Available online at www.sciencedirect.com

ScienceDirect

Dyes and Pigments 74 (2007) 363–370

DYES and PIGMENTS

www.elsevier.com/locate/dyepig

Sorption of ionic dyes onto untreated low-rank coal – oxihumolite: A kinetic study

Pavel Janoš*, Pavel Michálek, Lukáš Turek

University of Jan Evangelista Purkyně, Faculty of the Environment, Králova Výšina 7, 400 96 Ústí nad Labem, Czech Republic

Received 16 January 2005; received in revised form 17 February 2006; accepted 17 February 2006
Available online 17 April 2006

Abstract

The kinetics of the sorption of basic dyes – Methylene Blue (C.I. Basic Blue 9), Malachite Green (C.I. Basic Green 4), Rhodamine B (C.I. Basic Violet 3), Crystal Violet (C.I. Basic Violet 10) – as well as acid dyes – Egacid Orange (C.I. Acid Orange 7), Egacid Yellow (C.I. Acid Orange 11), Midlon Black (C.I. Acid Black 26) – onto a special kind of naturally weathered and oxidised young brown coal called oxihumolite was investigated in a batch arrangement. Both pseudo-first-order and pseudo-second-order kinetic models were applied successfully to evaluate the kinetic dependencies. The intraparticle diffusion model was used to examine diffusion processes taking place during the dye sorption. It was found that the diffusion rate parameters decreased with increasing dose of the sorbent and with increasing particle sizes of the sorbent, whereas an effect of an agitation mode and intensity was much less pronounced. The diffusion processes were identified as the main mechanisms controlling the rate of the dye sorption onto oxihumolite. Malachite Green exhibited faster kinetics of the sorption in comparison with other dyes. However, this different behaviour may not be explained from differences in such parameters as a molecular weight or a dye structure.

Keywords: Basic dyes; Acid dyes; Young brown coal; Sorption kinetics; Kinetic models

1. Introduction

Dyes and pigment are emitted into wastewaters from various industrial branches, such as from the dye manufacturing or textile finishing, and may significantly affect photosynthetic activity in aquatic systems. They represent one of the problematic groups of chemical pollutants, as they are hardly destroyed in conventional wastewater treatment plants and require usually special treatment strategies [1]. Adsorption techniques employing solid sorbents provide an attractive alternative for the treatment of contaminated waters, especially if the sorbent is inexpensive and does not require an additional pre-treatment step (such as activation) before its application.

Currently, the most commonly used adsorption agent in industry is activated carbon that was successfully used to remove various kinds of dyes from waters [2–6]. Although some kinds of activated carbons are prepared from low-cost waste materials, such as waste tires [6], sawdust [3], rice husk or straw [2], their prices remain rather high [7]. This fact together with problems with regeneration of the spent activated carbon hampers its large-scale application. Therefore, a number of non-conventional sorbents have been tried for the treatment of wastewaters. A review of the low-cost sorbents including their main operational characteristics and also a comparison with activated carbon was published recently by Babel and Kurniawan [7]. It was, however, focused on the removal of metal ions, although the sorption of some metal-containing dyes was also mentioned. For the dye removal, various natural materials, clays or rocks (pumice [8], diatomite [9]), were tested. Numerous studies have been focused on a utilization of wastes from industry or agriculture as sorbents. Of many examples reported in literature, the following may be mentioned: steel plant slag [10], red mud and fly ash [11,12], carbon slurry from the fertilizer industry [13], chitosan from the seafood processing industry [14,15], sawdust [16,17], leaf powder [18], peanut hull [19], orange peel [20], algae

---

* Corresponding author. Tel.: +420 475 284 148; fax: +420 475 284 158.
E-mail address: janos@fzp.ujep.cz (P. Janoš).

0143-7208/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2006.02.017

[21,22], sugarcane dust [23], spent brewery grains [24], or other biosorbents and wastes from agroindustry.

Highly effective and low-cost sorbents have been prepared from peat [25–28] and various kinds of low-rank coals [29–36] – materials containing humic substances as an active constituent. The coal-based sorbents are capable to retain various kinds of pollutants, ranging from inorganic ionic species (heavy metal cations [30,32,34]) to low-polarity organic compound (trichlorobenzene, naphthalene [35]), including, of course, ionic organic compounds, such as synthetic dyes [29,31,33,36]. Properties and the sorption ability of the carbonaceous materials depend strongly on their origin [32] and may be altered, to some extent, by their chemical modification [29,34]. From an economical point of view, however, a utilization of untreated raw materials is more favourable.

Large deposits of young brown coals are located in the North-Bohemian Coal Basin in the Czech Republic where also the oxidatively altered lignite analogues called "oxihumolites" occur [37]. The oxihumolites originated on the surface of lignite deposits by post-sedimentary oxidation. Similar kinds of low-rank coals from other localities are called leonardites. They are utilized in agriculture [38] and for industrial preparations of humic acid derivatives [39,40].

Unique sorption, ion-exchange, complex-forming and other properties of the oxihumolites have been only seldom exploited in wastewater treatment. The oxihumolite pre-treated (loaded) with Ca^{2+} ions was used successfully to remove heavy metal cations from wastewaters [41]. In our recent work [42], it was shown that the oxihumolite is capable to retain both basic as well as acid dyes from aqueous solutions without any pre-treatment procedure. However, effective applications of the oxihumolite as a sorbent require a more detailed knowledge of the sorption mechanisms. In the present work, a kinetic study was performed for the sorption of basic and acid dyes onto oxihumolite. Various kinetic models, namely the pseudo-first-order and pseudo-second-order models, were tested to fit the experimental kinetic dependencies. An intraparticle diffusion model was also used to examine diffusional processes affecting the rate of the dye sorption.

2. Materials and methods

2.1. Sorbent

The sorbent – oxihumolite – originated from the North-Bohemian Coal Basin, locality Vaclav, was obtained from SD-Humatex (North-Bohemian Mines), Bilina, Czech Republic. It was used without an additional pre-treatment except of grinding and a size classification by sieving. Two fractions were used for the kinetic measurements – the fraction with grain sizes less than 1 mm, from which fine powdered particles were removed, and the fraction with grain sizes of 2–3 mm. The specific surface area (standard BET procedure – N_2 sorption) of the sorbent was ca. 2.5 $m^2 g^{-1}$ and did not depend significantly on the grain size. The content of humic acids in the sorbent was ca. 67%, ash content was ca. 23% and the content of water was ca. 10%. An elemental composition of the organic part can be found elsewhere [37]. An inorganic part of the sorbent contained mainly compounds of aluminium (0.56% of Al in the sorbent), silicon (0.71%), calcium (0.19%) and iron (0.23%). Quartz (SiO_2) and mulite ($Al_6Si_2O_{13}$) were the main crystalline phase identified in the ash from oxihumolite. Non-negligible amounts of K, Na, Mg, S, Ti, P and Cl were also detected in the sorbent. The contents of heavy and toxic metals were very low – typically 5 $mg\,kg^{-1}$ of Cu, 10 $mg\,kg^{-1}$ (Ni), 1 $mg\,kg^{-1}$ (Zn) and 1 $mg\,kg^{-1}$ (Ba). Leachability of these elements from the sorbent was measured using a standard leaching test with water (DIN 38 414). The concentrations of heavy and toxic metals in the water extract were very low (below regulatory limits for waters), e.g. 0.02 $mg\,L^{-1}$ (Cu), 0.03 $mg\,L^{-1}$ (Ni), 0.04 $mg\,L^{-1}$ (Zn), 0.005 $mg\,L^{-1}$ (Cr), 0.0004 $mg\,L^{-1}$ (Cd), 0.007 $mg\,L^{-1}$ (As).

2.2. Dyes

Methylene Blue, Malachite Green and Crystal Violet were obtained from Lachema, Brno, Czech Republic. Rhodamine B was obtained from Merck, Darmstadt, Germany. Egacid Orange II, Egacid Yellow G and Midlon Black were obtained from Spolchemie, Ústí nad Labem, Czech Republic. Basic characteristics of the dyes are given in Table 1. Stock solutions with concentrations 0.01 and 0.001 $mol\,L^{-1}$ were prepared by dissolving the respective dyes in deionised water.

All 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

Kinetic experiments were carried out by shaking a known amount of the sorbent (typically 4–10 g) with 500 mL of

Table 1
Basic characteristics of the dyes

Dye	C.I. generic name	C.I. number	Molecular formula	Molecular weight	Chemical class
Methylene Blue	Basic Blue 9	52 015	$C_{16}H_{18}N_3S\cdot Cl$	319.88	Basic, thiazine
Malachite Green	Basic Green 4	42 000	$C_{23}H_{25}N_2\cdot Cl$	364.95	Basic, triarylmethane
Crystal Violet	Basic Violet 3	42 555	$C_{25}H_{30}N_3\cdot Cl$	408.03	Basic, triarylmethane
Rhodamine B	Basic Violet 10	45 170	$C_{28}H_{31}N_2O_3\cdot Cl$	479.06	Basic, triarylmethane
Egacid Orange II	Acid Orange 7	15 510	$C_{16}H_{11}N_2NaO_4S$	350.30	Acid, diazo dye
Egacid Yellow G	Acid Yellow 11	18 820	$C_{16}H_{14}N_4O_4S$	358.37	Acid, diazo dye
Midlon Black	Acid Black 26	27 070	$C_{32}H_{21}N_5Na_2O_7S_2$	697.65	Acid, diazo dye

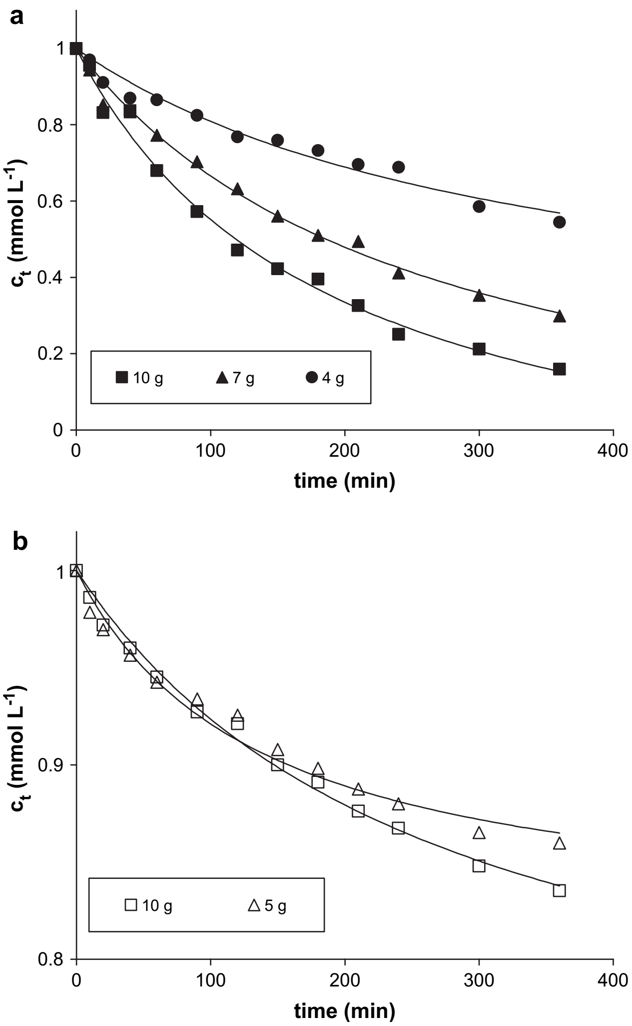

Fig. 1. Decrease of the dye concentration in solution with time for various weights of the sorbent. (a) Basic dye – Rhodamine B; (b) acid dye – Egacid Yellow. Initial dye concentration 1 mmol L^{-1}, volume of the solution 500 mL, grain sizes fraction of the sorbent <1 mm, agitation – horizontal shaking 200 min^{-1}. Solid lines calculated from the pseudo-second-order kinetic model.

the solution containing the dye (typically 1 mmol L^{-1}). The measurements were performed in PE bottles agitated with the aid of the horizontal shaker LT 2 (Kavalier, Sazava, Czech Republic) with an intensity of agitation 200 min^{-1}. Alternatively, slow rotation was used to examine an affect of the agitation mode on the sorption kinetics; a rotation (end-over-end) mixing device Reax 20 (Heidolph Instruments, Schwabach, Germany) was used in this case, operating with an intensity of agitation 5 min^{-1}. The measurements were carried out at "natural" pH values (ca. 3.7), without any pH adjustment. In the pre-determined time intervals, small portions of the mixture (less than 1 mL) were drawn, the solid phase was separated with the aid of a syringe nylon microfilter 0.45 μm, the dye concentration was determined spectrophotometrically, and the sorbed amount was calculated. Blank experiments with no sorbent added to the dye solution were performed in each series of measurements.

All the sorption experiments were carried out at a laboratory temperature 22 ± 1 °C in an air-conditioned box.

2.4. Analyses and data evaluation

Concentrations of the dyes in solutions were determined spectrophotometrically after a proper dilution using a UV/Vis spectrophotometer Cary 50 (Varian, Mulgrave, Australia). MS Excel and DataFit 8.0 (Oakdale Engineering, USA) software were used for calculations and data evaluations.

3. Results and discussion

Using an experimental arrangement described in the previous section, the kinetic dependencies were measured for various dyes and various weights of the sorbent, whereas the other experimental parameters (volume of the dye solution, initial dye concentration, grain size fraction of the sorbent, agitation mode) were kept constant. As examples, the dependencies of the concentrations of the dye in solution, c_t, vs. contact time are shown in Fig. 1a for the basic dye Rhodamine B, and

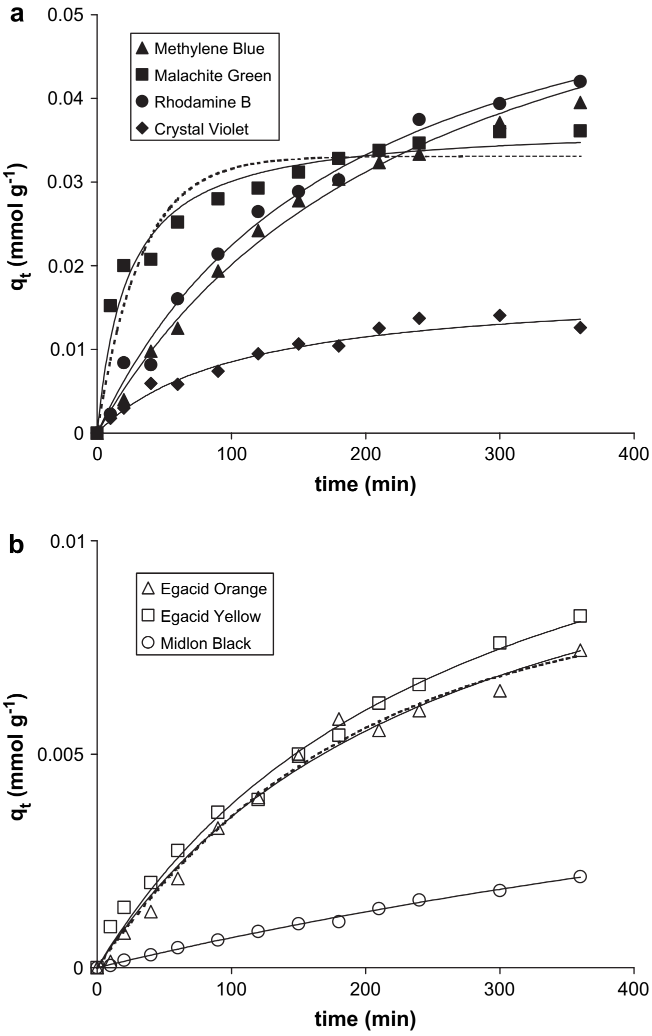

Fig. 2. Dependencies of the sorbed amounts on time. (a) Basic dyes; (b) acid dyes. Weight of the sorbent 10 g, other conditions as in Fig. 1. Solid lines calculated from the pseudo-second-order kinetic model, dashed lines calculated from the pseudo-first-order kinetic model.

Table 2
Parameters of the kinetic models for the sorption of basic dyes onto oxihumolite

Weight of the sorbent (g)	Pseudo-first-order model – Eq. (2)			Pseudo-second-order model – Eq. (4)		
	k_1 (min^{-1})	q_e (mmol g^{-1})	R^2	k_2 (g mmol^{-1} min^{-1})	q_e (mmol g^{-1})	R^2
Methylene Blue						
4	0.0052	0.0451	0.962	0.0534	0.0501	0.959
7	0.0074	0.0438	0.990	0.1086	0.0444	0.989
10	0.0060	0.0400	0.985	0.0587	0.0392	0.982
Malachite Green						
4	0.0414	0.0606	0.934	0.918	0.0664	0.968
7	0.0356	0.0414	0.918	1.090	0.0460	0.971
10	0.0309	0.0331	0.882	1.191	0.0369	0.949
Rhodamine B						
4	0.0040	0.0710	0.964	0.0286	0.1041	0.969
7	0.0052	0.0581	0.989	0.0464	0.0846	0.991
10	0.0067	0.0456	0.991	0.0831	0.0643	0.991
Crystal Violet						
4	0.0070	0.0253	0.928	0.1609	0.0354	0.924
7	0.0091	0.0162	0.918	0.4027	0.0211	0.917
10	0.0098	0.0137	0.946	0.5281	0.0177	0.944

for the acid dye Egacid Yellow in Fig. 1b. A simple re-calculation allows to plot the dependencies of the sorbed amounts, q_t, as functions of contact time, as shown in Fig. 2a and b for various basic and acid dyes, and for a single dose of the sorbent. As can be seen, the sorption rate was rather fast at the initial stage and then it slowed down gradually. Typical times to approach the equilibrium were several hours. Similar dependencies were obtained in most systems described in literature, e.g. for the sorption of acid dyes on carbon [4], basic dyes on peat particles [25,27,28] or metal complex dyes on sawdust [17]. Even faster kinetics was observed for the biosorption of basic dyes onto dead fungal biomass, when most of the dye was retained within the first 10 min [43]. Khraisheh et al. [44], on the other hand, found for the sorption of reactive dye on activated carbon that only 20% of the available sorption capacity was achieved during the first 6 h.

As can be seen from Fig. 2, Malachite Green exhibited markedly faster sorption kinetics in comparison with other dyes. The reason is not quite clear. Most of the basic dyes used in this study (Malachite Green, Rhodamine B, Crystal Violet) belong to the group of triarylmethane dyes, but they differ in the substituents and in the position of ionogenic groups in their molecule. In this stage of investigations, however, it is not possible to establish a relationship between the dye structure and the sorption rate. It seems also that the nature of ionogenic group (acidity/basicity) is not a factor affecting the sorption rate significantly.

3.1. Pseudo-first-order and pseudo-second-order kinetic models

Pseudo-first-order and pseudo-second-order models are most commonly used to describe the kinetics of the sorption of dyes on solid sorbents [2,17,27,28,45–47], although, as pointed out by Ho and McKay [27], the application of a single kinetic model to the sorption on solid sorbents may be questionable because of the heterogeneity of the sorbent surfaces and diversity of sorption phenomena (transport, surface reactions). Ho and McKay [48] revised critically the published kinetic data for many sorbent–sorbate systems and showed that, in most cases, the pseudo-second-order model is more suitable than pseudo-first-order model. Recently, Azizian [49] derived a general equation that converts to the pseudo-first-order model for lower initial concentrations of solute, and to the pseudo-second-order model for high solute concentrations.

The pseudo-first-order equation (suggested originally by Legergren [50]) is expressed as follows:

Table 3
Parameters of the kinetic models for the sorption of acid dyes onto oxihumolite

Weight of the sorbent (g)	Pseudo-first-order model – Eq. (2)			Pseudo-second-order model – Eq. (4)		
	k_1 (min^{-1})	q_e (mmol g^{-1})	R^2	k_2 (g mmol^{-1} min^{-1})	q_e (mmol g^{-1})	R^2
Egacid Orange						
5	0.0035	0.0137	0.987	0.1066	0.0217	0.987
10	0.0053	0.0086	0.990	0.2938	0.0129	0.988
Egacid Yellow						
5	0.0076	0.0144	0.932	0.3966	0.0186	0.946
10	0.0049	0.0097	0.989	0.2569	0.0143	0.991
Midlon Black						
5	0.0005	0.0212	0.997	0.0069	0.0401	0.997
10	0.0014	0.0054	0.996	0.0822	0.0096	0.996

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{1}$$

After integration and applying the boundary conditions, for $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, the integrated form of Eq. (1) becomes:

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \tag{2}$$

where q_e and q_t are the amounts of the dye adsorbed per unit mass of the sorbent at equilibrium and time t, respectively, and k_1 is the first-order kinetic constant.

The pseudo-second-order equation is expressed as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{3}$$

After integration for the similar boundary conditions as above, the following equation can be obtained:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \tag{4}$$

where k_2 is the second-order kinetic constant. Eqs. (2) and (4) are often presented in their linearized forms [17,27,28,48].

Both models were tested to fit the experimental dependencies. The model parameters (k_1, k_2 and q_e) were obtained with the aid of a non-linear curve-fitting procedure, and are listed in Table 2 for basic dyes (and various weights of the sorbent) and in Table 3 for acid dyes. It was ascertained from a comparison of the predicted (best fitted) time dependencies with experimental data that both kinetic models describe adequately the dye sorption. For the sorption of Malachite Green, a slightly better fit was achieved when the pseudo-second-order model was used – compare the R^2 values (coefficients of determination) in Table 2 and also the curves in Fig. 2a.

Tables 2 and 3 show that the sorbed amounts at equilibrium (q_e) decrease with increasing weight (dose) of the sorbent, which may be deduced also from Fig. 1 taking into account equilibrium isotherms (a similar kind of dependencies was used to construct the so-called pseudo-isotherms from kinetic measurements [46]). The rate constants, in general, are expected to increase with an increase in the sorbent dose [27], which was confirmed (with a few exceptions) by the data in Tables 2 and 3. No distinct relationship can be established between the values of the rate constants and the nature or structure of the dye. As mentioned above, higher sorption rates were observed for Malachite Green that is reflected in the higher values of the kinetic constants k_1 and k_2.

3.2. Intraparticle diffusion model

It is assumed that the adsorption process consists of several steps [4,51,55–57]:

- migration of the dye from bulk of the solution to the sorbent surface,
- diffusion of the dye through the boundary layer,
- intraparticle diffusion, and
- adsorption of the dye on the (internal) sorbent surface.

The dye sorption is governed usually by either liquid phase mass transport rate or intraparticle mass transport rate [2,4,47,54]. Hence, diffusive mass transfer is incorporated in the sorption process [16,25,26].

In diffusion studies, the rate can be expressed in terms of the square root time. The mathematical dependence of q_t vs. $t^{0.5}$ is obtained if the sorption process is considered to be influenced by diffusion in the spherical particles and convective diffusion in the solution [16,25,26]. The root time dependence, also known as a Weber–Morris plot [55], may be expressed by the following equation [4,17,27,28]

$$q_t = k_{ID} t^{0.5} \tag{5}$$

where k_{ID} is a diffusion rate parameter [15,26]. Eq. (5) is reported as an intraparticle diffusion model in literature [2,4,17,27,28,56] suggesting that the sorption process is

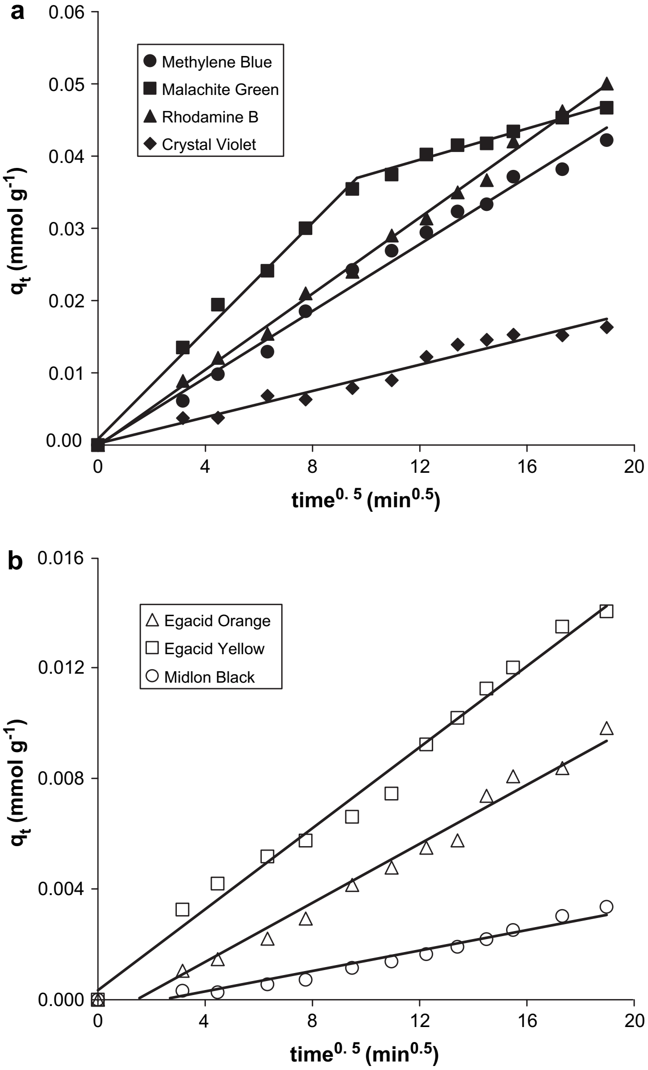

Fig. 3. Dependencies of q_t vs. $t^{0.5}$ – intraparticle diffusion model. (a) Basic dyes; (b) acid dyes. Weight of the sorbent 7 g for basic dyes and 10 g for acid dyes, other conditions as in Fig. 1.

considered to be controlled by the internal diffusion [44,47,57,58] with a minor effect of the external diffusion [44].

The experimental kinetic dependencies were evaluated using the intraparticle diffusion model – Eq. (5). For most of the dyes, the $q_t - t^{0.5}$ plots were straight lines in the whole time interval studied. The only exceptions were the dependencies for the sorption of Malachite Green that consisted of two separate sections with different slopes. Similar multilinearity was also observed in the case of the sorption of basic dyes onto peat [26,28], and was explained as a result of the presence of various kinds of pores (macropores vs. micropores) in the sorbent structure. However, this will hardly explain the differences in the sorption behaviour between Malachite Green and, for example, Crystal Violet, because the structures and molecular weights of these dyes are very similar.

Examples of the square root time plots are shown in Fig. 3a for the basic dyes and in Fig. 3b for acid dyes. The diffusion rate parameters, k_{ID}, were estimated from the plots according to Eq. (5) and are listed in Tables 4 and 5 for basic and acid dyes, respectively, and for various sorbent doses. As can be seen, the k_{ID} parameter decreased with increasing dose of the sorbent, which is consistent with observations of Allen et al. [26], who have found a similar tendency for the sorption of Basic Yellow 21 onto peat. The increased dose of the sorbent results in an increase in the overall rate of the dye removal from solution. This causes a rapid decrease in the dye concentration with a corresponding reduction in the driving force for intraparticle diffusion [26,53].

For selected dyes – Rhodamine B and Egacid Orange – an effect of an intensity of agitation was examined. Two agitation modes were compared – a rapid horizontal shaking with an intensity of agitation 200 min^{-1}, and slow rotation with an intensity of agitation 5 min^{-1}. In general, the agitation rate affects the boundary layer resistance to mass transfer [25]. As can be seen from Fig. 4a and b, however, the agitation mode and intensity did not exhibit a very pronounced effect on the sorption rate. A minor effect of the agitation rate on the dye sorption was observed also by Sun and Yang [28]. This indicates that the sorption was controlled mainly by the diffusion inside the particle pores, which remained almost unaffected by the agitation [53].

The particle sizes of the sorbent may affect the amounts of dyes adsorbed [2], and also the sorption kinetics [25,26,53]. The external particle surface area increases as the particle sizes decrease. It was shown that the surface mass transfer coefficient may be correlated to the average particle diameters [52]. As can be seen from Fig. 4a and b, the slopes of the square root plots (the diffusion rate parameters, k_{ID}) decreased with increasing particle sizes of the sorbent, in accordance with the findings of Allen et al. [26]. However, contradictory results can be found in literature with regard to the effect of particle sizes on the mass transfer during the sorption process, as some authors observed only negligible effects (see e.g. the discussion in Ref. [53]). In general, more pronounced effects of the particle sizes may be expected at relatively low sorbate concentrations and at high doses of the sorbent [53,59].

Table 4
Parameters of the intraparticle diffusion model for the sorption of basic dyes onto oxihumolite – effect of the dose of the sorbent

Weight of the sorbent (g)	$k_{\mathrm{ID}} \times 10^3$ (mmol g^{-1} min$^{-0.5}$)	R^2
Methylene Blue		
4	3.58	0.944
7	2.32	0.989
10	2.20	0.963
Malachite Green[a]		
4	6.62	0.968
7	3.52	0.976
10	3.09	0.947
Rhodamine B		
4	3.00	0.973
7	2.61	0.997
10	2.02	0.996
Crystal Violet		
4	1.33	0.918
7	0.90	0.914
10	0.79	0.921

[a] Model parameters determined from the initial time period up to 90 min.

4. Conclusions

It was found that the sorption of both basic as well as acid dyes onto oxihumolite is a quite rapid process – most of the dye was retained within the first several hours of contact. The kinetic dependencies may be described adequately both by pseudo-first-order as well as pseudo-second-order kinetic model, although, at least in the case of the sorption of Malachite Green, the pseudo-second-order model gave a slightly better fit to the experimental data. The intraparticle diffusion model was also applied successfully to the examined systems.

Malachite Green exhibited faster sorption kinetics in comparison with the other dyes. Unfortunately, it is not possible to establish any distinct relationship between the dye structure and the rate of the sorption in this stage of investigations. It seems that the nature of ionogenic groups (acidity/basicity) does not play a crucial role in the sorption kinetics.

Table 5
Parameters of the intraparticle diffusion model for the sorption of acid dyes onto oxihumolite – effect of the dose of the sorbent

Weight of the sorbent (g)	$k_{\mathrm{ID}} \times 10^3$ (mmol g^{-1} min$^{-0.5}$)	R^2
Egacid Orange		
5	0.63	0.969
10	0.38	0.970
Egacid Yellow		
5	0.72	0.988
10	0.49	0.989
Midlon Black		
5	0.20	0.935
10	0.13	0.952

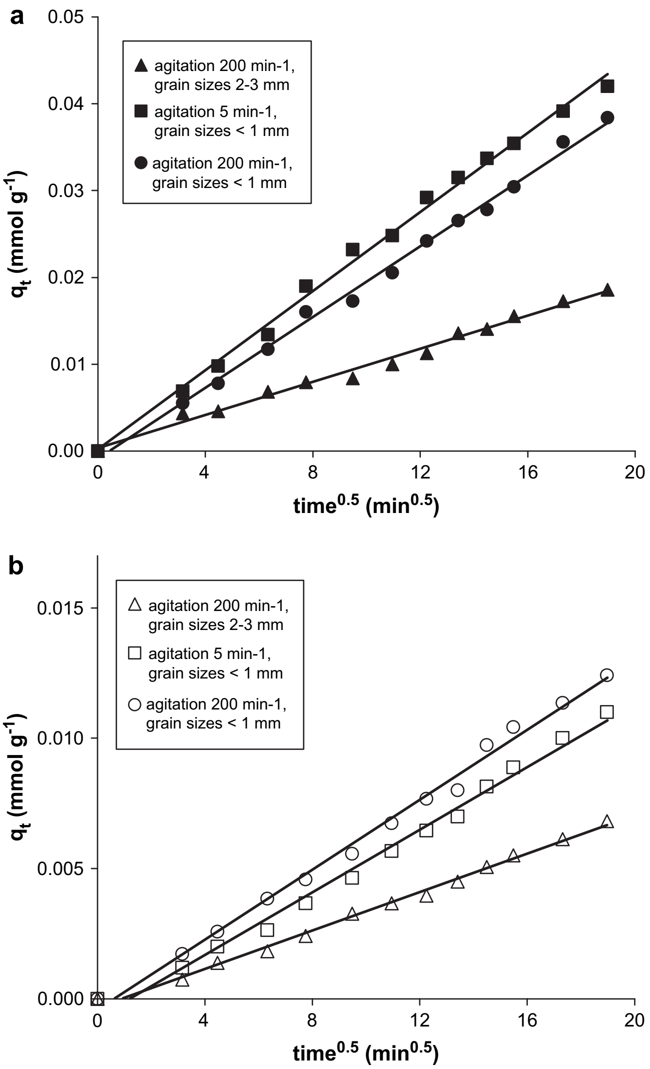

Fig. 4. Effects of agitation mode and particle sizes of the sorbent on the dye sorption. (a) Basic dye – Rhodamine B; (b) acid dye – Egacid Yellow. Weight of the sorbent 10 g, other conditions as in Fig. 1.

For selected dyes (Rhodamine B, Egacid Yellow), effects of an agitation mode and grain sizes of the sorbent were examined. It was found that the diffusion rate parameters decreased with increasing particle sizes, whereas an effect of the agitation was much less pronounced. This suggests that the diffusion inside the particles of the sorbent is the main process controlling the rate of the dye sorption onto oxihumolite.

Acknowledgements

SD-Humatex, Bilina is thanked for providing samples of oxihumolite for this study. Spolchemie, Ústí nad Labem is thanked for providing the acid dyes. Financial support from the Czech Science Foundation (Grant No. 104/03/1248) is gratefully acknowledged.

References

[1] Krull G, Döpkens E. Recycling of dyehouse effluents by biological and chemical treatment. Water Science and Technology 2004;49(4):311–7.

[2] Kannan N, Sundaram MM. Kinetics and mechanism of removal of methylene blue by adsorption on various carbons – a comparative study. Dyes and Pigments 2001;51(1):25–40.

[3] Malik PK. Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of Acid Yellow 36. Dyes and Pigments 2003;56(3):239–49.

[4] Choy KKH, Porter JF, McKay G. Intraparticle diffusion in single and multicomponent acid dye adsorption from wastewater onto carbon. Chemical Engineering Journal 2004;103(1–3):133–45.

[5] Yang X, Al-Duri B. Kinetic modeling of liquid-phase adsorption of reactive dyes on activated carbon. Journal of Colloid and Interface Science 2005;287(1):25–34.

[6] Tanthapanichakoon W, Ariyadejwanich P, Japthong P, Nakagawa K, Mukai SR, Tamon H. Adsorption–desorption characteristics of phenol and reactive dyes from aqueous solution on mesoporous activated carbon prepared from waste tires. Water Research 2005;39(7):1347–53.

[7] Babel S, Kurniawan TA. Low-cost adsorbents for heavy metals uptake from contaminated water: a review. Journal of Hazardous Materials 2003;97(1–3):219–43.

[8] Akbal F. Adsorption of basic dyes from aqueous solution onto pumice powder. Journal of Colloid and Interface Science 2005;286(2):455458.

[9] Al-Ghouti M, Khraisheh MAM, Ahmad MNM, Allen S. Thermodynamic behaviour and the effect of temperature on the removal of dyes from aqueous solution using modified diatomite: a kinetic study. Journal of Colloid and Interface Science 2005;287(1):6–13.

[10] Ramakrishna KR, Viraraghavan T. Dye removal using low cost adsorbents. Water Science and Technology 1997;36(2–3):189–96.

[11] Wang S, Boyjoo Y, Choueib A, Zhu ZH. Removal of dyes from aqueous solution using fly ash and red mud. Water Research 2005;39(1):129–38.

[12] Janoš P, Buchtová H, Rýznarová M. Sorption of dyes from aqueous solutions onto fly ash. Water Research 2003;37(20):4938–44.

[13] Bhatnagar A, Jain AK. A comparative adsorption study with different industrial wastes as adsorbents for the removal of cationic dyes from water. Journal of Colloid and Interface Science 2005;281(1):49–55.

[14] Sakkayawong N, Thiravetyan P, Nakbanpote W. Adsorption mechanism of synthetic reactive dye wastewater by chitosan. Journal of Colloid and Interface Science 2005;286(1):36–42.

[15] Chatterjee S, Chatterjee S, Chatterjee BP, Das AR, Guha AK. Adsorption of a model anionic dye, eosin Y, from aqueous solution by chitosan hydrobeads. Journal of Colloid and Interface Science 2005;288(1):30–5.

[16] McKay G, Poots VJP. Kinetic and diffusion processes in colour removal from effluent using wood as an adsorbent. Journal of Chemical Technology and Biotechnology 1980;30:279–92.

[17] Özacar M, Sengil IA. A kinetic study of metal complex dye sorption onto pine sawdust. Process Biochemistry 2005;40(2):565–72.

[18] Bhattacharyya KG, Sharma A. Kinetics and thermodynamics of Methylene Blue adsorption on Neem (*Azadirachta indica*) leaf powder. Dyes and Pigments 2005;65(1):51–9.

[19] Gong R, Sun Y, Chen J, Liu H, Yang C. Effect of chemical modification on dye adsorption capacity of peanut hull. Dyes and Pigments 2005;67(3):175–81.

[20] Arami M, Limaee NY, Mahmoodi NM, Tabrizi NS. Removal of dyes from colored textile wastewater by orange peel adsorbent: equilibrium and kinetic studies. Journal of Colloid and Interface Science 2005;288(2):371–6.

[21] Kumar KV, Ramamurthi V, Sivanesan S. Biosorption of malachite green, a cationic dye onto *Pithophora* sp., a fresh water algae. Dyes and Pigments 2006;69(1–2):102–7.

[22] Özer A, Akkaya G, Turabik M. The removal of Acid Red 274 from wastewater: combined biosorption and bioaccumulation with *Spirogyra rhizopus*. Dyes and Pigments 2006;71(2):83–9.

[23] Ho YS, Chiu WT, Wang CC. Regression analysis for the sorption isotherms of basic dyes on sugarcane dust. Bioresource Technology 2005;96(11):1285–91.

[24] Silva JP, Sousa S, Rodrigues J, Antunes H, Porter JJ, Goncalves I, et al. Adsorption of acid orange 7 dye in aqueous solutions by spent brewery grains. Separation and Purification Technology 2004;40(3):309–15.

[25] McKay G, Allen SJ, McConvey IF, Otterburn MS. Transport processes in the sorption of colored ions by peat particles. Journal of Colloid and Interface Science 1981;80(2):323–39.

[26] Allen SJ, McKay G, Khader KYH. Intraparticle diffusion of a basic dye during adsorption onto sphagnum peat. Environmental Pollution 1989;56(1):39–50.

[27] Ho YS, McKay G. Kinetic of sorption of basic dyes from aqueous solution by sphagnum moss peat. Canadian Journal of Chemical Engineering 1998;76:822–7.

[28] Sun Q, Yang L. The adsorption of basic dyes from aqueous solution on modified peat–resin particle. Water Research 2003;37(7):1535–44.

[29] Mittal AK, Venkobachar C. Sorption and desorption of dyes by sulfonated coal. Journal of Environmental Engineering 1993;119(4):366–8.

[30] Allen SJ, Brown PA. Isotherm analyses for single component and multi-component sorption onto lignite. Journal of Chemical Technology and Biotechnololgy 1995;62(1):17–24.

[31] Mohan SV, Rao NC, Karthikeyan J. Adsorptive removal of direct azo dye from aqueous phase onto coal based sorbents: a kinetic and mechanistic study. Journal of Hazardous Materials 2002;90(2):189–204.

[32] Hanzlík J, Jehlička J, Šebek O, Weishauptová Z, Machovič V. Multi-component adsorption of Ag (I), Cd (II) and Cu (II) by natural carbonaceous materials. Water Research 2004;38(8):2178–84.

[33] Khan TA, Singh VV, Kumar D. Removal of some basic dyes from artificial textile wastewater by adsorption on Akash Kinari coal. Journal of Scientific and Industrial Research 2004;63(4):355–64.

[34] Burns CA, Boily JF, Crawford RJ, Harding IH. Cd(II) binding by particulate low-rank coals in aqueous media: sorption characteristics and NICA-Donnan models. Journal of Colloid and Interface Science 2004;278(2):291–8.

[35] Lu Y, Pignatello JJ. History-dependent sorption in humic acids and a lignite in the context of a polymer model for natural organic matter. Environmental Science and Technology 2004;38(22):5853–62.

[36] Karaca S, Gürses A, Bayrak R. Investigation of applicability of the various adsorption models of methylene blue adsorption onto lignite/water interface. Energy Conversion and Management 2005;46(1):33–46.

[37] Kurková M, Klika Z, Kliková C, Havel J. Humic acids from oxidized coals. I. Elemental composition, titration curves, heavy metals in HA samples, nuclear magnetic resonance spectra of HAs and infrared spectroscopy. Chemosphere 2004;54(8):1237–45.

[38] Gonet SS, Dziamski A, Gonet E. Application of humus preparations from oxyhumolite in crop production. Environment International 1996;22(5):559–62.

[39] Novák J, Kozler J, Čežíková J, Janoš P, Tokarová V, Madronová L. Humic acids from coals of the North-Bohemian coal field. I. Preparation and characterisation. Reactive and Functional Polymers 2001;47(2):101–9.

[40] Rasmussen HW, Allen LH. Method for producing calcium fulvate from humus material. U.S. Patent 6 204 396; 2001.

[41] Horáček J, Soukupová L, Punčochář M, Slezák J, Drahoš J, Yoshida K, et al. Purification of waste waters containing low concentrations of heavy metals. Journal of Hazardous Materials 1994;37(1):69–76.

[42] Janoš P, Šedivý P, Rýznarová M, Grötschelová S. Sorption of basic and acid dyes from aqueous solutions onto oxihumolite. Chemosphere 2005;59(6):881–6.

[43] Bhole BD, Ganguly B, Madhuram A, Deshpande D, Joshi J. Biosorption of methyl violet, basic fuchsin and their mixture using dead fungal biomass. Current Science 2004;86(12):1641–5.

[44] Khraisheh MAM, Al-Degs YS, Allen SJ, Ahmad MN. Elucidation of controlling steps of reactive dye adsorption on activated carbon. Industrial and Engineering Chemistry Research 2002;41(6):1651–7.

[45] Ho YS, Chiang CC. Sorption studies of acid dye by mixed sorbents. Adsorption 2001;7(2):139–47.

[46] Ho YS. Pseudo-isotherms using a second order kinetic expression constant. Adsorption 2004;10(2):151–8.

[47] Mohan SV, Karthikeyan J. Adsorptive removal of reactive azo dye from an aqueous phase onto charfines and activated carbon. Clean Technologies and Environmental Policy 2004;6(3):196–200.

[48] Ho YS, McKay G. Pseudo-second order model for sorption processes. Process Biochemistry 1999;34(5):451–65.

[49] Azizian S. Kinetic models of sorption: a theoretical analysis. Journal of Colloid and Interface Science 2004;276(1):47–52.

[50] Lagergren S. Zur theorie der sogenannten adsorption gelöster stoffe. Kungliga Svenska Vetenskapsakakademiens. Handligar 1898;24:1–39.

[51] McKay G. The adsorption of dyestuffs from aqueous solutions using activated carbon: an external mass transfer and homogeneous surface diffusion model. AIChE Journal 1985;31(2):335–9.

[52] McKay G, Otterburn MS, Sweeney AG. Surface mass transfer processes during colour removal from effluent using silica. Water Research 1981;15(3):327–31.

[53] Al-Qodah Z. Adsorption of dyes using shale oil ash. Water Research 2000;34(17):4295–303.

[54] Furusawa T, Smith JM. Fluid-particle and intraparticle mass transport rates in slurries. Industrial and Engineering Chemistry Fundamentals 1973;12(2):197–203.

[55] Weber WJ, Morris JC. Journal of the Sanitary Engineering Division-ASCE 1963;89:31.

[56] Tsai WT, Chang YM, Lai CW, Lo CC. Adsorption of basic dyes in aqueous solution by clay adsorbent from regenerated bleaching earth. Applied Clay Science 2005;29(2):149–54.

[57] Edeskuty J, Amundson NR. Effect of intraparticle diffusion: agitated nonflow adsorption systems. Industrial and Engineering Chemistry 1952;44(7):1698–703.

[58] Markovska L, Meshko V, Noveski V, Marinkovski M. Solid diffusion control of the adsorption of basic dyes onto granular activated carbon and natural zeolite in fixed bed columns. Journal of the Serbian Chemical Society 2001;66(7):463–75.

[59] Cooney DO, Adesanya BA, Hines AL. Effect of particle size distribution on adsorption kinetics in stirred batch systems. Chemical Engineering Science 1983;38(9):1535–41.