



# Kinetic studies of dyes sorption from aqueous solutions onto the strongly basic anion-exchanger Lewatit MonoPlus M-600

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## ABSTRACT

The sorption of Tartrazine, Allura Red, Sunset Yellow and Indigo Carmine from aqueous solutions onto the strongly basic anion-exchanger (Lewatit MonoPlus M-600) of dimethylethanolamine functional groups and styrene–divinylbenzene matrix was investigated. The experimental data obtained at 50, 100, 200, 300 and 500 mg/dm<sup>3</sup> initial concentrations at 20 °C were applied to the pseudo-first order, pseudo-second order and Weber–Morris kinetic models. The calculated sorption capacities ( $q_{1,cal}$ ) and the rate constant of the first-order adsorption ( $k_1$ ) were determined. The pseudo-second order kinetic constants ( $k_2$ ) and capacities ( $q_{2,cal}$ ) were calculated from the plots of  $t/q_t$  vs.  $t$ ,  $1/q_t$  vs.  $1/t$ ,  $1/t$  vs.  $1/q_t$ ,  $q_t/t$  vs.  $q_t$  and  $1/q_2 - q_t$  vs.  $t$  for type 1, type 2, type 3, type 4 and type 5 of the pseudo-second order expression, respectively.

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## 1. Introduction

Synthetic dyes are widely used as colouring agents in a variety of products, such as textiles, paper, leather, gasoline and foodstuff. Due to large-scale production and extensive application, dyes can cause considerable environmental pollution and are a serious health-risk factor. According to the estimate, around 10–15% of the dyes used enter as a waste into the environment through effluent [1]. Hence, the removal of residual colour from wastewaters becomes of fundamental importance.

Colour effluents are usually treated by physical or chemical processes. Among several chemical and physical methods, a sorption process is often one of the most effective methods for dyes removal. To find an effective and ideal adsorbent, researchers have exploited many low cost and biodegradable substitutes obtainable from natural resources for removal of different dyes from aqueous solutions under various operating conditions [2]. Activated carbon [3] is still the most popular and widely used adsorbent but the main problem with its use is that it is quite expensive. Good sorption capacities for dyes are found for such materials as chitin [4], peat [5], de-oiled soya [6], sawdust [7], but no successful regeneration has been reported. There is very little information in the literature about removal of dyes using ion-exchangers [8].

The aim of this study was, therefore, to apply the commercially available strongly basic anion-exchanger of dimethylethanolamine

functional groups for removal of food dyes. These studies investigated the kinetics sorption characteristics of Allura Red (AR), Tartrazine (T), Sunset Yellow (SY) and Indigo Carmine (IC) using Lewatit MonoPlus M-600 of gel structure. The effects of initial dye concentration and phase contact time on adsorption were investigated. The experimental data were analyzed using the pseudo-first and -second order kinetic models as well as the intraparticle diffusion equation. Kinetic constants were calculated.

## 2. Experimental

### 2.1. Materials

The four different food dyes Allura Red, Tartrazine, Sunset Yellow and Indigo Carmine (Sigma–Aldrich, Germany) were used. Their solutions were prepared by dissolving the accurately weighed amount of dye in 1 dm<sup>3</sup> of distilled water. The molecular structures and properties of tested dyes are shown in Fig. 1 and Table 1.

Lewatit MonoPlus M-600 (Bayer Chemicals, Germany) is a strongly basic, gelular anion-exchange resin of dimethylethanolamine functional groups. Its beads of uniform size (monodisperse) are based on a styrene–divinylbenzene copolymer. The total exchange capacity is 1.3 mequiv./cm<sup>3</sup>.

### 2.2. Adsorption studies

The adsorption of Allura Red, Tartrazine, Sunset Yellow and Indigo Carmine onto Lewatit M-600 was studied by means of laboratory batch method. The samples of dry resin (0.25 g) were

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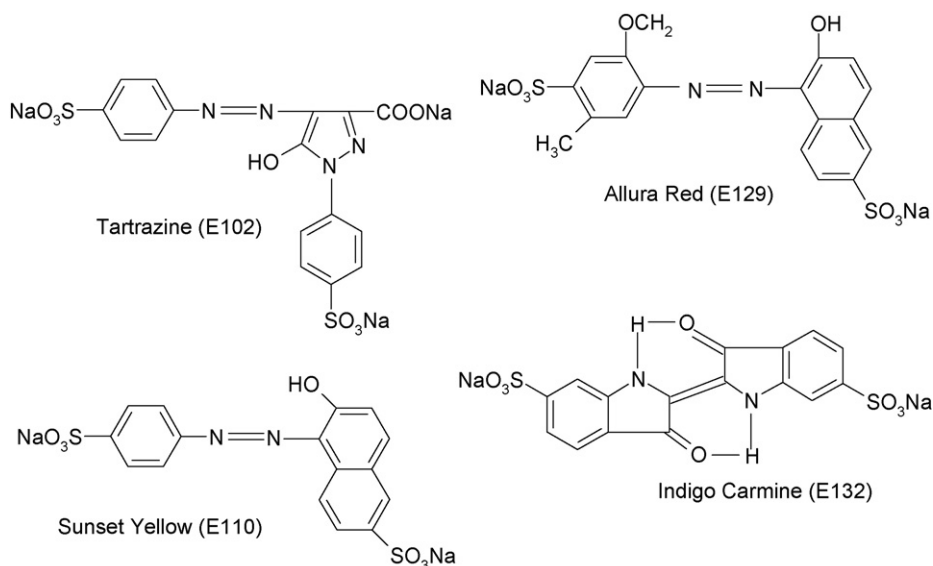


Fig. 1. Structures of food dyes: T, AR, SY and IC.

Table 1  
Characteristics of food dyes used.

Dye	Allura Red AC	Tartrazine	Sunset Yellow FCF	Indigo Carmine
Properties				
Formula	C <sub>18</sub> H <sub>16</sub> N <sub>2</sub> O <sub>8</sub> S <sub>2</sub> Na <sub>2</sub>	C <sub>16</sub> H <sub>9</sub> N <sub>4</sub> Na <sub>3</sub> O <sub>9</sub> S <sub>2</sub>	C <sub>16</sub> H <sub>10</sub> N <sub>2</sub> Na <sub>2</sub> O <sub>7</sub> S <sub>2</sub>	C <sub>16</sub> H <sub>8</sub> N <sub>2</sub> Na <sub>2</sub> O <sub>8</sub> S <sub>2</sub>
Synonyms	Food Red 17, E129	Acid Yellow 23, E 102, Acilan Yellow GG	E 110, Acid Yellow TRA, Food Yellow 3	E 132, Acid Blue 74
Physical form	Red powder, dye content 80%	Orange powder, dye content 90%	Orange powder, dye content 90%	Dark blue powder, dye content 90%
λ <sub>max</sub> (nm)	502	430	482	611
Molecular weight	496.42	534.36	452.36	466.35

shaken mechanically with 25 cm<sup>3</sup> of corresponding dye solution for 1–240 min at 20 °C. Dye solutions of five different initial concentrations (50, 100, 200, 300 and 500 mg/dm<sup>3</sup>) were used.

At the end of the predetermined time interval, the anion-exchanger was removed by the filtration and the dye concentration was determined using the UV–vis spectrophotometer (Specord M42). The data obtained from the adsorption tests were used to calculate the adsorption capacity,  $q_t$  (mg/g) from Eq. (1):

$$q_t = \frac{C_0 - C_t}{w} \times V \quad (1)$$

where  $C_0$  and  $C_t$  are the concentrations of the dye in the solution before and after sorption respectively (mg/dm<sup>3</sup>),  $V$  is the volume of the solution (dm<sup>3</sup>) and  $w$  is the mass of the dry anion-exchanger (g).

Kinetic experiments related to the effect of initial concentrations were performed at the natural pHs of solutions.

### 3. Results and discussion

#### 3.1. Kinetic parameters

Adsorption process proved to be effective for the removal of various pollutants from aqueous solutions. The prediction of batch kinetics is necessary for designing of 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. Kinetic models based on the concentration of solute and on the dose of sorbent have been proposed by several researchers [9].

In order to investigate the mechanism of sorption, the rate constant of chemical sorption and intraparticle diffusion for the dyes

were determined using the equations of a pseudo-first order system by Lagergren, pseudo-second order mechanism and intraparticle diffusion by Weber and Morris, respectively [5,9–12].

The Lagergren pseudo-first order rate expression is generally described using the following equation:

$$\frac{dq_t}{dt} = k_1(q_1 - q_t) \quad (2)$$

where  $q_1$  and  $q_t$  are the amounts (mg/g) of dye adsorbed at equilibrium and at time  $t$  (min) respectively; and  $k_1$  is the constant rate (1/min).

After integration by applying the boundary conditions ( $q_t = 0$  at  $t = 0$  and  $q_t = q_t$  at  $t = t$ ), Eq. (2) can be rearranged for linearized data plotting:

$$\log(q_1 - q_t) = \log(q_1) - \frac{k_1}{2.303} t \quad (3)$$

In order to confirm the applicability of the model, the plot of  $\log(q_1 - q_t)$  against  $t$  should be a straight line. In a true first-order process, experimental  $\log(q_1)$  should be equal to the intercept of the straight line [5,13].

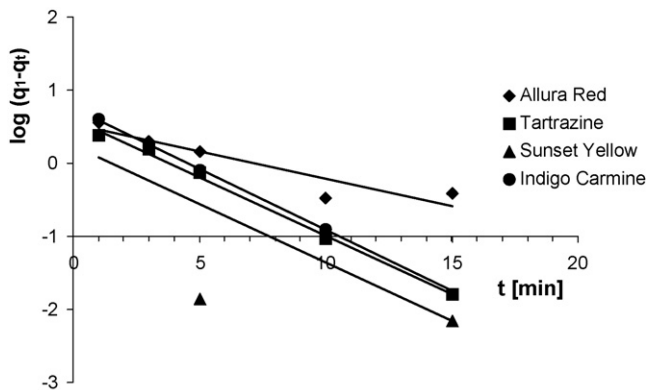
However, if the intercept does not equal  $\log(q_1)$  then the reaction is not likely to be the first order even if these plots have high correlation coefficients with the experimental data. In many cases, the first-order equation does not fit well for the whole range of contact time and is generally applicable over the initial stage of adsorption processes [14].

The kinetic parameters for AR, T, SY and IC solutions of different initial concentrations according to the pseudo-first order equation are listed in Table 2. Fig. 2 shows that after a short time period, the experimental data deviated from linearity.

**Table 2**

Pseudo-first order kinetic parameters obtained by using the linear method at different initial concentrations of dye solutions.

Dye	Parameters	50 mg/dm <sup>3</sup>	100 mg/dm <sup>3</sup>	200 mg/dm <sup>3</sup>	300 mg/dm <sup>3</sup>	500 mg/dm <sup>3</sup>
Allura Red	$q_{1,cal}$ (mg/g)	3.412	8.996	18.519	23.297	26.193
	$k_1$ (min <sup>-1</sup> )	0.171	0.0791	0.0168	0.0150	0.0164
	$r^2$	0.861	0.992	0.811	0.979	0.950
Tartrazine	$q_{1,cal}$ (mg/g)	4.077	12.523	22.452	27.729	39.208
	$k_1$ (min <sup>-1</sup> )	0.369	0.4522	0.3488	0.3258	0.3004
	$r^2$	0.996	0.970	0.984	0.991	0.988
Sunset Yellow	$q_{1,cal}$ (mg/g)	1.704	6.174	21.372	27.879	44.781
	$k_1$ (min <sup>-1</sup> )	0.367	0.3694	0.3384	0.1328	0.0487
	$r^2$	0.594	0.972	0.999	0.892	0.996
Indigo Carmine	$q_{1,cal}$ (mg/g)	5.784	8.827	24.306	27.266	43.648
	$k_1$ (min <sup>-1</sup> )	0.384	0.3726	0.3531	0.1459	0.0704
	$r^2$	0.999	0.998	0.967	0.923	0.979

**Fig. 2.** Pseudo-first order kinetics sorption of T, AR, SY and IC onto Lewatit M-600 at 50 mg/dm<sup>3</sup> initial concentration.

The values of correlation coefficient ( $r^2$ ) of the pseudo-first order kinetic model in the plot of  $\log(q_1 - q_t)$  vs.  $t$  for Indigo Carmine and Sunset Yellow were extremely high (0.999) when the sorption occurred from the solution of 50 and 200 mg/dm<sup>3</sup>, respectively. The calculated sorption capacities ( $q_{1,cal}$ ): 5.784 mg/g for IC and 21.372 mg/g for SY are compared with the experimental ones (5.0 and 20.0 mg/g). The same dependence was observed for IC solutions of the initial concentrations 100, 200 and 300 mg/dm<sup>3</sup>.

**Table 4**

Pseudo-second order kinetic parameters obtained by using the linear method at different initial concentration of Allura Red solutions.

Type	Parameters	50 mg/dm <sup>3</sup>	100 mg/dm <sup>3</sup>	200 mg/dm <sup>3</sup>	300 mg/dm <sup>3</sup>	500 mg/dm <sup>3</sup>
Type 1	$q_{2,cal}$ (mg/g)	5.609	9.708	18.245	28.800	55.618
	$k_2$ (g/(mg min))	0.064	0.018	0.015	0.011	0.00003
	$h$ (mg/(g min))	2.016	1.649	1.030	0.825	0.109
	$r^2$	0.992	0.939	0.834	0.921	0.766
Type 2	$q_{2,cal}$ (mg/g)	6.039	6.711	18.689	7.321	-0.838
	$k_2$ (g/(mg min))	0.049	0.056	0.0023	0.017	0.076
	$h$ (mg/(g min))	1.791	2.565	0.801	0.916	0.053
	$r^2$	0.997	0.954	0.951	0.998	0.900
Type 3	$q_{2,cal}$ (mg/g)	6.059	7.011	31.449	7.357	-0.645
	$k_2$ (g/(mg min))	0.048	0.049	0.0008	0.017	0.130
	$h$ (mg/(g min))	1.786	2.447	0.762	0.914	0.054
	$r^2$	0.997	0.954	0.935	0.998	0.900
Type 4	$q_{2,cal}$ (mg/g)	5.935	8.601	13.078	8.500	-8.493
	$k_2$ (g/(mg min))	0.051	0.026	0.005	0.012	0.004
	$h$ (mg/(g min))	1.827	1.974	0.897	0.852	0.322
	$r^2$	0.966	0.754	0.131	0.886	0.118
Type 5	$q_{2,cal}$ (mg/g)	23.485	11.446	18.569	23.40	26.302
	$k_2$ (g/(mg min))	0.200	0.018	0.001	0.0007	0.0007
	$h$ (mg/(g min))	110.676	2.366	0.352	0.398	0.489
	$r^2$	0.791	0.947	0.835	0.982	0.963

**Table 3**

Comparison of the pseudo-second order models.

Type	Linear form	Plot
Type 1 pseudo-second	$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2} t$	$t/q_t$ vs. $t$
Type 2 pseudo-second	$\frac{1}{q_t} = \left( \frac{1}{k_2 q_2^2} \right) \frac{1}{t} + \frac{1}{q_2}$	$1/q_t$ vs. $1/t$
Type 3 pseudo-second	$\frac{1}{t} = \frac{k_2 q_2^2}{q_t} - \frac{k_2 q_2^2}{q_2}$	$1/t$ vs. $1/q_t$
Type 4 pseudo-second	$\frac{q_t}{t} = k_2 q_2^2 - \frac{k_2 q_2^2 q_t}{q_2}$	$q_t/t$ vs. $q_t$
Type 5 pseudo-second	$\frac{1}{q_2 - q_t} = \frac{1}{q_2} + k_2 t$	$1/(q_2 - q_t)$ vs. $t$

However, in the case of the others dye solutions of initial concentrations ranging from 50 to 500 mg/dm<sup>3</sup>, the  $r^2$  values were proper for the application of the first order model. All the calculated equilibrium capacities differed significantly from experimental values. This finding suggested that the adsorption of Allura Red, Sunset Yellow and Tartrazine onto the anion-exchanger of gel structure was not the first order reaction.

In order to analyze the experimental data the pseudo-second order model was also used. The pseudo-second order kinetic rate equation is expressed as:

$$\frac{dq_t}{dt} = k_2(q_2 - q_t)^2 \quad (4)$$

**Table 5**  
Pseudo-second order kinetic parameters obtained by using the linear method at different initial concentration of Tartrazine solutions.

Type	Parameters	50 mg/dm <sup>3</sup>	100 mg/dm <sup>3</sup>	200 mg/dm <sup>3</sup>	300 mg/dm <sup>3</sup>	500 mg/dm <sup>3</sup>
Type 1	$q_{2,cal}$ (mg/g)	5.457	11.500	23.920	33.748	56.523
	$k_2$ (g/(mg min))	0.136	0.043	0.015	0.015	0.0010
	$h$ (mg/(g min))	4.049	5.705	8.431	17.532	29.068
	$r^2$	0.998	0.996	0.984	0.999	0.997
Type 2	$q_{2,cal}$ (mg/g)	5.084	13.328	21.341	32.929	53.678
	$k_2$ (g/(mg min))	0.204	0.0245	0.022	0.017	0.010
	$h$ (mg/(g min))	5.260	4.350	10.126	18.545	27.42
	$r^2$	0.951	0.988	0.935	0.998	0.987
Type 3	$q_{2,cal}$ (mg/g)	5.172	13.499	22.452	32.963	53.939
	$k_2$ (g/(mg min))	0.187	0.0236	0.019	0.017	0.009
	$h$ (mg/(g min))	5.001	4.298	9.472	18.514	28.486
	$r^2$	0.951	0.988	0.935	0.998	0.986
Type 4	$q_{2,cal}$ (mg/g)	5.300	12.729	24.102	33.360	58.545
	$k_2$ (g/(mg min))	0.165	0.0286	0.015	0.016	0.008
	$h$ (mg/(g min))	4.643	4.627	8.609	18.091	26.762
	$r^2$	0.903	0.902	0.815	0.993	0.956
Type 5	$q_{2,cal}$ (mg/g)	-0.075	-0.039	-0.459	-0.835	-2.244
	$k_2$ (g/(mg min))	4.186	7.214	0.665	0.376	0.154
	$h$ (mg/(g min))	0.024	0.011	0.140	0.262	0.779
	$r^2$	0.784	0.677	0.732	0.747	0.799

where  $q_2$  and  $q_t$  are the amounts (mg/g) of dye adsorbed at equilibrium and at time  $t$  (min) respectively; and  $k_2$  is the constant rate of the pseudo-second order adsorption (g/(mg min)).

After taking into account the boundary conditions,  $q_t = 0$  at  $t = 0$  and  $q_t = q_t$  at  $t = t$ , the integrated form of Eq. (4) can be rearranged to obtain Eq. (5):

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{1}{q_2} t \quad (5)$$

and

$$h = k_2 q_2^2$$

where  $h$  is the initial sorption rate (mg/g min).

The values of  $k_2$  and  $q_2$  can be determined from the slope and intercept of the plot  $t/q_t$  vs.  $t$ , respectively. This dependence is defined as type 1 of the pseudo-second order expression.

Similarly, the pseudo-second order kinetic constant  $k_2$  and  $q_2$  can be calculated from the plots of  $1/q_t$  vs.  $1/t$ ,  $1/t$  vs.  $1/q_t$ ,  $q_t/t$  vs.  $q_t$  and  $1/q_2 - q_t$  vs.  $t$  for type 2, type 3, type 4 and type 5 pseudo-

second order expression, respectively [10,11]. Table 3 shows the linear forms of Eq. (5).

The calculated kinetic constants according to the five linear forms of the pseudo-second order model at different food dye concentrations are compared in Tables 4–7. Figs. 3–6 illustrate experimental data using the equation of four pseudo-second kinetic models (types 1–4) for the sorption of AR, T, SY and IC on Lewatit MonoPlus M-600 from the solution of initial concentration 100 mg/dm<sup>3</sup>. Similar patterns were obtained for the other initial concentrations. It was observed that  $k_2$ ,  $h$  and  $q_{2,cal}$  obtained from the five linear forms of the pseudo-second order equations were different.

Kinetics sorption of Allura Red solutions on Lewatit MonoPlus M-600 was relatively well-described using model 1 of the pseudo-second expression (Table 4). Types 2–4 could not be taken into account because of big differences in experimental and calculated sorption capacities in spite of high values of correlation coefficients. Decrease of kinetic constants as well as initial sorption rates was noticed with the increase of initial concentration.

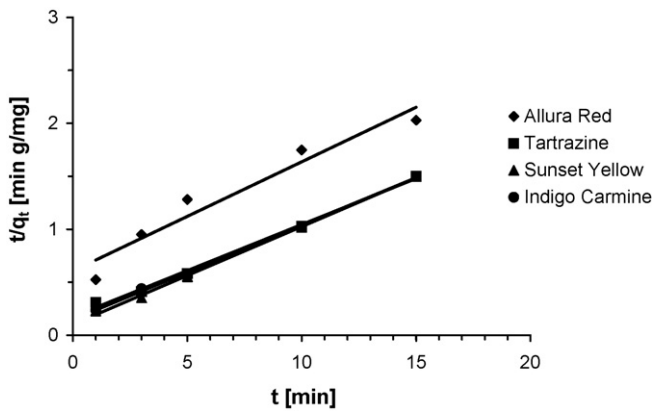
**Table 6**  
Pseudo-second order kinetic parameters obtained by using the linear method at different initial concentration of Sunset Yellow solutions.

Type	Parameters	50 mg/dm <sup>3</sup>	100 mg/dm <sup>3</sup>	200 mg/dm <sup>3</sup>	300 mg/dm <sup>3</sup>	500 mg/dm <sup>3</sup>
Type 1	$q_{2,cal}$ (mg/g)	5.489	10.818	23.920	32.641	38.977
	$k_2$ (g/(mg min))	0.136	0.085	0.015	0.0063	0.0039
	$h$ (mg/(g min))	4.105	9.906	8.431	6.715	5.952
	$r^2$	0.986	0.999	0.996	0.9177	0.954
Type 2	$q_{2,cal}$ (mg/g)	5.163	11.913	26.493	28.260	38.806
	$k_2$ (g/(mg min))	0.185	0.051	0.010	0.011	0.0058
	$h$ (mg/(g min))	4.922	7.181	7.229	8.154	8.700
	$r^2$	0.820	0.979	0.998	0.989	0.936
Type 3	$q_{2,cal}$ (mg/g)	5.603	12.055	26.564	28.642	41.646
	$k_2$ (g/(mg min))	0.129	0.048	0.010	0.0098	0.0041
	$h$ (mg/(g min))	4.034	7.035	7.214	8.063	7.126
	$r^2$	0.819	0.980	0.998	0.989	0.936
Type 4	$q_{2,cal}$ (mg/g)	5.843	11.768	25.669	31.564	34.898
	$k_2$ (g/(mg min))	0.108	0.053	0.011	0.0073	0.0056
	$h$ (mg/(g min))	3.674	7.400	7.482	7.313	6.859
	$r^2$	0.666	0.901	0.973	0.831	0.772
Type 5	$q_{2,cal}$ (mg/g)	-0.0868	-0.856	-0.595	-102.824	47.461
	$k_2$ (g/(mg min))	8.268	0.659	0.534	0.019	0.0016
	$h$ (mg/(g min))	0.062	0.483	0.189	202.089	3.645
	$r^2$	0.565	0.915	0.771	0.768	0.998

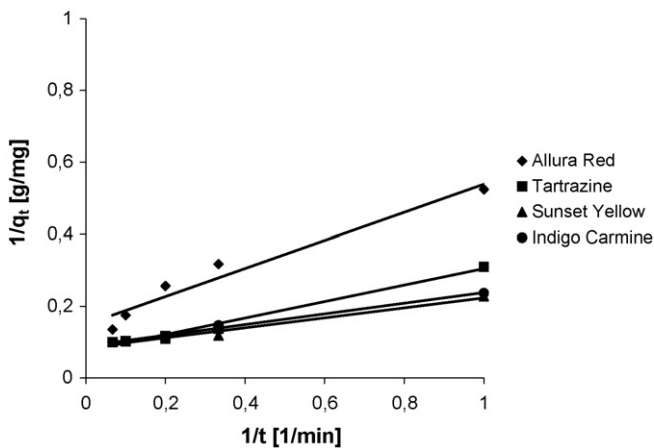
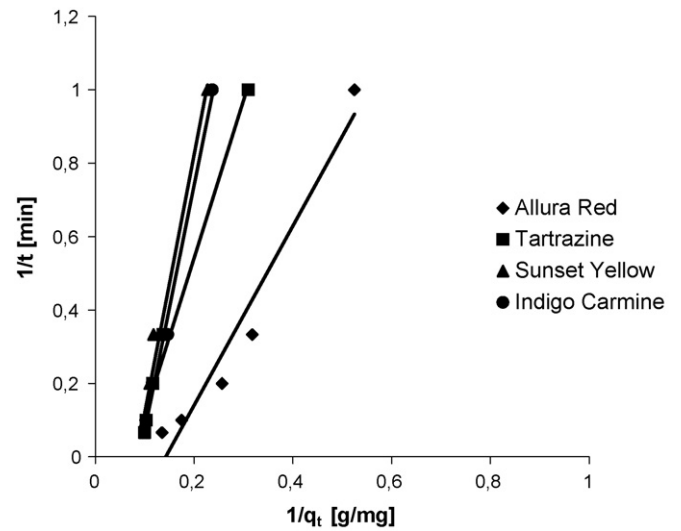
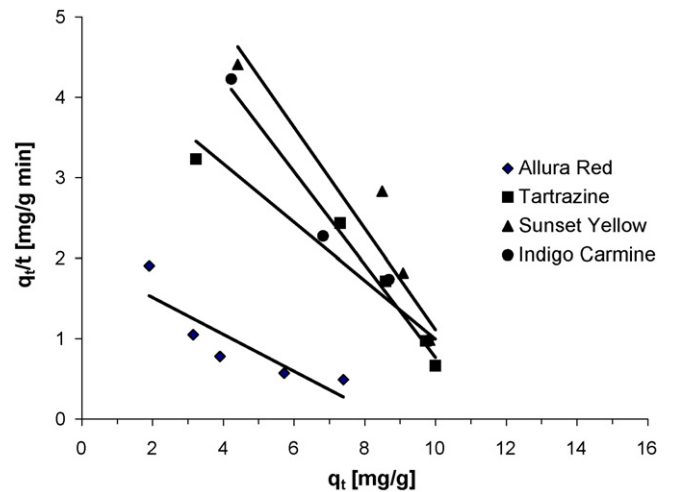
**Table 7**

Pseudo-second order kinetic parameters obtained by using the linear method at different initial concentration of Indigo Carmine solutions.

Type	Parameters	50 mg/dm <sup>3</sup>	100 mg/dm <sup>3</sup>	200 mg/dm <sup>3</sup>	300 mg/dm <sup>3</sup>	500 mg/dm <sup>3</sup>
Type 1	$q_{2,cal}$ (mg/g)	6.541	11.209	24.410	39.096	48.144
	$k_2$ (g/(mg min))	0.0392	0.0537	0.0127	0.0038	0.0033
	$h$ (mg/(g min))	1.677	6.751	7.572	5.821	7.582
	$r^2$	0.963	0.998	0.994	0.970	0.975
Type 2	$q_{2,cal}$ (mg/g)	10.877	11.155	22.754	37.321	46.080
	$k_2$ (g/(mg min))	0.0096	0.0542	0.0161	0.0043	0.0045
	$h$ (mg/(g min))	1.141	6.739	8.354	5.982	9.970
	$r^2$	0.979	0.994	0.993	0.997	0.969
Type 3	$q_{2,cal}$ (mg/g)	11.664	11.195	22.889	37.562	47.626
	$k_2$ (g/(mg min))	0.0082	0.0534	0.0159	0.0042	0.0038
	$h$ (mg/(g min))	1.118	6.697	8.302	5.965	8.643
	$r^2$	0.979	0.994	0.993	0.997	0.968
Type 4	$q_{2,cal}$ (mg/g)	8.488	11.330	24.063	40.545	45.433
	$k_2$ (g/(mg min))	0.018	0.0509	0.0135	0.0035	0.0040
	$h$ (mg/(g min))	1.309	6.537	7.796	5.695	8.158
	$r^2$	0.619	0.977	0.958	0.913	0.847
Type 5	$q_{2,cal}$ (mg/g)	-0.562	-0.971	-2.715	-2.889	50.543
	$k_2$ (g/(mg min))	0.9028	0.0531	0.1827	0.232	0.0029
	$h$ (mg/(g min))	0.284	0.500	1.347	1.933	7.528
	$r^2$	0.896	0.897	0.861	0.910	0.993

**Fig. 3.** Type 1 of pseudo-second order kinetic model obtained by using linear method for sorption of T, AR, SY and IC from 100 mg/dm<sup>3</sup> solutions on Lewatit M-600.

There was a good correlation of experimental capacities with calculated  $q_{2,cal}$  for Tartrazine solutions using the linear form of types 1–3 of the pseudo-second order kinetic expression (Table 5). It was confirmed by the values of  $r^2$  ranging from 0.935 to 0.999.

**Fig. 4.** Type 2 of pseudo-second order kinetic model obtained by using linear method for sorption of T, AR, SY and IC from 100 mg/dm<sup>3</sup> solutions on Lewatit M-600.**Fig. 5.** Type 3 of pseudo-second order kinetic model obtained by using linear method for sorption of T, AR, SY and IC from 100 mg/dm<sup>3</sup> solutions on Lewatit M-600.**Fig. 6.** Type 4 of pseudo-second order kinetic model obtained by using linear method for sorption of T, AR, SY and IC from 100 mg/dm<sup>3</sup> solutions on Lewatit M-600.

Type 4 provided lower values of  $r^2$  (from 0.815 to 0.993). The initial sorption rate ( $h$ ) as well as the constant rate ( $k_2$ ), increased with the increasing initial concentration in the range 50–500 mg/dm<sup>3</sup>.

Sunset Yellow kinetic sorption onto Lewatit MonoPlus M-600 from the solutions of initial concentrations 50 and 100 mg/dm<sup>3</sup> was described by type 1 of the pseudo-second order equation (Table 6). Correlation coefficients equal to 0.986 and 0.999, respectively. The calculated sorption capacities were close to the experimental values. At 300 mg/dm<sup>3</sup> initial concentration types 2 and 3 provided good values of calculated sorption capacities: 28.26 and 28.642 mg/g, respectively ( $r^2 = 0.989$ ). According to types 1 and 4 of the pseudo-second order kinetic models the  $q_{2,cal}$  values were insignificantly higher than the experimental ones with lower correlation coefficients: 0.917 and 0.831, respectively.

Type 5 of the pseudo-second order expression represented very poorly the kinetic data of tested food dyes onto Lewatit M-600. Lower  $r^2$  values (from 0.565 to 0.982) for all initial concentrations with the exception of 500 mg/dm<sup>3</sup> for SY and IC were found. As follows from Table 4 type 5 of the pseudo-second order model failed to predict the  $q_2$  of Allura Red solutions. Furthermore, for the initial dye concentrations ranging from 50 to 300 mg/dm<sup>3</sup>, type 5 pseudo-second order expression produced negative  $q_e$  values, which was experimentally and practically impossible (Tables 5–7). The reasonably higher  $r^2$  values for type 5 expressions suggested that it could be used to represent the kinetics of Indigo Carmine and Sunset Yellow onto Lewatit MonoPlus M-600 from the solutions of initial concentration 500 mg/dm<sup>3</sup> (Tables 6 and 7).

The intraparticle diffusion model proposed by Weber and Morris in 1963 [13,15] was also taken into account in the experiments. They concluded that sorption is proportional to the square root of contact time:

$$q_t = k_i t^{0.5} \quad (6)$$

where  $k_i$  is the intraparticle diffusion rate (mg/(g min<sup>0.5</sup>)).

When the intraparticle diffusion model controls the sorption, the graph of  $q_t$  against  $t^{0.5}$  should be a straight line passing through the origin. The rate constant can be calculated from the slope of the line [13,15–19].

Fig. 7 illustrates the intraparticle diffusion kinetics of Tartrazine by Lewatit MonoPlus M-600 at various initial dye concentrations. The values of intraparticle diffusion rates ( $k_i$ ) estimated from the slopes increased from 0.841 to 10.549 mg/(g min<sup>0.5</sup>) with the increasing initial concentration from 50 to 500 mg/dm<sup>3</sup> for Tartrazine. The values of  $r^2$  decreased consistently from 0.919 to 0.836. The intraparticle diffusion rates ( $k_i$ ) calculated according to Weber and Morris equation changed from 1.131 to

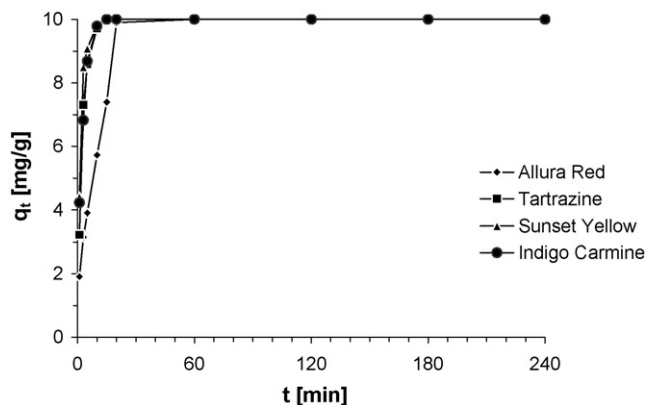


Fig. 8. Influence of phase contact time on AR, T, SY and IC from aqueous solution of initial concentration 100 mg/dm<sup>3</sup> using Lewatit M-600.

1.755 mg/(g min<sup>0.5</sup>), from 0.877 to 6.957 mg/(g min<sup>0.5</sup>) and from 1.321 to 6.722 mg/(g min<sup>0.5</sup>) for AR, SY and IC, respectively.

Deviations from the intraparticle diffusion kinetics occurred with the initial dye concentration increase. These deviations may be attributed to some repulsion between Lewatit M-600 and food dyes molecules due to concentration density.

### 3.2. Effect of phase contact time

A series of contact time experiments for four food dyes have been carried out with the initial dye concentration of 100 mg/dm<sup>3</sup> at 20 °C. Fig. 8 shows that the amount of the adsorbed dye onto the strongly basic anion-exchanger Lewatit MonoPlus M-600 of  $-N^+(CH_3)_2C_2H_5OH$  functional groups increased with time. The contact time necessary to reach equilibrium was 20 min. The initial dye concentration had little influence on the time of contact necessary to reach equilibrium with the exception of Allura Red solutions.

### 3.3. Effect of initial dye concentration

The relationship between contact time and dye concentration uptake by the strongly basic anion-exchanger Lewatit MonoPlus M-600 was studied through batch experiments that were carried out at five different initial concentrations ranging from 50 to 500 mg/dm<sup>3</sup> at 20 °C.

For Tartrazine the sorption capacity at equilibrium increased from 5 to 50 mg/g with the increasing in the initial dye concen-

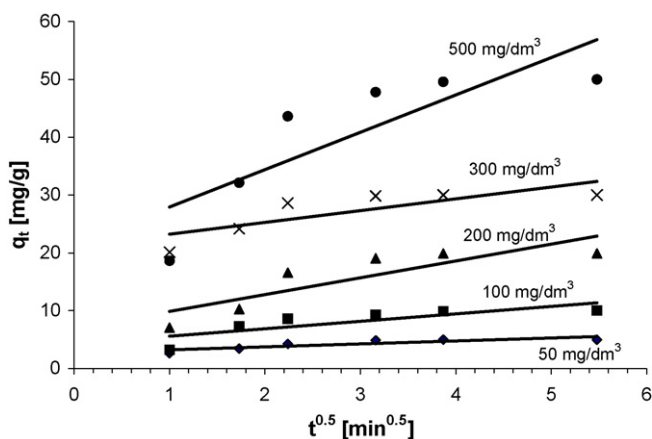


Fig. 7. Intraparticle diffusion kinetics of Tartrazine on Lewatit M-600 at various initial dye concentrations.

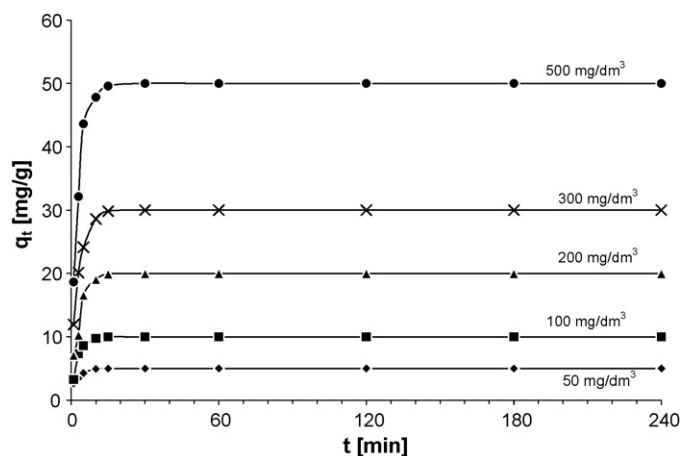


Fig. 9. Uptake of Tartrazine from aqueous solutions of initial concentrations ranging from 50 to 500 mg/dm<sup>3</sup> using Lewatit M-600.

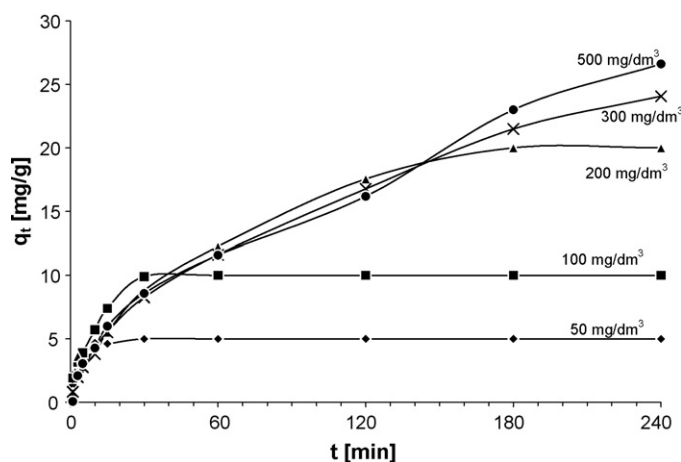


Fig. 10. Uptake of Allura Red from aqueous solutions of initial concentrations ranging from 50 to 500 mg/dm<sup>3</sup> using Lewatit M-600.

trations from 50 to 500 mg/dm<sup>3</sup> (Fig. 9). The same changes of the above mentioned values were obtained for IC and SY solutions.

The experimental results of sorption of Allura Red on Lewatit MonoPlus M-600 at various concentrations are shown in Fig. 10. The equilibrium uptake in this case occurred after 30 min in the solution of initial concentrations 50 and 100 mg/dm<sup>3</sup>. The sorption capacity was equal to 20, 24.1 and 26.6 mg/g for the dye solutions of initial concentrations 200, 300 and 500 mg/dm<sup>3</sup>, respectively.

#### 4. Conclusions

The kinetics sorption of such food dyes as Tartrazine, Allura Red, Sunset Yellow and Indigo Carmine on the strongly basic anion-exchanger Lewatit M-600 were fast, reaching over 99% of the total sorption capacity within 20 min. Increases in the initial dye concentration resulted in the increasing uptake capacity.

It can be generally assumed that the sorption process of these dyes fitted the pseudo-second order kinetic model. The best results were obtained using types 1 and 2 of the pseudo-second order kinetic equation, type 5 poorly represented the kinetic data of the tested food dyes onto Lewatit MonoPlus M-600.

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