

Removal of caprylic acid impregnated on resins using organic solvents and water

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In this study, organic solvents and water were used to remove caprylic or octanoic acid from resins. The conventional batch method of stirring with a solvent-extractor produced a reasonable quantity of unbound acid in the liquid phase (0.00433–0.0772 g.L⁻¹). Removal characteristics were investigated with water, ethylene glycol (MEG), diethylene glycol (DEG), ethanol and butanol. For the anionic and cationic resins in both exposure times studied, the order of maximum removed amount was: using water (95%) > MEG (60%) ≈ DEG (50%)>ethanol(25%)>butanol (20%). On the other hand, the removal percentage was very low and similar in the mixed resin system. In spite of being soluble in alcohols, caprylic acid was a little removed from resins when attacked by them.

Keywords: caprylic acid; resins; DEG; MEG; exposure time.

INTRODUCTION

Regeneration and reusability of an adsorbent are highly appreciated in industry due to the factors of economy, environmental aspects and operational convenience. However, regeneration was not often employed in some cases because of the difficulty and inconvenience of the procedure. Recently, Punyapalakul *et al.* (2013) [1] found that the reused Plasma Arc Cured (PAC) resin had a significant loss of adsorption capacity, while functional silicas with better regeneration ability required a high-cost synthesis. In the case of adsorbent MIPs (Molecularly Imprinted Polymers), Yu *et al.* (2008) [2] obtained a satisfactory regeneration in a percentage of 95% for the adsorbent MIP, whereas the mixture of acetone and sodium hydroxide (NaOH) solution as regeneration solvent was not "green" or ecologically correct.

In relation to dry washing, some alternative commercial adsorbents have been discussed in recent research studies [3-5]. One of these adsorbents is the Purolite® PD206 resin, which has shown good performance in biodiesel purification [3]. The adsorption of biodiesel contaminants on PD 206 resin can occur in two ways: by ion exchange or by physical adsorption.

The regeneration of resins or adsorbents must be efficient to increase the removal of contaminants and the life time of the adsorbent material. In addition, the optimization of the regeneration methods is essential to increase the efficiency and economy of the dry washing processes.

Recently, Stapea *et al.* (2016) [6] published a work involving resins used in dentistry, in which a solvent, DMSO, was tested as a compound of new potential that could promote the adhesion of the hydrophilic resin to the dentin of the human tooth. In this case the researchers sought to improve the thermo-mechanical properties of the resin by introducing an organic solvent. Different concentrations of DMSO in water were employed in the study. According to Ekambaram *et al.* (2015) [7], in addition to influencing the mechanical and physical properties of resins, solvents have a great impact on resin-dentin bonding. In this sense, the second assertion of the researchers must be explored so that experimental studies can define a solvent that positively affects the bond that one wishes to strengthen or weaken.

Solubility data [8,9] have confirmed that caprylic acid has some solubility in water and is highly soluble in some organic solvents [8]. This fact encouraged the research on the possibility to extract this solute from Purolite resins employing pure organic compounds or water. Among available solvents, in this research we used diethylene glycol (DEG), monoethylene glycol (MEG), ethanol and butanol. Therefore, this work will be developed in considering the potentialities of the solvents by checking the removal of caprylic acid from three different resins. The experimental work will answer what solvent has affinity to caprylic acid and could be used with success to regenerate resins previously used in biodiesel production [10-13].

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METHODOLOGY

The experimental procedure for desorption of caprylic acid using pure organic compounds or water will be described below. The experiment was similar to that used by Franco *et al.* [14]. Desorption experiment was performed using a 150-mL glass vessel placed on a magnetic stirrer. The pure solvent was weighed on a semi-analytical balance (SHIMADZU, AUW Series, $\pm 10^{-2}$ g). One gram of resin previously contaminated with caprylic acid was added to the vessel and the system was stirred at 300 rpm for about 15-30 min. After stirring, the equipment (IKA, RH Basic) was switched off and the solid-liquid mixture was decanted for a few minutes. Using a glass syringe, 15.0 mL of the decanted mixture was sampled and titrated with 0.01 N sodium hydroxide solution (V_{NaOH} , mL) with phenolphthalein as an indicator. Thus, the concentration of caprylic acid in the liquid phase can be determined by potentiometric titration with alkaline solution using a drop of phenolphthalein as indicator. In the literature the use of a mixture of ether and ethanol (1:1) as diluents of the sample to be titrated was recommended. In this case, for every 2 g of sample it is recommended to use 25 mL of dilution mixture. In this research, 15 mL of sample were collected in duplicate, so that the dilution can be initially dispensed. Different solvent extractors were used. The reagents available were of P.S. grade 99.5% purity and were purchased from Dinâmica Química Contemporânea LTDA. Anionic, cationic and mixed (Purolite) resins were contaminated by caprylic acid and submitted to regeneration treatment taking into account the following parameters: type of resin, exposure time and type of solvent. The experiments were conducted at controlled temperature using a thermostatic bath, as well as at room temperature.

Solid Sample Preparation

Ten grams of resin were weighed into a beaker and two drops of caprylic acid measured with microsyringe (Hamilton; 100 μL) were added. The mass of added acid (0.0552 ± 0.0030 g) to the resin can be measured by knowing its density, as well as by using an analytical balance. The vial (VIDROLABOR®) containing the contaminated solid was shaken in a centrifuge for a given period of time, about one hour. The sample remained at rest according to the contact time to be tested. This exposure time varied from 14 to 170 hours, or more. After this period the sample was used for the desorption tests. After the treatment, the liquid

sample was titrated and the results were presented for the desorption of caprylic acid from anionic, cationic and mixed resins. The effect of the exposure time of the resin to the acid can be observed. All experiments were conducted at room temperature (25-27°C).

Tables and Figures illustrate the results for the regeneration studies of anionic, mixed and cationic resins. Most of the titration analyzes were done in duplicate or triplicate with δ being the standard deviation. The mass (m) and final acid concentration in the liquid mixture is given by $C \pm \delta$ in g.L^{-1} .

As the exposure time of octanoic acid with the resin increases, the desorption of this solute turns to be more difficult. This is extremely disadvantageous for the process of regeneration. Tests with all resins used in the biofuels line should be carried out using organic solvents and water. The final concentration of the acid in solution (C , g.L^{-1}) will allow to obtain the mass of extracted acid. It is believed that some resins, if contaminated with this acid, after 24 h of exposure, cannot be regenerated. Only a solid phase evaluation can define its possible re-use in adsorption processes.

RESULTS AND DISCUSSION

The comparison among five solvents (water, ethanol, butanol, MEG and DEG) for acid-contaminated resin treatment was carried out doing blank tests as an initial study. Solvents permeated the resin and acid will be desorbed from the pores and then, dissolved in the liquid phase. Acid molecules that were not desorbed will stay on the resin surface during this process and connect to each other.

The acid removal performance of solvents was examined by doing experimental blank tests with the clean (not used) resin as it could contain some acid that belongs to the fresh resin. As it can be seen from Table 1, MEG and DEG extract a higher amount of acid from the resins. Results show that all solvents remove an amount of acid which can influence the final results of removing. In Table 1, 15 mL of sample was titrated and then the volume of NaOH solution (0.01 mol/L) used can confirm that there is some acid removed which is not caprylic acid.

In order to exemplify the removal results, together with the concentration and final mass levels of acid in the liquid phase (C_{Liq}^{ac} , m_{Liq}^{ac}), and residual mass of acid in the solid m_{Res}^{ac} , it was chosen to present the data for the tests with the anionic resin (Table 2).

Table 1. Volume of the NaOH solution (mL) used for titration of a sample in the blank extraction process of 1.0 g of original resin.

Solvent	Resin		
	Mixed	Cationic	Anionic
water	0.25	0.35	0.25
MEG	1.55	1.45	0.95
DEG	1.2	1.45	1.35
ethanol	0.55	0.65	0.55
butanol	0.35	0.55	0.55

Table 2. Results for the removing of caprylic acid from the anionic resin exposed to the contaminant for 170 hours.

Solvent	$C_{Liq.}^{ac.}/g.L^{-1}$	$m_{Liq.}^{ac.}/g$	$m_{Res.}^{ac.}/g$
water	0.0527±0.005	0.00264	0.00271±0.0004
MEG	0.0772±0.006	0.00390	0.00148±0.0002
DEG	0.0167±0.003	0.00082	0.00460±0.0005
ethanol	0.00935±0.001	0.00047	0.00489±0.0007
butanol	0.00432±0.001	0.00011	0.00510±0.0008

Table 3. Results for the removing of caprylic acid from the cationic resin exposed to the contaminant for 170 hours.

Solvent	$C_{Liq.}^{ac.}/g.L^{-1}$	$m_{Liq.}^{ac.}/g$	$m_{Res.}^{ac.}/g$
water	0.0671±0.006	0.0034	0.00398±0.0003
MEG	0.0627±0.006	0.0032	0.00219±0.0002
DEG	0.0094±0.0008	0.0005	0.00399±0.0003
ethanol	0.0577±0.005	0.0029	0.00244±0.0002
butanol	0.0072±0.0007	0.00036	0.00230±0.0002

Table 4. Results for the removing of caprylic acid from the mixed resin exposed to the contaminant for 170 hours.

Solvent	$C_{Liq.}^{ac.}/g.L^{-1}$	$m_{Liq.}^{ac.}/g$	$m_{Res.}^{ac.}/g$
water	0.0193±0.003	0.00096	0.00438±0.0003
MEG	0.0526±0.008	0.00265	0.00271±0.0002
DEG	0.0236±0.004	0.00120	0.00420±0.0003
ethanol	0.0094	0.00048	0.00487±0.0004
butanol	0.0094	0.00047	0.00487±0.0005

Note that alcohols are unsuitable for removal of caprylic acid from resins; water and MEG are the most recommended ones. Figs. 1 and 2 show the effect of time exposure on the acid removal ability. The influence of the dielectric constant on caprylic acid removal ability is shown in Figs. 1 and 2. Thus, the x-axis contains dielectric constant data for butanol (17.1), ethanol (24.3), diethylene glycol (31.7), monoethylene glycol (41.2) and water (76.7), respectively. Comparing the two exposure

times (14 h and 170 h), it is clear that the results of acid removal are different. We believe that it is because, as Fig. 2 shows, the caprylic acid will be much stickier at high contact time of solute and resin.

Also, the influence of the solvent is clear for the cases studied. It is noted that water acted as the most appropriate solvent to remove the solute from all resins and that butanol, which has a lower dielectric constant, was unsuitable for the process.

Summing up, the removal efficiency depended largely on the solvent type and less on the exposure time.

From Fig. 1, none of the solvents proved to be suitable for recovering the mixed resin, which should probably be discarded after to its use. Also, results in Fig. 1 are presented for two experiments which were carried out using the same resin. Fig. 2 shows that the exposure time of the resin to the acid influences the percentage of removal from the resin, so that lower removal values are observed when the exposure time is eleven times greater. In the two exposure times, a similar behavior of the solvents, regarding the removal, is observed for the three resins studied. Solvents with higher dielectric constant are more suitable for removal of caprylic acid.

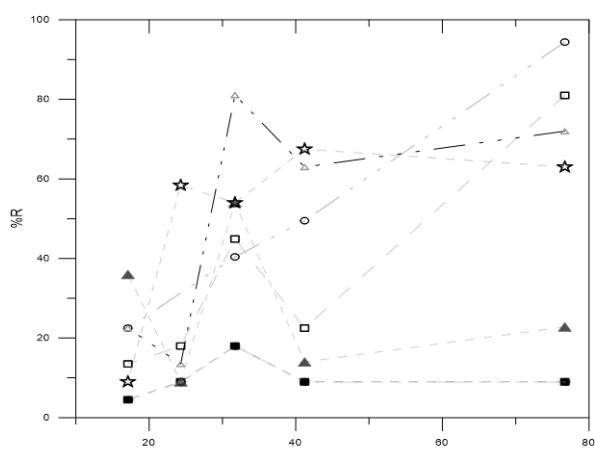


Fig. 1. Removal of caprylic acid as a function of dielectric constant of extractor solvent. (14 hours of exposure). (type of resin: ○☆ Anionic; ■▲ Mixed; □△ Cationic)

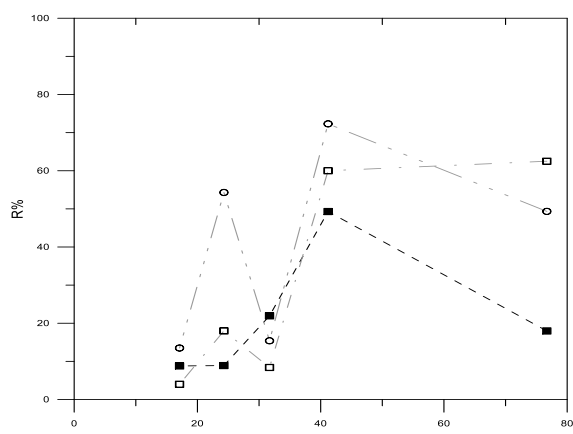


Fig. 2. Removal of caprylic acid as a function of dielectric constant of extractor solvent. (170 hours of exposure). (type of resin: ○ Anionic; ■ Mixed; □ Cationic)

Although the removal results using MEG and DEG solvents showed pronounced variation for the

experiments with 170 h of contamination, water continues to be the best solvent, when comparing the costs of the removing process. What is clear from the removal measurements is that for all the resins impregnated with acid, alcohols are not recommended as solvents.

CONCLUSIONS

Among all solvents employed, water was the most suitable solvent to remove caprylic acid from the solid phase. On the other side, the use of alcohols to clean resins contaminated with caprylic acid is not recommended.

As the time of contact of resin with the acid increases, the removal of the acid from the resin through the use of extractor solvents becomes more difficult.

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REFERENCES

1. P. Punyapalakul, K. Suksomboon, P. Prarat, S. Khaodhiar, *Sep. Sci. Technol.*, **48**, 775 (2013).
2. Q. Yu, S. Deng, G. Yu, *Water Res.*, **42**, 3089 (2008).
3. M. Berrios, R. L. Skelton, *Chem. Eng. J.*, **144**, 459 (2008).
4. K. Suppalakpanya, S. B. Ratanawilai, C. Tongurai, *Applied Energy*, **87**, 2356 (2010).
5. Z. J. Predojevic, *Fuel*, **87**, 3522, (2008).
6. T. H. S. Stapea, A. Tezvergil-Mutluaya, M. M. Mutluaya, L. R. M. Martins, R. L. do Prado, E. C. G. Pizic, L. Tjaderhane, *Journal of the Mechanical Behavior of Biomedical Materials*, **64**, 220 (2016).
7. M. Ekambaram, C. K. Y. Yiu, J. P. Matinlinna, *Int. J. Adhes.*, **57**, 22 (2015).
8. K. T. Tan, M. M. Gui, K. T. Lee, A. R. Mohamed, *J. Supercritical Fluids*, **53**, 82 (2010).
9. S. Budavari, *The Merck Index: An Encyclopedia of Chemicals, Drugs, and Biologicals*, 12th edn., Merck, ISBN 0911910123, 1996.
10. D. R. Lide, *CRC Handbook of Chemistry and Physics*, 70th edn., Boca Raton (FL), CRC Press, 1990.
11. P. Valle, A. Velez, P. Hegel, G. Mabe, E. A. Brignole, *J. Supercritical Fluids*, **54**, 61 (2010).
12. M. M. Gui, K. T. Lee, S. Bhatia, *J. Supercritical Fluids*, **49**, 286 (2009).
13. J. M. Marchetti, V. U. Miguel, A. F. Errazu, *Renewable and Sustainable Energy Reviews*, **11**, 1300 (2007).
14. M. R. Franco Júnior, N. R. A. F. Rocha, W. A. Pereira, N. P. Merlo, *Bulg. Chem. Commun.*, **51**(3), (2019).