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Nonliving biomass of marine macrophytes as arsenic(V) biosorbents

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Abstract The present study was aimed at assessing the performance of different nonliving macrophytes sampled in the Adriatic coast in arsenic(V) sorption. Full factorial experiments were carried out where the main factors were the macrophyte species (brown algae: *Cystoseira*, *Dictyopteris*, and *Eisenia*; green algae: *Caulerpa* and *Ulva*; red algae: *Ceramium*, *Gracilaria*, and *Porphyra*; and seagrass: *Zostera*), biosorbent washing pre-treatment (deionized water, acid pH 2 and basic pH 10), equilibrium pH (in the range 1 to 8), under relatively high (10 mg L^{-1}) and relatively low (100 μg L^{-1}) arsenic concentration. All species exhibited significant adsorption. Indeed, they showed a good performance, with the highest observed value of about 1.3±0.1 mg g^{-1} for the red alga *Ceramium* and the seagrass *Zostera*, comparable with those of activated carbon and other low-cost adsorbents reported in the literature under similar experimental conditions. Moreover, red algae known in the literature to be bad cationic metal sorbents showed very good arsenic sorption performance. This work shows that the performance of arsenic biosorption depends on many factors: the different composition and structure of outer layer of the macrophytes, arsenic speciation and functional group availability under different pH, and eventual counter-ion interactions with arseniate.

Keywords Adsorption · Arsenic removal · Bioremediation · Heavy metal · Seagrass · Seaweeds

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Introduction

Arsenic is an element that is widely distributed in the earth's crust and it is ordinarily a steel gray metal-like material that occurs naturally (Cullen and Reimer 1989). There are two forms of arsenic in nature: organic and inorganic. The inorganic forms of arsenic, in particular arsenic(V), are more mobile than the organic forms and hence pose more of the risk of leaching into groundwater (Dembitsky and Rezanka 2003). The aquifers can be also contaminated by arsenic from the activities of mining. Indeed, acid mine drainage typically poses an additional risk to the environment by the fact that it often contain high concentration of metals (iron, zinc, manganese, aluminum, and heavy metals) and metalloids (e.g., arsenic; Akcil and Koldas 2006). Moreover, even copper smelting generates large amount of wastewater containing considerable amounts of inorganic compounds such as heavy metals and arsenic species (Hansen et al. 2006). Last but not least, drinking water can be harmful to humans due to the presence of trace arsenic (Azcue and Nriagu 1995; Wang and Mulligan 2006). World Health Organization (WHO) in 1993 and National Health and Medical Research Committee (NHMRC) Australia, in 1996 recommended Maximum Contaminant Level (MCL) of arsenic in drinking water as 10 and 7 μg L^{-1}, respectively (WHO 1993; NHMRC 1996). The MCL of arsenic in drinking water has also been reduced from 50 to 10 μg L^{-1} by European Commission in 2003 (ECD 1998). Environmental Protection Agency (EPA), USA, decided to move forward in implementing the same MCL of arsenic that is recommended by WHO for drinking water in 1993 (EPA 1998). Japan and Canada have reduced the MCL for arsenic in drinking water to 10 and 25 μg L^{-1}, respectively. The MCL for arsenic in countries such as India, Bangladesh, Taiwan, China, Vietnam, etc., is also 50 μg L^{-1} (Nordstrom 2002). In spite of the availability of some conventional techniques for arsenic removal from contaminated water (Choong et al. 2007),

Table 1 Factors and levels investigated in the study of As(V) biosorption at relatively high concentration (10 mg L^{-1})

Factor	Levels						
Macrophyte	*Ulva rigida*	*Caulerpa racemosa*	*Cystoseira compressa*	*Dictyopteris polypodioides*	*Gracilaria bursa-pastoris*	*Ceramium ciliatum*	*Zostera marina*
pH	6			7	8		
Pre-treatment	No			Acid pH 2	Basic pH 10		

development of new laboratory-based techniques along with enhancement and cost reduction of conventional techniques are essential for the benefit of the common people (Beolchini et al. 2006; Mondal et al. 2006; Beolchini et al. 2007).

Mohan and Pitmann (2007) reviewed the existing purification methods for drinking water, wastewater, industrial effluents, and technological solutions for arsenic. During the last decades, the use of biosorbents as nonliving biomass of marine algae has become interesting due to high adsorption capacities, low costs of the sorbent (Gavrilescu 2004). In fact, seaweed have been used for pharmaceutical reasons for detoxification of heavy metals in the human body due to a very efficient adsorption of the contaminants, and this effect could be used to remove heavy metals from industrial wastewaters. Different algae have been used in wastewater treatment in recent years (Jalali et al. 2002; Davis et al. 2003; Lodeiro et al. 2005; Tüzen et al. 2009). In particular, the brown algae have since proven to be the most effective and promising substrates for the removal of metallic cations (Davis et al. 2003; Pennesi et al. 2012; Sari and Tüzen 2009b). This capacity depends on their basic biochemical constitution that is responsible for this enhanced performance among biomaterials. More specifically, it is the properties of cell wall constituents, such as alginate and fucoidan, which are chiefly responsible for heavy metal chelation (Davis et al. 2003; Ghimire et al. 2008). Recent work has shown that brown algae are used successfully also in the removal of As(V). Hansen et al. (2006) have shown that arsenic biosorption capacity by *Lessonia nigrescens* Bory de Saint-Vincent is high and is pH dependent with the best arsenic sorption at low pH (2.5).

The wastewater treatment with synthetic resins often produces water contaminated by low concentrations of arsenic. To make wastewater acceptable for reuse or for returning to the environment, the concentration of contaminants must be reduced to a non-harmful level. In this study, we applied an innovative low-cost technique for the removal of low concentrations of As(V) from contaminated water through the use of nonliving biomass of marine algae (beach material). The objective of the present work was to assess what Phyla of algae accomplish the biosorption of As(V) better and to evaluate the influence of pH on this process.

Materials and methods

The biosorbent materials were obtained from eight species of seaweed and one species of seagrass. The seaweeds including several species belonging to the phylum Chlorophyta (*Ulva rigida* C. Agardh, *Caulerpa racemosa* J. Agardh), Ochrophyta (*Cystoseira compressa* Gerloff & Nizamuddin, *Dictyopteris polypodioides* J.V. Lamouroux and *Eisenia bicyclis* Setchell), and the Rhodophyta (*Gracilaria bursa-pastoris* P.C. Silva, *Ceramium ciliatum* Ducluzeau, and *Porphyra tenera* Kjellman). The seagrass was *Zostera marina* Linnaeus. Samples were collected from Italian beaches of the Adriatic Sea: Palombina, Portonovo, Passetto, Gabicce (Marche region; central Italy), and Torre Guaceto (Puglia region; south Italy). After collection, samples were extensively washed with deionized water to eliminate impurities and dried at room temperature for 3–4 days (until a stable weight was observed) and stored in bottles until use. Before biosorption tests, each dried biomass sample was reduced in small fragments (size fraction of 0.5–1 cm). Where specified, biomass was washed either in acid solution (HCl; pH 2) or in basic solution (NaOH; pH 10) for 4 h under vigorous stirring at room temperature, with a ratio solid/washing solution 1/10. Further drying was then performed and the biosorbent stored before biosorption tests.

Chemicals A concentrated arsenic solution was prepared by dissolving 150 mg of arsenic oxide (As_2O_5 analytical grade, Sigma Aldrich) in 1 L of deionized water. The solution was diluted according to the experimental design (see chapter 2.4).

Arsenic sorption test Before each test, 5 g of dried biomass was put in 100 mL of distilled water for 30 min in order to

Table 2 Factors and levels investigated in the study of As(V) biosorption at relatively low concentration (100 μg L^{-1})

Factor	Levels							
Macrophyte	*Porphyra tenera*		*Ceramium ciliatum*			*Eisenia bicyclis*		
pH	1	2	3	4	5	6	7	8

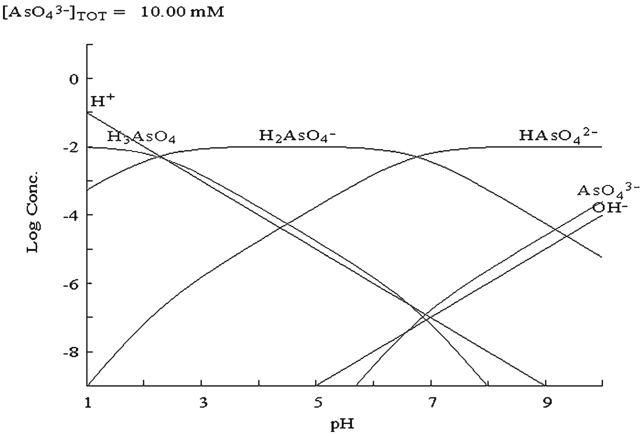

Fig. 1 Prediction of arsenic(V) speciation as a function of pH (Puigdomenech 2009)

rehydrate the biomass. At the beginning of the experiment, a known volume of the concentrated arsenic solution was added. The suspension pH was adjusted with 0.1 M HCl and 0.1 M NaOH and controlled during the whole biosorption test, according to the experimental conditions. One mL aliquots of test solution were sampled periodically and centrifuged for arsenic determination. As(V) uptake, q (mg g^{-1}), was calculated as the difference in metal concentration in the aqueous phase before and after sorption, according to Eq. A.1:

$$q = V(C_i - C)/W \tag{A.1}$$

where V is the volume of As(V) solution (L), C_i and C are the initial and concentration of As(V) in solution (mg L^{-1}), respectively, and W is the mass of dry seaweed (g).

Experimental design Tables 1 and 2 show factors and levels investigated. In the first experiments (Table 1), factors investigated were: macrophyte type, pH, and pre-treatment of biosorption material with acidic and basic solutions. The biomass was treated as follows: (1) only washing with deionized water; (2) acid washing (pH 2) to remove possible cations; and (3) basic washing (pH 10) to remove possible anions.

In the second series of experiments (Table 2) factors investigated were: macrophyte type and pH. For both series of experiments a full factorial design was implemented (Montgomery 2009).

Analytical determinations The pH measurements were made using a pH meter (ISteK 730p). All samples were diluted with HNO_3 at pH 2 and stored at 4°C before the analysis. Arsenic concentration in the liquid phase was determined by inductively coupled plasma atomic emission spectrometry (Jobin Yvon JY 24, method EPA200.7.2001).

Results and discussion

Nonliving marine algae are capable of heavy metals sorption from dilute aqueous solutions. Such sorbents have produced encouraging results; many works are present in the literature where sorption ability of marine macrophytes is demonstrated with cationic metals such as lead, cadmium, zinc, and chromium (Filho et al. 1999; Hashim and Chu 2004; Lodeiro et al. 2005; Pennesi et al. 2012; Seki and Suzuki 2002; Stirk and Van Staden 2000). The present work deals with arsenic biosorption where the metal speciation is different. In fact, it is known that arsenic is stable as anion, according to the solution pH. Figure 1 shows As(V) speciation as a function of pH, as predicted by the Medusa software (Puigdomenech 2009). It can be observed that the neutral species H_3AsO_4 predominates in the pH range 1–2, the negatively charged $H_2AsO_4^-$ in the pH range 3–6, and the bivalent negatively charged $HAsO_4^{2-}$ in the pH range 7–10. It is well-known that biosorption is based on physicochemical interaction between the metal and functional groups of the cell wall, such as ion exchange, coordination bond, and complexation (Niu et al. 2007; Vegliò and Beolchini 1997; Pennesi et al. 2012); consequently, the solution equilibrium pH is expected to have a key role on arsenic biosorption both influencing its speciation and functional groups availability.

Table 3 Arsenic-specific uptake (mg g^{-1}) of different marine macrophytes: effect of pH and washing pre-treatment

Pre-treatment	pH	*Ceramium*	*Ulva*	*Caulerpa*	*Dictyopteris*	*Zostera*
Deionised water	6	1.24±0.06	0.76±0.04	0.38±0.02	0.92±0.05	0.87±0.04
	7	1.08±0.05	0.59±0.03	0.41±0.02	1.00±0.05	0.72±0.04
	8	0.88±0.04	0.24±0.01	0.45±0.02	0.92±0.05	0.59±0.03
Acid solution pH 2	6	1.31±0.07	0.20±0.01	0.39±0.02	0.95±0.05	1.09±0.05
	7	1.21±0.06	0.14±0.01	0.39±0.02	0.61±0.03	0.89±0.04
	8	1.11±0.06	0.88±0.04	0.23±0.01	0.93±0.05	0.97±0.05
Basic solution pH 10	6	1.00±0.05	0.96±0.05	0.39±0.02	0.71±0.04	1.31±0.07
	7	1.12±0.06	0.94±0.05	0.83±0.04	0.65±0.03	1.28±0.06
	8	0.81±0.04	1.10±0.06	0.48±0.02	0.63±0.03	1.31±0.07

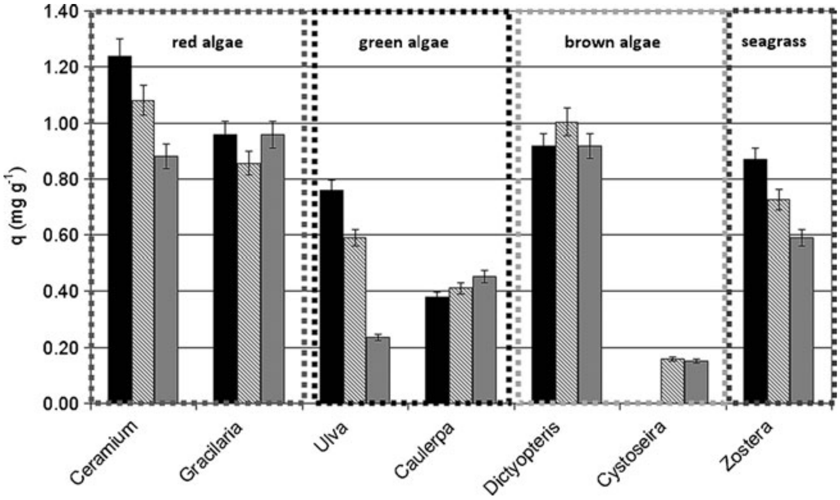

Fig. 2 Effect of equilibrium pH on arsenic-specific uptake by different macrophytes pretreated by washing with deionized water (arsenic initial concentration 10 mg L^{-1}, biosorbent 5 gL^{-1}, room temperature; pH 6 *black bars*, pH 7 *diagonal lines bars*, pH 8 *gray bars*)

The first series of experiments (Table 1) was aimed at assessing arsenic sorption abilities of different marine macrophytes at relatively high arsenic concentration (10 mg L^{-1}) considering biosorption as a tertiary treatment downstream of arsenic co-precipitation with iron. Main factors investigated were the macrophyte species, biosorbent pre-treatment, and equilibrium pH. The first factor was chosen in order to confirm what has been established elsewhere (Pennesi et al. 2012) for lead biosorption performances: brown algae>seagrasses> green algae>red algae: considering that arsenic speciation is different, dissimilar results may be achieved. Pre-treatment of the biosorbent would change its performance, modifying main counter-ions bound to the cell wall functional groups: simple washing by deionised water, protonation with acid (pH 2), and basic washing (pH 10) for anions substitution by OH^{-}, potential competitors with arseniate, were chosen as pre-treatment. The equilibrium pH is expected to affect sorption performances, as previously reported, both acting on arsenic speciation and functional groups availability: pH was in the range 6–8, simulating natural conditions after iron co-precipitation. Table 3 reports all the observed values for arsenic-specific uptake at equilibrium (60-min contact). Figure 2 shows the equilibrium specific uptake observed for different macrophytes and pH, when simple washing by deionized water was realized as sorbent pre-treatment. Figure 3 shows the effect of sorbents pre-treatment for the two species *Zostera* (seagrass; Fig. 3a) and *Ceramium* (red algae; Fig. 3b). It can be observed that in any case arsenic-specific adsorption did not exceed 2 mg g^{-1}, in the investigated range.Data reported in Fig. 2 and in Table 3 suggest also that all typologies of the investigated macrophytes exhibited significant adsorption: red, green, and brown algae and seagrasses. The worst arsenic sorbent was *Cystoseira* (Fig. 2), a brown alga which has shown very good lead sorption abilities (Pennesi et al. 2012). However, the other brown alga, *Dictyopteris*, showed a very good performance, comparable with the highest observed values of arsenic-specific uptake. The great divergence of the arsenic adsorption capacity between these brown algae (i.e., *Cystoseira* and *Dictyopteris*) suggests that not only functional groups on the cell wall play a key role, but also thallus structure; this may be particularly true for arseniate that has a steric structure bigger than simple metallic cations.

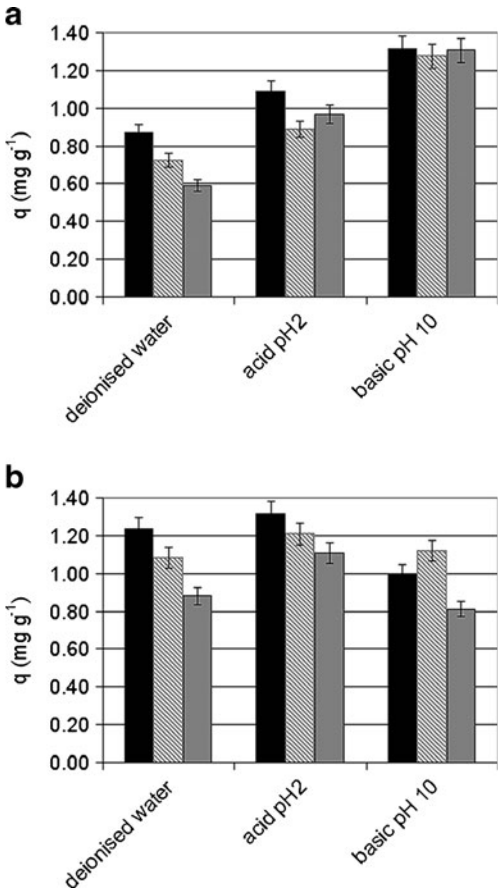

Fig. 3 Effect of biosorbent pre-treatment on arsenic-specific uptake by *Zostera* (**a**) and *Ceramium* (**b**) for different pH in the range 6–8 (arsenic initial concentration 10 mg L^{-1}, biosorbent 5 gL^{-1}, room temperature; pH 6 *black bars*, pH 7 *diagonal lines bars*, pH 8 *gray bars*)

Table 4 Output of the three-way analysis of variance

Source	df	MS	*F* value	*p* value
Macrophyte (A)	4	1.694	128.41	–***
Pre-treatment (B)	2	0.460	34.82	–***
pH (C)	2	0.014	1.10	ns
A×B	8	0.422	31.95	–***
A×C	8	0.075	5.69	–***
B×C	4	0.130	9.78	–***
A×B×C	16	0.090	6.85	–***
Residuals	90	0.013		

ns not significant, *df* degree of freedom, *MS* mean square

***$p<0.001$

Consequently, the poor sorption of *Cystoseira* is probably attributed to the bushy and arborescent thallus (Gerloff and Nizamuddin 1975), which may cause anchoring problems to arsenate ion due to steric obstruction. The achieved results also showed that red algae (i.e., *Ceramium* and *Gracilaria*), demonstrated to be very poor lead sorbents (Pennesi et al. 2012), seem to be good for As(V). With respect to biosorbent pre-treatment, data shown in Fig. 3a and b, suggest that its effect was not the same for the different materials: for example, a washing under basic conditions seems to enhance *Zostera* performance and to be ineffective for *Ceramium* sorption abilities. The results of analysis of variance (Table 4) revealed that both the effects macrophytes and the pre-treatment had a significant effect on arsenic-specific uptake, while the principal effect of pH was not statistically significant, in the investigated range of pH 6–8. On the other hand, the interactions among all the investigated factors were important, meaning that the effect of a factor (e.g., pH) changed when the level of others (e.g., pre-treatment) was different. This can be explained taking into account the effect on arsenic biosorption of many causes: the different composition of macrophyte cell wall, tallus structure, arsenic speciation, and functional group availability under different pH, eventual counter-ion interactions with arseniate. The second series of experiments (Table 2) was a detailed investigation on the pH effect in the range of pH 1–8 for red (*Porphyra*, *Ceramium*) and brown algae (*Eisenia*) for a relatively low initial arsenic concentration (100 μg L^{-1}) simulating a drinking water treatment. Figure 4 shows the estimated values for arsenic-specific uptake in all the experimental treatments. It is evident that arsenic sorption performance significantly decreases with pH, with the highest value around 7 μg g^{-1} for all the tested biosorbents at pH 1 and progressively lower values for pH varying from pH 2 to 8. Generally, red algae, previously reported known to be not good sorbents for cationic metals (Davis et al. 2003; Pennesi et al. 2012) were shown in the present work to have a good arsenic sorption performance, comparable with the other tested marine macrophytes. Similar results have been reported by Lee et al. (2000), concerning the adsorption of Cr(VI) by the red seaweed *Pachymeniopsis* sp. compared to brown and green seaweeds. In the case of negatively charged species, like As(V) and Cr (VI), sorption involves positively charged sites on the cell wall of seaweeds, as ammine groups, while many works in the literature (Davis et al. 2003; Ghimire et al. 2008; Pennesi et al. 2012) report the involvement of negatively charged groups, like carboxylic groups in cationic metals sorption: consequently, it is not strange to find different sorption performance for the two typologies of metals (cationic vs. anionic). Hashim and Chu (2004), observing the lower adsorption capacities of red seaweeds compared with brown and green seaweeds for metallic cations, also ascribed this to the presence of cationic sites on the wall of red algae, in the proteinaceous cuticles of their external surface (Graham and Wilcox 2000). Consequently, the better performance of red algae and the relatively poor one of brown algae can be explained by the abundance of positively charged amminic sites which attract

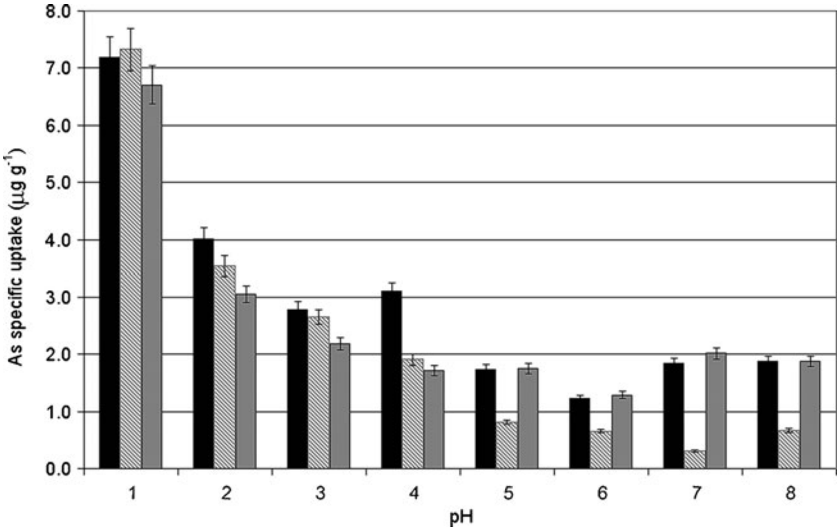

Fig. 4 Effect of pH on arsenic sorption by *red* (*Porphyra*, *Ceramium*) and brown algae (*Eisenia*) pretreated by washing with deionized water (initial As 100 μg L^{-1}, room temperature, sorbent 10 gL^{-1}; *Porphyra* (*black bars*), *Ceramium* (*diagonal lines bars*), *Eisenia* (*gray bars*)

arseniate and the scarcity of negatively charged carboxylic groups which act as repulsing agents for arseniate ions, and it is exactly the opposite for brown algae. Moreover, methyl groups of carrageenans in the red seaweeds lower the overall negative charge of the cell wall: therefore, the repulsive action to anions, like arsenate ions, is less significant than in the Ochrophyta and Chlorophyta. The action of methyl groups has been demonstrated by Seki et al. (2005) on methylated yeast. In fact, they have observed that the adsorption of Cr(VI) and As(V) increased with methylated carboxyl groups (and so the neutralization of such groups): that suggested the negative charge of carboxyl groups inhibited the adsorption/access of anions Cr(VI) and As(V). Concerning the effect of pH, it seemed to have a significant effect in the range pH 1–8; as previously reported it has influence both on arsenic speciation and on functional groups availability. Arsenic seems to be stable as a neutral H_3AsO_4 in the range of pH 1–2 (Fig. 1), as monovalent and bivalent anions in the pH range 3–8. Furthermore, a decrease of pH involves both a neutralization of negative charges on biosorbent's wall, as a consequence of a smaller dissociation of anion groups (COO^-), and an increase of positive charges due to protonation of ammine groups (NH^{4+}) (Zouboulis et al. 1999; Kefala et al. 2000). Both these events act towards a greater adsorption of anions. Sorbent pre-treatment by basic washing also was statistically significant for arsenic biosorption; nevertheless, its effect was different for the tested macrophytes and the tested pH. Generally, a basic pre-treatment removes eventual anions on

Table 5 Comparative evaluation of activated carbons and various low-cost adsorbents for arsenic removal

Adsorbent	pH	Concentration (mg L^{-1})	Temperature (°C)	Capacity (mg g^{-1})		References
				As(III)	As(V)	
Iron-oxide-coated sand	7.6	0.1	22	0.041	0.043	Thirunavukkarasu et al. (2003)
Activated carbon	6.4–7.5	157–737 As(V) 193–992 As(III)	25	29.9	30.48	Mohan and Pitmann (2007)
Orange juice residue	7–11 As(III) 2–6 As(V)	–	30	70.43	67.43	Akhter et al. (1997)
Fresh biomass	6	50–2,500	30	128.1	–	Kamala et al. (2005)
Red mud	7.25 As(III); 3.50 As(V)	2–30	25	0.884	0.941	Altundogan et al. (2002)
Immobilized biomass	6	50–2,500	30	704.1	–	Mohan and Pitmann (2007)
Tea fungal biomass	7.20	1.3 As(III) 0.9 As(V)	30	1.11	4.95	Murugesan et al. (2006)
Human hairs	–	0.090–0.36	22	–	0.012	Wasiuddin et al. (2002)
Chitosan/chitin mixture	–	–	–	–	0.010	Elson et al. (1980)
Water lettuce (*Pistia stratiotes* L.)	–	–	–	–	1.43	Basu et al. (2003)
Activated carbon from olive pulp and olive stone, carbon	7	5–20	25	1.393	–	Budinova et al. (2006)
Lessonia nigrescens (brown algae)	2.5	50–600	25	–	45.2	Mohan and Pitmann (2007)
Maugeotia genuflexa (green algae)	6	10 As(III)	20	57.48	–	Sari et al. (2011)
Xanthoria parietina (lichen)	6	25 As(III) As(V)	20	63.8	60.3	Sari and Tüzen (2010)
Inonotus hispidus (macrofungus)	6 As(III) 2 As(V)	10 As(III) As(V)	20	51.9	59.6	Sari and Tüzen (2009a)
Ceramium ciliatum (red algae)	6–8	10 As(V)	RT	–	0.88–1.24	Present study
Gracilaria bursa-pastoris (red algae)	6–8	10 As(V)	RT	–	0.86–0.96	Present study
Ulva rigida (green algae)	6–8	10 As(V)	RT	–	0.24–0.76	Present study
Caulerpa racemosa (green algae)	6–8	10 As(V)	RT	–	0.38–0.45	Present study
Dictyopteris polypodioides (brown algae)	6–8	10 As(V)	RT	–	0.92–1.0	Present study
Cystoseira compressa (brown algae)	6–8	10 As(V)	RT	–	0.0–0.72	Present study
Zostera marina (seagrass)	6–8	10 As(V)	RT	–	0.59–0.87	Present study

RT room temperature

adsorbent surface and replaces these anions with hydroxyl groups. The positive effect of such pre-treatment, where observed, can be ascribed to the removal of anions in competition with arsenic for the same binding sites. In fact, it has been observed that the presence of HCO_3^- and Cl^- in solution interfered with arsenate ions removal (Mohan and Pitmann 2007). On the whole, sorption of As(V) on biological materials is complex and involves different binding mechanisms: ion exchange, complexation, and electrostatic interaction. In view of the complexity of the composition of cell walls, it is possible that these adsorption's mechanisms occur simultaneously to different extent for the different macrophytes and pH (Haque et al. 2007). The key role of the cell wall structure may explain also the positive effect of the basic pre-treatment observed only for green seaweeds and seagrasses and not for brown seaweeds. In fact, the cuticle of seagrasses contains hydroxy acids that have a linear long chain, while the polysaccarides of brown seaweeds have either a cycle structure or a complex structure with a big steric obstruction and so it represents an obstacle for the adsorption. The green seaweeds have a cell wall mainly composed of cellulose and their cell wall structure is less complex than the cell wall of brown seaweeds (Graham and Wilcox 2000). Therefore, the basic pre-treatment results can be effective only if there is a simpler structure of the cell wall and a consequent poor steric obstruction, as in the case of the seagrass (i.e., *Zostera*), and the green seaweeds (i.e., *Caulerpa* and *Ulva*). Moreover, we cannot exclude that arsenic can interact with negatively charged groups: in fact, the possibility of interaction between carboxylic groups and arsenate ions for the geometric configuration of such ions in which the central atom of As(V) can be partially positive has been reported (Haque et al. 2007).

A further aim of this study was to assess in general the macrophyte arsenic sorption abilities. Table 5 compares the results observed in the present work with available data in the literature. It appears that the macrophytes used had good capacity adsorbents and are comparable with those of activated carbon and other low-cost adsorbents (e.g., *L. nigrescens*; Table 5) (Mohan and Pitmann 2007).

In conclusion, the present work assessed the performance of different nonliving macrophytes on As(V) sorption. All species of the investigated macrophytes exhibited significant adsorption: red, green, and brown algae and seagrasses. Furthermore, red algae known to be bad cationic metal sorbents, showed very good arsenic sorption performance. The equilibrium pH confirmed its key role on arsenic biosorption both influencing its speciation and functional groups availability in the range pH 1 to 8; it was however not significant in the range pH 6–8. It was also shown that in some cases, the morphology of the macrophyte influences the biosorption capacity (i.e., it decreases with thallus complexity), although at pH=1 such effect is canceled by the predominance of arsenic neutral form. The biosorbent acid washing did not significantly improve arsenic sorption, while it was reported elsewhere that a protonation of active sites for cationic metals sorption enhances biosorption performance (Pennesi et al. 2012). On the other hand, the effect of the basic washing was not the same for the different materials: it enhanced arsenic sorption of seagrasses and green seaweeds, while it was not significant for brown and red seaweeds.

As a whole these results have opened new perspectives for the utilization of marine macrophytes as low-cost sorbents in the removal of arsenic from wastewater.

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