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SYNTHESIS OF CELLULOSE ANTHRANILIC ACID (CAA) RESIN AND USED IT FOR REMOVAL OF TOXIC METAL IONS AS Co (II), Ni (II), AND Cr (II) FROM INDUSTRIAL EFFLUNT'S USING BATCH METHOD AND DETERMINE THEIR DISTRIBUTION COFFICIENT (Kd) VALUE

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ABSTRACT

To synthesized cellulose based natural polysaccharide-based resin containing functional group as anthranilic acid in laboratory and determine their adsorption behavior by using batch method. The resin selectively removed toxic metal ions from industrial effluents. The CAA resin used for removal of toxic metal ions as Co (II), Ni (II) and Cr (II) from aqueous solution of these metal ions and industrial effluents. Ni^{2+} shows maximum adsorption at High pH 7 and Cr^{2+}, Co^{+2}, shows maximum adsorption at pH 4.

KEY WORDS

Natural resin, industrial effluents, adsorption behavior and toxic metal ions, Kd value.

1. INTRODUCTION

Water pollution due to the disposal of heavy metals continues to be a great concern worldwide. Consequently, the treatment of polluted industrial waste water remains a topic of global concern since waste water collected from municipalities, communities and industries must ultimately be returned to receiving or the land[1].

The pollution of heavy metals occurs in much industrial waste water such as produced by metal plating facilities, mining operations, battery manufacturing processes, the production of paints and pigments and ceramic and glass industries. This waste water from industries, commonly includes Co^{+2}, Ni^{+2} and Cr^{+2} Whenever toxic heavy metals are exposed to the natural ecosystem, accumulation of metal ion in human bodies will occurs through either direct intake or food chains. Therefore, heavy metals should be prevented from reaching the natural environment[3].

In the order to remove toxic heavy metals from water systems, conventional methods have been used such as chemical precipitation, coagulation, ion exchange, solvent extraction and filtration evaporation and membrane methods[4].

2. OBJECTS

The object of the present investigation is to develop such chemicals preferably using the raw materials that are locally available from industrial or agriculture resources. Among natural polymers cellulose is of special interest due to its easy availability and wide application spectrum both in natural as well as modified from.

In the view of the above we have attempted to develop polysaccharide matrix-based ion exchangers with different functional groups incorporated in the same. Cellulose gives hydrophilic base for the preparation of chelating resins and are effective and compatible in metal ion separation from solution and industrial effluent. Acid (CAA) resin was used for removal of Co (II), Ni (II) and Cr (II) in aq. solution and steel industries[5].
The natural polysaccharide cellulose anthranilic acid (CAA) resin, has been prepared is used for removal heavy metal ions from industries waste water.

3. METHODOLOGY

3.1 Synthesis Of Cellulose Anthranilic Acid (CAA) Resin

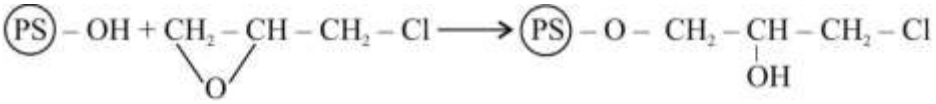
The Synthesis of cellulose Anthranilic Acid resin accomplished in the following steps.

A. Preparation Epoxy Propyl Ether of cellulose

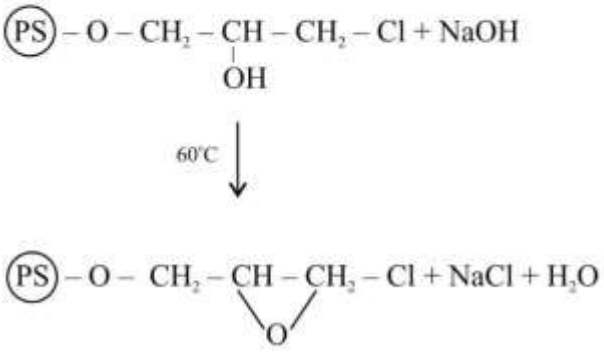
32.4 g. of cellulose powder (0.2 mol) was taken in round bottom flask and it was slurried with dioxane. 15 ml of 40% (w/v) sodium hydroxide was added to it to make it alkaline, till pH reached to 8.5 and the solution is stirred at 60°C. 9.25 g. epichlorohydrin (0.2 mole) was added with constant stirring. the stirring was further continued for 5 hours at 60°C. The product epoxy propyl ether of cellulose powder was filtered under vacuum[6] and washed with methanol to remove impurities and dried.

B. Preparation of cellulose Anthranilic Acid (CAA) Resin

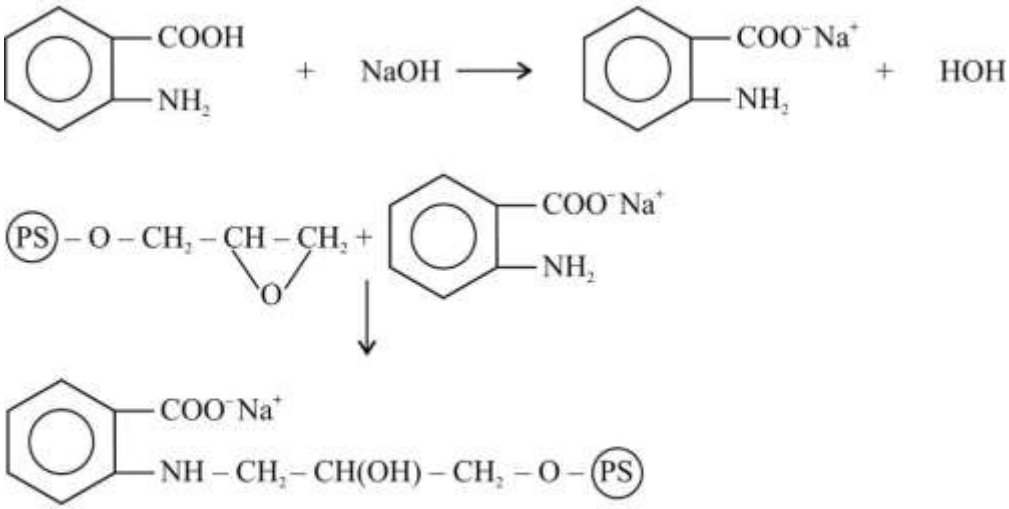
Epoxy propyl ether of cellulose was then allowed to react with 13.71g (0. 1 mole) of Anthranilic acid and the stirring was continued for another 4 hours at 60°C. The product so formed was filtered under vacuum and washed with methanol, containing few drops of HC1 to remove inorganic impurities and to neutralise excess of NaOH and finally washed with methanol and dried. The yield of cellulose anthranilic acid resin is 42.2 gm and degree of substitution (DS) is 0.45. The reaction scheme is shown in "Figure no 1.



Cellulose Epichlorohydrin Chlorohydrin of Cellulose



Epoxy propyl ether of Cellulose



Cellulose Anthranilic Acid (CAA) Resin.

(PS) = Cellulose Powder

4. EXPERIMENT AND ANALYSIS

4.1). Preparation Of Stock Solutions of Metal Ions

i) Chromium Chloride Cr (III)

We take a 5.1294 gm of chromium chloride [$CrC1_3.6H_2O$] was dissolved in minimum quantity of conc. H_2SO_4 in a 1000 ml volumetric flask. Volume was made upto the mark by adding demineralized water. The resultant solution contains 1000 ppm chromium.

ii) Nickel Sulphate Ni (II)

We take a 6.72 g Nickel Sulphate $NiSO_4.7H_2O$ It was dissolved in minimum quantity of conc. H_2SO_4 in a 1000 ml volumetric flask. Volume was made up-to the mark by adding demineralized water. The resultant solution contains 1000 ppm Nickel.

iii) Cobalt Nitrate Co (II)

We take a 5.59 g of cobalt Nitrate [$Co(NO_3)_2\ 6H_2O$] is dissolved in minimum quantity of conc. H_2SO_4 and the volume was made upto 1000 ml to give 1000 ppm Co (II) solution.

4.2). Determination Of Distribution Coefficient By Batch Method

The molar distribution coefficient 'K_d' of metals showing pronounced adsorption on chelating resins is Co (II), Ni (II), Cr (II) were determined by batch[7] method. 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,

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

i). Chelation of Cobalt (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 1 ml of 1000 ppm Co (II)

solution was added to each flask. The contents were stirred. magnetically for 1 hour and then filtered. The filtrates were analyzed for cobalt by AAS. The results are given in Table 1

TABLE NO.1

'K_d' values for Co (II) on CAA resin

pH	Absorbance	Conc. Of Co (II) in Filtrate (ppm)	Amount of Co (II) in solution (mg)	Amount of Co (II) in resin (mg)	'K_d'	% Adsorption of Co (II) by resin	Metal Exchange Capacity mg/g
2	0.341	21.4	0.8785	0.1215	81.10	12.15	1.7355
3	0.255	15.25	0.6255	0.3745	351.9	37.45	5.3488
4	0.215	11.8	0.4855	0.5145	622.88	51.45	7.3499
5	0.285	15.2	0.6225	0.3775	354.79	37.75	5.3928
6	0.283	15.3	0.6785	0.3715	346.87	37.15	5.3071
7	0.295	16.9	0.6935	0.3065	259.08	30.65	4.3784
8	0.315	18.2	0.7455	0.2545	199.76	25.45	3.6356

Inference: On CAA resin, cobalt shows highest value of distribution coefficient at pH 4.

ii). Chelation of Nickel (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 1 ml of 1000 ppm Ni (II) solution was added to each flask. The contents were stirred magnetically for I hour and then filtered. The filtrates were analyzed for nickel by AAS. The results are given in Table 2

TABLE NO.2

'K_d' Values for Ni (Ii) On CAA Resin

pH	Absorbance	Conc. Of Ni (II) in Filtrate (ppm)	Amount of Ni (II) in solution (mg)	Amount of Ni (II) in resin (mg)	'K_d'	% Adsorption of Ni (II) by resin	Metal Exchange Capacity mg/g
2	0.397	18.9	0.7765	0.2235	168.93	22.35	3.1927
3	0.385	19.1	0.7855	0.2145	160.43	21.45	3.0642
4	0.365	16.5	0.6785	0.3215	278.35	32.15	4.5927
5	0.345	15.9	0.6555	0.3445	309.52	34.45	4.9213
6	0.285	14.3	0.5885	0.4115	411.08	41.15	5.8784
7	0.255	12.7	0.5195	0.4805	540.49	48.05	6.8642
8	0.285	13.7	0.5635	0.4365	455.16	43.65	6.2356

Inference: The distribution values for Ni (II) on CAA resin increases with pH, with a maximum value of pH '7'

iii). Chelation of Chromium (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 was added to get the pH of 8. 0.070 gm of the dry resin and 1 ml of 1000 ppm Cr (III) solution was added to each flask. The contents were stirred magnetically for 1 hour and then filtered. The filtrates were analysed for chromium by AAS. The results are given in Table 3

TABLE NO.3

'K_d' Values for Cr (Iii) On CAA Resin

pH	Absorbance	Conc. Of Cr (III) in Filtrate (ppm)	Amount of Cr (III) in Solution (mg)	Amount of Cr (III) in resin (mg)	'K_d'	% Adsorption of Cr (III) by resin	Metal Exchange Capacity mg/g
2	0.305	12.5	0.5125	0.4875	557.14	48.75	6.9642
3	0.205	8.4	0.3465	0.6535	1111.39	65.35	9.3356
4	0.255	10.6	0.4355	0.5645	760.78	56.45	8.0642
5	0.335	12.6	0.5185	0.4815	545.91	48.15	6.8784
6	0.358	14.3	0.5855	0.4145	414.08	41.45	5.9213
7	0.375	15.2	0.6225	0.3775	354.79	37.75	5.3928
8	0.85	12.3	0.6265	0.3735	433.79	37.35	5.3356

Inference: It is seen that chromium shows maximum adsorption at the pH 3 on the CAA resin.

5. RESULT AND DISCUSSION

Resin CAA is highly selective for the removal of heavy metal ion from their aqueous[8] solution as well as industrial effluents. 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 Ni^{2+}, Co^{2}, Cr^{+2} with CAA resin at the pH of their maximum adsorption.

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

$Cr^{2+} > Co^{2+} > Ni^{2} >$

1111.39>622.88>540.49

6. CONCLUSION

Ni^{2+} shows maximum adsorption at High pH 7. Cr^{2+}, Co^{+2}, shows maximum adsorption at pH 4.
Thus the resin CAA shows high affinity for Ni^{2+} at pH 7, therefore these metal ions can be separated from other metal ions at pH 7.

7. ACKNOWLEDGMENT

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