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A GREEN APPROACH FOR REDUCTION IN BLEACH CHEMICALS CONSUMPTION BY REMOVING HEXENURONIC ACID USING XYLANASE ENZYMES IN PULP BLEACHING PROCESS

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Agenda

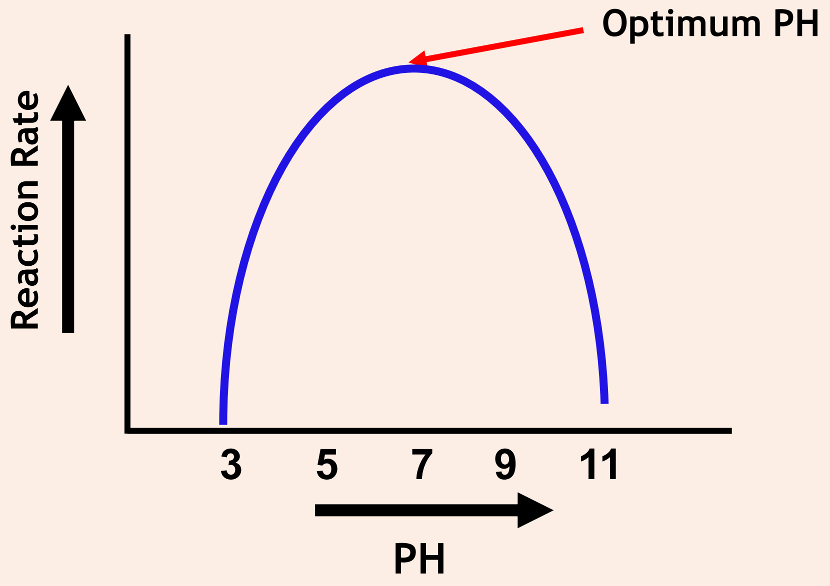
- Enzymes
- Factors Affecting Enzyme Action
- Conventional and Enzymatic Bleaching
- Hexenuronic Acid (Hex-A)
- Mechanism of Hex-A Formation
- Trend of Hex-A Removal During ECF Bleaching
- Summary

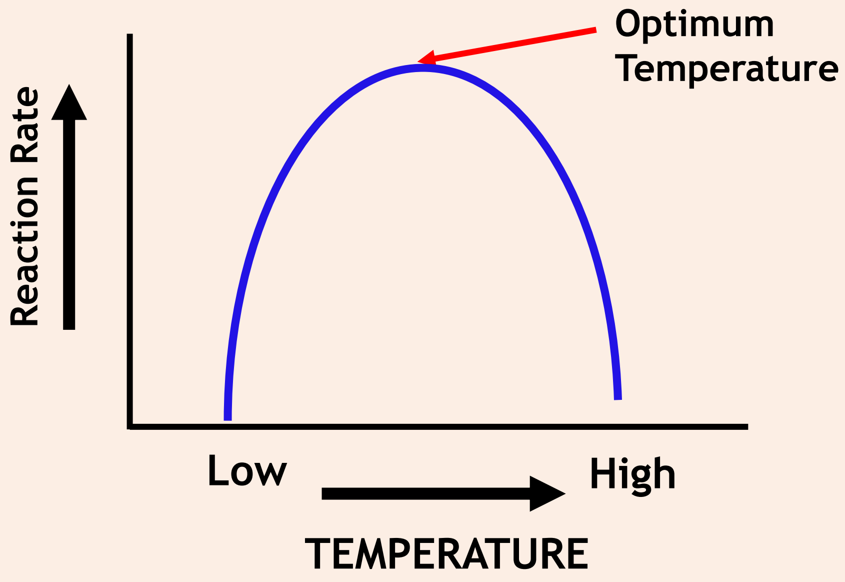
https://www.knowpulp.com/www_demo_version/english/pulping/bleaching/1_general/frame.htm

Enzymes ?

- Selective catalysts for biological reactions
- Enzyme specificity- Lock and key model
- Increase the rate of reaction
- Lowering the activation energy
- Activity lost if denatured
- May contain cofactors such as metal ions or organic (vitamins)

Factors Affecting Enzyme Action





- PH
- Temperature
- Substrate Concentration
- Enzyme Concentration
- Retention Time
- Mixing

Conventional Bleaching ?

It is the process of removing color part of the pulp by using chemical processing

Advantages:

- Reduces remaining lignin amount to much extent
- Increases brightness and whiteness of pulp

Disadvantages:

- Generate lots of hazardous chemicals
- Increases AOX generation in bleach effluents

Bleaching chemicals: Cl_2, ClO_2, H_2O_2, NaOH, Hypo etc..

Enzymatic Bleaching ?

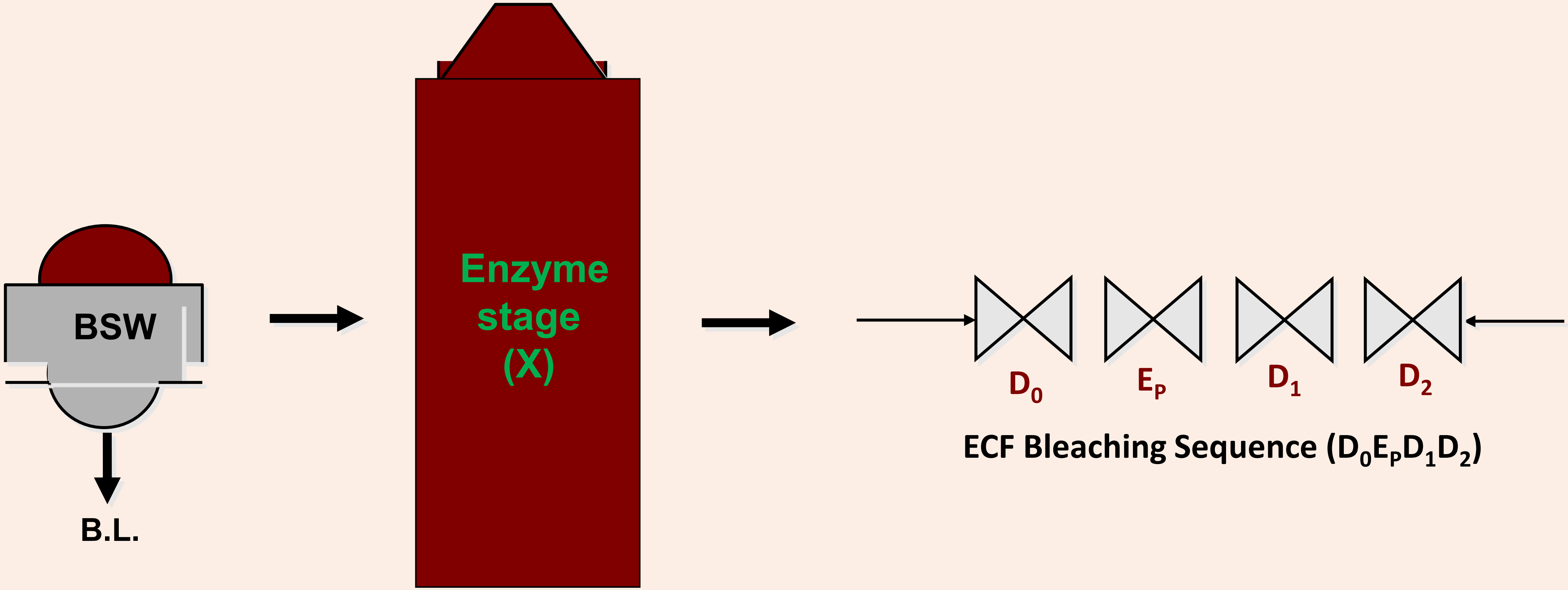
It is the process of removing color part of the pulp by using enzymes before and/or after the bleaching process

Advantages: **Green manufacturing practices**

- Improves brightness and whiteness of pulp
- Reduces the consumption of hazardous chemicals (ClO_2 and NaOH)
- AOX reduction and increases BOD/COD ratio

Disadvantages: No side effects, 100% eco-safe

Unbleached Pulp and Dosing point for Enzymatic Bleaching



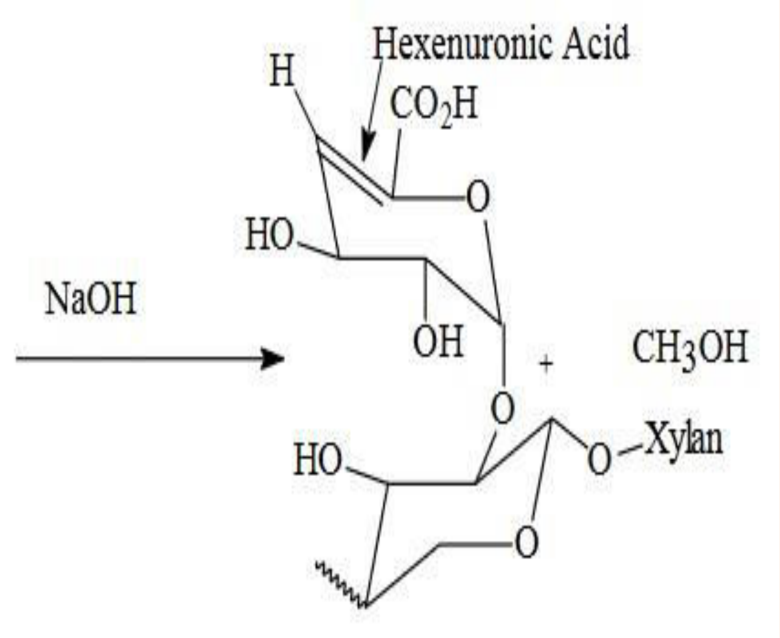
BSW- Brown Stock Washer
B.L.- Black Liquor

Hexenuronic Acid (Hex-A)- $C_{13}H_{20}O_{10}$

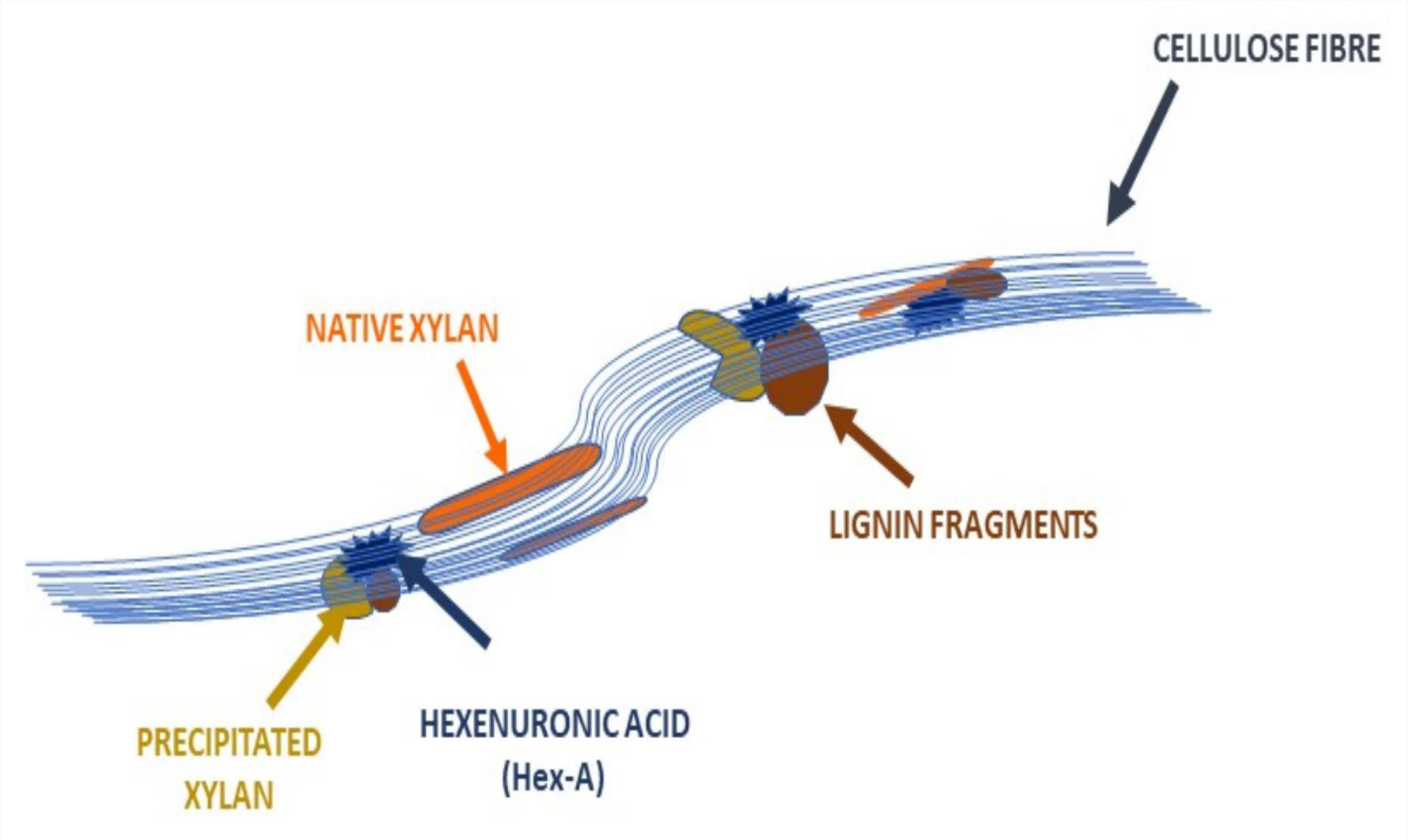
Hexenuronic Acid (Hex-A) is a Bicyclic Organic compound produced during Kraft cooking process

- Hexenuronic Acid bound with re-precipitated xylan and entrap lignin components
- Hex-A reduces penetration of bleach chemicals onto the fibre surface
- Hex-A increases consumption of bleach chemicals
- Hex-A also give false indication of Kappa number estimation

Mechanism of Hexenuronic Acid Formation



https://en.wikipedia.org/wiki/Hexenuronic_acid



Schematic diagram of bounded Hexenuronic Acid (Hex-A) with Xylan

Enzymes and Unbleached Pulp Characterisation

Enzyme Code	Xylanase Activity (IU/ml)
EnzyA	19192±553
EnzyB	14123±350
EnzyC	46876±226
EnzyD	25315±259

Initial pulp Properties	Mean±S.D
Kappa number	18.5±0.21
Brightness, %ISO	31.7±0.28
Viscosity, cp	12.8±0.10
Hex-A, mmol/kg	21.3±0.31

Enzyme Treatment and ECF Bleaching Sequence

Parameter	X stage	D_o stage	E_P stage	D_1 stage	D_2 stage
Consistency, %	10	5	10	10	10
Treatment time, min.	90	45	120	180	180
Treatment Temp., °C	55	60	80	75	75
pH	8.0	1.8-2.0	10.5-11.0	3.0-4.0	3.0-4.0
Where; X- Enzyme treatment stage, E_P- Extraction stage, D_o, D_1 and D_2- Chlorine dioxide stages					

Application conditions used during enzymatic bleaching of eucalyptus pulp

Results- Enzyme (X) Stage

Parameter	Control	EnzyA	EnzyB	EnzyC	EnzyD
End Kappa No.	18.3±0.10	16.4±0.17	16.6±0.20	15.2±0.10	15.7±0.20
Brightness, %ISO	31.9±0.10	33.5±0.17	33.3±0.35	34.5±0.20	33.9±0.10
Hexenuronic acid, mmol/kg	20.90±0.69	18.47±0.46	18.95±0.59	17.56±0.37	18.08±0.44
Viscosity, cp	12.1±0.10	12.4±0.10	12.2±0.10	12.8±0.20	12.6±0.10

Effect of EnzyA, EnzyB, EnzyC and EnzyD on pulp properties after Enzyme (X) stage

Final Pulp and Bleach Effluent Properties

Parameter	KF	Control	EnzyA	EnzyB	EnzyC	EnzyD
Post Color (PC) No.	0.22	0.60±0.03	0.43±0.03	0.45±0.04	0.39±0.01	0.41±0.04
	0.187		0.50±0.04	0.53±0.04	0.44±0.03	0.46±0.02
Shrinkage, %	0.22	4.6±0.20	5.9±0.31	6.1±0.45	5.4±0.20	5.8±0.25
	0.187		5.4±0.26	5.6±0.30	5.1±0.15	5.2±0.23
BOD, $kgtp^{-1}$	0.22	45.4±0.87	38.1±0.60	40.5±0.70	34.6±0.42	36.2±0.35
	0.187		41.8±0.45	43.5±0.50	38.7±0.45	39.9±0.50
COD, $kgtp^{-1}$	0.22	75.6±0.26	66.2±0.59	68.2±0.46	55.1±0.40	65.4±0.60
	0.187		70.1±0.70	71.8±0.64	63.2±0.40	68.8±0.38

Effect of EnzyA, EnzyB, EnzyC and EnzyD on final pulp and bleach effluent properties

Final Pulp Brightness Improvement (Stage-wise)

Parameter	KF	Control	EnzyA	EnzyB	EnzyC	EnzyD
D_o stage	0.22	54.7$\pm$0.55	56.8$\pm$0.67	56.5$\pm$0.65	57.8$\pm$0.50	57.1$\pm$0.40
	0.187		56.1$\pm$0.47	56.0$\pm$0.45	57.2$\pm$0.25	56.4$\pm$0.36
E_P stage	0.22	75.6$\pm$0.61	77.4$\pm$0.57	77.1$\pm$0.40	77.9$\pm$0.47	77.5$\pm$0.60
	0.187		76.6$\pm$0.57	76.5$\pm$0.61	77.2$\pm$0.46	76.9$\pm$0.40
D_1 stage	0.22	85.3$\pm$0.42	86.3$\pm$0.47	86.1$\pm$0.35	86.9$\pm$0.36	86.4$\pm$0.29
	0.187		85.7$\pm$0.78	85.5$\pm$0.61	86.1$\pm$0.50	85.8$\pm$0.60
D_2 stage	0.22	87.3$\pm$0.62	88.2$\pm$0.67	88.1$\pm$0.82	88.8$\pm$0.68	88.5$\pm$0.57
	0.187		87.2$\pm$0.62	87.1$\pm$0.35	87.9$\pm$0.36	87.6$\pm$0.72

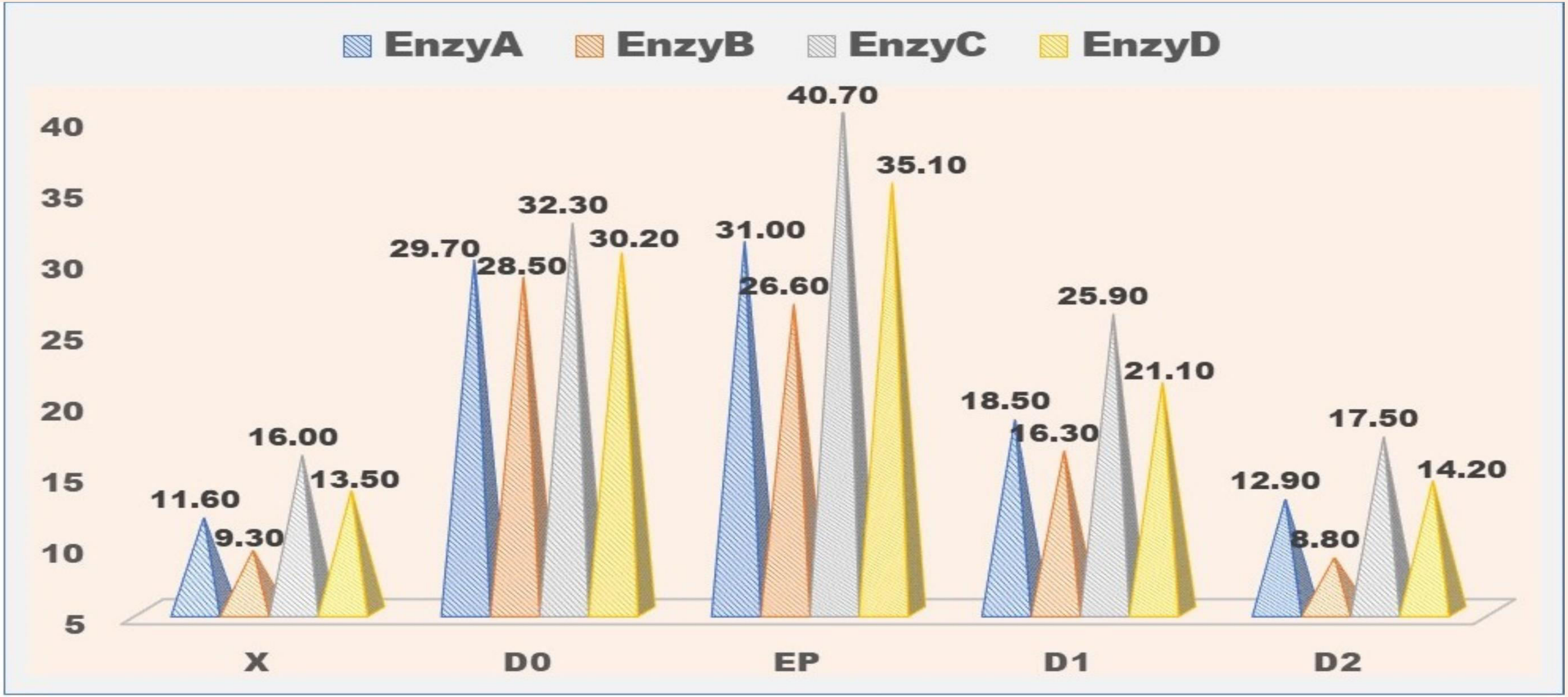
Effect of EnzyA, EnzyB, EnzyC and EnzyD on final pulp Brightness at equivalent and reduced KF

Hex-A Reduction (Stage-wise)

Parameter	KF	Control	EnzyA	EnzyB	EnzyC	EnzyD
D_o stage	0.22	13.10±0.40	9.21±0.71	9.37±0.64	8.87±0.33	9.14±0.49
	0.187		9.81±0.76	10.21±0.45	9.26±0.23	9.57±0.56
E_P stage	0.22	4.10±0.19	2.83±0.17	3.01±0.34	2.43±0.30	2.66±0.35
	0.187		3.23±0.39	3.44±0.46	2.81±0.52	2.97±0.42
D_1 stage	0.22	2.70±0.24	2.20±0.35	2.26±0.33	2.00±0.26	2.13±0.12
	0.187		2.41±0.46	2.53±0.55	2.24±0.37	2.36±0.16
D_2 stage	0.22	2.40±0.28	2.09±0.09	2.19±0.11	1.98±0.31	2.06±0.26
	0.187		2.31±0.18	2.39±0.39	2.10±0.20	2.22±0.33

Effect of EnzyA, EnzyB, EnzyC and EnzyD on Hex-A reduction at equivalent and reduced KF

Trend of Hex-A Removal During ECF Bleaching



Trend of Hex-A reduction (%) with enzymes (EnzyA, EnzyB, EnzyC and EnzyD) at different stages of ECF bleaching sequences

Bleach Chemical Consumption Reduction

Particulars	ClO_2, $kgtp^{-1}$	Savings, $kgtp^{-1}$	NaOH, $kgtp^{-1}$	Savings, $kgtp^{-1}$
Control	26.3	---	20.1	---
EnzyA	23.1	3.2	17.1	3.0
EnzyB	23.3	3.0	17.4	2.7
EnzyC	22.4	3.9	16.1	4.0
EnzyD	22.8	3.5	16.7	3.4

Summary

- **After Enzyme (X) Stage;**
  - 16.0% Hex-A reduction
  - 2.6 units of brightness gain and
  - 16.9% reduction in Kappa number as compared to control
- **After last dioxide (D_2) stage;**
  - 17.5% Hex-A reduction
  - 1.5 units of brightness gain over control in final bleached pulp
  - Due to reduction in the Hex-A components from bleached pulp, brightness reversion (post color number) was also reduced up to 35.0%
  - Maximum reduction of BOD and COD up to 23.8% and 27.1%, respectively
- **Enzymatic treatment also leads to bleach chemicals savings of 14.8% and 20.0% for chlorine dioxide and sodium hydroxide respectively.**

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