Biotechnology for Textile Waste Valorization

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Textile industry generates a large amount of waste. Thus, many researches have been performed in order to eliminate pollution. Biotechnology could be a feasible solution for the textile waste valorization. The paper presents a preliminary study to recover polyethyleneterephtalate (PET) from cotton blends by treatments with two commercial cellulases which destroy the cotton from the mixture. The influence of different factors: the type of enzyme and the textile material (blends or only cotton) on the biodegradation is studied. The obtained results seem promising for finding a new solution for textile waste valorization.

Keywords: Biodegradation, textile waste, cotton, polyethyleneterephtalate recovering

The sustainable development is one of the main targets of a modern economy [1]. Biotechnology represents a green solution for a sustainable development in textile industry. Enzymes started to be used with success in different textile processes like: scouring of cotton, anti-pilling and handle improving treatments for cotton, wool and polyester, anti-felting effect for wool, biostoning of denim, silk degumming, etc.[2]. The problem to be solved in this respect is that of textile material waste, taking especially into account the increasing world population. Cotton is one of the most spread raw materials as indicated [3] by the global textile fibers consumption (table 1). It may be used alone or in blend with synthetics like polyethylene terephtalate.

Table 1
TEXTILE FIBER CONSUMPTION

Fiber category	10^6 tones
Cotton	18.76
Regenerated cellulose	2.32
Wool	1.74
Synthetic	16.04

It is well known that at this stage of development of textile industry there are few environmentally friendly processes. All the textile materials based on natural or man-made fibers involves consume of large quantities of chemicals, water and energy and generation of air discharges, wastewaters and solid waste. A product life-cycle analysis for polymeric blends made from cotton and PET [4] gave the following environmental impact (table 2).

There are two types of solid textile wastes: pre-consumer and post-consumer. The pre-consumer wastes, generated during the industrial process, are usually recycled being used for other fibers, blends or non woven materials. The post-consumer waste is one of the components of municipal solid waste. According to the literature, in USA, one of the larger world consumer, textile made 3.2 –4% from the composition of municipal waste [5].

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Table 2
BALANCE OF CONSUME FOR A COTTON/POLYESTER MATERIAL

Impact	Per Ton
Total energy consumed (GJ)	350
Total water consumed	9200
Total textile waste generated (%)	25

There are some solutions proposed for solving the problem of post-consumer textile waste based on cotton [6]:
- energy recovering by burning;
- agricultural solution;
- composite materials;
- biotechnological procedure.

Energy recovering by burning

Incineration of textile waste represents a procedure for recovering in part the energy involved in the production of textile material. Campbell and coworkers [7] proposed a procedure for co-combustion of coal and textiles in a small-scale circulating fluidized bed boiler. Other procedures for recovering the energy were proposed [6]. The application of gasification brings a number of benefits like: decomposition below melting point of ash and decrease of the amount of flue gas originating in the process.

A problem in connection with the thermal degradation of waste is that of possible Dioxin emission. The analysis of polychlorinated dibenzo-dioxins (PCDD) and polychlorinated dibenzo-furans (PCDF) from the incineration of recycling products has lead to the conclusion that textiles have the highest potential to produce these very toxic compounds [8]. Dioxin is the most potent carcinogenic compound and has also teratogenic effects.

Agricultural solution

Composting the cotton mill waste produced stable organic material useful for soil improvement and growth substrates. Addition of different organic or inorganic compounds is benefic for the compost quality. The product may be used for agricultural application, for instance as substrate for growing mushrooms [9]. From the cotton textile waste only the pure cotton material, being biodegradable, may be used for agricultural purposes, not blends with different synthetic components.

Composite materials

Textile waste could be used as component of different composite materials. An example is the valorization of textile from automotive industry for an environmentally friendly green concrete [10]. Textile waste cutting, mixed with cement makes a composite material looking like concrete but which can be cut like wood [11]. Cotton waste in a matrix of polyacrylo-nitrile has been used for a water absorbent material [12]. Still the technologies for such materials are complex and costly.

Biotechnological procedure

Biotechnological solution could be more appropriate for solving the problems of textile waste. A biotechnological solution for solving the problem of textile waste of blends from cotton and PET was proposed [13]. The textile waste had been treated with a mixture of xylanase and cellulase and the polyester fibers were separated by simple filtration. The residual polyester [14] has proved to have similar properties with synthetic standard samples (table 3). The recover of polyester is a proper solution from an ecological point of view due to the fact that polyester is a non biodegradable material and also its synthesis involves consume of chemicals and energy.

Table 3
PROPERTIES OF POLYESTER FIBERS

Parameter	Initial fiber	Residual fiber
Average molecular weight (Da)	16900	16573
Number density (dtex)	155	137
Breaking force (cN)	193	181
Tenacity (cN/tex)	12.5	14.9
Elongation (%)	31.2	28.6

The expensive costs of enzymes, as well as the absence of knowledge concerning cotton biodegradation optimal conditions, make the procedure unrealistic.

The purpose of this study is to find some information concerning the interaction of enzyme with the substrate depending on the enzyme type and the material structure. Also pretreatments have been used for making the cotton more available for the enzyme.

Material and methods

Enzymes

Roglyr Bio 1536 supplied by Rotta, an enzyme based on cellulase; used on all the cellulosic fibers, preferable on cotton. Optimal condition: *p*H 5.0, temperature 55-60^{0}C.

Denimax 601 S supplied by Novozym, a cellulolytic aggressive enzyme with good robustness working across broad *p*H and temperature ranges.

Materials

Textile materials

- cotton fiber;
- 100% cotton fabric, scoured and bleached, 110 g/m^2;
- fabric blend cotton/polyester 50/50 %, desized and alkaline scoured , 134 g/m^2;
- fabric blend cotton/polyester 50/50 %, printed; 106 g/m^2;
- fabric blend cotton/polyester 50/50 %, dyed , 110 g/m^2;
- fabric blend cotton/polyester 33/67 %, yarn dyed , 104 g/m^2;
- 100% cotton knitted fabric waste, 120 g/m^2.

All the chemical reagents (acetic acid, sulphuric acid, hydrochloric acid, sodium acetate, mono- and di-sodium phosphate, ammonia solution 34%), are p.a and have been supplied by Reactivul Bucharest.

Methods

General procedure

Samples of the textile materials have been treated with buffered solution (liquor ratio 1/20) based on phosphate or acetate of the commercial enzymes in the indicated optimal conditions for the enzyme activity. The samples transformation has been determined by measuring the weight loss due to the biotreatments in comparison with the weight loss in a similar solution without the enzyme.

$$\%W = W_i - W_f/W_i \qquad (1)$$

where: W_i = Initial weight;
W_f = Final weight after treatment

All the samples have been kept in solution for 8 h at 50-55^{0}C, followed by 16 h to room temperature. Then the enzymes have been deactivated by heating 20 min at 80^{0}C, the textile samples separated by filtration on glass filter, washed with hot water and dried. All the experiments have been done in triplicate.

The weight of all the samples was determined on a Sartorius thermo-analytical balance MA 100 in order to avoid the influence of relative humidity.

For the blends of cotton with polyester the accurate analysis of cotton content has been determined by the classical procedure, dissolution in sulphuric acid [15]. All the analysis confirmed the fact that the enzyme does not biodegrade the polyester part.

Pretreatment procedure

The textile material has been pretreated by the following procedures:

- Physical pretreatments:
  - mechanical fragmentation;
  - counter pile mapping with cards;
- Chemical pretreatment:
  - boiling in hydrochloric acid solution 3%, 120 min , followed by washing with hot and cold water.

Results and discussion

The study of biotreatments of cotton tried to put in evidence the influence of the textile substrate structure and history of the material, the enzyme types and previous pretreatment.

The influence of textile material

Cotton is a natural cellulose fiber having a supramolecular nanostructure stabilized by numerous hydrogen bonds making difficult the enzyme access [16]. The degree of biodegradation depends, according to the

Sample	Material weight loss (%)	Cotton weight loss (%)
Cotton fiber	1.80	1.80
Cotton fabric 100%	2.26	2.26
Fabric blend Cotton/PES 50/50 desized and bleached	2.33	4.66
Fabric blend Cotton/PES 50/50 dyed	6.37	12.87
Fabric blend Cotton/PES 50/50 printed	2.32	4.64
Fabric blend Cotton/PES 33/67 yarn dyed	3.01	9.03

Table 4
WEIGHT LOSS OF THE SAMPLES TREATED WITH DENIMAX 601S, AT *p*H 6.0

experimental results, on the degree of cristallinity of the fiber which depends on the way of work up. More work up have been done, less crystalline will be the cotton part.

The results obtained with Deni Max 601S, recommended as very aggressive enzyme, were shown in table 4. The commercial enzyme was used in a concentration of 10% (o.w.f) in phosphate solution with *p*H 6.0, worked up according to the general method described before.

The experimental results showed that more worked up materials biodegraded more than the less worked up ones. The cotton/PET blends presented higher degradation than pure cotton. These results confirm that the disruption of the crystalline area of cotton by knitting and weaving in blends or finishing processes helps the enzymatic attack on the cotton substrate.

The influence of enzyme

Another problem is generated by the enzymes composition. For cellulose biodegradation a complex of cellulases has to be used. It is formed by the following types of enzymes, according to the way of the polymer fragmentation [17]:

- endoglucanases (E.C. 3.2.1.4) - EG
- exoglucanases or celobiohydrolases (E.C. 3.2.1.91) - CBH
- β-Glucosidases or celliobases (E.C. 3.2.1.21) -β-G

Each enzyme has its role in the biodegrading process and depending on the purpose of the enzymatic treatment, a surface polishing or real biodegradation takes place [18]. Both endo- and exoglucanases have the same specificity for the 1-4 glucans but hydrolyses it in different ways [19]. An efficient hydrolytic process takes place by the simultaneous action of these enzymes [20]. The endoglucanases cut randomly the polymer chain of cellulose, generating new ends for the exoglucanases. These enzymes have an active site shaped so to allow attack only at the end of the polymer chain [21]. Most of celobiohydrolases cut at the nonreducing end of the biopolymer but some of them act at the reducing end leading to a complete and productive biodegradation [22]. The cooperation mechanism of endo- and exoglucanases is not entirely known. For celobiohydrolase of primer importance seems to be the binding domain. The results obtained suggest that the binding domain place an important role in the cellulose crystalline structure disruption [23]. Similar results have been evidenced before [24].

Moreover, celobiosedehydrogenase, an extra cellular haemoflavoenzyme, oxidizes the reducing end of cellulose and cellooligosaccharide. It completes the biodegradation process by transforming the corresponding sugars in 1,5-lactones, and easily hydrolyzed to carboxylic acid [25]. Together with cellobiases the cellobiosedehidrogenase helps to eliminate cellobiose an inhibitor of cello-biohydrolases [26].

The mechanism of action of all these enzymes was presented in a review paper (fig. 1) [27].

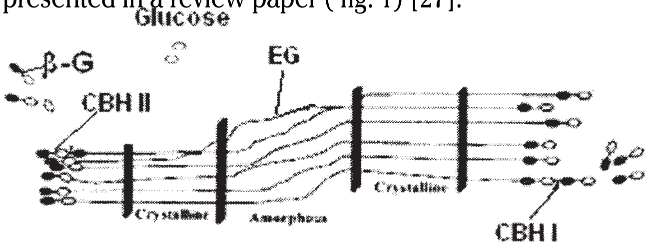

Fig.1. Cotton biodegradation by different types of cellulases

All the literature data confirm the importance of the enzyme composition for a complete biodegradation. The multi-cellulase complex, known as cellulosome, has better activity than isolated enzymes [28]. Also, synthetic mixtures of cellulase type enzymes in known ratio give better results in cellulose saccharification [29]. For industrial application pure enzyme are by far too expensive. Thus, in the present study a number of commercial enzymes with unfortunately unknown real content have been used. Depending on the commercial enzyme type and textile material, the following results have been obtained (table 4 and 5).

The pretreatment influence

These preliminary results indicated that the used commercial enzymes have not a very efficient activity in the experimental conditions. Accordingly, in order to have

Table 5
THE INFLUENCE OF ENZYME TYPE ON THE COTTON BIODEGRADATION

Enzyme / Substrate	Roglyr Bio 1536	DeniMax 601S
	Cotton weight loss (%)	
Cotton fabric 100%	8.03	2.73
Fabric blend Cotton/PES 50/50 desized and bleached	9.18	7.52

Enzyme / Substrate	Roglyr Bio 1536			DeniMax 601S		
	Cotton weight loss (%)					
	1	2	3	1	2	3
Cotton fabric 100%	12.18	7.78	16.08	3.34	3.29	6.89
Fabric blend Cotton/PES 50/50	22.12	11.5	18.14	9.39	7.85	7.40
Waste of 100% cotton knitted fabric	7.85	6.51	15.59	3.73	1.44	5.34

1-mechanical fragmentation; 2-counterpile mapping with cards; 3-boiling in hydrochloric acid;

Table 6
THE INFLUENCE OF PRETREATMENT ON THE COTTON BIODEGRADATION

higher cotton losses a number of pretreatments of the textile materials have been performed. The textile materials were subjected to mechanical and chemical pretreatments. The experimental results are presented below (table 6).

The physical pretreatments are more helpful leading to higher biodegradation of the textile substrate. The highest weight loss have been obtained for the first type of pretreatment and as expected for blends there were registered higher losses.

Conclusions

Enzymatic treatments lead to the partial biodegradation of cotton.

The type of enzyme is of importance due to the necessary ratio between the different types of cellulases. According to the experimental results Roglyr Bio 1536 has a better action compared with DeniMax 601S.

A pretreatment is necessary for enhancing the hydrolysis of the substrate a mechanical fragmentation being the most efficient.

The diminishing of the cellulose substrate cristallinity, by knitting and weaving or finishing processes, generates a higher biodegradation. The cotton from the blends with polyester degraded better than pure cotton making possible the recovery of polyethyleneterephtalate.

New investigations will be done concerning an efficient use of cotton degradation products.

Further investigations have been developed for improving the cotton degradation.

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