Cationic Dyes Removal from Textile Wastewaters by Using Ecofriendly Adsorbents

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The use of cheap and ecofriendly adsorbents, as: hemp fibres, cellolignine, peat and cotton, have been studied as an alternative substitution of AOPs for the removal of some cationic dyes with compact condensed structures from textile wastewater. The sorption capacity of adsorbents was evaluated spectrometrically and removal degree for cationic dyes was calculated, as well as Langmuir and Freundlich models were applied to describe the sorption isotherm and the characteristic parameters are calculated. A kinetic study concerning sorption/desorption process was elaborated.

Keywords: cationic dye, ecofriendly adsorbent, removal degree, sorption isotherm

Textile industry uses large amounts of water and agents with considerable toxicity such as, dyes, inorganic salts, surfactants, and different auxiliaries, especially in dyeing process. It is not surprising that these substances have become a major environmental concern. Many of these compounds affect the environment via wastewater facilities. Colour, as a discernible indicator of pollution in the aqueous environment, is the first to attract the attention of each Environmental Agency of the world.

Dyes are considered to be particularly aggressive organic compounds for the environment because most of them, due to the complex structure, are completely resistant to biodegradation processes. Many dyes are very stable and resistant to chemical agents and light. The presence of dyes resulted from dyeing process in wastewaters modifies the colour of water and leads to some environmental problems [1]:
- modification of the illumination grade of aquatic medium which leads at the diminution of photosynthesis process and auto-purification capacity of water;
- besides, if their chemical structure is not stable, then can be decomposed, providing toxic organic compounds, e.g. aromatic amines which lead carcinogenous effects.

For this reason, the textile wastewaters treatment by physical processes is found to be inefficient. But the physico-chemical processes for the pre-treatment are recommended. A number of methods, like coagulation/ flocculation, chemical oxidation, reverse osmosis, ion exchange, electrochemical treatments, solvent extraction, adsorption using activated carbon, are usually used for the treatment of dye bearing wastewaters. Many of these procedures are cost prohibitive, however, and therefore are not viable options for treatment of textile wastewaters.

The adsorption process is one of the effective methods for removal dyes from the wastewaters. Activated carbon (powdered or granular) is one of the most widely used adsorbents because it has excellent adsorption efficiency for dyes [2, 3]. But, commercially available activated carbon is very expensive and through regeneration process of this adsorbent is possible to lose the adsorption capacity for dye. In the last years many studies lead to finding commercially cheaper non-polluted adsorbents for the dyes removal.

Biological treatments are costly and sometimes inefficient for the degradation of dyes form textile wastewaters [4]. Also, the combination of advanced oxidation processes (AOPs) with the biodegradation is a suitable alternative for the textile wastewater that permits to obtain 90% of the chemical oxygen demand (COD) reduction [5].

Nowadays, the ecofriendly adsorbents are a very appreciate alternative comparative with Advanced Oxidative Procedures (AOPs) [6-8] due to the fact that the dyes are retained on the adsorbents without formation of some any toxic compounds [9, 10].

The objective of the present research was to investigate the adsorption/desorption process of blue cationic dyes, derived from aminothioloquinoline and aminothiazolo-indazole heterocyclic systems [11], on cheap ecofriendly adsorbents. Hemp fibres, cellolignine, peat and cotton B26 were used for removal of selected blue cationic dyes. The sorption capacity of adsorbents was evaluated by amount of absorbed dye. The removal degree for each cationic dye is calculated, as well. Linear Langmuir and Freundlich models were applied to describe the sorption isotherm and the characteristic parameters are calculated.

Experimental part

In this study, the adsorption/desorption process of non-toxic blue cationic dyes obtained by original synthesis [12-15] on ecofriendly adsorbents was investigated by discontinuous method at laboratory scale in the following stages:
- the study of adsorption equilibrium – known quantities of dye (10-50 mg/L) used in dyeing process are mixed with selected adsorbents. The mixture is vigorously stirred until the equilibrium is achieved. Finally, the concentrations at equilibrium by analysis were determined and the retention percentage of cationic dye on adsorbent (R%) and their sorption capacity q (mg/L) were calculated.
- desorption of cationic dye from adsorbent was investigated by decantation and refilling technique. At the end of adsorption study, the supernatant was removed with the aid of pipette and then analysed for determination of residual concentration. The same decanted supernatant quantity was replaced with other eluent as distillate water.

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with following characteristics: salinity 0.0 ‰, resistivity better than 17.5 MΩ cm and pH 5.5;
- the kinetic study was realized. A known eco-friendly adsorbent quantity (1 g/L) was introduced in a known quantity of dye (10 mg/L). Certain intervals of time, some quantities of sample were collected. These samples were filtrated by filter (0.45 µm) and then analysed by analytical techniques.

Reagents and materials
Cationic dyes (Table 1) derived of compact condensed systems 2-aminothiazolo[4,5-b]quinoxaline-6-carboxylic acid, 2-aminothiazolo[5,4-b]quinoxaline-7-carboxylic acid, 2-aminothiazolo[4,5-f]indazole and 2-aminothiazolo[5,4-f]indazole were obtained by original syntheses and published in many articles [12-15]. These non-toxic blue dyes [9] were selected due to their complex chemical structure and in view of their extended application in the textile industry. Therefore, selection of dyes was realized depending on the following criteria: the affinity face on the textile fibre; the colour of the obtained compound; the stability in time of the chosen dyes. The presence of ionizing groups on the structure of cationic dyes provides bonding affinity on the polyacrylic fibres and the primary laboratory tests [12-15] were shown very good tintorial proprieties. The dyeing quality was determined by the standard AATCC (Calculation of Small Colour Differences for Acceptability) Test Method 173-1998 applied in the textile industry and the results are reported. Table 1 presents the chemical structures and some characteristics (wavelength, absorbance, extinction molar coefficient) of original blue cationic dyes.

Ecofriendly adsorbents: hemp fibres (<25mm) and free from any contamination, cellolignine (residual product obtained after treating the wood with dilute mineral acid at 150-160°C, with following composition: 45-48% cellulose; 32-35% lignin; 4-8% pentosan and 1-1.5% ash), eutrophic peat, Tara Barsei, Brasov County (characteristics: brown colour; 49 g/kg organic carbon content; 7.8 g total proteins; 3.44% ash; pH 35; specific area 192 m²/g) and cotton B26 with specific surface $S_p=31.71$ m²/g, were used for removal of selected blue cationic dyes.

Spectrophotometric techniques
The dyes from wastewaters were analyzed by VIS spectroscopy and certainly by visualization of colour of residual waters. The VIS electronic spectra were performed with Specord 250 UV-VIS spectrophotometer with double-monochromator, variable spectral resolution and cooled double detection and PC system, in quartz cells ($l=1$ cm).

Results and discussion
In this work some cheaper ecofriendly adsorbents for the removal of dyes are tried. The choice of non-pollutants adsorbents was based on requirements concerning high selectivity, large capacity of sorption, favourable kinetic features (highly hydrophobic that determines a rapid kinetics of the sorption process), physicochemical stability, mechanical strength, high porosity and availability at low cost [1-3]. Because of compatibleness between these criteria and their adsorptive features, these non-polluted and cheaper adsorbents constitute, in many instances, a solution of election. These researches started from some disadvantages of conventional adsorbents based on synthetic polymers (e.g. high prices, difficulties in obtaining, pollution produced during their synthesis), in accordance with the tendency of replacing chemically synthesized compounds with ecofriendly materials which protected the environment [1].

| Table 1 | CHEMICAL STRUCTURES AND CHARACTERISTICS OF BLUE CATIONIC DYES |
|------------------|------------------|------------------|------------------|
| **Cationic dyes** | **Structure of dyes** | **$\lambda_{max}$ [nm] (Absorbance) $\varepsilon_{max}$** |
| Blue Light cationic dye derived of compact condensed system 2-aminothiazolo[4,5-b]quinoxaline-6-carboxylic acid, CD1 | ![Structure of CD1][1] | $\lambda_{max}=555$ nm (1.050) $\varepsilon_{max}=23570$ |
| Blue Violet cationic dye derived of compact condensed system 2-aminothiazolo[5,4-b]quinoxaline-7-carboxylic acid, CD2 | ![Structure of CD2][2] | $\lambda_{max}=608$ nm (1.350) $\varepsilon_{max}=28230$ |
| Blue Light cationic dye, derived of compact condensed system 2-aminothiazolo[5,4-f]indazole, CD3 | ![Structure of CD3][3] | $\lambda_{max}=594.3$ nm (1.198) $\varepsilon_{max}=22510$ |
| Blue cationic dye, derived of compact condensed system 2-aminothiazolo[4,5-f]indazole, CD4 | ![Structure of CD4][4] | $\lambda_{max}=593$ nm (1.328) $\varepsilon_{max}=22560$ |

[1] Image of Structure of CD1
[2] Image of Structure of CD2
[3] Image of Structure of CD3
[4] Image of Structure of CD4
The experimental data concerning adsorption of blue cationic dyes shown that on superior limit of equilibrium concentration area, the adsorption capacity of dye on ecofriendly adsorbent (hemp fibres, peat, cellolignine and cotton B26), remained practically constant. The Langmuir and Freundlich model were utilized for interpretation of equilibrium data.

The kinetic study concerning sorption/desorption process of selected dyes from aqueous solution included the drawing of sorption isotherms and effects of hysteresis analysis. The sorption isotherms describe the relation between concentration at equilibrium of adsorbed in solid state and liquid state at constant temperature.

**Langmuir isotherm**

The Langmuir isotherm assumes monolayer deposition on homogeneous adsorbent surface. The mathematical expression of Langmuir isotherm can be given as rational form (1),

\[ q_e = \frac{K_L \cdot C_e}{1 + a_L \cdot C_e} \]  

(1)

The linearization of the above equation results

\[ \frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} \cdot C_e \]  

(2)

The binding constant \((K_L)\) and the sorbent capacity \((a_L)\) can be estimated by plotting \(C_e/q_e\) against \(C_e\).

**Freundlich Isotherm**

The Freundlich isotherm is an empirical model used for the study of multilayer sorption. The isotherm is adopted to describe reversible adsorption and not restricted to monolayer formation. The mathematical expression of the Freundlich model can be written as

\[ q_e = K_F \cdot C_e^b \]  

(3)

where \(K_F\) and \(b\) are the constants which give adsorption capacity and adsorption intensity respectively. A linear form of the Freundlich model can be written as follows

\[ \ln q_e = \ln K_F + b \ln C_e \]  

(4)

Plot of \(\ln q_e\) versus \(\ln C_e\) gives a straight line with slope \(K_F\) and intercept \(b\). It can be observed from the correlation coefficient \((R^2)\) that the Langmuir isotherm model fits well than the Freundlich isotherm (fig. 1) for the selected dye on cotton B26. From the above analysis, it can be concluded that the adsorption of dye on ecofriendly adsorbent follows monolayer adsorption.

The values of the correlation coefficient, \(R^2\), are very good for the both Langmuir and Freundlich isotherm models, especially for adsorption of cationic dyes on cotton, hemp and peat (e.g. fig. 1 – adsorption of CD1 on cotton B26 and figures 2 and 3 – adsorption isotherms of CD1 on cotton B26). The maximum value of dyes adsorption capacity on cotton B26 on equilibrium concentration domain is between 26.23 mg/g and 26.94 mg/g (table 2).

The study, which followed to compare the sorption capacity of all natural adsorbents, shown that Langmuir isotherm describes very well the adsorption of cationic dyes, especially, CD1 and CD4 dyes, on cotton and peat (table 2 and e.g. figs. 1, 2, 3). It should be noted that in the dyeing process of polycrylic fibers with CD1, respectively CD4 dyes, the affinity of these dyes on fibers was remarkable, as shown the published researches [12-15]. The same studies indicated that, in subsequent dyeing process (washing with hot and cold water), in washing waters were lost about 4-5% of the total amount of dyes used in dyeing. In the case of CD3 and CD4 dyes, the final loss of dyes is about 7%, respectively 9% [12-15].

In case of sorption and desorption, the ratio of the Freundlich exponents gives information about hysteresis form. If \(n_{des}/n_{sorb} = 1\), it is not observed the hysteresis phenomenon; if \(n_{des}/n_{sorb} < 1\), the hysteresis phenomenon is positive, and if \(n_{des}/n_{sorb} > 1\) the hysteresis is negative. Obviously, the sorption/desorption process depends on several factors, as: type of adsorbent, their physico-chemical and structural properties; adsorbent mass which influences the process by the number of sorption centers (e.g. fig. 3 the retaining process of dyes on peat increases with the increase of peat quantity and R% ~ 97); the initial concentration of dye (the removal coefficient R increase with concentration of cationic dye) is the last factor which influences the sorption process.
By processing the equilibrium data using Langmuir model (K_L, the equilibrium constant of adsorption process) can be calculated the value of Gibbs standard energy for adsorption process, \( \Delta G_{298}^{\circ} \) (table 2). The mathematical expression is:

\[
\Delta G_{298}^{\circ} = -RT\ln K_L
\]  

(5)

The values of Gibbs standard energy for studied adsorption processes are contained between -19.142 kJ/mole and -22.270 kJ/mole. These values include the adsorption process in category of physical processes. Also, the maximum values of capacity adsorption of selected dyes on ecofriendly adsorbents concluded that natural adsorbents can be used with success in advanced treatment of textile wastewaters.

The experimental studies demonstrated that doses of adsorbent influenced the process by the number of adsorption centres. In figures 4 and 5 are presented the results concerning the influence of adsorbent amount on adsorption process of 50 mg/L dye CD4. The presence of CD4 dye in aqueous phase was determined by spectrophotometric technique (fig. 6). It was observed that removal process increases with the amount of peat which was introduced in system, by the affinity of dye on peat being smaller comparative with the affinity of dye on the cotton B26. The affinity of studied dyes for all ecofriendly adsorbents decreases as following: cotton>hemp>peat>celloignine. The removal degree of dye was calculated with equation: \( R\% = \left( \frac{C_0 - C}{C_0} \right) \cdot 100 \), where:

<table>
<thead>
<tr>
<th>Adsorbent/dye</th>
<th>Langmuir isotherm</th>
<th>Freundlich isotherm</th>
<th>( \Delta G_{298}^{\circ} ) [kJ/mole]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( R^2 )</td>
<td>( q_e [\text{mg/g}] )</td>
<td>( K_L [\text{L/mg}] )</td>
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<tr>
<td>Hemp/CD1</td>
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<td>0.083</td>
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<td>Peat/CD1</td>
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<tr>
<td>Peat/CD2</td>
<td>0.97079</td>
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<td>Peat/CD4</td>
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<td>Celloignine/CD1</td>
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<td>Celloignine/CD3</td>
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<td>Celloignine/CD4</td>
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<td>13.02</td>
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</tr>
<tr>
<td>Cotton B26/CD1</td>
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</tr>
<tr>
<td>Cotton B26/CD2</td>
<td>0.99812</td>
<td>26.23</td>
<td>0.0943</td>
</tr>
<tr>
<td>Cotton B26/CD3</td>
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<td>26.52</td>
<td>0.0914</td>
</tr>
<tr>
<td>Cotton B26/CD4</td>
<td>0.99992</td>
<td>26.94</td>
<td>0.0982</td>
</tr>
</tbody>
</table>

Table 2
ESTIMATED PARAMETERS FROM LANGMUIR AND FREUNDLICH ISOTHERMS FOR SORPTION OF CATIONIC DYES ON ECOFRIENDLY ADSORBENTS

Fig. 4. Dependence of removal degree of dye CD4 on studied adsorbents (5 g/L; 10 g/L; 20 g/L; 30 g/L; 50 g/L)

Fig. 5. Dependence of removal degree on time for adsorption of 10 mg/L, 25 mg/L and 50 mg/L cationic dye CD4 on cotton

Fig. 6. Adsorption of dye CD4 (50 mg/L) on a peat increasing quantity (5 g/L; 10 g/L; 20 g/L; 30 g/L; 50 g/L)
C<sub>0</sub> and C is the initial and equilibrium concentration of studied compounds in aqueous system (mg/L).

Conclusions

In this work, the equilibrium and kinetics of adsorption process for some blue cationic dyes, obtained by synthesis from compact condensed systems 2-aminothiazolo-quinoxaline and 2-aminothiazolo-indazole, on different ecofriendly adsorbents, were studied.

The Langmuir and Freundlich models, to interpret the obtained results, were used. The analysis of experimental data, according to Langmuir and Freundlich isotherms, permitted to determine the maximum adsorption capacity of dyes, ordered the sorbents after adsorption capacity and could calculated the Gibbs standard energy. The obtained values for Gibbs energy have placed the adsorption process in physical adsorption category. This aspect was not mentioned in literature. The adsorption/desorption process was elucidated by following aspects: type of adsorbent, their physico-chemical and structural properties; adsorbent mass which influences the process by the number of sorption; the initial concentration of dye (the removal coefficient R increase with concentration of cationic dye).

The researches indicated that the removal percentage of dyes on ecofriendly adsorbents was higher on cotton (R% ~90) and lower on cellolignine (R% ~49). The maximum values of capacity adsorption of selected dyes on ecofriendly adsorbents concluded that natural adsorbents can be used with success in advanced treatment of textile wastewaters.

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References

9. RADULESCU, C., Rev. Chim. (Bucharest), 54, no. 12, 2003, p. 986
10. RADULESCU, C., STIHI, C., Rev. Chim. (Bucharest), 60, no. 8, 2009, p. 810
11. RADULESCU, C., Sisteme Heterociclice Compact Condensate, Editura Bibliotheca, Târgoviște, 2004
12. RADULESCU C., CONSTANTINESCU, G.C., Rev. Chim. (Bucharest), 55, no. 4, 2004, p. 269
15. RADULESCU, C., TĂRĂBĂȘANU-MIHAILĂ, C., Rev. Chim. (Bucharest), 55, no. 1, 2004, p. 25

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