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CYCLODEXTRINS TO RECOVER TEXTILE DYES IN WASTE WATER

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Abstract: *Cyclodextrins are cyclic oligosaccharides with a special toroid shape, obtained by the action of glucosyltransferase enzyme (CGTase) on starch molecule. Their peculiar structure allows the accommodation of different guest molecules inside their cavity forming molecular inclusion complexes. There are different types depending on the glucose units that are formed, called native. The cyclodextrins can be modified incorporating different groups (hydroxipropyl, methyl...) that changes their properties. Due their versatility in size, properties and the variety of inclusion complex can form is employed in many different industries like pharmacy, food or cosmetics to protect the molecule or to reduce their volatility. As the guest molecule is not bond with the cyclodextrin with the appropriate conditions it can release easily. In textile industry had been use in different areas: to remove surfactants from washed textiles, to substitute surfactants, in the dyeing process, in detergents… Due their capacity to fix onto textile allows the functionalization of the fabrics giving them new properties like UV protection, antimicrobial or insect repellents depending on the guest molecule, in. The project DYES4EVER employs the cyclodextrins to encapsulate dyes not fixed during the dye process that remains in the wastewater and aims to go one step further and reuse the dyes recovered as a raw material in new dyeing processes.*

Key words: *reuse, textile dyes, cyclodextrins, inclusion complex, epichlorohydrin-Cyclodextrin .*

1. INTRODUCTION

1.1 Layout

Cyclodextrins (CDs) are cyclic oligosaccharides obtaining treating enzymatically starch with cyclodextrin trans glycosylase. α-, β-, and γ-CDs comprise 6, 7, and 8 D-glucose units, respectively, connected through α-1,4 linkages. Each CyD is shaped more or less like a thick-walled bucket, with a hydrophobic cavity and hydrophilic exterior. This unique structure enables CDs to form an inclusion complex, entrapping the whole, or part, of a "guest" molecule inside its cavity, principally by means of weak forces, such as van der Waals forces, dipole-dipole interactions, and hydrogen bonding. [1].

The most familiar applications of cyclodextrins are in pharmacy [2] to drug release and masking taste, in nutrition [3] to remove fats and for flavor release and cosmetics [4] to protect the active ingredients. The applications of cyclodextrin is growing and it can find use in agro industry [5] [6] to encapsulate pesticides, herbicides or insect repellents and in environmental sciences to removal organic pollutants from water, soil and air [7].

Is this point where DYES4EVER project is focused: in remove textile dyes from the wastewater and recover to reuse in new process of dyeing improving their life cycle. The investigation was focus in direct dyes in concrete in: direct yellow 106, direct red 83:1 and Direct black 112.

2. EXPERIMENTAL

2.1. Materials

Epichlorohydrin, Cyclodextrins, Sodium borohydride and sodium hydroxide were purchased from Sigma-Aldrich.

2.2. Methods

In a first step an Epichlorohydrin-Cyclodextrin was synthetized. The procedure described by Solms and Egli [8], and extended by Komiyama et al. [9] was used with some modifications, consisting of an increase in the amount of crosslinking agent in order to obtain mechanically stable polymers containing the same amounts of β-CD or γ-CD, as it can see in table 1

Table 1: *Experimental conditions carried out in the experiments.*

Epichlorohydrin (g)	Tª (ºC)	Time (h)	NaOH (mL)	$NaBH_4$ (mg)	CDs	CDs (g)
132	50	2	13	30	HP- βCD	12
132	50	2	13	30	γ-CD	12

There are several methods of preparing CDs inclusion complexes [10] depending on the type of molecule to encapsulate. The employed in the previous works done in the lab were stirring the wastewater solution with CDs in a ratio 50:1 v/w and filtering off the precipitated complex. This method is replicate in the prototype constructed in Colorprint Fashion facilities, which collect part of the waste water and after 2 h. of stirring is emptied by filtering off to recover the Epi-CDs polymer with the dye encapsulated.

Fig. 1: *Recovery prototype*

The last step is use the complex formed between EPI-CDs polymer and dyes as a raw material in a new lab dyeing process with the conditions showed in table 2.

Table 2: *Experimental conditions in dyeing process.*

wof.complex (%)	Liquor rate	Temperature (ºC)	Time (min)	Auxiliaries (g/l)
6	1/15	95	60	15 Sodic sulphate

3. RESULTS AND DISCUSSION

The water waste (figure 2) was analyzed before and after treated with the two cyclodextrins polymers with the results showed in the figure 3.

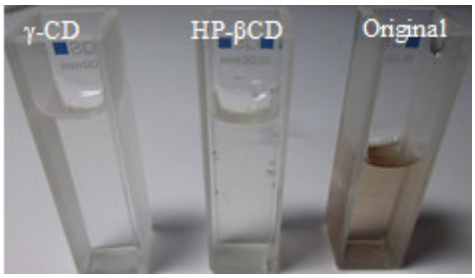

Fig. 2: *wastewater.*

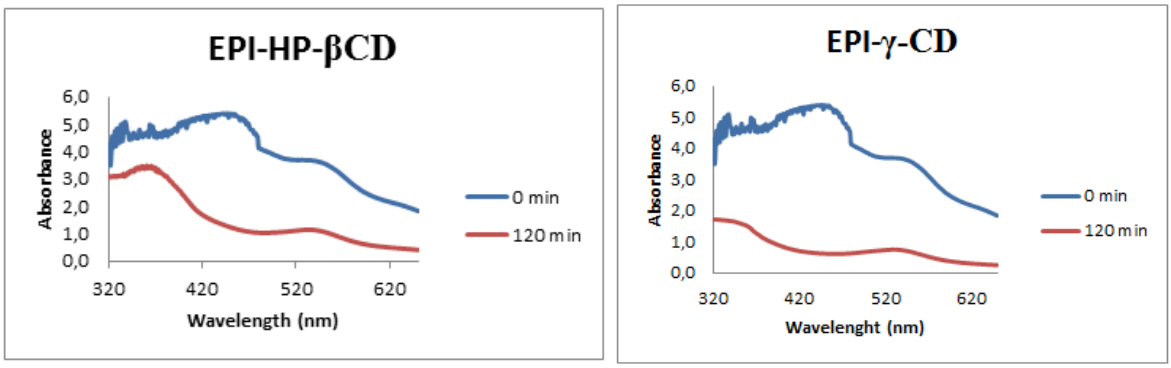

Fig. 3: *Recovery prototype*

In the figure 4 the textile dyed are showed. The named as original is the textile obtained with the formulation mix of three direct dyes that generate the waste water with which is form the complex. This complex recovered is used as a new material to dyed in the first use and recovered and use again in the second dyeing process.

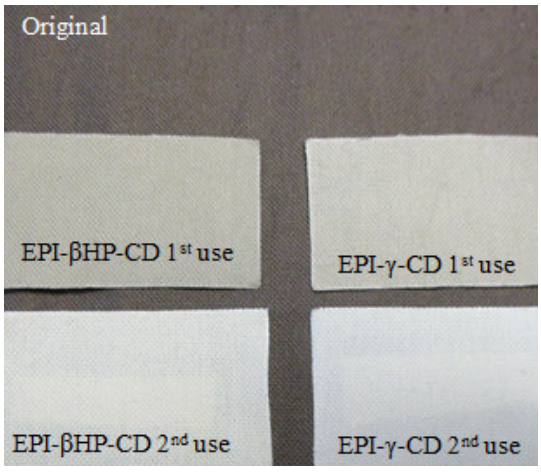

Fig. 4: *Recovery prototype*

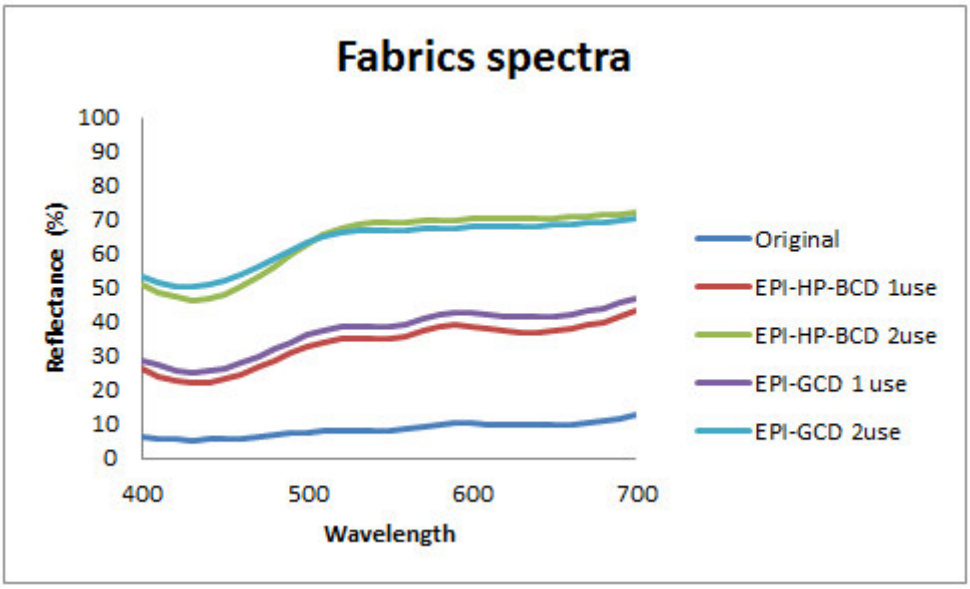

Fig. 5: *Spectra of fabrics dyed.*

4. CONCLUSIONS

The cyclodextrins are good agents to encapsulate dyes un-fixed in the waste water after a dyeing process reducing the amount of dye in the water effectiveness. The dye recovered could be use in news dyeing process obtaining a textile dyed with very low intensity that the original formulation but with the same spectra despite to encapsulate three different dyes with different release form. The EPI-HP-β-CDs polymers obtain slightly better results about the intensity of the fabric that the obtained with the EPI-γ-CDs polymers.

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