International Research Journal of Management and Commerce
Volume 3, Issue 2, February 2016 **Impact Factor 5.564**
ISSN: (2348-9766)

Website- www.aarf.asia, **Email** : editor@aarf.asia , editoraarf@gmail.com

Synthesis of 2-Amino Pyrimidine derivative of wood flour and its use in removal of Nickel (II) from polluted water

Harsukh Ram Chharang

Department of Chemistry, SBRM Govt. College, Nagaur (Raj.)

ABSTRACT

Removal of heavy metals from polluted water is done to avoid water pollution. In present work synthesized resin, 2-Amino Pyrimidine derivative of wood flour is used for removal of Ni (II) from polluted water samples prepared in laboratory. Wood flour(Polysaccharide cellulose) is an easily available wood product. By chelation Ni (II) ions are chelated on the newly synthesised chelating resin and get removed from water sample. The chelation process was studied as a function of pH (3.5 to 6.5), contact time (≃60 min.), initial concentration (10 ppm) and temperature (30°±1°C) keeping constant amount of wood flour (0.1 g). The concentration of Ni (II) ions in the filtrate was determined using corresponding calibration curve. It was observed that the pH has marked effect on removal of Ni (II). Result shows that about 64 % removal of Ni (II) takes place at pH at 5.54. At this pH chelation of Ni (II) ions was studied with varying amounts of resin having same initial concentration, temperature and contact time. It was observed that with increasing amount of APWF resin, the distribution coefficient (K_d) and percentages removal values increase and at 0.5 g dose these reach to maximum 3667 and 88 % respectively and remains constant at higher doses of resin.

Key Words: Heavy metals, Wood flour, Calibration curve, Ni (II), Chelation, Absorbance, Polluted water, 2-Amino Pyrimidine derivative of wood flour (APWF).

INTRODUCTION

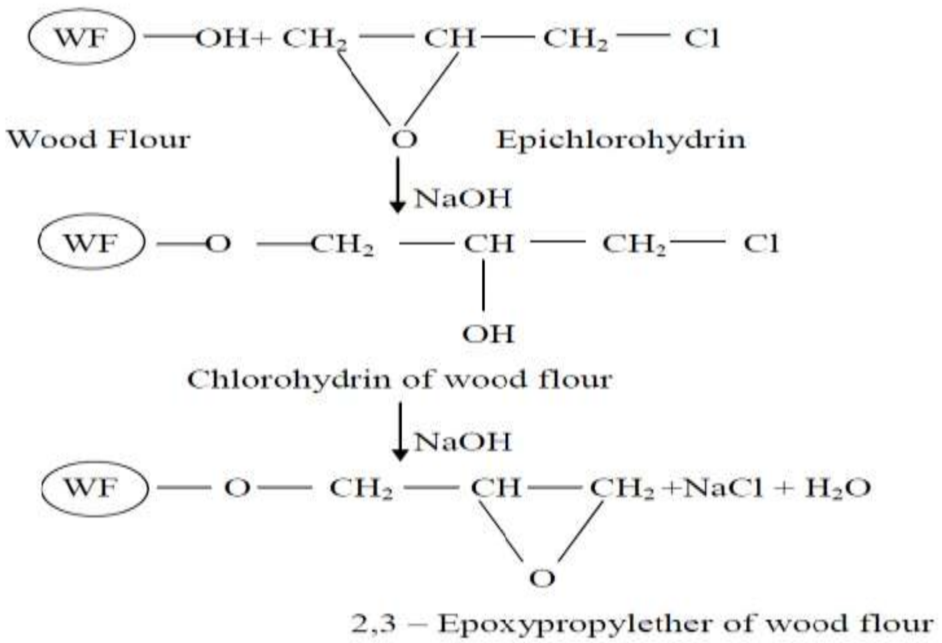
Excess dose of heavy metals in natural environment results various problems in both animals andplants. The metals are of special concern due to their recalcitrant and persistency properties in nature.Although some metals are essential at low levels serving as nutrients for animals and plant life but toxic athigher levels. Presence of heavy metals in water changes the physicochemical characteristics of theaqueous phase, which have direct influence on the types and distribution of aquatic biota[1]. Toxic metals can bedistinguished from other pollutants since they are not bio degradable and can be accumulated in nature.The heavy metals have a great affinity for sulphur and attack sulphur bonds in enzymes, thusimmobilizing the later. Other vulnerable sites are protein carboxylic acid (-COOH) and amino (-NH_2)groups. Heavy metals bind to cell membrane, affecting transport processes through the cell wall. Theyalso tend to precipitate phosphate bio compounds or catalyze their decomposition[2]. Ni (II) is commonlyfound in polluted water. It is used in a number of industries including electroplating because of itsresistance to corrosion, high strength over a wide range of temperatures and good alloying properties.Although Ni (II) is comparatively less toxic than the other heavy metals but its higher concentrationpresent in water may cause of severe damage to lungs. Concentration of Ni (II) more than 0.3ppm causesgrowth reduction in chicks, when it is ingested with diet. Other diseases like diarrhea, renal edema,vomiting, respiratory problems and dermatitis also caused due to higher concentration of Ni (II) presentin water[3]. To avoid above harmful effects of Ni (II), it is essential that it must be removed from polluted water. Many methods are used for removal of Ni (II) ions from solutions or polluted water such as electrolytic methods, ion exchange, precipitation, flocculation, complexation, biological treatment and adsorption[4-11]. In present work we selected chelation method for removal of Ni (II) due to its high efficiency, easy mechanism and low cost[12-15]. We synthesised 2-Amino Pyrimidine derivative of wood flour and used it to remove Ni (II) from polluted water/solution. The naturally occurring polysaccharides are fibrous in nature, which imparts the ease of accessibility of functional groups even the macro molecules in the surrounding solutions. The effective capacities of the chelating resins based on polysaccharide are higher than those of other chelating resins based on synthetic polymers. The wood flour is easily available and can be easily processed was used as matrix to form chelating resin for metal removal from polluted water. Wood flour resin may be economically viable substance for water treatment if used in place of commercially high cost resins.

MATERIAL AND METHODS

(A) Synthesis of Cross Linked wood flour

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

The reaction mixture was then 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 wood flour was further used for derivatization.



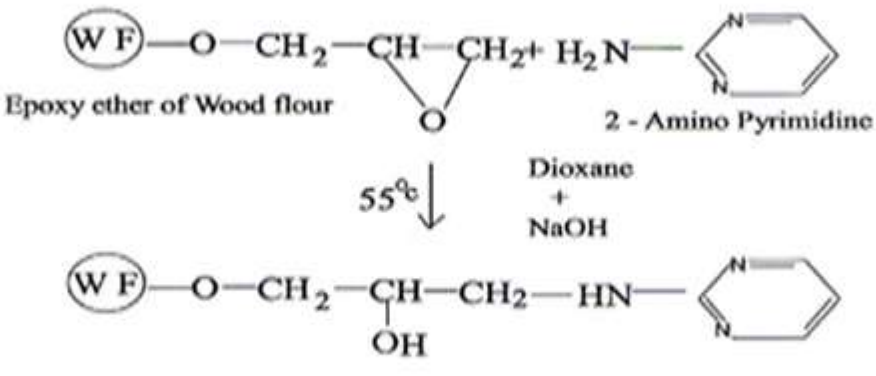
Scheme 1 : synthesis of cross linked wood flour

(B) Synthesis of 2-Aminopyrimidine derivative of wood flour (APWF)

We took 0.05 mole of cross linked wood flour in a 500ml round bottom flask and it was slurred with dioxane. To the round bottom flask 10ml of 50% aqueous sodium hydroxide was added slowly with constant stirring at 55ºC.

9.5 gm (0.1mole) of 2-Amino pyrimidine was dissolved in dioxane and it was added slowly to the reaction vessel. The contents of the flask were constantly stirred for five hours at 55ºC on water bath. The product was filtered on a buchner funnel and washed with 80% aqueous methanol containing few drops of nitric acid to remove the inorganic impurities from the product.Washing were continued till the filtrate was free from 2-Amino pyrimidine.

The product was made strongly acidic by adding sufficient amount of 1.0 NHCl and was filtered immediately. Successive washings were done with 150ml portions of 0.1 N NaOH &0.1 N HCl. The product was air dried and was again suspended in 200 ml of 0.1N HCl. Supernatant liquid was decanted and the sediment was washed four to five times by decantation to remove the resin particles that did not settle. The supernatant liquid at the end was clear and free from acid. The product was finally washed with absolute alcohol. Much of the alcohol was removed by filtration and the remaining alcohol was evaporated in vacuum. The product was free flowing brownish powder.



Scheme 2 : synthesis of 2-Amino Pyrimidine derivative of wood flour(APWF)

REAGENTS

All the chemicals used were of analytical grade obtained from E. Merck. Stock solutions of 2000 mg/L each of the Ni (II) 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 Ni (II) solutions and Calibration Curve

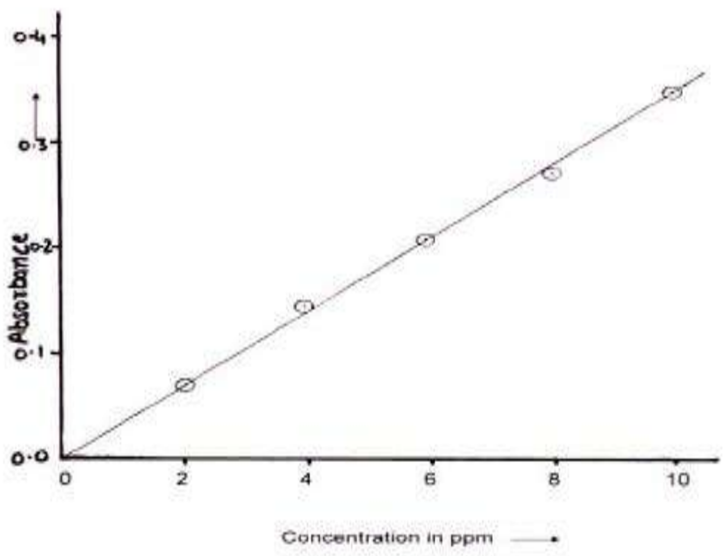
To 10 ml of Nickel solution, 5 ml 10 % citric acid was added and neutralized with 6M ammonia (litmus) withabit excess (about 5ml). The solution was transferred to a separatory funnel and diluted to 50ml.Then tothis solution 5ml dimethyl glyoxime solution (1% in ethyl alcohol)was added and extracted thrice with5ml portions of $CHCl_3$ shaking vigorously for one–half minute each time. Then chloroform extracts wereshaken with 20ml of 0.5 M ammonia and separated the layers. Separated aqueous layer was shaken with5ml of $CHCl_3$ and treated the later with washed $CHCl_3$. To return Nickel to the aqueous phase chloroformextracts were shaken twice for 1 minute each with 5 ml portions of 1MHCl. Then transferred the acidsolution to a beaker, diluted up to about 50 ml and to this solution 1 ml of 10% citric acid,3ml of 2%potassiumpersulphate solution, 15ml of 2M NaOH and 1ml dimethyl glyoxime were added and heated to 60°C andkept at 60°-70°C for 5 minutes. Now after cooling up to room temperature, it was diluted to 100ml. Theabsorbance of Ni-DMG red complex was measured at 465nm comparing against reagent blank. Using standard Nickel solutions of different concentrations, calibration curve was plotted and concentration of unknown solution of Nickel can be determined using the calibration curve.

Table 1

Absorbance for standard Ni (II) Solution

S.No.	Concentration (ppm)	Absorbance
1	2	0.07
2	4	0.15
3	6	0.21
4	8	0.27
5	10	0.35

Figure 1 : Calibration Curve for Ni (II) Solutions



RESULT AND DISCUSSION

A. Chelation of Ni (II)on constant amount of APWF resin with varying pH.

0.1 g of dry resin and 25ml of 20ppm solution of Ni (II) were taken in different sets. Appropriate amounts of 0.2M acetic acid and 0.2M sodium acetate were added to each set to obtain desired pH. The total volume of sodium acetate-acetic acid buffer was kept 25ml in each set. The contents were stirred magnetically. The filtrates were analysed for Ni (II) concentration spectrophotometrically. The results are given in Table 2.

The distribution coefficient (Kd) and percentage removal of Ni (II) are calculated by applying following Formula -

$$K_d = \frac{\text{Amount of Ni (II) in wood flour derivate (APWF) Phase/g of dry wood flour derivate}}{\text{Amount of Ni (II)in solution/ml of solution}}$$

$$\%\text{RemovalofNi (II)} = \frac{\text{(Initial concentrationof Ni (II) sol. — concentration of Ni (II) solution after treatment with wood flour derivate)}}{\text{Initial concentration Ni (II) solution}} \times 100$$

Table 2

Chelation of Ni (II) on constant amount of APWF resin, with varying pH.

Amount of APWF added = 0.1 g | Initial concentration = 10 ppm

Volume of Ni (II) of 20 ppm =25 ml

Total volume = 50 ml. | Temperature = 30°± 1° C

S.No	Vol. of 0.2 M acetic acid (ml)	Vol. of 0.2 M sodium acetate (ml)	pH	O.D. of filtrate	Conc. Of Ni (II) in filtrate (ppm)	Amount of Ni (II) in sol. (mg)	Amount of Ni (II) in APWF (mg)	K_d	% Removal
1	23	2	3.51	0.25	8.4	0.430	0.070	81	14
2	19	6	4.02	0.22	7.4	0.380	0.120	158	24
3	15	10	4.53	0.19	6.4	0.330	0.170	158	34
4	7	18	5.04	0.17	5.7	0.295	0.205	347	41
5	3	22	5.08	0.13	4.4	0.230	0.270	587	54
6	1	24	5.54	0.10	3.4	0.180	0.320	889	64
7	0.5	24.5	6.50	0.14	4.7	0.245	0.255	520	51

Inference

It is observed that with the increase of pH the K_d values for Ni (II) on APWF increases. At pH 5.54 the distribution coefficient value is maximum (889) and removal percentage is 64%. On pH more than 5.54 the K_d value and removal percentage decreases.

B.Chelation of Ni (II) on varying amount of APWF resin at constant pH.

Different amounts of APWF resin were taken in each flask and 1 ml of 0.2M acetic acid 24 ml of & 0.2M sodium acetate were added to get the pH 5.54. Now 25ml (20 ppm) solution of Ni (II) was then added to each set. The contents were stirred magnetically and equilibrated over night. The filtrates were analysed forNi (II) concentration. The results are given in Table 3.

Table 3

Chelation of Ni (II) on varying amounts of APWF resin at constant pH.

Volume of Buffer = 25 ml Initial concentration = 10 ppm
(1ml Acetic acid + 24ml Na-Ac)
Volume of Ni (II) of 20 ppm =25 ml Temperature = 30°± 1° C
Total volume = 50 ml. pH = 5.54

S.No.	Amount of APWF added (mg)	O.D. of Filtrate	Conc. Of Ni (II) in Filtrate (ppm)	Amount of Ni (II) in solution (mg)	Amount of Ni (II) in APWF (mg)	K_d	% Removal
1	100	0.12	4.0	0.195	0.305	782	61
2	200	0.10	3.3	0.160	0.340	1063	68
3	300	0.09	3.0	0.145	0.355	1224	71
4	400	0.08	2.7	0.130	0.370	1423	74
5	500	0.04	1.3	0.060	0.440	3667	88
6	600	0.04	1.3	0.060	0.440	3667	88

Inference

It is observed that at constant pH 5.54, the K_d value and percentage removal of Ni (II) increases with amount of APWF. It reaches maximum at 500 mg amount of APWF. At this amount, K_d is 3667 and percentage removal is 88%. It remains constant on further increase of amount of resin.

CONCLUSION

In the present work, we have synthesized a chelating resin derived from a polysaccharide cellulose (wood flour), an easily available wood product. Wood is the most abundant and renewable natural resource easily available to the mankind. The cellulose of wood is a linear polymer ofD-anhydro glucopyranose and stabilized by hydrogen bonding. Attempts were therefore made to prepare few derivatives from wood flour without any pretreatment with object to the material as chelating resin for different toxic trace metals.2-Amino pyrimidine was incorporated in hydrophilic wood flour matrix to give wood flour based chelating resins of -N-N- type. By chelation Ni (II) ions are chelated on the newly synthesised chelating resin and get removed from water sample.2-Amino pyrimidine derivative of wood flour shows maximum removal of Ni (II) atpH 5.54.

REFERENCES

1. H. Kaur;Environmental Chemistry.Pragati Prakashan, Meerut, 2005
2. A.K. De;Environmental Chemistry.Wiley Eastern Limited, New Delhi, 1989
3. S.S. Dara;A Text Book of Environmental Chemistry and Pollution Control. S. Chand & Company Ltd. New Delhi, 1993
4. Dingwag Chen, Ajay K Rasy;Removal of toxic metal ions from polluted water by semiconductor photocatalysis.Chemical engineering science, Volume 56, Issue 4, 2001, 1561-1570.
5. Ashok K Pandey, Shri Dhar Pandey and Virendar Mistra;Removal of toxic metals from leachates from hazardous solid waste and reduction of toxicity to microtox by the use of calcium alginate beads containing humic acid.Ecotoxicology and Environmental Safety, Volume52,Issue 2, 2002, 92-96.
6. A L Zouboulis, M X Loukidou and K A Matis;Bio sorption of toxic metals from aqueous solution by Bacteria strain isolated from metals polluted soils.Process Biochemistry, Volume 39,Issue 8, 2004, 909-916
7. Sandra Maria Dal Basco, Ricardo Sarti Jimer and Wagner Alves Carvalho;Removal of toxic metals from polluted water by Brazilian natural Scolecite.Journal of colloid and Interface Science, Volume 281, Issue 2, 2005, 424-431.
8. Syed Moosa Hasany and Rashid Ahmad;The potential of cost effective coconut husk for the removal of toxic metal ions for environmental protection.Journal of environmental management, Volume 81, Issue 3, 2006, 286-295.
9. Amany H Sikaily, Ahmed Nemr, Azza Khaled and Ola Abdel Wehab;Removal of toxic chromium from polluted water using green alga ulva lactuca and its activated carbon.Journal of hazardous materials, Volume 148, Issue 1-2, 2007, 216-288.
10. Ozgui Ozay, Sema Ekici, Yskup Baran, Nahit and Nurettin Sahiner;Removal of toxic metals ions with magnetic hydrogels.Waste Research, Volume 43,issue 17, 2009, 4404-4411.
11. Sarika Singh , K C Baruck and D Bahadur;Surface engineered magnetic nano particles for removal of toxic metal ions and bacterial pathogens.Journal of hazardous materials, Volume192, Issue 3, 2011, 1539-1547.
12. Harsukh Ram Chharang and Atul Kumar Sharma; Romoval of Mercury (II) using Synthesised 5-Amino-2-Hydroxy Benzene Sulphonic Acid derivative of Wood Flour.Journal of Interdisciplinary Cycle Research, Vol 3, Issue 2, July-December 2011.
13. Harsukh Ram Chharang and Atul Kumar Sharma; Romoval of Chromium (VI) using Synthesised 5-Amino-2-Hydroxy Benzene Sulphonic Acid derivative of saw dust. IJREAS, Vol 2, Issue 10, October 2012.
14. Harsukh Ram Chharang and Bhanwar Lal; Removal of Copper (II) using Synthesised 5-Amino-2-Hydroxy Benzene Sulphonic Acid derivative of Wood Flour.Bull. Env. Pharmacol. Life Sci., Vol 2 (7) June 2013 : 38-40.
15. Bhanwar Lal;Romoval of Nickel (II) using Synthesised 5-Amino-2-Hydroxy Benzene Sulphonic Acid derivative of Wood Flour.Research Journal of Chemical and Environmental Sciences, Vol 1, Issue 3, Augest 2013.