Synthesis, Characterization of Novel cross linked BE-TH resin and its application in treatment of industrial waste water

Rajni Bais, Gazala Khan, Seema Parveen* and Ram Lal Saini

Department of Chemistry, Jai Narain Vyas University, Jodhpur (Raj.), India

ABSTRACT

Green chemistry emphasizes the importance of developing unique, eco-friendly solutions to protect human health and ecosystems. In order to examine this concept for minimizing industrial waste and lessening the environmental impact of hazardous chemicals, new greener procedures for heavy metal extraction from industrial waste must be implemented. Because of their low cost and ease of synthesis, plant based resins are increasingly being used in the treatment of water resources in accordance with the goals and objectives of green chemistry. To remediate harmful industrial effluents, cross linked Bajra Epoxy Tryptophan Hydroxamate (BE-TH) resin were produced in the current study. The FT-IR spectroscopy and Scanning electron microscopy were used to determine the BE-TH resin's characterization. The uptake of metal ions by the BE-TH resin was studied by batch equilibrium experiment. The adsorption of different metal ions such as Cd(II), Zn(II) and Fe(II) take place successfully on the BE-TH resin. The maximum percentage removal Cd (II) and Zn (II) occurred at the pH range of 7-7.5. The results have established good potentiality for the BE-TH resin to be used as an adsorbent for the removal of toxic metals from industrial waste water.

Introduction

Heavy metal ion-containing industrial effluents are poured into natural water systems, causing significant environmental damage. Even if only a little amount of heavy metals were consumed, human health would've been imperiled (Connel *et al.,* 2008, Gode *et al.,* 2006; Baraka *et al.* 2007). As a result, wastewater contaminated with metals must be cleaned before being released into the environment. Metal salts such as As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Se, Tl, and V, are extremely toxic to humans, sea animals, and ecosystems (Ali *et al.,* 2019; Pasichnaya *et al.,* 2020; Ali and Khan, 2018: Korkmaz *et al.,* 2019; Fu and Xi , 2020). Due to their high solubility in aquatic environments and tendency to be absorbed and bioaccumulated in living cells, industries that produce effluent rich in heavy metals such as Cd, Cr, Ni, As, and Zn are regarded the most hazardous (Barakat, 2011). Fe has aesthetic, cosmetic, and technical consequences due to its unpleasant odour and taste, capacity to harm water systems due to corrosivity, scaling, or sedimentation, as well as potential to impede the efficiency of remediation for other contaminants. As a result, the World Health Organization (WHO) has defined a secondary contaminant threshold of 0.3 mg/l for Fe (US-EPA, 2021, EPA, 2015). In children, chronic toxicity of Cd causes harm to the respiratory, renal, skeletal, and cardiovascular systems, as well as the development of lung, kidney, prostate, and stomach malignancies (US EPA, 2010, WHO, 2011a). Textile wastewater

covers a range of refractory and toxic substances, such as different dyes and heavy metal ions which pollute the environment permanently and pose a major hazard to human health if released directly. As a result, the textile printing and dyeing business is now regarded as one of the most hazardous. (Holkar *et al.,* 2016; Huang and Song 2018, Tkaczyk *et al.,* 2020. Yaseen and Scholz, 2019). The waste water from steel industry usually found to contain toxic metals such as Cd, Zn, Pd and Cu which causes adverse effect to human health when entered in food chain. As a consequence, technology must be developed that can not only treat wastewater but also extract heavy metals from industrial effluent. The adsorption process has received a lot of attention in recent years and became one of the most effective methods for removing hazardous metal ions from industrial wastewater. Adsorption is a surface process in which aqueous heavy metal ions are physically or chemically trapped on the adsorbent, or both. The cheapest adsorbents have been created by modifying a range of industrial or agricultural by-products (Ahalya *et al.,* 2003, Abdel-Raouf and Abdul-Raheim, 2017). Bajra (Pearl millet) is a renewable and unexploited starch source, with its grain containing up to 70% starch. When compared to other grains, pearl millet could be a less expensive source of starch for making functional foods (Sneh Punia, 2021). There are numerous methods for modifying starch, resulting in a variety of starch utilization in both the food and non-food industrial sector (Ashogbon *et al.,* 2014, Alcázar-Alay and Meireles, 2015, Haroon *et al.,* 2016). Song used AM (acrylamide) and acrylacyloxyethyltrimethylammonium chloride (AAC) for grafting on maize starch and [$(NH_4)_2S_2O_8$] ammonium persulfate with urea as a co-initiator. The products have been shown to be significantly efficient than cationic polyacrylamide in wastewater treatment. (Song, 2010). Cross-linking corn starch with epichlorohydrin yielded cross-linked amino-starch (CAS) and dithiocarbamate starch (DTCS), according to Li and coworkers (ECH). The chelating starch derivatives CAS and DTCS were employed in the adsorption of Cu^{2+} removal and recovery of heavy metal ions from Faridabad ground water (Raigar, 2021). Bertrand Sancey discovered that treating industrial wastewaters with sorption utilising a starch-based sorbent as a non-conventional material is also a viable option. The goal of this work was to modify bajra (pearl millet) to create a biodegradable ion-exchange resin, and then examine its properties so that it might be used as an adsorbent for the removal of toxic metal ions from industrial wastewater. To the best of our knowledge synthesis and characterization of bajra based BE-TH resin (Fig. 1) for treatment of industrial waste water is a novel approach. So far no research has been reported on synthesis and application of BE-TH resin in treatment of industrial effluents.
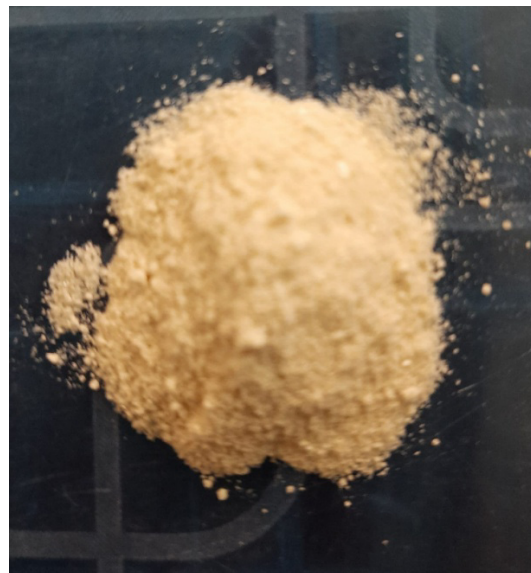

Fig. 1. BE-TH Resin

Experimental

Materials and Methods

Bajra was combined with reagent-grade epichlorohydrin. E. Merk and Sarabhai M. Chemicals provided A.R. quality solvents such as dioxane and methanol, respectively.

Metal analysis was carried out using a Perkin-Elmer 2380 atomic absorption spectrophotometer (AAS) using KBr pellets, I.R. spectra of the produced resin were recorded using a Schimadzu IR 400 spectrophotometer.

Sample collection- The industrial effluents sample was collected from NeelKanth steel industry, Jodhpur, Rajasthan.

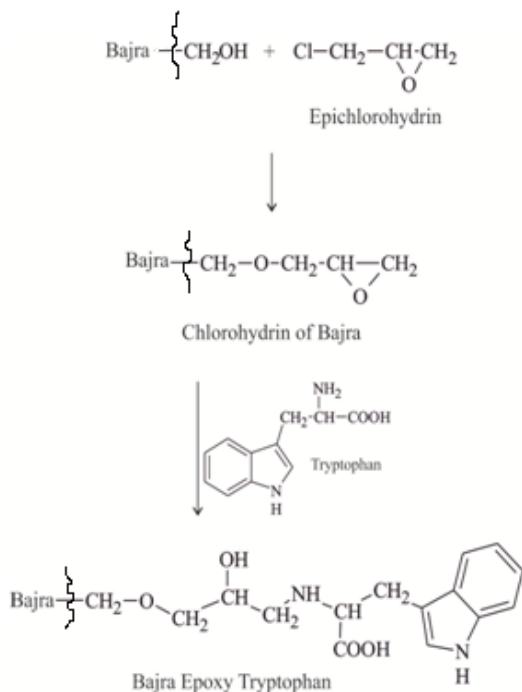Preparation of Bajra Epoxy Tryptophan Hydroxamate resin (BE-TH):

Preparation of Cross linked Bajra and its derivative

In a conical flask, 3.55 g of bajra powder was digested in dioxane for one and a half hour, subse-

S520

Eco. Env. & Cons. 28 (May Suppl. Issue) : 2022

quently 3.6 ml of epichlorohydrin and 50% aqueous sodium hydroxide solution were added to make the flask alkaline with continuous shaking. The solution was stirred for 5 hours at 50-55 ^{0}C, then the mixture was stirred for 5 hours. The resulting product is then filtered and dioxane washed. This mixture is rinsed with a mixture of 80 percent aqueous methanol and nitric acid. The filterate was washed again and again until it was free of chloride ions and alkalinity. Finally, solvent ether was used to clean it. The goods was washed and dried. The resulting cross-linked bajra is shown in scheme.1, which was employed for further derivatization.

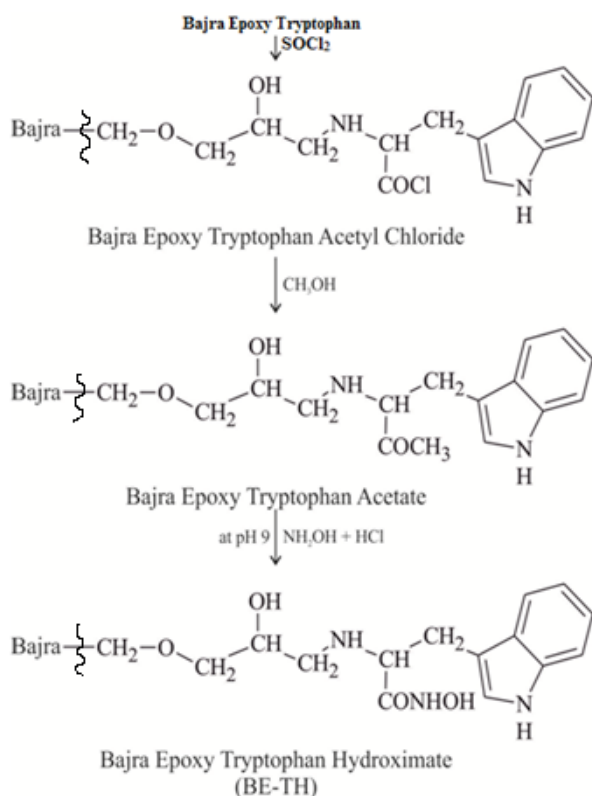### Preparation of Bajra Epoxy Tryptophan

0.025 moles of epoxy ether of Bajra was slurred with dioxane in a 500 ml round bottom flask, to which 8 ml of 50 % aqueous NaOH was slowly added with continual stirring at 50 °C. 4.45 g recrystallized Tryptophan diluted in dioxane was taken. Slowly, this was introduced to the reaction vessel. The resulting mixture was consistently stirred at 50-55 °C, and the solution was agitated for five hours. To eliminate inorganic contaminants from the product, it was filtered through a Buchner funnel and rinsed with 80 percent aqueous methanol adding a few drops of nitric acid. The resulting Bajra Epoxy Tryptophan derivative so prepared is shown in scheme. 1.

Scheme 1. Preparation of Bajra Epoxy Tryptophan

Preparation of Bajra Epoxy Tryptophan Hydroxamate

In a round bottom flask, Bajra Epoxy Tryptophan derivative is taken. Excess methanol was added, and the container was cooled to 5° C before adding 3 ml of thionyl chloride. To obtain the hydroxamate of the ester, a CH_3OH solution of 3 g hydroxyl amine hydrochloride was added, with the pH kept at 9 by Na_2HCO_3 solution. The resulting derivatized Bajra was filtered and rinsed with double distilled water before being dried (Scheme-2)

Scheme 2: Preparation of Bajra Epoxy Tryptophan Hydroxamate (BE-TH) Resin

Characterization of BE-TH resin

The Kjeldahl method, which is used to estimate nitrogen, and the back titration method, which is used to determine total ion exchange capacity, was used to characterise the formation of crosslinked BETH resin. Other characteristics such as bulk density, moisture content, degree of cross linking and total ion exchange capacity were carried out using stan-

dard methodologies, and the results are summarised in table.

1. Moisture content

$$\% \text{ Moisture content} = \frac{W_1 - W_2}{w_1} \times 100$$

W_1= Weight of wet resin
W_2 = Weight of dry resin

2. Nitrogen content

$$\% \text{ Nitrogen content} = \frac{1.4 \times V \times N}{W}$$

V = volume of HCl consumed
N = Normality of HCl (N/2)
W= weight of resin (g)

3. Bulk density

Bulk density= M / V
   M= mass of dry resin
   V= total volume of the wet resin

4. Total ion exchange capacity- In a conical flask, 1 gram of BE-TH resin was placed, and 250 ml (V1) of standardise NaOH solution (N/20) added to 5 ml of 5% NaCl was added and kept it overnight. Further a conical flask was filled with 25 mL of supernatant solution from the prepared solution, and a burette was filled with N/20 HCl solution. The pink coloration was then removed by adding 2 drops of phenolphthalein to the supernatant suspension and titrating with HCl solution. The following findings were obtained during titration:

   Q (meq/g) = (0.05 X V_1) – 8(0.05 X V_2) /w
   Where: V_1 is the volume of standardize NaOH solution

   V_2 is the volume of HCl consumed
   W = weigh of dry resin (g)
   Assay of Metal ions uptake by BETH resin
   The metal adsorption by the resin was measured using the batch equilibrium method. 0.084g of dried resin was placed in each of six glass stoppered flasks, and 40 mL of buffer (made by mixing varying quantities of 0.2 M acetic acid and 0.2 M sodium acetate) was injected to each flask to adjust the pH to 3.5, 4.0, 4.5, 5.0, 5.5, and 6.0, respectively. Each flask

received 1 mL of 1000-ppm metal ion solution, which was stirred for 1 hr. After attaining equilibrium, the two phases were separated using the batch method, and the metal content of an aliquot of the filtrate was measured by flame atomic absorption spectrometry (FAAS).

Results

The various parameters like Moisture content, Nitrogen content, Bulk density and Total ion exchange capacity for the BE-TH resin were calculated as follows and results are given in Table 1.
1. % Moisture content = 1- 0.955/1 x 100= 4.5 %
2. % Nitrogen content-
Weight of resin = 2 g
   Volume of HCl consumed =8.5ml
   % Nitrogen content = 1.4 x 8.5 x0.5 /2 = 2.975 %
3. Bulk density= 0.955/1 = 0.955 g/cm³
4. **Total ion exchange capacity** (Q)
   Q = (0.05 X 250.0) – 8(0.05 X 18.5) / 0.955 = 5.340 meq /g
Characteristics of Industrial waste water sample- The industrial effluents sample collected from Neelkanth Steel industry, Jodhpur, Rajasthan, contains heavy metal ions such as Cd(II), Pb(II), Zn(II), Cu(II), Ni(II) and Fe(II) along with the opacity and debris. The following are the features of the Neelkanth Steel Industry sample given in Table 2.
Distribution coefficient (D_f) of metal ions- The distribution coefficient (D_f) of metal ions obtained by

Table 2. Characteristics of waste water samples from Neelkanth Steel industry, Jodhpur, Rajasthan

Characterisation	Observation
pH	4.5
Colour	Green
Total Hardness	968
Metal ion	Concentration (ppm)
Cu^{+2}	2.45
Cd^{+2}	0.35
Zn^{+2}	8.95
Pb^{+2}	0.95
Ni^{+2}	0.75
Fe^{+2}	1.75

Table 1. Different Characteristics of BE-TH resin.

Resin	% Moisture content	% Nitrogen content	Bulk density (g/cm³)	Total ion exchange capacity (Q) (meq/g)
BE-TH	4.5	2.975	0.955	5.340

S522

Eco. Env. & Cons. 28 (May Suppl. Issue) : 2022

using Batch equilibrium experiment is given in Table 3.

The percentage adsorption of the examined metal ions as a function of pH using BE-TH resins is shown in Fig. 2.The maximum percentage removal of Cd (II) and Zn (II) ions were observed near neutral pH.The effect of dose of BE-TH resin used has a considerable impact on the uptake of metal ions given in Fig. 3. BE-TH resin attained maximum adsorption with an adsorbent dosage of 2 g and thereafter remained constant until 5g. The Cd (II) and Fe (II) showed 80% and 70% of adsorption with 2g and 1g of BE-TH resin respectively. The effect of contact time on percentage removal of metal ions by BE-TH resin was very high initially, then slowed down later

and finally it becomes constant shown in Fig.4. The 35% of Cd and 40% of Zinc removed in first 15 and 20 minutes respectively.

FT-IR Analysis-

The FT-IR spectrum for the BE-TH resin is shown in Fig .5.The IR spectrum shows a narrow peak in the region of 3037 cm^{-1} is assigned to –OH stretching in NHOH. The –CH$_2$stretching band observed at 1095cm^{-1}. The sharp peak at 3399 cm^{-1} is attributed to –NH stretching in –NH$_2$ The –C=O stretching band is observed at 1654 cm^{-1}. The peak observed at 864cm^{-1} is due to stretching of –C-O-C- of oxirane (epoxy) group.
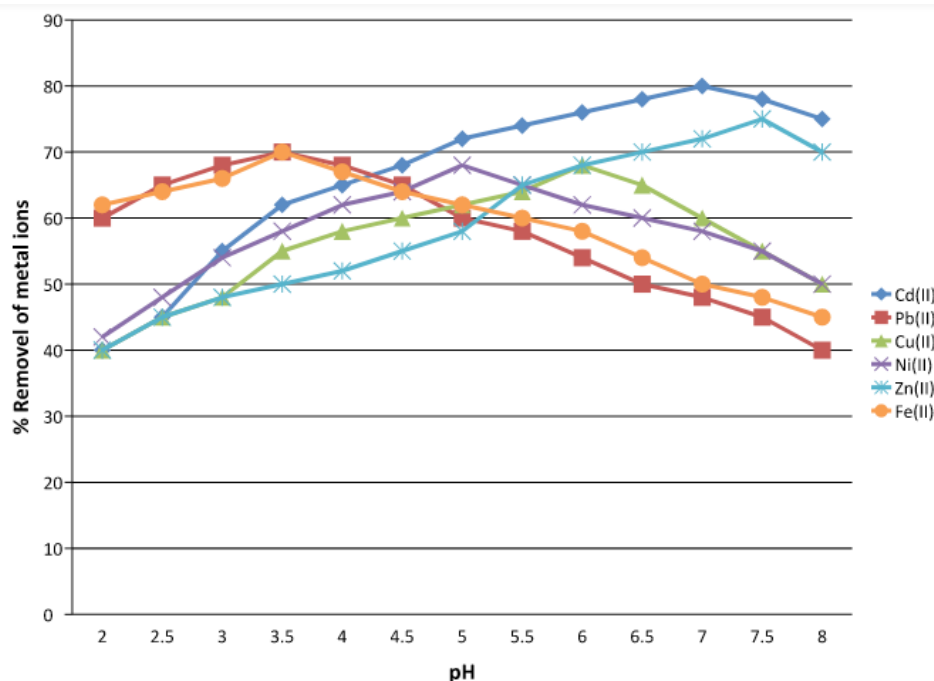

Fig. 2. Effect of pH on % removal of metal ions by BE-TH resin

Table 3. Distribution coefficient (D$_f$) of different metal ions from industrial effluents

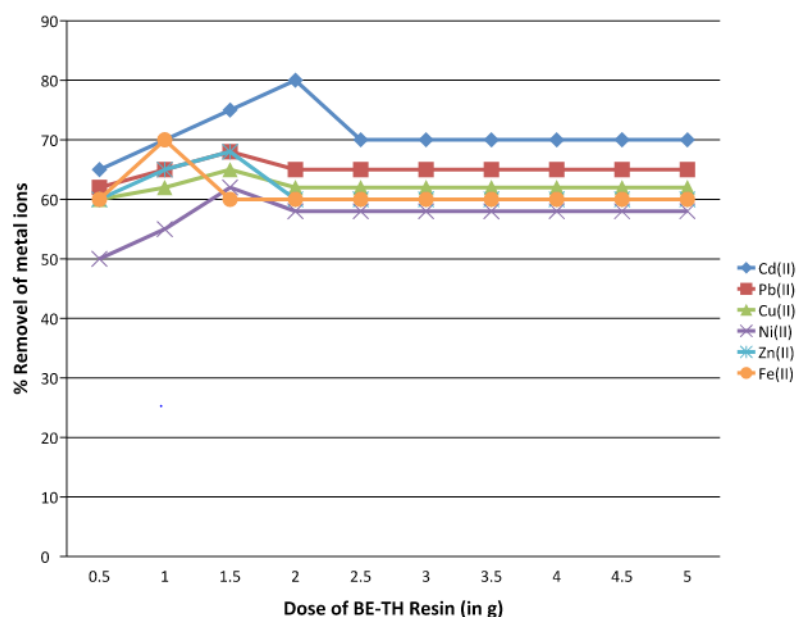| pH	Distribution coefficient (D$_f$) (in ml/g)					
	Cd (II)	Pb (II)	Cu (II)	Ni (II)	Zn (II)	Fe (II)
3.5	348	1087	325	129	310	280
4.0	456	1355	349	210	425	410
4.5	789	795	458	456	750	745
5.5	890	810	657	567	810	805
6.0	1835	615	569	788	1780	2085
6.5	1950	——	656	856	1830	1815
7.0	2045	——	——	789	1980	1965
7.5	1025	——	——	610	2010	1946
8.0	980	——	——	580	1890	——

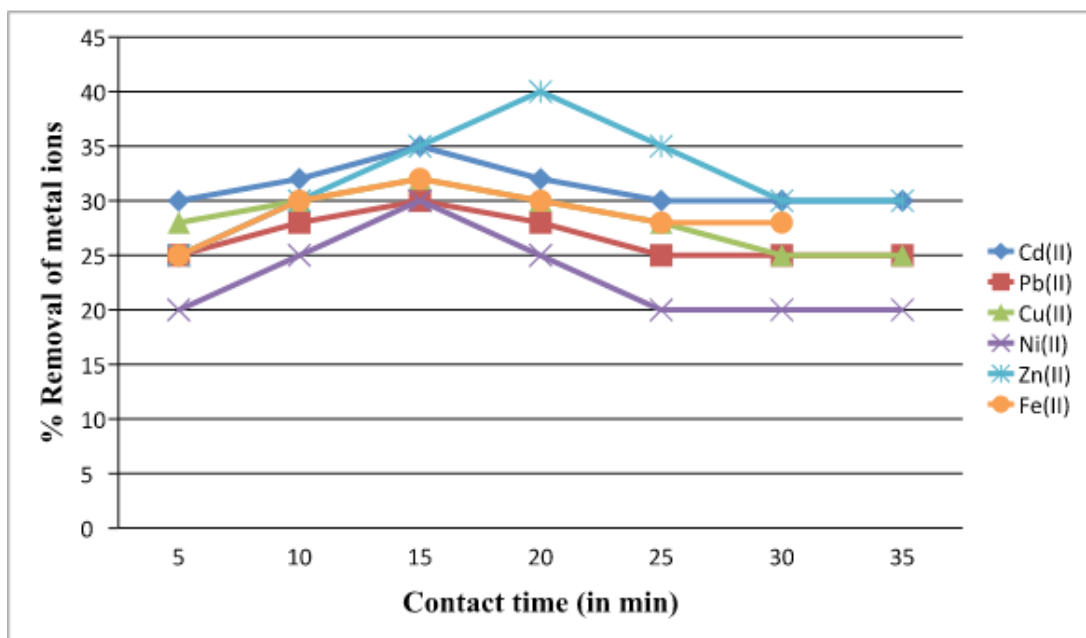**Fig. 3.** Effect of BE-TH resin doses(in g) on percentage removal of metal ions.

Fig. 4. Effect of BE-TH resin contact time (in min) on percentage removal of metal ions.

SEM Interpretation: The newly synthesized BE-TH resin surface is macroporus, craggy, honeycomb and unequal size of particles given in Fig.6.

Discussion

Distribution coefficient (D_f) of metal ions-The distribution coefficient (D_f) of metal ions obtained by using Batch equilibrium experiment is strongly influenced by pH given in Table 3. The distribution coefficient value increases first and then decreases with rising pH, according to the data obtained. Cadmium and zinc have maximum removal at pH 7.0 and 7.5 respectively, as per their Distribution coefficient (D_f) figures in Table 3. The BE-TH resin has been shown to be very selective for Fe at pH- 6.0.
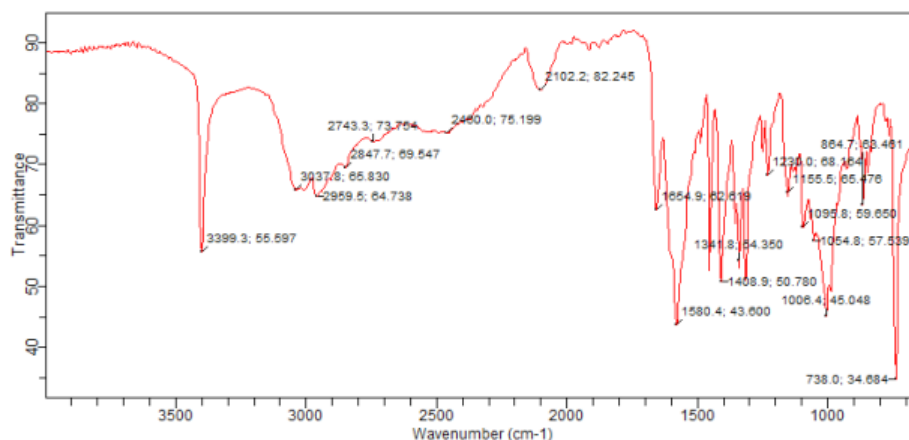
S524

Eco. Env. & Cons. 28 (May Suppl. Issue) : 2022

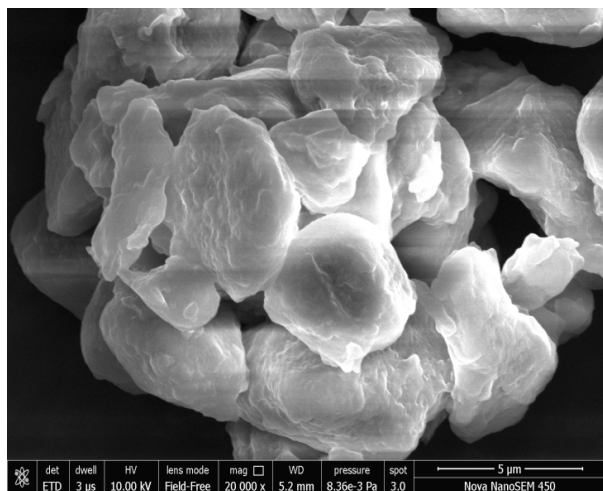
Fig. 5. FT-IR spectrum for the BE-TH resin

Fig. 6. Scanning Electron microscope image of BE-TH resin

Effect of pH: The pH of the solution controls the surface charge of the sorbent, as well as the degree of ionisation and speciation of the adsorbate, as it has a significant impact on metal adsorption. The results shown in Fig. 2 depict the sorption process to be more favourable near neutral conditions which is also reflected on the relatively low acidity of the chelating polymers. The results are in very good agreement with Mohammed A. Sharaf *et al.* (Sharaf, 2007). The maximum percentage removal of Fe and Pb were found at pH 3.5. These outcomes are also found parallel to that obtained by Rao et.al (Rao, 2005).

Effect of dose of BE-TH resin- The number of binding sites accessible for adsorption was dictated by the dose of BE-TH resin added to the solution. Using different BE-TH doses, the influence of the adsorbent dose on the percentage removal of metal ions was investigated which is given in Fig. 3. The results provided are consistent with those of Taha.M et al. (Taha, 2020).

Effect of contact time with BE-TH resin-The percentage removal of metal ions by BE-TH resin was very high initially, then slowed down later and finally it becomes constant shown in Fig. 4. The number of free binding sites is clearly responsible for the initial high adsorption rate. During the first stage of the adsorption process, the macroporus resin becomes practically saturated with metal ions. Following that, the metal ions must go farther and deeper into the pores, encountering significantly higher resistance, resulting in a lower driving force and adsorption rate. Approximately similar results were reported by Wang *et al.* with respect to Cd(II) (Wang, 2010)

FT-IR Analysis: The FT-IR interpretation of BE-TH resin confirmed the presence of hydroxamate group as it showed a peak at 3037cm⁻¹ which is correspond to –OH stretching in NHOH. Further the presence of epoxy group in BE-TH resin was confirmed by a distinct peak observed at 864cm⁻¹correspond to the –C-O-C- of oxirane (epoxy) group.

SEM Analysis : The Scanning electron microscopy technique is to study the surface topography of BE-TH resin. The macroporous resin allows big molecules or ions to not only enter but also to be eluted during the regrowth of the sponge-like structure. As a result, they serve two purposes: ion exchange via functional groups and reversible sorption and elution via macroporous structure. They are also immune to organic contamination, resulting in a longer resin life when compared to traditional gel type ion

exchangers, as well as significantly improved water quality due to organic species adsorption by the macroporous structure(Hubicki and Kolodyriska, 2012).

The BE-TH resin was prepared by cross-linking of Bajra with epichlorohydin and tryptophan amino acids modified with NH_4OH and HCl. The Hyroxamate and Epoxy group functional group in the BE-TH resinwere successfuly confirmed by FT-IR analysis. The batch equilibrium experiment and study of various parameters like effect of pH, effect of BE-TH resin doses and effect of contact time shows that BE-TH resin has good adsorbtion capacity. The BE-TH resin is found to be particularly effective for the adsorption of Cd(II), Zn(II) and Fe(II) metal ions.Based on the results of the experiments, we suggest that the cross linking BE-TH resin can be employed as a low-cost, convenient adsorbent for removing a variety of heavy metal ions from industrial wastewater in order to achieve the goals and objectives of green chemistry.

Acknowledgement

References

Ali, H. and Khan, E. 2018. Bioaccumulation of non-essential hazardous heavy metals and metalloids in freshwater fish. Risk to human health. *Environmental Chemistry Letters*. 16(3) : 903-917.

Ali, H., Khan, E. and Ilahi, I. 2019. Environmental chemistry and ecotoxicology of hazardous heavy metals: environmental persistence, toxicity, and bioaccumulation. *Journal of Chemistry*. 2019.

Abdel Raouf, M. S., Abdul Raheim, A. R. M. 2017. Removal of heavy metals from industrial waste water by biomass-based materials: A review. *Journal of Pollution Effects and Control.* 5 (1): 1–13.

Ahalya, N., Ramachandra, T. V. and Kanamadi, R. D. 2003. Biosorption of heavy metals. *Res. J. Chem. Environ*. 7(4) : 71-79.

Alcazar-Alay, S. C., and Meireles, M. A. A. 2015. Physicochemical properties, modifications and applications of starches from different botanical sources. *Food Science and Technology*. 35 : 215-236.

Ashogbon, A. O. and Akintayo, E. T. 2014. Recent trend in the physical and chemical modification of starches from different botanical sources: A review. *Starch.* 66(1-2) : 41-57.

Baraka, A., Hall, P. J. and Heslop, M. J. 2007. Preparation and characterization of melamine–formaldehyde–DTPA chelating resin and its use as an adsorbent for heavy metals removal from wastewater. *Reactive and Functional Polymers*. 67(7) : 585-600.

Barakat, M. A. 2011. New trends in removing heavy metals from industrial wastewater. *Arabian Journal of Chemistry*. 4(4) : 361-377.

Connell, D. W.O., Birkinshaw, C. and O'Dwyer, T. F. 2008. Heavy metal adsorbents prepared from the modification of cellulose: A review. *Bioresource Technology*. 99(15): 6709-6724.

Fu, Z. and Xi, S. 2020. The effects of heavy metals on human metabolism. *Toxicology Mechanisms and Methods*. 30(3) : 167-176.

Gode, F. and Pehlivan, E. 2006. Removal of chromium (III) from aqueous solutions using Lewatit S 100: the effect of pH, time, metal concentration and temperature. *Journal of Hazardous Materials*. 136(2) : 330-337

Haroon, M., Wang, L., Yu, H., Abbasi, N. M., Saleem, M., Khan, R. U. and Wu, J. 2016. Chemical modification of starch and its application as an adsorbent material. *Rsc Advances*. 6(82) : 78264-78285.

Holkar, C. R., Jadhav, A. J., Pinjari, D. V., Mahamuni, N. M. and Pandit, A. B. 2016. A critical review on textile wastewater treatments: possible approaches. *Journal of Environmental Management*. 182 : 351-366.

Huang, Y. L., Zheng, Y. J., Song, Z., Chi, D., Wee, A. T., and Quek, S. Y. 2018. The organic–2D transition metal dichalcogenide heterointerface. *Chemical Society Reviews*. 47(9) : 3241-3264.

Hubicki, Z. and Kolodyriska, D. 2012. *Selective removal of heavy metal ions from waters and waste waters using ion exchange methods*. Ion Exchange Technologies. 7: 193-240.

Korkmaz, C., Ay, Ö., Ersoysal, Y., Köroðlu, M. A., and Erdem, C. 2019. Heavy metal levels in muscle tissues of some fish species caught from north-east Mediterranean: evaluation of their effects on human health. *Journal of Food Composition and Analysis*. *81*: 1-9.

Pasichnaya, Y. A., Gorbatiuk, L. O., Arsan, O. M., Platonov, N. A., Burmistrenko, S. P., Godlevskaya, O. A. and Gopinath, A. 2020. Assessment of a possibility of the use of aquatic macrophytes for biomonitoring and phytoindication of the contamination of natural waters by heavy metals. *Hydrobiological Journal*. 56(1).

Punia, S., Kumar, M., Siroha, A. K., Kennedy, J. F., Dhull, S. B. and Whiteside, W. S. 2021. Pearl millet grain as an emerging source of starch: A review on its structure, physicochemical properties, functionalization, and industrial applications. *Carbohydrate Polymers*. 260 : 117776.

Raigar Bala, M., Hooda, S., and Bargujar, S. 2021. Synthesis, Characterization and Application of Novel Guar gum-n,ndimethylaniline resin for waste water treat-

S526

Eco. Env. & Cons. 28 (May Suppl. Issue) : 2022

ment. *International Journal of Recent Scientific Research.* 12(6) : 41932-4193.

Rao, K. S.,Dash, P. K., Sarangi, G., Roy, G., Choudhary and Misra, V. N. 2005. Treatment of wastewater containing Pb and Fe using ionexchange techniques. *Journal of Chemical Technology & Biotechnology.* 80(8): 892–898.

Sharaf, M. A., Sayed, S. A., Younis, A. A., Farag, A. B. and Arida, H. A. 2007. Removal of trace contaminants from water using new chelating resins. *Analytical Letters.* 40(18) : 3443-3456.

Song, H. 2010. Synthesis and application of cationic starch graft polymer by using the complex initiation system. *Carbohydrate Polymers.* 82(3) : 768-771.

Taha, M. H., Masoud, A. M., Khawassek. Y., Hussein, A. E., Aly, H. F. and Guibal, E. 2020. Cadmium and iron removal from phosphoric acid using commercial resins for purification purpose. *Environmental Science and Pollution Research.* 27 (25).

Tkaczyk, A., Mitrowska, K., and Posyniak, A. 2020. Synthetic organic dyes as contaminants of the aquatic environment and their implications for ecosystems: A review. *Science of the Total Environment.* 717 : 137222.

Wang, F. Y., Wang, H. and Ma, J. W. 2010. Adsorption of cadmium (II) ions from aqueous solution by a new low-cost adsorbent—Bamboo charcoal. *Journal of Hazardous Materials.* 177(1-3): 300-306.

World Health Organization. 2011. WHO, *Adverse health effects of heavy metals in children. Children's Health and the Environment.* WHO *Training Package for the Health Sector. World Health Organization.* (*2020)*.

Yaseen, D. A. and Scholz, M. 2019. Textile dye wastewater characteristics and constituents of synthetic effluents: a critical review. *International journal of environmental science and technology.* 16(2): 1193-1226.