

Application of Poly(acrylamide-co-acrylonitrile) Hydrogel to Remove Soluble Water from Biodiesel and Evaluation in the Control Mechanism of the Mass Transfer Process in an Adsorption Process

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Fuels are contaminated with gases, solvents, dirt, soot, and sealants. Water is always present in biodiesel and high-water content may impact negatively the performance of fuels, such as damaging injection systems and leading up to corrosion of metal surfaces and the growth of fungi and bacteria. The present work shows an alternative technology to remove water from biodiesel by polymeric material. In this context, this work aims to synthesize hydrogel and to evaluate the influence of contact time on the water removal from biodiesel. Poly(acrylamide-co-acrylonitrile) hydrogel was synthesized by means of free radical polymerization. Batch experiments were conducted using particles of this copolymer and saturated-commercial biodiesel at 200 rpm at 25 and 40 °C. The water content of the samples was measured using Karl Fischer technique.

The control mechanism of the mass transfer process between the water present in the fuel and the hydrogel was studied considering pseudo-first order and pseudo-second order kinetic models. The pseudo-second-order model presented better fit from nonlinear experimental data for poly(AAm-co-AC) hydrogel at 25 and 40 °C. The latter had higher values of R^2 (0.9963) and maximum water removal capacity ($q_e = 247.7$ mg/g). The tests carried out in this research pointed out the ability of the hydrogel to reduce water content from biodiesel and to be applied on an industrial scale.

1. Introduction

Fuels are contaminated with gases, solvents, dirt, soot and sealants. Water is also one of the main sources of oil contamination and presents one of the biggest challenges of the production process, as its presence significantly compromises the quality of the same (Li et al., 2021). It is present in fuels as the three following forms: soluble, emulsified, and free. Usually, water contamination of fuels is associated with poor seals during the storage step or contact with the external environment. For instance, biodiesel stored in floating roof tanks allows rainwater to enter (Santos et al., 2019). In fixed roof tanks, wet air may enter through vacuum breaker valves. For biodiesel, a significant amount of water is added to wash and remove the excess catalyst, alcohol, soap, oils, greases, and residual glycerol (Dourado et al., 2021).

Biodiesel is more hydrophilic than fossil diesel, significantly increasing its water content upon contact with air humidity. The high hydrophilicity of biodiesel is attributed to the presence of polar methyl or ethyl esters. Thus, the affinity of biodiesel with water may vary according to its composition, and the higher the polarity, the higher the hydrophilicity of the fuel (Gonçalves et al., 2020).

High water contents may impact negatively the performance of fuels, damaging injection systems and leading to corrosion of metal surfaces and the growth of fungi and bacteria (Gonçalves et al., 2020).

Therefore, Brazilian and international standards define specifications of maximum water content in biodiesel to be marketed. In Brazil, the ANP (National Oil Agency - Resolution 45/2014) defined the upper limit in 350 ppm and in Europe, the upper limit is 500 ppm (ANP, 2014; EN 14214). The analytical method for water content determination is defined according to ASTM (American Society for Testing and Materials) D6304 (ASTM, 2014). Industrially, different technologies are applied to remove water from fuels such as coalescing filters, distillation, and salt beds (Santos et al., 2019). Although these techniques are widely used, each one has its own disadvantage such as high investment, excessive energy expenditure, complexity of operation, fuel contamination, and saline effluent generation (Palanisamy et al., 2021). Polymeric hydrogels have been studied as a new technology to remove water from fuels. These materials have hydrophilic structure and three-dimensional networks capable of holding large amounts of water (Sharma et al., 2022). The polymer is synthesized based on natural or synthetic products. Synthetic materials have advantages such as increased water holding capacity, longer service life, and diverse applications. The polymer can be classified according to different forms, including the charge of the groups linked to the polymer chains and the preparation methods (homopolymer, copolymer, and interpenetrating network) (Sharma et al., 2022).

Hydrogel application occurs in different segments with emphasis on application in agriculture, medicine, hygiene products, and food additives (Sharma et al., 2022). Based on previous work by our research team, Santos et al. (2019), Gonçalves et al. (2020) and Dourado et al. (2021) expanded the use of hydrogel to remove water from biodiesel. Santos et al. (2019) evaluated the application of poly(acrylic acid-co-acrylamide) and poly(sodium acrylate-co-acrylamide) hydrogels for the removal of water from commercial biodiesel. The polymers were able to remove approximately 80 % of the water at 40 °C from 1650 ppm being the initial water content. Gonçalves et al. (2020) used the poly(acrylamide-co-acid acrylic) obtaining 53 % water removal. Dourado et al. (2021) applied polyacrylic acid and sodium polyacrylate and the results showed that the final water content was lower than 1100 ppm from 6977 ppm (initial water content). Thus, the present work proposes the synthesis of poly(acrylonitrile-co-acrylamide) hydrogel to remove water from biodiesel and obtain biodiesel with reduced water content (≤ 350 ppm). The batch experiments were designed to allow the analysis of the effect of contact time between hydrogel and biodiesel on the water removal and to understand the mass transfer mechanisms involved. Mathematical models of adsorption kinetics allow the kinetic behaviour of the solid-liquid system to be known, and therefore kinetic models of the pseudo-first order and pseudo-second order were evaluated.

2. Methodology

2.1 Materials

Reagents used in the experimental procedures were acrylamide (AAm) ultrapure (Amresco), acrylonitrile (AC) (Dinamica 99 %), N,N'-methylene-bis-acrylamide (mBAAm) (USB 99 %), N,N,N,N'-tetramethyl-ethylenediamine (TEMED) (Sigma-Aldrich 99 %), potassium persulfate (Fisher Scientific 99 %). The biodiesel used to perform the experimental procedures was purchased from local businesses. The water content of biodiesel before saturation was 585 ppm.

2.2 Synthesis of acrylamide hydrogel copolymerized with acrylonitrile via free radical

Hydrogel synthesis was performed using 2.5 g AC, 3 g AAm and 0.015 mol of crosslinking agent MBAAm. To the respective mixture it was added 0.057 mol/L TEMED, 0.02 g of sodium persulfate as a polymerization reaction initiator and water to allow solubilization of the medium. After the aqueous mixture was prepared, nitrogen was bubbled into the reaction medium until completion of the reaction, where it was possible to visualize the gel formation. After approximately 24 hours (relative to the end of the reaction), the excess of monomers was removed by washing procedure with distilled water and the sample was oven dried at 70 °C until a constant mass was obtained (Santos et al., 2019). Figure 1 shows the dry poly (AAm-co-AC) hydrogel.



Figure 1: Poly (AAm-co-AC) hydrogel particles.

2.3 Tests of water removal from biodiesel

For water removal experiments, commercial biodiesel was initially saturated with distilled water for 1 hour. After this time, the aqueous and oily phases were expected to separate, and a separatory funnel was used to obtain saturated biodiesel. 100 mL of saturated biodiesel was added to an erlenmeyer and placed in contact with 0.4 g of hydrogel. The tests were carried out in a batch system with controlled temperatures of 25 and 40 °C and performed in triplicate. The samples were agitated using a shaker (IKA Model KS 4000 ic control) with a constant speed of 200 rpm. Biodiesel water content was determined by automatic coulometric titration (Metrohm, model 860 KF Thermoprep), according to EN ISO 12937.

Equation 1 and Equation 2 were used to quantify the hydrogel water removal capacity (q_e) and the percentage removal of water from biodiesel (%R), respectively (Ramos et al., 2022).

$$q_e = (C_o - C_e) \times \frac{V}{M} \quad (1)$$

$$\% R = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

Where q_e is the water removal capacity at equilibrium ($\text{mg}\cdot\text{g}^{-1}$), V is the biodiesel volume (L), M is the amount of hydrogel (g), C_o and C_e is the initial and equilibrium water concentration in the biodiesel ($\text{mg}\cdot\text{L}^{-1}$), respectively. To evaluate the controlling mechanism of the mass transfer process between the water present in the fuel and the hydrogel, the pseudo-first order (Eq3) and pseudo-second order (Eq4) kinetic models were studied (Ramos et al., 2022).

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (3)$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (4)$$

Where q_e and q_t are the amounts of water adsorbed per gram of adsorbent at equilibrium and time t , respectively ($\text{mg}\cdot\text{g}^{-1}$), k_1 is the pseudo-first order rate constant (min^{-1}) and k_2 is the pseudo-second order rate constant ($\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$) (Ramos et al., 2022).

3. Results

3.1 Effect of contact time between hydrogel and biodiesel

Contact time is one of the factors that can influence the hydrogel's ability to remove water. Table 1 presents the results obtained by the poly (AAm-co-AC) hydrogel to remove water from biodiesel as a function of time. The initial water content for saturated biodiesel was 1333 ppm.

As can be seen, the water was removed during all the assessed contact time. Removal was gradually increased and the equilibrium time achieved by the hydrogel was 48 h at 25 °C and 32 h at 40 °C. For 48 h at 25 °C, the water removal percentage was 60.34 % and the removal capacity was 194.79 mg of water/g of hydrogel. At 40 °C for 32 h, the percentage was higher than at 25 °C and 72.17 % of water was removed and the removal capacity was 219.20 mg of water/g of hydrogel. From equilibrium, it is said that the hydrogel reached its maximum saturation, not removing more water from biodiesel (Ilaiyaraja et al., 2017).

Table 1: Experimental data on the hydrogel water removal capacity (q_t) and the percentage removal of water from biodiesel (%R) by poly (AAM-co-AC) hydrogel as a function of time at 25 °C and 40 °C.

Time (hours)	poly(AAm-co-AC)			
	25 °C		40 °C	
	% R	q_t (mg/g)	% R	q_t (mg/g)
1	18.28	59.32	10.09	36.54
8	38.75	126.00	41.85	150.64
16	46.33	150.03	65.65	199.72
24	51.65	167.48	68.79	208.83
32	55.42	179.57	72.17	219.20
40	57.90	187.28	73.80	224.21
48	60.34	194.79	73.53	222.30
72	61.45	199.04	73.72	223.04

It was found that the increase in temperature allowed larger amounts of water to be retained by the hydrogel. In the literature, it is easy to find systems directly dependent on temperature, contributing positively to the adsorption processes. According to Santos et al. (2019), through statistical analysis, the authors reported that temperature has a significant effect on the dependent variable (water content), obtaining greater removal of water from biodiesel when the temperature increased from 25 °C to 40 °C. Thus, the authors verified an endothermic process during water removal between biodiesel and hydrogel.

The same behavior was analyzed in the present work. When the temperature ranged from 25 to 40 °C, the percentage of removal increased from 62 % to 74 % for 72 h, also indicating an endothermic process. Also, the increase in temperature allows the crosslinked hydrogel bonds to expand, favoring the incorporation of larger amounts of water (Santos et al., 2019). In addition, fuel viscosity decreases and water solubility in fuel increases with temperature increasing (Romanova et al., 2019). Thus, hydrogels had a greater ability to remove water from biofuel at 40°C.

Regarding the 350 ppm and 500 ppm limit of water established by ANP 45/2014 and EN 14214/2008, respectively, the hydrogel operating at 25 °C was not effective enough to remove water, so that the water concentration specifications are met. At this temperature and considering 72 h, the water content in the fuel was 502.37 ppm. However, when the temperature of the experiment was increased to 40 °C and the contact time was 72 h, the biodiesel water content was 320 ppm and this value is lower than required by the standards. It was possible to verify that the hydrogel had potential to remove water present in biodiesel. Although this temperature is not usual room temperature, it is not distant from 25 °C. Besides, when we consider that this polymer can be applied in storage oil tanks, long times, as 72 h, may not be a technical problem. For future experiments, it is expected that hydrogel application can be optimized so that even low water contents will be removed in low temperatures, making the technology even more competitive. Regarding the 350 ppm and 500 ppm limit of water established by ANP 45/2014 and EN 14214/2008, respectively, the hydrogel operating at 25 °C was not effective enough to remove water, so that the water concentration specifications are met.

3.2 Kinetic Mathematical Modeling

The experimental data from Table 1 were used to adjust the adsorption kinetics parameters of the proposed models. Some mechanisms interfere with the adsorption process, highlighting mass transfer and chemical reactions. Therefore, two kinetic models were studied, Lagergren's pseudo-first order and pseudo-second order, in order to know the kinetic behavior of the solid-liquid system (Ramos et al., 2022).

Lagergren's pseudo-first order kinetic equation (Eq3) is one of the most widely used models in the literature to describe the adsorption mechanism. The pseudo-first-order model assumes that adsorption is reversible and occurs on a heterogeneous surface. The pseudo-second order model describes the sorption process considering chemisorption as a limiting step of the adsorption rate (Aliprandini et al., 2020). Equation 4 describes the pseudo-second order model equation.

Table 2 presents the model kinetic parameters for water removal in biodiesel.

Table 2: Kinetic parameters for poly(AAm-co-AC) hydrogel.

Temperature	Model	$k_1(\text{h}^{-1})$	$k_2(\text{g}/\text{mg}\cdot\text{h})$	q_e (mg/g)	R^2
25 °C	Experimental	--	--	199.04	--
	1 ^(a)	$(1.34 \pm 0.3) \cdot 10^{-1}$	--	186.6 ± 8.8	0.8548
	2 ^(b)	--	$(1.14 \pm 3.8) \cdot 10^{-3}$	204.4 ± 8.4	0.9440
40 °C	Experimental	--	--	223.04	--
	1 ^(a)	0,1438	--	221.7	0.9897
	2 ^(b)	--	$(8,4 \pm 1,2) \cdot 10^{-4}$	247.7	0.9963

(a) pseudo-first order and (b) pseudo-second order

Based on the values presented for the adjustment coefficients (R^2) (Table 2), it was identified the mathematical equation that best described the proposed separation process. The pseudo-second order model presented the best adjustment (greater R^2) to the nonlinear experimental data for poly(AAm-co-AC) hydrogel at 25 and 40 °C. Notably, at 40 °C higher values of R^2 and maximum water removal capacity (q_e) were obtained. If adsorption increases with increasing temperature, so, the system is better fitted by pseudo-second order. This conclusion may be indicative of chemisorption.

4. Conclusion

Poly(AAm-co-AC) hydrogel showed efficiency in removing water from commercial biodiesel. The hydrogel had its capacity maximized when the temperature was increased from 25 °C to 40 °C, demonstrating its significant effect on water retention by the hydrogel. The longest contact time led to the highest removal percentages, so in 72 hours, 62% (25 °C) and 74% (40 °C) of water were adsorbed. The adsorption kinetics of the system followed the pseudo-second order model, so the rate limiting step was chemisorption. The concentration of water remaining in biodiesel after treatment at 40 °C meets the specification defined by the ANP following ENISO 12937. It means that the final water content was lesser than 350 ppm, corresponding to approximately 320 ppm.

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