UNDERSTANDING THE INTERACTION OF METAL OXIDE NANOPARTICLES WITH BACTERIA AND ITS IMPLICATIONS ON TREATMENT OF MUNICIPAL WASTEWATER

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by

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CERTIFICATE

This is to certify that the thesis entitled **"UNDERSTANDING THE INTERACTION OF METAL OXIDE NANOPARTICLES WITH BACTERIA AND ITS IMPLICATIONS ON TREATMENT OF MUNICIPAL WASTEWATER"** being submitted by**Mr. BARANIDHARAN S** to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy** is a record of the original bonafide research work carried out by him under my guidance and supervision. The thesis work, in my opinion, has reached the requisite standards fulfilling the requirement for the Degree of Doctor of Philosophy.

The results contained in this thesis have not been submitted in part or in full to any other University or Institute for the award of any degree or diploma.

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ABSTRACT

The widespread use of various nanoparticles (NPs) in different consumer products may lead to their release into urban wastewater treatment plants (WWTPs) and influence the operation of WWTPs due to its potential toxicity.However, investigations of the potential mixture impacts of NPs on both short term and long term effect on activated sludge are sparse.

The objective of this study was to understand the toxic effect of mixture of metal oxide nanoparticles on biological functioning of activated sludge. It was studied using four sub-objectives. In the first sub-objective, three NPs (Ag_2O, $TiO_2$and mixture of both) were selected to illustrate the toxic effect of mixture of NPs on biological functioning by performing 5-d BOD (concentration tested: 0.1, 1 and 10 mg/L), specific oxygen uptake rate (SOUR) inhibition and time-dependent COD study (concentration tested: 1 mg/L; 5-h exposure duration).Mixture of NPs at 10 mg/L in solution pH inhibited SOUR by 34.17±2.4% and was found to be more toxic to activated sludge (maximum reduction in BOD_5 =22% in comparison to control) than compared to individual NP toxicity.The rank of toxicities of NPs using minimum concentration (MC) giving significant effect than control was found to be as following: (least toxic) Ag_2O < TiO_2< Mixture of TiO_2 and Ag_2O (most toxic). COD reduction in 5-h was found to be most affected by TiO_2 NPs with regards to control (24% reduction) than other two types of NPs (22%). These findings indicate the effect of mixture of NPs on biological functioning of activated sludge in a quantitative manner, for the first time as per author's knowledge. When mixture of NPs was added to study the short term effect on activated sludge, the predicted toxicity was higher than the observed value, showing an antagonistic effect.

The second sub-objective focused on investigating the stability of mixture of two metal oxide nanoparticles in simulated wastewater. Aggregation and sedimentation behaviors of silver

oxide (Ag_2O), titanium dioxide (TiO_2) and mixture of these two NPswere thoroughly studied in three water types (ultrapure, ultrapure with nutrients and ultrapure with nutrients and glucose) (pH : 4, 7, and 10;ionic strength: 0, 0.01, 0.1 M).

Ionic strength and pH significantly increased the size of metal oxide NPs ($p < 0.05$). Aggregation was reported to be maximum at alkaline medium than acidic and neutral mediums. Ag_2O NPs size remained in nm while TiO_2 NPs size ranged inμm. The settling rate was found to be maximum for TiO_2 followed by particles in suspension containing mixture of NPs and Ag_2O NPs.Strong correlation was found between the NP size and sedimentation rate among all the three NPs when investigated in simulated wastewater condition ($p < 0.05$).

The third sub-objective evaluated the influence of three NPs (Ag_2O, TiO_2, mixtureof both) on biological reactor performance in a biological reactor. Among the NPs tested it was found that 1 and 10 mg/L of mixture of NPs had more impact on the COD removal efficiency than the individual NPs. When tested among the three NPs, maximum reduction in COD (76.3%) was observed after 150 days of exposure by mixture of NPs at 500 mg/L COD loading, whereas for 10 mg/L it was after 180 days of exposure (70.2%) by mixture of NPs at 250 mg/L COD loading. When tested among the individual NPs, TiO_2 had higher reduction in COD than Ag_2O NPs at 10 mg/L and vice versa for 1 mg/L. From the study results, it was evident that the COD removal was dependent more on NP type and concentration than organic loading rate which had insignificant effect of NPs removal. This study results revealed that metal ion concentration in sludge was found to be higherthan in supernatant irrespective of the NPs tested. When compared among the NPs tested both in individual and in mixture, dissolved Ti ion concentration was found to be high than dissolved Ag ion concentration thus reiterating the fact that TiO_2NPs have greater affinity towards the sludge than Ag_2O NPs. From the microscopic analysis it was found

that NPs of all size were found inside the activated sludge where the size of NPs was ranging from individual NPs to size greater than> 100 nm. The results suggest that 10 mg/L of mixture of NPs have greater impact than the individual NPs on activated sludge wastewater treatment performance.

The fourth sub-objective aimed to determine the presence of NPs in Indian water for the first time as per author's knowledge.Six water samples from inlets and outlet of two different municipal WWTPs (activated sludge and extended aeration), ground water and surface water in three independent sampling events were characterized using Dynamic Light Scattering,Transmission Electron Microscope,X-Ray Fluorescence and Inductively Coupled Plasma.Particle size distribution (PSD) revealed that over 90 % of particles were > 250 nm, where the least size of particles was found in ground water sample (196 ± 70 nm) and larger size fraction was found to be in the inlet of $WWTP_2$(501±87 nm). Results revealed that plant operating with extended aeration process had 42 % reduction in size of particles, whereas 58 % reduction was found in plant operating with activated sludge process. TEM analysis indicated the presence of both individual and aggregated particles of different shapes in all tested water types.Further XRF scan revealed, the presence of Ag, Ti, Zn in the concentration range of µg/L (Ti<Ag<Zn). More emphasis is needed for monitoring NPs in different Indian water types which can help in evaluating the pollution. The results have important implications for Indian regulatory bodies to monitor NPs presence in environment and to protect human health in India.

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