

CONCENTRATION AND REMOVAL OF ARSENIC USING SULFATE REDUCING BACTERIA (SRB)

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DEPARTMENT OF BIOCHEMICAL ENGINEERING AND BIOTECHNOLOGY

INDIAN INSTITUTE OF TECHNOLOGY DELHI

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by

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DEPARTMENT OF BIOCHEMICAL ENGINEERING AND BIOTECHNOLOGY

Submitted

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to the



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Certificate

This is to certify that the thesis entitled “**Concentration and Removal of Arsenic using Sulfate Reducing Bacteria (SRB)**” being submitted by **Mr. Satyendra Singh** is worthy of consideration for the award of the degree of **Doctor of Philosophy**. The thesis has been prepared under our supervision and guidance in conformity with the rules and regulations of **Indian Institute of Technology Delhi** and is a record of the original bonafide research work. The results presented in this thesis have not been submitted in part or full to any other universities or institutes for the award of any other degree or diploma.

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Abstract

Abstract

The demand of drinking water is increasing day by day. Contamination of drinking water by natural and anthropogenic activities is increasing the scarcity of safe drinking water. The drinking water polluted with arsenic has always been a major concern for environment and society. The development of an economic and eco-friendly process to address the problem has always been a challenge. The presence of metalloid arsenic in ground water and in potable water has a serious impact on human health. In the earth's crust, arsenic is twentieth most abundant element. The ground water gets arsenic contamination naturally during different geological activities such as eruption of rocks. The arsenic contamination in surface water is created by human activities like improper use and disposal of mining waste, industrial waste and arsenical pesticides.

Arsenic contamination of ground water needs more attention of environmental and process engineers for its removal. Separation of arsenic from drinking water can be done by restricting its mobility by changing it from one form to another. There are many unit operations available to address the issue of arsenic removal from water. Conventional chemical methods like coagulation, adsorption and precipitation are practiced to remove it from water. Oxidation to a less harmful state, arsenic (V), using chemical or biological conversion from its most toxic form, arsenic (III), is another approach for its removal. Ion exchange and membrane filtration are also promising treatment options. Among all the above mentioned processes, membrane based arsenic removal process is the most efficient and economic.

The present study was performed under a broad objective of arsenic removal from ground or potable water with higher recovery of arsenic-free drinking water using polymeric membrane based separation process and safe release of membrane generated

concentrate biologically, in the form of arsenic sulphide (As_2S_3), which was performed separately in a bioreactor with the help of sulfate reducing bacteria (SRB). The polyacrylonitrile (PAN) based modified & poly (4-styrenesulfonic acid) (PSSA) ultrafiltration (UF) membrane and other commercial nanofiltration (NF) membranes were tested for arsenic removal or its concentration. All these membranes were tested for different chemical parameters and membrane filtration parameters for optimum removal of arsenic. The pH of the feed solution played a major role on arsenate ion separation through charged ultrafiltration (UF) membranes. The membranes were subjected to arsenic concentrations in the feed ranging from 250 ppb to 50 ppm to test the removal efficiency and other process limiting parameters like concentration polarization. Among all the tested membranes, polyacrylonitrile (PAN) based modified ultrafiltration membrane showed maximum ($> 95\%$) rejection at $\text{pH} \geq 7$ in low TDS, arsenic spiked, synthetic water. The arsenic removal mechanism through polyacrylonitrile (PAN) based modified ultrafiltration membrane followed Donnan exclusion principle.

The polyacrylonitrile (PAN) based modified ultrafiltration membrane was further subjected to test its efficacy for arsenic removal in high TDS (~ 700 ppm) potable water. Filtration of arsenic spiked high TDS water resulted in increased flux and reduced arsenic rejection as low as 4- 6%. The presence of hardness causing minerals, calcium and magnesium were found to be the main culprit for reversibly changing the modification properties of the PAN membrane. It was observed that presence of 50 ppm calcium and magnesium ions reduced arsenic rejection by 20 % and 10% respectively. The other monovalent and divalent naturally occurring co- and counter-ions did not show significant effect on arsenic removal (85-92%). The higher operating transmembrane pressure (up to 10 kg/cm^2) did not improve the arsenic rejection

(~96%). In the arsenic concentration mode operation, the arsenic got concentrated 8.5 fold and volumetric concentration ratio (VCR) 10.3 fold with an average rejection of 97%.

The remediation study demonstrated that the arsenic concentration of greater than 30 ppm is toxic to microbial community specially lactate utilizing SRB. The real time PCR (qPCR) data also confirmed that up to 30 ppm of arsenic was not inhibitory to the microbial community. The optimum pH for bio-precipitation of arsenic to arsenic sulphide was 6.5 at which 20 ppm arsenic got removed by precipitation and adsorption. 81 and 19% arsenic removal were obtained by precipitation and adsorption, respectively. The continuous stirred tank reactor (CSTR) operation showed that without adjusting the reactor pH, maximum 67% arsenic removal was achieved at steady state operation of CSTR at 3 days hydraulic retention time (HRT).

The results of this research work for the first time showed that making arsenic free ground or potable water using modified PAN based ultrafiltration (UF) membrane and followed by restricting the mobility of membrane concentrated arsenic by biologically converting it into arsenic sulphide is possible. The process technology based on this research findings is significantly advantageous (economic and eco-friendly) compared to existing technologies for complete arsenic removal from ground or potable water.

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Abbreviations

AAS	- Atomic absorption spectroscopy
AS-DV	- Auto sampler- DV
ASRS	- Anionic self-regenerating suppressor
CSTR	- Continuous stirred tank reactor
Da	- Dalton
DAD	- Diode array detector
DGGE	- Denaturing gradient gel electrophoresis
DNA	- Deoxyribonucleic acid
<i>Dsr</i>	- Dissimilatory sulfate reductase gene
EDTA	- Ethylenediaminetetraacetic acid
FPD	- Flame photometric detector
<i>FTHSF</i>	- Formyltetrahydrofolate synthetase gene
FTIR	- Fourier transform infrared spectroscopy
GC	- Gas chromatograph
HPLC	- High pressure liquid chromatograph
HRT	- Hydraulic retention time
IC	- Ion chromatograph
ISI	- Indian Standard Institute
LMH	- Litre meter ⁻² hour ⁻¹
MEUF	- Micellar-enhanced ultrafiltration
MIC	- Minimum inhibitory concentration
MWCO	- Molecular weight cut-off
NCL	- National Chemical Laboratory
NF	- Nanofiltration
PAN	- Polyacrylonitrile
PCR	- Polymerase chain reaction
PEG	- Polyethylene glycol
ppb	- Parts per billion
ppm	- Parts per million
PSSA	- Poly (4-styrenesulfonic acid)
PSSA-Li	- Poly (4-styrenesulfonic acid) of lithium salt

PTFE	- Polytetrafluoroethylene
qPCR	- Real time or quantitative polymerase chain reaction
RID	- Refractive index detector
RO	- Reverse osmosis
SDS	- Sodium dodecyl sulfate
SRB	- Sulfate reducing bacteria
TAE	- Tris-acetate-EDTA buffer
TDS	- Total dissolve solid
TMP	- Transmembrane pressure
UF	- Ultrafiltration
VCR	- Volumetric concentration ratio
WHO	- World Health Organization