

# A new biosorbent with controlled grain (I). Efficient elimination of cationic dyes from textile dyeing wastewater

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**Abstract**— *Environmental care is an increasing concern in our society, and therefore integrated, circular economy allowing to close the industrial cycle is an urging demand. This project employs a residue of the food industry to recover the wastewaters from the textile industry, allowing closing the loop in two different industrial processes. Orange peel is a very abundant residue in the food industry. By chemical modification of the orange peel, we aim to produce a biosorbent to be employed in the treatment of the textile industry wastewater containing cationic dyes. In this project, we evaluate the capacity of the treated orange peels as cationic interchanger with different dissolutions of copper (II). Finally, their capacities as biosorbents were evaluated with four cationic dyes, examining the influence of different parameters like: biosorbent concentration, contact time, temperature and pH of the medium. An adsorption between 51 and 92 % was reached with the first treatment and also the possibility of the biosorbent recovery.*

**Keywords**— *basic dyes, biosorbent, biosorption, orange peel, wastewaters.*

## I. INTRODUCTION

A trend in wastewater treatment of industrial processes is to perform primary treatments in the most troublesome waters. In this first part of the study the new way to obtain a biosorbent with controlled particle size is presented and also the results of batch tests for the elimination of dyes, as well as the reuse of biosorbent that have allowed the subsequent development of continuous process of decoloration of wastewater from dyeing of textile materials.

Dyes are widely used in dyeing textiles and food, so they constitute one of the greatest challenges in the treatment of industrial wastewater due to its visual impact and increase of the organic load and toxicity (Vieira 2000). The dye molecules distinguish three functional parts: the chromophore, which is responsible for giving the colour property to the dye molecule; the auxochrome, which provides affinity to the textile fibre and intensifies the colour, and the solubilizing groups (Zollinger2001).

These substances are persistent in wastewater and constituting a pollution problem . The dyes are found in the waste of the textile industries from their own production. Their main effect on the aquatic life is the limitation of photosynthetic activity as a result of the decrease in the light penetration and the toxicity affecting aquatic life due to the presence of aromatic and halogenated compounds and/or heavy metals(Robinson 2001).

The dyes currently used are mainly synthetic. Due to its diverse and complex reactive nature, the chemical stability of the dyes converts them in compounds difficult to treat with a general method. According to the conditions in which the dyeing process occurs, the dyes are classified into: acidic, cationic, direct, disperse, reactive, sulphur, vat and others (Aksu 2005).

The textile finishing industry is an industrial sector that consumes water, energy and auxiliary chemical products; therefore, the treatment of wastewater is important. These effluents have significant concentrations of dye, organic contaminants, heavy metals, surfactants and chlorinated compounds.

The treatment of textile effluents is carried out in two stages: homogenization, and physicochemical or biological treatment. Within this scheme, it is possible to selectively treat the dyeing wastewater, discolor, and incorporate them in the overall treatment system. Each method has its own technical and economic limitations and, usually, the use of a single process is not efficient enough to ensure the colour degradation and the mineralization of the compounds formed (Supaka 2004; Buitrón 2004).

Biological processes have been considered as effective alternatives to treat coloured effluents (Van der Zee 2005;Pandey 2007) but the elevated permanence times needed of some dyes and auxiliary products are now the major constraints for their application (Rai 2005).

There are many techniques used in dye removal, which include both physical and chemical processes, for example: ozonation, advanced oxidative processes, photochemical processes, membrane filtration, etc. (Robinson 2001)

The lines of research to obtain new low-cost adsorbents materials have focused, primarily, to produce activated carbon. Different activated carbons have been prepared from shell Walnut (Yalcin 2000; Bello 2002) rice husks, peach stones (Abdel-Nasser 2001), and from other waste materials. However, due to the high cost of the aforementioned substances, we have also considered low cost biosorbents as, for example, agro-industrial waste without any type of treatment. Namely, rice husks, cork and orange peels have been found to yield results such as sufficient retention of dyes. In fact, the valorisation of vegetable residues such as biosorbents, is gaining increasing significance in the environmental field (Brown 2000).

Adsorption is a transfer of matter that is being reintroduced as an alternative to dye removal. There are three kinds of adsorption according to the type of interaction given between the solute and the adsorbent. If the adsorption is done by an ion exchange mechanism, the ions of the substance of interest are concentrated in an area of the adsorbent material as a result of the electrostatic attraction between the two; this is called electrostatic adsorption. However, if the adsorbed molecule is not fixed in a specific place of the surface, but it is rather free to move into the interface, the adsorption is done due to the Van der Waals forces and it is called physisorption. Therefore, if the adsorbate has strong links in the active sites of the adsorbent, one can say that adsorption is of chemical nature. It may be highlighted that, in the physisorption, the adsorbed species preserve its chemical nature, while during the chemisorption the adsorbed species undergo a chemical transformation, giving place to different species (Appelo 2005). The systems based on physisorption can allow the reuse of the adsorbent, probably better than the systems based on chemisorption are able to.

The main parameters are: the specific surface of biosorbent, pH, temperature, the nature of the adsorbent, the nature and concentration of the adsorbate, the contact time and even the solute ionic force (Santos 2003). In the interaction between adsorbate and adsorbent, the factors that affect the process are: the adsorbate solubility (at lower solubility, best adsorption); molecular structure of the solute (as more branched best adsorption); molecular weight (large molecules show better adsorption); polarity (lower polarity has better adsorption and degree of saturation) (Fetter 2001).

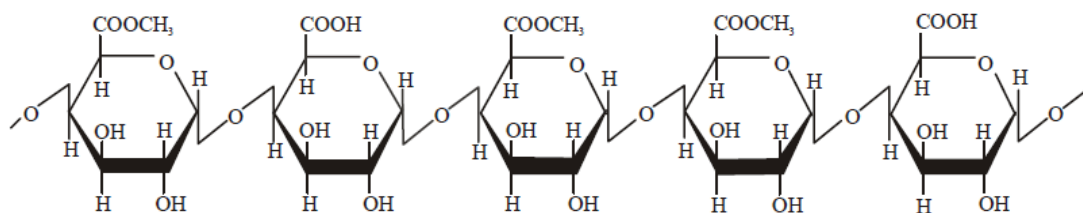
The biosorption is an adsorption process that consists of the catchment of different chemical species by a biomass (living or dead), such as: algae, fungi, bacteria, shells of fruits, agricultural products and some types of biopolymers through physicochemical mechanisms as the adsorption or an ionic exchange (Chojnacka 2010).

The biosorption process involves a solid phase -biomass- (sorber or adsorbent) and a liquid phase (solvent) that contains the dissolved species (adsorbate), which is to be retained by the solid. To carry out this process affinity should exist between the adsorbent and the adsorbate, so that those are transported toward the solid, where they are retained by different mechanisms. This operation continues until a balance between the dissolved adsorbate and the adsorbent is established and bound to the solid. This process continues until a steady state of concentration is reached. The use of dead biomass has advantages compared to the use of living biomass, since it is not necessary to add nutrients to dead biomass. Additionally, the adsorbent is immune to the toxicity or to the adverse conditions of the operation so the processes are not governed by biological limitations anymore (McKay 1986).

The cellular walls of biosorbent materials contain polysaccharides, proteins and lipids, and, therefore, functional groups with capacity to bind heavy metals and cationic molecules in their surface. The main functional groups present here are the amino, carboxylic, hydroxilic, phosphate and thiol groups that differ in their affinity and specificity of joining different metal ions (Ghimire 2003).

The orange peel (*Citrus sinensis*) is obtained as a byproduct of orange juice manufacturing, and is eliminated as scrap. However, the orange peel and other citrus fruits have been widely used in the elimination of heavy metals and textile dyes (Annadurai 2002; Arami 2005; Pavan 2006; Pérez 2007; Popuri 2007; Hameed 2008; Li 2008; Gupta 2009; Lu 2009; Arjona 2016).

The bioadsorption in orange peels is because they contain pectin in their composition. Pectin is a natural high molecular compound widely-existing in cell wall and middle lamella structure of all higher plants (Qiu, Tian, Qiao, & Deng, 2009). Pectin is usually considered as a complex polysaccharide which consists of  $\alpha$ -1,4-linked D-galacturonic acid, which is partly methyl esterified, and the side chain contains various neutral sugars, such as L-rhamnose, L-arabinose, and D-galactose (Mohnen, 2008; Xie, Li, & Guo, 2008). Pectin properties include gelatification, thickening and stabilization, giving it widespread use in food, medical, chemical, textile and other industrial fields (Sato et al., 2011).



**FIGURE 1: PECTIN A POLYMER OF  $\alpha$ -GALACTURONIC ACID WITH A VARIABLE NUMBER OF METHYL ESTER GROUPS**

When the proportion of methoxy groups is low and, therefore, the proportion of COO-groups available is high, the links that are established between the molecules can be made through divalent cations (Ca<sup>2+</sup>, Cu<sup>2+</sup>, etc. . .).

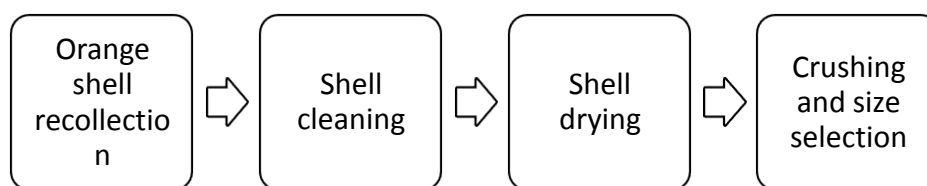
The main objective of this study is to develop and optimize the treatment of orange peel to obtain a reusable biosorbent, which will allow the removal of heavy metals and cationic dyes from wastewater.

## II. MATERIAL AND METHOD

### 2.1 The process of the biosorbent preparation

The first stage is the collection and cleaning of the orange peels. It is important to select peels of oranges in good state, without fungi, worms or parts in decomposition. Then the edible part (endocarp) is separated, so that the shell (flavelo and albedo) is free from pulp residues. The process continues by rubbing the peel surface with detergent to remove the waxes, which had been added to improve the appearance of the fruit in the commercial circuit.

The second stage is drying till reaching a constant weight. The process continues with the crushing and screening, selecting a particle size between 500  $\mu$ m and 1000  $\mu$ m. All those operations are presented in figure 2:



**FIGURE 2 PHYSICAL RECONDITIONING PROCESS OF THE ORANGE SHELL**

The selected particle size fraction was subjected to a clarification treatment with tetrahydrofuran (THF) in a Soxhlet equipment, to extract the lipid fraction, the essential oils and the bioflavonoids.

In this research, the orange peel was subjected to a first treatment in acid medium to clean the surface and extract secondary products, followed by a second treatment in an alkaline medium with calcium hydroxide to reticulate the Ca<sup>2+</sup> in the surface of the orange peel. The removal of metals in dissolution by the Ca<sup>2+</sup> reticulated pectin occurs basically due to a phenomenon of ion exchange between the Ca<sup>2+</sup> and metal ions in solution until equilibrium is reached.

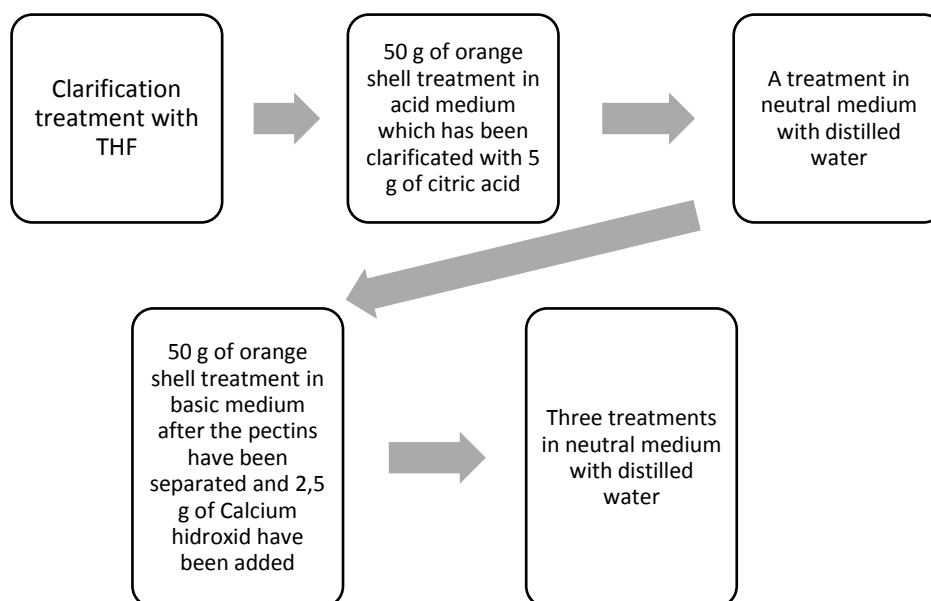
The procedure was:

The orange peel was clarified with THF in the Soxhlet equipment. Experimentally, it proceeded as follows:

- 500 mL of distilled water, 50 g of orange peel and 5 g of citric acid were added to a vessel and were treated for 45 minutes with ultrasonic equipment, and was filtered.
- 500 mL of water distilled was added to the solid fraction, (orange peel subject to the process of extraction), and was treated again for 45 minutes with ultrasonic equipment to eliminate the remains of the acid added in the previous process and was filtered again.
- In the resulting solid fraction, 500 ml of distilled water and 2.5 g of calcium hydroxide were added and it was treated again for 45 minutes with the ultrasonic.

The solid fraction was separated and treated with 500 mL of distilled water for 45 minutes with ultrasound. This last operation was repeated two times more with the objective of eliminating the excess of alkali in dissolution and eliminate

possible particles that could have stayed in suspension (fine) which could constitute an interference in the spectrophotometric determination of the dyes when they were subjected to the action of the cationic exchanger



**FIGURE 3: CHEMICAL CONDITIONING PROCESS OF THE ORANGE PEEL**

The equipment used in the treatment of orange peel was Ultrasonic LC 30 H from Elmasonic with frequency set of 37 KHz.

## 2.2 Procedure for controlling the efficiency of preparation of the biosorbent

The verification of the characteristics of the biosorbent obtained was made with a series of synthetic solutions of Cu (II). Experimentally, it proceeded as follows:

- 0.5 g of biosorbent and 25 mL of a known Cu (II) solution in a test tube equipped with a screw cap were added and a controlled stirring was followed for 10 minutes.
- A 5 ml aliquot of the Cu (II) solution was extracted and 5 mL of 5% potassium iodide solution was added and shaken manually, in order to check the formation of iodine.
- Then 5 ml of dichloromethane were added and it was shaken again manually. A pink coloration of the organic layer confirmed the formation of iodine.

In the case that the organic phase of dichloromethane remained colourless, it is interpreted as that the biosorbent (cation exchanger) has adsorbed the totality of the Cu (II). In the case that a light pink colour appears it means as that the cation exchanger had not completely absorbed the Cu (II) and enough iodine has been formed to detect it in the dichloromethane phase, according to the reaction:  $5I^- + 2Cu^{2+} \rightarrow Cu_2I_2 + I_3^-$

Under the described conditions, 0.5 grams of the described biosorbent were completely removed, through an ion exchange mechanism, 200 ppm (mg/L) of dissolution of Cu (II) prepared from  $CuSO_4 \cdot 5H_2O$ .

Dissolution of 500 ppm of Cu (II) was used to show that it had overcome the adsorption capacity of the quantity used in the biosorbent. Under those conditions a light pink coloration appeared during the organic phase

The following table shows the results obtained by the adsorption of synthetic aqueous solutions of Cu (II) (25 mL at different concentrations) with 5.0 g of the biosorbent. This test was measured by the atomic absorption at 324.8 nm.

**TABLE 1**  
**EFFICIENCY OF THE BIOSORBENT IN THE REMOVAL OF CU (II)**

Initial Cu (II) concentration (ppm)	Final Cu (II) concentration (ppm)	Cu (II) retained (%)
5.00	1.25	<b>75.00</b>
10.00	1.15	<b>88.50</b>
30.00	2.69	<b>91.03</b>
100.00	3.64	<b>96.36</b>

The results show that the biosorbent obtained from orange peel allows the exchange of cations in an aqueous solution. It is also observed that as the initial concentration of the Cu (II) solution increases, the efficiency increases.

The removal of Copper (II) by the calcium pectinate is mainly due to an ion exchange process between the Ca (II) and the ions that are in the solution (Jang 1990). In this way, the Cu (II) displaces the Ca (II) initially attached to the polygalacturonic chain until reaching equilibrium concentrations in both phases.

In order to explain this biosorption process, the following model has been proposed: Initially, a fast mechanism of Cu(II) ion migration towards the surface of the bioadsorbent and in the second, slower stage, the migration of the Cu(II) ion to the active site displacing the Ca (II) ion.

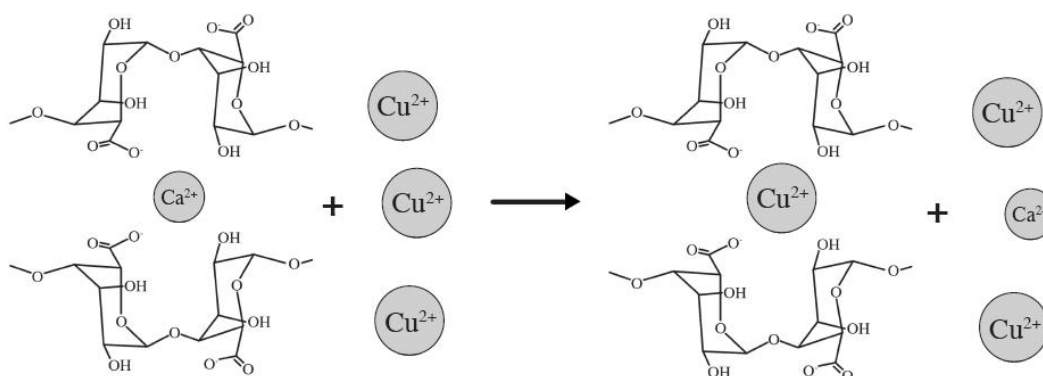


FIGURE 4 Cu (II) BIOSORPTION MODEL

### 2.3 Decolouration of textile wastewaters containing cationic dyes

Four cationic dyes were used in this research: C.I. Basic Blue 3; C.I. Basic Yellow 21; C.I. Basic Red 18 and C.I. Basic Green 4. The removal achieved was between 50% and 90%, using a batch shaken process at controlled pH 4.26 and a contact time of 45 minutes at 25 °C with a solution of 30 ppm (0.03 g/L) of the dye. Table 2 presents the molecular and the structural formula of the dyes and their molar mass.

TABLE 2  
CATIONIC DYES USED

Name	Molecular formula	Molecular weight (g/mol)	Structural formula
C. I. Basic Blue 3	C <sub>20</sub> H <sub>26</sub> ClN <sub>3</sub> O	359.9	
C. I. Basic Yellow 21	C <sub>22</sub> H <sub>25</sub> ClN <sub>2</sub>	352.9	
C. I. Basic Red 18	C <sub>19</sub> H <sub>25</sub> Cl <sub>2</sub> N <sub>5</sub> O <sub>2</sub>	426.3	
C. I. Basic Green 4	C <sub>23</sub> H <sub>25</sub> ClN <sub>2</sub>	364.9	

## 2.4 Recovery of the biosorbent (cationic exchanger)

The treatment to which orange peel has been submitted has two purposes. The first is extract partially the content of pectin and the second is the saponification of the ester (methyl) groups, so that Ca (II) ions facilitate the formation of three-dimensional structures with the chemically modified orange peel (biosorbent).

In contact with concentrated solutions of other cations, the movement of the calcium cation concerned is achieved demonstrating behaviour of ionic exchange. However, in the case of copper ionic exchange it is strongly retained in the three-dimensional structure, in a virtually irreversible way, which promotes the movement of calcium ions in the solution that is in contact with the biosorbent but not the displacement of Cu (II).

In the case of cationic dyes, which are very voluminous molecules, the biosorption mechanism does not occur by ion exchange. Electrostatic attractions and / or hydrogen bridges produce the surface adsorption of these molecules.

The biosorbent can be reused when treated with a polar solvent such as ethyl alcohol, since cationic dyes are dissolved in this medium.

After that, the biosorbent is treated with calcium chloride to enhance the three-dimensional structure that acts as a biosorbent. In this way, the cationic exchanger can be reused to adsorb new cationic dyes (basic dyes).

## III. RESULTS AND DISCUSSION

The influence of pH, temperature, biosorbent concentration, contact time of the biosorbent with cationic dye, the influence of moisture on the biosorbent, and the possibility of eliminating dye have been verified by successive treatments. In addition, the biosorbent regeneration process and the efficiency of the recovery have also been verified.

### 3.1 Influence of the pH

The influence of the pH on the interaction between the biosorbent (cationic exchanger) and the four cationic dyes (C.I. Basic Blue 3; C.I. Basic Yellow 21; C.I. Basic Red 18 and C.I. Basic Green 4) were determined. Dissolutions of 30 ppm (mg/L) of the four dyes were prepared at different pH values: 8.2; 5.2 and 4.0 and determined how much dye was left in the dissolution when treating 25 ml aliquots with 0.5 g biosorbent for 30 minutes. The results are shown in Table 3.

**TABLE 3**  
**COMPARISON BETWEEN THE BIOSORPTION AT PH 8.2; 5.2 AND 4.0**

	Biosorption (%)			Biosorption variation between max. and min. value (%)
	pH = 8.2	pH = 5.2	pH = 4.0	
<b>C.I. Basic Red 18</b>	91.33	91.00	89.00	2.33
<b>C.I. Basic Yellow 21</b>	51.67	52.33	54.67	3.00
<b>C.I. Basic Blue 3</b>	64.33	65.67	67.00	2.67
<b>C.I. Basic Green 4</b>	90.33	92.00	88.67	3.33

It was found that pH does not have a significant influence on the process of removal of the dyes, since the variation between the different dyes is less than 4 %. Therefore, due to the low influence of pH, it was decided to work in the conditions in which usually the textile industry works for the dyeing processes with cationic dyes: a regulatory solution of pH of acetic acid and sodium acetate with the concentration of 1 M (pH  $\approx$  4.26).

### 3.2 Influence of the temperature

The biosorbent efficiency was compared at 25 ° C and 65 ° C. The textile industry has its usual thermal recovery processes of the baths of dye, and therefore, the temperature of the bath that arrives to the columns of adsorption is an ambient temperature of around 25°C.

In the pH conditions described in the previous section (pH  $\approx$  4.26, with a pH buffer solution of acetic acid and sodium acetate), the efficiency of the biosorbent has been compared at 25 ° C and 65 ° C. The results are shown in the table 4:

**TABLE 4**  
**COMPARISON BETWEEN THE ADSORPTION AT 25 AND 65 °C**

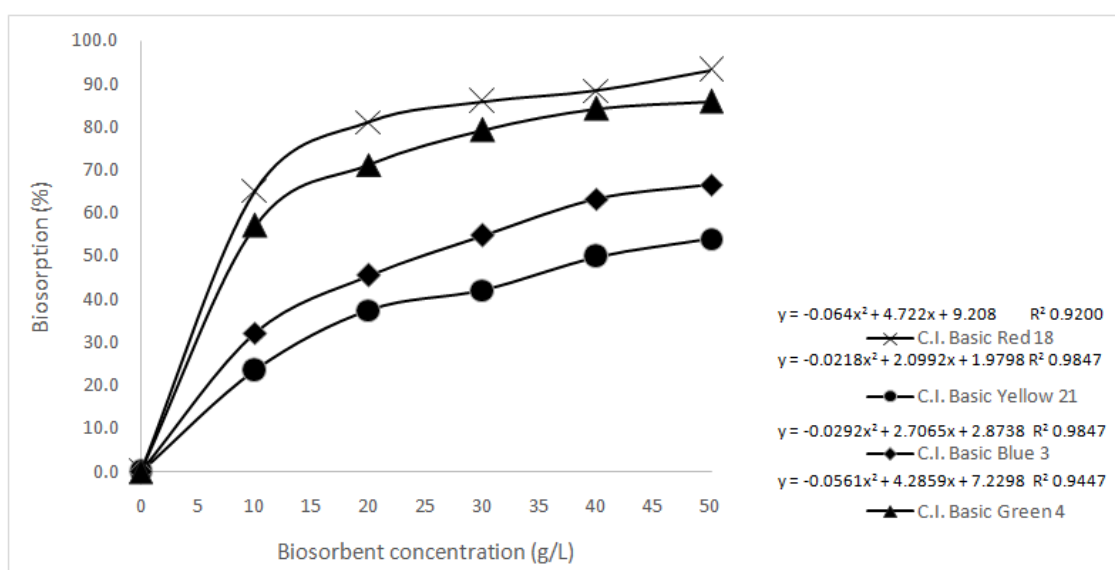
	Biosorption (%)		Variation (%)
	25 °C	65 °C	
<b>C.I. Basic Red 18</b>	81.0	80.5	0.5
<b>C.I. Basic Blue 3</b>	39.3	42.6	3.3
<b>C.I. Basic Yellow 21</b>	24.5	24.9	0.4
<b>C.I. Basic Green 4</b>	54.7	62.3	7.6

In the case of the C.I. Basic Red 18 the difference in the % of adsorption between the two temperatures is 0.5 %. In the case of the C.I. Basic Blue 3 the difference is 3.3 %. For the C.I. Basic Yellow 21, the variation is 0.4 %. Finally, for the C.I. Basic Green 4, the variation is 7.6 %.

Due to these results, it was decided to continue working at 25 °C as this favors its transfer to the industrial sector of dye treatment of wastewater.

### 3.3 Influence of the biosorbent concentration

At the pH and temperature predetermined values, the following process was to establish the optimum concentration of biosorbent and the contact time. Therefore, solutions of 30 ppm of each of the four cationic dyes were prepared in a pH  $\approx$  4.26 (with a pH buffer solution of acetic acid and sodium acetate), then different quantities of biosorbent were added to 25 ml aliquots of each dissolution. The results are shown in Figure 5.



**FIGURE 5. DYE BIOSORPTION DEPENDING ON THE BIOSORBENT CONCENTRATION**

Fixed the values of the pH  $\approx$  4.26 and the temperature (25 °C), the influence of the concentration of biosorbent in the elimination of cationic dyes of the wastewater of the textile industry was confirmed.

According to the results, it was considered that the optimal biosorbent mass for 25 ml of the different dissolutions of 30 ppm (mg / L) was 1.0 g, which is equivalent to say 0.04g biosorbent / ml dissolution or 40 g / L, since from this value the biosorption percentage did not increase significantly.

At low concentrations of biosorbent, between 10 and 20 g/L, a dye adsorption between 65 and 81 % takes place for the C.I. Basic Red 18, between 23 and 37 % for the C.I. Basic Yellow 21, between 32 and 45 % for the C.I. Basic Blue 3 and between 57 and 71 % for the C.I. Basic Green 4.

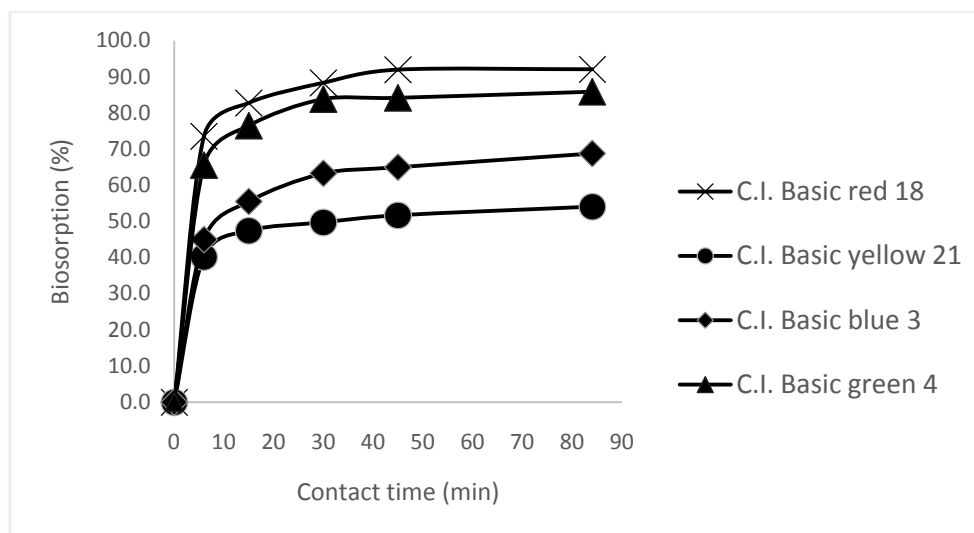
The increase of the concentration of the biosorbent between 20 and 50 g/L results in smaller increase in the adsorption of dyes.

With 40 g / L of adsorbent, a removal of 88.4% is achieved for C.I Basic Red 18, 49.8% for C.I. Basic Yellow 21, 63.3% for C.I. Basic Blue 3 and 84.2% for C.I. Basic Green 4.

In view of these results it is recommended that the industrial conditions of biosorbent concentration are of 40 g / L.

### 3.4 Contact time influence between biosorbent and the residual dyeing bath

At the optimal biosorbent concentration we proceeded to make a series of experiments in which 25 mL aliquots of dye was added 1 g of biosorbent (40 g/L). All dyes were prepared to a initial concentration of 30 ppm (mg/L), at pH 4.26 and 25 ° c. In these conditions, the time of contact between the biosorbent and dye was in the range between 6 and 84 minutes. The results are presented in Figure 6:



**FIGURE 6: RESIDUAL CONCENTRATION OF THE FOUR CATIONIC DYES DEPENDING ON THE CONTACT TIME**

There is an asymptotic behaviour in the adsorption of dye from the 45 min of contact time.

At short contact times, from 6 to 15 min, between 73.6% and 82.8% is eliminated for C.I. Basic Red 18, between 40.2% and 47.5% for C.I. Basic Yellow 21, between 45.0% and 55.5% for C.I. Basic Blue 3 and between 65.6% and 76.5% for C.I. Basic Green 4. In the table 6, the initial rates of dye biosorption (at 6 minutes) in the table 5

**TABLE 5  
INITIAL BIOSORPTION RATES (AT 6 MIN)**

	Initial biosorption rates (% biosorption / min)
<b>C.I. Basic Red 18</b>	12.26
<b>C.I. Basic Yellow 21</b>	6.70
<b>C.I. Basic Blue 3</b>	7.50
<b>C.I. Basic Green 4</b>	10.93

When comparing the biosorption at 15 and 45 minutes it was observed that the retention of cationic dyes increased from 82.8% to 92.0% by C.I Basic Red 18, from 47.5% to 51.7% by C.I. Basic Yellow 21, from 55.5% to 65.0% by C.I. Basic Blue 3 and 76.5% to 84.2% by C.I. Basic Green 4.. According to our results, the optimal contact time between the residual dyeing bath and the new biosorbent is 45 min

It was found that dyes that have a low initial rate also have a lower adsorption in the recommended conditions. This fact shows that there is a relationship between the chemical structure of the dye, the efficiency of the process and the initial rates.

In the recommended conditions of concentration of biosorbent (40 g/L) and contact time (45 min), the biosorption of the four cationic dyes by effect of the biosorbent are shown in table 6.



**TABLE 6**  
**THE FOUR CATIONIC DYES BIOSORPTION AT RECOMMENDED CONDITIONS**

	<b>Biosorption (%)</b>
<b>C.I. Basic Red 18</b>	92.0
<b>C.I. Basic Yellow 21</b>	51.7
<b>C.I. Basic Blue 3</b>	65.0
<b>C.I. Basic Green 4</b>	84.2

In all cases this supposes an important elimination of dye from the wastewater.

### 3.5 Biosorbent reuse: adsorption at low concentrations

The efficiency of removal of cationic dyes was determined after two, three or four successive treatments with fresh biosorbent, until a residual concentration of 2 ppm or less is reached. The residual bath of the first treatment is subjected to a second biosorption treatment with 40 g/L of fresh biosorbent, and then, if necessary, to a third or fourth treatment with the same concentration of biosorbent. In all cases, the cationic dye solution is fixed at pH 4.26 and 25 °C.

The results of each treatment efficiency are shown in table 7:

**TABLE 7**  
**EFFICIENCY OF THE SUCCESSIVE TREATMENTS AT LOW CONCENTRATIONS**

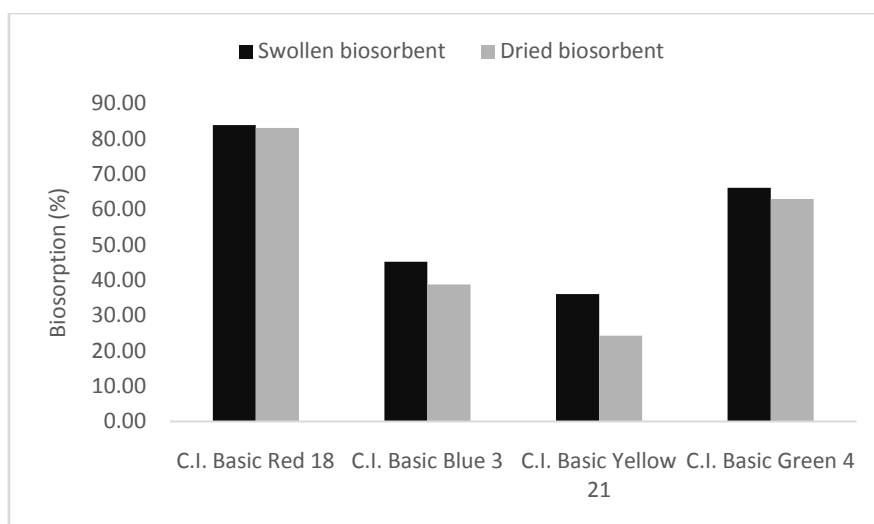
	<b>Efficiency of 1st treatment (%)</b>	<b>Efficiency of 2nd treatment (%)</b>	<b>Efficiency of 3rd treatment (%)</b>	<b>Efficiency of 4th treatment (%)</b>	<b>Final efficiency (%)</b>
<b>C.I. Basic Red 18</b>	92.0	100.0	-	-	100.0
	$C_i = 30.0$ ppm	$C_{i1} = 2.4$ ppm			$C_f = 0.0$ ppm
<b>C.I. Basic Yellow 21</b>	51,7	51,0	58,8	38,8	94.0
	$C_i = 30.0$ ppm	$C_{i1} = 14.5$ ppm	$C_{i2} = 7.1$ ppm	$C_{i3} = 2.9$ ppm	$C_f = 1.8$ ppm
<b>C.I. Basic Blue 3</b>	65,0	62,7	68,5	-	96.0
	$C_i = 30.0$ ppm	$C_{i1} = 10.5$ ppm	$C_{i2} = 1.2$ ppm		$C_f = 1.2$ ppm
<b>C.I. Basic Green 4</b>	84,2	82,4	-	-	97.3
	$C_i = 30.0$ ppm	$C_{i1} = 4.7$ ppm			$C_f = 0.8$ ppm

Successive biosorbent treatments always increase the efficiency of removal of the cationic dyes from wastewater.

With two successive treatments it is possible to eliminate 100% of C.I. Basic Red 18 of the sample. For C.I. Basic Yellow 21, four treatments are required to remove 94% of dye. In the case of C.I. Basic Blue 3, it is possible to eliminate 96% of the dye with three treatments. Finally, with two treatments, 97% of C.I. Basic Green 4 is removed.

### 3.6 Influence of pre hydration of the biosorbent

The efficiency of the biosorption process of cationic dyes from biosorbent powder or previously hydration biosorbent in distilled water for 24 h at 25 °C has been tested. 25 mL of cationic dye solution at pH 4.26 and 25 °C and 30 ppm were added with 20 g/L of biosorbent (0.5 g of biosorbent). The results are shown in figure 7:



**FIGURE 7. COMPARISON BETWEEN THE ADSORPTION OF THE FOUR CATIONIC DYES WITH MOIST AND DRIED BIOSORBENT**

It is therefore concluded that the hydration biosorbent tends to have a higher efficiency than the dried biosorbent. This base the subsequent development of a continuous process of treatment with the biosorbent used in this work.

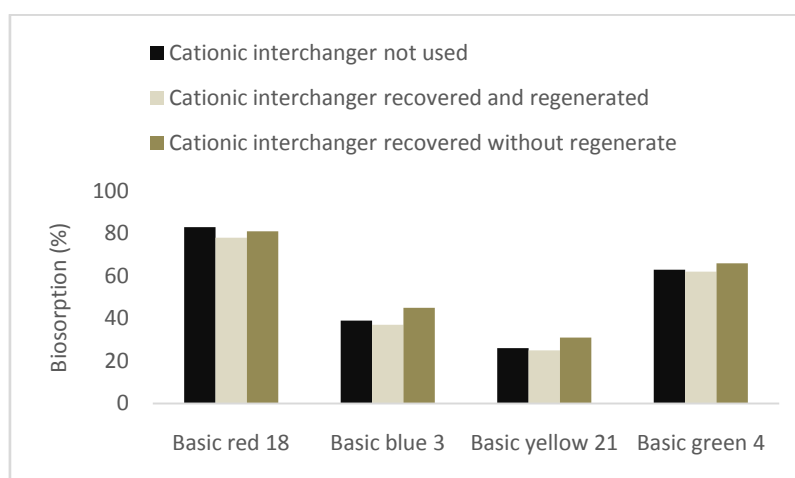
### 3.7 Influence of higher dyestuffs concentrations in the wastewater

An initial dyeing bath of 2 % owf of dyestuffs, and bath relation 1:40, if the bath exhaustion is 80 %, approximately 100 ppm (mg/L) of the dye may remain in the bath. Therefore, the biosorption of dye solutions at concentrations of 60, 90, 120 ppm and even 240 ppm has been studied. This study has been carried out at the same conditions (25 mL of solution at pH 4.26 and 1.0 g of treated citric derivate biosorbent) with higher or, at least, similar efficiency levels previously obtained.

### 3.8 Recovery of the cationic exchanger

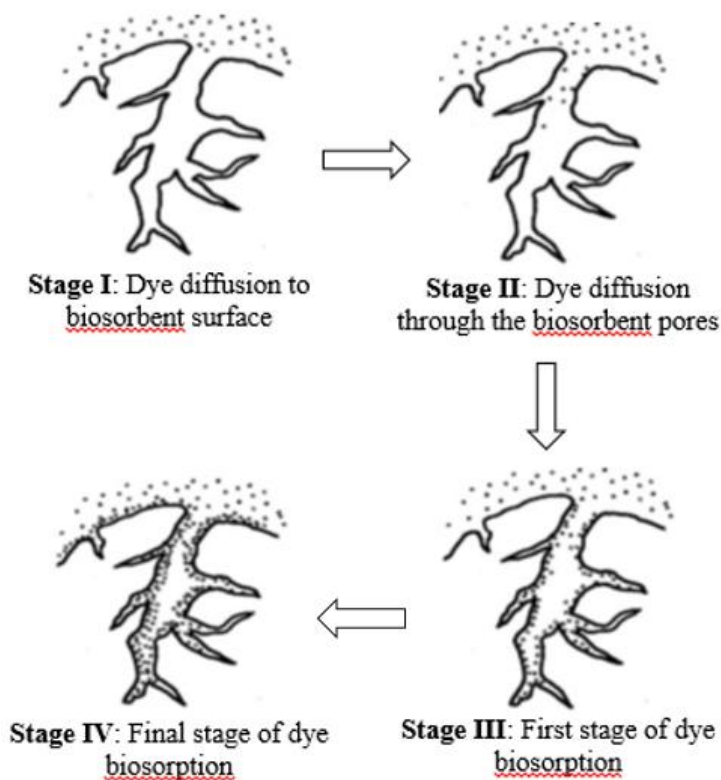
Finally, the recovery of the biosorbent was studied. For 1.0 g of used biosorbent two successive extractions of 25 mL of ethyl alcohol were added and stirred in a mechanical shaker for 45 minutes.

Then the regeneration of the biosorbent with calcium chloride ( $\text{CaCl}_2$ ) followed in order to cross-link the calcium ion in the cellulosic wall. For this process a solution of 0.2 M of  $\text{CaCl}_2$  was prepared and 0.5 g of cationic exchanger was treated with 25 mL of the solution (with a concentration of 20 g/L). Finally, a last treatment with distilled water was undertaken so as to eliminate the possible excess of calcium chloride. The biosorption of dye yields were compared with regenerated biosorbent and recovered biosorbent, without the calcium chloride treatment. The tests were done with solutions of 25 mL at pH 4.26 and 25 °C with a dye concentration of 30 ppm and with 0.5 g of biosorbent (20 g/L). The results shown in Figure 8 indicate that the biosorbent increased the efficiency when it was not cross-linked.



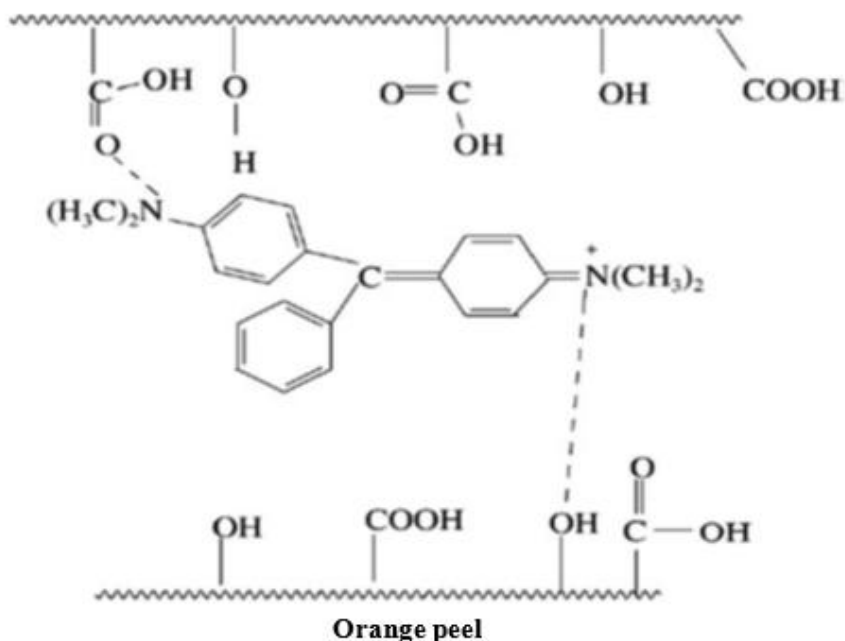
**FIGURE 8. EFFICIENCY COMPARISON BETWEEN REGENERATED BIOSORBENT AND BIOSORBENT WITHOUT REGENERATION**

Our results confirm the work of (Sivakumar 2010), that this is not anionic exchange mechanism, but that electrostatic attractions and/or hydrogen bonds adsorb the dyes. In figure 9 is shown how (Sivakumar 2010) reported a four-stage adsorption mechanism for removal of C.I. Acid Blue 92, C.I. Basic Red 29, C.I. Reactive Red 4 and C.I. Direct Blue 53 by precursor wood.



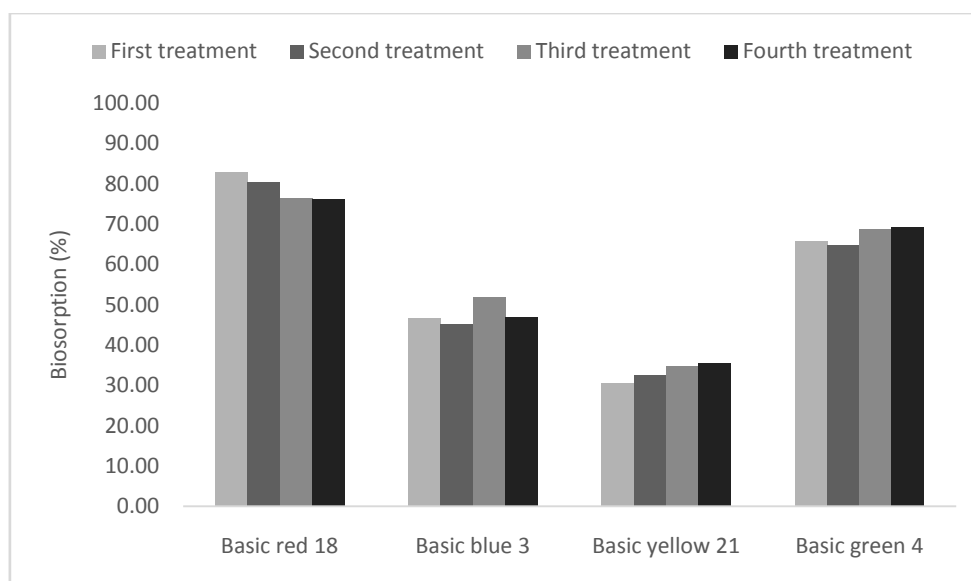
**FIGURE 9. PROPOSED FOUR-STAGE MECHANISM OF THE DYE ADSORPTION (SIVAKUMAR 2010)**

In Figure 10, the proposed mechanism for the C.I. Basic Green 4 is shown.



**FIGURE 10. PROPOSED MECHANISM FOR THE BIOSORPTION OF THE C.I. BASIC GREEN 4**

In the view of those results with ethyl alcohol we chose the recovery of the adsorbed dye, and the biosorbent was used for four more biosorption cycles. Figure 10 shows the results:



**FIGURE 11. ADSORBED PERCENTAGE OF THE DYES IN SUCCESSIVE TREATMENTS**

With the bioadsorbent developed in this work, it has been shown that the elimination of cationic dyes of the textile waste water is not produced by ion exchange but its efficacy is based on bonds by Hydrogen Bridge and by forces of London.

#### IV. CONCLUSION

The removal of heavy metals by treated orange peel is basically done through an ionic exchange phenomenon between Ca (II) and the metal ions in solution until the equilibrium is reached. That way, Ca (II), linked to the polygalacturonic chains, is displaced by the metal ion.

The saponification process (desmetoxilation) and the pectins reticulation sensible to the Ca(II) ion are usually done in two steps. At the first step, the desmetoxilation with NaOH is done, while in the second step the reticulation by CaCl<sub>2</sub> takes place. In this project, both steps were simultaneously done using Ca(OH)<sub>2</sub>.

The testing of this method has been rendered effective through a removal of Cu (II), using 0.5 grams of the biosorbent, through an ion exchange mechanism, almost 100 ppm of dissolution of Cu (II). It is accepted that this removal is done mainly because of an ionic exchanger process, in a way that Ca(II) is initially linked to the pectin chains and displaced by Cu (II) until reaching the equilibrium conditions. Furthermore, the biosorbent presents a high selectivity to the Cu (II) even in presence of other cations (Hang 1970).

In the light of these results, it is possible to assert that the removal of the cationic dyes used is not explained by a simple mechanism of ionic exchange, leaving the establishment of a better-adjusted mechanism according to experimental data for a later study.

The physical-chemical treatment developed in this work in the orange peel shell has achieved a final stable product (biosorbent), which can be reused several times.

Its application in the removal of cationic textile dyes has been tested yielding positive results at laboratory level. Nevertheless, the experimental results discard that, with this type of organic molecules, this biosorbent works as a cationic exchanger.

It has been demonstrated that 40 g/l of the biosorbent is effective in the removal of 30 ppm of cationic dyes, for 45 minutes of stirring, obtaining yields ranging from 52 to 92%.

It is possible to reach the total removal of the biosorbed dyes if the process is successively repeated, which suggests the developing of a new removal procedure as a continuous process.

The removal of cationic dyes has been studied in a solution with higher dyestuff concentrations (between 60 and 240 ppm) at the same conditions with higher or, at least, similar efficiency. This means that the dilution of the wastewater is not necessary to treat with this biosorbent.

It has been demonstrated that it is possible to recover the biosorbent and to reuse it with a constant efficiency for at least four cycles.

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