INDIAN JOURNAL OF SCIENCE AND TECHNOLOGY

RESEARCH ARTICLE

OPEN ACCESS
Received: 21-05-2024
Accepted: 25-06-2024
Published: 26-07-2024

Citation: Rathore M, Vikram Singh A (2024) Synthesis and Characterization of a New Ion Exchange Cellulose -1- Butane Sulphonic Acid (CBSA) Resin and its Application for Removal of Hazardous Metal Ion (Pb^{2+}) from Industrial Waste Water by Batch Method . Indian Journal of Science and Technology 17(28): 2960-2966. https://doi.org/10.17485/IJST/v17i28.1741

* **Corresponding author**.

monikarathorejnvu@gmail.com

Funding: None

Competing Interests: None

Published By Indian Society for Education and Environment (iSee)

ISSN
Print: 0974-6846
Electronic: 0974-5645

Synthesis and Characterization of a New Ion Exchange Cellulose -1- Butane Sulphonic Acid (CBSA) Resin and its Application for Removal of Hazardous Metal Ion (Pb^{2+}) from Industrial Waste Water by Batch Method

Monika Rathore[1]*, Aresh Vikram Singh[1]

1 Department of Chemistry, Faculty of Science, New Campus, Jai Narain Vyas University, Jodhpur, 342001, Rajasthan, India

Abstract

Objective: The purpose of this work is to develop and evaluate a new cellulose-1-butane sulphonic acid resin and use it for the elimination of hazardous metallic ions from textile industry effluent. **Method:** In the laboratory, a new cellulose-based resin containing 1- Butane sulphonic acid group has been synthesized. 1-Butane sulphonic acid group has been introduced into cellulose matrix through modified Porath's method. **Findings:** Development of cellulose-1-butane sulphonic acid resin based on natural polysaccharides for the removal of lead ions, a dangerous metal, from industrial wastewater. Cellulose -1-Butane sulphonic acid resin's adsorbed metal ions were efficiently eluted using varying strengths of HCl solution. The resin could then be washed with pure, acidic distilled water to restore it to its H^+ cationic exchanger state ten times. The hazardous metal ion Pb^{2+} can be specifically extracted from industrial waste water using the cellulose-1-Butane Sulphonic Acid (CBSA) resin. **Novelty:** Ion exchange capacity, pH titration, FTIR spectra, elemental analysis, and moisture levels were used to characterize the CBSA resin. At various pH levels, the distribution coefficient value (K_d) of lead metal ions has been methodically investigated using the batch method.

Keywords: Effluent; Distribution Coefficient; Resin; Waste Water; Polysaccharide

1 Introduction

The effluent from the mineral extraction, tanning leather, the electroplating process battery, and steel industries has been discovered to include heavy metal ions, including ferrous, copper, zinc, lead, and others. Heavy metal ions have a negative impact on human and environmental life when they surpass tolerance thresholds. The astronomical increase in world population, modern industrialization and civilization, domestic and agricultural activities and other geological, environmental and global changes are responsible for water pollution. The polysaccharides have unique functional characteristics and biological activities for Guar Gum 1-Butane Sulphonic Acid[1] and exchange resin [2] for waste water[3]. The industry continues to be one of the most significant causes of pollution of aquatic ecosystems due to a diverse kind of wastes especially toxic heavy metal ions such as arsenic, cadmium, chromium, copper, lead, mercury, zinc, etc. In addition, many of them are known to be toxic or carcinogenic even at low concentration. They are not biodegradable and tend to accumulate in living organisms causing serious diseases and disorders Therefore, many industries have a need to treat wastewater either of domestic or industrial origin to obtain very high-quality water for demanding purposes.

Various technologies and methods, such as ion exchange, precipitation, solvent extraction, chemical and electrochemical technique, advanced oxidation process, reverse osmosis and adsorption procedure have been developed for the removal and recovery of metal ions from industrial effluent. Agricultural solid wastes based adsorbent materials in the remediation of heavy metal ions from water and wastewater by adsorption[4], like Guar Gum 1-Butane Sulphonic Acid) Resin and Study of their Physicochemical Characterization. The newly synthesized CBSA resin was further diagnosed by SEM, TGA and FTIR spectral analysis. Metal ion distribution coefficient (K_d values at pH 7) for Fe^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+} and Pb^{2+} are 86.66, 60.95, 69.42, 49.44 and 45.65, respectively[5]. Comprehensive review of polysaccharide-based bio nanocomposites for food packaging applications[6], Polysaccharides as Economic and Sustainable Raw Materials for the Preparation of Adsorbents for Water Treatment[7], Functionalized polysaccharide-based flocculants for solid liquid separation of wastewater[8] and Synthesis of a polyacrylamide chelating resin and application in metal ion extractions[9]. The use of the advanced oxidation process in the ozone + hydrogen peroxide system for the removal of cyanide from water [10], followed by Tamarind Kernel Powder (TKP) and its biosorbents that went through chemical modification are crucial for removing heavy metals from industrial effluents including Fe^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+} [11], Protection of biodiesel and oil [12] and removal of bio refractory compounds in industrial wastewater by chemical and electrochemical pretreatments [12], Synthesis and characterization of a new guar [12], for eco-friendly environment[13] Development and Application of Newly Synthesized Tamarind 2-Hydroxy -2- Methyl Butyric Acid (THMBA) Resin for Elimination of Hazardous Metal Ions from Industrial Effluents[14], Guar gum Diamino Benzoic Acid (GDABA) resin[13] have been studied for review the elimination of hazardous metal ions from the industrial wastewater. However, most of these technologies are either extremely expensive or too inefficient in the treatment of wastewater. It is observed that adsorption among other methods is a cost-effective technique and simple to operate. Adsorption involves the accumulation of substances on the surface of a solid or liquid. Adsorption is of two types, which are physical adsorption or Van Der Waals adsorption and chemical adsorption or Langmuir adsorption. Recently, numerous approaches have been studied for the development of cheaper and more effective adsorbents containing natural polymers. Among these, polysaccharides such as tamarind kernel powder (TKP)[15], and starch deserve particular attention. These biopolymers represent an interesting and attractive alternative as adsorbents because of their structure, physico-chemical characteristics, chemical stability, high reactivity and excellent selectivity towards metals, resulting from the presence of chemical reactive groups (hydroxyl, acetamido or amino functions) in polymer chains. Furthermore, it is commonly known that polysaccharides, which are plentiful, renewable, and biodegradable resources, can interact chemically and physically with a broad range of molecules. For this reason, adsorption on polysaccharide derivatives may be the preferred low-cost method for component extraction and separation during water purification.

The creation and Characterisation of a novel cellulose-1-butane sulphonic acid resin, as well as its use in the elimination of harmful metal ions from textile industry effluent, are the goals of this work. Because it is quick, easy on the environment, and affordable, the removal of heavy metal ions using cellulose -1-butane sulphonic acid resin is currently regarded as one of the most promising methods.

2 Methodology

The chemicals used in the synthesis of resin are tabulated in Table 1.

2.1 Preparation of Stock solution of lead

In a 1000 mL volumetric flask, 3.357 g of lead acetate ($Pb\ (CH3COOH)_2$) was dissolved in a couple of millilitres of acetic acid, and the volume was increased to the mark to produce a 1000 ppm lead solution.

2.2 Determination of ion exchange capacity

Using a 10% aqueous solution of potassium chromate solution as an indicator, a direct titration using a 0.11N silver nitrate solution was used to determine the ion exchange capacity of freshly synthesized CBSA resin. The ion exchange capacity was

Table 1. Materials used for development and application of newly synthesized Cellulose 1-Butane Sulphonic acid (CBSA) resin

S. No.	Chemical	Specification
1	Cellulose	Ases chemical works, Jodhpur
2	Dioxane (AR)	S. D fine chem. Pvt. Ltd. Boisar
3	Sodium hydroxide (AR)	Sarabhai M. Chemicals Baroda, India
4	Epichlorohydrin	Loba Chemie Pvt. Ltd. Mumbai
5	Methanol	E Merk. Bombay, India
6	Hydrochloric acid	Sarabhai M. Chemicals Baroda, India
7	1-Butane Sulphonic Acid	Sarabhai M. Chemicals, Baroda, India

computed using the subsequent formula.

$$\text{Ion exchange capacity} = \frac{Solution\ volume\ x\ milliequivalents\ of\ titrant\ used}{volume\ of\ aliquote\ x\ (100-w)\ x\ wet\ weight\ of\ sample}$$

2.3 Methodology steps

We have tried to develop an ion exchange resin based on cellulose by adding 1-butane sulphonic acid as a functional group to it. Because it is hydrophilic, cellulose, a naturally occurring polysaccharide, can be utilised as a chelating agent.

2.3.1 Synthesis of CBSA resin

Porath's method was approached to synthesize the BSA resin in a two-step procedure.

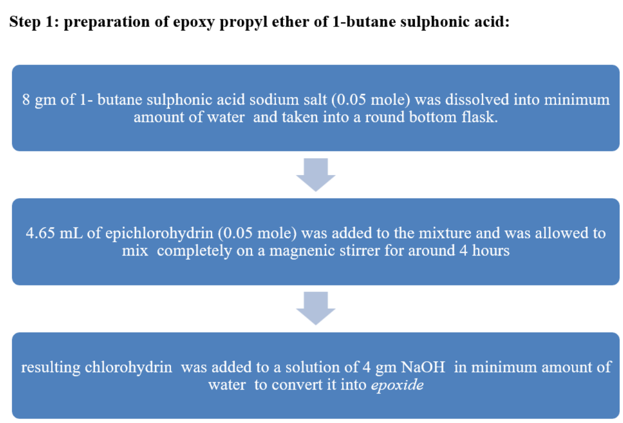

Fig 1. Preparation of epoxy propyl ether of 1-butane sulphonic acid

2.4 Calculation of distribution coefficient by batch method

The molar distribution coefficient 'Kd' value of Pb^{+2} ion was calculated by using the batch method. 25 mg of cellulose 1-butane sulphonic acid was taken in a glass stoppered conical flask which was containing 1 mL of 1000 ppm metal solution analogous to 1 mg metal ions. In it suitable buffers were added for pH adjustments. After this the contents of conical flasks were then allowed to stir on a magnetic stirrer and then equilibrated. The two phases obtained on equilibration were then separated by using Whatman 42 filter paper and a portion of filtrate obtained was examined for the concentration of metal in filtrate. Calibration curves were plotted for various metals, through the examination of standard solution series of metal ions with the help of atomic absorption spectrophotometer. Air acetylene flame and different wavelengths of the main resonance line were used for the estimation of various metals. The respective distribution coefficients were calculated by using the following formula.

$$K_d = \frac{amount\ of\ metal\ ion\ in\ resin\ \frac{phase}{gm}\ of\ dry\ resin}{amount\ of\ metal\ ion\ in\ \frac{solution}{ml}\ of\ solution}$$

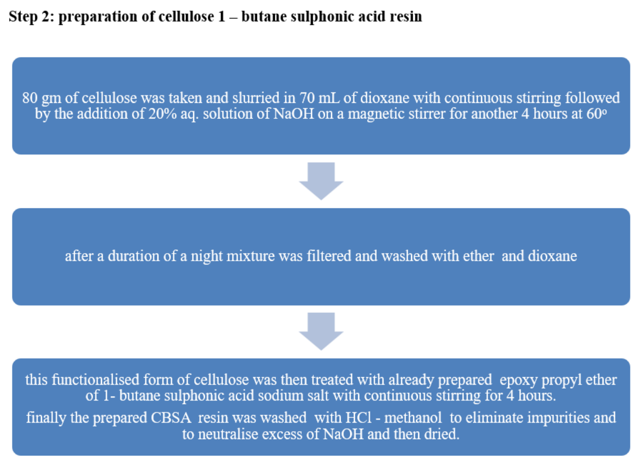

Fig 2. Preparation of cellulose 1 – butane sulphonicacid resin

2.5 Elemental analysis

2.5.1 Determination of Sulphur content

Using Messenger's method, the amount of sulphur in the form of barium sulphate was calculated. A 250 ml beaker was filled with 0.2g of CBSA resin. This was combined with 25 millilitres of distilled water, one gramme of potassium hydroxide, and a tiny bit of potassium permanganate. Following four to five hours of heating the reaction combination, it was cooled, and 25 millilitres of strong hydrochloric acid were added to the cooled liquid. This mixture was heated to a colourless consistency. After filtering it, 1 millilitre of strong hydrochloric acid was applied to the filtrate. Following that, the filtrate was mixed with a 2 percent $BaCl_2$ solution until all of the $BaSO_4$ had precipitated. After filtering, washing, and oven drying, the BaSO4 was finished. The weight of $BaSO_4$ was measured using a weight balance.

2.5.2 Calculation for Sulphur content in CBSA Resin

Weight of resin taken = 0.2 g

Weight of $BaSO_4$ formed = 0.0194 g

233 g of $BaSO_4$ contains = 32 g of S

0.1922 g of $BaSO_4$ = $\frac{32}{233}$ x 0.0194 = 0.0026 g of S

0.2 g of resin contains = 0.0026 g of S

1 g of resin contains = $\frac{0.0026}{0.2}$ g of sulphur

100 g of resin contains = $\frac{0.0026}{0.2}$ x 100 = 1.30 % of S

Cellulose 1-butane sulphonic acid resin contain 1.30 % of sulphur as estimated by messenger's method.

2.6 Determination of Kd value of Pb (II) metal ion on CBSA resin: chelation of Pb (II) on CBSA resin

Various amounts of 0.2 M acetic acid and 0.2 M sodium acetate were taken in different glass stopper conical flasks to obtain solutions of desired pH i.e., 2-7. Similarly, pH 8 was obtained by adding a mixture of suitable amounts of 0.2 M NH_4OH and 0.2 M NH_4Cl. During experiment, 0.075 g of dry CBSA resin and 1 ml of 1000 ppm Pb (II) solution was added in each flask containing different pH solutions followed by stirring on a magnetic stirrer and filtration. Filtrates were examined for Pb^{+2} metal ion. Results so obtained are summarized in Table 2.

2.7 Determination of moisture content

For a day, 5g of well cleaned and dried resin in its chloride form was baked at 80°C until it was fully dry. The weight of the dried resin was once more measured once it had fully dried. The resin's moisture content is shown by the weight differential.

Table 2. Chelation of Pb (II) on CBSA resin

pH	Absorbance	Concentration of Pb (II) in filtrate (ppm)	Amount of Pb (II) in solution (mg)	Amount of Pb (II) in resin (mg)	'Kd'	% absorption of Pb (II) by resin	Metal exchange capacity mg/g
2	2.950	11.6	0.4780	0.5220	600.00	52.20	6.960
3	2.238	8.8	0.3629	0.6371	965.30	63.71	8.494
4	1.475	5.8	0.2413	0.7587	1744.13	75.87	10.115
5	**0.788**	**3.1**	**0.1280**	**0.872**	**3750.53**	**87.20**	**11.626**
6	1.373	5.4	0.2218	0.7782	1921.48	77.82	6.973
7	3.509	13.8	0.5669	0.4331	418.45	43.31	5.774
8	4.171	16.4	0.6759	0.3241	263.49	32.41	4.321

2.8 pH analysis

The investigation of the impact of an ionic polymer's structure on its chemical behaviour utilised the batch approach. An equilibrium pH titration curve was plotted for this purpose. After washing and drying the newly generated derivative overnight at 50 ^{0}C, the excess acid was removed by converting it to its hydrogen ion form. Eight to nine flasks containing 0.1g of resin were filled with a solution of 1 N NaCl in progressively decreasing amounts and 1 N NaOH in progressively increasing amounts. Following this, the necessary quantity of deionized water was added to each flask to maintain a 25 mL volume of solution. To ensure that the final pH of the solution remained constant, these flasks were securely closed and allowed to acclimatize on a magnetic stirrer. The obtained values are listed in Table 2 and a pH titration curve plotted and is shown in Figure 3.

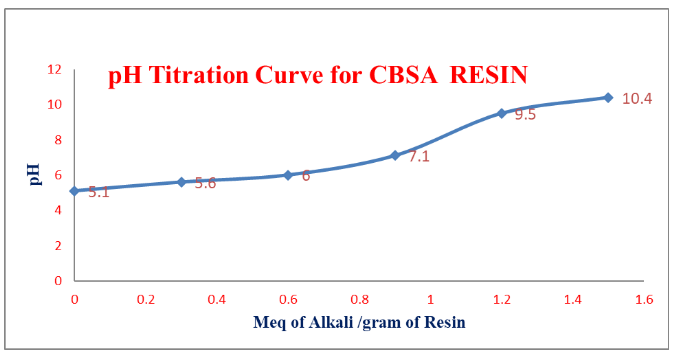

Fig 3. pH analysis for Cellulose 1-Butane Sulphonic acid (CBSA) resin

3 Result and Discussion

Many researchers have worked on production of activated carbon from renewable resources such as industrial and agricultural waste[15]. FTIR demonstrated that carboxyl and hydroxyl groups were involved in the biosorption of the metal ions[16] and chemical composition as 6.2% of 3,5-diethyl and 40% of ethyl thioisobutyrate[17]. The research results can provide a reference for the process improvement of sewage treatment plants and the safe reuse of wastewater[18].

3.1 FTIR Characterization

The FTIR spectra of CBSA resin shows a peak at 2899.6 cm^{-1}, which is attributed to CO stretching vibrations at 1218.8 cm^{-1} and another variable peak at 1587.8 cm^{-1} for C=0 Stretching. A strong peak in the resin 1250 - 1050 cm^{-1} (1021.3 cm^{-1}) denotes C-O stretching vibrations. The CBSA resin shows symmetric O-H Stretching in the resin at 3272.6 cm^{-1}. The spectra of polysaccharides are generally observed in the region 3500 to 3000 cm^{-1}, which denotes -OH stretching frequencies. The IR spectra of CBSA resin is shown in Figure 4.

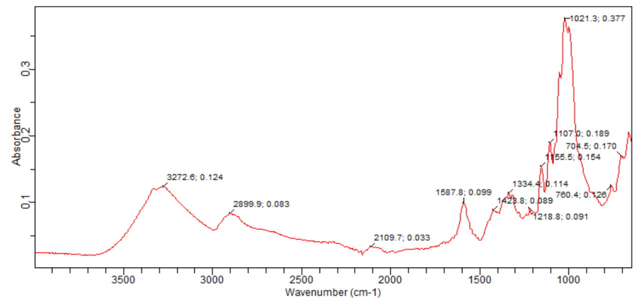

Fig 4. FTIR Characterization for Cellulose 1-Butane Sulphonic acid (CBSA) resin

Table 3. 3

Flask No.	Volume of 0.1 N NaOH (ml)	Volume of IN NaCI (ml)	Volume of deionized water (ml)	Final pH
1	0.0	1.4	23.6	5.1
2	0.3	1.2	23.5	5.6
3	0.6	1.0	23.4	6.0
4	0.9	0.8	23.3	7.1
5	1.2	0.6	23.3	9.5
6	1.5	0.4	23.1	10.4
7	1.8	0.2	23.0	11.0
8	2.1	0.0	22.9	11.2

3.2 Distribution coefficient of Pb (II) metal ion from industrial waste

Natural polysaccharide derivative functionalized CBSA resin has a strong affinity for removing dangerous metal ions from industrial effluents. After examining the different findings, it can be said that when pH rises, Kd values for the elimination of zinc metal ions first rise and subsequently fall. The Kd value for Pb^{2+} ion at the pH of maximum adsorption is 3750.53, according to equilibrium experiments of Pb^{+2} with CBSA. Additionally, it can be deduced that the Pb (II) distribution coefficient value on CBSA resin peaked at pH 5 in a buffer including NH_4OH and NH_4Cl. This indicates that at pH 5, CBSA resin exhibits a strong attraction for Pb.

3.3 Moisture content

The weight of completely oven dried resin was found to be 4.6g which indicates the presence of 0.4g or 8% moisture.

3.4 Effect of pH

The study of the pH titration curve (Figure 3) obtained for CBSA resin shows that this resin is stable over a wide pH range of 6 to 10.

3.5 Ion exchange capacity of CBSA resin for Pb (II) metal ion

Ion exchange capacity of CBSA resin was found to be 11.626 mg/g for Pb (II) ion.

3.6 Estimation of sulphur content

1.30% of sulphur was estimated in CBSA resin using messenger's technique of quantitative sulphur analysis

4 Conclusion

This study has used cellulose based natural polysaccharide because of its effective and low-cost procedure in decontamination of effluent water for extraction and separation of compounds. The adsorbed metal ions on Cellulose -1- Butane sulphonic acid resin was effectively eluted by different strength of HCl solution and the resin could be regenerated 10 times to its H^+ cation exchangerform after elution of the metal ions followed by washing with acidic and pure distilled water. The new synthesized Cellulose -1- Butane sulphonic acid resin is hydrophilic and biodegradable so that after effluent treatment used resins can be disposed of without facing any environmental problem. Cellulose 1-butane sulphonic acid resin contain 1.30 % of sulphur as estimated by messenger's method. Thus, present research reveals that newly synthesized Cellulose -1- Butane sulphonic acid resin can be effectively used for removal of toxic heavy metalions from industrial effluent. The removal of heavy metal ions by Cellulose -1- Butane sulphonic acid resin is now considered as one of the most promising techniques due to cost-effective, eco-friendly and rapidness.

Acknowledgement

Authors are thankful to the Head, Department of Chemistry, Jai Narain Vyas University, Jodhpur, Rajasthan, INDIA for research laboratory facilities.

References

1) Gaur S, Joshi R, Singh AV. Preparation of Gbsa (Guargum 1-Butane Sulphonic Acid) Resin and Study of their Physicochemical Characterization and Use for Removal of Toxic Metal from Effluents. *Oriental Journal of Chemistry*. 2023;39(5):1226–1231. Available from: https://bit.ly/46lS4yL.
2) Rathore M, Singh I, Bhati PS, Nagar S. Synthesis of natural polysaccharide based cellulose anthranilic acid ion exchange resin for extraction of heavy toxic nature metal ion (cadmium) from industrial waste water (Steel Industry. *Research Journal of Chemical Sciences*. 2022;12(1):36–41. Available from: https://www.isca.in/rjcs/Archives/v12/i1/6.ISCA-RJCS-2021-018.php.
3) Fakhri V, Aliakbar J, Fatemeh LV, Hung CS, Vahid P. Polysaccharides as eco-friendly bio-adsorbents for wastewater remediation: Current state and future perspective. *Journal of Water Process Engineering*. 2023;54:103980–103980. Available from: https://doi.org/10.1016/j.jwpe.2023.103980.
4) Sen TK. Agricultural Solid Wastes Based Adsorbent Materials in the Remediation of Heavy Metal Ions from Water and Wastewater by Adsorption: A Review. *Molecules*. 2023;28(14):5575–5575. Available from: https://doi.org/10.3390/molecules28145575.
5) Choudhary GK, Anju A, Prakash C, Kumari S, Choudhary M, Chowdhary V. Development and Application of Newly Synthesized Mango Seed Starch 6-Amino Hexanoic Acid Resin for Elimination of Toxic Heavy Metal Ions from Industrial Effluents. *Oriental Journal of Chemistry*. 2023;39(4):990–995. Available from: http://dx.doi.org/10.13005/ojc/390423.
6) Altaf A, Usmani Z, Dar AH, Dash KK. A comprehensive review of polysaccharide-based bio nanocomposites for food packaging applications. *Discov Food*. 2022;2(10). Available from: https://doi.org/10.1007/s44187-022-00011-x.
7) Díaz BG, Rossi E, Errea MI. Polysaccharides as Economic and Sustainable Raw Materials for the Preparation of Adsorbents for Water Treatment. *Polysaccharides*. 2023;4:219–255. Available from: https://doi.org/10.3390/polysaccharides4030016.
8) Shaon D, Priyapratim P, Sagar P. Functionalized polysaccharide-based flocculants for solid liquid separation of wastewater. *Journal of the Indian Chemical Society*. 2021;98. Available from: https://doi.org/10.1016/j.jics.2021.100066.
9) Kumar V, Dwivedi SK, Oh S. A critical review on lead removal from industrial wastewater: Recent advances and future outlook. *Journal of Water Process Engineering*. 2022;45:102518–102518. Available from: https://doi.org/10.1016/j.jwpe.2021.102518.
10) Zakaria KK, Farag HA, El-Gayar DA. Removal of Cu2+, Fe2+ and SO42— ions from industrial wastewater by ion exchange resins contained in a rotating perforated cylindrical basket of different heights. *Sci Rep*. 2023;13. Available from: https://doi.org/10.1038/s41598-023-29956-4.
11) Prakash C, Choudhary GK, Chowdhary V. Development and Utilization of Newly Synthesized Tamarind-6-Amino Hexanoic Acid (TAMHA) Resin for Removal of Toxic Heavy Metals Ions from Industrial Effluents. *Oriental J Chemistry*. 2024;40(2):594–598. Available from: http://dx.doi.org/10.13005/ojc/400235.
12) Carlos BD, Ivonne LH, Gabriela RM, Bryan B, Patricia BH. Removal of Bio refractory Compounds in Industrial Wastewater by Chemical and Electrochemical Pretreatments. 2009. Available from: https://doi.org/10.1021/ie800560n.
13) Rathore M, Singh AV. Development and Application of newly synthesized Guar gum Diamino Benzoic Acid (GDABA) resin for elimination of hazardous waste metal Ions from industrial effluents. *Oriental Journal of Chemistry*. 2023;39(1):216–221. Available from: http://dx.doi.org/10.13005/ojc/390127.
14) Anju A, Prakash C, Choudhary GK, Kumari S, Choudhary M, Chowdhary V. Development and application of newly synthesized Tamarind-2-Hydroxy-2-Methyl Butyric Acid (THMBA) resin for elimination of hazardous metal ions from Industrial Effluents. *Oriental J Chemistry*. 2023;39(2):505–510. Available from: http://dx.doi.org/10.13005/ojc/390233.
15) Tejada CT, Gonzalez-Delgado AD, Villabona-Ortiz A. Removal of Cr (VI) from Aqueous Solution using Orange Peel-based Biosorbents. *Indian Journal of Science and Technology*. 2018;11(13):1–13. Available from: https://dx.doi.org/10.17485/ijst/2018/v11i13/121602.
16) Ningchuan F, Xueyi G, Sha L, Yanshu Z, Jianping L. Biosorption of heavy metals from aqueous solutions by chemically modified orange peel. *Journal of Hazardous Materials*. 2011;185(1):49–54. Available from: https://doi.org/10.1016/j.jhazmat.2010.08.114.
17) Diedhiou D, Candy FM, Vandenbossche L, Raynaud V, Sock C, Rigal O. Chemical Composition of the Essential Oil of Neem (Azadirachta indica A. Juss.) Seeds Harvested in Senegal. *Indian Journal of Science and Technology*. 2023;16(2):118–122. Available from: https://doi.org/10.17485/IJST/v16i2.1650.
18) You-Wei J, Gui-Jing, Shuang W, Yue Z, Hong-Fei Q, Qiao T, et al. Halogenated aliphatic and phenolic disinfection byproducts in chlorinated and chlorinated dairy wastewater: Occurrence and ecological risk evaluation. *Journal of Hazardous Materials*. 2024;465:132985–132985. Available from: https://doi.org/10.1016/j.jhazmat.2023.132985.