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PAPER

Magnetic separation of fatty acids with iron oxide nanoparticles and application to extractive deacidification of vegetable oils†

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The magnetically assisted removal of fatty acids from organic solutions and vegetable oils using iron oxide magnetic nanoparticles (MNPs) was investigated. The effect of contact time and concentration on the adsorption of oleic acid from ethanol–hexane solutions was investigated at room temperature using equilibrium batch experiments. The results showed that the adsorption is rapid (<2 h) and follows a pseudo-second-order model. The adsorption isotherm was found to follow the Langmuir model and the maximum adsorption capacity of oleic acid was determined to be 125 mg g⁻¹. FTIR analyses of the magnetically separated MNPs demonstrated the covalent binding of the carboxylic group to the particle surface in a bidentate/bridging manner. Thermogravimetric analyses showed that the adsorption capacity of MNPs is very similar for the most common fatty acids in vegetable oils (palmitic, stearic, oleic and linoleic acids). Desorption of fatty acids was readily achieved upon basic treatment and the regenerated magnetite nanoparticles were found to be recyclable for repeated use. The separation of fatty acids from olive and sunflower oils was investigated without added solvent. MNPs were found to remove up to 85% of the fatty acids in the oil within 2 h with a 10 wt% load at room temperature, without alteration of the pigment composition.

1. Introduction

The presence of free fatty acids (FFA) in vegetable oils has important implications not only in terms of oil quality in food¹ but also in biodiesel production.² FFA, virtually absent in oils of living tissue, are released after the oilseed has been harvested by enzymatic hydrolysis of triglycerides as well as by the effect of moisture or heat.³ In food, the presence of FFA alters the taste and affects the conservation and the long-term quality of edible oils. The release of acids is responsible for the development of an undesirable rancid flavor and the formation of toxic oxygenated compounds.⁴ Moreover, FFA are more sensitive to oxidation than their parent triglycerides and this oxidation leads to rancidity in edible oils and fat-containing foods.⁴ In biodiesel production, the homogeneous catalysts used for the transesterification of oils with short-chain alcohols are quite sensitive to free fatty acids which react with the basic catalyst and form soap.² In conventional methods for biodiesel production, the FFA content in the feedstock must be lower than 0.5 wt%, thereby requiring the use of highly refined oils.²

Conventional methods for removal of FFA, *i.e.* deacidification, include chemical, physical or miscella refining.⁵ The most

commonly used method in industry is chemical refining, which is performed by saponification of FFA using an inorganic base. This process reduces the FFA to an acceptable level, but presents several disadvantages:⁵ (i) a significant loss of oil which results from alkali catalyzed side saponification of triglycerides and occlusion in soapstock which can hold as much as 50% of its weight of oil and (ii) the production of large amounts of wastes which have to be treated to meet the statutory requirements. Physical refining is also a feasible process for deacidification of highly acidic oils since it minimizes the loss of oil, but it requires high operating temperatures which often lead to the formation of side products such as polymers and *trans*-isomers.⁶ Moreover, in some cases the refined oil is subject to undesirable alterations in color and a reduction of stability to oxidation.⁷ Miscella deacidification based on solvent extraction is not widely used due to multiple drawbacks like mass transfer limitations, complicated removal of solvent and the requirement of special expensive enclosed and explosion-proof equipment.^{8,9}

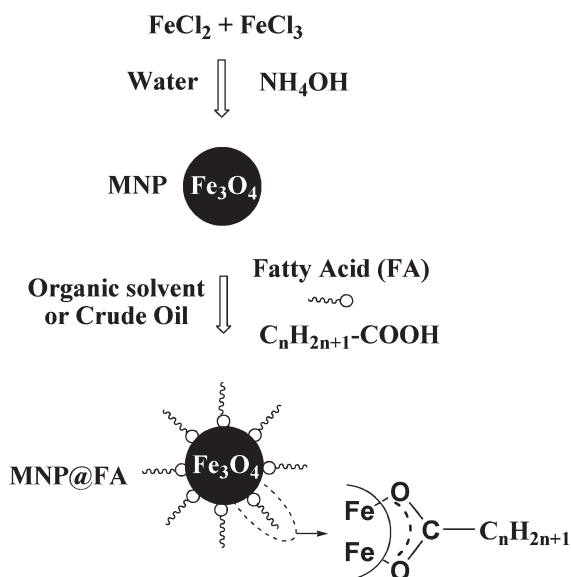
Although the basic unit operations in vegetable oil processing have remained relatively unchanged for the past 5–6 decades,⁵ a great research interest is nowadays devoted to the development of efficient refining processes that meet the requirements of sustainable chemistry. Some alternative approaches including biological deacidification,¹⁰ esterification,^{11,12} solvent and supercritical fluid extraction,^{13,14} and membrane processing¹⁵ have been proposed. Considering the concepts of green chemistry, removal of FFA by adsorption on solids appears to be a valuable alternative environmentally friendly method since adsorption processes can operate at low temperature without the

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need of adding organic solvents or reactants and facilitate the separation by filtration, decantation or centrifugation of the adsorbent. Some recent studies have demonstrated the applicability of adsorption processes for removing FFA from vegetable oils using ion-exchange resins,¹⁶ granulated and activated carbon,^{17,18} activated earth,¹⁸ chitosan,¹⁸ or porous aluminosilicates.¹⁹

In this context we anticipated that iron oxide magnetic nanoparticles (MNPs) should be excellent candidates for adsorption-based removal of FFA for the following reasons. (1) Nanoparticles exhibit large surface area with remarkable accessibility of the binding sites,²⁰ thus promising rapid and efficient adsorption. (2) The chemical and physical properties of iron oxides have been widely studied and the methods for producing iron oxide NPs are well documented, simple and inexpensive.^{21,22} (3) Iron oxide particles are biocompatible, biodegradable and non-toxic and hence have found a variety of applications in biology and medicine.^{21,23,24} These last two points highlight the interest of iron oxide particles as a non-toxic and low-cost adsorbent. (4) Magnetic nanoparticles are of great interest in separation processes because they can be easily separated and recovered using an external magnet. MNPs have been used as adsorbents for magnetically assisted separations of biomolecules as well as pollutants like heavy metal ions or dyes.^{23,25,26} They also found applications as supports for facilitated separation/recovery of catalysts.²⁷ The magnetic separation constitutes a considerable advantage of using magnetic sorbents in adsorption processes because the recovery of particles from solution with the use of a magnetic field is more selective, efficient and usually much faster than filtration and centrifugation.²⁶ (5) Last but not least, iron oxide particles are known to exhibit high affinity for carboxylic acids, including fatty acids. Oleic acid is now commonly used as a hydrophobic ligand to prepare dispersions of MNP in organic solvents.^{22,28–33} The stability arises from the binding of the carboxylic groups to the particle surface, which results in the formation of a hydrophobic layer of long hydrocarbon chains (Scheme 1).^{30,31} Korolev *et al.* have reported thermodynamic



Scheme 1 Schematic representation of the synthesis of MNPs and interactions with fatty acids.

studies of the adsorption of oleic, linoleic and linolenic acids in organic solvents on magnetite particles.³⁴ However, the magnetically assisted separation of FFA and its application for the deacidification of vegetable oils have been never studied.

In this work, we studied the adsorption of fatty acids on MNPs and the potential applications for magnetically assisted removal of FFA from vegetable oils. The adsorption of oleic acid (OA) and other FFA from organic solution (hexane–ethanol) was first investigated. The kinetics and isotherm of adsorption were investigated to determine the optimal conditions and adsorption capacity. Thermogravimetric and FTIR analyses of the magnetically separated particles were performed to examine the binding and coordination mode of FFA on MNPs. A method for the desorption of FFA and the recycling of the adsorbent was developed and found to permit repeated use of MNPs. The applicability of MNPs for removal of FFA from crude vegetable oils, without added solvent, was then examined on two samples of olive and sunflower oils with different FFA contents. The selectivity of MNPs for FFA and their performance for reducing the acidity of oils were investigated.

2. Experimental section

2.1. Materials and methods

Reagents. Iron(III) chloride hexahydrate ($\geq 99\%$), iron(II) chloride tetrahydrate ($\geq 99\%$), potassium hydroxide ($> 90\%$), palmitic acid (PA, $\geq 99\%$), stearic acid (SA, $> 99\%$) and linoleic acid (LA, $\geq 99\%$) were obtained from Sigma-Aldrich. Ammonium hydroxide (aqueous solution 25 wt%) was obtained from Fluka and oleic acid (OA, $\geq 90\%$) from Alfa-Aesar. All other chemicals were of reagent grade and used as received.

Virgin olive and sunflower oils were obtained from a local food store in Versailles, France. These oils were analyzed in our laboratory and presented acidity values of $(0.88 \pm 0.03)\%$ and $(0.07 \pm 0.02)\%$, respectively, expressed as weight fraction of OA.

Instrumentation. Magnetic separations were performed using two N48 NdFeB magnets ($50 \times 15 \times 15$ mm) from Supermagnete.

FTIR spectra were acquired using a Nicolet FT-IR 560 Magna spectrometer. Thermogravimetric analyses (TGA) were performed by a simultaneous TG-DTA measurement using a Perkin-Elmer STA-600. The samples were heated from 20 to 600 °C at a heating rate of 5 °C min⁻¹ under O₂. UV-visible spectra were recorded on a Perkin-Elmer Lambda 19 UV/VIS/NIR spectrometer. X-ray diffraction (XRD) patterns were recorded on a Siemens D5000 diffractometer with Cu-K α ($\lambda = 1.5405$ Å) radiation over a 2θ range from 10 to 70° using a step size of 0.018 and a counting time per step of 20 s. Elemental analyses were performed by the Service de Microanalyse, ICSN CNRS, Gif/Yvette (France).

Atomic force microscopy (AFM) measurements were made in the tapping mode with a Digital Instrument 3100 and a Nanoscope IIIa controller. Tapping mode etched silicon probes from Veeco (TESP-SS, spring constant k_0 20–80 N m⁻¹ and constant force f_0 300–371 kHz) with a 3.5–4.5 nm radius of curvature were used. Mica substrates were cleaved prior to sample

deposition. The MNPs were diluted 4×10^4 times in *n*-hexane. 10 μL of the dilute solution was deposited on 9 mm mica disks and allowed to dry at room temperature for 12 h.

2.2. Preparation of iron oxide nanoparticles (MNPs)

MNPs were prepared by using the co-precipitation technique.^{32,33} Two aqueous solutions of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (2.76 g in 20 mL deionized water) and $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (1.00 g in 20 mL deionized water) were mixed together with vigorous stirring (ratio $\text{Fe}^{3+}/\text{Fe}^{2+} = 2$). MNPs were precipitated by dropwise addition of ammonia solution (25 wt%, 20 mL) until the pH reached 9.0. The dispersion was then stirred for 60 min to complete the reaction. The dispersion was centrifuged at 5000 rpm for 20 min and the aqueous supernatant was discarded. The black precipitate was washed with water and centrifuged until neutral pH (5×10 mL Millipore water), then washed with ethanol (5 mL) and finally dried under vacuum at 50 °C. To facilitate the subsequent dispersion of the particles, the resultant solid was ground to a fine powder using a mortar.

2.3. Acidity measurement

The amount of FFA in oils is usually characterized by the “acidity value”, which is the content in wt% of free fatty acid contained in the oil.¹ Since oleic acid is the most abundant FFA, the acidity of vegetable oils is expressed, unless otherwise stated, in grams of oleic acid per hundred grams of oil, assuming that all FFA are OA.

The concentration of FFA in vegetable oils was determined using the normalized ISO 660:2009 titration method:¹ 7 g of sample was weighed in an Erlenmeyer flask and the exact weight was recorded (W_s). In a second Erlenmeyer flask 1 mL of phenolphthalein solution (in ethanol) was added to 50 mL of a mixture of ethanol–ethyl ether (50 : 50 v/v) and the solvent mixture was titrated with 0.01 N KOH until the appearance of a pale pink color (taken as the endpoint of the titration). The volume of KOH used was recorded (V_1). The neutralized solvent mixture was quickly added to the sample and mixed vigorously. This mixture was titrated until the appearance of a pale pink color and the amount of KOH used was recorded (V_2). Eqn (1) was used to calculate the acidity expressed as the wt% of oleic acid in the sample. All measurements were performed in triplicate and the end result was the average of three titrations.

$$\% \text{Oleic acid} = \frac{(V_2 - V_1)282N}{10W_s} \quad (1)$$

where V_2 and V_1 are the volumes of KOH solution in mL, N is the exact normality of the KOH solution, W_s is the exact weight in grams of oil, and 282 is the molecular weight of OA (g mol^{-1}).

2.4. Solid–liquid extraction procedures

Adsorption kinetics and isotherm. The model experiments were performed by adding 30 mg of as-prepared dry magnetite in 30 mL of a solution of OA (concentration ranges from 10 to 2000 mg L^{-1}) in a mixture of *n*-hexane–ethanol (50 : 50 v/v).

The resulting suspension was sonicated for 30 min at room temperature and then stirred mechanically at 200 rpm till the chosen reaction time. The sorbent was separated with an external magnet and OA loaded magnetic particles were collected. The isolated OA loaded MNPs were washed with acetone and then dried under vacuum at 50 °C before characterization (TGA, IR, AFM and elemental analyses).

The residual OA concentration in the supernatant was determined using the titration method described above. The amount of adsorbed OA (Q_e) in mg per g of MNP was calculated by material balance of the initial and equilibrium concentrations of the solution using eqn (2).

$$Q_e = \frac{(C_{\text{ini}} - C_e)V}{m} \quad (2)$$

where C_{ini} and C_e (mg L^{-1}) denote the initial and equilibrium concentrations of OA, respectively, V is the total volume of the solution in liters and m is the mass of the dry MNPs used in grams.

Adsorption of other fatty acids. Experiments were performed as described above under equilibrium conditions using 30 mg of dry MNPs and 30 mL of a 250 mg mL^{-1} solution of FA in hexane–ethanol (50 : 50 v/v). The resulting suspension was sonicated for 30 min and then stirred mechanically at 200 rpm for 90 min at room temperature.

Desorption and repeated use. OA loaded MNPs isolated from adsorption experiments, using equilibrium conditions, were immersed in 30 mL of a 0.1 N solution of NaOH in ethanol–water (50 : 50 v/v) and the mixture was sonicated for 30 min and mechanically stirred for 90 min. The MNPs were then separated by an external magnet and washed with water until neutral pH (5×10 mL Millipore water), then with ethanol (5 mL) and finally dried under vacuum at 50 °C. The OA adsorption experiments (adsorption–desorption cycle) were repeatedly performed using the same batch of MNPs. The amount of OA adsorbed for each cycle was determined by titration as described in section 2.3. The adsorption capacity was determined for 6 cycles.

Removal of FFA from vegetable oils (sunflower and olive oils). The extraction experiments were performed by directly adding the MNPs to the oil. The resulting suspension was sonicated for 30 min and then stirred mechanically at 200 rpm for 90 min at room temperature. The MNPs were separated by an external magnet and the supernatant was titrated (as described in section 2.3) to determine the remaining concentration of FFA in the oil. All measurements were performed at least in triplicate.

2.5. Determination of iron concentration in vegetable oils

The concentration of iron in olive and sunflower oils before and after the separation of FFA with MNPs has been determined a standard fluorescence analytical method using 1,10-phenanthroline as a fluorescent probe.³⁵ This method has a detection limit of 2.4×10^{-8} mol L^{-1} (1.35 ppb). The samples for analyses were obtained by acidic extraction of iron using the previously reported procedure.³⁶ The experimental procedure and the analyses of the results are detailed in the ESI.†

3. Results and discussion

Iron oxide magnetic nanoparticles (MNPs) were synthesized by the co-precipitation method from an aqueous solution of Fe(II) and Fe(III) chloride in the presence of ammonium hydroxide.^{31–33} The as-synthesized particles were characterized by X-ray powder diffraction (see Fig. S1 in the ESI†). The X-ray diffraction patterns revealed the characteristic peaks of inverse spinel magnetite Fe₃O₄ crystal and indicated an average size of 8 nm.

3.1. Kinetics and isotherm of adsorption of oleic acid from organic solvent (or study of the adsorption of oleic acid from organic solvent)

In order to determine the optimal conditions for magnetic separation of FFA and to get some mechanistic insights on the adsorption process, we first studied as a model the adsorption of oleic acid (OA) on MNPs from solution in ethanol–hexane (50 : 50 v/v). The amount of OA adsorbed on MNPs was quantified by measuring the remaining acid concentration in the solution after magnetic separation of the particles.

Adsorption kinetics. Fig. 1 shows the effect of contact time, from 5 to 120 min, on the amount of adsorbed OA at room temperature. The experimental curve shows that the adsorption process is rapid since the equilibrium is reached after 60 min. The amount of adsorbed OA at the equilibrium is 92 mg per g of MNP (about 0.33 mmol g⁻¹). For subsequent batch experiments, we took a contact time of 90 min which was more than sufficient to establish equilibrium.

To further characterize the adsorption process, we have tried to adjust the experimental data with different kinetic models of adsorption. It was found that the pseudo-second-order rate equation (eqn (3))³⁷ fitted well the kinetic data of adsorption of OA on MNP.

$$\frac{dQ_t}{dt} = k_2(Q_c - Q_t)^2 \quad (3)$$

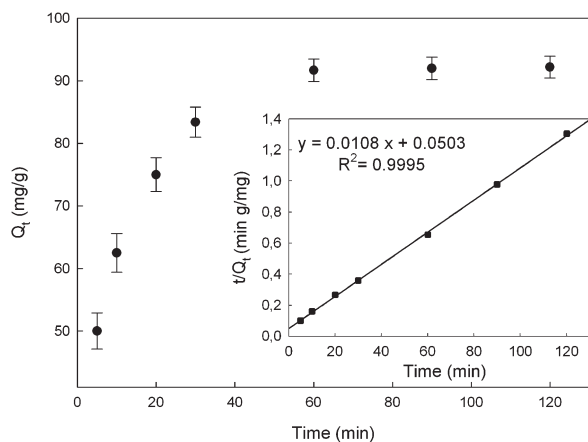


Fig. 1 Effect of contact time on the adsorption of oleic acid in ethanol–hexane solution. Inset: t/Q_t vs. time. Experimental conditions: 30 mg MNPs, 30 mL OA solution ($C_{ini} = 250 \text{ mg L}^{-1}$), 298 K.

where k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$) is the second-order rate constant, and Q_c and Q_t (mg g^{-1}) are the amounts of OA adsorbed at equilibrium and at any time t (min), respectively.

Integration for the boundary conditions $t = 0$ ($Q_t = 0$) to t_{eq} ($Q_t = Q_c$) followed by linearization leads to eqn (4).

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_c^2} + \frac{t}{Q_c} \quad (4)$$

By plotting t/Q_t vs. t , a straight line is obtained as shown in Fig. 1 (inset). The calculated values of k_2 and Q_c are $0.002 \text{ g mg}^{-1} \text{ min}^{-1}$ and 92 mg g^{-1} , in good agreement with the experimental data, respectively. The high correlation coefficient demonstrates the applicability of the kinetic model and hence indicates that the adsorption of OA on MNPs follows a pseudo-second-order chemisorption mechanism.³⁷ The initial adsorption rate v_0 ($v_0 = k_2 Q_c^2$) is equal to $16.9 \text{ mg g}^{-1} \text{ min}^{-1}$ ($3.6 \text{ mmol g}^{-1} \text{ h}^{-1}$): this fast adsorption kinetic is a key point for the design of efficient adsorption systems.

Adsorption isotherm. The adsorption process involves the mass transfer of a solute (adsorbate) from the liquid phase to the adsorbent surface till the thermodynamic equilibrium concentration of the adsorbate is attained.^{17–19,37,38} Therefore, the equilibrium amount of adsorbed solute varies with the initial concentration, and adsorption isotherms are useful for predicting the performance of adsorption systems as well as for selecting the most appropriate conditions. Fig. 2 shows the effect of the initial concentration of OA on the adsorption. The amount of OA adsorbed on MNP sharply increases on increasing the initial concentrations (up to 300 mg L^{-1}). The shape of the adsorption curve suggests that the adsorption of OA follows a Langmuir adsorption model which assumes a surface with homogeneous binding sites in terms of adsorption energy with a limited number of adsorption sites and a monolayer coverage without lateral interactions between adsorbed species. The Langmuir

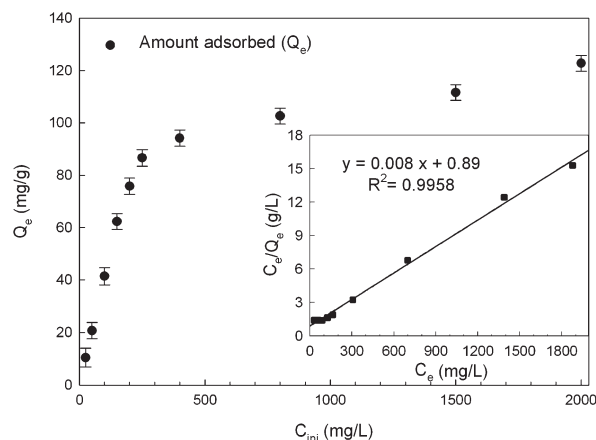


Fig. 2 Effect of initial concentration of oleic acid on the adsorption. Inset: C_e/Q_e vs. C_e (Langmuir model). Experimental conditions: 30 mg MNPs, 30 mL OA solution in ethanol–hexane, 90 min, 298 K.

model is represented by eqn (5) and (6) in its linearized form for plotting and analysis purposes.

$$Q_e = \frac{Q_{\max} b C_e}{1 + b C_e} \quad (5)$$

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{b Q_{\max}} \quad (6)$$

where Q_{\max} (mg g^{-1}) is the maximum uptake of OA, b (L mg^{-1}) is the Langmuir constant related to the affinity of the sorbate for the binding sites, and C_e (mg L^{-1}) and Q_e (mg g^{-1}) are the equilibrium concentrations of OA in the liquid and solid phases, respectively.

The linear variation of C_e/Q_e vs. C_e (inset Fig. 2) with a good correlation coefficient demonstrates the applicability of the Langmuir model for OA concentrations ranging from 25 to 2000 mg L^{-1} and allows the calculation of Q_{\max} (125 mg g^{-1}) and b (0.009 L mg^{-1}).

The values of the dimensionless separation factor R_L calculated using eqn (7)^{37,38} were found to be smaller than 0.04 over the whole range of concentrations studied. Since a value of $R_L < 1$ represents favorable adsorption,^{37,38} it can be concluded that the adsorption of OA on magnetite NPs is highly favorable at room temperature.

$$R_L = \frac{1}{1 + b C_0} \quad (7)$$

where C_{ini} is the initial concentration of OA expressed in mg L^{-1} and b is the Langmuir adsorption equilibrium constant (L mg^{-1}).

The calculated maximum adsorption capacity (Q_{\max}) allows us to compare magnetite NPs with other adsorbents previously used for FFA adsorption. Ribeiro *et al.* reported that the adsorption capacity of granulated carbons for FFA from crude vegetable oil in hexane was 9.8 mg g^{-1} .¹⁷ Maximum adsorption capacities for FFA in crude catfish oil of 71.2, 65.5 and 57 mg g^{-1} for chitosan, activated carbon and activated earth, respectively, have been reported by Sathivel *et al.*¹⁸ Recently, adsorption of FFA on porous magnesium silicates was studied in crude palm oil by Clowutimon *et al.* with an adsorption capacity of 185 mg g^{-1} at $50 \text{ }^\circ\text{C}$.¹⁹ Jamal *et al.* reported an adsorption capacity of 250 mg g^{-1} of wet resin for the separation of OA with quaternary ammonium functionalized ion-exchange resins soaked with methanol from 5 wt% OA–soybean oil mixtures at $50 \text{ }^\circ\text{C}$.¹⁶ These data indicate that the MNPs used in this study may compete favorably with other adsorbents while presenting the outstanding advantages of being non-toxic and easily magnetically separated.

Desorption and repeated use. Another key point for the design of efficient separation systems is the possibility to regenerate the adsorbent and to recycle it for repeated use. To regenerate the native, FA surface-free, MNPs, we used the methodology employed for desorption of dyes from TiO_2 surfaces where the desorption took place by immersion in a 0.01 M solution of NaOH in aqueous ethanol.³⁹ The desorption results from the development of a negative charge on the oxide surface at pH above its point of zero charge ($\text{pzc} \sim 6$ for TiO_2).⁴⁰ In our case, we found that desorption of OA adsorbed on magnetite NPs required more basic conditions, in agreement with the higher pzc

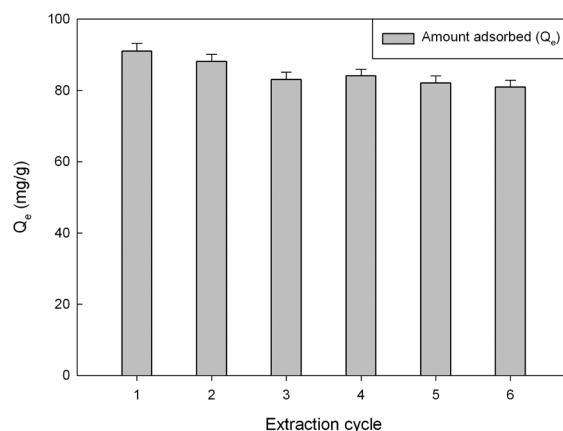


Fig. 3 Adsorption capacity of MNPs during repeated use. Experimental conditions for adsorption: 30 mg MNPs, 30 mL of OA solution in ethanol–hexane (250 mg L^{-1}), 90 min, 298 K ; for desorption: 30 mL of NaOH (0.1 N) solution in 1 : 1 ethanol–water, 298 K .

of iron oxide ($\text{pzc} \sim 9$). Quantitative desorption was achieved upon treatment with a 0.1 N solution of NaOH in EtOH– H_2O (1 : 1) at room temperature. Interestingly, after desorption and washing with water, the MNPs can be reused for subsequent adsorption. Fig. 3 shows the adsorption capacities of the same batch of MNPs after repeated adsorption–desorption cycles. These results demonstrate that MNPs can be used for at least 6 adsorption cycles with good conservation of their adsorption capacity since the decrease of the adsorption capacity is limited to about 10% after 6 uses. The adsorption capacity reached a roughly constant value of $83 \pm 2 \text{ mg g}^{-1}$ after 2 cycles and we did not observe any deactivation over the number of experiments performed in the lab.

This is a relevant advantage of the MNPs with respect to other previously reported adsorbents for removal of FFA, which were not recyclable.

3.2. Characteristics of the separated OA loaded MNPs

The OA coated MNPs separated after the adsorption experiment under saturated conditions have been characterized in terms of particle size and chemical composition.

Fig. 4 shows a representative AFM image of MNPs magnetically separated after adsorption of OA, which indicates that the adsorbent retains its nanometric size. Small NPs in the 8–10 nm diameter range close to those of the native particles together with some larger aggregates (100–125 nm) are observed. From these AFM analyses the specific surface area was estimated to be around $105 \text{ m}^2 \text{ g}^{-1}$ (see ESI† for details). Interestingly, considering this calculated value of the specific surface area of the adsorbent, the maximum adsorption capacity (Q_{\max}) of 125 mg g^{-1} corresponds to a surface area per oleic acid molecule adsorbed on the surface of 39 \AA^2 , a value very close to the previously reported area (38 \AA^2) in a densely packed oleic acid monolayer on magnetite NPs,³¹ suggesting an almost complete coverage of the particle surface. The observed conservation of the nanometric structure after adsorption accounts for the remaining binding capacity during recycling.

Thermogravimetric analyses (TGA) provide quantitative evidence of the adsorption of oleic acid. Fig. 5a shows the TGA

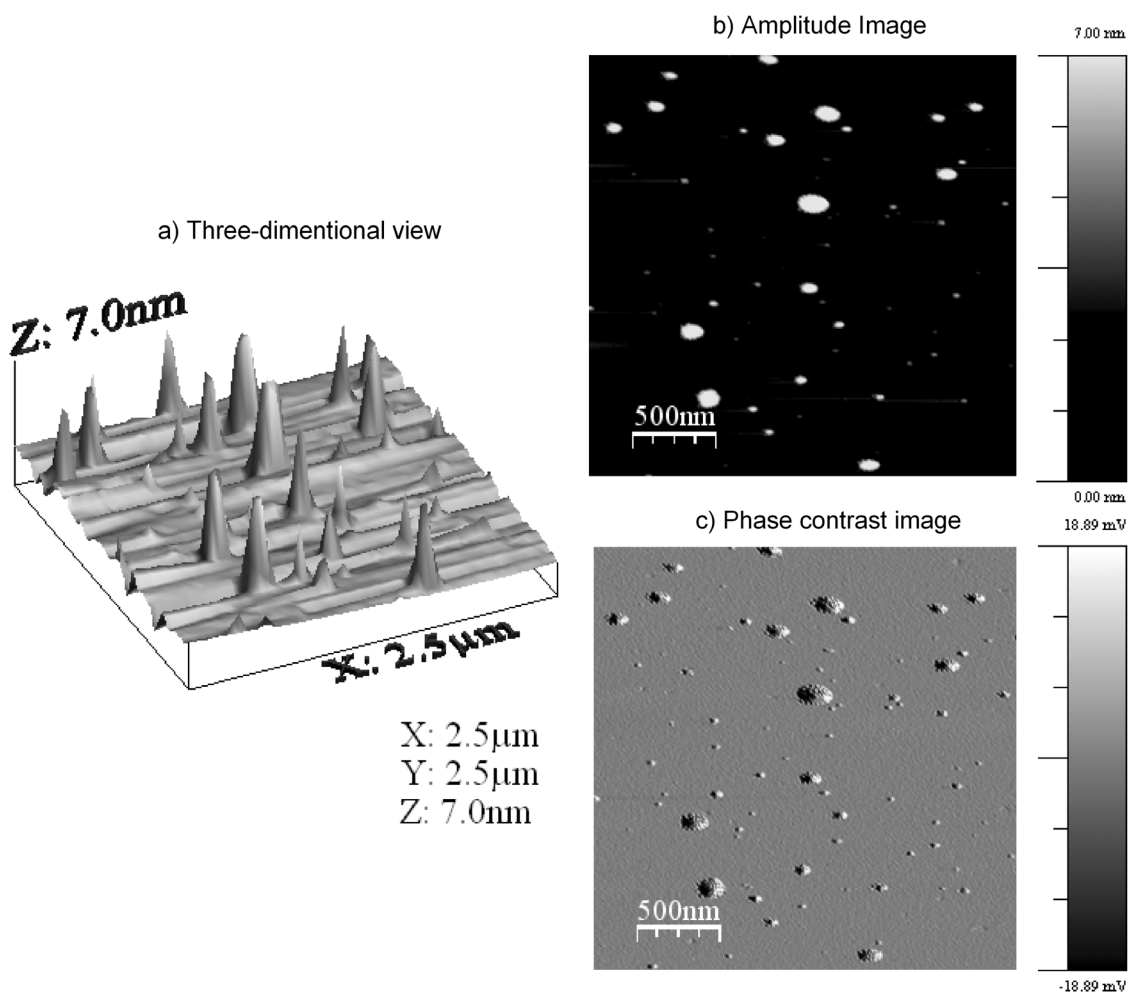


Fig. 4 AFM images of oleic acid-coated MNPs, isolated from adsorption experiments under equilibrium conditions, using tapping mode on mica substrate. (a) Three-dimensional view; (b) amplitude image; (c) phase contrast image.

curves for the starting MNPs and the OA loaded NPs isolated after adsorption. The weight loss of about 7.5% between 200 and 400 °C corresponds to the decomposition of adsorbed oleic acid molecules. The amount of OA adsorbed deduced from TGA is in good agreement with those estimated from carbon elemental analysis (see Table S5 in the ESI†). This estimated OA load on separated MNPs (0.26 mmol g^{-1}) is slightly lower than the OA uptake deduced from titration of the acid remaining in solution (0.33 mmol g^{-1}): this may result from a partial desorption of oleic acid during the washing of particles before analysis.

The FTIR spectra of the MNPs before and after the OA adsorption, given in Fig. 6, confirm the adsorption of OA through chemical interactions between the carboxylic groups and the iron oxide particles and provide information on the coordination mode. The IR spectrum of the starting MNPs shows the vibration bands of the Fe–O bond of the iron oxide core at 590 cm^{-1} and the bands of the OH groups at 3420 and 1637 cm^{-1} . The adsorption of OA in $\text{Fe}_3\text{O}_4@OA$ is confirmed by the appearance of the C–H stretching bands at 2926 and 2850 cm^{-1} as well as the two asymmetrical and symmetrical carboxylate vibrations at 1524 and 1402 cm^{-1} . These carboxylate stretches indicate that oleic acid is attached to the surface of

Fe_3O_4 particles through covalent bonding between a carboxylate (COO^-) group and Fe atoms as depicted in Scheme 1.^{41,42} The observed position and separation of the carboxylate stretching bands suggest a bidentate and/or bridging coordination, in agreement with previous reports on oleic acid stabilized iron oxide particles.^{41,42}

Interestingly, as illustrated in Fig. 7, FTIR analysis of the separated particles can be used to estimate the initial concentration of OA from the area of the C–H stretching bands in the $2800\text{--}3000 \text{ cm}^{-1}$ region. The peak areas for particles separated after adsorption experiments from solutions with different OA concentrations increase linearly with the initial concentration. Under our experimental conditions, the linear calibration applies to a range of concentrations from 100 to 350 mg L^{-1} with a sensitivity of $0.388 \pm 0.04 \text{ L mg}^{-1}$ (regression coefficient > 0.99).

3.3. Comparative adsorption of other FFAs on MNPs

The composition of FFA in vegetable oils depends on their origin (see Table S2 in the ESI†).⁴³ In order to determine the potential of MNPs for removing all FFA from oils, we compared

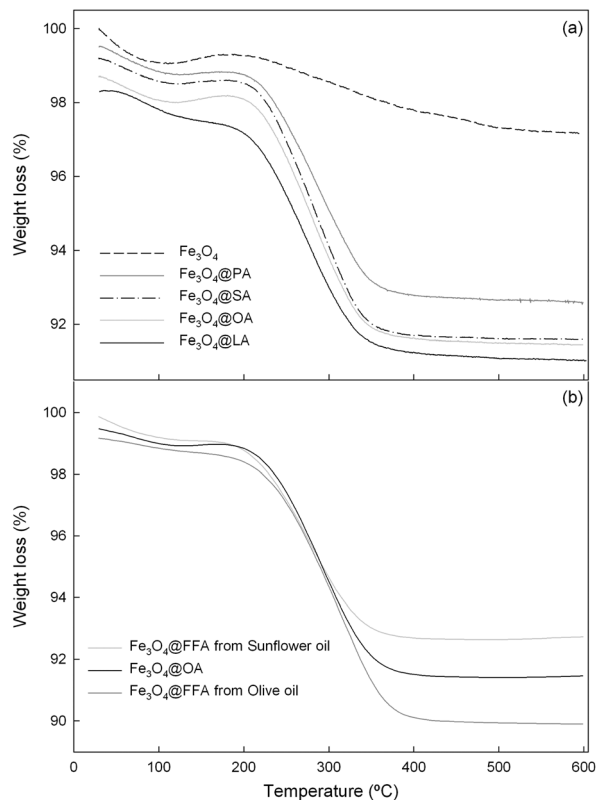


Fig. 5 TGA curves of starting MNPs (Fe_3O_4) and MNPs (Fe_3O_4 @FA) isolated after adsorption experiments under equilibrium conditions. (a) MNPs isolated after adsorption of oleic, stearic, palmitic and linoleic acid (OA, SA, PA and LA) from ethanol-hexane solutions. (b) MNPs isolated after treatment of sunflower and olive oils.

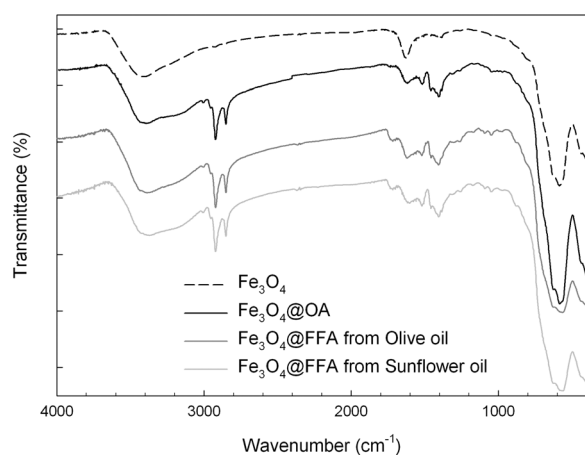


Fig. 6 FTIR spectra of starting MNPs (Fe_3O_4) and coated MNPs isolated after adsorption of oleic acid from ethanol-hexane solution (Fe_3O_4 @OA), and after treatment of olive and sunflower oils (Fe_3O_4 @FFA).

the adsorption capacity of MNP towards some of the other most abundant saturated and unsaturated FFA: stearic acid (SA), linoleic acid (LA) and palmitic acid (PA).

Fig. 5 shows the TGA curves of MNPs separated after adsorption of the different fatty acids (OA, SA, LA and PA) under

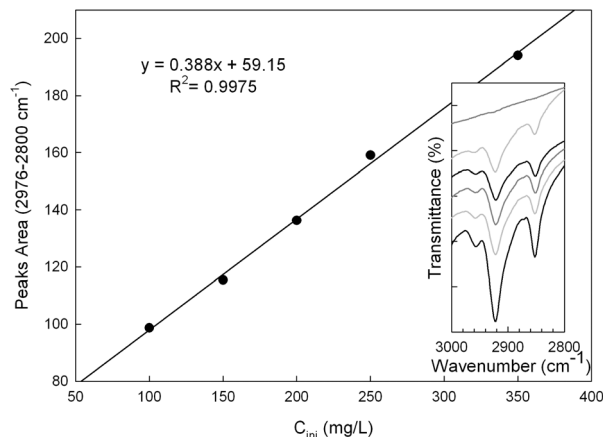


Fig. 7 Variation of the C-H bands area in the FTIR spectra of MNPs isolated after adsorption of oleic acid in ethanol-hexane solutions at different OA concentrations (C_{ini}). Inset: part of the FTIR spectra of MNPs isolated at different initial OA concentrations. Experimental conditions: 30 mg MNPs, 30 mL OA solution in ethanol-hexane, 90 min, 298 K.

similar conditions. It can be seen that the TGA curves are quite similar, with weight losses ranging from 7.1 to 7.7% (detailed values are given in Table S4 in the ESI†). DT-TGA curves (given in Fig. S3 in the ESI†) show that each of the FA coated MNPs have slightly different maximum decomposition peak temperatures (274, 283, 284 and 288 °C for LA, PA, OA and SA, respectively) which vary in the same order as the boiling points of the fatty acids (Table S3 in ESI†).

The values of the molar amount of FA adsorbed per g of MNP, deduced from TGA, are 0.27 and 0.26 mmol g^{-1} for saturated fatty acids (PA and SA) and unsaturated fatty acids (OA and LA), respectively. These values indicate that the studied saturated and unsaturated fatty acids are adsorbed similarly regardless of their hydrocarbon chain length and the presence of unsaturation. The binding mode through coordination of the carboxylate accounts for the observed similar binding capacities independently of the alkyl chain. These findings confirm the observations made by other researchers that, although oleic acid is the most common surfactant used to prepare organic dispersions of iron oxide NPs, saturated fatty acids and medium chain-length carboxylic acids (PA, SA as well as C_8 - C_{14} carboxylic acids) can also be used as capping agents.^{29,31,33,42,44} Moreover, it has been shown that C_8 - C_{18} carboxylic acids adsorbed in a similar manner on magnetite nanoparticles.^{31,33}

These results indicate that MNPs are a valuable adsorbent for removing fatty acids regardless of their aliphatic chain and hence could find applications in the deacidification of oils.

3.4. Magnetic separation of FFA from vegetable oils: selectivity and efficiency

According to green chemistry concepts, the applicability of MNPs for removing FFA from vegetable oils and deacidification has been investigated by treating crude oils with NPs without any added solvent at room temperature, thereby providing an environmentally friendly (solvent-free and non-toxic adsorbent)

and energy efficient process. Olive oil and sunflower oil samples, which differ in their acidity values (0.88 and 0.07%, respectively), their FFA composition (see Table S2 in the ESI†) as well as in their color (green and pale yellow, respectively) and thus their pigment composition, were chosen as models.

Selectivity for FFA compared to pigments. In the food industry and cooking, the color of oils is an important factor in the appreciation of the consumers. Moreover, the presence of pigments plays an important role in stability of oils. Chlorophylls and phenolic compounds decrease the autoxidation of oil in the dark; carotenoids and tocopherols exhibit both antioxidant and prooxidant activity depending on the oil system.⁴ Therefore, for future applications in FFA removal, the adsorbent should exhibit a high selectivity for FFA over pigments. Fig. 8 shows the UV-visible absorption spectra of olive and sunflower oils before and after treatment with MNPs. The absence of spectral changes clearly indicates that the color is not affected and demonstrates that there is no adsorption of pigments: in olive oil the absorbances of chlorophylls and pheophytins at 668 nm¹⁷ as well as carotenoids at 450 nm¹⁷ are not modified. These observations highlight the remarkable selectivity of MNPs for FFA compared to pigments. This is a relevant advantage of MNPs over other adsorbents like activated earth and powdered or granulated carbon which were found to exhibit higher affinity for pigments than for FFA.¹⁷

Adsorption of FFA on MNPs in crude vegetable oils. The FTIR spectra of MNPs isolated after treatment of olive and sunflower oils, given in Fig. 6, are very similar to those of OA loaded NPs isolated from organic solutions. The presence of the two vibration bands of coordinated carboxylate groups (1524 and 1408 cm⁻¹) clearly indicates the covalent binding of FFA to the MNPs. Compared to OA coated MNPs isolated from treatment in organic solvents, the only difference is the appearance of a weak band at 1738 cm⁻¹ which can be attributed to the C=O stretching of the ester group of triglycerides (the IR spectrum of the vegetable oils given in Fig. S5 in the ESI† shows a strong absorption at 1744 cm⁻¹ for the ester). This finding suggests some co-adsorption of triglycerides probably through hydrophobic interactions with the FA monolayer. However, the low

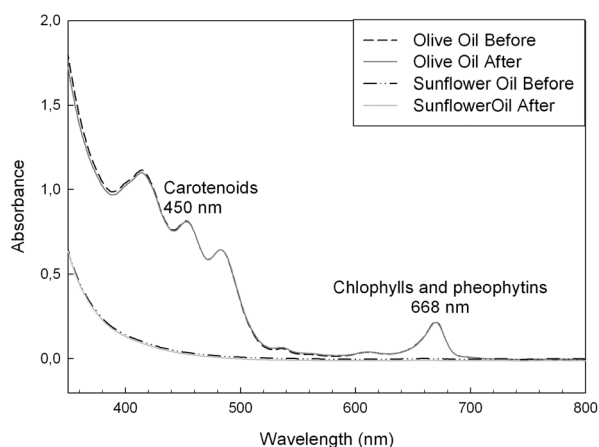


Fig. 8 Absorption spectra of the olive and sunflower oils before and after treatment with MNPs.

intensity of this vibration band is indicative of limited co-adsorption.

Thermogravimetric analyses confirm the finding that MNPs retain their affinity for FFA present in vegetable oils and provide quantitative information. The TGA curves for MNPs isolated after treatment of olive and sunflower oils are given in Fig. 5b together with those of OA loaded NPs isolated from organic solution under similar experimental conditions. The weight loss for NPs separated from olive oil (8.9%) is slightly higher than those obtained for the reference OA loaded NPs (7.4%), in good agreement with carbon elemental analysis (see Table S5 in the ESI†). The slight increase in the organic content may be the result of some triglycerides co-adsorption. However, the co-adsorption of triglycerides is limited since the estimated molar ratio of triglycerides relative to adsorbed FFA does not exceed 8% and does not compete with the binding of FFA. For MNPs isolated after treatment of sunflower oil the weight loss is slightly lower (7.1%), in agreement with carbon elemental analysis (66 ± 7 mg g⁻¹). The much lower concentration of FFA in sunflower oil (0.07%) than in olive oil (0.88%) accounts for this observed lower content of organics adsorbed on NPs.

Efficiency of MNPs for deacidification of vegetable oils. Olive and sunflower oils were treated with MNPs at room temperature for 2 h and the remaining acidity was determined after magnetic separation of the adsorbent. The results given in Table 1 show that MNPs efficiently reduce the acidity of oils even at low loads (0.5–10 wt%). For olive oil, 85% of the free fatty acids are removed in the presence of 10 wt% MNPs. For the less acidic sunflower oil, 70% of the FFA are removed with a 10 wt% load of MNPs and a reduction of the acidity of more than 55% is achieved even at very low adsorbent load (1 wt%). The calculated amounts of FFA removed per g of MNP indicate that the amount of adsorbed FFA is close to the maximum adsorption capacity for the most acidic oil. These results indicate that the MNPs can compete favorably with other adsorbents while presenting the advantage of being highly selective for FFA over other oil components. Activated earth, activated carbon and chitosan were found to remove 45–55% of FFA in catfish oil with a 3.5 wt% adsorbent load at 25 °C after 4 h.¹⁸ Quaternary ammonium functionalized ion-exchange resins soaked with methanol were found to remove >93% of oleic acid from 5 wt% OA–soybean oil mixtures at 50 °C within 4 h with 20 wt% resin loading; from the reported data, one can estimate that about 50% of oleic acid is removed with 10 wt% resin loading.¹⁶ Although the reduction of acidity was not quantified in the paper by Cloutimon *et al.*, one can estimate from the reported adsorption data that porous magnesium silicates removed >90% of FFA

Table 1 Deacidification of vegetable oils^a

	Olive oil		Sunflower oil		
Acidity (wt%)	0.88%	0.88%	0.07%	0.07%	0.07%
MNP load (wt%)	10%	1%	10%	1%	0.5%
Acidity after treatment	0.13%	0.79%	0.02%	0.03%	0.04%
% FFA removed	85%	10%	71%	57%	43%
mg FFA removed/g MNP	75	90	5	40	60

^a 2 h, room temperature.

from crude palm oil with 2 wt% adsorbent loading at 50 °C within 1 h.¹⁹ It is worth noticing that none of these adsorbents have been demonstrated to be recyclable.¹⁶ This comparison with other adsorbents reported in the literature shows that MNPs have a quite acceptable efficiency and have the advantages of operating at room temperature in a short time (2 h) and being recyclable. Compared to the ion-exchange resins, they also have the advantage of not requiring the use of solvent.

It is worth noticing that there is no leakage of iron in the oil during the treatment with MNPs. Actually, crude vegetable oils contain traces of metals such as copper and iron.⁴⁵ Edible oils manufactured without refining contain relatively high quantities of iron and the usual concentrations of iron in good quality oils usually range from 2 to 5 ppm.⁴⁵ We have determined the concentrations of iron in olive and sunflower oils before and after treatment with MNPs using a fluorescence method³⁵ and found that there were no significant variations of the iron contents in the oils after removal of FFA with MNPs (see the ESI† for details).

4. Conclusion

MNPs were found to remove fatty acids from organic solution and crude oils efficiently and selectively. In addition to being non-toxic and biodegradable, the magnetite nanoparticles can also be easily separated using a simple magnet and recycled after basic treatment. The model study of the adsorption of OA from organic solution showed that the adsorption is rapid at room temperature, with equilibrium reached within less than 2 h. The adsorption kinetic was found to follow a pseudo-second-order model in accordance with a chemisorption mechanism. The adsorption isotherm data were found to be well described using the Langmuir single-site model with a maximum adsorption capacity of 125 mg OA per g of NP. FTIR spectra of the isolated fatty acid loaded NPs demonstrate the covalent binding of the carboxylate group to the particle surface in a bidentate/bridging manner. Accordingly, thermogravimetric analyses of NPs isolated after adsorption of different C16–C18 fatty acids revealed that the adsorption capacity does not significantly depend on the alkyl chain. Interestingly, it was found that desorption of FA is readily achieved by treatment with a basic solution, thus allowing facile regeneration of the native magnetic adsorbent. Using this procedure, it has been proved that MNPs can be re-used for at least 6 adsorption cycles with a good conservation of the adsorption capacity. The adsorption spectra of olive and sunflower oils after treatment revealed the selectivity of MNPs for FFA over pigments. MNPs were found to be able to remove up to 85% of FFA in crude vegetable oils within 2 h at room temperature with a 10 wt% adsorbent loading, suggesting that MNPs may be a promising adsorbent for deacidification of edible oils.

Owing to their affinity and selectivity for carboxylic acids as well as their facile separation, iron oxide magnetic particles may find valuable applications in chemistry, for instance as scavengers to facilitate the treatment of organic reactions where carboxylic acids (either as unreacted starting reagent or by-product) have to be removed. Further studies are currently being undertaken to investigate the chemical transformations of the fatty

acids⁴⁶ adsorbed on magnetite and hence potential applications in biodiesel production or for valorization of the isolated unsaturated fatty acids.

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