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The potential use of ultrasound-assisted bleaching in removing heavy metals and pigments from soybean oil using kinetic, thermodynamic and equilibrium modeling: Linear and nonlinear approach and error analysis

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Abstract

In this research, the sorption behavior (kinetic, isotherm and thermodynamic modeling) of heavy metals (Cu (II) and Fe (II)) and pigments (carotenoid and chlorophyll) on activated bentonite clay was investigated for soybean oil under industrial (IBM) and ultrasonic bleaching method (UBM). The results indicated that a nonlinear fitting approach with a higher coefficient of determination (R^2) and lower Chi-square (χ^2) values was more appropriate to estimate kinetic and isotherm parameters than the linear fitting approach. The adsorption of metal ions and pigments on activated bentonite clay under UBM was quite well by the pseudo-first-order model. In both bleaching methods, the equilibrium adsorption data follows the Freundlich isotherm model, presenting the sorption occurrence tends to be on a heterogeneous surface by multi-layer adsorption. The results indicated that the adsorption thermodynamics was endothermic nature and the process was spontaneous between 35 and 65 °C.

Keywords Adsorption . Modeling . Freundlich . Bentonite clay . Endothermic.

Introduction

Soybean oil consumption rate increase consistently owing to the unique properties of its fatty acid profile mainly polyunsaturated fatty acids (PUFA ~ 57 %), monounsaturated fatty acids (MUFA ~ 22 %), and saturated fatty acids (SFA ~ 15 %) (Abedi and Sahari 2014). Soybean oil is mostly consumed in main applications including, food (as salad, frying, cooking and shortening oil, as well as magerine oil), cosmetic, pharmaceutical, and biodiesel industries. According to global production of oils and fats (FAO-Trade and Markets Division, 2020), in the 2019/2020 crop year, soybeans were the important variety of oilseed in the world. That year, soybeans were

53 produced (336.11) million metric tons, placed first grade in worldwide owing to fatty
54 acid profile, and also in vitamin E and A (Huth et al. 2015; Dai et al. 2016), followed
55 by rapeseed (68.2), sunflower oil (54.97), peanut (45.38), cotton seed (44.84), palm
56 kernel (19.85) and copra (5.86) million metric tons. In the United States, soybean oil
57 is the most consumed type of edible oil by volume. Canola oil came in second place,
58 followed by palm oil ([https://www.statista.com/statistics/267271/worldwide-oilseed-](https://www.statista.com/statistics/267271/worldwide-oilseed-production-since-2008/)
59 [production-since-2008/](https://www.statista.com/statistics/267271/worldwide-oilseed-production-since-2008/)). Further extraction of soybean oil from soya seeds using the
60 solvent extraction method, is purified using various series of sequential steps
61 consisting of degumming, neutralization, bleaching, and deodorization (Erickson
62 1995; More and Gogate 2018). Among all these steps, bleaching is a leading step as
63 adsorption operation with emphasis aims at removing pigments, residual soaps and
64 residual phosphatides, oxidation products and trace metals using activated clay
65 (Erickson 1995; More and Gogate 2018), in order to reduce their deleterious impact
66 on oil stability (Abedi et al. 2015).

67 The relevant pigments found in vegetable oils are the chlorophylls and carotenoids.
68 Carotenoids are yellow-red pigment, which can be categorized into carotenes and
69 xanthophylls. Meanwhile, the β - carotene is the most predominant carotenoid in crude
70 vegetable oils. The carotenoids removal is valuable to enhance the visual appearance
71 of bleached oil for the consumer; however its permanence improves oxidative stability
72 of the oil. However, chlorophyll removal is more significant than the carotenoids,
73 which heating cause to decompose it into pheophytins, resulting oil with opaque and
74 dark color appearance. The main step in color reduction occurs in bleaching process.
75 The soybean oil bleaching process must be conducted to eliminate chlorophyll, which
76 is engaged in photosensitized oxidation, and to break down peroxides into lower

molecular weight carbonyl compounds that are removed with deodorization (Proctor and Brooks 2005; Hussin et al. 2011; Abedi et al. 2020a, b).

Normal amount of chlorophyll in crude soybean oil are in the range of 100 to 200 ppb. Erickson evaluated the reduction in chlorophyll in oil processing would be expected to be in the range of 10 to 20 ppb. Acceptable limit levels of chlorophyll and peroxide value should be 50 ppb content and a zero peroxide value to maintain the optimal oxidative stability of the finished oil. Chlorophyll levels more than 50 ppb following bleaching may lead to a green/gray color in the refined oil. This faint green tinge is hindered by yellow and red colors. The final step of deodorization may diminish the yellow and red to values low enough to permit the green/gray color to be apparent. Hence, the oil is rebleached if the green/gray color becomes problematic (Erickson 1995; More and Gogate 2018).

The occurrence of trace metals including copper (Cu), iron (Fe), cobalt (Co), nickel (Ni), manganese (Mn), calcium (Ca), and magnesium (Mg) in edible oils, not only are toxic, but also can enhance the rate of oil oxidation, affecting the oil's shelf life and storage stability (Proctor and Brooks 2005).

The adsorption process comprise of attaching contaminants to the surface of activated clay in two ways: chemisorption and physisorption. The chemisorption, the contaminant is bonded on the surface of activated clay via ionic bonding or covalent bond, caused by exchange of electrons between the sorbent surface and contaminant whereas in the physisorption process was conducted by van der Waals bonding with no substantial manipulation happen in electronic structure (Didi et al. 2009).

Application of ultrasonic in oil refining process such as olive, rapeseed, soybean, , palm, and canola compared with the traditional has several advantages mainly low energy consumption, higher throughput and shorter processing time (Jahouach-Rabai

et al. 2008; Chandrapala et al. 2012; Su et al. 2013; Abedi et al. 2015, 2017, 2020a; Asgari et al. 2017, 2018; Icyer and Durak 2018; Roohi et al. 2019). However, few surveys have reported the adsorption kinetics behavior and thermodynamic aspects associated with the compounds adsorption of oils on sorbent surface. Kinetics, equilibrium and thermodynamics of the bleaching step of rice bran oil (Pohndorf et al. 2016), soybean oil (Abedi et al. 2020a), palm oil (Silva et al. 2013; Almeida et al. 2019) and olive oil (Asgari et al. 2018) were investigated. To understand the mechanism of heavy metals and pigments removal from edible vegetable oils under commercial bleaching, the insight into the adsorption kinetic, isotherm and thermodynamic models is necessary. In this regard, linear and nonlinear forms of kinetic, isotherm and thermodynamic models of oil bleaching under commercial and ultrasonic are used to predict model parameters. Although several kinds of research have been performed on target pollutants adsorption by bleaching clays either in natural or acid-activated form (Su et al. 2013; Abedi et al. 2015; Icyer and Durak 2018), low studies can be found in the literature to characterize adsorption mechanism in terms of operating parameters (Asgari et al. 2018) (Abedi et al. 2020a).

Therefore, the overarching aim of this study is to evaluate the performance of ultrasonic bleaching method (UBM) in refining soybean oil from heavy metals (Cu (II) and Fe (II)) and pigments (carotenoid and chlorophyll) by activated bentonite clay in terms of ultrasonic power (25 and 40 kHz), clay content (0.5–2 %), temperature (35–65 °C), and time (0–30 min) as compared with industrial bleaching method (IBM). The specific aims of this study are listed below: (1) compare the linear and nonlinear forms of equilibrium isotherms models (Langmuir, Freundlich, and Tempkin) to determine the accurate design parameters of metals and pigments adsorption, (2) compare the linear and nonlinear forms of kinetic models (pseudo-

first-order, pseudo-second-order, and intraparticle diffusion) to elucidate the adsorption mechanism, (3) Analyze the experimental data to a better comprehend the bleaching time effect on the adsorption of metals and pigments via thermodynamic parameters such as standard enthalpy (ΔH°), standard entropy (ΔS°), and standard free energy (ΔG°).

Material and Methods

Materials

Neutralized soybean oil for bleaching process was purchased from Narges Oil Company (Shiraz, Fars Province, Iran). All the chemicals used in this work were purchased from Merck Co. (Darmstadt, Germany) and were analytical grade.

Bleaching process

Bleaching experiments were carried out by adding various amounts of activated bentonite clay (0.5, 1, 1.5 and 2 % (w/v)) to 50 mL oil sample. The oil sample is treated by ultrasonic horn. Horn ultrasonic bleaching process was carried out by the ultrasonic processor UP400S Hielscher (400 W, 25, and 40 kHz) at amplitude 100% at a bleaching time of between 0 and 30 min and a bleaching temperature of 35, 45, 55 and 65 °C in batch conditions. An immersible probe is dipped in the liquid at the 1 cm top of the tank and emits the sound vibration into the solution via a titanium alloy rod 14 mm diameter. The reactor is a cylindrical jacket glass vessel (volume 100 ml). After agitation, the mixture was filtered through the centrifuge at 14000 rpm for 20 min and the supernatant solution was further filtered using Whatman 42 filter paper. The bleaching under the mentioned condition without the ultrasonic process is considered as control (IBM). All tests were performed in triplicate.

Mineral measurement

Atomic absorption spectrophotometry (AA-680 Shimadzu, Kyoto, Japan) was employed to determine the residual Fe(II) and Cu(II) concentrations in bleached oil during the temperature (35, 45, 55 and 65 °C) and time (0, 5, 10, 15, 20, 25 and 30 min), following the AOAC official method 999.11. Briefly, 5 g sample was dried at 105 °C for 24 h. Then, samples were ashed at 450 °C for 6 h under gradual increase (<50 °C/h). The resultant white ash was dissolved in 3 ml HCl and HNO₃ (3/1 ratio) and valium were adjusted to 25 ml using deionized water. The final solution was filtered via filter paper (Whatman, Grade 1) and the concentrations of the elements (Fe and Cu) were measured as previously described (Vafaei et al. 2018). All assays were carried out in 5 replicates and mineral contents were expressed in mg/kg.

The effect of ultrasonication on the reduction of particle size and cleaning of surface is presented in Fig. 1.

Pigments measurement

The chlorophyll and carotenoid content of bleached oils were measured according to the method proposed by (Abedi et al. 2015). In this regard, 7.5 g of oil was dissolved in cyclohexane up to a final volume of 25 mL. Then, chlorophyll and carotenoid level of bleached oils was recorded by a UV–VIS Spectrophotometer (UV S-2100; Scinco, Seoul, South Korea) at 670 and 470 nm, respectively, using the following Eq (1 and 2):

$$\text{chlorophyll } \left(\frac{\mu\text{g}}{\text{kg}} \right) = A_{670} \times \frac{10^9}{613} \times 100 \times d \quad (1)$$

$$\text{carotenoid } \left(\frac{\text{mg}}{\text{kg}} \right) = A_{470} \times \frac{10^6}{2000} \times 100 \times d \quad (2)$$

Kinetic studies

In order to examine the effect of bleaching time (0-30 min) on adsorption of metal ion and pigments onto activated bentonite clay under IBM and UBM, 1 % of bleaching clay at 65 °C was selected. In this regard, 1 % (w/v) of activated bentonite clay was added to 50 mL oil samples containing metals and pigments at 65 °C. The solution was agitated for varying amounts of time (5, 10, 15, 20, 25, and 30 min), followed by filtration. Finally, the concentrations of metal ions and pigments were measured by atomic absorption spectrophotometry and UV–VIS Spectrophotometer, respectively. The amount of metals and pigments adsorbed at various time intervals and at equilibrium time was calculated by the following equation:

$$q_t = \frac{(C_o - C_t) \times V}{m} \quad (3)$$

$$q_e = \frac{(C_o - C_e) \times V}{m} \quad (4)$$

where C_t is the amount of metals and pigments adsorbed at any time (t), C_o and C_e are the initial and equilibrium concentrations of metals and pigments, respectively. The volume of soybean oil solution in L is represented by (V) and m is the amount of activated bentonite clay in g. The kinetics of metal ions and pigments onto activated bentonite clay can be determined with three common kinetic models. In this study, the kinetic of metal ions and pigments adsorption within activated bentonite clay under IBM and UBM was evaluated with the pseudo-first-order, pseudo-second-order and the intraparticle diffusion models. For the analysis of data, the linear and nonlinear forms of these models were used and the results were compared. The nonlinear forms of pseudo-first-order, pseudo-second-order, and the intraparticle diffusion models can be expressed by Eqs. (5) – (7), respectively (Gil et al. 2018).

$$200 \quad \text{Pseudo -first -order model : } q_t = q_e (1 - e^{-k_1 t}) \quad (5)$$

$$201 \quad \text{Pseudo -second -order model : } q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t} \quad (6)$$

$$202 \quad \text{Intraparticle diffusion model : } q_t = k_p t^{0.5} + C \quad (7)$$

203 where q_e (mg g⁻¹) and q_t (mg g⁻¹) are the adsorption capacities of activated bentonite
 204 clay under IBM and UBM at equilibrium time and time t , respectively. The k_1 , k_2
 205 and k_p are the pseudo-first-order rate constant (min⁻¹), pseudo-second-order rate
 206 constant (gmg⁻¹min⁻¹), and intraparticle diffusion model rate constant (mgg⁻¹min^{-0.5}),
 207 respectively, t (min) is the bleaching time and C is the intercept of intraparticle
 208 diffusion model. The linear forms of pseudo-first-order, pseudo-second-order, and the
 209 intraparticle diffusion models can be calculated according to Eqs. (8) – (10),
 210 respectively (Batool et al. 2018).

$$211 \quad \text{Pseudo -first -order model : } \log(q_e - q_t) = \log q_e - k_1 t \quad (8)$$

$$212 \quad \text{Pseudo -second -order model : } \frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (9)$$

$$213 \quad \text{Intraparticle diffusion model : } \log q_t = \log(k_p C) + 0.5 \log t \quad (10)$$

214

215 **Equilibrium studies**

216 To study the influence of bleaching clay usage on the adsorption efficiency, 50 mL
 217 soybean oil solutions containing metal ions and pigments with various activated
 218 bentonite clay dosages (0.5, 1, 1.5, and 2 % (w/v)) were agitated at 65 °C for 30 min.
 219 After filtration, the residual concentrations of metal ions and pigments were measured
 220 by atomic absorption spectrophotometry and UV–VIS Spectrophotometer,
 221 respectively. To distinguish the distribution of metal ions and pigments between

solution and solid phase, the Langmuir, Freundlich, and Tempkin models in nonlinear forms were used as Eqs. 11 to 13 (Aljeboree et al. 2017; Hashemi and Amiri 2020).

$$\text{Langmuir model : } q_e = \frac{K_L q_m C_e}{(1 + K_L C_e)} \quad (11)$$

$$\text{Freundlich model : } q_e = K_F (C_e)^{1/n} \quad (12)$$

$$\text{Tempkin model : } q_e = \frac{RT}{b_T} \ln(A_T C_e) \quad (13)$$

where q_e is the amount of metals and pigments adsorbed in solid phases (mg g^{-1}), q_m is the maximum adsorption capacity (mg g^{-1}), C_e is the amount of bleaching clay in the solution (mg L^{-1}), K_F is the Freundlich coefficient corresponded to the adsorption capacity ($(\text{mg g}^{-1})(\text{L mg}^{-1})^{1/n}$), n is the constant corresponded to the adsorption intensity, K_L is the Langmuir coefficient corresponded to the energy of adsorption (L mg^{-1}), T and R are the absolute temperature (K) and the universal constant ($8.314 \text{ J mol}^{-1} K^{-1}$), respectively, A_T is the Temkin isotherm constant related to the maximum binding energy (L mg^{-1}), b_T is the Temkin constant corresponded to the heat of sorption (J mol^{-1}). The linear forms of the Langmuir, Freundlich, and Tempkin models can be calculated according to Eqs. (14) – (16), respectively (Nassar 2010).

$$\text{Langmuir model : } \frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (14)$$

$$\text{Freundlich model : } \ln q_e = \frac{1}{n} \ln C_e + \ln K_F \quad (15)$$

$$\text{Tempkin model : } q_e = \frac{RT}{b_T} \ln(A_T) + \frac{RT}{b_T} \ln C_e \quad (16)$$

Thermodynamic Studies

In order to determine whether the adsorption process is spontaneous or not, the prediction of the thermodynamic parameters such as standard enthalpy (ΔH^o), standard entropy (ΔS^o), and standard free energy (ΔG^o) is necessary. These thermodynamic parameters can be predicted from the following equations (Nassar 2010; Arshadi et al. 2014; Aljeboree et al. 2017; Gil et al. 2018) :

$$\ln k_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (17)$$

$$k_d = \frac{q_e}{C_e} \quad (18)$$

$$\frac{d \ln k_d}{dt} = \frac{\Delta H^o}{RT^2} \quad (19)$$

$$\Delta G^o = \Delta H^o - T \Delta S^o \quad (20)$$

$$\Delta G^o = -RT \ln k_d \quad (21)$$

where k_d is the equilibrium constant, q_e is the concentrations of metal ions and pigments adsorbed on activated bentonite clay at equilibrium ($mg L^{-1}$), C_e is the equilibrium concentration of metal ions and pigments in the solution ($mg L^{-1}$), R is the ideal gas constant ($8.314 Jmol^{-1}K^{-1}$), T is the temperature (K).

Goodness of fit

To check the performance of kinetic and isotherm models that best describes the interaction between the activated bentonite clay and metal ions as well as pigments, two statistical criteria is used. The coefficient of determination (R^2) and Chi-square statistic test (χ^2) have been used to check model fit. These criteria are given as (Hashemi and Amiri 2020):

$$R^2 = \frac{\sum_{i=1}^n \left[\left[(q_e)_{cal} - (\overline{q_e})_{cal} \right] \left[(q_e)_{exp} - (\overline{q_e})_{exp} \right] \right]}{\sum_{i=1}^n \left[(q_e)_{exp} - (\overline{q_e})_{exp} \right]^2 \sum_{i=1}^n \left[(q_e)_{cal} - (\overline{q_e})_{cal} \right]^2} \quad (22)$$

$$\chi^2 = \sum_{i=1}^{i=N} \frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,cal}} \quad (23)$$

where $q_{e,exp}$ is the equilibrium adsorption capacity obtained from the measured data (mgg^{-1}), $q_{e,cal}$ is the equilibrium adsorption capacity obtained from the models (mgg^{-1}), $(\overline{q_e})_{cal}$ and $(\overline{q_e})_{exp}$ are the average of the calculated and observed equilibrium adsorption capacity, respectively. The higher (R^2) and lower (χ^2) values show a better agreement between the experimental data and model predictions.

Statistical analysis

The statistical software package, Minitab software Version 16, was used for the regression analysis of the experimental data and to obtain the regression coefficients. Statistical assumptions mainly normality of data distribution and homogeneity of variances were determined by Shapiro–Wilk and Levene's tests, respectively. Then, oneway and two-way analysis of variance ANOVA were performed for physicochemical and bleaching data (factors and products), respectively to investigate the effect of bleaching methods on considered parameters. The adsorption experiments were conducted as a function of four major factors namely frequency (25 and 40 kHz), time (0, 5, 10, 15, 20, 25 and 30 min), clay content (0.5, 1, 1.5 and 2 %) and temperature (35, 45, 55 and 65 °C). Bleaching process was full filled at temperature 65 °C with the speed of 600 rpm. The Least Significant Difference (LSD) test was utilized for post -hoc analyses.

Results and Discussion

The effect of sonication on metal ions and pigments adsorption

The concentrations of heavy metals including Fe(II) and Cu(II) ions and pigments namely carotenoids and chlorophyll in bleached oil under industrial and sonication process was presented in Table 1-4. The adsorption trends of metals and pigments on activated clay under ultrasonication were significantly ($p < 0.05$) more than industrial condition at same temperature. Trace metals and pigments were reduced under cavitation in the suspension containing clay particle due to some reasons:

1) pyrolytic reactions and thermal decomposition inside or near the bubbles; 2) radical reactions following by mainly hydroxyl and free radicals formation during ultrasonic processing could have damaged the carotenoid and chlorophyll structure, inducing sonochemical degradation (Tiwari et al. 2008; Abedi et al. 2015). Meanwhile, the concomitant consumption of clay and sonication could have promoted a synergic effect on the reduction of pigment content and metals; 3) in order to initiation acoustic cavitation, a surface require for generation of nuclei bubbles. This surface should not be dissolved in fluid, which can include container wall, fluid contamination and clay particles. Bubbles grow when exposure to the pressure lower than threshold pressure. Numerous parameters can affect threshold pressure mainly, applied ultrasound intensity and frequency, the presence of fine particles and gases in the liquid (Niazi et al. 2014; Abedi et al. 2015, 2017). According to (Roohi et al. 2019), clay particles might reduce the threshold pressure and accelerate the bubbles cavitation. 4) Sonication at various concentrations of solids, causing a release of energy due to the collapse of the cavitation bubbles (Farmer et al. 2000). The cavitation phenomenon simply produces very high-velocity particle-to-particle

collisions (Farmer et al. 2000; Abedi et al. 2017) and induces high shear forces, macro-turbulence and perturbation in microporous particles, and finally, causing the reduction in the particle size, increasing surface area and surface cleaning effect. The reduction in the particle size of the clays is one of the other application of sonication which were evaluated by (Wiewióra et al. 2003; Franco et al. 2004; Pérez-Maqueda et al. 2005; Pérez-Rodríguez et al. 2006; Poli et al. 2008; Sompech et al. 2012; Ali et al. 2014; Pradhan et al. 2016; Retamal Marín et al. 2018). Moreover, cavitation at the liquid–solid interface leads to surface peeling, erosion, particle breakdown, thus, ultrasonic of a suspension containing particles can constantly produce new surfaces of clay ready for absorbing of impurities, increasing mass transfer of oil pigments and trace metals on clay microporous surface particles (Farmer et al. 2000). Cavitation in suspension containing suspended powder particles is divided into two categories: i) cavitation in suspension containing large particles generates shear stress and shock waves, which eventually result in their fragmentation while cavitation in suspension containing tiny particles may cause particles collisions and particle abrasion (Thompson and Doraiswamy 1999; Zhao et al. 2007; Abedi et al. 2015)

Effect of time and temperature of sonication on metal ions and pigments adsorption

Regarding to obtained results in Table 1-4, there are substantial ($P < 0.05$) differences among treatments (ultrasonic frequency, and treatment temperature as well as time) on the reduction of metals and pigments. (Jahouach-Rabai et al. 2008) and (Abedi et al. 2015) revealed that the collapse of bubbles and cavitation happen when the oil is treated by sonication upon a period of time greater than 20 min. In mentioned studies, the changes in pigment were observed at range 20–30 min. Temperature has a direct

337 impact on the kinetics of adsorption. In general, every 10 °C rise in temperature
338 doubles the reaction rate (the Van Hoff rule). The optimal temperature range for oil
339 bleaching is 85–120 °C depending on oil type and clay activity (i.e. residual and
340 surface acidity) ([Proctor and Brooks 2005](#)).

341 According to Table 2, the iron and copper as well as pigments elimination in soybean
342 oil medium improved with increasing the temperature from 35 to 65 °C under IBM
343 and UBM conditions. With increasing 10 °C in temperature range (35-65 °C), the
344 elimination of iron and copper in IBM, UBM-40 kHz, and UBM-25 kHz conditions
345 were about in range (3-24% and 12.5-24%), (22.5-100% and 15-53%) and (42.5-
346 100% and 53-100%), respectively. The percent reduction of carotenoids were
347 determined in range (6.97-25.3), (20.7-70.5) and (38.1-51.1) while chlorophylls was
348 recorded in range (9.2-18.3), (24.8-37.8) and (22.9-32.3) following IBM, UBM-40
349 kHz, and UBM-25 kHz conditions, respectively. The adsorption of Fe(II) and Cu(II)
350 ions on activated clay enhanced with increasing the temperature and time of bleaching
351 process in both of industrial and ultrasonic conditions. In general, doubles the reaction
352 rate occur with 10 °C rise in temperature (the Van Hoff rule). The optimal
353 temperature for the adsorption of polar compounds such as trace metals and pigment
354 adsorption (chlorophyll and carotenoid) are around 60–80 °C and 100–120 °C,
355 respectively ([Proctor and Brooks 2005](#)).

356 The most considerable effect of adsorption was observed for sonication at higher
357 temperature (65 °C) and time (30 min) due to occurrence of cavitations and facilitate
358 in particles size reduction ([Ali et al. 2014](#)). The exfoliation and delamination
359 improved due to cavitation and natural evaporation bubbles of the water at this
360 temperature ([Ali et al. 2014](#)). Temperature had contradictory effect as follow; as the
361 temperature of the solutions rises, bubbles generate and grow quickly, which acts a

cushion which lead to reduce violence of bubbles collapse as a result of inhibit the successful transfer of acoustic energy (Thompson and Doraiswamy 1999), while the evaporation of water bubble in oil sample as a result of increasing temperature induce to decrease inside vapour tension and accelerate the cavitation with higher the violence of the collapses (Ali et al. 2014; Abedi et al. 2015, 2017). The increase in temperature can decrease threshold of cavitation by reduction in the oil viscosity. (Santos et al. 2005) and (Fasina and Colley 2008) illustrate viscosity variation as a function of temperature. According to the Arrhenius model (Eq. 1), the viscosity of an oil reduces by approximately 30% for each 10 °C rise in temperature due to a higher thermal movement among molecules, reducing intermolecular forces, making flow among them easier and reducing viscosity (Santos et al. 2005).

$$\mu = A \times \exp \left[\frac{E_a}{RT} \right] \quad (24)$$

where μ is the rate constant namely: the collision or frequency factor, E_a is the activation energy (J mol⁻¹), A is the pre-exponential factor, R is the universal gas constant (8.314 Jmol⁻¹K⁻¹), T is the absolute temperature (K).

The effect of frequency of sonication on metal ions and pigments adsorption

The frequency is considered as one the main parameter of the ultrasound for improving cavitation bubbles. An increase in the frequency from 25 to 40 kHz of sonication remarkably decreased the reduction rate of pigment discoloration and metal absorption on activated clay (Table 1-4).

1) Cavitation yield decline as frequency increases, thence scattering and attenuation of sound waves occur.

2) The formation of cavitation bubbles accelerate at the lower frequency, the formed bubble size maximize to the largest size (60–100 μm) and their life time minimized; therefore, bubbles collapse take place very quickly, causing the formation of a comparatively large amount of heat and shock wave (Priego-Capote and De Castro 2004; Proctor and Brooks 2005; Kulkarni and Rathod 2014; Abedi et al. 2017; Roohi et al. 2019). Regarding the results from (Merouani et al. 2013) and (Brotchie et al. 2009) mean size along with range (mean of the distribution) of active bubble becomes smaller, when the ultrasound frequency increases for all employed acoustic amplitudes. 3) The generation of unstable cavitation facilitates at lower frequency, leading to violent collapse of the cavitation bubbles and locally high temperatures and pressures (up to 50 MPa or even higher) that conduct more rapid agitation and mass transfer, whereas moderate physical impacts, namely microstreaming, are the major effects of ultrasonic waves at high frequency (Vilkhu et al. 2008; Brotchie et al. 2009; Kulkarni and Rathod 2014; Abedi et al. 2015; Asgari et al. 2018). 4) The bubble formation accelerates further increase acoustic frequency, producing the high number of bubbles, which acts as a barrier throughout the liquid suspension. The collapse of cavitation bubbles reduced owing to inhibit the successful transfer of acoustic energy (Priego-Capote and De Castro 2004; Merouani et al. 2013; Abedi et al. 2017).

The adsorptions concentration of Fe(II) and Cu(II) elements in all temperatures and times in frequency 25 kHz were considerable ($p < 0.05$) higher than 40 kHz (Table 1-2).

Kinetic results

The contact time is a key parameter in the adsorption process, especially for the adsorption of metal ions and pigments of soybean oil bleaching (Abedi et al. 2020a),

consequently the correlations between reaction time and adsorption kinetics were studied in terms of pseudo-first-order, pseudo-second-order, and intraparticle diffusion models in the range of 0-30 min and the results are reported in Tables 5-8. The adsorption of metal ions and pigments on activated bentonite clay under UBM was rapid during the first 20 min and can be described quite well by the pseudo-first-order model. The R^2 values of the pseudo-first-order model for the adsorption of heavy metals (Cu (II) and Fe (II)) and pigments (carotenoid and chlorophyll) onto the activated bentonite clay under IBM and UBM were higher than those computed by other models ($R^2 > 0.93$). Moreover, χ^2 values of the pseudo-first-order model under IBM and UBM were lower than those computed by other models. The good agreement of pseudo-first order model with heavy metals (Cu (II) and Fe (II)) and pigments (carotenoid and chlorophyll) adsorption indicates that the adsorption is physisorption (Arshadi et al. 2014; Amiri et al. 2016, 2018). It can be clearly seen that the intraparticle diffusion model also played a non-negligible role in the adsorption of metal ions and pigments on activated bentonite clay under IBM and UBM (see Tables 5-8). According to the intraparticle diffusion model, the adsorption of metal ions and pigments on activated bentonite clay under IBM and UBM can be divided into three main steps. In step I, the metal ions and pigments diffused to the external surface and occupied some adsorption sites of activated bentonite clay quickly. In step II, the metal ions and pigments were adsorbed gently due to the intraparticle diffusion and reached equilibrium in the final step (Amiri et al. 2018). In all cases, a nonlinear fitting approach with a higher coefficient of determination (R^2) and lower Chi-square (χ^2) values was more appropriate to estimate kinetic parameters than the linear fitting approach. The rate constants of the pseudo-first-order model for the adsorption of heavy metals (Cu (II) and Fe (II)) and pigments (carotenoid and chlorophyll) onto

the activated bentonite clay were in the order of UBM-25 kHz (0.059 min⁻¹ for Fe(II), 0.062 min⁻¹ for Cu(II), 0.055 min⁻¹ for carotenoid, 0.068 min⁻¹ for chlorophyll) > UBM-40 kHz (0.056 min⁻¹ for Fe(II), 0.053 min⁻¹ for Cu(II), 0.05 min⁻¹ for carotenoid, 0.058 min⁻¹ for chlorophyll) > IBM (0.053 min⁻¹ for Fe(II), 0.051 min⁻¹ for Cu(II), 0.043 min⁻¹ for carotenoid, 0.056 min⁻¹ for chlorophyll). The greater rate constant of the pseudo-first-order model shows that the adsorption of heavy metals and pigments onto activated bentonite clay under UBM-25 kHz is more suitable. Moreover, the calculated adsorption capacities by the pseudo-first-order model for the adsorption of heavy metals and pigments onto the activated bentonite clay were in the order of UBM-25 kHz (0.0058 mg g⁻¹ for Fe(II), 0.0023 mg g⁻¹ for Cu(II), 0.426 mg g⁻¹ for carotenoid, 29.77 mg g⁻¹ for chlorophyll) > UBM-40 kHz (0.0054 mg g⁻¹ for Fe(II), 0.0022 mg g⁻¹ for Cu(II), 0.397 mg g⁻¹ for carotenoid, 27.74 mg g⁻¹ for chlorophyll) > IBM (0.0019 mg g⁻¹ for Fe(II), 0.0007 mg g⁻¹ for Cu(II), 0.211 mg g⁻¹ for carotenoid, 17.45 mg g⁻¹ for chlorophyll). The non-linear fitting of adsorption kinetics for the adsorption of heavy metals and pigments is represented in Fig 2-5 according to the pseudo-first-order, pseudo-second-order, and intraparticle diffusion models under IBM (Fig 2a-5a), UBM-25 kHz (Fig 2b-5b), and UBM-40 kHz (Fig 2c-5c) for soybean oil, suggesting that the pseudo-first-order is more suitable to predict the adsorption kinetics characteristic. A similar result under UBM was reported in previous research by Asgari et al (2018) for carotenoids removal from olive oil onto activated bentonite clay, which shows the kinetics adsorption followed pseudo-first-order model. In a previous research, Abedi et al (2020) reported that the adsorption of Fe(II), Cu(II), carotenoids and chlorophylls on activated bentonite clay under HVEF follows the pseudo-first-order model.

Thermodynamic results

The influence of the temperature on the adsorption of heavy metals (Cu (II) and Fe (II)) and pigments (carotenoid and chlorophyll) onto the activated bentonite clay under IBM and UBM was assessed. Fig 6a-d show the amounts of metals and pigments adsorbed at temperatures of 35, 45, 55 and 65 °C. It is found that the quantities of metals and pigments adsorbed onto the activated bentonite clay under IBM and UBM increase in the order of IBM < UBM-40 kHz < UBM-25 kHz with the increase of the temperature from 35 to 65°C, representing that the adsorption is suited at higher temperature. The increment in the q_e values with increasing the temperature is associated to the endothermic nature of the adsorption process ([Arshadi et al. 2014](#); [Amiri et al. 2016, 2018](#); [Gil et al. 2018](#); [Hashemi and Amiri 2020](#)). Plots of $\ln(K_d)$ versus $1/T$ to adsorb Fe(II) (see Fig 7), Cu(II) (see Fig 8), carotenoid (see Fig 9), and chlorophyll (see Fig 10) on activated bentonite clay under IBM and UBM are represented. The calculated thermodynamic parameters (ΔH° , ΔS° , and ΔG°) of the metal ions and pigments on the activated bentonite clay are summarized in Table 9 and 10, respectively. The results indicate that $\Delta H^\circ > 0$ (see Table 9 and 10), denoting that the adsorption process is endothermic, which is confirmed by the increase in the metal ions and pigments uptake capacity with increasing the temperature. The values of ΔH° for physisorption are between 2.1 and 20.9 kJ mol⁻¹, and for the chemical adsorption are in the range of 20.9 to 418.4 kJ mol⁻¹. The ΔH° values acquired in the present research under IBM and UBM for Fe(II) and Cu(II) ions adsorption onto the activated bentonite clay are in the range of 93.49 to 203.32 kJ mol⁻¹ and for carotenoid and chlorophyll are in the range of 46.39 to 125.56 kJ mol⁻¹. These values are higher than 20.9 kJ mol⁻¹, demonstrating that the rate limiting step in the process is chemically controlled. The negative values of ΔG° in higher temperatures under UBM

show that the adsorption of metal ions and pigments is spontaneous in this temperature range. In addition, the decrease in ΔG° values with an increase of temperature demonstrates that the adsorption process is thermodynamically favorable at greater temperatures (see Tables 9 and 10). It is noteworthy that the adsorption mechanisms are physisorption and chemisorption when ΔG° values ranged from -20 and 0 kJ mol⁻¹ and -80 to -400 kJ mol⁻¹, respectively (Nassar 2010; Amiri et al. 2016, 2018). From the results of Tables 9 and 10, the ΔG° values are changed up to -20 kJ mol⁻¹, indicating the physisorption mechanism is involved in the uptake of the metal ions and pigments by activated bentonite clay. The data indicate that $\Delta S^\circ > 0$ (see Table 9 and 10), demonstrating that an aleatory state at the adsorbent/adsorbate interactions. A similar result under UBM was reported in previous research by Asgari et al (2018) for carotenoids and chlorophylls elimination from olive oil onto activated bentonite clay. In a previous research, Abedi et al (2020) reported that the adsorption of Fe(II), Cu(II), carotenoids and chlorophylls on activated bentonite clay under HVEF were endothermic and spontaneous.

Equilibrium results

The equilibrium studies are used to display the mechanism of heavy metals (Cu (II) and Fe (II)) and pigments (carotenoid and chlorophyll) adsorption onto the activated bentonite clay under IBM and UBM (Abedi et al. 2020a). Therefore, the linear and non-linear forms of the Langmuir, Freundlich, and Tempkin models were employed to study the adsorption mechanism of heavy metals and pigments onto the activated bentonite clay. The equilibrium parameters are calculated and presented in Tables 11-14. It can be found that the non-linear forms of isotherm models were better than those of linear form models due to the higher coefficient of determination and lower Chi-square values (see Tables 11-14). Among which, the Freundlich model

satisfactorily described the equilibrium sorption data and was more favorable to explain the adsorption process in terms of R^2 and χ^2 . Therefore, the multilayer adsorption of heavy metals (Cu (II) and Fe (II)) and pigments (carotenoid and chlorophyll) onto the heterogeneous surface of activated bentonite clay was occurred. Similar results were reported by Asgari et al (2018) and Abedi et al. (2020). The calculated adsorption capacities (K_F) by the Freundlich model for the sorption of heavy metals and pigments onto the activated bentonite clay were in the order of UBM-25 kHz ($0.436 (mgg^{-1})(Lmg^{-1})^{1/n}$ for Fe(II), $0.429 (mgg^{-1})(Lmg^{-1})^{1/n}$ for Cu(II), $0.765 (mgg^{-1})(Lmg^{-1})^{1/n}$ for carotenoid, $29.91 (mgg^{-1})(Lmg^{-1})^{1/n}$ for chlorophyll) > UBM-40 kHz ($0.412 (mgg^{-1})(Lmg^{-1})^{1/n}$ for Fe(II), $0.406 (mgg^{-1})(Lmg^{-1})^{1/n}$ for Cu(II), $0.649 (mgg^{-1})(Lmg^{-1})^{1/n}$ for carotenoid, $27.41 (mgg^{-1})(Lmg^{-1})^{1/n}$ for chlorophyll) > IBM ($0.345 (mgg^{-1})(Lmg^{-1})^{1/n}$ for Fe(II), $0.338 (mgg^{-1})(Lmg^{-1})^{1/n}$ for Cu(II), $0.589 (mgg^{-1})(Lmg^{-1})^{1/n}$ for carotenoid, $17.41 (mgg^{-1})(Lmg^{-1})^{1/n}$ for chlorophyll). According to the Freundlich model, the values of $1/n$ are in the range of 0-1, suggesting that, the adsorption of heavy metals (Cu (II) and Fe (II)) and pigments (carotenoid and chlorophyll) onto the activated bentonite clay under IBM and UBM is suitable. Higher values of K_F and lower values of $1/n$ for UBM specially at a frequency of 25 kHz show that, this method can be used instead of IBM for soybean oils bleaching (see Tables 11-14).

Conclusion

In this research, efficacy of IBM and UBM was evaluated for adsorption of heavy metals (Cu (II) and Fe (II)) and pigments (carotenoid and chlorophyll) onto the activated bentonite clay from soybean oil using kinetic, thermodynamic and

equilibrium modeling. For this regard, a comparison of R^2 and χ^2 statistical indices was employed to finding the best kinetic and isotherm models using linear and non-linear approaches. The kinetic behavior of heavy metals (Cu (II) and Fe (II)) and pigments (carotenoid and chlorophyll) was well described by pseudo-first-order equation, and the isotherms followed the Freundlich model. Improved metal ions and pigments elimination in oil medium can be obtained on processing activated bentonite clay with the ultrasound technology. According to the results of this study, the adsorption of heavy metals (Cu (II) and Fe (II)) and pigments (carotenoid and chlorophyll) on activated bentonite clay under UBM is spontaneous ($\Delta G^\circ < 0$), and endothermic ($\Delta H^\circ > 0$) with an increase of the randomness at adsorbent/adsorbate interface ($\Delta S^\circ > 0$). It was concluded that the UBM, particularly at a frequency of 25 kHz, presented greater potential adsorption of metal ions and pigments from soybean oil compared with the IBM. Under the same conditions in time and temperature, the effect of metal ions and pigments elimination in ultrasonication were more than industrial process due to size reduction, scrubbing and cleaning effect of sonication on activated bentonite. The effect of metal ions and pigments elimination in 12 and 10 min of sonication are about equivalent to that with industrial bleaching in 30 min, therefore, the processing time can be decreased more than about two and three times, respectively. Trace elements and pigments removed under lower frequency (25 kHz) than higher frequency (40 kHz), due to improvement in cavitation and collapse of bubbles which result in collision in the particles, followed by reduce in surface area. The metal ions and pigments elimination rate can be increased by 100% at lower time of the ultrasonic-assisted technology combined with activated bentonite clay in solution due to their synergistic effect.

560 **Ethics approval and consent to participate**

561 We verify that we have seen and have approved the submitted manuscript. Our
562 manuscript does not report on or involve the use of any animal or human data or
563 tissue.

564 **Consent for publication**

565 None.

566 **Author contributions**

567 All authors conceived of the presented idea. Dr. Elahe Abedi carried out the
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576 **Availability of data and materials**

577 Data cannot be made publicly available; readers should contact the corresponding
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Figure Caption

Figure 1. The effect of ultrasonication on the reduction of particle size and cleaning of surface.

Figure 2. The experimental kinetic data and predicted values of Fe(II) ions on bentonite clay under IBM (a), UBM-25 kHz (b) and UBM-40 kHz (c) for soybean oil.

Figure 3. The experimental kinetic data and predicted values of Cu (II) ions on bentonite clay under IBM (a), UBM-25 kHz (b) and UBM-40 kHz (c) for soybean oil.

Figure 4. The experimental kinetic data and predicted values of Carotenoid on bentonite clay under IBM (a), UBM-25 kHz (b) and UBM-40 kHz (c) for soybean oil.

Figure 5. The experimental kinetic data and predicted values of Chlorophyll on bentonite clay under IBM (a), UBM-25 kHz (b) and UBM-40 kHz (c) for soybean oil.

Figure 6. The influence of temperature for the adsorption of (a) Fe(II); (b) Cu(II); (c) carotenoid; and (d) chlorophyll onto activated bentonite clay under IBM and UBM. Industrial bleaching method (IBM), Ultrasonic bleaching method (UBM).

Figure 7. Plot of $\ln(K_d)$ versus $1/T$ for the adsorption of Fe(II) on activated bentonite clay under (a) IBM, (b) UBM-25 kHz, and (c) UBM-40 kHz. IBM; industrial bleaching method, UBM; ultrasonic bleaching method.

Figure 8. Plot of $\ln(K_d)$ versus $1/T$ for the adsorption of Cu(II) on activated bentonite clay under (a) IBM, (b) UBM-25 kHz, and (c) UBM-40 kHz. IBM; industrial bleaching method, UBM; ultrasonic bleaching method.

Figure 9. Plot of $\ln(K_d)$ versus $1/T$ for the adsorption of carotenoid on activated bentonite clay under (a) IBM, (b) UBM-25 kHz, and (c) UBM-40 kHz. IBM; industrial bleaching method, UBM; ultrasonic bleaching method.

Figure 10. Plot of $\ln(K_d)$ versus $1/T$ for the adsorption of chlorophyll on activated bentonite clay under (a) IBM, (b) UBM-25 kHz, and (c) UBM-40 kHz. IBM; industrial bleaching method, UBM; ultrasonic bleaching method.

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Table 1. The Fe(II) and Cu(II) content (mg kg⁻¹) at 65°C

Time (min)	Industrial bleaching method (IBM)		Ultrasonic bleaching method (UBM)			
	Fe(II)*	Cu(II)	UBM-25 kHz		UBM-40 kHz	
			Fe(II)	Cu(II)	Fe(II)	Cu(II)
0	0.063 ^{aA}	0.024 ^{aA}	0.063 ^{aA}	0.024 ^{aA}	0.063 ^{aA}	0.024 ^{aA}
5	0.063 ^{aA}	0.024 ^{aA}	0.060 ^{bB}	0.021 ^{bB}	0.062 ^{aA}	0.022 ^{abAB}
10	0.058 ^{bA}	0.022 ^{abA}	0.051 ^{cBC}	0.018 ^{cC}	0.054 ^{bB}	0.020 ^{bB}
15	0.051 ^{cA}	0.021 ^{bA}	0.028 ^{dC}	0.011 ^{dC}	0.039 ^{cB}	0.014 ^{cB}
20	0.049 ^{cA}	0.018 ^{cA}	0.012 ^{eC}	0.03 ^{eC}	0.018 ^{dB}	0.007 ^{dB}
25	0.045 ^{dA}	0.017 ^{cA}	0.005 ^{fC}	ND ^{fC}	0.010 ^{eB}	0.003 ^{eB}
30	0.042 ^{eA}	0.016 ^{cA}	ND ^{gC}	ND ^{fB}	0.004 ^{fB}	ND ^{fB}

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847 * Each data represents the mean value from three replicates and values with similar letters are not
848 significantly different in each row (P<0.05). ND means not detected.

849 ** Different lowercase letters in each column and capital letters in each row indicate significant
850 statistical difference in iron and copper ($p \leq 0.05$).

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Table 2. The Fe(II) and Cu(II) content (mg kg⁻¹) at 30 min

Temperature (°C)	Industrial bleaching method (IBM)		Ultrasonic bleaching method (UBM)			
	Fe(II)	Cu(II)	UBM-25 kHz		UBM-40 kHz	
			Fe(II)	Cu(II)	Fe(II)	Cu(II)
35	0.062 ^{aA}	0.024 ^{aA}	0.061 ^{aA}	0.015 ^{bC}	0.062 ^{aA}	0.020 ^{aB}
45	0.060 ^{aA}	0.024 ^{aA}	0.040 ^{bC}	0.007 ^{bC}	0.048 ^{bB}	0.017 ^{bB}
55	0.057 ^{bA}	0.021 ^{bA}	0.023 ^{cC}	ND ^{bC}	0.033 ^{cB}	0.008 ^{cB}
65	0.043 ^{cA}	0.016 ^{cA}	ND ^{dC}	ND ^{bC}	0.020 ^{dB}	0.003 ^{dB}

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* Each data represents the mean value from three replicates and values with similar letters are not significantly different in each row (P<0.05). ND means not detected.

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** Different lowercase letters in each column and capital letters in each row indicate significant statistical difference in iron and copper (p ≤ 0.05).

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Table 3. The Carotenoid (mg kg⁻¹) and Chlorophyll (µg kg⁻¹) content at 65°C

Time (min)	Industrial bleaching method (IBM)		Ultrasonic bleaching method (UBM)			
	Carotenoid*	Chlorophyll	UBM-25 kHz		UBM-40 kHz	
			Carotenoid*	Chlorophyll	Carotenoid*	Chlorophyll
0	5.51 ^{aA}	509.9 ^{aA}	5.51 ^{aA}	509.9 ^{aA}	5.5 ^{aA}	509.9 ^{aA}
5	5.43 ^{aA}	473.8 ^{aA}	5.01 ^{bB}	436.1 ^{bB}	5.1 ^{aA}	478.0 ^{abAB}
10	5.12 ^{bA}	437.3 ^{abA}	3.87 ^{cBC}	374.8 ^{cC}	4.3 ^{bB}	414.2 ^{bB}
15	4.82 ^{cA}	404.7 ^{bA}	3.03 ^{dC}	325.5 ^{dC}	3.5 ^{cB}	361.8 ^{cB}
20	4.24 ^{cA}	395.1 ^{cA}	2.78 ^{eC}	267.0 ^{eC}	3.1 ^{dB}	302.3 ^{dB}
25	3.76 ^{dA}	350.7 ^{cA}	1.56 ^{fC}	202.5 ^{fC}	1.8 ^{eB}	248.6 ^{eB}
30	2.83 ^{eA}	284.4 ^{cA}	0.48 ^{gC}	125.9 ^{fB}	0.82 ^{fB}	160.7 ^{fB}

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* Each data represents the mean value from three replicates and values with similar letters are not significantly different in each row (P<0.05). ND means not detected.

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** Different lowercase letters in each column and capital letters in each row indicate significant statistical difference in iron and copper (p ≤ 0.05).

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Table 4. The Carotenoid (mg kg⁻¹) and Chlorophyll content (µg kg⁻¹) at 30 min

Temperature (°C)	Industrial bleaching method (IBM)		Ultrasonic bleaching method (UBM)			
	Carotenoid*	Chlorophyll	UBM-25 kHz		UBM-40 kHz	
			Carotenoid*	Chlorophyll	Carotenoid*	Chlorophyll
35	5.45 ^{aA}	465.7 ^{aA}	4.5 ^{aA}	376.8 ^{bC}	4.9 ^{aA}	434.7 ^{aB}
45	5.12 ^{aA}	421.8 ^{aA}	3.5 ^{bC}	282.6 ^{bC}	3.0 ^{bB}	334.6 ^{bB}
55	3.79 ^{bA}	348.8 ^{bA}	1.0 ^{cC}	202.6 ^{bC}	1.6 ^{cB}	236.4 ^{cB}
65	2.83 ^{cA}	284.4 ^{cA}	0.48 ^{gC}	125.9 ^{fB}	0.82 ^{fB}	160.7 ^{fB}

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* Each data represents the mean value from three replicates and values with similar letters are not significantly different in each row (P<0.05). ND means not detected.

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** Different lowercase letters in each column and capital letters in each row indicate significant statistical difference in iron and copper (p ≤ 0.05).

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Table 5. Fitting parameters of adsorption kinetics for Fe(II) ions under IBM and UBM

System	Model	Kinetics parameters	Value		R ²		χ^2	
			Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear
IBM	Pseudo-first-order	$k_1(\text{min}^{-1})$	0.077	0.053	0.912	0.938	0.0008	0.0002
		$q_1\text{ (mg g}^{-1}\text{)}$	0.0026	0.0019				
	Pseudo-second-order	$k_2\text{ (g (mg min)}^{-1}\text{)}$	0.0058	0.0066	0.693	0.752	0.004	0.0032
		$q_2\text{ (mg g}^{-1}\text{)}$	0.0034	0.0029				
	Intraparticle diffusion	$k_i\text{ (mg (g min}^{1/2}\text{)}^{-1}\text{)}$	-	0.0004	0.937	0.844	0.0014	0.0028
		kiC/C	0.011	-0.0004				
System	Model	Kinetics parameters	Value		R ²		χ^2	
			Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear
UBM-25 kHz	Pseudo-first-order	$k_1(\text{min}^{-1})$	0.104	0.059	0.887	0.962	0.002	0.0011
		$q_1\text{ (mg g}^{-1}\text{)}$	0.0088	0.0058				
	Pseudo-second-order	$k_2\text{ (g (mg min)}^{-1}\text{)}$	0.0054	0.0068	0.619	0.687	0.0047	0.0039
		$q_2\text{ (mg g}^{-1}\text{)}$	0.0094	0.009				
	Intraparticle diffusion	$k_i\text{ (mg (g min}^{1/2}\text{)}^{-1}\text{)}$	-	0.0012	0.961	0.831	0.0013	0.003
		kiC/C	0.0035	-0.0012				
System	Model	Kinetics parameters	Value		R ²		χ^2	
			Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear
UBM-40 kHz	Pseudo-first-order	$k_1(\text{min}^{-1})$	0.091	0.056	0.851	0.964	0.0088	0.0011
		$q_1\text{ (mg g}^{-1}\text{)}$	0.0082	0.0054				
	Pseudo-second-order	$k_2\text{ (g (mg min)}^{-1}\text{)}$	0.0057	0.0069	0.594	0.634	0.0048	0.0045
		$q_2\text{ (mg g}^{-1}\text{)}$	0.0096	0.0089				
	Intraparticle diffusion	$k_i\text{ (mg (g min}^{1/2}\text{)}^{-1}\text{)}$	-	0.0011	0.956	0.797	0.0012	0.008
		kiC/C	0.0014	-0.0013				

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874 **Table 6.** Fitting parameters of adsorption kinetics for Cu(II) ions under IBM and UBM
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System	Model	Kinetics parameters	Value		R ²		χ^2	
			Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear
IBM	Pseudo-first-order	$k_1(min^{-1})$	0.202	0.051	0.632	0.967	0.002	0.001
		$q_1\ (mg\ g^{-1})$	0.0027	0.0007				
	Pseudo-second-order	$k_2\ (g\ (mg\ min)^{-1})$	0.0052	0.0065	0.682	0.759	0.0038	0.0033
		$q_2\ (mg\ g^{-1})$	0.0039	0.0032				
	Intraparticle diffusion	$k_i\ (mg\ (g\ min^{1/2})^{-1})$	-	0.0005	0.966	0.858	0.0026	0.0028
		kiC/C	0.0063	-0.0004				
System	Model	Kinetics parameters	Value		R ²		χ^2	
			Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear
UBM-25 kHz	Pseudo-first-order	$k_1(min^{-1})$	0.389	0.062	0.737	0.967	0.021	0.001
		$q_1\ (mg\ g^{-1})$	0.023	0.0023				
	Pseudo-second-order	$k_2\ (g\ (mg\ min)^{-1})$	0.0045	0.0064	0.537	0.654	0.0046	0.0036
		$q_2\ (mg\ g^{-1})$	0.0036	0.0029				
	Intraparticle diffusion	$k_i\ (mg\ (g\ min^{1/2})^{-1})$	-	0.0012	0.961	0.831	0.0003	0.002
		k_iC	0.005	-0.0012				
System	Model	Kinetics parameters	Value		R ²		χ^2	
			Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear
UBM-40 kHz	Pseudo-first-order	$k_1(min^{-1})$	0.258	0.053	0.536	0.96	0.012	0.009
		$q_1\ (mg\ g^{-1})$	0.0137	0.0022				
	Pseudo-second-order	$k_2\ (g\ (mg\ min)^{-1})$	0.0036	0.0057	0.584	0.631	0.0042	0.0035
		$q_2\ (mg\ g^{-1})$	0.0034	0.0028				
	Intraparticle diffusion	$k_i\ (mg\ (g\ min^{1/2})^{-1})$	-	0.0011	0.958	0.797	0.009	0.01
		kiC/C	0.0038	-0.0013				

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Table 7. Fitting parameters of adsorption kinetics for carotenoid under IBM and UBM

System	Model	Kinetics parameters	Value		R ²		χ^2	
			Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear
IBM	Pseudo-first-order	$k_1(min^{-1})$	0.055	0.043	0.861	0.973	0.012	0.008
		$q_1\ (mg\ g^{-l})$	0.263	0.211				
	Pseudo-second-order	$k_2\ (g\ (mg\ min)^{-l})$	0.0068	0.0047	0.746	0.854	0.069	0.045
		$q_2\ (mg\ g^{-l})$	0.325	0.262				
	Intraparticle diffusion	$k_i\ (mg\ (g\ min^{1/2})^{-l})$	-	0.037	0.972	0.775	0.009	0.032
		kiC/C	0.02	-0.045				
System	Model	Kinetics parameters	Value		R ²		χ^2	
			Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear
UBM-25 kHz	Pseudo-first-order	$k_1(min^{-1})$	0.069	0.055	0.869	0.967	0.054	0.035
		$q_1\ (mg\ g^{-l})$	0.513	0.426				
	Pseudo-second-order	$k_2\ (g\ (mg\ min)^{-l})$	0.0078	0.0068	0.746	0.815	0.098	0.088
		$q_2\ (mg\ g^{-l})$	0.501	0.489				
	Intraparticle diffusion	$k_i\ (mg\ (g\ min^{1/2})^{-l})$	-	0.078	0.965	0.887	0.04	0.08
		kiC/C	0.086	-0.063				
System	Model	Kinetics parameters	Value		R ²		χ^2	
			Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear
UBM-40 kHz	Pseudo-first-order	$k_1(min^{-1})$	0.067	0.05	0.847	0.989	0.06	0.04
		$q_1\ (mg\ g^{-l})$	0.498	0.397				
	Pseudo-second-order	$k_2\ (g\ (mg\ min)^{-l})$	0.0088	0.0078	0.678	0.741	0.096	0.079
		$q_2\ (mg\ g^{-l})$	0.568	0.512				
	Intraparticle diffusion	$k_i\ (mg\ (g\ min^{1/2})^{-l})$	-	0.073	0.985	0.849	0.05	0.07
		kiC/C	0.058	-0.07				

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Table 8. Fitting parameters of adsorption kinetics for chlorophyll under IBM and UBM

System	Model	Kinetics parameters	Value		R ²		χ^2	
			Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear
IBM	Pseudo-first-order	$k_1(min^{-1})$	0.065	0.056	0.914	0.967	1.34	0.22
		$q_1(mg\ g^{-1})$	19.67	17.45				
	Pseudo-second-order	$k_2(g\ (mg\ min)^{-1})$	0.0088	0.0078	0.817	0.897	1.78	1.39
		$q_2(mg\ g^{-1})$	19.85	18.69				
	Intraparticle diffusion	$k_i(mg\ (g\ min^{1/2})^{-1})$	-	3.13	0.959	0.922	0.28	0.5
		kiC/C	0.882	-1.97				
System	Model	Kinetics parameters	Value		R ²		χ^2	
			Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear
UBM-25 kHz	Pseudo-first-order	$k_1(min^{-1})$	0.106	0.068	0.841	0.968	3.2	0.63
		$q_1(mg\ g^{-1})$	41.39	29.77				
	Pseudo-second-order	$k_2(g\ (mg\ min)^{-1})$	0.0028	0.0089	0.798	0.845	4.15	3.47
		$q_2(mg\ g^{-1})$	39.76	33.48				
	Intraparticle diffusion	$k_i(mg\ (g\ min^{1/2})^{-1})$	-	5.72	0.957	0.945	0.71	1.84
		kiC/C	1.27	-3.16				
System	Model	Kinetics parameters	Value		R ²		χ^2	
			Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear
UBM-40 kHz	Pseudo-first-order	$k_1(min^{-1})$	0.077	0.058	0.91	0.962	7.7	5.7
		$q_1(mg\ g^{-1})$	35.41	27.74				
	Pseudo-second-order	$k_2(g\ (mg\ min)^{-1})$	0.0088	0.0081	0.623	0.721	9.6	8.1
		$q_2(mg\ g^{-1})$	41.56	37.56				
	Intraparticle diffusion	$k_i(mg\ (g\ min^{1/2})^{-1})$	-	5.27	0.943	0.889	6.2	6.4
		kiC/C	0.615	-4.52				

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Table 9. Thermodynamic parameters for Fe(II) and Cu(II) adsorption by activated bentonite clay under IBM and UBM. IBM; industrial bleaching method, UBM; ultrasonic bleaching method, ΔH° ; standard enthalpy, ΔS° ; standard entropy, ΔG° , standard free energy.

System	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	T (K)	ΔG° (kJ mol ⁻¹)
IBM			308	10.72
			318	8.03
Fe(II)	93.49	268.72	328	5.35
			338	2.66
			308	15.44
Cu(II)	151.26	440.93	318	11.04
			328	6.63
			338	2.22
UBM-25 kHz			308	8.79
			318	2.48
Fe(II)	203.32	631.56	328	-3.83
			338	-10.14
			308	1.61
Cu(II)	193.1	621.63	318	-4.61
			328	-10.82
			338	-17.04
UBM-40 kHz			308	9.16
Fe(II)	137.33	416.12	318	5.00
			328	0.84
			338	-3.32
Cu(II)	105.64	517.73	308	4.69
			318	1.42
			328	-1.85
			338	-5.13

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Table 10. Thermodynamic parameters for carotenoid and chlorophyll adsorption by activated bentonite clay under IBM and UBM. IBM; industrial bleaching method, UBM; ultrasonic bleaching method, ΔH° ; standard enthalpy, ΔS° ; standard entropy, ΔG° , standard free energy.

System	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	T (K)	ΔG° (kJ mol ⁻¹)
IBM			308	10.69
			318	6.96
Carotenoid	125.56	372.93	328	3.23
			338	-0.49
			308	5.82
Chlorophyll	54.67	158.59	318	4.23
			328	2.65
			338	1.066
UBM-25 kHz			308	3.03
			318	0.55
Carotenoid	79.27	247.54	328	-1.92
			338	-4.39
			308	2.33
Chlorophyll	46.39	143.02	318	0.908
			328	-0.52
			338	-1.95
UBM-40 kHz			308	4.61
Carotenoid	93.32	288.01	318	1.73
			328	-1.15
			338	-4.03
Chlorophyll	60.98	184.73	308	4.08
			318	2.23
			328	0.388
			338	-1.46

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Table 11. Fitting parameters of adsorption isotherms for Fe(II) ions under IBM and UBM

System	Model	Kinetics parameters	Value		R ²		χ^2	
			Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear
IBM	Langmuir	$K_L (Lmg^{-1})$	0.151	0.134	0.763	0.857	0.065	0.044
		$q_m (mg\ g^{-1})$	0.0032	0.0023				
	Freundlich	K_F $((mgg^{-1})(Lmg^{-1})^{1/n})$	0.376	0.345	0.851	0.938	0.043	0.037
		n	1.33	1.26				
	Tempkin	$A_T (Lmg^{-1})$	1.42	1.36	0.799	0.888	0.063	0.041
		$b_T (Jmol^{-1})$	7.14	5.22				
System	Model	Kinetics parameters	Value		R ²		χ^2	
			Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear
UBM-25 kHz	Langmuir	$K_L (Lmg^{-1})$	0.164	0.141	0.777	0.889	0.063	0.042
		$q_m (mg\ g^{-1})$	0.0077	0.0066				
	Freundlich	K_F $((mgg^{-1})(Lmg^{-1})^{1/n})$	0.467	0.436	0.898	0.937	0.041	0.036
		n	3.01	2.86				
	Tempkin	$A_T (Lmg^{-1})$	4.11	3.41	0.871	0.899	0.043	0.04
		$b_T (Jmol^{-1})$	11.56	9.91				
System	Model	Kinetics parameters	Value		R ²		χ^2	
			Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear
UBM-40 kHz	Langmuir	$K_L (Lmg^{-1})$	0.157	0.138	0.746	0.889	0.057	0.039
		$q_m (mg\ g^{-1})$	0.0072	0.0062				
	Freundlich	K_F $((mgg^{-1})(Lmg^{-1})^{1/n})$	0.436	0.412	0.886	0.964	0.042	0.031
		n	2.89	2.46				
	Tempkin	$A_T (Lmg^{-1})$	3.65	3.26	0.854	0.921	0.046	0.034
		$b_T (Jmol^{-1})$	8.19	7.56				

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Table 12. Fitting parameters of adsorption isotherms for Cu(II) ions under IBM and UBM

System	Model	Kinetics parameters	Value		R ²		χ^2	
			Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear
IBM	Langmuir	$K_L\ (Lmg^{-1})$	0.151	0.139	0.754	0.834	0.064	0.046
		$q_m\ (mg\ g^{-1})$	0.0033	0.0013				
	Freundlich	K_F $((mgg^{-1})(Lmg^{-1})^{1/n})$	0.364	0.338	0.843	0.901	0.047	0.039
		n	1.33	1.21				
	Tempkin	$A_T\ (Lmg^{-1})$	1.48	1.39	0.791	0.867	0.061	0.043
		$b_T\ (Jmol^{-1})$	8.63	6.1				
System	Model	Kinetics parameters	Value		R ²		χ^2	
			Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear
UBM-25 kHz	Langmuir	$K_L\ (Lmg^{-1})$	0.159	0.144	0.765	0.876	0.057	0.043
		$q_m\ (mg\ g^{-1})$	0.0052	0.0043				
	Freundlich	K_F $((mgg^{-1})(Lmg^{-1})^{1/n})$	0.453	0.429	0.894	0.921	0.039	0.037
		n	2.83	2.79				
	Tempkin	$A_T\ (Lmg^{-1})$	3.76	3.87	0.864	0.898	0.051	0.04
		$b_T\ (Jmol^{-1})$	11.89	10.7				
System	Model	Kinetics parameters	Value		R ²		χ^2	
			Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear
UBM-40 kHz	Langmuir	$K_L\ (Lmg^{-1})$	0.155	0.141	0.741	0.869	0.054	0.041
		$q_m\ (mg\ g^{-1})$	0.0044	0.0036				
	Freundlich	K_F $((mgg^{-1})(Lmg^{-1})^{1/n})$	0.427	0.406	0.867	0.934	0.04	0.034
		n	2.66	2.46				
	Tempkin	$A_T\ (Lmg^{-1})$	3.74	3.65	0.834	0.901	0.048	0.038
		$b_T\ (Jmol^{-1})$	9.3	7.6				

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Table 13. Fitting parameters of adsorption isotherms for carotenoid under IBM and UBM

System	Model	Kinetics parameters	Value		R ²		χ^2	
			Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear
IBM	Langmuir	$K_L\ (Lmg^{-1})$	0.192	0.174	0.785	0.926	0.061	0.036
		$q_m\ (mg\ g^{-1})$	0.257	0.231				
	Freundlich	K_F $((mgg^{-1})(Lmg^{-1})^{1/n})$	0.634	0.589	0.917	0.987	0.037	0.028
		n	1.46	1.34				
	Tempkin	$A_T\ (Lmg^{-1})$	2.36	2.22	0.887	0.945	0.039	0.033
		$b_T\ (Jmol^{-1})$	8.15	5.79				
System	Model	Kinetics parameters	Value		R ²		χ^2	
			Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear
UBM-25 kHz	Langmuir	$K_L\ (Lmg^{-1})$	0.224	0.186	0.882	0.946	0.054	0.033
		$q_m\ (mg\ g^{-1})$	0.479	0.448				
	Freundlich	K_F $((mgg^{-1})(Lmg^{-1})^{1/n})$	0.778	0.765	0.921	0.991	0.034	0.025
		n	3.46	3.23				
	Tempkin	$A_T\ (Lmg^{-1})$	4.87	4.63	0.906	0.974	0.036	0.029
		$b_T\ (Jmol^{-1})$	15.89	11.86				
System	Model	Kinetics parameters	Value		R ²		χ^2	
			Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear
UBM-40 kHz	Langmuir	$K_L\ (Lmg^{-1})$	0.211	0.181	0.798	0.901	0.059	0.036
		$q_m\ (mg\ g^{-1})$	0.436	0.419				
	Freundlich	K_F $((mgg^{-1})(Lmg^{-1})^{1/n})$	0.684	0.649	0.891	0.978	0.039	0.031
		n	2.74	2.65				
	Tempkin	$A_T\ (Lmg^{-1})$	3.65	3.49	0.876	0.931	0.046	0.033
		$b_T\ (Jmol^{-1})$	12.49	8.59				

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Table 14. Fitting parameters of adsorption isotherms for chlorophyll under IBM and UBM

System	Model	Kinetics parameters	Value		R ²		χ^2	
			Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear
IBM	Langmuir	$K_L\ (Lmg^{-1})$	0.295	0.251	0.786	0.889	0.065	0.045
		$q_m\ (mg\ g^{-l})$	23.87	21.48				
	Freundlich	K_F $((mgg^{-1})(Lmg^{-1})^{1/n})$	18.65	17.41	0.899	0.981	0.042	0.033
		n	1.78	1.45				
	Tempkin	$A_T\ (Lmg^{-1})$	2.87	2.74	0.887	0.965	0.044	0.038
		$b_T\ (Jmol^{-1})$	39.67	33.58				
System	Model	Kinetics parameters	Value		R ²		χ^2	
			Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear
UBM-25 kHz	Langmuir	$K_L\ (Lmg^{-1})$	0.322	0.274	0.787	0.901	0.063	0.043
		$q_m\ (mg\ g^{-l})$	36.89	32.85				
	Freundlich	K_F $((mgg^{-1})(Lmg^{-1})^{1/n})$	31.45	29.91	0.891	0.981	0.047	0.035
		n	3.96	3.79				
	Tempkin	$A_T\ (Lmg^{-1})$	4.58	4.36	0.868	0.937	0.05	0.039
		$b_T\ (Jmol^{-1})$	70.31	65.85				
System	Model	Kinetics parameters	Value		R ²		χ^2	
			Linear	Nonlinear	Linear	Nonlinear	Linear	Nonlinear
UBM-40 kHz	Langmuir	$K_L\ (Lmg^{-1})$	0.301	0.259	0.785	0.871	0.066	0.044
		$q_m\ (mg\ g^{-l})$	34.89	29.78				
	Freundlich	K_F $((mgg^{-1})(Lmg^{-1})^{1/n})$	29.42	27.41	0.851	0.946	0.048	0.039
		n	2.91	2.79				
	Tempkin	$A_T\ (Lmg^{-1})$	3.74	3.65	0.846	0.901	0.051	0.042
		$b_T\ (Jmol^{-1})$	45.68	41.36				

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966
967
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969
970
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972

Figures

Figure 1

The effect of ultrasonication on the reduction of particle size and cleaning of surface.

Figure 2

The experimental kinetic data and predicted values of Fe(II) ions on bentonite clay under IBM (a), UBM-25 kHz (b) and UBM-40 kHz (c) for soybean oil.

Figure 3

The experimental kinetic data and predicted values of Cu (II) ions on bentonite clay under IBM (a), UBM-25 kHz (b) and UBM-40 kHz (c) for soybean oil.

Figure 4

The experimental kinetic data and predicted values of Carotenoid on bentonite clay under IBM (a), UBM-25 kHz (b) and UBM-40 kHz (c) for soybean oil.

Figure 5

The experimental kinetic data and predicted values of Chlorophyll on bentonite clay under IBM (a), UBM-25 kHz (b) and UBM-40 kHz (c) for soybean oil.

Figure 6

The influence of temperature for the adsorption of (a) Fe(II); (b) Cu(II); (c) carotenoid; and (d) chlorophyll onto activated bentonite clay under IBM and UBM. Industrial bleaching method (IBM), Ultrasonic bleaching method (UBM).

Figure 7

Plot of $\ln(K_d)$ versus $1/T$ for the adsorption of Fe(II) on activated bentonite clay under (a) IBM, (b) UBM-25 kHz, and (c) UBM-40 kHz. IBM; industrial bleaching method, UBM; ultrasonic bleaching method.

Figure 8

Plot of $\ln(K_d)$ versus $1/T$ for the adsorption of Cu(II) on activated bentonite clay under (a) IBM, (b) UBM-25 kHz, and (c) UBM-40 kHz. IBM; industrial bleaching method, UBM; ultrasonic bleaching method.

Figure 9

Plot of $\ln(K_d)$ versus $1/T$ for the adsorption of carotenoid on activated bentonite clay under (a) IBM, (b) UBM-25 kHz, and (c) UBM-40 kHz. IBM; industrial bleaching method, UBM; ultrasonic bleaching method.

Figure 10

Plot of $\ln(K_d)$ versus $1/T$ for the adsorption of chlorophyll on activated bentonite clay under (a) IBM, (b) UBM-25 kHz, and (c) UBM-40 kHz. IBM; industrial bleaching method, UBM; ultrasonic bleaching method.