Preparation and characterization of nanoporous powders from bentonite by hydrochloric acid leaching and using as bleaching earth

Nilgün Yener¹ · Cengiz Biçer² · Abdullah Devrim Pekdemir³ · Yüksel Sarıkaya⁴ · Müşerref Önal⁴

Received: 3 December 2019 / Accepted: 16 March 2020 / Published online: 20 March 2020
© Springer Nature Switzerland AG 2020

Abstract

A calcium bentonite (CaB) was leached by hydrochloric acid (HCl) solutions to improve the adsorptive properties such as nanoporosity, acidity, and decoloration power. The mass ratio of HCl/CaB was changed between zero and 1.00 according to the anhydrous CaB + HCl mixture. Different powders were obtained from the heating of the aqueous mixtures at 90 °C for 16 h under a reflux condenser. The raw CaB and obtained powders were investigated by different methods such as X-ray diffraction, chemical analyses, adsorption, pH-metry, and tintometry techniques. A calcium rich-smectite (CaS) are found in the CaB as major clay mineral, whereas illite (I) and metahalloysite (MH) as minor ones. The impurities are opal-A (OA), opal-CT (OCT), quartz (Q), calcite (C), orthoclase (O), and clinoptilolite (CLN). The fraction of the dissolved cations from the C, CaS, I, and CLN increases with the increasing of HCl concentration. The remaining K⁺ and Al³⁺ cations are located in the undissolved orthoclase. An amorphous silica OA (SiO₂·nH₂O) remained at the end of completed leaching. The gradual increase in the adsorptive properties, acidity, and bleaching power is due to the formation of new nanopores. Gradual decrease after their maxima is caused from the degradation of the layered structure for clay minerals. The maximum bleaching power tentatively intensifies with the increasing of the used powder mass.

Keywords Acid leaching · Bentonite · Bleaching · Crystallinity · Nanoporosity

1 Introduction

Bentonites are one group of the clays. The major clay minerals in bentonite are smectites. Pure smectite minerals seldom found in the nature. However, different non-clay minerals found in bentonites as impurities [1]. The 2:1 unit layer of smectites is formed by the one octahedral (O) sheet between two tetrahedral (T) sheets [2, 3]. The sheets bonded to each other with the oxygen bridges in the T–O–T (2:1) layers. The dominant central tetrahedral cations are Si⁴⁺, but Al³⁺ substitutes for it frequently whereas Fe³⁺ rarely. Otherwise, the central octahedral cations may be Al³⁺, Fe³⁺, Fe²⁺, Mg²⁺, and Li⁺. The abundance

one of these cations determined the type of smectite found in bentonites. Because of the isomorphous substitutions of such cations with lower-charge ones, the 2:1 layers possess negative charges. These negative charges are neutralized by Na⁺ or Ca²⁺ situated in the interlayer spaces and around the edges of the 2:1 layers. If the Na⁺ or Ca²⁺ is dominant, then the mineral is called sodium-rich smectites (NaS) or calcium-rich smectites (CaS). The value of basal spacing, d(001), of the anhydrous NaS and CaS is approximately 1.0 nm. The air dried NaS has one water sheet between the 2:1 layers whereas CaS has two ones. Therefore, their thickness are almost 1.26 nm and 1.54 nm, respectively. Such cations are exchangeable with

✉ Müşerref Önal, onal@science.ankara.edu.tr | ¹Department of Biochemistry, Medical School, Dokuz Eylül University, Inciralti, İzmir, Turkey. ²Ege Teknik CNC, 4. Industrial Site, 29/18 Bornova, İzmir, Turkey. ³Institute of Mineral Research and Exploration, 06800 Ankara, Turkey. ⁴Department of Chemistry, Faculty of Science, Ankara University, 06100 Tandoğan, Ankara, Turkey.

all inorganic or organic ones via a cation exchange process under certain conditions. The equivalent content of the Na^+ and/or Ca^{2+} in a unit mass of the smectite minerals as well as silicates is defined as the cation exchange capacity (CEC). On the other hand, NaS suspended in water for a long time whereas CaS flocculated rapidly [4].

Ideal chemical formula for each smectite is given in the following forms [1].

where $R_{0.33}^+$ is the exchangeable cation as Na^+ or/and $\text{Ca}_{0.33/2}^{2+}$ and $R_{0.33}^{3+}$ is the octahedral cation as $\text{Al}_{0.33}^{3+}$ or/and $\text{Fe}_{0.33}^{3+}$.

The void space between and inside of the particles with the internal width less than 2 nm, between 2 and 50 nm, and larger than 50 nm are called micropore, mesopore, and macropore, respectively [5]. Diameter of cylindrical pore and distance between opposite walls of a silt are taken as internal pore width. Recently, the voids with the internal width between 2 and 100 nm are named as nanopores.

The specific pore volume (V) is defined as the total volume of the micro- and mesopores in a unit mass solid. The specific surface area (S) is equal to the total area of inner and outer walls of the micro- and mesopores in a unit mass solid. Smectites and bentonites as well as other clay mineral and clays are micro- and mesoporous materials having different adsorptive properties depending on the mineralogy, crystal structure of the minerals and their chemical composition [6, 7].

Bentonites have been modified by acid activation [8–10] heat treatment [11, 12], ion exchange [13–15] to extend the using areas [16–18]. The acid leached bentonites are mainly employed as bleaching earth [19–21] and catalyst [22]. They are raw materials for the preparation of organoclays [23, 24], pillared clays [25], nanocomposites [26], and electrodes [27, 28]. New adsorbents and different organic chemical have been obtained through the pyrolysis of the spent bleaching earths [29–31]. The goal of the present study is to obtain a powder with the maximum bleaching power for an alkali refined cottonseed oil through hydrochloric acid leaching of a bentonite.

2 Materials and methods

A calcium-rich bentonite (CaB) of light green color obtained from the Enez/Edirne bed, Turkey, was used as raw material. The CaB was leached with a dilute acetic acid solution to remove carbonates and washed with distilled water until free of acetate ions [32]. The carbonate-free CaB dried at 105 °C for 4 h, and stored in a tightly closed plastic bottle.

Sixteen samples each having a mass 20 g were taken from the stock CaB and leached with 400 mL HCl solutions. The mass ratio of HCl/CaB was changed between zero and 1.00 based on the dried CaB and pure HCl mixture. Accordingly, the corresponding concentrations of the leach-solution increases from zero to up 1.4 molL⁻¹. Each sample was suspended in the aqueous solution of HCl under magnetic stirring in a round-bottom flask. The heterogeneous mixtures were heated at 90 °C for 16 h in the continuous stirred flasks under a reflux condenser. Each leached CaS sample was centrifuged. The obtained precipitates were washed with distilled water until free of Cl⁻ ions. After drying at 105 °C for 4 h, they were stored in tightly closed plastic bottles.

The X-ray diffraction (XRD) patterns of the samples were recorded from the random mounts using a Rikagu D-max 2200 Powder Diffractometer with a Ni filter and CuK_α ray with a wavelength of 0.15418 nm.

Before chemical analysis, each sample was heated at 1000 °C for 2 h, and the decrease in mass was taken as the loss on ignition (LOI). The metal content of the each ignited sample was determined using Hitachi Z-8200 Atomic Absorption Spectrometer. The results were calculated as the mass percentage of the metal oxides.

The CEC of each sample was determined by the methylene blue (MB) standard method [33–35]. The N₂ adsorption/desorption (N₂-AD) data at 77 K of the samples were determined using a volumetric Pyrex glass adsorption instrument connected to high vacuum [36]. The samples were outgassed at 150 °C and 4 h under vacuum of 10⁻⁵ mmHg before the adsorption experiments. The pH-value for each aqueous suspension having CaB of 2% by mass was measured using an Orion equipment.

Sample of alkali refined cottonseed oil [37] were heated to 85 °C with magnetic stirring under reduced pressure at 80 mmHg in a glass equipment. Then, leached bentonite sample was added to the oil and stirred 10 min. Mass percent of the solid was 2% in the suspension. The suspension was filtered by applying vacuum. A Lovibond Tintometer was used to obtain the red color index of the bleached oils [38–40]. These experiments were repeated in duplicate. Similar experiments

were performed by changing the mass percent of the leached sample having maximum bleaching power.

3 Results and discussion

3.1 Mineralogy of the bentonite

The XRD-reflections (Fig. 1) indicate the minerals in the raw bentonite and its two hydrochloric acid leached samples [1, 41]. The bentonite contains major clay mineral as CaS as well as illite (I), and metahalloysite (MH) minor ones. The average structural formula for I is given as: $R^{+}_{0.89}(Al_{1.85}Fe^{3+}_{0.05}Mg_{0.10})Si_{3.20}Al_{0.80}O_{10}(OH)_2$, where R^{+} is generally K^{+} and not exchangeable [1]. Illite is 2:1 layered clay mineral like as smectites. Also, a mixture of the 2:1 layers of smectites and illite can be found in a clay mineral. The chemical formula for MH is: $Al_4Si_4O_{10}(OH)_8$ which is T-O (1:1) layered clay mineral in kaolin group. The nonclay mineral in the bentonite and their chemical formula are: calcite (C: $CaCO_3$), quartz (Q: SiO_2), opal-CT and opal-A (OCT and OA: $SiO_2 \cdot nH_2O$), clinoptilolite [CLN: $(Na,Ca)_{4-6}Al_6(Al,Si)_4Si_{29}$

$O_{72} \cdot 24H_2O$], and orthoclase (O: $KAlSi_3O_8$) [34]. Here, Q, OCT, and OA are the crystalline, paracrystalline, and amorphous silica polymorphs, whereas CLN and O are the zeolite and feldspar minerals, respectively.

The thickness of 2:1 layer for CaS and I was calculated from Bragg equation using the position of the 001 reflections as 1.54 nm and 0.99 nm, respectively (Fig. 1). Similarly, the thickness of 1:1 layer for MH is found as 0.71 nm. The 2:1 layers of CaS and I greatly degraded when the HCl/CaB ratio reached up to 0.26 (Fig. 2). Also, CLN dissolved at the same interval. In the contrary, MH, O, Q, OCT, and OA not affected from the leaching (Figs. 1, 2). The most broad peak in the interval $15^\circ < 2\theta < 30^\circ$ indicated the formation of OA from the undissolved silicon [42–44]. Consequently, the greatest deformation in the 2:1 layers of the CaS appeared by changing HCl/CaB ratio between 0.10 and 0.20 in the leaching mixture (Fig. 3).

3.2 Crystallinity

The shape of the 001-reflection (Fig. 1) indicates the well crystallized CaS in the CaB. The intensity (I) of

Fig. 1 The XRD-patterns for raw, carbonat free, and completely dissolved by the hydrochloric acid leached bentonite powders (CaS:calcium smectite, I:illite, MH: metahalloysite, C:calcite, OA:opal-A, OCT:opal-CT, Q:quartz, O:orthoclase, CLN:clinoptilolite)

Fig. 2 Change in intensity of the most characteristic smectite reflection from 001 surfaces depending on the HCl/CaB ratio at the leaching process (CaS:calcium smectite, I:illite, MH: metahalloysite, O:orthoclase, CLN:clinoptilolite)

Fig. 3 The changes in the relative intensity (I/I_0) and full width at half-maximum peak height ($FWHM$) of the 001 reflection with HCl/CaB ratio by the leaching (I and I_0 : peak intensities before and after acid-leached bentonite powders, $[HCl]$: molarity of the leach-solution)

001-reflection for CaS decreased by the progress of the acid leaching whereas its full width at half-maximum peak height ($FWHM$) increased (Fig. 2). The change in relative intensity (I/I_0) and $FWHM$ of the 001 peak (Fig. 3) revealed that the crystallinity of the CaS decreased greatly when the HCl/CaB ratio changed from 0.10 to 0.20 by the leaching process.

3.3 Chemical composition

The chemical analyses show that the CaO % decreased from 4.90 to 1.85 by the extraction of the acetic acid solution which is due to the dissolution of the calcite (Table 1). The self-mass fraction ($x = m/m_0$) of the dissolved cations in the CaB decreased in the sequence of Ca^{2+} , Na^+ , Mg^{2+} , $Fe^{2+,3+}$, Al^{3+} , and K^+ with the increase of HCl/CaB ratio by the leaching (Fig. 4). The exchangeable cations (Ca^{2+} ,

Na^+) and the structural cations (Mg^{2+} , $Fe^{2+,3+}$, Al^{3+}) can be located only octahedral sites dissolved completely when the HCl/CaB ratio reached approximately to 0.40. Consequently, under these conditions the crystal structure of the CaS, I, and CLN destroyed completely. This finding was compatible with the XRD-result.

The dissolved Al^{3+} content increased more slowly with the increasing of HCl/CaB ratio and remained constant when it is about 0.50. Similarly, the dissolved K^+ content has a constant value at same conditions. The remainder Al^{3+} content is due to the undissolved MH and whereas K^+ from O (Fig. 4). These findings were also verified by the XRD-results (Fig. 2).

3.4 Cation exchange capacity

The equivalent amounts of the Na^+ and Ca^{2+} cations dissolved from one kilogram bentonite were calculated from the chemical analyses of the acid-leached powders. Because of the formation H-smectite by replacing protons with Na^+ and Ca^{2+} cations, the CEC remained constant (Fig. 5) before destroy of the layers in the CaS by the acid leaching. The CEC disappeared when the crystal of the CaS was completely collapsed in the CaB.

3.5 Surface area and pore volume

The N_2 adsorption capacity (n) of the powders increased with the increasing of HCl/CaB ratio by the leaching process (Fig. 6). Here p , p^0 , and $x = p/p^0$ are the equilibrium pressure, vapor pressure of the liquid nitrogen at $-196^\circ C$, and relative equilibrium pressure, respectively. The shape of the isotherms indicated that the powders contain micro- and mesopores. Hysteresis over the interval $0.50 < x < 0.96$ is due to the fact that capillary condensation beginning at the narrowest pores and capillary evaporation at the largest pores.

The specific surface area (S) for the samples was determined using standard BET method from the nitrogen adsorption isotherms in the relative equilibrium pressure interval from 0.05 to 0.30 [45]. The pores of inner width less than 50 nm filled completely by liquid nitrogen at $x = 0.96$ [5]. So, the specific pore volume (V) was taken as liquid nitrogen volumes at $x = 0.96$.

Total percentage of the dissolved metal oxides, R_xO_y ($MgO + Fe_2O_3 + Al_2O_3$) %, was obtained from the chemical

Table 1 The result of chemical analyses for the raw bentonite (B0) and carbonate-free bentonite (B1) samples as mass percent of the oxides

Samples	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	LOI
B0	55.75	16.42	5.63	2.74	4.90	0.70	2.41	11.49
B1	59.22	17.05	5.59	2.25	1.85	0.53	2.40	11.04

Fig. 4 Self mass fraction ($x = m/m_0$) of dissolved cations with increasing with the ratio of HCl/CaB during the process (m_0 and m : mass% of the element oxides in the carbonate-free bentonite before leaching and their dissolved values by the leaching, [HCl]: molarity of the leach-solution)

analyses of the powders. The increase in S and V arise from the increasing of R_xO_y % (Fig. 7), they have maxima when HCl/CaB ratio is 0.40 and then decreased to lower values. The gradual increase in S and V values up to their maxima was originated from the opening new pores by the progress of the leaching. In the contrary, the gradual decrease in same values after their maxima was due to destroy of the layers. The maximum increase in the S and V were 400% and 300%, respectively. Consequently, the optimal HCl/CaB ratio, temperature, and time to prepare the most porous powder are 0.40, 90 °C and 16 h, respectively.

3.6 Bleaching

Bleaching is an adsorption step in the edible oil refinement to remove color organic pigments, oxidation products and metal traces. The pH-value (acidity) of the aqueous suspensions for hydrochloric acid leached bentonite samples and red color index of the oil bleached by these adsorbents change depending on the mass percent of the dissolved metal oxide (Fig. 8). The bleaching power

Fig. 5 Change in the cation exchange capacity for the leached samples with respect to the equivalent amount of dissolved exchangeable cations

of the prepared samples depends on their chemical compositions, specific pore volume, specific surface area, and acidity (Figs. 7, 8). Color organic pigments, oxidation products and metal cations remove from the oil via physical and chemical adsorptions onto used bleaching earth [7, 8, 18, 21]. The cottonseed oil becomes to light yellow color after the bleaching. The dissolved R_xO_y % by mass in the sample provides maximum bleaching at 8% (Fig. 8). The bleaching power greatly increases with respect to the mass percent of this most suitable sample (Fig. 9). Besides bleaching different edible oils, the obtained acid leached bentonite can be used in other processes such as clarification of wine, beer, and fruit juice. Various adsorbent and organic chemicals can be prepared by pyrolysis of the spent bleaching earth having several organic pigments.

4 Conclusions

The powders with different properties were prepared by hydrochloric acid leaching of a calcium bentonite at 90 °C for 16 h. The obtained results are consecutively given in the following forms.

Fig. 6 Adsorption/desorption isotherms of nitrogen at 77 K on the different hydrochloric acid leached bentonite powders (n : adsorption capacity, $x = p/p^0$: relative adsorption equilibrium pressure, p : adsorption equilibrium pressure, p^0 : vapor pressure of the liquid nitrogen at working temperature)

Fig. 7 Change in the specific surface area (S) and specific pore volume (V) with the mass percent of dissolved structural cations R_xO_y % (R_xO_y : $Al_2O_3 + Fe_2O_3 + MgO$)

Fig. 8 Change in the pH-value of the aqueous suspension for the leached samples and red color index of the bleached oil depending on the mass percent of the dissolved structural metal oxide (R_xO_y : $Al_2O_3 + Fe_2O_3 + MgO$)

Fig. 9 Decreasing of the red color index (increasing bleaching) with respect to the mass percent of the used sample that has the maximum bleaching power (BP)

1. The clay and zeolite minerals dissolved completely with a certain amount hydrochloric acid whereas silica and feldspar minerals not affected.
2. Opal-A which is an amorphous silica formed at the end of these dissolutions.
3. Crystallinity of the dissolved minerals decreased tentatively and then degraded completely.
4. The cations dissolved in the order of Ca^{2+} , Na^+ , Mg^{2+} , $\text{Fe}^{2+,3+}$, Al^{3+} and K^+ depending on the increasing of hydrochloric acid content.
5. When HCl/CaB ratio in the leaching is 0.40; the surface area, pore volume, surface acidity, and bleaching power reach to their maxima.
6. The optimum conditions to obtain a bleaching earth with the maximum bleaching power change according to the raw bentonite, content and type of the used acid, time and temperature of the leaching.
7. Beside content and physiochemical properties of the used powder, the optimum conditions to obtain maximum bleaching change according to the kind of edible oil as well as temperature and time of the process.
8. Consequently, the results arrived in this study is not overall. Thus, the optimum bleaching parameters for each pair of bentonite and vegetable oil would be individually determined.

Acknowledgements This study was supported by Ankara University Research Fund (Project No: 17H0430010).

Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

1. Moore DM, Reynolds RC Jr (1997) X-ray diffraction and the identification and analysis of clay minerals. Oxford University Press, Oxford
2. Komadel P (2003) Chemically modified smectites. *Clay Miner* 38:127–138
3. Bergaya F, Theng BKG, Lagaly G (2006) Handbook of clay science. Elsevier, Amsterdam
4. Özgüven E, Pekdemir AD, Önal M, Sarıkaya Y (2020) Characterization of a bentonite and its permanent aqueous suspension. *J Turkish Chem Soc* 7:11–18
5. Rouquerol F, Rouquerol J, Sing KSW, Llewellyn P, Mourin G (2014) Adsorption by powders and porous solids. Elsevier, Amsterdam
6. Zhu R, Chen Q, Zhou Q, Xi Y, Zhu J, He H (2016) Adsorbent based on montmorillonite for contaminant removal water: a review. *Appl Clay Sci* 129:239–258
7. Uddin MK (2017) A review on the adsorption heavy metals by clay minerals, with special focus on the past decade. *Chem Eng J* 30:438–462
8. Ujeneza E, Njenga HN, Mbui ND, Kariuki DN (2014) Optimization of acid activation conditions for Athi River Bentonite Clay and application of the treated clay in palm oil bleaching. *IOSR J Appl Chem* 7:29–38
9. Al-Essa K (2018) Activation of Jordanian bentonite by hydrochloric acid and its potential for olive mill wastewater enhanced treatment. *J Chem-NY* 8385692:1–10
10. Komadel P (2016) Acid activated clays: materials in continuous demand. *Appl Clay Sci* 131:84–99
11. Noyan H, Önal M, Sarıkaya Y (2006) The effect of heating on the surface area, porosity and surface acidity of a bentonite. *Clay Clay Miner* 54:375–381
12. Önal M, Sarıkaya Y (2007) Thermal behavior of a bentonite. *J Therm Anal Calorim* 90:167–172
13. Önal M (2007) Swelling and cation exchange capacity relationship for the samples obtained from a bentonite by acid activation and heat treatments. *Appl Clay Sci* 37:74–80
14. Yener N, Biçer C, Önal M, Sarıkaya Y (2012) Simultaneous determination of cation exchange capacity and surface area of acid activated bentonite powders by methylene blue sorption. *Appl Surf Sci* 258:2534–2539
15. Park CW, Kim BH, Yang HM, Sea BK, Lee KW (2017) Enhanced desorption of Cs from clays by a polymeric cation-exchange agent. *J Hazard Mater* 327:127–134
16. Murray HH (2000) Traditional and new applications for kaolin, smectite, and palygorskite; a general overview. *Appl Clay Sci* 17:207–221
17. Huang Z, Li Y, Chen W, Shi J, Zhang N, Wang X, Li Z, Gao L, Zhang Y (2017) Modified bentonite adsorption of organic pollutants of dye wastewater. *Mater Chem Phys* 202:266–276
18. Awad AM, Shaikh SMR, Jalab R, Gulied MH, Nasser MS, Benamar A, Adham S (2019) Adsorption of organic pollutants by natural and modified clays: a comprehensive review. *Sep Purif Technol* 228(115719):1–39
19. Mukosa-Tebandeke IZ, Ssebuwufu PJM, Nyanzi SA, Nyakairu GW, Ntale M, Lugolobi F, Andreas S (2015) Adsorption behavior of acid-leached clays in bleaching of oil. *Am J Anal Chem* 6:495–512
20. Noyan H, Önal M, Sarıkaya Y (2007) The effect of sulphuric acid activation on the crystallinity, surface area, porosity, surface acidity, and bleaching power of a bentonite. *Food Chem* 105:156–163
21. Almeida ES, Carvalho ACB, de Souza Soares ID, Valadares LF, Mendonça ARV, Silva IJ Jr, Monteiro S (2019) Elucidating how to different types of bleaching earths widely used in vegetable oils industry remove carotenes from palm oil Equilibrium, kinetics and thermodynamics parameters. *Food Res Inter* 121:785–797
22. Chitnis SR, Sharma MM (1997) Industrial application of acid activated clays as catalysts. *React Funct Polym* 32:93–115
23. Breen C, Watson R (1998) Acid-activated organoclays: preparation, characterization and catalytic activity of poly-cation-tri-ated bentonites. *Appl Clay Sci* 12:479–494
24. De Poiva LB, Morales AR, Diaz FRV (2008) Organoclays: properties, preparations and applications. *Appl Clay Sci* 42:8–24
25. Adams JM (1987) Synthetic organic chemistry using pillared cation exchanged and acid-treated montmorillonite catalysts-a review. *Appl Clay Sci* 2:309–342
26. Çelik M, Önal M (2012) Synthesis, characterization and properties of conducting polypyrrole/Na-Montmorillonite nanocomposites. *J Thermoplast Compos* 25:505–520
27. Falares P, Lezou F, Pomonis P, Ladavas A (2006) Al- pillared acid-activated montmorillonite modified electrodes. *J Electroanal Chem* 486:156–165
28. Bayraktepe DE, Yazan Z, Önal M (2019) Sensitive and cost effective disposable composite electrode based on graphite, nano-smectite and multiwall carbon nanotubes for the simultaneous

- trace level detection of ascorbic acid and acetylsalicylic acid in pharmaceuticals. *Talanta* 203:131–139
29. Sedghamiz MA, Raeissi S, Attar F, Salami M, Mehrabi K (2019) In-situ transesterification of residual vegetable oil in spent bleaching clay with alkali catalyst using CCD-RSM design of experiment. *Fuel* 237:515–521
30. Sedghamiz MA, Attar F, Raeissi S (2019) Experimental investigation of acid regeneration of spent bleaching clay de-oiled by the in situ transesterification process at various operating conditions. *Process Saf Environ* 124:121–127
31. Bachmann SAL, Valle R de CSC, Vegini AA, Tavares LBB (2020) Determination of optimum conditions for thermal regeneration and characterization of a spent bleaching earth. *J Environ Chem Eng.* <https://doi.org/10.1016/j.jece.2019.103503>
32. Ostrum ME (1961) Separation of clay minerals from carbonate rocks by using acid. *J Sediment Petrol* 31:123–129
33. Hang PT, Brindley GW (1970) Methylene blue absorption by clay minerals. Determination of surface areas and cation exchange capacities (clay- organic studies XVIII). *Clay Clay Miner* 18:203–212
34. Rytwo G, Serban C, Nir S, Margulies L (1991) Use of methylene blue and crystal violet for determination of exchangeable cations in montmorillonite. *Clay Clay Miner* 39:551–555
35. Kahr G, Madson FT (1995) Determination of the cation exchange capacity and surface area of bentonite, illite, and kaolinite by methylene blue adsorption. *Appl Clay Sci* 9:327–336
36. Sarıkaya Y, Aybar S (1978) The adsorption of NH_3 , N_2O , and CO_2 gases on the 5A molecular sieve. *Commun Fac Sci Univ Ankara* B24:33–39
37. Mounts TL (1981) Chemical and physical effects of processing fats oils. *J Am Oil Chem Soc* 58:51A–54A
38. Omar S, Girgis B, Taha F (2003) Carbonaceous materials from seed hulls for bleaching of vegetable oils. *Food Res Int* 36:11–17
39. Ribeiro JAA, Almeida ES, Neto BAD, Abdelnur PV (2018) Identification of carotenoid isomers in crude and bleached palm oils by mass spectrometry. *Food Sci Technol* 89:631–637
40. Silva SM, Sampaio KA, Ceriani R, Verhé R, Stevens C, Greyt WD, Meirelles AJA (2014) Effect of type of bleaching earth on the final color of refined palm oil. *LWT Food Sci Technol* 59:1258–1264
41. Chipera SJ, Bish DL (2001) Baseline studies of the clay minerals society source clays: powder X-ray diffraction analyses. *Clay Clay Miner* 49:398–409
42. Kahraman S, Önal M, Sarıkaya Y (2005) Characterization of silica polymorphs in kaolins by X-ray diffraction before and after phosphoric acid digestion and thermal treatment. *Anal Chim Acta* 552:201–206
43. Önal M, Kahraman S, Sarıkaya Y (2007) Differentiation of α - cristobalite from opals in bentonites from Turkey. *Appl Clay Sci* 35:25–30
44. Önal M, Sarıkaya Y (2007) The effect of heat treatment on the paracrystallinity of an opal- CT found in a bentonite. *J Non Cryst Solids* 353:4195–4198
45. Brunauer S, Emmett PH, Teller E (1938) Adsorption of gases in multimolecular layers. *J Am Chem Soc* 60:308–319

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.