Separation of Oleic Acid from Soybean Oil Using Mixed-Bed Resins

Yousuf Jamal and Bryan O. Boulanger*

Environmental and Water Resources Division, Zachry Department of Civil Engineering, Texas A&M University, 3136 TAMU, College Station, Texas 77843

Two mixed bed ion-exchange resins (Dowex Monosphere MR-450 UPW and Amberlite MB-150) were investigated for their ability to remove oleic acid from a laboratory-prepared 5 % (w/w) oleic acid/soybean oil mixture. The performance of the heterogeneous mixed-bed resins to remove oleic acid from the mixture was investigated for resin loading and reaction duration while the mixing rate, reaction temperature, and initial oleic acid composition of the mixture were kept constant. Both resins removed > 93 % of the oleic acid in the sample within 4 h with a 20 % (w/w) resin loading in a nonpressurized batch reactor system at 50 °C. The maximum adsorption capacity for Amberlite MB-150 and Dowex Monosphere MR-450 UPW was determined to be 0.27 $g \cdot g^{-1}$ (oleic acid/wet resin) and 0.26 $g \cdot g^{-1}$ (oleic acid/wet resin), respectively. Ion-exchange of oleic acid onto the quaternary ammonium site of the mixed-bed resin was determined to be the mechanism of oleic acid removal. The presented research has promising application in the areas of refining edible oils and biodiesel production from free fatty acid-containing feed stocks.

Introduction

Feed stocks of crude edible oils used in food products, nutraceuticals, and biodiesel production contain triglycerides and low amounts of diglycerides, monoglycerides, free fatty acids (FFAs), and additional trace components. Creating high-quality finished products from crude edible oils requires refining the crude oil to remove FFAs and other contaminants. Physical refining methods (such as distillation[1–3] and membrane separation[1–3]) and chemical refining methods (such as esterification with strong acids,[4–6] supercritical extraction,[7–9] and enzyme treatment[10–12]) have been used to remove FFA from crude oil. However, current research has moved toward the development of alternative processing methods to remove FFA that are less energy-intensive and consume less solvents, acids, and bases.[13]

Recently, ion-exchange resins have been explored as an alternative refining method to remove FFA from crude oil. Acidic[5,14–16] and basic[17,18] ion-exchange resins have both been used to remove FFAs from oil and solvent systems. In basic resin ion-exchange systems the mechanism of FFA removal appears to be adsorption to the basic site, although no step-by-step evaluation of the reaction mechanism is presented in the literature to the best of our knowledge. In acidic ion-exchange resin systems, FFA removal is accomplished by the esterification of FFAs at the acidic functional site in the presence of methanol or ethanol. Esterification of FFAs on acidic ion exchange resins is a pretreatment option of increasing interest in biodiesel processing.[14,19–22] In this case the mechanism of FFA removal is catalyzing the esterification reaction rather than ion exchange.

While ion-exchange resins have historically been used to remove contaminants in aqueous waste streams via ion exchange, reports of using resins to facilitate ion-exchange in nonpolar systems are increasing because of their direct potential use in biodiesel production.[16,22–24] While the application of ion-exchange resins to sorb or react with FFAs in nonpolar systems appears promising on the basis of these reports, additional characterization of the mechanisms, sorption capacity, and kinetics behind sorption of FFAs to individual ion-exchange resins in nonpolar systems is needed.

The present work seeks to add to the current knowledge by elucidating FFA adsorption from a nonpolar system onto mixed bed ion-exchange resins. The amount of FFA adsorbed by the resins, the kinetics of the reaction, and adsorption isotherms of oleic acid removal from degummed soybean oil are investigated for two commercially available resins with oleic acid used as the FFA component. The adsorption of oleic acid onto the resins from soybean oil was investigated for various resin loadings and reaction durations, while the mixing rate, reaction temperature, and initial oleic acid composition of the mixture were kept constant.

The mechanism of removal was determined by evaluating oleic acid removal using commercially available acidic and mixed-bed resins with and without the presence of methanol. Isotherm and kinetic studies were completed using a 15 % by weight resin loading for the mixed-bed resins. Single-site Langmuir and Freundlich isotherm models were used to evaluate the data.

Experimental Section

Materials. Degummed soybean oil, technical grade oleic acid (90 %), reagent grade toluene (99.5 %), reagent grade isopropyl alcohol (99.5 %), 0.1 N potassium hydroxide, reagent grade methanol, mixed-bed resins (Dowex Monosphere MR-450 UPW and Amberlite MB-150), and acidic resins (Amberlyst 36 wet and Dowex Monosphere M-31) were all purchased from Sigma-Aldrich (St. Louis, MO). These four resins are supported on a styrene-divinyl benzene matrix, are of similar particle size range (between 360 μm and 850 μm), and contain sulfonic acid (all resins) and quaternary ammonium (mixed-bed resins) fuctional groups. Phenolphthalein was purchased from Fisher Scientific (Pittsburgh, PA).

Reactor Design. Triplicate three-neck borosilicate glass flat-bottom flasks (1000 mL) were used as a reactor system to

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* Corresponding author. Fax: 979.862.1542. E-mail: yousuf.jamal@neo.tamu.edu and bboulanger@tamu.edu.

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evaluate each experimental condition. All reactants and a magnetic stir bar were placed/poured into each of the three flasks through one of the necked openings. The reaction vessel's contents were kept at a constant temperature by mixing in a water bath on top of a combination heating and stirring plate. During the reaction, one of the three-necked openings was used to insert a thermometer, which measured the temperature of the fluid inside each reactor vessel. All of the necked openings, including the opening with the thermometer, were covered with parafilm during the experiments.

Experimental Procedure for Evaluating Oleic Acid Removal and Kinetics. All experiments started by soaking a premeasured amount of mixed-bed resin (Dowex Monosphere MR-450 UPW and Amberlite MB-150) or acidic resin (Amberlyst 36 wet and Dowex Monosphere M-31) in 22.5 g of methanol inside each of the three individual reactor flasks. The resin was soaked for 12 h while stirring at 550 rotations per minute (rpm). After 12 h the methanol was decanted, leaving behind the soaked resin. Approximately 1 h prior to beginning an experimental run, an 800 mL mixture of 5 % oleic acid in soybean oil (weight/weight nominal) was made up in a 1 L glass beaker.

The 5 % oleic acid in soybean oil mixture was heated while stirring to 50 °C and held at 50 °C for 30 min to remove residual moisture and break any emulsified oil. Following heating, triplicate 2.5 g subsamples of the mixture were taken from the 5 % oleic acid in soybean oil mixture. Each of the subsamples was used to determine the mixture's exact oleic acid composition by titration.

Once the measured oleic acid composition of the mixture was determined, a 200 g portion of the mixture was placed into each of the triplicate reaction flasks already containing the resin. The resin and oleic acid/soybean oil mixture was mixed for 24 h at 550 rpm while being held at 55 °C.

The exact amount of resin used in each experiment was varied to evaluate the effect of resin loading on oleic acid reduction and to determine isotherm model parameters. The mixed-bed resin loadings evaluated were (5, 10, 15, and 20) % by weight of the oleic acid/soybean oil mixture. The acidic resin was used to determine which functional group was responsible for oleic acid removal and was only evaluated at a 15 % by weight resin loading. During the 24 h reaction duration for each experimental condition, 2.5 g subsamples were taken from each of the three replicate reactors to determine the mean oleic acid composition in each reaction mixture at an interval of (2, 4, 8, 12, 16, 20, and 24) h. At the end of each experimental run, the heating/stir plate was turned off, and the resin was allowed to settle out of the liquid phase for five minutes.

The settled reacted mixture was then transferred into 50 mL polyethylene centrifuge tubes and centrifuged for 15 min at 9000 rpm to separate out the resins. Recovered resins were stored separately for later reuse.

Influence of Methanol Addition. Experiments were also carried out under a 15 % mixed-bed resin loading with and without methanol to determine if adding excess methanol to the system would cause the resin was to act as a catalyst (via esterification of oleic acid) instead of an ion-exchange medium. The experimental setup described above was altered to include 22.5 g of methanol into the reactor for a total reactor composition of 22.5 g of methanol, 200 g of the 5 % oleic acid in soybean oil mixture, and 20 % mixed-bed resin loading as a weight percent of the oleic/soybean mixture. The FFA value in the oil phase was measured at (2 and 4) h to determine if there was any effect of methanol on the removal of oleic acid compared to the system without methanol. The system was also monitored for the presence of a second phase.

Experimental Procedure for Isotherms. Isotherm experiments were conducted for mixed-bed resins at resin loadings of (10, 15, 20, 25, and 30) % at an initial FFA concentration of 53 $g \cdot g^{-1}$ (oleic/soybean oil). The amount of FFA sorbed to the resin was determined through mass balance. Single-site Langmuir and Freundlich models were used to evaluate mixed-bed resin isotherm data.

Isotherm and Reaction-Rate Model Fitting. The experimental data was fit to isotherm and reaction-rate models using an Excel macro developed to minimize the root-mean-square error of predicted versus observed data.

Desorption Studies. At the end of the isotherm studies, each of the 15 % mixed-bed resin samples from individual triplicate reactors was evaluated for desorption by three different methods. One of the reactor's resins was placed into a clean 200 g sample of soybean oil and rapidly mixed for 24 h. The second reactor's resin was placed into a 0.45 μm filter within a funnel and rinsed with 22.5 g of methanol five times. The third reactor's resin was also placed into a 0.45 μm filter within a funnel but was rinsed with 22.5 g of methanol with 5 % sodium hydroxide five times. The resulting rinses were then added to individual 200 g samples of soybean oil, and the resulting FFA of the oil was measured.

Measuring Oleic Acid in the Reaction Mixture. The oleic acid composition of the subsampled reaction mixtures was determined using the American Oil Chemists' Society method for the determination of FFA (AOCS Ca 5a 40).[25] Briefly, 37.5 g of both toluene and isopropyl alcohol were combined in the bottom of a titration flask. Two milliliters of phenolphthalein indicator and 2.5 g of the reaction mixture were added to the titration flask. The mixture was then titrated against 0.1 N potassium hydroxide (KOH) until a light pink color appeared and remained in the solution for 30 s. The volume of 0.1 N KOH consumed was recorded and used to calculate the oleic acid composition in the sample using the oleic acid composition of a prepared soybean oil only blank as a benchmark.[25]

The mean and 95 % confidence intervals of oleic acid from the triplicate reactor vessels were then determined using Excel functions for each of the time interval subsamples.

Results

Oleic Acid Removal. The impact of reaction duration and resin loading for both mixed-bed resins is presented in Figure 1. After 8 h oleic acid removal from the liquid fraction ceased for both resins. However, the amount of oleic acid removed from the liquid fraction at 8 h was directly proportional to the resin loading. For both resins, the maximum removal was observed for the highest resin loading evaluated in this study (20 % loading by weight of the oil). Amberlite MB-150 and Dowex Monosphere MR-450 UPW resulted in (98.0 and 95.3) % removal of oleic acid from the soybean oil fraction at 8 h, respectively.

The nominal difference in removal is related to the distribution of acidic and basic functional groups on each resin. While both resins contain sulfonic acid functional groups as the acidic site and quaternary ammonium functional groups as the basic site, the ratio of basic to acidic sites is higher for the Amberlite resin (60:40) compared to the Dowex Monosphere MR-450 UPW resin (50:50).

Kinetics. Figure 2 shows the experimental and modeled kinetic data for oleic acid sorption to both mixed-bed resins for a 15 % resin loading. The mass sorbed onto the resin increased for both

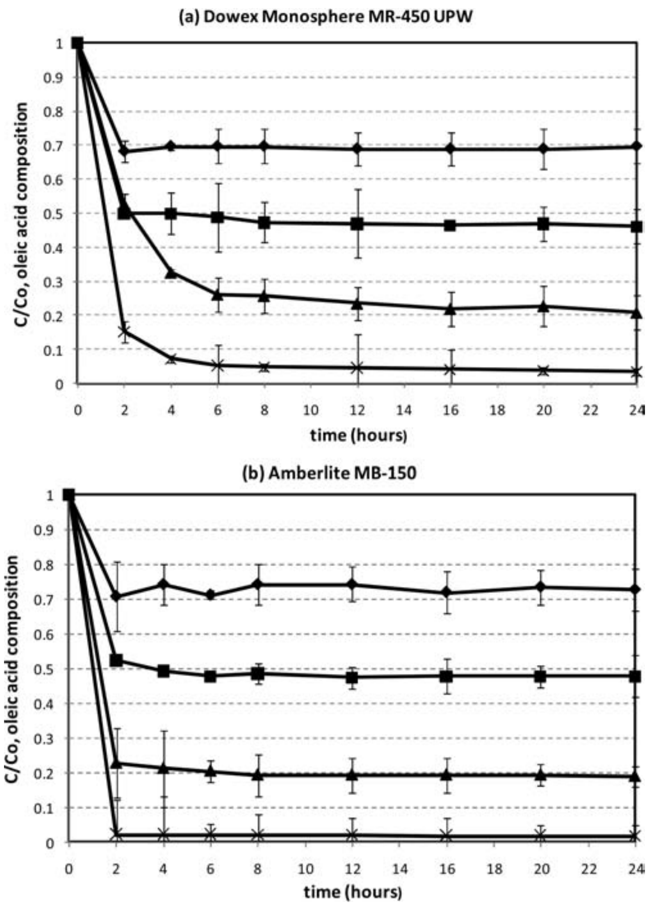

Figure 1. Oleic acid reduction over time in reactors as a function of resin loadings (◆, 5 %; ■, 10 %; ▲, 15 %; and ×, 20 % by weight) for (a) Dowex Monosphere MR-450 UPW and (b) Amberlite MB-150. Each presented data point represents the mean fraction of oleic acid remaining in each of the triplicate reactors as a function of the initial oleic acid composition (5 % by weight) and time. Error bars represent the 95 % confidence intervals. The solid lines demonstrate the trend but are not a fit of the data.

resins reaching a maximum value of $0.81 \cdot C_O$ (7.9 g oleic acid) for Amberlite MB-150 after 8 h and $0.79 \cdot C_O$ (7.8 g oleic acid) for Dowex Monosphere MR-450 UPW at 24 h. The kinetic data was then modeled with pseudofirst-order, pseudosecond-order, and modified second-order kinetic models to determine the kinetic model fitted parameters that would best describe the data.[26] The modeling data are presented in Table 1.

The experimental data form a continuous curve indicating single-layer adsorption through ion exchange. The data also show a higher rate of sorption over the first four hours followed by incremental sorption after four hours. For Amberlite MB 150, all three kinetic models describe the data well with correlation coefficients (r^2) all greater than 0.999 and normalized standard deviations (Δq) less than 0.94 %. The Dowex Monosphere MR-450 UPW data demonstrate r^2 values all greater than 0.986 but have a wider range of Δq (from 1.42 to 4.80 %) compared to the Amberlite MB-150 results.

While any of the three models can be used to describe the sorption of oleic acid to Amberlite MB-150 resin data, the pseudofirst-order model best describes the Dowex Monosphere MR-450 UPW data with an r^2 of 0.999 and a Δq of 1.42 %. The similarity in shape of the experimental data between the two evaluated resins was expected because both resins contain the same functional groups and the same backbone support of styrene-divinylbenzene copolymer.

Influence of Methanol. Presence of methanol in the system did not have an effect on the removal of FFA through adsorption or esterification. At four hours the mean ± 95 % confidence interval mass of oleic acid remaining in both systems containing the mixed-bed resin was 0.32 ± 0.03 (93.6 % removal) with methanol present and 0.31 ± 0.04 (93.7 % removal) without methanol present in the reactors. Using a two-sample t test assuming equal variances, no difference in the mean oleic acid concentration is observed in the oil phase when methanol was present at a 95 % confidence interval after four hours. Additionally, only a single phase was observed in the reactor, indicating that esterification did not occur. The data for 2 h show the same trend, indicating that adsorption and not catalysis is responsible for removing oleic acid in mixed-bed resin systems. Because there was no observed difference in means at two and four hours, methanol also does not appear to impact adsorption kinetics, although additional observations are required to confirm this hypothesis.

Isotherms. The experimental data for adsorption of oleic acid by both resins are plotted with isotherm modeling results in Figure 3. The maximum adsorption capacity (q_m) observed for Amberlite

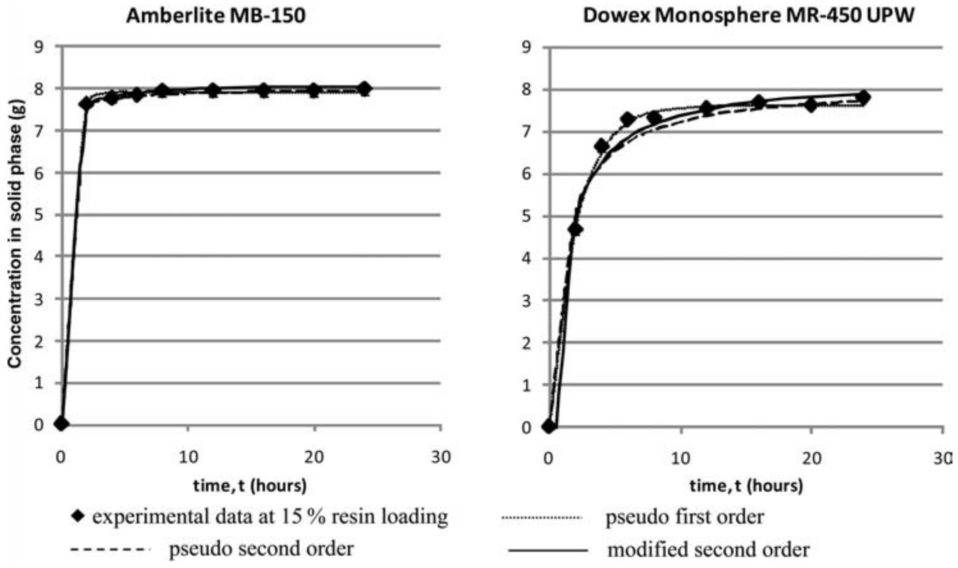

Figure 2. Experimental data plotted with kinetic models for oleic acid adsorption on mixed-bed resins. The plotted data are the mean concentrations in the solid phase for the triplicate set of reactors. The 95 % confidence intervals fall within the marker and do not appear on this graph.

Table 1. Kinetic Model Parameters for the Exchange of Oleic Acid on Amberlite MB-150 and Dowex Monosphere MR-450 UPW Mixed-Bed Resins[a]

resin	kinetic model	model equation	fitted parameters	r^2	Δq (%)
Amberlite MB-150	pseudofirst order	$m_t = m_e[1 - \exp(-k_1 t)]$	$m_t = 7.9[1 - \exp(-1.62t)]$	0.999	0.85
	pseudosecond order	$m_t = t/(1/k_2 m_e^2) + (t/m_e)$	$m_t = t/1/((0.9)(8.0^2)) + (t/8.0)$	0.999	0.66
	modified second order	$m_t = m_e(1 - [1/\beta + k_2 t])$	$m_t = 8.1(1 - [1/1.0 + 6t])$	0.999	0.95
Dowex Monosphere MR-450 UPW	pseudofirst order	$m_t = m_e[1 - \exp(-k_1 t)]$	$m_t = 7.62[1 - \exp(-0.48t)]$	0.999	1.42
	pseudosecond order	$m_t = t/(1/k_2 m_e^2) + (t/m_e)$	$m_t = t/1/((0.1)(8.1^2)) + (t/8.1)$	0.990	4.80
	modified second order	$m_t = m_e(1 - [1/\beta + k_2 t])$	$m_t = 8.3(1 - [1/0.8 + 0.81t])$	0.987	3.60

[a] m_e = amount of oleic adsorbed at equilibrium (g); m_t = amount of oleic adsorbed at any time (g); t = reaction duration (hours); k_1 and k_2 are the first- and second-order rate constants (hr^{-1}); β is an initial resin loading describing constant; r^2 = correlation coefficient; $\Delta q\ (\%) = 100 \cdot ((\sum[(m_{t,\text{experimental}} - m_{t,\text{modeled}})/m_{t,\text{experimental}}]^2)/(n - 1))^{1/2}$ where n = number of data points.

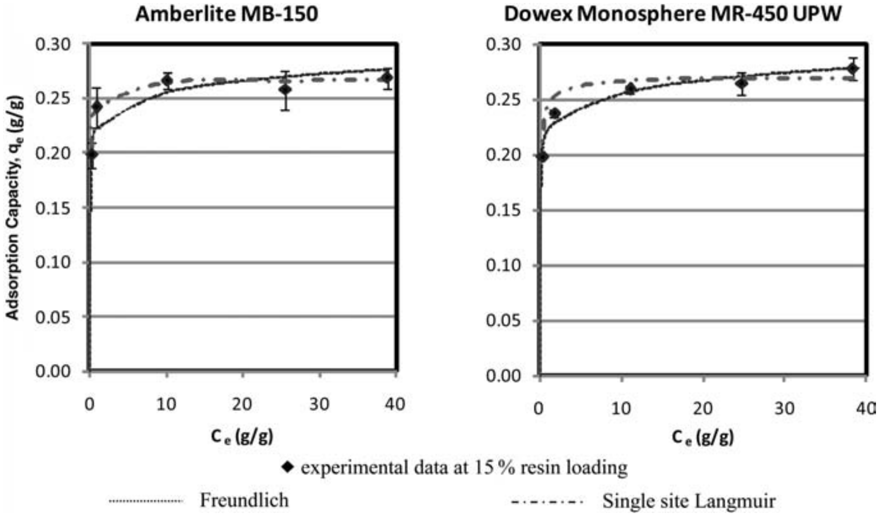

Figure 3. Experimental data plotted with isotherm models for oleic acid adsorption on mixed-bed resins. The plotted data are the mean concentrations in the solid phase for the triplicate set of reactors. Error bars represent the 95 % confidence intervals.

Table 2. Isotherm Model Parameters for Exchange of Oleic Acid on Amberlite MB-150 and Dowex Monosphere MR-450 UPW Mixed-Bed Resins[a]

resin	kinetic model	model equation	fitted parameters	r^2	Δq (%)
Amberlite MB-150	single-site Langmuir	$q_e = Q_o b C_e / 1 + b C_e$	$q_e = (0.267)(8.9)C_e / 1 + 8.9C_e$	0.998	1.71
	Freundlich	$q_e = K_f C_e^{1/n}$	$q_e = 0.222 C_e^{1/(16.9)}$	0.986	5.37
Dowex Monosphere MR-450 UPW	single-site Langmuir	$q_e = Q_o b C_e / 1 + b C_e$	$q_e = (0.27)(7.7)C_e / 1 + 7.7C_e$	0.994	3.57
	Freundlich	$q_e = K_f C_e^{1/n}$	$q_e = (0.220) C_e^{1/(15.5)}$	0.997	2.66

[a] q_e = amount of oleic adsorbed at equilibrium ($\text{g} \cdot \text{g}^{-1}$); C_e = concentration of oleic in liquid phase ($\text{g} \cdot \text{g}^{-1}$). Langmuir constants: Q_o = adsorption capacity ($\text{g} \cdot \text{g}^{-1}$), b = energy of adsorption (1/g). Freundlich constants: K_f = adsorption capacity ($\text{g} \cdot \text{g}^{-1}$), n = intensity of adsorption. r^2 = correlation coefficient; $\Delta q\ (\%) = 100 \cdot ((\sum[(q_{\text{experimental}} - q_{\text{modeled}})/q_{\text{experimental}}]^2)/(n - 1))^{1/2}$ where n = number of data points; t = reaction duration (hours).

MB-150 and Dowex Monosphere MR-450 UPW was 0.27 $\text{g} \cdot \text{g}^{-1}$ and 0.26 $\text{g} \cdot \text{g}^{-1}$, respectively. The experimental data was then modeled with single-site Langmuir and Freundlich isotherm models to determine the model fitted parameters that would best describe the data.[26] The modeling data are presented in Table 2.

Both the single-site Langmuir and the Freundlich isotherm models described the experimental data with r^2 values between 0.985 and 0.999 and Δq values from (1.71 to 5.37) %, respectively. Prior to running the experiment, we anticipated that a multiple-site Langmuir model may be required to describe the system, because two distinct functional sites are present on the surface of the resin. However, because the single-site isotherm fits the data, we hypothesized that only one of the sites present in the mixed-bed resin is responsible for the adsorption of oleic acid. Currently, exchange of the anionic FFA with the cationic quaternary ammonium site is the mechanism supported through conceptual understanding, an additional experiment, and by the literature.

Cren et al. performed similar isotherm adsorption studies using the strongly basic exchange resin Amberlyst A26 OH and found oleic acid bound to the quaternary ammonium ion functional group on the surface of the resin. They report a maximum adsorption capacity of 0.342 $\text{g} \cdot \text{g}^{-1}$ (acid/wet resin)[18] which is slightly above our observed values of (0.27 and 0.26) $\text{g} \cdot \text{g}^{-1}$ (acid/(wet) resin). This difference in results can be explained by the presence of the acidic functional group on the surface of the mixed-bed resins. Ihara also demonstrated that the sorption of fatty acid sodium salts occurred on weakly basic ion-exchange resins Amberlite IRA94 and IRA68.[27] The single-site Langmuir model fitted the Ihara data set for each sodium salt evaluated. However, the overall interpretation of their results was limited to fitting the model within their paper, and no additional information was given into the mechanism of removal or adsorption capacity.[27]

An additional experiment was also performed to evaluate the hypothesis that the quaternary site was responsible for the adsorption of FFA in our system. Two acidic resins, Amberlyst 36 (wet) and Dowex Monosphere M-31, were evaluated to determine the extent of oleic acid adsorption to the sulfonic acid functional group present in the mixed-bed resins and the acidic resins selected. After 24 h of reaction, the FFA levels in the mixture were reduced by 1.9 % for the system containing 15 % Dowex Monosphere M-31 and 0.02 % for the system containing 15 % Amberlyst. The lack of oleic acid adsorption to the two acidic resins provides definitive evidence that the quaternary ammonium functional group is responsible for the adsorption of oleic acid to the mixed-bed resins.

Desorption. Oleic acid levels were nondetectable following all desorption treatments (clean soybean oil, methanol rinsing, and 5 % sodium hydroxide in methanol rinse) indicating a strong affinity for the retention of oleic acid on the resin. Cren et al. reported similar findings from their desorption experiments, indicating that only a very small amount of physical adsorption accounted for the oleic acid removal observed in their system.[17,18] While oleic acid does not appear to desorb from the resin under the conditions evaluated in this research, additional research is required to find a wash process that will successfully regenerate the resin's surface. This research is currently underway in our laboratory.

Conclusion

The two mixed-bed resins evaluated in this study, Amberlite MB-150 and Dowex Monosphere MR-450 UPW, were both found to remove oleic acid from a laboratory-prepared 5 % oleic acid/soybean oil mixture through ion-exchange of oleic acid to the quaternary ammonium functional group on the resins. The sulfonic acid functional group was not determined to be an important exchange site or found to catalyze the esterification of oleic acid when methanol was present in the system.

Kinetic and isotherm models were used to describe the data observations. The maximum adsorption capacity for Amberlite MB-150 and Dowex Monosphere MR-450 UPW was determined to be (0.27 and 0.26) $g \cdot g^{-1}$, respectively. The isotherm data was well-correlated ($r^2 > 0.985$) to both the Freundlich and single-site Langmuir isotherm models. The nominal difference in the adsorption capacity and kinetic and isotherm model correlations for the two mixed-bed resins is caused by the difference in quaternary ammonium/sulfonic acid functional group ratio for Amberlite MB-150 (60:40) and Dowex Monosphere MR-450 UPW (50:50) resins. Despite the nominal difference in structure, both resins were able to adsorb > 93 % of the oleic acid in the mixture within four hours, suggesting that adsorption to mixed-bed resins will be a promising refining process to remove FFA from edible oils and biodiesel feed stocks.

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Literature Cited

(1) Hafidi, A.; Pioch, D.; Ajana, H. Effects of a Membrane-Based Soft Purification Process on Olive Oil Quality. *Food Chem.* **2005**, *92*, 607–613.

(2) Hafidi, A.; Pioch, D.; Ajana, H. Soft Purification of Lampante Olive Oil by Microfiltration. *Food Chem.* **2005**, *92*, 17–22.

(3) Koris, A.; Vatai, G. Dry Degumming of Vegetable Oils by Membrane Filtration. *Desalination* **2002**, *148*, 149–153.

(4) Chongkhong, S.; Tongurai, C.; Chetpattananondh, P. Continuous Esterification for Biodiesel Production from Palm Fatty Acid Distillate Using Economical Process. *Renewable Energy* **2009**, *34*, 1059–1063.

(5) Prateepchaikul, G.; Somnuk, K.; Allen, M. Design and Testing of Continuous Acid-Catalyzed Esterification Reactor for High Free Fatty Acid Mixed Crude Palm Oil. *Fuel Process. Technol.* **2009**, *90*, 784–789.

(6) Zhang, J.; Jiang, L. Acid-Catalyzed Esterification of Zanthoxylum Bungeanum Seed Oil with High Free Fatty Acids for Biodiesel Production. *Bioresour. Technol.* **2008**, *99*, 8995–8998.

(7) Bernardo-Gil, M. G.; Casquilho, M.; Esquível, M. M.; Ribeiro, M. A. Supercritical Fluid Extraction of Fig Leaf Gourd Seeds Oil: Fatty Acids Composition and Extraction Kinetics. *J. Supercrit. Fluids* **2009**, *49*, 32–36.

(8) Chen, C.-R.; Wang, C.-H.; Wang, L.-Y.; Hong, Z.-H.; Chen, S.-H.; Ho, W.-J.; Chang, C.-M. J. Supercritical Carbon Dioxide Extraction and Deacidification of Rice Bran Oil. *J.Supercrit. Fluids* **2008**, *45*, 322–331.

(9) Soto Ayala, R.; Luque de Castro, M. D. Continuous Subcritical Water Extraction as a Useful Tool for Isolation of Edible Essential Oils. *Food Chem.* **2001**, *75*, 109–113.

(10) Cramer, J. F.; Dueholm, M. S.; Nielsen, S. B.; Pedersen, D. S.; Wimmer, R.; Pedersen, L. H. Controlling the Degree of Esterification in Lipase Catalysed Synthesis of Xylitol Fatty Acid Esters. *Enzyme Microb. Technol.* **2007**, *41*, 346–352.

(11) Negishi, S.; Shirasawa, S.; Arai, Y.; Suzuki, J.; Mukataka, S. Activation of Powdered Lipase by Cluster Water and the Use of Lipase Powders for Commercial Esterification of Food Oils. *Enzyme Microb. Technol.* **2003**, *32*, 66–70.

(12) Robles Medina, A.; Esteban Cerdán, L.; Giménez Giménez, A.; Camacho Páez, B.; Ibáñez González, M. J.; Molina Grima, E. Lipase-Catalyzed Esterification of Glycerol and Polyunsaturated Fatty Acids from Fish and Microalgae Oils. *J. Biotechnol.* **1999**, *70*, 379–391.

(13) Bhosle, B. M.; Subramanian, R. New Approaches in Deacidification of Edible Oils--a Review. *J. Food Eng.* **2005**, *69*, 481–494.

(14) Chung, K.-H.; Park, B.-G. Esterification of Oleic Acid in Soybean Oil on Zeolite Catalysts with Different Acidity. *J. Ind. Eng. Chem. (Washington, D.C.)* **2009**, *15*, 388–392.

(15) Marchetti, J. M.; Errazu, A. F. Comparison of Different Heterogeneous Catalysts and Different Alcohols for the Esterification Reaction of Oleic Acid. *Fuel* **2008**, *87*, 3477–3480.

(16) Russbueldt, B. M. E.; Hoelderich, W. F. New Sulfonic Acid Ion-Exchange Resins for the Preesterification of Different Oils and Fats with High Content of Free Fatty Acids. *Appl. Catal., A* **2009**, *362*, 47–57.

(17) Cren, É. C.; Cardozo Filho, L.; Silva, E. A.; Meirelles, A. J. A. Breakthrough Curves for Oleic Acid Removal from Ethanolic Solutions Using a Strong Anion Exchange Resin. *Sep. Purif. Technol.* **2009**, *69*, 1–6.

(18) Cren, E. C.; Meirelles, A. J. A. Adsorption Isotherms for Oleic Acid Removal from Ethanol + Water Solutions Using the Strong Anion-Exchange Resin Amberlyst A26 Oh. *J. Chem. Eng. Data* **2005**, *50*, 1529–1534.

(19) Marchetti, J. M.; Miguel, V. U.; Errazu, A. F. Heterogeneous Esterification of Oil with High Amount of Free Fatty Acids. *Fuel* **2007**, *86*, 906–910.

(20) Kim, H.-J.; Kang, B.-S.; Kim, M.-J.; Kim, D.-K.; Lee, J.-S.; Lee, K.-Y.; Sang-Eon Park, J.-S. C.; Kyu-Wan, L. In *Development of Heterogeneous Catalyst System for Esterification of Free Fatty Acid Contained in Used Vegetable Oil*, Proceedings of the 7th International Conference on Carbon Dioxide Utilization, Seoul, South Korea, 2003; Elsevier: New York.

(21) Park, Y.-M.; Lee, D.-W.; Kim, D.-K.; Lee, J.-S.; Lee, K.-Y. The Heterogeneous Catalyst System for the Continuous Conversion of Free Fatty Acids in Used Vegetable Oils for the Production of Biodiesel. *Catal. Today* **2008**, *131*, 238–243.

(22) Shibasaki-Kitakawa, N.; Honda, H.; Kuribayashi, H.; Toda, T.; Fukumura, T.; Yonemoto, T. Biodiesel Production Using Anionic Ion-Exchange Resin as Heterogeneous Catalyst. *Bioresour. Technol.* **2007**, *98*, 416–421.

(23) Özbay, N.; Oktar, N.; Tapan, N. A. Esterification of Free Fatty Acids in Waste Cooking Oils (Wco): Role of Ion-Exchange Resins. *Fuel* **2008**, *87*, 1789–1798.

(24) Feng, Y.; He, B.; Cao, Y.; Li, J.; Liu, M.; Yan, F.; Liang, X. Biodiesel Production Using Cation-Exchange Resin as Heterogeneous Catalyst. *Bioresour. Technol.* **2010**, *101*, 1518–1521.

(25) Firestone, D. *Official Methods and Recommended Practices of the American Oil Chemists' Society*, 4th ed.; American Oil Chemists' Society: Champaign, IL, 1989.

(26) Inbaraj, B. S.; Sulochana, N. Mercury Adsorption on a Carbon Sorbent Derived from Fruit Shell of *Terminalia Catappa*. *J. Hazard. Mater.* **2006**, *B133*, 283–290.

(27) Ihara, Y. Adsoprtion of Fatty Acid Sodium Salts on Ion Exchange Resins. *J. Appl. Polym. Sci.* **1986**, *32*, 5665–5667.

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