

**MODELING OF WATER PURIFICATION PROCESS USING  
NANO-BIOSORBENT TO REMOVE DYES AND HEAVY  
METALS**

**A PROJECT**

*Submitted in partial fulfilment of the  
requirement for the award of the  
degree of*

**BACHELOR OF TECHNOLOGY**

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**May, 2022**

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## NATIONAL INSTITUTE OF TECHNOLOGY

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### CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the project titled “**MODELING OF WATER PURIFICATION PROCESS USING NANO-BIOSORBENT TO REMOVE DYES AND HEAVY METALS**” in the particular fulfilment of the requirements for the award of the Degree of Bachelor of Technology and submitted in Chemical Engineering Department, National Institute of Technology Hamirpur, is an authentic record of my own work carried out during a period from July 2021 to May 2022 under the supervision of **Dr. Subhajit Majumder**, Assistant Professor Grade I, Chemical engineering Department, National Institute of Technology Hamirpur.

The matter presented in the project report has not been submitted by me for the award of any other degree of this or any other Institute/University.

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This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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## **ACKNOWLEDGEMENT**

We thank the almighty God for his blessings so that we could write the report and use our capabilities to the best of this report. Our deepest heart gratitude is to our parents who strived to get us where we are now. We pay our deep sense of gratitude to Dr. Radhe Shyam, Head of the Department of Chemical Engineering, National Institute of Technology, Hamirpur for permitting us to undergo this undergraduate project. We express our heartfelt gratitude to Dr. Subhajit Majumder, for his guidance. Without his constant support and encouragement at every step, we would not have been able to bring this project work to this step. We sincerely thank him for his patience and correcting our mistakes.

## Table of Content

Candidate's Declaration.....	i
Acknowledgement.....	ii
List of Figures.....	vi
List of Tables.....	viii
<b>CHAPTER - 1 Introduction.....</b>	<b>01</b>
1.1 Motivation.....	03
<b>CHAPTER – 2 Literature survey.....</b>	<b>05</b>
2.1 Limitation of Present Work.....	19
2.2 Scope of Project Work.....	20
2.3 Objectives of Project.....	20
<b>CHAPTER – 3 Dyes and heavy metals: Properties and selection.....</b>	<b>21</b>
3.1 Dyes.....	22
3.2 Heavy Metals.....	23
3.3 Selection of Methylene Blue.....	24
<b>CHAPTER – 4 Nano-biosorbents for the removal of methylene blue dye.....</b>	<b>27</b>
4.1 Biochar and Fe <sub>2</sub> O <sub>3</sub> -biochar nanocomposite.....	27
4.1.1 Synthesis of Biochar and Fe <sub>2</sub> O <sub>3</sub> -biochar nanocomposite.....	27
4.1.2 Removal of Methylene Blue with the help of Biochar and Fe <sub>2</sub> O <sub>3</sub> -biochar nanocomposite.....	28
4.2 Agrobacterium fabrum biomass along with iron oxide nanoparticles as biosorbent...28	
4.2.1 Synthesis of Magnetic properties.....	28
4.2.2 Preparation of biomass.....	28
4.2.3 Removal of Methylene Blue with the help of Agrobacterium fabrum biomass along with iron oxide nanoparticles.....	29
4.3 Surfactant-Modified Sawdust.....	29
4.3.1 Preparation of Surfactants-Modified Sawdust.....	29
4.3.2 Methylene Blue removal with Surfactants-Modified Sawdust.....	29
4.4 Poly m-phenylenediamine grafted dextrin based nano-biosorbent.....	30

4.4.1 Synthesis of nano biosorbent composite Dextrin-g-poly m-phenylenediamine (DgPmPDA).....	30
4.4.2 Methylene Blue removal using Poly m-phenylenediamine grafted dextrin based nano biosorbent.....	31
4.5 Gum ghatti - graft – poly(4-acryloylmorpholine) hydrogel incorporated with magnetite nanoparticles.....	31
4.5.1 Synthesis of nanobiosorbent composite Gum ghatti-graft-poly(4-acryloylmorpholine) gel.....	32
4.5.2 Methylene Blue removal using Gum ghatti-graft-poly(4-acryloylmorpholine)gel and composite gel and magnetite nanocomposite.....	32
4.6 Rice husk as biosorbent.....	33
4.6.1 Synthesis of Rice husk as biosorbent.....	33
4.6.2 Removal of Methylene Blue with the help of Rice husk.....	33
<b>CHAPTER – 5 Selection of nano-biosorbent for dye and heavy metal removal.....</b>	<b>34</b>
5.1 Comparative study of different nano biosorbent for effective MB and heavy metal removal.....	34
5.2 Introduction to nano biosorbent.....	35
5.3 Lead as Heavy metal toxicant.....	36
5.3.1 Effect of Lead on Human, Soil and Water.....	36
5.3.2 Heavy Metals in Textile Industries.....	38
<b>CHAPTER – 6 Biosorption: Modeling and Analysis.....</b>	<b>39</b>
6.1 Mechanism of Biosorption.....	39
6.1.1 Biosorption and bio-accumulation.....	39
6.1.2 Biosorption mechanism.....	40
6.2 Modeling of Biosorption.....	41
6.3 Fixed bed adsorption.....	41
6.4 Adsorption Kinetics.....	43
6.4.1 Kinetic Models.....	44
6.4.2 Diffusion Models.....	44
6.4.3 Adsorption Isotherms.....	45
6.4.4 Langmuir isotherm model.....	45
6.4.5 Freundlich isotherm model.....	46
6.4.6 Dubinin-Radushkevich isotherm model.....	46

6.4.7 Temkin isotherm model.....	47
6.4.8 Modified BET isotherm model (Harkin Jura Model).....	47
6.4.9 Elovich model.....	48
6.4.10 Jovanovic model.....	48
6.5 Adsorption Modeling.....	48
6.6 Kinetic Modeling.....	53
6.7 Discussion.....	58
6.8 Biosorption Modeling.....	60
6.8.1 Steps involved in biosorption of Pb(II).....	60
6.8.2 Steps involved in biosorption of MB dye.....	62
6.9 Discussion.....	64
6.10 Conclusion.....	65
<b>CHAPTER - 7 Mechanism of dye and heavy metal removal.....</b>	<b>66</b>
7.1 Mechanism of Dye and metal ion removal.....	66
7.1.1 Complex Formation.....	67
7.1.2 Ion Exchange.....	67
7.1.3 Electrostatic Attraction or Coordination.....	68
7.1.4 Chelation.....	68
7.1.5 Electrostatic Attraction.....	68
7.1.6 Hydrogen Bonding.....	68
7.1.7 $\pi$ - $\pi$ interactions.....	69
7.2 Structure characterization of DgPmPDA@GO nano biosorbent.....	69
7.3 Hypothesis of dye and metal ion removal mechanism.....	70
7.4 Factors Effecting Adsorption of Pb and MB by nano-biosorbent.....	70
7.5 Regeneration and reusability of a dextrin-based nano biosorbent grafted with poly m-phenylenediamine.....	74
7.6 Factors affecting desorption of Pb and MB dye.....	76
7.7 Disposal methods for heavy metal and dye.....	78
7.8 Discussion.....	81
<b>CHAPTER - 8 Conclusions.....</b>	<b>82</b>
Appendix.....	84
References.....	87

## List of Figures

Fig.1.1: Effects of dyes on aquatic and land ecosystem.....	03
Fig.3.1: Classification Of dyes.....	22
Fig.3.2: Implications of heavy metals on human health.....	23
Fig.6.1: Process involved in the entire adsorption of a single pollution molecule.....	41
Fig.6.2: Adsorption zones.....	43
Fig.6.3: Mono and Multilayer adsorption depicted with capillary condensation.....	43
Fig.6.4: Langmuir Isotherm for Lead and MB dye.....	49
Fig.6.5: Freundlich isotherm for Lead and MB dye.....	49
Fig.6.6: Modified BET model for Lead and MB dye.....	50
Fig.6.7: Temkin model for Lead and MB dye.....	51
Fig.6.8: Dubnin-Radhuskevich Model for Lead and MB dye.....	52
Fig.6.9:Elovich model for Lead and MB dye.....	52
Fig.6.10:Jovanovic model for Lead and MB dye.....	53
Fig.6.11: Pseudo-first Order model for Pb(II) and MB.....	54
Fig.6.12: Pseudo second Order model for Pb(II) and MB.....	54
Fig.6.13: Intraparticle Diffusion model (Webber and Morris) for Pb(II) and MB.....	55
Fig.6.14: Kinetics of Pb(II).....	62
Fig.6.15: Percentage Removal vs time.....	62
Fig.6.16: Kinetics of MB dye.....	63
Fig.6.17: Percentage Removal vs time.....	64
Fig.7.1: Different mechanisms of Biosorption.....	67
Fig.7.2: Different resonance structures of methylene blue.....	69
Fig.7.3: $Q_e$ vs pH plot.....	71
Fig.7.4: $Q_e$ vs Adsorbent Dosage plot.....	72



Fig.7.5: $Q_e$ vs Contact Time plot.....	72
Fig.7.6: $Q_e$ vs Initial Concentration plot.....	73
Fig.7.7: $\ln(K_d)$ vs $1/T$ .....	74
Fig.7.8: Adsorption percentage(Regeneration and reusability).....	78
Fig.7.9: Removal Efficiency.....	79
Fig.7.10: Desorption efficiency.....	77
Fig.7.11: Desorption percentage.....	77
Fig.7.12: Secure landfill.....	79
Fig.7.13: Deep well disposal.....	80

## List of Tables

Table 1.1: Heavy Metals: Sources and permissible Ranges.....	01
Table 2.1: Literature Survey.....	05
Table.3.1: Classes of dyes and their Chemical Structures.....	21
Table 5.1: Comparison of different nano biosorbent.....	34
Table 5.2: Heavy metal contents ( $\text{mg kg}^{-1}$ ) in various textile (average of replicates $\pm$ standard deviation).....	38
Table 6.1 Comparative study of different adsorption and kinetic models.....	56

## CHAPTER - 1

### Introduction

Dyes are staple to many industries like tanning, cosmetics, pharmaceutical, pulp and paper, textile and many others [1]. Most of the waste released by these industries have major share of dye affected wastewater. The effluents from these industries have the potential to harm the environment and human health. Because of their high visibility at low concentrations and their recalcitrance, these dyes are a substantial cause of contamination in the hydrosphere, posing a risk to aquatic life by decreasing penetration of sunlight and preventing photochemical reactions, among other things [2]. Excessive dye exposure can cause irritation, respiratory difficulties, and, some dyes, are also carcinogenic in nature. Furthermore, the presence of dyes in wastewater adds to a high chemical oxidation requirement as well as a foul odour [3]. As a result, dyes must be successfully removed from wastewater before further disposal to the surroundings and hence it has acquired a lot of attention in the recent years [1,2].

Heavy metal removal from water bodies is especially important because it persists in the environment. Harmful heavy metals produced in aquatic environment from a variety of sources, including fertiliser manufacturing, quarrying, and smelting, pollute water and soil ecosystems. Metals like arsenic, lead, copper, mercury and cadmium in drinking water can cause skin cancer, allergic dermatitis, hypertension, and other health problems. Increased industrial activity has resulted in harmful metal toxicity in reservoirs, streams, and other bodies of water[21].

Table 1.1: Heavy Metals: Sources and permissible Ranges [21,22]

Heavy Metal	Industries associated	Permissible ranges	
		WHO ( $\mu\text{g/l}$ )	Indian ( $\text{mg/l}$ )
Arsenic	Smelting processes, electrolysis, thermal power plants, battery manufacturing, solid waste incineration	10	0.20
Mercury	Incineration of hospital waste, hydropower, coal-based power generation plants	6	0.01

Lead	Metal ores extraction, processing, lead acid battery incineration, coal combustion, ceramics, and glassware	10	0.10
Cadmium	Metal electroplating, industrial effluent, phosphate fertilisers, plastic stabilisers, and paints are all examples of industrial effluents.	3	2.00
Chromium	Electroplating, tanning, paper and pulp, chromate preparation, dye manufacture, petroleum and petrochemical products.	50	1.00
Copper	The main sources of copper emission in the stream of water are insecticides, electroplating, and the pulp and paper industry.	200	3.00
Nickel	Electrodeposition, textiles, thermal power plants, ceramics and batteries	100	3.00

As a result, an environment conscious, cost-effective, and efficient technology for removing heavy metals and dyes from discharge water is required. There can be many techniques to treat the dye and heavy metal affected wastewater, but we can broadly classify all these techniques as physical, chemical and biological techniques [4]. The Chemical techniques includes Coagulation-Flocculation, Ozonation, Photocatalytic and Electrochemical methods. Physical techniques use methods like Ion exchange, Membrane Filtration and Adsorption and the Biological techniques use the Bio-remediation of dye affected wastewater using fungi, bacteria and yeasts [16].

Adsorption has the distinct advantage of eliminating the entire dye molecule, as opposed to other removal procedures that just degrade the dye while leaving dangerous residual moieties (such as heavy metals) in the discharge [5] also adsorption provides high efficacy and due to its convenience, adsorption is the most popular of these approaches [3]. The phenomenon of adsorption occurs when the interface between gas/liquid molecules is concentrated on the surface of a porous substance. The component that accumulates at the interface is known as adsorbate, while the substance that interacts with a solid is known as adsorbent [2].

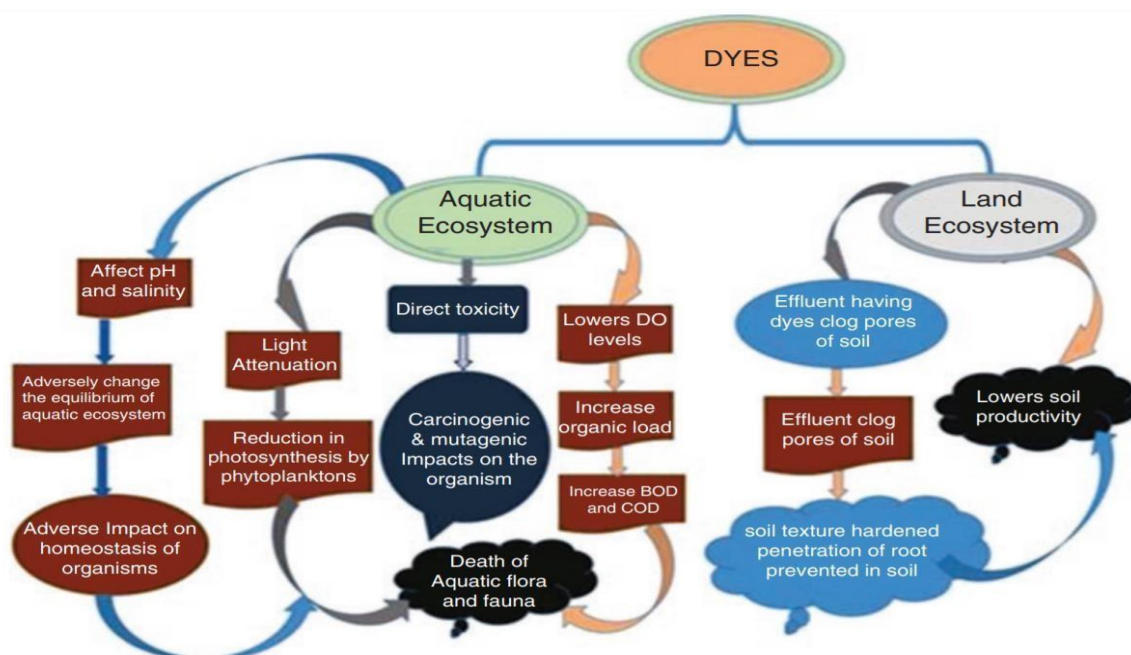


Figure 1.1: Effects of dyes on aquatic and land ecosystem[7].

Due to the extremely high porosity and huge surface area (500–2000 m<sup>2</sup> /g), activated carbon is commonly used in industries for dye removal. However, activated carbon, is relatively expensive due to high production costs. Furthermore, replenishment of activated carbon necessitates a high-pressure stream, which adds to the processing system's operating costs. This high cost has prompted researchers to look for more cost-effective and effective dye removal adsorbent materials [3]. In the recent decade, researchers have focused their attention on low-cost nano-adsorbents because materials show enhanced mechanical, optical, magnetic, and electrical properties at nano scale, thus better adsorption rates and high reactivity is observed in many nanomaterials [6]. In this study we have concentrated our efforts upon the Modeling aspect of wastewater purification using nano-bio sorbents to remove dyes and heavy metals from it.

### 1.1 Motivation

Due to the rapid expansion of modernization, massive amounts of pollutants are emitted from industries, posing substantial environmental hazards. One of the most important families of pollutants is dye, which is more persistent in water and difficult to biodegrade due to its stable and complex structure of molecules and artificial origin [7]. We cannot deny the importance of

dyes in today's industrialized era, at least 100,000 distinct types of dyes are commercially accessible. It is estimated that 1.6 million tonnes of dyes are generated annually to meet the industrial demand and 10 to 15 percent of this total volume is lost as wastewater and released in the environment without prior treatment.

Similar to dyes the importance and hazards of heavy metals in the industrial effluents cannot be ignored. As a corollary, this dye affected wastewater have become a major threat to our ecosystem [3].

Water is a valuable commodity that is both crucial and completely essential for life to exist. Even though water covers 71 percent of the earth's surface, barely 2.5 percent of it is freshwater, and only 0.007 percent of it drinkable [2]. Thus, there is a very strong need to create new dye removal procedures that are both inventive and low-cost to ensure the safe discharge of the effluents in the waterbodies. Bio sorbents are naturally abundant, cheap, environmental friendly and can adsorb dyes as well as heavy metals with great efficiency without leaving behind any toxic residual and on the nano scale the performance is enhanced even more [7].

## CHAPTER – 2

### Literature Survey

This chapter covers the outline of the literature work we have referred to during this project, the gaps in the present work and the scope of the project work. Furthermore, the objectives have also been decided and asserted in this chapter. Given below is the table mentioning the main research paper papers we have cited along with a summary of their major finding

Table 2.1: List of literature reviewed along with the author's name, year of publication, title and summarizing its major findings of the particular literature.

S.No.	Name of the Author	Year	Title	Major Findings	References
1.	Venceslau M. Correia, Tom Stephenson & Simon J. Judd	1994	Characterisation of textile wastewaters: A Review	In this paper, brief study is conducted on wastewater coming from the textile industries and these textile wastes are characterised by high volume and extreme variability in composition, which includes non-biodegradable dyes and toxic substances. This variation in composition is due to the different industrial processes and different chemicals and materials using in that industry.	[11]
2.	Yongming Lu and Ebtisam Wilkins	1996	A mathematical model for the biosorption	<i>Saccharomyces cerevisiae</i> is a type of yeast. For the recovery of copper ions from aqueous solution, yeast was entrapped in alginate, as both yeast and alginate can take metal ions. When the equilibrium copper ion concentration in the fluid was less than 1 mg/l, the Freundlich isotherm was shown to be successful in describing biosorption, and a linear biosorption was assumed. The	[29]

				biosorption isotherm was discovered to be unaffected by immobilized yeast densities ranging from 6 to 17%.	
3.	Fatemeh Afshariani, Aliakbar Roosta	2005	Experimental study and mathematical modeling of biosorption of methylene blue from aqueous solution in a packed bed of microalgae <i>Scenedesmus</i>	The microalgae <i>Scenedesmus</i> was used to investigate the sorption of methylene blue from aqueous solutions in batch and continuous systems. The sorption capacity of methylene blue on the <i>Scenedesmus</i> was determined in the first part of the study at various temperatures (22 C, 30 C, and 37 C) and pH values (5, 7 and 9). At a pH of 9 and a temperature of 30 C, the maximum uptake was found to be 87.69 (mg/g). The biosorbent's high potential was revealed by scanning electron microscopy (SEM) characterization.	[28]
4.	Yasemin Bulut, Haluk Aydın	2005	A kinetics and thermodynamics study of methylene blue adsorption on wheat shells	The removal of methylene blue from aqueous solutions using wheat shells (WHS) was investigated at various contact times, temperatures, pH, adsorbent doses, and initial dye concentrations. Within 60 minutes, the adsorption process reaches equilibrium. The extent of dye removal decreased as adsorbent dosage was increased, and it also increased as contact time, temperature, and solution concentration were increased. The Langmuir and Freundlich isotherms are used to describe adsorption isotherms. The Langmuir equation fits the data better than the	[27]



				Freundlich equation.	
5.	Suntud Sirianuntapioon, Parawee Srisornsak	2007	Removal of disperse dyes from textile wastewater using bio-sludge	This work emphasis on the resting bio-sludge of a domestic wastewater treatment system and its use as an adsorbent for both natural matter and disperse dye because of its high adsorption capacity and its capacity to be reused subsequent to washing with a diluted alkali solution. The biological treatment, especially the GAC–SBR system, are more suitable for treating raw TWW due to the high removal efficiencies of disperse dyes.	[13]
6.	Adrian Demayo, Margaret C. Taylor, Kenneth W. Taylor, Peter V. Hodson b & Paul B. Hammond	2009	Toxic effects of lead and lead compounds on human health, aquatic life, wildlife plants and livestock	Brief study on effects of Lead on environment was there. Natural distribution of lead was there, how lead exists in nature in the form of ores and other forms and the production of lead.	[31]
7.	Mohamad M. Ayad and Ahmed Abu El-Nasr	2010	Adsorption of Cationic Dye (Methylene Blue) from Water Using Polyaniline Nanotubes Base	With variations in MB concentration, equilibrium and kinetic studies for the adsorption of cationic MB dye from aqueous solutions onto polyaniline NTs polymer were investigated in this study. The pseudo-first order, pseudo-second-order, and intraparticle diffusion models were used to investigate the kinetic mechanism. Langmuir, Freundlich, and Tempkin isotherm models were used to analyse the equilibrium data.	[25]

				The Langmuir adsorption isotherm was found to be reasonably good at correlating experimental data.	
8.	Umar Farooq, Janusz A. Kozinski, Misbahul Ain Khan, Makshoof Athar	2010	Biosorption of heavy metal ions using wheat based bio sorbents	Biosorption is a technique which is offering the use of economical alternate biological materials. Metal ions in water get attached in these bio materials because of presence of Functional groups like carboxyl, hydroxyl, sulphydryl and amido. Straw and bran from Triticum aestivum (wheat), one of major food crop around the world, are produced as by-products materials. Westudied about the utilization of straw and bran for the removal/minimization of metal ions from waste waters.	[14]
9.	R. Ansari, B. Seyghali A. Mohammad -khan, and M.A. Zanjanchi	2012	Application of Nano Surfactant Modified Bio sorbent as an Efficient Adsorbent for DyeRemoval	The adsorption of MB from aqueous solutions was examined using sawdust treated with sodium dodecyl sulphate (SDS/SD). Batch and fixed-bed column systems were used in the adsorption tests. On the adsorption of MB dye, the impacts of crucial parameters such as pH, initial dye concentration, flow rate, and bed depth have been investigated. It was concluded that surfactant modified sawdust is substantially more successful for basic MB dyeremoval than SD, and that the depleted SDS/SD column can be easily regenerated with good performance using dilute HCl solution.	[3]

10.	Muftah H. ElNaas and Manal. A. Alhaija	2013	Modeling of Adsorption Process	In this work complete examination of many models for batch and continuous adsorption processes for adsorption of various toxicants has been performed. A rigorous investigation of isotherm, kinetics, and packed-bed models is also presented in this chapter, emphasising their importance in the design of commercial adsorption units.	[34]
11.	Seema Tiwari I.P.Tripathi H.L.Tiwari	2013	Effects of Lead on Environment	Because of its stability in contaminated sites and the complexity of biological toxicity mechanisms, lead is one of the most abundant heavy metals, and its toxic effects cause environmental and health problems. Lead is especially dangerous for children, leading to mental retardation when abnormal concentrations in body fluid exist. To reduce the risk of lead poisoning, you must first understand the problem. The negative effects of lead on various components of the environment, such as soil, water, and humans, were investigated in this article.	[33]
12.	Anuj Kumar Yadav, C.K. Jain and D.S. Malik	2014	Toxic characterization of textile dyes and effluents in relation to human health hazards	Studied about the harmful toxic effects of dyes and heavy metals on human health. It is clear that wastewater coming from textile industries contain different toxic dyes and heavy metals which are dangerous for living beings. In the review, a large portion of the textile wastewater parameters are found over	[10]

				as far as possible endorsed by CPCB and BIS and not prescribed to deliver into the climate with no earlier treatment. The untreated wastewater might prompt defilement in the surface bodies and groundwater reservoir.	
13.	Fana Sungur and Fatih Gülmez	2015	Determination of Metal Contents of Various Fibers Used in Textile Industry by MP-AES	Microwave plasma-atomic emission spectroscopy was used to determine the concentrations of metals (Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Tl, and Zn) in various textile fibres (cotton, acrylic, polyester, nylon, viscose, and polypropylene) of various colours (red, white, green, blue, yellow, orange, black, brown, purple, pink, navy, burgundy, beige (MP-AES). Textile fibres were collected from various textile plants in the Turkish city of Gaziantep-Kahramanmaraş.	[32]
14..	Kok Bing Tan, Mohammad taghi Vakili, Bahman Amini Horri , Phaik Eong Poh, Ahmad Zuhairi Abdullah, Babak Salamatnia	2015	Adsorption of dyes by nanomaterials: Recent developments and adsorption mechanisms	This review focuses on recent advances in the use of NMs for colour adsorption from wastewater. For each nanomaterial, specific adsorption mechanisms, enhancements, particularly for boosting adsorption capacities, and toxicity are explored. The evidence suggests that nanoparticles can be employed to efficiently remediate coloured effluent.	[2]

15.	Haijao Lu, Jing ang Wang, Marco Stoller, Ting Wang, Ying Bao, and HongxunHao	2016	An Overview of Nanomaterials for Water and Wastewater Treatment	NMs have enhanced properties such as high reactivity and bettercatalysis and adsorption. This work focused on zero-valent metal nanoparticles, metal oxidenanoparticles, CNTs, and NCs. In addition, their applications in water and wastewater treatment were thoroughly examined along with this future prospect of the technology are mentioned.	[4]
16.	Neeta A. Salvi, S. Chattopadhyay	2016	Biosorption of Azo dyes by spent Rhizopus arrhizus biomass	Formation of Rhizopus arrhizus biomass and biosorption of azo dyes by spent Rhizopus arrhizusbiomass.	[18]
17	Pedro Yahico Ramos Suzaki, Mauricio Tombini Munaro, Carnia Contini Triques, Sirlei Kleinübing, Márcia Regina Fagundes Klen, Luiz Mario de Matos Jorge, Rosangela Bergamasco Carina Triques, Jaiana	2016	Kleinübing, Márcia Regina Fagundes Klen, Luiz Mario de Matos Jorge, Rosangela Bergamasco Carina Triques, Jaiana	To describe the biosorption of binary heavy metal systems, a phenomenological mathematical Modeling approach was used. The biosorption of Cu(II)-Ni(II) systems onto residue of alginate extraction from Sargassum filipendula validated the mathematical model proposed here. To better understand the competition between the ions in the process, equilibrium studies were conducted. Cu(II) ions had a stronger affinity for the biosorbent, whereas removal was highly reliant on the presence of Cu(II) ions (i.e., Cu(II) ions inhibit Ni(II) removal).	[26]

18.	Bianca Mella, Brunna Samuel de Carvalho Barcellos, Dimitrius Extralazonda Silva Costa, and Mariliz Gutterres	2017	Treatment of Leather Dyeing Wastewater with Associated Process of Coagulation Flocculation/Adsorption/Ozonation	Dyes use in leather industry, their toxic effect and methods for removal of these dyes from effluent.	[16]
19.	Nhamo Chaukura,	2017	Sorptive removal of methylene blue	MB dye was removed from synthetic wastewater using BC and	[8]
20.	K. El Ass, F. Erraib, M. Azzi, A. Laachach	2017	Removal of Pb(II) from aqueous solutions by low cost adsorbent: Equilibrium, Kinetic and Thermodynamic studies.	In a batch adsorption process, the ability of Moroccan clay, known locally as Ghassoul, to remove Pb(II) ions from aqueous solutions was investigated with respect to several experimental conditions, including pH, contact time, initial metal ions concentration, temperature, and ionic strength. By fitting the adsorption data with Langmuir, Freundlich, and Dubinin–Radushkevich isotherms, the suitability of the adsorbent was determined.	[23]
21.	Nimibofa Ayawei, Augustus Newton Ebelegi, and Donbebe Wankasi	2017	Modeling and Interpretation of Adsorption Isotherms	In this study various adsorption isotherm models were studied along with their error analysis.	[35]
22.	Rais Ahmad, Anam Mirza	2017	Synthesis of Guar gum/bentonite a novel	Innovative and eco-friendly The removal of Pb (II) and crystal violet dye from aqueous solution was	[24]

			<p>bionanocomposite: Isotherms, kinetics and thermodynamic studies for the removal of Pb (II) and crystal violet dye.</p>	<p>investigated using a guar gum/bentonite bionanocomposite that was synthesised, characterised, and tested. SEM, EDX, FT-IR, XRD, TGA, BET, and TEM techniques were used to characterize the bio nanocomposite. With particle sizes ranging from 3 to 11 nm and increased thermal stability, the bio nanocomposite showed a porous, crystalline nature. The Pseudo-second order kinetic model best described the adsorption kinetics of Pb (II) and crystal violet. Freundlich (for Pb) and Langmuir (for Crystal violet) models accurately described the adsorption isotherm. pH, dose, contact time, and temperature all influenced the adsorption of Pb (II) and crystal violet.</p>	
23.	Edna C Murimba Willis Gwenzi	2017	<p>Sorptive removal of MB from simulated wastewater using biochars derived from pulp and paper sludge</p>	<p>Fe<sub>2</sub>O<sub>3</sub>-biochar NC produced from PPS. The morphology analysis revealed diverse adsorbent surfaces, and textural tests revealed that BC and NC has pore size ranging from 1.7 to 300 nm. NC shows better adsorption results than BC due to infused magnetic NP<sub>s</sub> and the adsorption was pseudo-first order and pseudo second order kinetics, respectively. The Freundlich and Langmuir isotherm models were used to calculate the isotherm data for BC and NC, respectively.</p>	[8]

24	Ehsn Nazarzede Zare Moslem Mansour Lakouraj Neda Kasirian	2018	Development of effective nano-biosorbent based on ploy-mphynylenediamine grafted dextrin for removal of Pb(II) and methylene blue from water	A nano-bio sorbent was created using modified dextrin. Pb(II) and MB was removed from water using this nano-biosorbent and various approaches were used to characterize the novel nano chelating adsorbent. Adsorption kinetics, isotherms, and thermodynamics were also examined.	[9]
25.	SujataMani, Pankaj Chowdhary, and Ram Naresh Bharagava	2018	Textile Wastewater Dyes: Toxicity Profile	Different methods of treatment for treating the textile wastewater have been studied like physical methods (adsorption, ion exchange, and membrane filtration), chemical methods (chemical precipitation, coagulation and flocculation, chemical oxidation), and biological methods .	[12]
26.	Swati Sharma & Abshar Hasan & Naveen Kumar & Lalit M. Pandey	2018	Removal of methylene blue dye from aqueous solution using immobilized Agrobacterium fabrum biomass along with iron. oxide nanoparticles as bio sorbent	By encapsulating iron oxide nanoparticles (NPs) and an Agrobacterium fabrum strain in calcium alginate, a nano-bio sorbent for the removal of methylene blue (MB) dye was created and studied. At pH 11, 160rpm, and 25 °C, the bio sorbent prepared here was optimised for maximum adsorption capacity.	[1]
27.	T.P. Krishna Murthy, B.S. Gowrishankar, M.N. Chandra Prabha, M. Kruthi, R. Hari Krishna	2018	Studies on batch adsorptive removal of malachite green from synthetic wastewater using acid treated coffee husk: Equilibrium, kinetics and	For batch adsorptive elimination of malachite green (MG) from synthetic dye solution, coffee husk treated with sulfuric acid (ACH) is utilised as a low-cost adsorbent. Powder X-ray diffraction, Raman spectroscopy, and scanning electron microscopy were used to study the structural and	[36]



			thermodynamic studies	topological features of the produced ACH adsorbent. pH (2–9), adsorbent dose (0.05–1 g/L), starting adsorbate concentration (25–150 mg/L), contact time (0–120 min), and temperature (30–60 °C) all had an influence on adsorption.	
28.	Wenqian Ruan, Jiwei Hu, Jimei Qi, Yu Hou, Chao Zhou, Xionghui Wei	2018	Removal of dyes from wastewater by nanomaterials: A review	Dye's classification and their toxicity was studied. Different dye removal techniques have been mentioned in this study with special emphasis on dye removal from wastewater by adsorption using NMs.	[15]
29.	Bruno Lellis, Cíntia Zani Fávaro Polonio, João Alencr Pamphile, Julio Cesar Polonio	2019	Effects of textile dyes on health and the environment and bioremediation potential of living organisms	The transformation of the dyes and other pollutants by the enzymatic action of plant, bacterial and fungal biomasses is possible by bioremediation. The modern biotechnology processes involve the creation of more degrading and resistant engineered organisms by making it a long-term solution.	[6]
30.	Shelby L. Foster, Katie Estoque, Michael Voecks, Nikki Rentz and Lauren F. Greenlee	2019	Removal of Synthetic Azo Dye Using Bimetallic Nickel-Iron Nanoparticles	This study is about the synthesis of Bimetallic Nickel-Iron nanoparticles. Removal of azo dye using Bimetallic nickel-iron nanoparticles.	[17]

31.	Agnes Pholosi*, Eliazer B. Naidoo, Augustine E. Ofomaja	2020	Intraparticle diffusion of Cr(VI) through biomass and magnetite coated biomass: A comparative kinetic and diffusion study	The kinetics, diffusion, equilibrium, and mechanism of Cr(VI) uptake were studied at various temperatures, as well as the effect of the inorganic- organic nanocomposite combination on the kinetics, diffusion, equilibrium, and Cr(VI) absorption mechanism. NTP-NC FE-SEM-EDX examination revealed that the compound was homogeneous, including Fe, O, and C, and that the iron oxide was well disseminated throughout the composite. Intraparticle diffusion Modeling found that the first adsorption behaviour of NTP was classified as strong initial adsorption and NTP- NC was categorized as approaching complete initial adsorption.	[37]
32.	Asim Ali Yaqoob, Tabassum Parveen, Khalid Umar and Mohamad Nasir Mohamad Ibrahim	2020	Role of Nanomaterials in the Treatment of Wastewater: A Review	Water Treatment Methodologies, advantages, and disadvantages each of one, various type of adsorbent and future perspective about it	[20]
33.	Mohammad A. Al-Ghouti and Dana A. Da'ana	2020	Guidelines for the use and interpretation of adsorption isotherm models: A review	The goal of this study is to develop criteria for selecting the best isotherm model by analysing numerous adsorption models and applying mathematical error functions such as linear regression analysis, nonlinear regression analysis, and error functions for adsorption data optimization. The	[38]

				paper looked at 15 mono-parametric adsorption isotherm models with one, two, three, four, and five variables.	
34.	Moumita Sardar, Madhumita Manna, Manisha Maharana, and Sujit Sen	2020	Remediation of Dyes from Industrial Wastewater Using Low-Cost Adsorbents	The numerous advancements on adsorption processes for dye removal from industrial wastewater are covered in this study. The understanding of dyes, their classification and adverse effects, different treatment approaches, and dye adsorption utilizing distinctive low-cost adsorbents are studied extensively. Special emphasis on adsorptive methods have been given because of its due to its low cost and efficacy in colour removal.	[5]
35.	Prajwal Kulal, Vishalakshi Badalamoole	2020	Efficient removal of dyes and heavy metal ions from wastewater using Gum ghatti – graft–poly(4-Acryloylmorpholine ) hydrogel incorporated with magnetite nanoparticles	The gum ghatti-graft-poly(4acryloylmorpholine) polymer was found to be an effective adsorbent for cationic dyes (in this study MB was used) and metal ions when implanted with magnetite nanoparticles produced in situ with the best suited pH range of 6.5-7.5. This NC exhibited superparamagnetic properties as well as good regeneration results.	[7]

36.	Renata Farias Oliveira, Keila Guerra Pacheco Nunes, Ivone Vanessa Jurado, Ianka Cristine Benício Amador, Diego Cardoso Estumano, Liliana Amaral Féris	2020	Cr (VI) adsorption in batch and continuous scale: A mathematical and experimental approach for operational parameters prediction	The goal of this research is to determine the effectiveness of hexavalent chromium adsorption onto granular activated carbon (GAC) and to anticipate which mathematical models best characterise the adsorption behaviour. To analyse the characteristics of the adsorption process, synthetic and industrial effluent were used to test the effects of pH, contact time, and absorbent content. Breakthrough curves were determined using fixed-bed column experiments. The Bayesian Criteria Information (BIC) and Markov Chain Monte Carlo (MCMC) methods were used.	[39]
37.	Keerti Jain, Anand S.Patel, Vishwas P. Pardhi and Swaran JeetSingh Flora	2021	Nanotechnology in Wastewater Management: A New Paradigm  Towards Wastewater Treatment	Nano particles materials has various unique properties, like high sensitivity, high surface to volume ratios, reactivity, high adsorption capacity and using these properties of nanoparticles we discussed about introductive part of various methodology for water purification.	[19]
38.	Manisha Maharana, Madhumita Manna, Moumita Sardar,and Sujit Sen	2021	Heavy Metal Removal by Low- Cost Adsorbents	In this study special emphasis is given upon cost effective adsorbents such as clay, coal, peat moss, and chitosan are used to remove heavy metal ions. They all proved as inexpensive and effective bio sorbent for this purpose. Agricultural and industrial wastes, in addition to conventional adsorbents, are emerging as effective heavy metal removal alternatives. Adsorbate concentration, temperature, pH, level	[21]

				of surface alteration, and adsorbent properties are all important factors in metal adsorption.	
39.	Swarup Biswas and Soma Nag	2021	Biomass-Based Absorbents for Heavy Metal Removal	In this study the treatment of metal tainted wastewater was performed by the bacterial biomass, algal biomass, and fungal biomass were used. Because most natural bio sorbents have a limited adsorption capacity, researchers used a variety of pre-treatment procedures to boost the adsorption capacity. Physical and chemical activation are two types of pre-treatment. In physical activation, the adsorbents are heated to a high temperature at a controlled rate. Various acids, bases, and other compounds are used in chemical treatment.	[22]

## 2.1 Limitation of Present Work

- i Most of the techniques described in these works require an experimental set-up, and no studies have been done on the Modeling side of nano-biosorption.
- ii The studies have been performed on a laboratory scale only, and there is a lack of evidence regarding their commercial viability.
- iii Most of the biosorbents used in these studies do not exist at the nanoscale, and their surface properties have not been thoroughly investigated.
- iv Most studies were conducted using active biomass, due to which the biosorption efficiency is not high.

## **2.2 Scope of Project Work**

The main purpose of this project work is to study the importance of treatment of dye-affected wastewater and thus develop the mathematical model for wastewater treatment using adsorption by using Nano Bio sorbents as cost-effective and environmentally friendly adsorbents. It requires the theoretical and practical understanding of the adsorption process as well as the market scenario revolving around the industries that are the major culprits responsible for the discharge of these coloured effluents into the environment. Different such industries and dyes will be investigated, and further studies will be conducted on a particular dye. In a similar fashion, different bio sorbents will also be taken into consideration while developing the mathematical model. The adsorption mechanism will be studied, and the equations will be modelled based on Langmuir and Freundlich isotherms. The effects of different reaction conditions such as pH, temperature, concentration, etc., will be studied and the optimum results will be derived.

## **2.3 Objectives of the Project Work**

- i To target the major dye and heavy metal discharging industries and identify particular dyes and heavy metals.
- ii To select the nano-bio sorbent by comparative study and to understand its synthesis.
- iii To develop the mathematical model for wastewater treatment using biosorption.
- iv To understand the mechanism of dye and heavy metal removal from the waste.
- v To comprehend the in-depth investigation into the regeneration of the nano-bio sorbent.
- vi To study the different parameters like temperature, pH, etc., affecting the biosorption.
- vii To study the fate of dye, metal ions, and biosorbents after the completion of biosorption.

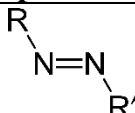
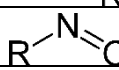
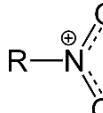
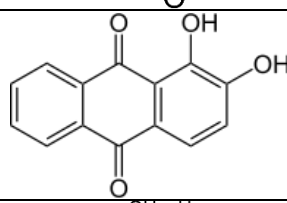
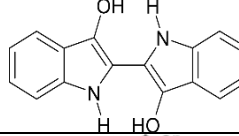
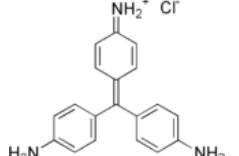
## CHAPTER – 3

### Dyes and heavy metals: Properties and selection

Dyes are inorganic or organic chemicals with synthetic and compound unsaturated aromatic structures of molecules that achieve qualities such as colour, intensity, fastness, and complete aqueous solubility. Synthetic dyes are resistant to fading in moisture, sunlight, and a variety of substances due to their chemical composition, and their acidic qualities make them more powerful and durable to biodegrade when coupled with water.[5]

Currently, over 10,000 dyes are commercially accessible. Dyes are made up of two main components: chromophore and auxochrome. Chromophores, or electron acceptors in dye molecules, are basically electron withdrawing groups that are responsible for colour creation due to their capacity to absorb light near the UV range. The chromogen is an aromatic molecule comprising anthracene, benzene, or naphthalene rings and binding chromophores with delocalized electrons that create a conjugated system. Ethylene, azo, carbonyl, methine, carbon with sulphur group, carbon with nitrogen group, nitro, chionids or nitroso groups are the most important chromophores[1, 5].

Table.3.1: Classes of dyes and their Chemical Structures [1]

Class	Chromosphere	Example
Azo Dye		Reactive Black 1
Nitroso		Acid green 1
Nitro		Acid Yellow 24
Anthraquinone		Reactive Blue 4
Indigoid		Acid Blue 71
Triarylmethane		Malachite Green

Auxochrome, on the other hand, is an electron donor that can not only complement but also increase the casting of chromophore by altering the overall strength of the electronic system and giving the dye's solubility and adhesion to the fibre through stable chemical bonds. The carboxyl, hydroxyl, sulfonate and amino groups are the most prevalent auxochromes. In nature, basic or acidic groups organize chemical bonds.

### 3.1 Dyes

#### 3.1.1 Dye classification

Basic chemistry, industrial application, supply of materials, nuclear structure, type of chromophores, colour index, and specific technique of bonding are all examples of how dye might be organised (e.g., physical forces or robust bonds). Cationic, anionic, and non-ionic dyes are classified according to how well they dissolve particle charge in solution. The solubility of dyes can be used to classify them. Acid, basic, direct, mordant, metal complex, and reactive dyes are examples of soluble dyes, while sulphur, azotic, vat, and disperse dyes are examples of insoluble dyes. However, dyes are classified primarily depending on their application methods, suppliers and chemical structures. [2,5]

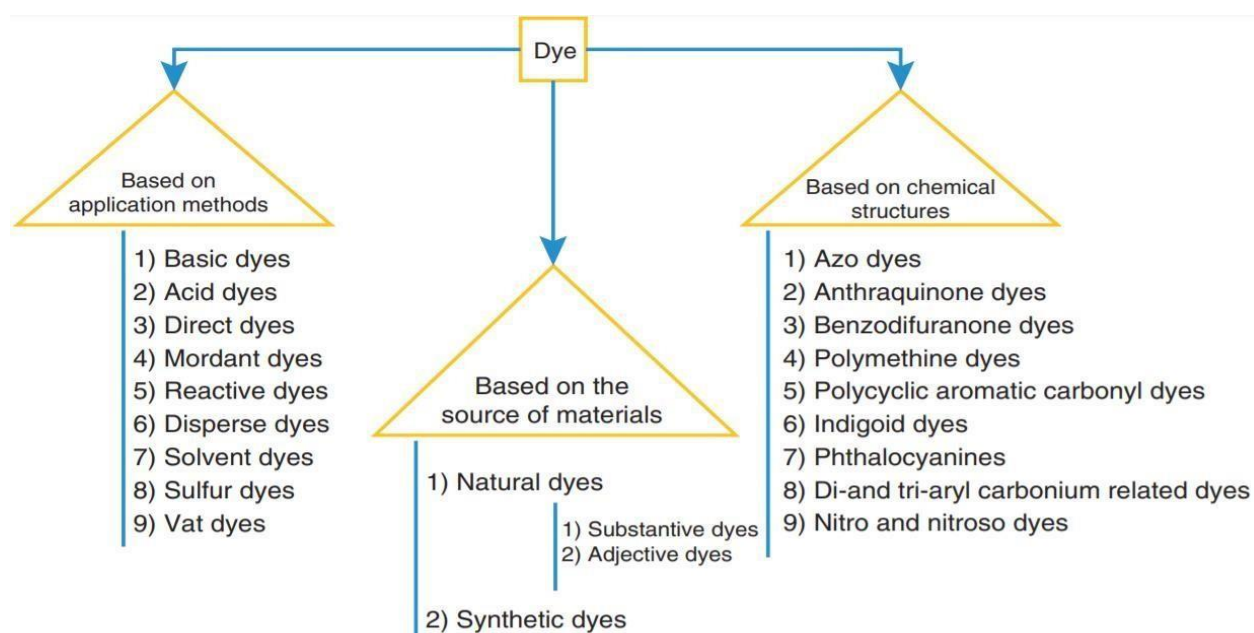


Figure.3.1: Classification Of dyes [5]



### 3.2 Heavy metals

Any metallurgical chemical element with a relatively high density that is hazardous or toxic at even at lower concentrations is known as heavy metal. The atomic weights of these elements are higher and they are denser. This category consists metals like arsenic, lead, and chromium and when they come into contact with live beings, they can cause toxicity at a very low level [21]. They are not biodegradable and can enter the human body through drinking water, breathing air, or eating food. Although some heavy metals are required for the efficient operation of the body's metabolic system. A lack of essential nutrients results in a variety of disorders. Several disasters have occurred in recent decades as a result of toxic metal pollution in aquatic streams. Mercury poisoning of humans was caused by the accumulation of mercury in fish. The poisoning of the environment by such harmful metals has resulted in an increase in worldwide public health during the last few decades. Human exposure to heavy metals has increased dramatically as a result of rising energy demand and their use in many industrial, agricultural, residential, and technology applications. Heavy metals have been identified as a high-priority contaminant [22].

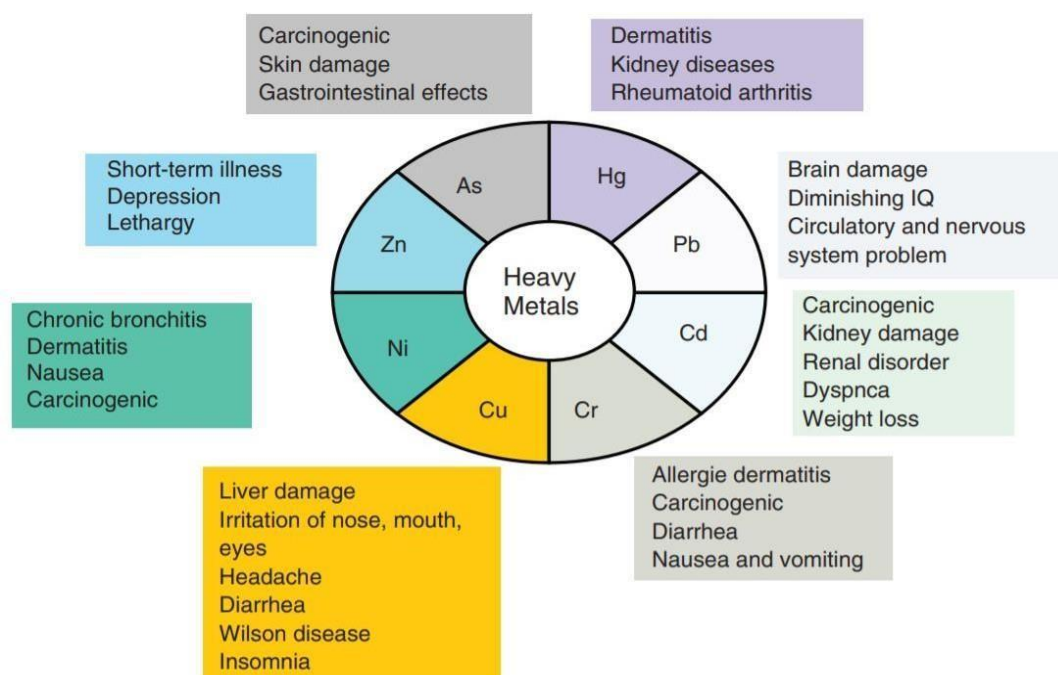


Figure 3.2: Implications of heavy metals on human health [21]

The major heavy metal dischargers are the industries like leather, mining, pharmaceutical, pulp and paper, petroleum industries, textile industries, steel plants and many such industries.

According to the WHO, almost one billion people do not have access to safe drinking water, and this number is steadily rising. As a result of their exposure to harmful metals, millions of individuals are suffering from various diseases. After oxygen, clean water scarcity is the world's second most pressing concern. As a result, it is past time to implement an easy and economical approach for wastewater reclamation employing low-cost adsorbents in order to ensure our long-term survival on this planet.[21]

### **3.3 Selection of methylene blue**

We concentrated on a great deal about various dyes coming from various industries in their wastewater. In practically all industries like paper and pulp, textile, tannery and pharmaceutical, we found that Methylene Blue dye is playing its part on little and large scope. So, we chose to contemplate on Methylene Blue Dye and its removal techniques.

#### **Textile industry**

The textile industry is spread globally, generating around 1 trillion dollars, contributes with 7% of the total world exports and employs around 35 million workers around the world.[11] The textile industry is responsible for an extensive list of environmental impacts. The textile dyes, along with a large number of industrial pollutants, are highly toxic and potentially carcinogenic so that they are related to environmental degradation and various diseases in animals and humans. [12]

In India, more than 80,000 tonnes of dyestuff and pigment are produced. Textile industries are the biggest purchaser of dyestuffs up to 80 percent. Methylene Blue (MB) is a synthetic dye. It is an aromatic-cationic dye and is used extensively in textile industry, the most common and widely used dye in textile industries for dyeing wool, silks, and cotton. Most of the time, the dyes we are using to dye our fabric doesn't stick to the fabric surface and as a result of which these dyes come as a water in the water coming out from textile industries. Exposure to MB can lead to skin damage and burning sensation in the eyes, its ingestion can cause nausea, vomiting, and detrimental effects such as methemoglobinemia. [11, 12]

Heavy metal ions such as Cr (VI), Pb (II), Cd (II), and Zn (II) can be found in wastewater from the textile industry (II). As a result, it is essential to remove these ions from wastewater. [21]

## **Paper and pulp industry**

Paper and pulp are an important industry because of its demand. It's important industry but we can't discard the effect of waste which it's generating. The paper and pulp industry faces series of challenges to the generation of large amounts of wastes. Substantial quantity of water is used in paper production processes in the pulp and paper industry wherein, according to the quality and kind of paper manufactured, the water consumption amount differs. Paper is coloured by adding dye in pulp before sheet is formed. To get a blue coloured paper the common dye which is used by Paper and Pulp industry is Methylene Blue.

Using Methylene Blue dye in manufacturing process of paper increases it's change to get in to the water coming as waste from industry. As a result of which this dye enters to the ecosystem and causes harm.

There are different heavy metals that are used in pulp and paper industries. Major such contaminants are cadmium, barium and copper [21]. Thus it becomes important to remove this dye from our wastewater.

## **Tannery industry**

With the improvement of tannery industry, tannery wastewater has become one of the significant wellsprings of industrial pollution [16]. As per measurable information accumulated from all over the world, there are 300 million bits of cowhide prepared across the world calfskin showcases consistently which results that the measure of tannery wastewater produced yearly is around 300 millions of tons. This industry is one of the major heavy metal releasing industries, and the most prominent contaminants released by this industry includes chromium, cobalt, lead, nickel, cadmium, selenium to arsenic. These heavy metals have huge impact on environment as well as on the workers who comes in direct contact with these contaminants.[22]

## **Pharmaceutical industry**

In Pharmaceutical industries Methylene Blue is used for manufacturing medicines. Methylene Blue is used in human and veterinary medicine for several therapeutic and diagnostic procedures, including as a stain in bacteriology, as a redox colorimetric agent, as a targeting agent for melanoma, as an anti haemoglobinaemic, as an antidote, and as an antiseptic and disinfectant. One of the most common clinical applications of methylene blue is for the treatment of methemoglobinemia induced by overexposure to drugs, to industrial chemicals

such as nitrophenols or to environmental poisons such as excessive nitrate in well-water, or cyanide compounds.

The heavy metal used in pharmaceutical industry includes some of the major toxicants like, chromium, cobalt, lead, nickel, cadmium, arsenic and selenium. These contaminants are released into waterbodies without prior treatment and results in heavy damage to our ecosystem.[21]

### **Selection of MB dye**

After going through different manufacturing industries and their products, we have understood that methylene blue is contributing its part in every industry. In textile industries, it is used on large scale and in industries like leather and pharmaceutical we have witnessed its limited usage. It is no wonder that how obvious this dye is in the colourant industry due to its extensive and versatile use, and it makes it an unavoidable water pollutant. To protect our water resources and to reuse this wastewater it becomes mandatory to remove methylene blue dye completely from the effluents. This is a dark-coloured dye, due to which it resists sun rays to reach the bottom of water bodies[8]. Due to which process of photosynthesis stops. Also, we studied about the toxic effects of dyes and how it affects the aquatic flora and fauna. Also, Methylene Blue is a basic dye, and biosorbents works exceptionally well with basic dyes because of their polymeric hydrocarbon structure and pi bond interaction along with hydrogen bonding, it becomes easier for biosorbents to adsorb these types of dyes with better efficacy[9,15]. After going through all the crucial points in our study we have decided to work upon the removal of methylene blue dye using nano-biosorbents.

## CHAPTER - 4

### **Nano-biosorbents for the removal of methylene blue dye and heavy metals**

Adsorption is the process of removing atoms, molecules or ions from the liquid, gas or dissolved solid to a surface. The particles which are being removed are known as adsorbate and the surface on which these particles get adsorbed is known as adsorbent.

Adsorbents can vary in size but the most effective range of the adsorbents which can adsorb the particles up to maximum efficiency falls in nano range. Studies were made on nano adsorbents for the removal of heavy metals and dyes.[2] The research to develop eco-friendly and economical process for removal of pollutants from water is going on. A lot of processes like membrane filtration, adsorption, ion-exchange and precipitation have been developed for the removal of these pollutants. It has been found that adsorption process is an efficient method to expel these organic pollutants inorganic matters and heavy metals from waste water. The adsorbent which is used most commonly is coal-based carbon. This adsorbent high surface area and high adsorption capacity.[3] The coal-based carbon adsorbent is an effective adsorbent for removing the pollutants from wastewater but this is very expensive. Now research for the inexpensive and eco-friendly adsorbents has been done. Natural adsorbents commonly known as bio sorbents were used for the removal of pollutants, dyes, heavy metals from the wastewater. It has been found that lignocellulosic biomass wastes, especially nutshells, are able to remove the heavy metals, dyes from the wastewater. [24]

#### **4.1 Biochar and Fe<sub>2</sub>O<sub>3</sub>-biochar nanocomposite**

Pulp and paper sludges are used to make these. Both had pore sizes ranging from 1.7 to 300 nanometers. Methylene blue dye is removed from waste water using this biosorbent.

##### **4.1.1 Synthesis of Biochar and Fe<sub>2</sub>O<sub>3</sub>-biochar nanocomposite**

Sludge from pulp and paper is collected and dewatered. The residue is air-dried for two days after dewatering and then oven dried for 24 hours at 70 degrees Celsius. Biochar is made by tightly packing dried material into a closed steel container and pyrolyzing it for 2 hours at 750 degrees Celsius. Dry material is soaked in FeCl<sub>3</sub>.6H<sub>2</sub>O solution (80% w/v) at a mass to make Fe<sub>2</sub>O<sub>3</sub> -biochar nanocomposite.

#### **4.1.2 Removal of methylene blue with the help of biochar and Fe<sub>2</sub>O<sub>3</sub>-biochar nanocomposite**

The electrostatic interaction between the absorbent surfaces and the cationic methylene blue dye molecule causes adsorption. At pH 12-14, the Fe<sub>2</sub>O<sub>3</sub>-biochar nanocomposite and biochar remove the most methylene blue. Biochar has a maximum adsorption capacity of 33 mg/g based on the Langmuir isotherm, and Fe<sub>2</sub>O<sub>3</sub>-biochar nanocomposite has a maximum adsorption capacity of 50 mg/g based on the Langmuir isotherm. Methylene blue is removed more effectively by Fe<sub>2</sub>O<sub>3</sub>-biochar nanocomposite than by biochar [8].

#### **4.2 Agrobacterium fabrum biomass along with iron oxide nanoparticles as bio sorbent**

A nano-bio sorbent is prepared for the removal of methylene blue (MB) dye by encapsulating iron oxide nanoparticles (NPs) and *Agrobacterium fabrum* strain, in calcium alginate.

##### **4.2.1 Synthesis of magnetic nanoparticles**

The synthesis of magnetic nanoparticles is done by Co-precipitation method. 100 mL of deoxygenated water is added to the 1.04 g of FeCl<sub>2</sub>·4H<sub>2</sub>O and 2.64 g of FeCl<sub>3</sub>·6H<sub>2</sub>O and mixed at room temperature gently. The solution is vortexed at 600 rpm using a stirrer maintained at 80°C under the reducing environment. The hydrolysis of iron precursors to magnetite nanoparticles (MNPs) is confirmed by the formation of black precipitate on adding drops of 25% NH<sub>4</sub>OH, a reducing agent. This synthesis of nanoparticles was performed for 2 hours for reduction of iron salts to nanoparticles completely. The obtained precipitates then repeatedly washed with distilled water until the pH of 7 reached and kept for drying overnight.

##### **4.2.2 Preparation of biomass**

*Agrobacterium fabrum* is isolated, found to be highly tolerant to lead (Pb) and exhibits an excellent Pb adsorption capacity. Glycerol stock of this isolated strain is used to prepare 1% inoculum by growing it in Luria-Bertani (LB) media at pH 7.4 and 37 °C overnight. Later, biomass is separated by centrifugation at 10,000 rpm for 20 min at 4 °C. Then biomass pellets were rinsed thoroughly with the distilled water and kept for drying overnight and later lyophilized to form a dry powder. An equal ratio of these synthesized iron oxide MNPs and lyophilized biomass is mixed evenly in 2% (w/v) sodium alginate solution without any lump formation. The solution prepared is slowly dropped by using the peristaltic pump at uniform rate in 3.5% calcium chloride solution (w/v) and MNP biomass- calcium alginate (MBCaAb) beads were formed. The encapsulation is done by calcium alginate. The prepared MBCaAb beads are kept overnight and the beads gets hardened after encapsulation. Later on, these

beads were cleaned with distilled water until reaching the pH 7 and preserved at 4 °C for further use.

#### **4.2.3 Removal of methylene blue with the help of *Agrobacterium fabrum* biomass along with iron oxide nanoparticles**

MBCaAb beads (dry weight) was added individually to different concentrations of methylene blue dye (C<sub>0</sub>) 25, 50, 100, and 200 mg/L respectively in a 250 mL conical flask. Optimization of pH for dye biosorption was studied in the range from 3 to 12 by using 0.1 N NaOH and HCl. Further, experiments were performed at optimized pH. Batch experiments were carried out at 25, 30, 37, and 45 °C temperatures for 3 h. The adsorption process occurred rapidly and attains an equilibrium within first 60 min. [15]

#### **4.3 Surfactants-modified sawdust**

Sawdust is a biological waste product that is readily available and inexpensive in woodworking industries. It comprises polyphenolic groups in several organic molecules (lignin, cellulose, and hemicellulose), making it particularly good at binding basic dyes.

##### **4.3.1 Preparation of surfactants-modified sawdust**

Sawdust was first cleaned with distilled water to remove any dust or contaminants before being dried in an air circulating oven for 5 hours at a temperature of around 60 degrees Celsius. Before alteration, the sawdust was sieved (35–50 mesh) to ensure consistent modification and repeatable outcomes.

In this preparation method, 35 g of Sawdust were treated with 500 mL of SDS solution (10 g/L), and the mixture was shaken for 12 hours at room temperature. Filtered surfactant-modified sawdust particles (SDS/SD) were washed with abundant distilled water and dried at 50°C (in oven). SDS/SD particles were sieved (35–50 mesh) before USE in order to acquire more repeatable data.

##### **4.3.2 Methylene blue removal method with surfactants-modified sawdust**

In a glass column, continuous flow sorption experiment was carried out (1.0 cm internal diameter and 50 cm height). Separately, 1.0 g of each of the selected adsorbents (SD, and SDS/SD) were packed into glass columns of the same size. At a constant flow rate of 3 mL/min, MB dye solutions with a constant concentration of 50 mg/L and appropriate pH values (6 for SD and 10 for SDS/SD) were passed through the columns. Dilute NaOH and HCl solutions were used to modify the pH levels. At regular intervals, outlet solutions were collected for

examination of remaining dye concentration.

The studies were conducted out using MB solution with various known concentrations (20, 50, 100 mg/L) to explore the influence of initial dye concentration. Experiments with three different bed depths, 3.1 cm (0.60g), 5 cm (1.0 g), and 18.8 cm (3.0 g), were also carried out at the same influent MB concentration (50 mg /L) and flow rate (3 mL /min). [3]

#### **4.4 Poly m-phenylenediamine grafted dextrin based nano-bio sorbent**

Polysaccharides such as chitosan, starch, alginate and cellulose are plentiful, sustainable, and inexhaustible substances with a high potential for chemical and physical interactions with a variety of waste compounds or ions. Dextrin (Dex) is a polysaccharide that is plentiful and inexpensive, and it is widely utilised in the textile and food industries. It's a moderate polysaccharide made up of d-glucose units linked together by alpha -(1,4) or alpha-(1,6) glycoside linkages. Dex is a product of starch or glycogen hydrolysis that has been utilised to make biodegradable materials.

It is generally known that altered polysaccharide bio sorbents have better adsorption capabilities than untreated polysaccharide bio sorbents. Graft copolymerization is an old method for chemically modifying polysaccharides. The presence of N and S atoms in the primary structure of conjugated polymers is accountable for contaminant adsorption. Because of the significant amounts of amine and imine functional groups in the polymer chains, polyaniline (PANI) and its derivatives have demonstrated good adsorption capability among conducting polymers, and they are used as adsorbents for the removal of heavy metal ions/dyes from industrial effluents solutions.

A potential route of adsorption was proposed in which MB adsorption and chelation were controlled by  $\pi$ -stacking interactions, H-bonding interactions, and electrostatic attraction, and Pb(II) adsorption was controlled by electrostatic attraction.

##### **4.4.1 Synthesis of nano-bio sorbent composite dextrin-g-poly m-phenylenediamine (DgPmPDA)**

Dex was mixed with distilled water and was stirred for 30 minutes at 50°C. Once this solution comes at the room temperature 1M HCl is added to it at 0-5 °C and left in an inert environment solution for 30 min. The APA solution and mPDA solution was added one by one in a dropwise manner and the solution is left undisturbed for 12 hours in nitrogen atmosphere. The resulting solution was rinsed and filtered and DgPmPDA is obtained.



## **Graphine Oxide(GO)**

A combination of graphite flakes and  $\text{KMnO}_4$  was treated with concentrated  $\text{H}_2\text{SO}_4/\text{H}_3\text{PO}_4$ . This mixture was then heated to  $50\text{ }^\circ\text{C}$  and stirred for 12 hours. The reaction mixture was cooled to room temperature and then poured into the ice-cold water containing 30% hydrogen peroxide. The mixture was centrifuged and washed with distilled water, 30%  $\text{HCl}$ , and ethanol. Then the resulting powdered is heated in a vacuum oven at  $90\text{ }^\circ\text{C}$  for over a day, and GO is thus finally obtained.

After the synthesis of both the GO and DgPmPDA, the nano-bio sorbent composite is composed using the solution blending technique using a magnetic stirred.

### **4.4.2 Methylene blue removal using Poly m-phenylenediamine grafted dextrin based nano-bio sorbent**

The resulted nano-bio sorbent was effective in removing the MB as well as  $\text{Pb(II)}$  from the waste water water. The optimum pH ranges were 6-7 for  $\text{Pb(II)}$  adsorption and 8-9 for the adsorption of MB.

The adsorption process starts pacing up after 30 minutes and reached its equilibrium at 120 mins. Thus 90-120 mins were observed as the optimum contact times.

The maximum adsorption observed was 76.33 (mg/g) and 80.00 (mg/g) for MB and  $\text{Pb(II)}$  respectively, at initial concentration of 80 and 100 (mg/L) for MB and  $\text{Pb(II)}$  respectively. [9]

### **4.5 Gum ghatti – graft – poly(4-acryloylmorpholine) hydrogel incorporated with magnetite nanoparticles**

Gum ghatti (Ggh), also known as Indian gum, is an extract of the *Anogeissus latifolia* tree that has outstanding gelling, hardening, gelatinization, and interfacial properties. It is a non-starch polysaccharide with an exceedingly complicated structure made up of sugars like D-galactose, D-mannose, L-arabinose, D-xylose, and D-glucuronic acid. It is widely used in the culinary, pharmaceutical, and paper sectors. Because of their longevity, bio - compatibility, and environmental safety, Ggh-based hydrogels functionalized with various vinyl and acrylic polymer units have been successfully used for the adsorption of dye and heavy metal ions from aqueous solution.

4-Acryloylmorpholine is a biodegradable, water-soluble monomer with amide and ether functional groups. Because of the presence of the morpholine group, acryloylmorpholine-based polymers are said to have excellent adsorption characteristics.

Magnetic nanomaterials are a type of nanomaterials in which magnetite nanoparticles serve as a strengthening ingredient. They have the advantages of magnetic separation with an externally applied magnetic field as well as high nano-scale material efficiency. They are effective in treating large amounts of waste water in a short period of time.

A graft polymerized composite of these three components have been fabricated for effective removal of Methylene blue and heavy metals from the waste water.

#### **4.5.1 Synthesis of nano-bio sorbent composite Gum ghatti-graft-poly (4-acryloylmorpholine) gel**

To achieve a homogeneous solution, Ggh was dispersed in 20 mL distilled water and kept stirring. A amount of 2 mL AcM was poured to the aforesaid solution and stirred until it fully dissolved. Aqueous solutions containing 0.066 mmol KPS and 0.097 mmol MBA were added to the resulting combination. The resultant solution was treated in a household microwave oven at 80 W for 80 seconds with intermittent cooling and heating after complete mixing. To remove undissolved constituents and the homopolymer from the gel, it was first treated with acetone, then methanol, and finally distilled water.

#### **Combining composite gel and magnetite nanocomposite**

In a beaker containing 100 mL of an aqueous phase containing 2.1 g ferric chloride and 5.8 g ferrous chloride, around 0.5 g of dry (Ggh-g-PAcM) gel was inserted and allowed to settle for 10 hours. After that, the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  loaded swollen gel was placed for 8 hours in a beaker containing 100 mL of 0.5 M  $\text{NH}_4\text{OH}$  solution. After that, the black coloured gel was collected and rinsed multiple times with distilled water. Ggh-g-PAcM/ $\text{Fe}_3\text{O}_4$  was the name given to the resultant nanocomposite, which was processed in a  $500^\circ\text{C}$  oven for over a day

#### **4.5.2 Methylene Blue removal using Gum ghatti-graft-poly(4-acryloylmorpholine) gel and composite gel and magnetite nanocomposite**

The performance of the hydrogel and nanocomposite in adsorbing heavy metal ions ( $\text{Cu(II)}$  and  $\text{Hg(II)}$ ) and Methylene Blue from aqueous solutions was observed to be effective. Due to the increased surface area, the inserted  $\text{Fe}_3\text{O}_4$  nanoparticles occupied the available empty space in the gel, increasing the hydrogel's adsorption capacity. The best model for understanding the

adsorption process was found to be the Freundlich isotherm model. For both dyes and metal ions, kinetic investigations demonstrated that the adsorption process followed a pseudo second order model. Biosorption was endothermic, with negative overall Gibbs free energy for the process, followed by a rise in entropy. The regeneration capabilities of both the adsorbents were found out to be exceptionally good. [7]

#### **4.6 Rice husk as bio sorbent**

Rice husk is a type of organic waste that is widely produced. It's a common byproduct of rice milling and agro-based biomass production. Rice husk is a cellulose-based fibre that contains amorphous silica in the amount of 20%.

##### **4.6.1 Synthesis of Rice husk as bio sorbent**

To remove the contaminants, RH was washed five times with deionized water. After 4 days of natural drying in the sun, the RH was dried in the air for 12 hours at 105°C, then sieved to get RH particles with a particle size of 0.5–0.84 mm (termed as the dried RH).

Furthermore, the dried RH (about 10 g each batch) was treated for 4 hours at 60°C with 200 rpm stirring in a 100 mL 15 M H<sub>2</sub>SO<sub>4</sub> solution.

After the filtration, the acid-modified rice husk was washed with deionized water (until the liquid became neutral) and dried in an oven at 105°C for 12 hours, followed by torrefaction at 300°C under N<sub>2</sub> (termed as the torrefied RH, TRH). Before the adsorption studies, the dry RH and TRH were stored in a desiccator.

##### **4.6.2 Removal of Methylene Blue with the help of Rice husk**

1g of MB was dissolved in 1L distilled water to make the dye stock solution (1000 mg/L). In a Batch adsorption experiment, A conical flask was filled with 25 mL of 50 mg/L dye solutions and 0.05 g of adsorbent, which was swirled together until equilibrium was reached. A UV-visible spectrophotometer was used to measure the absorbance of the MB dye at different time intervals after around 2 mL of the solution was put to the cuvette. All of the experiments were carried out at room temperature and were performed three times to find accurate results.

Changing the concentration of MB dye has an effect. When lesser concentrations of 10 mg/L and 20 mg/L were applied with an adsorbent dose of 0.05 g, about 100 percent clearance was achieved. However, with dye doses of 40 mg/L and 50 mg/L, the percentage removal was reduced to ninety five percent and ninety three percent, respectively.

## CHAPTER – 5

### Selection of nanobiosorbent for dye and heavy metal removal

In the previous chapter we have discussed about the various biosorbents used for heavy metal and methylene blue dye removal. In this chapter our discussion will be focused on the comparison of the biosorbents and their selection, along with the selection of heavy metal ion. Further project work will be carried out with accordance to the selected nanobiosorbent, heavy metal ion and methylene blue.

#### 5.1 Comparative study of different nano biosorbents for effective MB and heavy metal removal

Table 5.1: Comparison of different nano biosorbents

Biosorbent	Adsorption capacity (mg g <sup>-1</sup> )	Isotherm Followed	Kinetics Followed	Heavy Metal removed	Reference
Biochar and Fe <sub>2</sub> O <sub>3</sub> -biochar nanocomposite	50	Langmuir	Pseudo 2nd order	-	[8]
Surfactants-Modified Sawdust	129.68	Langmuir and Freundlich	-	-	[3]
Poly m-phenylenediamine grafted dextrin based nanobiosorbent	76.33 and 80	Langmuir and Freundlich	Pseudo 1st and 2nd order	Pb(II) and Methylene blue	[10]
Gum ghatti – graft – poly(4-acryloylmorpholine) hydrogel incorporated with magnetite nanoparticles	116.8, 137.8, 249.9, and 235.1	Freundlich	Pseudo 2nd order	Methylene blue, rhodamine 6G, Cu(II) and Hg(II)	[7]
Nanomagnetic Fe <sub>3</sub> O <sub>4</sub> with Fish Scales	68.72	Langmuir and Sips	Pseudo 2nd order	-	[41]
Spinel Ferrite with nano bio-Silica	253.6	Langmuir and Freundlich	Pseudo 2nd order and Elovich	-	[42]

After comparing these nanobiosorbents we have selected Poly m-phenylenediamine grafted dextrin based nanobiosorbent as our nanobiosorbent for effective MB and heavy metal removal.

## **5.2 Introduction to nanobiosorbent**

To remove heavy metal ions and dyes from aqueous solutions, adsorbents such as zeolites, metallic oxides, activated carbon, agricultural residue, conducting polymers, and polysaccharides have been utilized. Polysaccharides such as chitosan, starch, cellulose, and alginate are plentiful, biodegradable, and renewable resources with a high potential for chemical and physical interactions with a variety of waste compounds or ions. Dextrin (Dex) is a polysaccharide that is abundant and inexpensive, and it is widely utilized in the textile and food industries. It's a low-molecular-weight polysaccharide made up of d-glucose units linked together by alpha-(1, 4) or alpha-(1, 6) glycoside linkages. Dex is a product of starch or glycogen hydrolysis that has been utilized to make biodegradable materials.

Modified polysaccharide adsorbents have been shown to have higher adsorption capabilities than unmodified polysaccharide adsorbents. Graft co-polymerization is an old approach for chemical modification of polysaccharides. Graft co-polymerization of conducting polymers to polysaccharides has been documented in several publications as an excellent adsorbent for contaminant removal. Pollutant adsorption is caused by the presence of N and S atoms in the primary chain structure of conducting polymers. Because of the substantial numbers of amine and imine functional groups in the polymer chains, polyaniline (PANI) and its derivatives have shown good adsorption performance and are utilized as adsorbents for the removal of heavy metal ions/dyes from industrial effluents systems.

By grafting PANI and its variants onto polysaccharides, the adsorption characteristics can be enhanced. Many research organizations have been working on biomaterial-based nanocomposites for a variety of purposes. Nanocomposite polymeric adsorbents have garnered a lot of attention in recent years because of their excellent adsorption performance, ease of synthesis, wide availability, cost-effectiveness, and presence of diverse functional groups. To improve the properties of the parent materials, graphene oxide (GO) components are utilised as fillers in composites. Because of their superior physical and chemical qualities, they have indeed been extensively used in the water purification industry. For example, GO-based hybrids can be used as an adsorbent to remove heavy metal ions and dyes from wastewater/aqueous solutions due to their huge surface area and hydrophilicity.

GO-based composites have been synthesized by a number of research groups for a variety of

purposes, including water filtration. In this work Pb(II) and methylene blue removal with a high-performance multifunctional nanobiosorbent based upon dextrin-g-poly m-phenylenediamine (DgPmPDA) and GO has been studied. This is a new, low-cost, and ecologically sustainable nano-biosorbent.

The behavior of biosorption onto the nano-biosorbent was investigated under various settings, including varying contact periods, solution pH, adsorbent doses, starting concentrations, and temperature. Isotherms, and kinetics of MB and Pb(II) adsorption onto the nano-biosorbent were examined [10].

### **5.3 Lead as heavy metal toxicant**

Lead is found in the earth's crust (igneous rocks) at a concentration of 12.5 mg/kg, making it the 36th most abundant element in the periodic table. Lead concentrations in sedimentary rocks have been estimated to range from 7 mg/kg (sandstones) to 20 mg/kg (shales). Lead concentrations in deep-sea sediments are estimated to be between 9 and 80 mg/kg (clay) (carbonate). The typical range of lead concentrations in soil is 2 to 200 mg/kg, with an average value of 10 mg/kg (dry weight).[31]

With the possible exception of Pb(I), lead can exist in several valence states: Pb(O)-metal, Pb(I), Pb(II), and Pb(IV), all of which are potentially harmful to the environment. Unburned lead alkyl vapours and lead halides are released into the atmosphere by gasoline additives, primarily tetraethyl lead, the primary anthropogenic source of lead in the environment. The main lead compounds found in fresh automobile exhaust are PbBrCl and (PbO)<sub>2</sub>PbBrCl. Primary lead emissions are converted to a wide range of lead species by chemical reactions in the atmosphere. PbCCh, PbO<sub>x</sub>, (PbO)<sub>2</sub>PbCO<sub>3</sub>, PbSO<sub>4</sub>, and 2PbBrCl were the most common species found.[31]

#### **5.3.1 Effect of lead on human, soil and water**

##### **On Human**

Increased lead levels are a major issue in developing countries such as India. When lead is inhaled or ingested, it is a very dangerous poison, especially for children. Excessive lead exposure may be the most serious environmental health risk for children. Air, drinking water, food, household dust, play area soil and dust, interior and exterior paints, and improperly glazed ceramics and toys are all sources of lead for children. Lead poisoning is most dangerous in children aged six and under. Children grow at a rapid rate, forming stronger bones, developing stronger muscles, and forming numerous connections in their brain.

Permanent harm to health can occur when lead is used instead of essential nutrients to build bones, muscles, and brain connections. Lead can be harmful even at low levels, and high levels of lead can be fatal, causing seizures, unconsciousness, and death. Lead is a common contaminant in the environment. The negative health effects of lead exposure in children and adults are well documented, and there is no safe blood lead threshold for children.[33]

### **On Soil**

Lead is a trace element found in trace amounts in all biological materials, including soil, water, plants, and animals. It serves no physiological purpose in living organisms. Smelting operations, the application of wastewater treatment sludges to soil, transportation, rain, snow, hail, and other sources of lead contamination are the most common. Human activities are responsible for approximately 98 percent of the lead in the atmosphere. Plants detect lead through their roots, which also store the majority of the metal. Animals are particularly susceptible to lead poisoning after grazing on contaminated pasture. Food and air carry lead into organisms. The accumulation was studied in food grains, vegetables, spices, medicinal plants, and wild species. Lead in dust can also be found in wind-blown soil. Variations in lead content in soil could also be due to historical factors like traffic congestion, industry, and soil type.[33, 31]

### **On Water**

Unless there is a specific source of contamination, lead is unlikely to be present in source water. Lead, on the other hand, has long been used in plumbing materials and solder that come into contact with drinking water as it travels from its source to homes. Lead is leached into tap water as a result of the corrosion of lead-based plumbing materials. The higher the lead concentration in drinking water and the more lead-contaminated drinking water consumed, the higher the risk of lead poisoning. The reported permissible limits for Pb in the air, drinking water, soil, and food are 0.10-0.30  $\mu\text{g}/\text{m}^3$ , 5  $\text{mg}/\text{L}$ , 300  $\text{mg}/\text{kg}$ , and 1.1  $\text{mg}/\text{kg}$ , respectively. Rain and runoff water in central India's industrial cities is contaminated with lead levels several times higher than the permissible limits of 5  $\text{mg}/\text{L}$ . The medicinal plants, species, and leafy vegetables that grow in contaminated soil were found to contain levels of lead that exceeded the permissible limit of 1.1  $\text{mg}/\text{kg}$ . Rain and runoff water in central India's industrial cities is contaminated with lead levels several times higher than the permissible limit of 5  $\text{mg}/\text{L}$ . Lead levels in medicinal plants, species, and leafy vegetables grown in contaminated soil exceeded the permissible limit of 1.1  $\text{mg}/\text{kg}$ . [33]

### 5.3.2 Heavy Metals in Textile Industries

Because it necessitates a large amount of chemicals, the textile industry has been labelled as one of the world's worst polluters. Textiles use over 2000 different chemicals, ranging from dyes to transfer agents. The use of catalysts in the synthesis of some dye intermediates can result in antimony, copper, and chromium residues in dyestuffs. Metal complexes such as copper, lead, nickel, cobalt, and chromium are found in some reactive dyes. Metallic impurities from the raw materials used in the manufacturing process can also be found in dyestuffs with metal-free chromophores. Chemical residues from the manufacturing process can be found in traditional fabrics, which can evaporate into the air we breathe or be absorbed through our skin. Some of the chemicals can cause cancer or harm to children even before they are born, while others can cause allergic reactions in some people. Long-term exposure to heavy metals has been linked to kidney failure, emphysema, allergies, and even cancer. As a result, determining the the metal content of textile materials is extremely important.[32]

Table 5.2: Heavy metal contents ( $\text{mg kg}^{-1}$ ) in various textile (average of replicates  $\pm$  standard deviation).[32]

<b>Textile Fibers</b>	<b>Pb</b>	<b>Cu</b>	<b>Al</b>	<b>Mn</b>	<b>Cr</b>
<b>Cotton</b>	$1.57 \pm 0.10$	$3.16 \pm 0.20$	$5.52 \pm 0.30$	$1.44 \pm 0.09$	$0.11 \pm 0.01$
<b>Acrylic</b>	$1.68 \pm 0.10$	$2.35 \pm 0.14$	$3.74 \pm 0.23$	$0.35 \pm 0.02$	$0.25 \pm 0.02$
<b>Polyester</b>	$1.08 \pm 0.07$	$2.04 \pm 0.13$	$2.70 \pm 0.16$	$0.39 \pm 0.02$	-
<b>Nylon</b>	$0.74 \pm 0.04$	$2.01 \pm 0.12$	$2.46 \pm 0.16$	$0.62 \pm 0.04$	-
<b>Viscose</b>	$0.66 \pm 0.04$	$2.11 \pm 0.13$	$3.18 \pm 0.20$	$0.39 \pm 0.02$	-
<b>Polypropylene</b>	$1.37 \pm 0.08$	$2.94 \pm 0.19$	$4.70 \pm 0.30$	$0.37 \pm 0.02$	$0.37 \pm 0.02$



## **CHAPTER - 6**

### **Biosorption: Modeling and Analysis**

Heavy metals, dyes, pesticides, industrial chemicals and other substances that can be dangerous to wild animals and humans at low quantities are the most significant micro-pollutants in waters. Currently available wastewater treatment systems are frequently inefficient or expensive. Significant quantities of conventional waste, such as egg shells, bone fragments, peat, mushroom, sea grass, filamentous fungi, and carrots, can successfully remove toxic from pickled water, according to research.

Biosorption is a term used to describe a group of processes in the cell wall that include physical and chemical adsorption, ion exchange, electrostatic forces, complex formation, chelation, and micro-precipitation. These processes occur before anaerobic or aerobic biodegradation. It has a high level of selectivity and efficiency (high performance and low cost). Biosorbents can be made from natural resources like marine algae or weeds, or from industrial waste such excess activated sludge or fermentation wastes [40].

#### **6.1 Mechanism of biosorption**

##### **6.1.1 Biosorption and bio-accumulation**

Biosorption is defined as the passive adsorption of toxic substances by dead, inactive or biologically derived materials. Biosorption is a consequence of several metabolic processes independent of the cell membrane, the mechanisms responsible for the absorption of the pollutant vary according to the type of applied biomass. Bio accumulation is defined as the phenomenon occurring in living organisms. More specifically, bio accumulation is defined as the absorption of toxic contaminants by living cells or organisms. Compounds are passively or actively transported into cells, accumulated inside them, and they also enter the metabolic cycle through the cell membranes. Bio-accumulation is therefore often dependent on cell metabolisms.

Biosorption and bio accumulation both have benefits and problems. In general, using live organisms for continual water treatment from very harmful organic/inorganic contaminants is not a good idea. The accumulating substance quantity may attain partition equilibrium, or saturation, if the dangerous substance concentration is too high or the process step takes too long. The organism's metabolism will be disrupted and death may occur as a result of the high accumulated pollutant concentration. Using inert, dead biomass, this problem can be

avoided. In addition, if the adsorption mechanism is reversible, chemicals can be desorbed and returned to the treated wastewater if the concentration falls. A high sorption capacity is required to avoid desorption. Because of different constraints such as nutritional requirements, aeration, maximum cell density, and so on, this is not always possible in processes involving living cells. This explains well why we have opted for biosorption over bio-accumulation [40].

### **6.1.2 Biosorption Mechanism**

Heavy metal and organic compound biosorption occurs as a result of physicochemical interactions between the metal and the chemical bonding on the biosorbent's surface. Physisorption, ion exchange, and chemical sorption are among the mechanisms which are involved [40].

Contaminant sequestration from aqueous phase onto the surface of bio-material particles can be divided into four processes:

- (i) Diffusion from bulk solution across the liquid film surrounding the bio-material particles (film diffusion or external mass transfer)
- (ii) Adsorption onto adsorbent sites on the surface of the bio-material particles (surface adsorption)
- (iii) Internal diffusion into the bio-material particles (intraparticle or internal mass transfer diffusion) and
- (iv) Adsorptive diffusion

The analysis of kinetic parameters for contaminant removal from aqueous solution by bio-materials can be accomplished using two types of kinetic models:

- (i) Kinetic models (Pseudo-first order, Pseudo-second order etc.) that describe the interactions between pollutant molecules or ions and active sites on the adsorbent surface. These models do not include for diffusion, yet it is generally understood that intraparticle diffusion can alter kinetic data.
- (ii) Diffusion models (Webber and Morris model, Bangham diffusion model etc.) presume that the interactions between contaminant and active sites is instantaneous in comparison to diffusion steps, and hence these diffusion steps govern the total rate. [34, 37]

The nature of organic contaminants varies greatly. As a consequence, molecule size, charges, solubility, hydrophobicity, and reactivity all have an impact on biosorption. The biosorption method can also have a considerable impact on the type of biosorbent used and the makeup of the effluent [40]

## 6.2 Modeling of Biosorption

To establish the maximal Biosorbent absorption capacity for a adsorbate and to comprehend the sorption mechanism, the equilibrium distribution of the adsorbed pollutant (adsorbate) between the Biosorbent and the aqueous phase is necessary. Sorption kinetics, in addition to adsorbate distribution at equilibrium, gives vital information regarding the sorption process, particularly the rate of pollutant removal. When used in water treatment technology, biosorption kinetics information is critical for determining the optimal residence duration of the wastewater at the solid biomass phase interface.[40]

## 6.3 Fixed bed adsorption

The pollutant to be adsorbed will be transferred from the bulk fluid to the adsorbent bed as the polluted fluid passes through a fixed bed. There are several processes involved in the total adsorption process of a single pollutant molecule:

- Mass transfer from the bulk of the fluid to the adsorbent particle's surface via the boundary layer around the particle.
- Internal diffusion through the pores of the adsorbent is the second phase of diffusion.
- Adsorption onto the particle's surface is the third phase.

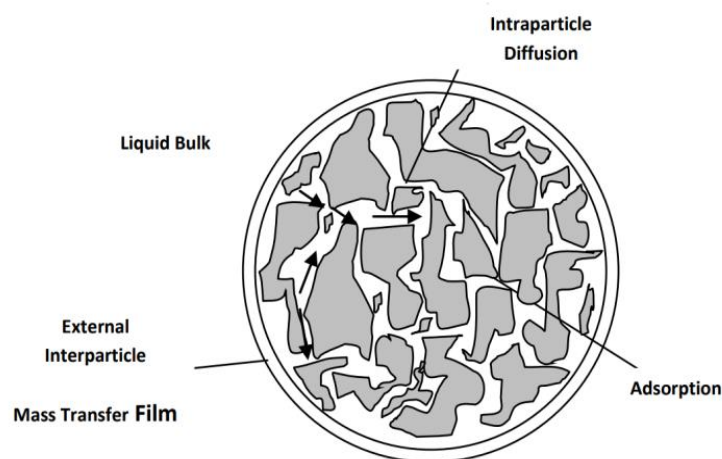


Fig:6.1 Processes involved in the entire adsorption of a single pollution molecule.[34]

In wastewater treatment applications, mass transfer, particularly intraparticle mass transfer,

dominates the total adsorption process. In batch-type contact procedures, an amount of material is mixed with a certain volume of water until the pollutants reach a desired concentration. The solid is then either discarded or regenerated for use with an additional volume of solution. If finely powdered adsorbent is employed in this sort of device, it may be difficult to separate the spent adsorbent from the water. In contrast, the use of big solid particles, which are eliminated more quickly when exhausted, necessitates longer contact times between the solution and adsorbent, necessitating the use of larger containers to hold the water during treatment.

Continuous-flow column operations offer an advantage over batch operations because adsorption rates are dependent on the solute content in the treated solution. The adsorbent is in continual contact with a fresh solution during column operation. Therefore, the concentration of the solution in contact with a particular adsorbent layer in a column varies relatively slowly. For batch treatment, the concentration of solute in contact with a certain amount of solid declines considerably more rapidly as adsorption progresses, consequently diminishing the adsorbent's ability to remove the solute.

Typically, fixed bed adsorbers are cylindrical, vertical tanks. Horizontal containers are occasionally employed, however vertical orientation is recommended to prevent poor or unequal flow distribution when particle motions or bed settling occur. For liquid phase applications, buoyancy forces must also be taken into account. Typically, the flow velocity in the upward direction should be low enough to prevent bed rising. In certain applications, however, it is advantageous to permit some bed expansion to prevent pressure drop. As the minimum velocity required to generate lifting is exceeded, the pressure drop increases somewhat with additional velocity increases. However, excessive growth might cause the bed to become thoroughly mixed. If this were to occur on a fixed bed, it would be analogous to the batch process and pose a risk of diminished product purity. If the liquid contains suspended particulates, it may be advantageous for the flow to be downhill. In water treatment applications, the adsorbent bed can serve as a particle trap and a method for eliminating flavor, odor, and contaminants.[37]

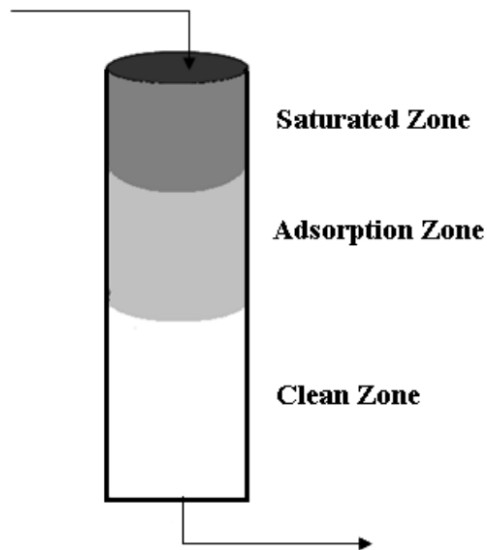


Fig:6.2 Adsorption Zones[34]

#### 6.4 Adsorption Kinetics

Kinetic studies covers reaction mechanism and the time required to attain equilibrium. It is also highly dependent on physical and chemical properties of the adsorbents, which determine the adsorption behavior, which can be either film or pore diffusion or a blend of both based on the system hydrology [34]. It can also be understood as the process which explains the rate of adsorbent uptake, which determines the adsorption residence time and is one of the most essential factors in determining adsorption efficiency.[36]

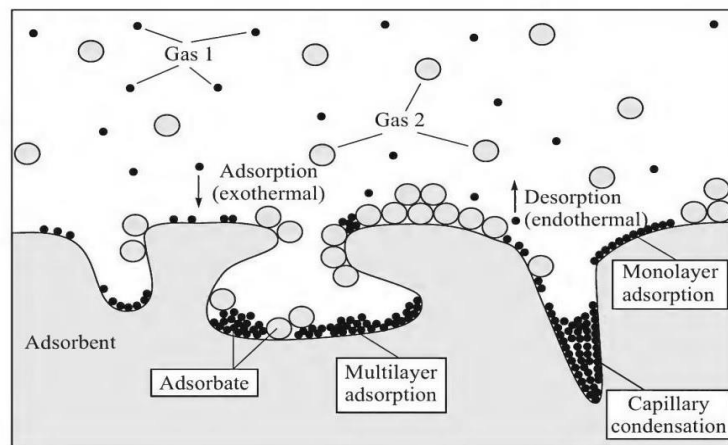


Figure 6.3. Mono and Multilayer adsorption depicted with capillary condensation [B.K. Dutta, Principles of Mass Transfer and Separation Processes, Chapter 12: Adsorption]

### 6.4.1 Kinetic Models

#### 1. Pseudo first order model

To explain the adsorption of a solute from a liquid solution, the Lagergren pseudo-first order model is most typically utilised [37]. Lagergren's pseudo-first order equation is given by:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \dots (6.1)$$

Here  $q_t$  and  $q_e$  are the contaminant quantities adsorbed at time  $t$  and equilibrium (mg/g) respectively, and  $k_1$  is the adsorption process's pseudo-first order rate constant (1/min).

#### 1. Pseudo second order model

The rate limiting step in this model is surface adsorption, which comprises chemisorption, in which adsorbate extraction from a solution is owing to physicochemical existing between the two phases; the kinetics rate equation is written as [34]:

$$\frac{dq_t}{dt} = k_1(q_e - q_t)^2 \dots (6.2)$$

### 6.4.2 Diffusion Models

#### 1. Webber and Morris Model

If a straight line is obtained when plotting metal ions adsorbed versus the square root of the contact period, intraparticle diffusion is rate limiting in the adsorption process.

$$q_t = k_i t^{0.5} + C \dots (6.4)$$

where  $k_i$  denotes the intraparticle diffusion rate constant (g/mg min) and  $C$  denotes the boundary layer effect or surface adsorption, it was discovered that the larger the intercept, the greater the contribution of surface adsorption to the rate-limiting step [37].

### 6.4.3 Adsorption Isotherms

Adsorption normally involves removing solutes from a solution and concentrating them on a surface till the concentration of solutes remained in the solution equals the amount at the surface. The amount of solute absorbed per unit mass of adsorbent,  $q$ , is defined as a function of the concentration of solute remaining in solution,  $C$ , to characterize this equilibrium. An adsorption isotherm is a type of statement of this type. The adsorption capacity or loading is determined by the fluid-phase concentration, the adsorption capacity, temperature and other environmental factors (especially the initial conditions of the adsorbent).[34]

Usually, data on adsorption capacity is collected at a constant temperature using a variety of adsorbates. The data is represented as an isotherm, and the concentrations (or partial pressures for a vapour or gas) are plotted (concentration vs. loading at constant temperature). There are numerous conceptual and empirical models. To depict the many types of adsorption isotherms, have been constructed. Langmuir, Freundlich, Dubinin-Radushkevich, Temkin, Toth, and a number of other isotherm models were developed over the previous decade using three core techniques [38].

### 6.4.4 Langmuir isotherm model

The Langmuir isotherm is an empirical model in which the adsorbed layer is one molecule thick (monolayer adsorption) and the adsorption process takes place at similar and analogous definite localised spots. The Langmuir isotherm model implies that adsorption is homogeneous, with each molecule having the same sorption activation energy and constant enthalpies. There should be no adsorbate transmigration in the surface plane, and all sites should have equal affinity for the adsorbate [38].

$$q_e = \frac{q_m b c_e}{1 + b c_e} \dots \dots \dots (6.6)$$

where  $q_e$  (mg/g) represents the equilibrium quantity of solute adsorbed in mg per gram of

solid,  $C_e$  (mg/l) represents the equilibrium concentration of the solute in solution, and  $q_m$  (mg/g) and  $b$  (l/mg) represent the maximum absorbance for the solid phase load capacity and the energy constant related to the heat of adsorption, respectively [34].

#### 6.4.5 Freundlich isotherm model

The reversible and non-ideal adsorption process is described by the Freundlich adsorption isotherm model. Unlike with the Langmuir isotherm model, the Freundlich model is not limited to monolayer development, allowing it to be applied for multilayer adsorption

Adsorption heat and affinities do not need to be spread equally across the heterogeneous surface in this isotherm model. The surface heterogeneity, as well as the exponential distribution of active sites and active site energies, are defined by the Freundlich isotherm model expression.

$$q_e = a_F C_e^{\frac{1}{n}} \dots \dots \dots (6.7)$$

Here,  $a_F$  and  $n$  are constants

#### 6.4.6 Dubinin-Radushkevich isotherm model

The Dubinin-Radushkevich adsorption isotherm model is commonly used to represent the mechanism of adsorption with a Gaussian energy distribution onto heterogeneous surfaces. The adsorption of vapours and gases on highly porous sorbents such as activated charcoal and zeolites is frequently described using this paradigm. This model was successful in predicting high solute activity as well as the moderate adsorbate concentration range, which can be explained to the inaccurate asymptotic behaviour. When pressure is low, however, the Dubinin-Radushkevich isotherm model does not predict Henry's law. This model is based on the notion that physical adsorption processes have a multilayer character that includes Van der Waal's forces. This isotherm model is typically used to differentiate between chemical and physical metal ion adsorption. This isotherm model is temperature dependent. It is regarded as a defining and distinctive characteristic [38].

$$\ln q_e = q_s - K \epsilon^2 \dots \dots (6.8)$$

$$\epsilon = RT \ln 1 + \frac{1}{C_e} \dots \dots (6.9)$$



#### 6.4.7 Temkin isotherm model

The Temkin empirical Isotherm model was originally developed to describe hydrogen adsorption onto platinum electrodes in an acidic solution, which is referred to as a chemisorption system. This isotherm model accounts for the contact between the adsorbent and the adsorbate while ignoring presence of extreme concentration values. This model predicts that, as a function of temperature, the adsorption heat of all molecules in the layer decreases linearly rather than logarithmically as the surface coverage increases. Only an intermediary concentration range is covered by this adsorption isotherm model.

$$q_e = \frac{RT}{b_T} \ln A_t + \frac{RT}{b_t} \ln C_e \dots \dots \dots (6.10)$$

Because binding energies are assumed to be equally distributed in its equation, this model is excellent at forecasting gas phase equilibrium when it is not necessary for it to be arranged in a closely packed structure with same alignment. This isotherm model, but at the other hand, is inapplicable to current complicated adsorption systems, such as aqueous-phase adsorption isotherms [38]

#### 6.4.8 Modified BET isotherm model (Harkin Jura Model)

The BET model is regarded as a variant of the Langmuir model. It includes the same hypotheses as the Langmuir model, as well as several additional simpler hypotheses, such as: The second, third, and higher layers all have the same adsorption energy. This energy is the same as fusion heat, which is unaffected by exchanges between the adsorbent and the adsorbate. The initial layer, on the other hand, has a different energy than the remaining layers.

The Harkin-Jura isotherm model assumes that multi layer adsorption on the surface of the adsorbents can have a heterogeneous distribution of pores. The following is a diagram of the isotherm model [38].

$$\frac{1}{q_e^2} = \frac{B_{HJ}}{A_{HJ}} - \left( \frac{1}{A_{HJ}} \right) \log C_e \dots \dots \dots (6.11)$$

Here,  $A_{HJ}$  and  $B_{HJ}$  are constants.

#### 6.4.9 Elovich model

This model's equation is based on the kinetic principle, which states that adsorption sites increase exponentially with adsorption, implying multilayer adsorption. The equation was originally created to describe the kinetics of gas chemisorption onto solids [38].

The Elovich model's written as follows:

$$\frac{qe}{qm} = K_E C_e e^{\frac{qe}{qm}} \dots (6.12)$$

Linear form of Elovich model is:

$$\ln\left(\frac{qe}{C_e}\right) = \ln(K_E qm) - \frac{qe}{qm} \dots (6.13)$$

The slope and intercept of the plot of  $\ln(q_e/C_e)$  versus  $q_e$  can be used to calculate maximum adsorption capacity of adsorbant and Elovich constant. Elovich Model is used to calculate the Adsorption Capacity and if we get high adsorption capacity by Elovich model then it means that our adsorption fits the Elovich Model and adsorption process is Multilayer, if it does not fits Elovich model then that means our adsorption process is not multilayer [38].

#### 6.4.10 Jovanovic model

The Jovanovic model is based on the Langmuir model's assumptions, as well as some of the mechanical contacts which are between the adsorbent and the adsorbate. The Jovanovic isotherm's linear form is written as follows:

$$\ln(q_e) = \ln(q_{max}) - K_J C_e \dots (6.14)$$

$q_e$  is the amount of adsorbate present at equilibrium condition in adsorbent (mg/l),  $q_{max}$  is the maximum adsorbate uptake calculated from the plot of  $\ln q_e$  versus  $C_e$ , and  $K_J$  is the Jovanovic constant [38].

### 6.5 Adsorption Modeling

Different adsorption isotherm models are applied to the derived data set from the paper [10] and the plotting work is carried out using MS Excel. Initially the constants in every model are found by plotting graphs based on the experimental values derived from the paper [10]. Then the modeling is done by using MS Excel. Best fit isotherm is then derived using the value of regression coefficient  $R^2$ . The model with the value closet to unity was considered as the best fit.

## 1. Langmuir isotherm model

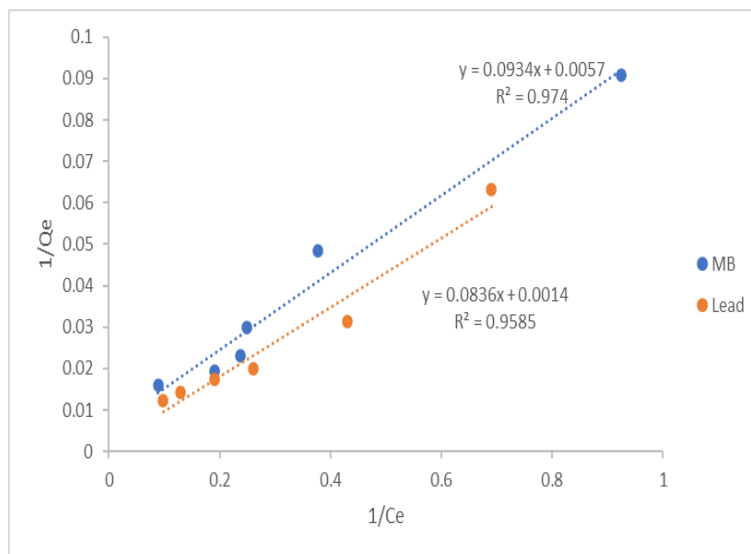


Fig.6.4 Langmuir Isotherm for Lead and MB dye

The graph between  $1/Q_e$  vs  $1/C_e$  has been produced, and the regression coefficient  $R^2$  values have been computed. As shown in Fig. 6.4, the  $R^2$  values for MB and Pb(II) are 0.974 and 0.9585, respectively. In comparison to lead ion, Langmuir's model matches MB better. This shows that the monolayer adsorption process for MB dye is more likely. It also supports the theory that MB dye adsorption is homogenous, with each molecule having the same sorption activation energy and constant enthalpies. The value of the regression coefficient for various models can be used to validate this mechanism.

## 2. Freundlich isotherm model

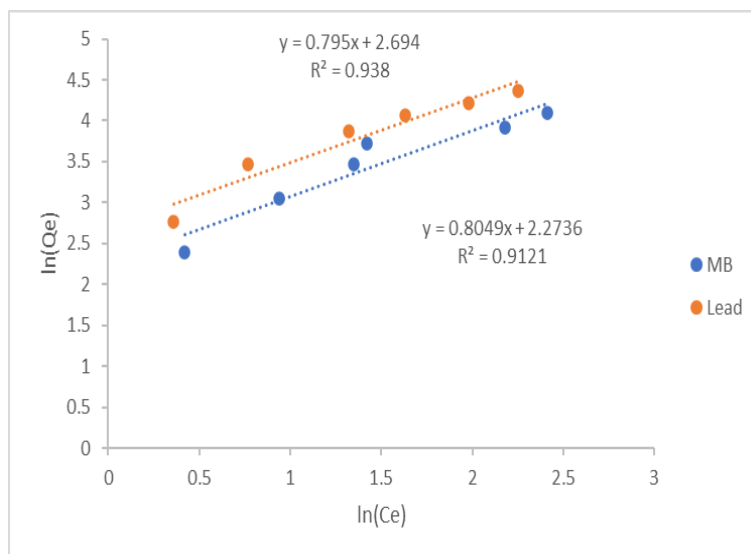


Fig.6.5 Freundlich Isotherm for Lead and MB dye

The graph has been plotted between  $\log$  of  $Q_e$  and  $\log$  of  $C_e$ , and the values of regression coefficient have been computed. As shown in Fig.6.5, the  $R^2$  values for MB and Pb(II) are 0.9121 and 0.938, respectively. Unlike with the Langmuir isotherm model, the Freundlich model is not limited to monolayer development, allowing it to be applied for multilayer adsorption. Adsorption heat and affinities do not need to be spread equally across the heterogeneous surface in this isotherm model. According to the values of regression coefficient Langmuir model fits better.

### 3. Modified BET model (Harkin-Jura model):

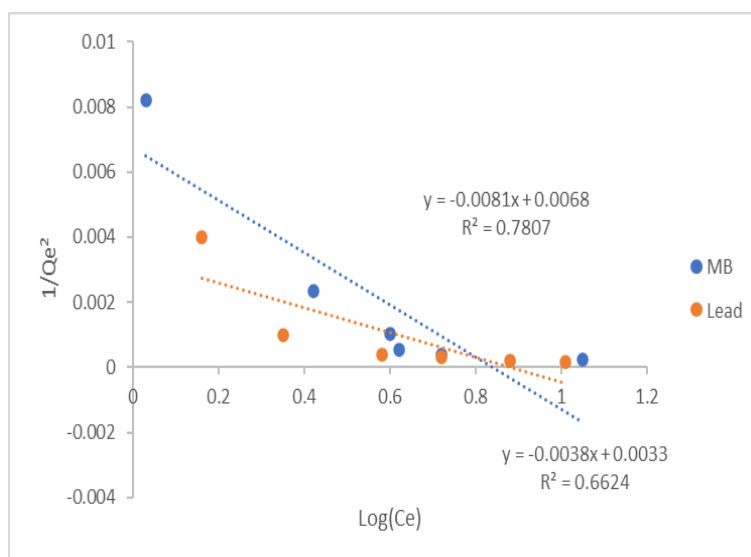


Fig.6.6 Modified BET model for Lead and MB dye

The graph has been plotted between  $1/(Q_e)^2$  vs  $\log$  of  $C_e$ , and the values of regression coefficient have been computed. As shown in Fig.6.6, the  $R^2$  values for MB and Pb(II) are 0.66 and 0.78, respectively. It is regarded as a variant of the Langmuir model. It includes the same hypotheses as the Langmuir model, as well as several additional simpler hypotheses, such as: The second, third, and higher layers all have the same adsorption energy. This energy is the same as fusion heat, which is unaffected by exchanges between the adsorbent and the adsorbate. This model does not fit well for our system which is realized through the values of regression coefficient.

#### 4. Temkin Model

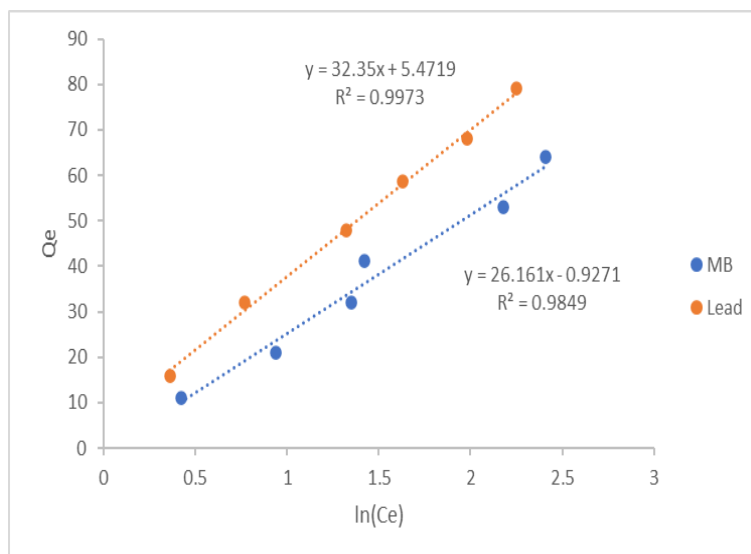


Fig.6.7 Temkin model for Lead and MB dye

The graph has been plotted between  $Q_e$  vs log of  $C_e$ , and the values of regression coefficient have been computed. As shown in Fig.6.7, the  $R^2$  values for MB and Pb(II) are 0.98 and 0.99, respectively. The Temkin Isotherm model was originally developed to describe hydrogen adsorption onto platinum electrodes in an acidic solution, which is referred to as a chemisorption system. The high values of regression coefficient describes that as a function of temperature, the adsorption heat of all molecules in the layer decreases linearly rather than logarithmically as the surface coverage increases. This isotherm model accounts for the contact between the adsorbent and the adsorbate while ignoring presence of extreme concentration values.

#### 5. Dubnin-Radhuskevich Model

The graph has been plotted between log of  $Q_e$  and  $E^2$ , and the values of regression coefficient have been computed. As shown in Fig.6.8, the  $R^2$  values for MB and Pb(II) are 0.82 and 0.89, respectively. The Dubinin-Radushkevich adsorption isotherm model is often used to simulate the mechanism of adsorption onto heterogeneous surfaces with a Gaussian energy distribution. The adsorption of vapours and gases on highly porous sorbents such as activated charcoal and zeolites is frequently described using this paradigm. This isotherm model is typically used to differentiate between chemical and physical metal ion adsorption thus the value of regression coefficient for metal ion is higher than that of the dye.

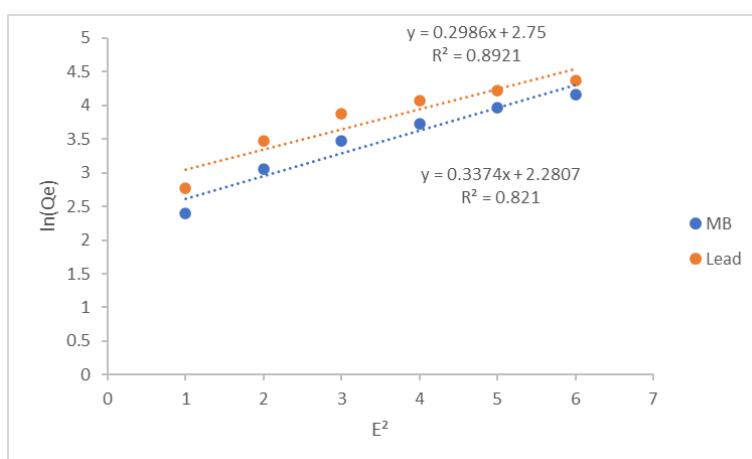


Fig.6.8 Dubnin-Radhuskevich Model for Lead and MB dye

## 6. Elovich model

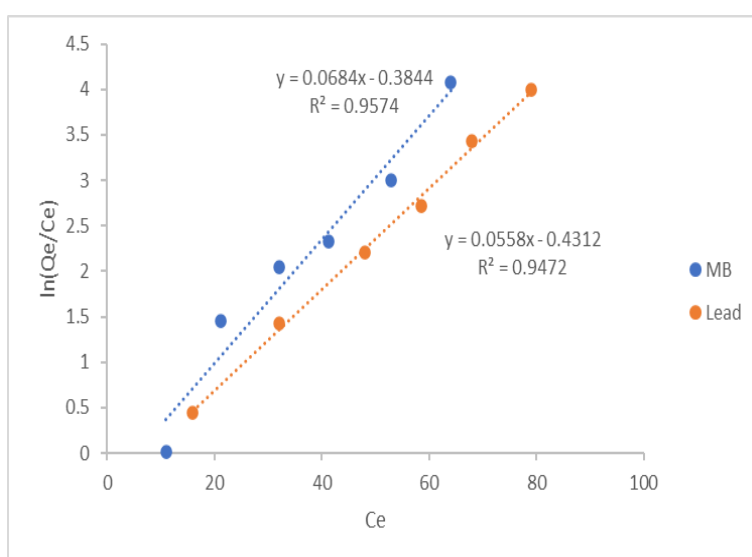


Fig.6.9 Elovich Model for Lead and MB dye

The graph has been plotted between  $Q_e/C_e$  vs  $C_e$ , and the values of regression coefficient have been computed. As shown in Fig.6.9, the  $R^2$  values for MB and Pb(II) are 0.95 and 0.94, respectively. This model is based on the kinetic principle, which states that adsorption sites increase exponentially with adsorption, implying multilayer adsorption. The equation was originally created to describe the kinetics of gas chemisorption onto solids. The value of regression coefficient is higher for MB dye giving possibility of chemisorption for the dye.

## 7. Jovanovic model

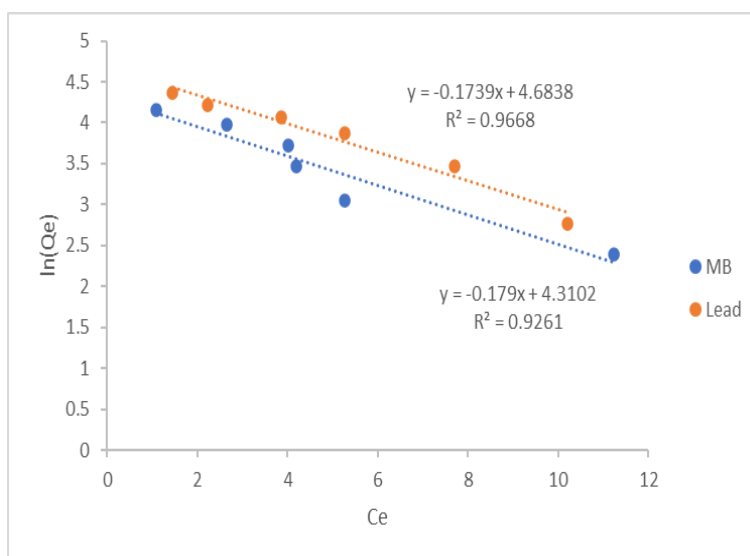


Fig.6.10 Jovanovic Model for Lead and MB dye

The graph has been plotted between log of  $Q_e$  and  $C_e$ , and the values of regression coefficient have been computed. As shown in Fig.6.10, the  $R^2$  values for MB and Pb(II) are 0.923 and 0.926, respectively. The Jovanovic model is based on the Langmuir model's assumptions, as well as some of the mechanical contacts which are between the adsorbent and the adsorbate.

## 6.6 Kinetic Modeling

Different kinetic and intraparticle diffusion models are applied to the derived data set from the paper[10] and the plotting work is carried out using MS Excel. Initially the constants in every model are found by plotting graphs based on the experimental values derived from the paper [10]. Best fit isotherm is then derived using the value of  $R^2$ . The model with the value closet to unity was considered as the best fit.

## 1. Pseudo-first Order :

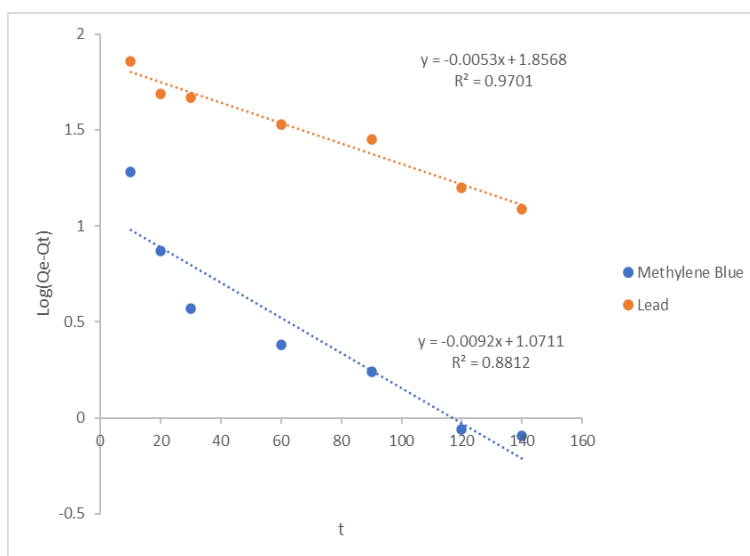


Fig.6.11 Pseudo-first Order model for Pb(II) and MB

The graph has been plotted between log of ( $Q_e - Q_t$ ) vs time, and the values of regression coefficient have been computed. As shown in Fig.6.11, the  $R^2$  values for MB and Pb(II) are 0.88 and 0.97 respectively. This implies that the metal ion follows pseudo first order kinetics, which is the rate limiting step for this process.

## 2. Pseudo-Second Order Model:

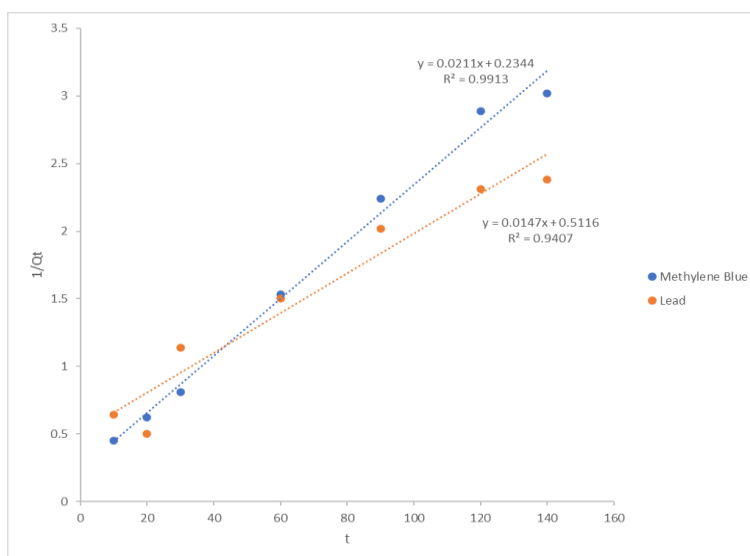


Fig.6.12 Pseudo second Order model for Pb(II) and MB

The graph has been plotted between log of  $1/Q_t$  vs time ,and the values of regression coefficient have been computed. As shown in Fig.6.12, the  $R^2$  values for MB and Pb(II) are 0.99 and 0.94 respectively. This implies that the MB dye follows pseudo second order



kinetics. The rate limiting step in this model is surface adsorption, which comprises chemisorption, in which adsorbate extraction from a solution is owing to physicochemical existing between the two phases. Thus we can hypothesised that MB dye is adsorbed by chemisorption.

### 3. Intraparticle Diffusion Model:

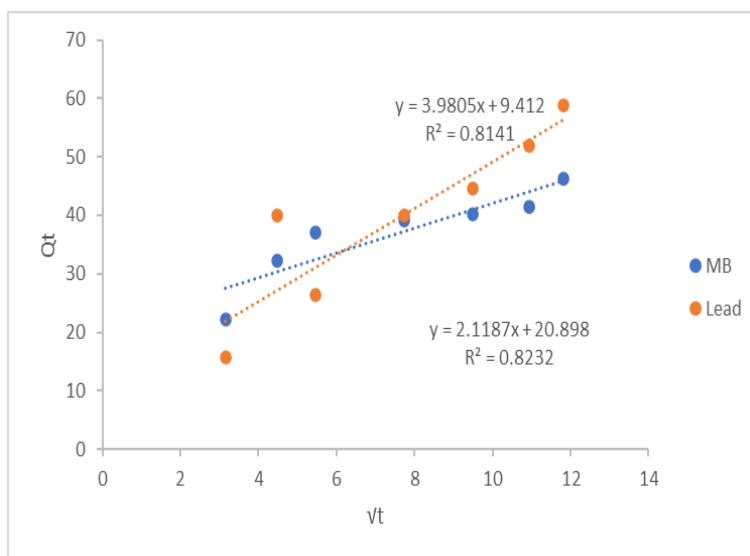


Fig.6.13 Intraparticle Diffusion model (Webber and Morris) for Pb(II) and MB

The graph has been plotted between log of  $Q_t$  vs  $(t)^{0.5}$ , and the values of regression coefficient have been computed. As shown in Fig.6.13, the  $R^2$  values for MB and Pb(II) are 0.82 and 0.81 respectively. This model also includes the effects of boundary layer. straight line is not obtained when plotting metal ions and dye adsorbed versus the square root of the contact period hence intraparticle diffusion is rate not limiting in the adsorption process.

Table 6.1 Comparative study of different adsorption and kinetic models

Modeling Type	Model	Parameter	Pb(II)	MB	Validation from the work referred[10]	
					Pb(II)	MB
Adsorption Isotherm	Langmuir Fig(6.4)	$Q_m$ (mg/g)	666.66	158.73	800	163.3
		$K_L$ (L/mg)	0.0182	0.0678	0.040	0.030
		$R^2$	0.95	0.97	0.95	0.97
	Freundlich Fig(6.5)	$K_F$ (mg/g)	14.79	9.45	14.62	10.89
		$n$	1.25	1.19	1.26	1.35
		$R^2$	0.93	0.91	0.93	0.95
	Modified BET Model Fig(6.6)	$B_{HJ}$	2.07	2.04	-	-
		$A_{HJ}$	238.09	99.00	-	-
		$R^2$	0.78	0.66	-	-
	Temkin Model Fig(6.7)	$A_T$ (L/g)	446.68	811.26	-	-
					-	-
		$B_T$ (J/mol)	73.13	80.95	-	-
	Dubnin-Radhuskevich Model Fig(6.8)	$q_s$ (mg/g)	4.2066	3.216	-	-
		$K(\text{mol}^2/\text{KJ}^2)$	0.0001	0.0001	-	-
		$R^2$	0.89	0.82	-	-
	Elovich Model Fig(6.9)	$R^2$	0.94	0.95	-	-
	Jovanovic	$R^2$	0.92	0.92	-	-

	model Fig(6.10)					
Kinetic Model	Pseudo-first order Fig(6.11)	$Q_e(\text{mg/g})$	71.91	11.77	69.39	11.90
		$K_1 (\text{min}^{-1})$	0.012	0.021	0.011	0.020
		$R^2$	0.9701	0.88	0.95	0.88
	Pseudo-second order Fig(6.12)	$Q_e(\text{mg/g})$	47.39	68.02	67.56	46.72
		$K_2(\text{m}^{-1}\text{min}^{-1})$	0.0018	000042	0.0004	0.0023
		$R^2$	0.94047	0.9913	0.93	0.98
	Intraparticle Diffusion Fig(6.13)	$C(\text{mg/l})$	9.412	20.898	-	-
		$k_i$	3.9805	2.1187	-	-
		$R^2$	0.8141	0.8232	-	-

## 6.7 Discussion

It can be inferred from the Table 6.1 (mentioned above) that Temkin model (Fig 6.7) fits best for adsorption isotherms having regression coefficient values as 0.98 and 0.94 for metal ion and dye respectively. But owing to the fact that Temkin model is valid only for gaseous systems we will go for the second best fit which is the Langmuir isotherm model (Fig 6.4) having the values of regression coefficient as 0.94 and 0.97 for metal and dye respectively. For the kinetic model it can be observed that Pseudo First order model (Fig 6.11) and Pseudo Second order model (Fig 6.12) is followed by Pb(II) and MB respectively. The intraparticle diffusion model doesn't fit well for our system (Fig 6.13) shows that mass diffusion step is not rate controlling. The rate is controlled by kinetic steps only which explained by Fig 6.11 and Fig 6.12.

### 6.7.1 Comparison from the work referred:

#### Adsorption Isotherm:

The results which we have drawn were based on the data set from the paper [10] according to which the isotherm followed by MB and Pb(II) was Langmuir model, hence the suggested mechanism was monolayer adsorption process taking place at similar and analogous definite localised spots. The Langmuir isotherm model implies that adsorption is homogeneous, with each molecule having the same sorption activation energy and constant enthalpies. There should be no adsorbate transmigration in the surface plane, and all sites should have equal affinity for the adsorbate.

The work which we have referred have the values of regression coefficient as 0.94, 0.97 for Pb(II) and MB respectively and in our work the values of regression coefficient are obtained as 0.9464 and 0.93 for Pb(II) and MB respectively. The values obtained by reproducing the present work have error of 0.68% for Pb(II) and for MB error obtained was 4.12%.

This shows that our work is in accordance with the already drawn results.

We have also fitted the data on three different isotherm models among which Temkin model shows the best fit for both Pb(II) and MB. The regression coefficient values obtained for the Temkin model were 0.9857 and 0.944 for Pb(II) and MB respectively. This isotherm model accounts for the contact between the adsorbent and the adsorbate while ignoring presence of extreme concentration values. This model predicts that, as a function of temperature, the adsorption heat of all molecules in the layer decreases linearly rather than logarithmically as

the surface coverage increases. Only an intermediary concentration range is covered by this adsorption isotherm model. Because binding energies are assumed to be equally distributed in its equation, this model is excellent at forecasting gas phase equilibrium when it is not necessary for it to be arranged in a closely packed structure with same alignment. This isotherm model, but at the other hand, is inapplicable to current complicated adsorption systems, such as aqueous-phase adsorption isotherms.

### **Kinetic Study:**

It has been observed that the intraparticle diffusion is not rate limiting step as the value of  $R^2$  for Webber Morris model was obtained as 0.8141, 0.8232 for Pb(II) and MB respectively. This is clear that adsorption capacity does not varies as the  $t^{0.5}$  which suggest that interactions between contaminant and active sites is rate determining and the diffusion steps were instantaneous, and hence interactions between contaminant and active sites these steps govern the total rate.

For the metal ion it is observed that Pseudo First order model is followed which suggests that rate of reaction is directly proportional to the concentration of the Pb(II) ion where as for the dye Pseudo Second Order model was followed and hence the rate was directly proportional to the square of the concentration of the MB dye. The rate limiting step in this model is surface adsorption, which comprises chemisorption, in which adsorbate extraction from a solution is owing to physicochemical existing between the two phases. Our observations and the work which we have referred were in alignment for the kinetic study.

In this comparison the value of different parameters were calculated by first plotting the experimental data and then finding the slope and intercept for the different models. The comparison of different models and their effectiveness for Pb(II) and MB are as follows:

#### **1.For MB dye:**

##### ***Adsorption study***

Temkin model shows the best fit for our MB dye followed by Langmuir model, Elovich Model, Jovanovic model, Freundlich model, Dubnin-Radhuskevich Model and Modified BET Model.

##### ***Kinetic study***

Pseudo-second order shows the best fit for our MB dye followed by Pseudo-first order and Intraparticle diffusion.

## 2. For Pb(II) metal ion:

### *Adsorption study:*

Temkin model shows the best fit for Pb(II) ion followed by Langmuir model, Freundlich model, Jovanovic model and Elovich Model, Dubnin-Radhuskevich Model and Modified BET Model.

### *Kinetic study:*

Pseudo-first order shows the best fit for Pb(II) ion followed by Pseudo-second order and Intraparticle diffusion.

Although the best fit for adsorption is Temkin Model but we will use Langmuir Model because Temkin Model has this limitation that it is valid for gaseous system only. We are dealing with liquid system, therefore we will use Langmuir Model.

In this comparative study we have used the data set from the paper [10] we have validated our observations. In this work we have additionally studies about the different adsorption and kinetic models which were not present in the current work which we have cited.

## 6.8 Biosorption Modeling

We have already discussed how every individual step in the biosorption of MB and Pb(II) is taking place on DgPmPDA@GO nano-biosorbent. Now we will incorporate all those equations together to form one adsorption model. We will follow the stepwise approach and carry our work according to some of the stated assumptions.

### **Assumptions:**

1. The biosorption will not be carried out simultaneously for the metal ion and the dye molecule, rather it will occur individually according to the pH of the system which is discussed in the further chapters.
2. The Intraparticle diffusion effects are ignored as Kinetic steps were rate controlling for our system.

### 6.8.1 Steps involved in biosorption of Pb(II):

Bulk Diffusion Step:

$$J_i = K_L(C_f - C_p) \dots(6.15)$$

Where,  $J_i$  : mass flux;

$K_L$  : mass transfer coefficient

$C_f - C_p$  : concentration difference(driving force)

### 1. Surface Adsorption Step:

We have observed that the adsorption of Pb(II) on DgPmPDA@GO nano-biosorbent shows the best fit for the Temkin Model but that model is only valid for gaseous systems and the second best fit which was the Langmuir model will be followed.

$$q_e = \frac{q_m b C_e}{1 + b C_e} \dots (6.16)$$

### 2. Kinetic Modeling Step:

The adsorption of Pb(II) on DgPmPDA@GO nano-biosorbent follows Pseudo First order Kinetics.

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \dots (6.17)$$

Kinetic modeling was performed using MATLAB and the results of kinetic modeling has shown below in the Fig 6.14. Concentration vs Time data was plotted using the Pseudo first order model for different initial concentrations ranging from 1mg/l to 30mg/l. The trend observed shows that after 200 minutes the concentration drop becomes almost stagnant, this is so because of the reduced concentration driving force.

Removal Percentage vs Time plot is presented in Fig 6.15 for different concentration ranging from 1mg/l to 30mg/l. The graph shows that maximum removal at higher concentrations (15,20,15,30 mg/l) has observed before 100 minutes. This explains us that percentage removal is also controlled by concentration driving force.

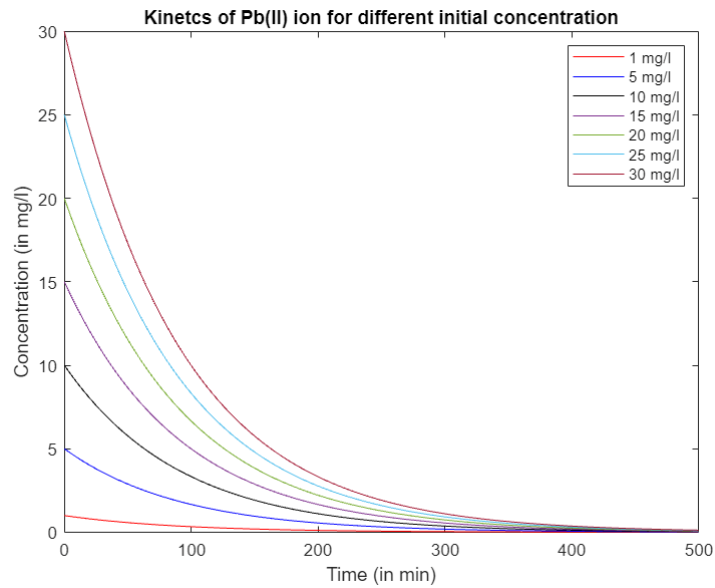


Fig.6.14 Kinetics of Pb(II)

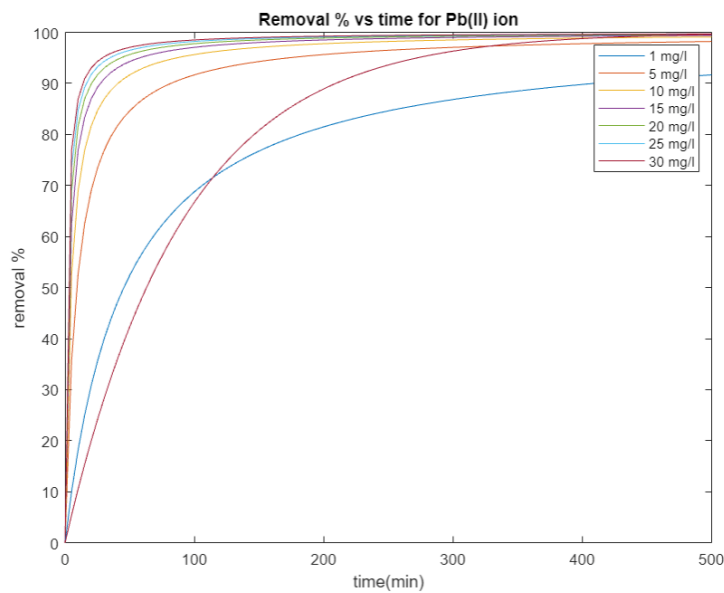


Fig.6.15: Removal percentage vs Time

### 6.8.2 Steps involved in biosorption of MB dye:

#### 1. Bulk Diffusion Step:

$$J_i = K_L(C_f - C_p) \dots(6.18)$$

Where,  $J_i$  : mass flux;

$K_L$  : mass transfer coefficient

$C_f - C_p$  : concentration difference(driving force)



## 2.Surface Adsorption Step:

We have observed that the adsorption of MB Dye on DgPmPDA@GO nano-biosorbent shows the best fit for the Temkin Model but that model is only valid for gaseous systems and the second best fir which was the Langmuir model will be followed.

$$q_e = \frac{q_m b C_e}{1 + b C_e} \dots (6.19)$$

## 3. Kinetic Modeling Step:

The adsorption of MB dye on DgPmPDA@GO nano-biosorbent follows Pseudo second order Kinetics.

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \dots (6.20)$$

Kinetic modeling was performed using MATLAB and the results of kinetic modeling has shown below in the Fig 6.16. Concentration vs Time data was plotted using the Pseudo second order model for different initial concentrations ranging from 1mg/l to 30mg/l. This graph shows steep drop in concentration during the first 50 minute of the process. The drop in concentration is steeper in this Figure because of the pseudo second order nature of the graph. Removal Percentage vs Time plot is presented in Fig 6.17 for different concentration ranging from 1mg/l to 30mg/l. In this Figure the percentage removal is lower at lower concentrations because of the lower concentration difference, but a similar trend is observed in this plot as well that most of the removal takes place during the first 100 minutes of the process. After sometime the percentage removal becomes saturated.

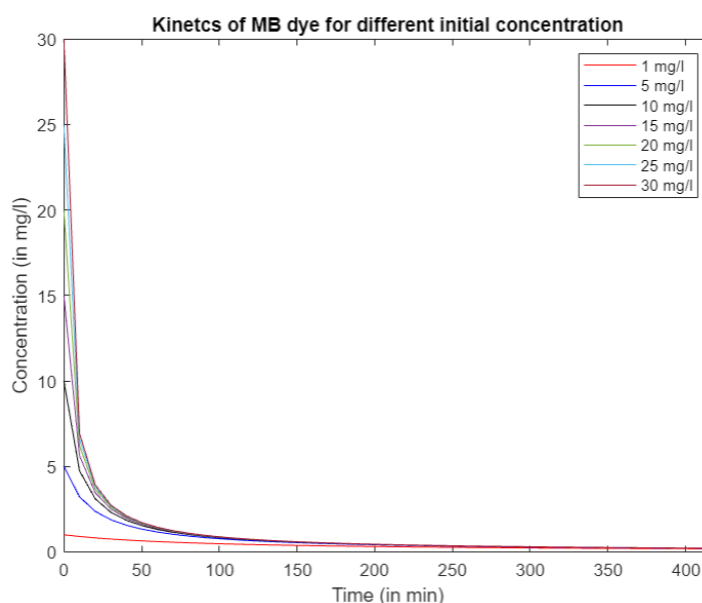


Fig.6.16 Kinetics of MB dye

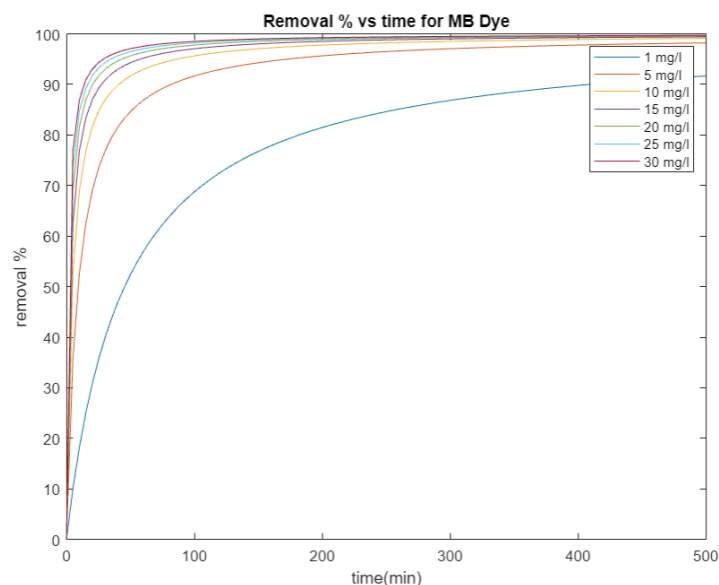


Fig 6.17: Removal percentage vs Time

## 6.9 Discussion

We have started this chapter with the studying the differences between biosorption and bioaccumulation and have stated that why we have opted biosorption over bioaccumulation. Further we have discussed about the biosorption mechanism and how it is ruled by various factors like kinetic and mass diffusion steps. Then for better understanding of our system we have studied different various types of adsorption isotherm models and kinetic models and it was found that for our system Kinetic step is rate controlling. Pseudo first order and pseudo second order kinetics is followed by PB(II) ion and MB dye respectively. For the adsorption isotherm best fit for both the models was Temkin model but as we know that Temkin model is only limited to gaseous system we have chosen Langmuir isotherm model as the suitable fit for our system.

Then the biosorption Modeling steps were discussed one by one. We have assumed that our system follows the Two film theory of mass transfer and hence the bulk diffusion step was given by the equation mentioned above. Then the next step was surface adsorption and as discussed earlier we have concluded that Langmuir isotherm model as the suitable for our system. For the surface kinetics step Pseudo first order and pseudo second order kinetics is followed by PB(II) ion and MB dye and thus the equations are solved using ODE45 solver of MATLAB (see Appendix) and these graphs are obtained. We have performed the calculations for different values of initial concentration as 1,5,10,15,20,25 and 30 mg/l for both dye and metal ion and observed these results.

It can be clearly seen that initially there is a huge concentration drop and as time proceeds the

system tends to become nearly stagnant which we can observe in Fig 6.14 and Fig 6.16. Similar trend has been observed over the different ranges of concentration.

This is the common trend shown by all the three graphs for the dye in our work. Thus, it could be concluded that the concentration driving force is very high for the first quarter in our system.

## **6.10 Conclusion**

The heavy metal Lead ion ( $\text{Pb(II)}$ ) and the textile dye Methylene Blue were chosen for study. The DgPmPDA@GO nano-biosorbent based on poly m-phenylenediamine grafted dextrin and graphene oxide (DgPmPDA@GO nano-biosorbent) was used in this study to remove  $\text{Pb(II)}$  and MB from industrial waste water. For various experimental data collected from referred work, various Adsorption Isotherms and Kinetic Models were investigated. The Temkin Isotherm was found to be the best fit for explaining Methylene Blue and  $\text{Pb(II)}$  adsorption on DgPmPDA@GO nano-biosorbent, while pseudo-first order and pseudo-second order kinetic models were found to be the best fit for explaining kinetics of  $\text{Pb(II)}$  and Methylene Blue, respectively. [10]

## Chapter 7

### Mechanism of dye and heavy metal removal

In this chapter we have discussed about the mechanism of removal of methylene blue dye and PB(II) ion using our nanobiosorbent. The chemistry of the process is thoroughly discussed in the chapter. Furthermore, the characterization of the our selected nanobiosorbent and the factors affecting the biosorption are taken into the account and are read and cited briefly in this chapter.

#### 7.1 Mechanism of Dye and metal ion removal:

The binding of sorbate to the biosorbent is a complicated process that occurs during biosorption. Bonding of metal ions through physical (electrostatic contact or van der Waals forces) or chemical (displacement of either bound metal cations (ion exchange) or protons) binding, chelation, reduction, precipitation, and complexation are all examples of biosorbents. Biosorbents comprise chemical/functional compounds that can bind and adsorb metal ions, such as amine, amide, imidazole, thioether, sulfonate, carbonyl, sulfhydryl, carboxyl, phosphodiester, phenolic, imine, and phosphate. These procedures are controlled and characterised by a number of essential elements, and those elements are as follows:

- the molecular weight, ionic radius, and oxidation state of the targeted metal species
- the chemical, stereochemical, and coordination features of metal ions
- The structure and nature of the biosorbent (in the case of microorganisms—living/non-living)
- the bonding site's kind (biological ligand)
- process variables such as pH, temperature, sorbate and sorbent concentrations, and other competing metal ions
- The bonding sites' accessibility

These factors play crucial role in the metal and dye speciation during biosorption. [44]

The following are some of the possible metal ion adsorption mechanisms onto biosorbents:

- Complex Formation
- Ion Exchange

- Electrostatic Attraction or Coordination
- Chelation

### 7.1.1 Complex formation

The creation of a complex is described as the association of two or more species. Between the metal ion and the ligands, mononuclear (monodentate) complexes develop wherein the metal atom fills the center point. The metal atom at the centre of a polynuclear (multidentate) complex can have a positive, negative, or neutral charge depending on the number of binding ligands involved. Because multidentate ligands comprise several ligands, complex formation to the monodentate ligand is superior to multidentate ligand complex formation. Covalent bonds connect the metal ion to the ligands during this process.

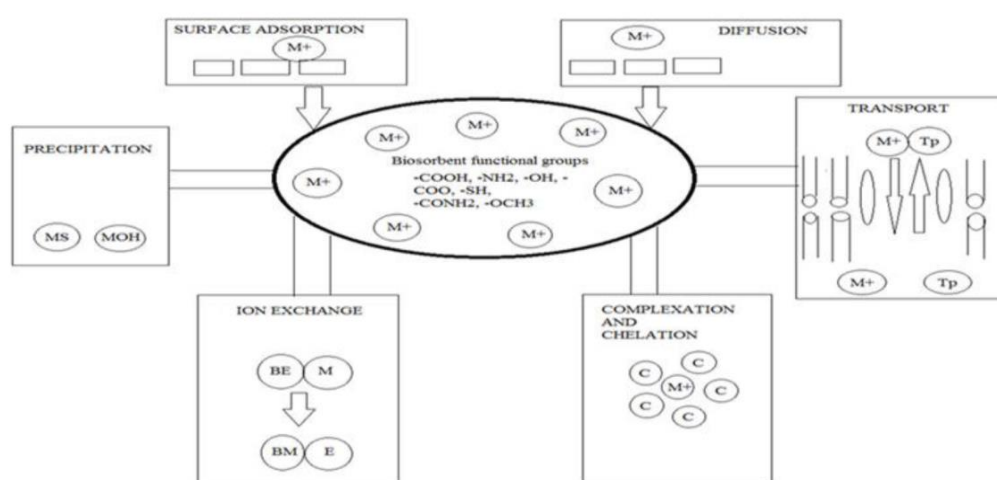


Fig 7.1: Different mechanisms of Biosorption by: (i)  $M^+$ : heavy metal ions, (ii) C: chelating agents, (iii) BE: molecules with exchangeable ions, (iv) BM: molecules with metal ions, (v) Tp: transport protein. [44]

### 7.1.2 Ion exchange

The process of ion exchange is a key term in biosorption. It is the process in which the exchange of binary metal ions with counter-ions takes place on the biosorbent's surface during biosorption. The majority of the purification process relies on the ion exchange mechanism. Cation or anion exchange are the two types of ion exchange. Cation exchangers include carboxyl groups, whereas anion exchangers include amino/imidazole groups.

### 7.1.3 Electrostatic attraction or coordination

This process the removal is carried as metal ion takes up a lone pair of electrons from the non-metal atom, the metal atom in the complex is attached to its immediate neighbours by a coordinate covalent bond. The donor (coordinating atom) is the non-metal atom, and the acceptor is the metal atom that takes the electron pair. Coordinate compounds are those that have these types of bonds in their structure. =O, -NH<sub>2</sub>, -NH, -N=, -OH, -S-, -O-R, and =NOH are some examples of coordinating groups.

### 7.1.4 Chelation

It refers to the process in which a chelating chemical attaches to a metal ion in multiple locations at the same time to produce a cyclic structure. The reaction to build stable complex via multiple linking primarily involves polydentate ligands. The structure becomes more stable as the number of ligand binding sites increases. Chelates are much more persistent than complexes as they have multiple binding sites for the metal ion.[44]

The following are some of the possible cationic dye adsorption mechanisms onto biosorbents:

- electrostatic attraction
- hydrogen bonding
- $\pi$ - $\pi$  interactions

### 7.1.5 Electrostatic attraction:

The negatively charged sites on the surface of our Nanobiosorbent and the cationic MB molecules in the solution can form weak electrostatic attractions. The oxygen-containing functional groups (carboxylic and phenolic groups) become ionised when  $\text{pH}_{\text{solution}} > \text{pHPZC}$ , and the pH of the solution reduces after adsorption. The surface charges of biosorbents are also explained by the pKa values of the carboxylic (2.0–4.0) and phenolic (8.0–9.0) groups. When the solution pH exceeds their pKa values, both the carboxylic and phenolic groups can dissociate and become predominantly negatively charged. The negatively charged carboxylate (-COO-) groups form when the (-COOH) carboxylic groups dissociate. As a result, the carboxylic groups are directly responsible for MB binding to the biosorbent surface. [43]

### 7.1.6 Hydrogen Bonding

Between the surface hydrogens of the hydroxyl groups (H-donors) on the adsorbent's surface

and the appropriate atoms (i.e., nitrogen and oxygen; H-acceptors) of MB, hydrogen bonding interactions can occur (this phenomenon is also known as dipole-dipole hydrogen bonding). Between the hydroxyl groups on the nanobiosorbent's surface and the aromatic rings of MB, hydrogen bonding interactions can also occur (this phenomenon is also known as Yoshida hydrogen bonding). [43]

#### 7.1.7 $\pi$ - $\pi$ interactions

Mattson and colleagues first proposed  $n$ -interactions (or  $n$ -electron donor-acceptor interactions) (1969). The carbonyl oxygens on the adsorbent's surface act as electron donors, while the aromatic rings of MB act as electron acceptors in  $n$ -interactions. [43]

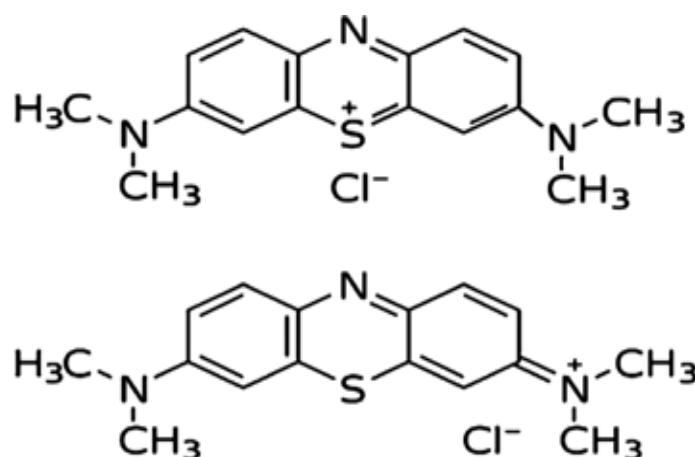


Fig 7.2 Different resonance structures of methylene blue. [45]

### 7.2 Structure characterization of DgPmPDA@GO nano-biosorbent

In the work which we have cited it was observed that the stretching vibration of O-H was related with a large absorption peak in the FT-IR (Fourier Transform Infra Red) spectra of GO, while the C=O, aromatic C=C, and C-O stretching vibrations were associated with 1710, 1631, and 1230  $\text{cm}^{-1}$ , respectively. The typical absorption peak of C=N and NH<sub>2</sub> is shown in the FT-IR spectrum of DgPmPDA at 1580 and 3400, respectively. Furthermore, O-H, N-H, C-H, C=C, and C-O-C stretchings correspond to peaks at 3400-3200, 2950-2860, 1476, and 1151  $\text{cm}^{-1}$ , respectively. The existence of the DgPmPDA (3400-3200, 3100-2900, 1580 and 1151  $\text{cm}^{-1}$ ) and GO (1710  $\text{cm}^{-1}$ ) matching peaks in the DgPmPDA@GO nano-biosorbent indicated the presence of both DgPmPDA and GO in the nano-biosorbent.

The samples of our nanobiosorbents and its constituents are also gone through XRD measurements. They were done to investigate the crystal lattice of generated substances. The XRD pattern of GO was amorphous, with two peaks at  $2\theta = 10^\circ$  and  $42.02^\circ$ , respectively. The

XRD pattern of DgPmPDA revealed an unique amorphous peak that related to the Dex and PmPDA, indicating that the grafting of PmPDA onto the Dex backbone was effective. Peaks at  $2\theta = 10^\circ$ ,  $25.5^\circ$ , and  $42.02^\circ$  were found in the XRD pattern of DgPmPDA@GO nano-biosorbent, indicating its amorphous structure and agreeing with the XRD patterns of GO and DgPmPDA.

### 7.3 Hypothesis of dye and metal ion removal mechanism

The FTIR spectra of DgPmPDA@GO nano-biosorbent before and after adsorption were used to demonstrate the adsorption mechanism of both Pb(II) and MB on DgPmPDA@GO nano-biosorbent. The spike at  $3419\text{ cm}^{-1}$  associated to -OH (or -NH<sub>2</sub>) groups shifted to  $3408\text{ cm}^{-1}$  in the FTIR spectra of DgPmPDA@GO-Pb(II), reflecting the electrostatic interactions along with chelation association between the amino and hydroxyl groups of DgPmPDA@GO and Pb(II). Furthermore, the spectra show  $1710\text{ cm}^{-1}$  (for carboxylic acid C=O) and  $1580\text{ cm}^{-1}$  (for quinoid C=C) changed to  $1695\text{ cm}^{-1}$  and  $1570\text{ cm}^{-1}$ , implying chelation and electrostatic attraction between the amine groups and carboxylic of DgPmPDA@GO and Pb (II). The overall adsorption is physical in nature, hence, is controlled by the electrostatic interactions between the biosorbent and metal ion.

For the dye molecule the spike was observed at  $3419\text{ cm}^{-1}$  in the FTIR spectrum of DgPmPDA@GO-MB connected to the stretching vibrations of -OH and -NH<sub>2</sub> shifted to  $3410\text{ cm}^{-1}$  in MB, indicating electrostatic interactions as well as H-bonding interactions between the active sites of cationic MB dye and the amine groups and hydroxyl groups of DgPmPDA@GO. Also, the absorption peaks  $1710\text{ cm}^{-1}$  (carboxylic acid C=O) and  $1580\text{ cm}^{-1}$  (quinoid C=C) moved to  $1700\text{ cm}^{-1}$  and  $1575\text{ cm}^{-1}$ , indicating electrostatic attractions as well as H bonding and  $\pi$ -stacking connections between both the MB and the DgPmPDA@GO aromatic rings. [ DEXTRIN PAPER]

### 7.4 Factors Effecting Adsorption of Pb and MB dye by nano-biosorbent

#### 1. Solution pH:

pH of the solution can change the surface charge of adsorbent and adsorbate. At pH value 2, the adsorption capacities for both Pb and MB dye are minimum due to competitive adsorption between Pb(II), cationic MB and available H<sup>+</sup> for protonation of the nano-biosorbent active sites. With increasing pH value adsorption capacities also increased and reached maximum level around pH 6.0 for Pb(II) and pH 8.0 for MB. For Pb(II) if pH value is higher than 6.0, hydrolysis of Pb(II) occurs which results in the formation of PbOH<sub>3</sub><sup>-</sup> ion and Pb(OH)<sub>2</sub>. MB is cationic dye so adsorbed at pH > 6.0. If pH > 8.0, due to electrostatic repulsion there is no



significant increase in adsorption capacity.

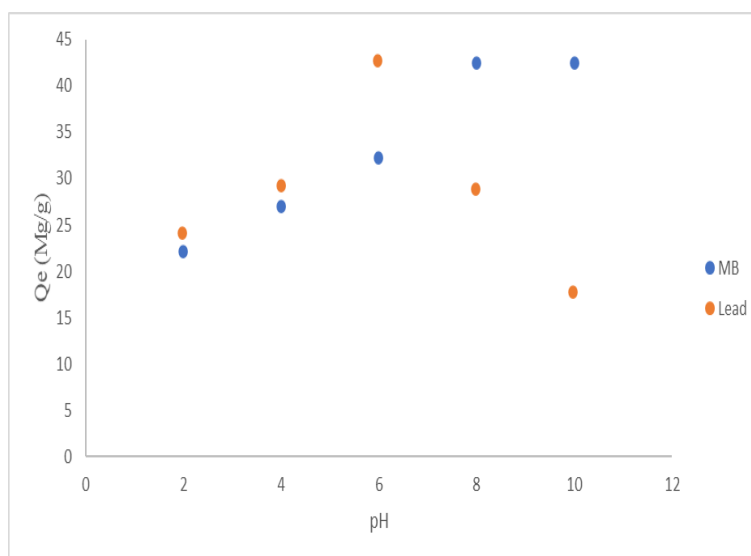


Fig 7.3: Qe vs pH

In Fig 7.3 the trend of adsorption capacity vs pH has been shown. It can be inferred from the mentioned Figure that at pH 2 the lowest adsorption is observed. It could be due to the competitive adsorption in the acidic medium. The optimum pH for Pb(II) is at 6 and for the dye it is at 8. This could be due to the fact that at in basic medium Pb(II) ion tends to precipitate and for the dye neutral to mild basic conditions are favourable because of less ionization.

## 2. Adsorbent dosage:

The adsorption capacities for both Pb(II) and MB increases when the amount of nano-biosorbent is decreased. Adsorption capacities increases with the increased amount of containments(Pb and MB) available to be adsorbed per unit mass of nano-biosorbent. Maximum adsorption capacities are 87.50 mg/g for Pb(II) and 76.25 mg/g for MB with DgPmPDA@GO adsorbent dosage of 20 mg. When dosage of DgPmPDA@GO adsorbent is 120 mg the percentage removal for both Pb(II) and MB reach to >98%. Fig 7.4 shows the trend between the adsorption capacity and the adsorption capacity. It can be observed from Fig 7.4 that as the amount of biosorbent is decreased the adsorption capacity increases. So it can be inferred that it follows an inverse relation.

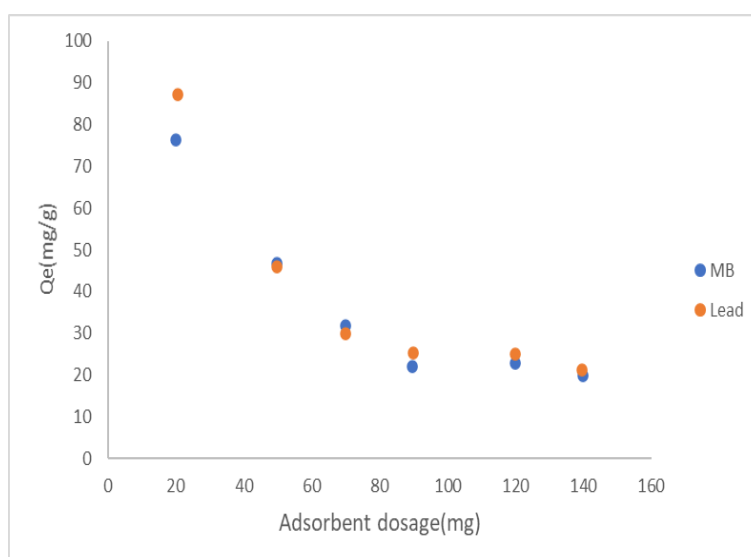


Fig 7.4: Qe vs Adsorbent Dosage

### 3. Contact Time:

Initially as adsorption proceeds, free binding sites becomes lower which results in decrease in adsorption rate and finally adsorption capacity was saturated. Adsorption capacities for Pb(II) and MB dye increases within 30 min and reached equilibrium in 120 min. After equilibrium time there is no significant changes in adsorption capacity.

It can be inferred from the Fig 7.5 that rise in adsorption capacities are seen upto first 30 mins of the process and then the process tend towards achieving equilibrium and after 120 mins no significant changes are observed.

This shows that equilibrium is achieved after 120 mins and the system becomes saturated.

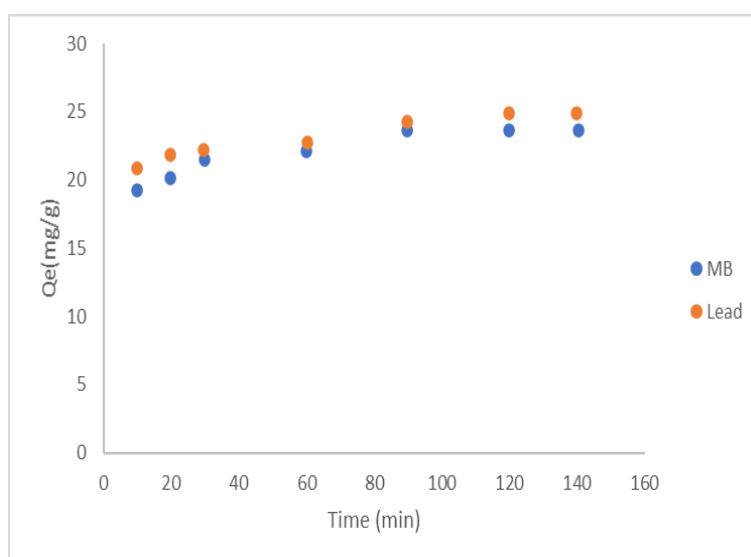


Fig 7.5: Qe vs Contact Time

#### 4. Initial Pb(II) and MB concentration:

Initial heavy metal ion and dye concentration is the main driving force for mass transfer from solution to the adsorbent. Thus, increase in initial concentration of heavy metal ion and dye indicates stronger interactions between metal ion or dye and accessible sites on the adsorbent surface. Adsorption capacities for both Pb(II) and MB dye increase with the initial pollutant concentration in range of 20 to 150 mg/L. Fig 7.6 shows the trend between the adsorption capacity and initial pollutant concentration. This can be observed from the Fig 7.5 that it follows a proportional relation and for the dye it is nearly linear. The results can be explained using the concept of mass transfer. As the driving force for the mass transfer increase the mass transfer rate or mass flux increases.

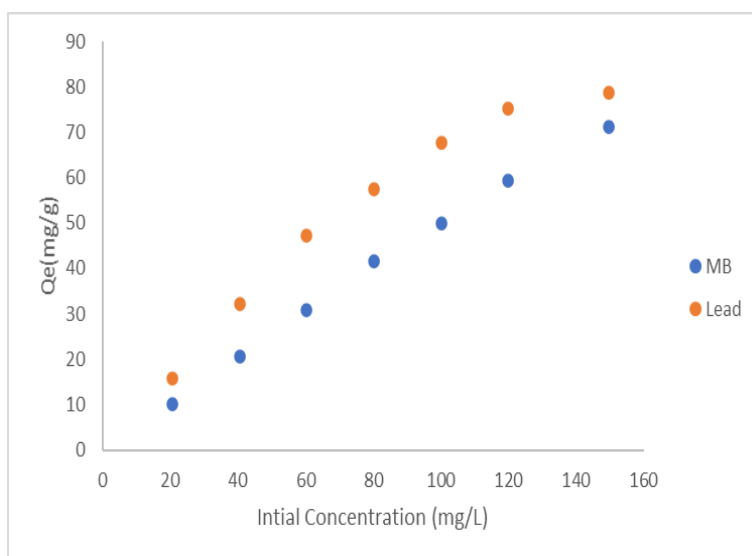


Fig7.6: Qe vs Initial concentration

#### 5. Temperature:

Dependency of temp. on adsorption process is related with thermodynamic parameters such as  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$ .

Values of these parameters can be calculated from following equations

$$K_d = q_e/c_e \dots (7.1)$$

$$\Delta G^\circ = -RT \ln K_d \dots (7.2)$$

$$\ln K_d = (\Delta S^\circ/R) - (\Delta H^\circ/RT) \dots (7.3)$$

Here,  $K_d$  – Distribution coefficient (ml/g)

R- universal gas constant (8.314 J/mol K)

T- Absolute Temperature (K)

$\Delta H^\circ$ -Enthalpy(J/mol) and  $\Delta S^\circ$ - Entropy (J/mol K)

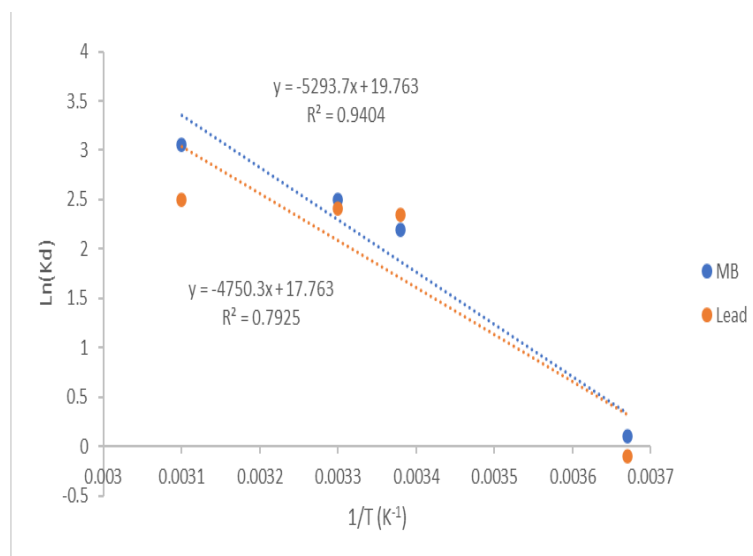


Fig7.7:  $\ln(K_d)$  vs  $1/T$

The value of  $\Delta G^\circ$  comes negative for both Pb(II) and MB dye indicates adsorption process is thermodynamically spontaneous. Absolute value of  $\Delta G^\circ$  increases with the increase in temperature which indicates that adsorption process is more favorable at high temperature.

Positive value of  $\Delta H^\circ$  indicates adsorption process is endothermic in nature and positive value of  $\Delta S^\circ$  indicates increase in randomness at adsorbent and adsorbent interface, revealing good affinity of nano-biosorbent towards MB dye and Pb(II).

## 7.5 Regeneration and reusability of a dextrin-based nano-bio-sorbent grafted with poly m-phenylenediamine

### 7.5.1 Analysis of regeneration

After sorption, the nano-bio-sorbent are going to be introduced to associate HCl resolution with varied pH values and left to desorb at temperature.

HCL is an eluent that aids in the release of metal ions from the adsorbent's binding sites. An appropriate eluent should neither harm or alter the biosorbents structure, be environmentally friendly, inexpensive, have a high affinity for the adsorbate, and be easy to separate from the adsorbate.

When the pH level is lower, It can be seen that the desorption rate increases as the HCl concentration rises, but then plateaus at 0.2 M HCl.

Desorption can be done in a batch or in a column, however desorption is easier in a packed column setup. When the sorption process is carried out in a column, it is preferable to carry out the desorption process in the same column. When the sorption process becomes saturated, for example, switching to desorption by letting the eluent to flow through the column is preferable. It's critical to keep a close eye on the procedure to avoid overstretching the bio-sorbent; however, this is dependent on the strength of bio-sorbent.

The nano-bio-sorbent was separated and distilled water was used to wash it.

The reusability of nano-bio-sorbent was tested using a series of adsorption-desorption cycles in HCl solution.

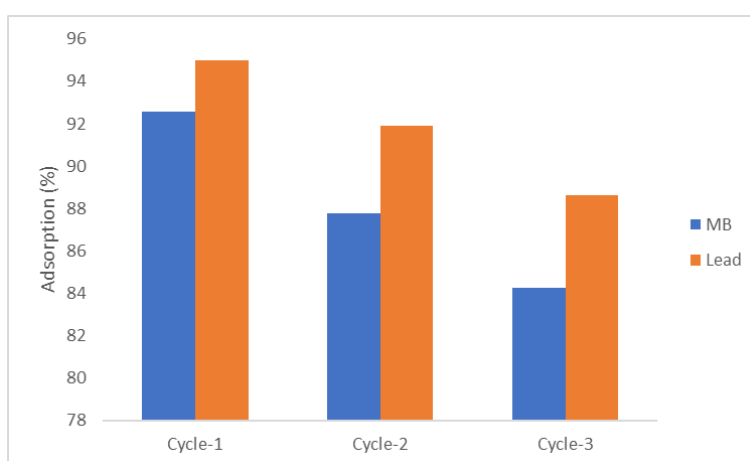


Fig.7.8: Adsorption % (Regeneration and reusability)

**The desorption percentage  $D\% = \frac{A}{B} * 100$ .....(7.4)**

where A- is that the quantity of pollutants desorbed to the extraction medium (mg) and B is that the quantity of pollutants adsorbate on the nano-bio-sorbent (mg).

Adsorption–desorption tests for Pb(II) and MB complexes were performed in a highly acidic medium (pH<2) to evaluate desorption and reusability of the DgPmPDA@GO nanobiosorbent. Batch desorption investigations were carried out at ambient temperature under acidic conditions (HCl, 0.1 M), and the desorption efficiencies were then compared.

After three cycles, adsorption decreased by 3.5 percent for Pb(II) and 4.25 percent for MB, while desorption decreased by 5% for Pb(II) and 6.25 percent for MB. The adsorption ability of the DgPmPDA@GO nano-bio-sorbent was almost completely maintained after three cycles, according to these findings. It can be concluded that the DgPmPDA@GO nano-bio-sorbent is an excellent adsorbent that can be used for Pb(II) and MB removal and recovery without sacrificing adsorptive performance significantly.

The Pb(II) and MB adsorption onto the DgPmPDA@GO nano-bio-sorbent depend on the pH of the solution, adsorbent dosage, contact time, initial concentrations of Pb(II) and MB, and temperature. The optimum pH values for Pb(II) and MB adsorption were 6 and 8

All these results are cited from the paper “ Development of effective nano-biosorbent based on poly m-phenylenediamine grafted dextrin for removal of Pb (II) and methylene blue from water”[10].

## 7.6 Factors Affecting desorption of Pb and MB dye

### 7.6.1 Effect of the type of desorbing Agent

It is critical to choose a suitable desorption solvent in this process to achieve high removal efficiency. The target analytes were eluted with Tap Water, De-ionized water, HCl, H<sub>2</sub>SO<sub>4</sub>, and NaOH as desorption solvents (1 mL each time, washed twice). Shaking for 30 minutes at ambient temperature resulted in desorption. In comparison to Tap Water, De-ionized water, HCl, H<sub>2</sub>SO<sub>4</sub>, and NaOH the experimental findings showed that HCl had the best desorption ability (Figure 7.9) As a result, HCl was chosen as the desorption solvent.

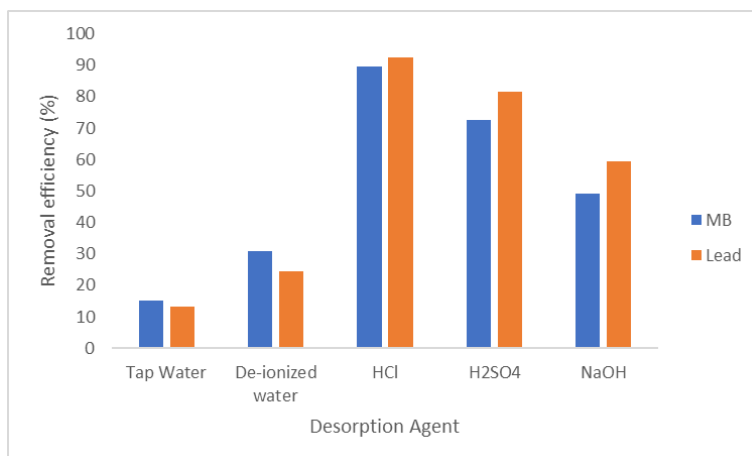


Fig.7.9: Removal efficiency affected by different desorption agents

### 7.6.2 Desorption solvent volume

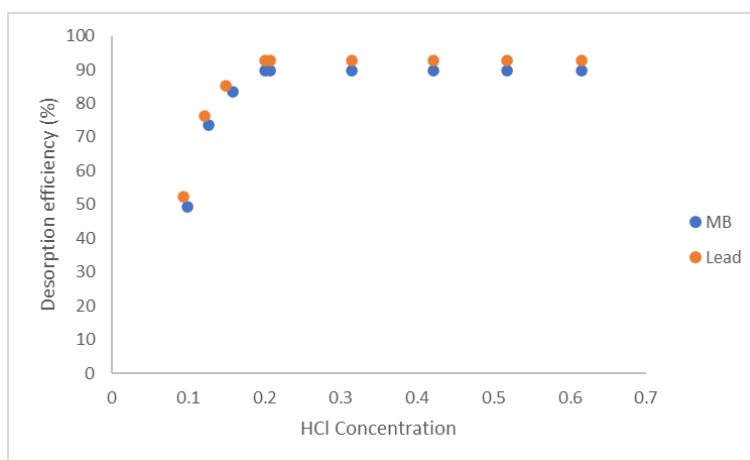


Fig.7.10: Desorption efficiency based on HCl concentration

The desorption solvent Concentration was also tuned after the desorption and sample solvents were chosen; the results are shown in Figure.7.10 , 0.2 M of HCl was sufficient to achieve full analyte desorption. When the pH level is lower, It can be seen that the desorption rate increases as the HCl concentration rises, but then plateaus at 0.2 M HCl

### 7.6.3 No. of Cycle

Adsorption–desorption tests for Pb(II) and MB complexes were performed in a highly acidic medium ( $\text{pH} < 2$ ) to evaluate desorption and reusability of the DgPmPDA@GO nanobiosorbent. Batch desorption investigations were carried out at ambient temperature under acidic conditions (HCl, 0.2 M), and the desorption efficiencies were then compared. After three cycles, adsorption decreased by 3.5 percent for Pb(II) and 4.25 percent for MB, while desorption decreased by 7.42% for Pb(II) and 7.20 percent for MB

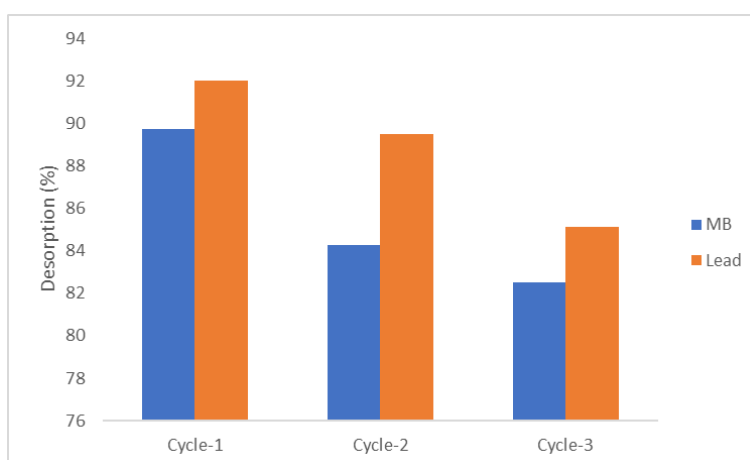


Fig.7.11: Desorption percentages of Pb(II) and MB during 3 cycles

## **7.7 Disposal methods for Heavy metal and Dye**

After the process of biosorption the adsorbed material i.e lead and methylene blue dye is considered as hazardous or toxic waste and is disposed of accordingly. They falls under the K-list which basically includes the hazardous wastes created as a result of specific industrial operations are classified as source-specific wastes. K-listed hazardous waste must be classified into one of the 13 categories listed below[45].

- Preservation of wood
- Manufacturing of organic compounds
- Manufacturing pesticides
- Refining of petroleum
- Manufacturing of veterinary medicines
- Manufacturing of inorganic pigments
- Manufacturing of inorganic chemicals
- Manufacturing of explosives
- Production of iron and steel
- Production of primary aluminium
- Ink formulation
- Secondary lead processing
- Coking (processing of coal to produce coke)

Also, these adsorbates falls into the category of chemical hazardous wastes.

This category includes Synthetic organics, inorganic metals, salts, acids and bases, and flammables and explosives are the five categories of hazardous chemical waste. Some of the substances are dangerous because they put people's lives at danger.



### 7.7.1 Disposal Methods:

Disposal of these hazardous residues can be done by the following methods:

#### Secure Landfilling

Some hazardous wastes were disposed of in conventional landfills, resulting in large amounts of dangerous materials seeping into the ground. These pollutants eventually find their way into natural water systems. As a result, a landfill must have a barrier for collecting hazardous substances that may remain in the discarded waste in order to prevent chemicals from infiltrating the soil. Hazardous wastes are now stabilised and solidified before being disposed of, and the process varies depending on the type of hazardous waste. A landfill is a type of waste disposal facility where hazardous material is buried and kept in the ground. Figure shows an example of a recommended design. Before being disposed of, the wastes are placed in sealed barrels. The hazardous-waste landfill features two impermeable liners as well as leachate collection systems. A network of pipes is put above each liner in a double leachate collection system. The upper layer prevents leachate from accumulating in the fill, while the lower layer serves as a backup. The collected leachate is taken to a treatment plant for further processing. To reduce the amount of leachate in the fill and minimise the risk of environmental damage, an impermeable top or cover is placed over the finished landfill.

The following is a list of the key components found in landfill leachate. Calcium, magnesium, iron, sodium, ammonia, carbonate, sulphate, and chloride are major elements and ions.

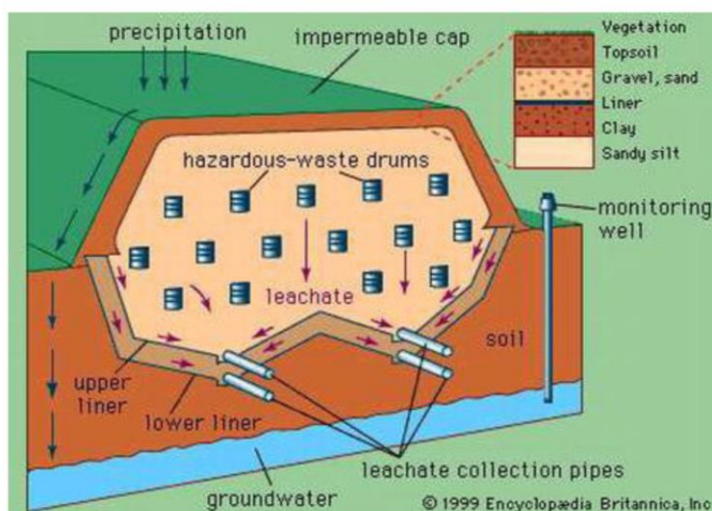


Fig:7.12: Secure Landfill[45]

Manganese, chromium, nickel, lead, and calcium are all trace metals. Leachate is created by hazardous waste, primarily from industries. In comparison to other components of leachate, heavy metals concentration is of greater importance[45].

### **Disposal in deep wells**

Injection of liquid industrial waste into a deep well, as depicted in Figure, is another option for disposal. Deep well injection is a method of disposing of liquid waste. This option involves injecting treated or untreated liquid waste into geologic formations that will not allow contaminants to migrate into possible drinkable water aquifers. High pressures are used to drive the liquid into the pores and crevices of the rock. The chosen rock unit is porous and permeable (often sandstone or cracked limestone) and must be separated from above and below by low permeability layers (for example, shale). Although deep-well injection is cost-effective and requires little or no waste processing, it raises the risk of hazardous material spilling and eventually damaging subsurface water resources[45].

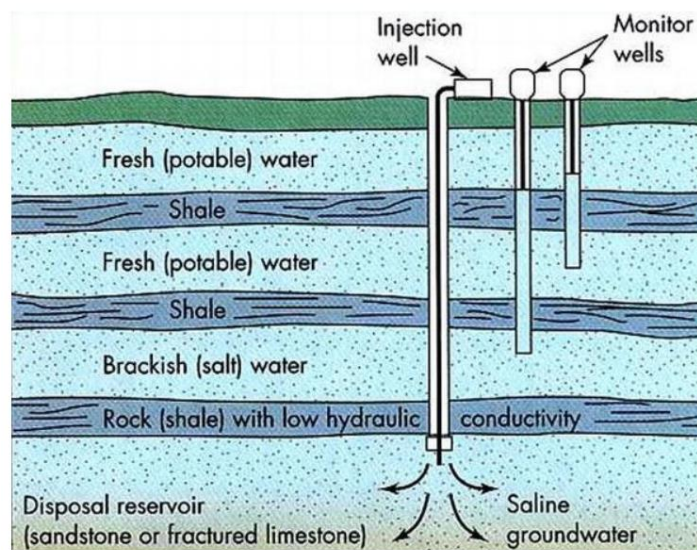


Fig.7.13: Disposal in deep wells[45]

### **Disposal of bedrock**

The majority of solid hazardous waste is disposed of in bedrock, and a range of bedrock types are being examined as host rocks. It is based on the multiple barrier (or multi barrier) idea, which involves encircling solid hazardous waste with a variety of materials to prevent waste leakage or groundwater invasion. The nature of the host rock, as well as some possible downsides, are key concerns. Stainless steel canisters, or spent fuel rods encased in corrosion-resistant metals like copper or stainless steel and buried deep below in stable rock structures. Granite, volcanic tuff, salt, thick basalts like the Columbia River plateau basalt, and shale are

all suitable geological formations[45].

## **7.8 Discussion**

Absorption mechanism of both Pb(II) and methylene blue on nanobiosorbent is demonstrated by FT-IR spectra of DgPmPDA@GO Nano biosorbent before and after adsorption. The overall adsorption is physical adsorption and hence it is controlled by electrostatic interaction between the biosorbent and metal ion. Electrostatic attraction and chelation are responsible for adsorption mechanism. The spikes observed in case of methylene blue indicates that electrostatic interaction and hydrogen bonding interaction between dye molecules and amino, hydroxyl groups of DgPmPDA@GO nanobiosorbent are responsible for adsorption mechanism. For Pb(II) the pH is to be maintained at 6 for better adsorption and adsorption of methylene blue occurs best at pH of 8. After increase in pH beyond this level, there will be no significant increase in adsorption capacity. Adsorption capacity increases with increased amount of contaminants which are available to be adsorbed per unit mass of the nanobiosorbent. In first 30 minutes there is sudden increase in absorption capacities and by 120 minutes equilibrium state is achieved. The concentration difference is the driving force and therefore increase in initial concentration of heavy metal and dye indicates the stronger interaction between the metal Ion or dye molecules and the active site of the adsorbent.

## Chapter 8

### Conclusions

In this report we study about different industries where dyes and heavy metals are being used. Textile industries uses dyes in a significant amount and waste generated from textile industries contain high amount of dyes and heavy metals. Methylene blue is one of most abundantly used dye and lead is most commonly found heavy metal ion in the wastewater coming from textile industries. Biosorption is a popular, cost effective and highly efficient process in removal of heavy metals and dyes by using sorption mechanism. Biosorbents are environment friendly adsorbents and when these biosorbents are used in nano range then their adsorption surface increases and enhances the process efficiency. Poly m-phenylenediamine grafted dextrin and graphene oxide based nanobiosorbent is used for removing Lead and Methylene blue dye from wastewater. Adsorption of lead and methylene blue dye on nanobiosorbent (DgPmPDA@GO) depends on different factors like pH of the solution, dosage of adsorbent, contact time, temperature and initial concentration of Lead and MB dye. Different isotherms like has been studied for adsorption, the results which we have drawn were based on the data sets to which the isotherm followed by MB and Pb(II) was Langmuir model, hence the suggested mechanism was monolayer adsorption process taking place at similar and analogous definite localised spots. The Langmuir isotherm model implies that adsorption is homogeneous, with each molecule having the same sorption activation energy and constant enthalpies. For the metal ion it is observed that Pseudo First order model is followed which suggests that rate of reaction is directly proportional to the concentration of the Pb(II) ion where as for the dye Pseudo Second Order model was followed and hence the rate was directly proportional to the square of the concentration of the MB dye. The rate limiting step in this model is surface adsorption, which comprises chemisorption, in which adsorbate extraction from a solution is owing to physicochemical existing between the two phases. Complex Formation, Ion Exchange, Electrostatic Attraction or Coordination and Chelation were possible metal ion adsorption mechanisms onto biosorbents. Electrostatic Attraction, Hydrogen bonding and  $\pi$ - $\pi$  interactions were possible metal ion adsorption mechanisms onto biosorbents.  $6 < \text{pH} < 8$  is the range of pH for good adsorption of Lead ion and Methylene Blue. Maximum adsorption capacities are 87.50 mg/g for Pb(II) and 76.25 mg/g for MB with DgPmPDA@GO adsorbent dosage of 20 mg. When dosage of DgPmPDA@GO adsorbent is 120 mg the percentage removal for both Pb(II) and MB reach to >98%. Adsorption capacities for Pb(II) and MB dye increases within 30 min and reached

equilibrium in 120 min. After equilibrium time there is no significant changes in adsorption capacity. This shows that equilibrium is achieved after 120 mins and the system becomes saturated after this there is no significant change. Adsorption capacities for both Pb(II) and MB dye increase with the initial pollutant concentration in range of 20 to 150 mg/L, this increase in initial concentration of heavy metal ion and dye indicates stronger interactions between metal ion or dye and accessible sites on the adsorbent surface. Absolute value of  $\Delta G^\circ$  increases with the increase in temperature which indicates that adsorption process is more favourable at high temperature. Nanobiosorbent is regenerated after treating with HCl. After three cycles, adsorption decreased by 3.5 percent for Pb(II) and 4.25 percent for MB, while desorption decreased by 5% for Pb(II) and 6.25 percent for MB. The adsorption ability of the DgPmPDA@GO nano-bio-sorbent was almost completely maintained after three cycles. Type of Desorbing Agent, Desorption Solvent Volume and number of cycles are different factors affecting the desorption of Pb and MB dye. Landfill, disposal in deep wells, disposal of bedrock are different methods for disposal of Pb ion and MB dye after the treatment. The DgPmPDA@GO nanobiosorbent could be a suitable biosorbent for removal of Heavy Metals and Dyes in wastewater.

## Appendix

### Code for Kinetics of MB dye ion

```
% "Kinetics of MB dye"
```

```
Ca0=1;
```

```
Cb0=5;
```

```
Cc0=10;
```

```
Cd0=15;
```

```
Ce0=20;
```

```
Cf0=25;
```

```
Cg0=30;
```

```
% initial values
```

```
C0=[Ca0,Cb0,Cc0,Cd0,Ce0,Cf0,Cg0];
```

```
tspan= linspace(0,1000,100);
```

```
[t,C]=ode45(@myodefun,tspan,C0);%function call
```

```
% plotting results
```

```
Figure;
```

```
plot(t,C(:,1),"r",t,C(:,2),"b",t,C(:,3),"k",t,C(:,4),t,C(:,5),t,C(:,6),t,C(:,7));
```

```
xlabel("Time (in min)");
```

```
ylabel("Concentration (in mg/l)");
```

```
axis([0 200 0 30])
```

```
title("Kinetics of MB dye for different initial concentration");
```

```
legend("1 mg/l", "5 mg/l", "10 mg/l", "15 mg/l", "20 mg/l", "25 mg/l", "30 mg/l");
```

```
display(C);
```

```
%function
```

```
function dCdt= myodefun(t,C)
```

```
Ca=C(1);
```

```
Cb=C(2);
```

```
Cc=C(3);
```

```
Cd=C(4);
```

```
Ce=C(5);
```

```
Cf=C(6);
```

```
Cg=C(7);
```

```
K1= 0.011;
```

```

dCadtd= -K1*Ca*Ca;
dCbdt= -K1*Cb*Cb;
dCcddt= -K1*Cc*Cc;
dCdtdt= -K1*Cd*Cd;
dCedt= -K1*Ce*Ce;
dCfdt= -K1*Cf*Cf;
dCgdt= -K1*Cg*Cg;
dCdt=[dCadtd;dCbdt;dCcddt;dCdtdt;dCedt;dCfdt;dCgdt];
end

```

### Code for Kinetics of Pb(II) metal ion

```

% "Kinetics of Pb(II) ion"
Ca0=1;
Cb0=5;
Cc0=10;
Cd0=15;
Ce0=20;
Cf0=25;
Cg0=30;
% initial values
C0=[Ca0,Cb0,Cc0,Cd0,Ce0,Cf0,Cg0];
tspan= linspace(0,500,100);
[t,C]=ode45(@myodefun,tspan,C0);%function call
% plotting results
plot(t,C(:,1),"r",t,C(:,2),"b",t,C(:,3),"k",t,C(:,4),t,C(:,5),t,C(:,6),t,C(:,7));
xlabel("Time (in min)");
ylabel("Concentration (in mg/l)");
axis([0 500 0 30] )
title("Kinetics of Pb(II) ion for different initial concentration");
legend("1 mg/l", "5 mg/l", "10 mg/l", "15 mg/l", "20 mg/l","25 mg/l","30 mg/l");
display(C);
%function
function dCdt= myodefun(t,C)

```

```
Ca=C(1);
Cb=C(2);
Cc=C(3);
Cd=C(4);
Ce=C(5);
Cf=C(6);
Cg=C(7);
K1= 0.011;
dCadtdt= -K1*Ca;
dCbdt= -K1*Cb;
dCcddt= -K1*Cc;
dCdtdt= -K1*Cd;
dCedtdt= -K1*Ce;
dCfdtdt= -K1*Cf;
dCgdt= -K1*Cg;
dCdt=[dCadtdt;dCbdt;dCcddt;dCdtdt;dCedtdt;dCfdtdt;dCgdt];
end
```



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