



Synthesis of Natural Polysaccharide based Cellulose Anthranilic Acid (CAA) Resin for Removal of Toxic Metal Ions Pb(II) and Fe(II) From Industrial Effluent's by Batch Method and Their Physical Characterizations

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ABSTRACT

A cellulose based natural resin containing anthranilic acid as a functional group has been synthesized in laboratory and their adsorption behavior for toxic metal ions has been determined by using batch method and column separation experiment. The Cellulose anthranilic acid resin (CAA) was characterized on the basis of ion exchange capacity, bulk density, FTIR spectra. The CAA resin selectively remove heavy toxic metal ions from industrial effluents. The resin used for removal of heavy metal ions as Fe⁺² and Pb⁺² from aqueous solution and effluents of prince steel industry, Jodhpur. Fe⁺² and Pb⁺² shows maximum adsorption on CAA resin at pH 5 and 3.

KEY WORDS : Natural resin, industrial effluents, adsorption behavior and toxic metal ions.

Received 18.06.2021

Revised 26.07.2021

Accepted 03.08.2021

INTRODUCTION

Ion exchange technology has proved to be cost effective compared to chemical precipitation and solvent extraction techniques. For the effluent to be discharged to a sewage or for its reuse, it has to be treated with selective ion exchanger [1].

The removal of metal ions from and industrial waste is attracting the attention of scientists and technologists, due to limitations of conventional water treatment process. Environment-friendly and low-cost technologies to being developed on promising materials including natural polymers[2] such as cellulose, starch, guar gum, chitin etc., which are not only eco-friendly and cost-effective but are effective also in remediation of common effluents present in the water and many technology for reduction of toxicity order to meet technology based removal of heavy metals from industrial waste water[3].

But now a days due to limits on of conventional water treatment process ion exchange tests are attracting the attention of scientist and technologist for the removal of metal ions from sewage and industrial waste and this process of separation of toxic Pb²⁺ metal ions from aqueous solution using strongly acidic cation exchange resin[4].

Ion exchange technologies are environment friendly and low-cost technologies which are being developed by promising materials including natural polymers. Natural polymers like cellulose, alginic acid, starch, guar gum, chitin etc offer an endless source of raw materials[5,6].

Chelating resins take up heavy metal cations[7,8] chelating ion exchangers behave chromatographically so that it is not practical for the streams containing more than one metals[9]. Therefore, a selective chelating cation or anion exchange resins are required for the treatment of such streams. Due to rising prices of petroleum products, polysaccharide matrix has been selected for the removal of metal ions from effluents.

In recent year, many techniques have been studied for the development of cheaper and more efficient natural biopolymers. biopolymer represent an interesting and smart alternative as absorbent because of their particular construction, physicochemical features, chemical permanence, great reactivity and outstanding choosiness to metals.

My research work depends on preparation of natural biopolymer-based ion exchange resin, in which chelating functional group have been incorporated. This type of insoluble functionalized resin provides flexible, wide working range, high stability and good capacity toward metal ions.

PHYSICAL CHARACTERIZATION OF CAA RESIN

FTIR Characterization

Agilent Technology Cary 630 FTIR instrument was employed for all the FTIR Spectral analysis of the synthesized resin [12].

FTIR Characterization of Cellulose Anthranilic Acid (CAA) Resin

FTIR spectral analysis of resin was done in H⁺ form. The characteristic bonds observed in the spectra of CAA results from C–H stretching at 2927.7 cm⁻¹, –C–H stretching at 2858.3 cm⁻¹, N–H bending at 1508.2 cm⁻¹, >C=O stretches of carboxylic acid at 1720.4 cm⁻¹, and –OH hydrogen bonded broad stretches at 3444.6 cm⁻¹ and N–H stretches perck at 3442 cm⁻¹.

The FTIR spectra is shown in Fig. 2

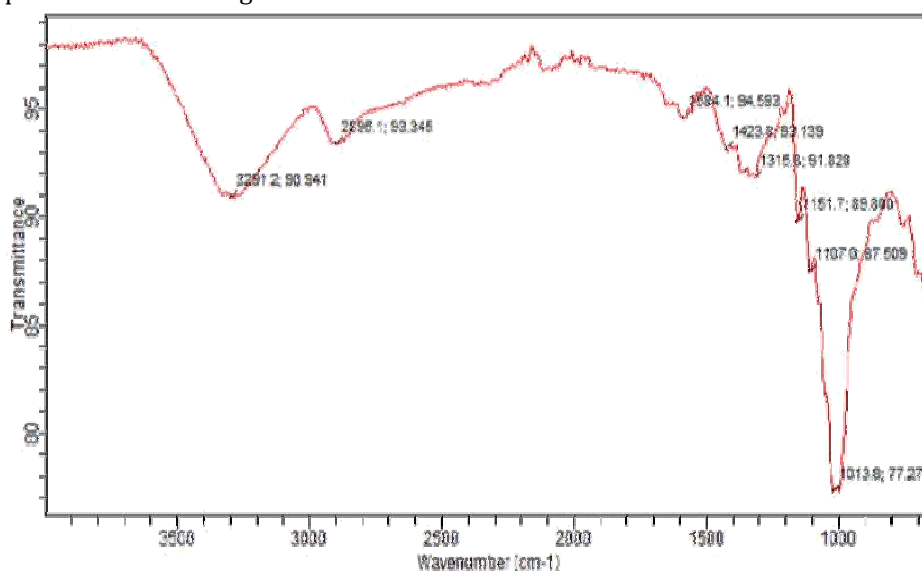


Fig.2 FTIR spectra of Cellulose Anthranilic Acid (CAA) Resin

Moisture Contents

A physical property of the ion exchange resin with changes in cross linkage is the moisture contents of the resin.

Cellulose Anthranilic Acid (Caa)

1 g of the resin in hydrogen form was taken and dried to a constant weight in vacuum desiccator at 75 °C for 24 hours and the resin was weighted.

The weight of dried resin	:	0.92 g
Weight of the moisture	:	0.08 gm
Moisture percentage	:	8%

Ion Exchange Capacity Determination

The total capacity of an ion exchange resin is define as the total number of chemical equivalents available for exchange per some unit weight or unit volume of resin. The capacity may be expressed in terms of milli equivalents per dry gram of resin or in terms of milli equivalents per millilitre of wet resin.

This situation is reversed when a wet volume basis is used to measure [12] capacity on a resin. Although few functional groups are introduced into a highly cross-linked resin. Thus the capacity on a wet volume basis increases as cross linking increases.

Resin capacity is usually expressed in terms of equivalents per litre (eq/L) of resin. An equivalent is the molecular weight in grams of the compound divided by its electrical charge, or valency. For example a resin with an exchange capacity of 1 eq/L could remove 35.7 g divalent zinc (Zn²⁺, molecular weight of 65) from solution.

The determining of total ion exchange capacity of the synthesized[13] resin by following method Back titration procedure was followed for the determination of capacity of resin. One gram resin was taken in an Erlenmayer flask and 200 ml of standardized NaOH (0.05N) containing 5 ml of 5% NaCl solution was added and was allowed to stand overnight. 25 ml aliquot of supernatant solution was back titrated with standard solution of 0.05 N HCl using phenolphthalein as indicator. Finally total ion exchange capacity [Q(Meq/g)] was calculated using the formula:

$$Q \text{ (Meq/g)} = \frac{(0.05N \times V_1) - 8(0.05N \times V_2)}{M}$$

$V_1 =$ Volume of 0.05 N NaOH solution
 $V_2 =$ Volume of 0.05 N HCl consumed

$$Q \text{ (Meq/g)} = \frac{(0.05 \times 200) - 8(0.05 \times 13.5)}{0.85}$$

$$= 10 - 8(0.675) / 0.85$$

$$= 5.41$$

Bulk Density Of The Dry Resin**Procedure:**

10 g of the resin dried to a constant weight and it was poured to a 100 cm³ measuring cylinder. The cylinder was poured gently on a hard rubber filter until the volume of the resin does not change. The volume of the stationary layer was read. The results are as under:

Resin	Bulk Density (g/cm ³)
CAA	1.39

pH Titration Of CAA Resin

The cellulose derivative were firstly converted to hydrogen ion form. The resins were then washed with water to remove excess acid and dried at 50° C overnight. 0.1 g portion of the resins were taken in 8–9 different flasks successively decreasing amount of 1 n NaCl solution was added to each flask and increasing amount of 0.1 N NaOH was added in successive flasks. Deionized water was then added to each flask as required to keep the ratio of solution volume to resin weight constant (25 ml solution per 0.1 g of resin). The tightly closed flask were equilibrated by magnetic stirrer until the pH of the solution attained constant value. The observed pH values are given in the tables below

TABLE NO.1: pH TITRATION OF CROSS- LINKED CELLULOSE ANTHRANILIC ACID (CAA)

Flask No.	Volume of 0.1 N NaOH (ml)	Volume of 1 M NaCl (ml)	deionized water (ml)	Final pH
1	0.0	1.4	23.6	6.3
2	0.3	1.2	23.5	7.5
3	0.6	0.1	23.4	8.7
4	0.9	0.8	23.3	9.4
5	1.2	0.6	23.2	10.1
6	1.5	0.4	23.1	11.3
7	1.8	0.2	23.0	11.9
8	2.1	0.0	22.9	12.3

EXPERIMENT AND ANALYSIS**Preparation Of Stock Metal Solutions****(Ferrous Ammonium Sulphate)Fe (II)**

We take a volumetric flask and dissolved 7.022 gm of ferrous ammonium sulphate [(NH₄)₂(FeSO₄)₂.6H₂O]. It was dissolved in 2-3 ml conc. H₂SO₄ and the volume was made upto 1000 ml to give 1000 ppm Fe (II) Solution.

B. (Lead Nitrate)Pb(II)

We take a 1.5985 g of Pb(NO₃)₂, It was dissolved in minimum quantity of conc. HNO₃ in a 1000 ml volumetric flask, volume was made up to the mark by adding demineralized water. The resultant solution contains 1000 ppm lead.

Instruments

pH meter: Digital pH meter model 5651, supplied by Electronics Corporation of India (ECI) was used in the determination of pH values.

AAS: Varian model 175 Atomic Absorption Spectrophotometer was used in the quantitative determination of metals ion concentration in traces.

Magnetic Stirrer: Magnetic stirrer manufactured by Metrex Scientific Pvt. Ltd. was used.

Determination Of Distribution Coefficient By Batch Method

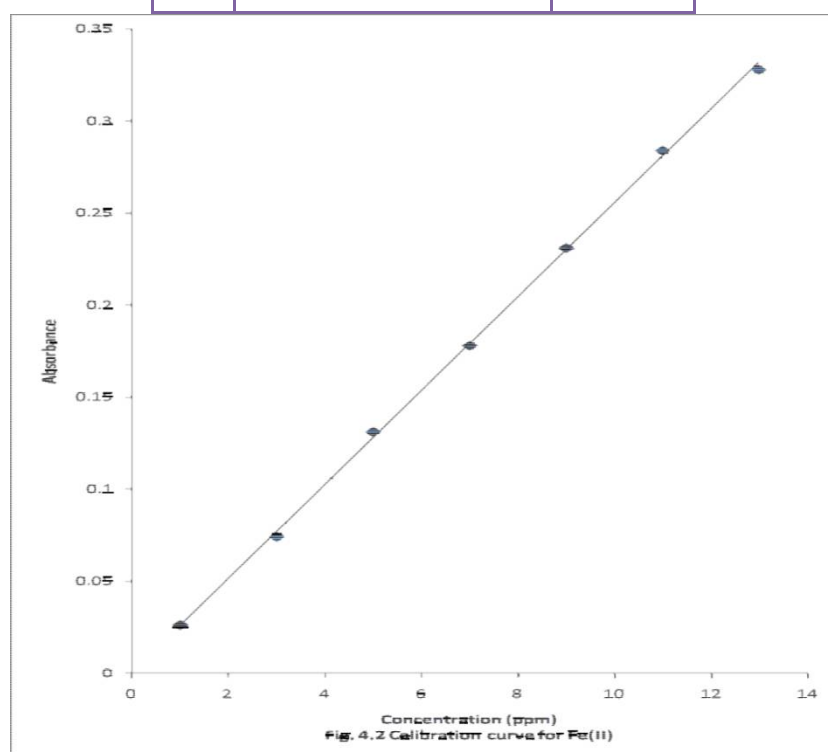
The molar distribution coefficient 'K_d' of metals showing pronounced adsorption on chelating resins is Fe(II) and Pb(II), were determined by batch method[14]. The weighed amount of different resins were used.

The concentration of metal ion in filtrates were determined using corresponding calibration curve. Finally the distribution coefficient were calculated using the formula,

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

TABLE NO.2: DETERMINATION OF DISTRIBUTION COEFFICIENT FOR IRON FE (II) SOLUTION

S. No.	Concentration (ppm)	Absorbance
1	1	0.026
2	3	0.074
3	5	0.131
4	7	0.178
5	9	0.231
6	11	0.284
7	13	0.328



The calibration curve is given in Fig. 3

Chelation of Fe (II) on CAA resin

In different glass stoppered conical flasks appropriate amounts of 0.2 M acetic acid and 0.2 M sodium acetate were added to get the desired pH i.e. 2 to 7. In the same way appropriate amounts of 0.2 M NH_4OH and 0.2 M NH_4Cl were added to get the pH of 8, 0.070 g of the dry resin and 1ml of 1000 ppm Fe(II) solution was added to each flask. The contents were stirred magnetically for 1 hour and then filtered. The filtrates were analysed for iron. The results are given in Table 3

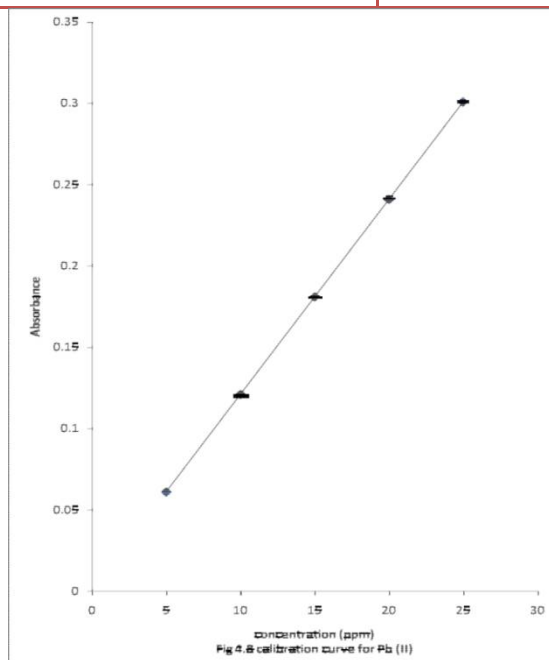
TABLE NO.3: ' K_D ' VALUES FOR FE (II) ON CAA RESIN

pH	Absorbance	Conc. Of Fe (II) in Filtrate	Amount of Fe (II) in solution	Amount of Fe (II) in Resin	' K_d '	% Absorption of Fe (II)	Metal Exchange Capacity
		(ppm)	(mg)	(mg)		by resin	mg/g
2	0.435	16.7	0.6854	0.3146	269.11	31.46	4.4941
3	0.318	12.5	0.5150	0.4850	554.28	48.50	6.9285
4	0.163	6.71	0.2755	0.7245	1544.77	72.45	10.3448
5	0.153	2.2	0.0922	0.9078	5894.80	90.78	12.9685
6	0.135	3.1	0.1245	0.8755	4034.56	87.55	12.5071
7	0.155	5.3	0.2156	0.7844	2114.28	78.44	11.2056
8	0.296	11.3	0.4655	0.5345	675.72	53.45	7.6356

Inference: Maximum distribution coefficient value for Iron (II) on CAA resin is attained at pH 5.

TABLE NO. 4: Determination of Distribution coefficient for lead Pb (II) Absorbance of Standard Lead Solution

S.No.	Concentration(ppm)	Absorbance
1	5	0.061
2	10	0.121
3	15	0.181
4	20	0.241
5	25	0.301



The calibration Curve is given in Fig 4

Chelation of Lead on CAA resin

In different glass stoppered conical flasks appropriate amounts of 0.2 M acetic acid and 0.2 M sodium acetate were added to get the desired pH i.e. 2 to 7. In the same way appropriate amounts of 0.2 M NH_4OH and 0.2 M NH_4Cl were added to get the pH of 8. 0.070 g of the dry resin and 1 ml of 1000 ppm Pb(II) solution was added to each flask. The contents were stirred magnetically for 1 hour and then filtered. The filtrates were analysed for lead by CAA. The results are given in Table 5

TABLE NO. 5 'K_d' VALUES FOR PB (II) ON CAA RESIN

Ph	Absorbance	Conc. of	Amount of	Amount	'K _d '	%	Metal
		Pb (II) in filtrate (ppm)	Pb (II) in solution (mg)	of Pb (II) in (mg)		Adsorption of Pb (II) by resin	Exchange Capacity mg/g
2	0.209	18.20	0.7465	0.2535	199.05	25.35	3.62
3	0.203	16.91	0.6935	0.3065	259.08	30.65	4.378
4	0.217	18.45	0.7565	0.2435	189.05	24.35	3.47
5	0.235	19.91	0.8165	0.1835	131.73	18.35	2.621
6	0.245	20.37	0.8355	0.1645	115.76	16.45	2.34
7	0.265	21.86	0.8965	0.1035	67.82	10.35	1.47
8	0.273	22.23	0.9115	0.0885	56.69	8.85	1.25

Inference: Lead shows maximum adsorption on the pH 3 at on the resin.

Determination Of K_d By Batch Method For Metal Ions Of Prince Steel Industry, Jodhpur (Raj.)

The effluents from smelters, mines and other non ferrous metal industries pose a serious problem in the removal of heavy metal ions i.e. copper, lead, zinc, cadmium and iron. These heavy metal ions are present in the effluent at a level above the permissible limit. The lime treatment considerably reduces the concentration of undesirable metal ions, however such treatment still leaves the residual metal ions concentration at a level considered unsafe for discharge into stream. Therefore it is necessary to develop more sophisticated treatment to remove the heavy metal ions from the effluent of these industries. Cation exchangers can effectively reduce the concentration of toxic metal ions to a desired safe limit.

In context to above, we have synthesized and used CAA for the treatment of effluent of Prince Steel Industries. The Effluent sample containing heavy metal[15] ions was collected from the Prince Steel Industries, Jodhpur, Rajasthan. These sample contains heavy metal ions [16] along with other metal ions as shown in below Table 6

TABLE NO.6: Characteristics of effluents contaminated with heavy metal ions obtained from Prince Steel Industries, Jodhpur (Raj.)

Colour	Dirty Brown/Green
pH	4.3
Total Hardness (ppm)	833
Metal ions concentration in ppm	
Lead	0.65
Iron	1.02

The distribution coefficient K_d of metal ions on resins were determined by Batch method. In all cases for the determination of K_d, 100 ml sample solution was taken in a conical flask and the pH was adjusted by appropriate buffer. seventy milligrams of resin were added to the solution and stirred on a magnetic stirrer for 2 hours and the contents were equilibrated. The solution was filtered through whatman filter paper No. 40. The residue on the filter paper was equilibrated with 4N HCL and the metal ion concentration in the filtrate as well as in the residue was estimated using atomic absorption spectrophotometer. The calibration curves for different metal ions were plotted, by analyzing a series of standard solutions of metal ions using AAS.

The concentration of metal ion in filtrate were determined by the calibration curves and distribution coefficient K_d were calculated using the formula:

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

The distribution coefficient (K_d) values of metal ions of Prince Steel Industry on CAA resin are given in table 7.

TABLE NO.7: DISTRIBUTION COEFFICIENT (K_d) VALUES OF Fe (II) OF PRINCE STEEL INDUSTRY ON CAA RESIN

pH	Absorbance	Conc. Of Fe (II) In Filtrate (ppm)	Amount of Fe (II) in Solution (mg)	Amount of Fe (II) in resin (mg)	' K_d '	Metal Exchange Capacity (mg/g)
3	0.025	3.6	0.162	0.0070	221.51	7.97
4	0.023	6.8	0.147	0.0063	3286.17	2.23
5	0.029	6.2	0.142	0.0031	3561.47	2.20
6	0.021	7.2	0.138	0.0029	3402.65	2.44
7	0.031	4.8	0.124	0.0022	7793.11	3.79

TABLE NO. 8: DISTRIBUTION COEFFICIENT (K_d) VALUES OF Pb (II) OF PRINCE STEEL INDUSTRY ON CAA RESIN

Ph	Absorbance	Conc. Of Pb (II) In Filtrate (ppm)	Amount of Pb (II) in Solution (mg)	Amount of Pb (II) in resin (mg)	' K_d '	Metal Exchange Capacity (mg/g)
3	0.015	1.26	0.19	0.050	1649.55	2.07
4	0.013	2.24	0.14	0.054	2069.37	4.63
5	0.011	3.16	0.13	0.065	3155.43	9.97
6	0.009	3.13	0.11	0.077	371.21	1.17
7	0.007	2.16	0.7	0.067	711.51	1.53

RESULT AND DISCUSSION

Resin CAA resin is very selective for the removal of heavy metal ion from their aqueous solution as well as samples of Prince Steel Industry, Jodhpur (Raj.). On the basis of results, it can be concluded that distribution coefficient (K_d) value first increases and then decreases with increasing pH. The equilibrium adsorption studies of Fe^{2+} and Pb^{2+} with CAA, resin at the pH of their maximum adsorption follows the following sequence:

The metal equilibrium studies with CAA resin follows the following order of ' K_d ' values at the pH of their maximum adsorption.

$Fe^{2+} > Pb^{2+}$

5894.8 > 259.08

Fe^{2+} and Pb^{2+} shows maximum adsorption at pH 5 and 3.

The ' K_d ' values of heavy metal ions with CAA resin of samples of Prince Steel Industry, Jodhpur (Raj.) follows the following sequence:

$Fe^{2+} > Pb^{2+}$

9910.62 > 3155.43

CONCLUSION

These reagents are dual functioning reagents, acting as flocculants cum selective ion binders. They can be used as large scale on the commercial basis. The polysaccharide used in the preparation of the reagents is basically a flocculant. It is cheap and also available in abundance. It is possible to incinerate the floc and recover the metals. Since the reagents are directly added to the effluent, there is no limitation to the quantity of water that can be treated in one batch. In case of conventional ion exchangers, such restrictions are imposed by the size of the resin bed and flow rate.

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 I have no word to express his greatness and kindness. He always supported me in my research work. I want to convey regards to all the teachers of Department of Chemistry J.N.V. University, Jodhpur for giving me good suggestions during my research.

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CITATION OF THIS ARTICLE

P S Bhati, I Singh, S Nagar and A V Singh . Synthesis of Natural Polysaccharide based Cellulose Anthranilic Acid (CAA) Resin for Removal of Toxic Metal Ions Pb(Ii) and Fe(Ii) From Industrial Effluent's by Batch Method and Their Physical Characterizations. Bull. Env.Pharmacol. Life Sci., Vol 10[9] August 2021 : 36-44