

PHOTOINITIATED SYSTEM AND PROCESS FOR REMOVAL OF TOXIC CHEMICALS FROM VEGETABLE OILS

5 **FIELD OF INVENTION**

[0001] The present invention generally relates to oil processing, and more particularly a photoinitiated process and system for removal of toxic chemicals in vegetable oils.

10 **BACKGROUND**

[0002] 3-monochloropropane-1,2-diol (3-MCPD) and glycidyl esters (GE) are two known compounds typically formed endogenously when vegetable oils are heated at high temperature, such as during deep-frying using vegetable oil and during oil refinery process.

15 The presence of these compounds has raised a potential public health in their free forms, which are usually release during digestion, present toxic properties such as nephrotoxicity, carcinogenicity and genotoxicity.

[0003] To date, the mitigation of these compounds includes their removal after
20 deodorization process and reducing their precursors. However, these approaches require a significant structural or equipment change in the refinery facilities, not only the unit operators as well as refinery conditions (temperature and pressure) and processing steps resulting to additional cost. Alternative ways have been considered to reduce the formation of these undesired chemicals especially in oil refinery processes, since there have been
25 reports to indicate that changing or modifying oil deodorization process or systems may have an impact on the resulting overall quality of the oil in addition to generating additional wastes.

[0004] Accordingly, the reduction of these toxic chemical compounds remains a challenge
30 for oil manufacturers.

SUMMARY

[0005] In one aspect, the present invention provides a system for removing toxic chemicals
35 from a refined, bleached and deodorized oil (RBDPO) comprising: a treatment section for

removal of the toxic chemicals from the RBDPO comprising a photosensitive adsorbent and a light source; a regeneration section for separating the treated RBDPO from the adsorbent hence regenerating the adsorbent; wherein the adsorbent comprises graphite functionalized with a copper oxide such that when the toxic chemicals from the RBDPO feed are in contact
 5 with the functionalized adsorbent and exposed to the light, the adsorption of the toxic chemicals is initiated, therefore enabling the separation of the toxic chemicals from the RBDPO.

[0006] Advantageously, the separation of the toxic chemicals from RBDPO enables ease of
 10 removal of the toxic chemicals from the feed.

[0007] In an embodiment, the light source is adapted for providing artificial or simulated sunlight.

15 [0008] In a further embodiment, the copper oxide is Copper (II) Oxide (CuO).

[0009] In yet a further embodiment, the graphite includes mesoporous S-doped graphite spheres.

20 [0010] In an embodiment, the toxic chemicals include 3-monochloropropane-1,2-diol (3-MCPD) and glycidyl esters (GE).

[0011] In a further embodiment, the treatment section comprises any combination of cylinders, mesh member and/or the like for supporting the adsorbent.

25

[0012] In another aspect, the present invention provides a photosensitive adsorbent for removing toxic chemicals from refined, bleached and deodorized palm oil (RBDPO), comprising a functionalized graphite, wherein when the toxic chemicals are in contact with the adsorbent and is exposed to sunlight, the adsorption of the toxic chemicals is initiated,
 30 therefore enabling the separation of the toxic chemicals from the RBDPO.

[0013] In an embodiment, the toxic chemicals include 3-monochloropropane-1,2-diol (3-MCPD) and glycidyl esters (GE).

35 [0014] In an embodiment, the adsorbent can withstand high oil processing temperature up to 250°C.

[0015] In another embodiment, the regeneration step further includes removing the toxic chemicals from the adsorbent by way of desorption.

[0016] In a further aspect, the present provides a process for removal of toxic chemicals from refined, bleached and deodorized oil (RBDPO) feed comprising: a treatment step comprising a photosensitive adsorbent and a simulated sunlight source for removing the toxic chemicals from the RBDPO; a regeneration step for separating the treated RBDPO from the adsorbent hence regenerating the adsorbent; wherein the adsorbent comprises graphite functionalized with a copper oxide such that when the toxic chemicals from the RBDPO feed are in contact with the functionalized adsorbent and exposed to the simulated sunlight, the adsorption of the toxic chemicals is initiated and therefore enabling the separation of the toxic chemicals from the RBDPO.

[0017] In another embodiment, the light source is adapted to project simulated sunlight and is positioned adjacent to the adsorbent section such that the adsorbent is sufficiently exposed to the simulated sunlight to initiate adsorption reaction between the functionalized surface of the adsorbent and the toxic chemicals in the feed.

[0018] In an embodiment, the toxic chemicals include 3-monochloropropane-1,2-diol (3-MCPD) and glycidyl esters (GE).

[0019] In yet another aspect, the present invention provides a photosensitive adsorbent for removing toxic chemicals from refined, bleached and deodorized palm oil (RBDPO), comprising a functionalized graphite, wherein when the toxic chemicals are in contact with the adsorbent and is exposed to sunlight, the adsorption of the toxic chemicals is initiated, therefore enabling the separation of the toxic chemicals from the RBDPO and subsequently removal of the toxic chemicals from the RBDPO.

[0020] In an embodiment, the adsorbent includes graphite. Typically, the adsorbent includes mesoporous S-doped graphite spheres.

[0021] In a further embodiment, the graphite is functionalized with copper oxide (CuO).

BRIEF DESCRIPTION OF DRAWINGS

[0022] The invention will be more understood by reference to the description below taken in conjunction with the accompanying drawings herein:

5

[0023] FIG. 1 provides a schematic diagram showing the adsorption of the toxic chemicals onto the functionalized mesh in accordance with an embodiment of the present invention; and

10 [0024] FIG. 2 shows an exemplary of the toxic chemicals removal system in accordance with an embodiment of the present invention;

[0025] FIG. 3 shows an example of simulated sunlight irradiance that may be configured for the light source in accordance with an embodiment of the present invention.

15

DETAILED DESCRIPTION

[0026] In line with the above summary, the following description of a number of specific and alternative embodiments is provided to understand the inventive features of the present invention. It shall be apparent to one skilled in the art, however that this invention may be practiced without such specific details. Some of the details may not be described at length so as not to obscure the invention. For ease of reference, common reference numerals will be used throughout the figures when referring to the same or similar features common to the figures.

25

[0027] Embodiments of the invention are described by way of illustration. As will be realized, the invention is capable of other and different embodiments and its several details are capable of modifications in various respects, all without departing from the scope of the present invention. It should be noted that the drawings include schematic description of how the process in accordance with the preferred embodiments can be carried out. The necessary pumps, valves, and other standard equipment or components may have not been illustrated since they are known in the art.

[0028] The present invention provides a process for removing toxic chemicals in vegetable oils in the presence an adsorbent that is accordingly modified to be selective to toxic chemicals

35

that are commonly produced when vegetable oil is heated at high temperature or during an oil refinery process where the refining process typically requires high temperatures to convert or transform oil into useful products. The adsorbent comprises a photosensitive adsorptive material, therefore able to chemically react with the targeted toxic chemicals to form an adsorptive network in the presence of sunlight. These toxic chemicals include 3-monochloropropane-1,2-diol (3-MCPD) and Glycidyl ester (GE).

[0029] The process removes chemicals from a refined, bleached and deodorized oil (RBDPO) comprising: a treatment step for removing the toxic chemicals from the RBDPO comprising a light source and a photosensitive adsorbent; and a regeneration step for separating the treated RBDPO from the adsorbent hence regenerating the adsorbent. In this embodiment, the adsorbent comprises graphite functionalized with Copper (II) Oxide (CuO) such that when the toxic chemicals from the RBDPO are in contact with the functionalized adsorbent, and exposed to the light, the adsorption of the toxic chemicals is initiated, therefore enabling the separation of the toxic chemicals from the RBDPO and subsequently removal of the toxic chemicals from the RBDPO.

[0030] The adsorbent comprises modified materials with responsive surface which is highly selective to 3-monochloropropane-1,2-diol (3-MCPD) and Glycidyl ester (GE). In an embodiment, the photosensitive adsorbent includes graphite, having a surface functionalized with Copper (II) Oxide (CuO) creating an adsorption surface for the toxic chemicals once exposed to sunlight. In the preferred embodiment, the CuO is immobilized on mesoporous S-doped graphite spheres (CuO@SPG).

[0031] The following steps may be carried out to functionalize CuO on the mesoporous S-doped graphite spheres. First, Cu^{2+} ($\text{Cu}(\text{NO}_3)_2$, 0.2 mol/L) was immobilized on the sulfonic-functional cation exchange resin ($\text{R-SO}_3\text{H}$) surface and dried at 50 °C to obtain $(\text{R-SO}_3^-)_2\text{Cu}^{2+}$ beads. Then $\text{Cu}(\text{OH})_2$ were obtained on the $(\text{R-SO}_3^-)_2\text{Cu}^{2+}$ surface upon rapidly precipitating the beads $(\text{R-SO}_3^-)_2\text{Cu}^{2+}$ composite along with cetyltrimethylammonium bromide (CTAB) (0.06 mol/L) and NaOH (1.25 mol/L) on a water bath (80 °C) for 1 h. Repetitive washing of the composite with water quantitatively removes CTAB and NaOH from the surface to achieve the black $(\text{R-SO}_3^-)_2\text{-Cu}(\text{OH})_2$ precursor and then dried at 80 °C for 12 h. Finally, the obtained sample was pyrolyzed in a tube furnace at 150 °C for 1 h to obtain the CuO@SPG.

[0032] The photoinitiated adsorption process is able to remove with 3-MCPD and GE once in contact with the RBDPO containing said chemicals. The chemical bonding therefore enables the separation of these chemicals from the RBDPO and subsequently removal of the chemicals from the RBDPO easily. An example of photoinitiated mechanism of the photosensitive adsorbent is shown in **FIG. 1**. The CuO with oxygen-vacancy loaded is used due to lower bandgap energy that can enhance separation of electron-hole which promotes the generation of the electron under sunlight irradiation. The S-doped graphite spheres (SPG) surface itself is highly conductive and able to transfer the electron generated from CuO to its -SO₃⁻ group on the surface that activates the sulfur group and bind with 3-MCPD and GE via chemical addition reaction.

[0033] The present invention further provides a system for removing toxic chemicals in vegetable oils comprising: an oil refining section for producing a refined, bleached and deodorized oil (RBDPO); a treatment section for removal of the toxic chemicals from the RBDPO; the treatment section comprising a photosensitive adsorbent and a light source, a regeneration section for separating the treated RBDPO from the adsorbent hence regenerating the adsorbent.

[0034] An example of the treatment section in accordance with an embodiment of the present invention is shown in **FIG. 2A**. The RBDPO feed may be contained in a holding tank (20) in which an inlet (21) feeds the RBDPO stream into an adsorption column (22) comprising an adsorbent section (23) provided with a layer of the functionalized photosensitive adsorbent. The RBDPO feed stream flows in parallel to said adsorption section (23) and therefore contacts the functionalized surface of the adsorbent by gravitational force. During this process, a light source (24) adapted for projecting simulated sunlight may be positioned adjacent to the adsorbent section (23) such that the amount of simulated sunlight projected towards the adsorbent section (23) is sufficient to initiate adsorption reaction between the functionalized surface of the adsorbent and the toxic chemicals in the feed. An example of the simulated sunlight irradiation that may be used in the system is depicted in **FIG. 2B**. The toxic chemicals are separated from the RBDPO by way of physisorption/chemisorption. As a result, the toxic chemicals are retained (subsequently removed later) and the treated RBDPO is directed to the tank (20). To prevent a decrease in the quality of the treated feed due to sunlight irradiation, the treated feed may be directed to a chiller (25) which helps to maintain the feed temperature.

[0037] The treated feed may be directed to the tank (20) facilitated by a pump (20A). The adsorbent is oleophilic to allow the RBDPO to flow through with minimal resistance.

[0035] The photosensitive adsorbent comprises functionalized graphite spheres, wherein
5 when the toxic chemicals are in contact with the functionalized surface of the adsorbent a bonding is formed therefore enabling the separation of the toxic chemicals from the RBDPO and subsequently removal of the toxic chemicals from the RBDPO. The adsorbent may be used in different configurations such as in a packed adsorption column or supports such as combination of cylinders, mesh member and/or the like.

10

[0036] The adsorbent is thermally stable, therefore capable of operating at any high temperature of the oil after deodorization process, i.e., up to 250°C. It is capable of removing the toxic chemicals 3-MCPD and GE regardless of its concentration in RBDPO, therefore analysis of raw materials in refinery, bleaching and deodorization process can be minimized.
15 Further, the adsorbent can be provided in packed adsorption columns which is modular, has small footprint, with low capital and operation expenses, resulting in a facile approach to improve existing plant layout. Additionally, the adsorbent is composed of CuO functionalized on SPG spheres, which is chemically stable, and the copper metal ions from the CuO on SPG spheres will not leach out into the RBDPO, minimizing the risk of metal pollution from the
20 adsorbent in the treated RBDPO.

[0037] While the invention has been described as required in terms of preferred embodiments and specific operating ranges and conditions, those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications
25 other than those specifically described.

CLAIMS

- 5 1. A system for removing toxic chemicals from a refined, bleached and deodorized oil (RBDPO) feed comprising:
a treatment section for removal of the toxic chemicals from the RBDPO comprising a photosensitive adsorbent and a light source;
a regeneration section for separating the treated RBDPO from the adsorbent hence
10 regenerating the adsorbent;
wherein the adsorbent comprises graphite functionalized with a copper oxide such that when the toxic chemicals from the RBDPO feed are in contact with the functionalized adsorbent and exposed to the light, the adsorption of the toxic chemicals is initiated, therefore enabling the separation of the toxic chemicals from the RBDPO.
- 15 2. The system according to claim 1, wherein the light source is adapted for providing artificial or simulated sunlight.
- 20 3. The system according to claim 1, wherein the copper oxide is Copper (II) Oxide (CuO).
4. The system according to claim 1, wherein the graphite includes mesoporous S-doped graphite spheres.
- 25 5. The system according to claim 1, wherein the toxic chemicals include 3-monochloropropane-1,2-diol (3-MCPD) and glycidyl esters (GE).
6. The system according to any one of the preceding claims, wherein the treatment section comprises any combination of cylinders, mesh member and/or the like.
- 30 7. A process for removal of toxic chemicals from refined, bleached and deodorized oil (RBDPO) feed comprising:
a treatment step comprising a photosensitive adsorbent and a simulated sunlight source for removing the toxic chemicals from the RBDPO;

a regeneration step for separating the treated RBDPO from the adsorbent hence regenerating the adsorbent;

wherein the adsorbent comprises a graphite functionalized with a copper oxide such that when the toxic chemicals from the RBDPO feed are in contact with the functionalized
5 adsorbent and exposed to the simulated sunlight, the adsorption of the toxic chemicals is initiated and therefore enabling the separation of the toxic chemicals from the RBDPO.

8. The process according to claim 7, wherein the light source is adapted to project simulated sunlight and is positioned adjacent to the adsorbent section such that the adsorbent is
10 sufficiently exposed to the simulated sunlight to initiate adsorption reaction between the functionalized surface of the adsorbent and the toxic chemicals in the feed.

9. The process according to claim 7, wherein the toxic chemicals include 3-monochloropropane-1,2-diol (3-MCPD) and glycidyl esters (GE).
15

10. The process according to claim 7, wherein the regeneration step further includes removing the toxic chemicals from the adsorbent by way of desorption.

11. A photosensitive adsorbent for removing toxic chemicals from refined, bleached and deodorized palm oil (RBDPO), comprising a functionalized graphite, wherein when the
20 toxic chemicals are in contact with the adsorbent and is exposed to sunlight, the adsorption of the toxic chemicals is initiated, therefore enabling the separation of the toxic chemicals from the RBDPO.

25 12. The adsorbent according to claim 11, wherein the adsorbent includes mesoporous S-doped graphite spheres.

13. The adsorbent according any one of claim 11 to 12, wherein the graphite is functionalized with copper oxide (CuO).
30