ENHANCED ADSORPTION OF METHYL ORANGE FROM AQUEOUS SOLUTIONS USING A FUNCTIONALIZED STYRENE-DIVINYLBENZENE COPOLYMER

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Abstract
The adsorption efficiency of the styrene-divinylbenzene copolymer functionalized with carboxylic acid groups (SDVBF) was investigated for methyl orange (MO) removal from aqueous solutions. The effects of contact time and of the initial concentration on the amount of MO adsorbed were studied. The kinetics of MO adsorption onto SDVBF copolymer was described by the pseudo-second order model. It was demonstrated that Redlich-Peterson model is the most suitable to describe the adsorption of MO onto SDVBF copolymer. The maximum adsorption capacity of the SDVBF adsorbent, resulted from the Langmuir isotherm was 53.12 mg g^{-1}.

Introduction
The widespread use of dyes generates large amounts of waste water, producing toxicological problems related to environmental protection [1]. Their presence, even in small quantities, causes changes in terms of waters color, besides the cumulative effect, reducing the amount of light that reaches the aquatic environment thus complicating the process of photosynthesis [2,3]. Most dyes are used in industries such as textiles, paper, plastics, cosmetics, paints, leather, food and pharmaceutical industries [2,3].
Over time there were developed many techniques for the removal of dyes from wastewater such as: flocculation [4], precipitation [5], coagulation [6], separation membranes [7] electrolysis [8], photolysis [9] and adsorption [10]. Among these methods, adsorption is considered by many authors as a superior technique because of high efficacy, low implementation cost, wide availability and simplicity in terms of design [11].
In this study we investigate the adsorption efficiency of the styrene-6.7%divinylbenzene copolymer functionalized with carboxylic acid groups (SDVB-F) for the removal of methyl orange (MO) from aqueous solutions.

Experimental
The preparation and characterization of the functionalized copolymer was presented in our previous work [12]. The adsorption experiments were performed at 25°C, in a thermostated shaker with an operating speed of 200 rpm and at the natural pH of the solution.
The MO concentration was monitored using a UV–Vis SHIMADZU spectrophotometer. The absorbance values were measured at the wavelength of maximum absorbance of 464 nm.

Results and discussion

The effect of different initial concentrations, ranging from 100 to 600 mg L^{-1}, on the adsorption of MO onto SDVBF copolymer is shown in Fig. 1.
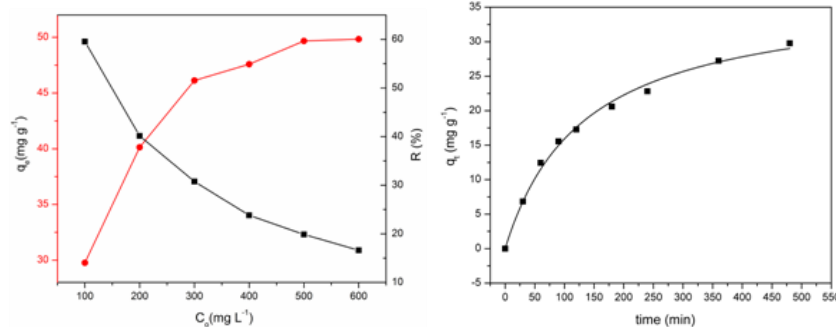

Figure 1. Effect of initial concentration on MO adsorption ontoSDVBF: m= 2 g L^{-1}.

Figure 2. Effect of contact time on MO adsorption onto SDVBF: C$_0$= 100 mg L^{-1},m=2 g L^{-1}.

The results are in accordance with the literature data, showing the increase of the amount of MO adsorbed at equilibrium and the decrease of the percentage of the pollutant removal with increasing the initial concentration which indicates that the MO removal is concentration dependent.

The amount of MO adsorbed onto SDVBF as a function of contact time is presented in Fig. 2.It can be observed the fast increase of the adsorbed amount of MO in the first 200 min of the process. This behavior can be explained by the large number of initially available vacant sites on the SDVBF surface, sites which are gradually occupied in time as a result of sorption process. It can be seen that equilibrium was reached in about 6 h.

The adsorption kinetics experiments were conducted at 25 °C, 100 mg L^{-1} initial concentration of MO and 2 g L^{-1} adsorbent dose.

The experimental data were fitted with four kinetic models namely Lagergren pseudo-first order, Ho and McKay pseudo-second-order, Elovich and intraparticle diffusion model proposed by Weber and Morris. The fitting plots of the MO adsorption data to the four kinetic models are shown in Fig.3. and the kinetic parameters are listed in Table 1.
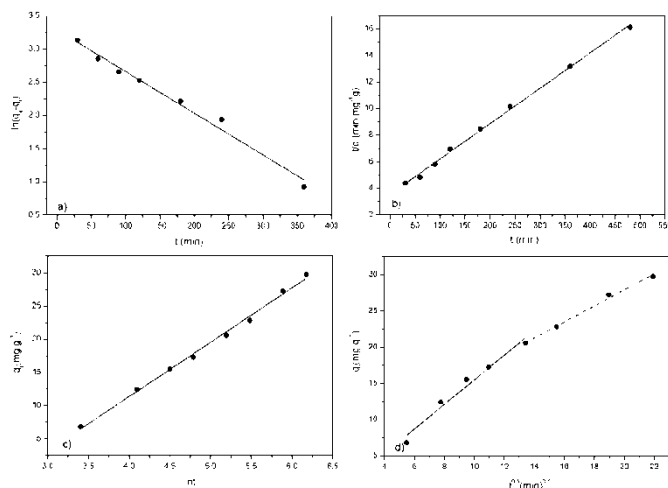

Figure 3. Adsorption kinetics of MO onto SDVBF: a) pseudo-first-order; b) pseudo-second-order; c) Elovich equation; d) intraparticle diffusion model.

Table 1. Kinetic parameters for the adsorption of MO onto SDVB-F.

Kinetic model	Kinetic parameters	
Pseudo-first-order model	$q_{e,\text{calc.}}$ (mg g^{-1})	26.84
	$q_{e,\text{exp.}}$ (mg g^{-1})	29.77
	$k_1 \cdot 10^3$ (min^{-1})	6.28
	R^2	0.98205
Pseudo-second-order model	$q_{e,\text{calc.}}$ (mg g^{-1})	37.56
	$q_{e,\text{exp.}}$ (mg g^{-1})	29.77
	$k_2 \cdot 10^4$ (g mg^{-1} min^{-1})	2.00
	R^2	**0.99733**
Elovich model	α (mg g^{-1} min^{-1})	0.60
	β (g mg^{-1})	0.12
	R^2	0.99484
Intraparticle diffusion model (second linear portion)	k_i (mg g^{-1} min$^{-0.5}$)	1.10
	c (mg g^{-1})	5.83
	R^2	0.99147

The linear plots of t/q versus t, and the values of the determination coefficients (R^2) close to unity (Table 1) indicate that the adsorption kinetics of MO is properly described by the pseudo-second-order model. The plot of q_t versus $t^{0.5}$ is not linear over the entire time range, which means that the adsorption mechanism of MO onto SDVBF is not controlled only by the intraparticle diffusion.

The experimental equilibrium data were fitted by the most used isotherm models namely: Langmuir, Freundlich and Redlich-Peterson. The fitting of the equilibrium experimental data of MO with the three isotherm models are shown in Fig.4, and the theoretical parameters of isotherms along with the corresponding determination coefficients (R^2) and Chi-square values (χ^2) are listed in Table 2.
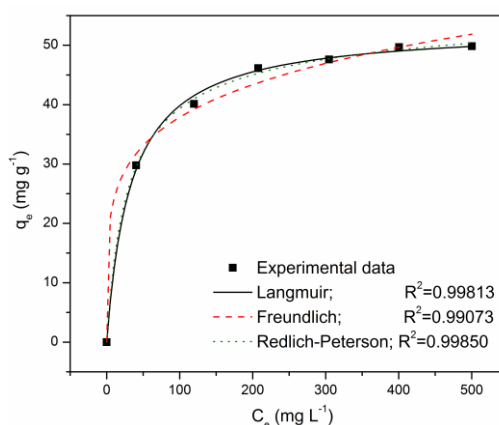
Figure 4. Isotherm plots for the adsorption of MO onto SDVBF.

Comparing the R^2 and χ^2 values of the analyzed isotherms (Table 2), it follows that the Redlich-Peterson model is the most suitable to describe the adsorption of MO onto SDVBF. It can be noticed the maximum adsorption capacity of the SDVBF resulted from the Langmuir isotherm of 53.12 mg g^{-1}, which is higher as compared with other results reported in the literature regarding the adsorption of MO onto different adsorbents [13].

Table 2. Isotherm parameters values for the adsorption of MO onto SDVBF.

Isotherm model	Parameter	Pollutant
		MO
Langmuir	q_m (mg g^{-1})	53.12
	K_L (L mg^{-1})	0.030
	R^2	0.99813
	χ^2	0.60769
Freundlich	K_F (((mg$^{1-(1/n)}$L$^{1/n}$)g^{-1}))	15.41
	n	5.120
	R^2	0.99073
	χ^2	3.01319
Redlich-Peterson	K_{RP} (L mg^{-1})	1.947
	α_R((L mg^{-1})$^\beta$)	0.049
	β	0.954
	R^2	0.9985
	χ^2	0.48748

Conclusion

The styrene-divinylbenzene copolymer functionalized with carboxylic acid groups has shown good adsorption capacity for removal MO from aqueous solutions. The kinetic studies indicated that the adsorption of MO onto SDVBF followed the pseudo-second-order model and the equilibrium adsorption data were best fit by the Redlich-Peterson isotherm.

Acknowledgements

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