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Short communication

Remediating industrial wastewater containing potentially toxic elements with four freshwater algae

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ABSTRACT

The present study was conducted to identify a cost effective method for removal of potentially toxic elements (PTEs) such as cadmium (Cd), chromium (Cr), lead (Pb) and nickel (Ni) from industrial wastewater (IWW), collected from Hayatabad Industrial Estate (HIE), Peshawar, Pakistan. For this purpose, four freshwater algae (*Cladophora glomerata*, *Oedogonium westii*, *Vaucheria debaryana* and *Zygnema insigne*) were used for the treatment of IWW. After treatment with algae, substantial decreases were observed in electrical conductivity (EC: 40.8–85.9%), biological oxygen demand (BOD: 7.3–52.4%), chemical oxygen demean (COD: 12.0–30.7%), total dissolved solids (TDS: 25.3–79%) and nitrate (13.5–76.8%) in IWW. Furthermore, the cultivation of algae increased the concentrations of dissolved oxygen (DO: 6.0–67.8%). The influence was greatly varied among the physicochemical parameters and increased with increasing the incubation time. The bioaccumulation potentials of algae such as *C. glomerata*, *O. westii*, *V. debaryana* and *Z. insigne* for selected PTEs were ranged from 22.5–80.3, 22.1–63.3, 9.10–92.1 and 17.4–93.0%, respectively. The effect of *C. glomerata* was highest for Cd (80.3%), whereas *O. westti* showed the highest removal capacity for Ni (66.3%). The influence of *V. debaryana* and *Z. insigne* were highest for Cr followed by Ni. This study revealed that phycoremediation is one of the environmentally friendly and economical feasible techniques used for IWW treatment.

1. Introduction

The rapid growth of industrialization and urbanization are considered as the major anthropogenic activities discharge potentially toxic elements (PTEs) in to environment from the last few decades (Khan et al., 2009). Different industries including textile, electroplating, mining, metal plating, storage batteries manufacturing, leather/tanning and steel discharge wastewater contaminated with high concentrations of PTEs such as Cd, Cr, Ni, Pb and Cu (Jahan et al., 2014; Xu et al., 2016).

Phycoremediation is a beneficial alternative technology used for the treatment of PTE contaminated water. The freshwater algae effectively remove PTEs from wastewater (Ajayan et al., 2015; Shamshad et al., 2015a). In living cells of algae, PTE sorption occurs through binding with the surface of cell and intracellular ligands. These ligand-bounded PTEs further accumulated by active biological transport (Kiran and Thanasekaran, 2011). The mechanisms for PTE removal depend upon different functional groups such as carboxylates, amines, and hydroxyls which form complexes with PTEs (Piotrowska-Niczyporuk et al., 2015) and reduce their concentrations in the treated media/water. The peptides of algae are also capable to form complexes with PTEs and later on these organo-metallic complexes separated in vacuoles for the purpose to regulate the concentrations of toxic metal ions in cytoplasm, which prevents the toxicological effects of PTEs (Cobbett and Goldsbrough, 2002). In the past, various studies have been demonstrated that algae improve the quality of wastewater and IWW by absorbing PTEs and nutrients such as nitrogen (N), phosphorous (P) and nitrate (NO_3) (Li et al., 2010; Shamshad et al., 2015a,b; Liang et al., 2015). Green algae have also shown high effectiveness on different physicochemical parameters such as total dissolved solids (TDS), dissolved oxygen (DO), biological oxygen demand

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(BOD), chemical oxygen demand (COD) and NO_3 (Malla et al., 2015; Sharma et al., 2014).

The PTE removal efficiency of algae vary from species to species and depends on various parameters such as pH, temperature, PTE concentrations and nutrient values of growing media, biomass of algae and its metabolic stage. Ajayan et al. (2015) reported that *Scenedesmus* has high potential for the uptake of PTEs (Cu, Cr, Zn and Pb) and can be used for phycoremediation of these PTEs present in wastewater. Previously, different published papers have demonstrated that several fresh water algae are capable to uptake PTEs from contaminated media and then accumulate in their bodies (Afkar et al., 2010). However, no one has worked on removal of PTEs through algae present in IWW generated by an industrial estate containing diverse types of production unites and industries. The present study was, therefore, aimed to quantify the efficiency of freshwater algae including *Cladophora glomerata*, *Oedogonium westii*, *Vaucheria debaryana* and *Zygnema insigne* for removal of PTEs present in IWW collected from Hayatabad Industrial Estate (HIE), Peshawar, Pakistan.

2. Materials and methods

2.1. Algae, collection and preparation

In this research work, four fresh water algae including *C. glomerata*, *O. westii*, *V. debaryana* and *Z. insigne* were collected from freshwater pond ecosystems, located in Islamia College University, Peshawar, Pakistan, and then properly washed as mentioned in our previous studies (Shamshad et al., 2015a). The clean algae were cultured and acclimated for 14 d in distilled water at temperature of 20 ± 3 °C. After 14 d, these acclimated algae were subsequently used for further experimental work.

2.2. Industrial wastewater (IWW) collection and analyses

Wastewater samples were collected from HIE (Peshawar, Pakistan) and processed as mentioned by Shamshad et al. (2015b) to remove the suspended solid materials. The IWW was analyzed for basic parameters such as pH, electric conductivity (EC), temperature, total suspended solids (TSS), and total dissolved solids (TDS), dissolved oxygen (DO) and biological oxygen demand (BOD_5) using the standard procedures adopted by American Public Health Association (APHA, 1992). Dissolved organic carbon (DOC) in IWW was measured using TOC analyzer (Shimadzo, Japan), while the concentrations of nitrate and sulfate were determined using water lab (DR/2010 HACH, USA). Further detail is given in Supporting Information (SI).

2.3. Experimental design

The remediation experiments were carried out in new plastic containers that were washed with diluted HNO_3 (10%) and finally with deionized water before use. Living algae such as *C. glomerata*, *O. westii, V. debaryana* and *Z. insigne* were added to the each plastic container. Two control treatments (one without algae and other used algae with distilled water) were run to confirm if something besides the algae could have affected the remediation of PTEs and other parameters. Each treatment was carried out in five replicates for 12 d under clean aerated environment at temperature of 20 ± 3 °C; light/dark duration of 14:10 h. The fluorescent lamps were used to provide light intensity of 3000 flux to these pots.

2.4. Extraction of PTEs

After harvesting, algae samples were dried and extracted for selected PTEs using a method mentioned by Rybak et al. (2012), detail is given in SI. PTE concentrations in the final extracts of algae were quantified using Atomic Absorption Spectrometer (Analyst 700 Perk Elmer). For precision and accuracy, the reagent blanks and standard reference materials were used in each batch. The plant reference material (GBW10015 (GSB-6)) was purchased from the National Research Center for Standards in China. The recovery rates of PTEs were satisfactory and ranged from 93.4 ± 6.2 to 103 ± 10.3%.

Table 1
Physicochemical properties of IWW collected from HIE, Peshawar, Pakistan.

Parameters	Mean ± STD[a]	PAK-NEQS[b]	USEPA[c]
pH	6.15 ± 0.2	6–10	6–9
EC ($\mu S\,cm^{-1}$)	863 ± 12	NA[d]	NA
Alkalinity ($mg\,L^{-1}$)	247 ± 11.5	NA	NA
DO ($mg\,L^{-1}$)	1.83 ± 0.5	4.0–6.0	NA
BOD5 ($mg\,L^{-1}$)	25 ± 4.7	80	10
COD ($mg\,L^{-1}$)	251 ± 10.6	150	4.0
Temperature (°C)	35.7 ± 4.4	40	NA
TSS ($mg\,L^{-1}$)	143 ± 5.4	200	5.0
TDS ($mg\,L^{-1}$)	462 ± 26.1	3500	500
Nitrate ($mg\,L^{-1}$)	31 ± 4.87	NA	0.1
Sulfate ($mg\,L^{-1}$)	143 ± 12.5	600	250
PTE concentrations ($mg\,L^{-1}$)			
Cd	1.48 ± 0.12	0.1	0.005
Cr	0.97 ± 0.07	1.0	0.01
Ni	0.85 ± 0.05	1.0	0.20
Pb	2.67 ± 0.13	0.5	0.015

[a] Standard deviations.
[b] Pakistan Environmental Protection Agency (2008).
[c] United States Environmental Protection Agency (2005).
[d] Not allocated.

2.5. Data analysis

Bioaccumulation of PTEs in algae and their removal efficiency were calculated, while the data were statistically analyzed using the statistical package (SPSS 16.0). See SI for detail.

3. Results

3.1. Characteristics of IWW

Table 1 summarizes the physicochemical characteristics of IWW collected from selected industrial estate. The pH value (6.15 units) was observed within maximum permissible limit (MPL) ranged from 6 to 10 set by Pakistan Environmental Protection Agency (Pak-EPA, 2008). The TSS contents ($143\,mg\,L^{-1}$) were observed below the limit ($200\,mg\,L^{-1}$) set by Pak-EPA but exceeded the MPL ($200\,mg\,L^{-1}$) set by USEPA (2005). Further detail about DO and BOD_5, COD NO_3 and sulfate concentrations is given in SI. The initial concentrations of PTEs such as Cd, Cr, Ni, and Pb in IWW were exceeded their respective MPLs set by USEPA (2005). However, the concentrations of Cr and Ni were within their respective MPLs set by Pak-EPA (2008), while Cd and Pb concentrations were exceeded the MPLs of Pak-EPA (Table 1, SI).

3.2. Effects of algae on physicochemical parameters

Fig. 1 shows the effects of selected algae on different physicochemical parameters. The data indicate that *C. glomerata* had significantly ($p < 0.01$) reduced EC (45.9–85.9%), BOD (13.0–33.2%) and COD (13.1–30.7%) during the incubation period. The contents of DO were increased with cultivation of algae and ranged from 14.2 to 64.5%. The influence of *O. westii* on EC, TDS, DO, BOD, COD, and nitrate was significant ($p < 0.05$) and increased with increasing the incubation time. Further detail is given in SI. In this study, *O. westii* effects were found lower than *C. glomerata*. The effects of *V. debaryana* on EC (40.8–76.7%), TDS (34.6–78.3%), DO (9.3–66.1%),