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# REMOVAL OF Zn(II) IONS FROM AQUEOUS SOLUTION BY SORPTION USING CELLULOSE FUNCTIONALIZED WITH REACTIVE DYES AS SORBENT

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**Abstract**

The influence of initial metal ion concentration and temperature on the adsorption of Zn(II) from aqueous solution onto amino ethyl cellulose (AEC) functionalized with Orange 16 reactive dye, was examined. Batch experiments were performed at pH of 4.0 and adsorbent dose of 8.0 g/L previously established as optimum, ranging the initial Zn(II) concentration between 22.74-181.92 mg/L and temperature between 2 and 60 °C. Three isotherm models (Langmuir, Freundlich and Dubinin – Radushkevich) were applied to the equilibrium data and the fitted parameters were used to determine the thermodynamic parameters of adsorption process. The adsorption equilibrium was well described by the Langmuir model. Maximum adsorption capacity of functionalized AEC for Zn(II) ions slightly increase with increasing of temperature, from 33.56 to 36.50 mg/g. In addition, the adsorption energy, calculated from Dubinin - Radushkevich model, indicate that the Zn(II) uptake process occurs via electrostatic interactions. Thermodynamic studies indicated that adsorption of Zn(II) onto functionalized AEC is and endothermic process ($\Delta H$ = 9.98 kJ/mol) and spontaneous ($\Delta G$ = - 14.50 ÷ - 19.64 kJ/mol), in the studied temperature range.

*Keywords:* functionalized amino ethyl cellulose, isotherm, reactive dye, thermodynamic study, Zn(II) ions

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## 1. Introduction

The development of industrial activities has determined the accumulation of heavy metals in surface and ground waters. The presence of heavy metals in water sources is detrimental for a variety of living species, because these pollutants are non-biodegradable and have a high toxic potential, even at low concentration (Lodeiro et al., 2006; Martins et al., 2004; Modoi et al., 2014).

Numerous industrial applications of heavy metals, such as copper, nickel, zinc, cadmium and lead, in important technological processes, such as metal finishing, electroplating, pigments, paper and pulp, fertilizers, metallurgy and leather industry etc. (Wang and Chen, 2009), have made that their wastewaters to represents the main source of environmental pollution with such pollutants (Abdel-Ghani and El-Chaghaby, 2014; Han et al., 2006). Hence, improved and innovative methods for the removal of heavy metals from industrial wastewater are constantly developed, and their implementation at large scale keeps on to be an issue that entails advanced studies.

Various physico-chemical methods, such as precipitation, ion exchange, adsorption, membrane processes, electrolytic methods etc. were already recommended and applied for the elimination or reduction of metal ions concentration from industrial effluents (Bilal et al., 2013; Dabrowski et al., 2004;

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Gantam et al., 2014; Llanos et al., 2010; Suditu et al., 2013; Tunali et al., 2012; Wan Ngah and Hanafiah, 2008). Since the majority of these methods are costly and difficult to be applied, an efficient alternative has been checked. Adsorption has been shown to be an effective and low-cost method for the removal of a large variety of heavy metal ions from aqueous solution, including Zn(II) ions.

Among the significant advantages of adsorption, some are very relevant, such as: effective and quantitative removal of heavy metals, ease of operation, possibility of recycling the retained metal ions, low sludge production and energy consumption (Crini, 2005; Dabrowski et al., 2004; Hlihor et al., 2015). However, all these advantages can be taken into account only when the adsorbent material is not very expensive.

In recent decades, cellulosic materials have attracted the attention as low-cost, highly efficient and renewable source of biomass, which can be exploited as sorbents in the treatment of industrial effluents (Abdel-Halim and Al-Deyab, 2011; Wan Ngah and Hanafiah, 2008). It is well known that cellulose one of is the most abundant natural materials, which is used in numerous applications, such as paper manufacturing, packing, preparation of biocomposites etc. (Singha and Guleria, 2014a; Sud et al., 2008). Besides, the potential use of cellulosic materials for wastewater remediation process has become the topic of intense studies due to their numerous functional groups. This is also supported by the growing concern in relation to the environmental problems.

Unfortunately, many studies from literature have shown that the adsorption capacity of cellulose is relatively low, because the hydroxyl groups present in its structure are rather involved into hydrogen bonding that into interactions with heavy metal ions from aqueous solution (Crini, 2005; Mahajan and Sud, 2013; Gautam et al., 2014; Singha and Guleria, 2014b). Therefore, in order to improve the adsorption capacity of cellulose it is necessary the introduction of new functional groups in its structure, by chemical modification (Abdel-Halim and Al-Deyab, 2012; O'Connell et al., 2008; Shibi and Anirudhan, 2006; Singha and Guleria, 2014b).

The engraftment of amino ethyl groups in cellulose structure, which is a simple and cheap procedure that require common chemical reagents, significantly improves the removal of pollutants from aqueous solution, but only in case of negative charged species. In case of heavy metal ions that are predominantly positively charged in aqueous solution, the removal efficiency is quite low, mainly due to the electrostatic repulsions. This different behaviour of amino ethyl cellulose in function of charge of species from aqueous solution was the starting point in the functionalization of this adsorbent with organic dyes, prior to be used for the retention of metal ions. Thus, on the surface of the synthesized amino ethyl cellulose was first retained a negatively charged organic dye (such as Orange 16), and then after washing and drying, the obtained material was used for the adsorption of metal ions.

In this study, the adsorption of Zn(II) ions from aqueous solution onto amino ethyl cellulose (AEC) functionalized with reactive dye (Orange 16) was studied, as a function of initial Zn(II) concentration and temperature. The data obtained from batch experiments were analyzed using Freundlich, Langmuir and Dubinin-Radushkevich isotherm models. The fitted parameters were then used to determine the thermodynamic parameters of adsorption process. The obtained values of thermodynamic parameters ($\Delta G$, $\Delta H$, $\Delta S$) shown that the adsorption process is spontaneous and endothermic.

## 2. Experimental

### 2.1. Materials

*Adsorbent*. The experiments were carried out using amino ethyl cellulose (AEC) functionalized with reactive dye Orange 16, as adsorbent. This was obtained by equilibrating 25 g of AEC with 1000 mL dye solution with 0.1 g/L concentration, at neutral pH, 24 hours of contact time and room temperature (Şuteu et al., 2008).

*Metal ion solution*. It was worked with a stock solution 1% of $ZnSO_4 \cdot 7H_2O$ in which the Zn(II) concentration was 2274 mg Zn(II)/L. The working solution has been prepared by appropriate dilution of stock solution, having knowing and desired concentrations.

### 2.2. Adsorption experiments

The adsorption experiments were performed through batch method by contacting a constant amount of adsorbent (0.4 g) with 50 mL of solution containing various amounts of Zn(II) ions, ranged between 23 and 182 mg/L. The previous results indicate that better adsorption efficiency of Zn(II) ions onto functionalized AEC was reached with adsorbent dose of 8 g/L and initial solution pH of 4, and these conditions were considered as optimum and used in all further experiments. The system was maintained at constant temperature in a thermostatic bath and under discontinuous stirring. After 24 hours, the concentration of the Zn(II) ions in the solution was determined spectrophotometrically (method with xylenol orange $10^{-3}$ M in order to obtained colored metallic complex with maximum wavelength at $\lambda$= 570 nm) using an UV-VIS Digital Spectrophotometer, model S 104D /WPA (Dean, 1995).

The adsorption efficiency of functionalized AEC was evaluated by determined two characteristic parameters: the amount of Zn(II) retained on mass unit of adsorbent q (mg/g) and percentage of Zn(II) removal R(%), using Eqs. (1-2), where: $C_0$ and $C$ are initial and the equilibrium concentration of Zn(II) in solution in mg/L, G is the amount of AEC (g) and V is the volume of solution (L).

$$q = \frac{C_0 - C}{G} \cdot V \quad (1)$$

$$R,\% = \frac{(C_0 - C) \cdot 100}{C_0} \quad (2)$$

*2.3. Adsorption thermodynamics*

The characteristic thermodynamic parameters were determined using Eqs. (3-4) (Crini and Badot, 2008), where: ΔG is free energy (kJ/mol), ΔH is enthalpy (kJ/ mol) and ΔS is adsorption entropy changes (kJ/mol K), R is the universal gas constant (8.314 J/mol K), T is the absolute temperature of solution (K) and $K_L$ is the values of Langmuir constant (L/mol).

$$DG = -RT \ln K_L \quad (3)$$

$$\ln K_L = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (4)$$

**3. Results and discussion**

*3.1. Effect of temperature on Zn(II) removal capacity*

The studies relating to the effect of temperature on Zn(II) ions adsorption from aqueous solutions onto functionalized AEC were carried out at three different temperatures (2 – 60°C), with initial concentrations of Zn(II) ions varying from 23 to 182 mg/L, at pH 4, and the obtained results are illustrated in Fig. 1.

It can be observed that the adsorption efficiency of Zn(II) onto functionalized AEC increase with the increasing of temperature. This increase of adsorption efficiency is determined mainly by two factors: (i) increase of metal ions mobility with increasing of temperature, and (ii) swelling effect within the internal structure of functionalized AEC, which make that internal functional groups from adsorbent structure to become available for interactions with Zn(II) ions. In consequence, the attractive forces between adsorbent surface and metal ions from aqueous solution will be stronger and the adsorption efficiency increases (Febrianto et al., 2009).

It should be also noted that the increase of adsorption efficiency with the rise of temperature is not uniform, and two distinct stages can be observed. In the first stage, at low Zn(II) ions concentration, the increase of adsorption efficiency with temperature is more pronounced, than in the second stage, where a flattening of adsorption isotherms can be noticed. The Zn(II) concentration that separates these two stages is around 20 mg/L, and this value is almost the same for all studied temperatures.

The increase of adsorption efficiency with increasing of temperature suggest that between Zn(II) ions from aqueous solution and functional groups from adsorbent surface occur strong interactions, and in consequence, the possible mechanism to be a ion exchange one (Singha and Guleira, 2014a).

*3.2. Adsorption equilibrium*

The absorption equilibrium isotherm are obtained plotting the amount of adsorbate retained on mass unit of adsorbent (*q*, mg/g) as a function of the adsorbate concentration at equilibrium in liquid phase (*C*, mg/L), and could be considered an important instrument to analyzed the adsorption process (Chong and Volenski, 1995; Febrianto et al., 2009).

In order to analyze the adsorption isotherms obtained at various temperatures, three isotherm models: Langmuir, Freundlich and Dubinin-Radushkevich (Chong and Volenski, 1995; Crini and Badot, 2008; Febrianto et al., 2009) were employed for fitting the equilibrium data.

- *Freundlich isotherm model* assumes that multilayer adsorption on heterogeneous surface occurs, with an exponential distribution of active sites of different energies, according to Eq. (5) where: $K_F$ and $n$ are constants related to the adsorption capacity and adsorption intensity (efficiency), respectively.

$$q = K_F C^{1/n} \quad (5)$$

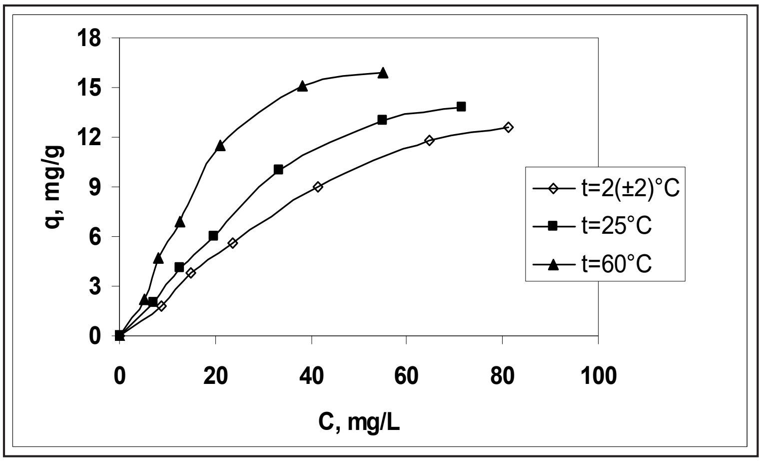



**Fig. 1.** Adsorption isotherms of Zn(II) ions on functionalized AEC, at different temperatures

- *Langmuir isotherm model* considers that the adsorption process occurs on homogeneous surface containing a finite number of energetically equivalent sites takes place, until complete monolayer coverage is formed, according to Eq. (6), where: $q_0$ is the maximum amount of adsorbed solute (mg/g); $K_L$ is the Langmuir constant, related to the binding energy of solute (L/mg).

$$q = \frac{K_L C q_0}{1 + K_L C} \quad (6)$$

- *Dubinin-Radushkevich isotherm model* states that one can speak about a Gaussian energy distribution onto a heterogeneous surface. It is usually applied to differentiate the physical and chemical adsorption by the mean free energy value, as given by Eqs. (7-8), where: $q_D$ is the maximum adsorption capacity, mg/g; $\beta_D$ – activity coefficient related to mean adsorption energy, mol$^2$/kJ$^2$; $\varepsilon$ - Polanyi potential defined by: $\varepsilon = RT\ ln(1 + \frac{1}{C})$ ; $E$ – mean free energy of adsorption, kJ/mol.

$$ln\, q = ln\, q_D - \beta_D \varepsilon^2 \quad (7)$$

$$E = \frac{1}{\sqrt{-2\beta_D}}, \ E = \frac{1}{\sqrt{-2\beta_D}} \quad (8)$$

The linear dependences of Langmuir, Freundlich and Dubinin-Radushkevich models for the adsorption of Zn(II) ions onto functionalized AEC are presented in Fig. 2. The isotherms parameters were calculated from the slope and intercept of the characteristic plot of each model (lg *q vs*.lg *C* – for Freundlich model; *1/C vs. 1/q* – for Langmuir model, and $\varepsilon^2$ *vs*. ln *q* – for Dubinin-Radushkevich model, respectively), and the obtained values are summarized in Table 1. The conformity between experimental data and the model predicted values was estimated using the linear correlation coefficient $R^2$, whose values were also mentioned in Table 1, for all cases.

The Freundlich constant n, which is used to estimate the adsorption intensity of the metal ion on the functionalized AEC surface, is higher than 1 in all cases, which means that the adsorption process is favourable even at high metal ion concentrations. On the other hand, the increase of this constant with the rise of temperature, suggest that the uptake of Zn(II) from aqueous solutions on functionalized AEC, probably takes place by ionic interactions. This assumption is sustained and by the variation of Freundlich constant ($K_F$) with temperature. The increases of $K_F$ values, which are a measure of the adsorption degree, with the increase of temperature, indicate that more adsorption would be expected at higher temperatures.

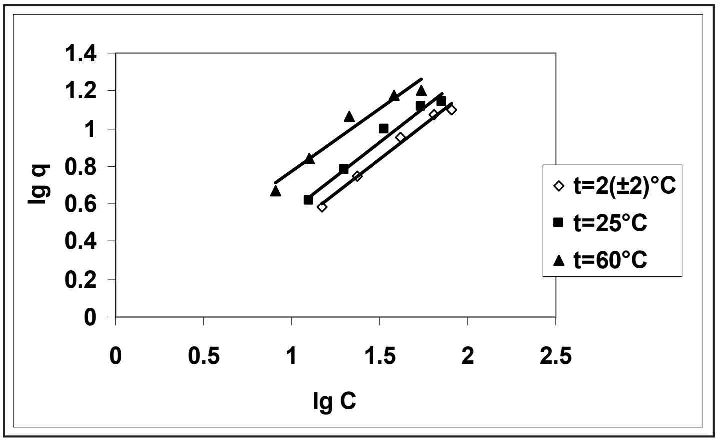
Unfortunately, the values of correlation coefficients shows that the Freundlich isotherm model is not so adequate to describe the adsorption process of Zn(II) ions onto functionalized AEC. On the basis of this criterion, the experimental data of Zn(II) ions adsorption on functionalized AEC are better described by the Langmuir isotherm model, where the correlation coefficients have higher values. According with the Langmuir isotherm model, the number of adsorption sites from adsorbent surface is limited and the metal ions adsorption occurs gradually until monolayer coverage is formed (Febrianto et al., 2009).

The value of maximum adsorption capacity ($q_0$), required to obtain a complete monolayer coverage, in case of Zn(II) ions adsorption onto functionalized AEC, at temperature of 25$^0$C is 34.6021 mg/g, and increases with increasing of temperature. This value is comparable with those reported in literature for the retention of Zn(II) ions onto various low-cost materials (Table 2), suggesting the potential applicability of functionalized AEC in removal processes of this metal ion from aqueous media.

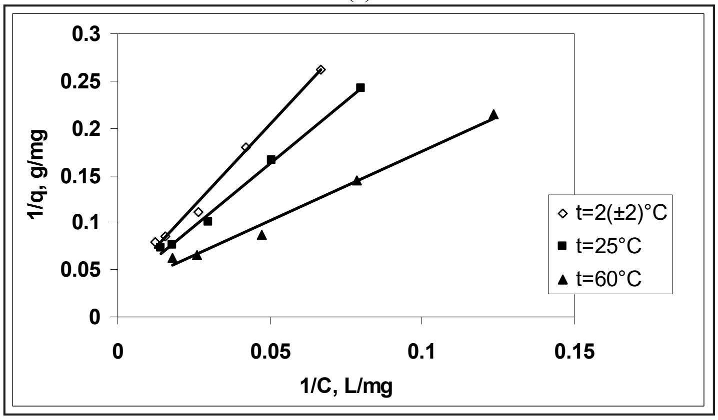
The relative low values of Langmuir constant, $K_L$ is due to a weaker binding between cationic ions and adsorbent surface. The adsorption capacity increases with the temperature probably due to increase of diffusion of ions toward the structure of the functionalized cellulose. Knowing that the values of mean free energy lower than 8 kJ/mol characterizes a physical adsorption mechanism, whereas values between 8 and 16 kJ/mol indicates an ion exchange mechanism (Dubinin and Radushkevich, 1947), the calculated values of this parameter will give important information about adsorption mechanism.

**Table 1.** Isotherms parameters for the adsorption of Zn (II) ions onto functionalized AEC

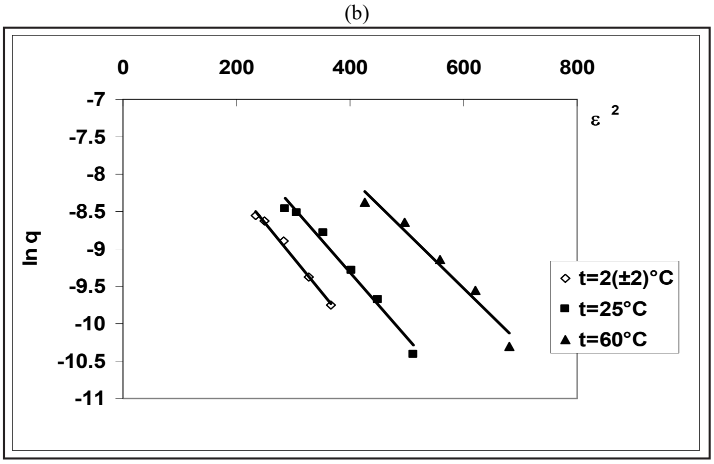
| ***Isotherm model*** | ***Isotherm parameter*** | ***Temperature, K*** | | |
|---|---|---|---|---|
| | | ***278*** | ***298*** | ***333*** |
| Freundlich | $n$ | 1.371 | 1.3926 | 1.5212 |
| | $K_F$, mg.L$^{1/n}$/g.mg$^{1/n}$ | 0.5497 | 0.7092 | 1.3041 |
| | $R^2$ | 0.9868 | 0.9736 | 0.9440 |
| Langmuir | $q_0$, mg/g | 33.6311 | 34.6021 | 36.4961 |
| | $K_L$, L/mg | 0.0087 | 0.0108 | 0.0184 |
| | $R^2$ | 0.9922 | 0.9945 | 0.9871 |
| Dubinin-Radushkevich | $E$, kJ/mol | 7.33 | 7.57 | 8.16 |
| | $\beta_D$, mol$^2$/kJ$^2$ | 0.0093 | 0.0087 | 0.0075 |
| | $q_D$, mg/g | 117.65 | 187.21 | 416.60 |
| | $R^2$ | 0.9921 | 0.9804 | 0.9622 |




(a)




(b)




(c)

**Fig. 2.** Freundlich (a), Langmuir (b) and Dubinin-Radushkevich (c) linear representations for the adsorption of Zn(II) ions on functionalized AEC

**Table 2**. Comparative values of Langmuir adsorption capacities for Zn(II) on various low-cost materials

| ***Adsorbent material*** | ***pH*** | ***$q_{max}$, mg/g*** | ***Reference*** |
|---|---|---|---|
| Bentonite | 4.5 | 52.91 | Mellah and Chegrouche, 1997 |
| Natural zeolite | 5.0 | 2.21 | Motsi et al., 2009 |
| Sphagnum sp. | 5.0 | 60.73 | González and Pokrovsky, 2014 |
| Lignin | 4.0 | 73.20 | Srivastava et al., 1994 |
| Sawdust-black locust | 4.5 | 5.23 | Sciban et al., 2006 |
| Waste activated sludge | 4.0 | 36.90 | Norton et al., 2004 |
| Functionalized AEC | 4.0 | 34.60 | This study |

In case of Zn(II) ions adsorption onto functionalized AEC, the values of mean free energy between 7.33 and 8.16 kJ/mol (Table 1) suggest that the adsorption mechanism is combined one, that imply both physical interactions (such as van der Waals, hydrogen, dipole – dipole), but also electrostatic attractions between the positive charged surface of the adsorbent and the cationic inorganic species.

### 3.3. Adsorption thermodynamics

Determination of the apparent thermodynamic parameters is important in order to evaluate the effect of temperature of Zn(II) adsorption onto AEC functionalized with reactive dye Orange 16, to evidence the nature of adsorption, and to appreciate the spontaneity of the adsorption process. Using the values of Langmuir constant $K_L$ (expressed in L/mol), the Gibbs free energy variation was calculated by Eq (3). The obtained values of Gibbs free energy change are then employed to determine other thermodynamic parameters, such as enthalpy change ($\Delta H^0$) and entropy change ($\Delta S^0$), on the basis of the van't Hoff equation (Eq. 4) (Crini and Badot, 2008).

- The values of thermodynamic parameters $\Delta H^0$ and $\Delta S^0$ estimated by plotting *ln* $K_L$ versus *1/T* (Fig. 3) are given in Table 3. In order to evaluate the degree of fitness of the van't Hoff equation to the experimental data, it was used the linear regression coefficient $R^2$ (Table 3).

The results presented in Fig. 3 and Table 3 showed that:

- The negative value of Gibbs free energy ($\Delta G^0$) increases while temperature increases. This behavior suggests that the Zn(II) ions adsorption onto functionalized AEC is thermodynamically feasible and spontaneous in nature. Moreover, it is known that $\Delta G^0$ values less than - 40 kJ/mol (Table 3) confirms the fact that the electrostatic interactions play an important role in the adsorption mechanism (Horsfall and Spiff, 2005).

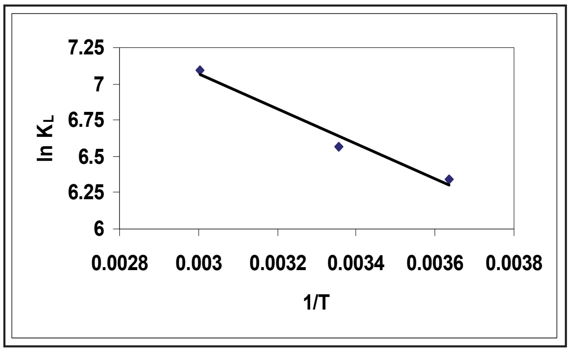



**Fig. 3.** Plots of ln K versus *1/T* for the retention of Zn(II) onto functionalized AEC

**Table 3.** Thermodynamic parameters obtained for Zn(II) adsorption onto functionalized AEC

| *T, K* | *$K_L$, L/mol* | *$\Delta G^0$, kJ/mol* | *$\Delta H^0$, kJ/mol* | *$\Delta S^0$, J/mol.K* | *$R^2$* |
|---|---|---|---|---|---|
| 275 | 568.844 | -14.5037 | 9.979 | 88.029 | 0.971 |
| 298 | 707.616 | -16.2575 | | 88.04 | |
| 333 | 1205.585 | -19.6421 | | 88.952 | |

- The positive values of enthalpy change ($\Delta H^0$) underline the endothermic nature of the adsorption process that is in agreement with the increase of adsorption capacity with increase of temperature. Its relative low value supports the statement that adsorption process occurs through a combination of physical van der Waals interactions and electrostatic attractions.

- The positive value of entropy change ($\Delta S^0$) is characteristic to the increased randomness at the solid-liquid interface during adsorption of heavy metal ions, indicating also some structural changes in both adsorbate and adsorbent. At the same time, the positive values evidenced the electrostatic interactions between opposite charge groups and may be a result of the increase in the degree of freedom of the adsorbed species.

## 4. Conclusions

The experimental results presented in this study indicate that the adsorption of Zn(II) ions from aqueous solution onto AE cellulose functionalized with reactive dye (Orange 16) is favoured by the increasing of temperature. The increase of temperature will favour the increase of solubility of pollutants species in the wastewater and also enhances the adsorption rates.

The experimental data of adsorption of Zn(II) ions from aqueous environment onto functionalized AEC were analyzed using Freundlich, Langmuir and Dubinin-Radushkevich models. The Langmuir isotherm model better characterizes the equilibrium adsorption data; the monolayer adsorption capacity was found to be 34.6021 mg/g at 25$^0$C. The value of adsorption energy determined by Dubinin-Radushkevich models suggested a physical adsorption process occurring via electrostatic interactions between adsorbent surface and metal ions. The values of thermodynamic parameters indicate a feasible, spontaneous and endothermic adsorption process between the surface of functionalized AEC and the Zn(II) ions from aqueous solution. Their values also confirm the physical nature of adsorption.

The results lead to conclusion that the functionalized celluloses with reactive dyes can be considered as a promising adsorbent for the removal of heavy metal ions from aqueous solutions.

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