BIOREMEDIATION OF BTEX POLLUTED SOIL WATER SYSTEMS UNDER VARYING ENVIRONMENTAL CONDITIONS

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JANUARY 2016

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by

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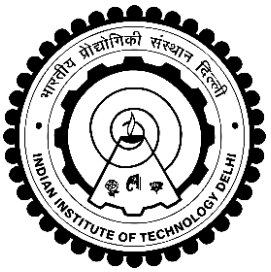
Submitted

in fulfillment of the requirements of the degree of

Doctor of Philosophy

to the



Indian Institute of Technology Delhi

January 2016

In the loving memory of

My Father

CERTIFICATE

This is to certify that the thesis, entitled **"*Bioremediation of BTEX Polluted Soil Water Systems under Varying Environmental Conditions* "**, being submitted by **Ms. Shreejita Basu** to the **Indian Institute of Technology, Delhi** for the award of Doctor of Philosophy, is a record of bonafide research work carried out by her under our joint supervision. The thesis work, in our opinion has reached the standard, fulfilling the requirements for the said degree. Further, we certify that this submission is Ms. Shreejita's own work and that, to the best of our knowledge and belief, it contains no material previously published or written by another person which to a substantial extent has been accepted for the award of any other degree or diploma of any University or Institute, except where due acknowledgment has been made in the text.

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Acknowledgements

I have been very lucky to be a part of two prestigious institutes, IIT Delhi and IIT Roorkee during my doctoral studies. I consider it a proud privilege to express my heartfelt gratitude to my supervisors, Prof. Shashi Mathur, Department of Civil Engineering, IIT Delhi and Dr. Brijesh K Yadav, Department of Hydrology, Indian Institute of Technology Roorkee for their excellent supervision during the course of this research work. Dr. Brijesh Yadav has been a source of vital support, constant motivation and valuable suggestions that has helped me immensely in shaping this dissertation. I would like to extend my gratitude to Prof. Shashi Mathur for providing me with his invaluable advice and feedback on my work. In addition to their technical guidance, they have set forth examples of personal attributes which I hope to emulate as a good human being.

I sincerely acknowledge my SRC members, Prof. B.J Alappat, Prof. T.R Sreekrishnan, and Dr. Arun Kumar for their valuable feedback. I am also grateful to Prof. S.M Hassanizadeh from Utrecht University for allowing me to visit his laboratory and imbibe knowledge in my field of expertise. I am thankful to the Council of Scientific and Industrial Research for funding me with the Junior and Senior Research Fellowship. I am equally thankful to Department of Science and Technology (DST) for proving funding as Ramanujan Fellow award (Ref. No SR/S2/RJN-01/2010) to Dr. Brijesh K Yadav. I wish to thank Prof. Himanshu Joshi, from IIT Roorkee for his cooperation in the experimental work carried out in the environmental hydrology lab. I would also like to thank Dr Naveen Navani

and his PhD student Ms. Manasi Gupta for their help in the microbial analysis conducted at Department of Biotechnology IIT Roorkee

For the successful and timely completion of this thesis I am deeply indebted to quite a number of people of which a few names simply cannot go without being mentioned here.

I wish to extend my sincere thanks to all my labmates and fellow researchers in Department of Hydrology IIT Roorkee, Mr Jahangeer, Mr Pankaj, Dr. Deepak Kumar, Mr Kuntal, Ms Shachi and Mr Shashi who have extended their support by all means to carry out my experiments. I would also like to thank Mr Sunil Yadav,Mr Shyam,Mr Vikram and Mr Ajay Vashisht. This acknowledgement shall remain incomplete unless I thank my fellow research scholars in IIT Delhi- Mr. Faiz Ahmad and Mr. Anuj Mathur for their help and encouragement during this study. The friendly help provided by Mr. Rajveer, Mr. Bikram and Mr. Gehlot is duly acknowledged and I am thankful to them for all help rendered by them during my stay at IIT Delhi. Apart from these, my special acknowledgement is due for my friends Lohit Jain, Jyoti Pakhale, Raktim Haldar, Aniket Chakraborty, Jatin Anand, Himanshu Tyagi, Shailza Sharma, Manjula Devak and Pawan rai. Lohit and I have shared endless moments of laughter and he has proven himself to be a dependable friend time and again. I express my regards and thanks to my parents as their contribution in whatever I have achieved till date is beyond comparison. It was their unconditional love, affection and encouragement that has helped me to move ahead in my difficult times and complete my work successfully. Last but not the least I would like to thank my elder sister for her constant encouragement and love without which I would not have been able to succeed.

January 2016 (Shreejita Basu)

Abstract

Hydrocarbons like BTEX compounds entering the soil-water system through anthropogenic activities can be long lasting sources of pollution, and thus, it is essential to look for remediation options that are environmentally benign. Bioremediation is a promising cost effective technique causing no harm to the contaminated ecosystem as compared to the traditional physicochemical methods. Natural microbes degrade contaminants from polluted soil water resources in bioremediation; however this process of natural bioremediation is quite slow under prevailing environmental conditions of a typical polluted site. So, in order to enhance the degradation rate, engineered bioremediation is practiced by addition of seeded cultures and/or nutrients, popularly known as bioaugmentation and biostimulation. Another key role in the success of bioremediation application is played by various site specific environmental conditions like temperature, moisture content, and oxygen availability. Research has also proven that plants play an important role when it comes to accelerate the degradation rate cost-effectively in enhanced bioremediation technique. Therefore, the main focus of this study is to investigate the most effective feasible way of bioremediating the BTEX contaminated soil water using the biostimulation and bioaugmentation techniques, separately and in-combine using locally available domestic wastewater and wetland plants in mixed as well continuous laboratory setups.

To achieve this, the combined impact of temperature and soil water content on biodegradation of toluene, the selected BTEX compound, was investigated first using two

sets of completely mixed batches with oversaturated and saturated soils at two temperature extremes of 30° C and 10 °C under aerobic conditions. It was found that the rate of toluene degradation was highest for oversaturated soil at 30 °C and lowest for saturated soil at 10 °C. Four different cases of bioremediation technique (bioremediation, biostimulation, plant-enhanced biostimulation and bioaugmentataion) were experimentally investigated then for decontaminating toluene polluted groundwater using completely mixed microcosms. Natural biodegradation of toluene was studied first under different varying substrate concentrations at room temperature (21.6 ±0.30 ^{o}C). Biostimulation was studied by mixing the polluted groundwater with a primary treated domestic wastewater for providing nutrients and other supplementary components to the native microbial population. Two pot-scale wetlands, one with and another without presence of toluene, having plants of *Canna genralis* and locally available domestic wastewater were used to study 3rd and 4th cases. The wetland system in presence of toluene was used here for developing the pre-grown microbial cultures to degrade toluene. The plant-assisted biostimulation, the third case, was studied by adding the polluted groundwater with the root-zone water of the wetland system developed without the presence of toluene. In the fourth case, the biostimulation was coupled with the bio augmentation strategy by mixing the groundwater with the root-zone water of the wetland system developed in presence of toluene. A comparative account of these four different bioremediation techniques was prepared for their respective rates of biodegradation, duration of lag phases, and the total time of degradation. It was observed that both the plant-assisted bioremediation techniques had better performance over simple biodegradation and biostimulation methods.

Subsequently, treatment wetlands with and without shoot biomass of *Canna Generalis* along with unplanted gravel bed were used to quantify the toluene uptake by the plants under controlled conditions. The residual concentration of the selected BTEX compound in the rhizosphere water was measured over the entire period of the experiment along with the water lost by evapotranspiration. The rate of biodegradation in all wetland mesocosms fitted best with the first order kinetics. The total removal time of the BTEX compound was found to be highest in the unplanted gravel bed mesocosm followed by wetlands without and with shoot biomass. The cumulative uptake of toluene in shoot biomass of the wetland plants initially increased rapidly and started to decrease subsequently till it reached a peak value. Continuity equations integrated with biodegradation and plant uptake sink terms were used to simulate residual concentration of toluene in rhizospheric water for comparison with the measured data of the experiments.

Thereafter, the results of the microcosm experiments were then used to investigate the fate and transport of dissolved toluene from a source zone to down-gradient receptors in a continuous soil-water plant system. For this, two sets of large scale column experiments were performed by connecting them with a treatment wetland having canna plants in one set and unplanted gravel bed in the second set. A continuous source of toluene contaminated water was supplied at the top of the column setups. A constant groundwater flow velocity of 0.625 cm/hr was maintained in the vertical direction. Free drainage was allowed at the bottom and a constant hydraulic head of 2.0 cm was maintained at the top boundary throughout the period of the experiments in both the cases. The observed microbial colonies using the plate counting method along with measured dissolved oxygen (DO) proved that the BTEX compound degraded aerobically at faster rate in the second set. Here again, plants

played positive role in enhancing biodegradation rate of the BTEX compound during its transport through the porous media. Finally the observed data of the column experiments were compared with the breakthrough curves obtained numerically solving the advection dispersion equation. The results of this research can be used to frame in-situ plant-assisted bioremediation techniques for hydrocarbon contaminated soil-water resources.

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Nomenclature

a_v	Air content
α_L	Longitudinal dispersivity
C_t	Contaminant concentration at time, t
Co	Initial contaminant concentration,t=0
D_r	Diffusion rate constant
D_g	Molecular diffusion coefficient in gas
D_w	Molecular diffusion coefficient in water
D_L	Longitudinal dispersivity
D	Hydrodynamic dispersion coefficient
D_m	Molecular diffusion coefficient
D_o	Free water diffusivity
f_{oc}	Fraction of organic carbon
J(z)	Contaminant influx
J(z+Δz)	Contaminant outflux
k_1	First order rate constant at time
k_o	Zero order rate constant
K_d	Adsorption coefficient
K_m	Michaelis-menten constant
K_{oc}	Organic carbon partioning coefficient
$\boldsymbol{\rho}_s$	Bulk density of soil
q	Soil water flux
|q|	Darcian fluid flux density
Q_{trans}	Water lost in transpiration
S_b	Sink term for biodegradation
S_D	Contaminant adsorbed to soil mass
τ_g	Tortuosity factor in liquid phase
τ_w	Tortuosity factor in gas phase
μ_{max}	Maximum specific growth rate
V_t	Total volume at time, t
v	Pore water velocity
X_o	Initial microbial density

Acronyms and Abbreviations

ADE	Advection Dispersion Equation
BTC	Breakthrough curve
BTEX	Benzene, Toluene, Ethyl Benzene, Xylene
CW	Constructed Wetland
DNAPL	Dense Non aqueous Phase Liquid
GCMS	Gas chromatograph mass spectrophotometer
FID	Flame Ionization Detector
LNAPL	Light Non aqueous Phase Liquid
MTBE	Methyl tertiary Butyl Ether
NAPL	Non Aqueous Phase Liquid
PAH	Poly Aromatic Hydrocarbons
PCB	Poly Chlorinated Biphenyls
PCE	Perchloroethylene
RCF	Root Concentration factor
TSCF	Transpiration Stream Concentration Factor
TW	Treatment Wetland
VOC	Volatile Organic Compound
UST	Underground Storage Tank