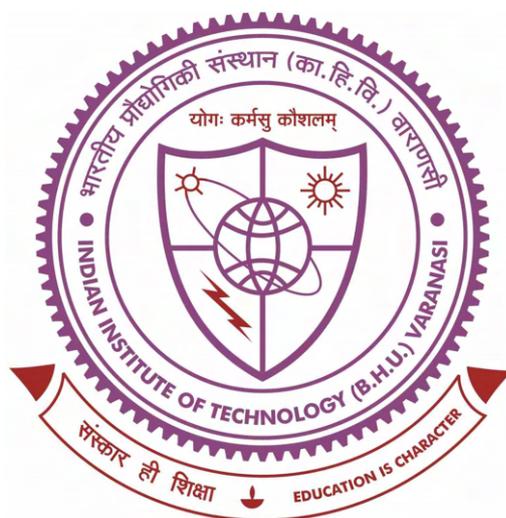


Removal of Copper, Nickel and Zinc from Contaminated Water using Novel Adsorbents



Thesis submitted in partial fulfilment

for the Award of

DOCTOR OF PHILOSOPHY

in

BIOCHEMICAL ENGINEERING

by

JYOTI SINGH

SCHOOL OF BIOCHEMICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY

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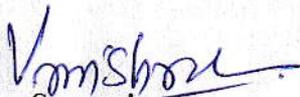
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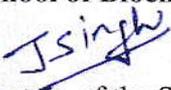
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List of Abbreviations

AAS	Atomic Absorption Spectrophotometer
ACGIH	American Conference of Governmental Industrial Hygienists
AC/ACTG	Activated carbon derived from <i>Tectona grandis</i>
ANN	Artificial Neural Network
ASTM	American Society for Testing and Materials
ATA	Azadirachta indica Twig Ash
ATSDR	Agency for Toxic Substances and Disease Registry
BET	Brunauer–Emmett–Teller
BIS	Bureau of Indian Standards
CPCB	Central pollution Control Board
Cu	Copper
D-R	Dubinin–Radushkevich
DTG	Derivative Thermogravimetry
ECEF	Electrocoagulation-Electroflotation
EDX	Energy-dispersive X-ray spectroscopy
F	Feldspar
FTIR	Fourier-transform infrared spectroscopy

FWHM	Full Width at Half Maxima
I	Illite
IARC	International Agency for Cancer Research
ICMR	Indian Council of Medical Research
L-M	Levenberg-Marquardt
M	Montmorillonite
MSE	Mean Square Error
MT	Metallothionein
Ni	Nickel
NTP	National Toxicology Program
OFI	Opuntia Ficus-indica
PIO	Pseudo First Order
PSO	Pseudo Second Order
Q	Quartz
Q	Reactive Oxygen Species
RSM	Response Surface Methodology
SEM	Scanning Electron microscopy
SRT	Statistical Rate Theory
TG	<i>Tectona grandis</i> Sawdust
TGA	Thermogravimetric analysis
USA	The United States of America
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

LIST OF ABBREVIATIONS

XRD X-ray Diffraction

ZiP Zinc Importer

Zn Zinc

ZnT Zinc Transporter

Abstract

Worldwide, approximately 80% of wastewater goes back to the waterways without being treated or reused, creating health, environmental, and climate hazards. Wastewater is generated either from domestic or industrial sources. Heavy metals are common in industrial effluent like cadmium, chromium, copper, arsenic, lead, nickel, and zinc, which are hazardous above permissible limits and have severe effects on humans, other species, and the environment. Heavy metals are easily absorbed by living organisms because they are highly soluble in aquatic environments. As a result, heavy metals must be removed from water before consumption using an inexpensive technique such as adsorption. Adsorption has the advantage of being a more cost-effective way of heavy metal removal when compared to other heavy metal removal processes. Adsorption of metals on the adsorbent allows metals to be removed from wastewater. In the present work, adsorption studies on Ni^{2+} , Cu^{2+} and Zn^{2+} ions removal by using novel adsorbents (Composite, *Azadirachta indica* Twig Ash, Activated carbon derived from *Tectona grandis* and Mould) showed significant effects of the variables like pH, initial adsorbate concentration, contact time, temperature and adsorbent dose. The optimum parameters for composite were observed as pH 6, initial Ni^{2+} , Cu^{2+} and Zn^{2+} ions concentration 100 mg/L, contact time 270 minutes for Cu^{2+} , Ni^{2+} and 330 minutes for Zn^{2+} ions, temperature 308 K and adsorbent dose 1 g. The optimum parameters for *Azadirachta indica* Twig Ash were pH 6, initial Ni^{2+} , Cu^{2+} and Zn^{2+} ion concentration 100 mg/L, contact time 210 minutes, temperature 308 K and adsorbent dose 1 g. The optimum parameters for Activated carbon derived from *Tectona grandis* were pH 9, initial Ni^{2+} , Cu^{2+} and Zn^{2+} ion concentration of 100 mg/L, contact time of 30 minutes, temperature of 308 K and adsorbent dose of 0.10 g. The optimum pa-

rameters for mould were pH 6, initial Ni²⁺, Cu²⁺ and Zn²⁺ ion concentration of 50 mg/L, contact time of 30 minutes and temperature 308 K. Surface characterization using proximate and ultimate analysis, Scanning electron microscopy with energy dispersive X-ray spectroscopy, Fourier-transform infrared spectroscopy, Brunauer–Emmett–Teller surface area, Thermogravimetric analysis and X-ray Powder Diffraction were done to analyze the physico-chemical characteristics of each novel adsorbent. Scanning electron microscopy micrograph of composite shows platelet-like particles clumped together with larger particles. Before adsorption, *Azadirachta indica* Twig Ash consisted of small particles of varying shape and size. In the scanning electron microscopy micrograph of Activated carbon derived from *Tectona grandis*, protrusions run through the biomass matrix. The diasporic particle size distribution revealed a range of forms and sizes for activated carbon particles. A sufficient adsorption zone were found on the surface of mould. Energy-dispersive X-ray spectroscopy of *Azadirachta indica* Twig Ash showed the presence of C and O mostly with minor amounts of Al, Mg, Ca, Na, Si, N, K, P, and S. Energy-dispersive X-ray spectroscopy of Activated carbon derived from *Tectona grandis* revealed C, O, Na, Al, S, Cl, and K and for mould revealed the presence of K, O, Fe, Mg, Al, and Si. Alumina rich octahedral centres of bentonite, bending vibration of the H-O-H group, and Si-O stretching of silica and quartz were detected in the composite's Fourier-transform infrared spectroscopy and *Azadirachta indica* Twig Ash demonstrated O-H stretching of carboxylic groups, N-H stretching of syringaldehyde, and C=O stretching. The O-H stretching vibration in *Tectona grandis* sawdust and Activated carbon derived from *Tectona grandis* confirmed the presence of alcohols and phenols in the structure. Fourier-transform infrared spectroscopy of mould revealed stretching vibrations of O-H groups linked to alcohols and phenolic chemicals. It had Si-O-Si, Si-O-Al, and Al-O stretching vibrations on tetrahedral and octahedral sheets. It also contained Al-Mg-OH stretching, indicating quartz. X-ray powder diffraction analysis found quartz, alumina, and hematite in composite and showed that *Azadirachta indica* Twig Ash was somewhat amorphous and should be used as an adsorbent. X-ray powder diffraction pattern for Activated carbon derived from *Tectona grandis* revealed amorphous graphitic carbon and for mould revealed montmorillonite,

illite, quartz, and feldspar. Composite, *Azadirachta indica* Twig Ash, and Activated carbon derived from *Tectona grandis* have Brunauer–Emmett–Teller surface areas of 447.31, 71.35, and 1270 m²/g, respectively. The ultimate composite analysis revealed 39.03% C, 14.46% N, 1.48% H, and 0% S. *Azadirachta indica* Twig Ash had 38.47% C, 1.89% H, 49.21% O, and 10.43% N. *Azadirachta indica* Twig Ash had 55.22 % fixed carbon, 8.51 % moisture, 14.78 % ash, and 21.49 % volatile matter. *Tectona grandis* sawdust had 67.3 % fixed carbon, 18.3 % moisture, 0.7 % ash, and 13.7 % volatile matter. Based on proximate analysis, the mould had low moisture (0.49%), ash (4.5%) and high volatile matter (95.01%). The study of adsorption dynamics for novel adsorbents using dimensionless numbers for copper, nickel and zinc ions showed that adsorption on the surface of Activated carbon derived from *Tectona grandis* and mould was transfer controlled as N_k lies between 10^{-4} and 10^{-3} for Ni²⁺, Cu²⁺ and Zn²⁺ ions. The process was diffusion controlled for *Azadirachta indica* Twig Ash for removal of copper, nickel and zinc ions as N_k fell between 10^1 and 10^4 . For composite, the process was diffusion controlled for copper and nickel ions as value of N_k was observed between 10^1 and 10^4 and mixed diffusion and transfer controlled for zinc ions as N_k lies between 10^{-3} and 10^1 . The artificial neural network modeling has been performed to compare the experimental and theoretical values. It has been found that using ANN both the experimental and theoretical values for novel adsorbent seemed to be in agreement with each other showing a high regression coefficient of 0.95 - 0.99; 0.98; 0.99 and 0.98 for Activated carbon derived from *Tectona grandis*, *Azadirachta indica* Twig Ash, composite and mould, respectively. Experimenters used isotherms such as the Langmuir, Freundlich, and Dubinin Radushkevich isotherms to match their results. For Cu²⁺, Ni²⁺ and Zn²⁺ ions, the maximum adsorption capacity of composite, *Azadirachta indica* Twig Ash, Activated carbon derived from *Tectona grandis* and mould were found to be 61.86 mg/g, 37.89 mg/g and 10.48 mg/g; 10.10 mg/g, 125 mg/g and 3.12 mg/g; 250 mg/g, 500 mg/g and 83.33 mg/g; 0.045 mg/g, 0.086 mg/g and 0.021 mg/g, respectively. The kinetics followed pseudo second order kinetic model for all novel adsorbents. Due to the positive Gibbs free energy, the adsorption on mould was non-spontaneous. Thermodynamic study for *Azadirachta indica* Twig Ash,

Activated carbon derived from *Tectona grandis* and composite indicated the endothermic and spontaneous nature of the adsorption. In desorption study, Activated carbon derived from *Tectona grandis* had the highest percentage of desorption, followed by the composite, *Azadirachta indica* Twig Ash and mould. The findings indicate that composite, *Azadirachta indica* Twig Ash, Activated carbon derived from *Tectona grandis* and mould have a high potential for usage as an effective and cost-effective adsorbent for heavy metal removal in a variety of applications.