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Removal of Industrial Dyes from Wastewaters Using Biosorbents

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Abstract: The paper presents studies on the removal of three industrial dyes: Acid Orange 7, Methylene Blue, and Alcian Blue onto several biosorbents. As potential biosorbents, seeds of *Salvia hispanica L* and *Linum*, and two types of chitosan derivatives (blank chitosan, and magnetic chitosan particles) were investigated. Batch experiments were carried out in order to examine the effects of the biosorbent nature, initial dye concentration and contact time on dyes removal. In case of cationic dyes the best results were obtained using *Salvia hispanica L.* with a yield up to 61.02 %. The removal percentage decrease in order: ShL > CHM > CH for two of investigated cationic dyes (Methylene Blue, and Alcian Blue). The highest removal percentage for the Acid Orange 7 was obtained using magnetic chitosan particles (64 %), and decreases in order: CHM > CH > ShL.

Keywords: biosorbent, dyes, wastewater, adsorption kinetics

1. Introduction

Colored effluents discharged by different industries such as textile, leather, paper, plastics are a major concern due to their adverse effects such as toxicity, carcinogenicity, impeding of light penetration, hypersensitivity reactions to many forms of life. The presence of even very small amounts of dyes in water is highly visible because the color is the first contaminant to be recognized by public perception of water quality [1-2]. Dyes are recalcitrant organic molecules, stable to light, heat and oxidizing agents and it is confirmed that are not easy to be removed from wastewaters [3]. It is difficult to define an universal method that could be used for the decontamination of industrial wastewaters. For wastewaters treatments several methods were investigated, such as biological methods (microbial discoloration [4], bioremediation systems), chemical methods (coagulation [5], filtration, precipitation, oxidation [6], electrochemical processes) and physical methods (membrane filtration) [7]. Among them adsorption was found superior to other techniques because of the low cost, flexibility, ease of operation and insensitivity to toxic pollutants [3, 8-9]. Researchers have been made an attempt to develop natural solid supports, which are able to remove pollutants from wastewaters at low cost [10-12]. The requierments of the low cost sorbents include abundancy in nature, minimal processing, or being a waste material from another industry [1, 2, 13-14]. The dye adsorption is mainly dependent on the dye's structure and the surface chemistry of the adsorbents. Chemical modification is an effective procedure for improving adsorption performance of a natural polymer, abundant in nature toward dye removal [15-17]. The purpose of this work is the study of the removal of three selected dyes from aqueous solutions using different types of biosorbents in adsorption batch experiments. Three particular dyes were selected, one acid dye and two cationic dyes, and the influences of process variables such as contact time, initial dye concentration, and biosorbent nature on dye removal were investigated. Kinetic studies have been carried out, as well.

2. Experimental

2.1. Materials

Acid Orange 7 (*AO7*) a monoazo acid dye, and two cationic dyes: Methylene Blue (*MB*) and Alcian Blue (*AB*) were used as adsorbate. The dyes were purchased from Merck, LOBA-Chemie, and were used as received without further purification.

The *Salvia hispanica L.* and *Linum* seeds were ground, resulting grinded seeds with small amount of oil, then washed several times with ethanol to remove the residual oil content, and finally washed with acetone to remove all the impurities. The resulting seeds were dried in an oven for a couple of hours and then used in adequate quantity for the future batch adsorption experiments.

The chitosan beads were obtained as previously described [18] by precipitation of 2% chitosan solution (2% acetic acid) into (1M NaOH and 26% v/v ethanol). The magnetic chitosan beads were prepared by the similar precipiatation procedure of the chitosan solution mixed with Fe_3O_4 nanoparticles.

2.2. Methods

Working solutions were prepared with water in order to determine concentrations similar to industrial colored wastewaters. UV-visible absorption spectra of the dyes were recorded using a CECIL CE 7200 Spectrophotometer in the wavelength range from 300 to 800 nm.

Batch experiments were carried out by adding 25 mg of biosorbent in 25 mL dye solution with different concentrations, ranging between $1x10^{-5}$ M and $5x10^{-5}$ M, in Erlenmeyer flasks.

The effect of initial concentration, contact time, and nature of the adsorbent on the dye adsorption was investigated under magnetically stirring at room temperature. The dye concentration in solution at the initial time and at time *t* were determined spectrophotometrically. Using the obtained experimental values the adsorption capacity (q_t), and the removal percentage (η) were calculated, using equations (1), and (2):

$$q_t = \frac{(C_0 - C_t)\,V}{W} \quad (1)$$

where: q_t = amount of dye adsorbed at time t (mg/g); C_0, C_t = dye concentration in solution at initial time, and at time t (mg/L); V = volume of solution (L); W = mass of dry adsorbent used (g).

$$\eta = \left(\frac{C_0 - C_e}{C_0}\right) \times 100 \quad (2)$$

where: C_e = the dye concentration at equilibrium (mg/L)

3. Results and Discussions

In the recent years, several chitosan derivatives have been used as sorbent for the dyes [19]. The efficiency for chitosan and its derivatives have been previously reported for Acid Orange 7 and Methylene Blue [20], but from our knowledge no data related to adsorption of Alcian Blue onto chitosan derivatives have been published. Moreover, it was demonstrated that the performance of chitosan for dyes removal is dependent by its origin, degree of N-acetylation, or chemical modification [12]. For a better evaluation of the other two sorbents we considered necessary to perform the adsorption experiments for all three selected dyes.

The chemical structures of the selected dyes, Acid Orange 7 (AO7), Methylene Blue (MB) and Alcian Blue (AB) are presented in Figure 1.

3.1. Influence of the nature of the biosorbent

The adsorption capacity of the biosorbent materials is influenced by several factors, mainly the nature and the chemical structure of the support [21]. In this study the adsorption capacities of the investigated materials in the dyes removal process were investigated using 0.025 g adsorbent in 25 mL of aqueous dye solutions ($1x10^{-5}$ M), under magnetic stirring, at 298 K and pH 6.8. The results presented in Figure 2 and Table 1 indicates a higher retention capacity of *Salvia hispanica L* (ShL) for the investigated cationic dyes.

The highest percentage of removal (64%) was achieved using magnetic chitosan particles (CHM) for removal of acid dye *AO7*, and *Salvia hispanica L*. seeds for the removal of the cationic dyes *MB* (61.02%) and *AB* (93.10%), respectively. The removal percentage decreases in the order: CHM > CH > ShL for the Acid Orange 7, and ShL > CHM > CH for Methylene Blue and Alcian Blue. Unfortunately, using *Linum* seeds we have not obtained favorable results for removal of any of the investigated dyes. The obtained results indicate that the dye adsorption is mainly dependent on the dye's structure and the surface chemistry of the adsorbents.

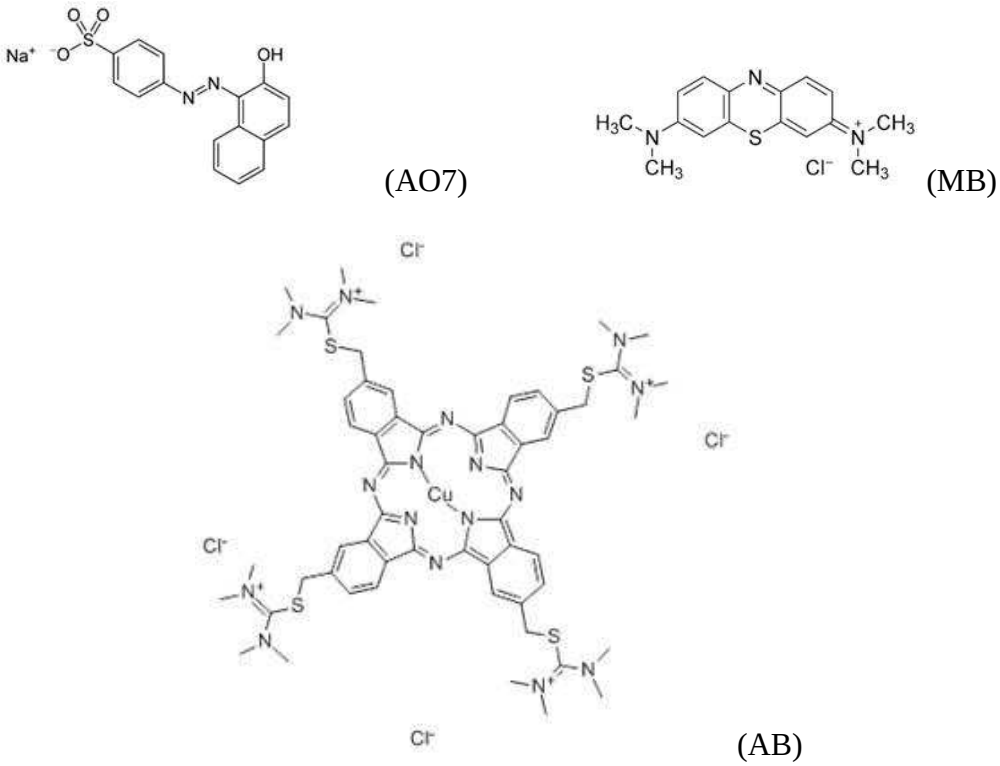

Figure 1. The chemical structures of Acid Orange 7 (AO7), Methylene Blue (MB), and Alcian Blue (AB)

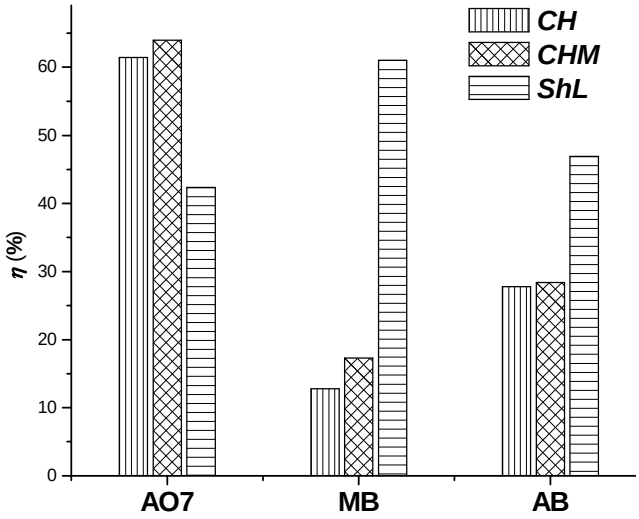

Figure 2. The influence of biosorbent nature on the removal percentage

3.2. Influence of the initial dye concentration and contact time

The effect of initial dye concentration plays a significant role in the amount of the adsorbed dye and removal percentage. In order to investigate the effect of initial dye concentration and the contact time on the dye removal efficiency, experiments were carried out for two concentrations, $1x10^{-5}$ M and $5x10^{-5}$ M, at 298 K. The amount of dye adsorbed onto the investigated biosorbents, as a function of contact time at different concentrations, is presented in Figure 3 and Table 1.

TABLE 1. Influence of different parameters for the adsorption of studied dyes on biosorbents

Dye	Biosorbent	C_i (mg/L)	Q_t (mg/g)	Contact time (min)	η (%)
AO7	ShL	1 x 10^{-5}	2.02	170	42.35
	CH	1 x 10^{-5}	2.15	160	61.44
	CHM	1 x 10^{-5}	2.24	100	63.99
	CHM	5 x 10^{-5}	10.50	220	59.93
MB	ShL	1 x 10^{-5}	1.95	100	61.02
	ShL	5 x 10^{-5}	7.01	180	43.82
	CH	1 x 10^{-5}	0.41	15	12.8
	CHM	1 x 10^{-5}	0.55	80	17.26
AB	ShL	1 x 10^{-5}	6.12	40	46.91
	ShL	5 x 10^{-5}	60.46	60	93.10
	CH	1 x 10^{-5}	3.61	150	27.82
	CHM	1 x 10^{-5}	3.69	170	28.40

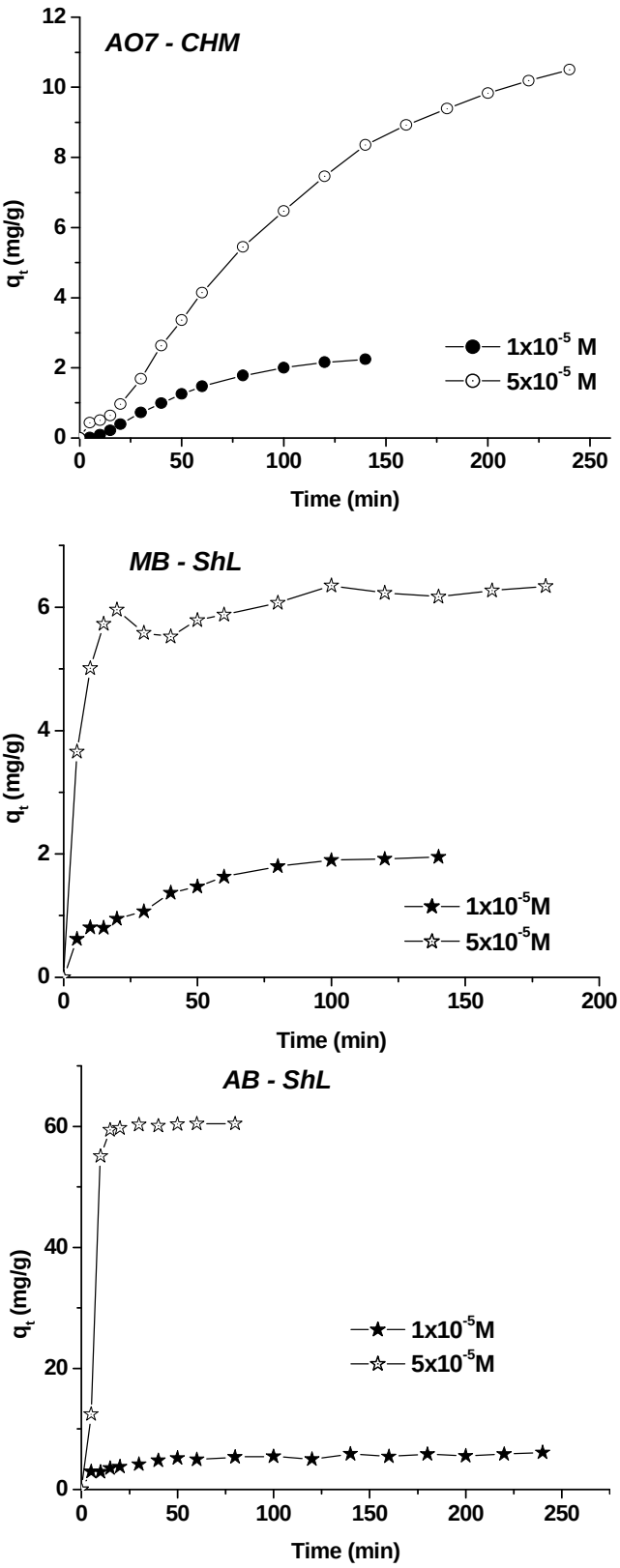

Figure 3. The influence of initial dye concentration and contact time on the adsorption of dyes onto *Salvia hispanica L.*, chitosan and magnetic chitosan particles

The amount of adsorbed dye increased with increasing initial dye concentration, due to the accelerated dye diffusion into the internal adsorption sites. The amount of the adsorbed dye was fast at the beginning of the process, and remained nearly constant when the equilibrium has been reached. The necessary time for reaching the equilibrium increased, while the removal percentages decreased with increasing the dye concentration (Table 1), indicating that the dye removal is concentration dependent.

The experimental data show that initially the amount of the adsorbed dye increased quickly, then it slowed down gradually, until the equilibrium was achieved.

3.3. Adsorption kinetics

In the kinetic experiments the results were determined at certain time intervals during the adsorption process. The experimental obtained data were analyzed using the first-order Lagergren model (3), and the pseudo second-order model (4).

$$log\left(q_e - q_t\right) = log\, q_e - \frac{k_1}{2.303}t \qquad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e}t \qquad (4)$$

where: k_1 is the Lagergren rate constant (min^{-1}), k_2 is the rate constant for the pseudo-second order kinetic model ($mg\ g^{-1}\ min^{-1}$).

The slope and intercept values of plots $\log(q_e-q_t)$ versus t, and t/q_t versus t, respectively, were used to determine the rate constants (k_1 and k_2) and the theoretical amount of the adsorbed dye ($q_{t,c}$). The analysis of the experimental data and determination of the parameters which describes the theoretical models were performed by the ORIGIN version 6.1 (OriginLab Corp., USA), using the correlation coefficients in order to determine the best fitting kinetic model.

The comparison of experimental and the theoretical adsorption capacities values, as well as the computed results estimated from equations 3 and 4, are presented in Table 2.

The obtained data gave poor fits with the first order model and good fits with the pseudo-second order model (higher regression coefficients), meaning that the adsorption depends on the adsorbate as well as the adsorbent and the chemical reaction is the main rate-controlling step of the adsorption process. A decrease of the pseudo-second order constant rate k_2 was observed, indicating that the necessary time for reaching the equilibrium increased with increasing the concentration, which is in agreement with the obtained experimental data.

The theoretical values of adsorption capacity were close to the experimental values in case of the pseudo-second order kinetics.

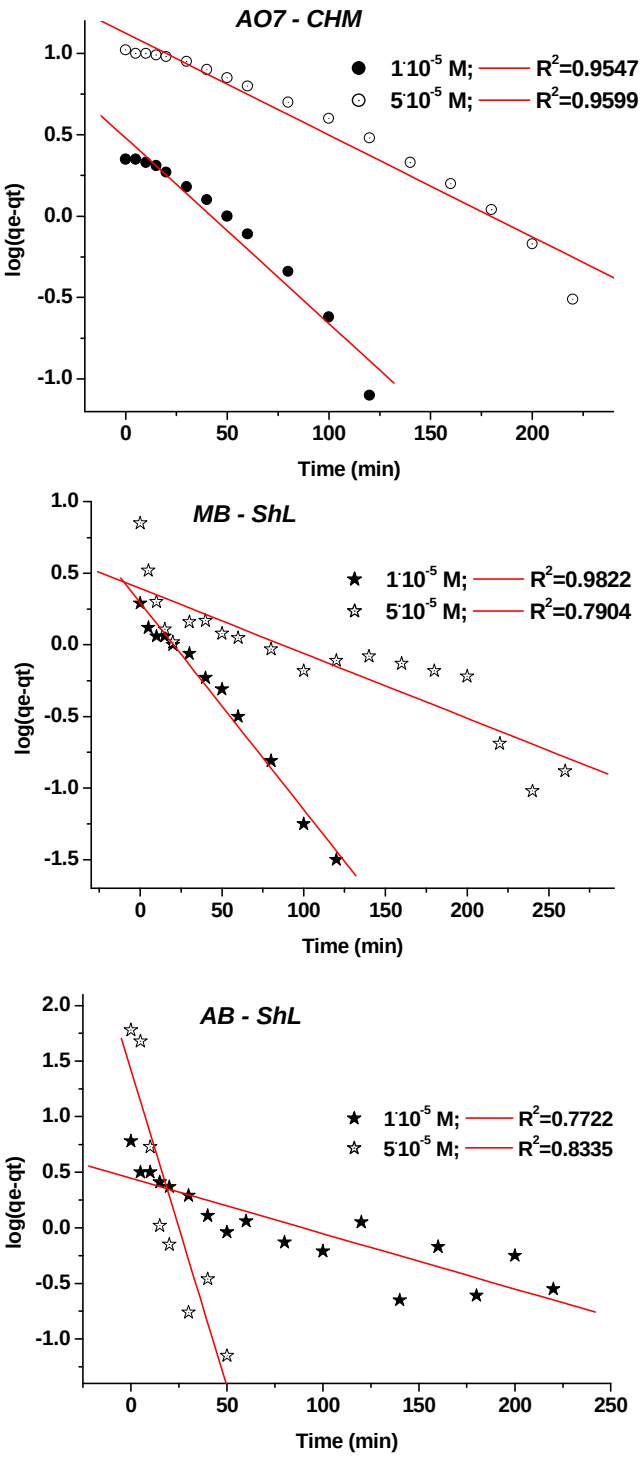

Figure 4. Lagergren plot for the adsorption of studied dyes on the most efficient biosorbents. Influence of concentration

TABLE 2. First order and pseudo-second order adsorption rate constants, and comparison of experimental and calculated q_e values for adsorption of the studied dyes on the investigated biosorbents

Dye	Biosorbent	C_i (mg/L)	$q_{e,exp}$ (mg/g)	First order kinetic model			Second order kinetic model		
				$q_{e,calc}$ (mg/g)	$k_1 \cdot 10^{-3}$ (min^{-1})	R^2	$q_{e,calc}$ (mg/g)	$k_2 \cdot 10^{-3}$ (mg g^{-1} min^{-1})	R^2
AO7	CHM	$1x10^{-5}$	2.24	3.02	2.63	0.9547	4.06	2.28	0.9811
		$5x10^{-5}$	10.50	13.31	1.44	0.9599	21.16	2.06	0.9809
MB	ShL	$1x10^{-5}$	1.95	1.97	33.25	0.9822	2.29	17.72	0.9859
		$5x10^{-5}$	7.01	2.48	10.43	0.7904	6.97	15.95	0.9956
AB	ShL	$1x10^{-5}$	6.12	2.80	11.47	0.7722	6.10	13.83	0.9937
		$5x10^{-5}$	60.46	26.32	13.10	0.8335	68.5	2.03	0.9401

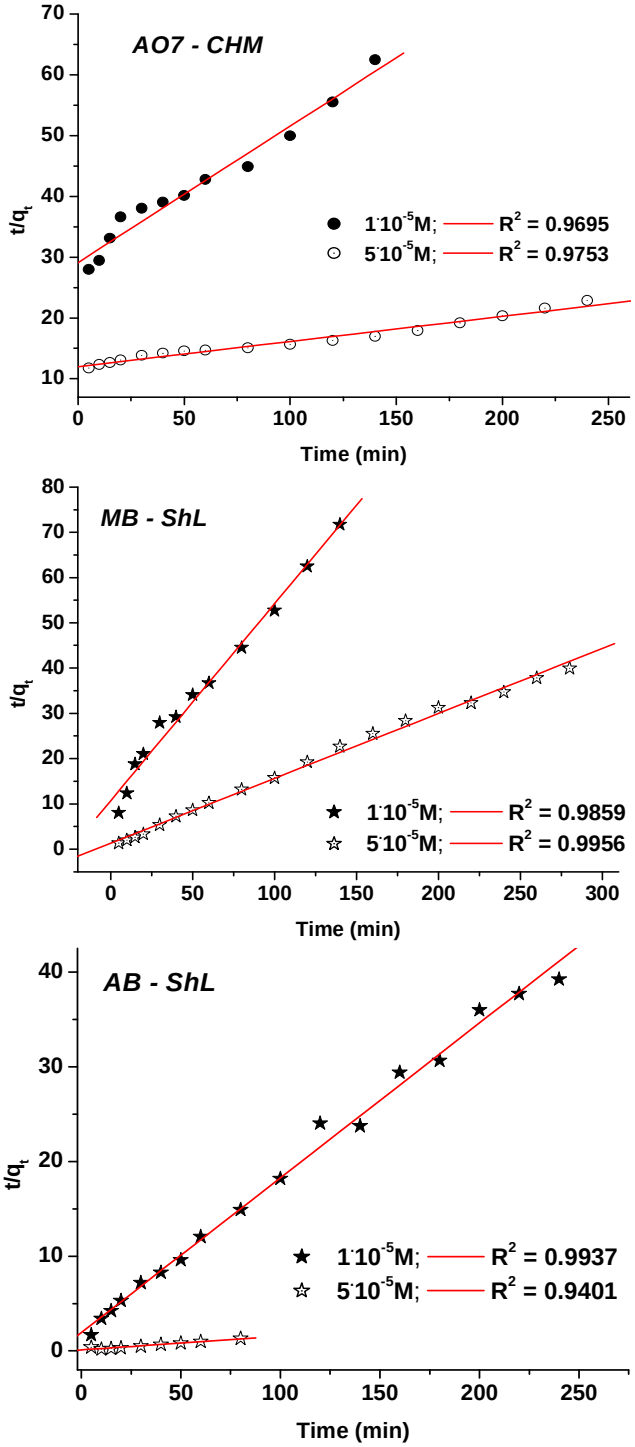

Figure 5. Second-order kinetic model fitting for the adsorption of studied dyes on the most efficient biosorbents. Influence of concentration

4. Conclusions

Although the *Linum* seeds did not register positive results, the *Salvia hispanica L.* seeds and the chitosan derivatives were successfully used as adsorbents for the removal of the investigated dyes. The different operational parameters monitorized during the process revealed that the initial dye concentration, contact time and nature of the biosorbent govern the overall process of adsorption. High removal percentage was obtained for low concentrations at room temperature. Increasing the initial dye concentration, the removal percentage decreased and the amount of the adsorbed dye increased indicating that the dye removal is concentration dependent. The kinetic studies showed that the adsorption followed the pseudo-second kinetic order. In conclusion, *Salvia hispanica L.* seeds and chitosan derivatives represent abundant and environmentally friendly promising materials for the development of a low cost adsorption technology for removal of dyes from industrial wastewaters.

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