

A Kinetic Model for Bleaching Vegetable Oils

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ABSTRACT: Very little data and very few kinetic models are available describing and evaluating the performance of bleaching processes, earths, and equipment. This work presents a general kinetic model for the adsorption of pigments by adsorbent earths in several edible oils. It reports the kinetic parameters found for two bleaching earths (one developed in the laboratory and one commercial) for the clarification of soybean oil, as well as their activation energies. The proposed kinetic model is second order in the dimensionless pigment concentration and is in good agreement with our experimental data. A very simple mechanistic explanation based on adsorption/deactivation is offered to justify its application. We also present mathematical modeling based on balance equations to show how the kinetic parameters can be used for bleaching earths and for industrial equipment evaluation and design, such as for the transient fed-batch stirred bleaching vessel. The model seems appropriate to represent data under different operating conditions such as temperature and adsorbent load. The simulation shows that startup procedures are very important in the bleaching process—at least as important as the batch step, in which the oil color reaches its desired standard.

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Bleaching is an important step in the refining of vegetable oils and is responsible for removing substances that give color to the oil (1). Appropriate design and operation of the bleaching process require a knowledge of kinetics so that engineering analyses can be properly carried out. This study was motivated by the limited kinetic data and descriptive models available for bleaching vegetable oils. To evaluate the oil bleaching step, scaleup procedures, and industrial equipment, a predictive model should be used. Some authors (2,3) have made use of an empirical model proposed by Brimberg (4) at Alfa Laval in Sweden several years ago:

$$\ln \frac{C}{C_o} = -k_B \sqrt{t} \quad [1]$$

where C is the pigment concentration at bleaching time t , C_o is the initial pigment concentration, and k_B is a rate constant. Unfortunately, this model has two major drawbacks: (i) It does not fit the data very well, particularly for more prolonged batch ex-

periments, requiring a kinetic parameter change for sequential experimental intervals, and (ii) it lacks an appropriate mechanistic basis, therefore consisting of an empirical fitting exercise. More recently, Langmaack and Eggers (5) took into account mass-transfer limitations (internal and external) and incorporated operating variables such as the amount of clay added and the power input into the vessel. Our analyses of mass-transfer resistances, however, showed that we may ignore possible internal diffusion limitations since the Thiele modulus is very low for industrial-sized particles such as those used here; therefore, the calculated effectiveness factor was always very close to one (see Table 1 for calculated values); external mass-transfer resistances were evaluated and ignored, according to the Mears criterion (6).

In this work we propose a simple kinetic model based on the basic principles of adsorption and chemical reaction engineering. The approach followed suggestions given by Levenspiel (7) to avoid complex descriptions in which parameter uncertainties mask the deviations that occur when fundamental changes are made in the process.

EXPERIMENTAL PROCEDURES

Two adsorbents were used for the clarification of soybean oil: (i) a bentonite-based formulation prepared in our laboratory, labeled MC20, and (ii) a commercial bleaching earth (Fulmont F180), used as a reference. The characteristics of MC20 are shown in Table 2.

Bleaching procedures and testing equipment followed recommendations of the American Oil Chemists' Society (8), with minor convenient adaptations as described elsewhere (3,9). They mostly consisted of using a three-necked flask—one neck for mechanical stirring (1750 rpm), another for nitrogen carrier gas (under 80 Torr) entrance and sample withdrawal, and the third for vacuum pump connection. Runs were carried out in batch mode at different temperatures and earth concentrations. Pigments present in the oil were then removed by adsorption. Oil samples of 2 mL (in duplicate) were withdrawn at regular intervals: initially every 3 min for 15 min, and then every 5 min. This sample size did not significantly modify the volume of oil in the flask (approximately 540 mL of oil). After centrifuging to separate the adsorptive earth, the oil was diluted in industrially bleached oil; samples were analyzed by using a spectrophotometer, with absorbance readings at 420 nm. Pigment concentration profiles were recovered and reported as relative absorbances using industrially bleached oil as a reference. Each run was carried out for 120 min, well above the usual time

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TABLE 1
Calculated Values of the First-Order Modified Kinetic Constant, k' , for the Clarification of Soybean and Corn Oils and the Variation in Mass-Transfer Parameters^a

Oil	Earth					
	Earth (%)	T (°C)	Parameter (k')	Thiele modulus	Effectiveness factor (h)	Weisz–Prater number (C_{WP})
Fulmont F180/soybean oil	0.5	100	0.05	0.292	0.994	0.085
	0.8	100	0.09	0.405	0.989	0.162
	1	100	0.08	0.379	0.991	0.142
	1	100	0.07	0.350	0.992	0.122
	1.5	100	0.22	0.630	0.975	0.387
	1.5	100	0.16	0.537	0.981	0.283
	2	100	0.38	0.830	0.957	0.659
	2	100	0.41	0.863	0.954	0.711
	3	100	0.36	0.810	0.959	0.629
	4	100	0.53	0.983	0.941	0.910
MC20/soybean oil	1	80	0.05	0.299	0.994	0.089
	1	90	0.08	0.387	0.990	0.148
	1	100	0.18	0.566	0.979	0.314
	1	110	0.39	0.846	0.955	0.683
Fulmont F180/corn oil	1	80	0.06	0.336	0.993	0.112
	1	90	0.08	0.389	0.990	0.150
	1	100	0.14	0.496	0.984	0.242
	1	110	0.25	0.669	0.971	0.435

^aFulmont F180, a commercial bleaching earth, used as a reference; MC20, a bentonite-based formulation prepared in our laboratory.

required and practiced in industry (usually 20–30 min), to fully evaluate color changes during the process. Blank experiments, without earth, were performed to verify possible color variations due to oil oxidation at different temperatures. Temperatures were varied from 80 to 120°C, and dried earth (105°C for 24 h) was fed from 0 to 4% (w/w). Some experiments were run without drying the earth to verify the effects of humidity (5% w/w) on color removal. Kinetic data were taken from 90 to 110°C and with dried earth to avoid interference from oil oxidation.

RESULTS AND DISCUSSION

The bleaching experiments showed a typical hyperbolic behavior in pigment concentration (i.e., absorbance) decay (Fig. 1). A second-order kinetic model was then developed and fitted by

regression analysis, giving good agreement with the experimental data.

Bleaching kinetic model. Kinetic data of soybean oil bleaching using the two adsorbents for different operating conditions are shown in Figures 1 and 2. Figure 3 shows similar behavior for corn oil bleaching.

The simplest mechanistic model for an irreversible adsorption process is based on an elementary step that can be written as $A + S \rightarrow A \cdot S$, where A represents the adsorbate (pigment being adsorbed) and S is the adsorption site on the bleaching earth. To establish a kinetic model compatible with our experimental observations, the following six assumptions were made: (i) The rate of color removal depends linearly on the pigment concentration in the oil (C) and on the population of adsorption sites (n_s , mol site·kg⁻¹ adsorbent), assuming that the loss of activity of the sites occurs in a fixed stoichiometric ratio (e.g.,

TABLE 2
Characteristics of the Adsorbent MC20

Composition (% w/w) ^a		Structural parameters	
SiO ₂	72.91	BET surface area (Gemini 2370 Micrometrics)	116 m ² ·g ⁻¹
Al ₂ O ₃	15.31	Pore diameter	68.10 Å
Fe ₂ O ₃	13.48	Particle average size	74 μm
MgO	0.71	Weight loss on ignition at 1000°C	5.76%
CaO	0.18		
K ₂ O	0.66		
MnO	0.01		
Na ₂ O	0.58		
P ₂ O ₅	0.01		
TiO ₂	0.40		

^aDetermined by X-ray fluorescence (Philips PW-2400).

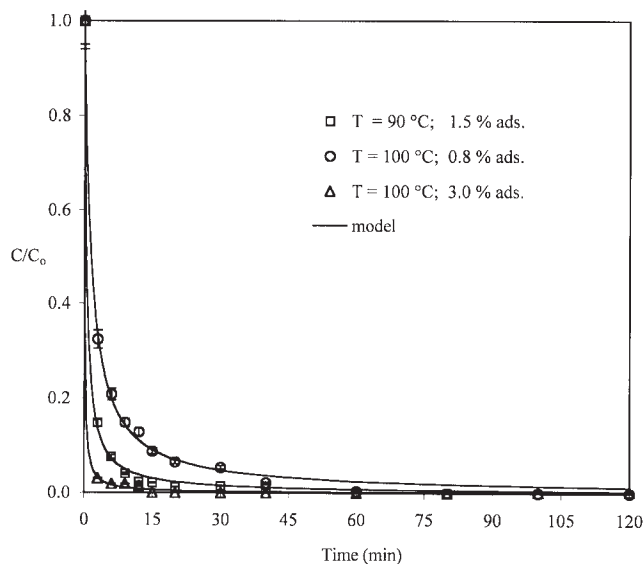


FIG. 1. Experimental data and model fitting for soybean oil bleaching at different temperatures and commercial adsorbent loads. Error bars indicate SD of the mean of experimental data. C , pigment concentration ($\text{mol pigment} \cdot \text{m}^{-3}$ oil); C_0 , initial pigment concentration ($\text{mol pigment} \cdot \text{m}^{-3}$ oil).

1:1); (ii) following the Beer–Lambert law for diluted solutions, the relative concentration of components that gives color to the oil was assumed to be proportional to the sample relative absorbance; (iii) the agitation intensity is high enough to avoid a mass-transfer limitation to the film that surrounds the adsorbent particles; (iv) under our experimental conditions, the bleaching process is kinetically controlled, since the adsorbent particle diameter is small enough, and therefore diffusional

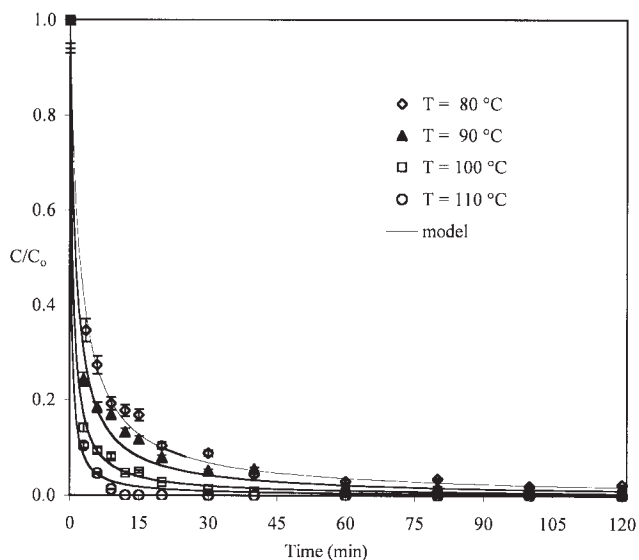


FIG. 2. The second-order model adjusted for soybean oil bleaching using 1% (w/w) of adsorbent MC20 (a bentonite-based formulation prepared in our laboratory). Error bars indicate SD of the mean of experimental data. For definitions see Figure 1.

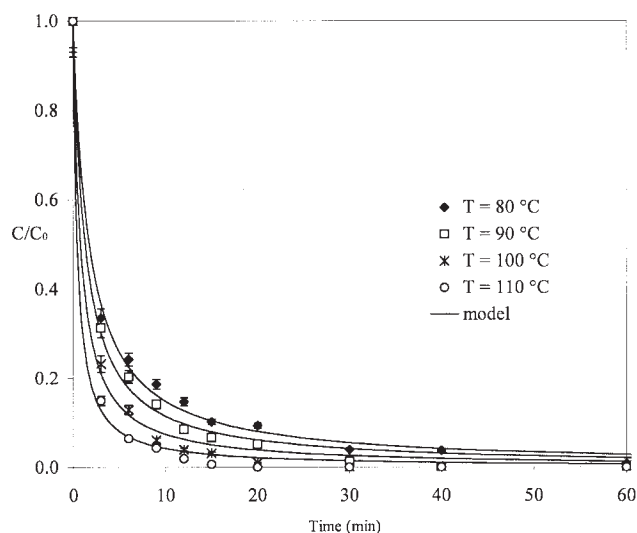


FIG. 3. Experimental data and model fitting for corn oil bleaching at different temperatures and commercial adsorbent loads. Error bars indicate SD of the mean of experimental data. For definitions see Figure 1.

resistance in the pores is not significant; (v) operation of the bleaching process is well controlled so that reactions of an oxidative nature do not occur; and (vi) color oscillation behavior observed during bleaching (color reversed), usually attributed to oxy-reduction processes, are not pronounced enough to be taken into account when a dried adsorbent is used. Oscillations in color that appeared when wet samples were tested (see Fig. 4) were not considered in the model.

Pigment balance. For a constant-volume batch system, the mole balance for the pigment can be written as:

$$-\frac{dC}{dt} = r_a \cdot \frac{W}{V} \quad [2]$$

where r_a is the pigment adsorption rate, W is the adsorbent mass, and V is the volume of vegetable oil.

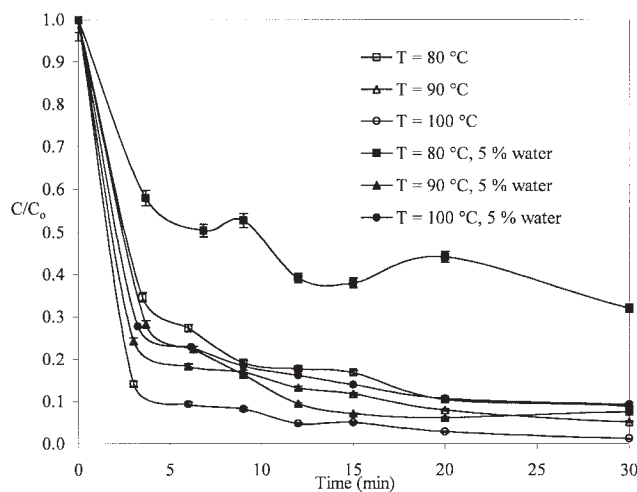


FIG. 4. Influence of water on the bleaching process. Soybean oil/1% of MC20 (earth). Error bars indicate SD of the mean of experimental data. For definitions see Figure 1.

Assuming the hypothesis formulated in (i),

$$r_a = k_a \cdot n_s \cdot C \quad [3]$$

where k_a is the rate adsorption constant. Replacing the adsorption rate in Equation 2, and writing C and n_s in dimensionless form:

$$\frac{d\Psi}{dt} = -k_a \cdot n_{so} \cdot \frac{W}{V} \cdot a \cdot \Psi \quad [4]$$

where $\Psi = C/C_o$ and $a = n_s/n_{so}$ [n_{so} , initial number of sites (mol site·kg⁻¹ adsorbent)]. Initial conditions were $\Psi = a = 1$.

Adsorption site balance. For the mole balance applied to the active sites (adsorption activity),

$$-\frac{dn_s}{dt} = r_d \quad [5]$$

Considering that each molecule is adsorbed in only one adsorption site, the adsorbence deactivation rate, r_d , can be written as

$$r_d = k_d \cdot n_s \cdot C \quad [6]$$

where k_d is the intrinsic adsorption deactivation rate constant.

By combining Equations 5 and 6 in a dimensionless form, we obtain the following equation:

$$\frac{da}{dt} = -k_d \cdot C_o \cdot a \cdot \Psi \quad [7]$$

Considering the nature of the process (i.e., for each pigment molecule removed from the oil, one adsorption site is "lost"), we assumed that the dimensionless rates for oil bleaching and site activity loss were the same, so that

$$\frac{d\Psi}{dt} = \frac{da}{dt} \therefore \Psi = a \quad [8]$$

since for $t = 0$, $\Psi = a = 1$. This is rather intuitive and is valid as long as the stoichiometry is maintained and there is no activity distribution for the adsorption sites.

Now, substituting a given by Equation 8 into Equation 4, we have

$$\frac{d\Psi}{dt} = -k_a \cdot n_{so} \cdot \frac{W}{V} \cdot \Psi^2 \quad [9]$$

or

$$\frac{d\Psi}{dt} = -k \cdot \Psi^2 \quad [10]$$

a *second-order* kinetic model [where k is the pseudo first-order bleaching rate constant (min⁻¹)], whose solution is given by

$$\Psi = \frac{1}{1 + kt} \quad [11]$$

On the other hand, substituting the value of Ψ given by Equation 8 into Equation 7, we may relate the adsorbent activity to the initial pigment concentration:

$$\frac{da}{dt} = -k_d \cdot C_o \cdot a^2 \quad [12]$$

Therefore, considering that $\Psi = a$, from Equations 9, 10, and 12 we can express k by the following relations and separate its dependence on the adsorbent load (W/V):

$$k = k_d \cdot C_o = k_a \cdot n_{so} \cdot \frac{W}{V} = k' \cdot \frac{W}{V} \quad [13]$$

where k' is the modified first-order adsorption constant (m³ oil·kg⁻¹ earth·min).

From Equation 13, it is easy to notice that k is quadratically dependent on the adsorbent concentration used in the clarification process since, according to the suggested model, k_a is an adsorption rate constant, and both n_{so} and W/V depend linearly on the amount of solid added to the vessel. Figure 5 shows the linear dependence of the modified constant $k' = k \cdot V/W$, as expected. Calculated values of k' are presented in Table 1 for the clarification of soybean and corn oils using different earth dosages, adsorbents, and temperatures.

The pseudo first-order kinetic constant, k , was determined for various temperatures and showed good Arrhenius correlation fitting. The corresponding activation energies found for soybean oil clarification were 78 kJ·mol⁻¹ ($r^2 = 0.98$) for MC20 and 75 kJ·mol⁻¹ ($r^2 = 0.96$) for the commercial earth (Fulmont F180), respectively. However, for the same conditions, using corn oil and the same commercial earth, the activation energy was 52 kJ·mol⁻¹ ($r^2 = 0.97$).

Adsorption vessel modeling. The industrial bleaching process is usually carried out in a large stirred vessel operating either in a semibatch or batch mode. Some processors also make use of a continuous filter to separate the bleaching earth

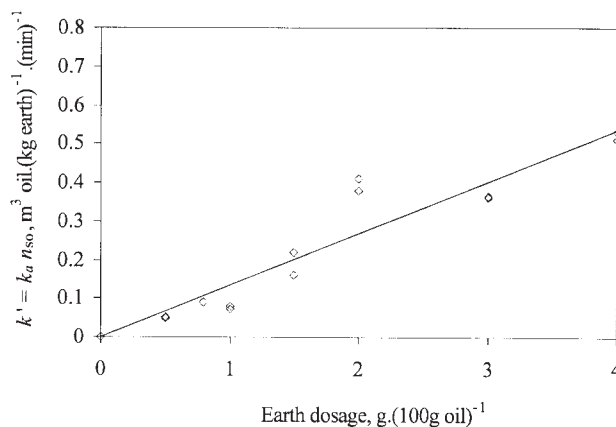


FIG. 5. Dependence of the kinetic parameter, $k' = k_2 \cdot (V/W)$, with earth dosage on the bleaching of soybean oil at 90°C [where k' is the modified first-order adsorption constant (m³ oil·kg⁻¹ earth·min⁻¹), k is the pseudo first-order bleaching rate constant (min⁻¹), V is the volume of vegetable oil (m³ oil), W is the mass of adsorbent (kg adsorbent), k_a is the adsorption kinetic constant, and n_{so} is the initial number of sites (mol site·kg⁻¹ adsorbent)].

TABLE 3
Bleaching Process Adsorption Model^a

Mass/mole balance	Conservation equation
Mass balance for the oil	$\frac{dM}{dt} = \gamma_{lo}\dot{m}_o - \gamma_{lp}\dot{m}_p$
Mass balance for the adsorbent	$\frac{dM}{dt} = \gamma_{so}\dot{w}_o - \gamma_{sp}\dot{m}_p$
Mole balance for the pigment in the oil	$\frac{d(xM)}{dt} = x_o\gamma_{lo}\dot{m}_o - x\gamma_{lp}\dot{m}_p - r_dW$
Mole balance for the adsorption sites	$\frac{d(n_sW)}{dt} = n_{so}\gamma_{so}\dot{w}_o - n_s\gamma_{sp}\dot{m}_p - r_dW$
Vessel level during startup	$\frac{dh}{dt} = \left(\frac{\dot{m}_o}{\rho_l} + \frac{\dot{w}_o}{\rho_s} \right) \cdot \frac{1}{A}$

^a M , mass of oil (kg); γ_{lo} , mass fraction of oil at the entrance (pure stream, kg oil·kg⁻¹ oil); \dot{m}_o , mass flow of oil that enters the vessel (kg·h⁻¹); γ_{lp} , mass fraction of oil in the paste (kg oil·kg⁻¹ paste); \dot{m}_p , mass flow of paste (slurry: oil + adsorbent, kg·h⁻¹); W , mass of adsorbent (kg adsorbent); γ_{so} , mass fraction of earth at the entrance (pure stream, kg adsorbent·kg⁻¹ adsorbent); \dot{w}_o , mass flow of adsorbent that enters the vessel (kg adsorbent·h⁻¹); x , molar concentration of pigment in the oil stream that leaves the vessel (mol pigment·kg⁻¹ oil); γ_{sp} , mass fraction of earth in the paste (kg adsorbent·kg⁻¹ paste); x_o , initial molar concentration of the pigment in the oil stream entering the vessel (mol pigment·kg⁻¹ oil); n_s , number of sites (mol site·kg⁻¹ adsorbent); n_{so} , initial number of sites (mol site·kg⁻¹ adsorbent); r_d , pigment adsorption rate (mol pigment·kg⁻¹ adsorbent·min⁻¹); r_d , adsorbent deactivation rate (mol site·kg⁻¹ adsorbent·min⁻¹); h , vessel level (m); ρ_l , oil density (kg·m⁻³); ρ_s , solid density (kg·m⁻³); A , vessel cross-sectional area (m²).

from the oil and/or to achieve some extra bleaching effect. When this is done in addition to vessel clarification, we have what is known as a press effect (10). The set of equations that represent adsorption vessel continuous operation, developed by Oliveira (9), is summarized in Table 3 and was used here to simulate the startup and batch operation modes.

The simulation results obtained by simultaneously solving the set of ordinary differential equations in Table 3, for startup and batch bleaching operations for soybean oil in an industrial bleaching vessel, for the kinetic parameters obtained for the commercial earth are shown in Figure 6. Polymath v. 4.02 (11) was used to solve the set of ordinary differential equations. Color removal is represented by the red color concentration in the Lovibond scale, a practical parameter still commonly used for the quality control of color in edible oil refineries. The correlation between the Lovibond red index (R_{Lovibond}) and the absorbance (A) of clarified soybean oil at 420 nm was given by Zanotta (3) as a third-order polynomial:

$$R_{\text{Lovibond}} = 8.97\alpha^3 - 15.89\alpha^2 + 11.92\alpha + 2.3 \quad [14]$$

where $\alpha = A/A_o$ (the initial absorbance of the oil), the relative absorbance at 420 nm, and was used to report the data shown in Figure 6. It is clear from the simulation shown in the figure that during the vessel filling operation (startup with an empty vessel), because of the fast adsorption kinetics, about one-third of the oil color was removed. At the end of the batch process (20 min), a color removal of about 55% was attained with re-

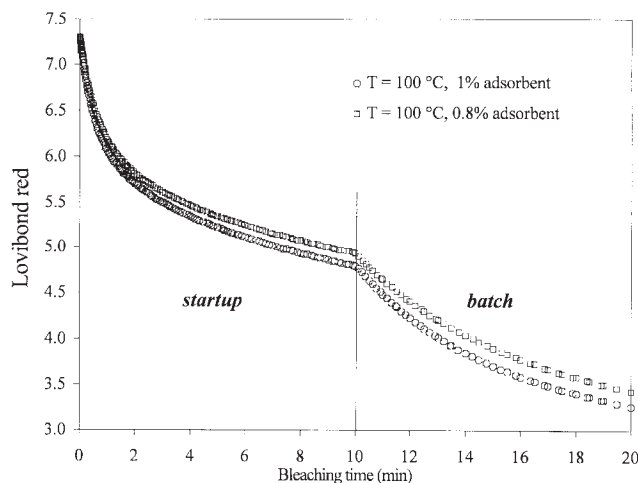


FIG. 6. Color removal (Lovibond red scale) for the startup and batch operation of the soybean oil bleaching process under realistic industrial vessel conditions (data not presented).

spect to the neutral oil bleached with 1% (w/w) earth dosage. However, when an 0.8% earth load was used, we still removed 53% of the color.

The kinetic model suggested by Brimberg (4) and referenced by other authors is quite limited since it does not represent the adsorption kinetics for a wide interval, nor does it physically interpret the clarification phenomenon. Therefore k_B , in Equation 1, assumes two or more values along the bleaching curve. This makes it of limited use for evaluating the oil bleaching process on an industrial scale.

The second-order kinetics approach described in this work provides a good fit with that of the experimental data for the bleaching of soybean oil, and some mechanistic basis is attributed to this behavior. The model, which was also successfully tested for soybean and corn oils (data not shown), may be useful to simulate transient steps during the industrial bleaching process, as well as in process and product (oil and adsorbent) evaluations.

A very simple but mechanistically justified second-order kinetic bleaching model is presented. Kinetic constants may be directly fitted from pigment relative concentration (or relative absorbance) decaying curves for a fixed adsorbent load. This may be useful, for instance, when comparing bleaching earths from different suppliers. We showed the results for soybean and corn oils, but the model seems quite appropriate for other oils as well, provided mass-transfer limitations are avoided. Alternatively, one may be interested in testing the influence of the earth load (adsorbent concentration of the bleaching batch). In that case, a modified kinetic constant may be directly evaluated from linearized C vs. t curves from Equations 2 and 3.

Kinetic parameters adjust to an Arrhenius plot, but activation energies are very dependent on the oil type, as indicated by soybean and corn oil clarification under the same batch conditions and for the same bleaching earth.

Simulation of the main bleaching process (not considering

press filter effects) shows the importance of the startup procedure, where oil and earth are being loaded into the vessel simultaneously. During that step, a considerable amount of color is removed; therefore, controlling the operating conditions is as important as in the "holding" step (batch process).

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