A NEW BIOMATERIAL FOR REMOVAL OF ARSENIC FROM DRINKING WATER

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ABSTRACT

Arsenic is a carcinogen and a potential health hazard known to produce skin, bladder, and lung cancers. A very large segment of the population living in and around Lahore and other cities of the Punjab in Pakistan is facing a threat from contaminated ground water having dangerously high levels of arsenic. The present research has shown the biomass of Calotropis procera roots and aerial parts to bring the level of arsenic in arsenic contaminated water to the EPA standard within very short time and more effectively then biomass of roots and aerial parts of Pteris vittata and Eichhornia crassipes. The rate of removal of arsenic from contaminated water by roots of Calotropis procera was determined as a first step towards developing a safe, easy, indigenous and practical method of arsenic removal.

Key Words : Asclapiadaceae, Calotropis procera, Drinking water, Arsenic removal

INTRODUCTION

Arsenic has been categorized as a Group of carcinogen by the environment Protection Agency (EPA), which can cause cancers of skin, bladder, and lung. Arsenic contamination of drinking water has contributed to countless cases of chronic arsenic poisoning in countries such as Chile, Argentina, China, Taiwan, Bangladesh, and India. Thousands of people living in the cities of the Punjab and Sindh in Pakistan are also facing a threat from unsafe ground water drawn through tube-wells containing dangerously high levels of arsenic. So far, little tangible effort has been made at the official level to counter the problem and monitor and bring the level of arsenic in drinking water to the WHO and EPA standards of 10 parts per billion (ppb) effective since January, 2006. To bring the arsenic concentrations in drinking water to EPA standards various alternate technologies have been developed or adapted that are capable of removing arsenic to trace levels but all of them are not affordable by poor population of developing world. Removal of arsenic from water by phyto-remediation and phytoremediation by dried biomass present a promising field for further exploration and research. Plants like Water hyacinth (Eichhornia crassipes) and Chinese Brake fern (Pteris vittata L.) have been found to be accumulator of arsenic but till now no new method based on phyto remediation has effectively been devised and employed. In search of a simple, affordable and easy method of arsenic removal, we focused our research on three abundantly grown plants in Pakistan namely Calotropis procera, Pteris vittata and Eichhornia crassipes and discovered

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Calotropis procera to be an excellent source of arsenic removal from water. Found on roadsides, disturbed areas, *Calotropis procera* is an abundant wild plant in urban and rural areas of Pakistan. Due to its medicinal value, it has been most extensively investigated but its property of removal for arsenic was discovered and put to use for the first time.

**MATERIAL AND METHODS**

Selection of site

A small village Old Kahna situated at 28 kilometers from Lahore with a population of around 27000 was selected as a test site. Water from three sources was collected namely five wastewater ponds populated with *Eichhornia crassipes* (water lily), tap water from thirty houses and water from five tube wells used for irrigation, all randomly selected. The samples of water were collected in triplicate from each location in clean plastic bottles with screw cap and stored at 4°C. The water samples were tested in situ with Arsenic Testing Kit (Highly sensitive: range 0-500 ppb of As\(^{3+/5+}\)) Merck and average values of arsenic concentrations were reported (Table 1). All chemicals used were of analytical grades.

**Plant Material Work-up**

*Calotropis procera* and *Pteris vittata* were collected from Lahore College for Women University (LCWU) campus and specimen vouchers were deposited in the Herbarium of LCWU. The aerial parts and roots of each plant were washed with distilled water to remove the dirt and dried in an oven at 60°C for one hour, cooled to room temperature and grinded to a fine powder. 100 ml of water samples from each location were tested for arsenic concentration in triplicates without treatment with powdered plant material and after treatment with plant material for 50 minutes and average concentrations reported. The control was double distilled water. For determination of rates water sample of known arsenic concentrations were prepared with arsenic standard (Merck, 1000mg/L with Nitric acid)\(^9,10\).

**RESULTS AND DISCUSSION**

For the collection of contaminated drinking water samples, Old Kahna a small town about 28 Kilo meters from Lahore was selected. The water supply in this town is mostly from tube-wells installed in the houses. The water samples were collected in the month of March 2007 from different locations randomly selected to determine the extent of arsenic contamination in ground waters as well as surface water (Table 1).

Waste water samples were collected from five ponds situated on the main roadside leading to Lahore in triplicates from old Kahna, Lahore with profuse growth of *Eichhornia crassipes* showing very high arsenic contamination of 150-200 ppb (Fig. 1).

Sample-3 was tap water samples taken from 30 houses randomly selected with arsenic concentration ranging from 25-200 ppb (Fig. 2).

### Table 1: Concentrations of Arsenic in Water Samples collected from Old Kahna, Lahore (measured at 27°C)

<table>
<thead>
<tr>
<th>S.N</th>
<th>Water samples</th>
<th>Locations</th>
<th>No. of Locations</th>
<th>Average Concentrations of Arsenic</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Sample-1</td>
<td>Water pond</td>
<td>5</td>
<td>175-200 ppb</td>
</tr>
<tr>
<td>2</td>
<td>Sample-2</td>
<td>Tube well</td>
<td>5</td>
<td>75-100 ppb</td>
</tr>
<tr>
<td>3</td>
<td>Sample-3</td>
<td>Tap water</td>
<td>30</td>
<td>25-200 ppb</td>
</tr>
</tbody>
</table>
Fig-1: Concentration of Arsenic in Sample-1 drawn from 5 ponds of Old Kahna. (The error bars are standard error of the means from three replicates).

Fig. 2: Average concentration of Arsenic in Sample-2 drawn from 5 Tube wells of Old Kahna compared with EPA standard.
This variation in concentration of arsenic in tap water, most probably depended upon the depth of the sunken tube-wells in the respective houses and storage facilities. Water samples were collected in triplicate in screw-capped clean plastic bottles and stored at 4ºC. A number of abundant and locally available wild plants i.e., *Eichhornia crassipes* (Ponte-deriaceae), *Pteris vitata* (Pteridaceae) and *Calotropis procera* (Asclapiadaceae, were collected from university campus and a voucher specimen deposited in the University Herbarium.

**Determination of Minimum Efficient Concentration (MEC)**

To avoid the use of larger amounts of biomass, we determined the Minimum Efficient Concentration (MEC) of plant material for removing arsenic from 100 ml of standard arsenic solution (200 ppb) to a level of EPA standard (5 ppb) within 50 minutes (minimum time period required by minimum quantity of dried biomass to bring the level of arsenic to EPA standard) by repeated experimentations (Fig. 4). The results showed that 12 g of oven dried and grinded aerial parts of *Calotropis procera* lowered the level of concentration of arsenic by 97.1%, while only one third amount of dried roots (4 g) of this plant were required to achieve the same results.

The time period of 50 minutes could have been reduced correspondingly by using larger amounts of dried biomass but this would have resulted in disposal of larger waste material. The level of arsenic concentration in the same standard solution decreased by 97.5 % within the same time span of 50 minutes but the minimum amount of dried aerial parts and dried roots of *Pteris vittata* required was 16.0 g and 12.0 g respectively. The minimum dried mass for aerial parts of *Eichhornia crassipes* required were 20.0 g, which brought the level of arsenic contamination from 200 ppb to 25 ppb (88.5%) in 50 minutes. The minimum masses of dried roots of *Eichhornia crassipes* were 15 g (a decrease of 94.2%). These results showed that the dried roots of these plants were...
more effective arsenic remover than their aerial parts as lesser amounts of biomass was required. The biomass of dried roots of *Calotropis procera* was three times more effective than biomass of aerial parts and was a most efficient source of arsenic removal from contaminated water. *Pteris vittata* was also very efficient but its larger amounts were required as compared to *Calotropis procera*. While *Eichhornia crassipes* was the least efficient of the three selected plants. 

**Determination of rate of arsenic removal**

To accurately measure the rate of arsenic removal by these plants, solutions of 200 ppb were prepared from Arsenic standard (Merck) in double distilled water which also served as control. The MECs of dried and grinded aerial parts and roots of these selected plants were separately suspended in 100 ml of the solutions and arsenic concentration measured after 10, 20 and 40 minutes time intervals using a stopwatch.

By comparing the results (Fig 4) it was evident the rate of removal of arsenic by aerial parts of *Calotropis procera* was better than other two plants. Under similar conditions the roots of *Calotropis procera* decreased the arsenic concentrations from 200 ppb to 50 ppb, 40 ppb and 5 ppb after 10, 20 and 40 minutes time interval by 12 g which was the most efficient.

These observations not only revalidated the effectiveness of MECs for different concentrations, it was also shown that with double concentrations of arsenic in water, doubling of MEC of roots gave the desired results with *Calotropis procera, Pteris vittata* and *Eichhornia crassipes* except for the aerial parts of *Eichhornia crassipes* whose capacity of removal of arsenic deteriorated between 20-40 minutes (Fig 1). This led us to the
Fig. 5: Rate of removal of As by biomass of aerial parts of *Calotropis procera*, *Eichhornia crassipes* and *Pteris vitatta.*

Fig. 6: Rate of removal of As by biomass of roots of *Calotropis procera*, *Eichhornia crassipes* and *Pteris vitatta.*

Conclusion that biomass of the roots of *Calotropis procera* were the most efficient arsenic remover, we selected this to determine its pH dependence and arsenic binding capacity and make its commercial use safe.

**pH Profile for Arsenic Binding**

Batch pH profile experiments were conducted based on a procedure previously reported on\(^2\). In summary, a 250 mg sample of the biomass was weighed and washed twice deionized water to remove any impurities or biomolecules present in the biomass. Fifty ml of 0.01 M HCl were added to the biomass to obtain a tissue concentration of 5 mg/ml. The pH
of this suspension was adjusted to 2.0, and 2 ml aliquots of the suspension were added to three 5 ml tubes. Similarly, the pH of the suspension was adjusted to 3.0, 4.0, 5.0, and 6.0 and three, 2 ml aliquots were collected at each pH. The suspensions were centrifuged at 2800 r.p.m and the supernatants were collected in separate tubes.

An arsenic metal solution of 0.1 mM concentration was prepared and the pH adjusted to 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0. At each pH, 2 ml of the metal solution were added to the respective biomass pellet and supernatant. In addition, 2 ml of the metal solution at each pH were added to three tubes for controls. All the tubes were reacted on a rocker for one hour. The tubes were then centrifuged at 2800 r.p.m. for five minutes, and the supernatants of the pellets were collected in separate tubes. After recording the final pHs of the tubes, the metal content was determined using flame atomic absorption spectroscopy. As the pH of the solution increases from 2.0 to 6.0, the metal showed an increase in binding to the biomass with optimum binding (97.11%) occurring at pH 6.0 augmenting the previously proposed mechanisms$^{3,6}$.

Metal-binding capacity experiments are underway.

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