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Dedicated to Professor Ionel Haiduc
on the occasion of his 80th anniversary

ISOTHERMS STUDY OF CONGO RED BIOSORPTION EQUILIBRIUM USING FIR (*ABIES NORDMANNIANA)* SAWDUST BIOMASS

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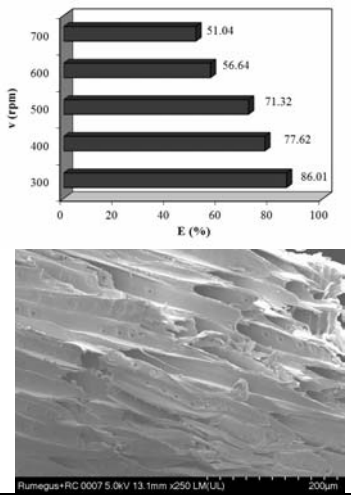
In this work, biosorption of Congo Red (CR) anionic dye, from synthetic aqueous solution using fir tree (*Abies nordmanniana*) sawdust biomass (FSB) (Transylvanian forests, Romania) was investigated. The considered biomass was characterized using Scanning Electronic Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). The effects of the initial biomass quantity and stirring rate over the biosorption process were considered. The biosorption equilibrium data were correlated with the most used isotherm models (Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich). Maximum adsorption capacity calculated using the Langmuir model was 28.1±0.1 mg/g. From Dubinin-Radushkevich isotherm the free energy of the system E = 0.326 kJ/mol was determined, whose value indicates a physisorption process. Also for this model, the coefficient of determination had the highest value (R^2 = 0.994). All these results indicate that *Abies nordmanniana* can be used as a cost effective biosorbent for the removal of CR dye from aqueous solutions.



INTRODUCTION

The textile industry uses large amounts of water for dyeing and washing and as a result, generates large quantities of wastewaters. Moreover, the presence of the low biodegradable synthetic dyes in effluents may conduct to chemical and/or biological reactions, which consume dissolved oxygen and destroy aquatic life. Consequently, the dyes removal from wastewater has become a major concern in the past years.

Among the different physical, chemical and biological treatments methods of dye removal from aqueous solutions, adsorption onto different adsorbents offer a suitable and cost-effective alternative.[1-5]

Various types of adsorbents have been applied for dyes removal including miscellaneous agricultural waste materials such as sawdust,[2,3,5-8] Jujuba seeds,[9] magnolia-leaf,[10] apricot stone,[11] orange peel powder,[12] tea waste,[13] fir cones,[14] etc.

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Congo Red, (CR), [1-naphtalene sulfonic acid, 3.30-(4.40-bisphenylenebis-(azo))-bis(4-amino)-disodium salt] is a typical anionic azo dye, which is synthesized by coupling tetrazotised benzidine with two molecules of naphtionic acid.[12] CR containing effluents are generated from textiles, printing and dyeing, paper, rubber, and plastics industries.[6] Due to its structural stability, CR is difficult to biodegrade and pose a major challenge in terms of removal from wastewaters. Also, CR metabolize to benzidine, a dangerous human carcinogenic and can cause allergic reactions in humans beings.[15] Taking into consideration these aspects, an increased interest has been focused in recent years on removing CR from the wastewater.

Taking into account that CR is difficult to remove using traditional adsorbents and that from our knowledge the system *Abies nordmanniana* sawdust biomass – Congo Red has not been previously investigated, the objective of this study was to explore the feasibility of using this green and low cost adsorbent for CR removal from synthetic aqueous solutions.

RESULTS AND DISCUSSION

FSB is considered to be a lignocellulosic material. In general, lignocellulosics have been included in the term biomass and are also called as photo mass, because they are a result of photosynthesis.[16] The three main components of biomass are hemicellulose, cellulose, and lignin. Cellulose is a significant pure organic polymer composed of anhydroglucose bound together in a large straight chain molecule, with a crystalline super molecular structure, due to the formation of the intramolecular and intermolecular hydrogen bonds between –OH groups. Hemicelluloses derived mainly from the chains of pentose sugars act as the cement material binding together the cellulose micelles and fibres.[17] Hemicellulose is a branched polymer, while cellulose is unbranched. Lignin is a cross-linked racemic molecule from sawdust, with hydrophobic and aromatic nature. Lignin contains alkyl phenols, has a complex three-dimensional structure, and forms a very complex matrix. This matrix consists of various functional groups including hydroxyl, methoxyl, and carbonyl, which impart a high polarity to the lignin macromolecule.[18]

The presence of the mentioned functional groups as well as of others (amino, carboxyl, amide, thiol, etc.) in the sawdust structure it is likely to confer to this material adsorptive properties.[17,19]

FSB characterization

SEM analysis

The SEM micrographs of the FSB surface before and after CR biosorption (15 kV; 12.7 mm), at 5.00 magnification reveal surface texture and porosity and are presented in Figure 1a,b. From the SEM analysis, it was found that there were holes and cave type openings on the surface of FSB before biosorption (a), so that, this image showed a rough and porous surface, which were covered after CR biosorption (b), and the FSB surface became smoother. Moreover, after dye biosorption the FSB surface seemed to have decreased porosity, due probably to the impregnation of CR onto the biomass surface. This behaviour is in good agreement with others from literature.[1,6,20]

FTIR analysis

IR spectroscopy was used to characterize the possible adsorbent-adsorbate (CR-FSB) interactions. The FTIR spectra of FSB (a) and FSB-CR (b) in the range of 4000-400 cm^{-1} are presented in Figure 2. The broad absorption band at 3462 cm^{-1} in the spectrum of FBS (a) corresponds to –OH and –NH (amine) symmetrical stretching vibrations. After CR biosorption, this band was shifted at 3449 cm^{-1}, in addition to an intensity decrease. The peak assigned to the –CH asymmetric stretching of methylene groups was observed at 2922 cm^{-1} and 2924 cm^{-1}, before and after CR biosorption (Figure 2). The peak at 1734 cm^{-1} was attributed to the stretching vibration of carboxyl groups and for FSB-CR (b) this peak was shifted at 1779 cm^{-1}.[12] C=O and C–N stretching were observed at 1658 cm^{-1} and at 1517 cm^{-1}, respectively. After CR biosorption these two bands were also shifted to 1650 and 1557 cm^{-1}, respectively, that are in good agreement with others literature data.[6,12,13] Peaks at 1270 cm^{-1} and 1073 cm^{-1} in the FTIR spectrum of FSB (Figure 2a) could be attributed to C-O stretching of phenolic group and six-member cyclic ether group of cellulose, respectively. After CR biosorption these wavenumber values were shifted at 1272 and 1052 cm^{-1}, respectively. These values are similar to those reported for pine[8] and meranti sawdust.[19,20]

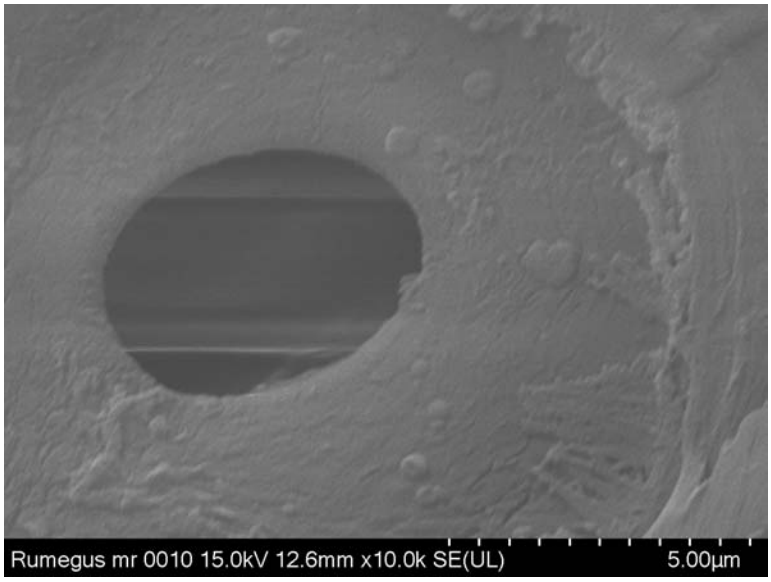

Fig. 1 – SEM images of FSB before (a) and after (b) CR dye biosorption.

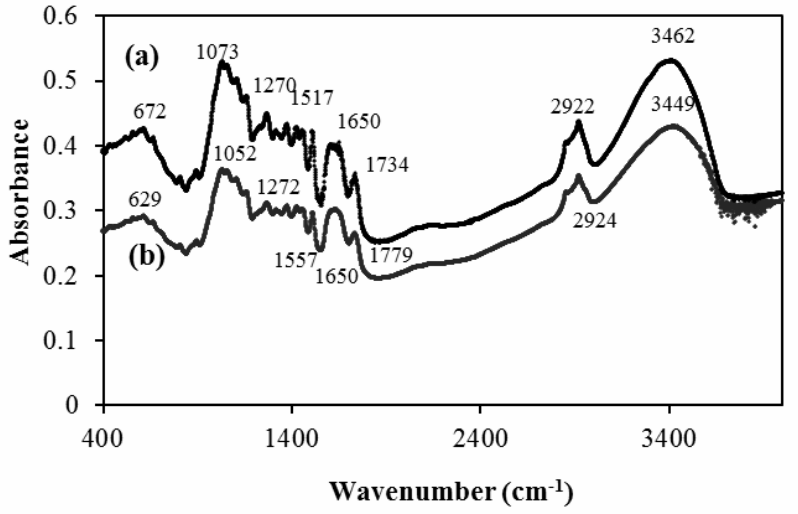

Fig. 2 – FTIR spectra of FSB before (a) and after (b) CR biosorption.

In conclusion, all the observed peaks displacements in the FTIR spectra clearly show that the functional groups including carboxylic, amino, and hydroxyl contribute to the biosorption of CR acid ions.[1]

Quantity of adsorbent and stirring rate influence over the biosorption process

Study of the effect of adsorbent quantity utilized gives an idea of the effectiveness of an adsorbent and the ability of a dye to be adsorbed with a minimum quantity.[15]

The effect of biomass quantity on the biosorption process was studied using different quantities of FSB (1.0-5.0 g) and 100 mL synthetic CR solution (50 mg/L). Experiments were conducted in batch conditions, under magnetic stirring (300 rpm) at room temperature (T = 295 K).

Experiments have shown that equilibrium was reached after about 180 minutes when 1.0-3.0 g FSB were used, and after about 150 minutes when 4.0 or 5.0 g FSB have been used. As shown in Figure 3 the maximum removal efficiency varies from 15.4 to 86.0% for 1.0 and 5.0 g of FSB, respectively. The best results were obtained for 4.0 g (83.9%) and 5.0 g (86.0%). The increase in biosorption efficiency with increasing biosorbent quantity is due to the increase in the number of available active sites and an increase in the adsorption driving force.[15]

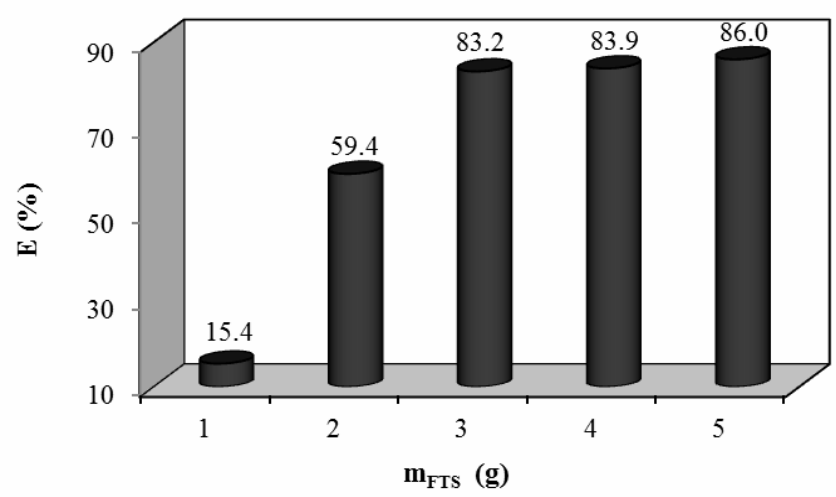

Fig. 3 – The effect of FSB quantity on maximum efficiency values for CR biosorption (100 mL solution, 50 mg/L, 0.4-0.6 mm, 295 K, 300 rpm, pH = 6).

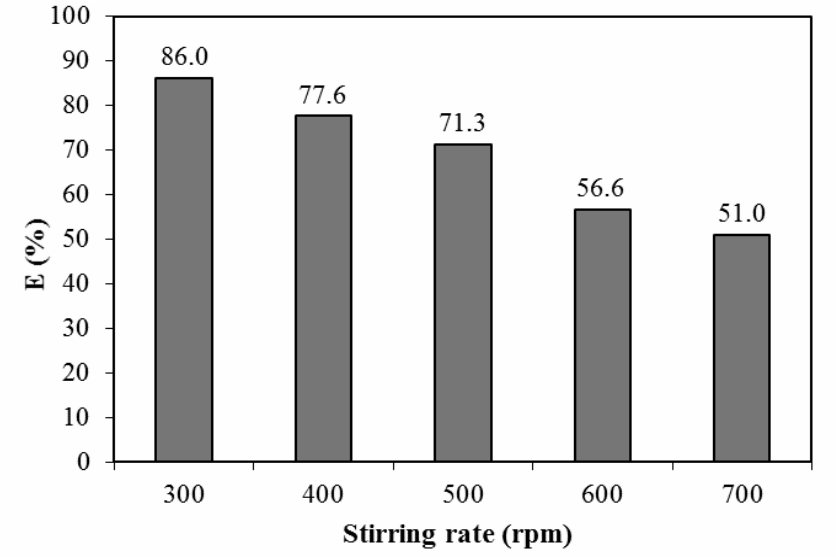

Fig. 4 – Influence of stirring rate over the efficiency of the biosorption process (100 mL solution, 50 mg/L, 5.0 g FSB, 0.4-0.6 mm, 295 K, pH = 6, 150 min).

The experiments of CR biosorption for 5.0 g FSB were repeated with various stirring rates in 300-700 rpm interval, at initial dye concentration of 50 mg/L. The results presented in Figure 4 showed that the highest efficiency was obtained at 300 rpm (86.0 %). Higher stirring rates will lead to a decrease in efficiency, 51.0 % (700 rpm), showing that due to the intense stirring, molecules are not able to reach the solid surface, therefore the biosorbed amount is going to be smaller for the same duration of the process (150 min). Such moderate speed gives probably, a good homogeneity for the mixture suspension in solution. The obtained results are in very good agreement with others from recent literature.[21] Similar adsorbent quantity and stirring rate behaviours for CR adsorption onto various adsorbents were reviewed by Salleh et al.[22]

Biosorption equilibrium study

Various isotherm equations have been used to describe the equilibrium nature of biosorption. Between the large number of isotherm models that can be utilized, the most popular are Langmuir (which is valid for homogeneous surfaces), Freundlich (suitable for highly heterogeneous surfaces), Temkin (which contains a factor that explicitly takes into consideration the interactions between adsorbing species and the adsorbate),[6] and Dubinin–Radushkevich (which is frequently applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface) models. The selection criterion for most suitable isotherm was the value of coefficient of determination, R^2, which should be closer to unit ($R^2 = 1$).

The experimental data at equilibrium, amount adsorbed and concentration, obtained using 25-125 mg/L CR solutions, 5.0 g FSB of 0.4-0.6 mm, at room temperature (295 K), pH = 6, and 300 rpm were considered.

Langmuir and Freundlich adsorption isotherms

Langmuir model is frequently used for adsorption of organic pollutants, heavy metals etc., this model is applicable for a monomolecular layer adsorption at specific homogenous sites on the adsorbent surface. The Langmuir isotherm equation has a hyperbolic form:[23,24]

$$q_e = \frac{q_m \cdot K_L \cdot C_e}{1 + K_L \cdot C_e} \quad (1)$$

where, q_e is the amount adsorbed at equilibrium (mg/g), q_m is the monolayer capacity of the biosorbent (mg/g), C_e is the concentration of CR in solution at equilibrium (mg/L), and K_L is related to the strength of adsorbent-adsorbate affinity (L/mg).

A linear form of eq. (1) is expressed as:

$$\frac{1}{q_e} = \frac{1}{q_m \cdot K_L} \cdot \frac{1}{C_e} + \frac{1}{q_m} \quad (2)$$

Isotherm parameters q_m and K_L can be obtained by plotting $1/q_e$ against $1/C_e$.

The important features of the Langmuir isotherm may be expressed in terms of parameter R_L, dimensionless constant referred to as separation factor or equilibrium parameter, [21,24] eq. (3):

$$R_L = \frac{1}{1 + K_L \cdot C_0} \quad (3)$$

where, C_0 is the highest intial concentration (mg/L), and R_L value indicates the biosorption nature to be either unfavourable if $R_L > 1$, linear if $R_L = 1$, favourable if $0 < R_L < 1$ and irreversible if $R_L = 0$.

Based on experimental data (Figure 5) q_m was determined to be 28.1±0.1 mg/g, K_L (Langmuir isotherm constant) is 3.64×10^{-3} L/mg, and the separation factor R_L is 0.653 indicating the fact that biosorption is favourable. The R^2 value is 0.937. The obtained results are in good agreement with other from literature on related systems for CR removal (apricot stone[21], *Eucalyptus* wood sawdust[24], activated carbon from pine cone biomass[25], Ni-doped magnolia-leaf-derived bioadsorbent[26], cationic modified orange peel powder[27], etc.)

Freundlich isotherm is an empirical model that takes into account the heterogeneity of the surface of the biosorbent and is expressed by logarithmic linear form, eq. (4):

$$\log q_e = \log K_F + \frac{1}{n} \cdot \log C_e \quad (4)$$

where, K_F and n are the Freundlich constants. The K_F constant is an indicator of the biosorption capacity of the biosorbent while n indicates biosorption intensity. If n lies between 1 and 10, this indicates a favourable biosorption process.[21,24,25,28]

The $\log q_e$ versus $\log C_e$ plot allows the determination of the Freundlich constants (Figure 6).

For CR biosorption onto FTS the following values were calculated: $K_F = 0.880$ ($mg^{(1-1/n)}L^{1/n}/g$) and $n = 3.36$, indicating that the biosorption process is favourable ($R^2 = 0.831$).

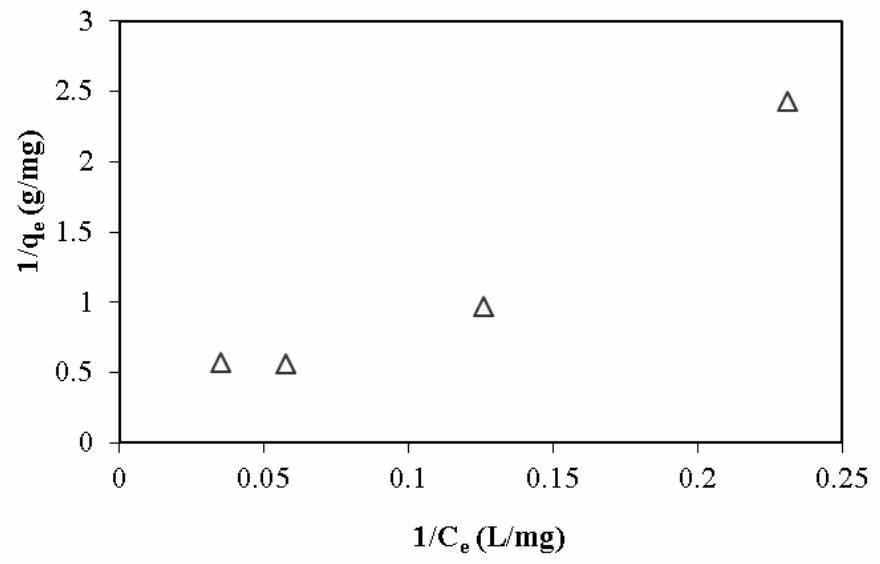

Fig. 5 – Langmuir biosorption model of CR dye on FSB.

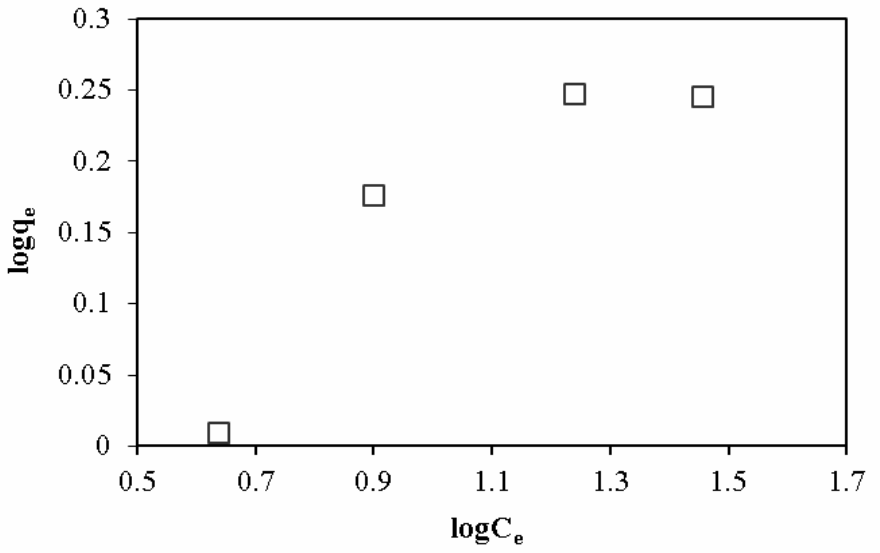

Fig. 6 – Freundlich biosorption model of CR dye on FSB.

Temkin isotherm

The Temkin isotherm contains a factor that explicitly takes into account the adsorbent-adsorbate interactions. By eliminating the extremely low and large value of concentrations, the model assumes that the heat of biosorption of all molecules in the layer would decrease linearly rather than logarithmic with coverage. As implied in the equation, its derivation is characterized by a uniform distribution of binding energies (up to some maximum binding energy). By plotting q_e against $\ln C_e$ and the constants were determined from the slope and intercept, Figure 7. The model is given by the following equation in logarithmic form, eq. (5):[28-30]

$$q_e = B \ln A_T + B \ln C_e \quad (5)$$

$$B = \frac{RT}{b_T} \quad (6)$$

where, A_T is Temkin isotherm equilibrium binding constant (L/g), b_T is Temkin isotherm constant (J/mol), R is universal gas constant (8.314 J/mol·K), T is absolute temperature (K), and B is a constant related to heat of biosorption.

The following values were determined for CR biosorption on FSB: A_T = 0.136 L/g, B = 0.729, which indicates a physical biosorption process (R^2 = 0.992).

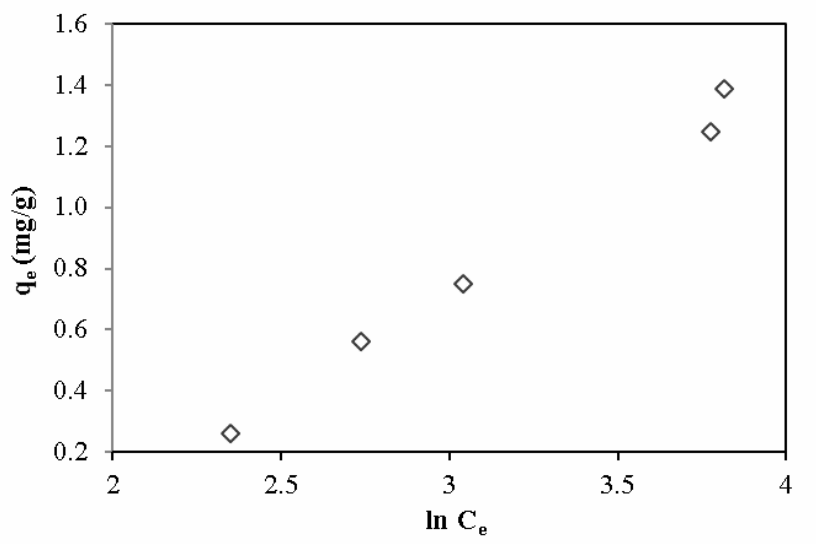

Fig. 7 – Temkin biosorption model of CR dye on FSB.

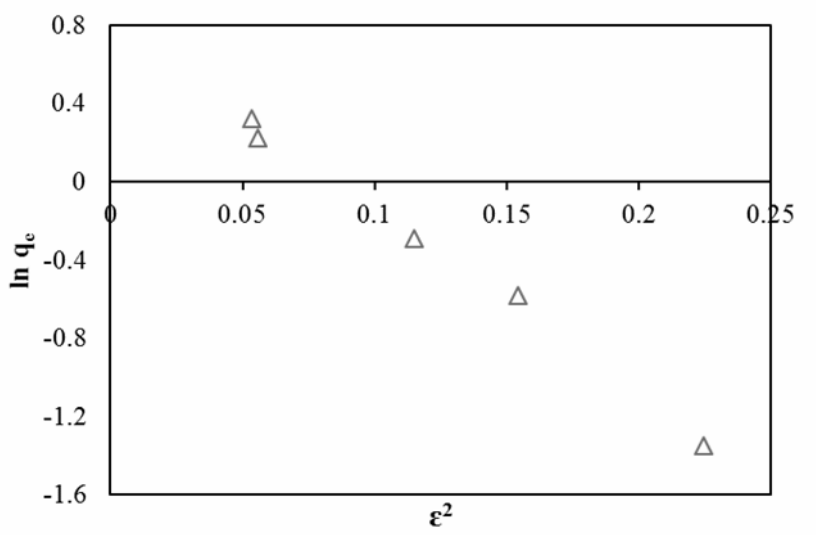

Fig. 8 – Dubinin–Radushkevich biosorption model of CR dye on FSB.

Dubinin–Radushkevich isotherm model

Dubinin–Radushkevich isotherm is frequently applied to express the biosorption mechanism with a Gaussian energy distribution onto a heterogeneous surface.[31] The model has often successfully fitted high solute activities and the intermediate range of concentrations data well.

$$q_e = q_s \exp(-K_D \varepsilon^2) \quad (7)$$

$$\ln q_e = \ln q_s - K_D \varepsilon^2 \quad (8)$$

$$\varepsilon = RT \ln(1 + \frac{1}{C_e}) \quad (9)$$

where, q_s is theoretical isotherm saturation capacity (mg/g) and K_D is Dubinin–Radushkevich isotherm constant (mol^2/kJ^2).

Dubinin–Radushkevich isotherm is usually applied to distinguish between physical and chemical adsorption using the mean free energy, E per molecule of adsorbate (for removing a molecule from its location in the sorption space to the infinity), which can be computed using eq. 10. Values smaller than 8 kJ/mol indicate a physical adsorption.[21,31-33]

$$E = \frac{1}{\sqrt{2K_D}} \quad (10)$$

From the linear plot of Dubinin–Radushkevich model, Figure 8, q_s was determined to be 1.35 mg/g and the mean free energy, E = 0.326 kJ/mol, indicating a physisorption process (R^2 = 0.994). These results are in good agreement with others from literature on similar systems.[21,34]

EXPERIMENTAL

Preparation and characterization of the biosorbent

The FSB was obtained from Mărgău village, Cluj County, Roumania, washed with distilled water, dried at 105°C for 24 h, grinded and sieved. 0.4-0.6 mm grain size was used throughout the experiments.

SEM analysis

Scanning electron microscope is an extremely useful tool for visual confirmation of surface morphology and the physical state of the surface. The images were obtained with a JEOL (USA) JSM 5510 LV apparatus. Prior to analyze, FSB samples were mounted on a stainless stab with a double stick tape. Then, they were coated with a thin layer of gold under vacuum to improve electron conductivity and image quality.

FTIR analysis

The fresh and used (separated from CR solution after biosorption and dried) FSB samples (0.4-0.6 mm) were prepared by encapsulating 1.2 mg of finely ground biomass particles in 300 mg. Infrared spectra were obtained using a JASCO 615 FTIR spectrometer, 400–4000 cm^{-1}, resolution 2 cm^{-1}.

Preparation of CR aqueous solutions

The CR used in this study was purchased from Sigma–Aldrich and used without further purification; C.I. No. is 22120, F.W. = 696.7, and λ_{max} = 497 nm. The chemical structure was presented somewhere else.[2] Dye stock solution (1000 mg CR/L) was prepared by dissolving the accurate quantity of solid substance, CR (analytical purity reagent), in double distilled water. From dye stock solution (1000 mg/L) experimental solutions with known concentration in 25-125 mg/L range were further prepared.

Biosorption study

The CR biosorption process was studied using the batch technique. Experiments were carried out by contacting different amounts of adsorbent under magnetic stirring, at 295 K and pH = 6, with 100 mL CR in aqueous solutions with different initial concentrations. It is reported that at and below pH = 2, the CR solution changes its color from red to dark blue and also the original red colour is different above pH > 10.[9] In this study, only the pH = 6 (the initial pH of solution) was utilized.

The CR concentration in aqueous phase was determined using an UV-VIS spectrophotometer (Jenway 6305). The experiments were repeated three times and averaged concentration values were further used.

Data evaluation

Biosorption process efficiency, E (%) and biosorption capacity, q_e (mg/g) were calculated using eqs. (11) and (12):

$$E \quad \frac{(C_0 \quad C_{t(e)})}{m} \frac{V}{1000} \tag{11}$$

$$q_e = \frac{(C_0 - C_e)}{m} \cdot \frac{V}{1000} \tag{12}$$

where, C_0 is the initial CR concentration (mg/L), $C_{t(e)}$ is time t and equilibrium CR concentration respectively (mg/L), V is the aqueous solution volume (mL), and m is the biosorbent quantity (g).

Experimental data were used to establish which equilibrium model describes better the biosorption process.

CONCLUSIONS

The ability of FSB (*Abies nordmanniana*) to biosorb CR dye from wastewater synthetic aqueous solutions was investigated. The FTIR analysis indicated that carboxyl groups on the FSB were the most important functional groups responsible for CR biosorption. Also, shifts of the main peaks and modified intensities were observed for the CR-FSB samples, indicating that the groups present on the biomass surface were involved in the removal of CR dye. The removal process showed that the biosorption equilibrium was reached between 150 and 180 minutes depending on the FSB quantity. Maximum CR removal efficiency, 86.0%, was obtained for 5.0 g FSB.

Between the four isotherm models considered, Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin, experimental data best fitted on the Dubinin–Radushkevich model (fact supported by the highest value of the coefficient of determination for Dubinin-Radushkevich model, R^2=0.994). The free energy value, E = 0.326 kJ/mol, (determined from Dubinin-Radushkevich model isotherm) indicated a physisorption process.

This study in small-scale batch gave rise to encouraging results therefore the study is going to be extended on fixed bed column experiments under the conditions applicable to the treatment of industrial effluents.

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