Food Chemistry 190 (2016) 103–109

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Application of metal–organic frameworks for purification of vegetable oils

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ARTICLE INFO

Article history:
Received 18 November 2014
Received in revised form 7 May 2015
Accepted 18 May 2015
Available online 18 May 2015

Keywords:
Metal–organic framework
Vegetable oil
Adsorption
Acid value
Peroxide value

ABSTRACT

Reported here is the synthesis of aluminum-, zinc- and titanium-containing metal–organic frameworks based on terephthalic acid and an investigation on the possibility of using these compounds as adsorbents for the purification of unrefined vegetable oils. It is found that aluminum-, zinc- and titanium-containing metal–organic frameworks improve the physicochemical properties of unrefined vegetable oils (more pleasant taste and odor) due to the binding of free fatty acids and peroxide compounds. It is established that the synthesized materials are more effective in these respects as compared with traditional adsorbents. An adsorption mechanism of free fatty acids and peroxides is proposed. Last but not least, the used MOF can be easily recycled at least five times, via solvent washing.

1. Introduction

Production of vegetable oils is among the leading industries in the world of agribusiness. One of the current tasks of the oil industry is to increase the quality and competitiveness of vegetable oils. Natural vegetable oils often do not meet modern requirements for food products, due to the high content of impurities (pigments, waxes, free fatty acids, sterols, etc.) (Gunstone, 2011; O' Brien, 2007). High levels of free fatty acids (FFA) worsen the taste and the odor of the vegetable oil, thereby reducing the storage life of the product. Vegetable oils are oxidized to form peroxides and hydroperoxides in the presence of oxygen/air and direct sunlight – causing spoilage of the product and giving it a rancid taste (O' Brien, 2007).

Traditional technologies for extracting impurities from vegetable oils, called refining, include the successive stages of chemical treatment of oils by acidic and alkaline agents (usually, phosphoric acid and sodium hydroxide), followed by adsorption, deodorization, and freezing to precipitate waxes (Gunstone, 2011). Furthermore, it includes the stage of phase separation by filtration (Gunstone, 2011). It was established (Prokofev, Razgovorov, Gordina, & Zakharov, 2011) that the difficult and time-consuming process can be simplified by the use of selected mineral sorbents such as low-cost clays and zeolites (Bulut & Yilmaz, 2010; Clowutimon, Kitchaiya, & Assawasaengrat, 2011; Prokofev & Razgovorov, 2010). However, such sorbents have low specific surface area (100–500 m^2/g) and unstable chemical composition (Ogata et al., 2013) Therefore, there is an increased interest in obtaining materials with high specific surface areas and high porosity.

In the past decade, there has been an increasing interest in the synthesis of porous metal–organic frameworks (MOFs) or coordination polymers, based on the connection of metal ions (nodes) and organic ligands (linkers), such as amines or carboxylates, usually including one or several benzene rings (Rosi, Eddaoudi, Kim, O'Keefi, & Yaghi, 2002). Compared to conventionally used sorbents such as zeolites, these organic structures have very high surface areas and provide the potential for more flexible rational design via controlling the architecture and functionalization of the pores.

Recently, MOFs have attracted extensive attention due to their potential applications in catalysis (Dhakshinamoorthy & Garcia, 2014; Lee et al., 2009; Liu, Chen, Cui, Zhang, & Su, 2014; Ma, Abney, & Lin, 2009; Ribeiro et al., 2013), molecular separation, adsorption of liquid hydrocarbons (Maes, Alaerts, Vermoortele, Denayer, & De Vos, 2010; Nuzhdin, Kovalenko, Fedin, & Bukhtiyarova, 2012; Yang et al., 2011) and sulfur (Liu, Wang, et al., 2014), chemical sensing, drug delivery (Ferey, 2009; Koukaras, Montagnon, Trikalitis, Zdetsis, & Froudakis, 2014), gas storage and separation, especially in hydrogen and methane storage (Luo, Wang, Li, Huo, & Liu, 2013; Ma & Zhou, 2010; Murray, Dinca, & Long, 2009). Thus, the chemistry of MOFs today is a rapidly developing field of coordination and supramolecular chemistry. To use such solids for a given food application, it is

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http://dx.doi.org/10.1016/j.foodchem.2015.05.078
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nevertheless important to focus on toxicologically acceptable MOFs. Apart from the first results dealing with the in vivo toxicity study at the preclinical level of several porous iron carboxylate-based MOFs, there has been no report on the toxicity of MOFs (Horcajada, Serre, McKinlay, & Morris, 2011). Therefore, one has to rely on toxicity data already reported for the metals and linkers themselves. Each metal possesses its own degree of toxicity, ranging from a few mg/kg up to more than 1 g/kg. Hence, in principle, all metals and linkers could be used for food applications but at doses below their degree of toxicity. The degree of toxicity of several metals (LD_{50}) is shown in Table S1 (Horcajada et al., 2011; Shugalei, Garabadgiu, Ilyushin, & Sudarikov, 2012). As can be seen from Table S1, all these metals have a low degree of toxicity. Most ligands used so far for the construction of porous MOFs are aromatic or aliphatic polycarboxylates. Some toxicity data are available (LD_{50}) (Table S2) and show, for instance, that typical polycarboxylic linkers are not very toxic (Horcajada et al., 2011). The number of publications devoted to MOFs, their synthesis, structure, study of the functional characteristics and attempts to find industrial application, increases exponentially (Ferey, 2008). Nevertheless, there are no reports on the use of MOFs for purification of vegetable oils.

In this paper the simple synthesis of aluminum-, zinc- and titanium-containing metal–organic frameworks (Al-MOF, Zn-MOF and Ti-MOF respectively) based on terephthalic acid is presented, and the possibility of using the synthesized compounds as sorbents for the purification of unrefined vegetable oils (sunflower, olive and linseed) is investigated.

2. Materials and methods

2.1. Chemicals

All chemicals were of p.a. grade and used as received. $Al(NO_3)_3{\cdot}9H_2O$ (98%), $Zn(NO_3)_2{\cdot}6H_2O$ (98%), titanium (IV) butoxide (97%), terephthalic acid (H_2BDC, 98%), N,N-dimethylformamide (DMF, 99%) were purchased from Sigma Aldrich.

2.2. Analyzed oils

Olive oil "Altero de oliva", sunflower oil "Kuban favorite" and linseed oil "Linseed oil" were used as received. Physicochemical parameters of oils are shown in Table S3, while fatty acids contents are shown in Table S4 (Enig, 2000).

2.3. Synthesis of Al-MOF and Zn-MOF

16.6 g (0.1 M) H_2BDC were dissolved into 300 ml DMF at reflux under stirring; subsequently, 0.1 M $Al(NO_3)_3{\cdot}9H_2O$ ($Zn(NO_3)_2{\cdot}6H_2O$) was added into the solution above. The reaction mixture was kept at reflux for 17 h. After cooling to room temperature, the product was centrifuged and washed for 2 times with DMF and for 5 times with ethanol. The collected powder was dried at 105 °C for 4 h and at 150 °C under vacuum for 6 h, and these

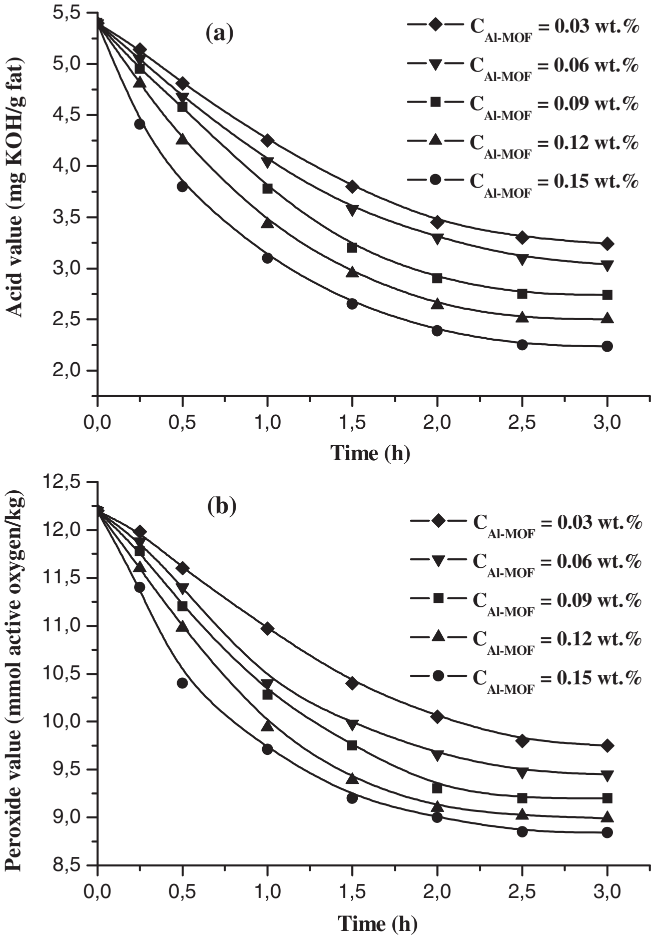


Fig. 2. Dependence of acid value (a) and peroxide value (b) of sunflower oil on time in the presence of additives of Al-MOF.

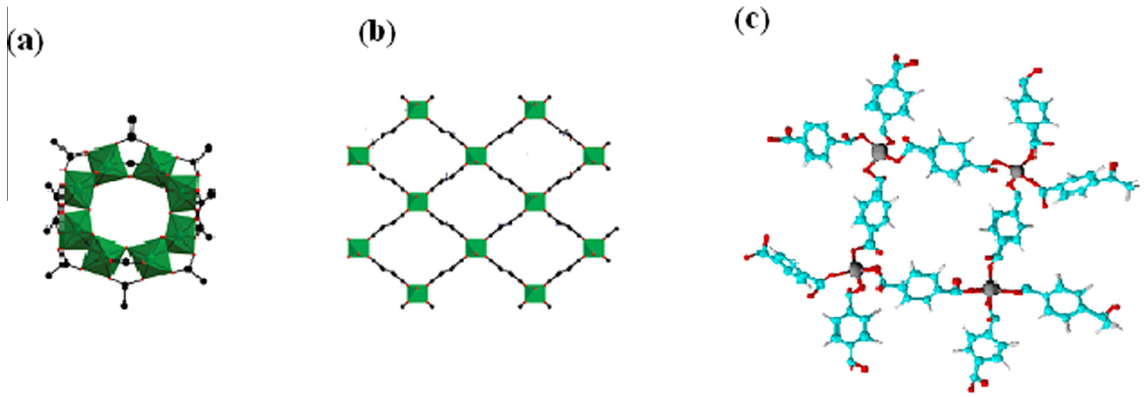


Fig. 1. Structure of Ti-MOF (a), Al-MOF (b) and Zn-MOF (c). (a): titanium polyhedra, carbon and oxygen atoms are in green, black and red, respectively; (b): aluminum octahedra, carbon and oxygen atoms are in green, black and red, respectively; (c): zinc, carbon and oxygen atoms are in black, cyan and red, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

samples are designated as Al-MOF and Zn-MOF ($Al(OH)[O_2C\text{-}C_6H_4\text{-}CO_2]$ and $Zn(OH)[O_2C\text{-}C_6H_4\text{-}CO_2]$), respectively. The yields for Al-MOF and Zn-MOF are 78.5% and 77.9% respectively (Vlasova, Naidenko, Kudrik, Makarova, & Makarov, 2015). Elemental data are shown in Table S5.

2.4. Synthesis of Ti-MOF

16.6 g (0.1 M) H_2BDC were dissolved into 300 ml DMF at reflux under stirring; 17 g (0.05 M) titanium (IV) butoxide were then added. The reaction mixture was refluxed for 6–7 h. After cooling to room temperature, the resulting solid was filtered, washed successively with dimethylformamide and acetone and dried at a temperature of 190–200 °C under vacuum for 3 h. This sample is designated as $Ti_8O_8(OH)_4[O_2C\text{-}C_6H_4CO_2]_6$, Ti-MOF. The yield is 70% (Kudrik, Makarova, Makarov, Salnikov, & Koifman, 2014). Data of elemental analysis are shown in Table S5.

2.5. Treatment of oils with MOFs

All experiments were performed at 25 °C in an air atmosphere; the oil (15 g) was mixed with the MOF as an adsorbent (0.03–0.15 wt.%) in a glass flask under stirring for different times. The liquid phase was then separated from the adsorbent by filtration, and titrated with 0.1 N KOH or 0.01 N $Na_2S_2O_3$ (Harutyunyan, Kornena, & Nesterov, 2004). Acid values were determined by a method based on the titration of free fatty acids in an ether fat-alcohol solution with an aqueous alkaline solution. Peroxide values were based on the amount of iodine, subsequently titrated with sodium thiosulfate in the presence of starch (Harutyunyan et al., 2004).

2.6. Regeneration of MOFs

Regeneration of spent MOF was performed by solvent washing. The spent MOF was washed with ethanol for 6 h using a Soxhlet extractor to remove adsorbed FFA and peroxide compounds (PC), and then dried under vacuum at 150 °C for 3 h. The performance of the regenerated MOF was tested as for the fresh adsorbent.

2.7. Characterizations

The crystalline structures of MOFs were determined by X-ray Diffraction (XRD) measurements using Bruker D8 Advance diffractometer with Cu-Kα radiation (λ = 1.5406 Å) running at a voltage of 50 kV and a current of 200 mA. Nitrogen adsorption–desorption measurements were carried out at 77 K. Specific surface areas were

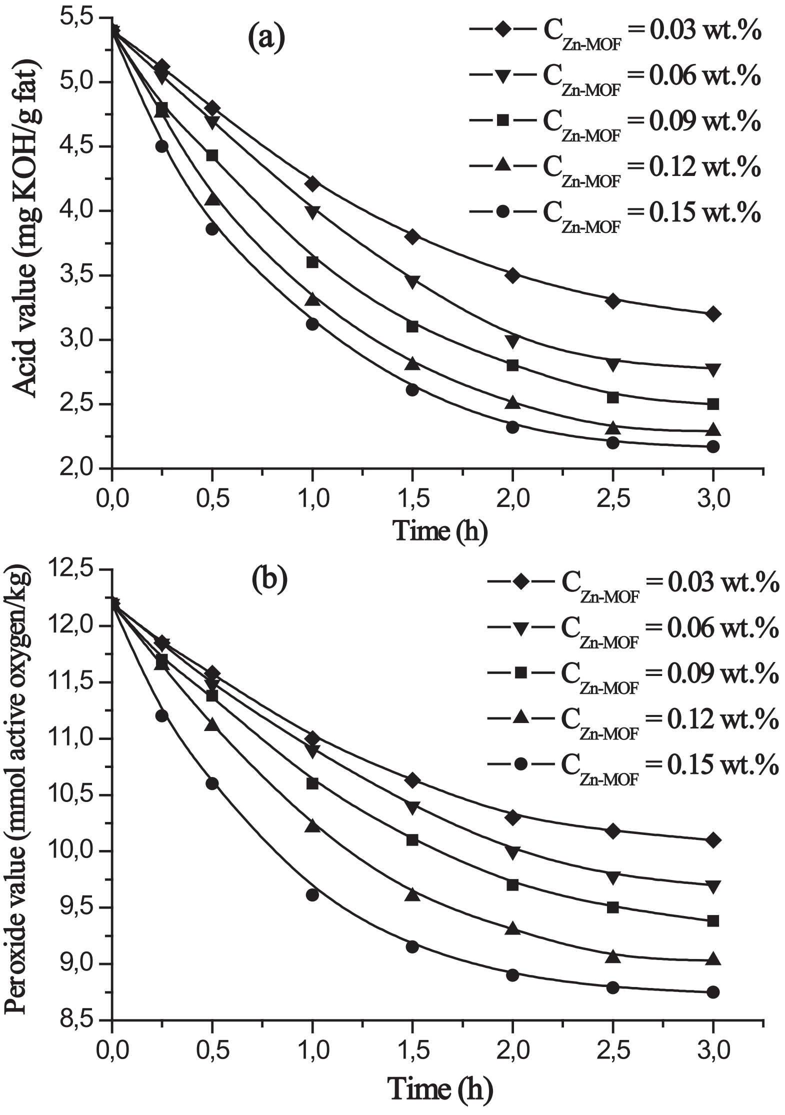


Fig. 3. Dependence of acid value (a) and peroxide value (b) of sunflower oil on time in the presence of additives of Zn-MOF.

determined using the Brunauer–Emmett–Teller (BET) equation; and the pore size distribution and pore volume were calculated by applying the nonlocal density functional theory (NLDFT) method. Thermal gravimetric analysis (TGA) was performed in air (5 °C min^{-1}) (Netzch Sta 449c Jupiter thermal analyzer). Elemental analysis was performed using a Perkin-Elmer 240 analyzer Flash EA 1112. IR spectra were registered using a Nicolet Avatar 360 spectrometer at room temperature in the range of 400–4000 1/cm, with potassium bromide pellets. The content of metal atoms in vegetable oils before and after extraction of free fatty acids and peroxide compounds by MOFs was determined by an atomic absorption spectrometer (AAC BUCK 210 VGP). The mixture of oil and MOFs was stirred using a magnetic stirrer (IKA C-MAG HS7). The data were analyzed using Origin 7.5.

2.8. Determination of acid value

Acid values (AV, mg KOH/g oil) were calculated according to the equation (Harutyunyan et al., 2004):

$$\text{AV} = 5.611 \times V \times K/m \tag{1}$$

where 5.611 is the number of mg of KOH contained in 1 ml of 0.1 N solution of potassium hydroxide;

V is the volume of 0.1 N solution of potassium hydroxide consumed for the titration, cm^3;
K is correction factor to the titer;
m is the mass of the analyzed oil, g.

2.9. Determination of peroxide value

Peroxide values (PV, mmol of active oxygen/kg) were calculated as (Harutyunyan et al., 2004):

$$\text{PV} = (V_1 - V_0) \times C \times 1000/m \tag{2}$$

where V_1, V_0 are the volumes of 0.01 M solution of sodium thiosulfate consumed for the titration of iodine liberated in the main and control experiments, respectively, cm^3;

C is the concentration of sodium thiosulfate solution, M;
1000 is the coefficient allowing recalculation of the result per kg fat;
m is the mass of the analyzed oil, g.

2.10. Determination of degree of extraction

The degree of extraction (DE, %) was calculated as:

$$\text{DE} = (\text{AV}_1 - \text{AV}_2)/\text{AV}_1 \times 100 \tag{3}$$

$$\text{DE} = (\text{PV}_1 - \text{PV}_2)/\text{PV}_1 \times 100 \tag{4}$$

where AV_1, AV_2 are acid values based on titrations of the oil prior to treatment with MOF, and after 0.5 h of contact the sorbent, respectively, in mg KOH per g fat;

PV_1, PV_2 are peroxide values likewise calculated based on titrations prior and after exposure to the MOF, in mmol active oxygen per kg.

3. Results and discussion

According to the infrared spectra, the synthesized Al-MOF has intense signals around 1416, 1674, 1613 and 3412 cm^{-1} relating to the vibrations of the C=C, coordinated and uncoordinated C=O and OH, respectively (Fig. S1). In Zn-MOF these bands are at 1390, 1662, 1611 and 3391 cm^{-1}, respectively (Fig. S1) – while in. Ti-MOF they are at 1401, 1645, 1585 and 3413 cm^{-1} (Fig. S1). Overall, these IR spectra are similar to those of other MOFs derived from terephthalic acid, both in terms of the nature and of the position of the main absorption bands (Liu et al., 2013; Loiseau et al., 2004). In contrast to the free terephthalic acid, the MOF display a splitting of the bands corresponding to C=O stretching vibrations in the region of 1500–1700 cm^{-1}.

The structures of the synthesized MOFs is shown in Fig. 1 (Devic & Serre, 2014; Dikio & Farah, 2013; Ferey & Serre, 2009). XRD data also confirm the formation of metal–organic framework. Fig. S2 shows XRD patterns of synthesized MOFs (Vlasova, Shalunova, Makarova, Kudrik, & Makarov, 2014). At small angles (till 11°) all materials are characterized by two intense peaks, which is typical for MOFs obtained by the hydrothermal method (Dan-Hardi et al., 2009; Liu et al., 2013; Yue et al., 2013). All synthesized MOFs have high thermal stability. Thermal degradation of Zn-MOF and Ti-MOF starts at temperatures above 410 °C (Fig. S3). Thermal degradation of Al-MOF starts at temperatures above 500 °C (Fig. S3). Nitrogen adsorption–desorption isotherms for Al-MOF (Vlasova et al., 2015), Zn-MOF (Vlasova et al., 2015) and Ti-MOF are shown in Fig. S4, and the physical properties of these three samples are given in Table S6. The data in Table S6 shows that the surface area (S_{BET}) depends on the valence of the cation. At the same time, the micropore volume is much less sensitive to the nature of the metal. By varying the metal cation, it is also possible to vary the pore size. As in the case of a S_{BET}, the minimum pore size is seen in the zinc complex, and the maximum pore size is seen in the titanium one.

The effect of Al-MOF, Zn-MOF and Ti-MOF on basic physicochemical parameters (acid value and peroxide value) of unrefined vegetable oils – sunflower, olive and linseed was studied.

Figs. 2–4 show the variations in acid and in peroxides value of sunflower oil in time, in the presence of Al-MOF, Zn-MOF

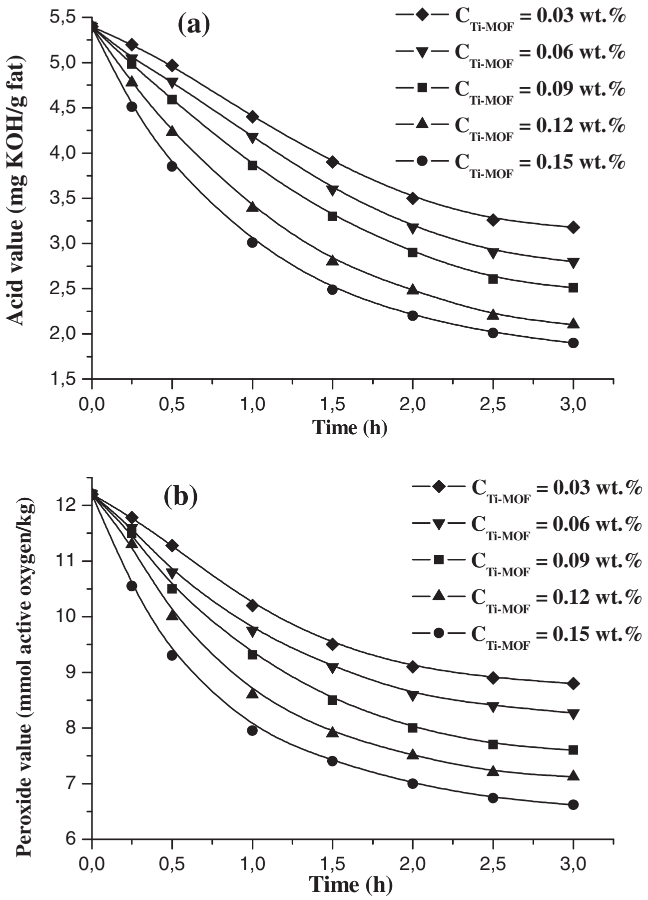


Fig. 4. Dependence of acid value (a) and peroxide value (b) of sunflower oil on time in the presence of additives of Ti-MOF.

Table 1
Effect of 0.15 wt.% MOFs on the extraction of impurities from vegetable oils.

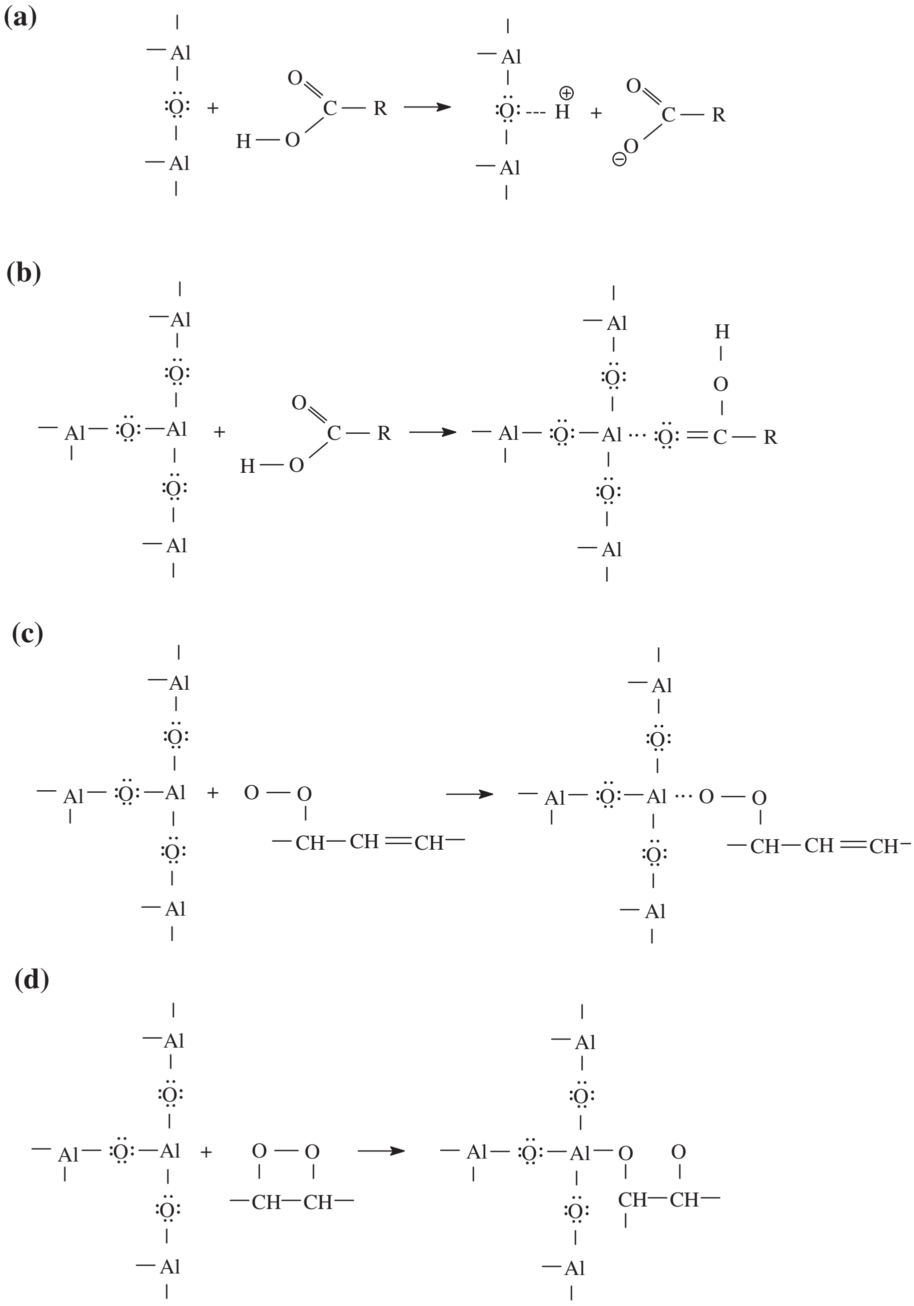
Oil	Degree of extraction[a] (%)					
	FFA			PC		
	Al-MOF	Zn-MOF	Ti-MOF	Al-MOF	Zn-MOF	Ti-MOF
Sunflower	58.7	59.8	64.8	27.5	28.3	45.7
Olive	30.0	30.0	31.2	20.3	21.1	23.2
Linseed	20.9	30.0	39.1	60	69.8	93.4

[a] Adsorption time 3 h.

and Ti-MOF respectively. These values are lowered in a time-dependent and dose-dependent manner by the MOFs thereby improving the physicochemical properties of unrefined vegetable oils. As a consequence of the extraction of FFA and PC, the oils have a more pleasant taste and odor due. Importantly, atomic absorption spectroscopy data also show that synthesized MOFs are almost absent in oils after extraction of FFA and PC.

A summary of the effects of all synthesized MOFs on the extraction of free fatty acids and peroxide compounds from all analyzed oils are summarized in Table 1.

Ti-MOF provides the highest degree of extraction of impurities from all analyzed vegetable oils, as compared to Al-MOF and Zn-MOF; the latter two behave similarly to each other in terms of yields. This result can be explained by the fact that titanium is a more redox active metal than aluminum and zinc, and hence more likely to decompose peroxides (the experimentally-observed decrease in peroxide values indicates the decomposition of peroxides).



Scheme 1. Adsorption mechanism of FFA (a and b) and PC (c and d) with the Al-MOF.

As can be seen from Table 1, the highest degree of extraction of peroxide compounds is observed, with all MOFs, in linseed oil – possibly due to the higher content of unsaturated fatty acids, which are easily oxidized by air and light.

The degrees to which the examined MOFs succeed in sorption of the substances polluting the oil are significantly higher than those of industrial adsorbents (for example, Suprime Pro-Activ, BM-500) or of natural ones based on diatomite and acid-activated bentonite (Bakun, Savostyanov, & Ponomarev, 2010; Ponomarev, 2011). Comparative characteristics of the adsorption capacity of some adsorbents are given in Table S7. These data also show that the synthesized MOFs remain distinctly more efficient than the natural adsorbents even at a lower temperature. On the other hand the industrial adsorbent Suprime Pro-Activ manages to perform (almost) similarly to our Ti-MOF on sunflower oil only at 80 °C (at the same concentration of adsorbent and time of contact with adsorbent and oil) (Ponomarev, 2011).

It is important to note that the MOF can be easily regenerated by ethanol washing after the adsorption of FFA and PC, and thereby recycled at least five times. Illustrating this fact, the, effect of the recycle times for Al-MOF on the degree of extraction of FFA from sunflower oil is shown in Fig. S5: the degree of extraction of FFA decreases by less than 5% at the second regeneration cycle, and then remains almost at the same level, with an overall decrease, after five cycles of utilization, of only ~10%. Moreover, the IR spectra of the fresh vs. the five-times-regenerated Al-MOF (Fig. S6) reveal no difference, which indicates that the sorbent is structurally intact at microscopic as well as macroscopic level. The XRD patterns of the fresh and fivefold regenerated Al-MOf are also essentially identical to each other (Fig. S7). Thus, Al-MOF maintains a high adsorption activity and structural integrity even after five cycles of usage.

The adsorption mechanism, in which the free acids and peroxides interact with the MOFs, is proposed to be similar to that used with kaolin clays (Prokofev & Razgovorov, 2010) as detailed below for Al-MOF. Free fatty acids present in the oil up to a concentration of 0.1 mol/l (and sometimes more) can be adsorbed, firstly, by neutralization of the carboxyl groups with the basic proton-acceptor centers on the surface of adsorbent according to the Brønsted mechanism (Scheme 1a).

Secondly, free fatty acids can be adsorbed by the interaction of coordinatively unsaturated Lewis centers in MOFs with the COOH-groups (Scheme 1b).

Peroxide compounds may employ their free pair of electrons to interact with the electron acceptor surface centers according to the Lewis mechanism (Scheme 1c and d). Obviously, where applicable, outer-sphere redox reactions with the metal surface or with other organic impurities adsorbed on the surface are also likely.

4. Conclusion

This study reports a set of newly synthesized MOFs, all of which are found to improve the physical and chemical properties of unrefined vegetable oils; this effect entails binding FFA and PC generated by inherent alteration/oxidation of the oils. Of these MOFs, Ti-MOF exhibits higher sorption capacity than Al-MOF and Zn-MOF, most likely due to its stronger redox activity. All MOFs are more effective and easily regenerable adsorbents as compared to traditional natural adsorbents. Last but not least, they can be easily regenerated by ethanol washing – and thus be recycled at least five times.

Acknowledgement

The present study was financially supported by the Ministry of Education and Science of Russian Federation.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.foodchem.2015.05.078.

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