INTRODUCTION

In the process of human evolution, some of the key issues confronting today’s society are safe
guarding the natural environment and maintaining a good quality of life. However, a slight imbalance
in any equilibrium in the environment is bound to manifest itself in the form of pollution. Toxic
metals/metalloids are the important member of dirty dozen clubs of pollutants. The scale of the
problem is illustrated by the frequently used term “Mass Poisoning”. Despite strict environmental
rules and regulations for wastewater management, particularly in developing countries, industrial
effluents released into water streams contain heavy metals. Deterioration of water quality due to
presence of toxic heavy metals in environmental water resources introduced by industrial pollution is
a serious matter of concern today.

Long-term intake of drinking water with elevated arsenic concentrations can cause the expansion of
Arsenicosis, the collective term for diseases caused by chronic exposure to arsenic(Hamadani et al.
2010). Arsenic toxicity causes skin lesions, damage mucous membranes, nervous system,
The major arsenic species found in environmental samples are arsenite As (III), arsenate As (V),
ar senious acids (H$_3$AsO$_3$), arsenic acids (H$_3$AsO$_4$), dimethylarsinate, monomethylarsonate,
ar senobetaine and arsenocholine. Among the arsenic compounds, arsenite (III) is 10 times more toxic
than arsenate (V) and 70 times more toxic than methylated species(O’Day et al. 2005).

The commonly used procedures for removing toxic metal/metalloid from aqueous streams include
Oxidation, Ion exchange, Reverse osmosis, Nanofiltration and Adsorption. These currently
practiced technologies for removal of pollutants from industrial effluents appear to be inadequate,
creating often-secondary problems with metal bearing sludge, which are extremely difficult to dispose
off. These conservative methods used for abatement of toxic metal/metalloid are as well often limited
because of technical, economical and environmental constraints(Johnston et al. 2001, Malik et al.
2009).

To combine technology with environmental safety is one of the key challenges of the new
millennium(Hoque at al. 2006). Biosorption is one of the phenomenon’s, which is based on one of the
twelve principles of green chemistry using renewable resources from biomaterials under the domain
of Green Technologies and can be defined as the ability of biological materials to accumulate heavy
metals from wastewater through metabolically mediated or physico-chemical pathways of uptake
(Ahalya et al. 2003). Bioremediation involves processes that reduce overall treatment cost through
the application of biomaterial which are particularly attractive as they lessen reliance on expensive
water treatment chemicals, negligible transportation requirements and offer genuine, local resources
as appropriate solutions to tackle local issues of water quality problems(Katsoyiannis et al. 2004).
In recent years, it is realized that biomaterials have been found to be associated with less sorption efficacy and stability, restricting their commercial use. Research interest has been focused on increasing the sorption capacity of the biomaterials through physical and chemical methods. Consequently, the major challenge for the biosorption processes was to select the most promising types of biomaterial from an extremely large pool of readily available and inexperience biomaterials.

The development of nanotechnologies is nowadays on the “crest of the wave” and has valuable contribution in science and technology which can make global dimensions for social and economic benefit. Latest progress is in the development of Green nanotechnology for solving many of the current problems involving water quality. Nanoparticles exhibit good adsorption efficiency especially due to higher surface area and greater active sites for interaction with metallic species.
A vigorous survey of the literature on the topic at International and National level has been conducted and presented in a concise manner.

**Biosorption; An emerging trend:** Bioremediation becomes a promising process to remediate the environmental pollutants (Vasudevan et al. 2001). It has many advantages like environmental friendly, good performance, possible recycling and low cost for remediation of toxic metals/metalloids. A range of plant biomaterials have been reported for efficient remediation of arsenic from water bodies.

| Plant Biomaterial used so far for remediation of Arsenic                  | As (III) | As (V) | As (III) & As (V) | As (III) | As (III) & As (V) | As (V) | As (V) | As (III) | As (III) & As (V) | As (V) | As (V) | Arsenic | As (III) | As (III) | As (III) & As (V) | As (V) | As (V) | Arsenic | As (III) | As (III) | As (III) & As (V) | As (V) | As (V) | Arsenic | As (III) | As (III) | As (III) & As (V) | As (V) | As (V) | Arsenic | As (III) | As (III) | As (III) & As (V) | As (V) | As (V) | Arsenic | As (III) | As (III) | As (III) & As (V) |
|------------------------------------------------------------------------|----------|--------|------------------|----------|------------------|--------|--------|----------|------------------|--------|--------|---------|----------|----------|------------------|--------|--------|---------|----------|----------|------------------|--------|--------|---------|----------|----------|------------------|--------|--------|---------|----------|----------|------------------|
| *Portulacaoleracea*                                                     |          |        |                  |          |                  |        |        |          |                  |        |        | Vankar & Tiwari, 2002 |
| Water lettuce                                                          |          |        |                  |          |                  |        |        | Basu et al. 2003 |
| Orange waste                                                           |          |        |                  |          |                  |        |        | Ghimire et al. 2003 |
| Cupresus Female Cone                                                   |          |        |                  |          |                  |        |        | Murugan & Subramaniam, 2004 |
| *Garcinia cambogia*                                                    |          |        |                  |          |                  |        |        | Kamala et al. 2005 |
| Unmodified and modified sawdust                                        |          |        |                  |          |                  |        |        | Igwe et al. 2005 |
| Cellulose Loaded Iron Oxyhydroxide                                     |          |        |                  |          |                  |        |        | Guo et al. 2005 |
| Methylated yeast biomass                                               | Arsenic  |        |                  |          |                  |        |        | Seki et al. 2005 |
| Sorghum biomass                                                        | As (V)   |        |                  |          |                  |        |        | Haque et al. 2005 |
| Chitosan                                                               | As (III) |        |                  |          |                  |        |        | Kartal & Imamura, 2005 |
| Coconut fiber                                                          | As (V)   |        |                  |          |                  |        |        | Igwe & Abia, 2006 |
| Powdered chitosan                                                      | Arsenic  |        |                  |          |                  |        |        | Chen & Chung, 2006 |
| Rice husk                                                              | As (III) | As (V) |                  |          |                  |        |        | Amin et al. 2006 |
| Bio-char                                                               | Arsenic  |        |                  |          |                  |        |        | Mohan et al. 2006 |
| Jute leaf, sugarcane powder                                            | As (V)   |        |                  |          |                  |        |        | Islam et al. 2007 |
| Bone char                                                              | As (V)   |        |                  |          |                  |        |        | Chen et al. 2008 |
| Banana peel                                                            | As (V)   |        |                  |          |                  |        |        | Memon et al. 2008 |
| *Piceaabies*                                                           | As (V)   |        |                  |          |                  |        |        | Urik et al. 2009 |
| *Withaniafrutescens*                                                   | As (III) |        |                  |          |                  |        |        | Chiban et al. 2009 |
| *Pteriscittata*                                                        | As (III) | As (V) |                  |          |                  |        |        | Wang et al. 2011 |
| Seaweed                                                               | As (III) | As (V) |                  |          |                  |        |        | Llorente-Mirandes et al. 2011 |
| Water hyacinth                                                         | As (III) | As (V) |                  |          |                  |        |        | Mahamadi, 2011 |
| Tea Waste                                                              | As (III) |        |                  |          |                  |        |        | Shaikh et al. 2011 |
| *Carpobrotusedulis*                                                    | As (III) | As (V) |                  |          |                  |        |        | Chiban et al. 2011 |
| Farm Rice                                                              | Total As |        |                  |          |                  |        |        | Rezaitabar et al. 2012 |
| Palm bark biomass                                                      | As (III) |        |                  |          |                  |        |        | Kamsonlian et al. 2012 |

**Cellulose; An important cost effective biosorbent:** As the most important skeletal components (Park et al. 2010, Teixeira et al. 2010) in plants, the polysaccharide cellulose is an almost inexhaustible polymeric raw material with fascinating structure and properties (Abdel-Halim et al. 2012, Coseria et al. 2012). It is formed by repeated connection of D-glucose building blocks (Ping and You-Lo, 2010). It is highly functionalized (Kim et al. 2007, Lee et al. 2011, Pahimanolis et al.
linear stiff-chain homo polymer is characterized by its hydrophilicity, chirality, biodegradability, broad chemical modifying capacity (Gilberto et al. 2010). Its formation (Sadeghifar et al. 2011) of versatile semi crystalline fibers morphologies due to sensitivity toward the hydrolysis and oxidation of the chain forming acetal groups, determine its chemistry, handling, environmental friendly and biocompatibility (Peng et al. 2011). Chemical reactivity is largely a function of the high donor reactivity of the OH groups (Klemm et al. 2005). The Degree of polymerization of native cellulose from various origins can fall in the range 1000 to 30,000, which corresponds to chain lengths from 500 to 15000nm (Ioelovich, 2012).

**Nano cellulose; Natural green resource:** Nanomaterials derived from renewable biomaterials, especially cellulose and lignocelluloses, will undoubtedly play a large role in the nanotechnology research effort (Dongping et al. 2007, Donia et al. 2012). Nanocellulose is a kind of natural green resource. A polymer composed of cellulose nanofibres (1-100nm) (Lu et al. 2010, Korotkov et al. 2012), whose functional properties are determined by the fibril structure is called Nanocellulose (Zimmermann et al. 2010, Antczak et al. 2012). Strengthening of functional groups in the biomaterial may lead to the designing of novel biomaterial with enhanced sorption efficiency and stability (Habibi et al. 2010, Hashaikeh et al. 2011).

The exhausted survey of the literature indicates:

- **Special emphasis is required to enhance sorption efficiency and environmental stability of biosorbents making them viable for commercial use.**
- **Abatement of arsenic has been largely attempted using inorganic coagulants. Not much attention has been paid on decontamination of arsenic using organic biomaterials.**
- **For the abatement of arsenic species advancements have been made on to inorganic nano materials. Toxicity issues of such compounds in health have been raised recently.**
- **Organic nanoparticles can easily be functionalized with various chemical groups to increase their affinity towards target species. The complexity of organic materials represents the achievement of structural order over many length scales with the full structure developed from the nested levels of structural hierarchy, in which self-assembled organic materials can form templates.**
Cellulose is most abundant and low cost renewable polymer resource for the sorption of cationic species and need modifications for the sorption of anionic species (Dieter et al. 2005).

No attention has been paid on the physico-chemical interaction of arsenic and cellulose which is strongly required for explaining the mechanistic aspects of different species of arsenic sorption.

<table>
<thead>
<tr>
<th>Functionalization on Cellulose/ Nanocellulose</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Type of modification</strong></td>
</tr>
<tr>
<td>Grafting of PEG-NH₂ of Nano cellulose</td>
</tr>
<tr>
<td>Grafting on Cellulose</td>
</tr>
<tr>
<td>Silylation</td>
</tr>
<tr>
<td>Silylation of Nano cellulose</td>
</tr>
<tr>
<td>Silylation</td>
</tr>
<tr>
<td>Acetylation of Nano cellulose</td>
</tr>
<tr>
<td>TEMPO oxidation of Nano cellulose</td>
</tr>
<tr>
<td>Fluorescently labelled NCC</td>
</tr>
<tr>
<td>Cationisation of Nano cellulose</td>
</tr>
<tr>
<td>Grafting of Nano cellulose</td>
</tr>
<tr>
<td>Grafting of Nano cellulose</td>
</tr>
<tr>
<td>Grafting of Nano cellulose</td>
</tr>
<tr>
<td>Grafting of Nano cellulose</td>
</tr>
<tr>
<td>Grafting</td>
</tr>
<tr>
<td>Esterification of Nanocellulose</td>
</tr>
<tr>
<td>Surface acetylation of Nanocellulose</td>
</tr>
<tr>
<td>Esterification of Nanocellulose</td>
</tr>
<tr>
<td>Silylation of Nanocellulose</td>
</tr>
<tr>
<td>Graft Copolymerization</td>
</tr>
<tr>
<td>Graft Copolymerization</td>
</tr>
<tr>
<td>Graft Copolymerization</td>
</tr>
<tr>
<td>Grafting of cellulose</td>
</tr>
<tr>
<td>Silane treatment of short cellulose fibres</td>
</tr>
<tr>
<td>Acetylation</td>
</tr>
<tr>
<td>Grafting of Nanocellulose</td>
</tr>
<tr>
<td>Amination of Nanocellulose</td>
</tr>
<tr>
<td>Carboxymethylation</td>
</tr>
<tr>
<td>Grafting onto cellulose microspheres</td>
</tr>
<tr>
<td>Grafting of Nanocellulose</td>
</tr>
</tbody>
</table>
OBJECTIVES

To convey the technology with the harmony of natural environment is the key challenge of this millennium. The treatment of environmental troubles requires discovery of newer, cost effective and eco-friendly methods based on biomaterials, using renewable resources. Functionalization of biomaterials for the waste water treatment is in great demand.

Keeping above views in mind, the present piece of work addresses the functionalization of cellulose/nanocellulose to enhance the sorption efficacy for arsenic species from water bodies.

It is proposed to carry out the present work with the following specific aims:

- **Functionalization** (*Grafting* through the combination of Periodate oxidation and reductive-amination reaction, *Silylation* with Aminosilane, *Cationization* using Epoxy propyl trimethylammonium chloride, EPTMAC and Epoxypropyl N-methylmorpholinium chloride, EPMMC and *Amination* by Ethylenediamine) in laboratory batch conditions and standardization of the optimum conditions for the evaluation of sorption efficiency of cellulose/nano cellulose for anionic arsenic species, As(III) and As(V) from water bodies.

- **Designing of functionalized cellulose/nano cellulose Filter aid** (Tea bags and non-woven Poly Propylene bags) to be used in arsenic remediation from water bodies.

- **Application of functionalized cellulose/nano cellulose material as filler in small bags for decontamination of arsenic in real waste water treatment.**
PLAN OF WORK

- Preparation of cellulose powder from wood pulp using green methods of enzymatic treatment and its functionalization, making it suitable for the sorption of anionic arsenic species [Designing of biomaterial for arsenic sorption].

- Preparation of nano cellulose from cellulose powder, its characterization for nano-scale particle size, morphology and structure (SEM, TEM, FTIR, XRD and TGA) followed by functionalization to enhance the sorption efficiency [Nanotech and Synthetic Enhancement in arsenic sorption efficiency].

- Standardization of the optimum conditions for the evaluation of sorption efficiency of functionalized cellulose/nanocellulose for anionic arsenic species (As III and As V) from aqueous system as a function of biomass dose, concentration of arsenic species, initial volume, contact time and pH [Process Optimization].

- Characterization of functionalized cellulose/nanocellulose to highlight the mechanistic aspects of sorption on the basis of the records of BET surface area, XRD, SEM, FTIR and TGA etc. [Academic interest].

- Regeneration of arsenic loaded tailored biomaterial by green eluting agents for its reusability [Cost effectiveness].

- Designing of functionalized cellulose/nanocellulose filter aids in small bags of non-woven poly propylene material for the use in arsenic remediation from water bodies [Decontamination of arsenic at Commercial scale].
METHODS AND METHODOLOGY

Proposed plan of work is depicted schematically as follows.

A. Preparation of Cellulose Powder from Wood pulp (Moran et al., 2008)

- Soak wood pulp in water followed by digestion with Caustic solution under controlled conditions of Time and temperature
- After the digestion process, material is washed and brought to pH 7
- Neutral pulp is treated with Cellulase enzyme in controlled pH, concentration, time and temperature
- At the end of the reaction, material is washed and cellulose powder is dried in fluid bed drier

B. Preparation of Nanocellulose from Cellulose Powder (Iovelich, 2012)

- Cellulose mixed with water
- Slowly added conc. Sulphuric acid
- Beaker placed into water bath at temp. 60-70 °C & heated at stirring up to 3 h.
- Cellulose sediment will be washed with water repeatedly
- Dried at 50 °C
- Water dispersion of Nanocellulose would be evaporated in vacuum at 80 °C.
C. Functionalization of Cellulose/Nano cellulose using standard reactions

I. Grafting through Periodate oxidation and reductive-amination scheme

II. Silylation with Aminosilane
III. Amination with Ethylenediamine

1. Cellulose/nano cellulose dissolved in distilled water
2. Potassium peroxydisulphate will be added as an initiator and kept under stirring
3. After 10 min 1.0 g of acrylamide will be added and stirred for 90 min. at 50°C and washed with deionised water dried at 50°C
4. After proper pH adjustment, the aminated cellulose/nanocellulose purified by washing with deionized water, and then dried in a vacuum oven at 50°C
5. Ethylenediamine will be added and refluxed for 8 h

IV. Cationization using EPTMAC and EPMMC

1. Cellulose/nano cellulose alkalinized with 5% NaOH with the ratio of 1M OH group equivalent to 1.5M NaOH for 15 min at room temperature with stirring
2. EPTMAC or EPMMC (1.5 equiv/cellulose hydroxyl group) will be added into suspensions, which then alkalinized by NaOH treatment and the mixture will be stirred for 5 hours
3. Suspensions will be sonicated and concentrated by reduced pressure evaporation in the room temperature
4. After 5 hours, the reaction will be quenched by water and diluted to 5-fold and dialyzed against distilled water for 5 days
D. Experimental conditions for sorption

Sorption efficiency at laboratory scale using standard practices would be carried out in batch experiments under various experimental conditions.

E. Standardization and characterization of arsenate and arsenite, Cellulose/Nanocellulose interactions for the evaluation of sorption and regeneration efficiency.
The preparation of functionalized cellulose/nanocellulose may lead to the formation of need based tailored biomaterial having enhanced sorption efficacy and environmental stability. Process development based on the use of Nanocellulose is deemed to be a strong foundation for the development of cost effective, ecofriendly, green nanotechnology for removal of Arsenic species from waste water particularly for rural and remote areas as a pretreatment step of waste water treatment. Functionalized cellulose/nanocellulose could be a potential challenge for inorganic materials.


