Removal of Free Fatty Acid from Plant Oil by the Adsorption Process

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Abstract. The food oil refinery process for deacidification is usually conducted by the neutralization after degumming. In this study, commercialized resins will be used as adsorbents to remove the free fatty acid (FFA) in food oil without using any solvent. Applying this environmental friendly green process, the energy efficiency will be increased and the waste water will be reduced compared to the traditional process. The selected adsorbent can be reused which may reduce the process cost. Instead of using alkali neutralization, the proposed process may reduce the concern of food oil security. The commercial resins A26OH and IRA900Cl were compared as adsorbents to remove the FFA in deacidification for refinery of food oil without adding any alkali chemicals. This process will be conducted to remove the FFA from peanut oil in this study. Besides, this study will get the adsorption isotherms for one of the better sorbents of A26OH or IRA900Cl to remove FFA from peanut oil under 25, 35, and 45°C. The Langmuir and Freundlich isotherm models were compared to fit the experimental data. The obtained isotherm data is important for the adsorption system design.

1. Introduction
Human may obtain the nutrients such as carbohydrates, proteins and lipids by food. Lipids are the main source of metabolic energy for human body. The main sources of edible lipids are the oils and fats, including plant and animal fats. In addition to glycerides, there are impurities such as phospholipids, free fatty acids (FFA) and others in crude oil that causes deterioration of the quality and curtailment of shelf life of oil whether plant oil or animal oil. Therefore, these impurities must be removed from crude oil through refining process. [1-3] There are quite a few refining process in business despite commercially available. In this study, using commercial resin as adsorbent in the absence of adding solvent for the adsorption process to remove FFA in plant oil. The application of environmentally friendly green process also enhances the use of energy, reduces the use of toxic substances and the generation of waste while improving efficiency and product quality, and emphasizes recyclable and reusable designs to mitigate environmental pollution load and impact, but also reduce the concern about food safety. [4-6]

2. Deacidification by ion exchange resins
The refining process of edible oil is conducted by steps of degumming, deacidification, bleaching and deodorization. The presences of FFA in edible oil raise the possibility of rancidity, even small amounts of fatty acids that reduce the quality of the oils. [7] Moreover, the presence of free fat causes generation of corrupt odours and accelerates oxidation process. [8] In recent years, many studies use strong anion exchange resins to adsorb oleic acid or FFA in plant oil, but all of the studies were operated continuously in packed beds with alcoholic solvents.
Hadijah used a strong anion exchange resin, IRA900Cl, for adsorption removal of free fatty acids in Kapok seed oil, Bagilumbang seed oil and Candle nut oil under a packed bed shown in Figure 1 with n-hexane as solvent under room temperature to obtain the impact of the effect of different plant oil variety on removal of acid value. The results are shown in Table 1, the removal rate of acid value is 95%, and the effect of deacidification is very good. And also recovery the ion exchange resin IRA900Cl after desorption and then carry out the deacidification of Bagilumbang seed oil for repeated 5 times. Repeated uses of 3 times of IRA900Cl within the deacidification effect are maintained at a fine level, the results are shown in Table 2. Additionally found that the use of IRA900 Cl for deacidification can achieve bleaching effect. [9]

Cren used a strong anion exchange resin, A26OH, to remove oleic acid in an oleic acid ethanoic solution under packed bed operation at room temperature to investigate the effect of flow rates and initial concentration of oleic acid. The results shown in Table 3, the removal rate of acid value is 97%, and the effect of deacidification is very well. And also found that the higher initial concentration of oleic acid or the lower flow rate, the higher removal rate of oleic acid. Conversely, the higher initial concentration of oleic acid or the higher flow rate, the higher adsorption amount of oleic acid [10]

![Figure 1. Schematic of packed bed set up for adsorption deacidification of different plant oils by using ion exchange resin IRA900Cl.](image)

| Oil variety     | Initial acid value of oil (mg KOH/g) | Acid value of oil after adsorption (mg KOH/g) | Removal rate of acid value (%) |
|-----------------|--------------------------------------|---------------------------------------------|------------------------------|
| Kapok seed oil  | 18.12                                | 0.59                                        | 96.74                        |
| Bagilumbang seed oil | 13.20                                | 0.56                                        | 95.76                        |
| Candle nut oil  | 10.80                                | 0.54                                        | 95.00                        |

| The number of reuses | Acid value of oil after adsorption (mg KOH/g) | Removal rate of acid value (%) |
|----------------------|-----------------------------------------------|------------------------------|
| 1                    | 0.56                                          | 95.76                        |
| 2                    | 0.59                                          | 95.53                        |
| 3                    | 0.59                                          | 95.53                        |
| 4                    | 5.60                                          | 57.58                        |
| 5                    | 10.32                                         | 21.82                        |
Table 3. The deacidification results of adsorption different plant oils by using ion exchange resin IRA900Cl \([10]\)

| Flow rate (mL/min) | Initial concentration of oleic oil (wt\%-%) | Operation time (min) | Removal rate of acid value (%) | Adsorption amount (g acid/g dry resin) |
|---------------------|-------------------------------------------|----------------------|-------------------------------|----------------------------------------|
| 19.4                | 4.21                                      | 198                  | 97.7                          | 1.23                                   |
| 19.5                | 6.13                                      | 155                  | 98.3                          | 1.29                                   |
| 30.0                | 4.22                                      | 136                  | 97.8                          | 1.17                                   |
| 30.0                | 6.34                                      | 95                   | 98.2                          | 1.22                                   |
| 16.7                | 4.90                                      | 180                  | 98.1                          | 1.18                                   |
| 33.2                | 4.90                                      | 120                  | 97.9                          | 1.13                                   |
| 26.3                | 3.59                                      | 176                  | 97.7                          | 1.13                                   |
| 24.5                | 6.50                                      | 124                  | 98.2                          | 1.22                                   |
| 24.9                | 5.19                                      | 135                  | 98.5                          | 1.23                                   |
| 24.0                | 5.26                                      | 133                  | 97.8                          | 1.24                                   |
| 24.3                | 5.18                                      | 132                  | 97.9                          | 1.18                                   |

3. Experimental method

3.1. Materials
Commercial ion exchange resin IRA900Cl (Amberlite®IRA900 chloride form) and A26OH (Amberlyst®A26 hydroxide form), and oleic acid with format of 65.0-88.0%, Ph. Eur. Grade were purchases from Sigma-Aldrich. Commercial oil Special Grad Peanut Oil was purchase from a manufacturer in Taoyuan Taiwan. Fresh Squeezed under Low-Temperature Peanut Oil was purchase from Master Chen Oil Workshop in Changhua Taiwan.

3.2. Pretreatment of oil
In order to increase the initial acid value of oil, add oleic acid directly into peanut oil. Since the content of free fatty acids in oils is often defined as the content of oleic acid in oils, the method of adding oleic acid directly into oils is also widely used in many studies.[9-11] In order to reduce the initial acid value of the oil, there are some manufacturers add good quality oil with low acid value into high-acidity oil products with poor quality to reduce the cost and acid value of their oil products. In this study, the peanut oil product from Master Chen Oil Workshop which has been through membrane filtration was added into commercial peanut oil that had not been filtered.

3.3. Pretreatment of adsorbents
Put 3 grams of ion exchange resin on a Petri dish covered with aluminium foil paper, placed into a constant temperature oven at 50°C for 3 hours to remove the moisture on the surface of adsorbent.

3.4. Adsorption equilibrium time
Loading commercial peanut oil, which acid value was unadjusted into 20 mL sample bottle, and add 1 wt% of ion exchange resin IRA900Cl and A26OH respectively. Then placed in a constant temperature circulating water bath under 35°C, the stirring speed was set to 550 rpm to operate 0.5, 1, 1.5, 2, 2.5, 3 hours adsorption respectively. After the adsorption, the ion exchange resins are separated from the oil by centrifugation. Finally, detecting the acid value of the deacidified peanut oil from which the adsorbent has been removed and calculate the adsorption efficiency index to compare the effect of the adsorbent. The adsorption equilibrium time obtained for this test is taken as the adsorption time of all subsequent experiments in this study.

3.5. Isothermal adsorption curve
Loading commercial peanut oil, which acid value was adjusted to 1, 3, 5, 8, 10, 13 mg KOH/g into 20 mL sample bottle respectively, and add 1 wt% of ion exchange resin A26OH. Then placed in a constant temperature circulating water bath under 35°C, the stirring speed was set to 550 rpm. The adsorption time was set as the adsorption equilibrium time obtained from Section 3.4. After the adsorption, the ion exchange resins are separated from the oil by centrifugation. Finally, detecting the acid value of the deacidified peanut oil from which the adsorbent has been removed and calculate the amount of adsorption; draw it into isothermal adsorption curve and further fit Langmuir and Freundlich adsorption isotherm models to understand the adsorption patterns.

4. Results and Discussion

4.1. Pretreatment of adsorbents
The specific surface areas of adsorbents with and without the pretreatment were measured by Laser Diffraction Method and the results are listed in Table 4. It can be seen from the table that the specific surface area of IRA900Cl is larger than that of A26OH, while the specific surface area of pretreated IRA900Cl is smaller than that of the one without pretreatment. However, the specific surface area of A26OH is not significantly changed due to the pretreatment. The surface picture results of the adsorbents with and without pretreatment by transmission electron microscope are shown in Figure 2. It can be seen from the figure that the treated adsorbent is cracked or even broken, and the surface of the adsorbent is smooth.

4.2. Adsorption equilibrium time
1 wt% ion exchange resin A26OH and IRA900Cl were used to adsorption FFA from pretreated peanut oil respectively under 35°C. Results of equilibrium concentration affected by adsorption time are shown in Figure 3. Results of removal rate of FFA affected by operation time are shown in Figure 4.

As shown in Figure 3. After 0.5 hours of adsorption, the equilibrium concentration decreased from 15.75 mg/g to 13.55 mg/g; after 1 hour of adsorption, the equilibrium concentration decreased slightly to 12.45 mg/g and maintained for 1.5 hours; after 2 hours, the decrease of equilibrium concentration was less. After the equilibrium concentration dropping to 11.7 mg/g and few changes to 3 hours, the adsorption equilibrium time of A26OH to could be regarded as 3 hours. The IRA900Cl adsorption for 0.5 hour equilibrium concentration from 15.75 mg/g down to 15 mg/g, is a relatively large drop; after 1 hour of adsorption, the equilibrium concentration decreased only to 14.8 mg/g; after two hours of adsorption, the equilibrium concentration also dropped to only 14.55 mg/g and maintained to 3 hours, so that IRA900Cl adsorption equilibrium time can be considered as 3 hours. A26OH was found to up to 25.5% of FFA removed from Figure 4, removal rate of FFA by IRA900Cl was less than 10%. A26OH adsorption was significantly higher than that of IRA900Cl, so the future use of A26OH as the experimental adsorbent in this study.

4.3. Isothermal adsorption curve
The ion exchange resin A26OH was used to adsorb peanut oil with different initial concentrations of FFA under 25, 35 and 45°C. The isothermal adsorption curve results were fitted to the Langmuir Isothermal adsorption model and the Freundlich isothermal adsorption model shown in Figure 5 and the fitting contanst results were given in Table 5. It was found from Table 5 that coefficient of determination (R²) for fitting Langmuir isothermal adsorption model were higher than Freundlich model under all the operation temperature; accordingly, Langmuir isotherm adsorption model was suitable to describe the adsorption for ion exchange A26OH to adsorb FFA from peanut oil. The maximum adsorption capacities (Qo) were found in Table 5, whether at any operation temperature, value is the same of 555.56 mg/g. And Freundlich experience index (n) was found that n> 1; hence the adsorption for ion exchange A26OH to adsorb FFA from peanut oil was favorable adsorption.
Table 4. The specific surface areas results of adsorbents with and without the pretreatment by Laser Diffraction Method

| Adsorbents       | Untreated IRA900Cl | Treated IRA900Cl | Untreated A26OH | Treated A26OH |
|------------------|---------------------|------------------|-----------------|--------------|
| Specific surface areas (m²/g) | 673.20              | 608.46           | 492.67          | 494.66       |

Figure 2. The surface picture results taken by transmission electron microscope (SEM) of (A) untreated IRA900Cl; (B) treated IRA900Cl; (C) untreated A26OH and (D) treated A26OH.

Figure 3. The equilibrium concentration results at different operation time with IRA900CI and A26OH as adsorbents to adsorption FFA in peanut oil.
Figure 4. The removal percentage results of FFA at different operation time with IRA900Cl and A26OH as adsorbents to adsorption FFA in peanut oil.

Figure 5. The isothermal adsorption curve and fitted curve results of Langmuir and Freundlich isotherm models by A26OH adsorbed peanut oil at 25, 35 and 45°C, respectively

Table 5. The regression constants of Langmuir and Freundlich isotherm models by A26OH adsorbed peanut oil at 25, 35 and 45°C, respectively

| Operation Temperature (°C) | Fitting Langmuir isotherm model | Fitting Freundlich isotherm model |
|---------------------------|---------------------------------|----------------------------------|
|                           | Q₀ | K_L   | R²  | n     | K_F   | R²  |
| 25                        | 555.56 | 0.26 | 0.99 | 5.52 | 252.35 | 0.95 |
| 35                        | 555.56 | 0.31 | 0.99 | 6.04 | 279.64 | 0.97 |
| 45                        | 555.56 | 0.44 | 0.99 | 8.03 | 331.44 | 0.95 |

5. Conclusion
In this study, commercial ion exchange resins A26OH and IRA900Cl were used as adsorbents in the deacidification step of plant oil refining process, and the free fatty acids in commercial peanut oil were adsorbed and removed without adding any solvent. By comparing the adsorption performance of different ion exchange resins, it was found that addition of 1 wt% adsorbent under 35°C resulted in removal of up to 25.5% free fatty acids by A26OH and less than 10% removal of free fatty acids by IRA900Cl. Therefore, adsorbent performance by A26OH is better than by IRA900Cl. The present study also described the adsorption of free fatty acids in the peanut oil using A26OH ion exchange resin. The isothermal adsorption curves at 25, 35 and 45°C respectively shown that adsorption at all temperatures is more consistent with Langmuir isothermal model, and the adsorption also found that
were favourable adsorption at all temperatures. For future study, the dynamic adsorption studies will be conducted in a packed-bed column and the data will be useful to design the real application column for oil refinery.

6. References

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