Ultrasound Assisted Synthesis of Hydroxylated Soybean Lecithin from Crude Soybean Lecithin as an Emulsifier

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Abstract: Soybean lecithin is a by-product obtained during degumming step of crude soybean oil refining. Crude soybean lecithin (CSL) contains major amount of phospholipids (PLs) along with minor amount of acylglycerols, bioactive components, etc. Due to presence of PLs, CSL can be used as an emulsifier. Crude soybean lecithin (CSL) was utilized to synthesize hydroxylated soybean lecithin (HSL) by hydroxylation using hydrogen peroxide and catalytic amount of lactic acid to enhance the hydrophilicity and emulsifying properties of CSL. To reduce the reaction time and to increase rate of reaction, HSL was synthesized under ultrasound irradiation. The effect of different operating parameters such as lactic acid, hydrogen peroxide, temperature, ultrasonic power and duty cycle in synthesis of HSL were studied and optimized. The surface tension (SFT), interfacial tension (IFT) and the critical micelle concentration (CMC) of the HSL (26.11 mN/m, 2.67 mN/m, 112 mg/L) were compared to CSL (37.53 mN/m, 6.22 mN/m, 291 mg/L) respectively. The HSL has better emulsion stability and low foaming characteristics as compared to CSL. Therefore, the product as an effective emulsifier can be used in food, pharmacy, lubricant, cosmetics, etc.

Key words: crude soybean lecithin, hydroxylation, by-product, ultrasound, hydroxylaed soybean lecithin, emulsifier

1 INTRODUCTION

Lecithin can be defined as a byproduct of oil processing, which is a complex mixture comprises of phospholipids (PLs) and triglyceride (TG) along with other minor components such as phytoglycolipids, phytosterols, tocopherols and fatty acids produced by degumming step of crude vegetable oils refining. The majority of commercial lecithin is derived from vegetable oils such as soybean. Lecithin contains major amount of phospholipids, which are polar lipids having surface-active properties. The important phospholipid components of soybean lecithin are phosphatidylcholine (PC) (13%-18%), phosphatidylethanolamine (PE) (10%-15%), phosphatidylinositol (PI) (10%-15%) and phosphatidic acid (PA) (5%-12%). Phospholipids (PLs) have both hydrophilic head and non-polar hydrophobic fatty acid tails. As amphipathic molecules, they tend to adsorb to surfaces or interfaces with the non-polar fatty acid tails facing the surface or oil phase and the polar heads facing the water phase, resulting in a decrease in the surface or interfacial tension. The presence of both hydrophilic and lipophilic groups in PLs makes them widely used as emulsifying agents or surface active agents. Soybean lecithin has potential application as a multifunctional additive for food, pharmaceutical and other industries. Lecithin is used in bread making as an anti-staling agent and in margarines as an anti-spattering and also can be used as anti-foaming agent in lubricants.

Soybean PLs mainly contain unsaturated fatty acids chain such as oleic, linoleic and linolenic, etc. An effective way to improve the emulsifying properties for o/w system and water dispersibility to increase the hydrophilicity of soybean lecithin is hydroxylation of unsaturated fatty acids present in PLs. Hydroxylation improves hydrophilic properties and enhances moisture retention to the lecithin. This process mainly involves the addition of hydroxyl groups at the points of unsaturation of fatty acids present in PLs using hydrogen peroxide under the catalytic action of water-soluble aliphatic carboxylic acids (e.g., lactic acid, acetic acid, tartaric acid, citric acid) as shown in Fig. 1. Lactic acid has been mostly used in hydroxylation of lecithin.

Abbreviations: PLs: Phospholipids, CSL: Crude soybean lecithin, HSL: Hydroxylated soybean lecithin, IV: Iodine value, PV: Peroxide value, AV: Acid value, SFT: Surface tension, IFT: Interfacial tension, CMC: Critical micelle concentration

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when the product is chosen for edible purposes. It is useful in baking application of fats and retard staling

The conventional hydroxylation methods involve reacting higher concentration of hydrogen peroxide in the presence of organic acids to obtain higher conversion rate. The use of higher concentration of hydrogen peroxide and exposure of soybean lecithin to higher temperatures for longer reaction times may degrade the lecithin. Due to the high heating efficiency in a short time, ultrasonic irradiation conditions can accelerate any type of organic reactions compared to conventional thermal heating. Under ultrasonic irradiation, as an acoustic pressure wave from a transducer propagates through the aqueous medium, changes in pressure causes cavitation bubbles to form oscillate and subsequently collapse and this phenomenon known as cavitation. In ultrasound assisted synthesis, microstreaming and microturbulence was generated during asymmetric cavity collapse and the physical effects was caused by shock waves, which helps for the process intensification. The reaction chemistry and propagation by a way of enhanced mass transfer and interphase mixing can be favoured by the use of sonochemical reaction. The use of ultrasound may facilitate operation at milder operating parameters. Ultrasonic irradiation also has the unique feature of providing environmentally friendly processes. Considering the large number of industrially important hydroxylation reactions, there have been relatively few publications dealing with the use of ultrasound in this area.

The objective of the present work is to provide a simple, rapid and an environmentally friendly ultrasound assisted process for hydroxylation of crude soybean lecithin using hydrogen peroxide and lactic acid at lower reaction times with higher conversion rates over conventional heating method. The effect of operating parameter such as lactic acid, hydrogen peroxide, temperature, ultrasonic power and duty cycle in synthesis of hydroxylated soybean lecithin (HSL) were studied. The surface tension reducing properties were compared. In this study, the Iodine value (IV), Peroxide value (PV), Acid value (AV), Surface tension (SFT), Interfacial tension (IFT), the Critical micelle concentration (CMC), emulsion stability and foamability of CSL and HSL were determined for the ultrasound irradiation method and compared with conventional method.

2 MATERIALS AND METHOD
2.1 Materials

Crude soybean lecithin (CSL) was obtained as gift samples from M/s Vav Life Sciences Pvt. Ltd., Mumbai, India. Hydrogen peroxide (30% aqueous solution), lactic acid (75%) and n-hexane (AR grade) were procured from M/s Thomas Baker, Mumbai. All the other reagents and solvents obtained from commercial sources were of analytical grade.

2.2 Experimental methods

2.2.1 Synthesis of hydroxylated soybean lecithin (HSL)

Crude soybean lecithin (CSL) (10 g) with n-hexane (30 mL), lactic acid (2-3% of lecithin, wt/wt) and hydrogen peroxide (5-20% of lecithin, v/vt) were charged in a 100 mL round bottom flask fitted with ultrasonic probe and reflux condenser. The reaction was carried out using ultrasonication and monitored by IV. The effect of different operating parameters such as lactic acid (2-3% of lecithin, wt/wt), hydrogen peroxide (5-20% of lecithin, v/vt), temperature (30-80°C), ultrasonic power (60-120 W), duty cycle (30-80%) for the synthesis of hydroxylated soybean lecithin (HSL) were studied. The product was dried under vacuum and analyzed for IV.

2.2.2 Properties of crude soybean lecithin (CSL) and hydroxylated soybean lecithin (HSL)

2.2.2.1 Determination of physico-chemical properties of CSL and HSL

The IV, AV, PV, viscosity, acetone insoluble and toluene insoluble matter were determined with usage of AOCS method (three measurements for each sample). The color was determined using Lovibond 3000 Comparator Gardner Color Unit. The fatty acid compositions of crude soybean lecithin (CSL) was determined using a gas chromatograph (Chemito 1000, Thermo Scientific, Nasik, India) equipped with a flame ionization detector and a BPX-5 column (30 m length, 0.25 mm).

2.2.2.2 Surface tension (SFT), interfacial tension (IFT) and critical micelle concentration (CMC) measurements

The surface tension and interfacial tension (IFT) against n-heptane for 0.05% concentrations of solution of CSL and HSL were measured at 25°C by Whelmy plate technique with Kruss K-100 tensiometer where standard platinum plate (PLO3) was used as a probe. Based on the variations

Fig. 1 Reaction scheme of synthesis of hydroxylated soybean lecithin (HSL) from crude soybean lecithin (CSL).
in surface tension with respect to concentration CMC was determined using Kruss K-100 tensiometer\(^5\). All the values are the averages of the three measurements.

2.2.2.3 Foamability test

Foaming power was measured by using a Ross & Miles apparatus for 0.05% concentrations of solutions of CSL and HSL\(^6\). For each sample solution, the experiment was repeated three times and the mean value of three of the results was calculated.

2.2.2.4 Emulsion stability test

The emulsifying power \(\mu\) (Emulsion stability) was defined as the necessary time for the separation of aqueous layer from the emulsion. Emulsion stability test was performed as per the procedure described by Aura et al.\(^7\). Accordingly, CSL and HSL were dissolved in sunflower oil at 0.05% (wt/v) of the total emulsification volume consisting of sunflower oil and water in 2:3, v/v. The contents were homogenized using homogenizer at 5,000 rpm for 60 s and the emulsion was poured into a 100 mL measuring cylinder. The time interval required to separate 10 and 20 mL aqueous layer from oily layer was recorded. The experiment was repeated 3 times for each sample and average of three tests was calculated. The longer time indicates the better emulsifying power.

3 RESULTS AND DISCUSSIONS

3.1 Physico-chemical properties of crude soybean lecithin (CSL)

The fatty acid composition and physico-chemical properties of CSL are listed in Table 1. Crude soybean lecithin contains large amounts of linoleic acid, oleic acid, palmitic acid followed by other constituents such as linolenic acid, stearic acid, etc. The IV of CSL was 91.38 g I\(_2\)/100 g due to the presence of higher amount of unsaturated fatty acids in CSL.

3.2 Study of effect of operating parameters on synthesis of hydroxylated soybean lecithin (HSL) from crude soybean lecithin (CSL)

3.2.1 Effect of the concentration of hydrogen peroxide

The addition of hydrogen peroxide as hydroxylating agent is one of the important parameter to determine the extent of conversion. In order to study the effect of the concentration of hydrogen peroxide on reduction in iodine value, different experiments were carried out with 5%, 10%, 15% and 20% hydrogen peroxide (v/wt of CSL) while keeping other parameters constant such as temperature of 50°C, reaction time of 90 minutes, lactic acid loading 3% (wt/wt of CSL), ultrasound power 100 W and duty cycle 70% and obtained results are plotted in the Fig. 2. It has been observed that the reduction in IV of CSL in the presence of ultrasound from 94.5-45.0 with an increase in the concentration of H\(_2\)O\(_2\) from 5% to 15%. With the increase in the quantity of H\(_2\)O\(_2\) in the reaction mixture, lowers the viscosity of the reaction mixture and hence resulting into the enhanced cavitation. This increase in the cavitation intensity leads to formation of enhanced emulsion with smaller drop sizes which gives rise to additional area for the reaction and hence enhanced reduction in IV. With further increase in the concentration of H\(_2\)O\(_2\) beyond 15%, there is no significant change in the reduction of IV. Further increase in H\(_2\)O\(_2\) beyond 15% may lead to decomposition of lecithin. Therefore, the optimal concentration of H\(_2\)O\(_2\) was found to be 15%.

3.2.2 Effect of the lactic acid loading

To study the effect of lactic acid concentration on the
hydroxylation reaction of CSL, the experiments were performed at four different concentrations viz. 2\%, 2.5\%, 3\% and 3.5\% (wt/wt of CSL) of lactic acid loading with constant reaction temperature of 50°C, reaction time of 90 minutes, 15\% \text{ H}_2\text{O}_2 (v/wt of CSL), ultrasonic power 100 W, duty cycle 70\%. The results obtained are shown in Fig. 3. It has been seen from the figure that an increase in the concentration of lactic acid from 2-3\% shows the faster reduction in IV. However, further increase in the catalyst concentration beyond 3\% has no significant effect on the conversion of CSL. The lactic acid acts as catalyst. The main function of lactic acid with \text{H}_2\text{O}_2 in the hydroxylation reaction was in making available sufficient amount of peroxy acids for hydroxylation of unsaturated fatty acid chain of CSL. Due to microstreaming effect of ultrasound, the rate of hydroxylation of CSL was faster as compared to conventional heating method. An increase in the lactic acid loading increases the active sites of catalyst. Hence, conversion was increased till 3\%. Furthermore, due to availability of the excess of lactic acid for hydroxylation beyond 3\% loading did not result in any further increase in the conversion. Therefore, the optimized amount of lactic acid loading was found to be 3\% (wt/wt of CSL).

3.2.3 Effect of the temperature

To investigate the effect of the reaction temperature on the hydroxylation reaction of CSL, the temperature was varied from 40°C to 55°C. The optimal parameters such as reaction time of 90 minutes, 15\% \text{ H}_2\text{O}_2 (v/wt of CSL), lactic acid loading 3\% (wt/wt of CSL), power dissipation of 100 W and duty cycle of 70\% were kept constant. The effect of reaction temperature on conversion of CSL is shown in Fig. 4, which shows that on increasing the temperature from 40 to 55°C, conversion of CSL to HSL increases. This increase in conversion with increase in temperature was mainly attributed to increase in miscibility of n-hexane in CSL and extent of cavitation at different temperature. Also the diffusion phenomenon is dominant at low temperature owing to high cavitation intensity as at low temperature rate of bubble generation is low but they collapse with high intensity\(^{10}\). Thus, the mass transport of the reactants on the catalytic sites is high. Increase in temperature decreases the viscosity and surface tension of the reaction mixture, which affects bubble formation and its subsequent collapse\(^{10}\). However, further rise in the temperature to 55°C, there was no significant change in the reduction of IV and further rise above 55°C may lead to the decomposition of CSL. Therefore, the optimum temperature found to be 50°C.

3.2.4 Effect of ultrasound power

To achieve an efficient cavitation for hydroxylation of CSL, ultrasonic power dissipation is an important parameter. To study the effect of ultrasound power on the hydroxylation reaction of CSL, the experiments were performed by varying the input power from 60-120W, while other parameters such as lactic acid loading 3\% (wt/wt of CSL), reaction temperature of 50°C, reaction time of 90 minutes, 15\% \text{ H}_2\text{O}_2 (v/wt of CSL), ultrasonic power 100 W, duty cycle 70\% kept constant. The obtained results have been shown in Fig. 5. It can be seen that conversion increases with an increase in the ultrasonic power from 60-100W. Further increase in the power beyond 100W has no significant effect on the conversion of CSL. This increase in the conversion with reduction in IV is attributed to the fact that, with an increase in power dissipation the cavitation intensity increases, which increases mixing and emulsification of two immiscible liquid layer. The cavitations intensity increases with an increase in the ultrasonic power, providing the formation of microturbulance, micro-streaming and micro-emulsion and hence enhances mass transfer\(^{21,22}\). Hence, the optimum power dissipation was taken to be 80 W.
3.2.5 Effect of Duty cycle

Ultrasonic duty cycle is an important operating parameter which affects the cavitational intensity. It is expressed in percentage indicates the ratio of ultrasound probe ON time and that of ON and OFF time taken together. Dey and Rathod et al. reported that the ultrasonicator can be used both in a pulse mode and a continuous mode\(^a\). Continuous mode is energy inefficient as compared to pulse mode and also causes erosion of the tip. The main purpose of using pulse mode ultrasound operation is to reduce the net power consumption in the system and to attain sufficient cooling of transducer, which will eventually enhance the durability of the equipments. To investigate the effect on reaction, the ultrasonic duty cycle was varied from 30\(^b\) to 80\(^c\) by keeping other optimal parameters such H\(_2\)O\(_2\) concentration\(^d\), lactic acid loading of 3\(^e\), wt/wt of CSL\(^f\), temperature\(^g\), reaction time\(^h\), ultrasonic power of 80 W constant. Effect of duty cycle on reduction of iodine value of CSL are shown in Fig. 6. It can be observed that as the ultrasound duty cycle increases from 30\(^b\) (3 s ON and 7 s OFF) to 70\(^c\) (7 s ON and 3 s OFF) the reduction of IV increases and then no significant increase in conversion was observed for further increase in the duty cycle to 80\(^c\) (8 s ON 2 s OFF). Hence the reaction was carried out in pulse mode at optimum duty cycle of 70\(^c\).

3.3 Comparison of ultrasonic irradiation with conventional stirring

The performance of ultrasound assisted hydroxylation of CSL was compared with the conventional route by carrying out the conventional reaction in a stirred batch reactor in absence of ultrasound irradiation. The optimized operating parameters of the ultrasonic irradiation such as 15\(^i\) H\(_2\)O\(_2\) (v/wt of CSL), lactic acid loading of 3\(^e\) (wt/wt of CSL) and temperature 50\(^c\) were used for the conventional stirring process and the obtained results were depicted in Fig. 7. The results showed that 52.38\(^i\) reduction in IV was obtained in 90 mins by the ultrasonic irradiation whereas the conventional stirring gave 15.24\(^i\) conversion in similar reaction time. An intense level of microturbulence and microemulsions was generated by ultrasonic irradiation which results in the increased interfacial area and eliminated mass transfer resistance. Therefore, it can be concluded that ultrasound assisted reaction is faster and requires less time in comparison of conventional stirring method.

3.4 Properties of CSL and HSL

3.4.1 Physico-chemical properties of CSL and HSL

The colour of hydroxylated soy lecithin obtained by ul-
Ultrasonic assisted hydroxylation with 15% hydrogen peroxide was found to be 15 Gardner units as against 18 Gardner units for crude soy lecithin which was shown in Table 2. Ultrasound assisted hydroxylation reaction was greatly accelerated using lactic acid (3%, wt/wt of CSL) and hydrogen peroxide (15%, v/wt of CSL) at 50°C with 100 W power and 70% duty cycle as compared to conventional method. Hydroxylation of the unsaturated fatty acids will result in the reduction in the degree of unsaturation which was determined through iodine value measurement. Under ultrasound irradiation, reduction in IV was observed up to 52.38% within 90 mins as compared to conventional thermal heating under similar reaction conditions, which suggests that as a result of CSL hydroxylation, double bonds of unsaturated fatty acids in PLs molecules were converted to C-C single bonds with hydroxyl groups. Moreover, lecithin with the level of peroxide value above 5 mmol O₂/kg should not be used in pharmaceuticals, cosmetics and food industries. Taking this into account, due to 52.38% reduction in IV and low peroxide value, the synthesized HSL can be used in food industries.

3.4.2 Surfactant properties of CSL and HSL
To understand the surface activity of CSL and HSL, the SFT, IFT and CMC measurements were carried out. The findings are tabulated in Table 2. The modification of the lecithin structure will influence the nature and extent of adsorption at the interface. Addition of hydroxyl group into the unsaturated bonds in the lecithin structure will alter its hydrophilicity that is the HLB, and its structure and consequently influence the surface active behaviour. Therefore, the effect of the hydroxylation on the surface and interfacial tension reduction can also be related to the degree and nature of surfactant adsorption at the air-liquid and liquid-liquid interface. 23, 24

The surface tension of 0.05% CSL was 37.53 mN/m. It was reduced to 26.11 mN/m for HSL. From this results we can infer that, hydroxylation of lecithin improved the surface tension reduction ability of lecithin. The interfacial tension of 0.05% surfactant solutions of CSL and HSL were 6.22 mN/m and 2.67 mN/m respectively. The IFT of HSL was found significantly lower than CSL. This could be due to the lecithin structure changes resulting from incorporation of hydroxyl group through hydroxylation, which alters the hydrophobic character of the surfactant and influences the nature of the surfactant arrangement at the interface.

To understand the role of surfactant adsorption, it is necessary to know the amount of material adsorbed at the interface. Hence, the critical micelle concentration (CMC) depicts the concentration of surfactant at the interface. CMC is known as an indicator of the effectiveness of surface tension reduction and it also helps to identify good emulsifier. 25 Introduction of the hydroxyl groups onto the lecithin structure helps to increase the hydrophilicity and the HLB. Therefore, HSL (112 mg/L) recorded a comparatively lower CMC than CSL (291 mg/L). Above the CMC value, the surface activity of an emulsifier does not enhance with the addition of an emulsifier in excess. Thus, the smaller the CMC of the emulsifier, the better its emulsion stability.

3.4.3 Emulsion stability
The nature and extent of packing of the phospholipids at the oil-water interface is an important factor for the emulsification behaviour of lecithin. It should be noted that the emulsification behaviour is influenced by the modification of hydrophobic group of lecithin. The presence of unsaturated fatty acids chains in PL molecules of lecithin make it more rigid and hence impacted negatively on its packing at the interface. The degree of the unsaturation was decreased through hydroxylation of CSL, which made the hydroxylated lecithin less rigid and flexible. This flexible structure of HSL will result in densely packed surfactant arrangement at the oil-water interface and it will increase the interaction between lecithin molecules and aqueous film at the oil-water interface, which eventually helps to improve the interfacial activity of lecithin. 26 Also, the increased interaction between surfactant and aqueous film at oil-water interface may provide a strong barrier to droplets coalescence which will enhances the emulsion stability.

### Table 2 Properties of crude soybean lecithin (CSL) and hydroxylated soybean lecithin (HSL)

| Properties                        | Crude soybean lecithin (CSL) | Hydroxylated soybean lecithin (HSL) |
|----------------------------------|------------------------------|-------------------------------------|
| IV (g I₂/100 g)                  | 91.38                        | 45.0                                |
| PV (mmol O₂/kg)                  | 2.6                          | 3.24                                |
| Acid value (mg KOH/ g)           | 22.6                         | 22.1                                |
| Surface tension (SFT) (0.05%) (mN/m) | 37.53                      | 26.11                               |
| Interfacial tension (IFT) (0.05%) (mN/m) | 6.22                      | 2.67                                |
| Critical micelle concentration (CMC) (mg/L) | 291                        | 112                                 |
| Colour Gardner                   | 18                           | 15                                  |
The results of emulsion stability of 0.05% solution of CSL and HSL are depicted in Fig. 8, which shows the time required for the separation of 10 and 20 mL aqueous layer from oily layer. The values indicated that the emulsion formed with hydroxylated soybean lecithin (36 min for 10 mL; 84 min for 20 mL) was more stable compared to crude soybean lecithin (24 min for 10 mL; 56 min for 20 mL).

3.4.4 Foamability test

CSL itself does not have good foaming properties. After hydroxylation of CSL, HSL shown better emulsification properties and water dispersibility as compared to CSL. Therefore, HSL showed low foaming characteristics than CSL (Fig. 9). Due to these properties, HSL can be used as defoamer or antifoamer to control the foam. It can be used as an antifoaming or defoaming lubricant additives to control the foam because foams results in the detrimental effect of small pin holes on the paper coated surface. Hence, an improved lubricant for coating moving webs can be provided with low foaming characteristics of HSL.

4 CONCLUSIONS

The present study demonstrated the applicability of ultrasound irradiation for the intensified synthesis of hydroxylated soybean lecithin (HSL) from crude soy lecithin (CSL). The optimum operating parameters for the present work were found to be H2O2 concentration of 15% (v/wt of CSL), lactic acid loading 3% (wt/wt of CSL), temperature 50°C, ultrasonic power 100 W, 70% duty cycle. In this process, ultrasonic irradiation at 22 kHz significantly enhanced the HSL synthesis from CSL with reduction in iodine value up to 52.38% over a reaction time of 90 min whereas conventional stirring method showed reduction in iodine value up to 15.24%. Cavitation generated using ultrasonic irradiation mainly affects the mass transfer rates, emulsification of the reaction mixture and ensures uniform distribution of the reactants. Therefore, the ultrasound-irradiated method was considered as a simple, rapid and efficient for the production of hydroxylated soybean lecithin. HSL has significantly reduced the SFT, IFT and CMC than the CSL. Considering the obtained degree of SFT, IFT reduction, the CMC value and better emulsion stability with low foaming characteristics, the HSL should be considered as more efficient emulsifier in food, pharmaceuticals, lubricants and cosmetics than the CSL.

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REFERENCES

1. Erickson, D.R. Practical Handbook of Soybean Processing and Utilization. 1st ed. Elsevier, pp. 297-299 (1995).
2. Ng, Tzi-Bun. Soybean - Applications and Technology. Inech, China, pp. 342-345 (2011).
3. Dasheill, G.L. Lecithin in food processing applications. in Lecithins: Sources, manufacture and uses (Szuhaj, B.F. ed.), American Oil Chemists’ Society Press, Champaign, pp. 213-236 (1989).
4. Endre, F.S; Szuhaj, B.F. Lecithins. in Bailey’s industrial oil and fat products (Hui, Y.H. ed.) Vol 1, 5th ed. Wiley, New York, pp. 311-395 (1996).
5. Agboola, S.O.; Singh, H.; Munro, P.A.; Dalgleish, D.G.; Singh, A.M. Stability of emulsions formed using whey protein hydroxylate: effects of lecithin addition and restoring. J. Agric. Food. Chem. 46, 1814-1819 (1998).
6. Bonekamp, A. Phospholipid technology and applications. in ADM specialty ingredients Vol 22, Oily Press, Hamburg, pp. 141-152 (2008).
7) Schmidt, J.C.; Orthoefer, F. Lecithin in baking applications. in Lecithins (Szuhaj, B.F.; List, G.R. eds.), American Oil Chemists’ Society Press, Champaign, pp. 203-211 (1985).
8) Julian, P.L.; Iveson, H.T.; Leichti, M.M. Process of treating phosphatides and product. US Patent 2,629,662 (1953).
9) Hsiao, M.C.; Lin, T.W. Ultrasound assisted rapid synthesis of ionic liquids 2011 IEEE: International Conference on Consumer Electronics, Communications and Networks (CECNet) (2011).
10) Kwiatkowska, B.; Bennett, J.; Akunna, J.; Walker, G.M.; Bremner, D.H. Stimulation of bioprocesses by ultrasound. Biotechnol. Adv. 29, 768-780 (2011).
11) Mason, T.I. (ed.) Chemistry with Ultrasound, Critical reports on applied chemistry Vol. 28, Elsevier Science Publications, London (1990).
12) Badgujar, K.C.; Bhanage, B.M. The combine use of ultrasound and lipase immobilized on co-polymer matrix for efficient biocatalytic application studies. J. Mol. Catal. B: Enzym. 122, 255-264 (2015).
13) Jadhav, A.J.; Holkar, C.R.; Goswami, A.D.; Pandit, A.B.; Pinjari, D.V. Acoustic cavitation as a novel approach for extraction of oil from waste date seeds. ACS Sustain. Chem. Eng. 4, 4256-4263 (2016).
14) Firestone, D. Official methods and recommended practices of the American Oil Chemists’ Society, 5th ed. AOCS Press, Champaign (1998).
15) Rosen, M.J. Surfactants and Interfacial phenomena. 3rd ed. A John Wiley & Sons Inc., Hoboken, NJ, pp. 277-302 (2004).
16) Ross, J.; Miles, G.D. An apparatus for comparison of foaming properties of soaps and detergents. J. Am. Oil. Chem. Soc. 18, 99-102 (1941).
17) Aura, A.M.; Forsell, P.; Mustranta, A.; Suortti, T.; Poutanen, K. Enzymatic hydrolysis of oat and soya lecithin: effects on functional properties. J. Am. Oil. Chem. Soc. 71, 887-891 (1994).
18) Vetal, M.D.; Lade, V.G., Ratnhod, V.K. Extraction of ursoic acid from Ocimum sanctum by ultrasound: Process intensification and kinetic studies. Chem. Eng. Process 69, 24-30 (2013).
19) Adewuyi, Y.G. Sonochemistry: Environmental Science and Engineering Applications. Ind. Eng. Chem. Res. 40, 4681-4715 (2001).
20) Gogate, P.R.; Wilhelm, A.M.; Pandit, A.B. Some aspects of the design of sonochemical reactors. Ultrason. So- nochem. 10, 325-330 (2003).
21) Maddikeri, G.L; Pandit, A.B.; Gogate, P.R. Ultrasound assisted interesterification of waste cooking oil and methyl acetate for biodiesel and triacetin production. Fuel Process Technol. 116, 241-249 (2013).
22) Dey, S.; Ratnhod, V.K. Ultrasound assisted extraction of b-carotene from Spirulina platensis. Ultrason. Sonochem. 20, 271-276 (2013).
23) Zrinyi, M.; Horvolgyi, Z.D. From colloids to nanotechnology (Progress in Colloid and Polymer Science Vol. 125), Springer (2004).
24) Rawicz, W.; Olbrich, K.C.; McIntosh, T.; Needham, D.; Evans, E. Effect of chain length and unsaturation on elasticity of lipid bilayers. Biophys. J. 79, 328-339 (2000).
25) Friberg, S.E.; Larsson, K. Food Emulsions. 3rd ed. Marcel Dekker, New York, pp. 141-188 (1997).
26) Nyankson, E.; Demir, M.; Gonen, M.; Gupta, R.B. Interfacially-active hydroxylated soybean lecithin dispersant for crude oil spill remediation. ACS Sustain. Chem. Eng. 4, 2056-2067 (2016).
27) Nikoloff, K.P. Surfactant-free lubricant for coating moving webs. US patent 5,858,933 (1999).