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Valorising Desizing Textile Effluent

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***Abstract:** Textile wet processing is an energy-intensive and water-consuming process. Right from pretreatment to finishing several basic, auxiliary, and specialty chemicals are used during the manufacturing of textiles. There are two main processes, namely sizing and desizing which are mutually responsible for increasing the Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) values of liquid effluent emerging after the pretreatment process. This review describes in detail the types of commercial sizing agents depending on their origin, performance, and environmental profile. The review further throws light on the possibilities of extracting energy-efficient, value-added products from the residual waste and effluent. Such recovery mechanisms can enhance sustainability and bring circularity to textile wet processing.*

***Keywords:** Desizing Technologies, Sizing Chemicals, Sustainability and Circularity, Textile Effluent, Valorizing Waste*

I. INTRODUCTION

Sizing is the process done in textile mills for lubricating warp yarn to protect it against wear and tear and breakage from the mechanical stress it undergoes during the weaving process. The applied sizing agent lubricates the warp yarn and enhances its strength, and as a result, the fibers become less prone to abrasion. Yarn breakages are avoided by sizing, thus reducing machinery downtime, which ensures faster and more efficient production.

Commercially starch, Polyvinyl alcohol (PVA), Carboxymethyl cellulose (CMC) and many more chemicals are used as sizing agents. Once the fabric is woven, the objective of the applied sizing chemical is over. After that, it must be removed to avoid interference during the subsequent textile wet processing steps.

The sizing agent is removed in the successive desizing process to make the material absorbent and accessible to the colorants and chemicals. Pretreatment processes like oxidative desizing or enzymatic desizing are commonly employed depending on the sizing agent used and substrate fiber. Desizing is a crucial step in processing woven, denim, and towels. Effective desizing enables even colorant uptake because of increased wettability and absorbency. The desizing process removes the sizing agent and some amount of natural impurities like fats, pectins, and dirt. Once the desizing process is over the bath is drained and the waste liquor is sent to effluent.

The waste desizing liquor is a major environmental concern because of dissolved organic and inorganic matter, lint, and residual chemicals. As a result, desizing liquors show high Biological Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) values [1]. Given below is a schematic diagram of the typical industrial process.

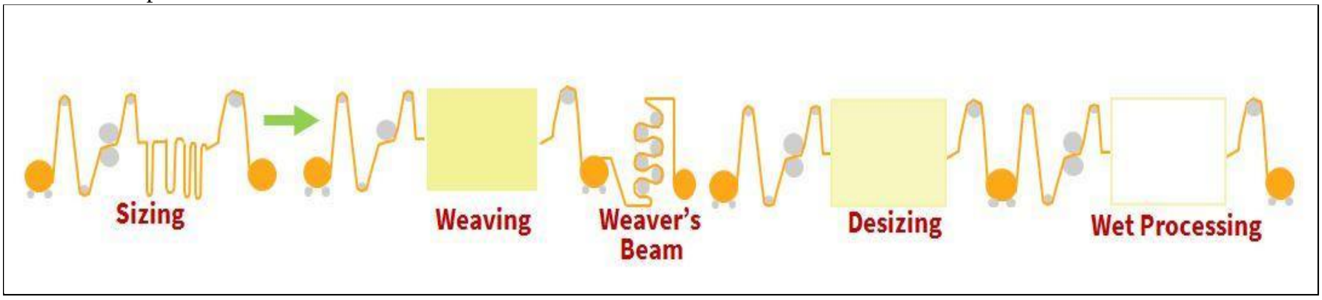

Figure 1- Representation of Sizing-Desizing Process Sequence

A range of chemicals are available for textile warp sizing. The classification of sizing agents based on their origin and their properties are discussed in the following sections of the review.

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Table 1- Classification of Textile [34] Sizing Chemicals

Origin/ Type	Sizing Agent	Source	+ Advantages	• Limitations	Derivatives
Natural	Starch	• Wheat • Potato • Maize • Rice • Tapioca	• Abundant and easily available • Economical • Good adhesion with cellulosic fibres • Safe to use and Easy to detect	• Non-recyclable • Modified starches are comparatively expensive • Skin formation	• Oxidized starch with carboxyl groups • Water-soluble starch ethers - e.g. carboxy methyl starch • Starch esters eg. starch acetate, • Cationic starch • Grafted starch
	Plant Protein sizes	• Corn • Gluten • Soy protein • Keratin • Algin	• Biodegradable • Strong adhesion	• Poor film flexibility • Average sizing performance	• Triethanolamine modified soy protein • Proteins plasticised with polyols and amines
	Animal Glue	• Animal bones, skin and other connective tissues	• Compatible with natural silk, viscose yarns • Biodegradable	• Perishable • Poor permeability • Susceptible to microbes	• Modified gelatin • Polyethylene glycol modified animal glue

Origin/ Type	Sizing agent	Source	+Advantages	-Limitations	Derivatives
Synthetic	CarboxyMethyl Cellulose (CMC)	• Refined cotton or wool pulp	• Good film formation • No skin formation	• Poor biodegradation • Swelling in desizing bath	• Cellulose ethers, • Hydroxy ethyl cellulose
	Polyvinyl Alcohol (PVA)	• Polyvinyl Acetate	• Ideal for blends • Lower Add-on • Recyclable • Good film elasticity	• Poor sizing paste stability • forms skin • foaming slow solubility • Poor Biodegradation	• PVA with phosphorylated starch /chitosan/ Polylactic acid additives
	Acrylic polymers	• Acrylic monomer	• Multiple synthesis routes • Easy to remove • High adhesion	• Poorly biodegradable	• Water Soluble acrylic acid derivatives e.g- acrylamides • Acrylonitrile or acrylic ester derivatives
	Polyester resins	• Terephthalate monomers • Used PET bottles	• Good for filament yarns • High abrasion resistance • Hairiness control	• Costly • Hot water soluble	• PTA and MEG resins

II. NATURAL SIZING AGENTS

A. Starch

Starch is the most common and one of the traditional lubricating agents used for warp sizing. Amongst all the sizing done around the globe, 75% of sizing agents are starch-based [2]. Textile sizing starch is mostly derived from edible sources like wheat and maize as they have better penetrating ability in coarse and dense fibers as well. Other non-edible sources like acorn starches also exist. The hydroxyl groups in the cyclic molecule of starch render it good adhesion with cellulosic fibres. Starch is used for sizing after its gelatinization. Retro-gradation, gelling behaviour, and viscosity stability are the main drawbacks of applying pure starch for sizing on high-speed weaving machines [3]. Nowadays modified starches are more common because of their ease of application, and no skinning behaviour [4]. Chemical modification can be brought about by oxidation, esterification, etherification, or grafting to get desired gelatinisation, viscosity, freeze-thaw stability, film flexibility [5]. Physical methods like gamma irradiation, mechanical lapping have been studied to alter adhesion, viscosity, stability, transparency and other film-forming properties of native starch [6]. However, modified starch sizing agents are costlier than native starches. Both are known for causing high BOD load in desizing effluents [7]. Other natural sizing agents are plant proteins and animal glue [8]. They are known to be sustainable sizing agents because of their biodegradability [9]. The amino groups in such sizing agents help in adhesion with protein fibres like natural silk. Animal bone glue is often supplied along with grease and preservatives as it's susceptible to micro-organisms. Though natural protein-based sizing agents are eco-friendly and biodegradable, they lack film flexibility and sizing performance [10].

B. Synthetic Sizing Agents

a. Carboxy Methyl Cellulose (CMC)

CMC is a water-soluble ether of alkali cellulose sourced from refined cotton/wood pulp and Chloroacetic acid [11]. It forms strong sizing film on cellulosic fibres thus making it difficult to be removed during desizing. Unlike starch, it forms no skin. Application of CMC is critical as it might precipitate in the sizing bath or swell in desizing bath [12]. Under high humidity, fabric might develop sticky marks. Crude CMC having high salt content can be corrosive to machinery. Aqueous CMC shows good emulsifying power, hygroscopic nature and miscibility. The sodium salt of carboxymethyl celluloses is used for sizing cotton and viscose fibres. Fabrics sized with CMCs are generally desized by hot detergent treatment. CMCs can choke membranes during processing [13].

b. Polyvinyl alcohol (PVA)

PVA is a hydrolysis product of polyvinyl acetate. It is a versatile sizing agent used for sizing synthetic blends and even cellulosic fibres. PVA sizes can be recovered by employing the ultrafiltration technique after desizing and again reused for sizing [14]. Thus, PVA is a versatile sizing agent which fits in the closed loop recycling process [15]. The sizing performance of PVA is influenced by its degree of polymerisation. PVA sizing film demonstrates high tensile strength, elasticity and abrasion resistance. The main problem with PVA sizes is they foam a lot and form skins [16]. The foaming nature of PVA effluent can be fatal for aquatic organisms when discharged untreated [17]. PVA size shows poor adhesion with hydrophobic fibres. PVA was once considered a versatile sizing agent owing to its warp reinforcement, and tear resistance.

c. Acrylic Polymers

Earlier acrylic acid and its salt derivatives were used for sizing nylon filament yarns. Polyacrylate sizes are known for the effective sizing of filament yarns. They can be developed by multiple synthesis strategies by interchanging copolymers of acrylic acid [18]. Many derivatives of acrylamide and acrylonitrile copolymers are commercialized as textile warp sizing agents. Owing to their hygroscopic nature and re-adhesiveness they cannot be used alone as sizing agents. They are often mixed with Starch or PVA. Copolymers like polyoxyethylene, polyvinyl methyl ether can be used to control hygroscopic nature and re-adhesion [19].

d. Water soluble polyester resins

The new age sizing agents are water-soluble polyester resins. They are sulfonated polyesters made from terephthalic acid and monoethylene glycol [20]. Compared to other sizing agents they show low viscosity, higher abrasion resistance and good flexibility. They are known to control hariness in yarns. It is mainly applied on polyester filament yarns and other staple fibres. Recently sustainable polyester resins derived from waste PET fabrics and plastic bottles have become popular as sizing agents [21]. Such resins might require additional antifoaming and antistatic agents while sizing polyester filaments. They show low COD/BOD and are considered to have better sizing performance.

C. Environmental Impact of Desizing Process

Nowadays, the acid desizing process is not being practised on large scale because of harsh processing conditions and fibre tendering. The oxidative desizing process carried out at a boil (98°C) temperature using alkali and oxidative persulphates is still common in small process houses. To avoid the risk of tendering cellulose fibre because of acid generation and to save energy, many processors are using enzymes. When starch is used as a sizing agent, enzymes belonging to the amylase class are used to break down the starch into its soluble components. Though enzymatic desizing is an energy-saving process performed at lower temperatures (70-80°C) the breakdown of sizing agent leads to effluent load.

During desizing of greige cotton fabric the Amylase enzyme breaks down starch and hydrolyses it into its sugar components like glucose and maltose. This increases the BOD/COD of desizing effluent because of increased carbohydrate content. Natural fibre desizing effluent accounts for 10000 -20000 mg/l of COD and 5000-10000 mg/l of BOD. Synthetic fibres result in comparatively lower BOD values ranging from 500-100 mg/l. The permissible limit for wastewater discharge prescribed by the Ministry of Environment and Forests, Government of India are 30mg/l BOD [22]. Therefore, the desizing wastewater requires adequate and sufficient treatment before being allowed to be discharged into surface waters. The waste desizing liquors have the potential of upcycling to generate value-added products. Many research studies have been reported that show the use of waste-desizing effluents for producing value-added products. Sophisticated techniques and advanced phenomena like Ion exchange, Ultra and Nanofiltration, Electrochemical oxidation, Aerobic treatment, Flocculation, Phyto and Bioremediation, Membrane technology, Hybrid anaerobic baffled reactor treatment, Anaerobic–aerobic processing, Ozonation etc are implemented for treating textile wastewater [23]. The effluent emerging out of the textile mills post pretreatment, coloration and finishing processes is collectively treated in ETP. However individual effluent treatment of emerging streams after every individual process is an easy, simple and more convenient technique than a centralized effluent treatment. High operating costs, higher treatment time, the requirement of well-trained personnel, lower efficiency and a large amount of sludge generation are the major challenges faced at the textile effluent treatment stage [24]. Researchers have come up with many physio-chemical or biochemical processes or a combination of both to address these issues [25].

D. Waste liquor -An alternative source for Enzyme extraction

Amylases are the main ingredient of any enzymatic desizing recipe when starch is used as a size. Finding alternative cost-effective sources for amylase production is necessary. Recent research has focussed on extracting enzymes from waste textile effluents. The most common source for extraction of amylase-producing organisms is soil or starchy materials like rotten fruits /vegetables.

A study reported the extraction of amylase from Aspergillus fungus isolated from textile mill effluent. The extracted amylase was used to perform enzymatic desizing of greige cotton fabric. The desized fabric showed good absorbency. The desizing efficiency of the amylase extracted using this novel approach was confirmed by TEGEWA ratings [26].

a. Deriving fuel and energy-efficient products from desizing wastewater

Catalytic thermal treatment for thermolysis of desizing wastewater was investigated wherein copper sulfate was used as a homogenous catalyst. The objective was to reduce COD and color of textile effluent. During the treatment copper leached in the aqueous medium. Post-treatment residue which is rich in copper could be used for blending with organic manure in agricultural fields. This thermal catalytic treatment claimed to remove 71.6% chemical oxygen demand (COD) at pH 4. The thermogravimetric results showed that catalytic treatment is a very fast process and can be done in a small reactor vessel in comparison to other methods[27][31][32]. Starch-desized effluents are a rich source of carbohydrates as the starch is hydrolyzed into disaccharides. The hydrolyzed disaccharides can serve as an ideal substrate for biogas-producing micro-organisms. In current scenario the sole aim of effluent treatment is not confined only to safe disposal. Deriving wealth from waste has become a new focus of research. In the quest to extract value-added products from desizing effluent, a process was developed for synthesizing methane. Methane gas was produced by anaerobic fermentation of desizing wastewater in a double-stage biogas reactor. An infrared gas sensor measured the methane content of produced biogas [28]. Hydrogen is considered as a clean fuel source and an alternative to fossil fuels. Fermentative bio-hydrogen production is possible from textile effluent. A recent study showed a method of coagulant pretreatment for increasing the yield of bio-hydrogen produced from desizing liquors. The research has described a two-stage biogas production for biohythane (a mix of hydrogen and methane) generation [29] In another study having a similar objective of using desized starch, a novel process of biogas and biomass production was developed .The high-strength organic waste from desizing effluent was treated by combining three phenomena-Granular activated carbon adsorption, Anaerobic digestion, and Microalgae cultivation. In the proposed process starch containing wastewater was first pretreated for adsorbing the organic matter and color of effluent on granular activated carbon. Post adsorption this effluent was anaerobically digested. Lastly, the effluent was treated by growing photoheterotrophic algae. The combined system achieved a total hydrogen, methane and ethanol energy production rate of 16.9 kJ/(L·d) and chemical oxygen demand removal of 89.5% [30]. A sustainable process was reported using ultraviolet UV-C radiation for desizing of PVA from cotton. It claims to save 67% water and achieving 68% of time and 83% of energy savings when compared with conventional process [31].

III. CONCLUSION

Liquid effluent, solid waste and gaseous emissions are inevitable in conventional textile wet processing. The consumption of important resources like water and energy is also unavoidable. The requirement of huge volumes of water and energy for textile wet processing has motivated textile manufacturers to look for alternative sustainable processes. Efforts are being made to develop safer chemistries and optimised processes. Recent research has shown environmentally friendly desizing options using indigenously produced enzymes. Majority of sizing across the globe is done by starch and its derivatives. It's crucial to tackle the effluent load it generates after desizing. The desizing liquors hold tremendous potential for energy, fuel generation and recovering value added products.

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