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REMOVAL OF ANIONIC DYE CONGO RED FROM SYNTHETIC WASTEWATER USING IMMOBILISED FIR SAWDUST (*ABIES ALBA*)

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ABSTRACT. The purpose of this paper was to establish the optimum experimental conditions for removal of Congo Red (CR) from aqueous solutions by biosorption on alginate immobilized fir tree sawdust *(Abies Alba)* beads. The studies were carried out under various experimental conditions. Dye concentration, fir tree sawdust quantity, stirring rate and working regime were considered in order to assess their influence on the biosorption process. Removal efficiencies up to 97% were reached in the case of immobile phase regime. Also, adsorption capacity increased with a decrease in the sawdust quantity and an increase of the initial dye concentration. The results indicate that this local immobilized material can be an attractive option for dye removal from diluted industrial effluents.

Keywords: *biosorption, Congo red, immobilized fir tree sawdust, alginate beads, kinetics*

INTRODUCTION

Wastewater effluents from many industries such as textile, rubber, paper, leather plastics, cosmetic, painting, etc. contain several kinds of synthetic dyes [1]. This dye-bearing wastewater exhibits high color. Thereby, a very small amount of dye in water is highly visible and therefore, the discharge of these effluents in the environment is worrying for both toxicological and aesthetical reasons [2].

As we know, dyes can be classified into cationic, anionic and nonionic dyes. Cationic dyes are basic dyes while the anionic dyes include direct, acid and reactive dyes [3]. The main problem in treating wastewater containing dyes is related to the high stability of these pollutant species, (they are resistant

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to moderate oxidizing agents and light, and cannot be removed completely by conventional methods of anaerobic degradation [4]).

Recently, numerous studies have been reported for the adsorption of cationic and anionic dyes by agricultural based adsorbents, such as rice husk [5], tea waste [6], coniferous pins bark powder [7], peanut hull [8], almond shell [9], lemon peel [10], etc.

Adsorption is a very effective separation technique and now it is considered to be superior to other techniques for wastewater treatment in terms of initial cost, simplicity of design, easy of operation and insensitivity to pollutant substances [11-14].

Congo Red (CR, chemical formula = $C_{32}H_{22}N_6Na_2O_6S_2$, FW = 696.68, λ_{max} = 497 nm) is a benzidine-based anionic diazo dye, i.e. a dye with two azo groups. The structure is as illustrated in Figure 1. This anionic dye, in general has been known to cause human allergic reactions and to be metabolized to benzidine, a human carcinogen [15].

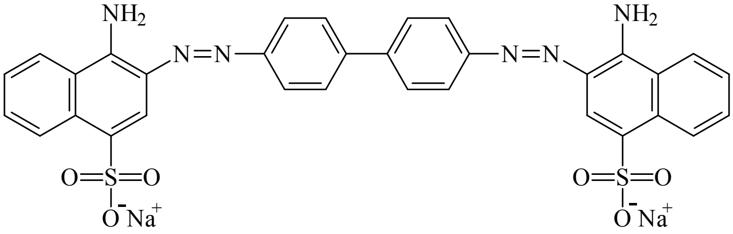

Figure 1. Structure of CR molecule

Abies Alba fir is a common tree from some forest areas in Transylvania (Romania). These trees are the main source for the local wood industry and their sawdust could be a good candidate as a green and economic alternative for Congo Red (CR) removal from wastewater. Previous studies realized on sawdust (timber, pine, *Shorea dasyphylla*, beech wood) showed that they can be used successfully to remove different dyes (methylene blue, direct brown, basic blue, acid blue) from wastewaters [16-19].

Different matrices that can be used for the immobilization of biomass such as alginate [20], chitosan [21], or polyvinylalcohol (PVA) with kaolin [22], etc. are available.

Predicting the rate at which adsorption takes place for a given system is probably the most important factor in adsorption system design, with adsorbate resistance time and the reactor dimensions controlled by the system kinetics [23]. In order to investigate the mechanism of adsorption, various kinetic models have been suggested. Numerous kinetic models have described the reaction order of adsorption system based on solution concentration. These include first-order [24] and second-order [25] reversible ones, and first-order [26] and second-order [27] irreversible one, pseudo-first-order [28] and pseudo-second-order [29] based on the solution concentration.

The goal of this study was to realize the Congo red biosorption onto immobilized fir tree sawdust (IFTS) from Romanian wood industry and to offer an effective and economical alternative to more expensive adsorption processes (commercial active carbon and resins). Therefore, biosorbent quantity, dye concentration, optimum stirring rate and working regime influence over the biosorption process were investigated in batch conditions. Kinetic models of the considered biosorption process were discussed.

RESULTS AND DISCUSSION

The effect of biomass quantity

The effect of biomass quantity on the biosorption of CR was studied using different masses of sawdust. To establish the optimal dose of adsorbent 100 mL synthetic solution of CR dye, with concentration 50 mg/L was used. Experiments were conducted in batch conditions under magnetic stirring at 300 rpm and room temperature (T = 22°C), using different amounts of sawdust, 1, 2, 3, 4 and 5 g, respectively, immobilized in sodium alginate (IFTS).

Experiments have shown that equilibrium was reached after about 180 minutes when 1, 2 and 3 g of sawdust were used, and after about 150 minutes when 4 or 5 g sawdust were used (Figure 2).

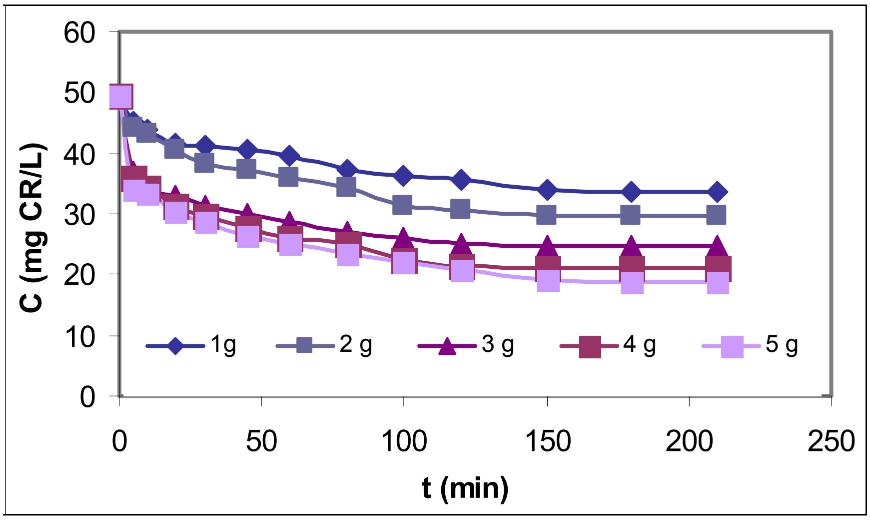

Figure 2. CR concentration time evolution for different initial sawdust quantities (100 mL solution, 50 mg CR/L, 300 rpm, room temperature).

The diagram from Figure 3, gives the maximum removal efficiency E (%) as a function of the biomass quantity. As shown in Figure 3 the maximum removal efficiency varies from 32.35 to 62.04% for 1 and 5 g of sawdust, respectively. The best results were obtained for 4 g (57.66 %) and 5 g (62.04 %). Taking into consideration the fact that the fir tree sawdust is a by-product, therefore is available in large quantities and at very low cost, the experiments were further considered using 5 g for maximum removal efficiency.

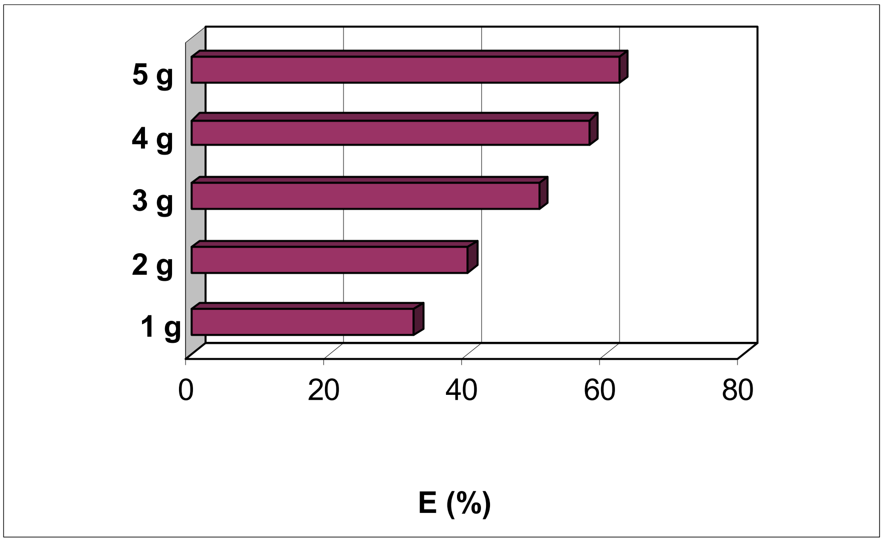

Figure 3. Influence of sawdust quantity over the maximum biosorption process efficiency (100 mL solution, 50 mg CR/L, 300 rpm, room temperature).

The effect of initial CR solution concentration over the biosorption process

Experiments were conducted using volumes of 100 mL CR aqueous solutions with the following concentrations: 50, 105, 150, 200 and 255 mg/L dye and were realized in batch conditions, with magnetic stirring at 300 rpm, at room temperature (T = 22°C) and 5 g of fir tree sawdust, immobilized in sodium alginate.

As the initial concentration decreases, the quantity of dye (CR) retained in the first 30 minutes decreases also due to the smaller difference that exist between the concentration of dye on the adsorbent surface and in the solution. As the initial concentration increases, biosorption process equilibrium was reached more difficult, after about 180 minutes, by comparison with just 80 minutes for small concentrations (50 – 105 mg CR/L) (Figure 4).

The biosorption was noted to occur in two phases of fast and slow rates. This variation could be explained by the easiness with which organic dye gain access to the adsorption sites (favoured by the small stirring rate and macroporosity of the lignocellulosic materials) and by the high activity of the adsorption sites. The formation of a plateau shows a maximum occupation of available biosorption sites, marking thus, the equilibrium achievement of the biosorbate/biosorbent system.

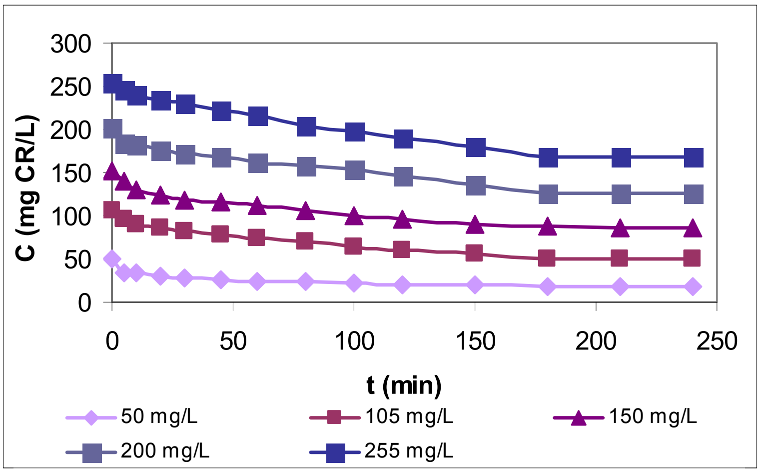

Figure 4. CR concentration time evolution for different initial concentrations (100 mL solution, 5g fir tree sawdust immobilized in alginate beads, 300 rpm, room temperature).

Experimental results showed that biosorption capacity increases with increasing concentration of CR dye in aqueous solution, from 0.51 mg/g when a 50 mg CR/L aqueous solution was used up to 1.43 mg/g when a 255 mg CR/L aqueous solution was used (Figure 5).

Establishing optimum stirring rate

The experiments of biosorption for 5g of fir tree sawdust immobilized in alginate were repeated with varying stirring rate at 300, 500 and 700 rpm, at initial dye concentration of 50 mg CR/L. The efficiency of each experiment is presented in Figure 6. The diagram obtained showed that the biosorption process was intensified with a decrease of stirring rate down to 300 rpm (62.04%). Higher stirring rates, (500 and 700 rpm) will lead to a decrease in efficiency from 45.98% (for 500 rpm) to 29.92% (for 700 rpm), showing that after a certain stirring speed, the minimization of the thin film layer formed at the beads surface will not lead to a further increase in the external diffusion rate.

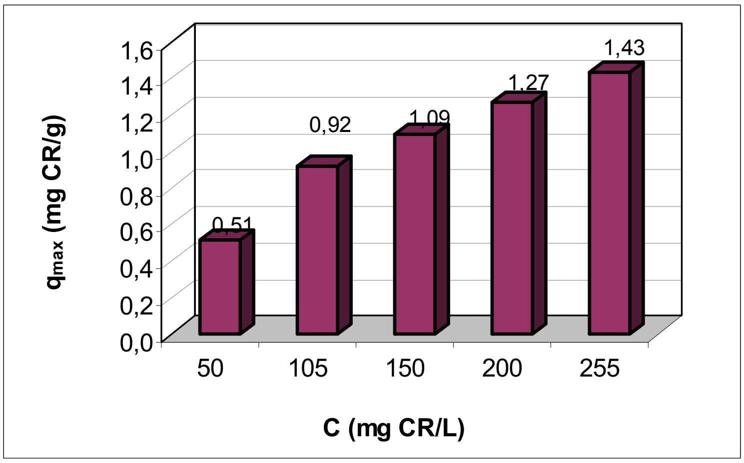

Figure 5. Influence of CR concentration over the biosorption capacity (100 mL solution, 5 g fir tree sawdust immobilized in alginate beads, 300 rpm, room temperature).

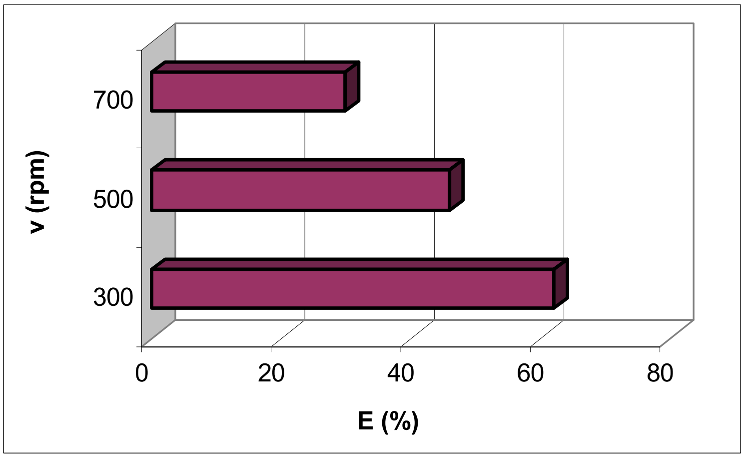

Figure 6. Influence of stirring rate over the maximum biosorption process efficiency (100 mL solution, 50 mg CR/L, 5 g fir tree sawdust immobilized in alginate beads, room temperature).

The influence of working regime on biosorption process

In figure 7, a comparison of maximum removal efficiencies is presented for the experiment conducted in *mobile* and *immobile phases regime*, at different initial concentrations (C_i = 50 – 255 mg CR/L). A closer inspection of this diagram conducts to the conclusion that for all five dye initial concentrations the *immobile phase regime* is the best solution, leading to the highest removal efficiencies 97.08% (50 mg/L), 96.92% (105 mg/L), 96.41% (150 mg/L), 95.68% (200 mg/L) and 95.14% (255 mg/L). Equilibrium was reached in 250 hours (10 day, approximately), for all five experiments.

In *mobile phase regime*, the same systems were studied and the conclusion was that this type of regime leads to maximum biosorption efficiency between 33.99% (for C_0 = 255 mg CR /L) and 62.04% (for C_0 = 50 mg CR /L), as it can be seen in Figure 7.

These results suggested that due to the size of the CR molecule, diffusion could have an important role in biosorption process, therefore we decided to conduct further experiments in immobile phase regime.

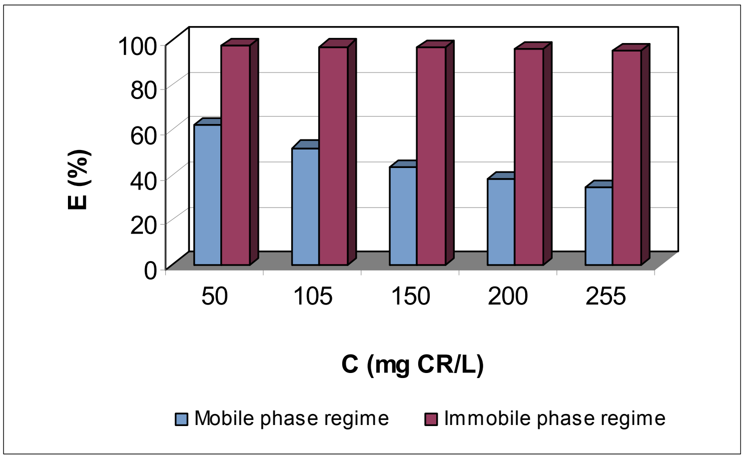

Figure 7. Influence of working regime over the maximum biosorption process efficiency (100 mL solution, 5 g fir tree sawdust immobilized in alginate beads, 300 rpm, room temperature).

Adsorption kinetics

Pseudo-first-order (Lagergren) [30] and pseudo-second-order (Ho) [31] models were used to study the adsorption kinetic of CR onto immobilized sawdust sample. Linear regression was used to determine the best fitting kinetic rate equation (correlation coefficients, R^2) [32].

Lagergren suggested a first order equation for the adsorption of liquid/ solid system based on solid capacity, which can be expressed as follows:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{1}$$

Integrating equation (1) from the boundary conditions t = 0 to t = t and q_t = 0 to $q_t = q_t$, gives:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{2}$$

where,

q_e and q_t are the amounts of CR adsorbed (mg/g) at equilibrium and time t, respectively

k_1 is the rate constant of first order adsorption (1/min).

In order to determine the rate constant and equilibrium of CR uptake, the straight line plots of $\ln(q_e-q_t)$ against t, eq. (2), were made at five different initial dye concentrations. Because correlation coefficients are modest (between 0.653 and 0.739, figure not shown), CR biosorption onto fir tree sawdust cannot be classified as first order.

The pseudo-second-order kinetic model is derived on the basis of the adsorption capacity of the solid phase, expresses as [27]:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \tag{3}$$

Integrating eq. (3) from the boundary conditions t = 0 to t = t and q_t = 0 to $q_t = q_t$, gives:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t \tag{4}$$

where,

q_e and q_t are the amounts of CR adsorbed (mg/g) at equilibrium and time t, respectively

k_2 is the rate constant of first order adsorption (g/mg·min).

Equation (4) can be rearranged in linear form, as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

In order to determine the rate constant and equilibrium of CR uptake, the straight line plots of t/q_t against t, eq. (5), were made at five different initial dye concentrations. Correlation coefficients between 0.921 and 0.997 were obtained (figure 8 and table 1), therefore Congo Red adsorption onto immobilized fir sawdust can be classified as pseudo-second-order.

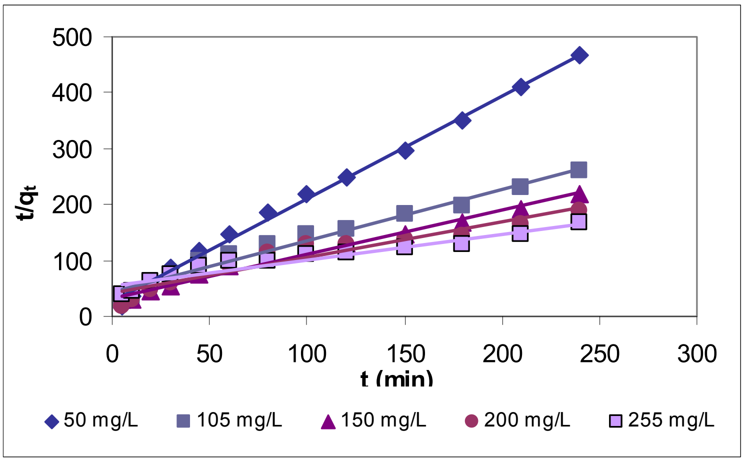

Figure 8. Plots of the second-order model, at different initial CR concentrations (mobile phase regime, 5 g fir tree sawdust immobilized in alginate beads, 100 mL CR solution).

Table 1. Second order adsorption rate constants, and calculated and experimental Q_e values for CR adsorption using different initial concentrations.

Concentration (mg CR/L)	$q_{e,exp}$ (mg/g)	k_2 (g/mg·min)	$q_{e,calc}$ (mg/g)	R^2
50	0.51	$15.04 \cdot 10^{-2}$	0.54	0.997
105	0.92	$4.62 \cdot 10^{-2}$	1.09	0.978
150	1.09	$3.29 \cdot 10^{-2}$	1.27	0.986
200	1.27	$2.43 \cdot 10^{-2}$	1.54	0.921
255	1.43	$1.91 \cdot 10^{-2}$	1.77	0.921

CONCLUSIONS

This study presented results obtained for Congo Red biosoption on popular Romanian fir tree sawdust (*Abies Alba*) from Transylvanian forests, in immobilized form as biosorbent. The biomass was subjected only to mechanical preparation in order to obtain the final biomass (washing, drying and sieving) which was further immobilized in alginate beads. The effects of the initial biomass quantity, initial dye concentration, stirring rate and working regime on biosorption process were studied. Higher biomass quantity, 50 mg CR/L initial dye concentration, reduced stirring rate and immobile phase regime were all favoring the biosorption process. Removal efficiencies up to around 62 % and a maximum adsorption capacity of 0.51 mg/g dye were obtained experimentally, in mobile phase regime, while for immobile phase regime removal efficiencies up to 97% were obtained.

In conclusion, for removal of this bulky anionic dye molecule with immobilized Romanian sawdust, the optimum conditions established experimental are high quantities of biosorbent, immobile phase regime (10 days or probably more, for higher concentrations), solution pH and room temperature.

Kinetics (pseudo-first- and pseudo-second-order) models of the considered biosorption process were discussed. The kinetic of the process was best described by the pseudo-second-order model, suggesting monolayer coverage and a chemisorption process. According to the obtained results it can be concluded that the fir tree (*Abies Alba*) sawdust it is a good biosorbent for Congo Red dye from aqueous solutions, especially in immobile phase regime.

EXPERIMENTAL SECTION

Biosorbent

The fir tree (*Abies Alba*) sawdust was obtained from a local sawmill in Mărgău vilage, Cluj County, Romania. Prior to its utilization the considered biomass was washed several times with distilled water in order to eliminate surface impurities, was dried at 105°C for 24 h. Finally the dried biomass was grinded and sieved (400-600 μm). The sieved sawdust was then stored in an airtight box before its utilization. No further chemical treatments were considered at this stage.

Preparation of Congo Red (CR) solutions

The dye stock solution *(*1000 mg/L) was obtained by dissolving the necessary quantity of solid substance, CR (analytical purity reagent) in distilled water. From this solution were further prepared solutions with known concentration in 50-255 mg CR/L range.

Immobilization of fir sawdust.

Our technique draws inspiration from the methods described by Akar et al., (silica-gel-immobilized waste biomass) [33], Rangsayatorn et al. (cells of *Spirulina platensis* TISTR 8217 immobilized in alginate and silica gel) [35] and Mata et al. (calcium alginate xerogels and immobilized *Fucus vesiculosus*) [35]. In this work, the beads were prepared by mixing 1-5 g of fir sawdust powder to 1 g of sodium alginate and an amount of water varying between 20 and 35 mL according to the quantity of the biosorbent and mixture viscosity. The mixture was blended until was homogeneous and fluid. Then, the mixture was dropped through a syringe using a 1.2 mm in diameter needle into a 0.2 M solution of $CaCl_2$ when beads with diameter between 1.5 and 2.0 mm were formed. Once the beads were formed, stirring was stopped and the beads were let at rest for at least two hours, then removed, washed with water and then conserved in demineralised water, and spin dried before further use.

Biosorption experiments

The Congo Red (CR) biosorption studies were realized using fir tree sawdust (*Abies Alba*) in alginate immobilized form (IFTS).

Biosorption process was conducted in batch conditions, under mobile phase regime (magnetic stirring), and also in immobile phase regime (the biosorbent was contacted with the solution and the process was realized without further stirring), through the contact of a certain amount of biosorbent with a volume of 100 mL dye aqueous solution of various concentrations. The biosorbtion process was realized until equilibrium was reached.

The CR concentration in solution was determined using a Jenway 6305 UV-VIS spectrophotometer at a wavelength of 498 nm and appropriate dilution. Samples were collected at established time intervals.

The influence of the following parameters on the efficiency of biosorbtion process was considered: initial concentration of CR, fir tree sawdust quantity, influence of stirring speed and working regime (with mobile and immobile phases).

All the experiments were repeated three times, the values presented were calculated using averaged concentration values.

Biosorption process efficiency expressed as percentage was calculated with equation (6):

$$E,(\%) = \frac{C_0 - C_t}{C_0} \times 100 \tag{6}$$

where: *E* – efficiency (%);

C_0 – CR initial concentration (mg/L);

C_t – CR time *t* concentration (mg/L).

Biosorption capacity was calculated using the equation (7):

$$q = \frac{(C_0 - C_t)}{w} \times \frac{V}{1000} \tag{7}$$

where: C_0 – CR initial concentration (mg/L);

C_t – CR time *t* concentration (mg/L);

V – aqueous solution volume (mL);

m – biosorbent quantity (g).

Experimental data were used to determine the optimum working conditions and to establish which kinetic model describes better the considered process.

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