PROCESS CHEMISTRY CENTRE

Metal ions in wood materials

Kim Granholm
Laboratory of Analytical Chemistry

COST Action 17.9.2013

Outline

Introduction

- Metal ions in wood and pulp
- Why are metal ions important?

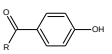
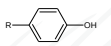
Developed analytical methods and results:

- I: Acid-base titrations
- II: Column chromatographic method
- III: Chelation of metal ions

Metal ions in wood

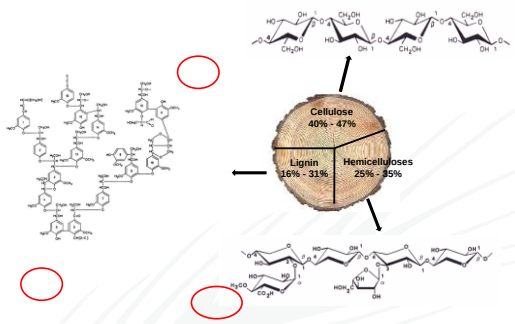
Concentration levels, ppm (*mg/kg*)	Elements
1000 – 100	Ca, K, Mg
100 – 10	F, Fe, Mn, Na, P, S
10 – 1	Al, B, Si, Sr, Zn, Ti
1 – 0.1	Ag, Ba, Cd, Cr, Cu, Ni, Rb, Sn
0.1 – 0.01	Bi, Br, Ce, Co, I, La, Li, Pb, Se, W
0.01 – 0.001	As, Eu, Gd, Hf, Hg, Mo, Nd, Pr, Sc, Sb

Acid groups in wood

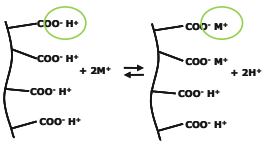
Group	Structure	pK_a
Carboxylic	R-COOH	4 - 5
	R-CH(OR´)COOH	3 - 4
Phenolic		7 - 8
		9.5 - 10.5
Alkoholic	R-CH(OH)-R´	> 13

Sjöström, E. Nord. Pulp Pap. Res.J. 4(1989)90-93

Chemical composition of wood



Ion Exchange



1

Metal ions in pulping and bleaching

- Wood raw material, process chemicals, corrosion of equipment, make up water
- Closed effluent systems ⟶ accumulation of metal ions
- TCF bleaching: H_2O_2 and O_3 are decomposed by Mn, Fe and Cu
  Mg stabilizes the decomposition ⟶ high Mg/Mn
- Scaling on equipments (e.g. $CaCO_3$ on black liquor evaporators)
- Colorization of the final paper product (e.g. Fe)

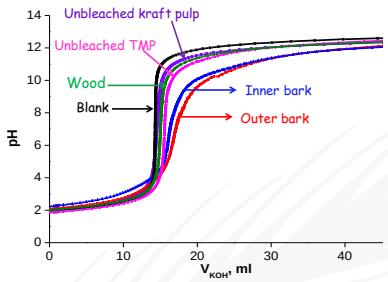
I: Potentiometric acid-base titration

Aim:
To determine the concentration of acid groups and their protonation constants in wood, pulp and bark

1.2-1.5 g (d.m) sample + 150 ml 0.1 M KNO_3
Acidified to pH 2 by HNO_3
Titrated with 0.1 M KOH

I: Potentiometric acid-base titration

Titration curves of spruce materials



1.2-1.5 g (d.m) sample +150 ml 0.1 M KNO_3
Acidified to pH 2 by HNO_3
Titrated with 0.1 M KOH

I. Potentiometric acid-base titration

Dissociation constants (pKa) of acid groups

Acid group	Spruce wood		Spruce TMP	Softwood kraft pulp	Spruce bark	
	Heartwood	Sapwood	Untreated	Unbleached	Inner	Outer
HR_1	4.0	3.9	4.2	3.7	3.9	3.9
HR_2	5.6	5.7	5.9	5.5	6.1	5.9
HR_3	7.9	7.9	7.9	7.5	8.4	8.2
HR_4	10.1	9.9	10.2	9.3	10.7	10.5

I: Potentiometric acid-base titration

Concentrations (μeq/g)

Acid group	Spruce wood		Spruce TMP	Softwood kraft pulp	Spruce bark	
	Heartwood	Sapwood	Un-treated	Un-bleached	Inner	Outer
HR_1	56	55	42	67	440	270
HR_2	20	18	11	20	66	74
HR_3	17	14	11	19	98	120
HR_4	50	43	72	30	590	520
Total	143	130	136	136	1194	984

I:Conclusions

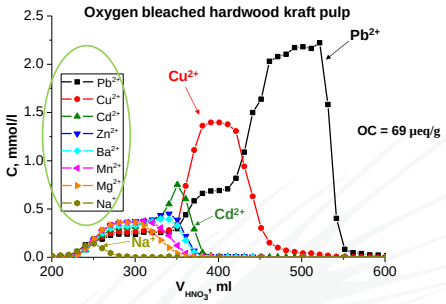
1. The total concentration of acid groups in wood, untreated TMP and unbleached kraft pulps are similar
2. Bark contains the highest concentration of acid groups
3. Chemical treatments generally creates new and more binding groups

II: Metal ion affinities to wood materials using a column chromatographic method

Aim:
To obtain affinity orders for metal ions to wood materials

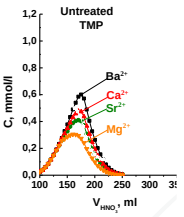
II:The column chromatographic method

II: The column chromatographic method



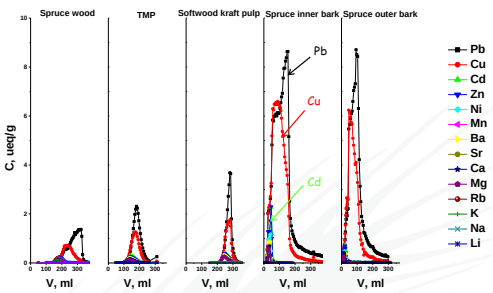
$Pb^{2+}>Cu^{2+}>Cd^{2+}>Zn^{2+}>Ba^{2+}>Mn^{2+}>Mg^{2+}>Na^+$

II: The column chromatographic method



$Ba^{2+}>Ca^{2+}>Sr^{2+}>Mg^{2+}$

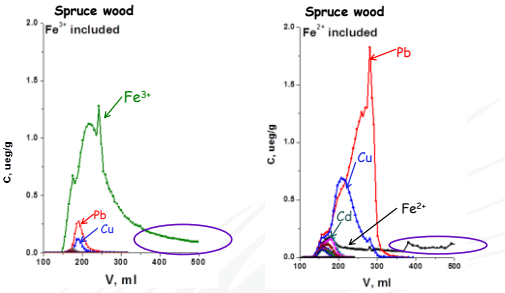
II: The column chromatographic method



Affinity order: Pb > Cu > Cd > Zn >.....

II: The column chromatographic method

Fe(II) or Fe(III) included



Affinity order: Fe(III) > Pb > Cu > Fe(II) > Cd.....

II: Conclusions

- All metal ions show specific sorption to tree- related materials
- Tree related materials show similar order of affinity for metal ions studied:

  For wood: $Fe^{3+} >> Pb^{2+} >> Cu^{2+} >> Fe^{2+} > Cd^{2+} > Zn^{2+} > Ni^{2+} > Ba^{2+} \geq Ca^{2+} \geq Mn^{2+} \geq Sr^{2+} > Mg^{2+} > Rb^{+} \sim K^{+} \sim Na^{+} \sim Li^{+}$

  - Alkali metal ions are most weakly bound
  - Pb and Cu very strongly bound
  - Fe (III) has highest binding strength
- Bark has the highest sorption capacity

  ➡ Potential bio-sorbent for removal of metal ions from wastewater

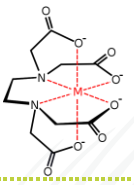
III: Chelation of pulp

Aim:

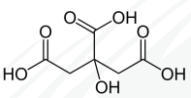
To remove Mn and Fe from pulps by chelation

Complexing agents:

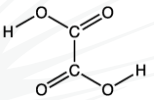
EDTA



Citric acid

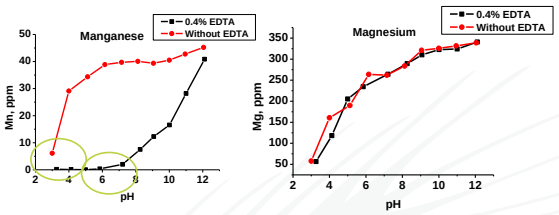


Oxalic acid



III: Chelaton of pulps

Softwood kraft pulp



Highest Mg/Mn ratio at pH = 5

III: Chelaton of pulps

Metal ions in softwood kraftwood after chelation at pH 5

	Mn (ppm)	*Fe (ppm)*	*Mg (ppm)*
Original	*48*	*6.9*	*310*
EDTA (0.4%)	*0.5*	*2.4*	*220*
EDTA (0.4%) + Ditionit (0.5%)	*0.1*	*0.9*	*190*
Citric acid (0.01M)	*2.8*	*2.3*	*18*
Oxalic acid (0.01 M)	*6.9*	*3.5*	*27*

III: Conclusions

- Mn can effectively and selectively be removed from pulps by chelation with EDTA
- A good chelation can be obtained at pH 4 - 6 for kraft pulps
- Fe was shown to be very difficult to be removed
- A reducing environment can improve the chelation of Mn and Fe
- Citric acid removes effectively Mn but also Mg

Thank You!