Annexure-IX

UNIVERSITY GRANTS COMMISSION
BAHADUR SHAH ZAFARMARG
NEW DELHI – 110 002

FINAL REPORT

1	**TITLE OF THE PROJECT**	Diminution of arsenic and fluoride from drinking water using electrocoagulation and nanoparticles based adsorbent
2	**NAME AND ADDRESS OF THE PRINCIPAL INVESTIGATOR**	Dr Manpreet Singh Bhatti Professor, Dept. of Botanical & Environmental Sciences, Guru Nanak Dev University Amritsar-143005, Punjab
3	**NAME AND ADDRESS OF THE INSTITUTION**	Guru Nanak Dev University, Grand Trunk Road, Amritsar-143005, Punjab
4	**UGC APPROVAL LETTER NO. AND DATE**	F. 43-314/2014 (SR), 01-07-2015
5	**DATE OF IMPLEMENTATION**	18-01-2016
6	**TENURE OF THE PROJECT**	3 Years 01-07-2015 to 30-06-2018
7	**TOTAL GRANT ALLOCATED**	Rs. 1360000
8	**TOTAL GRANT RECEIVED**	Rs 1083976 1st instalment - Rs 860000 2nd instalment - Rs 223976
9	**FINAL EXPENDITURE**	Rs 1054308 ***(Rs Ten lakh fifty four thousand three hundred eight only)*** Unspent balance of Rs. 29668/- have been refunded to UGC vide PSIBH19042167088. [Canara Bank, account no. 8627101002122 through Manager, Punjab & Sind Bank, Guru Nanak Dev University, Amritsar vide cheque no. 100530 dated 30-01-2019 through RTGS mode]

10. TITLE OF THE PROJECT

Diminution of arsenic and fluoride from drinking water using electrocoagulation and nanoparticles based adsorbent

11.OBJECTIVES OF THE PROJECT

(i) Development of batch/continuous flow electrocoagulation experimental setup for removal of arsenic and fluoride from drinking water under different process variables viz. pH, current density, treatment time and types of electrodes on the removal efficiency.

(ii) Study of arsenic and fluoride removal efficiency through nanoparticles based adsorbents.

(iii) Synergistic effect of electrocoagulation coupled with nanoparticles based adsorbents for enhancement in removal efficiency improved settling properties and minimizing energy consumption.

12.WHETHER OBJECTIVES WERE ACHIEVED: Yes

13. ACHIEVEMENTS FROM THE PROJECT

A low-cost portable method using visible range (520 nm) for arsenic concentration in drinking water was standardized (**Fig. 1**) and results were comparable with highly sophisticated techniques Inductively Coupled Plasma-Mass Spectrophotometer (**Fig. 2**).

High strength wastewater having 100 ppm arsenic strength was optimized for best electrode pair and optimum process conditions were established for energy-efficient arsenic removal. The process parameters viz. (i) pH, (ii) current density and (iii) treatment time were optimized for maximizing arsenic removal efficiency (**Fig. 3**).

Based on optimized process conditions, low strength arsenic water was investigated (> 50 ppb) within a short period (15 min) using a stainless steel electrode pair. The process is highly energy-efficient and can be used as a standalone treatment system in villages.

For fluoride treatment, real groundwater samples were collected from various villages of Punjab and the highest fluoride concentration ~ 4 ppm was investigated for electrocoagulation treatment by different electrode pairs and aluminium electrode gave best results.

Indigenously prepared iron nanoparticles did not give promising results and arsenic removal efficiency was low (< 10%). Thus, nanoparticles were not used due to low efficiency and also gave light brownish colour to the sample, which will make it unfit for drinking.

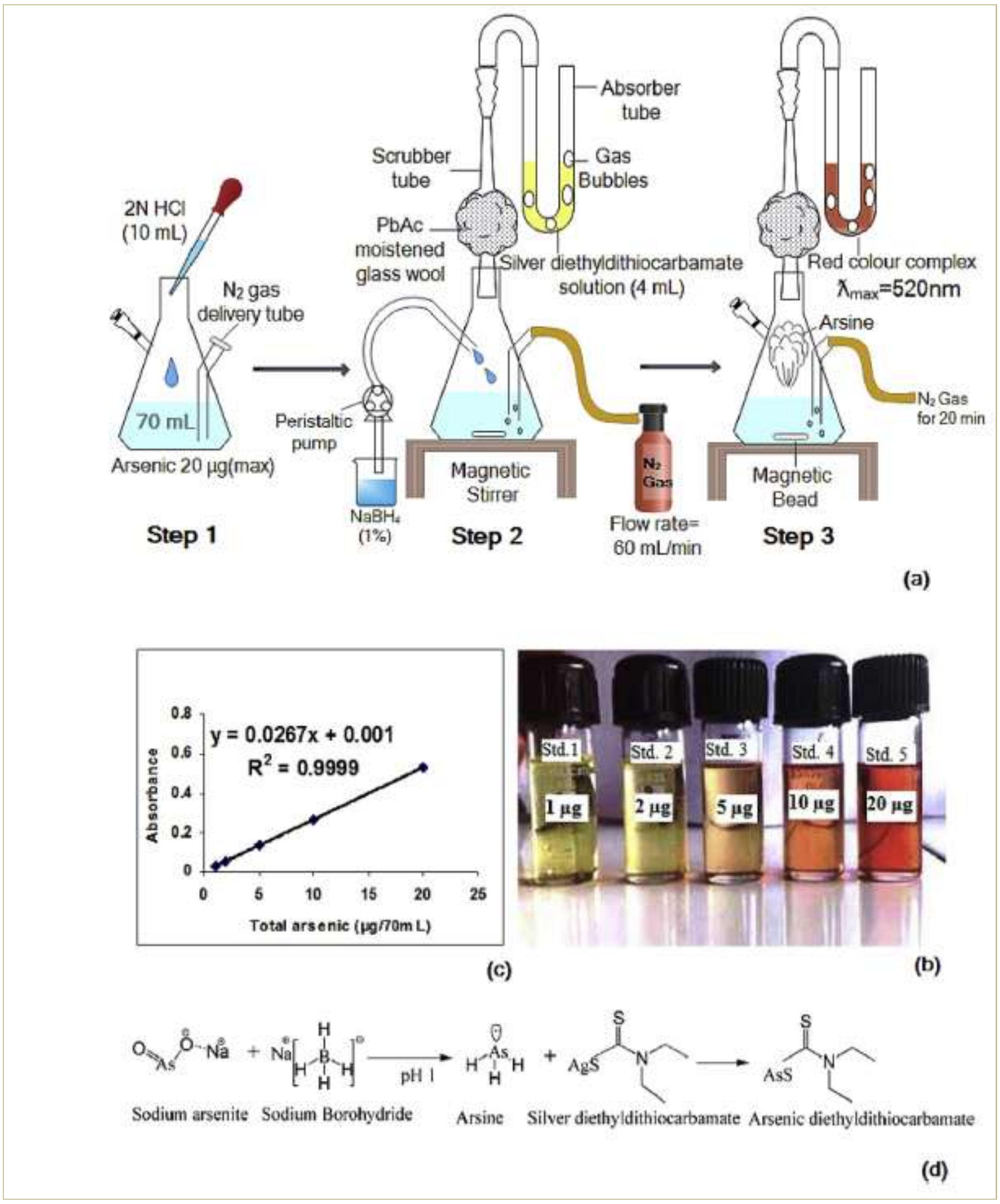
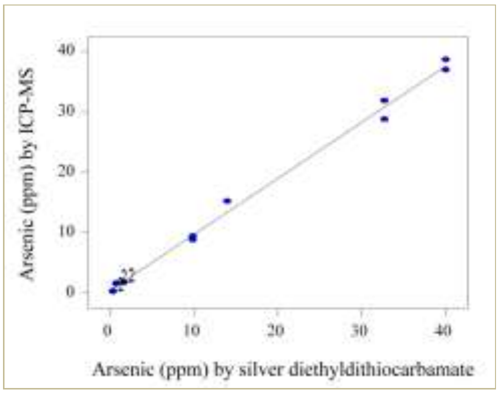


Fig. 1 (a) Schematic presentation (b) Colour intensity of standards (c) Standard curve and (d) Mechanism of silver diethyldithiocarbamate method for arsenic detection.
(Reproduced with permission from Journal of Cleaner Production, 198, pp.693-703)

Fig. 2 Arsenic concentration determined by spectrophotometric method (Silver diethyldithiocarbamate) *vs.* inductively coupled Plasma-Mass Spectrophotometer

(Reproduced with permission from Journal of Cleaner Production, 198, pp.693-703)



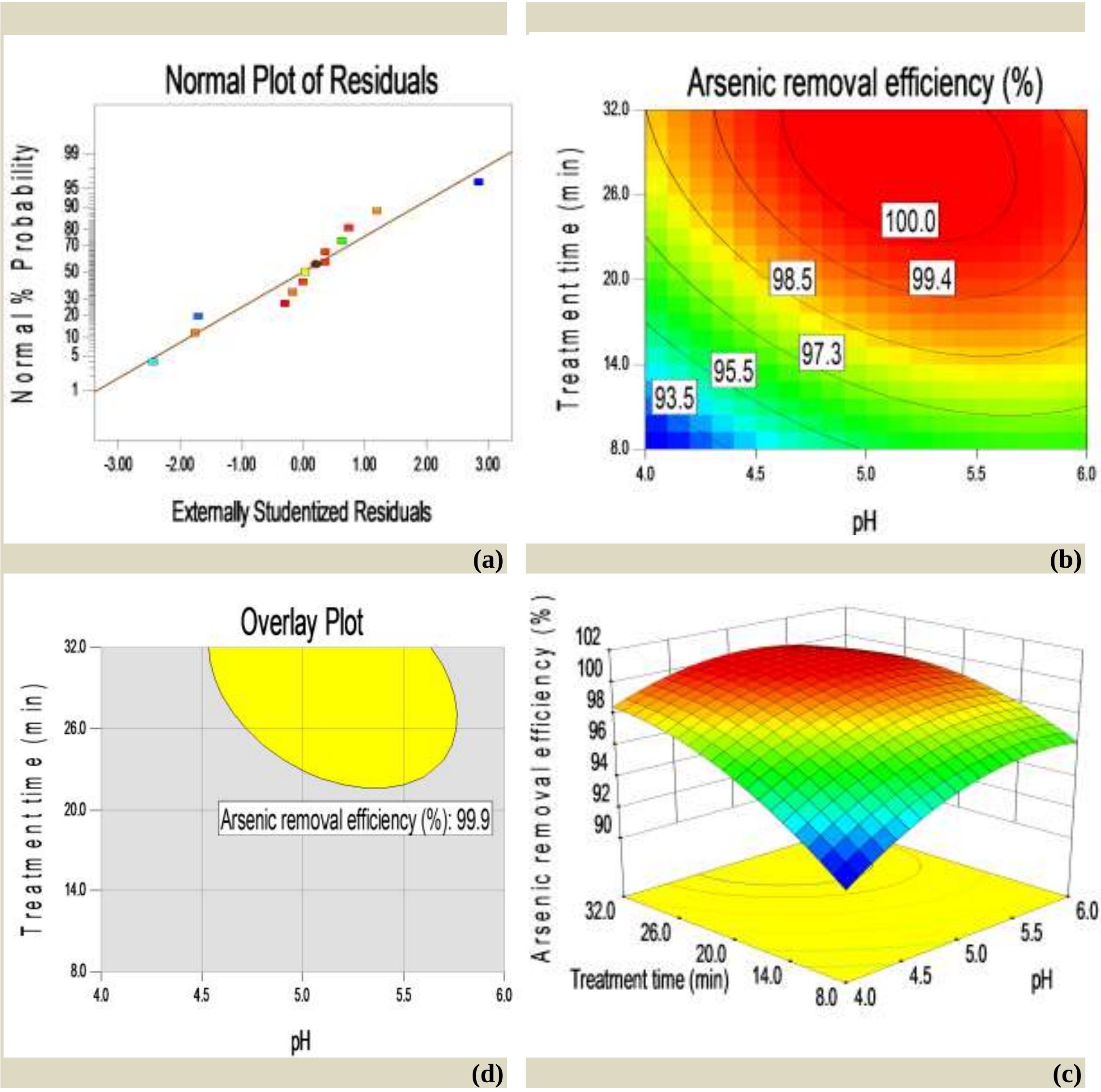


Fig. 3 (a) Normal percentage probability plot (b) 2-D (c) 3-D contour plot and (d) Overlay plot showing the effect of pH and treatment time on arsenic removal efficiency at a current density of 20 A/m^2 and 10 ppm arsenic concentration. *(Reproduced with permission from Journal of Cleaner Production, 198, pp.693-703)*

14. SUMMARY OF THE FINDINGS (in 500 words)

Electrocoagulation treatment of arsenic in water

Experiments were performed employing two factors Center Composite Design (CCD) strategy as per response surface methodology (RSM) approach. The independent variables were pH (4-6) and treatment time (8– 32) min. The fixed parameters are arsenic concentration (10 ppm) and current density (A/m^2). The maximum arsenic removal efficiency (99.6 %) was achieved at pH 5.2 and treatment time of 20 min. The minimum arsenic removal efficiency (92%) was achieved at pH 4 and treatment time of 8 min. The sequential experimental design strategy was used for data modelling, and quadratic model was best fitted. The two-factor interaction (2-FI) between pH and treatment time showed an antagonistic effect and this effect was stronger when both pH and treatment time were kept near their maximum ranges. Optimized pH was further investigated at a higher initial arsenic concentration (55 and 100 ppm). One-factor-at-a-time (OFAT) approach with the quadratic design was employed having treatment time (5 – 25) min as independent variables. For 55 and 100 ppm initial arsenic concentration, the maximum removal efficiency of 97 % and 86%, respectively was achieved at 25 min treatment time. To investigate the effect of current density on arsenic removal efficiency, experiments were performed at 20 A/m^2 and 40 A/m^2, at optimized conditions i.e. pH 5.2 and treatment time of 15 min. The removal efficiency was more than 95% at 10 ppm, which is subsequently reduced to 80% at 100 ppm. Historical data design was used to compare the results of spectrophotometer method (silver diethyldithiocarbamate) *vs.* Inductively coupled plasma-mass spectrophotometer (ICP-MS).

Use for sophisticated analytical techniques for process understanding of arsenic removal:

The plot between zeta potential values and electrolysis time indicated that with an increase in the time of electrolysis, the value of zeta potential decreases which indicated the adsorption of negatively charged arsenic species onto the flocs of monomeric and polymeric iron hydroxide/oxyhydroxide. FTIR spectra and cyclic voltammetry results corroborated to the oxidation of As(III) to As(V) prior to the adsorption. Mass spectra of sludge revealed the formation of high molecular weight complex during electrocoagulation. SEM analysis indicated that with increasing arsenic concentration, an amorphous character was predominant. The EDX analysis confirmed the presence of arsenic and iron in the sludge, and the removal of arsenic from the water samples. XRD analysis of sludge indicated the formation of iron arsenate species like $FeAsO_4$ and Fe_3AsO_7.

The arsenic removal efficiency of 99.6% was achieved at a pH of 5.2 and a treatment time of 20 min employing stainless steel electrode pair at an inter-electrode distance of 15 mm. The current density of 20 A/m^2 was found to be sufficient for treatment up to 55 ppm of initial arsenic concentration, but for 100 ppm, a higher current density of 40 A/m2 was required. The energy consumption was 0.213 KWh/m^3 at optimized process conditions. The empirical model for arsenic removal using different concentration is given in **Table 1**.

Table 1 Experimental models for arsenic removal efficiency using different initial arsenic concentrations

Arsenic (ppm)	**Design category**	**Experimental Model** Y = arsenic removal efficiency (%)
10	2 factor CCD	$Y = 35.975 + 19.190\ A + 1.021\ B – 0.085\ A \times B – 1.618\ A^2 – 0.009\ B^2$ where A = pH (4-6) and B = treatment time (8-32 min)
55	OFAT	$Y = + 13.921 + 6.26\ A - 0.117\ A^2$ A = treatment time (5-25 min)
100	OFAT	$Y = +18.654+ 2.688\ A$ A = treatment time (5-25 min)

Electrocoagulation treatment of fluoride water

The groundwater sample collected from Khalra village Tarn Taran, Punjab with high fluoride content (4 mg/L) was treated to check the process efficiency. The area had visible signs of dental and skeletal fluorosis cases among the inhabitants. Three different electrode pairs (Iron, aluminium and stainless steel) were used and aluminium electrodes were found to the best for removal of fluoride. At initial pH 7, maximum fluoride concentration was observed. Two factor CCD design was used having treatment time (3 - 37 min) and current density (10 – 40 A/m^2) as independent variables. The maximum fluoride removal efficiency of 70% was observed at pH 7, current density 40 A/m^2 and treatment time 37 min. Treated samples were analysed through ion chromatography depicting removal efficiency at the varied time (**Fig. 4**).

Use for sophisticated analytical techniques for process understanding of fluoride removal:

Removal kinetics plot explains the value of k increases (0.0064 min^{-1} to 0.0098 min^{-1}) as of current density changes from 10 A/m^2 to 40 A/m^2. This may be because at high current density, the production rate of coagulant increases which leads to an increase in the rate constant. Zeta potential results indicated that in the presence of fluoride ions, values of ζ–potential was negative which may be attributed to the OH^- surface-exchange mechanism of adsorption of fluoride onto aluminium oxide hydroxide. XRD results revealed that in absence of fluoride, boehmite (AlO(OH)) was formed. However, in fluoride-treated sludge, aluminium oxide fluoride and aluminium oxide were formed. SEM analysis results showed that in the presence of fluoride, floc size increased with agglomeration, complexation and destabilization of fluoride ions with aluminium oxide hydroxide. FTIR and Raman spectroscopy results revealed the substitution of the hydroxyl group by fluoride and occurrence of dimeric binuclear fluoro-aluminate complexes with three or two fluorine atoms in sludge. The empirical model for prediction of fluoride removal from simulated and real groundwater is given in **Table 2**. To check the interference of arsenic in the removal of fluoride, the groundwater sample was spiked with 300 ppb arsenite. The interference of arsenic was found to reduce fluoride removal efficiency by 6%. To achieve the drinking water discharge standards of 1.5 ppm for flouride, optimized treatment time was found to be 40 min. Under the optimized conditions, the residual fluoride concentration in treated water was found to be 1.2 mg/L with energy consumption of 1.64 KWh/m^3.

Table 2 Experimental models for fluoride removal efficiency using different initial fluoride concentrations

Real groundwater	**Design category**	**Experimental Model** Y = Fluoride removal efficiency (%)
Fluoride = 4 ppm Chloride= 66 ppm Sulphate=168 ppm	2 Factor CCD	$Y = -20.110 + 0.749\,A + 2.368\,B - 0.006\,A \times B - 0.008\,A^2 - 0.033\,B^2$ A = treatment time (3-37 min) and B = current density (10-40 A/m^2)

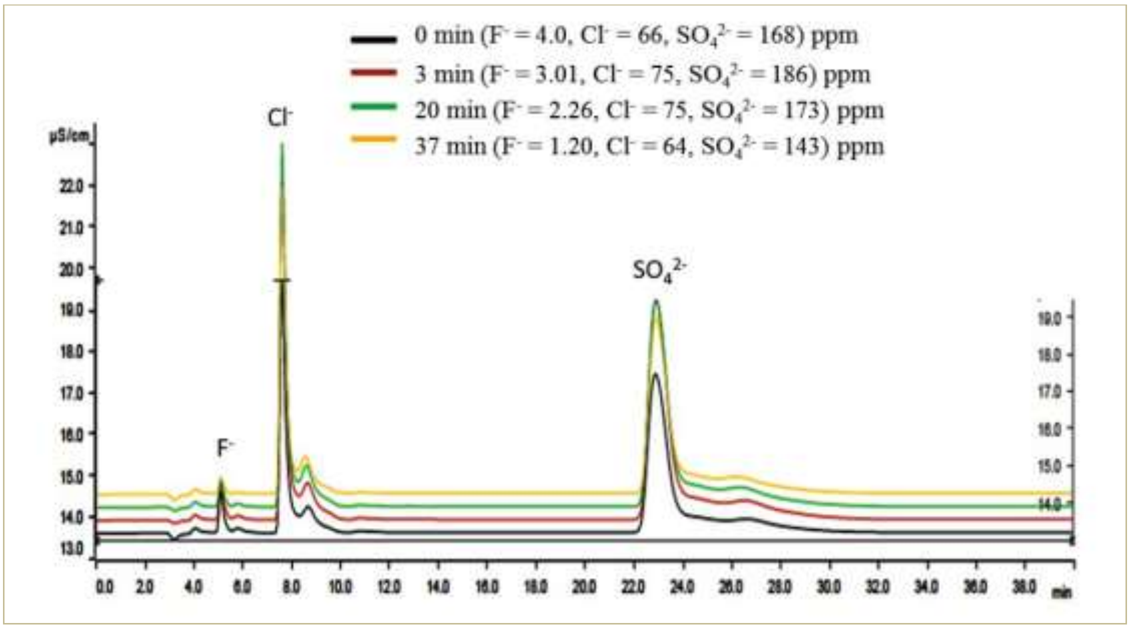


Fig. 4 Ion-chromatography of electrocoagulation treatment of fluoride for real groundwater sample at varied treatment time (0 min, 3 min, 20 min & 37 min)

In conclusion, electrocoagulation is a promising technology for the treatment of highly toxic substance (arsenic) and undesirable constituent in excess (fluoride) in groundwater as per BIS standard IS10500: 2012 as well as industrial effluent with minimum sludge generation.

15. CONTRIBUTION TO SOCIETY (GIVE DETAILS)

Arsenic and fluoride in groundwater in certain pockets of Punjab is a serious health hazard. Government-sponsored reverse osmosis (RO) plants installed in affected villages of Punjab is the only source of potable drinking water. The present study is an effort to test arsenic in groundwater using low-cost spectrophotometric method. The testing can also be done onsite and help in clearly demarcating the high arsenic wells in the area as arsenic is present at specific depth from ground level. Electrocoagulation treatment of arsenic contaminated groundwater (~ 100 ppb) can be used to achieve drinking water standards of 10 ppb in about 5 min of treatment time using non corroding stainless steel electrode. Similarly, electrocoagulation treatment of excess fluoride was achieved using aluminium electrode pair. The treatment may be economical viable in terms of energy efficiency and can generate potable water for public use. Also, published work on fluoride affected area will help the society in locating the non-potable water sources in different parts of Punjab.

16. WHETHER ANY PhD. ENROLLED/PRODUCED OUT OF THE PROJECT

- PhD awarded- 1 [Vishakha Gilhotra, Project Fellow completed her PhD in the year 2019]
- PhD ongoing- 1 [Laxmi Das is working on an extension of this work]

17. NO. OF PUBLICATIONS OUT OF THE PROJECT: 2

- Gilhotra, V., Das, L., Sharma, A., Kang, T.S., Singh, P., Dhuria, R.S. & **Bhatti, M.S.** (2018). Electrocoagulation technology for high strength arsenic wastewater: Process optimization and mechanistic study. *Journal of Cleaner Production, 198*, pp.693-703. (**Impact factor = 7.24)** DOI: https://doi.org/10.1016/j.jclepro.2018.07.023

- Gilhotra, V, Yadav, R. & Bhatti, M.S. (2020). Diminution of fluoride enriched groundwater using electrocoagulation: Process optimization and role of arsenic interference. *Desalination & Water Treatment*. *195*, pp.162-176. (**Impact factor = 0.85)** DOI: http://doi.org/10.5004/dwt.2020.25925

- Gilhotra, V. & **Bhatti, M.S.** (2017) 'A pragmatic model for removal of arsenic using iron electrocoagulation: A RSM based approach' at International Conference of Emerging Area of Environmental Science and Engineering organized by Department of Environmental Science & Engineering, Guru Jambheshwar University of Science & Technology, Hisar, Haryana on 18 Feb 2017. (***Abstract Published***)

- Gilhotra, V. & **Bhatti, M.S. (2019) '**Electrocoagulation treatment of fluoride contaminated groundwater' at 106th Indian Science Congress organized by Lovely Professional University, Phagwara, Punjab on 6 Jan 2019. (***Abstract Published***)

Dr Manpreet Singh Bhatti
(Principal Investigator)

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