

**ASSESSMENT OF SELECTED EMERGING  
CONTAMINANTS IN WASTEWATERS FROM RURAL,  
PERI-URBAN AND CITY AREAS OF DELHI NCR AND  
THEIR MICROALGAL REMEDIATION**

**FARHAT BANO**



**CENTRE FOR RURAL DEVELOPMENT AND TECHNOLOGY**

**INDIAN INSTITUTE OF TECHNOLOGY DELHI**

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**by**

**FARHAT BANO**

**CENTRE FOR RURAL DEVELOPMENT AND TECHNOLOGY**

**Submitted**

**in fulfilment of the requirements of degree of Doctor of Philosophy**

**to the**



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## CERTIFICATE

This is to certify that the thesis entitled “**Assessment of selected emerging contaminants in wastewaters from rural, peri-urban and city areas of Delhi NCR and their microalgal remediation**”, being submitted by Ms. **Farhat Bano** 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. She has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis. To the best of our knowledge, the results contained in this thesis have not been submitted in part or full to any other university or institute for award of any degree or diploma.

Date:

Place:

Dr. Anushree Malik  
Professor  
Centre for Rural Development  
and Technology  
Indian Institute of Technology Delhi  
New Delhi- 110016

Dr. Shaikh Z. Ahammad  
Associate Professor  
Biochemical Engineering  
and Biotechnology  
Indian Institute of Technology Delhi  
New Delhi- 110016

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## ABSTRACT

The objective of the present study was to assess the quality of drain wastewater in sparsely and densely populated different types of human settlements in Delhi NCR, in terms of both conventional and emerging contaminants (ECs) in two summer and two winter seasons and to investigate the potential of microalgal consortium for the removal of emerging contaminants from drain wastewater. Wastewater quality of 12 selected drain in Delhi NCR in different rural, peri-urban and city areas was evaluated in terms physiochemical characteristics – conductivity, TDS, pH, DO, BOD, COD, PO<sub>4</sub>, NO<sub>3</sub>, NH<sub>4</sub> and coliforms, as well as emerging contaminants - heavy metals and pharmaceutical and personal care products (PPCPs). Drain wastewater characterization was done for the period of two years (December 2016-June 2018) representing two seasons each year: peak winter and peak summer. The concentration of heavy metals at the selected drain sites was below the permissible limits of inland surface water discharge, with zinc and nickel present in highest concentrations. The peri-urban industrial sites were most contaminated with heavy metals. The abundance of PPCPs in drain wastewater and the highly polluted Yamuna river is much higher than the pristine Ganga river sites, indicating the human input of these due to extensive use and disposal. Methyl paraben, diclofenac, triclosan, ranitidine and carbamazepine were the most abundant PPCP contaminants in drain wastewater. However, their concentrations were found to be in pg L<sup>-1</sup>. The densely populated city and peri-urban drain sites showed the highest contamination with PPCPs. The variety of these PPCPs occurring in wastewater due to non-removal by conventional wastewater treatment systems, may have potential negative effects on the ecosystem. An environment friendly technology is required to remove both conventional and emerging contaminants from wastewater. A potential remediation technology based on microalgal consortium was investigated. For this, a wastewater obtained microalgal consortium from Hauz Khas lake in Delhi, named HL was examined for its emerging contaminant removal ability - heavy metal removal in single and multi-metal solutions; and PPCPs in individual solutions. The results show that under single metal exposure, HL showed better performance (57-98% removal) as compared to multi metal exposure (14-85% removal). The maximum removal was observed for Zn, Ni and Cu in both type of exposures. The biomass productivity for the consortium increased in both types of heavy metal spiking. For the PPCP removal, it was observed that the consortium was able to tolerate environmentally high concentrations of the selected drugs. The effective concentrations with 50% mortality values for the consortium for estradiol (EST), diclofenac

(DCF) and triclosan (TCS) was 16, 8 and 8 mg L<sup>-1</sup>, respectively. The consortium grew well in EST and DCF spiked media but could not tolerate TCS beyond 5 days. Substantial removal of EST (91.73%), DCF (74.68%) and TCS (78.47%) within the stationary phase of growth was achieved. It was also observed that the removal by microalgal consortium was higher than abiotic degradation in the same time. From the adsorption and bio-degradation experiments, it was concluded that bio-degradation by microalgae was the prominent removal mechanism for the selected PPCPs, and not adsorption. From SEM studies, it was observed that there were morphological deformation, clustering and cell disruption in microalgal cells due to the exposure to the PPCPs. Further, to assess the performance of native microalgal consortium under environmental concentrations of PPCPs, on-site, an LED based photobioreactor system (40L) was developed and fed with raw wastewater from the Barapulla drain in Delhi. PBR performance was assessed for winter and summer season for the removal of both conventional and emerging contaminants. The PBR was able to remove 41.35% COD, 41.28% PO<sub>4</sub> and 100 % NH<sub>4</sub> with an HRT of 4 days. Additionally, 25.67-59.63% removal of heavy metals and 21.93-100% removal of PPCPs was observed in the PBR. Thus, it can be concluded that microalgal-based treatment depicts a promising technology for both conventional and emerging contaminant removal under environmental conditions. The data generated from the mapping study of ECs occurring in the Delhi NCR is an important step towards understanding the scope of the problem of ECs in a highly populous country like India. Mapping of various conventional and emerging contaminants in different types of human settlements had not been previously done. This information can be useful for the regulatory authorities for making guidelines for the continuous discharge of the ECs and for investigating the potential to integrate environment friendly microalgal-based technology as a polishing step in the existing wastewater treatment systems to target and remove the ECs, along with the conventional contaminants.

## सार

वर्तमान अध्ययन का उद्देश्य दिल्ली एनसीआर में गर्मियों और सर्दियों के मौसमों में पारंपरिक और उभरते दोनों प्रकार के दूषित पदार्थों के संदर्भ में अलग-अलग और घनी आबादी वाले नाले की गुणवत्ता का आकलन करना था। नाली के अपशिष्ट जल से उभरते हुए दूषित पदार्थों को निकालना। विभिन्न ग्रामीण, पेरी-शहरी और शहर के क्षेत्रों में दिल्ली एनसीआर में 12 चयनित नाले की अपशिष्ट गुणवत्ता का मूल्यांकन भौतिक रासायनिक विशेषताओं (टीडीएस, ईसी, पीएच, डीओ, बीओडी, सीओडी, पीओ 4, एनओ 3, एनएच 4 और कोलीफॉर्म) के रूप में अच्छी तरह से मूल्यांकन किया गया था। उभरते दूषित (भारी धातुओं और PPCPs)। हर साल दो मौसमों का प्रतिनिधित्व करने के लिए दो साल (दिसंबर 2016-जून 2018) की अवधि के लिए सूखा अपशिष्ट जलकरण किया गया था: पीक सर्दी और पीक गर्मी। चयनित नाली स्थलों पर भारी धातुओं की प्रचुरता अंतर्देशीय सतह के पानी के निर्वहन की अनुमेय सीमा से कम थी, जिसमें जस्ता और निकल उच्चतम सांद्रता में मौजूद थे। पेरी-शहरी औद्योगिक साइटें भारी धातुओं से सबसे अधिक दूषित थीं। नाली के अपशिष्ट जल में प्रचुर मात्रा में पीपीसीपी और अत्यधिक प्रदूषित यमुना नदी, प्राचीन गंगा नदी स्थलों की तुलना में बहुत अधिक है, जो व्यापक उपयोग और निपटान के कारण इनका मानव इनपुट दर्शाता है। मिथाइल पैराबेन, डाइक्लोफेनाक, ट्राईक्लोसन रैनिटिडिन और कार्बामाज़ेपिन सबसे प्रचुर मात्रा में पीपीपी पोषक तत्व थे। हालाँकि, उनकी सांद्रता pg L-1 में पाई गई। घनी आबादी वाले शहर और पेरी-शहरी साइटों ने पीपीसीपी के साथ उच्चतम संदूषण दिखाया। पारंपरिक अपशिष्ट जल उपचार प्रणालियों द्वारा हटाने के कारण अपशिष्ट जल में होने वाले इन पीपीसीपी की विविधता, पारिस्थितिक तंत्र पर संभावित नकारात्मक प्रभाव डाल सकती है। इसलिए, पारंपरिक और उभरते दोनों दूषित पदार्थों को अपशिष्ट जल से निकालने के लिए एक लक्षित टिकाऊ प्रौद्योगिकी की आवश्यकता होती है। माइक्रोगल कंसोर्टियम पर आधारित एक संभावित उपचार तकनीक की जांच की गई। इसके लिए, एचएल नामक सूक्ष्म अपशिष्ट कंसोर्टियम को इसकी उभरती दूषित हटाने की क्षमता - एकल और बहु-धातु समाधानों में भारी धातु हटाने की जांच की गई; और व्यक्तिगत समाधान में PPCPs। परिणाम बताते हैं कि एकल धातु जोखिम के तहत एचएल ने मल्टी मेटल एक्सपोजर (14-85% हटाने) की तुलना में बेहतर प्रदर्शन (57-98% हटाने) दिखाया। दोनों प्रकार के एक्सपोजर में Zn, Ni और Cu के लिए अधिकतम निष्कासन देखा गया। कंसोर्टियम के लिए बायोमास उत्पादकता दोनों प्रकार के भारी धातु के स्पाइकिंग में वृद्धि हुई। पीपीसीपी हटाने के लिए, यह देखा गया कि कंसोर्टियम चयनित दवाओं के पर्यावरणीय उच्च सांद्रता को सहन करने में सक्षम था। ईएसटी, डीसीएफ और टीसीएस के लिए कंसोर्टियम के लिए 50% मृत्यु दर के साथ प्रभावी सांद्रता क्रमशः 16, 8 और 8 मिलीग्राम एल -1 थी। कंसोर्टियम एस्टा और डीसीएफ स्पाइक मीडिया में अच्छी तरह से विकसित हुआ लेकिन 5 दिनों से अधिक टीसीएस को बर्दाश्त नहीं कर सका। विकास के स्थिर चरण के भीतर ईएसटी (91.73%), डीसीएफ (74.68%) और टीसीएस (78.47%) को दूर किया गया। यह भी देखा गया कि सूक्ष्मजीवों के संघ द्वारा निष्कासन समान परिस्थितियों में एक ही समय में अजैविक क्षरण से अधिक था। जैव-सोखना और जैव-अपघटन प्रयोगों से, यह निष्कर्ष निकाला गया कि चयनित पीपीसीपी के लिए माइक्रोलेगा द्वारा जैव-अपघटन प्रमुख हटाने वाला तंत्र था न कि सोखना। एसईएम अध्ययनों से, यह देखा गया कि पीपीसीपी के संपर्क में आने के कारण सूक्ष्मजीव कोशिकाओं में रूपात्मक विकृति, क्लस्टरिंग और सेल व्यवधान थे। फ्यूचर, पीपीसीपी के पर्यावरणीय सांद्रता के तहत देशी माइक्रोआर्गेनल कंसोर्टियम के प्रदर्शन का आकलन करने के लिए, दिल्ली में बारापुल्ला ड्रेन से कच्चे अपशिष्ट जल के साथ ऑन-साइट एलईडी आधारित फोटोबाइक्टर सिस्टम (40L) विकसित किया गया

था। पीबीआर प्रदर्शन का मूल्यांकन सर्दियों और गर्मी के मौसम के लिए पारंपरिक और उभरते दोनों दूषित पदार्थों को हटाने के लिए किया गया था। PBR 4 दिनों के HRT के साथ 41.35% COD, 41.28% PO<sub>4</sub> और 100% NH<sub>4</sub> को निकालने में सक्षम था। इसके अतिरिक्त, 25.67-59.63% भारी धातुओं को हटाने और पीपीपीआर के 21.93-100% हटाने को PBR में देखा गया। इस प्रकार, यह निष्कर्ष निकाला जा सकता है कि माइक्रोएल-आधारित उपचार पर्यावरणीय परिस्थितियों में पारंपरिक और उभरते हुए दोनों दूषित पदार्थों को हटाने के लिए एक आशाजनक तकनीक को दर्शाता है। दिल्ली एनसीआर में होने वाले ईसी के मैपिंग अध्ययन से उत्पन्न डेटा भारत जैसे अत्यधिक आबादी वाले देश में ईसी की समस्या के दायरे को समझने की दिशा में एक महत्वपूर्ण कदम है। विभिन्न प्रकार की मानव बस्तियों में विभिन्न पारंपरिक और उभरते हुए दूषित पदार्थों का मानचित्रण पहले नहीं किया गया था। यह जानकारी नियामक प्राधिकरणों के लिए ईसी के निरंतर निर्वहन के लिए दिशानिर्देश तैयार करने और मौजूदा अपशिष्ट जल उपचार प्रणालियों में पर्यावरणीय रूप से टिकाऊ माइक्रोएल-आधारित प्रौद्योगिकी को एकीकृत करने की क्षमता की जांच करने के लिए उपयोगी हो सकती है, ईसी को पारंपरिक एक पॉलिश कदम के साथ लक्षित करने और दूषित पदार्थों को हटाने के लिए।

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