



Voltammetric detection of As(III) with *Porphyridium cruentum* based modified carbon paste electrode biosensor



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ABSTRACT

A novel biosensor based on carbon paste electrode modified with *Porphyridium cruentum* biomass was developed for the determination of As(III) in contaminated water. As(III) was first biosorbed–accumulated on the electrode surface at open circuit potential and then stripped off by applying anodic scan range of -0.8 to $+0.8$ V using differential pulse anodic stripping voltammetric technique. The best result was obtained at pH 6.0 with 0.1 M HNO₃ solution as stripping medium, allowing biosorption–accumulation time of 8 min using 5% *P. cruentum* biomass in graphite–mineral oil paste. Linear range for As(III) detection with the modified electrode–biosensor was observed between 2.5 and 20 $\mu\text{g L}^{-1}$. The FTIR spectrum of *P. cruentum* biomass confirmed the presence of active functional groups that participate in the binding of As(III). Scanning Electron Microscopy (SEM) indulged the surface morphology of modified electrode–biosensor before and after As(III) adsorption. Similarly, Atomic Force Microscopy (AFM) showed that the average roughness of the modified electrode decreased indicating the successful incorporation of *P. cruentum* biomass. Efficiency of the biosensor in the presence of different interfering metal (Na⁺, K⁺, Ca²⁺, and Mg²⁺) ions were also evaluated. The application of *P. cruentum* modified biosensor was successfully used for the detection of As(III) in the binary metal (Fe³⁺, Mn²⁺, Cd²⁺, Cu²⁺, Ni²⁺, Hg²⁺, and Pb²⁺) contaminated system. The accuracy of application of biosorption based biosensor for the detection of As(III) is as low as 2.5 $\mu\text{g L}^{-1}$.

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1. Introduction

Arsenic naturally exists in the earth's crust in low concentrations (Hussain et al., 2012). It has received much attention during recent years due to toxicity it may cause to humans (Bissen and Frimmel, 2003). The metalloid, on leaching from its geochemical formations, becomes a natural component of soil, water, and living organisms in a definite ratio (Mandal and Suzuki, 2002). Included among the anthropogenic origin of arsenic are insecticides (Welch et al., 2000), herbicides (Baker et al., 1969), wood preservatives (Bhattacharya et al., 2002), feed additives (Pergantis et al., 1997), and drugs (Bates et al., 1992), though its use in agrochemicals has been declining (Sanok et al., 1995). Arsenic may cause acute toxicity resulting in dysphasia, profuse diarrhea, dehydration, muscular cramps, and facial edema, or sub-acute toxicity as the

loss of appetite, erythema, jaundice, nervous weakness, and tingling of hand and feet (Jain and Ali, 2000; Choong et al., 2007). The element exists in the oxidation states of 0, -3 , $+3$, and $+5$ (Bissen and Frimmel, 2003). However, As(III) and As(V) are of greater significance due to their presence in the drinking water, which is regarded as the major route of inorganic arsenic entry into the human body (Khan and Ho, 2011). Depending on the groundwater pH, As(III) and As(V) may exist as the chemical species H₃AsO₃, H₂AsO₃[−], HAsO₃^{2−}, H₂AsO₄[−], H₃AsO₄, HAsO₄^{2−} and AsO₄^{2−} (Yan et al., 2000).

Most heavy metals exist in their cationic form and can be removed by conventional methods, including membrane filtration, precipitation, and ion-exchange (Arief et al., 2012). These methods, however, are not suitable for removing oxyanion forming elements such as arsenic (Dzombak and Morel, 1990). Arsenic removal is even more difficult as it has greater mobility under both the oxidizing and reducing conditions (Smedley and Kinniburgh, 2002). The process of biosorption, using the biomass of algae (Taboada-de la Calzada et al., 1998), bacteria (Stocker et al., 2003),

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fungi (Ridvan et al., 2003), and plant residues (Kamala et al., 2005) has been successfully used as an alternative for the removal of As(III) from water. The mechanism of this process is related to the ability of these biological materials to adsorb metal ions on their active sorption sites (Wang and Chen, 2009) mainly due to the presence of functional moieties, such as carboxyl, hydroxyl and amino groups on their surface (Volesky and Holan, 1995). The biosorption process is further useful as it performs efficiently at low metal levels, at which the conventional methods are not feasible, and is appropriately termed as 'metal-polishing' (Volesky, 2001). Most commonly used methods for the estimation of As(III) include UV–vis spectroscopy, inductively coupled plasma spectroscopy, hydride generation atomic absorption spectroscopy, and neutron activation analysis. Although these techniques are reliable for detection at low concentrations, they cannot be routinely used for *in-situ* analysis or screening as the instruments and their running and maintenance costs are high, and require trained technicians for their handling (Mays and Hussam, 2009). The field method used for arsenic detection in potable water is based on color development on mercuric bromide strips. This method has nevertheless given false results, specifically at levels below $70 \mu\text{g L}^{-1}$ (Stocker et al., 2003) and is thus not reliable for arsenic detection at a concentration below $10 \mu\text{g L}^{-1}$, a maximum permissible limit set by WHO for safe drinking water (WHO, 2006). An alternative method is electrochemistry-based, in which electrodes are used to measure, detect, and differentiate between various oxidation states of heavy metals (Mays and Hussam, 2009). The technique offers several benefits over others, such as simple sample preparation, easy to operate, and low in running and maintenance cost. However, commercial electrodes used for electrochemical As(III) analysis require extensive pretreatment and exhaustive adsorption or coating procedures that are time-consuming, costly and require technical handling skills (Giacomino et al., 2011). The ability of metal ions to interact with functional groups on the biomass surface, particularly at low concentrations, combined with the electrochemical technique offer the potential to develop a biosorption based biosensor for heavy metal analysis. Biosensors have been used in recent years for the detection of several metals (Yuce et al., 2010a; Alpat et al., 2008). Performance of biosensors has been further improved by using microorganisms as the electrode-modifying agents, as reported for the determination of Pb(II) with a biosensor modified with the biomass of *Rhizopus arrhizus* (Yuce et al., 2010b).

Pakistan is located in a region of arsenic-rich geochemical formations, which has resulted in high levels of arsenic in drinking water (Nickson et al., 2005). This alarming situation demands the development of a simple method for the estimation of arsenic in aqueous medium. The present study reports a low-cost, easy to make and operate, environment-friendly, and efficient sorption-based biosensor technique that uses the biomass of a unicellular red alga *Porphyridium cruentum* dispersed in a graphite–mineral oil paste made into a modified electrode. The main objective of the study was to develop a carbon paste electrode–biosensor able to detect As(III) in drinking water within the WHO limits of below $10 \mu\text{g L}^{-1}$. Various experimental conditions, such as deposition potential, pre-concentration time, pH of the arsenic-accumulating medium, biomass quantity, and metal ion concentration were optimized. The studies were further extended to investigate the working ability of biosensor in the presence of interfering alkali metal (AM) and alkaline earth metal (AEM) ions. The selectivity of the developed biosensor towards As(III) in the presence of other metal/heavy metal ions were also studied. The microalga *P. cruentum* (Rhodophyta) used in the present study to develop biosensor is one of the most widely studied microalgae due to its high contents of fatty acids, lipids, polysaccharides and pigment (Wijffels et al., 2013). However, its environmental application as

biosorbent/biosensor for the removal/detection from polluted water has not been studied yet. Therefore, present study is the first report of the use of *P. cruentum* to develop modified carbon paste electrode (PC-MCPE)–biosensor for the detection of As(III) in polluted water. This novel hand-made biosensor is expected to become a useful tool for arsenic-free water quality assurance in the arsenic-rich belt running through the developing-country region in south-Asia.

2. Materials and method

2.1. Chemicals

Mineral oil (light, white; Sigma-Aldrich, USA), graphite powder (7–11 μ particle size, 99%; Alfa Aesar, Germany), and analytical grade (Merck, Germany) AsO_3 , HCl, NaOH and HNO_3 .

2.2. Microalgal biomass production

Biomass used for the preparation of a modified carbon paste electrode–biosensor was of the unicellular red alga *P. cruentum* (CCAP 1380/1A) obtained from the Culture Collection of Algae and Protozoa, Switzerland. The microalga was grown in Erlenmeyer flasks in axenic culture in artificial sea water (ASW) medium (Jones et al., 1963). The pH of ASW medium was adjusted at 7.6. The culture flasks were incubated at $25 \pm 1^\circ\text{C}$ under cool white light continuous illumination ($75 \mu\text{E m}^{-2} \text{s}^{-1}$). After 25 day of growth, the microalgal biomass was harvested, washed with double-distilled water, freeze-dried, ground, passed through 250 μ particle size sieves, and stored in desiccators till further use.

2.3. Preparation of the microalgal biomass-based biosensor

Biomass quantity of *P. cruentum* was varied between 0.5% and 7.5% to optimize for maximum arsenic biosorption. The microalgal biomass was well-dispersed in appropriate quantities of graphite powder (64.25–67.25%) and mineral oil (28.25–32.25%) using pestle and mortar to obtain a homogenized paste of good consistency. A polyethylene plastic syringe (internal dia 5 mm \times 6 cm length) was chosen as the electrode body (Guo et al., 2011). Nozzle-tip of the syringe was removed with a razor blade before preparing the *P. cruentum*-modified carbon paste electrode (PC-MCPE). The biomass–graphite powder–mineral oil (B-GP-MO) paste was firmly packed into the syringe body and compressed with the syringe plunger to 1 cm height to make the modified sorbent-based biosensor. A copper wire (2 mm external dia \times 7 cm length) was inserted into the B-GP-MO paste inside the modified carbon paste electrode–biosensor body to allow the conductance of electric current. A schematic representation of this biosensor is shown as Fig. 1a. Electrical conductivity was checked using a multimeter. After preparing the modified carbon paste electrode–biosensor, its surface was smoothed and cleaned of any residual paste on the sidewalls using a shiny weighing paper. A fresh surface was obtained by removing some of the top-surface paste with the help of the syringe plunger. Unmodified carbon paste electrode (UMCPE) was prepared by mixing graphite powder (90%) and mineral oil (10%) only.

2.4. Experimental procedure

Electrochemical experiments were performed using a Reference 600 TM Potentiostat (Gamry, Germany) equipped with Gamry framework and Echem Gamry Analyst software to perform differential pulse anodic stripping voltammetry (DPASV). The equipment has three electrode cells containing supporting

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