# Design of Adsorption System Based on the Utitlisation of Low Cost Adsorbent for the Removal of Toxic Heavy Metals from Industrial Effluent

**Nekita Boraah**

**DEPARTMENT OF CIVIL ENGINEERING**

**INDIAN INSTITUTE OF TECHNOLOGY DELHI**

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by

**Nekita Boraah**

**Department of Civil Engineering**

*Submitted*

*in fulfilment of the requirements for the degree of*

**DOCTOR OF PHILOSOPHY**

to the

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***Dedicated to my Aita and Koka***

# Declaration by the Author

This thesis comprises my original work and contains no material previously published or written by another person except where due reference has been made in the text. I have clearly stated the contribution of others in jointly authored works, which I have included in my thesis.

I have clearly stated the contribution of others to my thesis, including statistical assistance, survey design, data analysis, significant technical procedures, professional editorial advice, financial support and any other original research contributions used or reported in my thesis. The content of my thesis is the result of work I have carried out since the commencement of my higher degree at IIT Delhi. It does not include a substantial part of the work that has been submitted to qualify for the award of any other degree or diploma by any other university/tertiary educational institution. I have clearly stated which parts of my thesis, if any, have been submitted to qualify for another award.

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Nekita Boraah

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# Certificate

This is to certify that the thesis entitled "Design of Adsorption System based on the Utilization of Low Cost Adsorbent for the Removal of Toxic Heavy Metals from Industrial Effluent" being submitted by **Nekita Boraah** to the Indian Institute of Technology Delhi for the award of the degree of **Doctor of Philosophy** is a record of bona fide research work carried out by her. **Nekita** has worked under our guidance and supervision and has fulfilled the requirements for submitting this thesis, which to our knowledge has reached the requisite standard. The results contained in this thesis are original and have not been submitted, in part or full, to any other university or institute for the award of any other degree or diploma.

**Prof. Sumedha Chakma**

**Civil Engineering**

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**Nekita Boraah**

# Abstract

The problem of water pollution due to the accumulation of heavy metals has been in trend from a long period of time. Heavy metals are the group of pollutants that have drawn extensive attention during recent years due to high-level toxicity, even at low concentrations. The main concern rises due to their non-decomposable nature, and they start getting accumulated in the organisms. So, even at their lowest concentrations, their presence in water poses a threat to humans and ecosystems. The main source of heavy metal contamination in waster is due to the disposal of industrial effluents without proper treatment. Many treatment technologies like ion-exchange, electrochemical methods, membrane filtration, photocatalysis and nanotechnology have been developed in order to treat wastewater but these technologies need high cost of installation along with high maintenance. Of all the technologies reported, adsorption has proved to be a versatile and affordable method for the treatment of wastewater. There has also been reports of low-cost adsorbents developed from wastes, naturally occurring soils, mineral deposits, aquatic and terrestrial biomasses that successfully removed heavy metals from wastewater. In addition to them, biochars have also proved to be highly efficient and low-cost adsorbents to treat heavy metals. Biochar is basically a carbonized product formed by the pyrolysis of raw biomass at a temperature of around 300-700°C. Different feedstocks are utilized to produce biochars; however, wood biochars are reported to be efficient in terms of its characteristics, produce a better yield of biochar, easily producible, cost-efficient and so, are in trend. This study takes into account two different types of wood feedstocks, neem wood (N) and old furniture waste wood (OF) and analyses them at two different pyrolysis temperatures based on their yield. The study initially analyses the trend and direction of research in this field using bibliometric analysis conducted with the help of VOSviewer. After preparation, grinding, washing and storing the biochars, they are then subjected

to different characterization techniques in order to understand the properties and their applicability in different fields of study. In this context, characterization techniques like BET, TGA, SEM/EDX, FTIR and elemental analysis were conducted and the properties of the biochars analyzed from the characterization techniques gave an idea of their applicability as adsorbents. In this study, the biochars are utilised for the remediation of toxic heavy metal species from industrial wastewater. In this context, out of the most toxic and hazardous group of heavy metals, three toxic heavy metal species, As, Cr and Pb have been considered for this study. Four biochars, N300, N500, OF300, OF500 and a composite (N-OF) were considered for this study. The biochars were analysed for their efficiencies using batch studies using synthetic wastewater and the parameters analysed using kinetics, thermodynamics and intraparticle diffusion studies. Of the four individual biochars, N500 showed the best removal efficiencies of 94.71% for As, 96.4% for Cr and 83.62% for Pb at different ranges of adsorbent dosage, pH and initial concentration. The results showed comparable outcomes for the biochar composite (N-OF), which was then considered for the continuous column studies that mimicked the performance in field conditions. The column study was further considered to analyse the effect of adsorbent bed shape, and two adsorbent beds (vertical and series horizontal) were designed and tested with industrial wastewater to evaluate their performance using real-time wastewater. The analysis also took into account the effect of flow direction in understanding the efficiency of removing heavy metals in a continuous column system. The column study showed that the efficiency of the biochars reduced when the system was subjected to continuous flow mode and an efficiency of 54.3% for As, 44.72% for Cr and 60.13% for Pb was recorded against batch efficiencies of 94.4% for As, 89.96% for Cr and 78.32% for Pb. The kinetics showed that the adsorption followed the pseudo second order while the pseudo first-order also showed a good fit, indicating the process being dominated by physico-chemisorption of the ions into the adsorbents. The intraparticle diffusion analysis also hinted at film diffusion being predominant over particle diffusion. The column models, however, showed that BDST model fits well with the experimental data for the adsorption of As, Cr and Pb. The effect of bed height was studied in order to understand the removal process with the increase or decrease in bed height. Also, the series horizontal column showed better efficiency than the vertical bed column when tested with industrial wastewater. In terms of flow direction, the upward flow of the adsorbate through the adsorbent bed showed better efficiency in removing As, Cr and Pb from industrial wastewater. The analysis of removal by the ETP present at the industry showed that the ETP was not capable of removing the metal ions from water efficiently. The desorption and regeneration studies showed that the efficiency of the biochars decreased after the $2^{nd}$ cycle of regeneration. Hence, after the utilisation of the biochars, the spent biochars were also studied for their disposal. The spent biochars were further pyrolyzed, which led to the reduction in their mass, and they were infused in concrete and soil. The addition of the spent biochar in concrete did not hamper the strength of the concrete, and the soil structures found application in decorative items for household purposes, which, in a way, reduced the probability of contamination that could have otherwise arisen due to open disposal.

# सार

भारी धातुओं के संचय के कारण जल प्रदूषण की समस्या लंबे समय से चलन में है। भारी धातुएँ प्रदूषकों का वह समूह है जिसने हाल के वर्षों में उच्च-स्तर की विषाक्तता के कारण, यहाँ तक कि कम सांद्रता पर भी, व्यापक ध्यान आकर्षित किया है। मुख्य चिंता उनके गैर-अपघटनीय स्वभाव के कारण उत्पन्न होती है, और वे जीवों में जमा होने लगते हैं। इसलिए, उनकी सबसे कम सांद्रता पर भी, पानी में उनकी उपस्थिति मनुष्यों और पारिस्थितिकी तंत्र के लिए खतरा बन जाती है। अपशिष्ट में भारी धातु संदूषण का मुख्य स्रोत उचित उपचार के बिना औद्योगिक अपशिष्टों का निपटान है। अपशिष्ट जल के उपचार के लिए आयन-विनिमय, विद्युत रासायनिक विधियाँ, झिल्ली निस्पंदन, फोटोकैटलिसिस और नैनो प्रौद्योगिकी जैसी कई उपचार प्रौद्योगिकियाँ विकसित की गई हैं, लेकिन इन प्रौद्योगिकियों को उच्च रखरखाव के साथ-साथ स्थापना की उच्च लागत की आवश्यकता होती है। रिपोर्ट की गई सभी प्रौद्योगिकियों में से, अपशिष्ट जल के उपचार के लिए सोखना एक बहुमुखी और सस्ती विधि साबित हुई है। कचरे, प्राकृतिक रूप से पाई जाने वाली मिट्टी, खनिज जमा, जलीय और स्थलीय बायोमास से विकसित कम लागत वाले अधिशोषक की भी रिपोर्ट मिली है, जो अपशिष्ट जल से भारी धातुओं को सफलतापूर्वक हटाते हैं। उनके अलावा, बायोचार भी भारी धातुओं के उपचार के लिए अत्यधिक कुशल और कम लागत वाले अधिशोषक साबित हुए हैं। बायोचार मूल रूप से लगभग 300-700 डिग्री सेल्सियस के तापमान पर कच्चे बायोमास के पायरोलिसिस द्वारा निर्मित एक कार्बनयुक्त उत्पाद है। बायोचार का उत्पादन करने के लिए विभिन्न फीडस्टॉक्स का उपयोग किया जाता है; हालाँकि, लकड़ी के बायोचार को इसकी विशेषताओं के संदर्भ में कुशल बताया गया है, बायोचार की बेहतर उपज देता है, आसानी से उत्पादित होता है, लागत-कुशल होता है और इसलिए, चलन में है। यह अध्ययन दो अलग-अलग प्रकार के लकड़ी के फीडस्टॉक्स, नीम की लकड़ी (N) और पुराने फर्नीचर के अपशिष्ट लकड़ी (OF) को ध्यान में रखता है और उनकी उपज के आधार पर दो अलग-अलग पायरोलिसिस तापमानों पर उनका विश्लेषण करता है।

अध्ययन शुरू में VOSviewer की मदद से किए गए ग्रंथ सूची विश्लेषण का उपयोग करके इस क्षेत्र में अनुसंधान की प्रवृत्ति और दिशा का विश्लेषण करता है। बायोचार को तैयार करने, पीसने, धोने और भंडारण करने के बाद, उन्हें अध्ययन के विभिन्न क्षेत्रों में गुणों और उनकी प्रयोज्यता को समझने के लिए विभिन्न लक्षण वर्णन तकनीकों के अधीन किया जाता है। इस संदर्भ में, बीईटी, टीजीए, एसईएम/ईडीएक्स, एफटीआईआर और मौलिक विश्लेषण जैसी लक्षण वर्णन तकनीकों का संचालन किया गया और लक्षण वर्णन तकनीकों से विश्लेषण किए गए बायोचार के गुणों ने अधिशोषक के रूप में उनकी प्रयोज्यता का विचार दिया। इस अध्ययन में, बायोचार का उपयोग औद्योगिक अपशिष्ट जल से जहरीली भारी धातु प्रजातियों के उपचार के लिए किया जाता है। इस संदर्भ में, भारी धातुओं के सबसे जहरीले और खतरनाक समूह में से, तीन जहरीली भारी धातु प्रजातियों, As, Cr और Pb को इस अध्ययन के लिए माना गया है। चार अलग-अलग बायोचार में से, N500 ने As के लिए 94.71%, Cr के लिए 96.4% और Pb के लिए 83.62% की सबसे अच्छी निष्कासन क्षमता दिखाई। परिणामों ने बायोचार कम्पोजिट (N-OF) के लिए तुलनीय परिणाम दिखाए, जिसे तब निरंतर स्तंभ अध्ययनों के लिए माना गया था, जो क्षेत्र की स्थितियों में प्रदर्शन की नकल करते थे। स्तंभ अध्ययन को आगे अधिशोषक बिस्तर के आकार के प्रभाव का विश्लेषण करने के लिए माना गया था और दो अधिशोषक बिस्तर (ऊर्ध्वाधर और श्रृंखला क्षैतिज) को डिज़ाइन किया गया था और वास्तविक समय के अपशिष्ट जल का उपयोग करके उनके प्रदर्शन का मूल्यांकन करने के लिए औद्योगिक अपशिष्ट जल के साथ उनका परीक्षण किया गया था। विश्लेषण ने एक सतत स्तंभ प्रणाली में भारी धातुओं को हटाने में दक्षता को समझने में प्रवाह दिशा के प्रभाव को भी ध्यान में रखा। स्तंभ अध्ययन से पता चला कि जब प्रणाली को निरंतर प्रवाह मोड के अधीन किया गया तो बायोचार्स की दक्षता कम हो गई और As के लिए 54.3%, Cr के लिए 44.72% और Pb के लिए 60.13% की दक्षता दर्ज की गई, जबकि बैच दक्षता As के लिए 94.4%, Cr के लिए 89.96% और Pb के लिए 78.32% थी। गतिकी ने दिखाया कि अधिशोषण छद्म द्वितीय क्रम का अनुसरण करता है जो अधिशोषकों में आयनों के

रासायनिक अधिशोषण की प्रक्रिया को इंगित करता है। अंतराण्विक विसरण विश्लेषण ने भी कण विसरण पर फिल्म विसरण के प्रमुख होने का संकेत दिया। हालांकि स्तंभ मॉडल ने दिखाया कि थॉमस मॉडल As, Cr और Pb के अधिशोषण के लिए प्रायोगिक डेटा के साथ अच्छी तरह से फिट बैठता है। बिस्तर की ऊंचाई में वृद्धि या कमी के साथ निष्कासन प्रक्रिया को समझने के लिए बिस्तर की ऊंचाई के प्रभाव का अध्ययन किया गया था। इसके अलावा, औद्योगिक अपशिष्ट जल के साथ परीक्षण किए जाने पर श्रृंखला क्षैतिज स्तंभ ने ऊर्ध्वाधर बिस्तर स्तंभ की तुलना में बेहतर दक्षता दिखाई। प्रवाह दिशा के संदर्भ में, अधिशोषक बिस्तर के माध्यम से अधिशोषक के ऊपर की ओर प्रवाह ने औद्योगिक अपशिष्ट जल से As, Cr और Pb को हटाने में बेहतर दक्षता दिखाई। उद्योग में मौजूद एसटीपी द्वारा निष्कासन के विश्लेषण से पता चला कि एसटीपी पानी से धातु आयनों को कुशलतापूर्वक हटाने में सक्षम नहीं था। विशोषण और पुनर्जनन अध्ययनों से पता चला है कि पुनर्जनन के दूसरे चक्र के बाद बायोचार की दक्षता कम हो गई। इसलिए, बायोचार के उपयोग के बाद, खर्च किए गए बायोचार को भी अनुप्रयोगों में शामिल करके उनके निपटान के लिए अध्ययन किया गया और इसलिए, खुले निपटान के कारण उत्पन्न होने वाली संदूषण की गतिविधि को कम किया गया।

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