

American Chemical Science Journal
4(5): 638-656, 2014

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Biosorption of Synthetic Dyes on Spruce Wood Shavings from Binary Solutions: A Comparison of Equilibrium Models

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Author's contribution

This whole work was carried out author P.J.

Original Research Article

Received 27 January 2014
Accepted 25th February 2014
Published 16th April 2014

ABSTRACT

Aims: To compare various models describing the sorption of synthetic dyes in multicomponent systems. For selected models, their predictive ability (an ability to predict the sorption behavior in multicomponent systems from the model parameters obtained in the single-component systems) was examined.

Place and Duration of Study: University of J. E. Purkyně in Ústí nad Labem, Faculty of the Environment, Czech Republic, January 2012 to June 2013.

Methodology: Equilibrium sorption experiments were performed in a batch arrangement, the dye concentrations were determined by spectrophotometry and HPLC, and the experimental data were evaluated by the method of non-linear regression.

Results: The single-component equilibrium data was evaluated successfully with the three-parameter isotherm equations, such as the Langmuir-Freundlich isotherm. To describe the experimental dependencies for multicomponent systems, various isotherms can be used (derived mostly from the well-known single-component isotherms), but not all of them are capable to predict the dye sorption in multicomponent systems from the model parameters obtained in the single-component system. To compare the predictive ability of various models, an Average Relative Deviation (ARD) and Root Mean Squared Deviation (RMSD) were used as estimators.

Conclusions: Untreated wood shavings from *Picea abies* are applicable as a low-cost non-conventional sorbent for the removal of synthetic dyes from aqueous solutions. The

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sorption of Egacid Orange (Acid Orange 7), Egacid Yellow (Acid Yellow 11) and Acid Red 88 as representatives of anionic azodyes with strongly acidic sulfonic group was studied in a single-component system, as well as in binary systems. Various isotherm equations were used to fit the equilibrium experimental data in both systems. Among the examined models, the Toth multicomponent isotherm exhibited quite good prediction ability, whereas the predictions based on a widely used competitive Langmuir model were rather poor.

Keywords: Biosorption; wood shavings; sulfonic azodyes; sorption isotherms; binary systems; predictive models.

1. INTRODUCTION

Synthetic dyes are widely used in many areas including textile, paper, leather, printing and other industries. The textile finishing consumes large volumes of water in various wet processes and produce great amounts of wastewaters polluted with residual colorants. The emitted dyes represent a serious environmental problem because of their poor biodegradability in conventional wastewater treatment plants. In addition to the biological treatment [1], many physical and chemical methods are commonly employed for the dye removal from wastewaters, including coagulation, flocculation, filtration, oxidation or reduction, complex-formation or neutralization [2]. Some advanced processes, such as photocatalytic decomposition of organic pollutants [3] or solar photo-Fenton oxidation [4] are studied extensively in recent time, but there are insufficient experiences with their large-scale application in the treatment of real colored wastewaters.

Adsorption techniques employing solid sorbents are widely used to remove certain classes of chemical pollutants from aqueous solutions. Currently, the most commonly used adsorption agent in industry is activated carbon. However, relatively high operating costs and problems with regeneration of the spent carbon hamper its large-scale applications. Therefore, an extensive research is carried out in recent time with the goal to find alternative and less expensive materials (sorbents) capable to remove chemical substances from waters. Natural materials and waste materials from industry or agriculture are typically classified as non-conventional sorbents because of their inexpensive production and local availability. Many of them have been tested for the dye removal, e.g. steel plant slag [5], fly ash [6], red mud [7], low-rank coal [8], or carbonaceous adsorbents from waste tyres [9].

Biosorption employing dead biomass, together with bioaccumulation and biotransformation [10] that utilize living microorganisms, have been increasingly used to bind and remove not only metal ions [11], but also organic pollutants [12] including synthetic dyes [13] – a utilization of sugarcane bagasse [14,15], rice milling waste [16], peanut husk [17,18] or coffee residues [19,20] for the wastewater decolouration may serve as examples. Sawdust and related waste materials from timber industry as relatively abundant, easily available and inexpensive sorbents have been used to remove unwanted chemical substances from waters, including dyes, oils, toxic salts and heavy metals – see a review of Shukla et al. [21]. Several authors tested various kinds of wood-based sorbents, e.g. pine sawdust [22], cedar sawdust [23], or beech wood sawdust [24], for the removal of both basic as well as acid dyes from aqueous solutions. To improve a sorption ability of wood-derived materials and other biosorbents towards various kinds of chemical pollutants, some more or less sophisticated pre-treatment procedures have been developed, including a relatively simple pre-treatment with mineral acids and bases or their salts. We have demonstrated in our previous work [25]

that spruce wood shavings chemically modified with HCl, Na₂CO₃ and Na₂HPO₄ are capable to remove both basic and acid dyes from aqueous solutions. Because the chemical pre-treatment may increase the cost of the sorbent substantially and thus abolish the main advantage of the non-conventional sorbents, we have focused in the following studies on an application of the untreated shavings.

The cell walls of the untreated wood shavings mainly consist of cellulose and lignin, and contain many hydroxyl groups that are effective in the binding of cationic species – typically heavy metal cations [12], presumably also basic (cationic) organic dyes [26]. Acid azodyes, on the other hand, exhibit an anionic nature because of the presence of one or more sulfonic groups, fully dissociated over an almost whole accessible pH range. Therefore, the above mechanism (cation-exchange) of the dye retention is hardly feasible in the case of the sulfonic azodye sorption on wood-based sorbents. It was speculated that the acid dye sorption is a physical process, in which non-specific (hydrophobic) interactions predominate, although coulombic repulsion forces play certainly a significant role [26]. Hu et al. [27] in their recent paper demonstrated clearly an importance of both hydrophobic and electrostatic interactions for the sorption of dye molecules bearing positive or negative charges (Methyl Orange was used as a representative of acid dyes). Blackburn [28] examined in detail possible interactions between the dye molecule and some natural polysaccharides, and showed that both hydrophobic and hydrophilic parts of the dye molecule take part in the sorption process. The dye sorption is viewed as a result of a complex interplay between many diverse attractive and repulsive forces, involving non-specific hydrophobic interactions between non-polar (less-polar) parts of sorbent and sorbate, coulombic attractive/repulsive forces between ionizable groups, intermolecular hydrogen bonding (Yoshida H-bonding, dipole-dipole bonding), van der Waals forces, and some others. Possible interactions between the sulphonicazodyes Egacid Orange and Egacid Yellow, and cellulose and lignin as the main wood constituents, are depicted in Fig. 1.

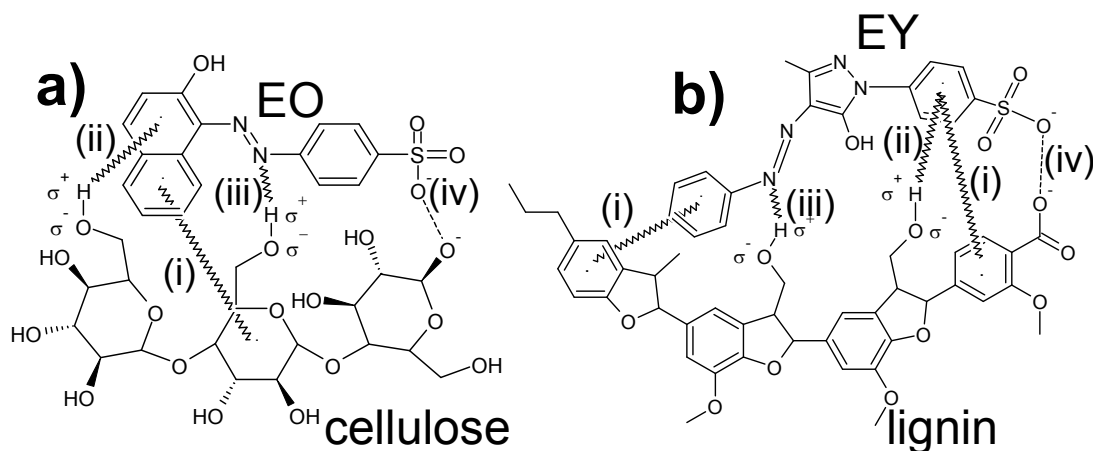


Fig. 1. Sorption of azodyes on wood.

Possible interactions between EO and cellulose (a), and between EY and lignin (b). (i) – hydrophobic interactions between less-polar parts in the sorbent and sorbate; (ii) – hydrogen bonding between hydroxyl groups and aromatic rings; (iii) – dipole-dipole hydrogen bonding interaction between hydroxyl groups and electronegative –N=N– groups; (iv) – repulsive forces between ionized groups.

Many papers have been published on the sorption of synthetic dyes on various synthetic and natural sorbents. However, a substantial part of these studies was performed with relatively

simple single-component model solutions, which is in a direct contrast with a complex multicomponent composition of real wastewaters. The evaluation of the sorption equilibria in multicomponent systems remains still a not satisfactorily solved problem, despite that many approaches can be found in literature, e.g. in [29-33]. Whereas several models are capable to fit equilibrium data in a multicomponent system (descriptive models), only a few of them are able to predict the sorption behavior in the multicomponent system from the data obtained in single-component systems (predictive models). In this work we compared several models describing the dye sorption in the binary systems, and for selected models we tested their predictive capability for the multicomponent biosorption of anionic azodyes on wood shavings.

2. MATERIALS AND METHODS

2.1. Sorbent

The wood material from *Picea abies* for the preparation of the sorbent was obtained from the local sawmill Riso (Sokolov, Czech Republic) in the form of thin shavings (chippings) with a thickness of ca. 0.1 – 0.2 mm. Before a further treatment, it was air-dried and size-classified by sieving to obtain uniform chippings with a typical diameter about 1 – 3 mm. The sorbent was washed with deionized water to remove impurities and very fine dusty particles, dried at 40°C overnight and stored in tightly closed PE bottles.

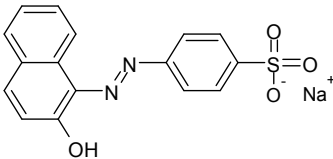
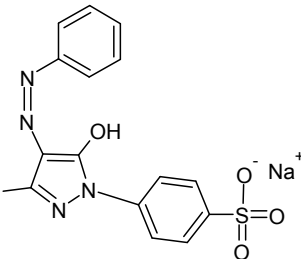
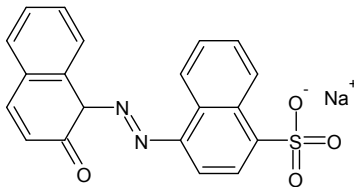
2.2. Chemicals

The azodyes used in this study are listed in Table 1. Egacid Orange (EO) and Egacid Yellow (EY) were obtained from Spolchemie, Usti nad Labem, Czech Republic, Acid Red 88 (AR88) was obtained from Sigma-Aldrich, Steinheim, Germany. Stock solutions of the dyes (typically 10 mmol/L) were prepared by dissolving the respective sodium salts in water, the working solutions were prepared by diluting before the sorption experiments. Other chemicals were of reagent-grade purity, obtained from Lach-Ner, Neratovice, Czech Republic. The solutions were prepared in deionised water from the system Demi Ultra 20 (Goro, Prague, Czech Republic) utilizing reverse osmosis and mixed-bed ion-exchange for the water purification.

2.3. Sorption Experiments

Equilibrium sorption experiments were carried out by shaking a known amount of the sorbent (typically 1 g) with 50 mL of the solution containing desired concentrations of the dyes. The dye solution together with the sorbent were agitated in the closed PE bottle for 24 hours using a horizontal shaker LT 2 (Kavalier, Sázava, Czech Republic) with an intensity of agitation 200 min⁻¹. It was checked that this time is sufficient to reach the sorption equilibrium. Then the solid phase was separated by sedimentation or filtration through 0.45 µm nylon microfilter, the concentrations of the dyes in the solution were determined spectrophotometrically or chromatographically, and the sorbed amounts were calculated. The equilibrium experiments in binary systems were carried out in an essentially the same arrangement as the experiments in single-component system, varying the ratio (initial concentrations) of the respective components.

Table 1. Azodyes used in this study.

Dye	Egacid Orange (EO)	EgacidYellow (EY)	Acid Red 88 (AR88)
C.I. Generic name	Acid Orange 7	Acid Yellow 11	Acid Red 88
C.I. Number	15510	18820	15620
Formula	$C_{16}H_{11}N_2NaO_4S$	$C_{16}H_{13}N_4NaO_4S$	$C_{20}H_{13}N_2NaO_4S$
Molecular weight	350.30	380.36	400.38
Structure			

2.4 Analyses and Data Evaluation

Concentrations of the dyes in single-component solutions were determined spectrophotometrically after a proper dilution using the UV/Vis spectrophotometer Cary 50 (Varian, Mulgrave, Australia). Liquid chromatography in a reversed-phase ion-interaction mode was used for the determination of individual dye concentrations in binary solutions. The liquid chromatograph consisted of the high pressure pump LaChrom L-7100 (Merck/Hitachi, Hitachi High-Technol. Corp., Tokyo, Japan), the Rheodyne 7125 injection valve with 20 μl sampling loop, vacuum degasser, and the variable wavelength UV detector LaChrom L-7400 (Merck/Hitachi) operating at 250 nm. Chromatographic separations were carried out on the Hibar column 125 \times 4 mm packed with octadecyl-bonded stationary phase Purospher STAR, RP-18e, 5 μm (Merck, Darmstadt, Germany) with mobile phase consisting of 75 % (v/v) methanol and 25 % (v/v) 0.2 mmol/L tetrabutylammoniumhydrogensulfate, the flow rate was 1 ml/min. It was confirmed that both analytical methods gave comparable results with a relative standard deviation of repeatability ranging from ca. 2 to 5 % in the given working range. MS Excel and DataFit 8.1 (Oakdale Engineering, USA) software were used for calculations and data evaluations.

3. RESULTS AND DISCUSSION

3.1. Single-component System

An example of the single-component isotherm for EO is shown in Fig. 2. The equilibrium data are usually evaluated according to the simplest models – Langmuir or Freundlich isotherm—after a proper transformation (“linearization”) of the isotherm equation (see Fig. 3).

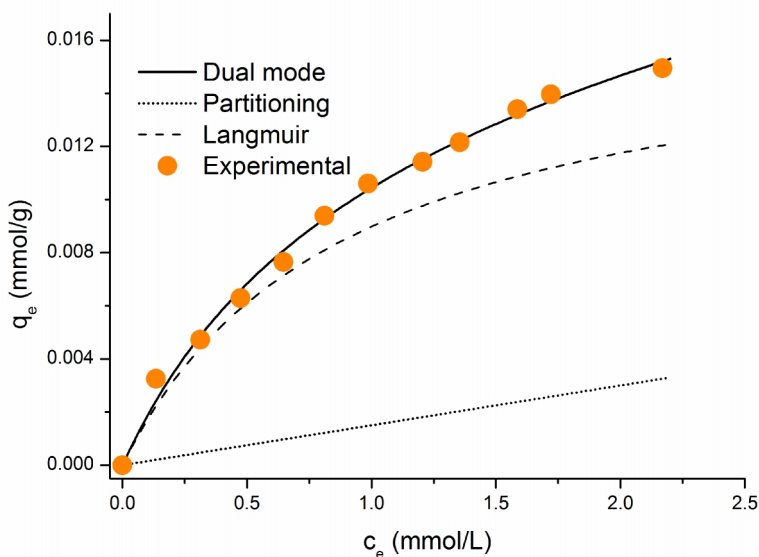


Fig. 2. Sorption isotherm for EO on spruce wood shavings.

Experimental data fitted with the curve calculated from the Dual Mode model. Dotted line represents a contribution of partitioning, whereas dashed line represents a contribution of Langmuir adsorption.

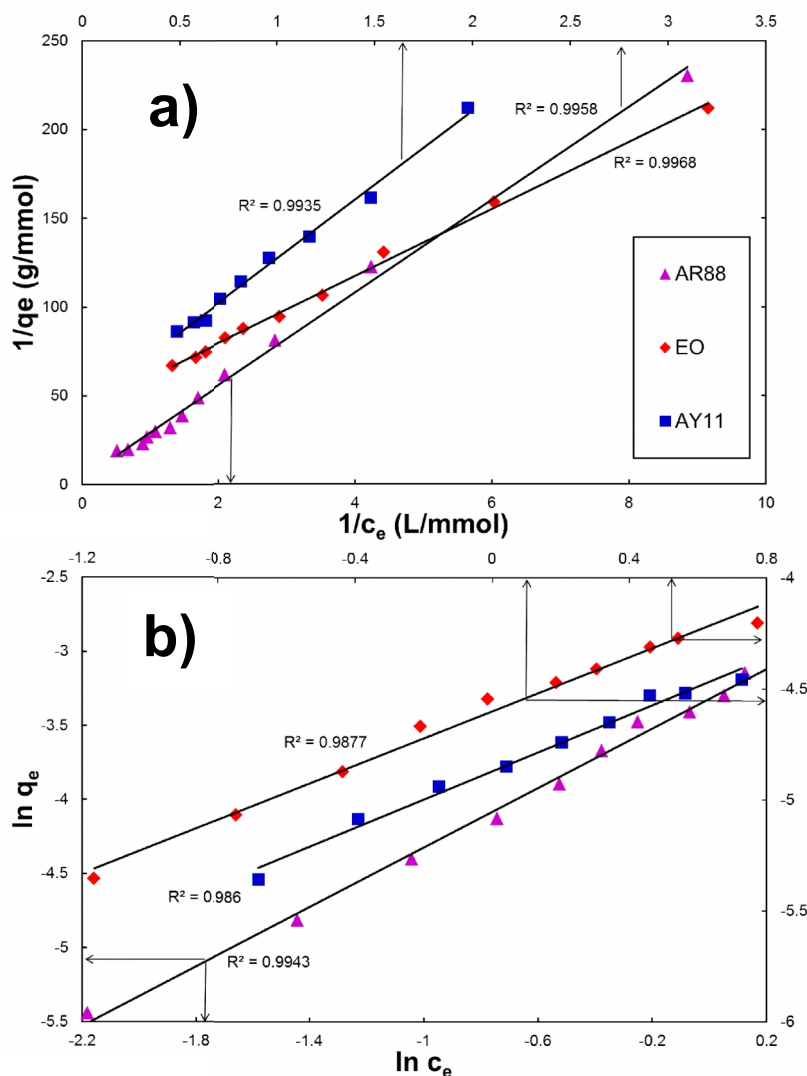


Fig. 3. Sorption isotherms for the sorption of EO, EY and AR88 evaluated according to the Langmuir (a) and Freundlich isotherm after linearization.

Simple Langmuir and Freundlich isotherms do not take into account a variety of mechanisms and binding forces possibly effective in the dye sorption. Stevertson and Banerjee [34] applied a slightly different approach to describe the sorption of organic compounds (2,4,5-trichlorophenol) on softwood fibers – in the Dual Reactive Domain Model combined two terms corresponding to two independent mechanisms effective in the sorbate retention, namely linear partitioning and non-linear adsorption of the Langmuir type. In Fig. 2, the sorption isotherm for EO was fitted with the dual-mode isotherm equation; a deconvolution of the fitted curve into linear (partitioning) and non-linear (Langmuir) components is shown here as well. It seems that both mechanisms contribute to the dye sorption on wood shavings. However, the partitioning term was negligible in the case of the sorption of the other examined dyes. Most of the isotherm equations (with exceptions of the Langmuir and Freundlich isotherms) contain three parameters reflecting the capacity of the sorbent, an

affinity between sorbent and sorbate, and a “heterogeneity” (in a broad sense) – see commonly used Langmuir-Freundlich isotherm. The so-called heterogeneity parameter may reflect a surface heterogeneity of the non-conventional sorbents, but also a stoichiometry of the binding (e.g. surface-complexation) reaction. It is generally believed that the Langmuir-Freundlich equation is more accurate over a wide concentration range than the Langmuir or Freundlich isotherms and provides more reliable estimations of the limiting value q_m (maximum sorption capacity), which is quite understandable, as it contains three adjustable parameters, in contrast to the Langmuir and Freundlich equations containing only two parameters. Note that the Langmuir-Freundlich isotherm (similarly to the Freundlich one) does not convert to a simple linear equation (Henry’s law) for low concentrations ($c_e \rightarrow 0$). Despite that the Langmuir-Freundlich isotherm belongs to the most popular isotherms with numerous applications in environmental chemistry [35]. In addition to the mentioned isotherms, several other models were tested for comparison; the isotherm equations commonly used to fit the equilibrium adsorption data are listed in Table 2.

Table 2. Single-component isotherms.

Name	Equation	Model parameters	References
Langmuir	$q_e = \frac{q_m K c_e}{1 + K c_e}$	q_m – maximum sorption capacity K – sorption affinity	[31,35]
Freundlich	$q_e = K_f c_e^n$	K_f – affinity parameter n – heterogeneity parameter	[31,35]
Langmuir-Freundlich	$q_e = \frac{q_m K c_e^n}{1 + K c_e^n}$	q_m – maximum sorption capacity K – sorption affinity n – heterogeneity parameter	[31,32,35]
Redlich-Peterson	$q_e = \frac{a_{RP} c_e}{1 + b_{RP} c_e^n}$	a_{RP} – Redlich-Peterson parameter b_{RP} – equilibrium constant n – heterogeneity parameter	[32]
Toth	$q_e = \frac{q_m K c_e}{(1 + K c_e^t)^{1/t}}$	q_m – maximum sorption capacity K – sorption affinity t – heterogeneity parameter	[31,35]
Khan	$q_e = \frac{q_m K c_e}{(1 + K c_e)^n}$	q_m – maximum sorption capacity K – sorption affinity n – heterogeneity parameter	[32]
Radke-Prausnitz	$q_e = \frac{a_r b c_e^p}{(a_r + b c_e^p)^{p-1}}$	a_r – maximum sorption capacity b – equilibrium constant p – Radke-Prausnitz parameter	[32]
Dual mode	$q_e = K_p c_e + \frac{q_{m,L} K_L c_e}{1 + K_L c_e}$	$q_{m,L}$ – sorption capacity of active sites (in the Langmuir sense) K_L – sorption affinity (in the Langmuir sense) K_p – partition coefficient	[34]
Polynomial	$q_e = \frac{q_m (A c_e + 2B c_e^2)}{1 + A c_e + B c_e^2}$	q_m – maximum sorption capacity A, B – parameters of polynomial isotherm	[30]

The isotherm parameters calculated from the experimental data using a non-linear regression are summarized in Table 3.

Table 3. Parameters of single-component isotherms

Isotherm/Parameter	EO	EY	AR88
Langmuir			
q_m (mmol/g)	0.0237 (0.0077) ^{a)}	0.0234 (0.0010)	0.1062 (0.0066)
K (L/mmol)	0.7976 (0.0078)	0.4980 (0.053)	0.5187 (0.0507)
SDEC $\times 10^4$	3.32	2.27	10.2
R^2	0.9939	0.9958	0.9951
Freundlich			
K_f (L ⁿ /mmol ⁿ⁻¹ g)	0.0118 (0.0002)	0.0084 (0.0001)	0.0351 (0.0006)
n	0.6446 (0.0185)	0.7965 (0.0187)	0.682 (0.0036)
SDEC $\times 10^4$	3.68	3.93	18.7
R^2	0.9948	0.9963	0.9850
Langmuir-Freundlich			
q_m (mmol/g)	0.0655 (0.0089)	0.0188 (0.0020)	0.0834 (0.0087)
K (L ⁿ /mmol ⁿ)	0.2096 (0.0752)	0.7910 (0.1685)	0.7867 (0.1566)
n	0.87 (0.06)	1.20 (0.10)	1.17 (0.08)
SDEC $\times 10^4$	2.76	1.90	8.70
R^2	0.9966	0.9970	0.9967
Redlich-Peterson			
a_{RP} (L/g)	0.0266 (0.0076)	0.0101 (0.0007)	0.0451 (0.0016)
b_{RP} (L ⁿ /mmol ⁿ)	1.5673 (0.7490)	0.2887 (0.1026)	0.2129 (0.0486)
n	0.74 (0.22)	1.39 (0.28)	1.76 (0.23)
SDEC $\times 10^4$	3.01	2.00	6.73
R^2	0.9976	0.9967	0.9981
Toth			
q_m (mmol/g)	0.0401 (0.0200)	0.0214 (0.0017)	0.0939 (0.0064)
K (L/mmol)	0.8059 (0.0684)	0.4669 (0.0586)	0.4747 (0.0454)
t	0.52 (0.33)	1.61 (0.45)	2.13 (0.40)
SDEC $\times 10^4$	2.91	1.99	7.12
R^2	0.9958	0.9967	0.9978
Khan			
q_m (mmol/g)	N	0.8551 (0.0037)	2.6980 (0.4084)
K (L/mmol)	N	0.0125 (0.0084)	0.0189 (0.0023)
n	N	25.03 (10.12)	17.64 (5.58)
SDEC $\times 10^4$		2.03	7.60
R^2		0.9966	0.9923
Radke-Prausnitz			
a_r (mmol/g)	0.4881 (0.5654)	0.2022 (0.0888)	2.7367 (0.4053)
b_r (L/mmol)	0.0206 (0.0539)	0.0620 (0.0387)	1.2787 (0.4517)
p	0.56 (0.06)	0.69 (0.10)	0.68 (0.08)
SDEC $\times 10^4$	3.71	3.95	18.8
R^2	0.9931	0.9968	0.9849
Dual mode			
$q_{m,L}$ (mmol/g)	0.0170 (0.0026)	0.0753 (0.0089)	0.5554 (0.7464)
K_p (L/g)	0.0015 (0.0010)	-0.0057 (N)	-0.0444 (N)
K_L (L/mmol)	1.12 (0.19)	0.22 (0.019)	0.17 (0.14)
SDEC $\times 10^4$	3.22	2.03	7.18
R^2	0.9973	0.9966	0.9978
Polynomial			
q_m (mmol/g)	0.0297 (0.0890)	0.0467 (4.223)	0.0686 (0.0039)
A (L/mmol)	0.5642 (1.695)	0.2018 (0.1828)	0.6483 (0.0431)
B (L ² /mmol ²)	0.0414 (0.5780)	0.0060 (2.349)	0.5193 (0.1785)
SDEC $\times 10^4$	3.32	1.99	7.49
R^2	0.9971	0.9923	0.9971

a) standard errors given in parentheses, SDEC – standard deviation error in calculation ($SDEC = \sqrt{RSS/n}$), RSS – residual sum of squares, R^2 – coefficient of multiple determination, N – non-realistic estimates (in the case of the dual-mode isotherm, the negative values were formally accepted and used for the sorption predictions in binary systems)

3.2. Binary systems EO-EY and EO-AR88

The sorption isotherms of EO on sawdust were measured in binary systems in a similar way as in the single-component system. The dependencies of the sorbed amounts of EO on the equilibrium EO concentration were measured for various initial concentrations of the other dye (EY or AR88); the experimental data are shown in Fig. 4.

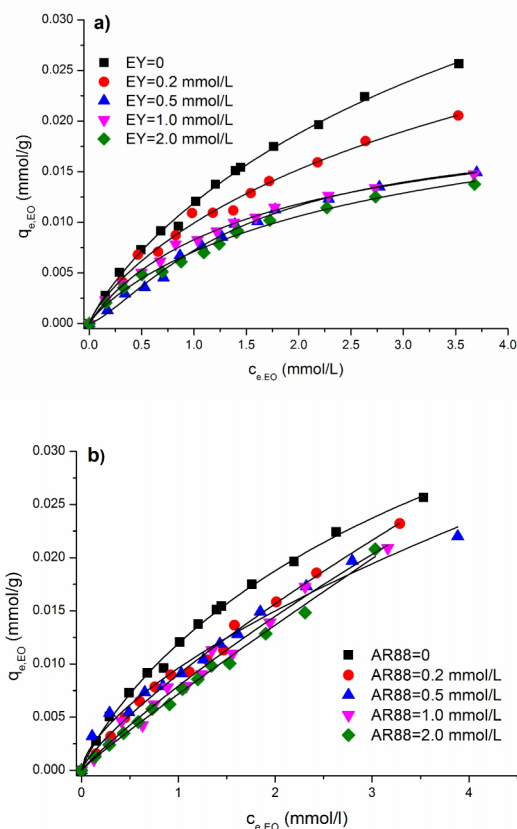


Fig. 4. Sorption isotherms for the sorption of EO in the presence of various initial concentrations of EY (a) or AR88 (b).

Various models can be used to describe the dye sorption from multicomponent systems; some of the binary isotherms are listed in Table 4. Using experimental data $c_{e,EO}c_{e,EY}$ ($c_{e,AR88}$) vs. $q_{e,EO}$ the model parameters were estimated by the method of a non-linear regression analysis (Table 5). As can be seen from the values of R^2 (coefficients of multiple determinations) and SDEC (standard deviation errors in calculation), the best fit to the experimental data was achieved with the Langmuir partially competitive, Langmuir-Freundlich and Redlich-Peterson sorption isotherms, which is quite expectable, as these models contain the highest number of adjustable parameters (together with the polynomial adsorption isotherm). A quite good fit was achieved also with the Toth isotherm.

Table 4. Isotherm equations for binary systems

Name	Equation	Model parameters	References
Langmuir competitive	$q_{e,A} = \frac{q_m K_A c_{e,A}}{1 + K_A c_{e,A} + K_B c_{e,B}}$	q_m – maximum sorption capacity K_A, K_B – sorption affinity	[36-38]
Langmuir non-competitive	$q_{e,A} = \frac{q_m (K_A c_{e,A} + K_C c_{e,A} c_B)}{1 + K_A c_{e,A} + K_B c_{e,B} + K_C c_{e,A} c_B}$	q_m – maximum sorption capacity K_A, K_B – sorption affinity K_C – sorption affinity constant related to uncompetitive sorption	[36,37,39]
Langmuir partially competitive	$q_{e,A} = \frac{q_m (K_A c_{e,A} + K_B K_C c_{e,A} c_{e,B})}{1 + K_A c_{e,A} + K_B c_{e,B} + (K_A K_C + K_B K_D) c_{e,A} c_{e,B}}$	q_m – maximum sorption capacity K_A, K_B – sorption affinity K_C, K_D – constants reflecting an affinity of compounds A and B for already occupied sites	[36,37,39]
Langmuir-Freundlich	$q_{e,A} = \frac{q_m K_A c_{e,A}^n}{1 + K_A c_{e,A}^n + K_B c_{e,B}^m}$	q_m – maximum sorption capacity K_A, K_B – sorption affinity n, m – heterogeneity parameters	[36,37]

Redlich-Peterson	$q_{e,A} = \frac{a_{RP} c_e}{1 + b_{RP} c_{e,A}^n + c_{RP} c_{e,B}^m}$	a_{RP} – Redlich-Peterson parameter b_{RP}, c_{RP} – equilibrium constants n, m – heterogeneity parameters	[36,37]
Jain-Snoeyink	$q_{e,A} = \frac{(q_{m,A} - q_{m,B})K_A c_{e,A}}{1 + K_B c_{e,B}} + \frac{q_{m,B} K_A c_{e,A}}{1 + K_A c_{e,A} + K_B c_{e,B}}$	$q_{m,A}, q_{m,B}$ – sorption capacities for compounds A and B K_A, K_B – sorption affinity	[36,40]
Toth	$q_{e,A} = \frac{q_m K_A c_{e,A}}{(1 + K_A c_{e,A}^t + K_B c_{e,B}^t)^{1/t}}$	q_m – maximum sorption capacity K_A, K_B – sorption affinity t – heterogeneity parameter	[41]
Dual mode	$q_{e,A} = K_{p,A} c_{e,A} + \frac{q_{m,L} K_A c_{e,A}}{1 + K_A c_{e,A} + K_B c_{e,B}}$	$q_{m,L}$ – sorption capacity of active sites (in the Langmuir sense) K_A, K_B – sorption affinity (in the Langmuir sense) $K_{p,A}$ – partition coefficient	[42]
Polynomial	$q_{e,A} = \frac{q_m c_{e,A} (A + C c_{e,B} + 2D c_{e,A})}{1 + A c_{e,A} + B c_{e,B} + C c_{e,A} c_{e,B} + D c_{e,A}^2 + E c_{e,B}^2}$	q_m – maximum sorption capacity A, B, C, D, E – parameters of polynomial isotherm	[30]

Subscript A relates to EO, subscript B relates to EY or AR88

Table 5. Parameters of binary isotherms

Isotherm/Parameter	EO - EY	EO - AR88
Langmuir competitive		
q_m (mmol/g)	0.0305 (0.0026) ^{a)}	0.0570 (0.0050)
K_A (L/mmol)	0.5355 (0.0824)	0.2235 (0.0289)
K_B (L/mmol)	0.9837 (0.1384)	0.2235 (0.0289)
$SDEC \times 10^4$	7.58	5.72
R^2	0.9339	0.9718
Langmuir non-competitive		
q_m (mmol/g)	0.0345 (0.0019)	0.0569 (0.0042)
K_A (L/mmol)	0.5858 (0.0658)	0.2468 (0.0277)
K_B (L/mmol)	6.658 (1.420)	4.700 (1.244)
K_C (L/mmol)	1.293 (0.375)	0.5893 (0.1970)
$SDEC \times 10^4$	5.18	4.80
R^2	0.9691	0.9801
Langmuir partially competitive		
q_m (mmol/g)	0.0470 (0.0032)	0.0472 (0.0039)
K_A (L/mmol)	0.3424 (0.0381)	0.3284 (0.0439)
K_B (L/mmol)	3.844 (0.702)	5.375 (1.323)
K_C (L/mmol)	0.2131 (0.0171)	0.1288 (0.0139)
K_D (L/mmol)	0.5216 (0.0654)	0.0392 (0.0286)
$SDEC \times 10^4$	3.67	4.51
R^2	0.9845	0.9824
Langmuir - Freundlich		
q_m (mmol/g)	0.1116 (0.0777)	0.0608 (0.0132)
K_A (L ⁿ /mmol ⁿ)	0.1238 (0.0989)	0.2305 (0.0648)
K_B (L ^m /mmol ^m)	0.7856 (0.1180)	0.6657 (0.0819)
n	0.6854 (0.0629)	0.9748 (0.0652)
m	0.4213 (0.0502)	0.4125 (0.0554)
$SDEC \times 10^4$	4.82	4.39
R^2	0.9733	0.9834
Redlich-Peterson		
a_{RP} (L/g)	0.0198 (0.0037)	0.0313 (0.0236)
b_{RP} (L ⁿ /mmol ⁿ)	0.5531 (0.2824)	1.720 (2.055)
c_{RP} (L ^m /mmol ^m)	1.285 (0.259)	1.511 (1.145)
n	1.03 (0.201)	0.45 (0.16)
m	0.44 (0.06)	0.41 (0.05)
$SDEC \times 10^4$	5.57	4.20
R^2	0.9644	0.9848
Jain-Snoeyink		
$q_{m,A}$ (mmol/g)	0.0108 (0.0022)	0.0541 (0.0417)
$q_{m,B}$ (mmol/g)	0.0023 (0.0019)	0.0526 (0.0617)
K_A (L/mmol)	2.903 (1.073)	0.2362 (0.1980)
K_B (L/mmol)	1.206 (0.154)	0.5065 (0.0559)
$SDEC \times 10^4$	6.68	5.72
R^2	0.9486	0.9718
Toth		
q_m (mmol/g)	0.0790 (0.0151)	0.0707 (0.0067)
K_A (L/mmol)	0.6559 (0.0564)	0.3058 (0.0302)
K_B (L/mmol)	0.3505 (0.0581)	0.2232 (0.0374)
t	0.35 (0.04)	0.40 (0.04)
$SDEC \times 10^4$	4.88	4.53
R^2	0.9726	0.9823
Dual mode		
$q_{m,L}$ (mmol/g)	0.0279 (0.0079)	0.0136 (0.0023)

Table 5 continued

$K_{p,A}$ (L/g)	0.0007 (0.0009)	0.0041 (0.0003)
K_A (L/mmol)	0.6521 (0.2435)	1.167 (0.3667)
K_B (L/mmol)	1.28 (0.53)	3.24 (1.39)
$SDEC \times 10^4$	7.56	4.77
R^2	0.9341	0.9804
Polynomial		
q_m (mmol/g)	0.0184 (0.0018)	N
A (L/mmol)	0.8350 (0.0823)	N
B (L/mmol)	10.126 (1.742)	N
C (L ² /mmol ²)	6.448 (1.322)	N
D (L ² /mmol ²)	0.2898 (0.1075)	N
E (L ² /mmol ²)	0.4693 (0.8735)	N
$SDEC \times 10^4$	3.90	
R^2	0.9825	

^{a)} standard errors given in parentheses, $SDEC$ – standard deviation error in calculation ($SDEC = \sqrt{RSS/n}$, RSS – residual sum of squares), R^2 – coefficient of multiple determination, N – non-realistic estimates. Subscript A relates to EO, subscript B relates to EY or AR88.

Examples of the experimental plots in the binary systems are shown in Figs. 5a and 6a. The Langmuir partially competitive model mentioned above is a typical descriptive model, as it contains some parameters that can not be derived from the single-component isotherms. Some other models (typically the Langmuir competitive isotherm) are classified as “purely predictive” [29], as they allow, at least in principle, to predict the sorption behavior of solutes in multicomponent mixtures using the parameters determined in single-component systems. For the given binary systems of dyes (EO – EY and EO – AR88), we attempted to predict the sorption behavior of EO in the presence of the other dye (EY or AR88) using some of the binary isotherms listed in Table 4 and the model parameters determined in the single-component systems, as listed in Table 3. Examples of the predicted curves are shown in Figs. 5b and 6b. The quality of the prediction was assessed from two points of view: i) as an agreement between the predicted values and the best-fitted curve, and ii) as an agreement between the predicted values and the experimental ones. In both cases, two criteria were used for an evaluation – average relative deviation (ARD) and root mean squared deviation (RMSD) defined by the following equations [43]:

$$ARD(\%) = 100 \times \left(\frac{1}{n} \sum_{i=1}^n \left(\frac{y_{p,i} - y_{0,i}}{y_{0,i}} \right) \right) \quad (1)$$

$$RMSD = \left(\frac{1}{n} \sum_{i=1}^n (y_{p,i} - y_{0,i})^2 \right)^{\frac{1}{2}} \quad (2)$$

n is the number of points ($n=65$), $y_{p,i}$ is the predicted value, $y_{0,i}$ is the best-fitted or experimental value. A comparison of the predictive ability of selected models is given in Table 6. To visualize the concentration regions, in which the predicted isotherm agrees (or disagrees) with the best-fitted curve, the relative deviation (predicted value vs. best-fitted one) was plotted as a function of the concentrations of both dyes in the binary solution; examples are shown in Figs. 5c) and 6c). The plots for squared deviations were constructed in a similar way - see Figs. 5d) and 6d). As can be seen from the values in Table 6, a simple and most popular competitive Langmuir model gives a relatively poor prediction of the sorption of dyes in the given binary systems. On contrary, rather good prediction was obtained with the aid of the Toth isotherm. In this case, however, one must adopt some reasonable rule for an estimation of the global heterogeneity parameter t [32]. In our case,

we utilized the value for EO as the global heterogeneity parameter for the predictions. It is evident that the purely predictive models provide only a rough estimation of the sorption behavior in multicomponent systems. More sophisticated models usually utilize some kind of an “interaction factor”, but their application requires additional measurements in multicomponent systems. Alternative approaches based mainly on the Ideal Adsorbed Solution Theory (IAST) – also purely predictive, but computationally laborious – compared and discussed recently Chan et al. [33].

Table 6. Comparison of predictive models

Model	Prediction vs. best-fit		Prediction vs. experimental data	
	ARD (%)	RMSD (mmol/g)	ARD (%)	RMSD (mmol/g)
<i>Binary system EO - EY</i>				
Langmuir competitive	48.81	0.00466	31.75	0.00413
Langmuir-Freundlich	39.44	0.00480	42.23	0.00486
Redlich-Peterson	N	N	N	N
Toth	15.91	0.00226	17.29	0.00246
Dual-mode	-84.11	0.06344	-93.69	0.06345
<i>Binary system EO – AR88</i>				
Langmuir competitive	13.30	0.00121	15.81	0.00167
Langmuir-Freundlich	23.76	0.00192	24.65	0.00209
Redlich-Peterson	11.14	0.00116	14.60	0.00142
Toth	-1.36	0.00093	1,03	0.00127
Dual-mode	24.20	0.00227	28.00	0.00269

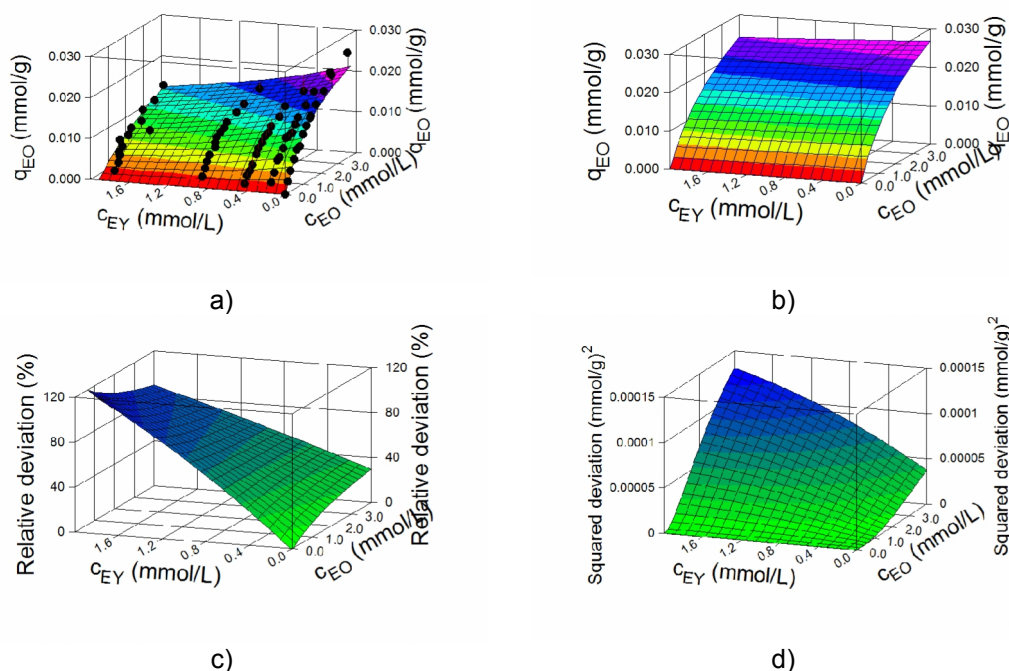


Fig. 5. Sorption of EO from binary EO – EY solution treated with the aid of the competitive Langmuir model.

a) Experimental data and best-fit curve; b) predicted curve; c) relative deviation (predicted vs. best-fit); d) squared deviation (predicted vs. best-fit).

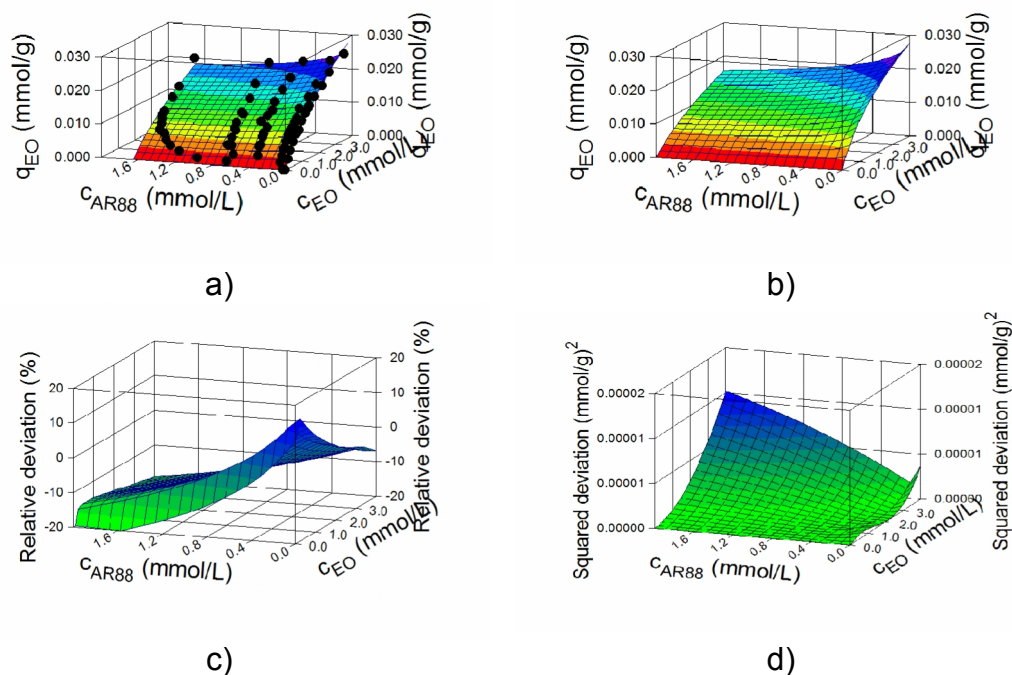


Fig. 6. Sorption of EO from binary EO – AR88 solution treated with the aid of the Toth model.

a) Experimental data and best-fit curve; b) predicted curve; c) relative deviation (predicted vs. best-fit); d) squared deviation (predicted vs. best-fit).

4. CONCLUSION

It was shown that the sulfonic azodyes can be removed from aqueous solutions by biosorption onto wood shavings. Various commonly used isotherm equations were applied successfully to describe the sorption equilibria in single-component as well as in binary systems. However, only some of the models allow to predict the sorption behavior of dyes in binary systems employing the model parameters derived from the single-component isotherms. The Toth multicomponent isotherm, for example, predicted the sorption of EO in the presence of EY or AR88 with a reasonable precision. The quality of predictions can be improved by an introduction of some kind of an interaction factor, which however requires additional measurements in the binary system.

ACKNOWLEDGEMENTS

Spolchemie, Ústínad Labem is thanked for providing some acid dyes for this study. Financial support from the Internal Grant Agency of the University of Jan Evangelista Purkyně in Ústínad Labem is gratefully acknowledged. Diploma students Eva Agapovová and Jitka Fikarová are thanked for their assistance in the experimental part of the work.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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