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## Adsorptive Removal of Unsaturated Fatty Acids using Ion Exchange Resins

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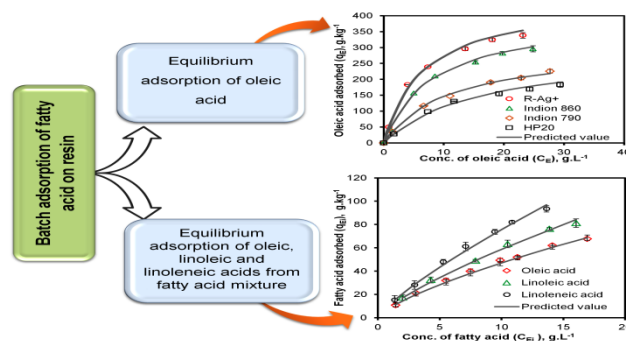
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### ABSTRACT

The main aim of present investigation was to elucidate efficacy of silver ion chromatography for selective separation of unsaturated (oleic, linoleic, and linolenic) fatty acids on a preparative scale. Accordingly, the present work was predominantly divided into two parts. In the first part, adsorption of oleic acid was carried using commercially available ion exchange resins and silver ion loaded resin (R-Ag<sup>+</sup>) prepared in the laboratory from non-polar and polar solvents in a batch mode. The maximum adsorption of oleic acid was found on R-Ag<sup>+</sup> (454.55 g.kg<sup>-1</sup>) when compared with other commercially available ion exchange resins from heptane at ambient temperature (303 K). The effect of temperature on adsorption of oleic acid on R-Ag<sup>+</sup> from heptane was investigated at 303, 313, and 323 K. Adsorption of oleic acid was favored at 303 K and further decreased with an increase in temperature. Experimental batch equilibrium data were modeled using Langmuir isotherm and Freundlich isotherm. Further, thermodynamic parameters *viz.*  $\Delta G_{\text{ads}}^0$ ,  $\Delta H_{\text{ads}}^0$ , and  $\Delta S_{\text{ads}}^0$  were estimated.

The negative values of  $\Delta G_{\text{ads}}^0$  and  $\Delta H_{\text{ads}}^0$  show that the adsorption of oleic acid on R-Ag<sup>+</sup> was spontaneous and exothermic in nature. Based on the results obtained in the first part, R-Ag<sup>+</sup> resin was subjected to adsorption of fatty acids from industrial fatty acids mixture using heptane as a solvent at 303 K. Multi-component Freundlich isotherm was used to model experimental batch equilibrium data. Linolenic acid and linoleic acid were preferentially adsorbed over oleic acid with selectivity of 1.40 and 1.16, respectively from industrial fatty acids mixture.

### Graphical Abstract



KEYWORDS: Adsorption; Freundlich isotherm; Langmuir isotherm; Polymeric resin; Unsaturated fatty acids

## 1. INTRODUCTION

Crude fats and oils produced by rendering, expression, or solvent extraction contain variable amounts of non-glyceride impurities, mainly free fatty acids.<sup>1</sup> Oils that are to be deodorized and marketed as neutral salad or cooking oils, as well as vegetable oils to be converted into shortenings and margarines should be free of the fatty acids. Free fatty acids are objectionable in all these products because they tend to smoke when the fat or oil is heated. The removal of free fatty acids is required not only for edible purposes, however, it is also needed for most of the oils which have to be processed further to modify or to make oleo-chemicals/derivatives.<sup>2</sup> Furthermore, an increased demand for fatty acids in soaps, fatty nitrogen compounds, surfactant, plasticizers, polymers, alkylated resins, lubricating greases, rubber products, candles, crayons, cosmetics, nutrient has led the pathway for separation of fatty acids from oils and fats.<sup>3-5</sup> Some of the unsaturated fatty acids such as oleic acid, linoleic acid, linolenic acid, etc. play a major role in metabolic activities in a human body. Oleic acid is an important unsaturated fatty acid known for its medicinal benefits. Oleic acid rich food lowers the risk of heart attack, arteriosclerosis, and aid in cancer prevention. Oleic acid, at plasma physiological concentrations, can also regulate the expression of important genes which helps in maintaining cell functioning.<sup>6,7</sup> Further, the deficiency of the linoleic acid leads to poor growth, fatty liver, skin lesions, and reproductive failure while deficiency of linolenic acid causes reduced vision, abnormal electroretinogram, and perhaps, impaired cognition and behavior.<sup>8</sup> Therefore, the separation of fatty acids from crude oil has gained tremendous attention in recent years.

The separation of fatty acids is usually complicated because of their similar physical properties. Various physical and chemical techniques have been developed for the separation and purification of fatty acids. Physical techniques involve distillation<sup>9</sup>, and membrane separation,<sup>10</sup> and chemical methods involve esterification,<sup>11, 12</sup> crystallization,<sup>13,14</sup> supercritical extraction<sup>15</sup> and saponification.<sup>16,17</sup> The pertinent details of these methods are given in supplementary data as Table S1. The physical methods are energy intensive, and the chemical methods consume considerable amount of solvents, acids, and bases. Therefore, it is imperative to develop an alternative technique to separate fatty acid which is techno-economically viable.

Adsorption is an attractive method for separation of fatty acids owing to its simple design, operation, cost-effectiveness, and energy efficiency. Literature reports adsorptive separation of fatty acids using various adsorbents such as zeolites,<sup>18</sup> strong anion exchange resin,<sup>19, 20</sup> weak base anion exchange resins,<sup>21</sup> iron oxide,<sup>22</sup> activated carbon,<sup>23</sup> mixed bed ion-exchange resins,<sup>24</sup> rice hull ash,<sup>25-27</sup> and clay.<sup>28-30</sup> These investigations primarily report adsorption equilibrium data and thermodynamic parameters. Although adsorptive separation of fatty acids is fairly investigated, it can be seen that the efficacy of the synthetic polymeric adsorbents and ion exchange resins is not investigated to the desired extent. Additionally, silver ion chromatography for the separation of fatty acids based on the degree of unsaturation and geometry has also been investigated adequately on the analytical scale.<sup>31,32</sup> However, silver ion chromatography with a view of preparative or production level separations of the fatty acids has not explored to a desirable extent to the best of authors knowledge. Therefore, it is essential to explore silver ion chromatography for separation of fatty acids and to compare its separation performance with commercially available ion exchange resins.

The present investigation has been divided into two parts. In the first part, adsorption of oleic acid was carried out on commercially available resins such as styrene- divinyl benzene copolymer (HP20 resin), weak base anion exchange resin (Indion 860), and strongly acidic cation exchange resin (Indion 790) using heptane, toluene, ethyl acetate, isopropyl alcohol (IPA), and methanol as a solvent. Subsequently, silver ion loaded resin (R- Ag<sup>+</sup>) has been prepared to investigate efficacy of silver ion chromatography over commercially available resins for adsorption of oleic acid on a preparative scale. The effect of initial concentration and temperature on adsorption of oleic acid has

been investigated and subsequently, adsorption equilibrium data has been modeled using Langmuir equation, Freundlich isotherm, and thermodynamic analysis has also been performed. Finally, in the second part, separation of fatty acids mixture (C<sub>12</sub>- C<sub>22</sub>) has been investigated on R- Ag<sup>+</sup> resin to validate the efficacy of silver ion chromatography based on the geometry and degree of unsaturation of fatty acids.

Table S1: Separation techniques for fatty acid

S.N.	Separation method	Summary	Reference
1	Distillation	Free fatty acid (FFA) containing 57.8 % (w.w <sup>-1</sup> ) oleic acid was subjected to vacuum distillation at 10 <sup>-6</sup> bar pressure. Oleic acid was found to be 2.3 % (w.w <sup>-1</sup> ) at the end of operation. Although appreciable separation efficiency (~96 %) was achieved, the requirement of high vacuum demands high initial cost of equipment. Further, vacuum distillation was energy intensive owing to high operating cost to maintain the vacuum.	[9]
2	Chemical method by esterification	Mixed crude oil containing 12 % (w.w <sup>-1</sup> ) was esterified with methanol in the presence of sulphuric acid as a catalyst at 60 °C for 12 h. Although 80 % FFA was converted in methyl ester, the reaction was time and energy demanding.	[12]
3	Crystallization	Crude palm oil containing 3 % (w.w <sup>-1</sup> ) FFA was subjected to crystallization with an optimized cooling rate of 17 °C.h <sup>-1</sup> from 70 °C to 25 °C. The residual FFA was observed to be 0.5 % (w.w <sup>-1</sup> ) after 2.94 h. The cooling rate was observed to be an important operating parameter for nucleation and crystal growth to achieve desired separation efficiency of FFA.	[13]
4	Supercritical extraction	The rice bran oil containing 10 % (w.w <sup>-1</sup> ) FFA was subjected CO <sub>2</sub> super critical extraction at 250 bar pressure until FFA content in oil reduced to 0.13 % (w.w <sup>-1</sup> ). Although CO <sub>2</sub> super critical extraction of FFA shows good separation efficiency, requirement of high pressure for a predetermined separation efficiency of FFA leads to high initial cost of equipment and operating cost.	[15]
5	Membrane separation	FFA mixture containing 50 % (w.w <sup>-1</sup> ) oleic acid with tripropylamine and elaidic acid was subjected to membrane separation using polydicyclopentadiene (PDCPD) membrane and dichloromethane and methanol as a diluents. The operation was, however, time intensive (72 h) with merely separation efficiency of 17 % for oleic acid.	[44]

## 2. MATERIALS AND METHODS

### 2.1. Materials.

All chemicals used during experimentation are reported in Table 1. These chemicals were used without further purification.

Table 1 Details of the chemicals used in the present work

Component	CAS No.	Suppliers	Purity <sup>&amp;</sup>	Analysis
Oleic acid	112-80-1	Merck Millipore Pvt. Ltd. India	99.0	GC*
Methanol	67-56-1	S. D. Fine Chemicals Pvt. Ltd. India	99.8	GC*
Isopropyl alcohol	67-63-0	Sisco Res. Lab. Pvt. Ltd. India	99.0	GC*
Ethyl acetate	141-78-6	S. D. Fine Chemicals Pvt. Ltd. India	99.5	GC*
Propyl acetate	109-60-4	S. D. Fine Chemicals Pvt. Ltd. India	99.0	GC*
Toluene	108-88-3	S. D. Fine Chemicals Pvt. Ltd. India	99.8	GC*
Hexane	110-54-3	S. D. Fine Chemicals Pvt. Ltd. India	95.0	GC*
Heptane	142-82-5	Loba Chemie Pvt. Ltd. India	99.0	GC*
Sodium sulfate	7757-82-6	Loba Chemie Pvt. Ltd. India	99.0	AAS <sup>\$</sup>
Sulfuric acid	7664-93-9	Merck Millipore Pvt. Ltd. India	95.0	Titration <sup>#</sup>
Silver nitrate	7761-88-8	Sisco Res. Lab. Pvt. Ltd. India	99.5	Titration

<sup>&</sup> = Purity (% w.w<sup>-1</sup>) \* = Gas chromatography; \$ = Atomic absorption spectroscopy; # Alkalimetric titration method

Fatty acid mixture (composition is given in Table 2) was supplied by Godrej Consumer Products Ltd, India as a gift sample. All the ion exchange resins were procured from Ion Exchange Pvt. Ltd. India. Table 3 reports the properties of HP20, Indion 860, and Indion 790 resins as provided by manufacturer.

Table 2 Composition of fatty acid mixture

Fatty acid	Composition, % (w.w <sup>-1</sup> )
Lauric acid (C 12:0)	1.23
Palmitic acid (C 16:0)	4.56
Stearic acid (C 18:0)	2.33
Oleic acid (C 18:1)	21.00
Linoleic acid (C 18:2)	30.00
Linolenic acid (C 18:3)	22.00
Arachidic acid (C 20:0)	14.32
Eicosenoic acid (C 20:1)	1.85
Eicosadienoic acid (C 20:2)	1.05
Behanic acid (C 22:0)	1.64

Table 3 Properties of polymeric resins

Parameters	HP20	Indion 860	Indion 790
Type	Plain copolymer	Weak base	Strong acidic
Matrix structure	Styrene-DVB	Styrene-DVB	Styrene-DVB
Functional group	Neutral	-NR <sub>2</sub>	-SO <sub>3</sub> <sup>-</sup>
Ionic form	-	Free base	H <sup>+</sup>
Moisture content (%)	50-60	47-55	45-55
Surface area (m <sup>2</sup> .gm <sup>-1</sup> )	600	35	32
Pore volume (mL.gm <sup>-1</sup> )	0.55	0.52	0.38
Pore diameter (Å)	250	339	280
Exchange capacity (mol.kg <sup>-1</sup> )	-	3.0	3.2
Cross linking (%)	7-10	7-8	7-8

## 2.2. Methods

### 2.2.1. Resin pretreatment

HP20 resin was thoroughly washed successively with distilled water and methanol. The resin was then dried in an oven at 333 K. Indion 860 and Indion 790 was washed with 5 % (w.v<sup>-1</sup>) NaOH and HCl solutions, respectively. The excess of NaOH or HCl was removed by washing the resin with ample amount of distilled water until neutral pH of solution was obtained. The resins were further washed with methanol and dried in an oven wherein temperature was maintained at 333 K and 393 K for Indion 860 and Indion 790, respectively and subsequently cooled to ambient temperature (303 K).

### 2.2.2. Loading of silver ion on Indion 790

Loading of silver ions on Indion 790 resin (initially in H<sup>+</sup> form) was carried out in a three-necked fully baffled stirred glass vessel of 150 cm<sup>3</sup> capacity. A known quantity of the resin (50 g) and aqueous silver nitrate solution (0.2 mol.L<sup>-1</sup>) were added to the vessel. The suspension was agitated with a six flat blade turbine impeller at 1200 rpm for 6 h. Samples were withdrawn at 30 min intervals to follow the approach to the equilibrium. The silver nitrate concentration in the liquid phase reached to constant value in 6 h. The mass balance for silver nitrate can be written as follows:

$$\left( \begin{array}{c} \text{Moles of silver} \\ \text{nitrate fed} \end{array} \right) = \left( \begin{array}{c} \text{Moles of silver nitrate} \\ \text{utilized to exchange H}^+ \text{ion} \end{array} \right) + \left( \begin{array}{c} \text{Moles of silver nitrate} \\ \text{remaining in the solution} \end{array} \right) \quad (1)$$

The moles of silver nitrate utilized to exchange H<sup>+</sup> ion were estimated using a titration method wherein 5 cm<sup>3</sup> solutions was titrated against 0.5 N NaOH solution. The moles of silver nitrate remaining in the solution were estimated by precipitation method wherein HCl (10 N) was added to form silver chloride precipitates. The silver chloride precipitate was separated by filtration, dried in oven at 353 K for 1 h, and subsequently weighed to estimate silver nitrate in the solution. The ion exchange capacity of the resin thus can be estimated from mass balance (eq 1). The ion exchange capacity of the resin was estimated to be 1.02 mol.L<sup>-1</sup>. The resin phase was then separated from the solution. The resin was further washed with a large volume of distilled water. Finally, it was washed with methanol and air-dried in a dark place.

### 2.2.3. Batch equilibrium studies

The batch equilibrium adsorption studies were carried out in specially fabricated glass cells to avoid the loss of solvents. The batch equilibrium studies were carried out for initial oleic acid concentration varying from 2.82 - 40 g.L<sup>-1</sup> using HP20, Indion 860, Indion 790, and R-Ag<sup>+</sup> resins from heptane, toluene, ethyl acetate, IPA, and methanol. A known amount of the resin (1 g) was taken in the cell and a solution of oleic acid in a solvent (25 cm<sup>3</sup>) of a known concentration was added into the cell. The cells were then kept in a thermostated water bath for 12 h to attain the equilibrium with continuous shaking. After the equilibrium was reached (6 h), the supernatant solution was separated from the resin. The volume changes of the resin, because of the sorption of solvent and oleic acid or fatty acid mixture, were estimated by measuring the initial volume of the dry resin and final volume of the swollen resin (after adsorption experiment) by standard calibrated glass tubes and also by microscopic observations. Based on equilibrium data analysis, the screening of resin and solvents were performed to retrieve the best resin and solvent using maximum adsorption capacity as a parameter. A similar adsorption procedure was repeated with selected resin and solvent to investigate the effect of temperature in the range of 303 to 323 K for adsorption of oleic acid and selective separation of unsaturated fatty acids from fatty acid mixture at 303 K. All experiments were carried out in triplicate and average values were reported with standard deviation.

### 2.2.4. Analytical procedure

The fatty acid (or mixture) was taken (0.1-0.8 cm<sup>3</sup>) in an excess amount of methanol (50 cm<sup>3</sup>). Sulfuric acid (98 % w.v<sup>-1</sup>) was added into the solution in catalytic amounts (6-8 drops) and the reaction mixture was refluxed for 180 min in a water bath at 343 K. After 180 min, the heat source

was removed and the mixture was cooled to room temperature (303 K). All fatty acid methyl esters (FAMES) were extracted into n-hexane (10 mL) and the organic phase was washed with distilled water to remove trace amounts of sulfuric acid. The organic phase was filtered through anhydrous sodium sulfate to remove all the moisture. The FAME mixture then was analyzed by gas chromatography on a Chemito 1000 gas chromatograph equipped with flame ionization detector (FID) using BPX- 70 capillary column (0.32 mm × 30 m with 0.25 × 10<sup>-6</sup> mm film thickness). The temperature program used for analysis is as follows:

Injector temperature : 260 °C

Detector temperature : 260 °C

Initial temperature : 120 °C

Temperature program : 120 °C to 240 °C with ramp of 3 °C.min<sup>-1</sup>.

### 2.2.5. Adsorption isotherm

The adsorption isotherm describes the relationship between the amount of the fatty acid adsorbed on the resin and the amount of the acid remaining in the liquid phase at equilibrium. In the present study, Langmuir adsorption and Freundlich adsorption isotherms have been employed to fit equilibrium adsorption data.

Langmuir adsorption isotherm can be expressed as follows:

$$\frac{q_E}{q_M} = \frac{K_L C_E}{1 + K_L C_E} \quad (2)$$

where  $q_E$  and  $q_M$  are the amount of oleic acid adsorbed at equilibrium (g.kg<sup>-1</sup>) and saturation adsorption capacity of the resin (g.kg<sup>-1</sup>) at a given temperature, respectively.  $C_E$  is the concentration of oleic acid at equilibrium (g.L<sup>-1</sup>) and  $K_L$  is Langmuir adsorption constant (L.g<sup>-1</sup>).  $q_M$  and  $K_L$  can be determined by rearranging eq 2 in the following form:

$$\frac{1}{q_E} = \frac{1}{K_L q_M} \cdot \frac{1}{C_E} + \frac{1}{q_M} \quad (3)$$

The plot of  $1/q_E$  against  $1/C_E$  yields a straight line. Therefore, the values of  $K_L$  and  $q_M$  can be obtained from the slope and intercept, respectively.

Freundlich adsorption isotherm can be expressed as follows:

$$q_E = K_F C_E^n \quad (4)$$

where  $q_E$  is the amount of the acid adsorbed at equilibrium (g.kg<sup>-1</sup>),  $C_E$  is the concentration of oleic acid in liquid phase at equilibrium (g.L<sup>-1</sup>),  $K_F$  is Freundlich constant (g<sup>1-n</sup>.L<sup>n</sup>.kg<sup>-1</sup>) and  $n$  is dimensionless Freundlich constant.  $K_F$  and  $n$  can be determined from the intercept and slope of the straight-line plot of  $\ln(q_E)$  against  $\ln(C_E)$ , respectively.

Freundlich adsorption isotherm for multi-component system can be expressed as follows<sup>33</sup>:

$$q_{E_i} = K_{F_i} C_{E_i} \left( \sum_{j=1}^k a_{ij} C_{E_j} \right)^{(n_i-1)} \quad (5)$$

where  $K_{F_i}$  is Freundlich constant of  $i^{\text{th}}$  component,  $C_{E_i}$  is the concentration of  $i^{\text{th}}$  component in liquid phase. For three component system the adsorption by each component can be given using following equations:

$$q_{E_1} = K_{F_1} C_{E_1} (C_{E_1} + a_{12} C_{E_2} + a_{13} C_{E_3})^{(n_1-1)} \quad (6)$$

$$q_{E_2} = K_{F_2} C_{E_2} (a_{21} C_{E_1} + C_{E_2} + a_{23} C_{E_3})^{(n_2-1)} \quad (7)$$

$$q_{E_3} = K_{F_3} C_{E_3} (a_{31} C_{E_1} + a_{32} C_{E_2} + C_{E_3})^{(n_3-1)} \quad (8)$$

where,  $q_{E_1}$ ,  $q_{E_2}$ , and  $q_{E_3}$  are amount of oleic acid, linoleic acid and linolenic acid adsorbed at equilibrium (g.kg<sup>-1</sup>) for corresponding liquid phase concentration  $C_{E_1}$ ,  $C_{E_2}$ , and  $C_{E_3}$ , (g.L<sup>-1</sup>),

respectively. Further,  $a_{12}$ ,  $a_{13}$ ,  $a_{21}$ ,  $a_{23}$ ,  $a_{31}$ , and  $a_{32}$  are competitive coefficients. The value of  $K_{Fi}$ ,  $C_{Ei}$  and  $a_{ij}$  can be obtained by non-linear regression analysis for  $i^{\text{th}}$  component.

### 2.2.6. Adsorption equilibrium constant

Adsorption equilibrium constant ( $K_0$ ) can be defined as the ratio of the activity of adsorbed acid molecule on the resin to the activity of the acid molecule in the liquid phase at equilibrium. Mathematically, the following expression can be written for  $K_0$ :

$$K_0 = \frac{a_A^S}{a_A^L} = \frac{\gamma_A^S q_E}{\gamma_A^L C_E} \quad (9)$$

where  $a_A^S$  and  $a_A^L$  denote the activity of oleic acid in the solid phase and liquid phase, respectively.  $\gamma_A^S$  and  $\gamma_A^L$  are activity coefficients of the oleic acid in the solid phase and liquid phase, respectively.  $q_E$  is the surface concentration of the acid ( $\text{g.g}^{-1}$ ) and  $C_E$  is a concentration of the acid at equilibrium ( $\text{g.g}^{-1}$  of solution). As the concentration of the acid in the liquid phase approaches zero, the activity coefficient approaches unity. Eq 9 can then be expressed as follows:<sup>19,34,35</sup>

$$\lim_{C_E \rightarrow 0} \frac{q_E}{C_E} = \frac{a_A^S}{a_A^L} = K_0 \quad (10)$$

The value of  $K_0$  can be determined by plotting  $\ln(q_E/C_E)$  versus  $C_E$  and extrapolating the data to set  $C_E$  equal to zero. A plot of  $\ln(q_E/C_E)$  versus  $C_E$  yields a straight line and the intercept of the line gives the value of  $K_0$  as confirmed by previous studies.<sup>21,36,37</sup>

### 2.3. Thermodynamic parameters

The standard Gibbs free energy change of adsorption can be estimated using following expression:

$$\Delta G_{\text{ads}}^0 = -RT \ln K_0 \quad (11)$$

where  $\Delta G_{\text{ads}}^0$  is standard Gibbs free energy change of adsorption ( $\text{kJ.mol}^{-1}$ ),  $R$  is universal gas constant ( $\text{kJ.mol}^{-1}.\text{K}^{-1}$ ),  $T$  is temperature of adsorption (K), and  $K_0$  is adsorption equilibrium constant. The values of the thermodynamic parameters, standard enthalpy change ( $\Delta H_{\text{ads}}^0$ ) and entropy change ( $\Delta S_{\text{ads}}^0$ ), can be calculated from linear relationship between the adsorption equilibrium constant ( $K_0$ ) and temperature using the following equation:

$$\ln K_0 = \frac{\Delta S_{\text{ads}}^0}{R} - \frac{\Delta H_{\text{ads}}^0}{RT} \quad (12)$$

The plot of  $\ln K_0$  against  $1/T$  yields straight line. The value of  $\Delta H_{\text{ads}}^0$  can be obtained from the slope while the value of  $\Delta S_{\text{ads}}^0$  can be obtained from the intercept of the line.

## 3. RESULTS AND DISCUSSION

### 3.1. Adsorption of oleic acid

#### 3.1.1. Screening of adsorbent

Figure 1 shows equilibrium adsorption of oleic acid on HP20, Indion 790, Indion 860, and R- $\text{Ag}^+$  resins from heptane at 303 K. The experimental adsorption data of oleic acid for all other solvents under consideration have been reported in Table 4. It can be seen from Figure 1 that the adsorption of oleic acid increases with an increase in initial concentration for all the resins with a similar trend. The oleic acid interacts with HP20 resin by dipole-induced dipole interaction and induced dipole- induced dipole interaction. In the case of Indion 860 resin, adsorption of the acid is due to the formation of hydrogen-bonded complex with the amino group on the resin matrix. The interaction between the lone pair of electrons on the tertiary amino nitrogen and acidic hydrogen of the acid is easily accepted as a Lewis acid-base interaction.<sup>21,38</sup>



Table 4 Batch equilibrium adsorption data for oleic acid

Solvent	HP20				Indion 790				Indion 860				R-Ag <sup>+</sup>			
	C <sub>0</sub> g.L <sup>-1</sup>	C <sub>E</sub> g.L <sup>-1</sup>	q <sub>E</sub> g.kg <sup>-1</sup>	SR -	C <sub>E</sub> g.L <sup>-1</sup>	q <sub>E</sub> g.kg <sup>-1</sup>	SR -	C <sub>E</sub> g.L <sup>-1</sup>	q <sub>E</sub> g.kg <sup>-1</sup>	SR -	C <sub>E</sub> g.L <sup>-1</sup>	q <sub>E</sub> g.kg <sup>-1</sup>	SR -			
Heptane	2.82	1.69±0.03	28.2±0.80	1.00	1.41±0.05	35.2±1.25	1.01	1.01±0.02	45.12±0.70	1.05	0.82±0.01	50.1±0.26	1.07			
	11.28	7.33±0.05	98.7±1.37	1.00	6.62±0.07	116.3±1.82	1.02	5.00±0.05	156.76±1.26	1.06	3.94±0.01	183.3±0.49	1.08			
	16.92	11.67±0.06	131.1±1.62	1.02	10.99±0.04	148.0±1.15	1.03	8.51±0.06	210.11±1.57	1.07	7.33±0.02	239.7±0.51	1.09			
	25.38	19.17±0.06	155.1±1.56	1.02	17.76±0.08	190.3±2.20	1.03	15.22±0.06	253.80±1.60	1.07	13.53±0.06	296.1±1.57	1.10			
	31.02	24.25±0.09	169.2±2.25	1.02	22.84±0.10	204.4±2.63	1.03	19.74±0.07	282.00±1.80	1.07	18.04±0.07	324.3±1.96	1.10			
	36.66	29.32±0.13	183.3±3.25	1.02	27.63±0.12	225.6±3.20	1.03	24.81±0.17	296.10±4.37	1.08	23.12±0.08	338.4±2.10	1.10			
	40.00	32.25±0.15	193.7±3.89	1.02	30.68±0.11	233.01±3.10	1.03	27.51±0.16	312.25±4.89	1.08	25.59±0.11	360.2±3.10	1.10			
Toluene	2.82	1.93±0.02	22.2±0.57	1.02	1.69±0.05	28.20±1.29	1.03	1.24±0.05	39.33±1.44	1.07	1.01±0.01	45.1±0.41	1.09			
	11.28	8.17±0.09	77.5±2.32	1.04	7.61±0.10	91.65±2.66	1.05	6.20±0.05	126.90±1.38	1.09	5.07±0.01	155.1±0.28	1.11			
	16.92	12.97±0.11	98.7±2.81	1.04	12.12±0.13	119.85±3.37	1.05	9.87±0.05	176.25±1.44	1.10	8.46±0.06	211.5±1.60	1.12			
	25.38	20.30±0.11	126.9±2.85	1.07	19.17±0.15	155.10±3.81	1.08	16.92±0.04	211.50±1.01	1.13	14.94±0.07	260.8±1.96	1.15			
	31.02	25.66±0.14	133.9±3.56	1.07	24.25±0.15	169.20±3.95	1.08	20.58±0.11	260.85±2.88	1.13	19.45±0.09	289.1±2.33	1.15			
	36.66	30.45±0.18	155.1±4.68	1.07	29.89±0.16	169.20±4.14	1.08	26.79±0.10	246.75±2.77	1.13	24.53±0.09	303.1±2.25	1.16			
	40.00	33.56±0.19	161.1±4.89	1.07	32.9±0.17	177.5±4.87	1.08	29.9±0.13	252.5±3.21	1.13	27.32±0.12	317.0±3.12	1.16			
Ethyl acetate	2.82	2.11±0.11	17.6±2.93	1.04	1.83±0.05	24.67±1.44	1.05	1.46±0.03	33.84±0.86	1.09	1.21±0.02	40.1±0.68	1.11			
	11.28	9.02±0.12	56.4±3.19	1.05	8.17±0.06	77.55±1.60	1.06	6.76±0.05	112.80±1.44	1.10	5.92±0.06	133.9±1.58	1.12			
	16.92	13.53±0.13	84.6±3.49	1.06	12.69±0.07	105.75±1.90	1.07	11.09±0.04	145.54±1.19	1.11	9.58±0.06	183.3±1.60	1.13			
	25.38	21.35±0.16	100.5±4.07	1.06	20.22±0.07	128.78±1.99	1.07	18.15±0.12	180.56±3.24	1.12	16.35±0.11	225.6±2.94	1.14			
	31.02	26.54±0.17	111.8±4.31	1.08	25.38±0.10	140.85±2.68	1.09	23.15±0.14	196.62±3.51	1.14	21.15±0.10	246.7±2.88	1.16			
	36.66	31.81±0.18	121.1±4.71	1.08	31.02±0.11	141.00±2.80	1.09	28.30±0.15	208.90±3.90	1.14	26.22±0.12	260.8±3.03	1.16			
	40.00	35.01±0.19	124.7±4.98	1.08	33.9±0.12	152.5±3.10	1.10	31.05±0.16	223.75±4.21	1.15	29.35±0.13	266.2±3.25	1.17			
IPA	2.82	2.290±0.04	13.2±1.15	1.07	2.05±0.02	19.03±0.53	1.08	1.69±0.05	28.20±1.44	1.13	1.63±0.04	29.6±3.03	1.15			
	11.28	9.588±0.10	42.3±2.57	1.08	8.74±0.05	63.45±1.44	1.09	7.61±0.07	91.65±1.81	1.14	7.33±0.05	98.7±0.21	1.16			
	16.92	14.38±0.10	63.4±2.52	1.09	13.81±0.05	77.55±1.58	1.10	12.12±0.11	119.85±2.88	1.15	11.56±0.06	133.9±0.21	1.17			
	25.38	22.27±0.10	77.5±0.21	1.12	21.43±0.06	98.70±1.73	1.12	19.45±0.14	148.05±3.75	1.16	18.89±0.06	162.1±0.21	1.18			
	31.02	27.35±0.10	91.6±2.68	1.11	26.50±0.07	112.80±1.87	1.12	24.81±0.17	155.10±4.33	1.17	23.97±0.09	176.2±0.21	1.19			
	36.66	32.71±0.11	98.7±2.75	1.12	31.91±0.12	118.54±3.13	1.13	29.77±0.15	172.18±4.88	1.18	29.32±0.09	183.3±0.21	1.20			
	40.00	35.94±0.18	101.5±4.52	1.13	34.95±0.13	126.25±3.52	1.14	32.93±0.17	176.75±4.33	1.19	32.12±0.11	197.0±0.21	1.22			
Methanol	2.82	2.45±0.06	9.16±1.63	1.09	2.27±0.01	13.74±0.43	1.10	1.97±0.05	21.15±1.44	1.15	1.83±0.01	24.6±3.03	1.17			

11.28	10.15±0.07	28.2±1.93	1.11	9.31±0.06	49.35±1.65	1.12	8.60±0.05	66.97±1.31	1.17	8.17±0.04	77.5±1.09	1.19
16.92	15.11±0.10	45.1±2.68	1.13	14.66±0.05	56.4±1.44	1.14	13.25±0.04	91.6±1.24	1.19	12.88±0.08	100.8±1.27	1.21
25.38	23.12±0.12	56.4±3.11	1.16	22.56±0.06	70.5±1.73	1.17	20.86±0.10	112.8±2.71	1.22	20.02±0.11	133.9±1.55	1.24
31.02	28.20±0.16	70.5±0.21	1.17	27.63±0.12	84.6±3.23	1.19	26.22±0.08	119.8±2.07	1.2	25.38±0.12	141.0±1.64	1.26
36.66	33.69±0.16	74.0±4.15	1.19	33.07±0.15	89.63±3.91	1.21	31.02±0.13	141.0±3.31	1.26	30.73±0.14	148.1±2.30	1.28
40.00	36.90±0.18	77.5±4.54	1.20	36.33±0.16	91.75±3.95	1.22	34.22±0.14	144.5±3.38	1.27	33.9±0.15	152.5±2.39	1.28

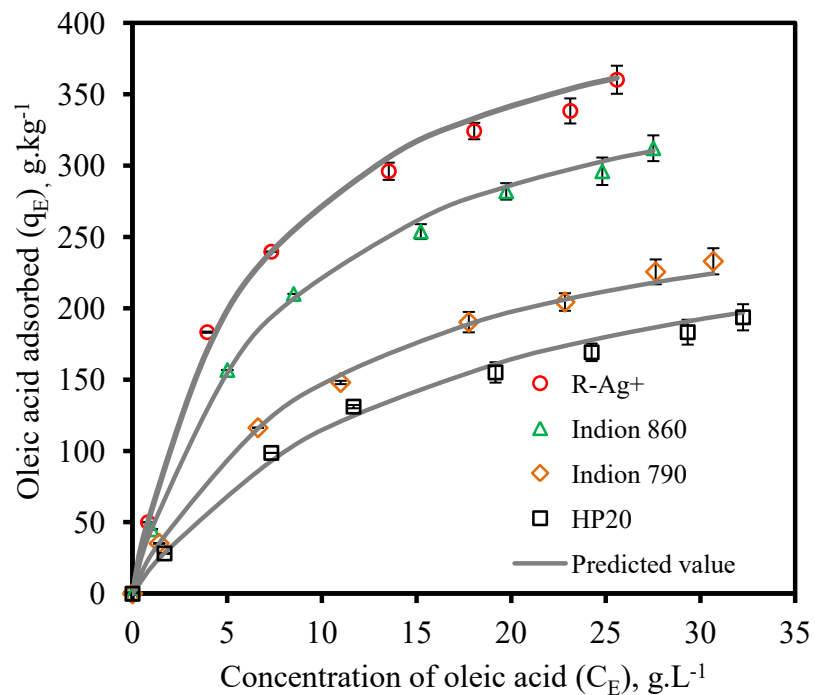


Figure 1 Screening of different resin (HP20, Indion 790, Indion 860, and R-Ag<sup>+</sup>) for adsorption of oleic acid from heptane

Thus, adsorption of the acid is expected to be higher on Indion 860 resin than that on HP20 resin. The interaction between the acid and Indion 790 resin is possibly attributed to the complexation between the unoccupied 1s orbital of hydrogen ion and the occupied  $2p\pi$  orbitals of the double bond of the acid. However, this interaction is very weak. If this is a case, the adsorption of the acid on Indion 790 resin should be less than the adsorption of acid on Indion 860 resin. For example, the maximum adsorption of oleic acid was found  $233.01 \text{ g.kg}^{-1}$  and  $312.25 \text{ g.kg}^{-1}$  from heptane on Indion 790 and Indion 860, respectively.

The adsorption of the acid on the  $\text{R-Ag}^+$  resin has been attributed to the interaction between silver ion ( $\text{Ag}^+$ ) and the double bond of the acid. This interaction is based on the ability of the acid to form  $\pi$ -n complex with silver ion. These complexes are of the charge-transfer type, i.e. the acid acts as an electron donor and the silver ion as an electron acceptor. The interaction exists between the occupied  $2p\pi$  orbitals of a double bond of the acid and the unoccupied 5s and 5p orbitals of the silver ion, and a probably weaker interaction between the occupied 4d orbitals of the silver ion and the free antibonding  $2p\pi^*$  orbitals of the olefinic bond.<sup>39-41</sup> Consequently, the maximum adsorption of oleic acid was observed on  $\text{R-Ag}^+$  resin. For example, the maximum adsorption of oleic acid was found  $233.01 \text{ g.kg}^{-1}$ ,  $312.25 \text{ g.kg}^{-1}$ , and  $360.20 \text{ g.kg}^{-1}$  from heptane on Indion 790, Indion 860, and  $\text{R-Ag}^+$  resin, respectively.

Literature reports adsorptive separation of fatty acids using various adsorbents such as zeolites,<sup>18</sup> strong anion exchange resin,<sup>19,20</sup> weak base anion exchange resins,<sup>21</sup> iron oxide,<sup>22</sup> activated carbon,<sup>23</sup> mixed bed ion-exchange resins,<sup>24</sup> rice hull ash,<sup>25-27</sup> and clay.<sup>28-30,42</sup> The summary of previous work on adsorption of fatty acid is given in Table 5 with relevant details. For example, Maddikeri et al.<sup>21</sup> have investigated adsorption of oleic acid on Indion 860 from sunflower oil and reported maximum adsorption capacity as  $441 \text{ g.kg}^{-1}$  at 293 K. However, in the present case, maximum adsorption capacity of Indion 860 was found to be  $400 \text{ g.kg}^{-1}$  at 303 K. The observed difference in the values can be attributed to the relative interaction of oleic acid with adsorbent and the diluent used to prepare the oleic acid stock solution. Cano et al.<sup>22</sup> have reported that the maximum uptake of oleic acid from hexane-ethanol (50:50) using iron oxide as the adsorbent is  $125 \text{ g.kg}^{-1}$ . Jamal and Boulanger<sup>24</sup> have reported that maximum adsorption of oleic acid is  $270 \text{ g.kg}^{-1}$  using mixed resin from soybean oil. Atia et al.<sup>26</sup> have reported the maximum adsorption capacity of rice hull ash for oleic acid as  $197.40 \text{ g.kg}^{-1}$  at 301 K, while Ilgen,<sup>20</sup> have reported the value of  $476.19 \text{ g.kg}^{-1}$  using Amberlyst A26 resin at 298 K.

Figure 1 also shows the fitting of Langmuir isotherm to experimental data. Langmuir isotherm shows good fit to the experimental data with a correlation coefficient ( $R^2$ ) of 0.99 and percentage average absolute deviation (% AAD) in the range of 1.56-3.98. The corresponding values for Freundlich isotherm were found to be in the range of 0.95- 0.98 and 7.75-12.98, respectively. The statistical analysis parameters ( $R^2$  and % AAD) for Langmuir isotherm and Freundlich isotherm are reported in Table 6 for all the solvents under investigation. The Langmuir isotherm and Freundlich isotherm constants are also reported in Table 6. The saturation adsorption capacity of  $\text{R-Ag}^+$  was estimated to be  $454.55 \text{ g.kg}^{-1}$  with the corresponding Langmuir adsorption constants of  $0.15 \text{ L.g}^{-1}$  using heptane as a diluent. Freundlich constants were estimated to be  $66.58 \text{ g}^{1-n}.\text{L}^n.\text{kg}^{-1}$  and 0.57 for oleic acid adsorption on  $\text{R-Ag}^+$  from heptane. The previous studies pertaining to adsorption of oleic acid on a given adsorbent typically indicate that Langmuir equation provides a good fit to the experimental adsorption data as illustrated in the present work.<sup>22,24,26,28,30</sup> Few studies are also available wherein experimental adsorption data were modeled by Freundlich isotherm.<sup>18,20,21</sup> For example, Maddikeri et al.<sup>21</sup> have investigated adsorption of oleic acid from sunflower oil on Indion 860 and reported the values of  $K_F$  and  $n$  as  $94 \text{ g}^{1-n}.\text{L}^n.\text{kg}^{-1}$  and 0.78, respectively. The present work reports  $K_F$  and  $n$  as  $51.04 \text{ g}^{1-n}.\text{L}^n.\text{kg}^{-1}$  and 0.59, respectively for adsorption of oleic acid on Indion 860 from heptane.

Table 5 Summary of previous work on adsorption of fatty acids

Adsorbate	Adsorbent	Kinetic model		Isotherm model		Thermodynamic parameter	Reference
		Type	Parameters	Type	Parameters		
Oleic acid	Zeolite	Pseudo second order	$k = 0.003 \text{ g.mg}^{-1}.\text{min}^{-1}$	Freundlich	$K_F = 84.29 \text{ mg}^{1-n}.\text{g}^{n-1}$ $n = 0.13$	$\Delta G_{348}^O = -10.66 \text{ kJ.mol}^{-1}$ $\Delta H^O = 33.89 \text{ kJ.mol}^{-1}$ $\Delta S^O = 0.13 \text{ kJ.mol}^{-1}.\text{K}^{-1}$	[18]
Oleic acid	Amberlyst A26	Pseudo second order	$k = 1.0250 \times 10^{-4} \text{ g.mg}^{-1}.\text{min}^{-1}$	Freundlich	$K_F = 246.83 \text{ mg}^{1-n}.\text{g}^{n-1}$ $n = 0.21$	-	[20]
Stearic acid	Indion 860	Pseudo-first-order	$k = 0.0131 \text{ min}^{-1}$	Freundlich	$K_F = 182 \text{ mg}^{1-n}.\text{g}^{n-1}$ $n = 0.54$ $q_M = 0.53 \text{ g.g}^{-1}$	$\Delta G_{293}^O = -13.4 \text{ kJ.mol}^{-1}$ $\Delta H^O = -48 \text{ kJ.mol}^{-1}$ $\Delta S^O = -0.12 \text{ kJ.mol}^{-1}.\text{K}^{-1}$	[21]
Oleic acid			$k = 0.0103 \text{ min}^{-1}$		$K_F = 142 \text{ mg}^{1-n}.\text{g}^{n-1}$ $n = 0.63$ $q_M = 0.49 \text{ g.g}^{-1}$	$\Delta G_{293}^O = -12.6 \text{ kJ.mol}^{-1}$ $\Delta H^O = -55 \text{ kJ.mol}^{-1}$ $\Delta S^O = -0.14 \text{ kJ.mol}^{-1}.\text{K}^{-1}$	
Oleic acid	Iron oxide	Pseudo second order	$k = 0.002 \text{ g.mg}^{-1}.\text{min}^{-1}$	Langmuir	298 K $q_M = 125 \text{ mg.g}^{-1}$ $K_L = 0.009 \text{ L.mg}^{-1}$	-	[22]
Oleic acid	Activated carbon	-	-	Freundlich	$K_F = 0.95 \text{ mg}^{1-n}.\text{g}^{-1}.\text{L}^n$ $n = 0.37$	-	[23]
Oleic acid	Mixed bed resin	Pseudo-first-order	$k = 1.62 \text{ h}^{-1}$	Langmuir	$q_M = 0.27 \text{ g.g}^{-1}$ $K_L = 8.9 \text{ g.g}^{-1}$	-	[24]
Palmytic acid	Rice hull ash	-	-	Langmuir	303 K $q_M = 15.82 \text{ mg.g}^{-1}$ $K_L = 0.94 \text{ g.mg}^{-1}$ 313 K $q_M = 20.16 \text{ mg.g}^{-1}$ $K_L = 1.32 \text{ g.mg}^{-1}$ 323 K $q_M = 21.51 \text{ mg.g}^{-1}$ $K_L = 1.68 \text{ g.mg}^{-1}$	$\Delta G_{303}^O = -22.2 \text{ kJ.mol}^{-1}$ $\Delta G_{313}^O = -24.4 \text{ kJ.mol}^{-1}$ $\Delta G_{323}^O = -25.8 \text{ kJ.mol}^{-1}$ $\Delta H^O = 31.7 \text{ kJ.mol}^{-1}$ $\Delta S^O = 0.178 \text{ kJ.mol}^{-1}.\text{K}^{-1}$	[25]
Oleic acid	Rice hull ash	-	-	Langmuir	301 K	$\Delta G_{301}^O = -23.1 \text{ kJ.mol}^{-1}$	[26]

					$q_M = 0.75 \text{ mmol.g}^{-1}$	$K_L = 181.72 \text{ g.mmol}^{-1}$				
Free fatty acids	Rice hull ash	-	-	Freundlich	$K_F = 25.19 \text{ mg}^{1-n} \cdot \text{g}^{-n-1}$	$n = 0.39$	-	[27]		
Capric acid	Montmorillonite	-	-	Langmuir	$q_M = 46.20 \text{ mg.g}^{-1}$	$K_L = 0.176 \text{ g.mg}^{-1}$	$\Delta G^O_{298} = -6.59 \text{ kcal.mol}^{-1}$	[28]		
Lauric acid					$q_M = 44.68 \text{ mg.g}^{-1}$	$K_L = 0.177 \text{ g.mg}^{-1}$	$\Delta G^O_{298} = -6.67 \text{ kcal.mol}^{-1}$			
Myristic acid					$q_M = 43.17 \text{ mg.g}^{-1}$	$K_L = 0.178 \text{ g.mg}^{-1}$	$\Delta G^O_{298} = -6.74 \text{ kcal.mol}^{-1}$			
Palmitic acid					$q_M = 41.45 \text{ mg.g}^{-1}$	$K_L = 0.18 \text{ g.mg}^{-1}$	$\Delta G^O_{298} = -6.82 \text{ kcal.mol}^{-1}$			
Stearic acids					$q_M = 40.13 \text{ mg.g}^{-1}$	$K_L = 0.181 \text{ g.mg}^{-1}$	$\Delta G^O_{298} = -6.90 \text{ kcal.mol}^{-1}$			
Stearic acid	Kaolinite	-	-	Langmuir	298 K $q_M = 18.80 \text{ mg.g}^{-1}$ $K_L = 0.25 \text{ g.mg}^{-1}$	308 K $q_M = 16.95 \text{ mg.g}^{-1}$ $K_L = 0.23 \text{ g.mg}^{-1}$	318 K $q_M = 16.12 \text{ mg.g}^{-1}$ $K_L = 0.19 \text{ g.mg}^{-1}$	$\Delta G^O_{298} = -19.98 \text{ kJ.mol}^{-1}$ $\Delta G^O_{308} = -20.33 \text{ kJ.mol}^{-1}$ $\Delta G^O_{318} = -20.50 \text{ kJ.mol}^{-1}$ $\Delta H^O = -12.30 \text{ kJ.mol}^{-1}$ $\Delta S^O = 0.026 \text{ kJ.mol}^{-1} \cdot \text{K}^{-1}$	[29]	
Stearic acid	Celtek clay	-	-	Langmuir	293 K $q_M = 26.70 \text{ mg.g}^{-1}$ $K_L = 0.14 \text{ L.mg}^{-1}$	298 K $q_M = 25.2 \text{ mg.g}^{-1}$ $K_L = 0.12 \text{ L.mg}^{-1}$	303 K $q_M = 23 \text{ mg.g}^{-1}$ $K_L = 0.1 \text{ L.mg}^{-1}$	308 K $q_M = 23 \text{ mg.g}^{-1}$ $K_L = 0.1 \text{ L.mg}^{-1}$	$\Delta G^O_{293} = -2.6 \text{ kJ.mol}^{-1}$ $\Delta G^O_{298} = -2.3 \text{ kJ.mol}^{-1}$ $\Delta G^O_{303} = -1.4 \text{ kJ.mol}^{-1}$ $\Delta G^O_{308} = -1.3 \text{ kJ.mol}^{-1}$ $\Delta G^O_{313} = -0.7 \text{ kJ.mol}^{-1}$ $\Delta H^O = -30.4 \text{ kJ.mol}^{-1}$ $\Delta S^O = -0.094 \text{ kJ.mol}^{-1} \cdot \text{K}^{-1}$	[30]

					$q_M = 22.2 \text{ mg.g}^{-1}$ $K_L = 0.09 \text{ L.mg}^{-1}$ 313 K $q_M = 21.3 \text{ mg.g}^{-1}$ $K_L = 0.08 \text{ L.mg}^{-1}$		
Oleic acid	Amberlyst A26	-	-	Langmuir	298 K $q_M = 1.33 \text{ g.g}^{-1}$ $K_L = 2.88 \times 10^{-6} \text{ g.g}^{-1}$ 313 K $q_M = 1.30 \text{ g.g}^{-1}$ $K_L = 2.55 \times 10^{-6} \text{ g.g}^{-1}$	-	[34]
Stearic acids	Bentonite	-	-	Langmuir	298 K $q_M = 36.40 \text{ mg.g}^{-1}$ $K_L = 0.22 \text{ g.mg}^{-1}$ 308 K $q_M = 35.7 \text{ mg.g}^{-1}$ $K_L = 0.20 \text{ g.mg}^{-1}$ 318 K $q_M = 35.10 \text{ mg.g}^{-1}$ $K_L = 0.18 \text{ g.mg}^{-1}$	$\Delta G_{298}^0 = -21.8 \text{ kJ.mol}^{-1}$ $\Delta G_{308}^0 = -22 \text{ kJ.mol}^{-1}$ $\Delta G_{318}^0 = -22.7 \text{ kJ.mol}^{-1}$ $\Delta H^0 = -9.2 \text{ kJ.mol}^{-1}$ $\Delta S^0 = 0.042 \text{ kJ.mol}^{-1} \cdot \text{K}^{-1}$	[42]
Oleic acid	Silver ion loaded resin (R-Ag <sup>+</sup> )	-	-	Langmuir	303 K $q_M = 454.55 \text{ g.kg}^{-1}$ $K_L = 0.151$	$\Delta G_{303}^0 = -9.19 \text{ kJ.mol}^{-1}$ $\Delta G_{313}^0 = -8.37 \text{ kJ.mol}^{-1}$ $\Delta G_{323}^0 = -7.65 \text{ kJ.mol}^{-1}$ $\Delta H^0 = -32.55 \text{ kJ.mol}^{-1}$ $\Delta S^0 = -0.077 \text{ kJ.mol}^{-1} \cdot \text{K}^{-1}$	Present study

$K_L$  = Langmuir adsorption constant;  $q_M$  = saturation capacity of the resin;  $K_F$  = Freundlich constant;  $n$  = Freundlich constant;  $\Delta H_{\text{ads}}^0$  = standard enthalpy change;  $\Delta S_{\text{ads}}^0$  = standard entropy change;  $\Delta G_{\text{ads}}^0$  = standard Gibbs free energy change

Table 6 Langmuir and Freundlich constants

Adsorbent	HP20				Indion 790				Indion 860				R-Ag <sup>+</sup>			
Langmuir constant																
Solvent	K <sub>L</sub>	q <sub>M</sub>	R <sup>2</sup>	AAD	K <sub>L</sub>	q <sub>M</sub>	R <sup>2</sup>	AAD	K <sub>L</sub>	q <sub>M</sub>	R <sup>2</sup>	AAD	K <sub>L</sub>	q <sub>M</sub>	R <sup>2</sup>	AAD
	L.g <sup>-1</sup>	g.kg <sup>-1</sup>	-	%	L.g <sup>-1</sup>	g.kg <sup>-1</sup>	-	%	L.g <sup>-1</sup>	g.kg <sup>-1</sup>	-	%	L.g <sup>-1</sup>	g.kg <sup>-1</sup>	-	%
Heptane	0.06	294.10	0.99	3.98	0.09	303.00	0.99	1.56	0.13	400.00	0.99	1.69	0.15	454.55	0.99	2.98
Toluene	0.05	256.40	0.99	2.48	0.07	256.40	0.99	2.28	0.10	344.80	0.99	3.96	0.12	416.70	0.99	1.39
Ethyl acetate	0.04	212.70	0.99	2.65	0.07	217.40	0.99	2.45	0.09	294.10	0.99	0.74	0.10	357.20	0.99	0.89
IPA	0.03	185.10	0.99	3.17	0.06	185.20	0.99	2.10	0.08	243.90	0.99	1.58	0.07	285.70	0.99	2.20
Methanol	0.03	149.30	0.99	4.49	0.04	153.90	0.99	2.39	0.06	208.30	0.99	2.49	0.07	217.40	0.99	1.93
Freundlich constant																
	K <sub>F</sub>	n	R <sup>2</sup>	AAD	K <sub>F</sub>	n	R <sup>2</sup>	AAD	K <sub>F</sub>	n	R <sup>2</sup>	AAD	K <sub>F</sub>	n	R <sup>2</sup>	AAD
	#	-	-	%	#	-	-	%	#	-	-	%	#	-	-	%
Heptane	22.67	0.65	0.96	10.55	31.12	0.62	0.98	7.75	51.04	0.59	0.96	10.68	66.58	0.57	0.95	12.98
Toluene	15.45	0.69	0.98	19.66	21.99	0.64	0.98	8.57	37.25	0.62	0.98	9.14	50.15	0.61	0.97	10.07
Ethyl acetate	11.01	0.72	0.98	6.98	18.40	0.64	0.97	8.86	29.68	0.62	0.97	8.97	39.62	0.62	0.97	9.35
IPA	7.33	0.77	0.97	4.57	12.75	0.67	0.98	6.51	22.33	0.63	0.97	8.99	24.09	0.64	0.97	9.88
Methanol	4.44	0.82	0.97	4.53	8.59	0.69	0.98	7.48	14.26	0.68	0.98	6.54	17.91	0.65	0.98	7.63

Freundlich constant for multi-component		R-Ag <sup>+</sup>			
Heptane		K <sub>F1</sub> = 9.39			
		a <sub>12</sub> = 0.11	n <sub>1</sub> = 0.73	R <sup>2</sup> = 0.98	% AAD = 3.95
		a <sub>13</sub> = 0.15			
-	-	K <sub>F2</sub> = 11.94			
		a <sub>21</sub> = 0.11	n <sub>2</sub> = 0.74	R <sup>2</sup> = 0.99	% AAD = 2.92
		a <sub>23</sub> = 0.16			
		K <sub>F3</sub> = 12.80			
		a <sub>31</sub> = 0.15	n <sub>3</sub> = 0.80	R <sup>2</sup> = 0.98	% AAD = 3.10
		a <sub>32</sub> = 0.16			

K<sub>L</sub> = Langmuir adsorption constant; q<sub>M</sub> = saturation capacity of the resin; R<sup>2</sup> = correlation coefficient; % AAD = percentage average

absolute deviation calculated using formula  $\left( \% \text{ AAD} = \frac{1}{m} \sum_{i=1}^m \left| \frac{q_{\text{exp},i}^* - q_{\text{calc},i}^*}{q_{\text{calc},i}^*} \right| \times 100 \right)$ ; K<sub>F</sub> = Freundlich constant; # = g<sup>1-n</sup>.L<sup>n</sup>.kg<sup>-1</sup>; n = Freundlich constant; a = competitive coefficient; Subscript 1, 2, and 3 = oleic acid, linoleic, and linolenic acid, respectively.



### 3.1.2 Effect of solvent on adsorption

Figure 2 shows effect of nature of solvent on adsorption of oleic acid on R-Ag<sup>+</sup> resin at 303 K. The experimental data pertaining to effect of solvents on adsorption of oleic acid on HP20, Indion 790, and Indion 860 at 303 K have been reported in Table 4. The adsorption behavior of the acid on the resin predominantly depends on the relative interaction of the acid with a solvent and the resin. Non-polar solvents like heptane and toluene interact with the acid by weak dipole-induced dipole interactions. Thus, the adsorption of the acid on the resin would be higher from these solvents. However, the interaction of the acid with the polar solvents is stronger as compared to that with non-polar solvents. The carboxylate group of the acid is expected to be highly solvated in polar solvents by hydrogen bonding. This is indeed the case as indicated by maximum adsorption of the acid from heptane followed by that in toluene. The adsorption was the least for methanol on all the resins. For example, the saturation capacity of R-Ag<sup>+</sup> resin was found for non-polar solvents like heptane (454.55 g.kg<sup>-1</sup>), followed by toluene (416.70 g.kg<sup>-1</sup>) as compared to its minimum value from methanol (217.40 g.kg<sup>-1</sup>). The corresponding Langmuir constants were found to be 0.15, 0.12, and 0.07 L.g<sup>-1</sup> for heptane, toluene, and methanol, respectively. Conclusively, the adsorption of the acid from different solvents follows the increasing order as: heptane > toluene > ethyl acetate > IPA > methanol for a given resin.

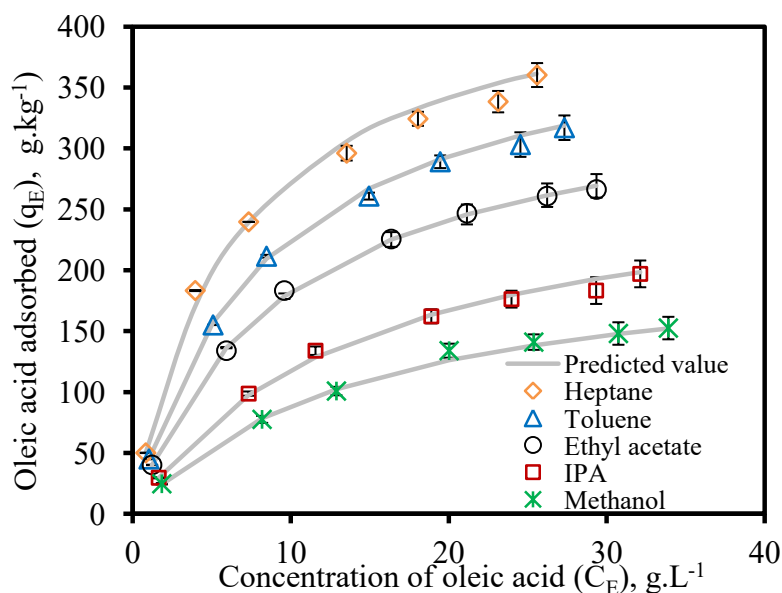


Figure 2 Equilibrium adsorption of oleic acid on R-Ag<sup>+</sup> resin from different solvents (Heptane, Toluene, Ethyl acetate, IPA, Methanol)

The molecular size of oleic acid also seems to affect its adsorption on the resin. The maximum adsorption capacity of oleic acid on Indion 860 resin was found to be 294.10 g.kg<sup>-1</sup> from ethyl acetate. The maximum adsorption capacity of similar resin was found to be 726 g.kg<sup>-1</sup> from ethyl acetate for acetic acid.<sup>38</sup> Oleic acid has a longer size (22.3 Å<sup>0</sup>) while acetic acid is relatively smaller in size (4 Å<sup>0</sup>). In the case of acetic acid, hydrogen bond between the acidic hydrogen and the nitrogen atom of the resin was responsible for adsorption. However, in the case of oleic acid the interaction of its longer hydrocarbon chain with the resin and solvent can modify its adsorption. Further, the larger size of oleic acid reduces its adsorption capacity due to the

blockage of some of the sites of the resin while this effect could be insignificant in the case of acetic acid.

### 3.1.3. Swelling of adsorbent

The resins were swollen due to the penetration of the acid and the solvent depending on their affinity for the resin during the adsorption of oleic acid on the different resins. Table 4 shows the swelling of the resins in terms of swelling ratio (defined as the ratio of the volume of swollen resin to the volume of dry resin) in a given solvent. The swelling of all the resins was found maximum in methanol, followed by IPA, and minimum in heptane. For example, the maximum swelling ratio for Indion 860 resin in different solvents was 1.08 for heptane, 1.13 for toluene, 1.15 for ethyl acetate, 1.19 for IPA, and 1.27 for methanol, respectively. Heptane is straight chain alkane molecule which mainly interacts with Indion 860 by weak van der Waals forces and consequently, swelling was found minimum in heptane. Toluene interacts with the polymeric backbone of the resin because of aromatic  $\pi$  electrons and hence swelling in this solvent is marginal as compared to heptane. The resins swell noticeably in polar aprotic solvent (ethyl acetate) and more in polar solvents (IPA and methanol). This is mainly attributed to their ability to act either as hydrogen bond donor and/or acceptor which in turn results into comparatively higher swelling of the polymer matrix.

### 3.1.4. Effect of temperature on adsorption

The R-Ag<sup>+</sup> resin show maximum adsorption capacity for oleic acid as compared to HP20, Indion 790, and Indion 860 from heptane at 303 K. Therefore, R-Ag<sup>+</sup> resin were considered to investigate the effect of temperature (303, 313, and 323 K) on adsorption of oleic acid from heptane. Figure 3 shows the effect of temperature on adsorption of oleic acid. The adsorption of oleic acid decreases with an increase in adsorption temperature from 303 to 323 K. Figure 3 also shows that Langmuir equation provides good fit to experimental adsorption data with the R<sup>2</sup> of 0.97 and % AAD in the range of 2.98-3.71, respectively at the investigated temperatures. The Langmuir constants, estimated using eq 3, are reported in Table 7.

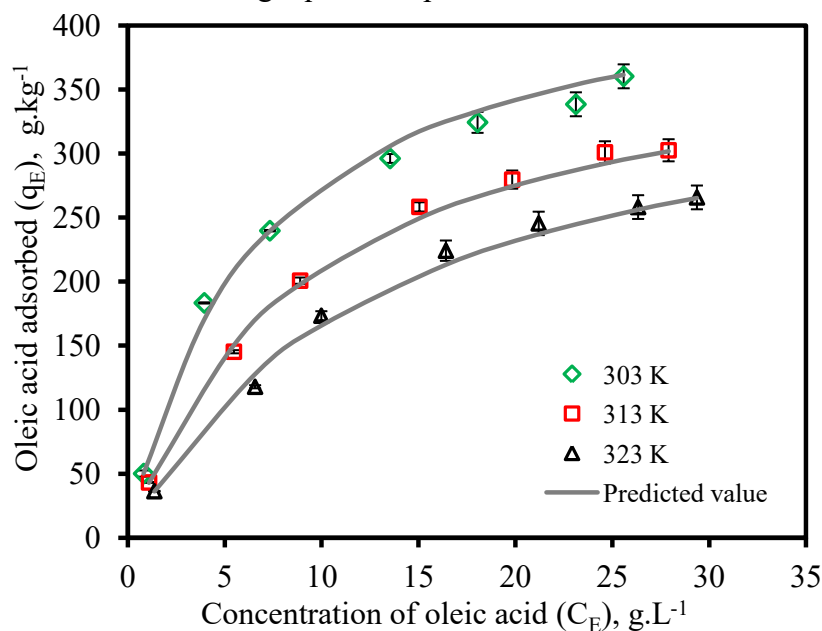


Figure 3 Effect of temperature (303, 313, and 323 K) for oleic acid adsorption on R-Ag<sup>+</sup> from heptane

Table 7 Thermodynamic and Langmuir parameters for adsorption of oleic acid on R-Ag<sup>+</sup> from heptane

Adsorbate	Temperature K	$K_L$ L.g <sup>-1</sup>	$q_m$ g.kg <sup>-1</sup>	$K_0$ -	$\Delta G_{ads}^0$ kJ.mol <sup>-1</sup>	$\Delta H_{ads}^0$ kJ.mol <sup>-1</sup>	$\Delta S_{ads}^0$ kJ.mol <sup>-1</sup> .K <sup>-1</sup>
Oleic acid	303	0.15	454.55	38.47	-9.19		
	313	0.11	400.00	25.02	-8.37	-32.55	-0.077
	323	0.07	384.61	17.28	-7.65		

$K_L$  = Langmuir adsorption constant;  $q_M$  = saturation adsorption capacity of the resin;  $K_0$  = adsorption equilibrium constant;  $\Delta H_{ads}^0$  = standard enthalpy change;  $\Delta S_{ads}^0$  = standard entropy change;  $\Delta G_{ads}^0$  = standard Gibbs free energy change

Oleic acid was appreciably adsorbed on R-Ag<sup>+</sup> resin with a saturation adsorption capacity of 454.55 g.kg<sup>-1</sup> and Langmuir adsorption constants of 0.15 L.g<sup>-1</sup> at 303 K as compared to adsorption temperature of 323 K where a saturation adsorption capacity of 384.61 g.kg<sup>-1</sup> and Langmuir adsorption constants of 0.07 L.g<sup>-1</sup> were estimated for adsorption of oleic acid. The values of saturation adsorption capacity and Langmuir adsorption constant, reported in Table 7, show that adsorption capacity of R-Ag<sup>+</sup> resin decreases with an increase in adsorption temperature. This may be due to a possible desorption of the oleic acid molecules at high temperature. Similar result has been reported by Maddikeri et al.<sup>21</sup> for adsorption of oleic acid on Indion 860 resin wherein Freundlich adsorption constant decreased from 142 to 44 mg<sup>1-n</sup>.g<sup>n-1</sup> for adsorption temperature from 293 to 313 K. Demirbas et al.<sup>42</sup> have also reported that adsorption capacity of bentonite decreases with an increase in adsorption temperature in range of 298 to 318 K for adsorption of stearic acid.

### 3.1.5. Thermodynamic parameters

Figure 4 shows effect of adsorption temperature on adsorption equilibrium constant ( $K_0$ ). The positive values of  $K_0$  indicate that the amount of oleic acid present per unit amount of resin is high as compared to the amount of oleic acid present per unit amount of the stock solution. Further,  $K_0$  increases with a decrease in adsorption temperature as shown in Table 7. This indicates that the amount of oleic acid adsorbed per kg of resin in equilibrium with oleic acid concentration in liquid phase is high at low temperature as compared to higher temperature. Similar results have been reported by Maddikeri et al.<sup>21</sup> for adsorption of oleic acid on Indion 860 resin and Demirbas et al.<sup>42</sup> for adsorption of stearic acid on bentonite as adsorbent. The values of  $\Delta G_{ads}^0$ , calculated using eq 11, have been observed to be negative at all the adsorption temperatures, indicating feasibility and spontaneity of the adsorption of oleic acid on R-Ag<sup>+</sup> resin.  $\Delta G_{ads}^0$  varies in the range of -7.65 to -9.19 kJ.mol<sup>-1</sup> for oleic acid adsorption, suggesting that the adsorption of oleic acid on R-Ag<sup>+</sup> resin was governed by the physical interaction.<sup>21,42,43</sup>

From Table 7, it can be seen that  $\Delta G_{ads}^0$  decreases with an increase in adsorption temperature. This is mainly attributed to weaker interaction between the oleic acid and resin at higher temperature with an enhanced solubility of oleic acid in heptane. Therefore, adsorption of oleic acid is favorable at lower temperature as compared to higher temperature. Bayrak<sup>28</sup> has

investigated the adsorption of stearic acid on montmorillonite at 298 K and reported  $\Delta G_{\text{ads}}^0$  as -28.87 kJ.mol<sup>-1</sup>. Demirbas et al.<sup>42</sup> have studied the adsorption of stearic acid on bentonite and reported that  $\Delta G_{\text{ads}}^0$  lies in the range of -21.80 to -22.70 kJ.mol<sup>-1</sup>.

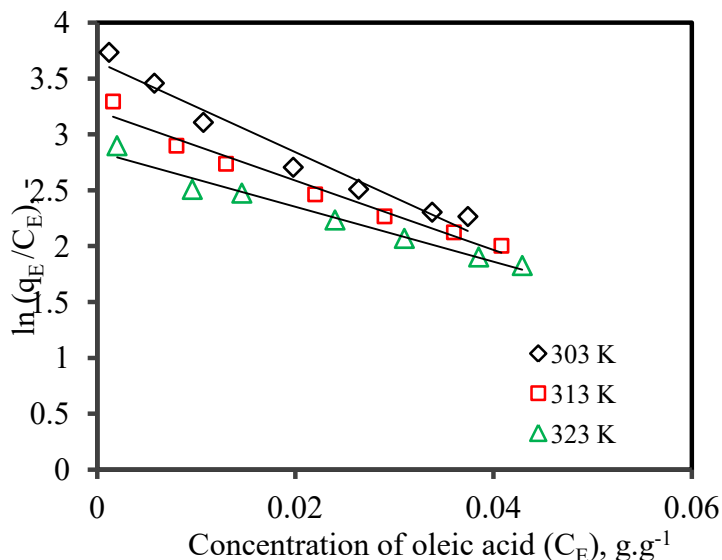


Figure 4 Plot for determination of adsorption equilibrium constant for oleic acid adsorption on R-Ag<sup>+</sup> resin

Maddikeri et al.<sup>21</sup> have investigated adsorption of oleic acid on Indion 860 and reported that  $\Delta G_{\text{ads}}^0$  lies in the range of -9.70 to -12.60 kJ.mol<sup>-1</sup>. In the present work,  $\Delta G_{\text{ads}}^0$  varies in the range of -7.65 to -9.19 kJ.mol<sup>-1</sup> for oleic acid adsorption on R-Ag<sup>+</sup>. The observed difference in the  $\Delta G_{\text{ads}}^0$  values is primarily due to the dependence of the adsorption process on the interactions between fatty acid and the type of adsorbent. It also depends on the diluent used to prepare the fatty acid stock solution. Maddikeri et al.<sup>21</sup> have used sunflower oil as a diluent while heptane was used to prepare oleic acid solution in the present work.

The value of  $\Delta H_{\text{ads}}^0$  and  $\Delta S_{\text{ads}}^0$  can be estimated from the slope and intercept of the straight line, respectively when  $\ln K_0$  is plotted against  $1/T$  (eq 12). The value of  $\Delta S_{\text{ads}}^0$  and  $\Delta H_{\text{ads}}^0$  are reported in Table 7. A negative value of  $\Delta H_{\text{ads}}^0$  indicates that the adsorption process is exothermic and thus decrease in temperature favors adsorption of oleic acid on R-Ag<sup>+</sup> resin. The change in entropy indicates the order-disorder in a given system. The lower value of change in entropy indicates that a given process occurs in an orderly manner and vice versa. The negative value of  $\Delta S_{\text{ads}}^0$  indicates that adsorption of oleic acid on R-Ag<sup>+</sup> occurs in an orderly manner.

### 3.2. Adsorption of fatty acid mixture

The adsorption of oleic acid on R-Ag<sup>+</sup> resin was found maximum from heptane as compared to all the other resins. Therefore, separation of a fatty acid mixture (C<sub>12</sub> to C<sub>22</sub>) has been attempted on R-Ag<sup>+</sup> using heptane as a diluent. Table 2 gives the composition of the mixture of the fatty acids. Figure 5 shows the adsorption of the fatty acids on R-Ag<sup>+</sup> resin wherein the symbols indicate experimental values and the solid lines represent the fitting of multi-component

Freundlich equation (eq 5) to experimental data with  $R^2$  and % AAD in the range of 0.98-0.99 and 2.92-3.95 %, respectively. The multi-component Freundlich parameters are reported in Table 6. The lower values of the Freundlich constant,  $n$  (less than 1), indicate favorable interaction of oleic acid, linoleic acid, and linolenic acid with  $R\text{-Ag}^+$  resin. Figure 6 shows the typical plot of  $\ln(q_E/C_E)$  versus  $C_E$  for oleic acid, linoleic acid, and linolenic acid using heptane as a solvent.

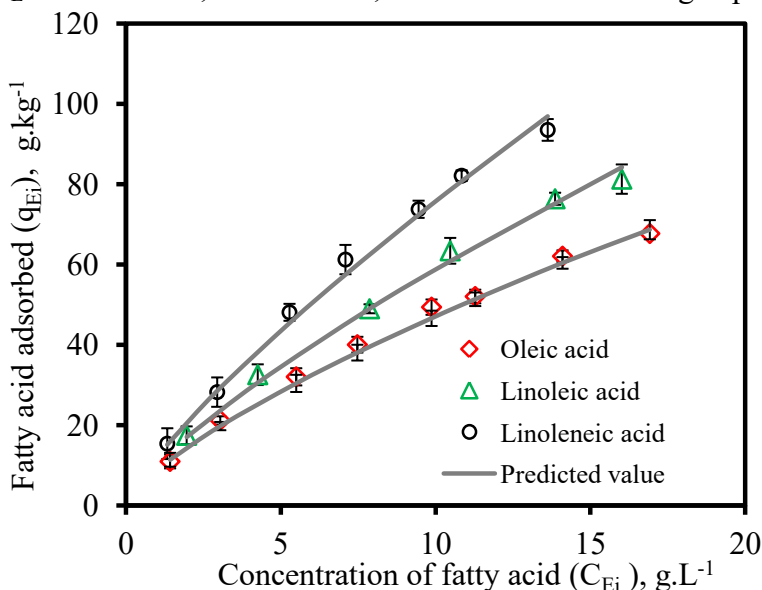


Figure 5 Equilibrium adsorption of oleic acid, linoleic acid, and linolenic acid from mixture of fatty acids on  $R\text{-Ag}^+$  from heptane

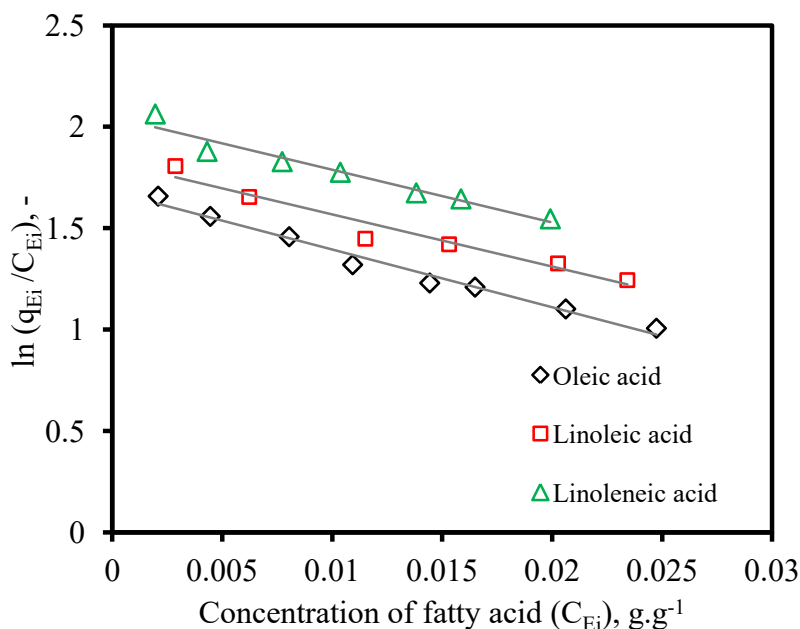


Figure 6 Determination of adsorption equilibrium constant for adsorption of oleic acid, linoleic acid, and linolenic acid on  $R\text{-Ag}^+$  resin from heptane

The linear relationship exists between  $\ln(q_E/C_E)$  and  $C_E$  and the value  $K_0$  can be determined by extrapolating the data to set  $C_E$  equal to zero. The values of  $K_0$  were found to be 5.36, 6.23, and

7.49 for oleic acid, linoleic acid, and linolenic acid, respectively. The positive values of  $K_0$  indicate that the amount of acid adsorbed per unit mass of the resin is high as compared to the amount of the acid present per unit mass of the liquid solution. The selectivity of linolenic acid and linoleic acid over oleic acid can be defined as a ratio of  $K_0$  of linolenic acid and linoleic acid to the  $K_0$  of oleic acid. Accordingly, the selectivity of linolenic acid and linoleic acid over oleic acid was estimated to be 1.40 and 1.16, respectively. These values indicate that the number of double bonds play an important role in the adsorption of the acids. The presence of three double bonds in linolenic acid results in greater interaction with the silver ion as compared to linoleic and oleic acids. In the presence of silver ion, the double bonds of linolenic acid orient themselves in such a way that maximum interaction is favored.

#### 4. CONCLUSIONS

The adsorption of oleic acid was favored in non-polar solvents for all the resins, with the maximum adsorption on the R-Ag<sup>+</sup> resin. Batch equilibrium adsorption data were modeled using Langmuir isotherm. The maximum adsorption of oleic acid was found to be 454.55 g.kg<sup>-1</sup> on the R-Ag<sup>+</sup> resin from heptane while minimum value was estimated to be 149.30 g.kg<sup>-1</sup> on HP20 from methanol. The resin swelling was found to be higher in the polar solvents as compared to non-polar solvents. The maximum swelling ratio was estimated to be 1.28 for R-Ag<sup>+</sup> in methanol while the minimum swelling ratio was found to be 1.02 for HP20 in heptane. The adsorption of oleic acid on R-Ag<sup>+</sup> resin from heptane decreases with an increase in temperature. The values of  $\Delta H_{\text{ads}}^0$  (-32.55 kJ.mol<sup>-1</sup>) and  $\Delta G_{\text{ads}}^0$  (-7.65 to -9.19 kJ.mol<sup>-1</sup>) indicate that the adsorption of oleic acid on R-Ag<sup>+</sup> was exothermic and physical in nature. Adsorption study of fatty acid mixture on R-Ag<sup>+</sup> resin revealed that linolenic acid and linoleic acid get preferentially adsorbed over oleic acid from heptane. The selectivity of linolenic acid and linoleic acid for oleic acid was found to be 1.40 and 1.16, respectively. Overall, efficacy of R-Ag<sup>+</sup> resin for the removal of free fatty acids from the solution has been demonstrated, and the design related thermodynamic information has been presented.

#### ASSOCIATED CONTENT

Supporting Information Table S1: Separation techniques for fatty acids (<https://pubs.acs.org/doi/10.1021/acs.jced.0c00700>)

#### NOTES

The authors declare no competing financial interest.

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#### NOMENCLATURE

$a_A^L$	=	activity of the acid in liquid phase, -
$a_A^S$	=	activity of the acid in solid phase, -
$a_{ij}$	=	competitive coefficient defined by eq 5, -
$C_E$	=	concentration of acid at equilibrium, g.L <sup>-1</sup>
$C_0$	=	initial concentration of the acid, g.L <sup>-1</sup>
$\Delta G_{\text{ads}}^0$	=	standard Gibbs free energy change, kJ.mol <sup>-1</sup>
$\Delta H_{\text{ads}}^0$	=	standard enthalpy change, kJ.mol <sup>-1</sup>

$K_L$	=	Langmuir adsorption constant, $L.g^{-1}$
$K_F$	=	Freundlich constant, $g^{1-n}.L^n.kg^{-1}$
$K_0$	=	adsorption equilibrium constant, -
$n$	=	Freundlich constant, -
$q_E$	=	amount of adsorbate adsorbed, $g.kg^{-1}$
$q_M$	=	saturation adsorption capacity of the resin, $g.kg^{-1}$
$R$	=	universal gas constant, $kJ.mol^{-1}.K^{-1}$
$T$	=	adsorption temperature, K
$\Delta S_{ads}^0$	=	standard entropy change, $kJ.mol^{-1}.K^{-1}$

### GREEK LETTERS

$\gamma_A^S$	=	activity coefficient of the acid in solid phase, -
$\gamma_A^L$	=	activity coefficient of the acid in liquid phase, -

### SUBSCRIPTS

$i$	=	$i^{th}$ component
$j$	=	$j^{th}$ component

### REFERENCES

1. Mičić, R.; Tomić, M.; Martinović, F.; Kiss, F.; Simikić, M.; Aleksić, A. Reduction of free fatty acids in waste oil for biodiesel production by glycerolysis: investigation and optimization of process parameters. *Green Process. Synth.* **2019**, *8*, 15-23.
2. Idris, N. A.; Lau, H. L. N.; Wafti, N. S. Abd.; Mustafa, N. K.; Loh, S. K. Glycerolysis of palm fatty acid distillate (PFAD) as biodiesel feedstock using heterogeneous catalyst. *Waste Biomass Valori.* **2020** <https://doi.org/10.1007/s12649-020-00995-6>.
3. Aktija, S. A.; Zirehpour, A. A.; Mollahosseini, M.; Taherzadeh, J.; Tiraferrie, A.; Rahimpour, A. Feasibility of membrane processes for the recovery and purification of bio-based volatile fatty acids: A comprehensive review. *J. Ind. Eng. Chem.* **2020**, *81*, 24-40.
4. Islam, M. S.; Christopher, L. P.; Alam, M. N. Separation and purification of  $\omega$ -6 linoleic acid from crude tall oil. *Separations* **2020**, *7*, 1-11.
5. Castejón, N.; Luna, P.; Senorans, F. J. Alternative oil extraction methods from *Echium plantagineum* L. seeds using advanced techniques and green solvents. *Food Chem.* **2018**, *244*, 75-82.
6. Yenuganti, V. R.; Viergutz, T.; Vanselow, J. Oleic acid induces specific alterations in the morphology, gene expression and steroid hormone production of cultured bovine granulosa cells. *Gen. Comp. Endocrinol.* **2016**, *232*, 134-144.
7. Sales-Campos, H.; De Souza, P. R.; Peghini, B. C.; da Silva, J. S.; Cardoso, C. R. An overview of the modulatory effects of oleic acid in health and disease. *Mini. Rev. Med. Chem.* **2013**, *13*, 1-10.
8. McCusker, M. M.; Jane, M. M.; Grant-Kels, M. D. Healing fats of the skin: the structural and immunologic roles of the  $\omega$ -6 and  $\omega$ -3 fatty acids. *Clin. Dermatol.* **2010**, *28*, 440-451.
9. Martins, P. F.; Ito, V.M.; Batistella, C. B.; Maciel, M. R. W. Deodorizer distillate using molecular distillation process. *Sep. Purif. Technol.* **2006**, *48*, 78-84.
10. Koris, A.; Vatai, G. Dry degumming of vegetable oils by membrane filtration. *Desalination* **2002**, *148*, 149-153.
11. Chongkhong, S.; Tongurai, C.; Chetpattananondh, P. Continuous esterification for biodiesel production from palm fatty acid distillate using economical process. *Renew. Energ.* **2009**, *34*, 1059-1063.

12. 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.
13. Mayamol, P. N.; Balachandran, E. C.; Samuel, E. T.; Sundaresan, E. A.; Arumughan, E. C. Process technology for the production of micronutrient rich red palm olein. *J. Amer. Oil Chem. Soc.* **2007**, 84, 587-596.
14. Elkacmi, R.; Kamil, N.; Boulmal, N.; Bennajah, M. Experimental investigations of oleic acid separation from olive oil and olive mill wastewater: a comparative study. *J. Mater. Environ. Sci.* **2016**, 7, 1485-1494.
15. Chen, C.; Wang, L.; Wang, C.; Ho, W.; Chang, C. Supercritical carbon dioxide extraction of rice bran oil and column partition fractionation of  $\gamma$ -oryzanols. *Sep. Purif. Technol.* **2008**, 61, 358-365.
16. Meher, L. C.; Dharmagadda, V. S. S; Naik, S. N. Optimization of alkali-catalyzed transesterification of *pongamia pinnata* oil for production of biodiesel. *Bioresour. Technol.* **2006**, 97, 1392-1397.
17. Elkacmi, R.; Kamil, N.; Bennajah, M.; Kitane, S. Extraction of oleic acid from morocane olive wastewater. *Biomed. Res. Int.* **2016**, 1-9.
18. Ilgen, O.; Dulger, H. S. Removal of oleic acid from sunflower oil on zeolite 13X: kinetics, equilibrium and thermodynamic studies. *Ind. Crops Prod.* **2016**, 81, 66-71.
19. Cren, É. 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.
20. Ilgen, O. Adsorption of oleic acid from sunflower oil on amberlyst A26 (OH). *Fuel Process Technol.* **2014**, 118, 69-74.
21. Maddikeri, G. L.; Pandit, A. B.; Gogate, P. R. Adsorptive removal of saturated and unsaturated fatty acids using ion-exchange resins. *Ind. Eng. Chem. Res.* **2012**, 51, 6869-6876.
22. Cano, M.; Bargoud, K. S.; Allard, E.; Larpent, C. Magnetic separation of fatty acids with iron oxide nanoparticles and application to extractive deacidification of vegetable oils. *Green Chem.* **2012**, 14, 1786-1795.
23. Vadi, M.; Ghaseminejad, E. Comparative study of isotherms adsorption of oleic acid by activated carbon and multi-wall carbon nanotube. *Orient J. Chem.* **2011**, 27, 973-978.
24. Jamal, Y.; Boulanger, B. O. Separation of oleic acid from soybean oil using mixed-bed resins. *J. Chem. Eng. Data* **2010**, 55, 2405-2409.
25. Adam, F.; Chua, J. H. The adsorption of palmytic acid on rice husk ash chemically modified with Al (III) ion using the sol-gel technique. *J. Colloid Interface Sci.* **2004**, 280, 55-61.
26. Atia, A. A.; El-Nahas, A. M.; Marie, A. M.; Al Mahdy, L. D. Adsorption of oleic acid on silica gel derived from rice ash hulls: Experimental and theoretical studies. *Adsorpt. Sci. Technol.* **2006**, 24, 797-814.
27. Clowutimon, W.; Kitchaiya, P.; Assawasaengrat, P. Adsorption of free fatty acid from crude palm oil on magnesium silicate derived from rice husk. *Eng. J.* **2011**, 15, 15-26.
28. Bayrak, Y. Application of Langmuir isotherm to saturated fatty acid adsorption. *Microporous Mesoporous Mater.* **2006**, 87, 203-206.
29. Sari, A.; Ip Idak, . Adsorption properties of stearic acid onto untreated kaolinite. *Bull. Chem. Soc. Ethiop.* **2006**, 20, 259-267.
30. Sari, A.; Soylak, M. Equilibrium and thermodynamic studies of stearic acid adsorption on



- Celtek clay. *J. Serb. Chem. Soc.* **2007**, 72, 485-494.
31. Dolowy, M.; Pyka, A. Chromatographic methods in the separation of long-chain mono and polyunsaturated fatty acids. *J. Chem.* **2015**, 1-20.
  32. Yurawecz, M. P.; Morehouse, K. M. Silver-ion HPLC of conjugated linoleic acid isomers. *Eur. J. Lipid Sci. Tech.* **2001**, 103, 609-613.
  33. Sheindorf, CH.; Rebhun, M.; Sheintuch, M. A Freundlich-Type Multicomponent Isotherm. *J. Colloid Interface Sci.* **1981**, 9, 136-142.
  34. Kumar, T. V. V.; Prabhakar, S.; Raju, B, G. Adsorption of oleic acid at sillimanite/water interface. *J. Colloid Interface Sci.* **2002**, 247, 275-281.
  35. 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.
  36. Khan, A. A.; Singh, R. P. Adsorption thermodynamics of carbofuran on Sn (IV) arsenosilicate  $\text{Li H}^+$ ,  $\text{Na}^+$  and  $\text{Ca}^{2+}$  forms. *Colloids Surf.* **1987**, 24, 33-42.
  37. Zhang, H.; Wang, Y.; Bai, P.; Guo, X.; Ni, X. Adsorptive separation of acetic acid from dilute aqueous solutions: adsorption kinetic, isotherms, and thermodynamic studies. *J. Chem. Eng. Data* **2015**, 61, 213-219.
  38. Anasthas, H.; Gaikar, V. Adsorption of acetic acid on ion-exchange resins in non-aqueous conditions. *React. Funct. Polym.* **2001**, 47, 23-35.
  39. Momchilova, S.; Damyanova, B. N. Stationary phases for silver ion chromatography of lipids: Preparation and properties. *J. Sep. Sci.* **2003**, 26, 261-270.
  40. Momchilova, S. M.; Nikolova-Damyanova, B. M. Advances in silver ion chromatography for the analysis of fatty acids and triacylglycerols - 2001 to 2011. *Anal. Sci.* **2012**, 28, 837-844.
  41. Momchilova, S.; Damyanova, B. N. Silver ion chromatography of fatty acids. *Encyclopedia of Lipidomics.* **2016**, 1-6.
  42. Demirbas, A.; Sari, A.; Isildak, O. Adsorption thermodynamics of stearic acid onto bentonite. *J. Hazard. Mater.* **2006**, 135, 226-231.
  43. Yu, Y.; Zhuang, Yuan-Y; Wang, Z. Adsorption of water-soluble dye onto functionalized resin. *J. Colloid Interface Sci.* **2001**, 242, 288-293.
  44. Gupta, A.; Bowden, N. B. Separation of *cis*-fatty acids from saturated and *trans*-fatty acids by nanoporous polydicyclopentadiene membranes. *ACS Appl. Mater. Interfaces.* **2013**, 5, 924-933.