Sorption of direct dyes from aqueous solution onto a synthetic adsorbent. Kinetic study.

Simona Gabriela Muntean[1], Sergiu Coseri[2], Georgeta Simu[3], Oana Paska[1]

[1]Institute of Chemistry Timisoara of Romanian Academy, 24 B-dul Mihai Viteazul, 300223 Timisoara, Romania;
[2] "Petru Poni" Institute of Macromolecular Chemistry, 41A Grigore Ghica Voda Alley, Iasi, 700487, Romania
[3]University of Medicine and Pharmacy "V. Babeş" Timişoara, Faculty of Pharmacy, Eftimie Murgu 2, 300041 Timişoara, Romania

ABSTRACT

The aim of this work was to investigate the efficiency of copolymer microbeads (styrene-divinylbenzene functionalized with trimethylamonium groups) as adsorbents for removal of direct dyes (orange *OD*, and green *GD*) from aqueous solutions. The influence of initial concentration, and contact time on the adsorption have been investigated. With increasing of the initial dye concentration, the amount of dye adsorbed increased, while the percentage removal decreased, indicated that the dye removal is concentration dependent. The adsorption kinetics of the removal of studied dyes has been investigated. The kinetics of adsorption is described by the first-order Lagergren model, and pseudo second-order. The correlation coefficients (R^2) were used to determine the best fitting kinetic model. The best fits were obtained with the second order kinetic model (higher values of R^2), meaning that the adsorption process for *OD* and *GD* dyes removal, can be described by the pseudo-second order kinetic model.

Keywords: Direct Dye; Adsorption; Kinetics

Introduction

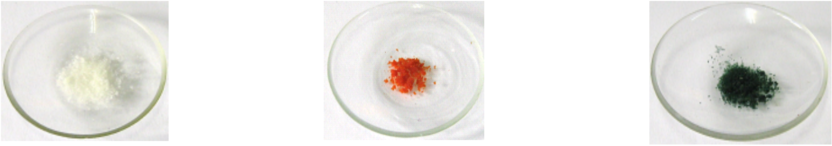
Wastewaters containing direct dyes discharged from various industries, in particular textile industry often causes many environmental problems [1, 2]. Direct dyes are highly soluble in water, so their removal from wastewaters is highly difficult [3]. Even dyes at very low concentrations in the effluent are highly visible, and are considered undesirable. The colored wastewaters are considered toxically for aquatic biosphere, and affect symbiotic process by reducing the photosynthetic activity [4, 5]. Several methods (coagulation/flocculation [6], chemical oxidation [7], membrane separation [8], adsorption [9], electrochemical reduction [10], microbiological decomposition [11], etc.) have been developed to remove color from dye-containing effluent, varying in effectiveness, economic cost and environmental impact. Currently the sorption technique is proven to be an effective and attractive process for the treatment of the coloured wastewaters. Due to their diversity in surface and porosity, high physical-chemistry stability, and regeneration and reuse for continuous process, polymeric adsorbents (polystyrene, polymaleic anhydride, polymethyl methacrylate and their derivatives) have been used as alternative to activated carbon in removal and recovery of organic pollutants from industrial wastewaters [12, 13].

The aim of the present work was to study the efficiency of copolymer microbeads, as adsorbent to remove direct dyes from aqueous solutions. For this purpose kinetic studies have been performed. The influences of process variables such as contact time, and initial concentration have been investigated.

Results and discussion

Characterization of copolymer microbeads

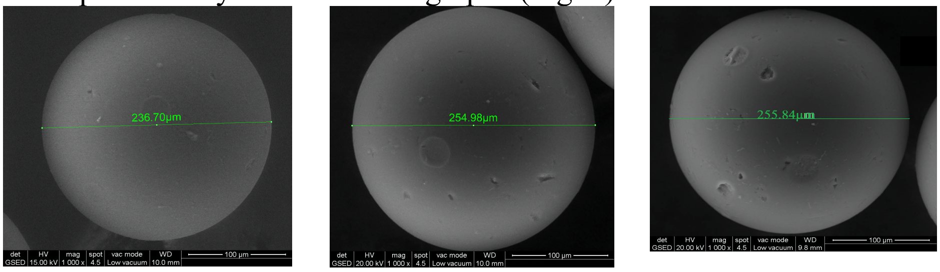
The samples of StDVB-NMe microbeads, before and after dye attachment, are presented in Figure 1.



(a) (b) (c)

Fig. 1. Samples of: (a) StDVB-NMe microbeads, (b) *OD* dye attached to StDVB-NMe, and (c) *GD* dye attached to StDVB-NMe

The surface morphology of the CoNMe microbeads, before and after adsorption experiments, are emphasized by electron micrographs (Fig. 3)



(a) (b) (c)

Fig. 2. SEM images for: (a) StDVB-NMe; (b) StDVB-NMe with *OD* dye; (c) StDVB-NMe with *GD* dye

As seen in Figure 2, the microbeads have a uniform and spherical form with almost compact structure and smooth surface characteristics.

The elemental analysis of the unmodified StDVB-NMe and dye-attached StDVB-NMe beads were carried out, and the attachment of the dyes were confirmed by an increase of the nitrogen content from 4.9 % in the original material to 5.8 % in StDVB-NMe with *OD* dye, and 5.4 % in StDVB-NMe with *GD* dye respectively.

Effect of initial dye concentration and agitation time

Effects of contact time on the adsorption capacity of StDVB-NMe at different initial dye concentrations are presented in Fig. 3, and Table 1. As shown in Figure 3, the adsorption is rapid in the initial stages, and after reaching the equilibrium, remained nearly constant, due to the saturation of the active centre available for `dye on the adsorbent surface.

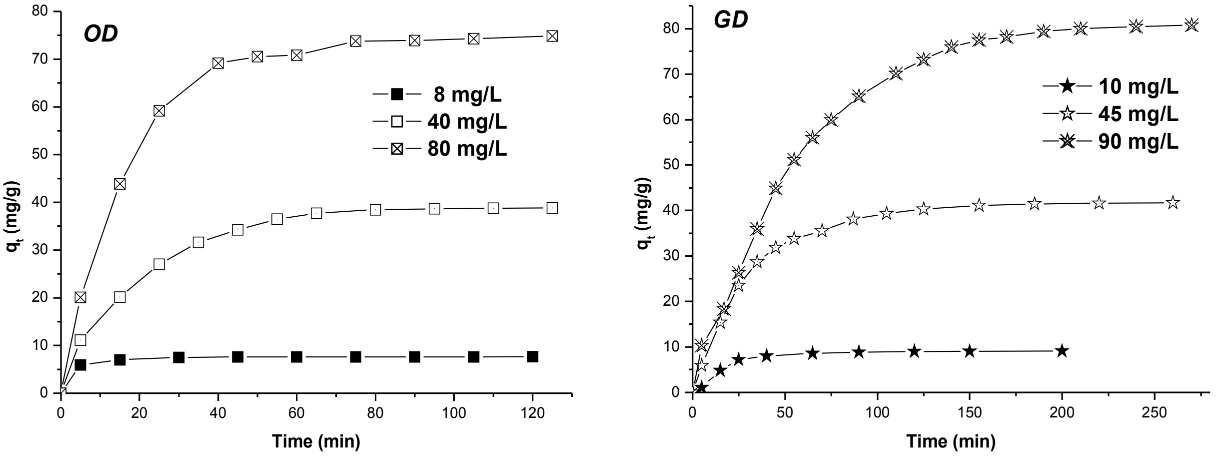


Fig. 3. Adsorption of studied dyes (*OD*, *GD*) at different initial dye concentrations.
Conditions: adsorbent dose 100mg/100mL; temperature 30±1°C, and pH 7.21.

Table 1. Amount and percentage of adsorbed dye

Dye	Dye concentration (mg/L)	q_e (mg/g)	t_e (min)	η (%)
OD	8	7.66	35	99.05
	40	39.11	75	98.13
	80	77.32	90	97.99
GD	10	9.07	95	98.53
	45	42.02	140	89.47
	90	81.48	210	88.47

Conditions: pH 7.21; temperature 30±1°C

The uptake of the studied dyes (mg/g) increased with the increase in initial concentration, while the percentage removal decreased (Table 1), indicated that the dye removal is concentration dependent. The necessary time for reaching the equilibrium increased with increasing the dye concentration, and with increasing the molar mass of investigated dyes *OD* < *GD*.

Adsorption kinetics

The adsorption kinetics of investigated dyes from aqueous solution on StDVB-NMe microbeads has been investigated. The experimental results were analyzed using the first-order Lagergren model and pseudo second-order kinetic model. The first-order rate expression of Lagergren (1) was used for determined the rate constants of first order adsorption k_1 (min^{-1}), for the removal of all three dye by investigated adsorbent:

$$\log(q_e - q) = \log q_e - \frac{k_1}{2.303}t \tag{1}$$

where: q_e and q are the amount of dye adsorbed on adsorbent at equilibrium and any time t, respectively (mg/g). The plot of $log(q_e-q)$ versus t will give a straight line, and the value of k_1 can be obtained from the slope of the graph (Figure 4).

The second-order kinetic model is expressed as:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (2)$$

where: k_2 is the pseudo-second-order equilibrium rate constant (g/mg min). A plot of t/q as a function of t is linear, and the value of k_2 is determined from the slope and intercept (Figure 5).

The correlation coefficients (R^2) were used to determine the best fitting kinetic model.

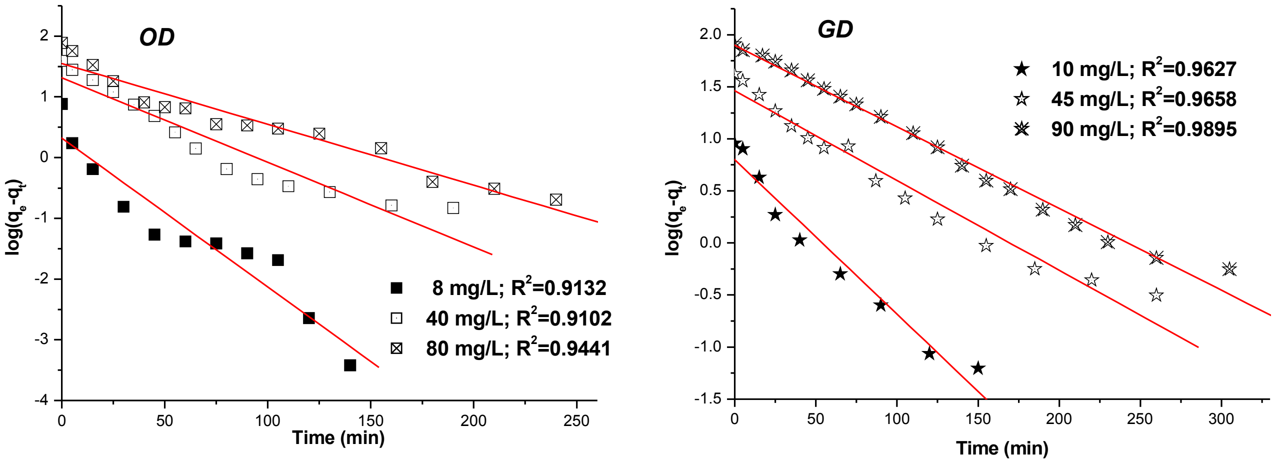


Fig. 4. Lagergren plot for the adsorption of *OD*, and *GD* dye on StDVB-NMe

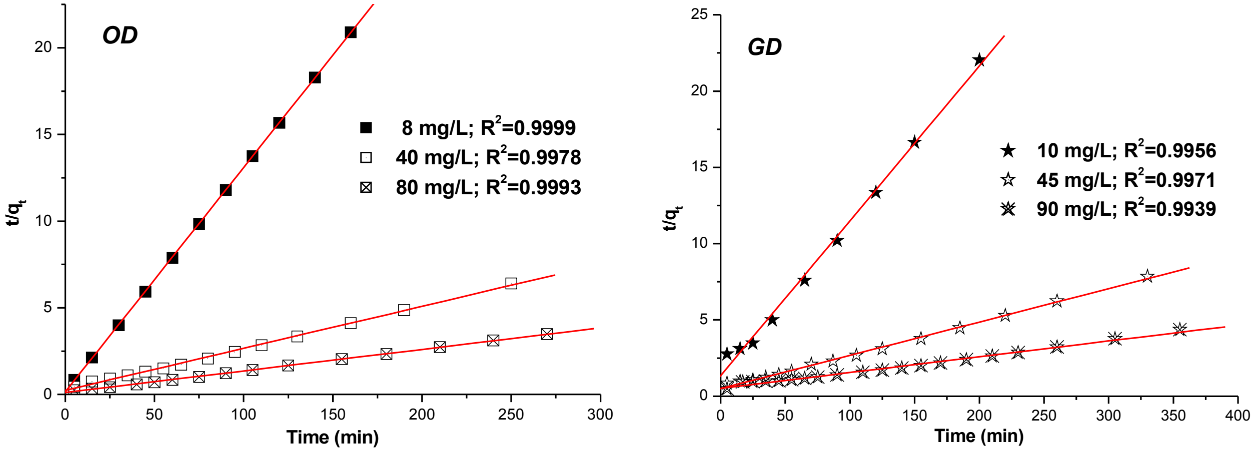


Fig. 5. Second-order kinetic model fitting for the adsorption of *OD*, and *GD* dye on StDVB-NMe.

Data obtained gave poor fits with the first order model, but very good fits with the pseudo-second order model for both systems, and at different initial concentration, as shown by the correlation coefficient (Figure 4, and Figure 5). The correlation coefficients for the linear plots of t/qt against time from the pseudo-second order rate law are greater than 0.993. This suggests that the adsorption of studied direct dyes onto copolymer microbeads follows the pseudo-second order model reactions.

The computed results obtained from the first and second order kinetic models, at different initial concentration of studied dyes are presented in Table 2.

Table 2. Comparison of experimental and calculated q_e values, and first order and pseudo-second order adsorption rate constants, for the adsorption of studied dyes on StDVB-NMe

Dye	Initial dye concentration (mg/L)	q_e (exp) (mg/g)	First order kinetic model		Second order kinetic model	
			q_e (calc) (mg/g)	k_1 x 10^{-2} (min^{-1})	q_e (calc) (mg/g)	k_2 x 10^{-2} (g/mg min)
YD	8	7.66	2.09	5.645	7.72	11.47
	40	39.11	20.65	2.303	41.27	0.244
	80	77.32	35.6	2.309	80.26	0.134

VD	10	9.07	6.31	3.418	9.84	0.773
	45	42.02	28.95	1.985	45.81	0.096
	90	81.48	79.47	1.808	83.81	0.026

Conditions: temperature 30ºC; adsorbent dose 100 mg/100mL; pH 7.11.

An increase in the initial dye concentration reduces kinetics of studied dyes sorption as shown in Table 2.

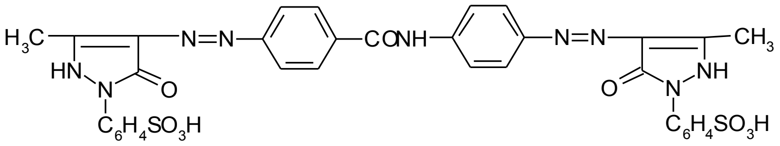
The mechanism of adsorption onto copolymer was deduced to be chemisorption and the rate-limiting step is being controlled mainly by external mass transfer.

In **conclusion**, from the obtained date we can estimate that the dye removal process can be performed with good results using StDVB-NMe microbeads as adsorbent. The adsorption process for the studied direct dyes removal, can be described by the pseudo-second order kinetic model.

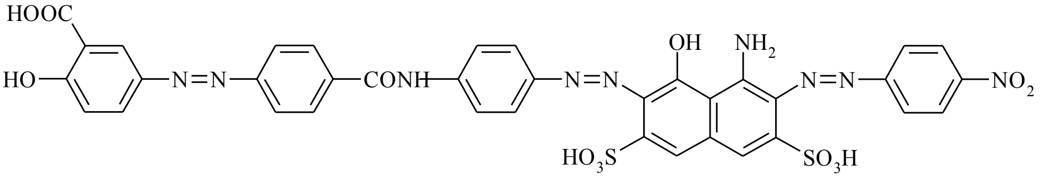
Experimental

Materials

Two types of direct dyes were used as adsorbate: a symmetrical disazo dye (*OD*) and a trisazo dye (*GD*). The chemical structures of the investigated dyes are shown in Figure 6. The synthesis and characterization of the studied dyes were presented in previous papers [14, 15].



OD



GD

The dyes were purified by several recrystallizations from distilled water and characterized by thin layer chromatography and UV-Vis spectroscopy and mass spectroscopy (FAB-MS).

For dyes removal we investigated a copolymer of styrene-divinylbenzene with quaternary ammonium functional groups supplied in the chloride form as counter-ions, (strongly anion exchanger resin).

Physico-chemical determinations

UV-visible absorption spectra of the dyes were recorded using a CECIL CE 7200 Spectrophotometer in the wavelength range 250 to 750 nm.

The structural characterization of the copolymer microbeads, before and after dye attaching, was performed by environmental scanning electron microscopy (ESEM). The ESEM studies were performed on Quanta 200 instrument. Samples were fixed by means of colloidal silver on copper supports. The samples were covered with a thin layer of gold, by sputtering (EMITECH K 550x). The coated surface was examined by using an Environmental Scanning 200, operating at 5 KV with secondary electrons in High Vacuum Mode.

The estimation of the nitrogen content in the StDVB-NMe and dye-attached StDVB-NMe beads has been performed by Energy Dispersive X-ray (EDX) analysis on the Quanta 200 (FEI) electron microscope equipped with EDX system.

Method

The dyes adsorption on the copolymer microbeads was studied in aqueous solutions. For dye immobilization on the copolymer microbeads (StDVB-NMe), 100mL of dye solution, and 0,1g copolymer were stirred magnetically at 250 rpm. The mixture was maintained under continuous stirring for a specific time *t* (equilibrium time). After reaction, the colored microspheres were separated through filtration, washed with distilled water (2×20 mL), and dried at 40°C for 24 hour.

The effect of initial concentration of the dye on the adsorption study was carried out using solutions of dyes with different concentrations ranging from $1 \cdot 10^{-5}$ M to $1 \cdot 10^{-4}$ M.

In the kinetic experiment, the changes of absorbance were determined at certain time intervals (0÷400 min) during the adsorption process.

The amount of adsorbed dye per unit copolymer (mg dye/g dry copolymer) was calculated using relation (3):

$$q_t = \frac{(C_0 - C_t) \cdot V}{W} \qquad (3)$$

where: q_t is the amount of dye adsorbed onto the copolymer unit at time *t* (mg/g), C_0 and C_t are the dye concentration in solution at initial time and at equilibrium (mg/L), V is the solution volume (L), and W is the amount of copolymer (g).

The percentage of dye removal (η) was evaluated using relation (4):

$$\eta = \frac{C_0 - C_e}{C_0} \times 100 \qquad (4)$$

where C_e is dye concentration at equilibrium (mg/L).

Acknowledgement

S. Coseri thanks POSDRU, the poject „Fondul Social European – Program de burse postdoctorale Cristofor I. Simionescu" – ID 55216.

References

1. Crini G., Badot P-M. (2008) *Prog. Polym. Sci.*, ***33***, 399-447.
2. Ahmad A.A., Hameed B.H., Aziz N. (2007) *J. Hazard Mater.*, ***141***, 70-76.
3. Prival M.J., Bell S.J., Mitchell V.D., Peipert M.D., Vaughan V.L. (1984), *Mutat. Res.,* ***136***, 33 -47.
4. Sanghi R., Bhattacharya B. (2002) *Color. Technol.*, ***118***, 256-269.
5. Freeman, H.S, Edwards, L.C. (2005) *Color. Technol.* , ***121***(5), 271-274.
6. Shi B., Li G., Wang D., Feng C., Tang H. (2007), *J. Hazard. Mater.*, ***143***, 567-574.
7. Vlyssides A.G., Loizidou M., Karlis P.K., Zorpas A.A., Papaioannou D. (1999), *J. Hazard. Matter.* ***70***, 41-52
8. Akbari A., Remigy J.C., Aptel P. (2002), *Chemical Engineering and Processing*, ***41***, 601-609.
9. Allen S. J., Koumanova B. (2005) *J. Univ. Chem. Technol. Metallurgy,* ***40(3)***, 175-192.
10. Socha A., Sochocka E., Podsiadły R., Sokołowska J., (2006) *Color. Technol.*, ***122***(4), 207-211.
11. Pearce C.L., Lloyd J.R., Guthrie J.T. (2003), *Dyes Pigments*, ***58***, 179-196.
12. Qiu Y., Ling F. (2006) *Chemosphere*, ***64***, 963-971.
13. Dhodapkar R., Rao N.N., Pande S.P., Nandy T., Devotta S. (2007), *React. Functional Polymers,* ***67***, 540-548
14. Grad M., Simu G., Hora S., Chicu S.A., Sisu E. (2004), *Chem. Bull. "Politechnica" Univ. (Timisoara)*, ***49(63)***, 31-34.
15. Simu G., Funar-Timofei S., Hora S., Kurunczi L. (2004), *Mol. Crys. Liq. Cryst.*, ***416***, 97-104.