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# Removal of an Anionic Reactive Dye by Chitosan and its Regeneration

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*Abstract:* - Chitosan, a waste from the food industry, was employed for the removal of Reactive Black 5, a water-soluble anionic dye, from aqueous solution. Adsorption of this dye onto chitosan was studied with respect to pH, contact time and dye concentration. Optimum pH was ranging from 1 to 3. The addition of chitosan to dye solution strongly affected the pH of solution and sorption efficiency. To avoid this pH variation, the initial pH was set at 2.3 (no change in final pH). Reactive Black 5 was efficiently adsorbed on chitosan. The maximum sorption capacity was close to 480 mg g<sup>-1</sup>. The aim of this study was also to screen a variety of non-toxic desorbing agents, in order to find out possible application in multiple sorption-desorption cycles. Sorption and desorption experiments have been carried out in batch system, at room temperature. Desorption studies showed that the dye adsorbed on chitosan could be effectively desorbed using diluted KOH and NaOH solutions (0.01 M). The successive sorption-desorption studies using NaOH, indicated that chitosan could be regenerated and reused several times.

*Key-Words:* - Chitosan, Reactive Black 5, Biosorption, Desorption, Sorbent Regeneration

## 1 Introduction

The wastewater treatment for long time has been a main problem of the textile industry. These effluents contain various kinds of synthetic dyestuffs. More than 100,000 commercially available dyes exist and more than 700,000 tones per year are produced annually. Due to their good solubility, synthetic dyes are common water pollutants and they are frequently found in trace quantities in industrial wastewater [1].

The presence of dyeing effluent in a watercourse has a serious environmental impact. Dyeing effluent has high biological oxygen demand (BOD; measure of organic matter in effluent and oxygen required by bacteria in respiratory process to break down the organic matter) [2].

Physico-chemical processes such as electro-coagulation, ozonation, photocatalysis, membrane filtration and adsorption have been employed for the treatment of dye containing wastewater.

Among these technologies, adsorption process is considered to be promising technology which involves phase transfer of dye molecules onto adsorbent leaving behind the clear effluent [3, 4]

Many studies have been undertaken to find low-cost sorbents, which include peat, bentonite, steel-plant slag, fly ash, maize cob, wood shavings and silica. However, these low-cost sorbents generally have low uptake, which means that large amounts of sorbents are needed. Although good sorption capacities for dyes are found for such materials as cellulose, sugarcane bagasse, rice husk, and coconut husk, successful regeneration has not been reported. Therefore, new, economical, easily available and highly effective sorbents still need to be found [5].

Chitosan (Fig. 1) is a polysaccharide prepared by alkaline deacetylation of chitin (second abundant polymer in nature after cellulose) [6].

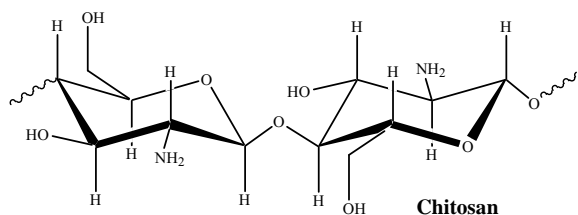


Fig. 1: Chemical structure of chitosan

Chitin is obtained from the exoskeleton of crustaceans, the cuticles of insects and the cell walls of fungi. However, chitin and chitosan are only commercially extracted from crustaceans (crab, krill, and crayfish) primarily because a large amount of the crustacean's exoskeleton is available as a by-product of food processing [7].

Chitosan and its derivatives have been widely studied for dye adsorption from aqueous solutions: the cationic character, along with the presence of reactive functional groups in polymer chains, has given it particular possibilities as efficient biosorbent. It is evident from the abundant literature data that this biomaterial offers a great potential in the adsorption field and might be a promising adsorbent for environmental purpose [8].

In recent years, numerous studies on chitosan-based biomaterials for dye removal demonstrated that these versatile biosorbents are efficient and have a high affinity for many classes of dyes, including acid, direct, mordant, reactive and disperse dyes. However, only a limited number of published studies can be found on its regeneration and on possibility of its reuse. This work may contribute to improve the knowledge of this subject.

In the present work the adsorption and the desorption of an anionic dye Reactive Black 5 have been investigated. Such parameters as pH, initial dye concentration, and contact time on RB5 adsorption were carried out. Efficiency of desorption varying several parameters such as contact time, type and concentration of eluent were evaluated. Several sorption and desorption cycles were operated showing the possibility to recycle the sorbent.

## 2 Experimental

### 2.1. Materials

The adsorbent used in this research is a chitosan in form of flakes supplied by Aber Technologies

(Plouvien, France). The material was previously characterized by the FT-IR technique and SEC (coupled with refractometer and laser light scattering measurements) for the determination of the degree of deacetylation and polymer weight, which were 87% and 125,000 g mol<sup>-1</sup>, respectively. For this study, chitosan flakes with particle size of 125 – 250 μm was selected.

Reactive Black 5 (RB5) is commonly used in dye houses and is regarded as a contaminant in the discharged effluents. Chemical structure of Reactive Black 5 is presented in Fig. 2. Reactive Black 5 (Remazol Black B, C<sub>26</sub>H<sub>21</sub>N<sub>5</sub>Na<sub>4</sub>O<sub>19</sub>S<sub>6</sub>) was supplied by Aldrich (France) (C.I. number: 20505). Its molecular weight is 991.82 g mol<sup>-1</sup>. This dye is characterized as a diazo compound bearing two sulphonate and two sulphatoethylsulphon groups that have negative charges in an aqueous solution. The commercial salt is supplied as a mixture of the active material and an inert product: the actual true dye content is 55%. This has been taken into account for the evaluation of true dye concentrations.

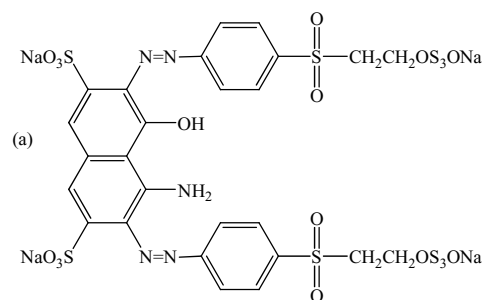


Fig. 2: Chemical structure of Reactive Black 5

All other chemicals used in this study (i.e., ethanol, H<sub>2</sub>SO<sub>4</sub>, NH<sub>3</sub>, NaOH, NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, KOH, KHCO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, NaCl, KCl, CaCl<sub>2</sub> · 2H<sub>2</sub>O, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>NO<sub>3</sub>, NaNO<sub>3</sub>, KNO<sub>3</sub> and C<sub>6</sub>H<sub>5</sub>Na<sub>3</sub>O<sub>7</sub> · 2H<sub>2</sub>O) were of analytical grade and were employed without further purification. All experiments were carried out using distilled water. The pH of the solution was adjusted with H<sub>2</sub>SO<sub>4</sub> or NaOH solutions (0.01 to 1 M).

### 2.2. Methods

#### 2.2.1. Adsorption studies

The experiments on the effect of pH on dye adsorption were carried out to investigate the relationship between the dye uptake and the final pH at equilibrium [9]. The study of the influence

of pH on dye sorption efficiency was performed by mixing a known amount of chitosan (50 mg) with a fixed volume (150 mL) of a dye solution containing 100 mg L<sup>-1</sup> of the dye for 72 hours at constant temperature of 21°C ± 1.5°C. After the system reached the equilibrium state, the final pH was measured, and approximately 6 mL of solution were filtered using a 1.2-µm-pore size membrane. The filtrate was analyzed for the dye content using a spectrophotometer (Shimadzu UV 160-A, Japan) at optimum wavelength of RB5 ( $\lambda_{\text{max}} = 597 \text{ nm}$ ). The dye spectrum may be affected by the pH of the solution, for analytical purpose, a drop of concentrated solution of H<sub>2</sub>SO<sub>4</sub> was systematically added to the samples to maintain a constant pH for the different samples. The dye concentration in the filtrate ( $C_e$ , mg L<sup>-1</sup>) was measured to determine the sorption efficiency and the concentration of the dye in the sorbent or sorption capacity ( $q$ , mg g<sup>-1</sup>) was calculated from the mass balance equation:

$$q = \frac{V(C_i - C_e)}{m}, \quad (1)$$

where  $q$  is the sorption capacity (mg g<sup>-1</sup>),  $C_i$  is the initial dye concentration (mg L<sup>-1</sup>),  $C_e$  is the equilibrium dye concentration (mg L<sup>-1</sup>),  $V$  is the volume (L) and  $m$  is the weight of chitosan (g).

To evaluate the sorption capacity of chitosan at pH 2, the sorption isotherm experiments of RB5 were conducted with 20 mg of chitosan in 300 mL of working solution volume. The initial concentration was altered from 10 to 100 mg L<sup>-1</sup>. After 3 days of contact, the pH of the solution was measured, and samples were analyzed for dye content. As above, the mass balance equation (1) was used to calculate  $q$ , the amount of dye sorbed on the polymer.

Sorption kinetic experiments were performed using 100 mg of sorbent with 1 L of RB5 solution, with a concentration of 100 mg L<sup>-1</sup>. Samples were regularly withdrawn, filtered and analyzed as above. A small fraction of the dye (less than 3%) was retained on the filter membrane; this small variation in the concentration due to filtration was neglected.

### 2.2.1. Desorption studies

Batch studies were conducted in order to test different desorbing agents for RB5 release from chitosan. The raw chitosan (50 mg) was first loaded with 150 mL of the dye at fixed pH (2.3)

and initial dye concentration (100 mg L<sup>-1</sup>). As desorbing agents deionized distilled water, ethanol and 0.01 M aqueous solutions of mineral acid: H<sub>2</sub>SO<sub>4</sub>, alkalies (NH<sub>3</sub>, NaOH, NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>, KOH, KHCO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>) and salts (NaCl, KCl, CaCl<sub>2</sub> · 2H<sub>2</sub>O, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>NO<sub>3</sub>, NaNO<sub>3</sub>, KNO<sub>3</sub> and C<sub>6</sub>H<sub>5</sub>Na<sub>3</sub>O<sub>7</sub> · 2H<sub>2</sub>O) were used. Desorption efficiency was determined by the following equation:

$$\%D = \frac{(C_{ed})}{(C_i - C_e)} \cdot 100, \quad (2)$$

where  $\%D$  is the desorption efficiency (%),  $C_i$  is the initial dye concentration before adsorption (mg L<sup>-1</sup>),  $C_e$  is the equilibrium dye concentration after adsorption (mg L<sup>-1</sup>) and  $C_{ed}$  is the dye concentration at equilibrium after desorption (mg L<sup>-1</sup>).

For the studies on influence of NaOH concentration on RB5 desorption several samples containing fixed amount of dry dye-saturated chitosan (50 mg) from adsorption of RB5 ( $C_i$  of 100 mg L<sup>-1</sup>,  $V = 0.15 \text{ L}$ , pH 2.3) were put in contact with 50 mL of NaOH solution (Concentration range: 0.001 – 1 M).

Desorption kinetic studies were performed by mixing 300 mg of dry dye saturated chitosan with 1 L of 0.01M NaOH solution. Samples were collected at fixed contact times, filtered and analyzed as above.

Several cycles of adsorption-desorption were monitored with the most efficient desorbing agent (NaOH) in order to investigate the regeneration ability of chitosan. For this study 50 mg of chitosan which was used for the adsorption of 100 mg L<sup>-1</sup> (pH 2.3 and  $V = 0.15 \text{ L}$ ) of RB5 was separated from the dye solution by filtration and dried overnight at room temperature. Dye saturated chitosan was put in contact with 50 mL of NaOH for 30 min. After each cycle, chitosan was washed with deionized water to neutrality.

## 3. Results and Discussion

### 3.1 Adsorption studies

#### 3.1.1. Influence of initial pH on adsorption of RB5 on chitosan

The pH of the dye solution plays an important role in the whole adsorption process and particularly on the adsorption efficiency. The variation in the

adsorption of RB5 was studied in the range of pH 1 – 7, and the results are shown in Fig. 3.

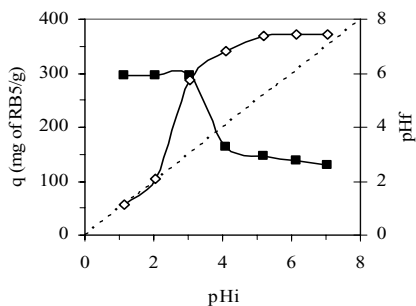


Fig. 3: Effect of pH on the adsorption of RB5 on chitosan ( $C_i = 100 \text{ mg/L}$ , chitosan dosage  $333 \text{ mg/L}$ , agitation time 72 hours).

It can be seen that that the adsorption of RB5 was strongly dependent on the pH of the solution. The highest sorption capacities were obtained in the pH range 1 – 3. Under these conditions dye removal was almost complete.

The higher dye removal that was obtained at acidic pH may be explained in terms of electrostatic attraction between dye and chitosan [10].

The  $pK_a$  of chitosan depends on the degree of deacetylation and degree of neutralization of the amine groups [11]. It tended toward 6.5 for the chitosan used in present study. So, below pH 6.5, most of the amine groups were protonated. The protonation of amine groups was necessary for the attraction of anionic sulphonic groups. Above pH 3, a significant decrease in sorption efficiency was observed. The decrease in protonation of the chitosan reduced the density of available sorption sites, and sorption efficiency decreased accordingly.

It can be observed also from Fig. 3 that final pH after adsorption varied significantly with initial pH of dye solution. It can be seen that using initial pH 3, the final pH exponentially increased: the number of amine groups available for protonation increased and consequently the pH significantly increased. In fact, when the initial pH was in the range 4-7, the final pH hardly changed (6.8-7.4). Thus, the pH control is an important parameter and the sorption process for RB5 removal needs to be operated at  $\text{pH} < 3$ . For this reason further experiments on dye sorption on chitosan were carried out at initial pH 2.3 where no change in final pH was observed.

### 3.1.2. Influence of the initial dye concentration on adsorption capacity

The RB5 concentration at equilibrium ( $q_e$  in  $\text{mg g}^{-1}$ ) was plotted against equilibrium concentration ( $C_e$  in  $\text{mg L}^{-1}$ ) (Fig. 4). This figure shows the relationship between the amount of RB5 adsorbed per mass unit of chitosan and its final concentration in the solution. The quantity of sorbent was kept constant.

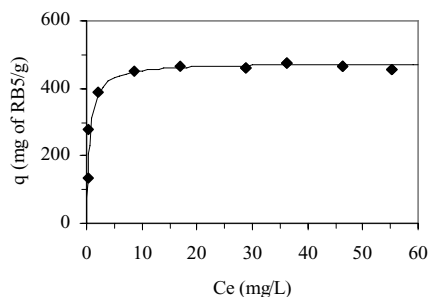


Fig. 4: Influence of RB5 concentration on adsorption capacity at pH 2.3.

Fig. 4 clearly indicates that the sorption capacity initially strongly increases with the initial concentration of RB5 and then tends to a plateau. This is due to the saturation of the sorption sites on chitosan.

### 3.1.3. Influence of contact time on RB5 sorption on chitosan

The adsorption data of RB5 versus contact time is presented in Fig. 5. The adsorbate concentration in the solution ( $q_t$  in  $\text{mg g}^{-1}$ ) was determined at different times from  $100 \text{ mg L}^{-1}$  initial dye solutions and in the presence of 0.1 g of sorbent.

The sorption capacity was increased constantly with increasing contact time reaching to a maximum point of 430 mg of dye per g of chitosan in 48 hours. Therefore 48 hours is fixed as the optimum contact time.

An increase observed on the biosorption capacity with increasing contact time is due to availability of biosorption sites on chitosan surface.

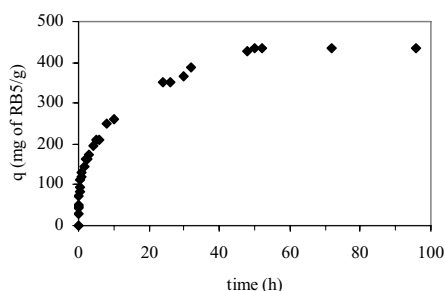


Fig. 5: Effect of contact time on RB5 sorption capacity ( $C_i = 100 \text{ mg L}^{-1}$ , Chitosan dosage of  $100 \text{ mg L}^{-1}$ , pH 2.3).

### 3.2 Desorption studies

The use of chitosan for dye recovery can be limited by the cost of the polymer compared to other sorbents obtained from waste materials. The recycling of the polymer has to be considered in the design of the process [12]. The recovery of the dye is also an important parameter for the economics of the process. For this reason, it is desirable to desorb the dye and to regenerate the material for another cycle [13]. A literature survey on chitosan regeneration showed very few references. The recuperation of this biopolymer and its ability for sorption-desorption cycles is generally poorly described, especially for dyes.

#### 3.2.1. Desorption of RB5 with different desorbing agents

Desorption studies as a function of desorbing agent were conducted to explore, the possibility of recovery of chitosan and dye, which in turn is expected to make the biosorption process economical [14].

In this paper dye saturated chitosan was employed for dye recovery experiments using distilled water, ethanol and 0.01 M aqueous solutions of acid, alkalies and salts in order to find the best desorbing agent. The results showed that water, ethanol, and almost all studied mineral salts did not desorb RB5 and that  $\text{H}_2\text{SO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{NaHCO}_3$  and  $\text{KHCO}_3$  desorbed only negligible amounts of the dye (less than 5%) (data not shown). As illustrated in Fig 6, dilute solutions of highly alkaline agents (NaOH,  $\text{Na}_2\text{CO}_3$ , KOH,  $\text{K}_2\text{CO}_3$  and  $\text{NH}_3$ ) (pH > 11) were very efficient (desorption yield in range of 60-90%). These results can be correlated to the fact that in basic solutions the electrostatic interaction between chitosan and dye becomes much weaker and the

adsorbed dye leaves the adsorption sites of chitosan.

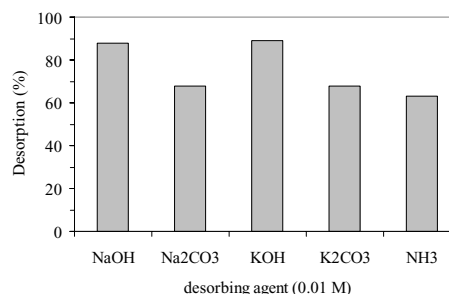


Fig. 6: Percentage of RB5 released from chitosan employing alkaline desorbing agents at concentration 0.01 M (Conditions: Adsorption: 50 mg of chitosan,  $C_i$  of RB5 =  $100 \text{ mg L}^{-1}$ ,  $V = 0.15 \text{ mL}$ , pH 2.3, contact time 48 hours; Desorption:  $V = 0.15 \text{ mL}$ , contact time: 15 min).

Thus, sodium hydroxide was chosen as a desorbing agent for further desorption studies with dye saturated chitosan.

#### 3.2.2. Influence of NaOH concentration on desorption efficiency of RB5

Influence of concentration of NaOH on desorption of reactive Black 5 from dye-saturated chitosan was presented in Fig. 7. It can be observed that the maximum desorption of RB5 (84%) from chitosan could be reached using 0.01 or 0.05 M NaOH solutions.

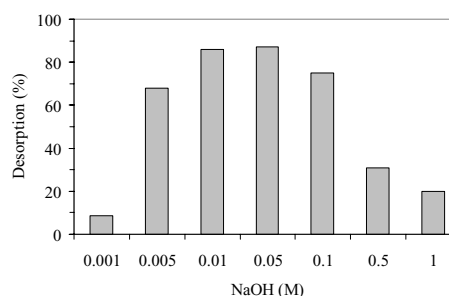


Fig. 7: Influence of NaOH concentration on desorption of RB5 (Adsorption:  $C_i$  of RB5 =  $100 \text{ mg L}^{-1}$ , pH 2.3,  $V = 0.15 \text{ L}$ , contact time: 48 hours; Desorption: 50 mL, contact time: 30 min.).

It should be noted that with increasing NaOH concentration the desorption efficiency decreased, suggesting that higher strength of NaOH was disadvantageous. The same trend was reported by Patel and Suresh [3] during desorption of RB5

from dye-loaded *Aspergillus foetidus*.

### 3.2.3. Influence of contact time on RB5 desorption from dye-loaded chitosan

Influence of contact time on desorption of RB5 from dye-saturated chitosan using 0.01 M NaOH was presented in Fig. 8.

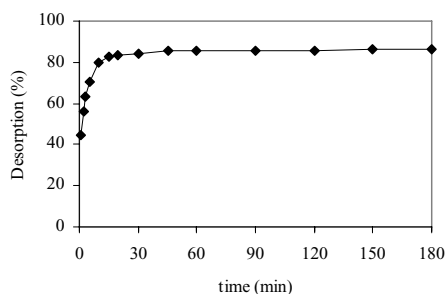


Fig. 8: Influence of contact time on RB5 desorption (Conditions: Adsorption: chitosan dosage of 300 mg L<sup>-1</sup>, pH 2.3, contact time: 48 hours; Desorption: 1L of 0.01 M NaOH).

It can be observed that desorption of Reactive Black 5 was very fast and the equilibrium was reached within first 30 minutes. This means that desorption was much faster than sorption step.

### 3.2.4. Chitosan regeneration and re-adsorption of RB5 in successive cycles

In order to regenerate the biosorbent material, a desorption step was carried out after each adsorption cycle, when the chitosan was saturated. After each step, the sorbent was washed with deionized water in order to neutralize. This study was carried out in ten consecutive cycles of adsorption and desorption.

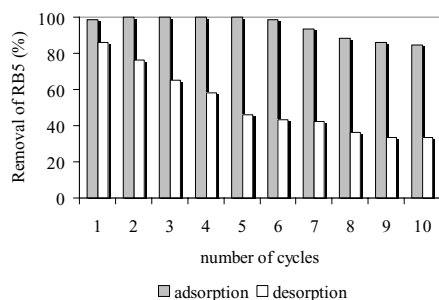


Fig. 9: RB5 adsorption-desorption cycles (adsorption: C<sub>i</sub> of RB5 = 100 mg L<sup>-1</sup>, pH 2.3, V = 0.15 L, contact time: 48 hours; Desorption: 50 mL of 0.01M NaOH, contact time: 30 min.).

Figure 9 shows that chitosan retained good

adsorption efficiency even after 10 cycles. The efficiency of Reactive Black 5 adsorption onto chitosan started to decrease after 6<sup>th</sup> cycle due to low desorption of the bound RB5 ions from chitosan (desorption decreased below 50%).

## 4 Conclusion

Chitosan, a waste from the food industry, is an effective cationic sorbent with high maximum adsorption capacity for anionic azo dye – Reactive Black 5 in acidic solution ( $q = 477 \text{ mg g}^{-1}$ ). The effect of process parameters on RB5 adsorption from solution have been investigated (pH, initial dye concentration and contact time). It is found that the adsorption of RB5 is dependent upon these variables. By considering the adsorption of acid dyes on chitosan surface, such mechanism as ionic attraction between anionic sulphonate groups of dissolved dye molecules and the cationic amino groups of protonated chitosan may be involved. Raw chitosan has a great potential as a reusable dye sorbent. Furthermore, it can be regenerated easily by 0.01 M NaOH solution and can bind dye molecules with high uptake for repeated reuse. Thus chitosan is a promising biosorbent for treating textile wastewater.

## ACKNOWLEDGMENTS

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## References:

- [1] G. Crini, Non-Conventional Low-Cost Adsorbents for Dye Removal: a Review, *Bioresource Technology*, Vol.97, 2006, pp. 1061-1085.
- [2] R.S. Blackburn, Natural Polysaccharides and Their Interactions with Dye Molecules: Applications in Effluent Treatment, *Environmental Science and Technology*, 38, 2004, pp. 4905-4909
- [3] R. Patel, S. Suresh, Kinetic and Equilibrium Studies on the Biosorption of Reactive Black 5 Dye by *Aspergillus Foetidus*, *Bioresource Technology*, 99, 2008, pp. 51-58.
- [4] G. Gibbs, J.M. Tobin, E. Guibal, Influence of Chitosan Preprotonation on Reactive Black 5 Sorption Isotherms and Kinetics, *Industrial & Engineering Chemistry Research*, 43, 2004, pp. 1-11.

- [5] S.W. Won, H.-J. Kim, S.-H. Choi, B.-W. Chung, K.-J. Kim, Y.-S. Yun, Performance, kinetics and equilibrium in biosorption of anionic Dye Reactive Black 5 by the Waste Biomass of *Corynebacterium glutamicum* as a low-cost biosorbent, *Chemical Engineering Journal*, 121, 2006, pp. 37-43
- [6] G. Crini, F. Gimbert, C. Robert, B. Martel, O. Adam, N. Morin-Crini, F. De Giorgi, P.-M. Badot, The Removal of Basic Blue 3 from Aqueous Solutions by Chitosan-Based Adsorbent: Batch Studies, *Journal of Hazardous Materials*, in press
- [7] G. Crini, Kinetic and Equilibrium Studies on the Removal of Cationic Dyes from Aqueous Solution by Adsorption onto a Cyclodextrin Polymer, *Dyes and Pigments*, 77, 2008, pp. 415-426.
- [8] G. Gibbs, J.M. Tobin, E. Guibal, Sorption of Acid Green 25 on Chitosan: Influence of Experimental Parameters on Uptake kinetics and Sorption Isotherms, *Journal of Applied Polymer Science*, 90, 2003, pp.1073-1080.
- [9] S.W. Won, H.-J. Kim, S.-H. Choi, B.-W. Chung, K.-J. Kim, Y.-S. Yun, Performance, kinetics and equilibrium in biosorption of anionic dye Reactive Black 5 by the waste biomass of *Corynebacterium glutamicum* as a low-cost biosorbent, *Chemical Engineering Journal*, 121, 2006, pp. 37-43.
- [10] Y.C. Wong, Y.S. Szeto, W.H. Cheung, G. McKay, Adsorption of Acid Dyes on Chitosan-Equilibrium and Isotherm Analyses, *Process Biochemistry*, 39, 2004, pp. 693-702
- [11] M. Ruiz, A.M. Sastre, E. Guibal, Palladium Sorption on Glutaraldehyde Crosslinked Chitosan, *Reactive and Functional Polymers*, 45, 2000, pp. 155-173.
- [12] G. Crini, Recent Developments in Polysaccharide-Based Materials Used as Adsorbents in Wastewater Treatment, *Progress in Polymer Science*, 30, 2005, pp. 38-70
- [13] E. Guibal, Interactions of Metal Ions with Chitosan-Based Sorbents: a Review, *Separation and Science Technology*, 38, 2004, pp. 43-74
- [14] M. Arami, N.Y. Limaee, N.M. Mahmoodi, N.S. Tabrizi, Removal of dyes from colored textile wastewater by orange peel adsorbent: equilibrium and kinetic studies, *Journal of Colloid and Interface Science*, 288, 2005, pp. 371-376.