GREEN AND SUSTAINABLE Solutions for heavy metal removal from wastewater

GREENAND SUSTAINABLE Solutions for heavy metal Removal from Wastewater

Haziqatulhanis Ibrahim Norazlianie Sazali Ahmad Fauzi Ismail Wan Norharyati Wan Salleh

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PREFACE

This book takes an innovative and environmentally conscious look at the field of heavy metal adsorption. The authors started a thorough investigation into nanocellulose that came from *Pandanus amaryllifolius* (PA) and was then changed into nanocrystalline cellulose (NCC). These researchers' thorough investigation has yielded a viable and eco-friendly method to eliminate heavy metals from wastewater, highlighting the enormous potential of materials and procedures inspired by nature.

The reader will embark on a comprehensive investigation of heavy metals, current water treatment techniques and the intriguing topic of the adsorption process as they go through the pages. Furthermore, this book will explore the revolutionary possibilities of sustainable solutions and nanotechnology, providing a thorough grasp of the scientific ideas and real-world applications that hold the key to a cleaner and greener future.

Readers will learn insights that can help them comprehend how the techniques and characterisations highlight the interesting nature of the nanoworld in the following chapters. The writers cordially encourage readers to go with them on this insightful trip, and uncover the possibilities and optimism contained inside the pages of this book as they demonstrate their unshakable dedication to sustainable solutions.

Hopefully, this book will be a source of knowledge, inspiration and a driver of change in our global effort towards a cleaner and more sustainable world. The authors warmly encourage readers to delve into this book and discover the fascinating developments in heavy metal adsorption technology.

ACKNOWLEDGEMENT

The authors want to convey profound gratitude and recognition to all those who have played a part in the creation and advancement of this book "Green and Sustainable Solutions for Heavy Metal Removal from Wastewater." Without the steadfast support, expertise and guidance of the individuals and organisations mentioned, this endeavour would not have come to fruition.

Foremost, we offer our sincere thanks to our families, whose unwavering encouragement, understanding and patience have been our steadfast companions throughout this journey. Their love and encouragement have been a consistent wellspring of motivation. We also wish to acknowledge the reviewers and editors who diligently scrutinised and enhanced the manuscript. Their meticulous attention to detail, perceptive insights and suggestions have markedly enriched the quality of this book.

Last but not least, we extend our appreciation to our readers, who have shown an interest in this book. We trust that the knowledge and perspectives shared in these pages will be proven valuable in advancing the field and nurturing fresh developments in heavy metal removal. Once again, we express our deepest gratitude to all who have contributed to the realisation of this book. Your support and participation have played an indispensable role in bringing this work to life.

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REVIEW ON HEAVY METALS IN WASTEWATER

Abstract

The presence of heavy metals in wastewater, and the various methods used to remove and recover them are subjects of concern. The development of effective remediation procedures is imperative due to the significant challenges posed by heavy metal contamination to both the environment and public health. The first step is to get a fundamental understanding of the causes of heavy metal contamination, and the effect on ecosystems and human health. With an emphasis on one primary technique, this section examines the benefits of adsorption over alternative processing techniques. Adsorption is valued for its quick kinetics, selectivity based on solid adsorbent materials, adaptability in targeting different metals and ease of operation.

Keywords

Heavy metals, Wastewater, Adsorption, Environmental

INTRODUCTION

Access to clean water is becoming increasingly challenging due to rising development and industrialisation. It is a common practice to discharge large volumes of industrial effluents into bodies of water, which can affect both oceans and river streams (Thekkudan et al., 2017). These effluents contain organic pollutants and substances that contain heavy metals. Heavy metals like Ni²⁺, Cu²⁺ and Zn²⁺ are known to be among the most harmful and toxic to the environment. According to Yaakub et al. (2020), marine life is especially susceptible to the harmful effects of these pollutants, which pose a threat to other species, including humans, through the food chain.

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Both Yaakub et al. (2020) and Zhao et al. (2011) found that wastewater from industries contains heavy metals that have carcinogenic properties. These heavy metals can lead to potential health hazards such as hypertension, fatal malformation and renal damage. Heavy metals are not suitable for biodegradation and have the potential to accumulate in the environment, which makes it difficult to get rid of them. Even though certain metals are necessary for the proper functioning of the body, an imbalance in the concentration of metals can have negative consequences. Copper(Cu), nickel(Ni) and manganese(Mn) deficiencies, for instance, can result in arterial weakening, growth depression and infertility (Karim et al., 2014; Cannas et al., 2020). These are just some of the potential consequences of these deficiencies.

All over the world, there has been an increase in the number of initiatives that aim to combat water pollution and improve water treatment systems. To remove heavy metals from wastewater, several different techniques are utilised (Chingombe et al., 2005). These techniques include electroplating, membrane filtration, ion exchange, precipitation and reverse osmosis. Taking into consideration the potential adverse effects on health that are associated with heavy metal exposure, the objective is to regulate metal intake in order to achieve a balance between the necessary metals, and the avoidance of excessive or inadequate consumption.

HEAVY METALS IN WASTEWATER

The human body can withstand tiny levels of metals under normal conditions without developing serious health issues. However, heavy metal poisoning of water has grown to be a major global problem. According to Fu and Wang (2011), heavy metals are defined as metals with an atomic weight between 63.5 and 200.6, and a specific gravity greater than 5.0. Human industrial activity and the direct dumping of municipal waste into water streams threaten the quality of the water. Only 1% of continental freshwater is accessible for everyday usage, and given the current

patterns of global population growth, the lack of clean water will quickly become a major problem on a worldwide scale.

The presence of the aforementioned harmful chemicals in water endangers the ecosystem and all living organisms, particularly marine life. These heavy metals, which cannot biodegrade like organic contaminants, pose a major risk to both humans and animals. Table 1.1 lists permissible levels of heavy metals in drinking water and Table 1.2 lists some of the recognised health hazards. Common industrial processing activities that release heavy metals into water bodies include mining, metal plating and fertiliser industry.

WHO (2004) WHO (2003a)
WHO (2003a)
JECFA (2000)
WHO (2003b)
WHO (2003c)
WHO (2003d)
WHO (2005)

Table 1.1: Permissible levels or heavy metals in drinking water.

Table 1.2: Health hazards carried by the heavy metal's exposure.

Heavy metals	s Health hazards	References
Copper	Neurological illness, Hypertension, Noseirritation and Autism	Dobrowolski et al. (2017) Shahzad et al.
Cadmium	Carcinogenic, Lung fibrosis, Dyspnoea	(2018) WHO. (2003c,
Chromium	Carcinogen, Lung tumour	2003d, 2004)

Heavy metal	s Health hazards	References
Lead	Carcinogenic, Anaemia,	Dobrowolski et
	Muscle and joint sore, high	al. (2017)
	blood pressure	Shahzad et al.
Zinc	Restlessness	(2018)
Nickel	Chronic bronchitis, lung	WHO. (2003c,
	cancer	2003d, 2004)

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Natural sources of the metal copper include rock, soil and water. According to Zoroddu et al. (2019), copper is also crucial for cellular functions in human bodies. However, excessive copper levels in water systems and high copper intake in people can have serious negative effects on health (National Research Council Committee on Copper in Drinking, 2000). Because these metal ions were improperly released into the water systems, copper(II) was able to enter human bodies through the food chain. The electroplating industry and copper smelting are two of the few sources that expose people to copper metal (Dong et al., 2019; Huang et al., 2018). Copper salts used in industry to control algae in reservoirs also increase the content of copper in water bodies. Copper poisoning is classified into two levels: acute and severe. Acute exposure produces nasal irritation and hypertension, while severe exposure causes neurological disease, anaemia and autism (National Research Council Committee on Copper in Drinking, 2000).

EXISTING WATER TREATMENT METHODS

Heavy metals of various types are frequently found in the large amounts of wastewater produced by manufacturing industries. Pollutants in the wastewater must first be treated and eliminated before the waste can be discharged into the water system.Since many years ago, studies have been conducted to develop practical and efficient methods to get rid of heavy metals, including membrane filtration, ion exchange, chemical precipitation, adsorption and electrooxidation. Due to its simplicity, chemical precipitation has traditionally been used to remove heavy metals; however, this method is not very efficient when there is a low concentration of metal ions. According to Kazeminezhad and Mosivandto (2017), significant amounts of sludge are created as a result of the precipitation, unequivocally demonstrating that the method is not very cost-effective.

The removal of unneeded metals from wastewater has also been accomplished using the ion exchange method. This process has the drawback of requiring chemical reagents to regenerate resins for ion exchange, which could lead to extremely serious secondary pollution. Additionally, this method is expensive and cannot be applied to large-scale water management. Although membrane fouling, low permeate flux, process complexity and high cost are some issues that can limit the use of this technique in wastewater treatment, membrane filtration is an effective way to remove heavy metals from water. Table 1.3 summarises other traditional heavy metal uptake methods.

In order to remove heavy metals from wastewater with low concentrations of pollutants, adsorption has long been recognised as an appealing, easy and affordable method. As claimed by Hadi et al. (2016) and a group of researchers who conducted a critical evaluation of the method's suitability for the removal of heavy metals, adsorption was found to be an excellent operational method due to its simple operating process and low cost compared to other approaches. A suitable reversible desorption method can also be used to recover the adsorbent cost compared to other approaches.

Technology	Advantages	Disadvantages	References
Ion exchange	 Relatively high regeneration Metal selective 	 Secondary pollution by resins recentration 	Dong et al. (2018): Joseph
		• Potentially alter the	et al. (2020)
		mineral composition	
Electrooxidation	Electrooxidation • Robust performance	• Electrode fouling and	Garcia-Segura
	• Efficient at ambient condition	degradation	et al., (2018);
		Possible generation of	Radjenovic &
		harmful by-products	Sedlak. (2015)
Membrane	• Low generation of solid waste	• Fouling of membrane	Riaz et al.
filtration	 Consume low chemicals 	 Susceptible to membrane 	(2016)
	• Require small space area for equipment	damage or breakage	
Flotation	• Ability to remove small particles	 Generation of sludge 	Taseidifar et
	• Low retention times		al. (2017)
Adsorption	• Easy to operate	 Adsorption capacity 	Bailey et al.
	 Varieties of target metals 	depends on the type of	(1999);
	 Selective of metal depending on solid 	adsorbent used	Dobrowolski et
	sorbent		al. (2017)
	• Fast kinetics		

Table 1.3 Existing methods for water treatment.

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Adsorption for removal of heavy metal ions

According to Singh et al. (2018), adsorption is a process in which a liquid solute or adsorbate accumulates on an adsorbent surface. The fundamental mechanism of adsorption is shown in Figure 1.1. Physical adsorption (physisorption) and chemical adsorption (chemisorption) are the two categories into which adsorption can be subdivided. The attraction between the sorbent surface and the adsorbate was assessed to distinguish between the two types of adsorptions. In contrast to chemical bonding, which has a strong attraction between molecules, physisorption involves natural interactions between molecules and weak van der Waals forces. In order to remove metals, a variety of materials have been investigated, including oxide-based adsorbent, carbon nanotubebased adsorbent and graphene-based adsorbent (Anjum et al., 2016). Although it has been suggested as a potential low-cost adsorbent, cellulosic-based adsorbent has been gaining attention from researchers worldwide due to its abundance and lower cost (Pyrzynska, 2019; Ulmanu et al., 2003; Wang & Chen, 2009). As a result of their interactions with surface functional groups, polysaccharides like cellulose, chitin and alginate demonstrated high metal binding capacity.

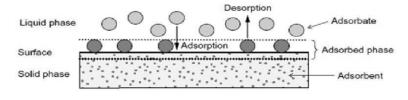


Figure 1.1: Simple illustration of adsorption (Worch, 2012)

Adsorption parameters

The adsorption process for the removal of heavy metals involves multiple factors. Several variables influence the process, including the acidity level of the solution, the amounts of metal ions present and the quantity of the selected adsorbent used. Thoroughly optimising these parameters is crucial to make a significant advancement in the large-scale removal of heavy metals. To attain the desired outcomes, it is imperative to enhance the adsorption capacity through the development of more diverse conditions. This strategic optimisation implementation facilitates the creation of a highly efficient method that can effectively eliminate metal contaminants on a large scale.

pH Level

The pH level is a critical parameter during the adsorption of heavy metal ions, influencing both the degree of ionisation of the adsorbate and the solubility of the metal ions. As highlighted by Joseph et al. (2019), pH is considered a crucial factor in the efficiency of the adsorption process, especially for heavy metals that typically exist in a cationic state under acidic to neutral pH conditions.

In the case of copper(II) ions, studies by Acheampong et al. (2013), Gündoan et al. (2004) and Kaur et al. (2019) reported that the adsorption of copper(II) increases within the pH range of 2 to 6. This is attributed to the fact that copper(II) ions, which carry a positive charge, exhibit enhanced affinity for adsorption at lower pH levels. The positive charge of copper(II) ions competes favourably with hydronium ions (H_3O^+), resulting in effective attachment to the surface of the adsorbent material.

However, beyond a certain pH threshold, it was observed that the adsorption capacity of copper(II) decreased. This phenomenon is explained by the fact that at higher pH levels, the positive charge on copper(II) ions diminishes, reducing their ability to attach to the adsorbent surface. Additionally, at elevated pH levels, there is a limited number of available active sites for adsorbate binding, leading to a decrease in the overall performance of the adsorption process.

Furthermore, Joseph et al. (2019) noted that the precipitation of copper(II) as $Cu(OH)_2$ begins when the pH level exceeds 7. This reaction hinders the completion of the adsorption process, as the formation of $Cu(OH)_2$ prevents copper ions from effectively attaching to the adsorbent surface. This information underscores the importance of maintaining an optimal pH range for effective heavy metal adsorption.

Initial Concentration

The initial concentration of heavy metals in a solution is a critical factor that significantly influences the speed and efficiency of their absorption through the adsorption process. A greater initial concentration of heavy metals results in a higher adsorption capacity, mainly due to the concentration gradient between the solution and the adsorbent that drives the adsorption process. Put it simply, a greater initial concentration yields a larger quantity of metal ions available for adsorption, thereby facilitating a more efficient attachment to the surface of the adsorbent.

Nevertheless, there exists a pivotal constraint to this association. Once the initial concentration exceeds the optimal level, the adsorption performance starts to deteriorate. The main reason for this is the scarcity of binding sites on the adsorbent's surface. Once the initial concentration exceeds the optimum level, the binding sites become fully saturated, indicating that there are no more available sites for additional metal ions to attach to. As a result, the intake of additional metal ions is hindered, resulting in reduction in the overall effectiveness of the adsorption process.

Past research, referenced by Memon et al. (2009) and Pourfadakari et al. (2017), suggested that the optimal adsorption capacity is attained within certain concentration ranges. In their findings, the optimal initial concentration for heavy metals falls within the range of 10 to 100 parts per million (ppm). The adsorption process operates most efficiently within this concentration range, achieving a balance between an adequate number of metal ions for effective adsorption and not overwhelming the binding sites on the surface of the adsorbent.

Adsorbent Dosage

The total amount of adsorbent used is crucial in the process of adsorption, as it directly affects the effectiveness and overall

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percentage of metal contaminants removed from a solution. According to El-Tawil et al. (2019), the efficiency of the process can be improved by increasing the quantity of adsorbent up to a specific threshold. This phenomenon can be attributed to the presence of a greater number of adsorbing sites on the surface of the adsorbent material, which in turn allows for an increased likelihood of metal ions binding to and being eliminated from the solution. In essence, increasing the quantity of adsorbent up to an optimal dosage is directly proportional to enhanced adsorption efficiency.

Nevertheless, Gorzin and Bahri Rasht Abadi (2018) offered a different viewpoint, stating that beyond a specific threshold, augmenting the number of adsorbent leads to a decline in adsorption capacity. This phenomenon can be attributed to the saturation of metal ions on the surface of the adsorbent. This saturation creates a state of unsaturation, where the addition of more adsorbent does not have a significant impact on the removal process. Gorzin and Bahri Rasht Abadi (2018) observed that there is no noticeable rise in the percentage of removal once the optimal dosage is reached. According to their findings, additional increases in dosage result in a decrease in removal efficiency.

The divergent results highlight the intricacy of determining the optimal amount of adsorbent to be used in the adsorption process. Attaining an ideal equilibrium is vital, as insufficient adsorbent can lead to ineffective metal elimination, while an excessive amount may result in diminishing returns and decreased efficiency. The disparities in observations underscore the necessity for a meticulous and context-dependent methodology to ascertain the suitable dosage while considering the distinct attributes of the adsorbent and the desired metal ions. When designing adsorption processes to remove heavy metals, researchers and practitioners need to take into account these subtle dynamics. It is important to select a dosage that is in line with the desired outcome to achieve maximum efficiency and removal percentage.

Adsorption Isotherm models

The adsorption isotherm is a useful tool to understand the correlation between the quantity of adsorbate on the adsorbent surface and the concentration of heavy metal ions, given a fixed pH and temperature. This was emphasised by Singh et al. (2018). This isotherm offers a succinct depiction of the interaction between ions and adsorbents, specifically in batch adsorption situations with different initial concentrations of metal ions.

Within the field of adsorption studies, various models have been formulated to elucidate adsorption mechanisms, with the Langmuir and Freundlich models being particularly prominent. These models are commonly utilised to analyse empirical data and acquire an understanding of the adsorption process. One crucial aspect of their usefulness resides in their capacity to offer theoretical frameworks to comprehend the process of adsorption.

The Langmuir isotherm model postulates that adsorption occurs on a uniform surface with a limited number of identical and energetically equivalent adsorption sites, forming a monolayer. It implies that once a site for adsorption is filled, no additional adsorption can occur on that particular site. Conversely, the Freundlich isotherm model is founded on the concept of adsorption occurring in multiple layers on a surface that is not uniform, thereby accommodating a range of adsorption energies. It is not constrained by a predetermined number of adsorption sites, which enhances its flexibility in real-world situations.

Table 1.4, as cited by Singh et al. (2018), illustrates a juxtaposition of the Langmuir and Freundlich models. These models facilitate the fitting of experimental data acquired from adsorption studies, assisting in the determination of the utmost adsorption capacity and offering insights into the adsorption mechanism. Researchers can evaluate the suitability of theoretical frameworks and enhance their comprehension of adsorption behaviour by comparing experimental results with the predicted values from these models.

Adsorbent

Historically, activated carbon-based materials have been predominant among adsorbents utilised for the removal of heavy metals from wastewater. Activated carbon is acknowledged for its highly effective adsorption capabilities; however, a notable drawback is its costliness, as highlighted in studies by Lim et al. (2012). Consequently, researchers have explored alternative adsorbents to address cost concerns while maintaining high adsorption efficiency.

In recent years, there has been a notable shift towards using less expensive and environmentally friendly adsorbents, a trend highlighted by various researchers. The exploration of materials such as clay and zeolites as adsorbents has been extensively reported in earlier research (Muhamad et al., 2018; Srinivasan, 2011), demonstrating a diverse range of materials under consideration. Researchers are now increasingly opting for green adsorbents that offer excellent adsorption performance at a lower cost.

Studies by Igwegbe et al. (2015), Lu et al. (2013), Mohamed et al. (2015) and Tibolla et al. (2018) emphasised the efficacy of various affordable and environmentally friendly adsorbents. Examples include banana peel, sweet potato waste, papaya carica, cellulose and chitosan, which are readily available and possess adsorption properties suitable for heavy metal removal. This shift towards utilising such materials is aligned with the broader goal of developing sustainable and cost-effective solutions for wastewater treatment. Table 1.5 summarises the benefits and drawbacks of popular adsorbents based on earlier studies, offering a comprehensive overview of the characteristics and suitability of different materials. This comprehensive exploration of alternative adsorbents underscores the ongoing efforts to optimise and diversify the range of materials employed in wastewater treatment, striking a balance between effectiveness, costefficiency and environmental impact.

Isotherms	Model	Linear	Parameters	Description	References
	equations	form			
Langmuir	$q_e = q_m K_L$	\mathcal{C}_{e}	Ce (mg/L):	Assuming monolayer	Singh et al.
	$L C_e$	q_e	Metal ions	adsorption process	(2018)
	$\frac{1}{1+K_LC_e}$		concentration at		
	1	$= \frac{1}{q_m K_L} c_e$	equilibrium	The affinity and the	
		, -		favourableness	
		$+\frac{K}{K}$	qe (mg/g):	between the adsorbent	
		11167	The amount of	and the adsorbate can	
			metal ion adsorbed at	be predicted by using	
			equilibrium	Langmuir constant KL	
			K _L (L/mg): Langmuir constant	constant separation factor, R_L ;	
			$q_m (mg/g)$:	$\mathbf{R}_L = (1/1 + \mathbf{K}_L \mathbf{C}_0)$	
			Maximum adsorption capacity	were, C ₀ = Initial	
				concentration of adsorbate (mg/L)	

Table 1.4: Details of adsorption isotherm models.

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Isotherms	Model equations	Linear form	Parameters	Description	References
				 Irreversible (RL= 0) Favourable (0 < RL 	
				<1) 3) Linear (RL = 1) 4) Unfavourable (RL >	
Freundlich		lna	Co (mo/L).	1) Assumino multilaver	Maleki
	$q_e = K_F C_e n$	$= \ln K_F$	Metal ions	5	&Karimi-
		_ 1 1 آمر	concentration at		
		$\frac{1}{n}$	equilibrium	ue of	
			00 (mo/o).	favourability of	Singn et al. (2018)
			The amount of		
			sort	Irreversible $(1/n = 0)$ Favourable $(0 < 1/n < 1)$	
			1/n: The heterogeneity factor	1_ Unfavourable (1/n > 1)	
			NF (L/g): Freundlich constant		

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Adsorbent	Advantages	Disadvantages	References
Activated	Effective adsorbent	 Limited selectivity 	Hegazi. (2013)
carbon	• Ability to generate high adsorption capacity	• Expensive regeneration	
		• Energy-intensive	
Zeolite	 Provide large surface area 	• Hard to separate the	Muhamad et al.
		material	(2018)
	• Superior thermal, chemical and mechanical stability	after adsorption	
		 Not suitable to be reused 	
Chitosan	Renewable and biodegradable	• Low mechanical resistance	Matusiak &
	 Good metal ion selectivity 	Pore size is difficult	difficult Bastrzyk. (2018)
		ed	
Clay	 Exhibit porous structure 	 Low adsorption capacity 	Srinivasan. (2011)
	 Large specific surface area 		
	• High chemical and mechanical stability		
Cellulose	 Most abundant polysaccharide on Earth 	• Low heavy metal	Mohamed et al.
	 Presence of hydroxyl group for ease of further 	adsorption capacity	(2017)
	Compatible with most of biological compound	 Poor physical stability 	Ummartyotin&
	 Possess high thermal stability 		Manuspiya. (2015)

Table 1.5 Adsorbent reported in past works by various researchers.

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CONCLUSIONS

This section's conclusion emphasises how critical it is to address wastewater contaminated with heavy metals. Effective treatment options are still desperately needed since heavy metals continue to present serious risks to the environment and public health. Adsorption is becoming a very useful strategy in the realm of therapeutic techniques. It is a potential method to remove heavy metals due to its ease of use, adaptability in targeting a variety of metals, selectivity based on solid sorbent materials and quick kinetics. Furthermore, the development of novel adsorbent materials and improvements in adsorption processes point to a promising future for water treatment. The review's summary of research findings and trends shows how the field of heavy metal pollution mitigation is developing. Researchers, environmentalists and legislators attempting to tackle the intricate issue of heavy metal pollution in water supplies may find this review to be a useful resource. This research illustrates the possibility for more advancement and innovation in this crucial field while highlighting the critical role that adsorption plays in overcoming these obstacles.

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AUTHORS' BIODATA

Haziqatulhanis Ibrahim, born in June 1996, is a driven academic with a passion for research. She earned her bachelor's degree from Curtin University Malaysia in Miri, Sarawak, and subsequently pursued a Master of Science at Universiti Malaysia Pahang Al-Sultan Abdullah (UMPSA). In October 2023, she proudly graduated with her master's degree,



marking the culmination of her educational journey. Her unwavering aspiration is to become a dedicated and accomplished researcher, making meaningful contributions to her field.



Born on 11 March 1989, in Pontian, Johor, Assoc. Prof. Ir., Ts. Dr. Norazlianie Sazali is a highly accomplished professional in gas engineering. She obtained her bachelor's degree from Universiti Malaysia Pahang Al-Sultan Abdullah (UMPSA) in 2012, followed by a master's degree from Universiti Tun

Hussein Onn Malaysia (UTHM) in 2015. Driven by her research passion, she pursued a PhD in gas engineering from Universiti Teknologi Malaysia (UTM). Currently serving as the Director of Penerbit UMPSA and a dedicated senior lecturer at UMPSA since 2018, her impressive research record includes over 130 indexed articles in WoS/Scopus, with an h-index of 18. Elsevier recognised her exceptional expertise by listing her as one of the top 2% of world scientists in 2020–2022.

Green and Sustainable Solutions for Heavy Metal Removal from Wastewater

Professor Datuk Ts. Dr. Ahmad Fauzi Ismail, the Founder and First Director of Advanced Membrane Technology Research Centre (AMTEC), excels in diverse areas of membrane research. His expertise lies in the development of polymeric, inorganic and innovative mixed matrix membranes for water



desalination, wastewater treatment, gas separation, palm oil refining, removal of emerging contaminants using photocatalytic membranes, haemodialysis membrane development, and polymer electrolyte membrane for fuel cell applications. In 1997, he earned a PhD in Chemical Engineering from the University of Strathclyde, preceded by an MSc. and BSc. from Universiti Teknologi Malaysia in 1992 and 1989, respectively. He has authored and co-authored over 550 journal articles. His efforts have resulted in the establishment of AMTEC as a recognised Higher Institution Centre of Excellence (HICOE). Presently, he serves as the Vice Chancellor of Universiti Teknologi Malaysia.



Dr. Wan Norharyati Wan Salleh is a highly accomplished senior lecturer as well as a research fellow of the esteemed Advanced Membrane Technology Research Center (AMTEC) at Universiti Teknologi Malaysia (UTM). She obtained her B. Eng. (Chemical Engineering) and PhD (Gas Engineering)

degrees from UTM in 2008 and 2012, respectively. Her passion and dedication to research are evident in her extensive publication record, with numerous scientific papers published in high-impact international refereed journals and academic books. She has authored and co-authored over 200 research papers, which have garnered approximately 4,340 citations and resulted in an impressive h-index of 39. Throughout her career, Dr. Wan Norharyati has led 11 research grants and been involved in over 40 research projects. Her expertise lies in membrane science and technology, specifically in the development of composite and photocatalytic membranes for water and wastewater treatment, as well as polymer-based carbon membranes and polymer/inorganic membranes for gas separation.

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