RISK ASSESSMENT AND SYNTHESIS OF MAGNETIC BIOCHAR COMPOSITES FROM PAPER MILL SLUDGE FOR REMOVAL OF PENTACHLOROPHENOL

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by

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CERTIFICATE

This is to certify that the thesis entitled, **"Risk assessment and synthesis of magnetic biochar composites from paper mill sludge for removal of pentachlorophenol"** being submitted by **Ms. Parmila Devi** 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 my guidance and supervision in conformity with the rules and regulations of Indian Institute of Technology Delhi.

The research report and results presented in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

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(Parmila Devi)

ABSTRACT

Huge quantity of sludge is generated during the paper manufacturing process in the pulp and paper industry. The disposal and management of the generated sludge is a big challenge as it contains significant amount of heavy metals, organic toxins and pathogenic microorganisms. Accumulation and bio-availability of heavy metals in the sludge is a limiting factor for its disposal and utilization. Pyrolysis is a promising sludge treatment method for the heavy metals immobilization leading to a significant reduction in the bioavailability and leaching potential of the heavy metals in the biochar. Therefore, efforts have been made in the present study to immobilize the heavy metals present in the sludge using pyrolysis. The risk analysis was performed to study the bioavailability and eco-toxicity of heavy metals in biochar obtained from pyrolysis of pulp and paper mill effluent treatment plant sludge. The sludge was pyrolyzed at different temperatures (200 – 700^{o}C) and the resultant biochar were analyzed for fractionation of heavy metals by sequential extraction procedure. It was observed that all the heavy metals get enriched in biochar matrix after pyrolysis, but the bioavailability and eco-toxicity of the heavy metals in biochar were significantly reduced as the mobile and bioavailable heavy metal fractions were transformed into the relatively stable fractions. Moreover, it was observed that the leaching potential of heavy metals decreased after pyrolysis and the best results were obtained for biochar pyrolyzed at 700^{o}C. Further, the sorption behaviour of the biochar was determined on the basis of degree of carbonization and bulk and surface properties of the biochar. It was found that the sorption behaviour varied from linear to non-linear depending on fractions of uncarbonized and carbonized organic matters in the biochar. The carbonized fraction acts as an adsorption media whereas uncarbonized fraction acts as a partition media. The individual fractions of adsorption and partition were quantified by isotherm separation method and isotherm parameters were correlated with biochar properties. It was found that H/C, O/C and (N+O)/C atomic ratios

were negatively correlated with adsorption capacity, while surface area, total pore volume and pore diameter were positively correlated to the biochar adsorption capacity.

The biochar pyrolyzed at 700 ^{o}C (BC700) showed best results in the terms of adsorption performance and environmental friendliness. However, the tedious separation process of the exhausted powdered biochar from the effluent and the regeneration/disposal problem of the exhausted biochar limit its commercial applications. Therefore, zero-valent iron (ZVI) was incorporated in the biochar matrix to modify the biochar to magnetic biochar composite which facilitate the separation of the exhausted biochar from the effluent. ZVI has powerful magnetic and reducing properties, which makes it most suitable magnetic reducing media for mixing with the biochar to obtain the modified magnetic biochar composites. The zero-valent iron magnetic biochar composites (ZVI-MBC) were synthesized from the paper mill sludge biochar and used for the treatment of the synthetic and real effluent containing pentachlorophenol (PCP). During the synthesis of ZVI-MBC, $NaBH_4$ was used as the reducing agent to reduce Fe (II) to Fe (0) and cetyltrimethylammonium bromide was added as surfactant. The effect of the molar ratio of $FeSO_4$ to $NaBH_4$, dose of the surfactant and the ZVI to biochar ratio on the PCP removal efficiency was investigated. It was found that the ZVI-MBC combines the advantages of biochar and ZVI particles for the simultaneous adsorption and dechlorination of PCP in the effluent and the complete removal of PCP was obtained in 240 min. The ageing tests showed that biochar prevents the formation of oxide film on the ZVI particles and leaching tests confirmed the stability of ZVI on biochar matrix as very low iron leaching was noticed. Although, ZVI-MBC was efficient in dechlorination of PCP from the aqueous solution but the dechlorination reaction was too slow to achieve the desired dechlorination in practical period of time. One of the practical approaches for enhancing the dechlorination rate of the ZVI-MBC is the impregnation of ZVI-MBC with a catalyst (Ni). Therefore, the Ni-ZVI magnetic biochar composites (Ni-ZVI-MBC) were synthesized by doping of Ni on ZVI-MBC surface. The synthesized Ni-ZVI-MBC were characterized and analyzed for the stability of Ni and ZVI particles in biochar matrix. It was found that the removal of PCP with Ni-ZVI-MBC involves simultaneous adsorption and dechlorination mechanism resulting in higher PCP removal efficiency. The presence of Ni as a catalyst in Ni-ZVI-MBC enhances the dechlorination rate and prevents the accumulation of PCP in the biochar matrix. The effect of operating parameters (solution pH, Ni loading, initial PCP concentration in the solution and temperature) on adsorption and dechlorination efficiency was studied. The dechlorination efficiency of Ni-ZVI-MBC was found to increase with an increase in Ni loading and the optimum Ni loading was found to be 0.5 wt %. The adsorption and dechlorination kinetics of PCP removal were studied and it was found that adsorption is the rate limiting step in PCP removal by Ni-ZVI-MBC.

The disposal of the exhausted adsorbent becomes a problem as it contains concentrated amount of the pollutants. So, the feasibility of usage of exhausted adsorbents for brick formation was evaluated. The bricks were prepared using geopolymerization technique using NaOH as polymerization agent. The geopolymer bricks showed good compressive strength and met ASTM standards. The concentration of heavy metals in the leachate was found within the permissible limits prescribed by Indian Standards for Industrial and Sewage Effluents Discharge (inland surface water) suggesting that the use of the geopolymer brick will not cause any harm to the environment.

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ABBREVIATIONS

BOD – Biochemical oxygen demand (mg/L)

COD – Chemical oxygen demand (mg/L)

EDX – Electron dispersive X-ray spectroscopy

FTIR – Fourier infrared transform spectroscopy

GC-MS – Gas chromatography mass spectroscopy

HPLC – High pressure liquid chromatography

SEM – Scanning electron microscopy

TDS – Total dissolved solids (mg/L)

TOC – Total organic carbon (mg/L)

TSS – Total suspended solids (mg/L)

XRD – X-ray diffraction spectroscopy

NOMENCLATURE

ETP – Effluent treatment plant

HMW – High molecular weight

LMW – Low molecular weight

MMW – Medium molecular weight

Ni-ZVI-MBC – Nickel zero-valent iron magnetic biochar composites

PAHs – Polycyclic aromatic hydrocarbons

PCP – Pentachlorophenol

PMS – Paper mill sludge

ZVI – Zerovalent iron

ZVI-MBC – Zero-valent iron magnetic biochar composites