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Application of MOFs and natural clays for removal of MCPD and GEs from edible oils

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SUMMARY: The aim of this study was to investigate the removal of 3-monochloropropane-1,2-diol (3-MCPD) and glycidyl esters (GEs) from edible oils by using Metal Organic Frameworks (MOF) and natural clays. First, the model oil was treated with adsorbents and titanium (IV) butoxide-terephthalate MOF (Ti-MOF) and kaolin were selected as the best performing MOF along with natural clay, respectively, for the removal of 3-MCPD and GEs. The effects of treatment conditions were also investigated, 6.0% adsorbent level, 120 min treatment time and 95 ºC temperature were determined to be the best treatment parameters. Finally, palm oil samples were treated with Ti-MOF and kaolin under the selected conditions and removal of 3-MCPD and GEs was obtained at up to 27% and 58%, respectively. In conclusion, MOFs and natural clays showed good potential for the removal of 3-MCPD and GEs, and the efficiency of the treatment can be improved by modifying the adsorbents.

KEYWORDS: *3-MCPD; Glycidyl esters; MOFs; Natural clays; Palm oil*

RESUMEN: ***Aplicación de EOMs y arcillas naturales para la eliminación de MCPD y EG de aceites comestibles.*** El objetivo de este estudio fue investigar la eliminación de 3-monocloropropano-1,2-diol (3-MCPD) y ésteres de glicidilo (EG) de aceites comestibles mediante el uso de estructuras orgánicas metálicas (EOMs) y arcillas naturales. El aceite modelo se trató en primer lugar con adsorbentes, se seleccionaron titanium (IV) tereftalato de butóxido (Ti-EOM) y caolín como EOM y arcilla natural, respectivamente, para el mejor rendimiento en la eliminación de 3-MCPD y EG. También se investigaron los efectos de las condiciones de tratamiento y se seleccionaron como los mejores parámetros un nivel de adsorbente de 6,0%, un tiempo de tratamiento de 120 min y temperatura de tratamiento de 95ºC. Finalmente, las muestras de aceite de palma se trataron con Ti-EOM y caolín en las condiciones seleccionadas y se obtuvo una eliminación de 3-MCPD y EG de hasta 27% y 58%, respectivamente. En conclusión, los EOMs y las arcillas naturales mostraron un buen potencial para la eliminación de 3-MCPD y EG, y la eficiencia del tratamiento se puede mejorar modificando los adsorbentes.

PALABRAS CLAVE: *3-MCPD; Aceite de palma; Arcillas naturales; EOM; Ésteres de glicidilo*

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1. INTRODUCTION

The fatty acid esters of glycidol (GEs) and 3-monochloropropane-1,2-diol (3-MCPD) are food-processing contaminants. 3-MCPD, which is a type of chloropropanol, is formed as a result of the interaction of acylglycerol with chloride ions at high temperatures (Arisseto *et al*., 2018). In the review of Rahn and Yaylayan (2011), four proposed mechanisms for 3-MCPD ester formation are mentioned: direct nucleophilic attack on glycerol carbon carrying an ester group, direct nucleophilic attack on glycerol carbon carrying a hydroxyl group, the formation of acyloxonium ion and the formation of an epoxide ring. GEs are generally formed from monoacylglycerols and diacylglycerols at high temperatures without chloride (Cheng *et al*., 2017a). In the review of Cheng *et al*. (2017a), four mechanisms for GE formation are mentioned: common reactive intermediate formation by the deacidification of 1,2-diacylglycerols, common reactive intermediate formation by the dehydration of monoacylglycerols, direct intramolecular rearrangement followed by the elimination of fatty acids for diacylglycerols, direct intramolecular rearrangement followed by the elimination of water for 1-monoacylglycerols. Generally, these contaminants are formed during the refining of oils, during the deodorization step (Larsen, 2009). They are present in all refined vegetable oils according to the surveys carried out by MacMahon *et al*. (2013) and Custodio-Mendoza *et al.* (2019). These contaminants have also been detected in oil-based foods such as margarine, potato chips, bread, crackers, infant formulas, breakfast cereals, coffee creamer, roasted malt and cooked meats. The reported levels of these contaminants in foodstuffs are generally much lower than the levels in refined vegetable oils. Therefore, studies mostly focus on refined vegetable oils, especially palm oil (Larsen, 2009).

Studies have shown that free 3-MCPD and glycidol, which are the free forms of 3-MCPD esters and GEs, can be harmful to human health, and even if they are present in ester form, they can be hydrolyzed to their free forms in the gastrointestinal tract. According to the International Agency for Research on Cancer (IARC), free 3-MCPD is classified as a possible human carcinogen (group 2B), while glycidol is classified as probably carcinogenic to humans (group 2A) (IARC, 2000; IARC, 2013; Arisseto *et al*., 2018). JECFA has established a provisional maximum tolerable daily intake of 4 μg/kg body weight for 3-MCPD and 3-MCPD esters singly or in combination (JECFA, 2016). According to Commission Regulations (EU) (2020), the maximum level of GEs should be 1000 μg/kg in vegetable oils and fats for general uses and 500 μg/kg in vegetable oils and fats for infant formulas. The maximum level of 3-MCPD should be 1250 μg/kg in vegetable oils and fats for general uses, 2500 μg/kg in pomace olive oils for general uses and 750 μg/kg in vegetable oils and fats for infant formulas.

When the health effects of 3-MCPD and glycidyl esters and their levels in oils are considered, the removal of these contaminants or the prevention of their formation becomes an important issue. The main factors affecting 3-MCPD and GEs formation in oils can be listed as follows: the presence of glycerol, mono-, di- and tri-acylglycerols, the presence of chloride ions (originating from water, steam, bleaching earth or other materials used in refining, natural organochloride and pesticides), bleaching earths activated by acids (especially HCl), and the time and temperature of thermal treatments. Considering these factors, three main approaches are recommended to reduce the levels of 3-MCPD and GEs: the removal of the precursors, modifications to oil processing parameters, and the removal of contaminants (Larsen, 2009; Matthaus and Pudel, 2013; Cheng *et al*., 2017a; Arisseto *et al*., 2018). Some methods studied in the literature to mitigate 3-MCPD and GEs levels in foodstuffs are as follows: the use of natural and synthetic antioxidants (Wong *et al*., 2019), the removal of precursors and reorganization/optimization of the refining process (Matthäus *et al*., 2011; Ramli *et al*., 2011; Zulkurnain *et al*., 2012; Zulkurnain *et al*., 2013; Li *et al*., 2016), the enzymatic removal of contaminants (Bornscheuer and Hesseler, 2010), the removal of contaminants by adsorbent materials (Strijowski *et al*., 2011; Shimizu *et al*., 2012) and the removal of contaminants by oil modifications (Kyselka *et al*., 2018).

Metal–organic frameworks (MOF) are synthesized polymers constructed through chemical reactions between metal-containing units and organic linker molecules to create open crystalline structures with permanent porosity, dynamic flexibility and diverse morphologies. They have been used for gas adsorption and storage, separation, sensors, drug de-

livery, and selective adsorption applications (Stock and Biswas, 2012; Furukawa, *et al*., 2013; Ma *et al*., 2014). To the best of our knowledge, there is only one study about MOF application for the removal of 3-MCPD and related substances from oils (Ahn *et al*., 2020). In this study, a series of Fe-MIL-88s with different ligand types, which were modified by carboxylation and deprotonation processes, were synthesized and used for the removal of 3-MCPD and glycidol. They found that, among different types of this MOF, Fe-MIL-88 BDC showed the most efficient adsorption performance. The present study differs from the study of Ahn *et al*. (2020) in that seven different MOFs and four different natural clays were used for the same purpose. Hence, this study expands the knowledge concerning this subject.

The main objective of this study was to evaluate the usage of MOFs as new and potential adsorbent materials in the removal of 3-MCPD and GEs from edible oils. For this purpose, seven different MOFs and four different natural clays were used and their structural properties were determined. After the treatments, the remaining 3-MCPD and GE contents in the model oil samples were measured and the efficiencies of the adsorbents were compared. Some process parameters like level of adsorbent addition, temperature and time were also studied with the two best-performing adsorbents in order to determine the optimum conditions for the adsorption treatments. Finally, the best-performing adsorbents were used under the best treatment conditions for the removal of 3-MCPD and GEs from commercial palm oil, which is a natural source of these contaminants.

2. MATERIALS AND METHODS

2.1. Materials

The seven different MOFs used in this study were synthesized and characterized in our laboratory. These MOFs were as follows: titanium (IV) butoxide-terephthalate MOF (Ti-MOF), synthesized according to Vlasova *et al*., (2016); gamma-cyclodextrine-potassium hydroxide MOF (γ-CD-MOF), synthesized by the method described in Moussa *et al*., (2016); chrome nitrate-terephthalate MOF (Cr-MOF), synthesized by the method of Li *et al*. (2015); aluminum chlorate-terephthalate MOF (Al-MOF), synthesized by the method of Ma *et al*. (2014); zinc nitrate-2,5-furandicarboxylicacid MOF (Zn-MOF), synthesized according to Bu *et al*. (2012); magnesium-MOF (Mg-MOF), synthesized by the method described in Spanopoulos *et al*., (2015); and zinc-2-methylimidazole zeolitic-type MOF (ZIF-8-MOF), synthesized according to Park *et al*. (2006). After synthesis, these MOFs were placed into amber-colored glasses and stored at room temperature throughout the study. The abbreviated MOF names given in parentheses are used throughout the paper.

The commercial pre-activated bleaching earth (CBE) was provided by the Trakya Birlik Oil Processing Factory (Tekirdağ, Turkey); natural zeolite and natural kaolin clay were provided by the Türkzeolit Mining Ind. and Trade. Inc. (Istanbul, Turkey); and natural sepiolite was provided Anadolu Industrial Mine Inc. (Istanbul, Turkey). Extra virgin olive oil and commercial palm oils were bought from Komili Oil (Balıkesir, Turkey) and Besler Oil Factory (Istanbul, Turkey), respectively. Glycidyl palmitate (99.1%, High Purity Compounds, Cunnersdorf, Germany), glycidyl stearate (96.5%, High Purity Compounds, Cunnersdorf, Germany) and 3-MCPD (98%, Sigma- Aldrich, St. Louis, USA) were purchased. All chemicals, solvents, and standards used in the analyses were of analytical or chromatographic grade and purchased from Sigma (St. Louis, MO, USA), Merck Co. (Darmstadt, Germany) and local stores.

2.2. Characterization of the adsorbents

The surface areas and pore properties of the adsorbents were determined using a Quantachrome Nova 4000E instrument (Quantachrome Instruments, Boynton Beach, FL, USA) with nitrogen gas and the Brunauer-Emmett-Teller (BET) and Langmuir models (Moussa *et al*., 2016).

The morphologies of the adsorbents were determined with a JSM-7100F (JEOL, Japan) scanning electron microscope (SEM). First of all, samples were placed onto a specimen holder carbon band with double-sided scotch tape. Then, they were coated with Au-Pd (80–20%) under vacuum (0.8 mbar) and 10 mA voltage using a Quorum coating device. Finally, samples were examined under accelerated voltage of 15 kV and 150–15,000-fold magnifications (Peerajit *et al*., 2012).

The X-ray diffraction (XRD) patterns of the samples were determined using a PANalytical Empyrean

model (Netherland) X-ray diffractometer under 40 kV and 40 mA CuKa (λ = 0.1546 nm), within the range of 4-40º at a scanning rate of 0.02-0.6 (sec^{-1}).

2.3. Preparation of the model oil

First, active silica gel was added to extra virgin olive oil (EVOO) at a ratio of 0.5:1 (w/w), stirred at 50 ºC for 3 hours, and filtered with filter paper (Whatman no. 1 filter paper, 11 µ pore, 125 mm diameter) for the removal of naturally-present impurities from the EVOO. Then, 3-MCPD, glycidyl palmitate and glycidyl stearate were added to this oil at a ratio of 125 mg/kg, 72 mg/kg and 72 mg/kg, respectively. Finally, this model oil was placed into amber-colored glass bottles and stored in a cool, dark place for the duration of the study.

2.4. Adsorbent treatments of the model oil

15 g of model oil was weighed for each treatment, and each of the adsorbents was added into the oils at a ratio of 3% (w/w). They were then shaken in an incubator (Certomat IS, Sartorius Stedium Biotech, Germany) at 95 ºC for 1 h. Finally, the treated oils were filtered through a Whatman no. 1 filter paper (11 µ pore, 125 mm diameter), placed into amber-colored glass bottles, and stored in a refrigerator in the dark for the duration of the study.

2.5. 3-MPCD and GEs analyses of the treated oils

The amounts of 3-MPCD and GEs in the samples were measured according to the AOCS Cd 29c-13 Method (AOCS, 2017). The analysis was carried out with a GC-MS (GC/MS-QP2010, Shimadzu Co., Nishinokyo, Japan) equipped with a Rxi-5MS column (30m x 0.25mm ID x 0.25µm film thickness, Restek Co.). The working conditions of the GC were as follows: splitless, 2 µl injection volume, 0.83 ml/min flow rate, 250 °C inlet temperature and helium as carrier gas. The oven temperature program was as follows: held at 100 °C for 1 min, increased to 160 °C (20 °C/min) and held at that temperature for 1 min, increased to 180 °C (4 °C/min), then to 330 °C (30 °C/min) and held at that temperature for 4.70 min. The working conditions of the MS detector were as follows: 200 °C ion source temperature, 280 °C interface temperature, 5 min solvent-cutoff-time. 3-MCPD-d5 was used as internal standard.

2.6. Effects of the process parameters on the adsorption treatment

As a result of the analyses, Ti-MOF and kaolin were selected as the best MOF and natural clay for removing 3-MPCD and GEs, respectively. With these two adsorbents, the effects of adsorbent addition level (0.5%, 1.5%, 3.0%, 6.0%), treatment temperature (25 °C, 50 °C, 95 °C, 150 °C) and time (15, 45, 60, 120 min) were evaluated under the same treatment conditions described in the adsorbent treatments of the model oil section. After treatment, the 3-MPCD and GE contents in the treated and control samples were measured and the best process parameters were determined.

2.7. Adsorbent treatments of commercial palm oils

Finally, Ti-MOF and kaolin were used under the best treatment conditions (6.0%, 95 °C, 120 min), for the removal of 3-MCPD and GEs from commercial palm oil samples (RBD: Refined, Bleached and Deodorized; DEO: Deodorized), which are natural sources of these contaminants. After the treatments, the 3-MPCD and GE contents in the treated and control samples were measured.

2.8. Statistical analysis

The whole study was repeated twice. Each analysis for each replicate was done in triplicate. The collected data were analyzed using one-way ANOVA and treatment groups were compared with Tukey's tests. Minitab Ver. 16.1.1 (Minitab, 2010) and SPSS (SPSS, 1994) package software programs were used for statistical analyses. There was a minimum 95% level of confidence in this study.

3. RESULTS AND DISCUSSION

3.1. Structural properties of the adsorbents

The surface areas and pore properties of MOFs and natural clays are shown in Table 1. Surface area and pore volume are important parameters which affect the treatment efficiency of adsorbents. Clearly, there is a great variation among the adsorbents in terms of surface area values. The highest surface area was measured for Al-MOF (1415.53 m^2/g), while the lowest value was for γ-CD-MOF (4.55 m^2/g). There is also a great variation among the adsorbents in terms of pore vol-

Table 1. The surface areas and pore properties of MOFs and natural clays

	Surface Area (m^2/g)	Pore Volume (cm^3/g)	Pore Radius (Å)
Ti-MOF	226.65 ± 3.21^{e}	0.27 ± 0.01^{h}	44.45 ± 0.89^{f}
γ-CD-MOF	4.55 ± 0.07^{k}	1.24 ± 0.00^{a}	707.63 ± 1.55^{a}
Cr-MOF	717.45 ± 15.90^{c}	0.77 ± 0.00^{d}	33.95 ± 0.87^{g}
Al-MOF	1415.53 ± 57.07^{a}	0.46 ± 0.01^{f}	19.37 ± 0.40^{i}
Zn-MOF	19.70 ± 2.33^{i}	1.05 ± 0.01^{b}	203.20 ± 0.94^{b}
Mg-MOF	66.50 ± 1.89^{h}	0.65 ± 0.00^{e}	96.85 ± 0.08^{d}
ZIF-8-MOF	1020.25 ± 48.84^{b}	0.55 ± 0.01^{f}	18.42 ± 0.01^{i}
Sepiolite	314.57 ± 13.90^{d}	0.91 ± 0.01^{c}	114.67 ± 0.05^{c}
Zeolite	181.25 ± 9.82^{f}	0.24 ± 0.00^{h}	62.05 ± 2.23^{e}
Kaolin	9.625 ± 1.44^{j}	0.03 ± 0.00^{i}	20.29 ± 0.01^{h}
CBE	143.20 ± 7.32^{g}	0.36 ± 0.01^{g}	99.89 ± 1.47^{d}

*Results are expressed as mean ± SEM. Different superscript letters in the same columns indicate statistically significant differences. The whole study was replicated two times and each analysis for each replicate was done in triplicate (n = 6). The data were analyzed by using one-way ANOVA and groups were compared with Tukey's tests ($P \leq 0.05$). Ti-MOF, titanium (IV) butoxide-terephthalate MOF; γ-CD-MOF, gamma-cyclodextrine-potassium hydroxide MOF; Cr-MOF, chrome nitrate-terephthalate MOF; Al-MOF, aluminum chlorate-terephthalate MOF; Zn-MOF, zinc nitrate-2,5-furandicarboxylicacid MOF; Mg-MOF, magnesium-MOF; ZIF-8-MOF, zinc-2-methylimidazole zeolytic type MOF; CBE commercial bleaching earth.

umes. The highest pore volume was measured for γ-CD-MOF (1.24 cm^3/g), while the lowest value was for kaolin (0.03 cm^3/g). As a result, it can be said that γ-CD-MOF and kaolin seem insufficient for utilization as adsorbents because of their low surface area values. In one study, the surface areas of Zn-MOF, Al-MOF and Ti-MOF were found to be 380, 1196 and 1310 m^2/g and the pore volumes were measured at 0.29, 0.76 and 0.97 cm^3/g, respectively (Vlasova *et al*., 2016). In the study of Ahn *et al*. (2020), the surface areas of different versions of Fe-MIL-88 MOF varied between 2.58 and 13.74 m^2/g. In a review, the structural properties of different MOF types were listed and it was observed that the surface areas varied between 46 and 2222 m^2/g (Du *et al*., 2018). Obviously, there are significant differences among MOF types in terms of surface areas and pore properties. These differences are even observed in the same MOF types synthesized in different studies. Overall, it was clear that the surface areas and pore properties of adsorbents depend on ligand type, synthesis conditions and the modifications applied.

The SEM images of MOFs and natural clays are presented in Figure 1. Obviously, the morphological properties of the adsorbents are different from each other. Ti-MOF has clustered spheres, Al-MOF has needle-like crystals, Zn-MOF has cubic crystals and ZIF-8-MOF has hexagonal crystals. Besides these certain geometric shapes, there are also amorphous bulk structures. In one study, the morphology of Ti-

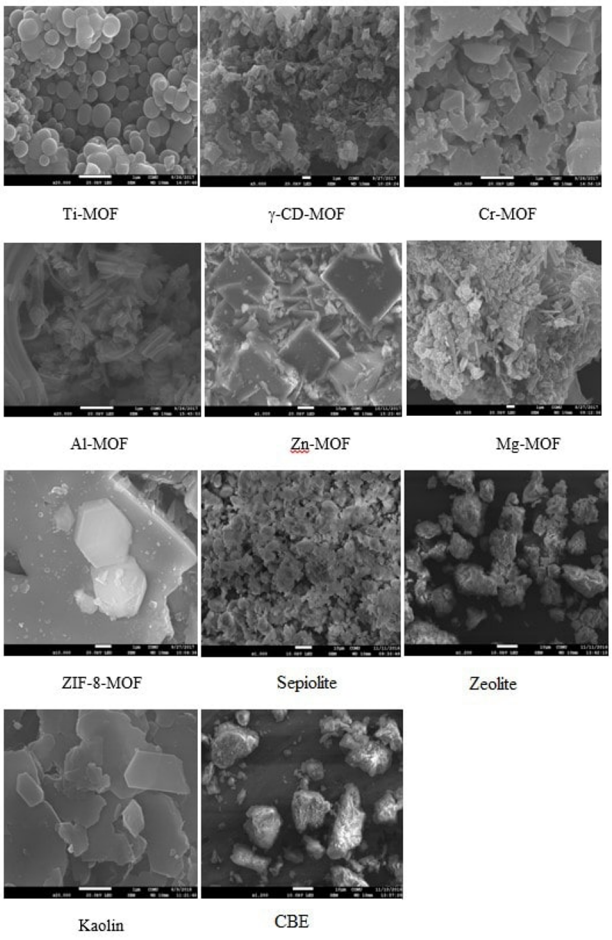

Figure 1. The scanning electron microscopy (SEM) images of MOFs and natural clays. Ti-MOF, titanium (IV) butoxide-terephthalate MOF; γ-CD-MOF, gamma-cyclodextrine-potassium hydroxide MOF; Cr-MOF, chrome nitrate-terephthalate MOF; Al-MOF, aluminum chlorate-terephthalate MOF; Zn-MOF, zinc nitrate-2,5-furandicarboxylicacid MOF; Mg-MOF, magnesium-MOF; ZIF-8-MOF, zinc-2-methylimidazole zeolytic type MOF; CBE commercial bleaching earth.

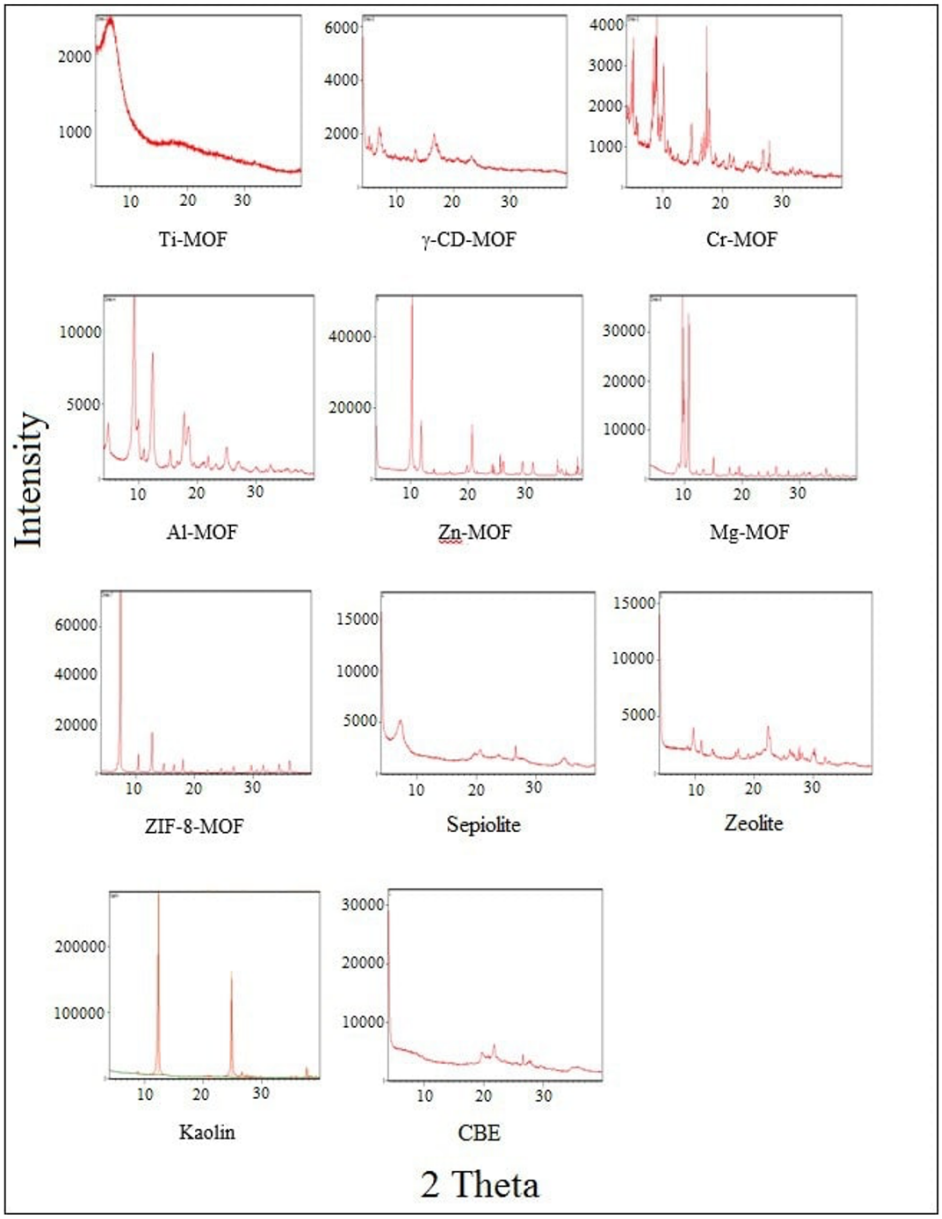

Figure 2. The X-ray diffraction (XRD) patterns of MOFs and natural clays. Ti-MOF, titanium (IV) butoxide-terephthalate MOF; γ-CD-MOF, gamma-cyclodextrine-potassium hydroxide MOF; Cr-MOF, chrome nitrate-terephthalate MOF; Al-MOF, aluminum chlorate-terephthalate MOF; Zn-MOF, zinc nitrate-2,5-furandicarboxylicacid MOF; Mg-MOF, magnesium-MOF; ZIF-8-MOF, zinc-2-methylimidazole zeolytic type MOF; CBE commercial bleaching earth.

MOF was determined as ovoidal or flat-cubed with round corners, like in our study (Xiao *et al*., 2019). In the study of Fallah and Sohrabnezhad (2019), the SEM image of Cr-MOF was similar to the one in this study. In the study of Lee *et al*., (2015) MOFs with different morphologies from amorphous spheres to crystalline hexagonal rods were presented. Naturally, there is a great variation among the adsorbents in terms of morphological properties.

X-ray diffraction (XRD) patterns of the adsorbents are presented in Figure 2. This analysis provides information about the crystal structures of solids. In the study of Vlasova *et al*. (2016), the XRD patterns of Al, Zn, and Ti-MOF were obtained. A major peak was observed at about 4-6° for Ti-MOF and the same peak was also detected in this study. In addition to this peak, there were two peaks at around 11 and 18° in the study of Vlasova *et al*.

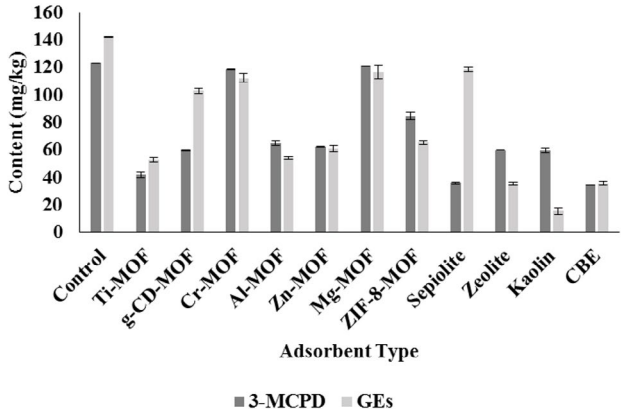

FIGURE 3. 3-MCPD and GE contents in the control and treated model oil samples. Results are expressed as mean ± SEM. Error bars represent standard error of mean. The whole study was repeated twice and each analysis for each replicate was done in triplicate (n = 6). The data were analyzed using one-way ANOVA and the groups were compared with Tukey's tests ($P \leq 0.05$). 3-MCPD, 3-monochloropropane-1,2-diol; GEs, glycidyl esters; Ti-MOF, titanium (IV) butoxide-terephthalate MOF; γ-CD-MOF, gamma-cyclodextrine-potassium hydroxide MOF; Cr-MOF, chrome nitrate-terephthalate MOF; Al-MOF, aluminum chlorate-terephthalate MOF; Zn-MOF, zinc nitrate-2,5-furandicarboxylicacid MOF; Mg-MOF, magnesium-MOF; ZIF-8-MOF, zinc-2-methylimidazole zeolytic type MOF; CBE commercial bleaching earth.

(2016), but not detected in this study. The XRD patterns of Zn-MOF and Al-MOF in this study were also similar to that study. In another study, the XRD patterns of γ-CD-MOF were presented (Moussa *et al*., 2016). Although there were some differences, similar peaks were observed for γ-CD-MOF in our study. According to Li *et al*., (2015), Cr-MOF showed peaks at around 3°, 5°, 6°, 9°, 10° and 17° and similar peaks were also observed in our study. The XRD patterns for ZIF-8-MOF were presented in the study of Park *et al*. (2006) and it was very similar to this study. Although there are some slight differences, the results generally concur with the literature. The determined peaks in the samples indicate that they all included certain types of crystal structures. In addition, the XRD patterns of natural clays indicate the presence of some amorphous structure besides crystallinity.

3.2. 3-MCPD and GE contents in the treated model oil samples

The 3-MCPD and GEs contents of the samples after the adsorbent treatments, and the removal, based on the calculation over the control sample, are presented in Figure 3. In the control (not treated with any adsorbent) oil sample, 3-MCPD and GE contents were determined as 123.51 mg/kg and 142.44 mg/kg, respectively. These contents were lower than the added amounts, probably because of losses during operation or the level of purity of the added compounds. These differences do not matter because the removal was calculated over these control values. Among MOFs, the highest removal was observed for Ti-MOF (65.97% and 62.95%) for 3-MCPD and GEs. Among natural clays, CBE yielded the lowest remaining 3-MCPD (71.86% reduction), and kaolin yielded the lowest remaining GEs (89.09% reduction). Obviously, there is a variation among the adsorbents in terms of removal. Although the mechanism of the interaction between adsorbent and 3-MCPD/GEs is not investigated in this study, it is thought that selective adsorption of 3-MCPD and GEs from oils mostly depends on the presence of high affinity groups in adsorbents and structural properties (pore size, specific volume, surface area etc.).

In another study, activated bleaching earth was used to remove glycidyl esters from diacylglycerol oils and it was observed that glycidyl esters in varying amounts were reduced to the limit of quantification value (0.1 mg/kg) (Shimizu *et al*., 2012). In addition, a glycerol diolate model oil system containing glycidyl palmitate was used to investigate the elimination mechanism and it was determined that the elimination of glycidyl esters by activated bleaching earth occurs by transformation rather than adsorption. In another study, acid-washed oil-palm-wood-based activated carbon was investigated for the removal of glycidyl palmitate from a hexadecane solution, as a model oil system, and it was observed that removal can reach up to 95% depending on process conditions (Cheng *et al*., 2017b). In a study about MOF treatment, carboxylated and deprotonated Fe-MIL-88s with different ligand types were used for the removal of 3-MCPD and glycidol from model media (isopropyl alcohol/toluene, 1:1, w/w) and removal reached up to 95%, depending on process conditions and MOF type (Ahn *et al*., 2020). Generally, higher removal was achieved in these studies compared to the present study. In the study of Ahn *et al*. (2020), the adsorption mechanism of 3-MCPD and glycidol was investigated and they found that carboxylated Fe-MIL-88s had higher adsorption capacity for both 3-MCPD and

glycidol compared to non-functionalized MOFs, probably due to the esterification of 3-MCPD and glycidol with deprotonated carboxyl groups. It is obvious that in addition to the structural properties of the adsorbents, the functional groups on the surface were also effective. This also explains why the kaolin and Ti-MOF used in this study were more effective despite having a lower surface area than some other absorbents.

The MOFs and natural clays used in our study showed good potential for the removal of 3-MCPD and GEs, and the efficiency of the treatment can be improved by adding some functional groups onto the surface of the adsorbents and optimizing the process conditions.

3.3. Effects of the treatment parameters

Ti-MOF and kaolin were selected as the best performing adsorbents among MOFs and natural clays, respectively, to investigate the effects of adsorbent addition levels, treatment temperatures and treatment times.

Figure 4 presents the effect of the level of adsorbent addition (0.5%, 1.5%, 3.0%, 6.0%) on the removal of 3-MCPD and GEs with the two selected adsorbents at 95 °C treatment temperature and 60 min treatment time. As the addition level increased, the removal of 3-MCPD and GEs increased for both adsorbents. Therefore, higher adsorbent addition levels could be used for more efficient 3-MCPD and GEs removal, but the cost of the adsorbent must also be considered.

The effect of treatment time (15, 45, 60 and 120 min) on the removal of 3-MCPD and GEs at 95 °C treatment temperature and 3.0% adsorbent addition level is shown in Figure 5. Clearly, the removal of 3-MCPD and GEs increased for both adsorbents with the increase in treatment time. Hence, the effectiveness of the treatment can be improved by increasing treatment time but the processing price should also be considered.

Figure 6 shows the effect of treatment temperature (25 °C, 50 °C, 95 °C, 150 °C) on the removal

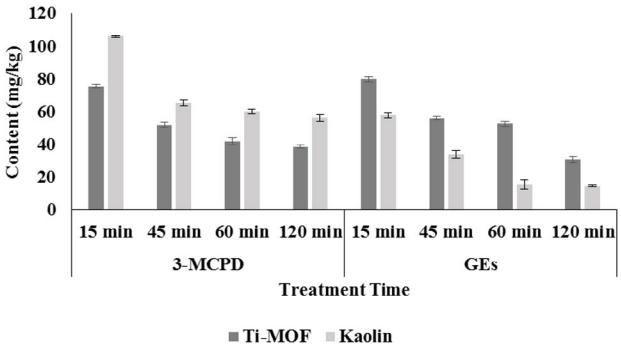

Figure 5. The effect of treatment time on the removal of 3-MCPD and GEs. Results are expressed as mean ± SEM. Error bars represent standard error of mean. The whole study was repeated twice and each analysis for each replicate was done in triplicate (n = 6). The data were analyzed using one-way ANOVA and groups were compared with Tukey's tests ($P \leq 0.05$). 3-MCPD, 3-monochloropropane-1,2-diol; GEs, glycidyl esters; Ti-MOF, titanium (IV) butoxide-terephthalate MOF.

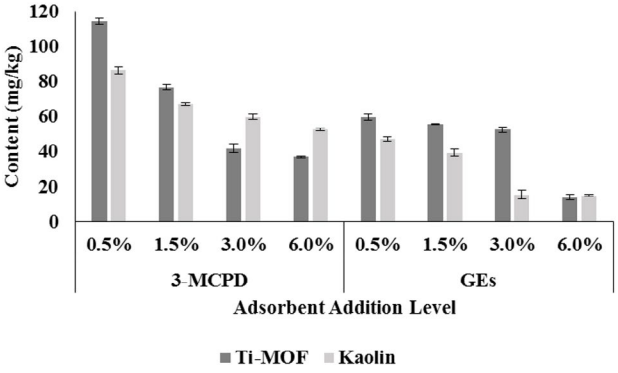

Figure 4. The effect of the level of adsorbent addition on the removal of 3-MCPD and GEs. Results are expressed as mean ± SEM. Error bars represent standard error of mean. The whole study was repeated twice and each analysis for each replicate was done in triplicate (n = 6). The data were analyzed using one-way ANOVA and groups were compared with Tukey's tests ($P \leq 0.05$). 3-MCPD, 3-monochloropropane-1,2-diol; GEs, glycidyl esters; Ti-MOF, titanium (IV) butoxide-terephthalate MOF.

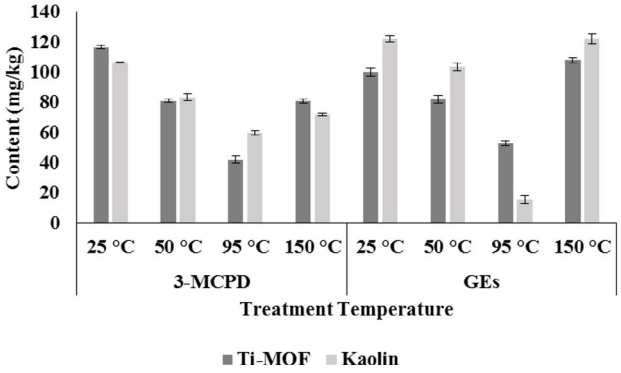

Figure 6. The effect of treatment temperature on the removal of 3-MCPD and GEs. Results are expressed as mean ± SEM. Error bars represent standard error of mean. The whole study was repeated twice and each analysis for each replicate was done in triplicate (n = 6). The data were analyzed using one-way ANOVA and groups were compared with Tukey's tests ($P \leq 0.05$). 3-MCPD, 3-monochloropropane-1,2-diol; GEs, glycidyl esters; Ti-MOF, titanium (IV) butoxide-terephthalate MOF.

of 3-MCPD and GEs with 3.0% adsorbent addition level and 60 min treatment time. The highest removal was obtained at 95 °C and it was observed that the removal decreased at lower and higher treatment temperatures. It is thought that at lower temperatures, the solubilities of 3-MCPD and GEs were not enough to penetrate into the adsorbents or kinetic energy was not enough for adsorption; while at higher temperatures, adsorbent affinity decreased or adsorbed contaminants dissolved back into the oil with increasing solubility and kinetic energy. As a result, 6.0% adsorbent level, 95 °C treatment temperature and 120 min treatment time were selected as the best treatment conditions for Ti-MOF and kaolin.

In one study, inorganic adsorbent materials were used to remove 3-MCPD esters and related substances from palm oil and the effects of process parameters on the efficiency of the treatment were investigated with the two most promising adsorbent materials (Strijowski *et al*., 2011). It was determined that as adsorbent level increased, the removal of the contaminants increased for both adsorbents. It was also observed that increasing treatment temperature and time improved the efficiency of synthetic magnesium silicate, while calcinated zeolite was not affected by these parameters. In another study, carboxylated and deprotonated Fe-MIL-88s with different ligand types were used for the removal of 3-MCPD and glycidol from model media (isopropyl alcohol/toluene, 1:1, w/w) (Ahn *et al*., 2020). It was observed that the removal of 3-MCPD and glycidol increased as adsorbent level, treatment temperature and time increased. Although there are some slight differences, the results generally concur with the literature.

3.4. Removal of 3-MCPD and GEs from palm oil

RBD and DEO palm oils were treated with Ti-MOF and kaolin for the removal of 3-MCPD and GEs, and the results are presented in Figure 7. Clearly, there are no significant differences in terms of removal between Ti-MOF and kaolin for both RBD and DEO palm oils. In RBD palm oil, the removal of 3-MCPD and GEs was measured at 26 and 56% for Ti-MOF and 28 and 58% for kaolin, respectively. In DEO palm oil, the levels of 3-MCPD and GEs were reduced by 26 and 56% with Ti-MOF and 25 and 56% with kaolin, respectively. It is obvious that these values are lower than the removal in the model oil system but this is a quite expected result because commercial palm oil is a more complex system than model oil.

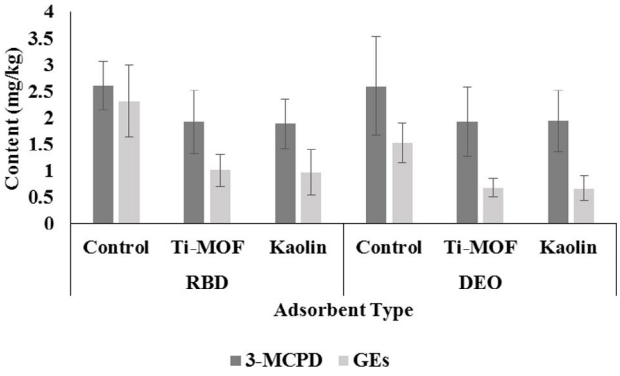

FIGURE 7. 3-MCPD and GEs contents in the control and treated palm oil samples. Results are expressed as mean ± SEM. Error bars represent standard error of mean. The whole study was repeated twice and each analysis for each replicate was done in triplicate (n = 6). The data were analyzed by using one-way ANOVA and groups were compared with Tukey's tests ($P \leq 0.05$). 3-MCPD, 3-monochloropropane-1,2-diol; GEs, glycidyl esters; Ti-MOF, titanium (IV) butoxide-terephthalate MOF; RBD, refined, bleached and deodorized; DEO, deodorized.

In one study, nine different commercially-available inorganic adsorbent materials were investigated for the removal of 3-MCPD esters and related substances from palm oil (Strijowski *et al*., 2011). Among all adsorbents, calcinated zeolite and the silicon calcium silicate were selected as the most promising adsorbents whose removal reached up to 40%. In another study, the carboxylated and deprotonated form of Fe-MIL-88-BDC, which is a type of MOF, was used for the removal of 3-MCPD and glycidyl ester from refined palm oil and both of these contaminants were reduced by 90% (Ahn *et al*., 2020). It is thought that the efficiency of the treatment in our study should be improved by modifying the adsorbents.

4. CONCLUSIONS

In this study, selected MOFs and natural clays were evaluated for the removal of 3-MCPD and GEs from edible oils. First, the structural properties and morphologies of the adsorbents were determined. Then, the 3-MCPD and GE removal capacities of the adsorbents were investigated using a model oil, and Ti-MOF and kaolin were selected as the best performing MOF and natural clay, respectively. The effects of treatment conditions on treatment efficiency were also analyzed and 6.0% adsorbent level, 95 °C treatment temperature and 120 min treatment time

were selected as the best treatment conditions. Furthermore, palm oils were treated with Ti-MOF and kaolin at selected treatment conditions and removal of about 25 and 55% were achieved for 3-MCPD and GEs, respectively. Overall, this study shows that MOFs and natural clays have good potential for the removal of 3-MCPD and GEs from edible oils, and for further studies, adsorbent modification is recommended in order to improve the efficiency of the treatment. Especially synthesis chemists may pay attention to adding specific ligands to the adsorbents, which have high affinity for chloride compounds to selectively remove those process contaminants from edible oils.

5. ACKNOWLEDGMENTS

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