Removal of Chromium (VI) using Synthesised 5-Amino-2-Hydroxy Benzene Sulphonic Acid derivative of saw dust

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Abstract

Removal of heavy metals from waste water is done for water treatment to avoid environmental pollution. In present work newly synthesised chelating resin, 5-Amino-2-Hydroxy Benzene Sulphonic Acid derivative of saw dust (AHBSASD) has been used for removal of Cr(VI) ions from polluted water samples prepared in laboratory. By chelation Cr(VI) ions are chelated on the newly synthesised chelating resins. The removal of Cr(VI) ions from polluted water by chelation process was studied as a function of pH (3.5-6), Contact time (60 min.), Initial Concentration (10ppm), doses of saw dust (0.1-0.6g) and Temperature (30±1°C). The concentration of Cr(VI) ions in the filtrate was determined using corresponding calibration curve. It was observed that the pH has marked effect on removal of Cr(VI). Result shows that about 68% removal of Cr(VI) takes place at pH at 5.54. At this pH chelation of Cr(VI) ions studied with varying amounts of resin having same initial concentration, temperature and contact time. It was observed that with increasing amount of AHBSASD resin the distribution coefficient (K_d) values increases and at 500 mg dose it reaches to maximum (81%) and remains constant at higher doses of resin.

Key Words: Chromium, Saw dust, Chelation, Chelating resin, Removal, Calibration Curve, AHBSASD, Absorbance.

Introduction

Toxic metals are added in aquatic system from industrial process, domestic sewage discharge and street dust. Heavy metals such as Hg, Pb, As, Co, Mn, Fe and Cr have been identified as deleterious to aquatic ecosystem and human health.[1-3]

Chromium is commonly found in waste water. Chromium is used in the manufacturer of stainless steel and other alloys. The trioxide is used in chrome

plating, copper stripping, photography and as a corrosion inhibitor. Chromium sulphate is used as mordant in textile manufacture, in leather tanning, in manufacturing green varnishes, paints, inks and glazes for porcelain. Chromium is also used in explosives and for preservative of wood. Waste from all the above industrial units can be a source of water pollution. Fertilizer materials are also a source of chromium pollution in water. Tri valent chromium has a law order of toxicity while hexa valent chromium is found to be much more toxic then the tri valent chromium. Chromium is very toxic by inhalation and dermal route and causes lung cancer, nasal irritation, nasal ulcer and hypersensitivity reactions like contact dermatitis and asthma. Chromium affects various components of the immune system and may result in immuno stimulation or immuno suppression. Chromium concentration in potable water supplies varies from 0.002 ppm to 0.1 ppm and in rain water it is about 0.003 ppm. The US EPA suggests 0.05 ppm as the chromium limit for domestic water supply. The environmental standers are usually set on the basis of chromium (VI) which is more toxic. The daily intake of Cr per person averages in the range 150 µg to 280 µg in different countries.

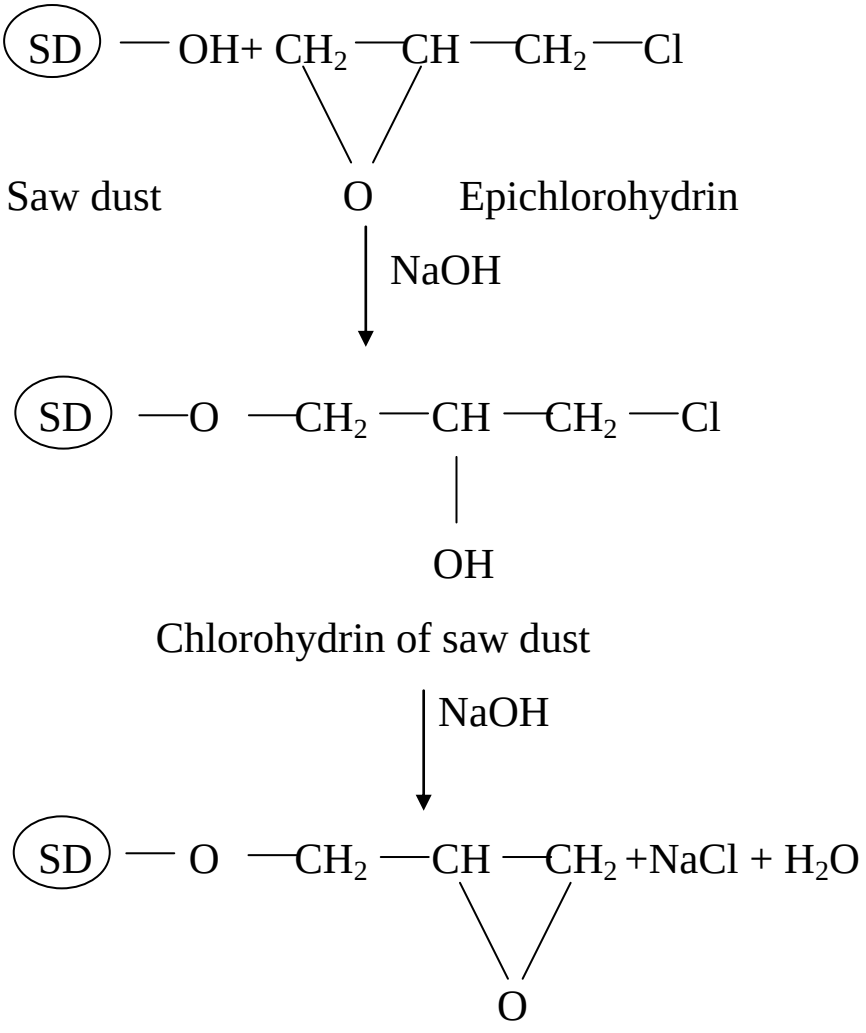
Many reports are available for removal of Cr (VI) from water and waste water using natural products and by products[4-15]. The present work deals with the study of removals of Cr (VI) from waste water using 5-Amino-2-Hydroxy Benzene Sulphonic Acid derivative of saw dust. The saw dust is selected as matrix because it is easily available and possess natural hydrophilicity which offers better compatibility for metal ions in solution. Saw dust resin may be economically viable substance for water treatment, if used in place of commercially high cost resin.

MATERIAL AND METHODS

(A) Synthesis of Cross Linked saw dust

486 g saw dust (corresponding to three anhydroglucose unit) was taken in a round bottom flask and it was slurred with dioxane. 15 ml of 40% (w/v) sodium hydroxide was added to it, to make it alkaline till pH reached 8.5. The contents of the flask were slurred magnetically at 45°C. Then 92.53 g (1 mole) epichlorohydrin was added with constant stirring. The stirring was further continued for four hours at 45°C.

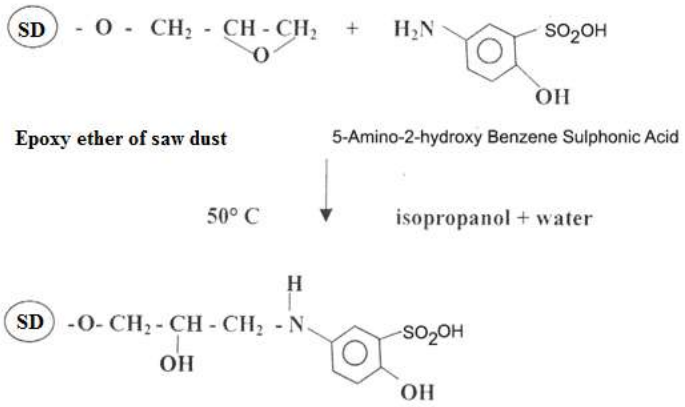
The reaction mixture was allowed to settle down. The supernatant liquid was decanted off and the product was filtered under vacuum and washed with 80% aqueous methanol containing few drops of nitric acid, to remove inorganic impurities and excess alkali in the contents. Washing was done till the filtrate was free from chloride ions and was no more alkaline. The washed product was dried in an oven at 40°C. Obtained cross linked saw dust was further used for derivatization.



Scheme 1 : Synthesis of Cross Linked Saw dust (Epoxy Ether of Saw dust)

(B) SYNTHESIS OF 5-AMINO-2-HYDROXY BENZENE SULPHONIC ACID DERIVATIVE OF SAW DUST (AHBSASD)

In a round bottom flask 0.01 mole of cross linked saw dust was taken and it was slurred with 70% aqueous isopropanol. 10 ml of 50% (w/v) aqueous sodium hydroxide was added to it gradually with continuous stirring at 45°C. Then 0.02 mole of 5-Amino-2-Hydroxy Benzene Sulphonic Acid was added slowly with stirring to the contents of flask. The stirring and heating was continued for 6 hours. The product thus formed was filtered on a Buchner funnel. Then washing of product was done with 50% aqueous methanol containing few drops of nitric acid to remove excess alkali and inorganic impurities. The washed product was dried in air and then was suspended in 0.1 N HCl and filtered immediately. The filtered product was successively washed with 0.1 N NaOH and 0.1 N HCl. The supernatant liquid was decanted and resin was washed several times to remove suspended particles and other impurities. The final washing was carried out with absolute alcohol and the product was dried under vacuum. The product was brownish powder.



Scheme 2 : Synthesis of 5-Amino-2-Hydroxy Benzene Sulphonic Acid derivative of saw dust

Reagents

All the chemicals used were of analytical grade obtained from E.Merck. Stock solutions of 2000 mg/L each of the Cr (VI) were prepared separately by dissolving required amounts in distilled water. Sample solutions of required concentrations were prepared by diluting the stock solutions. The pH of solutions was adjusted using 0.2M sodium acetate and 0.2M acetic acid.

Instrumentation

AGRONIC-511 digital pH meter was used to determine pH of the solutions. Spectrophotometric observations were obtained on an AIMIL-MAKE

"spectrochem" spectrophotometer. Magnetic stirrers manufactured by Metrex Scientific Pvt. Ltd. Were used for stirring.

Experimental Methods

Measurement of absorbance for standard Cr (VI) solutions and Calibration Curve

An aliquot (known vol.) of chromium (VI) solution was taken in a conical flask and was neutralized with concentrated NH_4OH till it becomes alkaline and then added slight excess of 18 N H_2SO_4 till it becomes acidic. Now added 4% $KMnO_4$ solution till dark red colour persists. Boiled the solution for 2 minutes. 2 ml sodium azide (0.5%) solution was added and boiled the whole solution till the colour faded completely. Cooled the contents and added 0.25 ml H_3PO_4. The solution was then transferred to a volumetric flask and diluted to 100 ml and mixed. Then 2.0 ml diphenyl carbazide solution (0.5% in acetone) was mixed thoroughly. Allowed to stand for 10 minutes. Cr (VI) reacts with diphenyl carbazide in acid medium to form a red-violet complex which is measured at 540 nm against a reagent blank. Calibration curve was plotted using chromium solutions of different concentrations comparing against solvent. The concentration of unknown solution can be determined by using the calibration curve.

Table 1 : Absorbance for standard Cr(VI) solutions

	Concentration (ppm)	Absorbance
1	2	0.06
2	4	0.12
3	6	0.19
4	8	0.26
5	10	0.32

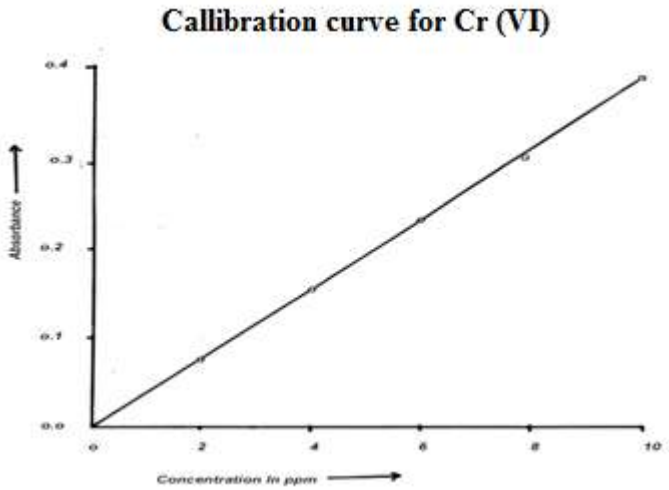


Figure 1 : Callibration Curve for Cr(VI) solutions

RESULT AND DISCUSSION

A. Chelation of Cr(VI) on constant amount of 5-Amino-2-Hydroxy Benzene Sulphonic Acid derivative of saw dust (AHBSASD) resin, with varying pH.

Different amounts of 0.2M acetic acid and 0.2M sodium acetate solution were added to get the desired pH (total volume of buffer in each case was 25ml). Now, 0.1g of dry resin and 25ml of 20ppm solution of Cr(VI) was added to each flask. The contents were equilibrated by magnetic stirring for 1 hour and filtered. Filtrates were analysed for the concentration of Cr(VI). The results are given in Table 2.

The distribution coefficient (K_d) and percentage removal of Cr(VI) are calculated by applying following Formula :-

$$K_d = \frac{\text{Amount of Cr(VI) in saw dust derivate (AHBSASD) Phase/g of dry saw dust derivate}}{\text{Amount of Cr(VI) Solution/ml of solution}}$$

$$\%\text{Removal of Cr(VI)} = \frac{\text{(Initial concentration of Cr (VI) sol. — Concentration of Cr(VI) solution after treatment with saw dust derivate)}}{\text{Initial concentration Cr(VI) solution}} \times 100$$

Table 2 : Chelation of Cr(VI) on constant amount of 5-Amino-2-Hydroxy Benzene Sulphonic Acid derivative of saw dust (AHBSASD) resin with varying pH.

Amount of AHBSASD resin added = 0.1 g Initial concentration = 10 ppm

Volume of Cr(VI) of 20 ppm = 25 ml

Total Volume = 50 ml Temperature = 30°±1°C

S. No.	Vol. of 0.2M acetic acid (ml)	Vol. of 0.2M sodium acetate (ml)	pH	O.D. of filtrate	Conc. Of Cr(VI) in filtrate (ppm)	Amount of Cr(VI) in sol. (mg)	Amount of Cr (VI) in AHBSASD (mg)	K_d	% removal
1	23	2	3.51	0.24	7.5	0.375	0.125	167	25
2	19	6	4.02	0.19	6.0	0.300	0.200	333	40
3	15	10	4.02	0.19	5.0	0.250	0.250	500	50
4	7	18	5.05	0.13	4.1	0.205	0.295	720	59
5	3	22	5.54	0.10	3.2	0.160	0.340	1062	68
6	1	24	6.03	0.14	4.4	0.220	0.280	636	56

Inference

It is observed that with the increase of pH the K_d values for Cr(VI) on AHBSASD increases. At pH 5.54 the distribution coefficient value is maximum (1062) and removal percentage is 68%. On pH more than 5.54 the K_d value and removal percentage decreases.

B. Chelation of Cr (VI) on varying amount of AHBSASD resin at constant pH.

Different amounts of AHBSASD resin were taken in each flask and 3 ml of 0.2M acetic acid 22 ml of & 0.2M sodium acetate were added to get the pH 5.54. Now 25 ml (20 ppm) solution of Cr(VI) was then added to each set. The contents were stirred magnetically and equilibrated over night. The contents were filtered and analysed. The results are given in Table 3.

Table 3 : Chelation of Cr(VI) on varying amount of AHBSASD resin at constant pH.

Volume of buffer = 25 ml Initial concentration = 10 ppm

(3 ml. Acetic acid + 22 ml Na-Ac)

Volume of Cr(VI) of 20 ppm = 25 ml Temperature = 30°C

Total Volume = 50 ml pH = 5.54

S.No.	Amount of AHBSASD added (mg)	O.D. of filterate	Conc. Of Cr(VI) in filterate (ppm)	Amount of Cr(VI) in sol. (mg)	Amount of Cr(VI) in AHBSASD (mg)	K_d	% removal
1	100	0.10	3.2	0.160	0.340	1062	68
2	200	0.09	2.9	0.145	0.355	1224	71
3	300	0.08	2.5	0.125	0.375	1500	75
4	400	0.07	2.2	0.110	0.390	1773	78
5	500	0.06	1.9	0.095	0.405	2132	81
6	600	0.06	1.9	0.095	0.405	2132	81

Inference

It is observed that at constant pH 5.54, the K_d value and precentage removal of Cr(VI) increases with amount of AHBSASD. It reaches maximum at 500 mg amount of AHBSASD. At this amount K_d is 2132 and percentage removal is 81%. It remains constant on further increase of amount of resin.

Conclusion

The saw dust gives hydrophilic base for preparation of chelating resins. The polysaccharide based resins are more effective and compatible in metal ion separation from solution and concentration in hydro metallurgical processes because of their hydrophilic character. The Naturally occurring polysaccharides are fibrous in nature, which imparts the case of accessibility of functional groups even to macro molecules in the surrounding solutions. With this am in view, we have synthesized 5-Amino-2-Hydroxy Benzene Sulphonic Acid derivative of saw dust, resin for removal of Cr(VI) from standard solutions and also their applications in removal of some toxic metal ions from waste water and effluents. it is clearly seen from Table-3 that 81% of Cr(VI) is removed at pH 5.54, and its distribution coefficient (2132) is also maximum at this pH. Results in Table-3 show that percentage removal of Cr(VI) is increased with increase in amount of AHBSASD resin at constant pH 5.54. It remains constant on further increase of amount of resin. Finally we concluded that 5-Amino-2-Hydroxy Benzene Sulphonic Acid derivative of saw dust is a good and economical resin for removal of toxic metals from solution and waste water.

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