Synthesis and Application of 2-Amino Pyrimidine derivative of wood flour in removal of Copper (II) ions from polluted water

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ABSTRACT

2-Amino pyrimidine derivative of wood flour has been used for the removal of Cu (II) ions from polluted water samples prepared in laboratory. By chelation Cu (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 6.0), 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 Cu (II) ions in the filtrate was determined using corresponding calibration curve. It was observed that the pH has marked effect on removal of Cu (II). Result shows that about 67 % removal of Cu (II) takes place at pH at 5.51. At this pH chelation of Cu (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 889 and 64 % respectively and remains constant at higher doses of resin.

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

INTRODUCTION

It is a matter of history that faecal pollution of drinking water caused water-borne diseases which wiped out entire population of cities. The major sources of water pollution are domestic waste from urban and rural areas and industrial wastes which are discharged into natural water bodies. Industrial effluents contains many types of toxic trace metal ions like Fe (II), Ni (II), Cr (VI), Zn (II), Cu (II), Hg (II) and Cd (II). Copper is the first metal known to be employed by man. Copper has many uses in industrial and house hold appliances. Salts of copper are used in controlling biological growths in reservoirs. The toxicity of copper affects the aquatic organisms. Although copper is an essential metal but the ingestion of higher levels of copper may results in nausea, metallic taste, vomiting, jaundice, hypertension, anuria and hemoglobinuria. Absorption of excess amount of copper results in vomiting and liver damage. A maximum concentration of 0.1 ppm copper has been prescribed for drinking water by US environmental protection Agency[1-3].

Many reports are available for removal of Cu (II) from water and waste water using natural products and byproducts.[4-12] The present work deals with the study of removal of Cu(II) from polluted water using 2-Amino Pyrimidine derivative of wood flour. The wood flour is selected because it is easily available at anywhere. It may prove economically viable substance for water treatment.[13-15]

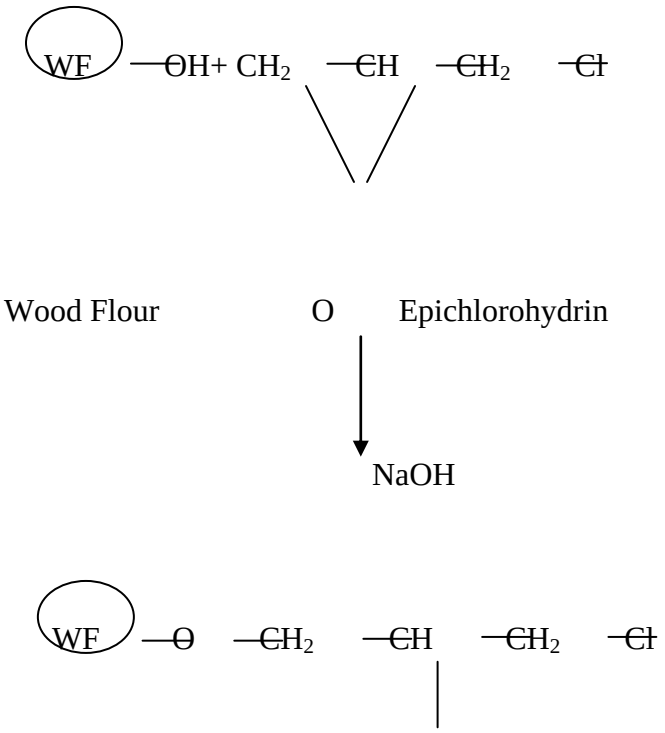
MATERIAL AND METHODS

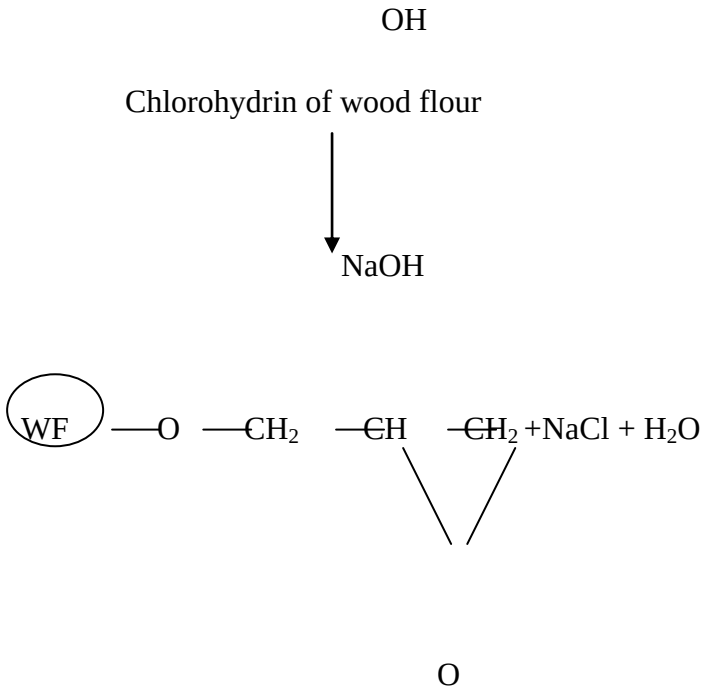
(A) Synthesis of Cross Linked wood flour

486 g wood flour (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 (1mole) epichlorohydrin was added with constant stirring. The stirring was 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.





2,3 – Epoxypropylether of wood flour

Scheme 1 : synthesis of cross linked wood flour

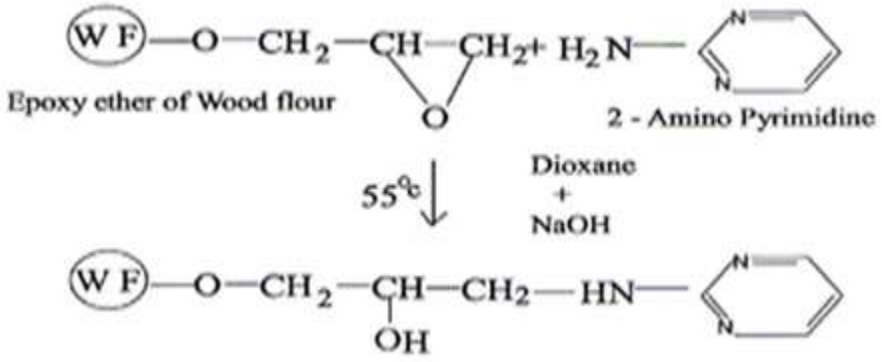
(B) SYNTHESIS OF 2-AMINO PYRIMIDINE DERIVATIVE OF WOOD FLOUR (APWF)

We took 0.05 mole of cross linked wood flour in a 500 ml 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 N HCl and was filtered immediately. Successive washings were done with 150 ml 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 Cu (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 0.2 M sodium acetate and 0.2 M 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 Cu (II) solutions and Calibration Curve

10 ml standard solution of copper (II) was taken in a beaker and 5ml of 20 % ammonium citrate solution was added. The pH of solution was adjusted to 9.0 by adding ammonium hydroxide. The solution was cooled to room temperature and diluted it to 25 or 30ml. Transfered the contents of beaker to a separatory funnel. 1.0 ml of sodium diethyl dithiocarbamate (0.1% aq.) was added to the contents of separatory funnel and was shaken with exactly 5 ml of carbon tetra chloride. Allowed the carbon tetra chloride layer to settle. When layer was free from water droplets, it was collected in a suitable cell. Aqueous phase remaining in separatory funnel was again extracted with carbon tetra chloride, until the last portion becomes colourless. Absorbance of extract was measured at 435 nm comparing against carbon tetra chloride.

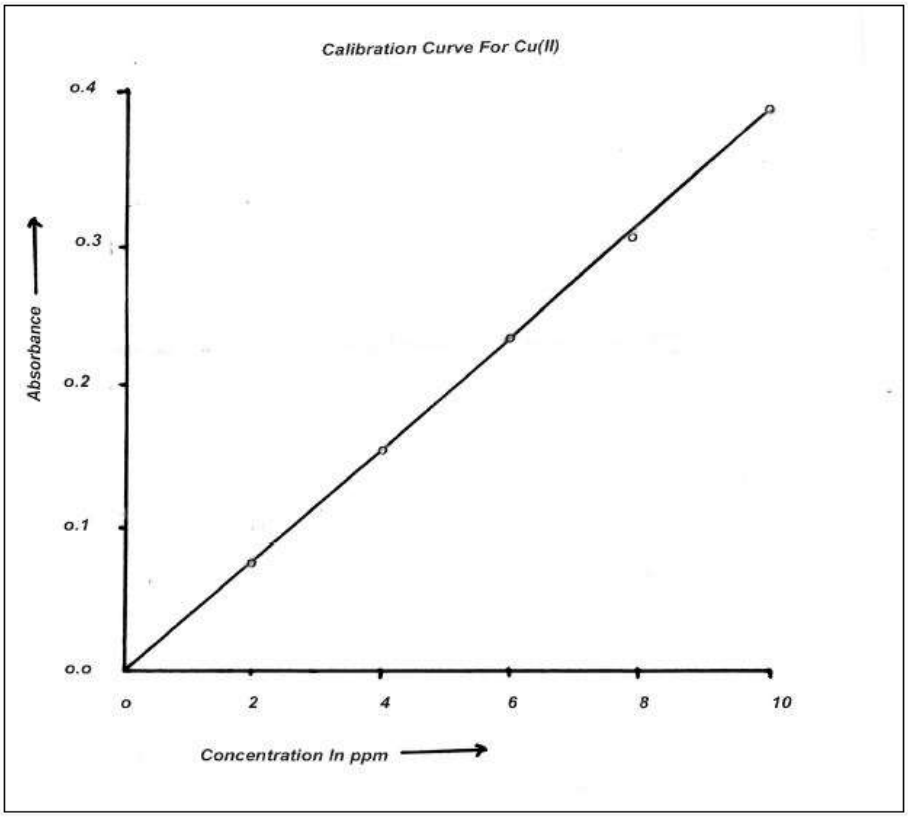
Similarly using standard Cu (II) solution of different concentrations, the calibration curve was plotted. The concentration of unknown solution can be determined by using the calibration curve.

Table 1

Absorbance for standard Cu (II) Solution

S.No.	Concentration (ppm)	Absorbance
1	2	0.08
2	4	0.15
3	6	0.23
4	8	0.30
5	10	0.38

Figure 1 : Calibration Curve for Cu (II) Solutions



RESULT AND DISCUSSION

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

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

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

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

(Initial concentration of Cu (II) sol. — concentration of Cu (II)

solution after treatment with wood flour derivate)

$$\%\text{RemovalofCu (II)} = \frac{\text{Initial concentration Cu (II) solution}}{\text{Initial concentration Cu (II) solution}} \times 100$$

Table 2

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

Amount of APWF added = 0.1 g Intial concentration = 10 ppm

Volume of Cu (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 Cu (II) in filtrate (ppm)	Amount of Cu (II) in sol. (mg)	Amount of Cu (II) in APWF (mg)	K_d	% Removal
1	23	2	3.50	0.30	7.9	0.415	0.085	102	17
2	19	6	4.01	0.27	7.0	0.375	0.215	166	25
3	15	10	4.52	0.21	5.6	0.300	0.200	333	40
4	7	18	5.00	0.16	4.2	0.235	0.265	563	53
5	3	22	5.51	0.11	2.9	0.165	0.335	1015	67
6	1	24	6.02	0.13	3.5	0.195	0.315	807	61

Inference

It is observed that with the increase of pH the K_d values for Cu (II) on APWF increases. At pH 5.51 the distribution coefficient value is maximum (1015) and removal percentage is 67 %. On pH more than 5.51 the K_d value and removal percentage decreases.

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

Different amounts of APWF resin were taken in each flask and 3 ml of 0.2 M acetic acid 22 ml of & 0.2 M sodium acetate were added to get the pH 5.51. Now 25ml (20 ppm) solution of Cu (II) was then added to each set. The contents were stirred magnetically and equilibrated over night. The filtrates were analysed for Cu (II). The results are given in Table 3.

Table 3

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

Volume of Buffer = 25 ml Initial concentration = 10 ppm

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

Volume of Cu (II) of 20 ppm =25 ml Temperature = 30°± 1° C

Total volume = 50 ml. pH = 5.51

S.No.	Amount of APWF added (mg)	O.D. of Filtrate	Conc. Of Cu (II) in Filtrate (ppm)	Amount of Cu (II) in solution (mg)	Amount of Cu (II) in APWF (mg)	K_d	% Removal
1	100	0.19	4.9	0.230	0.270	586	54
2	200	0.18	4.7	0.220	0.280	636	56

3	300	0.17	4.4	0.205	0.295	719	59
4	400	0.16	4.1	0.190	0.310	815	62
5	500	0.15	3.9	0.180	0.320	889	64
6	600	0.15	3.9	0.180	0.320	889	64

Inference

It is observed that at constant pH 5.51, the K_d value and percentage removal of Cu (II) increases with amount of APWF. It reaches maximum at 500 mg amount of APWF. At this amount, K_d is 889 and percentage removal is 64%. 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 of D-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 Cu (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 Cu (II) at pH 5.51.

REFERENCES

1. A.K. De;
Environmental Chemistry.

Wiley Eastern Limited, New Delhi, 1989

2. S.S. Dara;
A Text Book of Environmental Chemistry and Pollution Control.

S. Chand & Company Ltd. New Delhi, 1993

3. H. Kaur;
Environmental Chemistry.
Pragati Prakashan, Meerut, 2005

4. Dingwag Chen, Ajay K Rasy;
Removal of toxic metal ions from waste 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 waste 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 waste 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. Mikko Vepsalainen, Heli Kivisari, Martti Pullianen and Aimo Oikri;
Removal of toxic pollutants from pulp mill effluents by electroagulation.

Separetion and purification technology, Volume 81, Issue 2, 2011, 141-150.

13. 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.
14. 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.
15. 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.