

Water is a crucial and necessary chemical for all living organisms to survive. Water pollution is one of the most worrying environmental problems of today's world. The natural water resources have been polluted by both organic and inorganic pollutants as a result of extensive urbanization and industrialization. The environment, animals, and human beings are all greatly harmed by these pollutants, which consist of heavy metals and dyes [1]. Heavy metals cannot be degraded or destroyed. Heavy metals are known to be carcinogenic and are not biodegradable, causing them to accumulate in living things. Lead, cadmium, cobalt, nickel, copper and other toxic heavy metals are of special concern when treating industrial wastewaters. These heavy metals are frequently released in the aquatic systems due to effluents of following industries such as refineries, battery manufacturing, coal-fired power plants, mining operations, tanneries, phosphate fertilizers, pigments, metal smelters, paints, effluents from plastics, microelectronics, wood preservatives, brass and bronze manufacturing, steel production, electroplating, pharmaceuticals, galvanizing, paints, pigments, insecticides, and cosmetics [2, 3].

Dyes is released into waste streams, it becomes inert and difficult for it to biodegrade since it is an aromatic, colored organic substance with a synthetic origin and complicated, impatient molecular structures. Numerous organic dyes have been released into natural water resources or wastewater treatment systems by industries like textile, paper, and pulp manufacturing, agriculture, food technology, light-harvesting arrays, photo-electrochemical cells, hair coloring, dye and dye intermediates, pharmaceutical, etc. The textile industry is one of the biggest water consumers and dye pollutants among all industrial sectors. Accordingly, the environment and human health may suffer ongoing damage from these heavy metals and organic dyes. The ingestion of heavy metals and dyes can lead to multiple illnesses such as high blood pressure, anemia, nephritis, cancer, liver and kidney damage, central nervous system disorders, anemia, vomiting, anatomical defects, brain diseases, and lung cancer [4,5].

Pollutants are removed from waste water using a variety of techniques, including adsorption, coagulation, advanced oxidation, membrane separation, foam flotation, precipitation, ozonation, ion exchange, filtering, solvent extraction, electrolysis, chemical oxidation, liquid–liquid extraction, [6,7] etc. Due to its many advantages over other techniques, including its straightforward design, simple operation, high selectivity, versatility, non-toxicity, high separation efficiencies and sorption capacity, low temperature processing so adsorption and ion exchange are regarded as the most successful approaches in the field of removal of heavy metal and dyes. This is especially the case for waste water treatment processes. An extensive literature is available on types of adsorbents (activated carbons, surface modified zeolites, graphene oxide and its composites, biosorbents, tetravalent metal phosphonate, and chelating materials) utilized for the removal of metal ions and dyes [8,9]. Ion-exchange resins are extensively utilized for pre-concentrating and eliminating heavy metal ions from waste water. They have demonstrated to be extremely effective in metal recovery and separation. Selectivity and efficiency, however, are the most significant challenges in this field of study. Ion-exchange resins must have their surfaces modified in order to improve efficiency and increase selectivity toward metallic ions. The exchange/adsorption property of the adsorbents depends upon the functional groups present on their surfaces. Functional groups such as carboxylic, phenolic, amide and amine provide binding sites for metal ions. However, polymeric resin has not been modified with the point of view of insertion of chelating capacity in the resin, which can potentially be used for binding/exchange of metal ions. Mixed materials (organic/inorganic) are quite popular right now because they can create new solid-state structures and materials with novel composite qualities by combining the characteristics of their organic (dyes) and inorganic (metal ions) components. Metal phosphonate is produced when tetravalent metals are treated with phosphonic acid, which is the tetrahedral component of phosphoric acid, $PO(OH_3)$, where H or OH are substituted by R (R = alkyl/aryl containing ionogenic group) [10]. The prospective use of these materials in materials chemistry, as ion exchangers, and as adsorbents make them fascinating.

❖ The contents of the present thesis are summarized into seven chapters;

- 1. Introduction*
- 2. Materials, Methods and Characterizations*
- 3. Removal of Transition and Heavy Metal Ions by Using Modified Cationic Resin (MCR) as an Adsorbent*
- 4. Adsorption of Azo Dyes by Using Amberlite IRA-400(Cl⁻) Resin*
- 5. Removal of Transition and Heavy Metal Ions by Using Cerium Amino Tris Methylene Phosphonic Acid (Ce-ATMP)*
- 6. Adsorption of Cationic Dyes by Using Tin Amino Tris Methylene Phosphonic Acid (Sn-ATMP)*
- 7. Overall Conclusion*

Chapter 1: INTRODUCTION

- This chapter presents an extensive overview of the most important and relevant research findings in the area of study.

Chapter 2: MATERIALS, METHODS, AND CHARACTERIZATIONS

- Amberlite IRA-400(Cl⁻) resin (purchased from Merck India), disodium salt of ethylene diamine tetra acetic acid (from BIRCH), and all metal salts indicators (from S d fine-chem. limited and Loba-chem. limited). Ceric sulphate and Stannic chloride were purchased from Loba Chemicals, India. Hydro-Chem India Pvt. Ltd. furnished ATMP (amino tris-(methylene phosphonic acid), Glassware's were washed, cleaned and rinsed with dilute hydro chloric acid, distilled water and de-ionized water (D/W), respectively. methylene blue, malachite green, crystal violet and rhodamine B were purchased from Loba Chem. Pvt. Ltd. India. All reagents used in the present work were of analytical grade and solutions were prepared in de-ionized water. These all materials are in the present thesis have been shown in this chapter. This chapter will demonstrate the methods and many characterizations (FTIR, UV, XRD, SEM, EDS, TGA) employed in the

current work along with the criteria for data evaluation. Material structures of the studied are shown in Figure 1.

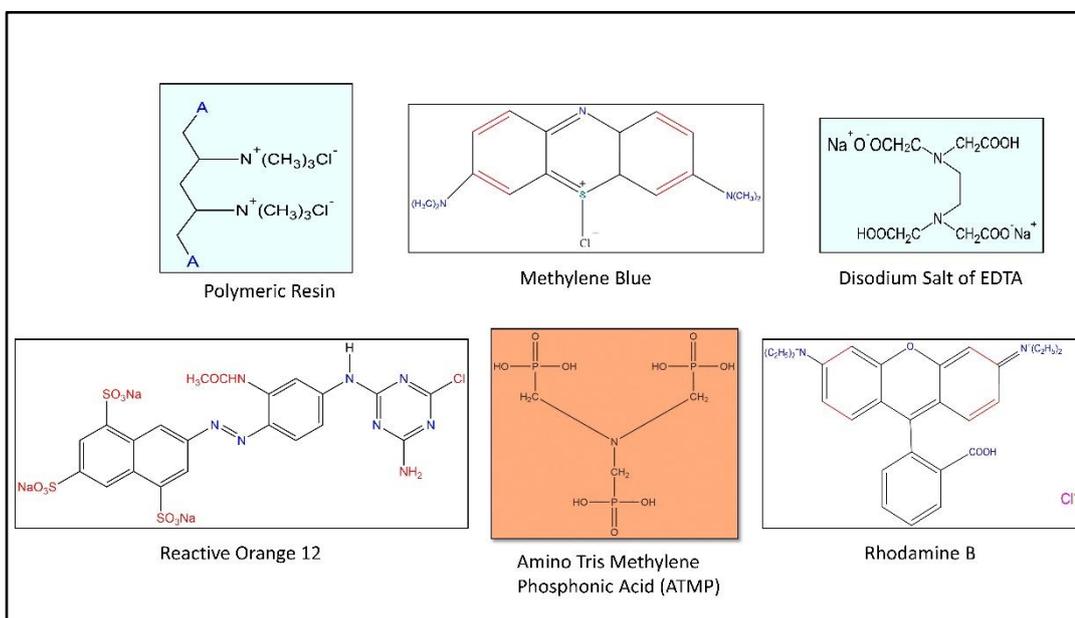


Figure 1: Structure of polymeric resin, Disodium salt of EDTA, Amino tris methylene phosphonic acid, Methylene blue, Rhodamine B, and Reactive orange 12.

Chapter 3: REMOVAL OF TRANSITION AND HEAVY METAL IONS BY USING MODIFIED CATIONIC RESIN (MCR) AS AN ADSORBENT

- In this chapter, modification inserts chelating characteristics in the above polymeric resin (modified chelating resin, MCR), which may be used to bind metal ions from external matrices. K_d values, evaluated for the transition and heavy metal ions towards MCR, have been presented in Table 1. occupancy of sites causes near saturation in ~ 120 min. K_d data have been analysed using Langmuir isotherm model at (299 K, 309 K, 319 K, 329 K). Thermodynamic parameters are used to support the nature of the adsorption process and various kinetics model have been computed. The % metal eluted in all cases is in the range of 60%–96%. A few of the resin containing metal ions outcomes are displayed in Figure 2, 3 and 4.

Table 1: Distribution coefficient (K_d) values (mL/g) with varying transition and heavy metal ions for MCR								
Metal ions	Ionic radii (\AA)	Distribution coefficient (K_d) values (mL/g) at different concentrations (M)						
		0.001M	0.002M	0.003M	0.004M	0.005M	0.006M	0.007M
Co^{2+}	0.72	164.7	212	128.81	105.55	91.66	64.7	39.13
Ni^{2+}	0.72	90.47	130.76	90.47	75	44.44	34.61	23.52
Cu^{2+}	0.74	104.54	122.22	80.55	45.45	34.86	34.4	28.57
Zn^{2+}	0.74	100	135.29	66.66	52.63	49.19	40	29.71
Cd^{2+}	0.97	114.28	214.81	100	64.70	50	42.85	38.46
Hg^{2+}	1.10	73.91	103.12	73.07	55.84	47.05	33.85	21.01
Pb^{2+}	1.44	133.33	341.17	91.66	63.15	43.93	39.88	36.58

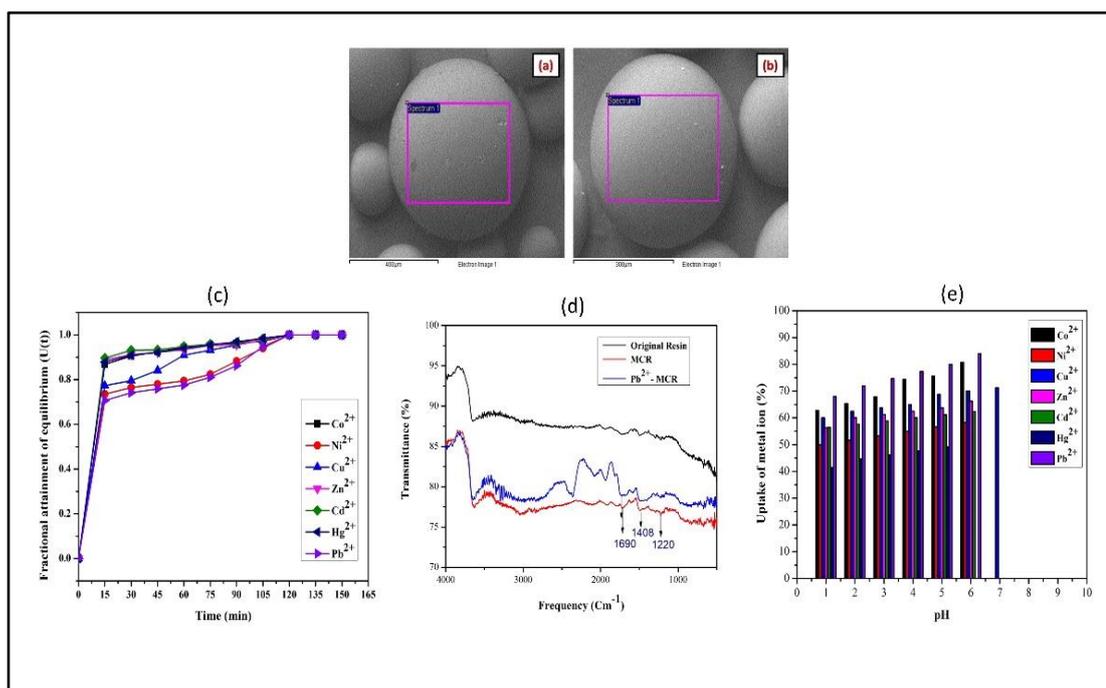


Figure 2: SEM micrographs of (a) Amberlite IRA-400(Cl^-) resin, (b) Modified cationic resin (MCR) (c) Fractional attainment of equilibrium for varying metal ions (d) FTIR of original resin, MCR and Pb^{2+} loaded resin (e) % uptake of metal ions vs. pH.

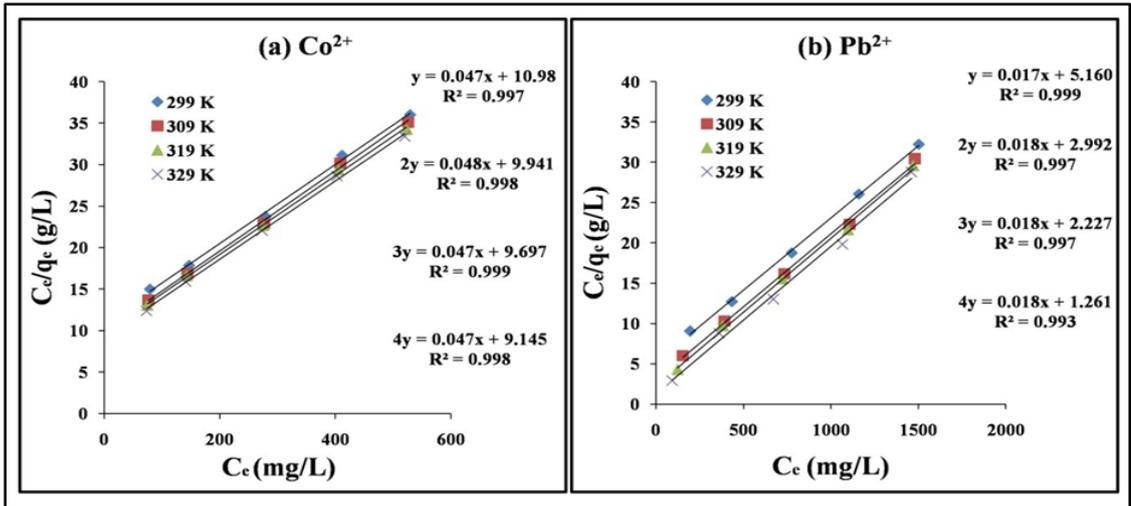


Figure 3: Langmuir adsorption isotherms of (a) Transition metal ion (Co^{2+}) and (b) Heavy metal ion (Pb^{2+}): 299 K, 309 K, 319 K and 329 K.

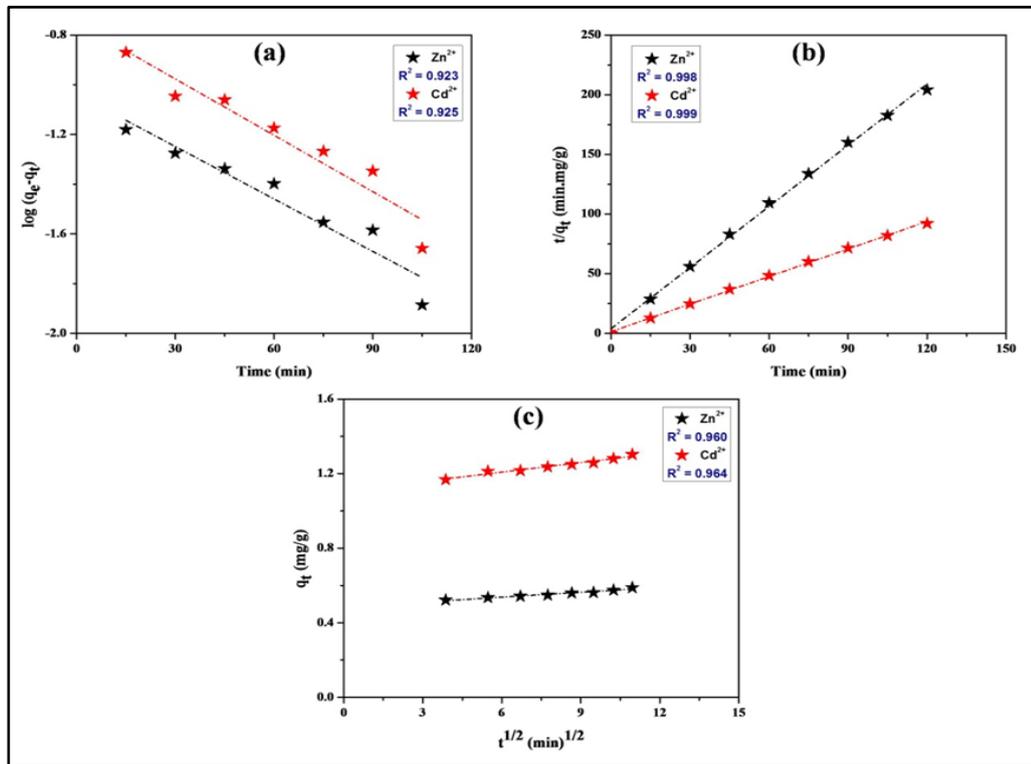


Figure 4: (a) Pseudo-first-order kinetics, (b) Pseudo-second-order kinetics, and (c) Intraparticle diffusion model for adsorption of transition metal ion (Zn^{2+}) and heavy metal ion (Cd^{2+}) on MCR.

Chapter 4: ADSORPTION OF AZO DYES BY USING AMBERLITE IRA-400(Cl⁻) RESIN

- In this chapter, Physical methods which include adsorption/ion exchange are effective for removing dyes without producing by products. Equilibrium experiments were carried out by contacting different amounts of resin particles with particular dyes solution. The focus of the present study was to assess the potentiality of this resin as low adsorbent for the removal of reactive orange 12 and acid yellow 49 from aqueous solution as an ideal alternative to the current expansive method of removing dyes from waste water. The kinetic data and equilibrium data were analyzed so that we can understand the adsorption process and different modes were applied to fit the experimental data. A few of the resin containing dyes outcomes are displayed in Figure 5.

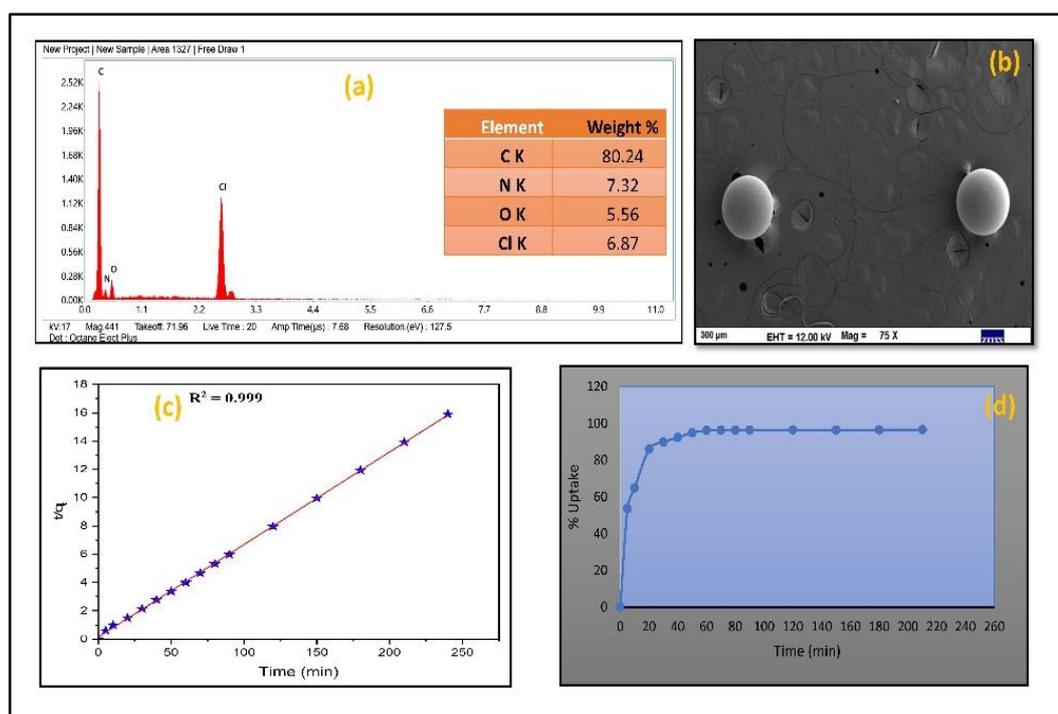


Figure 5: (a) EDS of Amberlite IRA-(400)Cl⁻ resin, (b) SEM image of Amberlite IRA-(400)Cl⁻ resin (c) Pseudo-second-order kinetics, and (d) Effect of Contact time on Amberlite IRA-(400)Cl⁻ resin.

Chapter 5: REMOVAL OF TRANSITION AND HEAVY METAL IONS BY USING CERIUM AMINO TRIS METHYLENE PHOSPHONIC ACID (Ce-ATMP)

- In this chapter, newly modified ion exchanger material of Ce-ATMP prepared by sol gel method. High K_d values for Cu^{2+} and Pb^{2+} (aqueous medium) are among Ce-ATMP's most promising attributes. K_d value rises throughout contact time (up to 60 min) and then fully sorbs on Ce-ATMP for 24 hours, at which point K_d value does not rise any further. The values of R^2 demonstrate that the Langmuir isotherms offer good fits to the experimental data. The current investigation revealed that the equilibrium constant (K) increased as the temperature rise for every metal ion evaluated, suggesting that ion exchange is the mechanism at work and that the metal ions had a strong affinity for the exchanger. As a result, it is probable that the ion exchange process can be explained by pseudo-second-order kinetics and endothermic as indicated by kinetics and thermodynamics studies. Symmetric bell-shaped curves also enable efficient separation. Some results are shown in figure 6.

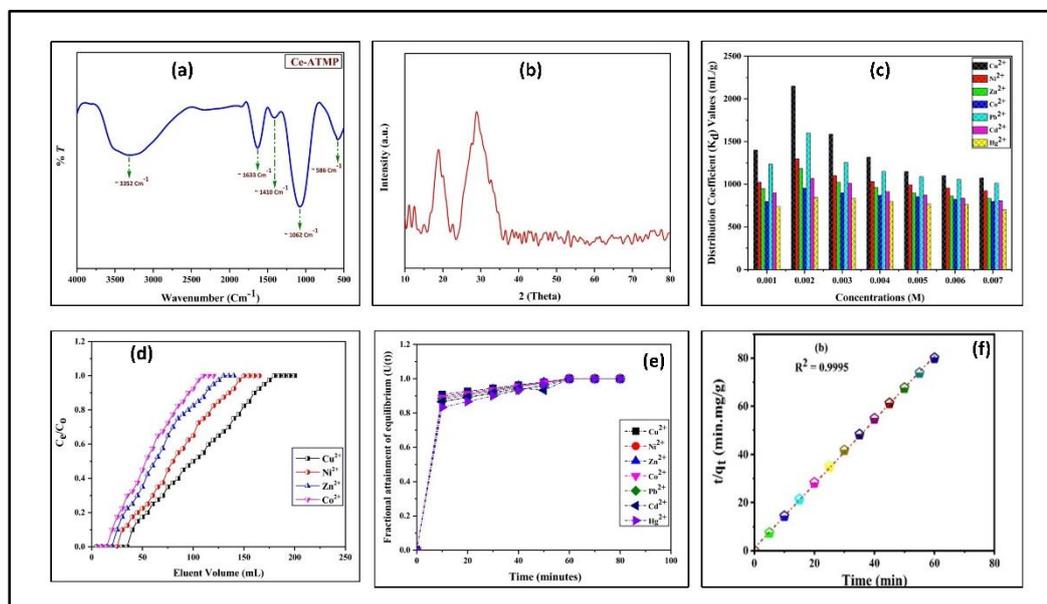


Figure 6: (a) FTIR of Ce-ATMP (b) XRD of Ce-ATMP (c) Effect of Concentration of the varying metal ions (d) BTC of transition metal ions (e) Effect of contact time of the varying metal ions (f) Pseudo-second-order kinetic model for adsorption of transition metal ion (Cu^{2+}) on Ce-ATMP.

Chapter 6: REMOVAL OF CATIONIC DYES BY USING TIN AMINO TRIS METHYLENE PHOSPHONIC ACID (Sn-ATMP)

- This chapter focus of all the adsorption parameters evaluated for the removal of cationic dyes by Sn-ATMP discussed in this study. The sorption behaviour of methylene blue, malachite green, crystal violet, rhodamine B towards Sn-ATMP has been studied at thermodynamic parameters such as ΔG° , ΔH° and ΔS° were calculated and results of kinetic studies indicated that the adsorption process followed the pseudo-second-order model, and rest of all parameters were discussed.

Chapter 7: OVERALL CONCLUSION

- The thesis end with overall conclusion of all the reported work drawn from the investigations.

❖ REFERENCES

1. Rafique, M.; Hajra, S.; Tahir, M. B.; Gillani, S. S. A.; Irshad, M. A Review on Sources of Heavy Metals, Their Toxicity and Removal Technique Using Physico-Chemical Processes from Wastewater. *Environ. Sci. Pollut. Res.* **2022**, 29 (11), 16772-16781.
2. Elbedwehy, A. M.; Abou-Elanwar, A. M.; Ezzat, A. O.; Atta, A. M. Super effective removal of toxic metals water pollutants using multi functionalized polyacrylonitrile and arabicgum grafts, *Polymers.* **2019**, 11, 1938.
3. Amiin, I. S.; Liu, X.; Pu, Z.; Li, W.; Li, Q.; Zhang, J.; Tang, H.; Zhang, H.; Mu, S. From 3D ZIF Nanocrystals to Co-N_x/C Nanorod Array Electrocatalysts for ORR, OER, and Zn-Air Batteries. *Adv. Funct. Mater.* **2018**, 28 (5), 1704638.

4. Boskabady, M.; Marefati, N.; Farkhondeh, T.; Shakeri, F.; Farshbaf, A.; Boskabady, M. H. The Effect of Environmental Lead Exposure on Human Health and the Contribution of Inflammatory Mechanisms, a Review. *Environ. Int.* **2018**, 120, 404-420.
5. Bashir, A.; Malik, L. A.; Ahad, S.; Manzoor, T.; Bhat, M. A.; Dar, G. N.; Pandith, A. H. Removal of Heavy Metal Ions from Aqueous System by Ion-Exchange and Biosorption Methods. *Environ. Chem. Lett.* **2019**, 17 (2), 729-754.
6. Parangi, T. F.; Chudasama, U. V. Synthesis, Characterization, and Proton Conduction Behavior of Thorium and Cerium Phosphonates. *ACS Omega* **2019**, 4 (2), 3716-3725.
7. Carolin, C. F.; Kumar, P. S.; Saravanan, A.; Joshiba, G. J.; Naushad, Mu. Efficient techniques for the removal of toxic heavy metals from aquatic environment: a review, *J. Environ. Chem. Eng.*, **2017**, 5, 2782-2799.
8. Shah, B.; Chudasama, U. Application of Zirconium Phosphonate - A Novel Hybrid Material as an Ion Exchanger. *Desalination Water Treat.* **2012**, 38 (1-3), 276-284.
9. Shah, B.; Chudasama, U. Kinetics, thermodynamics and metal separation studies of transition (Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+}) and heavy metal ions (Cd^{2+} , Hg^{2+} , Pb^{2+}) using novel hybrid ion exchanger-Zirconium amino tris methylene phosphonic acid, *Sep. Sci. Technol.*, **2019**, 54, 1560-1572.
10. Sinha, S.; Behera, S. S.; Das, S.; Basu, A.; Mohapatra, R. K.; Murmu, B. M.; Dhal, N. K.; Tripathy, S. K.; Parhi, P. K. Removal of congo red dye from aqueous solution using amberlite IRA-400 in batch and fixed bed reactors, *Chem. Eng. Commun.*, **2018**, 205, 2-12.

❖ List of the Research Publications

➤ Under the Thesis work

- 1) **S. N. Katariya**, S. Kumar, R. B. Yadav, Kinetics and thermodynamics of removal of metal ions using EDTA-modified cation ion exchange resin, *Desalination and Water Treatment*. **2021**, 233, 133-149.
[Doi:10.5004/dwt.2021.27537](https://doi.org/10.5004/dwt.2021.27537)
- 2) **S. N. Katariya**, T. Parangi, U. Chudusama, S. Kumar, R. B. Yadav, Synthesis, Characterization and Ion Exchange Behavior of Cerium Amino Tris-(Methylene Phosphonic Acid) (*Under Review*)

❖ List of the Papers presented in the Conferences/Seminars

- 1) Removal of Zn (II) ion by using modified chelating ion exchanger.
S. N. Katariya, R. B. Yadav, at an International Conference (IWA-RMTC 2018), Applied Chemistry Department, Faculty of Technology and Engineering, The Maharaja Sayajirao University of Baroda, Vadodara-390001, India, (10th - 12th December, 2018) (**Poster**).
- 2) Physico-chemical studies on the removal of cadmium and lead ion by using polymeric cation ion exchange resin.
S. N. Katariya, S. Kumar, R. B. Yadav, at an International Conference of Second DAE Symposium on Current Trends in Analytical Chemistry (CTAC-2021), Bhabha Atomic Research Center Trombay, Mumbai-400084, (20th - 23rd October, 2021) (**Poster**).
- 3) Removal of copper metal ion by using cerium amino tris methylene phosphonic acid.
S. N. Katariya, S. Kumar, R. B. Yadav, at an International Seminar on Advanced Materials and Applications (ISAMA 2022), Applied Physics Department and Applied Chemistry Department, Faculty of Technology and Engineering, The Maharaja Sayajirao University of Baroda, Vadodara-390001, India, (18th July, 2022) (**Poster**).

- 4) Kinetics, thermodynamics and removal of Cu (II) ion using modified resin.
S. N. Katariva, S. Kumar, R. B. Yadav, at National Conference on 8th all Gujarat Research Scholars' Meet (AGRSM-VIII), Indian Chemical Society, Vadodara Chapter and Department of Chemistry, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara-390002, India, (26th February, 2023) (**Oral**).

❖ **List of the Attended in the Conferences/Seminars/ Workshops**

- 1) National Webinar on "*Energy and Environment*" Organized by Applied Physics Department, Faculty of Technology and Engineering, The Maharaja Sayajirao University of Baroda, Vadodara-390001, India, from 9th & 10th July, 2020.
- 2) Virtual Faculty Development Programme on "*Analytical Chemistry*" Organized by Department of P. G. Studies and Research in Chemistry and Pharmacy, Rani Durgavati University, Jabalpur (M.P.), India, from 14th - 16th July, 2020.
- 3) International Webinar on "*Pivotal role of Chemistry/Chemical Engineering in Present Scenario - 2020*" Organized by Department of Humanities and Sciences, VNRVJIET, Hyderabad-500090, from 20th - 22nd July, 2020.
- 4) National Webinar on "*Chemical Catastrophes: Management and Planning*" Organized by Department of Chemistry, and Pharmaceutical Chemistry, Govt. Girls' P.G. College, Ujjain in Collaboration with Disaster Management Institute, Bhopal, on 27th July, 2020.
- 5) National Webinar on "*Recent Advances in Power Plant Chemistry*" Organized by Department of Applied Chemistry, Jabalpur Engineering College, Jabalpur, on 15th September, 2020.
- 6) Self-sponsored Online One Week Short Term Training Program on "*Challenges and Opportunities in Designing Nano architectonics of Nano porous Carbon Materials for Industrial Applications*" Organized by

- Department of Materials and Metallurgical Engineering, Maulana Azad National Institute of Technology, Bhopal, from 16th - 20th September, 2020.
- 7) TEQIP-III Sponsored One Week Online Short-Term Course on “*Chemistry of Advanced Functional Materials (CAFM-2020)*” Organized by Department of Chemistry, National Institute of Technology, Srinagar, from 21th - 25th September, 2020.
 - 8) GUJCOST and DST (Government of Gujarat) Sponsored Four days Faculty Development Programme on the Theme “*Green Chemistry and Technology for Sustainable Engineering*” Organized by Chemical Engineering Department, School of Engineering, P. P. Savani University from 18th - 21st January, 2021.
 - 9) AICTE Training and Learning (ATAL) Academy Online Faculty Development Programme (FDP) on “*Advances in Waste Treatment Technologies*” Organized by Civil Engineering Department, Government Engineering College, Modasa from 23rd - 27th August, 2021.
 - 10) E-symposium on “*Materials for Energy and Energy Storage*” Organized by Department of Humanities and Sciences, VNRJIET, Hyderabad-500090, from 3rd & 4th September, 2021.
 - 11) International Webinar on “*RSC-IIT Desktop Seminar with JMC-A*” Organized by Cryst Eng Comm and IISER Kolkata, on 27th October, 2021.
 - 12) National Symposium on “*Frontiers in Chemistry (NSFC-2022)*” Organized by Department of Chemistry, Faculty of Science, The Maharaja Sayajirao University of Baroda, Vadodara-390002, Gujarat, held on 25th June, 2022.

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