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Theoretical analysis of the adsorption of metal ions to the surface of melanin particles

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Abstract We have re-examined the problem of the interaction of melanins with metal ions. Metal ions are normal constituents of the pigment, but in some cases they can be related to pathologies, mainly at the level of the skin (Cu^{2+} and Fe^{3+}) and of the central nervous system (Fe^{2+} and Mn^{2+}). Our approach has been based on the mechanisms of adsorption on the particle surface, by the use of theoretical adsorption isotherms and kinetic models. Although this analysis doesn't give detailed information on the specific sites involved, it is useful to better characterize the surface behaviour of the colloidal melanin. The results obtained demonstrate that the affinity of melanin for metal ions is very high, comparable to the most efficient materials employed in decontamination and recovery techniques. Moreover, our results demonstrate that three-parameters models, such as Langmuir-Freundlich, Redlich-Peterson and Tóth equations, fit the experimental data with great accuracy and that the adsorption follows pseudo-second-order kinetics.

Keywords Synthetic melanins · Adsorption isotherms · Adsorption kinetics · Surface structure · Microporosity

Abbreviations

a	Adsorption rate in the Elovich equation ($\text{mmol}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$)
a_t	Inverse of the adsorptive potential constant in the Tóth equation ($\text{dm}^3\cdot\text{mg}^{-1}$)
b	Desorption constant in the Elovich equation ($\text{g}\cdot\text{mmol}^{-1}$)
C	Equilibrium concentration of ions in solution ($\text{mmol}\cdot\text{dm}^{-3}$)
E	Free energy of sorption ($\text{J}\cdot\text{mmol}^{-1}$)
k_1	Pseudo-1° order rate constant
k_2	Pseudo-2° order rate constant
k_p	Rate constant for intraparticle diffusion
K	Constant in the Langmuir, Freundlich and Langmuir-Freundlich isotherms ($\text{dm}^3\cdot\text{mmol}^{-1}$)
K_F	Freundlich constant ($\text{dm}^3\cdot\text{g}^{-1}$)
K_R	Redlich-Peterson constant (g^{-1})
K_S	Sips constant
K_1	1° Temkin constant
K_2	2° Temkin constant ($\text{dm}^3\cdot\text{mmol}^{-1}$)
q	Amount of adsorbed ions ($\text{mmol}\cdot\text{g}^{-1}$)
q_0	Monolayer adsorption capacity ($\text{mmol}\cdot\text{g}^{-1}$)
q_e	Amount of adsorbed ions at equilibrium ($\text{mmol}\cdot\text{g}^{-1}$)
q_m	Adsorption capacity ($\text{mmol}\cdot\text{g}^{-1}$)
R	Gas constant ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)
t	Tóth heterogeneity coefficient
T	Absolute temperature (K)
$1/n$	Freundlich heterogeneity index
α	Affinity coefficient ($\text{dm}^3\cdot\text{g}^{-1}$)
β	Constant in the Dubinin-Radushkevich isotherm ($\text{mmol}^2\cdot\text{J}^{-2}$)
γ	Heterogeneity coefficient
ε	Polany potential ($\text{J}\cdot\text{mmol}^{-1}$)
τ	Time (min)

1 Introduction

The term melanin refers to a class of natural pigments formed in the skin, eyes, hair and brain of animals in the form of colloidal aggregates and performs different physiological functions. Metal ions are normal constituents of

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natural melanins (Larsson and Tjälve 1978) and in some cases their role in the biosynthetic pathway of the pigment has been firmly established (Prota 1992). Moreover, when in contact with solutions containing metal ions, the pigment particles are able to bind them quantitatively, so that melanins have often been considered as ion-exchange substances (Liu et al. 2004). Thanks to this and related properties, many biophysical and structural aspects of natural melanins have been better understood.

Quantitative determinations of the amount of metals bound to the pigment, obtained with various experimental techniques, have been recently published (Liu et al. 2004; Szpoganicz et al. 2002; Andrzejczyk and Buszman 1992; Zecca et al. 2002) and, on the bases of the chemical structures of melanins, the binding sites resulted to be carboxylic acids, hydroxyl and amino groups. This basic structural aspect has been carefully investigated with various methods, in particular with EPR spectroscopy (Froncisz et al. 1980), Mössbauer spectroscopy (Bardani et al. 1982) and more recently, with resonance Raman microspectroscopy (Samokhvalov et al. 2004).

In a recent work by Simon and coll. (Hong et al. 2004), the mechanism of the binding of Mn^{2+}, Ca^{2+}, Zn^{2+}, Cu^{2+} and Fe^{3+} to EDTA-washed *Sepia* melanin has been unambiguously determined and a correlation between the concentration of Fe^{3+} and the production of oxygen reactive species has been demonstrated. This is particularly relevant not only for photobiology, but also for human pathology, as observed, for example, in the case of iron-neuromelanin interaction in the neurodegenerative processes, studied in great detail in recent years (Zucca et al. 2004; Zecca et al. 2001).

In the present work, we adopt a different and somewhat complementary point of view. This is based on the models that have been developed to describe the adsorption of molecules and ions on the surfaces of solids. This approach has been adopted firstly for the study of the adsorption of gases (BET and Langmuir models), but successively rigorous theories have been presented for the interaction of molecules and ions in aqueous solution with surfaces of colloids, in order to better understand heterogeneous catalytic processes and to improve technological applications (many ions pollute surface water and can be eliminated by adsorption on carbon, zeolites, chitosan, TiO_2, etc.).

Our analysis is based on the particle structure of melanins whose characteristics have recently been studied (Zajac et al. 1994; Liu and Simon 2003) and consists in considering and studying them in the same way as technical colloids. By this method, in principle, it is possible to derive parameters useful for the interpretation of the surface behaviour of the melanin particles, as we have recently demonstrated in the case of some drugs (Bridelli et al., 2006) and in the interpretation of N_2-BET curves (Crippa et al. 2003).

We have limited our attention to the adsorption of a series of metal ions on synthetic L-dopa melanins, as studied by Buszman and coll. and published several years ago (Buszman et al., 1987, 1988). The equations used in our analysis have been selected on the bases of their relative simplicity with the aim of deriving energetic and structural parameters from a straightforward fitting procedure.

2 Analysis of the binding

Our choice of the theoretical models for the interpretation of the isothermal adsorption curves, though arbitrary and restricted to well experimented cases, deserves some justification. In fact, as we will demonstrate more clearly in the analysis of the results, several models fit the experimental points rather well, from the classical ones (such as Langmuir or Dubinin-Radushkevitch equations) to the more recent Tóth theory. Such a situation allows us to derive a number of parameters, thanks to the different principles on which the various theories are based.

We give here a summary of the following equations used, with only some comments but with quotations from more specialized textbooks (Gregg and Sing 1982; Adamson and Gast 1997) and from specific papers for rigorous derivations. The symbols are the same used by us in a previous paper (Bridelli et al. 2006) and are described below.

2.1 The Langmuir isotherm

A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites. The curve is represented by the expression:

$$q = \frac{q_0 K C}{1 + K C} \tag{1}$$

where q is the amount adsorbed (mmol·g^{-1}), q_0 (mmol·g^{-1}) and K (dm^3·mmol^{-1}) are related to monolayer adsorption capacity and energy of adsorption, respectively, and C is the equilibrium solution concentration of solute. In the analysis of the results, q_0 is assumed as the total number of binding sites, N_t.

If it is presumed that two sites, A and B (or eventually, more) with different binding energies could be present, a modification of the classical Langmuir isotherm may be used. The two-site Langmuir equation has the form:

$$q = \frac{q_1 K_A C}{1 + K_A C} + \frac{q_2 K_B C}{1 + K_B C}$$

with the same meaning of the parameters.

2.2 The Freundlich isotherm

It is often used for heterogeneous surface energy systems. Its semiempirical expression is:

$$q = q_0(KC)^{1/n} \tag{2}$$

When the heterogeneity index is $1/n < 1$, the adsorption rate decreases with solution concentration as the low-energy sites are occupied. All the concentrations being expressed with the same units, the Freundlich constant K_F $(= q_0 K^{1/n})$ gives an estimate of the adsorption capacity.

2.3 The Temkin isotherm

It was proposed with the aim of considering the effects of adsorbate/adsorbate interactions on adsorption isotherms. The Temkin isotherm has been used in the following form:

$$q = \frac{RT}{K_1} \ln(K_2 C) \tag{3}$$

where K_2 ($\mathrm{dm^3 \cdot g}$) plays the role of an equilibrium constant.

2.4 The Dubinin-Radushkevich isotherm

This equation has often been used to describe the adsorption of metal ions. It is generally written in the form:

$$q = q_m e^{-\beta \varepsilon^2} \tag{4}$$

where q_m ($\mathrm{mmol \cdot g^{-1}}$) is the adsorption capacity (in the original treatment, the micropore volume), β ($\mathrm{mmol^2 \cdot J^{-2}}$) is a constant related to sorption energy and ε is the Polanyi potential (Adamson and Gast 1997). The constant β is related to the mean free energy E ($\mathrm{J \cdot mmol^{-1}}$) of sorption per molecule of the adsorbate transferred from infinity to the surface that can be calculated by the formula (Choy et al. 1999):

$$E = \frac{1}{\sqrt{2\beta}}$$

2.5 The Redlich-Peterson isotherm

In order to improve the fitting with the classical Langmuir and Freundlich equations, three parameters sorption isotherms that incorporate the features of both these isotherms are often used. The Redlich-Peterson equation (Onyango et al. 2004; Allen et al. 2003) is written as:

$$q = \frac{q_0 K C}{1 + \alpha C^{\gamma}} \tag{5}$$

where $q_0 K = K_R$ is often called Redlich-Peterson constant ($\mathrm{g^{-1}}$) and α ($\mathrm{dm^3 \cdot g^{-1}}$) represents an affinity coefficient. Again, γ is a heterogeneity index.

2.6 The Langmuir-Freundlich (Sips) isotherm

This three-parameters equation is based on the assumption of localized adsorption without interaction among sites, and is usually written in the form:

$$q = \frac{q_0 (KC)^{1/n}}{1 + (KC)^{1/n}} \tag{6}$$

where $K_S = q_0 K^{1/n}$ is sometime called Sips constant.

2.7 The Tóth isotherm

This model assumes adsorbate sorption on energetically heterogeneous surfaces with most sites having sorption energy lower than the maximum adsorption energy (Tóth 2000). A form applicable to liquid-phase adsorption is the following:

$$q = \frac{q_m C}{[1 + (a_t C)^t]^{1/t}} \tag{7}$$

where q_m ($\mathrm{mmol \cdot g^{-1}}$) is the total adsorption capacity, a_t ($\mathrm{mg \cdot dm^{-3}}$) plays the role of the inverse of an adsorptive potential and the parameter t characterize the heterogeneity of the adsorbent.

3 Kinetics

On the bases of the experimental kinetic data of Buszman et al. (1987), we have performed a study devoted to establish the best model to describe the mechanism governing the interaction between metal ions and melanin. In this work the analysis of the kinetic curves has been limited to a few classical models. This simplified approach is due to the scarce knowledge of melanin particle surfaces and to the limited number of available experimental points. These models are well known in the literature and have been successfully tested in experiments on the removal of ions from effluents by carbons and other adsorbers.

Pseudo first- and second-order equations have been used in the integrated forms as follows:

$$\ln(q_e - q) = \ln q_e - k_1 \tau \tag{8}$$

and

$$\frac{\tau}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \tau \tag{9}$$

where k_1 and k_2 are the rate constants of pseudo-first-order and pseudo-second-order adsorption respectively, q is the amount of adsorption at time t, and q_e is the amount of adsorption at equilibrium (both $\mathrm{mmol \cdot g^{-1}}$).

Equation (9) allows us to evaluate k_2 and q_e from the intercept and slope of the plot of τ/q vs. τ. Then the calculated values of q_e have been introduced in (8) without performing equilibrium experiments.

Another simplified model, the intraparticle diffusion model, has been tested to better identify the diffusion mechanism involved (McKay 1983). The theory is based on the adsorption dependence on the function (Dt/r^2), where r is the particle radius and D the diffusivity of the solute within the particle. The adsorption processes include the transport of the ion from the bulk solution to the interior surface of the pores. The treatment of the diffusion equation, for spherical particles and for the initial tract of the adsorption process, leads to the simple form:

$$q = k_p \tau^{1/2} \tag{10}$$

The presence of multi-linearity is indicative of two or more steps. In particular, the step corresponding to the adsorption stage where the intraparticle diffusion is rate limiting allows us to determine the rate constant k_p from the slope of this portion.

A theoretical model that is gaining in popularity in liquid phase sorption is the Elovich equation, proposed initially to describe the chemisorption of gas on solids (Low 1960). In its integrated form

$$q = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln\left(\tau + \frac{1}{ab}\right) \tag{11}$$

it allows easy calculation of the parameters a, representing the adsorption rate at zero coverage and b, indicative of the extent of surface coverage and activation energy.

4 Results and discussion

A discussion about metal ion interaction with melanins requests some preliminary observations in order to be stated on unequivocal bases. The first one concerns the pH conditions of the binding experiments. The functional groups that may be used as binding sites for metal ions are (Hong et al. 2004): carboxylic acid ($pK_a \sim 4.5$), phenol groups ($pK_a \sim 9$ and ~ 13) and amine group ($pK_a > 9$). The method of synthesis of the melanin adopted by Buszman et al. (1988) requests a lowering of the pH to ~ 2 to stop the reaction of autooxidation (Stępien et al. 1986). As the melanin prepared in such a way, when re-suspended in water at the concentration used, has a pH ~ 4 (Sarna et al. 1980), we can take this value as the condition of the binding experiments. As a consequence, only a percentage of carboxylic groups are deprotonated and the resulting net negative charge can contribute, through electrostatic attraction, to the interaction. The influence of the pH changes has been discussed in detail by Hong et al. (2004), with a cogent discussion of the role of the various kinds of cations on the final pH values. This implies a still more complicated picture that, in our opinion, gives more relevance to our simpler analysis that doesn't care, in principle, about the binding groups, but is limited to concepts such as homogeneous or not-homogeneous binding sites. It is perhaps necessary to underline at this point the deep conceptual difference between the technological point of view, where the study of the chemical mechanism prevails with the aim of achieving the optimization of the process, and our biophysical interest, limited to a qualitative description of possible biological reactions leading to the formation of a complex with a peculiar physiological and/or pathological role. In any case, the lack of chemical details should be counterbalanced by the possibility of calculating kinetic, energetic and other thermodynamic parameters.

Table 1 shows the results obtained applying the models listed above to the experimental determinations as presented by Buszman et al. (1988). Unfortunately, the authors of this paper report the experimental methods in detail, but without any evaluation of the experimental errors. From the literature the error in the estimation of the intensity in γ scintillation spectrometry (the method they used in the experiments) is reported to be less than 5% and this figure was adopted in the calculation of the fitting parameters. This prudential evaluation limits the significant figures in the data reported in the table where the last digit can be considered as affected by this uncertainty. The values of the non-linear R^2 are only the support of the good quality of the fittings and obviously are not a guarantee of the exactness of the data. We are also aware that a high correlation coefficient, by itself, is not sufficient to say an empirical equation is valid, but the examples reported in the literature encourage a certain degree of validity to be attributed to the results. Figure 1, related to Mn^{2+} ions, has been selected as representative of all the non-linear fittings. The analyses were performed using a calculation program where the values of the non-linear regression coefficients R^2 are directly given.

These values are indicative of the differences among the various models as applied to the different ions. Langmuir, Langmuir-Freundlich, Redlich-Peterson and especially Tóth theories, are able to interpret correctly the processes of adsorption. In this discussion we will base our analysis mainly on these. The worst results were obtained with Temkin and Dubinin-Radushkevich theories and the related numerical data have therefore been omitted from the table. A tentative analysis was performed with the two-sites Langmuir equation, but in all cases the sum of q_1 and q_2 was always equal to the value of q_0 obtained with the simple Langmuir equation. The heterogeneity index $1/n$ determined with the Langmuir-Freundlich model is high. As for $1/n = 1$ this isotherm reduces to the Langmuir isotherm, this can explain the rather good fits obtained with (1).

Table 1 Parameters values calculated from the fittings with the various adsorption isotherms

		Cd^{2+}	Co^{2+}	Cr^{3+}	Cu^{2+}	Fe^{3+}	Mn^{2+}	Ni^{2+}	Sn^{2+}	Zn^{2+}
Langmuir	q_0	1.82	0.31	0.95	0.78	1.58	0.14	1.88	0.46	0.31
	K	0.24	3.48	0.63	1.92	0.84	1.18	0.49	0.77	3.87
	R^2	0.996	0.997	0.992	0.976	0.995	0.999	0.986	0.978	0.989
Freundlich	1/n	0.71	0.52	0.44	0.37	0.63	0.57	0.59	0.50	0.54
	K_F	0.34	0.26	0.34	0.45	0.68	7.12	0.57	0.18	0.26
	R^2	0.993	0.972	0.959	0.860	0.972	0.976	0.955	0.992	0.947
Langmuir-Freundlich	1/n	0.92	1.05	1.00	1.48	1.17	1.03	1.33	0.63	1.21
	K_S	0.16	3.83	0.63	2.50	1.22	1.26	0.82	0.09	5.18
	q_0	2.23	0.30	0.95	0.68	0.31	0.14	1.49	1.03	0.27
	R^2	0.996	0.998	0.992	0.992	0.998	0.999	0.991	0.995	0.995
Redlich-Peterson	K_R	0.44	1.08	0.55	1.15	1.03	0.16	0.70	1.33	0.95
	α	0.26	3.47	0.51	1.14	0.36	1.07	0.11	6.12	3.13
	γ	0.97	1.00	1.06	1.20	1.68	1.05	1.82	0.59	1.32
	R^2	0.995	0.997	0.992	0.985	0.999	0.999	0.995	0.994	0.994
Tóth	q_m	0.46	1.06	0.55	0.96	1.04	0.16	0.68	3.00	0.88
	a_t	0.21	3.47	0.61	1.45	0.77	1.18	0.54	0.91	3.62
	t	0.85	1.04	1.10	2.00	1.56	1.09	2.88	0.25	2.00
	R^2	0.996	0.997	0.992	0.991	0.999	0.999	0.995	0.995	0.996

An interesting evaluation can be performed by comparing the values calculated for melanin with the results of the binding of ions to efficient adsorbers such as activated carbon, ion exchangers and other industrial materials. Some examples are indicative of the high capability of the melanin surface to adsorb metal ions. Dastgheib and Rockstraw (2002) fitted the results obtained on activated carbon with Freundlich and Langmuir-Freundlich models. After conversion of the units, the values of the parameters are comparable with ours.

The adsorption of Cu^{2+} and Zn^{2+} onto modified montmorillonite (Lin and Juang 2002) analyzed with the Dubinin and Langmuir models, and of Cu^{2+}, Cd^{2+} and Ni^{2+} on a silico-antimonate ion exchanger (with the Freundlich model) (Abou-Mesalam 2003), gives very similar parameter values. Similar agreements were found comparing melanin and zeolite in interaction with Zn^{2+}, Cu^{2+} and Pb^{2+}, when studied with Tóth, Redlich-Petersen, Langmuir-Freundlich and Dubinin-Radushkevich equations (Perić et al. 2004).

The conclusion we can draw from this short comparison is a confirmation of the elevated binding capacity of synthetic melanin towards many cations. Few quantitative studies were performed on natural melanins: the more accurate one indicates that Mn^{2+} binds more efficiently to beef eye eumelanin than to the synthetic analogue (the total binding capacity is 1.33 mmol/g (Lydén et al., 1984)). This finding has been recently confirmed for *Sepia* melanin (Hong et al. 2004) and we presume it can be considered as a general trend.

Through an overall consideration of the adsorption isotherms, we can classify the metal ions for their affinity towards the synthetic melanin adsorption sites as follows:

$$Mn^{2+} < Sn^{2+} < Co^{2+} < Zn^{2+} < Cd^{2+} < Cr^{3+} < Ni^{2+} < Cu^{2+} < Fe^{3+}$$

A comparison with the results of Dastgheib and Rockstraw (2002) on active carbon, shows that also in our case a correlation can be tentatively established with physical parameters such as electronegativity, and stability constant, but not with the size of the hydrated ion or the atomic weight and number. The predominance of negative surface charges justifies the selection of electronegativity as the main property influencing the metal ion uptake. Furthermore, the supposed complexation of metal ions with surface functional groups could be influenced by the stability constant of the ionic species in aqueous solution.

As previously mentioned, the parameters calculated by the fittings can, in principle, give useful information about the structure and the energy of interaction related to the adsorbing particles. In the absence of further information about the real topography of the surfaces, we limit ourselves to deriving only some inferences of general type.

(1) The parameter K (both from the Langmuir and the Redlich-Peterson equations) shows the maximum values in correspondence with the minimum values of the respective q_0. This can be verified in the cases of Mn^{2+}, Zn^{2+} and Co^{2+}. The contrary happens in the cases of

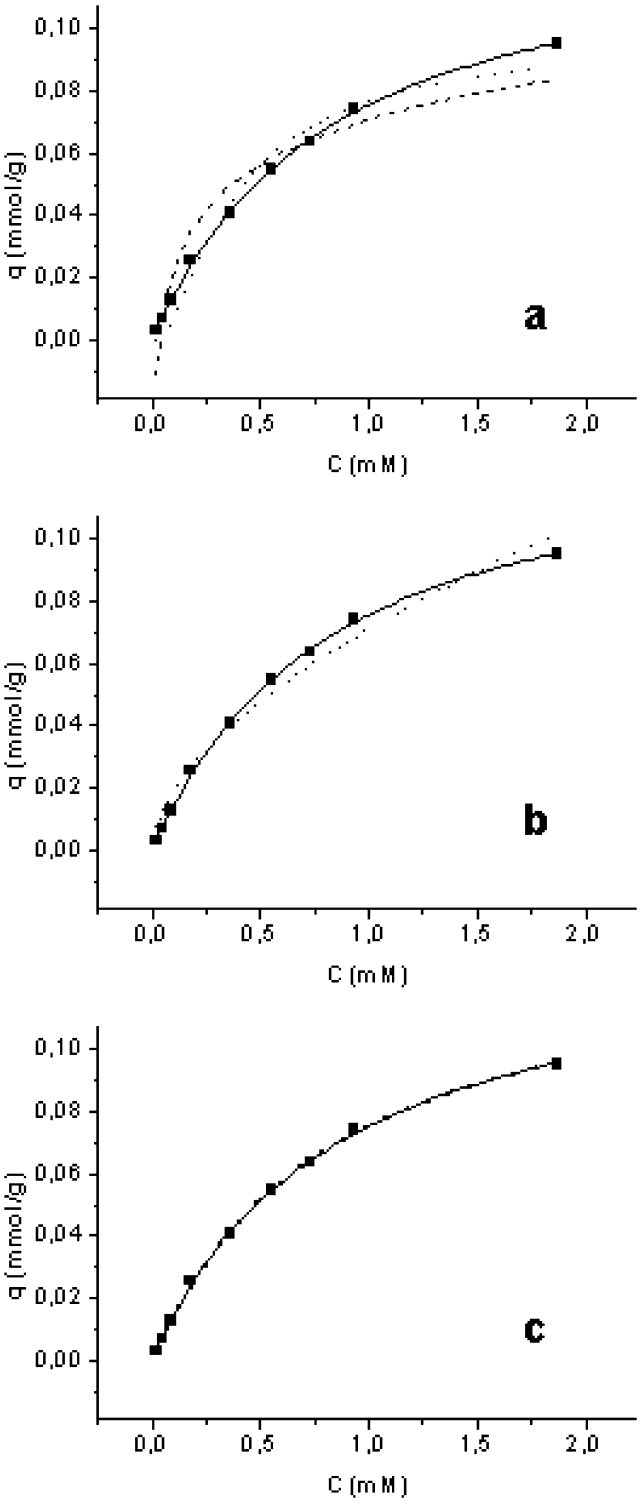

Fig. 1 Plots showing the fittings of the experimental points with different theoretical isotherms for the binding of Mn^{2+} to synthetic melanin. (**a**) — Tóth; – – – Temkin; · · · · Dubinin-Radushkevich; (**b**) — Redlich-Peterson; · · · · Freundlich; (**c**) — Langmuir; · · · · Langmuir-Freundlich

Cd^{2+} and Ni^{2+}. As a consequence, the product q_0K of the number of adsorption sites times an energetic constant varies from 0.17 $dm^3 \cdot g^{-1}$ (Mn^{2+}) to 1.50 $dm^3 \cdot g^{-1}$ (Cu^{2+}), assuming the higher values for copper and iron cations, namely the ions found in higher concentration in some natural melanins.

(2) The values of $1/n$ calculated from the Langmuir-Freundlich equations are high, indicating that the heterogeneity of the binding surface sites is generally not too elevated. This could appear in contrast with the results obtained on the adsorption of neutral molecules (Bridelli et al., 2006) but agrees with the hypothesis that only a few specific chemical groups are involved in the binding of ions.

(3) The constant a_t in the Tóth equation, shows very different values for different ions. No correlation can be found between a_t values and other parameters such as, for example, affinity.

(4) Though the Dubinin-Radushkevich equation fits the data well only in the case of Co^{2+} and consequently the data obtained from it must be considered very approximate, the calculated values of the mean free energy E of sorption per molecule (from 1.2 to 4.8 $J \cdot mmol^{-1}$ for Zn^{2+} and Co^{2+} respectively) are lower than those requested for ion-exchange mechanism (8–16 $J \cdot mmol^{-1}$) (Lin and Juang 2002).

We must be cautious before discussing the results of the kinetic analysis we performed using the above listed kinetic models. In the original Buszman et al. (1987) paper, the experimental points on which we applied the models were determined with the aim of testing the applicability of a comparative Scatchard analysis. Although they are few and no tentative evaluation of experimental errors is presented, we obtained some encouraging results. As before, we also adopted in this case the prudential estimate of 5% for the accuracy of the data generated by γ spectrometry.

Table 2 shows the values of the parameters and of correlation coefficients calculated from the experimental points fitted with the linear equations (9), (10) and (11). In the table, the notation n.d. (for Cd^{2+}) means that the dispersion of the experimental points doesn't allow any attempt of analysis. No fitting was possible with a pseudo-first-order model. The pseudo-second-order model gives very good results, as shown by the values of R^2, but unfortunately, as shown in Fig. 3, only the first 2 or 3 points are to be considered valid, the concentration of bound ion soon becoming practically constant and no further interpolation is reliable due to the experimental uncertainties. This explains the fact that the correlation coefficient results near one. An example is reported in Fig. 2. It should be noticed that the calculated values of q_e for the experiments performed with the concentration 10^{-3} M increases accordingly with the affinities evaluated by the adsorption isotherms. This allows us to evaluate the results of our analysis with more reliance.

Table 2 Parameters values obtained from the fittings with various kinetics models

Ion	C (M)	Pseudo 2nd order			Intraparticle diffusion		Elovich		
		q_e	k_2	R^2	$k_{p,2}$	R^2	a	b	R^2
Cu^{2+}	10^{-3}	0.65	0.06	0.999	0.018	0.890	0.006	0.106	0.956
	10^{-4}	0.10	0.33	0.999	0.003	0.947	−0.004	0.017	0.985
Co^{2+}	10^{-3}	0.20	0.28	0.999	0.005	0.910	0.041	0.027	0.959
	10^{-4}	0.07	0.49	0.992	0.002	0.756	−0.016	0.015	0.862
Mn^{2+}	10^{-3}	0.06	2.82	0.999	$7.8\cdot10^{-4}$	0.819	0.038	0.005	0.910
	10^{-4}	0.01	30.57	0.999	1.061	0.622	0.010	6.858	0.738
Ni^{2+}	10^{-3}	0.26	0.10	0.995	0.010	0.859	−0.087	0.058	0.940
	10^{-4}	0.07	0.82	0.998	0.002	0.831	0.008	0.011	0.912
Cd^{2+}	10^{-3}	0.27	0.72	0.999	n.d.		n.d.	n.d.	
	10^{-4}	0.04	1.63	0.996	n.d.		n.d.	n.d.	
Zn^{2+}	10^{-3}	0.26	0.08	0.972	0.006	0.642	0.043	0.030	0.570
	10^{-4}	0.08	0.73	0.999	0.002	0.893	0.014	0.011	0.960
Sn^{2+}	10^{-4}	0.03	0.35	0.969	$9.9\cdot10^{-4}$	0.991	−0.012	0.005	0.961
Cr^{3+}	10^{-3}	0.37	0.09	0.998	0.010	0.992	0.024	0.055	0.996
	10^{-4}	0.08	0.42	0.998	0.002	0.756	0.001	0.012	0.996
Fe^{3+}	10^{-3}	0.86	0.11	0.999	0.012	0.914	0.444	0.068	0.931
	10^{-4}	0.07	0.65	0.998	0.002	0.927	0.015	0.010	0.951

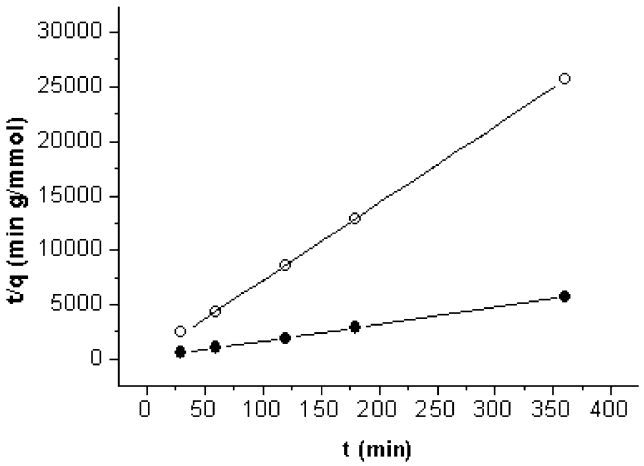

Fig. 2 Plot of the pseudo second-order adsorption kinetics of Mn^{2+} ions on synthetic melanin at different concentrations: ○ 10^{-4} M; ● 10^{-3} M

Ho and McKay (2000) and more recently Ho (2006) have discussed the meaning and the conditions of applicability of pseudo-second-order kinetics in which the initial adsorption rate increases with an increase in initial metal concentration and the rate limiting step may be the chemical adsorption but not the mass transport. Four conditions must be respected: (a) formation of a monolayer onto the surface of the particles; (b) same sorption energy for each ion, independent of surface coverage; (c) presence of localised adsorption sites and (d) rate of sorption almost negligible if compared with the initial rate. It is almost obvious that the presence of specific charged groups on the melanin surface constitutes the condition for fulfilling conditions (b) and (c).

The doubts raised by the analysis with a pseudo-second-order equation make the analysis performed with the Elovich theory interesting when this is possible as in the case of the adsorption of Cu^{2+}, Co^{2+}(10^{-3} M), Mn^{2+} (10^{-3} M), Ni^{2+}, Sn^{2+} (10^{-4} M), Zn^{2+} (10^{-4} M), Cr^{3+} and Fe^{3+}, if we accept R^2 values > 0.900. The Elovich equation allows us to evaluate the initial rate of adsorption through parameter a. Also in this case we have the confirmation of the behaviour of melanin similar to that of the very efficient carbon-based adsorbers (Cheung et al. 2001).

The data of adsorption against time at the two initial concentrations were further processed for testing the role of intraparticle diffusion as the rate controlling step. This incorporates the transport of adsorbate from bulk solution to the interior surface of the pores. The rate parameter for the intraparticle diffusion, k_p, is determined by (10). All the plots show the tendency to have the same general feature, a linearly increasing portion and a plateau, despite the experimental uncertainness that are in some cases very great. An example is represented in Fig. 3, again for the case of Mn^{2+}. The initial portion attributed to bulk diffusion is not observable. The linear trend indicates that the intraparticle diffusion controls the adsorption process. Approximate values of k_p are in the range between 9.95×10^{-4} mmol·g^{-1}·min$^{-1/2}$ (for Sn^{2+} 10^{-4} M) and 2×10^{-3} mmol·g^{-1}·min$^{-1/2}$ (for Co^{2+}, Ni^{2+}, Zn^{2+}, Cr^{3+} and Fe^{3+} 10^{-4} M). For the higher concentrations, they range

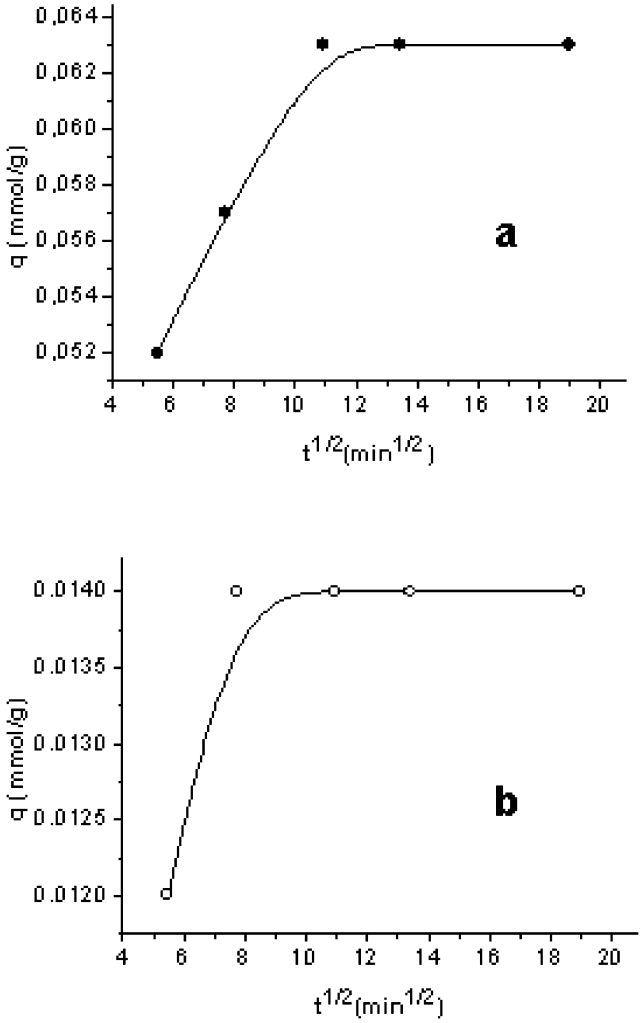

Fig. 3 Plot of the intraparticle diffusion model for adsorption of Mn^{2+} ions on synthetic melanin at different concentration: (**a**) 10^{-3} M; (b) 10^{-4} M

between 5×10^{-3} mmol·g^{-1}·min$^{-1/2}$ (for Co^{2+} 10^{-3} M) and 1.7×10^{-2} mmol·g^{-1}·min$^{-1/2}$ (for Cu^{2+} 10^{-3} M). No correlation with physical parameters of the ions was found. The intraparticle diffusion is slow and is probably the rate limiting step, namely the adsorption is governed by the diffusion within the pores of the melanin.

The specific binding sites deserve a conclusive comment. Our results are not in contrast with the coordination structures proposed on the bases of IR and EPR data (Froncisz et al. 1980). The implication of hydroxyl groups (Liu et al. 2004; Bilińska 2001), of the existence of hard and soft binding sites (Stainsack et al. 2003) and the involvement also of quinone-imine binding groups (Szpoganicz et al. 2002) can be the explication of the partial heterogeneity evaluated by us.

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