Research Journal of Chemical Sciences ISSN 2231-606X
Vol. **12(1),** 36-41, February **(2022)** *Res. J. Chem. Sci.*

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, Basni, Jodhpur, India) by batch method

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Available online at: www.isca.in, www.isca.me
Received 20th April 2021, revised 8th September 2021, accepted 25th December 2021

Abstract

In the laboratory, anthranilic acid (CAA) as a functional group was added to a natural cellulose-based modified ion exchange resin. Using the ion exchange mechanism, this modified ion exchange resin was employed to recover harmful heavy metal ions from contaminated industrial waste water. CAA resin was utilised to extract Cd(II) metal ions from aqueous solutions containing metal ions and industrial effluents containing Cd(II) ions from the Prince Steel Industry in Jodhpur. At pH 7, the Cd(II) ions showed the most adsorption on CAA resin. The resin with the highest Kd value is at this pH.

Keywords: Ion exchange resin, industrial effluents, metal ions and adsorption.

Introduction

Because of their selectivity against metal cations, ion exchange resin has been used in the deletion and extraction of transition hazardous heavy metal ions from polluted solutions. Because of their interplay and selectivity. Ion exchange systems based on natural polysaccharides are widely employed[1].

A modified approach was used to create a novel cellulose[2] based resin with multiple acidic functional groups. This sort of cellulose polysaccharide modified resin was quite effective and suited for recovering heavy hazardous metal ions from contaminated[3] waste-water businesses. Removal of such metal ions as Cd (II) using CAA modified ion exchange resin, which has been shown to be one of the most successful ways due to its environmental friendliness, low cost, and speed, because most of these resins have a di-viny benzene styrene backbone. And and petrochemicals are hydrophobic, expensive, and not as environmentally benign as they were were[4] Natural polysaccharide resins have a hydrophilic backbone and are quite inexpensive. The extraction and concentration of hazardous metal ions in solution, as well as the recovery of toxic heavy metal ions from industrial waste, mineral, textile, and metallurgical industries, are more effective, efficient, and compatible using polysaccharide-based cation ion exchange resin.

Object: The goal of this study is to create such chemicals utilizing basic ingredients that are readily available in the area, particularly from industrial or agricultural sources. Among natural polymers, I chose cellulose powder because it is readily available and has a wide range of applications. Cellulose has a wide range of applications, both in its natural and modified forms.

Methodology

I've tried to make polysaccharide matrix-based ion exchangers with various functional groups inserted into them. Cellulose provides a hydrophilic foundation for chelating resins, which are effective and compatible in the separation of metal ions from solution and industrial effluent. CAA resin was used to remove Cd (II) from aqueous solutions and in the steel industry[5].

The manufacture of cellulose or polysaccharide derivatives presents a number of challenges. Because cellulose contains both crystalline and amorphous regions, a precise treatment with sodium hydroxide is required before usage. The lack of homogeneity in NaOH distribution can cause serious issues with product quality and property control. These reactions take place at atmospheric pressure.

Because cellulose is a good insulator and these reactions are exothermic, the process is designed to allow for enough heat transport to avoid runaway reactions and hot patches, which can result in quality degradation[6]. The cellulose anthranilic acid (CAA) resin, a natural polysaccharide ion exchange has been created and is utilized to extract heavy hazardous metal ions from contaminated and waste water from the steel industry.

Epichlorohydrin was employed to etherify cellulose, and the resulting derivatives were then treated with polyamines. Epichlorohydrin is a white, mobile liquid with an aroma similar to chloroform.

Epoxy chloropropane is the most favored coupling agent for derivatisation of polysaccharides since it is highly reactive in nature and is frequently connected with a substance having an active (i.e. quickly reacted) hydrogen atom through the epoxy component. The introduction of an epoxide group into the polysaccharide according to the following technique is used to check for crossed linking or degree of cross linking:

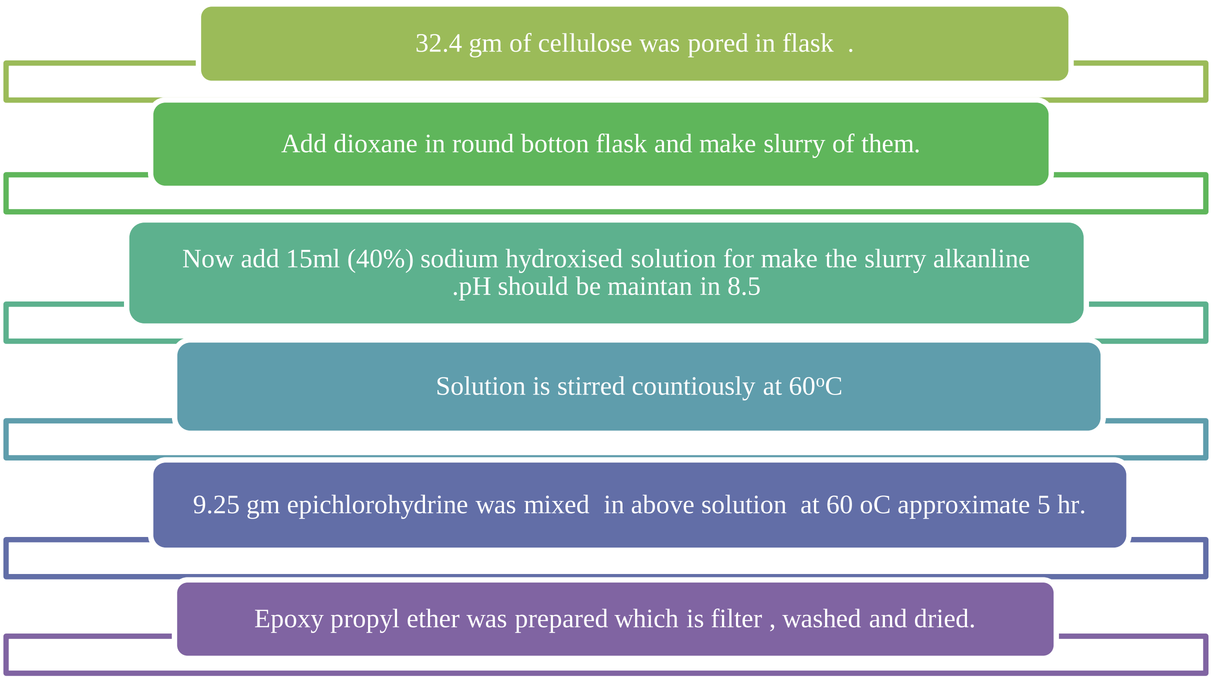

Figure-1: Synthesis of epoxy ether of polysaccharide[7].

Synthesis of cellulose Anthranilic Acid (CAA) Resin[7]

The synthesis of cellulose Anthranilic Acid resin is in two steps is as following:

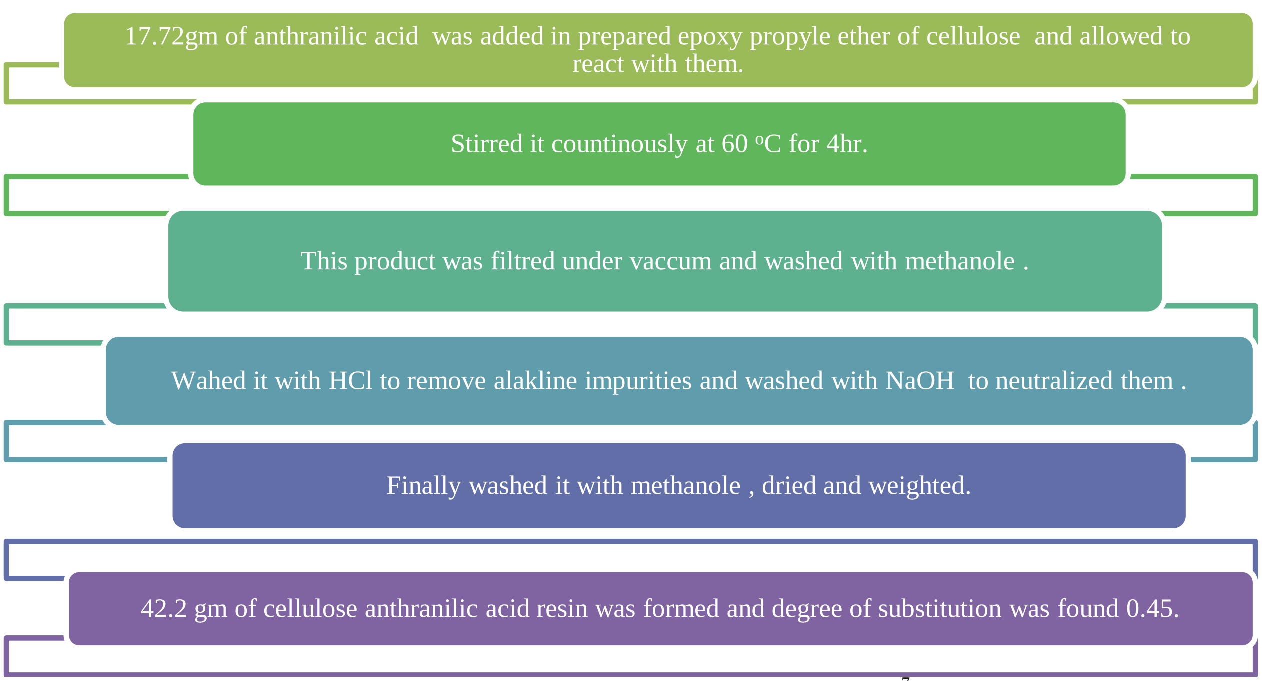

Figure-2: Flow diagram of Synthesis of CAA resin[7].

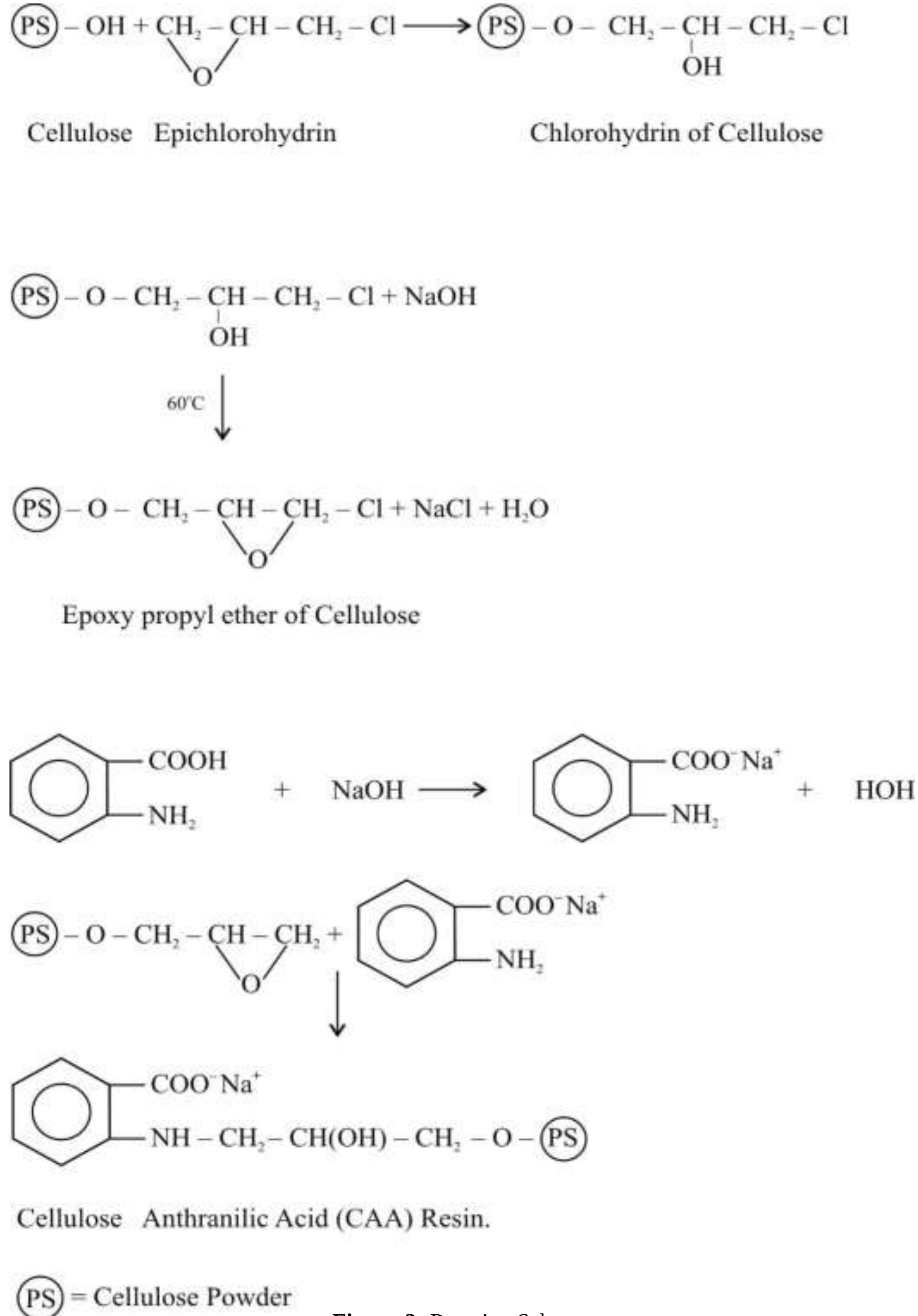

Figure-3: Reaction Scheme.

FTIR Characterization of Cellulose Anthranilic Acid (CAA) Resin: In H^+ form, FTIR spectrum investigation of produced CAA resin was performed. C–H stretching at 2927.7cm^{-1}, – C–H stretching at 2858.3cm^{-1}, N–H bending at 1508.2cm–1, >C=0 stretches of carboxylic acid at 1720.4cm^{-1}, –OH hydrogen bonded broad stretches at 3444.6 cm^{-1} and N–H stretches perck at 3442 cm^{-1} are the distinctive bonds identified in the spectra of CAA. Figure-4 shows the FTIR spectrum.

Instruments: pH meter: The pH readings were determined using a Digital pH meter model 5651 from Electronics Corporation of India (ECI).

Varian model 175 (AAS) Atomic Absorption is a term that refers to the process of the concentration of metal ions in traces was determined quantitatively using a spectrophotometer.

Metrex Scientific Pvt. Ltd. manufactured the magnetic stirrer that was used.

Preparation of Stock Solution: Cadmium Sulphate Cd (II): We took 2.015g of $CdSO_4$. H_2O and dissolved it in 1.5ml of conc. The volume of sulphuric acid was increased to 1000 mL in a volumetric flask, yielding a solution containing 1mg of Cd (II) per mL.

Determination of Kd value of Cd (II) metal ion on CAA resin: Chelation of Cadmium (II) on CAA resin[7]: Appropriate volumes of 0.2M acetic acid and 0.2M sodium acetate were poured to several glass stoppered conical flasks to achieve the desired pH range of 2 to 7. 0.070g of dry resin and 1 ml of 1000ppm Cd (II) solution were added to each flask in the same way that suitable volumes of 0.2M NH_4OH and 0.2M NH_4Cl were added to reach the pH of 8. The contents were magnetically agitated for 1 hour before being filtered. AAS was used to test the filtrates for cadmium. Table-1 summarizes the findings.

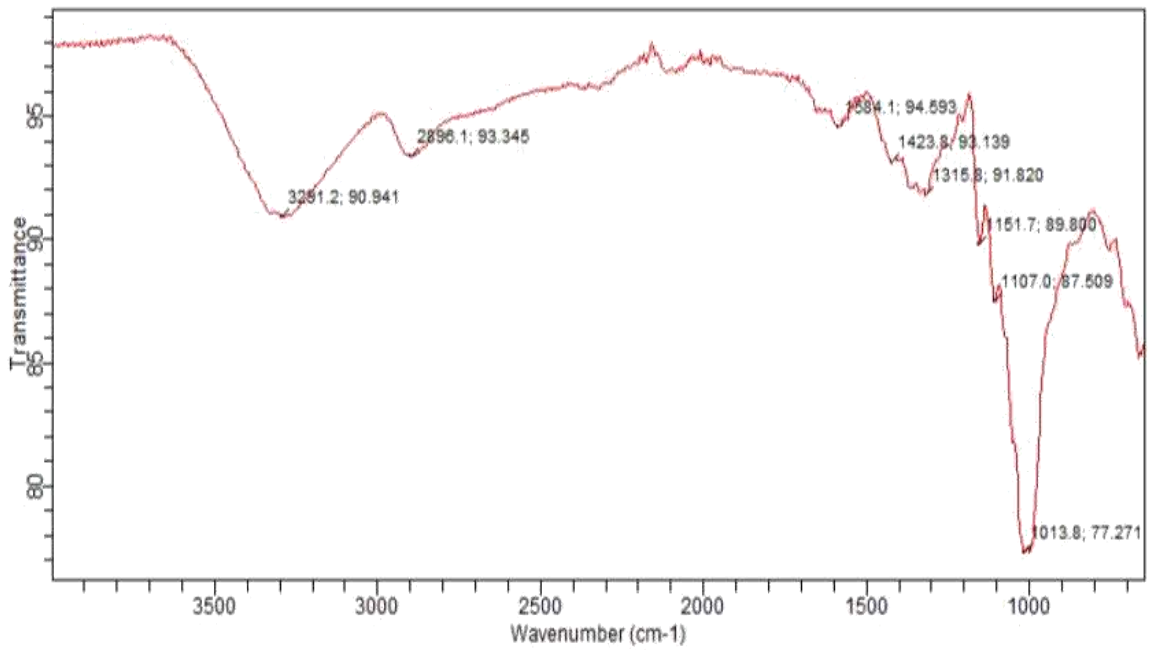

Figure-4: FTIR spectra of Cellulose Anthranilic Acid (CAA) Resin.

Table-1: 'K_D' values for Cd (II) on CAA resin.

pH	Absorbance	Cd (II) in Filtrate (ppm)	Cd (II) in Solution (mg)	Cd (II) in resin (mg)	'K_d'	% Adsorption of Cd (II) By ion exchanger	Metal Exchange Capacity mg/g
2	1.395	6.2	0.2525	0.7475	1722.35	74.75	10.6785
3	1.335	5.7	0.2355	0.7645	1916.04	76.45	10.9214
4	1.255	4.8	0.1975	0.8025	2388.39	80.25	11.4642
5	1.965	4.4	0.1795	0.8205	2663.96	82.05	11.7214
6	1.865	4.1	0.1675	0.8325	2900.69	83.25	11.8939
7	0.795	3.5	0.1425	0.8575	3500.00	85.75	19.2500
8	0.995	4.2	0.1735	0.8265	2811.22	82.65	11.8071

Inference: It is observed that maximum adsorption of Cd (II) on CAA resin at pH '7.0' in the presence of acetic acid and sodium acetate buffer[7].

Determination of K_d by batch method for metal ions of prince steel industry, Jodhpur (RAJ.): The removal of heavy metal ion cadmium from effluents from smelters, mines, and other non-ferrous metal businesses is a severe challenge. These heavy metal ions are detected in excess of the allowable limit in the effluent. As a result, more complicated treatment is required to remove the heavy[7] metal ions from these companies' effluent. Cation exchangers can successfully lower harmful metal ion concentrations to a safe level.

In light of the foregoing, we synthesized and applied CAA to the treatment of steel industry wastewater. Steel Industries in Jodhpur, Rajasthan, provided an effluent sample containing heavy metal ions.

As illustrated below, this sample contains heavy metal ions as well as other metal ions.

Table-2: Characteristics of effluents contaminated with heavy metal ions obtained from Steel Industries, Jodhpur (India).

Color	Dirty Brown/Green
pH	4.3
Total Hardness (ppm)	833
Various ions concentration in ppm	
Lead	0.65
Zinc	7.24
Copper	0.74
Iron	1.02
Cadmium	0.12

The Batch technique was used to estimate the Kd of metal ions on resins. In all cases, 100mL of sample solution was placed in a conical flask and the pH was adjusted using the appropriate buffer. 70 milligrams of resin were added to the solution and swirled for 2 hours on a magnetic stirrer to equilibrate the contents. Whitman filter paper No. 40 was used to filter the solution.

The metal ion concentration in the filtrate as well as the residue was determined using an atomic absorption spectrophotometer after the residue on the filter paper was equilibrated with 4N HCl. The calibration curves for various metal ions were plotted using AAS after evaluating a series of standard metal ion solutions. The calibration curves were used to quantify the concentration of metal ions in the filtrate, and Kd was calculated[7].

Table-3 shows the distribution coefficient (Kd) values of metal ions from Prince Steel Industry on CAA.

Results and discussion

CAA is a natural polysaccharide based resin which shows highly selectivity toward removal of toxic metal ions from stock solution of metal ions as well as industrial effluents. On the basis of the result we can concluded that kd value toward deletion of metal ions is increase and then decrease with rising value of pH of stock solution and effluents[8]. The equilibrium adsorption studies of Cd with CAA, resin at the pH of their maximum adsorption follows the result as shown below

Cd^{2+}
Kd value 3500.00

Cd^{2+} shows maximum adsorption at High pH 7. Thus the resin CAA shows high affinity for Cd^{2+}, at pH 7, therefore these metal ions can be separated from other metal ions at pH 7.

Thus we can conclude that modified resin of cellulose containing anthranilic acid as a functional group is very useful and suitable for extraction of selective metal ions from effluents.

CAA resin are now more considered one of the most effective and promising techniques due to very low cost and rapidness, because we know that most of them ion exchange resins was prepared by di-vinyl benzene styrene backbone and petrochemical which are very hydrophobic in nature, costly and not as eco-friendly as the were[9].

I have selected natural cellulose based resin CAA for deletion of toxic metal ions from industrial effluents because the natural polysaccharide resin has a hydrophilic backbone and very low cost.

Polysaccharide based cation ion exchanger resin are more effective, efficient and compatible for the separation and concentration of metal ions in solution, recovery of metal ions from steel industry effluents, textile, mineral and metallurgical industriesetc[10].

Conclusion

These reagents are dual functioning reagents, acting as flocculent cum selective ion binders. They can be used on a large scale on a commercial base. It is cheap and also available in abudance[11].

This experimental results which are reported in result section, validated that the CAA resin is an efficient and good adsorbent for deletion of metal ions from industrial effluents.

Table-3: Distribution coefficient Kd values of Cd (II) of prince steel industry on CAA resin

pH	Absorbance	Cd (II) in Filtrate (ppm)	Cd (II) in solution (mg)	Cd (II) in Resin (mg)	'K_d'	Metal Exchange Capacity(mg/g)
3	0.015	1.22	0.107	0.024	1235.07	1.50
4	0.013	2.70	0.098	0.027	1508.33	4.07
5	0.009	3.12	0.083	0.035	2191.71	6.83
6	0.007	3.53	0.055	0.043	4148.27	14.64
7	0.005	3.68	0.047	0.051	5766.57	21.22

Acknowledgment

I would like to express thanks to my research guide Dr. Aresh Vikram Singh, Professor, Department of Chemistry, Jai Narain Vyas University, Jodhpur, for his excellent guidance, encouragement, motivation and suggestions.

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