RESEARCH ARTICLE

Do Lichens have the Ability to Remove Arsenic from Water?

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Abstract

Arsenic (As) contamination of groundwater is a serious threat to human health. Apart from anthropogenic sources, favorable geological conditions also result in elevation of the arsenic problem in Asia, especially in South East Asia. More than 100 million people in South East Asian countries especially Bangladesh, West Bengal (India), Vietnam, China, drink and cook with arsenic-contaminated water, which causes chronic health problems for a long time. A large number of mechanism for removing As from drinking water includes the use of filters, which differ in their efficiency and applicability. In the present study, we propose the use of biofilters prepared from lichen biowaste for removal of arsenic from contaminated water. Six lichen species were tested for the applicability as biofilters. The physicochemical analysis confirmed the presence of high elemental (C, N, H, O) content in the treated lichen species. It was observed that species having high elemental content were able to remove arsenic more effectively.

Keywords: Arsenic, Groundwater, Lichen biofilter, Lichens.

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Introduction

Arsenic (As) is a naturally occurring toxic element. Its toxicity, mobility, and bioavailability in the soil are highly dependent on pH and redox potential (Bajpai *et al.,* 2009; Shukla *et al.,* 2014; Aide *et al.,* 2016). Asia especially South East Asia has a problem of As contamination of groundwater as a serious threat to human health. Arsenic-contaminated water can cause skin lesions, internal cancers, respiratory illnesses, cardiovascular diseases, and neurological problems (Cheng *et al.,* 2010). Bangladesh and Northern India, including the states of West Bengal, Madhya Pradesh, Bihar, and some parts of Uttar Pradesh are facing consequences of arsenic contamination. Reason for arsenic leaching in groundwater is attributed to the excessive use of tube wells as safe surface water is scarce in the region. When the tube wells, pump groundwater through geological layers rich with arsenic, the toxic metal is leached and the infiltrated waters become polluted (van Geen *et al.,* 2005; Cheng *et al.,* 2010).

Various physicochemical and biological techniques have been applied to remove heavy metals from wastewaters. Biological treatment based on living or non-living organisms may reduce the level of toxic metals to environmentally acceptable limits in a cost-effective manner. The major advantages of biological treatment over conventional treatment methods also include high efficiency of metal removal from dilute solution, minimization of chemical and/or biological sludge, no additional nutrient requirement and regeneration of biosorbent (Yalçin *et al.,* 2010). Lichens have certain characteristics that make them ideal biomonitoring organisms worldwide because of the perennial nature, absence of root or other special organs for the uptake of nutrients and lack of cuticle which enable them to absorb metals directly from the atmosphere. The high capability of lichens to accumulate air pollutants, resistance to environmental stress and longevity are the other features that make them most suitable organisms for biomonitoring studies (Garty, 2001). Lichens have the capacity to absorb elements within their thalli due to the presence of extra and intracellular compounds having a rich diversity of functional moieties attached to carbon skeleton, widely recognized as lichen secondary compounds, while surface adsorption is facilitated by lack of cuticle, rough surface and unique morphological structures like Purina, surface hairs. In the present study, an attempt has been made to determine the effectiveness and suitability of waste lichens collected from the perfume industry to filter arsenic from contaminated water together with screening of suitable lichen species for arsenic removal.

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Materials and methods

The raw material of lichens was collected from the waste of perfume industries located in Kannauj district of Uttar Pradesh. The samples were segregated and identified by the following literature (Awasthi, 2000; Divakar and Upreti, 2005). A total of six species of lichens [*Heterodermia diademata* (Taylor) D.D. Awasthi, *Phaeophyscia hispidula* (Ach.) Essl., *Usnea longissima* Ach., *Roccella montageni* Bél., *Parmotrema tinctorum* (Despr. ex Nyl.) Hale and *Sticta* sp.] were segregated from approximately 1.0 kg of perfumery waste (taken from Kannauj, Uttar Pradesh; Singh *et al.,* 2015) which was used for further experiment. The samples were cleaned with deionized water and dried at 90°C for 48 hours in an oven followed by 10% sulphuric acid digestion to make a rough surface for maximum accumulation. Treated samples were finally washed with deionized water (thrice) and oven dried for final column filling (Ahmadpour and Do, 1997). After each filtration, the deactivated carbon was washed with deionized water to remove adsorbed arsenic and further reactivated at 60°C for 24 hour and process repeated five times.

Results and discussion

The principal of biofilters lies on the characteristic of biosorption by biological entities, which involves non-active metal uptake by biological materials by the process of adsorption and absorption including ion exchange, coordination, and complexation. Cell walls contain a large number of polysaccharides and proteins which comprise of many functional groups, such as carboxyl, hydroxyl, sulfate, phosphate, and amino groups, which have an ability to bind metal ions. Furthermore, the performance of a biosorbent depends on its surface characteristics, which can be changed by the modification process to improve the efficiency of the biofilters by treating it with different concentrations of acid. The use of raw and modified biosorbents for removal of metal ions has gained importance in recent years (Yalçin *et al.,* 2010).

In the present study, six lichen species were tested for their efficiency as biofilters for arsenic removal from arsenic contaminated water (Table 1). Since the permissible limit of Arsenic is 50 μg L^{-1}, therefore the study was conducted at the threshold, and the performance of each species as biofilters was analyzed for applicability of the method for arsenic removal; thus water solution containing 50 ppm concentration of arsenic was filtered through the activated (treated) lichens thallus. Results show that treated lichen species efficiently removed arsenic from the solution and in filtered water arsenic was below the detection limit. It was observed that till four cycles arsenic was below detection limit in filtered water (after each cycle lichens was washed with deionized water and charged) while the arsenic content kept on increasing in the acid treated lichen sample (lichen biofilter), but after the fifth cycle, trace of arsenic were detected in the filter too, which implies that treated lichens got saturated (Table 2). As it is well known that adsorption and absorption are the two phenomenon involved in the removal process. Adsorption is a surface phenomenon, while absorption involves chemical bonding. The elemental analysis shows the presence of the high amount of elemental carbon and oxygen in all the lichen species; therefore it may be inferred that elemental carbon and oxygen will have a tendency to form chemical bonding with the metallic ion, i.e. arsenic (Table 1). Washing of lichen biofilters with deionized water only removes adsorbed arsenic, but in order to remove chemically bonded, arsenic chemical treatment is further required. In a similar study conducted by Yalçin *et al.* (2010) biosorption of Cu and Zn onto raw and autoclaved fruticose lichens *Roccella psychosis*, it was found that the modification process affected the biosorption yield and metal uptake efficiency. The present study shows that the lichen biofilters may be applied more economically/ effectively for removing less contaminated water which will improve its performance (as it will increase cycles) and will be more economical for commercial utilization.

Table 1: Elemental analysis (weight %, dry basis) along with initial arsenic content in the lichen samples analyzed

		Element (%)				
Lichen taxa	*As μg g^{-1}dw*	*C*	*N*	*H*	*O*	*Total*
Heterodermia diademata	BDL	58	2.5	5.2	30	95.7
Phaeophyscia hispidula	BDL	45	1.2	6.8	41	94.0
Usnea longissima	BDL	25	3.8	2.4	48	79.2
Roccella montagnei	BDL	29	2.9	5.7	35	72.6
Parmotrema tinctorum	BDL	52	4.15	6.9	35	98.0
Sticta sp.	BDL	41	3.12	5.6	45	94.7
water	BDL	–	–	–	–	–
pH	7	–	–	–	–	–
Charcoal weight	1.0 gm of charcoal	–	–	–	–	–

Table 2: Arsenic concentration detected in thallus and filtered water in each cycle (I - VI) (values are in ppm).

	Ist Filtration		*IInd Filtration*		*IIIrd Filtration*		*IVth Filtration*		*Vth Filtration*		*VIth Filtration*	
Lichen taxa	*Thallus*	*Filtered water*	*Thallus*	*Filtered water*	*Thallus*	*Filtered water*	*Thallus*	*Filtered water*	*Thallus*	*Filtered water*	*Thallus*	*Filtered water*
Heterodermia diademata	30.06	0.00	48.38	0.00	75.38	0.00	106.38	0.00	132.57	2.23	149.28	7.67
Phaeophyscia hispidula	22.89	0.00	41.66	0.00	59.16	0.00	80.16	0.00	95.39	4.34	104.71	5.46
Usnea longissima	19.50	0.00	46.88	0.00	64.38	0.00	90.38	0.00	102.66	4.15	110.82	8.25
Roccella montagnei	18.50	0.00	46.09	0.00	73.09	0.00	99.09	0.00	112.87	3.75	123.41	7.06
Parmotrema tinctorum	39.83	0.00	45.52	0.00	75.02	0.00	108.52	0.00	139.06	2.82	147.58	8.58
Sticta sp.	34.24	0.00	44.79	0.00	68.79	0.00	94.29	0.00	75.21	4.30	89.30	7.64
Mixture of all species	27.48	0.00	35.95	0.00	48.45	0.00	58.95	0.00	67.86	2.64	82.45	4.39

Table 3: Efficiency, effectiveness, and sustainability of arsenic removal technologies.

S. No.	*Parameters to be considered for ideal removal technique (Ghosh and Singh, 2009)*	*Performance of activated lichen thallus*
1.	How simple the device is in use, and operation and maintenance?	Easy to maintain with low maintenance cost
2.	What is its removal efficiency?	Capable of removing 100% As with a concentration of 50 ppm till 4 cycles
3.	How much is the outflow rate and cost?	80 drop/min = 50 ml/min. One time cost of glassware
4.	How eco-friendly the device is?	Prepared from nontoxic plant-based waste obtained from perfumery industry
5.	What mechanism in operation and maintenance is devised?	Activated carbon adsorbs the As content which may be re-used after reactivation

Among the six lichen species, it was observed that species containing high elemental content removed higher arsenic content from contaminated water. *Parmotrema tinctorum* containing 98.05% of the total elemental content removed 39.83 ppm of arsenic, while *Roccella montagnei* having 72.6% of total content, removed 18.50 ppm of arsenic out of 50 ppm. Thus results indicate that filter efficiency is directly linked with elemental content. One of the reasons for high elemental content in lichens lies on the fact that apart from basic carbon skeleton, lichens are known to contain a high percentage of carbon-based secondary chemical (CBSC's) rich in electron donor functional groups. Secondary metabolites from lichens can comprise of up to 20% of the dry weight (Dayan and Romagini, 2001, 2002). In an earlier study also, it has been observed that microorganisms having arsenic oxidation and reducing genes is also capable of reducing arsenic toxicity under their favorable conditions.

Moreover, microbes prove the most effective way to detoxification of arsenic which may be due to the presence of secondary metabolites (Chattopadhyay *et al*., 2017). Biotransformation potential of arsenic among three different fungal strains of *Tricoderma, Pencillium*, and *Fusarium* revealed that Penicillium has highest biotransformation activity (Su *et al*., 2011)

The present study thus shows lichens as a valuable bioresource for removal of hazardous metal contamination. Biofilters prepared from lichens fulfills parameters to be considered for ideal removal technique and for use its application as biofilters (Table 3). The present study proposes lichens as potential and cost-effective biofilters, however more studies are required to be carried for standardization and optimization of the technique for commercial application.

Conclusion

The result shows that acid treated lichen biowaste may be regarded as potential biofilters for arsenic removal. Experimental analysis shows the effectiveness and suitability of the proposed biofilter. Further modifications are required to be investigated for its large scale commercial application for wastewater treatment.

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