



## KINETICS STUDIES OF METAL-COMPLEX DYE ADSORPTION ON WASTE TEXTILE BASED ADSORBENT

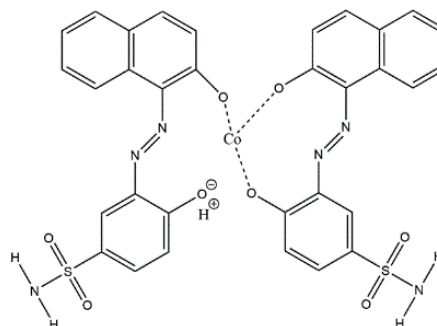
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This article represents a kinetic study of a metal-complex textile dye adsorption onto an adsorbent prepared from waste cotton textiles collected from a textile-fabrication facility. The qualitative and quantitative characterizations of the obtained adsorbent show that it is a relatively porous and inhomogeneous material. During adsorption, longer contact time causes a greater amount of dye on the adsorbent, *i.e.* with the duration of the adsorption process the concentration of dye in solution decreases. The kinetic parameters, rate constants, equilibrium adsorption capacities as well as the error statistical parameters, were calculated and discussed. It has been shown that the kinetic adsorption of a metal-complex dye onto the obtained adsorbent can be described best by the Hyperbolic tangent equation. The prepared adsorbent is relatively inexpensive, the raw material is easily available, therefore it could be an alternative for expensive adsorbents used for decolorization in the wastewater treatment processes.



### INTRODUCTION

Dyes and pigments are one of the problematic groups of chemicals which are released in the wastewaters of different industry branches, *e.g.* from the paint, textile, paper, carpet, cosmetics industries etc. Synthetic dyes have a complex aromatic structure that enables them to have physicochemical, thermal and optical properties.<sup>1</sup> The presence of these dyes in water is very noticeable; it affects the quality and transparency of water causing reduced light penetration and less solubility of gases in water. Many dyes and pigments are toxic with assumed carcinogenic and

mutagenic effects affecting the aqueous environment and people.<sup>2</sup> Removal of such compounds is complicated and difficult, and in addition to the appearance of physical and chemical methods, including adsorption, coagulation, precipitation, filtration, ozonation, or oxidation in order to treat dyed wastewaters.<sup>3</sup>

There are advantages and disadvantages of various methods for the removal of dyes from wastewaters, but only adsorption is considered to be superior over other techniques. The reasons are low cost, easy availability, simplicity of design, high efficiency, uncomplicated operation, biodegradability

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as well as the ability for dye treatment in more concentrated forms of.<sup>4</sup>

Most papers focus on novelties in materials serving as adsorbents. The kinetic studies in these papers, in which the experimental data are fitted by suitable models, serve only as a complement to the estimation of the adsorbent. Kinetic studies are developing models to describe the rate of adsorption. Ideally, with a minimum complexity, the model should: reveal the mechanism for limiting the rate and extrapolate the results in work-operating conditions that are of interest.<sup>5</sup>

The aim of this paper is to describe the kinetics of sorption of a typical metal-complex dye on an adsorbent made from waste cotton textile after being cut in the clothing plant. Based on this, valuable data can be obtained which are related to the rate and control mechanism of dye adsorption with the aim of optimizing the wastewater treatment. The kinetics of sorption, which describes the rate of dyes absorption, is one of the most important characteristic because it defines the efficiency of the sorption and capacity of use of the adsorbent in the bleaching of wastewater.

## EXPERIMENTAL

### 1. Materials

The adsorbent was obtained by chemical modification of cotton waste from the clothing plant. After collection, the textile waste (100% cotton knit) was finely cut with scissors and washed with non-ionic detergent Felosan NKB (CHT, Germany), in warm distilled water (60°C). After drying, the sample was treated with CaCl<sub>2</sub> solution (bath ration 1:100, 30 gL<sup>-1</sup> CaCl<sub>2</sub>) for 48 h at room temperature. This was followed by squeezing, then drying in air completely. Then, the dried samples were packed in aluminum foil and annealed at

400°C, for 90 min. Afterwards, spontaneous cooling followed, partial shredding and washing with distilled water. In the end, the complete drying (100°C) and manual grinding followed.

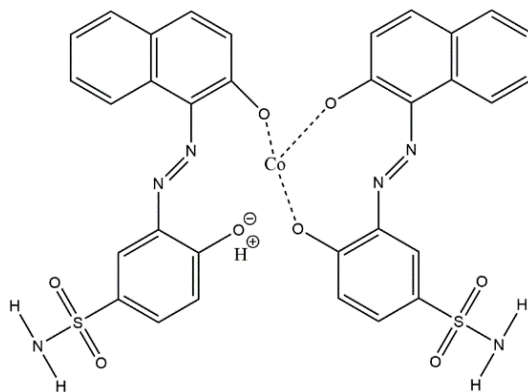
### 2. Adsorption process

The adsorption test was performed in glass reaction vessels in which the adsorbent was suspended in a metal-complex dye solution (adsorbate). Reaction vessels were placed on a shaker with circular moving (100 rpm) at a temperature of 20°C and held for certain period of time. The amount of adsorbent was constant, 1 g, whereas the solution in a constant amount of 100 mL contained a metal-complex dye of the following concentrations: 50, 100, 200, 300 and 400 mgL<sup>-1</sup>. Processing time, with continuous stirring, was 2, 5, 10, 20, 30, 40 and 60 min. The pH of the aqueous dye solution was adjusted to 2–3 by adding a sulfuric acid solution. The 60 min time was the equilibrium time because after this (checking went up to 90 min) there was no significant change in the amount of the adsorbed dye on the adsorbent.

The absorption measurement was performed on a UV-Vis spectrophotometer (*Cary 100 Conc UV-Vis, Varian*) at 490 nm (maximum wavelength of the spectrum of the used dye solution).

SEM measurements were performed on a TESCAN MIRA3 microscope using a secondary electron detector and EDS detector was used to measure the characteristic X-rays of the principal elements.

The used metal-complex dye belongs to the group of monoazo dyes with one sulfo and amino group and one benzene and naphthalene nucleus. Two dye molecules and one cobalt atom build a metal complex dye. The dye code is C.I. Acid Red 182, according to its molecular structure, it belongs to the group with single azo and metal-complexes dyes 1:2 (Fig. 1).



Sl. 1 – Structure of used metal-complex dye (using ChemBioDraw Ultra 14.0 software).

The adsorption capacity or the amount of the adsorbed dye (adsorbate) per unit mass of waste textile based material (adsorbent) at time  $t$  or at equilibrium,  $q_{t,e}$  (mg/g), was determined by the equation:<sup>3</sup>

$$q_t = \frac{(C_0 - C_t) \cdot V}{w}; \quad q_e = \frac{(C_0 - C_e) \cdot V}{w}; \quad (1)$$

where:  $w$  is a mass of adsorbent (g);  $V$  – volume of solution (L);  $C_e$  – dye concentration at equilibrium ( $\text{mgL}^{-1}$ ).

### 3. Kinetic reaction models

Modified Freundlich (MF) equation has the following form:<sup>6</sup>

$$q_t = k_{mF} \cdot C_0 \cdot t^{1/m_{mF}} \quad (2)$$

where:  $k_{mF}$  is apparent adsorption constant ( $\text{Lg}^{-1}\text{min}^{-1}$ );  $C_0$  is initial dye concentration ( $\text{mgL}^{-1}$ );  $t$  is contact time (min);  $m_{mF}$  is Kuo-Lotse constant. The values of  $k_{mF}$  and  $m_{mF}$  were used empirically to evaluate the effect of dye surface loading and ionic strength on the adsorption process. This model can describe diffusion processes controlled by surface; in particular, it can describe kinetics controlled by intra particle diffusion when  $m_{mF}$  tends to 2.<sup>7</sup>

Ritchie (RS) the second order equation has the following form:<sup>8</sup>

$$q_t = q_e \left[ 1 - \left( \frac{1}{1 + k_{RS} \cdot t} \right) \right] \quad (3)$$

where in:  $k_{RS}$  is Ritchie rate constant ( $\text{min}^{-1}$ );  $t$  is contact time (min). This model was suggested by Ritchie to provide an alternative method to the Elovich equation. As Ritchie has a different idea on the pseudo-second-order kinetics the Ritchie model is also applied on experimental data. The Ritchie mode was developed originally to describe the kinetics of gas–solid phase adsorption, but its use was extended to liquid-solid sorption. The basic assumptions of Ritchie second-order model are: one sorbate is sorbed onto two reaction sites, rate of sorption depends solely on the fraction of the sites witch are unoccupied at time  $t$ .<sup>8</sup>

Hyperbolic tangent (HT) mathematical equation is developed on the basis of the hyperbolic tangent function:<sup>9</sup>

$$q_t = q_e \cdot \left[ \tanh \left( \pi \cdot \frac{t}{t_{HT}} \right) \right]^{n_{HT}} \quad (4)$$

wherein:  $t_{HT}$  is required time for the adsorption to reach an equilibrium state (min);  $n_{HT}$  is heterogeneity of the adsorbent surface;  $t$  is contact time (min). This model is simple and can be used

easily for modeling of adsorption kinetics data in industrial scales to give the equilibrium time of adsorption. This predicted equilibrium time is much useful for controlling the industrial wastewater treatment process, which could benefit the industrial design and production cost. It is a perfect example of how basic science of model and engineering go hand in hand.<sup>10</sup>

The calculation and fitting isothermal equations to the kinetic data were checked on the basis of an statistical parameter, coefficient of determination ( $R^2$ ). This non-linear regression was appropriately realized by using computer software OriginPro 2016.

## RESULTS AND DISCUSSION

### 1. Surface morphology

The micrograph of Fig. 2 gives the appearance of particles with a magnification of  $\times 2000$ . The obtained adsorbent is a material with heterogeneous porous particles. Different shapes and forms of particles can be observed with the present cracks, cavities and channels which represent the basis of material micro-porosity. Porosity is characteristic for such adsorbents and it is enabled by the presence of particles of very irregular shapes, a high degree of amorphisation and a number of gaps in the structure.

In addition to the present differences in shape and size, pores also differ in their availability for adsorbate molecules, which is related to the fact that they can be closed, open at only one end or at both ends, isolated or interconnected.<sup>11</sup> The results of the EDS analysis revealed the quantitative composition of activated charcoal, *i.e.* the percentage of one element in relation to the sum of all detected elements. In the prepared adsorbent sample, the following ones were detected: C (8.36%), O (12.35%), Na (3.83%), Cl (50.74%), Ca (24.73%). According to the EDS data, as expected, Ca and Cl elements were dominant deriving from calcium chloride that activated the waste textile, whereas other elements originated from cellulosic material and oxidation by ambient air.

A study by Yokoyama *et al.*<sup>12</sup> describes a process for the purification of nitric nitrogen using charcoal activated with  $\text{CaCl}_2$ . It has been found that charcoal prepared in this way can contribute to the purification of water contaminated with nitric nitrogen. According to the EDX spectrum, the presence of elements Cl and

Ca was found, respectively, which confirmed that the particles of  $\text{CaCl}_2$  were present in the insoluble form,

due to binding with wooden component in the process of pyrolysis.

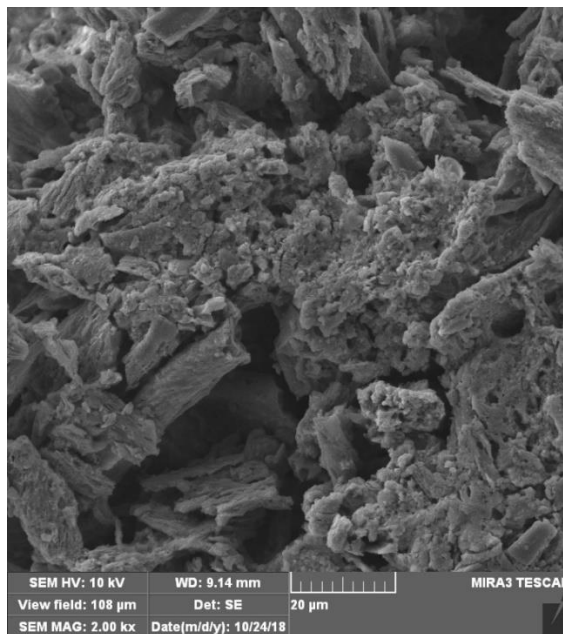


Fig. 2 – SEM micrograph of applied waste textile based adsorbent ( $\times 2,000$ ).

## 2. Effect of contact time and initial dye concentration

The structure, number and type of active sites as well as physical properties of the adsorbent have influence on the absorption capacity of the dye. The specifics of each dye sorption process has not been completely clarified, ionic exchange, complexing, coordination complexing, electrostatic interactions, hydrogen bonds, hydrophobic interactions, and physical sorption can be considered as fundamental interactions. It is possible that more than one factor may contribute to the sorption mechanism depending on various factors.<sup>6</sup>

The effect of the initial adsorbate concentration on the amount of adsorbed dye on the adsorbent was checked in the concentration range  $50\text{--}400\text{ mgL}^{-1}$  (Fig. 3). The initial dye concentration, especially higher values, provided an important driving force for overcoming the mass transfer resistance between the aqueous and solid phases. With increasing the contact time of dye, a steady increase in the slope of the curves for all dye concentrations starting from 50 to  $400\text{ mgL}^{-1}$  was noticeable. The curves for 40 and 60 min of contact almost coincided since there were small but still present differences in value for  $q_t$  in all cases.

It can be seen that the value of  $q_t$  increases continuously during adsorption, much faster at higher initial dye concentrations. At the lowest

concentrations, the change  $q_t$  to  $t$  is not particularly distinct, the curves extend almost horizontally (parallel) to the abscissa.

The initial rapid adsorption phase may be due to the increased number of vacancies available initially, resulting in an increased concentration gradient between adsorbate in solution and adsorbate on the adsorbent surface. This increase in the concentration gradient tended to increase the dye sorption rate in the initial stages. As time passes, the concentration gradient decreased due to amassing of dye molecules in the free areas, which led to a reduction of the sorption rate in later stages.

As time passes, the concentration gradient decreased due to amassing of dye molecules in the free areas, which led to a reduction of the sorption rate in later stages. Adsorption curves were single, smooth and continuous; they could lead to saturation and indicate the possible coverage by mono-layer from the dye molecules on the surface of the adsorbent caused by the strong attractive forces. Usually, rapid diffusion on outer surface was accompanied by the rapid diffusion through the pores in the matrix within the particles in order to achieve rapid equilibrium.<sup>4</sup>

Similar behavior is present at the other researchers, e.g. discussing the effect of the contact time and initial dye concentration on the adsorption of metal-complex dye by sorbent of saw dust from pine tree showed that the amount of the adsorbed

dye had increased with increasing contact time and reached equilibrium after 120 min for initial dye concentrations of 500, 1,000 and 2,000 mgL<sup>-1</sup>. The equilibrium time was independent of the initial dye concentration. But in the first 30 min, the initial adsorption rate was greater for a higher initial dye concentration. The diffusion of the dye molecules

through the solution onto the surface of the adsorbent was directly influenced by the dye concentrations, since the mixing rate was constant. Increase of the dye concentration accelerated the diffusion of dye from the solution onto the adsorbent due to the increased driving force of the gradient concentration.<sup>13</sup>

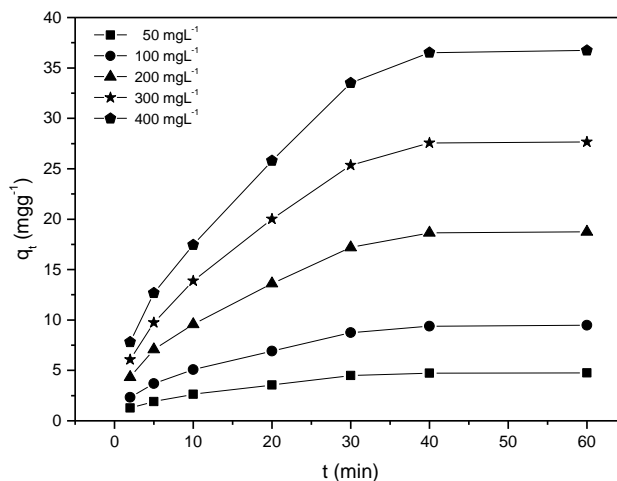
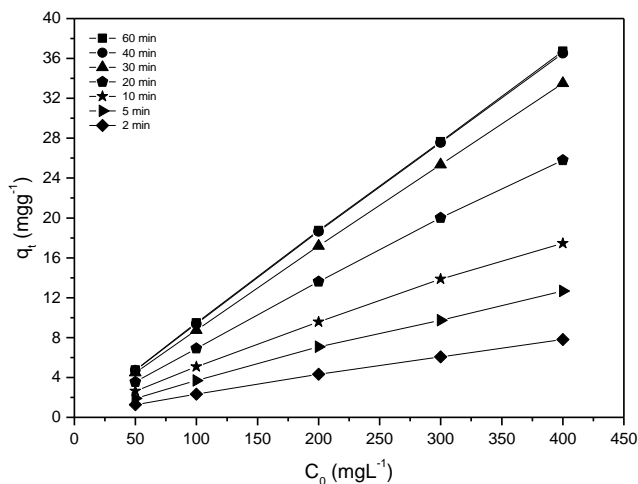


Fig. 3 – Influence of initial concentration and treatment time on adsorption capacity.

### 3. Kinetic models of adsorption

Information on the absorption kinetics of adsorbate is significant for determining the optimal operating conditions for a full batch process. The kinetics of sorption can be represented by the graph of sorption regarding time, and this dependence (diagram) is known as the kinetic isotherm. Kinetics depends on material factors, such as adsorbent and adsorbate as well as experimental factors, such as temperature or pH.<sup>4</sup>

Figure 4 shows the kinetics of dye sorption on adsorbent with experimental points and kinetic models, MF, RS, and HT, for the minimal and maximal concentration of metal-complex dye. It seems that, according to the curves of the models that fit the experimental points, the RS and HT equations best describe the kinetics of dye adsorption, i.e. the curves of these equations follow the paths closest to the experimental points, for both concentrations. Also, according to the appearance of curves in the diagrams in Fig. 4, MF model is noticeably inferior to other models and has a smaller contribution to the clarification of sorption kinetics.

In both diagrams of Fig. 4, it is noticed that at the beginning of the adsorption, all models fit the experimental data better, and that after ten minutes, the curves of all models move away from the experimental points. At the beginning of adsorption,

when there is no equilibrium, metal-complex dye molecules diffuse rapidly and bind to the surface of the adsorbent particles, migrate on the surface, and in the last stage diffuse into the pore of the adsorbent particles, binding to active sites by physical or chemical bonds.

This is in line with the Modified Freundlich model that describes an adsorption reaction that is initially rapid, followed by a slower adsorption rate, which results in a longer reaction time. The initial reaction rate has high adsorption energy associated with low surface saturation. The slow reaction rate is assumed to be the result of increased negative charge on the adsorbent surface, increased interaction between adsorbate molecules, and decreased adsorption energy with increased surface saturation. In this particular case, it can be said that adsorption implies a multi-stage process where the rate of adsorption is partly limited by diffusion within the particles, given the weakest but also relatively good coverage by the Modified Freundlich model.

On the other hand, the relatively short contact time necessary for achieving equilibrium conditions (60 min), apart from the evident processing advantages, is considered as an initial indication that adsorption of metal-complex dye on waste textile based adsorbent is a chemical-reaction controlled, rather than a diffusion controlled process.<sup>6</sup>

Since the applied dye has two dye molecules bound to a metal ion (cobalt), there is a high probability that both dye ions will bind to at least two positions in the adsorbent, provided that the metal ion will be able to create coordination bonds with the active sites around in the pores of particles, which is a confirmed Ritchie kinetic model that covers experimental points very well, though not the best.

According to the appearance of the curves in the diagrams of Fig. 4, the Hyperbolic tangent model is

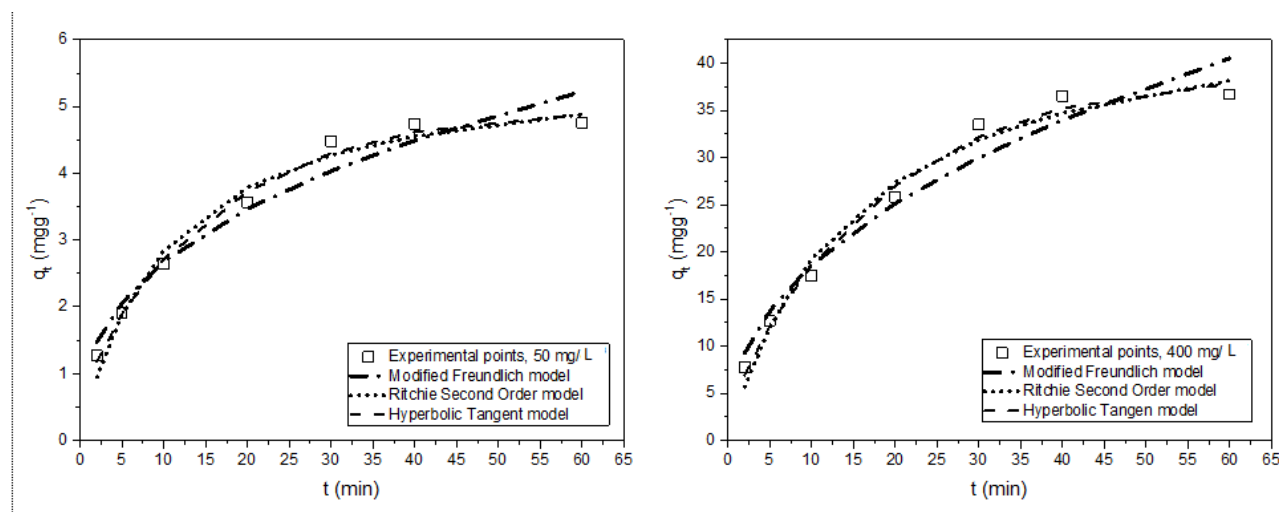


Fig. 4 – Kinetic modelling of metal-complex dye adsorption on the waste textile based adsorbent.

Table 1 shows the numerous values of the kinetic parameters of the used models for the dye adsorption with concentrations of 50 and 400 mgL<sup>-1</sup>. The results have shown the bond between the kinetic data for both concentrations with high correlation coefficients and small values of parameter errors thus confirming that they all applied models are generally suitable, with a note that RS and HT distinguish as the most beneficial ones.

Moving further on, based on both the maximum values of the determination coefficient ( $R^2 > 0.99$ ), the superior and perfect adaptation of experimental results of the model HT for both dye concentrations has been confirmed.

In addition to the statistical parameters for assessing the validity of the model, another comparative criterion can be used because of to the suitability of kinetic models because of the apparent confusion and ambiguity of the terms “similar”, “not trailing” or “almost equivalent”. This criterion involves comparing the calculated  $q_{e,cal}$  values (parameter from the model equation) with the experimental  $q_{e,exp}$  ones. Thus, for example, at a dye

adsorption concentration of 50 mgL<sup>-1</sup>, the applied kinetic models had the following values of adsorption capacity: RS ( $q_{e,cal} = 5.701$  mgg<sup>-1</sup>), HT ( $q_{e,cal} = 4.980$  mgg<sup>-1</sup>), the value obtained experimentally ( $q_{e,exp} = 4.756$  mgg<sup>-1</sup>), or for dye adsorption of concentration 400 mgL<sup>-1</sup>, the following values were found: RS ( $q_{e,cal} = 47.524$  mgg<sup>-1</sup>), HT ( $q_{e,cal} = 38.916$  mgg<sup>-1</sup>) and the value obtained experimentally ( $q_{e,exp} = 36.726$  mgg<sup>-1</sup>).

These values were close to the experimental adsorbed quantities (the HT model was particularly emphasized) and corresponded to the results of the statistical validity parameters of the model.

Due to the presence of small coverage of experimental points by MF model, it was suggested that the energy of adsorption was not reduced exponentially by the surface saturation, as well as a slower initial reaction of the adsorption.

According to the results for the RS the second order, the sorption rate did not seem to depend much on high concentration, but on the absorption of the dye molecules by adsorbent, as well as that each dye molecule was adsorbed at multiple sites on the surface.

The HT kinetic model, developed on the basis of hyperbolic tangent function, proved to be excellent for the used cellulose-based adsorbent-metal-complex dye system. The presented Hyperbolic tangent not only fitted well with the experimental data but it also gave the adsorption equilibrium time, so that the exact equilibrium time of the adsorption process could be predicted. In this case, the equilibrium time was 94 to 99 min, for the minimal and maximal initial dye concentration.

Similar results were obtained by the authors<sup>14</sup>

who proposed a new model of hyperbolic tangent for the analysis of sorption kinetics at the interface of Congo red dye and lignocellulosic biomass of jute fibers. The most important advantage of the proposed model is its ability to predict adsorption equilibrium time, which is very important for optimizing the design cost of the adsorption system. Based on the values of the correlation coefficient (0.999), the high performances of the new model of hyperbolic tangent have been confirmed for the kinetics modeling of the mentioned system.

Table 1

Parameters of kinetic reaction models with statistical error parameters

Kinetic model	Parameters	Values	
		50 mgL <sup>-1</sup>	400 mgL <sup>-1</sup>
Modified Freundlich	$k_{mF}$ (Lg <sup>-1</sup> min <sup>-1</sup> )	0.023	0.137
	$m_{mF}$	2.683	2.305
	$R^2$	0.949	0.949
Ritchie second order	$q_{e(RS)}$ (mgg <sup>-1</sup> )	5.701	47.524
	$k_{RS}$ (min <sup>-1</sup> )	0.099	0.068
	$R^2$	0.978	0.979
Hyperbolic tangent	$q_{e(HT)}$ (mgg <sup>-1</sup> )	4.980	38.916
	$t_{HT}$ (min)	94.901	99.130
	$n_{HT}$	0.531	0.626
	$R^2$	0.991	0.990

## CONCLUSION

In addition to calcium chloride, as activating agent, thermochemical conversion of waste cotton parts from the clothing plant to the powdered adsorbent was done. The resulting material was irregular in shape with heterogeneous porous particles, full of holes, cavities and channels. As expected, in the basic composition of the produced material, Ca and Cl elements dominated which were mainly derived from calcium chloride; there were also carbon, oxygen and sodium as well. The longer the contact time of metal-complex dye, and adsorbent of natural origin, the higher the amount of adsorbed color. This similar phenomenon was observed at higher initial concentrations of dye as well. Hyperbolic tangent kinetic model was the most efficient kinetic reaction model for nonlinear simulating of adsorption metal-complex dye onto the adsorbent from waste textiles. It is interesting to pay attention to the equilibrium time parameter in the presented model. The hyperbolic tangent model can predicate the equilibrium time very well, which is

very useful from a practical point of view. This model is simple and can be used easily for modeling of adsorption kinetics data in industrial scales to give the equilibrium time of adsorption. This predicted equilibrium time is much useful for controlling the industrial wastewater treatment process, which could benefit the industrial design and production cost.

By leveraging our ever-growing knowledge of wastewater adsorption and its kinetics model, it is possible to engineer a progressive Hyperbolic tangent kinetics models to give more industrial-guiding parameters under more flexible equilibrium definition.

The obtained kinetic information has a significant practical value for technological applications, since kinetic modeling successfully replaces time and material consuming experiments, necessary for process equipment design. It should be emphasized that the material obtained from the waste clothing cotton textile can be an efficient adsorbent for the removal of metal-complex dye from aqueous solution with a justified tendency of application in industrial conditions as well.

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