Adsorption Equilibrium and Kinetics Modeling for Tartrazine(E102) – Fe(II) Based Adsorbent System

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This paper presents the isotherm and kinetics modeling of yellow food dye, tartrazine (E102) adsorption from aqueous solution by in situ adsorbent support based on Fe(II)aq ions. The obtained experimental data were analyzed using Langmuir, Freundlich, Dubinin-Radushkevich and Temkin isotherm models and the characteristic parameters for each adsorption isotherm were determined. Also, two common kinetic models, pseudo-first-order and pseudo-second-order were studied. Based on the parameters of isotherm models and correlation coefficients values (R^2), we could estimate that tartrazine sorption equilibrium was accurately described by Langmuir model. The kinetic modeling of the experimental data, suggested that tartrazine adsorption process followed the pseudo second-order kinetic model.

Keywords: tartrazine, aqueous systems, isotherm models, kinetics

In the recent years water pollution with dyes has become an important environmental threat mainly because of the numerous industrial effluents.

The presence of dyes in natural waters prevents sunlight diffusion in water, causing therefore the decrease of the photosynthesis process of the aquatic plants and also the inhibition of the action of bacteria that are meant to degrade organic substances [1]. A large number of techniques used to remove different types of dyes from wastewater have been developed [2,3]. The most common physico-chemical treatment methods are adsorption [4,5], electrochemical coagulation [6] and photocatalytic decolourization [7].

Adsorption is one of the methods that are gaining more attention due to its simplicity and low cost for which the kinetic and equilibrium measurements can be made without any highly sophisticated instruments [8-9]. The investigated yellow azo dye, tartrazine (also known as E102 or FD&C Yellow 5) is used to color foods, cosmetics, and other products. It can be found in certain brands of: fruit cordial, colored fizzy drinks, instant puddings, cake mixes, soups, sauces, ice cream, sweets, chewing gum, marzipan, jelly, marmalade, mustard, yoghurt. Because of its hazardous health effects, foods and drinks containing tartrazine must be avoided and its emission in industrial effluents should be controlled. It was reported that tartrazine presence could lead to hyperactivity [10] and other behavioral problems [11], asthma [12–16], migraines, thyroid cancer [17], etc.

The aim of this study was to investigate the adsorption isotherms and kinetics modeling, for tartrazine removal from synthetic aqueous solutions by using *in situ* adsorbent support based on Fe(II)aq ions. The adsorption capacity, equilibrium and kinetic data were determined/ investigated in order to describe tartrazine (E102) adsorption process.

Experimental part
Materials and methods

Trisodium-5-hydroxy-1-(4-sulfonatophenyl)-4-(4-sulfonatophenylazo)-*H*-pyrazole-3-carboxylate (tartrazine), an azo dye (CI Number = 19140, EEC Number = E-102) with molecular formula $C_{16}H_9N_4Na_3O_9S_2$ and molecular weight 534.4 it was purchased from STERA CHEMICALS Bucharest. Fe(II)aq ions solution (0.2 M) was used to obtain the *in situ* adsorbent support and was prepared by dissolving $FeSO_4 \cdot 7H_2O$ (Merck) into distilled water.

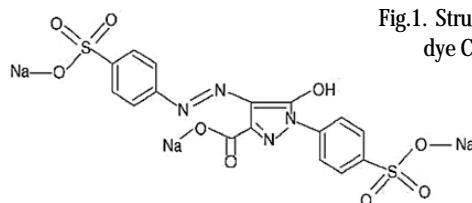All chemicals used in this study were of analytical reagent grade.

Fig.1. Structure of tartrazine dye $C_{16}H_9N_4Na_3O_9S_2$

Experimental procedure description

Adsorbent support. The *in situ* formation of the insoluble hydro species in the initial Fe(II), solution assume to take notice its oxidability. The presence of Fe(II) and Fe(III) species in solution under the established operating conditions depends on different factors, such as: *p*H, stirring, time, precipitation term, final composition of the reagent ($FeSO_4 \cdot 7H_2O$). Starting from Fe(II) solution, after 5 minutes, the predominant species in solution are :Fe(III) as $Fe(OH)_3$ and FeO(OH), also Fe(II) as $Fe(OH)_2$.

The sorption experiments were carried out under batch conditions by using a HEILDORPH VIBRAMAX 100 shaker. The *p*H of the solutions was adjusted by adding H_2SO_4 0.1 M or NaOH 0.2 M solutions and it was monitored during the whole period of the experiments with a ORION 290 A pH-meter. Tartrazine final concentrations in solution were analyzed by spectrophotometry (UNICAM UV2-100) at the wavelength λ=426nm.

The equilibrium adsorption studies were performed in the concentration range 5-500 mg / L, at room temperature (20 °C), *p*H = 8, for a molar ratio [dye]:[Fe] =1:20 /200 mL sample, under continuous stirring (200 rpm) for 5 min.

In order to investigate tartrazine adsorption kinetics onto the Fe(II) based adsorbent support, the contact time was varied after the samples brought to the desired *p*H, from 1 to 20 min in the following operating conditions: dye concentration: 20, 50, 100 mg/L, agitation rate: 200 rpm; temperature: 20°C; *p*H: 8.0; molar ratio [dye]:[Fe] =1:20. After each time interval, the samples were removed from the stirrer, the liquid phase was collected from the system using a plastic syringe.

Equilibrium sorption experiments

Several models have been reported in the literature to describe the experimental data of adsorption isotherms. [18-19] In this work, Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (fig. 2-5) models were used to describe the relationship between the amount of dye adsorbed and its equilibrium concentration.

The equilibrium adsorption capacity was determined by means of equation (1) [18]:

$$Q_e = \frac{(C_0 - C_e) \times V}{m} \qquad (1)$$

where:

Q_e equilibrium adsorption capacity (mg/g);
C_0 initial dye concentration (mg/L);
C_e final dye concentrations (mg/L);
V volume of solution (L);
m weight of adsorbent (g).

The linear forms of the isotherm models (Langmuir, Freundlich, Temkin and Dubinin-Radushkevich) used to correlate the adsorption data and to determine the isotherm parameters are given by the expressions presented in table 1.

Results and discussions

Adsorption isotherms

Tartrazine (E102) adsorption equilibrium was analyzed using Langmuir, Freundlich, Dubinin -Radushkevich and Temkin isotherm models (fig. 2 - 5).

Langmuir equation correlates with the amount of adsorbent, adsorbed at equilibrium in aqueous phase, when the entire area of the adsorbent is fully covered by one-molecular layer of adsorbate (monolayer adsorption). The representation of the 1/Ce vs 1/Qe plot is shown in figure 2.

Freundlich equation is used to determine the applicability of the surface energy for a heterogeneous adsorption process (multilayer adsorption). The linearized Freundlich isotherm model obtained for tartrazine adsorption onto *in situ* obtained adsorbent support based on Fe(II) is illustrated in figure 3.
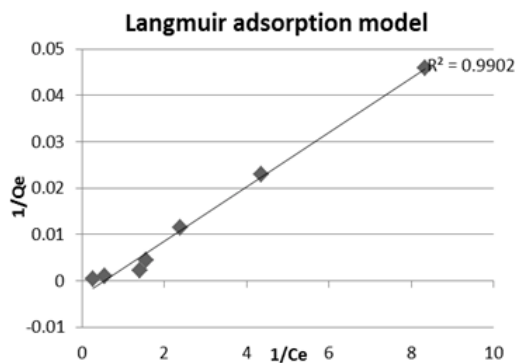

Fig.2. Langmuir isotherm model obtained for tartrazine (E102) adsorption (stirring rate: 200 rpm; temperature: 20°C; *p*H: 8,0; molar ratio [dye]:[Fe] =1:20 ; volume sample:200mL; time: 20 min).

Fig.3. Freundlich isotherm model obtained for tartrazine(E102) adsorption (stirring rate: 200 rpm; temperature: 20°C; *p*H: 8,0; molar ratio [dye]:[Fe] =1:20; volume sample:200mL; time: 20 min).
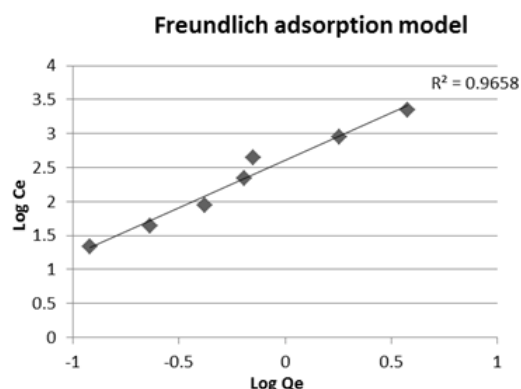
Figures 4 and 5 show the overlapping of the experimental data obtained for tartrazine adsorption to Temkin and Dubinin - Radushkevich isotherm models.

Table 2 lists the Langmuir, Freundlich, D-R and Temkin isotherm parameters, obtained for tartrazine adsorption onto an *in situ* adsorbent support based on Fe(II).

Adsorption model	Model equation	Parameters (meaning):
Langmuir	$\dfrac{1}{Q_e} = \dfrac{1}{Q_m} + \dfrac{1}{K_L Q_m} \times \dfrac{1}{C_e}$ $R_L = \dfrac{1}{1 + K_L C_0}$	Q_m - maximum monolayer adsorption capacity (mg/g); Q_e -amount of tartrazine adsorbed (mg/g); C_e - equilibrium concentration of the adsorbate (mg/g); K_L - Langmuir isotherm constant; R_L -separation factor; Langmuir isotherm: irreversible (R_L =0), favorable (0 $< R_L <$ 1), linear (R_L= 1), or unfavorable ($R_L >$ 1).
Freundlich	$\log Q_e = \log K_F + \dfrac{1}{n} \log C_e$	C_e - equilibrium concentration (mg/L); Q_e - amount of dye adsorbed at equilibrium time (mg/g); k and n - Freundlich constants; K_F - relative adsorption capacity of adsorbent;
Temkin	$Q_e = B_T \ln A_T + B_T \ln C_e$ $B_T = RT/b_T$	B_T and A_T: Temkin isotherm constant; T-temperature; R- universal gas constant(J/mol K)
Dubinin-Radushkevich	$\ln Q_e = \ln Q_m - K\varepsilon^2$ $E = \dfrac{1}{\sqrt{-2K}}$	K - constant related to mean adsorption energy (mol² kJ²) ; ε - Polanyi potential. E- adsorption energy(kJ/mol);

Table 1
LINEAR FORMS OF LANGMUIR, FREUNDLICH, DUBININ-RADUSHKEVICH AND TEMKIN ISOTHERM MODELS
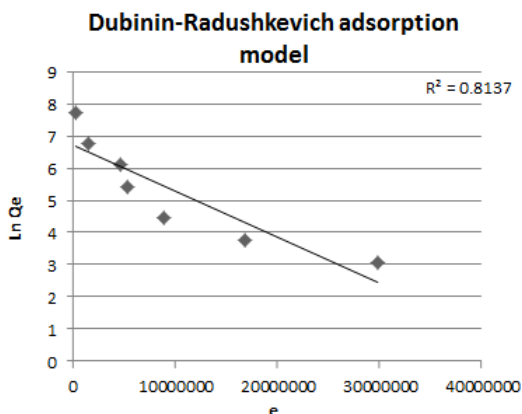
Fig.4. Dubbin-Radushkevich isotherm model obtained for tartrazine (E102) adsorption (stirring rate: 200 rpm; temperature: 20°C; *p*H: 8,0; molar ratio [dye]:[Fe] =1:20 ;volume sample:200mL; time: 20 min)
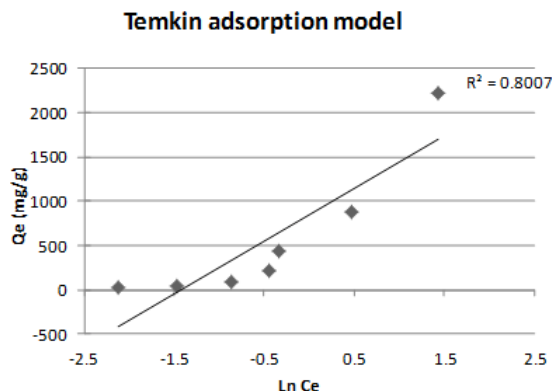

Fig.5. Temkin isotherm model obtained for tartrazine (E102) adsorption (stirring rate: 200 rpm; temperature: 20°C; *p*H: 8,0; molar ratio [dye]:[Fe] =1:20 ; volume sample:200mL; time: 20 min)

Table 2

LANGMUIR, FREUNDLICH, DUBININ-RADUSHKEVICH AND TEMKIN ISOTHERM PARAMETERS OBTAINED FOR TARTRAZINE ADSORPTION ONTO *IN SITU* ADSORBENT SUPPORT BASED ON Fe(II) IONS

Adsorption isotherm model	Parameters
Langmuir	Qm 434.78 mg/g K_L 0.3906 L/mg R_L 0.0256 R^2 0.9902
Freundlich	K_F 0.7752 mg/g 1/n 1.1128 n 0.8986 R^2 0.9658
Dubinin -Radushkevich	K -3 10^{-6} Kj/mol Qm 3.6996 mg/g E 333.33Kj/mol R^2 0.8137
Temkin	bt 19.87 B_T 122.56 KJ/mol^{-1} A_T 3.95 R^2 0.8007

Based on the correlation coefficients (R^2), it was established that the obtained results were correlated to the adsorption models in the following order: Langmuir> Freundlich> D-R> Temkin. The value of the maximum monolayer adsorption capacity, Qm (434.78 mg / g) determined from the intercept of the linearized Langmuir model (*1/Qe* vs. *1/Ce* plot)) was close to the maximum value of the adsorption capacity determined experimentally (443.25 mg / g), suggesting a good adsorption of tartrazine. The value of the separation factor, R_L (0. 0256) was situated was between 0-1, indicating therefore that Langmuir isotherm was favorable. K_F and 1/ *n* were calculated from the intercept and slope of the Freundlich plot (fig.3) and were found to be 0.7752 and 1.1128. The value of *n* is related to the distribution of bonded ions on the adsorbent surface. The value of the adsorption energy E (333.33 kJ / mol) was > 16 kJ/mol, which indicates that the adsorption mechanism of tartrazine using the *in situ* adsorbent support based on Fe(II)aq ions might involve chemical interactions [20].

Also, the positive value of energy adsorption, E, suggests that the adsorption process was endothermic [20,22]. The smaller values of the correlation coefficients (0.8137 and 0.8007) obtained for Dubinin -Radushkevich and Temkin models suggest that the aforementioned models are not suitable for tartrazine adsorption. The obtained results are in agreement with the data available in the literature [20,21,23] and suggest that tartrazine adsorption fitted better with Langmuir isotherm models.

Kinetics studies

The prediction of the kinetics is necessary for designing sorption systems. Chemical kinetics explains the rate of chemical reactions. The nature of sorption process depends on physical or chemical characteristics of the adsorbent and also on the system conditions. Diverse kinetic models based on the concentration of solute and on the dose of sorbent have been proposed by several researchers [24]. The data obtained for tartrazine adsorption using an *in situ* adsorbent support based on Fe(II)aq ions was correlated by two common kinetic models, pseudo-first-order kinetic and pseudo-second-order kinetic models. The model that best fitted the experimental data was selected based on the correlation coefficient (R^2), which is a measure for correlating the predicted values of a forecasting model with

| Kinetic models	Model equation*)	Parameters (meaning):	
Lagergren (pseudo-first order)	$$\frac{d_{qt}}{d_t} = k_1(q_e - q_t)$$ $$\log(Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303}t$$	qe and qt -amounts (mg/g) of dye adsorbed at equilibrium; Qe and Qt - adsorption capacities (mg/g) at equilibrium, respectively at time t; k_1 -rate constant of the first-order adsorption (min^{-1}) t-time(min)	**Table 3** LINEAR FORMS OF THE PSEUDO-FIRST-ORDER KINETIC AND PSEUDO-SECOND-ORDER KINETIC MODELS
Ho(pseudo second-order)	$$\frac{1}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e}t$$	Qe - adsorption capacity (mg /g) at equilibrium; K2 -rate constant of the second-order-order adsorption (min^{-1}); t-time(min)	
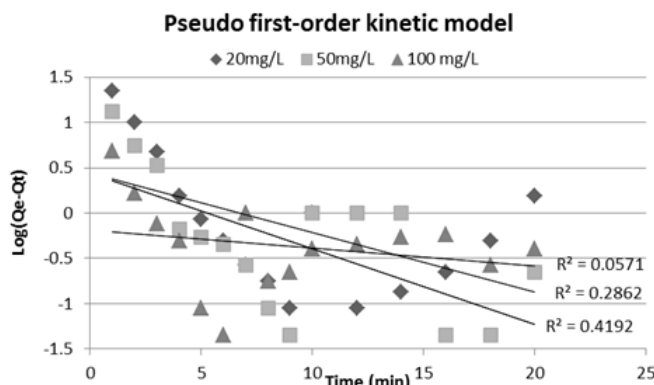
Fig. 6. The fitting of the pseudo first-order kinetic model obtained for tartrazine adsorption onto an *in situ* adsorbent support based on Fe(II)aq ions (dye concentration :100mg/L, agitation rate: 200 rpm; temperature: 20°C; *p*H: 8.0; molar ratio [dye]:[Fe] =1:20)

Fig. 7. The fitting pseudo second-order kinetic model obtained for tartrazine adsorption onto an , *in situ* adsorbent support based on Fe(II)aq ions (dye concentration: 100mg/L, agitation rate: 200 rpm; temperature: 20°C; *p*H: 8.0; molar ratio [dye]:[Fe] =1:20)
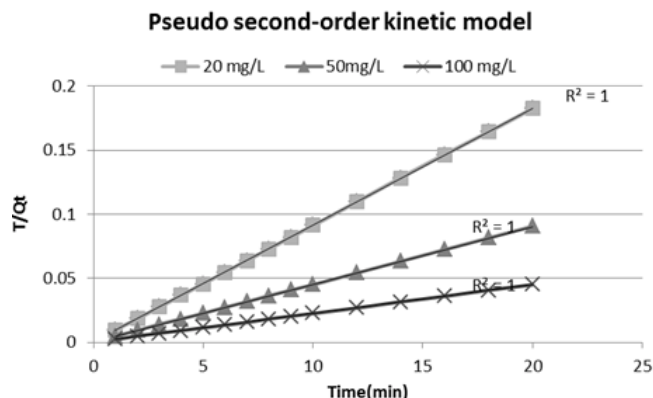
| Initial concdentration (mg/L) | Q_e (mg/g) | Pseudo-second order kinetic model | | |
		$k_{2)}$ (g/mg min)	$Q_{e\,cal}$ (mg/g)*	R^2
100	443.25	4.53 10^{-5}	434.78	1
50	220.89	6.02 10^{-6}	222.22	1
20	109.82	12.29 10^{-6}	109.89	1

*mg of dye/ g of Fe(II) adsorbent support

Table 4
PSEUDO-SECOND ORDER KINETIC PARAMETERS OBTAINED FOR TARTRAZINE ADSORPTION USING AN *IN SITU* ADSORBENT SUPPORT BASED ON Fe(II) IONS AT DIFFERENT INITIAL CONCENTRATIONS

experimental data obtained from adsorption at optimum parameters [24]. The linear form for the two kinetic models above mentioned is presented in the table 3.

In order to confirm the applicability of the model, the plot of log(*q*e-*q*t) against *t* should be a straight line. In a real first-order process, experimental log(*q*e) should be equal to the intercept of the straight line [24, 25].

The correlation coefficient, R^2 obtained from the plot *log(Qe - Qt)* vs. *t* of the pseudo first-order model was very low (fig. 7), suggesting that tartrazine adsorption did not followed pseudo first-order kinetics. Therefore, the constants for the pseudo first-order model were not considered.

Figure 7 illustrates the correlation of the experimental data according to the pseudo-second kinetic model obtained for tartrazine adsorption onto *in situ* adsorbent support based on Fe(II) ions (Ci=20–100mg/L, 20°C). The calculated kinetic constants from the linear form of the pseudo-second order model at different food dye concentrations are shown in table 4.

The correlation coefficients, R^2 derived from the pseudo second-order kinetic model (fig. 7) were higher than the ones obtained from the pseudo first-order kinetic model (fig. 6).

Also, the calculated equilibrium adsorption capacity, *Qe,cal,* determined from the pseudo second-order model fitted well with the experimental data (table 4). These results suggested that tartrazine adsorption onto the Fe(II)aq ions based adsorbent follows the pseudo second-order kinetic model and the adsorption mechanism might also involve chemical interactions [25-26].

Conclusions

The present study investigated the modeling and kinetics of tartrazine removal from aqueous solutions by using *in situ* adsorbent support based on Fe(II)aq ions.

The equilibrium data was analyzed using Langmuir, Freundlich, Dubinin–Radushkevich and Temkin adsorption isotherm models and respectively, the pseudo first-order and the pseudo second-order kinetic models. From the graphical representation of Langmuir isotherm model it

was observed that the 1/Ce vs 1/Qe plot exhibits a linear dependence with a correlation coefficient of 0.9902, higher than the one obtained for Freundlich isotherm (R^2 = 0.9658), suggesting that the experimental results are fitting better with Langmuir isotherm equation.

The maximum monolayer adsorption capacity, Q_m (434.78 mg / g) determined from the intercept of the liniarized Langmuir model (*1/Qe* vs. *1/Ce* plot) was close to the maximum adsorption capacity determined experimentally (443.25 mg / g), suggesting a good adsorption of tartrazine. Based on the correlation coefficients it was found that tartrazine adsorption onto the Fe(II)aq ions based adsorbent followed the pseudo-second order kinetic model. This result was also supported by the value of the calculated equilibrium adsorption capacity, *Qe,cal,* determined from the pseudo second-order model that fitted well with the experimental data.

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