Claire Grison, Peter Hesemann, Eddy Petit, et al.. Efficient removal of persistent and emerging organic pollutants by biosorption using abundant biomass wastes. *Chemosphere*, 2023, Special Issue: Soil and water pollution, 313, pp.137307. 10.1016/j.chemosphere.2022.137307 . hal-03866999

**HAL Id: hal-03866999**

**<https://hal.science/hal-03866999v1>**

Submitted on 9 Jun 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Efficient removal of persistent and emerging organic pollutants by biosorption using abundant biomass wastes

Pierre-Alexandre Deyris<sup>a</sup>, Franck Pelissier<sup>a</sup>, Claire M. Grison<sup>a</sup>, Peter Hesemann<sup>c</sup>, Eddy Petit<sup>b</sup>, Claude Grison<sup>a,\*</sup>

<sup>a</sup> Laboratoire de Chimie Bio-inspirée et Innovations Ecologiques (ChimEco), UMR 5021, Centre National de la Recherche Scientifique – Université de Montpellier, 34790, Grabels, France

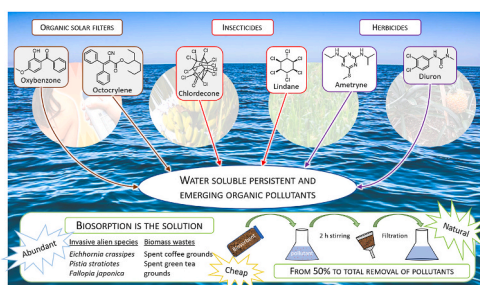
<sup>b</sup> Institut Européen des Membranes (IEM), UMR 5635, ENSCM, Centre National de la Recherche Scientifique, Université de Montpellier, 34095, Montpellier, France

<sup>c</sup> Institut Charles Gerhardt de Montpellier, Université de Montpellier, CNRS, ENSCM, Montpellier, France

## HIGHLIGHTS

- Persistent organic pollutants represent a serious threat to ecosystems.
- Roots of invasive alien species, coffee and tea grounds are efficient biosorbents.
- Excellent biosorption efficiency was obtained for removing UV-filters and pesticides.
- Discrimination between biosorbents could be observed for some pollutants.
- Solubility is the key point for selecting the best biosorbent/pollutant couple.

## GRAPHICAL ABSTRACT



### Keywords:

Persistent organic pollutants  
Emerging pollutants  
Biosorption  
Invasive alien species  
Coffee grounds  
Green tea grounds

Persistent and emerging organic pollutants represent a serious and global threat to human health and ecosystems. We describe here a simple, efficient and affordable technology for removing such organic pollutants from aquatic systems. Biosorption process was chosen, meeting these three criteria, and so that biosorbents should be biomass wastes combining the following characteristics: natural, cheap and abundant. Powdered dead roots from invasive alien species (*Eichhornia crassipes*, *Pistia stratiotes* and *Fallopiia japonica*), and wastes rich in tannins such as coffee grounds and green tea grounds were tested as biosorbents for removing extensively used organic pollutants: organic UV-filters, insecticides and herbicides. The elemental composition and morphology of the biosorbents were fully determined. The biosorption kinetics for each pair of biosorbent/pollutant was described by a pseudo-second order model. Excellent biosorption efficiency was obtained for 10  $\mu\text{M}$  solution of oxybenzone ( $89 \pm 1\%$ ), octocrylene ( $90 \pm 2\%$ ), lindane ( $88 \pm 0\%$ ) and diuron ( $90 \pm 1\%$ ) in only 2 h. And total removal of 10  $\mu\text{M}$  of chlordecone ( $100 \pm 0\%$ ) could be achieved, which could be of high concern for the population living in chlordecone-contaminated areas. As such pollutants can be found in aquatic ecosystems, an interference study

\* Corresponding author.

E-mail addresses: pierre-alexandre.deyris@umontpellier.fr (P.-A. Deyris), franck.pelissier@cns.fr (F. Pelissier), claire.grison.2@cns.fr (C.M. Grison), peter.hesemann@umontpellier.fr (P. Hesemann), eddy.petit@umontpellier.fr (E. Petit), claude.grison@cns.fr (C. Grison).

with salts showed that biosorption efficiency remained as efficient in reconstituted seawater. A principal component analysis was performed as an attempt to rationalise the biosorption results. The solubility of the organic pollutants in water and the concentration of tanins in the biosorbents were key parameters.

## 1. Introduction

Persistent and emerging organic pollutants and their degradation products are released continuously into the environment and are consistently being found not only in wastewaters but also in wetlands, water resources and even drinking water. This represents a serious and global threat to human health and ecosystems.

The list of emerging pollutants is particularly long. It includes pharmaceuticals (antibiotics, hormones, etc.) for human or veterinary uses, products for daily use (personal care products, cosmetics, UV-filters, detergents, antioxidants, etc.), products of industrial and household origins (surfactants, additives, solvents, flame retardants, plastic nanoparticles, etc.), pesticides (herbicides, fungicides, insecticides and other biocides).

Numerous studies have been conducted examining the occurrence and effects of pharmaceutical use in the aquatic environment. However, relatively little research has been conducted examining the use of personal care products although they are found more often and in higher concentrations than pharmaceuticals (Brausch and Rand, 2011). Organic UV-filters in cosmetic sun and personal care products have been massively used lately, due to the recent concerns with sunburns, premature skin ageing and the risk of developing skin cancer, related to sun exposure. However, they are inevitably released to the marine environment. For example, it has been estimated that 4000–6000 tons of organic UV-filters could be released in reef areas (Danovaro et al., 2008). The consequences of their release into aquatic systems are worrying, as they have shown human and ecotoxicity (Carve et al., 2021) and are now considered as a new pollutant type (Emmanouil et al., 2019). Indeed they have shown estrogenic effects, hence are classified as endocrine disruptors (Carstensen et al., 2022).

For example, oxybenzone, a common UV-filter, inhibits the reproduction of coral and fish via embryo toxicity and/or causing male fish to be feminized, coral bleaching, and/or death (DiNardo and Downs, 2018) (He et al., 2019). Also octocrylene-containing sunscreens cause coral bleaching, even at very low concentrations (10 µL/L), by promoting viral infection in their symbiotic algae (Danovaro et al., 2008).

Chemical pesticides, another type of persistent organic pollutants, are currently the predominant source of fresh water contamination (Boxall, n.d.). According to Food and Agriculture Organization of the United Nations, the full usage of pesticide worldwide in 2019 has reached 4.2 million tonnes (“FAO (2019) FAOSTAT. In,” 2020) and it is anticipated to increase with global warming and demographic pressure.

Chlordecone and lindane are synthetic and non-biodegradable chlorinated organic compounds, hence considered as highly persistent in the environment. However, they have been mainly used as agricultural insecticides. Chlordecone (or kepone) was used to control a wide range of pests on tobacco, ornamental shrubs, bananas and citrus trees. However, it has contaminated the population for more than 30 years. Exposure to this substance causes neurological symptoms, such as tremors and slurred speech. Moreover, a relationship between exposure to chlordecone and risk of prostate cancer has been established (Multigner et al., 2010). The International Agency for Research on Cancer has classified Chlordecone as group 2B, a possible human carcinogen (Report of the Persistent Organic Pollutants Review Committee on the work of its third meeting Addendum Revised risk profile on chlordecone, 2007).

Lindane was firstly used to kill lice and a variety of pests that attack agricultural products, livestock and trees. However, Lindane has been progressively eliminated from many applications since the mid-1970s in Europe and USA, due to its general toxicity to human and

the environment. Lindane can be absorbed through respiratory, digestive or cutaneous routes and damages human liver, kidney, neural and immune systems, and induces birth defects and cancer. Moreover, Lindane is long lived in the environment -it bioaccumulates in food chains (Nolan et al., 2012; Pagès et al., 2002) and its presence can still be detected in the blood of European citizens, although it has been banned for about 50 years (“Debates of the European Parliament, session of the January 14, 2008,” 2008).

Diuron and ametryne are active herbicides commonly used in agricultural activities. Diuron is however classified as highly toxic and may have toxic effects on the endocrine system and the reproductive system (Franco et al., 2021). Both herbicides were found in algae, fishes and macroinvertebrates located at various levels of the reef trophic web. Their widespread contamination may affect the reef ecosystem, as some of their symbiotic algae are particularly sensitive to photosystem II herbicides, particularly diuron, ametryne and related derivatives (Salvat et al., 2016).

Extensive research for wastewater treatment highlights the growing interest of the scientific community and the needs towards this problematic. Moreover, the regulation of chemical pesticides in drinking water has changed in Europe recently and reached a maximum limit of 0.10 µg/L for a single pesticide and 0.50 µg/L in total for cumulated pesticides (“DIRECTIVE (EU) 2020/2184 OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL on the quality of water intended for human consumption,” 2020).

Biotechnologies for the degradation and elimination of emerging contaminants have been described based on using membrane filtration strategies (bio-membrane reactors, use of algae, fungi and bacteria, enzymatic degradation), oxidation and adsorption oriented processes (activated carbon, clays, cyclodextrin polymers, metal-organic frameworks, molecularly imprinted polymers, chitosan, nanocellulose) (Morin-Crini et al., 2021). In recent years, new alternatives such as biosorption onto non-conventional materials (Aksu, 2005; Fenyvesi et al., 2020; Li et al., 2019; Rojas and Horcajada, 2020; Wang and Wang, 2016) have been reported. However, little research has led to industrial development. The implementation of a technical solution which is economically viable and environmentally friendly is rare (Morin-Crini et al., 2021).

We report the development of a simple, efficient and affordable biosorption technology of persistent and emerging organic pollutants based on using different types of waste biomass. The nature of the biosorbents is the key parameter for the biosorption efficiency and profitability. Our biosorbents were chosen as to be natural, low cost and abundant all around the world. They can be classified in two groups according to their origin and chemical composition:

- i) powdered dead roots of invasive alien species, which are found profusely in aquatic systems (*Eichhornia crassipes*, *Pistia stratiotes*) and wetlands (*Fallopia japonica*). Such biomaterials are rich in cellulose, hemicellulose and lignin but with a variable ratio of these three biopolymers, that might play complementary roles in the adsorption of organic molecules.

Moreover, in our previous study on rhizofiltration, an endocrine disruptor was found by chance in the roots of *Eichhornia crassipes*, coming from the plastic sheeting used as a pond liner (De Laet et al., 2019).

- ii) spent coffee grounds and green tea grounds, which were primarily brewed for consumption of coffee and tea generating organic

residues. Such organic wastes present a high concentration of tannins, a polyphenolic biopolymer, and have been extensively used in biosorption studies of metallic elements (Bihanic et al., 2021; Cases et al., 2021; Cybulska et al., 2022; Garcia et al., 2021; Grison et al., 2021, 2018; Grison and Lock Toy Ki, 2021; Lock Toy Ki et al., 2022; Stanovych et al., 2019).

Both biomaterials, because of their vegetal origin, are intrinsically rich in several mineral elements, as calcium and magnesium, which are Lewis acids and could interact with organic molecules bearing Lewis base properties (Ho, 1975).

Physicochemical properties -composition, morphology and structure-of these biomaterials were firstly compared. Biosorbents were then tested for removing organic UV-filters (oxybenzone and octocrylene), insecticides (chlordecone and lindane) and herbicides (diuron and ametryne) from water. The biosorption kinetics for each pair of biosorbent/pollutant was first established. Then the capacity of each biosorbent was investigated in ideal aqueous solutions. And an interference study with common salts was then performed to evaluate the robustness of biosorbents in reconstituted seawater. The relationship between the chemical properties of organic pollutants and the nature of the biosorbents was investigated to rationalise the differences in biosorption capacity of the biosorbents.

## 2. Material and methods

Oxybenzone (98% purity) and lindane (>98% purity) were purchased from Sigma-Aldrich. Octocrylene (>98% purity) and diuron (>98% purity) were purchased from TCI. Chlordecone (>99% purity) was purchased from Dr Erhenstorfer company and ametryn (99.5% purity) from ChemService. All chemicals were used without further purification.

### 2.1. Plants origin

*Eichhornia crassipes* was purchased from a specialized grower (Nymphaea company, France). The plants were placed in an outdoor tank under greenhouse filled with water to which guano was added as fertilizer.

*Pistia stratiotes* was directly collected by CNR (Compagnie Nationale du Rhône) from the Rhone river/Gardon river near Comps (Gard, France).

*Fallopia japonica* was collected by our laboratory at Thoiras (Gard, France) in collaboration with EPTB Gardons (Etablissement Public Territorial de Bassin).

Spent coffee grounds and green tea grounds were obtained directly from our laboratory.

### 2.2. Biosorbents preparation

After collection, aerial parts of *E. crassipes*, *P. stratiotes* and *F. japonica* were removed. The roots were air dried for 1 week and then ground and sieved with a knife mill FRITSCHE Pulverisette 19 in order to obtain particles under 0.5 mm size. These ground roots were washed with deionized water and finally oven-dried to obtain homogeneous powders.

The powder of *F. japonica* was then heated at 325 °C for 2 h and gave a new powder named *F. japonica* TT, which stands for *F. japonica* Thermally Treated.

Spent coffee and green tea grounds were washed with hot water until a colorless filtrate was observed and then oven-dried. The particle sizes of spent coffee grounds were between 1 and 0.5 mm for 30% and under 0.5 mm for 70%, thus this biosorbent was used with no further grinding. Green tea leaves were ground and sieved in order to obtain particles under 0.5 mm size.

### 2.3. Scanning Electron Microscope (SEM) images and Energy Dispersive Spectroscopy (EDS) analysis

Scanning Electron Microscope (SEM) images were obtained using a Hitachi S-4800 SEM. Samples were mounted on a support holder thanks to a double-sided conducting adhesive tape. Images were obtained using back-scattered electrons.

Energy Dispersive Spectroscopy (EDS) analysis with energy resolution 133 eV in scanning mode was performed using a Jeol JEM-2200FS Field Emission Electron Microscope at accelerating voltage of 200 kV. In each case, samples were ground into a thin powder, and suspended in hexane. Each suspension of samples was dropped off on a grid CF 300 – Cu (carbon film on 300 Mesh copper grids).

#### 2.3.1. Brunauer Emmett-Teller (BET) analysis

The specific surface area and pore size distribution of the samples were inferred from the measurements of adsorption–desorption of gaseous nitrogen at 77 K with the use of a Micromeritics Tristar unit.

Prior to the experiments, each sample was aged in EtOH for at least 24 h. The next stage involved further exchange of the remaining water in the sample by removing the ageing solution which is replaced with absolute ethanol. This operation was performed twice with at least 24 h between ethanol exchanges. The obtained sample was finally dried by exchanging the ethanol with liquid CO<sub>2</sub> followed by supercritical evaporation (Pierre and Pajonk, 2002).

### 2.4. Conditions of biosorption

All biosorption experiments were performed between 22 and 25 °C. Analysis conditions and calibration curves are presented in Supporting Information.

#### 2.4.1. General procedure 1 (GP1): adsorption of chlordecone and lindane

Due to their low UV-Vis response, the adsorption studies of lindane and chlordecone were performed by GC-FID.

In an Erlenmeyer-type flask equipped with a magnetic stirrer were added 250 mL of distilled water. Then, 250 µL of the desired pollutant-containing solution (10 mmol.L<sup>-1</sup> in propan-2-ol) were added under stirring. After 2 min of homogenisation, 4 mL of the initial solution were collected and filtered into a 15 mL falcon-type tube. Biomass wastes (250, 750 or 1250 mg) were finally added and the resulting suspension was stirred for 2 h. The mixture was filtered and 4 mL were also collected in a falcon-type tube. This procedure was simultaneously realized as triplicates.

A solution of biphenyl (7.2 mg/L) in ethyl acetate was realized. 1 mL of this solution was added to the 4 mL of the samples. The falcon-type tubes were sealed and vigorously shaken during 1 min. The tubes were then centrifuged for 3 min at 5300 rpm. The organic phase was transferred into a GC vial and analysed.

The identification of the samples was based on comparison of its retention time with those of the standard compounds. Three injections of each solution were used to obtain the curve. The calibration curve was linear (R<sup>2</sup> were presented in the supporting information 3. Calibrations). The calculations of the limits of detection and quantification were detailed in the supporting information 3. Calibration. All the limits were below the calibration curve.

#### 2.4.2. General procedure 2 (GP2): adsorption of oxybenzone, octocrylene, ametryn and diuron

The adsorption studies of both UV-filters, oxybenzone, octocrylene, ametryn and diuron, were performed by HPLC-UV.

In an Erlenmeyer-type flask equipped with a magnetic stirrer were added 250 mL of distilled water (or a solution of H<sub>2</sub>O/iPrOH 90:10 in the case of octocrylene). Then, 250 µL of the desired pollutant-containing solution (10 mmol.L<sup>-1</sup> in propan-2-ol) were added under stirring. After 2 min of homogenisation, 1 mL of the solution was collected and

filtered with a 0.45 µm syringe-filter into a HPLC vial. Biomass wastes (250, 750 or 1250 mg) were finally added and the resulting suspension was stirred for 2 h. The mixture was filtered and 1 mL was also collected and filtered with a 0.45 µm syringe-filter into a HPLC vial. This procedure was simultaneously realized as triplicates. The samples were thermostated at 15 °C and the injection volume varied between 100 µL and 40 µL depending on the compound quantification. Elution conditions are presented in SI (SI1 Reagents and instruments).

The identification of the samples was based on comparison of its retention time with those of the standard compounds. Three injections of each solution were used to obtain the curve. The calibration curve was linear ( $R^2$  were presented in SI: 3. Calibrations). The calculations of the limits of detection and quantification were detailed in the supporting information 3. Calibration. All the limits were below the calibration curve.

#### 2.4.3. General procedure 3 (GP3): kinetics monitoring of lindane and chlordane biosorption

In an Erlenmeyer-type flask equipped with a magnetic stirrer were added 250 mL of distilled water. Then, 250 µL of the desired pollutant-containing solution (10 mmol.L<sup>-1</sup> in propan-2-ol) were added under stirring. After 2 min of homogenisation, 4 mL of the initial solution were collected and filtered into a 15 mL falcon-type tube. Biomass wastes (750 mg) were finally added and the resulting suspension was stirred for 4 h 4 mL samples of the mixture were collected at 10, 20, 30, 40, 50, 60, 120, 180 and 240 min. Each sample were filtered into a falcon-type tube in order to isolate the solution from the biosorbent.

#### 2.4.4. General procedure 4 (GP4): kinetics monitoring of oxybenzone, octocrylene, ametryn and diuron biosorption

In an Erlenmeyer-type flask equipped with a magnetic stirrer were added 250 mL of distilled water (or a solution of H<sub>2</sub>O/iPrOH 90:10 in the case of octocrylene). Then, 250 µL of the desired pollutant-containing solution (10 mmol.L<sup>-1</sup> in propan-2-ol) were added under stirring. After 2 min of homogenisation, 1 mL of the solution was collected and filtered with a 0.45 µm syringe-filter into a HPLC vial. Biomass wastes (750 mg) were finally added and the resulting suspension was stirred for 4 h 1 mL samples of the mixture were collected at 10, 20, 30, 40, 50, 60, 120, 180 and 240 min. Each sample were filtered with a 0.45 µm syringe-filter into a HPLC vial. The samples were thermostated at 15 °C and the injection volume varied between 100 µL and 40 µL depending on the compound quantification. Elution conditions are presented in SI (SI1 Reagents and instruments).

#### 2.4.5. General procedure 5 (GP5) preparation of reconstituted seawater

The preparation of reconstituted seawater was realized following the reported distribution of elements in the seawater (Quinby-Hunt and Turehian, 1983). Regarding the very low concentration of many elements, only the most abundant elements were added (Na, Mg, Ca, S and Cl). For In an Erlenmeyer-type flask, Na<sub>2</sub>SO<sub>4</sub> (20.43 g), MgCl<sub>2</sub> (8.55 g), CaCl<sub>2</sub> (1.96 g), KCl (1.29 g) and NaCl (40.66 g) were added followed by 1.7 L of deionized water. The mixture was stirred until complete solubilisation of the salts. For more details, see SI 2.1.1.3. Synthetic sea water.

#### 2.4.6. General procedure 6 (GP6): kinetic monitoring of lindane and chlordane biosorption in reconstituted seawater

In an Erlenmeyer-type flask equipped with a magnetic stirrer were added 250 mL of synthetic sea water (see GP7). Then, 250 µL of the desired pollutant-containing solution (10 mmol.L<sup>-1</sup> in propan-2-ol) were added under stirring. After 2 min of homogenisation, 4 mL of the initial solution were collected and filtered into a 15 mL falcon-type tube. 750 mg of the best biomass wastes (Coffee grounds in these cases) were finally added and the resulting suspension was stirred for 4 h 4 mL samples of the mixture were collected at 10, 20, 30, 40, 50, 60, 120, 180 and 240 min. Each sample were filtered into a falcon-type tube in order

to isolate the solution from the biosorbent.

The identification of the samples was based on comparison of its retention time with those of the standard compounds. Three injections of each solution were used to obtain the curve. The calibration curve was linear ( $R^2$  were presented in SI 3. Calibrations). The calculations of the limits of detection and quantification were detailed in the supporting information 3. Calibration. All the limits were below the calibration curve. **2.5.7. General procedure 7 (GP7) kinetic monitoring of oxybenzone, octocrylene, ametryn and diuron biosorption in reconstituted seawater.**

In an Erlenmeyer-type flask equipped with a magnetic stirrer were added 250 mL of synthetic sea water (see GP7) (or a solution of Synthetic sea water/iPrOH 90:10 in the case of octocrylene). Then, 250 µL of the desired pollutant-containing solution (10 mmol.L<sup>-1</sup> in propan-2-ol) were added under stirring. After 2 min of homogenisation, 1 mL of the solution was collected and filtered with a 0.45 µm syringe-filter into a HPLC vial. 750 mg of the best biomass wastes (F. japonica T.T. for diuron and oxybenzone and Coffee grounds for ametryn and octocrylene) were finally added and the resulting suspension was stirred for 4 h 1 mL samples of the mixture were collected at 10, 20, 30, 40, 50, 60, 120, 180 and 240 min. Each sample were filtered with a 0.45 µm syringe-filter into a HPLC vial. The samples were thermostated at 15 °C and the injection volume varied between 100 µL and 40 µL depending on the compound quantification. Elution conditions are presented in SI (SI1 Reagents and instruments).

### 2.5. Statistical analysis

Relationships among biosorbents, organic pollutants and the biosorption were investigated by using a multivariate statistical analysis based on a principal component analysis (PCA).

PCA was performed using Unscrambler X 10.3. PCA was applied to a total of 99 experiments performed with the 6 biosorbents (root powder of *Eichhornia crassipes*, root powder of *Pistia stratiotes*, root powder of *Fallopia japonica*, coffee grounds and green tea grounds) and with a total of 12 variables (biosorption yield (Byield), water solubility (Ws), XLogP3, Hydrogen Bond Donor (HBD), Hydrogen Bond Acceptor (HBA), Rotatable Bonds (Rb) and Topological Polar Surface Area (PSA), biomass concentration (Bc), %hemicellulose, %cellulose, %lignin, % tannins).

All data were mean-centered and divided by standard deviation. This ensures that all variables had the same influence on the principal components (PCs). The cross-fold validation (random with 20 segments), the uncertainty Martens' test with the optimal number of PCs and Nonlinear Iterative Partial Least Square (NIPALS) algorithm were used for calculations. In accordance to the Kaiser's rule (Kaiser and Rice, 1974) (Kaiser and Rice, 1974), only factors with eigenvalues that exceed one were retained. According to Morrison (1967), PC-1 to PC-4, that account for 81% of the total variance, were presented. Factor loadings, whose absolute value was greater than 60% of the maximum factor loading in each PC, were considered (Jolliffe, 2010).

## 3. Results & discussion

### 3.1. Physicochemical properties of the biosorbents

The biosorbents were directly prepared from the fresh biomass, without any chemical transformation. This point is crucial, as many processes of biosorption rely on chemical modification of biomass, which is often not compatible for future industrial applications. Roots of aquatic and wetland plants (*E. crassipes*, *P. stratiotes*, *F. japonica*), spent coffee grounds and green tea leaves were only dried, ground (except for the coffee grounds), washed and dried again. A fourth biosorbent was prepared differently using the crude roots of *F. japonica*, which were thermally treated to destroy cellulose and hemicellulose, attempting to decrease the polarity of the biomaterial, and was named *F. japonica* TT

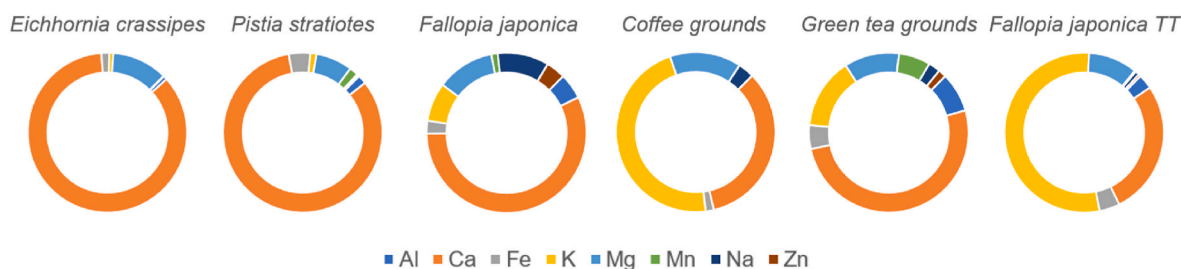


Fig. 1. Mineral composition of the biosorbents established by MP-AES.

(Thermally Treated).

### 3.1.1. Elemental composition of the biosorbents

The complete mineral composition of the biomaterials was determined by MP-AES, for anticipating possible interactions between metallic elements, naturally contained within the biomaterials, and the organic pollutants (Fig. 1).

Metallic compositions of the biomass wastes are quite different (Fig. 1). The analysis shows that biomass wastes derived from aquatic and wetland plants (*E. crassipes*, *P. stratiotes* and *F. japonica*) mainly contain calcium. The large presence of calcium ions might be interesting for adsorbing the selected organic pollutants, as they all display Lewis base properties (Ho, 1975).

Biomass wastes obtained from spent coffee grounds and green tea grounds, rich in tannins, and *F. japonica* TT, contain a high rate of potassium.

The presence of zinc should be noted for *F. japonica* and spent green tea grounds.

Energy dispersive X-ray spectroscopy (EDS) analysis showed that carbon and oxygen contribute most to the elemental composition of biomass wastes, which can be related to the organic composition of the biosorbents (SI4 Scanning electron microscopy). EDS also showed that biomass wastes derived from aquatic and wetland plants (*E. crassipes*, *P. stratiotes* and *F. japonica*) contain significant amounts of calcium, as also observed in MP-AES. For *P. stratiotes* and *F. japonica*, appreciable quantities of potassium and silicon were also observed. And root powder of *E. crassipes* contained also phosphorous.”

### 3.1.2. Morphology of the biosorbents

Besides their chemical composition, the morphology and texture of the biosorbents is a crucial parameter in view of the sorption properties of materials. We addressed this issue via scanning electron microscopy (SEM) and nitrogen sorption experiments. Whereas SEM allows getting a general overview on the morphology of the materials in terms of particle size and shape, nitrogen sorption gives more detailed insight in the porosity of the materials and allows for a detailed description of pore size, pore volume and pore size distribution on the mesoscopic scale. These two characterization methods therefore allow getting a complete set of information of textures, architectures and morphologies over several orders of magnitude, *i.e.* from the mesoscopic to the microscopic level.

The SEM images of the biosorbents are presented in Fig. 2. All materials display heterogeneous morphologies in terms of particle size and shape. Fiber-like morphologies can be observed in all samples.

Organization and order on the microscopic length scale can be seen in the non-treated root powder samples. Indeed, particles of *E. crassipes*, *P. stratiotes* and *F. japonica*, show fragments of dehydrated root tissues. A cross section of *E. crassipes* root, displaying intact vascular bundles and cortex with a flattened/dehydrated epidermis layer is clearly seen at the highest magnification (SI 4. Scanning electron microscopy).

The root powder of *F. japonica* TT that has been thermally treated show smaller particles with a sponge-like porosity compared to the non-treated sample. Similar morphology of sponge-like porosity can be

observed for green tea grounds. This feature can be favourable for applications in the field of biosorption.

Spent coffee grounds display heterogeneous sizes of particles with irregular pores, in line with the work of Mariana et al. (2018).

Porosity is an important parameter for the description of the morphological and textural properties of adsorbents. High porosity in terms of high specific surface area often improves the adsorption properties of adsorbents. In order to get more detailed information on the textural properties of the biosorbents, we performed nitrogen sorption experiments at 77 K, and the specific surface area of the samples was then determined via Brunauer-Emmett-Teller (BET) analysis. The materials used for these measurements were treated under conditions as close as possible to those of the biosorption conditions, using a super-critical CO<sub>2</sub> drying process for the preparation of the samples. This methodology is suitable for measuring the porosity of the biosorbents in solution, instead of in the air (García-González et al., 2012; Mukhopadhyay and Rao, 2008).

Our results indicate that the biosorbents generally display low mesoporosity or are non-porous. All samples displayed specific surface areas below 1 m<sup>2</sup>/g, except the root powder of *E. crassipes* that displays a specific surface area of S<sub>BET</sub> = 32 m<sup>2</sup>/g. This porosity, although rather limited, can be explained by the conserved internal root structure of *E. crassipes*, as shown in the SEM micrograph in Fig. 2.

## 3.2. Removal of the selected organic pollutants by biomass wastes

Biosorption of the organic pollutants was studied preparing contaminated solutions at the same concentration of 10 μmol.L<sup>-1</sup> for a comparative study of each pollutant. This concentration represents a compromise between the solubility of the pollutant in water and a concentration about 50 times above the DL and QL. Powders of the biomass wastes were introduced at 1–5 g.L<sup>-1</sup> in the contaminated solutions. This range of concentrations was considered reasonable for a potential industrial development.

Due to the hydrophobic nature of pollutants, a preliminary study was performed to evaluate the adsorption of the pollutants on the walls of the reactor. No pollutant could be detected in an EtOAc solution that was used to wash the walls of the reactor.

### 3.2.1. Kinetics studies

The biosorption kinetics was first investigated to determine the time required for a maximum adsorption of each organic pollutant (10 μmol.L<sup>-1</sup>) by each biomaterial (3 g.L<sup>-1</sup>). Experiments were conducted for different timings, from 10 min to 4 h (see SI 5. Biosorption results). In all systems, the biosorption was fast, as only 30 min to 1 h were required to reach the maximum level of removal.

The results were further analysed according to the pseudo-first and pseudo-second order models (Sahoo and Prelot, 2020). In all systems, their linearization and experimental fitting showed better coefficient of determination for the pseudo-second order model (see SI 6. Kinetic studies). Such kinetics model can be linked to a remarkably fast biosorption at the beginning, which could correspond to rapid filling of the adsorption sites, followed by the equilibrium, in which no more

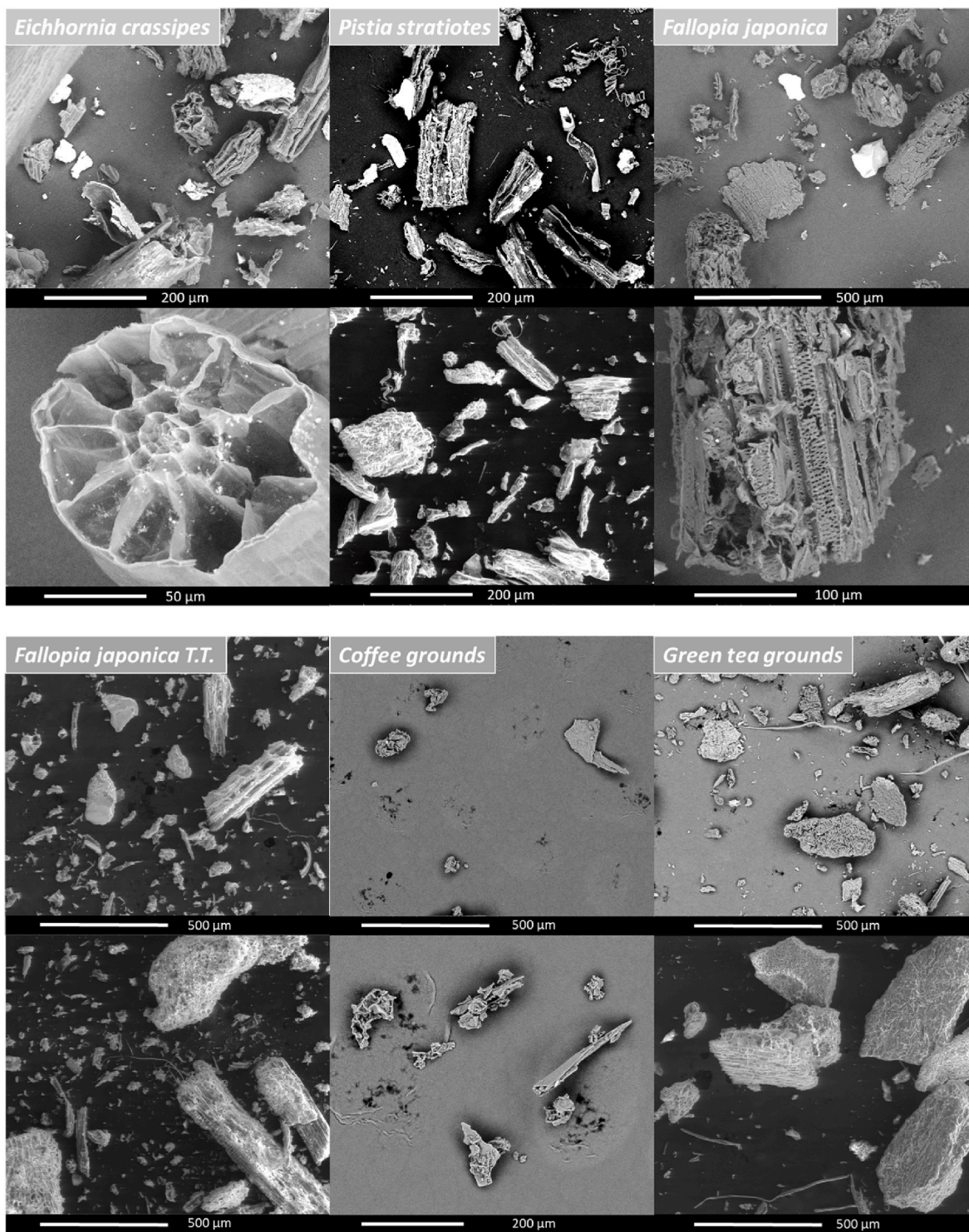


Fig. 2. SEM Images of biomass wastes.

adsorption was observed despite increasing the contact time.

### 3.2.2. Removal of organic UV-filters and pesticides by biosorption

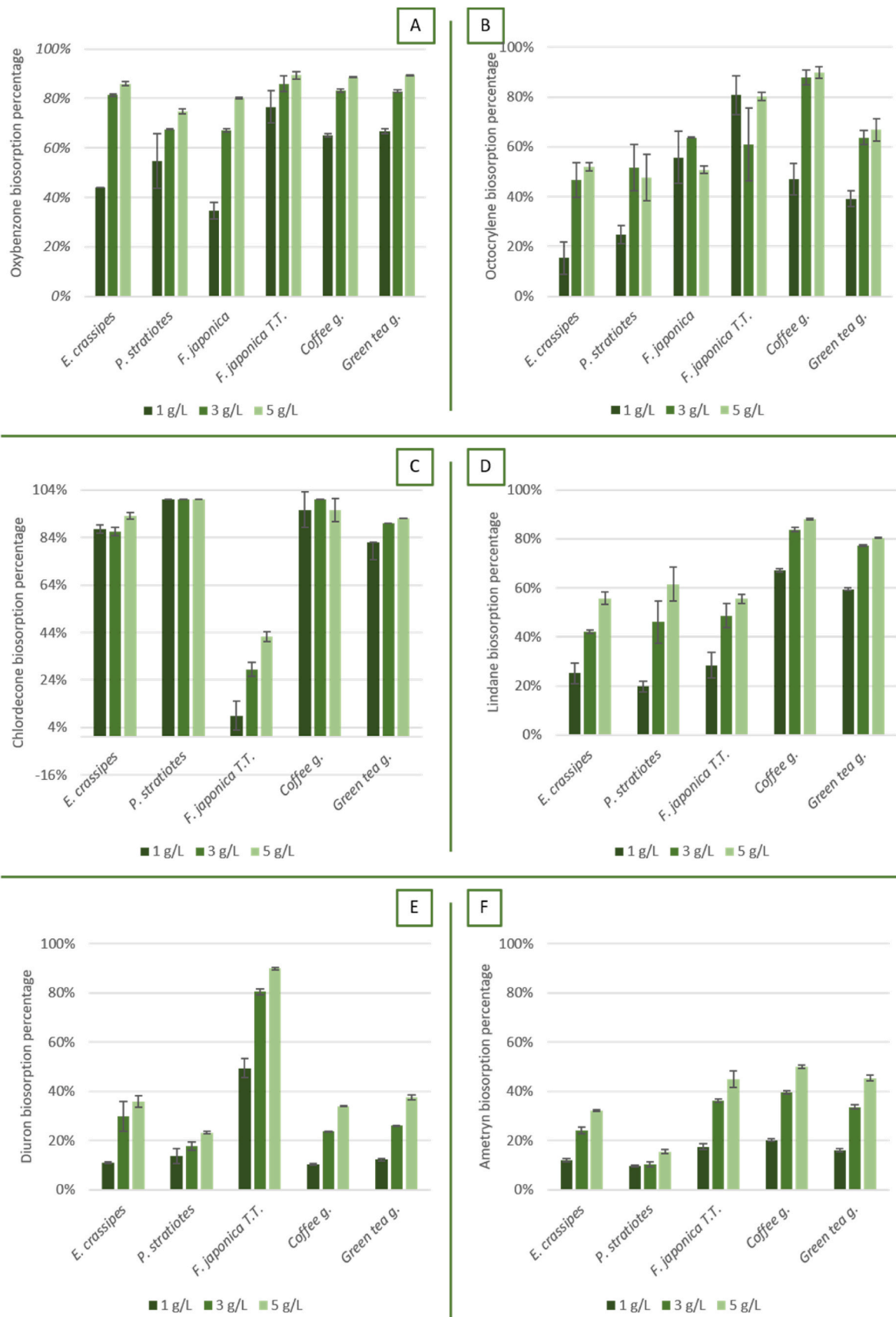
The adsorption capacity of each biowaste was evaluated on oxybenzone, octocrylene (Fig. 3A–B), ametryn and diuron (Fig. 3E–F) as described in Methods GP2, and on lindane and chlordecone as described in Methods GP1 (Fig. 3C–D). As the kinetics study showed that the equilibrium was reached between 30 min and 1 h for every system, the biosorption experiment lasted 2 h.

Maximal biosorption efficiency of oxybenzone and octocrylene was

very good, as it reached 89% and 90% respectively (Fig. 3 A & B). For oxybenzone, little difference was noted between biosorbents used at 5 g/L, giving a range of 75–89% of removal efficiency. However, the lowest concentration allowed discrimination among the biosorbents. Heat-treated *F. japonica* TT gave the best result even at 1 g/L, with 76% of removal efficiency.

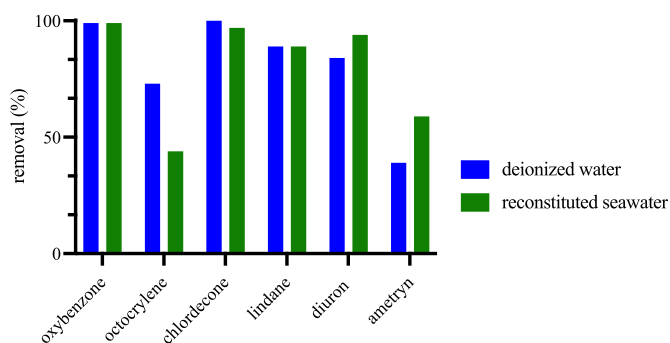
Discrimination among the biosorbents was clearer for octocrylene. Spent coffee grounds and root powder of *F. japonica* TT lead to the best removal of octocrylene from solution, with 90 and 81% of biosorption.

Excellent results were obtained for the biosorption of chlordecone,



**Fig. 3.** Removal of organic UV-filters (A: oxybenzone, B: octocrylene) and pesticides (C: chlordecone, D: lindane, E: diuron, F: ametryn) from aqueous solutions. Initial concentration of organic pollutant was 10  $\mu\text{mol/L}$ . Contact time was 2 h. Each experiment was conducted three times independently.





**Fig. 4.** Removal of organic pollutants from deionized water and reconstituted seawater. Initial concentration of organic pollutant was 10  $\mu\text{mol/L}$ . Oxybenzone, diuron were removed by the biosorbent derived from *F. japonica* TT (3 g/L); octocrylene, chlordecone, lindane and ametryn were removed by the biosorbent derived from spent coffee grounds (3 g/L). Contact time was 2 h.

which is promising for the population living in areas contaminated by such hazardous insecticide. Indeed root powder of *E. crassipes*, spent coffee and green tea grounds gave a range of 92–96% of removal efficiency; and root powder of *P. stratiotes*, even at the lowest concentration of 1 g/L, led to a total decontamination of the aqueous solution. This result is even more encouraging, considering the abundance of both aquatic plants in the chlordecone-contaminated areas (Méndez-Fernández et al., 2018; Rochette et al., 2020). Interestingly, heat-treated *F. japonica* TT was not efficient for removing this insecticide.

A very good removal efficiency of 88% was obtained for lindane using coffee grounds as biosorbent. Green tea grounds were also efficient at 80%, while the root powders of the aquatic plants could only remove half of the insecticide initial concentration.

Biosorption of diuron was very efficient, but surprisingly by only one biosorbent, the root powder of heat-treated *F. japonica* TT, which gave a 90% of removal efficiency at 5 g/L.

Biosorption of ametryn was clearly less efficient. Spent coffee and green tea grounds, and root powder of TT *F. japonica* were the best biosorbents, but could only remove half of the herbicide initial concentration.

### 3.2.3. Biosorption of pollutants in reconstituted seawater

An interference study was carried out in order to evaluate the biosorption performances in real aquatic systems (sea, lagoon, river, pond), where organic pollutants could be found. Interfering compounds can be salts, whose sodium, magnesium, calcium, sulfate and chloride are the most concentrated (Quinby-Hunt and Turehian, 1983).

Adsorption of each pollutant was compared in deionized water and

in reconstituted seawater (Fig. 4). The biomaterial, which previously gave the highest biosorption efficiency (Fig. 3), was used in this interference study.

In general, the biosorption efficiency was not impacted by the presence of salts; except for octocrylene and ametryn whose adsorption was respectively slightly less and more efficient in reconstituted seawater.

### 3.2.4. Comparison to literature

Several biomaterials, as plant-based, agricultural and microorganism-based sources, have been explored for removing organic pollutants by adsorption. A comparison between existing systems and the biosorbents reported here, versus lindane, diuron and ametryn is presented in Table 1.

In general, all biomaterials are efficient, which support the large interest in depollution by biosorption. However, these performances are reached in different experimental conditions that can include pH change (Abdel-Aty et al., 2015; Zhang et al., 2015), chemical modification of the biomaterial (Zhang et al., 2015) or high loading of biomaterial (Silva et al., 2013). Overall, spent coffee grounds and powder of invasive alien

**Table 2**

Factor loadings of the pollutant and biosorbent variables obtained by Principal Component Analysis (marked loadings are higher than  $60 \pm 2\%$  of maximum loading for each PC in absolute value).

		PC-1	PC-2	PC-3	PC-4
Characteristics of the organic pollutants	Water Solubility	<b>-0.451</b>	-0.013	-0.199	0.070
	Hydrogen Bond Donor	<b>-0.449</b>	-0.022	-0.261	0.068
	Hydrogen Bond Acceptor	<b>-0.472</b>	0.053	0.162	0.142
	XLogP3	0.097	0.105	<b>0.635</b>	0.007
	Rotatable Bonds	-0.222	0.111	<b>0.578</b>	0.046
Characteristics of the biosorbents	Polar Surface Area	<b>-0.481</b>	0.050	0.158	0.113
	Biosorbent concentration	0.032	0.009	0.028	<b>0.641</b>
	%Lignin	-0.025	<b>-0.603</b>	0.141	0.030
	%Cellulose	-0.013	<b>0.382</b>	0.148	<b>-0.344</b>
	%Hemicellulose	0.011	<b>0.582</b>	-0.113	-0.036
Biosorption efficiency	%Tannins	0.057	<b>0.348</b>	-0.192	<b>0.369</b>
	Biosorption yield	<b>0.277</b>	0.037	0.103	<b>0.536</b>
Statistics	Eigenvalue	3.88	2.36	2.19	1.28
	Proportion of total variance (%)	32	20	18	11

**Table 1**

Comparison of the biosorption efficiency between biosorbents.

Biosorbent	Organic pollutant	Conditions	Removal efficiency	Maximal biosorption capacity (mg/g)	References
<i>Pinus pinaster</i> bark powder (5 g/L)	lindane (20 $\mu\text{g/L}$ )	deionized water	80%	0.0032	Ratola et al. (2003)
Spent coffee grounds (3 g/L)	(3 mg/L)	reconstituted seawater	89%	0.89	This study
Microalgal biomass <i>Anabaena sphaerica</i> and <i>Scenedesmus obliquus</i> (1 g/L)	diuron (40 mg/L)	deionized water pH = 3	80%	32	Abdel-Aty et al. (2015)
Invasive alien species powder <i>Fallopia japonica</i> TT (3 g/L)	(2.3 mg/L)	reconstituted seawater	94%	0.72	This study
Cellulose/graphene composite (3 g/L)	ametryn (1 mg/L)	deionized water pH = 9	95%	0.31	Zhang et al. (2015)
Banana peel powder (60 g/L)	(10 $\mu\text{g/L}$ )	deionized water river water	96–98% 53–62%	0.0002–0.0001	Silva et al. (2013)
Spent coffee grounds (3 g/L)	(2.3 mg/L)	reconstituted seawater	59%	0.45	This study

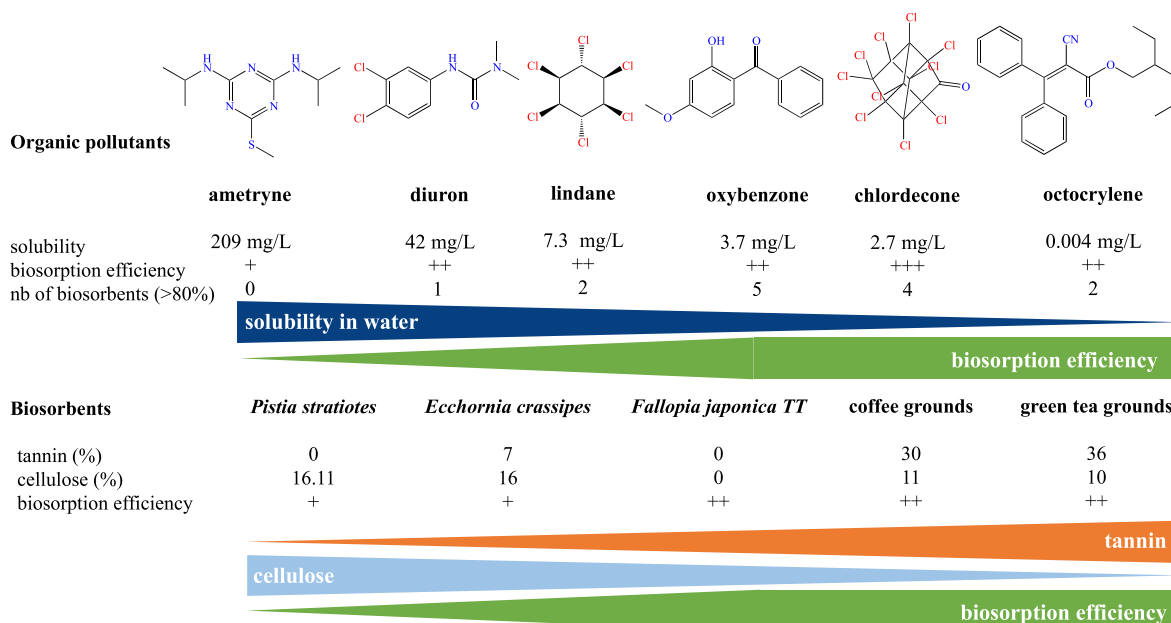


Fig. 5. Characteristics of organic pollutants and biosorbents related to biosorption efficiency.

species present a good maximal biosorption capacity. And they are not chemically modified, are used in reasonable quantity with no modification of pH. Their biosorption capacity remained high in reconstituted seawater, although different from real water samples, in which powder of banana peel was proved to remain efficient (Silva et al., 2013).

### 3.3. Principal component analysis

A principal component analysis (PCA) was performed as an attempt to rationalise the biosorption results (Table 2). The PCA was conducted considering variables from the organic pollutants (water solubility, XLogP3, Hydrogen Bond Donor, Hydrogen Bond Acceptor, Rotatable Bonds and Topological Polar Surface Area) and variables from the biosorbents (Biosorbent concentration, %hemicellulose, %cellulose, % lignin, %tannins).

Four principal components (PCs) explained 81% of the total variance. The first PC (PC-1), accounting for 32% of the total variance, described some characteristics of the organic pollutants, all related to their solubility in water. Although less important in absolute value, the factor loading of the biosorption efficiency cannot be excluded, since it corresponds to 59% of the maximum loading. PC-1 shows a negative correlation with water solubility of the pollutants and a positive correlation the biosorption efficiency. Indeed, the more soluble in water the organic pollutants are, the more difficult their interaction with water is breakable and the less they adsorb on the biosorbents (Fig. 5).

The PC-2 described the chemical composition of the biosorbents, showing that lignin is less present when cellulose, hemicellulose and tannins compose the biosorbent.

The PC-3 described the hydrophobicity and rotatable bonds of the compounds.

The PC-4, accounting for 11% of the total variance, was influenced by some characteristics of the biosorbents and the biosorption efficiency. As expected, the concentration of biosorbent is positively correlated with the biosorption efficiency. And the chemical composition of the biosorbents seems to have an effect, although weak, on the biosorption efficiency. The presence of tannin is positively correlated with the biosorption efficiency, while it is the opposite for the presence of cellulose (Fig. 5). Indeed, biomaterials containing tannins are better biosorbent of organic pollutants than biomaterials rich in cellulose, which is more hydrophilic and less prone to interact with organic

molecules than water.

## 4. Conclusion

Root powders of aquatic and wetland invasive alien species (*E. crassipes*, *P. stratiotes*, *F. japonica*) showed excellent capacities for the biosorption of chlordecone, oxybenzone, octocrylene and diuron in ideal aqueous solutions in only 2 h. Both spent coffee grounds and green tea grounds exhibited excellent biosorption efficiency for chlordecone, oxybenzone, octocrylene and lindane in ideal aqueous solutions in only 2 h. The biosorption of ametryne only was less efficient, as none of the biosorbents could remove more than half of the herbicide initial concentration. Similar biosorption capacity was obtained in reconstituted seawater for each pollutant, except for octocrylene whose adsorption was slightly lower. Principal component analysis suggested that biosorption efficiency could be directly related to the water solubility of the organic pollutants and the concentration of tanins in biosorbents, explaining the excellent removal of all pollutants except ametryn.

This biosorption technology allowed a double environmental service, as the rapid and efficient removal of pesticides and UV-filters from water, using abundant wastes, as invasive plants, coffee and tea grounds, as biosorbents. These results and the robustness of this method in brine provide strong motivation for the harvest and thereby the control of invasive plants proliferation, allowing the preservation of biodiversity of aquatic and wetland ecosystems. Further studies would be required under field condition, to challenge this methodology in the depollution of aquatic ecosystems.

## Author contributions statement

Pierre-Alexandre Deyris: Methodology, Experimental work of biosorption, GS analysis. Franck Pelissier: Mineral assessments and quantifications by HPLC. Claire M. Grison: Methodology, Experimental work of biosorption, Writing. Peter Heseaman: BET analysis. Eddy Petit: Principal Component analysis. Claude Grison: Conceptualization, Supervision, Writing.

## Declaration of competing interest

The authors declare that they have no known competing financial

interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

## Acknowledgements

The authors would like to thank Klorane Botanical Foundation for financial support. The authors also thank Dr. Nathalie Tanchoux for scCO<sub>2</sub> extraction experiments and Nicole Abdou for nitrogen sorption measurements.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2022.137307>.

## References

- Abdel-Aty, A.M., Gad-Allah, T.A., Ali, M.E.M., Abdel-Ghaffar, H.H., 2015. Parametric, equilibrium, and kinetic studies on biosorption of diuron by *Anabaena sphaerica* and *Scenedesmus obliquus*. *Environ. Prog. Sustain. Energy* 34, 504–511. <https://doi.org/10.1002/ep.12027>.
- Aksu, Z., 2005. Application of biosorption for the removal of organic pollutants: a review. *Process Biochem.* 40, 997–1026. <https://doi.org/10.1016/j.procbio.2004.04.008>.
- Bihanic, C., Lasbleiz, A., Regnier, M., Petit, E., Le Blainvaux, P., Grison, C., 2021. New sustainable synthetic routes to cyclic oxyterpenes using the cocatalyst toolbox. *Molecules* 26, 7194. <https://doi.org/10.3390/molecules26237194>.
- Boxall, A.B.A., n.d. New and Emerging Water Pollutants Arising from Agriculture 49.
- Brausch, J.M., Rand, G.M., 2011. A review of personal care products in the aquatic environment: environmental concentrations and toxicity. *Chemosphere* 82, 1518–1532. <https://doi.org/10.1016/j.chemosphere.2010.11.018>.
- Carstensen, L., Beil, S., Börnick, H., Stolte, S., 2022. Structure-related endocrine-disrupting potential of environmental transformation products of benzophenone-type UV filters: a review. *J. Hazard Mater.* 430, 128495 <https://doi.org/10.1016/j.jhazmat.2022.128495>.
- Carve, M., Nugegoda, D., Allinson, G., Shimeta, J., 2021. A systematic review and ecological risk assessment for organic ultraviolet filters in aquatic environments. *Environ. Pollut.* 268, 115894 <https://doi.org/10.1016/j.envpol.2020.115894>.
- Cases, L., Adler, P., Pelissier, F., Diliberto, S., Boulanger, C., Grison, C., 2021. New biomaterials for Ni biosorption turned into catalysts for Suzuki–Miyaura cross coupling of aryl iodides in green conditions. *RSC Adv.* 11, 28085–28091. <https://doi.org/10.1039/D1RA04478H>.
- Cybulska, P., Legrand, Y.-M., Babst-Kostecka, A., Diliberto, S., Leńiewicz, A., Oliviero, E., Bert, V., Boulanger, C., Grison, C., Olszewski, T.K., 2022. Green and effective preparation of  $\alpha$ -hydroxyphosphonates by cocatalysis. *Molecules* 27, 3075. <https://doi.org/10.3390/molecules27103075>.
- Danovaro, R., Bongiorno, L., Corinaldesi, C., Giovannelli, D., Damiani, E., Astolfi, P., Greci, L., Pusceddu, A., 2008. Sunscreens cause coral bleaching by promoting viral infections. *Environ. Health Perspect.* 116, 441–447. <https://doi.org/10.1289/ehp.10966>.
- De Laet, C., Matringe, T., Petit, E., Grison, C., 2019. Eichhornia crassipes: a powerful bio-indicator for water pollution by emerging pollutants. *Sci. Rep.* 9, 7326. <https://doi.org/10.1038/s41598-019-43769-4>.
- Debates of the European Parliament, Session of the 14/01/2008, 2008.
- DiNardo, J.C., Downs, C.A., 2018. Dermatological and environmental toxicological impact of the sunscreen ingredient oxybenzone/benzophenone-3. *J. Cosmet. Dermatol.* 17, 15–19. <https://doi.org/10.1111/jocd.12449>.
- DIRECTIVE (EU) 2020/2184 OF THE EUROPEAN PARLIAMENT and of the COUNCIL on the Quality of Water Intended for Human Consumption, 2020.
- Emmanouil, C., Bekyrou, M., Psomopoulos, C., Kungolos, A., 2019. An insight into ingredients of toxicological interest in personal care products and A small-scale sampling survey of the Greek market: delineating a potential contamination source for water resources. *Water* 11, 2501. <https://doi.org/10.3390/w1122501>.
- FAO, 2019. FAOSTAT, p. 2020.
- Fenyvesi, É., Barkács, K., Gruiz, K., Varga, E., Kenyeres, I., Záray, G., Szenté, L., 2020. Removal of hazardous micropollutants from treated wastewater using cyclodextrin bead polymer – a pilot demonstration case. *J. Hazard Mater.* 383, 121181 <https://doi.org/10.1016/j.jhazmat.2019.121181>.
- Franco, T.F., Parmejiani, R.S., Cunha, M.P.L., Miranda, A., Marques, R.C., Guimaraes, J. R.D., 2021. Characterization and distribution of pesticide use from 2015 to 2019, by health regions in the state of Rondônia (RO), Amazon, Brazil. *Rev. Bras. Ciéncia Aícola* 56, 445–458. <https://doi.org/10.5327/Z217694781013>.
- García, A., Deyris, P.-A., Adler, P., Pelissier, F., Dumas, T., Legrand, Y.-M., Grison, C., 2021. I - ecologically responsible and efficient recycling of Pd from aqueous effluents using biosorption on biomass feedstock. *J. Clean. Prod.* 299, 126895 <https://doi.org/10.1016/j.jclepro.2021.126895>.
- García-González, C.A., Camino-Rey, M.C., Alnaief, M., Zetzl, C., Smirnova, I., 2012. Supercritical drying of aerogels using CO<sub>2</sub>: effect of extraction time on the end material textural properties. *J. Supercrit. Fluids* 66, 297–306. <https://doi.org/10.1016/j.supflu.2012.02.026>.
- Grison, C., Adler, P., Deyris, P.-A., Diliberto, S., Boulanger, C., 2021. A green approach for the reduction of representative aryl functional groups using palladium cocatalysts. *Green Chem. Lett. Rev.* 14, 234–245. <https://doi.org/10.1080/17518253.2021.1898682>.
- Grison, C., Carrasco, D., Stanovych, A., 2018. Utilisation de matériaux naturels d'origine végétale riches en acides phénoliques pour la mise en oeuvre de réactions de chimie organique et le recyclage de catalyseurs. *FR3064496A1*.
- Grison, C., Lock Toy Ki, Y., 2021. Ecocatalysis, a new vision of green and sustainable chemistry. *Curr. Opin. Green Sustain. Chem.* 29, 100461 <https://doi.org/10.1016/j.cogsc.2021.100461>.
- He, T., Tsui, M.M.P., Tan, C.J., Ng, K.Y., Guo, F.W., Wang, L.H., Chen, T.H., Fan, T.Y., Lam, P.K.S., Murphy, M.B., 2019. Comparative toxicities of four benzophenone ultraviolet filters to two life stages of two coral species. *Sci. Total Environ.* 651, 2391–2399. <https://doi.org/10.1016/j.scitotenv.2018.10.148>.
- Ho, T.-L., 1975. Hard soft acids bases (HSAB) principle and organic chemistry. *Chem. Rev.* 75, 1–20. <https://doi.org/10.1021/cr60293a001>.
- Jolliffe, I.T., 2010. *Principal Component Analysis, Software Reprint of the Hardcover, 2002, second ed.* Springer Science+Business Media, LLC, New York.
- Kaiser, H.F., Rice, J., 1974. Little Jiffy, Mark IV. *Educ. Psychol. Meas.* 34, 111–117. <https://doi.org/10.1177/001316447403400115>.
- Li, X., Wang, B., Cao, Y., Zhao, S., Wang, H., Feng, X., Zhou, J., Ma, X., 2019. Water contaminant elimination based on metal-organic frameworks and perspective on their industrial applications. *ACS Sustain. Chem. Eng.* 7, 4548–4563. <https://doi.org/10.1021/acsschemeng.8b05751>.
- Lock Toy Ki, Y., García, A., Pelissier, F., Olszewski, T.K., Babst-Kostecka, A., Legrand, Y.-M., Grison, C., 2022. Mechanochemistry and eco-bases for sustainable michael addition reactions. *Molecules* 27, 3306. <https://doi.org/10.3390/molecules27103306>.
- Mariana, Marwan, Mulana, F., Yunardi Ismail, T.A., Hafdiansyah, M.F., 2018. Activation and characterization of waste coffee grounds as bio-sorbent. *IOP Conf. Ser. Mater. Sci. Eng.* 334, 012029 <https://doi.org/10.1088/1757-899X/334/1/012029>.
- Méndez-Fernandez, P., Kiszka, J.J., Heithaus, M.R., Beal, A., Vandersarren, G., Caurant, F., Spitz, J., Taniguchi, S., Montone, R.C., 2018. From banana fields to the deep blue: assessment of chlordecone contamination of oceanic cetaceans in the eastern Caribbean. *Mar. Pollut. Bull.* 137, 56–60. <https://doi.org/10.1016/j.marpolbul.2018.10.012>.
- Morin-Crini, N., Lichtfouse, E., Fourmentin, M., Ribeiro, A.R.L., Noutsopoulos, C., Mapelli, F., Fenyvesi, É., Vieira, M.G.A., Picos-Corrales, L.A., Moreno-Piraján, J.C., Giraldo, L., Sohajda, T., Huq, M.M., Soltan, J., Torri, G., Magureanu, M., Bradu, C., Crini, G., 2021. Remediation of emerging contaminants. In: Morin-Crini, N., Lichtfouse, E., Crini, G. (Eds.), *Emerging Contaminants Vol. 2, Environmental Chemistry for a Sustainable World*. Springer International Publishing, Cham, pp. 1–106. [https://doi.org/10.1007/978-3-030-69090-8\\_1](https://doi.org/10.1007/978-3-030-69090-8_1).
- Morrison, D.F., 1967. *Multivariate Statistical Methods, Multivariate Statistical Methods*. McGraw-Hill.
- Mukhopadhyay, M., Rao, B.S., 2008. Modeling of supercritical drying of ethanol-soaked silica aerogels with carbon dioxide. *J. Chem. Technol. Biotechnol.* 83, 1101–1109. <https://doi.org/10.1002/jctb.1996>.
- Multigner, L., Ndong, J.R., Giusti, A., Romana, M., Delacroix-Maillard, H., Cordier, S., Jégou, B., Thome, J.P., Blanchet, P., 2010. Chlordecone exposure and risk of prostate cancer. *J. Clin. Oncol.* 28, 3457–3462. <https://doi.org/10.1200/JCO.2009.27.2153>.
- Nolan, K., Kamrath, J., Levitt, J., 2012. Lindane toxicity: a comprehensive review of the medical literature: lindane toxicity. *Pediatr. Dermatol.* 29, 141–146. <https://doi.org/10.1111/j.1525-1470.2011.01519.x>.
- Pagès, N., Sauviat, M.-P., Bouvet, S., Goudey-Perrière, F., 2002. Toxicité du lindane sur la reproduction. *J. Soc. Biol.* 196, 325–338. <https://doi.org/10.1051/jbio/2002196040325>.
- Pierre, A.C., Pajonk, G.M., 2002. Chemistry of aerogels and their applications. *Chem. Rev.* 102, 4243–4266. <https://doi.org/10.1021/cr0101306>.
- Quinby-Hunt, M.S., Turehian, K.K., 1983. Distribution of elements in sea water. *Eos Trans. Am. Geophys. Union* 64, 130. <https://doi.org/10.1029/EO064i014p00130>.
- Ratola, N., Botelho, C., Alves, A., 2003. The use of pine bark as a natural adsorbent for persistent organic pollutants - study of lindane and heptachlor adsorption. *J. Chem. Technol. Biotechnol.* 78, 347–351. <https://doi.org/10.1002/jctb.784>.
- Report of the Persistent Organic, 2007. *Pollutants Review Committee on the Work of its Third Meeting Addendum Revised Risk Profile on Chlordecone*.
- Rochette, R., Bonnal, V., Andrieux, P., Cattani, P., 2020. Analysis of surface water reveals land pesticide contamination: an application for the determination of chlordecone-polluted areas in Guadeloupe, French West Indies. *Environ. Sci. Pollut. Res.* 27, 41132–41142. <https://doi.org/10.1007/s11356-020-10718-y>.
- Rojas, S., Horcajada, P., 2020. Metal-organic frameworks for the removal of emerging organic contaminants in water. *Chem. Rev.* 120, 8378–8415. <https://doi.org/10.1021/acs.chemrev.9b00797>.
- Sahoo, T.R., Prelot, B., 2020. Adsorption processes for the removal of contaminants from wastewater. In: *Nanomaterials for the Detection and Removal of Wastewater Pollutants*. Elsevier, pp. 161–222. <https://doi.org/10.1016/B978-0-12-818489-9.00007-4>.
- Salvat, B., Roche, H., Ramade, F., 2016. On the occurrence of a widespread contamination by herbicides of coral reef biota in French Polynesia. *Environ. Sci. Pollut. Res.* 23, 49–60. <https://doi.org/10.1007/s11356-015-4395-9>.
- Silva, C.R., Gomes, T.F., Andrade, G.C.R.M., Monteiro, S.H., Dias, A.C.R., Zagatto, E.A.G., Tornisielo, V.L., 2013. Banana peel as an adsorbent for removing atrazine and

- ametryne from waters. *J. Agric. Food Chem.* 61, 2358–2363. <https://doi.org/10.1021/jf304742h>.
- Stanovych, A., Balloy, M., Olszewski, T.K., Petit, E., Grison, C., 2019. Depollution of mining effluents: innovative mobilization of plant resources. *Environ. Sci. Pollut. Res.* 26, 19327–19334. <https://doi.org/10.1007/s11356-019-05027-y>.
- Wang, J., Wang, S., 2016. Removal of pharmaceuticals and personal care products (PPCPs) from wastewater: a review. *J. Environ. Manag.* 182, 620–640. <https://doi.org/10.1016/j.jenvman.2016.07.049>.
- Zhang, C., Zhang, R.Z., Ma, Y.Q., Guan, W.B., Wu, X.L., Liu, X., Li, H., Du, Y.L., Pan, C.P., 2015. Preparation of cellulose/graphene composite and its applications for triazine pesticides adsorption from water. *ACS Sustain. Chem. Eng.* 3, 396–405. <https://doi.org/10.1021/sc500738k>.