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Application of metal–organic frameworks for purification of vegetable oils

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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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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

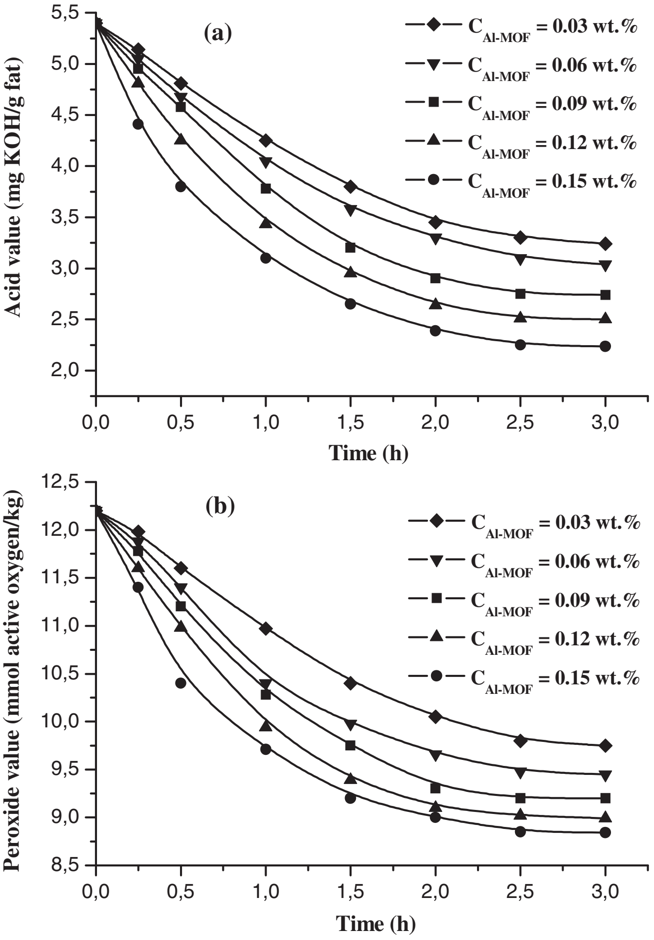

Fig. 2. Dependence of acid value (a) and peroxide value (b) of sunflower oil on time in the presence of additives of Al-MOF.

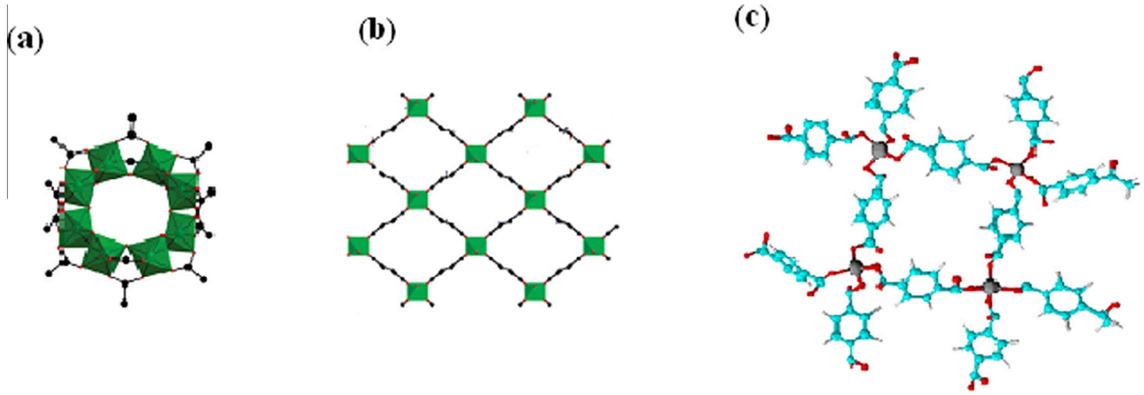

Fig. 1. Structure of Ti-MOF (a), Al-MOF (b) and Zn-MOF (c). (a): titanium polyhedra, carbon and oxygen atoms are in green, black and red, respectively; (b): aluminum octahedra, carbon and oxygen atoms are in green, black and red, respectively; (c): zinc, carbon and oxygen atoms are in black, cyan and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