KINETIC STUDY OF XANTHENE FOOD DYE SORPTION ON AGRICULTURAL BYPRODUCT

Laura Carmen Apostol[1,2], Maria Gavrilescu[2,3]
[1] Faculty of Food Engineering, "Stefan cel Mare" University of Suceava, Romania
[2]Department of Environmental Engineering and Management, Faculty of Chemical Engineering and Environmental Protection, "Gheorghe Asachi" Technical University of Iasi, Romania
*E-mail: laura.apostol@fia.usv.ro

Abstract
Erythrosine B is an important representative of the xanthene dye class, widely used in food, pharmaceutical and cosmetic industry. The local agriculture byproduct namely beans hulls was used to identify the interactions between the xanthene foods dye Erythrosine B with its components. The process was studied at natural solution pH (5.6) and a sorbent dosage of 20 g/L representing the favorable adsorption conditions established in the previous investigations.
The amount of dye adsorbed was found to vary with initial dye concentration and contact time. The data obtained from Erythrosine B sorption onto beans hulls was interpreted using four types of kinetics models: Lagergren pseudo-first-order, Ho's pseudo-second-order, Elovich and Weber and Morris intraparticle diffusion model.
According to the values obtained for correlation coefficient (R^2>0.99), the adsorption data fitted the pseudo-second-order model. The two and three linear section with different slope (for concentration higher than 10 mg/L) was assigned to two/three interparticle diffusion steps occurring during the adsorption process of the dye. The rate of Erythrosine B uptake onto beans hulls was found to be controlled by intraparticle diffusion considering that at last one stage has negative intercept values for three (10 mg/L, 30 mg/L and 50 mg/L) of the five studied concentrations.

Keywords: Beans hulls, Erythrosine B, kinetic models, sorption mechanism

Received: 28.11.2017 Reviewed: 24.01.2018 Accepted: 06.03.2018

1. INTRODUCTION

Food dyes are one of the most widely used and dangerous additives that have been around for a long time. They are synthesized originally from coal tar and now petroleum and have long been controversial because of safety concerns. Artificial food dye consumption has increased and children are the biggest consumers. Erythrosine B (CI 45,430) is an important representative of the xanthene dye class, widely used in food, pharmaceutical and cosmetic industry (Apostol and Gavrilescu, 2013). Despite its acceptance to be used, the dye effects have been represented by behavior disorder in children (Silbergeld *et al.*, 1982) and, due to the high iodine content, interference with thyroid function and, due to the high iodine content, interference with thyroid function (Bora *et al.*, 1969; Drumond *et al.*, 2012; Jennings *et al.*, 1990). The wastewater containing dyes is currently of major concern at global level whereas the volume of m^3/day (Ministry of the Environment, 2007).
The fate of Erythrosine B in the environment is less investigated. There is a lake of data regarding the amount of Erythrosine B in real aqueous effluents. Several studies regarding the removal this dye from artificial aqueous solution has been reported in the last period (Apostol and Gavrilescu, 2013). The studies are based on degradation methods: the photochemical degradation of Erythrosine B can lead to the formation of toxic byproducts (Apostol *et al.*, 2015), while the biodegradation process indicated that the decolorization of the dye may be due to enzymatic and adsorption phenomena, with inhibitory effect at high dye concentrations (Apostol *et al.*, 2012).
In this context the sorption process is often one of the effective methods to removes hazardous dyes from aqueous media. The low-cost, easily to obtained, highly efficient adsorbents has been investigated as a sustainable alternative to

the current expensive methods for dyes removal. Considering these aspects, adsorption can be a good choice for Erythrosine B sequestration by environmental friendly low cost adsorbents.

2. MATERIALS AND METHODS

Sorption kinetics experiments were carried out using 100 mL Erythrosine B solution at an agitation speed of 150 rpm using an isothermal shaker (IKA KS 4000 IC). The rate and mechanism of the reaction were studied at different physical parameters: dye concentration (10 – 100 mg/L) and temperature (20, 30, 40 and 50ºC). All the experiments were carried-out in duplicate and at the natural pH of the solution (pH = 5.6, according to Hanna pH meter provided with a combined glass electrode (Model Hanna HI1053B)). The solutions containing different Erythrosine B were determined spectrophotometrically at maximum absorption wavelength (524 nm). Amount of dye uptake per unit mass of sorbent at time t, (q_t, mg g^{-1}) and at equilibrium (q_e, mg g^{-1}) were calculated using Eqs. (1) and (2).

$$q_t = \frac{C_i - C_t}{m} * V \quad (1)$$

$$q_e = \frac{Ci - Ce}{m} * V \quad (2)$$

where:
C_i isthe initial dye concentration (mg L^{-1});
C_t and Ce, the concentration of dye at time t and at equilibrium (mg L^{-1});
m, the amount of dried sorbent used (g);
V, the volume of the solution (L).

3. RESULTS AND DISCUSSION

In the first part the adsorption of Erythrosine B was studied as a function of contact time to determine the required time for equilibrium reach. For the studied interval the results show that the amount of adsorbed dye increased with the increase of Erythrosine B concentration. The adsorption is initially fast and then becomes progressively slower with increasing contact time.
The process reached equilibrium in 6 h for the five Erythrosine B initial concentrations tested at room temperature: 10 mg/L, 20 mg/L, 30 mg/L, 50 mg/L and 100 mg/L. The initial Erythrosine B concentration influences the dye uptake and increase from 0.46 to 1.88 mg/g (Fig. 1).

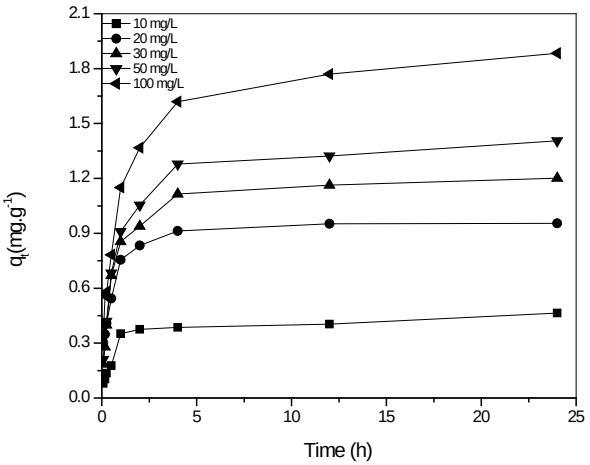

Fig. 1: Effect of contact time for different initial concentration of Erythrosine B

Adsorption processes at liquid - solid interface are frequently affected by the diffusional boundary layer, external mass transfer, and intraparticle diffusion.
In order to find out the potential rate-controlling steps involved in the process, in the second part of the study, four kinetics models were used for data analysis:

- the *Lagergren pseudo-first-order* model (Fig. 2a),
- the *Ho's pseudo-second-order* model (Fig. 2b),
- the *Elovich model* (Fig. 2c),
- the *intraparticle diffusion* using the model developed by Weber and Morris (Fig. 2b).

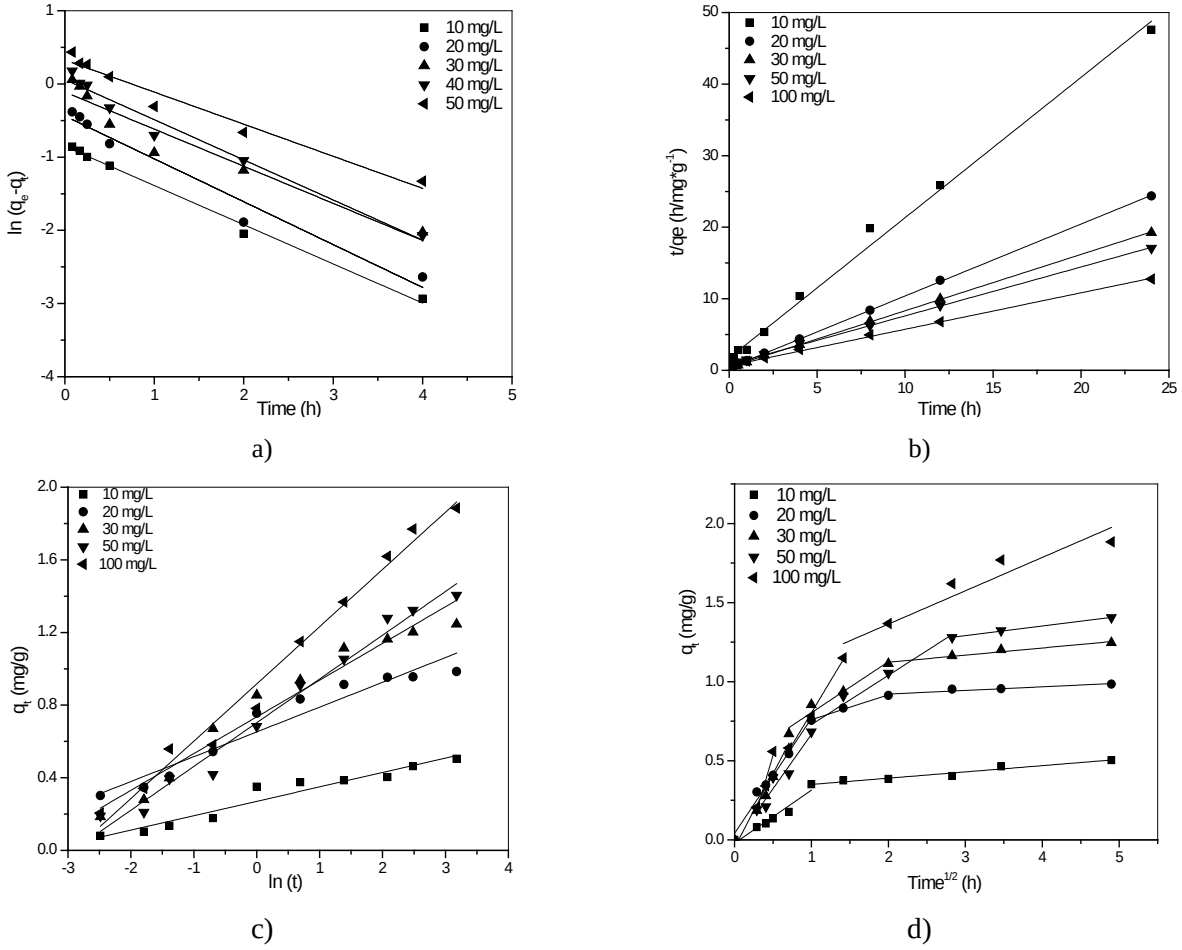

Fig. 2: a) Lagergren; b) Ho pseudo-second-order; c) Elocvich; d) Intraparticle diffusion modelapplied for Erythrosine B sorption on BH for different initial dye concentrations at 25ºC, pH 5.6, and 20 g/L sorbent dose

The Lagergren's pseudo-first-order model and Ho's pseudo-second-order model have been widely used to predict sorption kinetics. The pseudo-first-order equation is generally applicable over the initial stage of the adsorption processes whereas the pseudo-second-order equation predicts the behavior over the whole range of adsorption.

Comparing the results obtained by applying the two models the values of q_e obtained from pseudo-second-order model are much closer to the experimental results than q_e obtained from the Lagergeren's model (Tables 1). Also, the data obtained from the pseudo-second-order model have high values for R^2. This indicates that the adsorption kinetics are well represented by this model. The linear relationships between initial Erythrosine B concentration and k_2 *(g/mg*h)* - the rate constant obtained from *Ho's pseudo-second-order* model suggest that several mechanisms such as ion exchange and physical adsorption are involved in the adsorption process (Fig. 3) (Apostol et al., 2013).

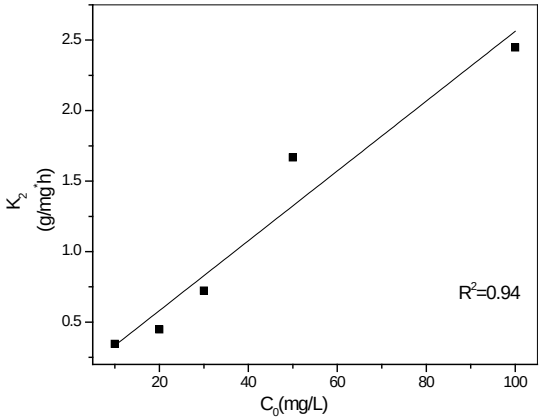

Fig. 3: Relationships between initial Erythrosine B concentration and the absorbtion rate (k_2 *(g/mg*h)* (t=25ºC, pH 5.6, and 20 g/L BH concentration)

Another simplified model, Elovich model, was tested because only one or two equation cannot define the mechanism for the sorption process of Erythrosine B on BH. The kinetic constants of Elovich equation are presented in Table 1.

Table 1: *Pseudo-first-order*, *pseudo-second-order*, *Elocvich and Intraparticle diffusion* rate constants for different initial dye concentrations at t=25ºC, pH 5.6, and 20 g/L sorbent concentration

Kinetic Model	$C_{0\ dye}$ ***(mg L^{-1})***									
	10		**20**		**30**		**50**		**100**	
Pseudo-first-order										
q_e *(mg/g)*	0.426		0.602		0.965		1.061		1.386	
k_1 *(h)*	0.595		0.580		0.548		506		0.438	
R^2	0.993		0.932		0.962		0.969		0.958	
Pseudo-second-order										
q_{exp} *(mg/g)*	0.463		0.955		1.201		1.405		1.884	
q_e *(mg/g)*	0.510		0.995		1.270		1.463		1.962	
k_2 *(g/mg*h)*	0.345		0.448		0.723		1.668		2.448	
R^2	0.997		0.999		0.999		0.998		0.997	
Elocvich										
α *(mg/g* h)*	1.072		1.463		1.510		1.534		1.738	
β *(g/mg)*	12.61		7.32		4.945		4.151		3.171	
R^2	0.952		0.937		0.953		0.978		0.982	
Intraparticle diffusion										
K_i *(mg/g* $min^{1/2}$)*	I	0.264	I	0.651	I	1.182	I	0.653	I	0.794
	II	-0.026	II	0.156	II	0.322	II	0.262	II	0.329
			III	0.023	III	-0.045	III	0.060	III	0.211
C_i	I	0.013	I	0.093	I	0.996	I	-0.0017	I	0.0284
	II	0.330	II	0.603	II	0.995	II	0.5354	II	0.6927
			III	0.876	III	0.956	III	1.1105	III	0.9728
R^2	I	0.998	I	0.179	I	0.994	I	0.978	I	0.969
	II	0.966	II	0.482	II	0.978	II	0.998	II	0.993
			III	1.032	III	0.984	III	0.996	III	0.879

The α coefficient values increase with Erythrosine B concentration raising, confirming the theory behind this model: as the surface coverage increases the rate of adsorption decreases.

The adsorption mechanisms of Erythrosine B on the beans hulls adsorbent were investigated

using intraparticle diffusion model (Smaranda *et al.*, 2014). As seen from Fig. 2d, the plot obtained by applying the intraparticle diffusion model developed by Weber and Moris were not linear over the whole time range. The two and three linear section with different slope (for concentration higher than 10 mg/L) was assigned to two/three interparticle diffusion steps occurring during the adsorption process.

At the beginning of adsorption there is a linear region representing the rapid surface loading, followed by the second linear region representing pore diffusion, and in the last part a horizontal linear region is representing equilibrium.

As it was find early by Apostol *et al.* (2016) for Erythrosine B sequestration by pumpkin seeds hulls, in the first portion the acid dye sorption was attributed to the diffusion of dye molecules through the solution, that to the external surface of adsorbent, or the boundary layer diffusion of solute molecules.

The second portion described the gradual adsorption stage, where intraparticle diffusion was rate limiting. The third portion was attributed to the final equilibrium stage for which the intraparticle diffusion started to slow down due to the extremely low dye concentration left in the solution or the rate of uptake might be limited by the size of adsorbate molecule, concentration of the adsorbate and its affinity to the adsorbent, diffusion coefficient of the acid dye in the bulk phase, the pore-size distribution of the adsorbent (Zhou *et al.*, 2011). This is confirmed since $K_{i3}<K_{i2}<K_{i1}$. The three different stages having three negative values for the intercept parameter suggests that intraparticle diffusion is the predominantly rate limiting step in the adsorption process.

5. CONCLUSION

The R^2 obtained from data interpretation of kinetics models were between 0.99 (pseudo-second order model) and 0.87 (intraparticle diffusion model), indicating that the experimental data are well described by Ho's pseudo-second-order model, suggesting that the sorption mechanism involves ion exchange and physical interactions. The mechanism of the sorption process of Erythrosine B onto beans hulls was predominantly intraparticle diffusion.

Acknowledgments

The work is supported by the Romanian National Authority for Scientific Research, CNCS-UEFISCDI, project number PN-III-P4-IDPCE-2016-0683, contract 65/2017.

4. REFERENCES

[1]. Apostol L.C., Pereira L., Pereira R., Gavrilescu M., Alves M.M., (2012), Biological decolorization of xanthene dyes by anaerobic granular biomass, Biodegradation, 23(5), 725–737.

[2]. Apostol L.C., Gavrilescu M., (2013), Erythrosine B in the environment. Removal processes, Food and Environment Safet, XII(3), 253–264.

[3]. Apostol L.C., Smaranda C., Diaconu M., Gavrilescu M., (2015), Preliminary Ecotoxicological Evaluation of Erythrosine B and its Photocatalytic Degradation Products, Environmental Engineering and Management Journal, 14(2), 465-471.

[4]. Apostol L.C., Ghinea C., Alves M.M., Gavrilescu M., (2016), Removal of Erythrosine B dye from water effluents using crop waste pumpkin seed hulls as adsorbent, Desalination and Water Treatment, 57(47), 22585-22608..

[5]. Bora S.S., Radichevich I., Werner S.C., (1969), Artifactual elevation of PBI from an iodinated dye used to stain medicinal capsules pink, J. Clin. Endocrinol. Metab., 29, 1269-1271.

[6]. Drumond F.M., de PaulaVenâncio C.V., de Lourdes Pires Bianchi M., Greggi Antunes L.M., (2012), Genotoxic and mutagenic effects of Erythrosine B, a xanthene food dye, on HepG2 cells, Food and Chemical Toxicology, 50(10), 3447-3451.

[7]. Jennings A.S., Schwartz S.L., Balter N.J., Gardner D., Witorsch R.J., (1990), Effects of oral erythrosine (2′,4′,5′,7′-tetraiodofluorescein) on the pituitary–thyroid axis in rats, Toxicol. Appl. Pharmacol., 103, 549-556.

[8]. Ministry of the Environment, (2007), Examples of Food Processing Wastewater Treatment, On line at: https://www.env.go.jp/earth/coop/coop/document/male2_e/007.pdf, Accessed on July, 2017.

[9]. Silbergeld E.K., Anderson S.M., Morris S.J., (1982), Interactions of Erythrosin B (U.S. FD & C Red 3) with rat cortical membranes, Life Sci., 31(10), 957-969.

[10]. Smaranda C., Comăniţă E.-D., Apostol L.C., Gavrilescu M., (2014), Assessment of *Phaseolus Vulgaris* L. Biomass as Low-Cost Adsorbent for the Removal of Congo Red Dye from Aqueous Solutions, Lucrări Ştiinţifice - Seria Agronomie, 57, 139-144.

[11]. Zhou Q., Gong W., Xie C., Yuan X., Li Y., Bai C., Chen S., Xu N., (2011), Biosorption of Methylene Blue from aqueous solution on spent cottonseed hull substrate for *Pleurotus ostreatus* cultivation, 29, 317–325.