Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1076355

57 (2016) 15813–15825
July

Taylor & Francis
Taylor & Francis Group

A critical review of the applicability of Avrami fractional kinetic equation in adsorption-based water treatment studies

Nurudeen Abiola Oladoja

Department of Chemistry, Adekunle Ajasin University, Akungba Akoko, Nigeria, Tel. +234 8055438642; email: bioladoja@yahoo.com

Received 8 March 2015; Accepted 22 July 2015

ABSTRACT

The need to stem the trend in the misuse and misinterpretation of the Avrami fractional kinetic equation in adsorption-based water treatment studies necessitated the present study. Taken into account, the theoretical basis and assumptions on which the derivation of the Avrami fractional kinetic equation is based, and the contexts in which it is being used in adsorption-based water research, the Avrami kinetic equation is being misused and misinterpreted. Most often, the mathematical model of the Avrami fractionary kinetic equation has no correlation with the proposed mechanism of sorption in the sorbent–sorbate system under investigation and the denotations given to the Avrami kinetic parameters obtained are flawed. In order to correct this problem, an exposé on the original Avrami kinetic equation and cases of misuse and misinterpretation of this kinetic equation are presented. The proposed mechanisms of interactions, in each of the cases reviewed, when correlated with the assumptions and theoretical basis of the Avrami fractional kinetic equation were found to be invalid. A review that detailed the issues on the use of Avrami equation and the alternative equation for fitting solution-based sigmoidal kinetic data were also provided.

Keywords: Avrami fractional kinetic equation; Avrami kinetic parameter; Adsorption; Water treatment; Wastewater; Kinetic modeling

1. Introduction

Adsorption is an important tertiary unit process in water and wastewater treatment operations. In order to design appropriate adsorption-based water treatment operations, the time-concentration profiles of the process are usually analyzed with different kinetic equations. The results of such kinetic analysis provide valuable insights into the reaction pathways and mechanism of the sorption reactions. It helps to define how sorption rates depend on the concentrations of sorbate in solution and how rates are affected by sorption capacity or by the character of the sorbent. Consequently, the prediction of the rate at which pollutant is removed from aqueous solutions helps to establish the residence time required for completion of the sorption reaction.

The modes of interactions between sorbent and sorbate are diverse and specific, thus large array of kinetic equations have been developed to describe the possible underlying mechanism of a given

This article was originally published with errors. This version has been corrected. Please see Corrigendum (http://dx.doi.org/10.1080/19443994.2015.1097078).

sorbent–sorbate system. Common kinetic equations that have been developed and used to describe the mechanisms of sorbent–sorbate interactions in adsorption-based water treatment operations, as documented by Ho et al. [1] include: sorption reaction models, e.g. first-order forward reaction, first-order reversible reaction, second-order reaction, Langmuir–Hinshelwood kinetics, and various order reaction models (e.g. zero-order, first-order reaction, second-order reaction, third-order reaction, Elovich-type equation, parabolic diffusion); sorption diffusion models (e.g. film diffusion control and particle diffusion control); pore diffusion control, and pseudo-second-order rate control.

In order to predict the rate-controlling kinetic or diffusion process, it has been shown [1] that the identification of a potential mechanism alone is usually not sufficient, but mathematical model should be consistent with a proposed mechanism for sorption. Unfortunately, the publications of reports on water-based adsorption studies that contravene this position are growing. Recently, the use of Avrami kinetic equation to analyze the time-concentration profiles of sorbent–sorbate interaction in adsorption-based water treatment processes is being reported. On the strength of the results obtained from different error analysis procedures, it is often claimed that the Avrami fractional kinetic equation fitted best to the data obtained from the kinetic experiment. Most often, the possible modes of sorbent–sorbate interactions, based on the type of sorbate and the surface functional groups on the sorbent, and the proposed sorption mechanism of the sorption process, being reported, do not correlate with the theoretical basis and assumptions of the Avrami fractional kinetic equation. In addition, the Avrami fractional kinetic parameters derived from the process are also given wrong denotations and interpretations.

In the selection of kinetic equation to predict the mechanisms of sorbent–sorbate interactions, it was postulated [1] that a preliminary appraisal of the sorbent–sorbate system may provide information indicating the sorption mechanism. Considering the theoretical basis on which the derivation of Avrami kinetic models was predicated and the context in which it is being applied in adsorption-based water research, it is glaring that this kinetic equation is being misused and misrepresented, hence the need to provide enlightenment on if, and when, the Avrami equation might be useful in water research.

2. The Avrami kinetic equation

Between 1939 and 1941, Melvin Avrami, based at the School of Mines, Columbia University, New York, developed a theory on the kinetics of phase change [2–4]. This same equation was predated by the equation of Kolmogorov [5], derived almost simultaneously by Johnson and Mehl [6] and subsequently, Erofeyev [7], which proposed that it comprises a generalized equation for the kinetics of solid-state chemical reactions. Consequent upon the contribution of Erofeyev, the equation is sometimes referred to as Avrami-Erofeyev equation. If the contribution of Kolmogorov is considered, it is also referred to as "Kolmogorov-Johnson-Mehl-Avrami" (KJMA) model. The Avrami-Erofeyev relationship assumes [8] that the transformation proceeds by a nucleation and growth mechanism and takes into account the coalescence and ingestion of other nuclei as the new phase grows. Nucleation is assumed to be random, that is, if the entire sample was divided into small equal volumes, then the probability of a nucleus forming in each element in unit time is the same. The theory also assumes isotropic growth (equivalent growth rate in all three crystallographic directions) and that the numbers of potential nucleation sites are limited.

Originally, the general theory of the kinetics of phase change, as proposed by Avrami [2] was developed with the experimentally supported assumptions that the new phase is nucleated by germ nuclei which already exist in the old phase, and whose number can be altered by previous treatment. Premised on the findings from this general theory, a transformation-time relations for random distribution of nuclei [3] and a comprehensive description of the phenomena of phase change, summarized in phase change, grain number, and microstructure formulas or diagrams [4] were subsequently introduced.

The well-known Avrami fractional kinetic equation describes changes in the volume of the crystals as a function of time during crystallization, and has the general form:

$$F = \frac{V - V_0}{V_\mathrm{m} - V_0} = 1 - e^{-kt^n} \tag{1}$$

where V is the volume of the crystals, V_0 is the initial crystal volume (usually zero), and V_m is the maximal crystal volume attained after crystallization is complete. Of course, mass can be used instead of volume in Eq. (1), k is a temperature-dependent constant (similar to a rate constant), n is the Avrami exponent (which reflects the dimensionality of "crystal" growth), and t, is the time. The Avrami exponent, n, value can be $3 \leq n \leq 4$ (for three-dimensional growth); $2 \leq n \leq 3$ (for two-dimensional growth) or $1 \leq n \leq 2$ (for one-dimensional growth).

This function is sigmoidal, with an initial lag period, where crystallization occurs very slowly, followed by a rapid increase in crystal volume or mass. Eventually, all the material which was supersaturated crystallizes out and a plateau is reached [9]. The linearized form of this equation by simple linear regression is presented in Eq. (2) viz.:

$$\ln[-\ln(1-F)] = \ln(k) + n\ln(t) \tag{2}$$

This linear form of the Avrami kinetic equation, presented in Eq. (2) has been successfully applied to a number of solid state processes, including phase transformations [8], decompositions [10], crystallization, and intercalation reactions [11–13].

3. Overview of misuse and misrepresentation of the Avrami fractional kinetic equation

3.1. Kinetic parameters of the interaction of Hg(II) with thin chitosan membranes [14]

The adoption of Avrami kinetic equation for the interpretation of the time-concentration profiles of sorbate–sorbent interactions in adsorption-based water treatment operations appear to have stemmed from the report of Lopes et al. [14]. The Avrami kinetic equation was applied to evaluate the kinetic parameters of the interaction of Hg(II) with thin chitosan membranes. The authors claim to have provided an alternative kinetic equation to determine time-related and/or temperature-related changes in the adsorption kinetic profiles. The authors have adapted the kinetic thermal decomposition modeling [15], without any justification, theoretical basis or assumption, other than the claim that the determination of the changes in adsorption rates as a function of the initial sorbate concentrations and the sorption time, as well as the determination of fractionary kinetic orders, could be performed using the Avrami kinetic equation.

The use of this equation in thermal decomposition modeling is appropriate because the process involves phase transformation, which formed the basis of this kinetic equation, but in the context in which the Avrami kinetic equation was used by Lopes et al. [14], no phase change or transformation could be ascertained; hence, the applicability of this equation is questionable and, at best, unjustified.

In the preliminary discussion of the sorption profile, Lopes et al. [14] posited that complexation and electrostatic attraction were the underlying mechanisms of interactions of Hg(II) with the active components of the chitosan membrane. Premised on the nonlinear fitting (results shown in Fig. 1) of the kinetic data to the linear form of the Avrami kinetic equation (Eq. (2)), it was concluded [14] that the sorption process occurred in two stages viz.: the relatively fast first stage of adsorption, which was attributed to the mass transfer of Hg(II) ions from the aqueous solution to the membrane surface and the last slow stage was attributed to the migration of the metallic ions or diffusion within the pores of membranes and the interaction of the ions with the available adsorption sites on the interior membranes, binding the pore, and capillary spaces.

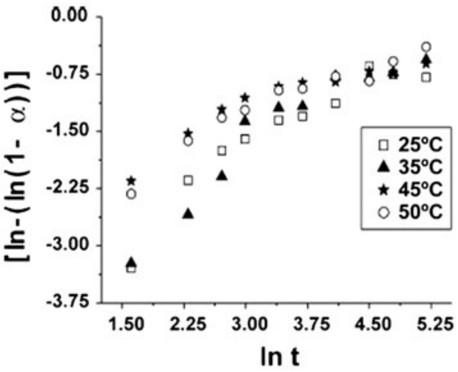

Fig. 1. Avrami kinetic linear plot of the sorption of Hg(II) on chitosan membrane [14].

Using the evidence provided by the authors as a basis to appraise the validity of using Avrami kinetic equation to the study described, it is evident that the use of this equation is unwarranted. To begin with, the poor linearity of the linear plot of the Avrami kinetic equation (as shown in Fig. 1), when fitted to the experimental data obtained from the sorption system is an enough justification to show that the Avrami kinetic equation gave poor fitting to the sorption system studied. In addition, no evidence of phase transformation of Hg(II) during the course of the sorption process could be proven; thus, the use of the Avrami kinetic equation to interpret the sorption data has no theoretical basis.

3.2. Kinetics and equilibrium parameters of Hg(II) adsorption on silica–dithizone [16]

Sílica–dithizone was synthesized and used to adsorb Hg(II) in solution at pH 6.0 and the Avrami kinetic equation was also used to elucidate the mechanism of the sorption process [16]. It was claimed that the use of the Avrami kinetic equation would enable the successful determination of the specific changes in kinetic parameters, as a function of temperature and reaction time. These claims were presumed to be the assumption of the Avrami kinetic equation. Avrami referred to the fact that specific changes in kinetic parameters could be obtained using the phase change equation proposed [2], but this is in relation to phase change by germ nuclei during a process that involves phase change. The results of the linear plots of the kinetic data, using Avrami kinetic equation, are presented in Fig. 2. The linearity of the plot (the linear coefficient values, r^2, not shown by the Authors) was poor, but the authors ascribed the trend to a two-stage adsorption process, as previously reported [14]. The relatively fast first stage of adsorption was attributed to mass transfer of Hg(II) ions from aqueous solution to the silica surface, while the last, slow stage was attributed to the migration of the metallic ions or diffusion within the pores of the silica and the interaction of the ions with the available adsorption sites on the interior, binding the pore, and capillary spaces.

Using the solution chemistry of Hg(II) (the sorbate) and the surface functional group on the Sílica–dithizone (the sorbent) as a basis, the possible sorbent–sorbate modes of interactions were postulated. It was reported that the solution chemistry of Hg is more complicated than that of other metals and in the presence of chloride ions, different species of HgCl being formed. Thus, it was concluded that the interaction of the Hg species with the silica-dithizone surface occurred through both nitrogen and/or sulfur atoms, using N=N, N–C, and C–S groups via complexation reaction. Considering the different species of the Hg species obtainable at the operating pH of the sorption system and the surface functional groups on the sorbent, the sorbent–sorbate interactions could not have occurred via a phase transformation procedure.

3.3. *Applications of Brazilian pine-fruit shell in natural and carbonized forms as adsorbents for the removal of Remazol Black B and methylene blue from aqueous solutions [17,18]*

Brazilian pine-fruit (*Araucaria angustifolia*) shell was utilized in natural form (PW) as well as the activated carbon material (AC-PW), produced from it, to remove Remazol black B textile dye (RB) from aqueous solutions [17]. In addition to the use of other kinetic equations (i.e. pseudo-first-order, pseudo-second-order, chemisorption, and intraparticle diffusion), the Avrami kinetic equation was used to fit the kinetic data obtained from the sorption process. Premised on the fact that the fractionary-order kinetic model gave the highest values of linear coefficient ($r^2 > 0.96$), the lowest error function values and the best fitting of the theoretical q_t (mg g^{-1}) values to the experimental q_t (mg g^{-1}) values (Table 1), in comparison with other kinetic models applied, at two different initial dye concentrations studied, it was assumed that the Avrami fractionary kinetic order suitably fitted the sorption process. On the basis of the results obtained when the effects of pH on the amount of dye sorbed by the sorbate was studied and the value of the pH$_{\mathrm{PZC}}$ (i.e. the pH of the point zero charge) of the sorbate, the authors proposed electrostatic attraction as the underlying mechanism of the sorbent–sorbate interactions. In a typical transformation reaction that is commonly encountered in water treatment processes (i.e. coagulation–flocculation process), electrostatic attraction, which results in charged neutralization, is one of the reaction mechanisms of the process that has been confirmed but the evidence of this process taking place in the reported study was not provided and could not be ascertained.

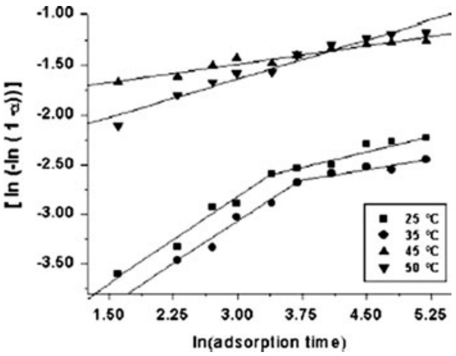

Fig. 2. Avrami kinetic linear plot of the sorption of Hg(II) on Sílica–dithizone [16].

Despite the inability of the authors to ascertain the process of phase change in the sorption process, the suitability of the Avrami kinetic equation to the process studied was further corroborated with the trends in the values of the Avrami kinetic parameters presented in Table 1. The author claimed that the values of the Avrami kinetic parameters, k_{Av}, obtained were independent of the initial sorbate concentrations studied. The authors did not take into consideration the original definition of the Avrami kinetic parameters (i.e. the k_{Av} is a temperature-dependent constant (similar to a rate constant) while, n_{Av}, is the Avrami exponent, which reflects the dimensionality of "crystal" growth). Since the parameter, k_{Av}, is only temperature-dependent constant and the experiment was conducted at fixed temperature, the values obtained could not have been initial concentration dependent. Hence, the claim that the values of the Avrami kinetic parameters, k_{Av}, obtained were independent of the initial sorbate concentrations studied has no theoretical basis. The values of the, n_{Av}, obtained was also ascribed to the resultant of the multiple kinetic order of the adsorption procedure, whereas this value is supposed to indicate the dimensionality of the crystal growth.

Table 1
Kinetic parameters for RB removal using PW and AC-PW as adsorbents [17]

	PW		AC-PW	
	100 mg dm^{-3}	200 mg dm^{-3}	100 mg dm^{-3}	200 mg dm^{-3}
Fractionary-order				
K_{Av} (h^{-1})	0.411	0.385	0.827	0.842
q_{e} (mg g^{-1})	22.5	40.2	39.6	78.5
n_{Av}	0.613	0.644	1.30	1.33
R^2_{adjusted}	0.9986	0.9999	0.9999	0.9999
F_{error}	0.210	0.0880	0.0844	0.145
Pseudo-first-order				
K_{f} (h^{-1})	0.522	0.481	0.809	0.824
q_{e} (mg g^{-1})	20.2	36.3	40.4	80.0
R^2_{adjusted}	0.9617	0.9695	0.9911	0.9899
F_{error}	1.011	1.783	1.244	2.632
Pseudo-second-order				
K_2 (g mg^{-1} h^{-1})	0.0298	0.0147	0.0194	0.0101
q_{e} (mg g^{-1})	23.2	42.1	47.8	94.5
h_0 (mg g h^{-1})	16.0	26.0	44.4	89.8
R^2_{adjusted}	0.9938	0.9963	0.9662	0.9638
F_{error}	0.444	0.624	2.425	4.980
Chemisorption				
α (mg g^{-1} h^{-1})	47.0	71.1	87.7	176.5
β (g mg^{-1})	0.230	0.123	0.0954	0.0483
R^2_{adjusted}	0.9938	0.9951	0.9406	0.9369
F_{error}	0.443	0.715	3.215	6.576
Intraparticle diffusion				
K_{id} (mg g^{-1} h$^{-0.5}$)	3.98	6.71	33.0	62.0

The same procedures applied in the interpretation of the kinetics of the sorption process, reported in the present study [17] were also employed in the interpretation of the kinetic data obtained when this same sorbents were used to remove methylene blue (MB) from aqueous solution [18] and the same conclusions were tendered.

3.4. Biosorption of Mn(II) by glutaraldehyde cross-linked chitosan beads [19]

The equilibrium and kinetic analysis of the sorption of Mn(II) from aqueous solution by glutaraldehyde cross-linked chitosan beads were performed [19]. The pseudo-second-order kinetic model, chemisorption model, the pseudo-first-order, fractional-order and Weber–Morris models were all employed to analyze the time-concentration profile of the sorption process. The linearity of the pseudo-second-order kinetic plot was the highest (>0.99) among the kinetic equations tested, but fitting of the kinetic data to the Avrami kinetic equation was also high ($r^2 > 0.96$). The results of the kinetic analysis was further evaluated with the Marquardt percentage standard deviation error function and based on the error function values obtained, the authors concluded that the kinetic data fitted to a better extent by the pseudo-second-order kinetic model and the chemisorption model, relative to the other kinetic models studied. Consequent upon the results obtained from the effects of pH on the sorption process, and the values of the $\mathrm{pH_{PZC}}$ of the cross-linked chitosan beads, electrostatic interaction was proposed as the mechanism of Mn(II) removal by the chitosan beads. If the role of electrostatic interaction is suspected as a mechanism of interaction, then justification for the use, in this study, of Avrami kinetic models, which is based on a phase change, is not apparent.

3.5. Organo-functionalized layered silicate for textile dye removal [20]

A member of the hydrous layered silicate family (an octosilicate), RUB-18, was synthesized, functionalized with silylating agent 3-trimethoxysilylpropylurea ($(CH_3O)_3Si(CH_2)_3NHCONH_2$) and used as a sorbent for Reactive Black 5 (RB-5) textile dye removal from aqueous solutions [20]. The kinetic models were fitted by employing a nonlinear method, with successive interactions calculated by the method of Levenberg–Marquardt and also by the simplex method, using the nonlinear fitting facilities of the software Microcal Origin 7.0. The R^2_{adjusted} values obtained for all the kinetic equations used (i.e. pseudo-first-order, pseudo-second-order, Avrami kinetic, and Elovich chemisorption) were high (>0.98). The kinetic models were also evaluated by an error function, which measures the differences in the amount of dye uptake (q_t (mg g^{-1})) by the adsorbent predicted by the models and the actual values (mg g^{-1}) measured experimentally. On the strength of the F_{error} values obtained, it was advanced that the Avrami kinetic model provided the best fit to the data compared to any of the other kinetic models.

The assertion that the removal of RB-5 dye by the organo-functionalized RUB-18 was best described by the fractional kinetic equation was further substantiated using the difference in the magnitude of variations in the values of the k_{Av} and k_{S} obtained, with increase in the initial dye concentrations, as an allusion (Table 2). It was reported [20] that the k_{Av} values showed a variation of 5.8%, when the initial concentration of the sorbate increased from 60.0 to 120.0 mg dm^{-3}. On the other hand, the percentage of variation of k_{S} (the pseudo-second-order rate constant) was 68.1%, when the initial concentration levels of the RB-5 dye were increased from 60.0 to 120.0 mg dm^{-3}. It should be noted that the two kinetic parameters being compared (i.e. k_{Av} and k_{S}) represent different parameters. The Avrami kinetic parameter, k_{Av}, is a temperature-dependent constant (similar to a rate constant) while, k_{S}, is the equilibrium rate constant of pseudo-second-order, whose dependency on any process variables being optimized varies.

The constant, k_{S}, value has been reported to be strongly dependent on the applied initial solute concentration [21]. It decreases with the increase in initial sorbate concentrations as a rule, which is a commonly known fact related to the interpretation of k_{S} as a time-scaling factor (obviously, the higher the initial sorbate concentration value is, the longer the time required to reach equilibrium becomes) [21–23]. Despite the widely reported dependency of k_{S} values on the initial sorbate concentration, reports of systems for which k_{S} is independent of initial solute concentration have also been reported [24–33]. The reported conflicting trends in the relationship between k_{S} and the initial sorbate concentrations was explicated via a theoretical analysis of kinetic models of sorption by Azizian et al. [34] that for the system that obeys the pseudo-second-order kinetic model, their observed rate constant is a complex function of the initial concentration of solute.

In this study, the optimum adsorption capacity of the sorbent occurred at pH 2.5–3.0, thus the underlying mechanism of sorption was assumed to have occurred via the protonation of the amino groups of the adsorbent, thus facilitating the adsorption of the negative charged dye. Evidence of phase change was also not demonstrated.

Table 2
Kinetic parameters for RB-5 removal using RUB-8 as adsorbent [20]

	C_0 (mg dm^{-3})	
	60.0	120.0
q_e *experimental* (mg g^{-1})	24.25	44.85
Fractionary-order		
K_{Av} (min^{-1})	0.01898	0.02008
q_e (mg g^{-1})	24.33	44.91
n_{Av}	0.8876	0.8738
R^2_{adjusted}	0.9998	0.9998
F_{error}	0.1139	0.2241
Pseudo-first-order		
K_f (min^{-1})	0.02047	0.02182
q_e (mg g^{-1})	23.78	43.82
R^2_{adjusted}	0.9975	0.9968
F_{error}	0.4200	0.8677
Pseudo-second-order		
K_2 (g mg^{-1} min^{-1})	7.900×10^{-4}	4.700×10^{-4}
q_e (mg g^{-1})	28.29	51.72
h_0 (mg g min^{-1})	0.6321	1.257
R^2_{adjusted}	0.9968	0.9971
F_{error}	0.4764	0.8255
Elovich Chemisorption		
α (mg g^{-1} h^{-1})	1.488	2.942
β (g mg^{-1})	0.1734	0.09513
R^2_{adjusted}	0.9817	0.9825
F_{error}	1.132	2.208

3.6. Carbon adsorbents prepared from the Brazilian pine-fruit shell for the removal of reactive orange16 dye and Procion Red MX 3B [35,36]

Activated (AC-PW) and nonactivated (C-PW) carbonaceous materials were prepared from the Brazilian pine-fruit shell (*A. angustifolia*) and tested as adsorbents for the removal of reactive orange16 dye (RO-16) from aqueous effluents [35]. Using the results obtained from the error analysis of the kinetic data as evidence, the Avrami fractionary kinetic equation was judged to give the best fit, presenting low error function values and also high r^2 values, for the two initial dye concentrations studied. The suitability of the Avrami kinetic model to the sorption process was also hinged on the assumptions reported earlier [20], on the magnitude of change in the values of the k_{Av} and k_{S} with the increase in the initial dye concentrations. Premised on the results obtained from the effects of acidity on the sorption capacity of the adsorbent, the mechanism of the sorbate sorbent interactions was assumed to have occurred through electrostatic interactions and not by a phase-change mechanism.

The removal of Procion Red MX 3B dye (PR-3B) from aqueous solution was studied using the AC-PW and C-PW [36]. Among all the kinetic equations tested, the Avrami kinetic equation was also reported to give the best description of the dye removal process. This conclusion was based on the results of the adoption of the same procedures reported [17,19,20] to have been used to validate the applicability of the kinetic equations to the kinetic experimental data. Using the results obtained from the effects of acidity on the amount of dye sorbed by the sorbent and the $\mathrm{pH_{PZC}}$ values of the sorbents, electrostatic attraction was proposed as the mechanism of interactions between the dye and each sorbents. Mechanisms of reactions related to phase change were not reported.

3.7. Pecan nutshell as biosorbent for the removal of toxic metals [37]

The feasibility of pecan nutshell (PNS, *Carya illinoensis*) serving as a biosorbent for the removal of Cr (III), Fe(III), and Zn(II) from aqueous solutions was investigated in a batch sorption procedure [37]. Among the five kinetic models tested, the adsorption kinetics were reported to fit best to the fractionary-order kinetic model (i.e. the Avrami kinetic model). The same procedures used for the validation of the Avrami kinetic equation and the conclusions proffered that have been reported [17,18,20,35,36] were adopted in this study. Using the results obtained from the sorption and desorption studies as a justification, the authors surmised that the mechanism of the metal ion removal occurred via electrostatic interactions between the carboxylic and phenolic groups of PNS with the metallic ion at pH ranging from 4.0 to 6.0, the operating pH. No evidence of phase change in the removal process was provided.

In another study, the ability of the PNS, as a biosorbent, was also evaluated in the removal of Cu (II), Mn(II), and Pb(II) from aqueous solutions in a batch process [28]. Among the four kinetic models tested, the fractionary-order kinetic model was adjudged to give the best fitting to the kinetic data obtained from the process. The validation of the kinetic fitting was performed following the procedures earlier reported [17,18,20,35–37]. The results obtained from the fitting of the experimental data to fractionary kinetic model, intraparticle diffusion model, and desorption experiments were assumed to be indicative of interaction of the carboxylic and phenolic groups on the PNS with the metallic ion, at pH ranging from 5.0 to 6.0 and not any form of phase change reaction process.

3.8. Determination of kinetic parameters from isothermal calorimetry for interaction processes of pyrimethamine with chitosan derivatives [39]

The interactions of the antifolate drug, pyrimethamine with chitosan derivatives, namely, chit-GLT (glutaraldehyde cross-linked chitosan gel beads), and chit-Cu (chit-GLT beads treated with copper solution) were investigated using isothermal calorimetry at 298 and 308 K [39]. The kinetic parameters of the interactions were studied using Avrami and pseudo-first- and second-order kinetic models. The Avrami kinetic model was reported to provide the best fitting to the experimental data. The procedures employed to determine the best kinetic model that described the sorption process were similar to those that have been reported [17,18,20,35,37,38]. The linear coefficient values (r^2) of the kinetic plot (Eq. (2)) were not reported, but the linear plot was segmented into three sections by the authors (Fig. 3). Thus, three different Avrami kinetic parameters (i.e. n and k_{Av}) were obtained for the three independent segmented portions of the graphs. The first values of n and k_{Av} were attributed to the interactions of the adsorbate with the surface sites of the adsorbent, while the values obtained for the intermediate linear segments were attributed to occupation of internal adsorption sites of materials. The different values of n, obtained in the experiment were also ascribed to the fact that all interaction processes presented different interaction mechanisms for

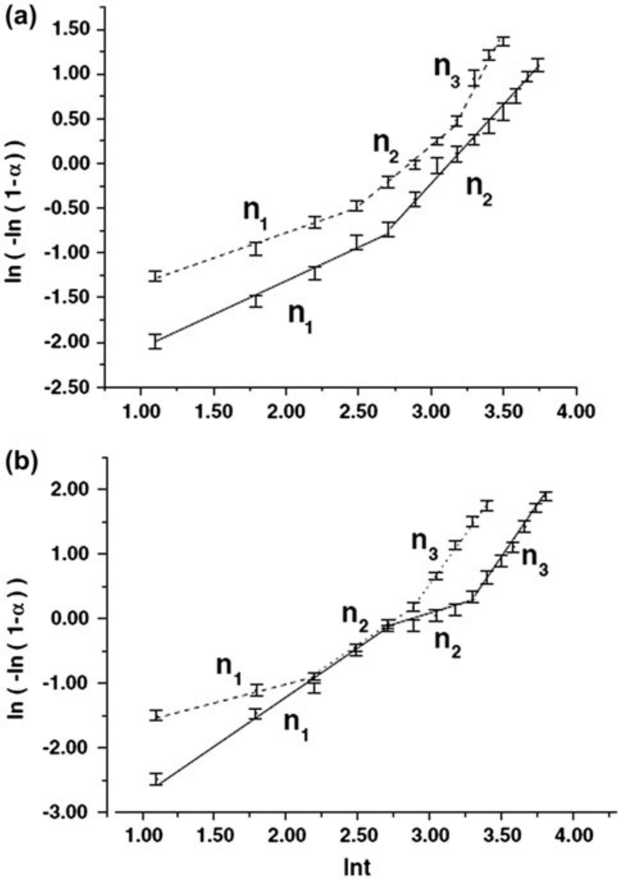

Fig. 3. Avrami plots for the interaction of pyrimethamine with the chitosan derivatives at (a) 298 K and (b) 308 K. Dash line is Pyr/chit-Cu and solid line is Pyr/chit-GLT [39].

all contact times evaluated and seemed to represent temperature dependence. The procedure adopted by the authors has no basis in the original Avrami kinetic equation, but an adoption of the interpretations provided by Lopes et al. [14], who claimed to have provided an alternative kinetic equation to determine time-related and/or temperature-related changes in the adsorption kinetic profiles. Consequent upon the results obtained from the calorimetry study, it was inferred that in chit-raw, the type of interaction that may be involved with the pyrimethamine is hydrophobic interactions. This is because chitosan has a strong potential for chemical interactions towards hydrophobic material, since it acts as a participant in hydrophobic interactions; owing to its remaining acetyl groups. It was also suggested that solution temperature plays a role in the chit-GLT-drug interaction by the residual aldehyde moieties on chit-GLT, through a Schiff-base formation reaction with NH_2 groups of pyrimethamine. For chit-Cu, the higher interaction energy values suggest reactions other than hydrophobic interactions and Schiff-base formation reaction. In this case, the covalent attachment of the drug with adsorbed Cu(II) was strongly suggested. No evidence of phase change was reported.

3.9. Organo-functionalized kenyaite for dye removal from aqueous solution [40]

A new nanomaterial, organo-functionalized kenyaite, was used to remove sumifix brilliant orange 3R (SBO) textile dye from aqueous solution in a batch wise process [40]. Based on the error function values (F_{error}), the kinetic data obtained were pronounced to best fitted to fractional-order and chemisorption kinetic models when compared with pseudo-first-order and pseudo-second-order kinetic models. The authors opined that the mechanism of the reaction occurred via an exchange process at the solid/liquid interface (Fig. 4). It was proposed that the sulfonate and sulfate-ethyl-sulfonate groups (negative charges) of the SBO ionically interacted with the protonated nitrogens, attached to the pendant chain, covalently grafted on the silicate layer. This interactive process is believed to be favored at $pH < 4$, when the basic nitrogen atoms are easily protonated to acquire a positive charge.

3.10. Sodic and acidic crystalline lamellar magadiite adsorbents for the removal of MB from aqueous solutions [41]

The potentials of two synthetic crystalline lamellar nanosilicates, sodic magadiite (Na-mag), and its converted acidic form (H-mag), were studied as adsorbents for the removal of the dye, MB from aqueous solutions in a batch procedure [41]. On the strength of the results obtained from the error analysis, the Avrami kinetic equation was assumed to give the best description of the sorption process. The mechanism of the sorption of MB by either Na-mag or H-mag was assumed to have occurred by interacting exchanger process at the solid–liquid interface (Fig. 5). For H-mag the adsorption was presumed to have followed two steps, while for Na-mag only one step was proposed. For H-mag, in the first step, it was believed that the lamellar silicate got equilibrated with the aqueous solution ($8.5 < pH < 10.0$), and the available silanol groups lost protons, to form interchangeable sodium silicate. In the second step, for both H-mag and for Na-mag, the MB became intercalated inside the lamella of the silicate, via an ion exchange process

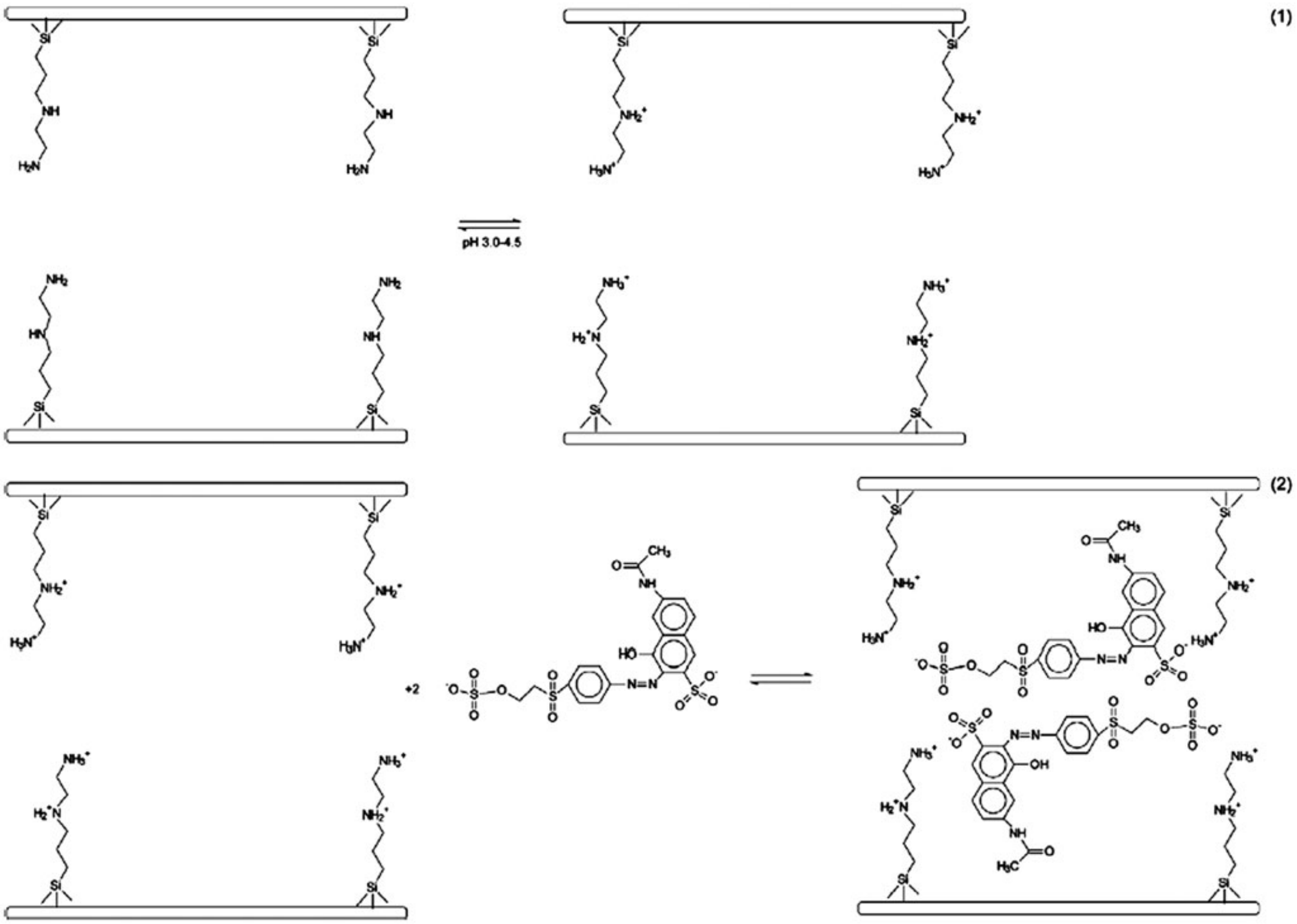

Fig. 4. Proposed mechanism of sorption of SBO by organofucntionalised kenyaite [40].

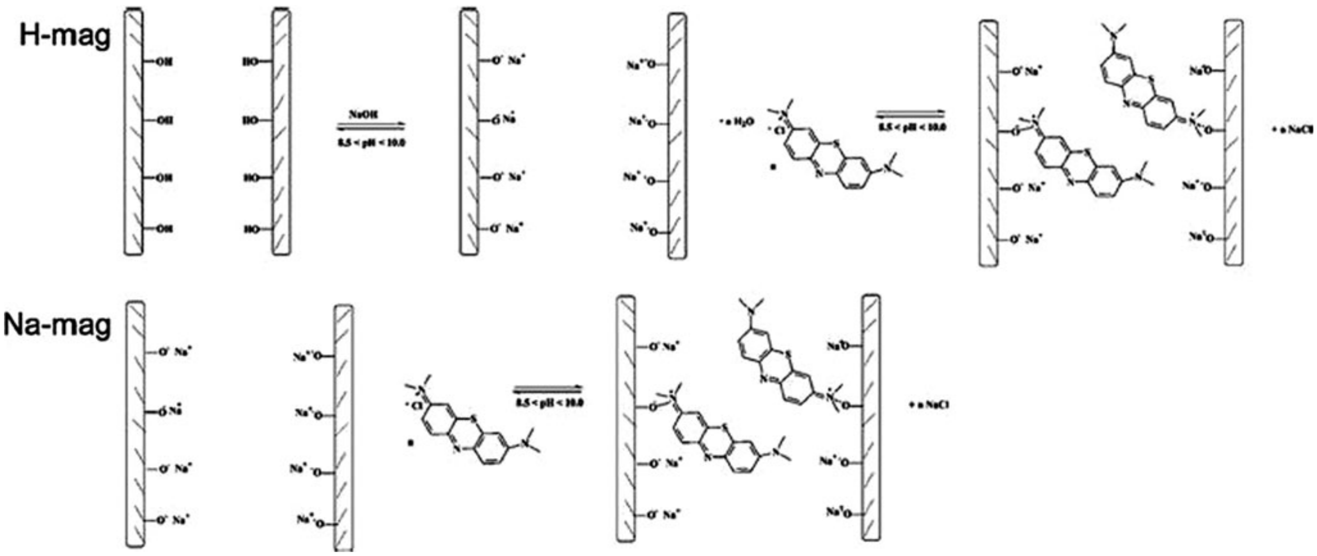

Fig. 5. Proposed mechanism of sorption of MB by H-mag and Na-mag [41].

between the positively charged MB and the sodium cation, originally bound to the silicate matrix. The role of ion exchange mechanism in the MB removal by the sorbents were also affirmed through the desorption studies.

3.11. Silica grafted with a silsesquioxane as adsorbent for anionic dye removal [42]

In this study, Silica was modified with a water soluble silsesquioxane, containing a double-charged 1,4-diazoniabicyclo[2.2.2]octane, to produce an adsorbent (Dabcosil-Al-SiO_2) for the removal of the dye, brilliant yellow (BY), from aqueous solution [42]. Adopting the procedure earlier reported [17,18,20,35–39] for testing the applicability of kinetic equation to a sorption process, the Avrami kinetic equation was argued to be the most suitable kinetic equation that fitted the sorption process. Consequent upon the fact that the BY is an anionic dye, containing two sulfonic groups and the adsorbent dabcosil-Al-SiO_2 possesses formal positive charges, the mechanism of interaction adsorbent–adsorbate was proposed to have occurred through an ion exchange mechanism.

3.12. Removal of anionic dyes in the presence of anionic surfactant using aminopropylsilica [53]

Aminopropyl-silica (Sil-NH_2) was synthesized and used to adsorb the dyes, commercially available as reactive yellow GR (yellow dye) and reactive red RB (red dye) from aqueous solutions at pH 4.0 [43]. The influence of the anionic surfactant SDS on the adsorption data was also studied. Adopting the procedure earlier reported [14,16,39] for the validation of the best kinetic model that described the process, the Avrami kinetic equation was judged to be the best. The proposed mechanism of the dye removal by the adsorbent was electrostatic attraction between the positively charged protonated amine group and the negatively charged functional group on the dye molecules.

4. Issues on the use of Avrami equation and the alternative equation for fitting solution-based sigmoidal kinetic data

A common feature of kinetic data for many solid-state reactions is their sigmoidally shaped kinetic curves. Unfortunately, the discussion that follows, such sigmoidally shaped kinetic data have proven difficult for the solid-state literature to fit in an agreed upon way. Especially lacking are clear physical insights, for example, even into the basic steps of nucleation and growth, from previously employed fitting methods [44].

The Avrami kinetic equation is based on the model put forth by Kolmogorov [5], Johnson and Mehl [6], Avrami [2–4] (the KJMA theory), and Erofe'ev [7]. The basic KJMA theory consists of four main assumptions [45,46] viz.:

1. that phase transformations occur via nucleation and growth;
2. that "germs" (i.e. nucleation sites) are distributed randomly, i.e. nucleation is homogeneous;
3. that the critical nucleus size is zero, so that nucleation is completely spontaneous; and
4. that the nucleation and growth laws are given a priori, meaning that the rate equations given are assumed and not based on experimental evidence or chemical or mechanistic insights or principles [44]. This is a common problem in the solid-state literature, one that leads to multiple, often increasingly complex equations to treat solid-state kinetic data [44].

The enormous amount of literature that has evolved over the last several decades provides compelling evidence for the assertion [47] that "formulating chemical mechanisms for reactions of solids has turned out to be far more difficult than was foreseen in early work."

Generally, the Avrami fractional kinetic equation often talk of nucleation and growth, but contain only a single rate parameter, k, a practice that causes considerable confusion. This confusion was the impetus for the research question postulated by Finney and Finke [44] that "how is it possible to talk about two chemical processes with only one rate constant? Something must be amiss here!?" It has also been noted that it is important for kinetic investigations of solid-state reactions to be able to distinguish the roles of nucleation and of growth [48]. In another treatise [49], the need for greater emphasis on chemical, rather than mathematical, representations of solid-state reaction kinetics was highlighted.

The main weakness of the Avrami model, as enumerated by Finney and Finke [44], include the difficulty in assigning physical meaning to the parameters k and n (i.e. the Avrami fractional kinetic parameters). Another significant weakness is that although k is often called a rate constant, it is not, since it is not defined by a specific chemical equation. Instead, k is a rate-related parameter, one that can be viewed as a convolution that includes the rate constants for chemically well-defined processes of nucleation and autocatalytic growth. Another issue is the Avrami parameter *n*, a parameter generally believed to be related to the dimensionality of nucleation; however, exactly how it relates to dimensionality cannot be easily extracted and is indeed a subject of continuing debate as are nonphysical values ("dimensions" in space) of $n < 1$ or $n \geq 4$. Another fundamental weakness of the Avrami equation and related equation-based solid-state literature is the large number of different models used to describe the kinetics of solid-state transformations. An issue with the Avrami and related models is that some are quite complicated without compelling evidence being available that more complicated models are warranted.

In order to overcome the disconnect between the observed kinetics vs. the concepts and words employed in the highly complex area of solid-state kinetics, efforts were made to see if there is not a minimal chemical mechanism that can provide statistically equivalent fits to solid-state and other phase-transformation kinetic data, classically treated by the Avrami kinetic model or its derivatives [44]. It was assumed that doing so is an important, missing piece of attempts to fit and draw chemical insight from solid-state kinetics, as made apparent by citations and quotations from the literature, which detail the presently confused state of solid-state kinetics and, especially, what those kinetics mean in terms of the underlying chemical mechanism(s).

Consequently, the one available, minimalistic, chemical mechanism-based kinetic model that is able to deconvolute nucleation from growth, a model originally developed for transition-metal nanocluster nucleation and growth in solution was tested. The Finke-Watzky two-step kinetic model of nucleation (k_1) and autocatalytic growth (k_2) are presented below [50]:

$$\text{Step 1}: \mathrm{A} \xrightarrow{k_1} \mathrm{B}$$

$$\text{Step 2}: \mathrm{A} + \mathrm{B} \xrightarrow{k_2} 2\mathrm{B}$$

The applicable rate equation for the kinetically important steps 1 and 2 is shown in Eq. (3):

$$-\frac{\mathrm{d}[A]}{\mathrm{d}t} = +\frac{\mathrm{d}[B]}{\mathrm{d}t} = k_1[A] + k_2[A][B] \tag{3}$$

The data from the solid-state reactions are typically given in terms of the amount of starting material transformed into product, *R*, which increases with time. In the Avrami equation, then, *R* also increases with time. The F–W model, in comparison, historically has fit data for the loss of concentration of the precursor, *A* (in the two steps reaction scheme illustrated above). The integrated rate equation for the loss of *A* over time is given in Eq. (4) [50].

$$[A]_t = \frac{\frac{k_1}{k_2} + [A]_0}{1 + \frac{k_1}{k_2[A]_0 \exp\left[\left(k_1 + k_2[A]_0\right)t\right]}} \tag{4}$$

This equation is known as the two-step chemical mechanism-based model (known as the Finke–Watzky (F–W) model) [50]. This two-step model tested was able to fit solid-state phase transformation kinetic data equally well, in comparison to fits obtained using the classic Avrami kinetic equation. The F–W model is a simple, Ockham's–Razor-based mechanism which fits a wide variety of sigmoidal data in nature [50–53] closely using only two chemically well-defined rate constants. These rate constants have clear meaning from their chemical-equation basis (at least in solution) and can, therefore, be connected rigorously and without confusion to useful chemical concepts/words, notably nucleation (k_1) and (autocatalytic) growth (k_2'), even if those words and concepts are oversimplifications that may have limitations for complex areas such as solid-state phase transitions. The F–W model has also been able to provide physical insights into at least solution nanocluster synthesis and stabilization [44].

5. Conclusion

(1) The Avrami kinetic model has been adapted from the kinetics of thermal decomposition modeling of phase changes to adsorption-based water treatment without any justification, theoretical, or other basis for doing so;
(2) The theoretical basis of the Avrami kinetic equation has no correlation with the proposed mechanism of sorbent–sorbate interactions in all the cases studied. In particular, there is no phase change in sorbent–sorbate interactions as needed before the applicability of the Avrami equation could make sense
(3) The Avrami kinetic parameters are given the wrong denotation or description, which is totally at variance with the original definition of the Avrami *k* and *n*, and without any justification for doing so.
(4) The conclusions reached, based on the values of the Avrami kinetic parameters obtained from the linear fittings of the kinetic experimental data, have no theoretical basis and, worse, no physical basis

(5) Moreover and significantly, for kinetic curves that are sigmoidal, there is now available a two-step, chemical mechanism known as the Finke–Watzky Mechanism, $A \rightarrow B$ (rate constant), $A + B \rightarrow 2B$ (rate constant) that is solution-based and is the chemical equivalent of the Avrami equation that can and should be used in place of the Avrami fractional kinetic equation

Acknowledgment

The author is grateful to the anonymous reviewers for the suggestions and contributions made to enhance the scientific merits of the manuscript

References

[1] Y.S. Ho, J.C.Y. Ng, G. McKay, Kinetics of pollutant sorption by biosorbents: Review, Sep. Purif. Methods 29(2) (2000) 189–232.

[2] M. Avrami, Kinetics of phase change. I. general theory, J. Chem. Phys. 7 (1939) 1103–1112.

[3] M. Avrami, Kinetics of phase change. II. Transformation-time relations for random distribution of nuclei, J. Chem. Phys. 8 (1940) 212–224.

[4] M. Avrami, Kinetics of phase change. III. Granulation, phase change, and microstructure, J. Chem. Phys. 9 (1941) 177–184.

[5] A.N. Kolmogorov, On the statistical theory of crystallization in metal, Izv. Akad. Nauk SSSR, Ser. Fiz. 1 (1937) 335 (Bull. Acad. Sci. USSR, Phys. Ser.).

[6] W.A. Johnson, R.F. Mehl, Reaction kinetics in processes of nucleation and growth, Trans. AIME, 135(8) (1939) 416–442.

[7] B.V. Erofeyev, Generalized equation of chemical kinetics and its application in reactions involving solids, C.R. (Dokl.) Acad. Sci. WRSS 52 (1946) 511–514.

[8] A.K. Sheridan, J. Anwar, Kinetics of the solid-state phase transformation of form β to γ of sulfanilamide using time-resolved energy-dispersive X-ray diffraction, Chem. Mater. 8 (1996) 1042–1051.

[9] A.G. Marangoni, On the use and misuse of the avrami equation in characterization of the kinetics of fat crystallization, J. Am. Oil Chem. Soc. 75(10) (1998) 1465–1467.

[10] J.D. Hancock, J.H. Sharp, Method of comparing solid-state kinetic data and its application to the decomposition of kaolinite, brucite, and $BaCO_3$, J. Am. Ceram. Soc. 55 (1972) 74–77.

[11] S.J. Price, J.S.O. Evans, R.J. Francis, D. O'Hare, Kinetics of metallocene intercalation into layered metal dichalcogenide hosts, Adv. Mater. 8 (1996) 582.

[12] G.R. Williams, A.I. Khan, D. O'Hare, Mechanistic and kinetic studies of guest ion intercalation into layered double hydroxides using time-resolved, *In-situ* X-Ray Powder Diffraction, in Structure and Bonding, in: X. Duan, D.G. Evans (Eds.), Layered Double Hydroxides, vol. 119, Springer, Berlin/Heidelberg, 2006, pp. 161–192.

[13] A.P. Wilkinson, J.S. Speck, A.K. Cheetham, *In situ* X-ray diffraction study of crystallization kinetics in $PbZr_{1-x}Ti_xO_3$, (PZT, x = 0.0, 0.55, 1.0), Chem. Mater. 6 (1994) 750–754.

[14] E.C.N. Lopes, F.S.C. dos Anjos, E.F.S. Vieira, A.R. Cestari, An alternative Avrami equation to evaluate kinetic parameters of the interaction of Hg(II) with thin chitosan membranes, J. Colloid Interface Sci. 263 (2003) 542–547.

[15] A. Putnis, Introduction to Mineral Sciences, Cambridge Univ. Press, Melbourne, 1995.

[16] A.R. Cestari, E.F.S. Vieira, E.C.N. Lopes, R.G. da Silva, Kinetics and equilibrium parameters of Hg(II) adsorption on silica–dithizone, J. Colloid Interface Sci. 272 (2004) 271–276.

[17] N.F. Cardoso, R.B. Pinto, E.C. Lima, T. Calvete, C.V. Amavisca, B. Royer, M.L. Cunha, T.H.M. Fernandes, I.S. Pinto, Removal of remazol black B textile dye from aqueous solution by adsorption, Desalination 269 (2011) 92–103.

[18] B. Royer, N.F. Cardoso, E.C. Lima, J.C.P. Vaghetti, N.M. Simon, T. Calvete, R.C. Veses, Applications of Brazilian pine-fruit shell in natural and carbonized forms as adsorbents to removal of methylene blue from aqueous solutions—kinetic and equilibrium study, J. Hazard. Mater. 164 (2009) 1213–1222.

[19] M. Suguna, A.S. Reddy, N.S. Kumar, A. Krishnaiah, Biosorption of Manganese(II) ions from aqueous solution by glutaraldehyde cross-linked chitosan beads: Equilibrium and kinetic studies, Adsorpt. Sci.Technol. 28(3) (2010) 213–228.

[20] B. Royer, N.F. Cardoso, E.C. Lima, T.R. Macedo, C. Airoldi, A useful organofunctionalized layered silicate for textile dye removal, J. Hazard. Mater. 181 (2010) 366–374.

[21] W. Plazinski, W. Rudzinski, A. Plazinska, Theoretical models of sorption kinetics including a surface reaction mechanism: A review, Adv. Colloid Interface Sci. 152 (2009) 2–13.

[22] J. Febrianto, A.N. Kosasih, J. Sunarso, Y.H. Ju, N. Indraswati, S. Ismadji, Equilibrium and kinetic studies in adsorption of heavy metals using biosorbent: A summary of recent studies, J. Hazard. Mater. 162 (2009) 616–645.

[23] S.R. Popuri, Y. Vijaya, V.M. Boddu, K. Abburi, Adsorptive removal of copper and nickel ions from water using chitosan coated PVC beads, Bioresour. Technol. 100 (2009) 194–199.

[24] M.A. Al-Ghouti, M.A.M. Khraisheh, M.N.M. Ahmad, S. Allen, Adsorption behaviour of methylene blue onto Jordanian diatomite: A kinetic study, J. Hazard. Mater. 165 (2009) 589–598.

[25] R. Aravindhan, N.N. Fathima, J.R. Rao, B.U. Nair, Equilibrium and thermodynamic studies on the removal of basic black dye using calcium alginate beads, Colloids Surf., A 299 (2007) 232–238.

[26] D. Kavitha, C. Namasivayam, Experimental and kinetic studies on methylene blue adsorption by coir pith carbon, Bioresour. Technol. 98 (2007) 14–21.

[27] M. Alkan, Ö. Demirbaş, M. Doğan, Adsorption kinetics and thermodynamics of an anionic dye onto sepiolite, Microporous Mesoporous Mater. 101 (2007) 388–396.

[28] Y. Vijaya, S.R. Popuri, V.M. Boddu, A. Krishnaiah, Modified chitosan and calcium alginate biopolymer

sorbents for removal of nickel (II) through adsorption, Carbohydr. Polym. 72 (2008) 261–271.

[29] J. Yu, M. Tong, X. Sun, B. Li, Cystine-modified biomass for Cd(II) and Pb(II) biosorption, J. Hazard. Mater. 143 (2007) 277–284.

[30] P.X. Sheng, K.H. Wee, Y.P. Ting, J.P. Chen, Biosorption of copper by immobilized marine algal biomass, Chem. Eng. J. 136 (2008) 156–163.

[31] N. Ertugay, Y.K. Bayhan, Biosorption of Cr (VI) from aqueous solutions by biomass of *Agaricus bisporus*, J. Hazard. Mater. 154 (2008) 432–439.

[32] N.A. Oladoja, R.O.A. Adelagun, I.A. Ololade, E.T. Anthony, M.O. Alfred, Synthesis of nano-sized hydrocalumite from a Gastropod shell for aqua system phosphate removal, Sep. Purif. Technol. 124 (2014a) 186–194.

[33] N.A. Oladoja, A.L. Ahmad, A.O. Adesin, Biogenic derived binary metal oxide as a reactive material for remediation of pyrophosphate contaminated aqua system, J. Water Process Eng. 3 (2014) 82–89, doi: 10.1016/j.jwpe.2014.05.013.

[34] S. Azizian, Kinetic models of sorption: A theoretical analysis, J. Colloid Interface Sci. 276 (2004) 47–52.

[35] T. Calvete, E.C. Lima, N.F. Cardoso, J.C.P. Vaghetti, S.L.P. Dias, F.A. Pavan, Application of carbon adsorbents prepared from Brazilian-pine fruit shell for the removal of reactive orange 16 from aqueous solution: Kinetic, equilibrium, and thermodynamic studies, J. Environ. Manage. 91 (2010) 1695–1706.

[36] T. Calvete, E.C. Lima, N.F. Cardoso, S.L.P. Dias, F.A. Pavan, Application of carbon adsorbents prepared from the Brazilian pine-fruit-shell for the removal of Procion Red MX 3B from aqueous solution—kinetic, equilibrium, and thermodynamic studies, Chem. Eng. J. 155 (2009) 627–636.

[37] J.C.P. Vaghetti, E.C. Lima, B. Royer, N.F. Cardoso, B. Martins, T. Calvete, Pecan Nutshell as biosorbent to remove toxic metals from aqueous solution, Sep. Sci. Technol. 44 (2009) 615–644.

[38] J.C.P. Vaghetti, E.C. Lima, B. Royer, B.M. da Cunha, N.F. Cardoso, J.L. Brasil, S.L.P. Dias, Pecan nutshell as biosorbent to remove Cu(II), Mn(II) and Pb(II) from aqueous solutions, J. Hazard. Mater. 162 (2009) 270–280.

[39] E.F.S. Vieira, A.R. Cestari, E.C.N. Lopes, L.S. Barreto, G.S. La´zaro, L.E. Almeida, Determination of kinetic parameters from isothermal calorimetry for interaction processes of pyrimethamine with chitosan derivatives, React. Funct. Polym. 67 (2007) 820–827.

[40] B. Royer, N.F. Cardoso, E.C. Lima, V.S.O. Ruiz, T.R. Macedo, C. Airoldi, Organofunctionalized kenyaite for dye removal from aqueous solution, J. Colloid Interface Sci. 336 (2009) 398–405.

[41] B. Royer, N.F. Cardoso, E.C. Lima, T.R. Macedo, C. Airoldi, Sodic and acidic crystalline lamellar magadiite adsorbents for the removal of methylene blue from aqueous solutions: Kinetic and equilibrium studies, Sep. Sci. Technol. 45 (2010) 129–141.

[42] D.S.F. Gay, T.H.M. Fernandes, C.V. Amavisca, N.F. Cardoso, E.V. Benvenutti, T.M.H. Costa, E.C. Lima, Silica grafted with a silsesquioxane containing the positively charged 1,4-diazoniabicyclo[2.2.2]octane group used as adsorbent for anionic dye removal, Desalination 258 (2010) 128–135.

[43] A.R. Cestari, E.F.S. Vieira, G.S. Vieira, L.E. Almeida, The removal of anionic dyes from aqueous solutions in the presence of anionic surfactant using aminopropylsilica—A kinetic study, J. Hazard. Mater. 138 (2006) 133–141.

[44] E.E. Finney, R.G. Finke, Is there a minimal chemical mechanism underlying classical Avrami–Erofe'ev treatments of phase transformation kinetic data? Chem. Mater. 21 (2009) 4692–4705.

[45] M. Fanfoni, M. Tomellini, The Johnson–Mehl–Avrami–Kohnogorov model: A brief review, Il Nuovo Cimento D 20 (1998) 1171–1182.

[46] F. Liu, F. Sommer, E.J. Mittemeijer, Parameter determination of an analytical model for phase transformation kinetics: Application to crystallization of amorphous Mg–Ni alloys, J. Mater. Res. 19 (2004) 2586–2596.

[47] A.K. Galwey, M.E. Brown, Solid-state decompositions—stagnation or progress? J. Therm. Anal. Calorim. 60 (2000) 863–877.

[48] A.K. Galwey, What can we learn about the mechanisms of thermal decompositions of solids from kinetic measurements? J. Therm. Anal. Calorim. 92 (2008) 967–983.

[49] A.K. Galwey, M.E. Brown Thermal Decomposition of Ionic Solids. Studies in Physical and Theoretical Chemistry, vol. 86, Elsevier, New York, NY, 1999 (Chapter 3), pp. 75–115.

[50] M.A. Watzky, R.G. Finke, Transition metal nanocluster formation kinetic and mechanistic studies. A new mechanism when hydrogen is the reductant: Slow, continuous nucleation and fast autocatalytic surface growth, J. Am. Chem. Soc. 119 (1997) 10382–10400.

[51] A.M. Morris, M.A. Watzky, J.N. Agar, R.G. Finke, Fitting neurological protein aggregation kinetic data via a 2-step, minimal/"Ockham's Razor" model: The Finke−Watzky mechanism of nucleation followed by autocatalytic surface growth, Biochemistry 47 (2008) 2413–2427.

[52] M.A. Watzky, A.M. Morris, E.D. Ross, R.G. Finke, Fitting yeast and mammalian prion aggregation kinetic data with the Finke−Watzky two-step model of nucleation and autocatalytic growth, Biochemistry 47 (2008) 10790–10800.

[53] A.M. Morris, M.A. Watzky, R.G. Finke, Protein aggregation kinetics, mechanism, and curve-fitting: a review of the literature, Biochim. Biophys. Acta 1794 (2009) 375–397.