Indian Institute of Technology Delhi

THE UNIVERSITY OF QUEENSLAND
AUSTRALIA

SYNTHESIS OF WASTE-DERIVED CARBON ADSORBENTS FOR EFFECTIVE REMOVAL OF PHENOL FROM WASTEWATER

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Synthesis of waste-derived carbon adsorbents for effective removal of phenol from wastewater

by

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Submitted

in fulfilment of the requirements for the joint degree of

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&

THE UNIVERSITY OF QUEENSLAND AUSTRALIA

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आपो हिष्ठा मयोभुवस्ता न ऊर्जे दधातन ।
महे रणाय चक्षसे ।।१।।
यो व: शिवतमो रसस्तस्य भाजयतेह नः ।
उशतीरिव मातर: ।।२।।
(पवित्र वेद से संकलित: ऋग्वेद सहिंता -10.9.1-2)

जल आनंद का स्त्रोत है ऊर्जा का भंडार है|
कल्याणकारी है ||
पवित्र करने वाला है |
और माँ की तरह पोषक तथा जीवनदाता है ||

Water is the source of
happiness, energy, health, and purity,
and is life-giving as a mother!
(Compiled from the Holy Veda: Rigveda Samhita -10.9.1-2)

O !! O

This thesis is dedicated to my beloved grandmothers,

women of grace, resilience, and boundless love.

"Swargeeya Shrimati Saroj Bala Jain"

स्वर्गीया श्रीमती सरोज बाला जैन

&

"Swargeeya Shrimati Vimla Devi Jain"

स्वर्गीया श्रीमती विमला देवी जैन

your love, care, and unfulfilled dreams echo in the pages of this thesis.

Every word is a tribute to the enduring impact of your guidance and extreme struggle in educating your children. Though you may not witness the completion of this chapter, your spirit resonates in every word, every discovery, and every achievement.

Thank you for being the driving force behind my dreams. In every page, in every line, and in every accomplishment, your presence is felt, and your legacy lives on.

With eternal love,

Marut Jain

…

Certificate

This is to certify that the thesis entitled "**Synthesis of waste-derived carbon adsorbents for effective removal of phenol from wastewater**" being submitted by **Mr. Marut Jain** to the "Indian Institute of Technology Delhi" and "The University of Queensland Australia" for the award of the degree of **Doctor of Philosophy** is a record of bonafide research work carried out by him. **Mr. Marut Jain** has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis, which, to our knowledge, has reached the requisite standard. The results 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.

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Abstract

Water remediation is an essential component of sustainable development. The increasing global population and rapid industrialization have contributed to the deterioration of water resources. Various organic pollutants found in industrial effluents pose a severe threat to environmental sustainability. Phenol is one of the most prevalent impurities, which has shifted the focus of researchers on the approaches for its efficient removal from aqueous solutions. Phenol, mainly found in industrial effluents, has adverse effects on ecosystems; hence, effective remediation strategies are necessary to address this issue. Carbon-based adsorbents have emerged as a promising solution in recent years owing to adsorbent efficiency in removing phenol from water, thereby offering a strategic solution for phenol adsorption and promoting sustainable water management. This dissertation underscores the potential applications of engineered carbon-based adsorbents for the effective adsorption of phenol.

In this scenario, graphene oxide (GO), magnetic graphene oxide (MGO), graphene aerogel (GA), and a novel hybrid aerogel (GO/CNTs) formed from GO and spent catalyst-generated carbon nanotubes (CNTs) were employed for the removal of phenol from water. All four adsorbents were assessed for phenol adsorption from wastewater, with both GA (404 m^2/g) and GO/CNTs (545.2 m^2/g) exhibiting outstanding potential for the adsorption of phenol (141 mg/g and 204 mg/g, respectively) as compared to powdered forms (108 mg/g for GO and 47 mg/g for MGO).

Another approach was followed to produce the advanced carbon adsorbents *via* pyrolysis from the various waste materials, *i.e.,* cow-dung, computer motherboard, and tyre. Synthesized activated carbon produced from different wastes exhibited specific surface area in this order *viz* cow-dung derived activated carbon (CDAC) (1146 m^2/g) > e-waste derived activated carbon (EAC) (930 m^2/g) > tyre derived activated carbon (TAC) (719 m^2/g). CDAC showed higher adsorption efficiency for phenol in a batch process (518 mg/g), followed by EAC (196 mg/g) and TAC (160 mg/g). CDAC adsorbent that showed enhanced adsorption capacity in the batch process was further utilized for continuous phenol adsorption in the column and exhibited 46 mg/g adsorption capacity, which was comparatively lower (only 8.8 %) than the batch process.

To further enhance the phenol adsorption capacity and to remove the adsorbents from wastewater, the derived activated carbon was efficiently converted into aerogel form *via* a

drying process. The process parameters (bed height, initial concentration of phenol, and flow rate) in column adsorption were optimized. EAC aerogel showed 130 mg/g adsorption efficiency in the column and retained ~90% of its efficiency compared to the batch process.

After successful implications of phenol removal from wastewater at the lab scale, the efficacy of synthesized adsorbent was further explored in petrochemical refinery wastewater treatment. In this regard, oily sludge from the refinery was used to synthesize the activated carbon. The activated carbon derived from oily sludge (OSAC) activated at 1073 K showed the highest adsorption capacity for phenol (527 mg/g) with around >90% phenol removal from refinery wastewater. Besides phenol, 24 other water quality parameters such as Iron, Nitrite, Hydrazine, Turbidity, COD, Fluoride, Ammonia, Sulphide, Alkalinity, Dissolved Oxygen, Cyanide, Ortho phosphate, Total Phosphate, Calcium Hardness, pH, Total Hardness, Sulphate, Chloride, Chlorine, Conductivity, Total Dissolved Solids, and Total Suspended Solids were also assessed. The synthesized adsorbents were recycled in five cycles. The discharge of contaminated adsorbent was done in the environment as per the USEPA standards, addressing the leaching property of the adsorbent.

Plausible adsorption mechanisms were further examined to validate the varying adsorption efficacy of the synthesized adsorbents. The adsorption data was fitted into the isotherm models to study the adsorption mechanism and interaction between adsorbate and adsorbent. Further, to determine the rate-limiting stage of adsorption, kinetic data were fitted into Pseudo-first-order, Pseudo-second order, Elovich, and Intra-particle diffusion kinetic models. RSM-CCD analysis was conducted to optimize the adsorption process parameters, which were further validated by statistical analysis.

A detailed analysis of the environmental impact of laboratory-scale production and application of CDAC and OSAC for phenol adsorption was done, delineating the experimental procedures and results and examining adsorption capacities and carbon characteristics. Utilizing a systematic life cycle assessment (LCA) approach, environmental impact throughout the activated carbon production lifecycle was accomplished. Overall, this dissertation deals with the efficient synthesis of different carbon-based adsorbents to effectively remove phenol from water and wastewater.

सार

जल उपचार सतत विकास का एक अनिवार्य घटक है। बढ़ती वैश्विक आबादी और तेजी से औद्योगिकीकरण ने जल संसाधनों की गिरावट में योगदान दिया है। औद्योगिक अपशिष्टों में पाए जाने वाले विभिन्न कार्बनिक प्रदूषक पर्यावरणीय स्थिरता के लिए एक गंभीर खतरा पैदा करते हैं। फिनोल सबसे प्रचलित अशुद्धियों में से एक है, जिसने अपशिष्ट जल से इसके हटाने के लिए शोधकर्ताओं का ध्यान केंद्रित किया है। फिनोल, मुख्य रूप से औद्योगिक अपशिष्टों में पाया जाता है, पारिस्थितिक तंत्र पर प्रतिकूल प्रभाव डालता है; इसलिए, इस मुद्दे को हल करने के लिए प्रभावी उपचार रणनीति आवश्यक है। कार्बन आधारित अधिशोषक हाल के वर्षों में पानी से फिनोल को हटाने में सोखने की दक्षता के कारण एक आशाजनक समाधान के रूप में उभरे हैं, जिससे फिनोल अधिशोषण के लिए एक रणनीतिक समाधान की पेशकश की जाती है और स्थायी जल प्रबंधन को बढ़ावा दिया जाता है। यह शोध प्रबंध फिनोल के प्रभावी अधिशोषण के लिए कार्बन-आधारित अधिशोषक के संभावित अनुप्रयोगों को रेखांकित करता है।

इस परिदृश्य में, ग्राफीन ऑक्साइड (GO), चुंबकीय ग्राफीन ऑक्साइड (MGO), ग्राफीन एरोजेल (GA), और ग्राफीन ऑक्साइड और उत्प्रेरक जनित कार्बन नैनोट्यूब (CNT) से गठित एक हाइब्रिड एरोजेल (GO/CNTs) को पानी से फिनोल हटाने के लिए नियोजित किया गया था। सभी चार अधिशोषकों का मूल्यांकन अपशिष्ट जल से फिनोल अधिशोषण के लिए किया गया था, GA (404 m^2/g) और GO/CNTs (545.2 m^2/g) दोनों के साथ पाउडर रूपों (GO के लिए 108 mg/g और MGO के लिए 47 mg/g) की तुलना में फिनोल (क्रमशः 141 mg/g और 204 mg/g) के अधिशोषण के लिए उत्कृष्ट क्षमता प्रदर्शित करते हैं।

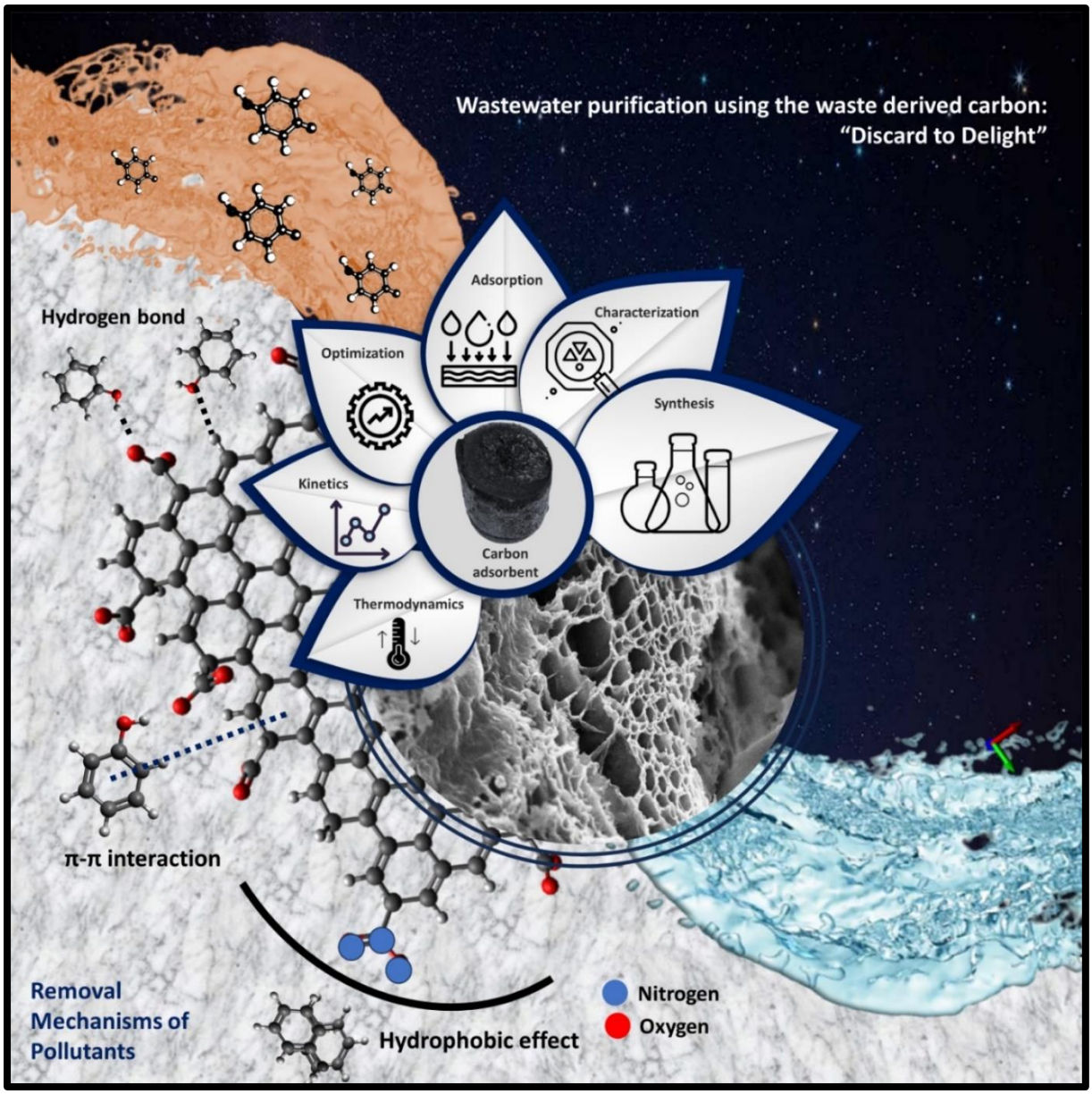
विभिन्न अपशिष्ट पदार्थों, यानी गाय के गोबर, कंप्यूटर मदरबोर्ड और टायर से पायरोलिसिस के माध्यम से उन्नत कार्बन अधिशोषक का उत्पादन करने के लिए एक अन्य दृष्टिकोण का पालन किया गया था। विभिन्न अपशिष्टों से उत्पादित संश्लेषित सक्रिय कार्बन ने इस क्रम में विशिष्ट सतह क्षेत्र अर्थात गाय के गोबर से व्युत्पन्न सक्रिय कार्बन (CDAC) (1146 m^2/g) > ई-अपशिष्ट व्युत्पन्न सक्रिय कार्बन (EAC) (930 m^2/g) > टायर व्युत्पन्न सक्रिय कार्बन (TAC) (719 m^2/g) का प्रदर्शन किया। सीडीएसी ने बैच प्रक्रिया (518 मिलीग्राम / जी) में फिनोल के लिए उच्च अधिशोषण दक्षता दिखाई, इसके बाद EAC (1 9 6 mg/g) और टीएसी (160 mg/g) है। CDAC अधिशोषण जिसने बैच प्रक्रिया में बढ़ी हुई अधिशोषण क्षमता दिखाई, आगे कॉलम में निरंतर फिनोल अधिशोषण के लिए उपयोग किया गया था, और 46 mg/g अधिशोषण क्षमता दिखाई, जो बैच प्रक्रिया की तुलना में तुलनात्मक रूप से कम (केवल 8.8%) थी।

फिनोल अधिशोषण क्षमता को और बढ़ाने और अपशिष्ट जल से अधिशोषक को हटाने के लिए, व्युत्पन्न सक्रिय कार्बन को कुशलतापूर्वक एरोजेल रूप में परिवर्तित किया गया। कॉलम अधिशोषण में प्रक्रिया मापदंडों (कार्बन की ऊंचाई, फिनोल की प्रारंभिक एकाग्रता, और प्रवाह दर) को अनुकूलित किया गया था। EAC एरोजेल ने कॉलम में 130 mg/g अधिशोषण दक्षता दिखाई और बैच प्रक्रिया की तुलना में ~ 90% अपनी दक्षता को बरकरार रखा।

प्रयोगशाला पैमाने पर अपशिष्ट जल से फिनोल हटाने के सफल निहितार्थ के बाद, पेट्रोकेमिकल रिफाइनरी अपशिष्ट जल उपचार में संश्लेषित अधिशोषण की प्रभावकारिता का और पता लगाया गया । इस संबंध में, सक्रिय कार्बन को संश्लेषित करने के लिए रिफाइनरी से तैलीय गाद का उपयोग किया गया था। 1073 K पर सक्रिय तैलीय गाद (OSAC) से प्राप्त सक्रिय कार्बन ने रिफाइनरी अपशिष्ट जल से लगभग >90% फिनोल हटाने के साथ फिनोल (527 mg/g) के लिए उच्चतम अधिशोषण क्षमता दिखाई। फिनोल के अलावा, 24 अन्य जल गुणवत्ता मानकों जैसे आयरन, नाइट्राइट, हाइड्राज़ीन, टर्बिडिटी, सीओडी, फ्लोराइड, अमोनिया, सल्फाइड, क्षारीयता, घुलित ऑक्सीजन, साइनाइड, ऑर्थो फॉस्फेट, कुल फॉस्फेट, कैल्शियम कठोरता, पीएच, कुल कठोरता, सल्फेट, क्लोराइड, क्लोरीन, चालकता, कुल घुलित ठोस और कुल निलंबित ठोस पदार्थों का भी मूल्यांकन किया गया। संश्लेषित अधिशोषक को पांच चक्रों में पुनर्नवीनीकरण किया गया था। संदूषित अधिशोषक का निस्सरण यूएसईपीए मानकों के अनुसार पर्यावरण में किया गया था, जो अधिशोषक के लीचिंग गुण को संबोधित करता है। संश्लेषित अधिशोषक की अलग-अलग अधिशोषण प्रभावकारिता को मान्य करने के लिए प्रशंसनीय अधिशोषण तंत्र की और जांच की गई। अधिशोषण डेटा को अधिशोषण तंत्र तथा अधिशोष्य एवं अधिशोष्य के बीच अन्योन्यक्रिया का अध्ययन करने के लिए समताप मॉडलों में फिट किया गया था। इसके अलावा, अधिशोषण की दर-सीमित चरण निर्धारित करने के लिए, गतिज डेटा को छद्म-प्रथम-क्रम, छद्म-दूसरे क्रम, एलोविच और इंट्रा-कण प्रसार गतिज मॉडल में फिट किया गया था। आरएसएम-सीसीडी विश्लेषण, अधिशोषण प्रक्रिया मापदंडों को अनुकूलित करने के लिए आयोजित किया गया था, जिन्हें सांख्यिकीय विश्लेषण द्वारा मान्य किया गया।

प्रयोगशाला पैमाने पर उत्पादन के पर्यावरणीय प्रभाव और फिनोल अधिशोषण के लिए CDAC और OSAC के आवेदन का एक विस्तृत विश्लेषण किया गया, प्रयोगात्मक प्रक्रियाओं और परिणामों को चित्रित करना और अधिशोषण क्षमताओं और कार्बन विशेषताओं का एक विस्तृत विश्लेषण किया गया। एक व्यवस्थित जीवन चक्र मूल्यांकन (LCA) दृष्टिकोण का उपयोग करते हुए, सक्रिय कार्बन उत्पादन जीवनचक्र में पर्यावरणीय प्रभाव पूरा किया गया। कुल मिलाकर, यह शोध प्रबंध जल और अपशिष्ट जल से फिनोल को प्रभावी ढंग से हटाने के लिए विभिन्न कार्बन-आधारित अधिशोषक के कुशल संश्लेषण से संबंधित है।

Graphical Abstract



This graphical abstract shows the different mechanisms of adsorption of pollutants onto the waste-derived carbon-based adsorbents in wastewater treatment, achieving the aim of "Discard to Delight."

*This art was awarded the **"Jo Underhill IMB Art Award 2023"** of The University of Queensland Australia under the **"People's choice Award"** category on 8th December 2023 at the Institute for Molecular Bioscience, The University of Queensland Australia.*

Declaration by author

This thesis is composed of 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 to jointly authored works that 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 work 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 by research candidature and does not include a substantial part of work that has been submitted to qualify for the award of any other degree or diploma in any university or other tertiary institution. I have clearly stated which parts of my thesis, if any, have been submitted to qualify for another award.

I acknowledge that an electronic copy of my thesis must be lodged with the University Library and, subject to the policy and procedures of The University of Queensland, the thesis be made available for research and study per the Copyright Act 1968 unless the Dean of the Graduate School has approved a period of embargo.

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30 March 2024, Brisbane (Australia)

Publications included in this Thesis

International Peer-reviewed Journal

1. **M. Jain,** A. Sahoo, D. Mishra, K. K. Pant, Z. Ziora, M. Blaskovich, Modelling and statistical interpretation of phenol adsorption behaviour of 3-Dimensional hybrid aerogel of waste-derived carbon nanotubes and graphene oxide, Chemical Engineering Journal, 2024, 151351. https://doi.org/10.1016/j.cej.2024.151351
2. **M. Jain,** S. Khan, A. Pandey, K. K. Pant, Z. Ziora, M. Blaskovich, Instructive analysis of Engineered Carbon materials for Potential Applications in Wastewater Treatment., Science of the Total Environment, 2021, 793, 148583 https://doi.org/10.1016/j.scitotenv.2021.148583
3. **M. Jain,** S. Khan, K. Sharma, P. Jadhao, K. K. Pant, Z. Ziora, M. Blaskovich, Current perspective of innovative strategies for bioremediation of organic pollutants from wastewater., Bioresour. Technol., 2021, 126305. https://doi.org/10.1016/j.biortech.2021.126305
4. **M. Jain,** S. Khan, K. K. Pant, Z. Ziora, M. Blaskovich, Statistical evaluation of cow-dung derived activated biochar for phenol adsorption: Adsorption isotherms, kinetics, and thermodynamic studies, Bioresour. Techol., 2022, 351, 127030. https://doi.org/10.1016/j.biortech.2022.127030

Book Chapters

1. **M. Jain,** A. Noor, A. Sahoo, K. K. Pant, Z. Ziora, M. Blaskovich, Microbial degradation of Petrochemical refinery wastewater pollutants. Biodegradation of Toxic and Hazardous Chemicals: Remediation and Resource Recovery (1st ed.). CRC Press. https://doi.org/10.1201/9781003391487
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National Jigyasa Science Journal (IIT Delhi)

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…….

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Abbreviations

2D: Two Dimensional
AC: Activated Carbon
ANOVA: Analysis of Variance
AOC: Assimilable Organic Carbon
BAC: Biological Activated Carbon
BAC: Biologically Activated Carbon
CCD: Central Composite Design
CDAC: Cow-dung derived Activated Carbon
CMC: Carboxy methyl cellulose
CNT: Carbon Nanotubes
COD: Chemical Oxygen Demand
CVD: Chemical Vapor Deposition
DTP: Dynamic Toxicity Characteristic Leaching Procedure
EAC: Electronic waste derived Activated Carbon
EBCT: Empty bed contact time
ECM: Engineered Carbon Materials
ENDs: Endocrine Disrupting Chemicals
FRC: Free Residual Chlorine
GAC: Granular Activated Carbon
GO: Graphene Oxide
GOA: Graphene Oxide Aerogel
GWP: Global Warming Potential
HiPco: High-pressure carbon monoxide
LCA: Life Cycle Assessment
MGO: Magnetic Graphene Oxide
MTMS: Methyl trimethoxy silane
MWCNTs: Multi-walled Carbon Nanotubes
NA: Nitric Acid
OS: Oily sludge
OSAC: Oily sludge derived Activated Carbon
PAC: Powdered Activated Carbon
PCB: Printed Circuit Board
PCPs: Personal Care Products
PRW: Petrochemical refinery wastewater
RCRA: Resource Conservation and Recovery Act
RGO: Reduced Graphene Oxide
RO: Reverse Osmosis
RSM: Response surface methodology
SA: Sulphuric Acid
S_{BET}: Total surface area
TAC: Tyre derived activated carbon
TCLP: Toxicity Characteristic Leaching Procedure
WoS: Web of Science