



# Demulsification and Oil Removal from Metalworking Fluids by Polyurethane Foam as Sorbent

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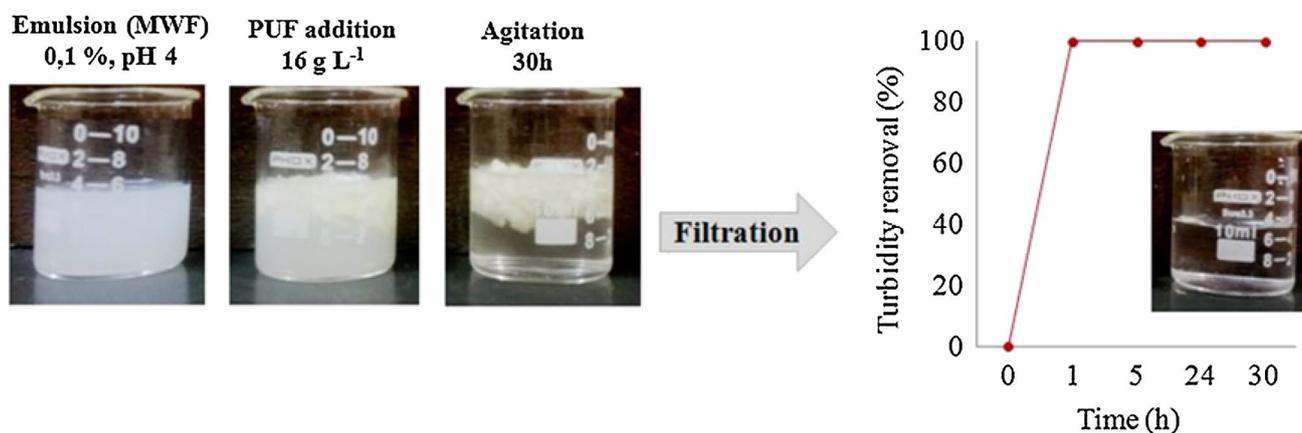
Accepted: 14 September 2020

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## Abstract

In this study polyurethane foam (p-PUF) was applied in tests of demulsification of metalworking fluids. The results showed the strong influence of the media pH on the oil adsorption. FTIR deconvolution elucidated that the acid media could improve the availability of urethane groups to participate of demulsification process. Results also showed that the foam has a maximum oil adsorption capacity of  $541 \text{ mg g}^{-1}$  at pH 6 the turbidity removal from metalworking fluids by p-PUF was of 86% while at pH lower than 4, turbidity removal was higher than 99%. The demulsification process happens because of two types of interaction: hydrophobic and electrostatic. The Freundlich model showed a better fit to the experimental data and MDSP error of 1.5. p-PUF was used even five times without losing its sorption capacity.

## Graphic Abstract



**Keywords** Polyurethane foam · Environmental contamination · Metalworking fluids ·  $\text{pH}_{\text{PCZ}}$  · Adsorption isotherms

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## Introduction

Metalworking fluid (MWF) is widely used in the metalworking industry for cutting or material machining. The MWF are functionally important, because they promote cooling of the workpiece and tools, improve the finishing of the surface of the working piece, also promote the cleaning of the workpiece by removing splinters arising from the cut and they also have economic importance, once they reduce wear of the tools and protect workpieces, machinery and tools from corrosion [1, 2]. The MWF can be separated in to two main groups: water

based (emulsions and solutions) and oil based. It can also be added antifoaming agents, bactericides, anticorrosive, emulsifier, among others agents, in order to improve MWF special properties [3]. The use of MWF in the industry is of great importance and the generation of residual water containing huge amount of oil calls for attention to the necessity of an efficient treatment of this residue. Oils and grease in the residual water can exist in different forms: free, scattered, emulsified and dissolved. The differences are based mainly on the size of the oil drops inside the residual water. On an oil–water mixture, free oil is characterized by the size of the oil drop superior to 150  $\mu\text{m}$ , scattered oil (mechanically emulsified) by the size of the drop going from 20  $\mu\text{m}$  to 150  $\mu\text{m}$  and the emulsified is characterized by the formation of highly stable emulsions with a drop size smaller than 20  $\mu\text{m}$ . Dissolved oils are characterized by the size of the molecules been less than 5  $\mu\text{m}$ , such as benzene, phenols, toluene and xylene [4, 5].

Many works have studied the application of different technologies (mechanical, physical, chemical and biological, and its combinations) to the treatment of oil–water emulsion residues. Electrochemical coagulation [5], separation by membrane [6], anaerobic bioreactor [7], ozone-bacteriological hybrid treatment [8], adsorption in different materials: bentonite, activated carbon and coal [9], clay-chitosan composite [10], rice husk modified with polyethylenimine [11], zeolites [12] and steel industry residue [13]. Adsorption process are interesting forms of treatment to this effluent, since it can use low cost adsorbents, obtain high efficiency in the demulsification and oil removal from water and has the possibility of recovering the adsorbent material in several cycles of treatment.

Polyurethane foams (PUF) are cellular polymers with low density that have their volume expanded through a chemical process by the action of an additive called the blowing agent. The polymeric structure of the PUF is formed from polycondensation reactions between diisocyanate groups (NCO) with hydroxyl groups from polyol forming the urethane groups ( $-\text{OCONH}-$ ) and their properties or applications vary according to the different types of diisocyanates and polyols used in their manufacturing process [14]. In recent years polyurethane foams have also been applied in effluent treatment processes. These materials have high sorption capacity of pollutants, possibility of recovery of the adsorbed compound and in some works the foams are reused without loss of its sorbent properties. These materials have been applied in a sorption studies and removal of contaminants from water such as metals [15–17], dyes [18–20], pesticides [21–23], and oils [24–26]. In

many of these studies, the sorption properties of polyurethanes are improved by the use of fillers, which can influence the cost of the obtained product, either by the demand for adjustments in the processing parameters, since the fillers can alter the viscosity of the reaction system, or by the need to increase the chemical compatibility between the polyurethane and the filler employed [27].

In this study, a pristine polyurethane foam (p-PUF) was synthesized from vegetable oil and applied as a demulsifying agent to separation of oil/water from metalworking fluids. The adsorption process was studied through isothermal models (Langmuir and Freundlich) and parameters as pH influence and foam recyclability were also evaluated in this research.

## Experimental

### Materials

The polyurethane foam was synthesized using the following reagents: isocyanate (Biopol p-MDI, 4,4-diphenylmethane diisocyanate, average functionality equal to 2.6 and average molar mass equal to 349.9  $\text{g mol}^{-1}$ ) a biopolyol (Biopol@411, 311  $\text{mg KOH g}^{-1}$ ) derivative from castor oil, glycerol, pentane from Synth, dimethyl cyclohexylamine (DMCHA) from Sigma Aldrich, the silicon Tegostab. Other reagents used in this work such as NaOH is from Neon, NaCl, HCl and  $\text{H}_2\text{SO}_4$  from Synth. The lubricant oil used to prepare the MWF was from Petronas, with 8.3% of its composition being sodium sulfonate (anionic surfactant).

### Synthesis and Characterization of Polyurethane Foam

A polyurethane foam (p-PUF) with glycerol as crosslinking was used as sorbent to evaluate MWF oil removal. The foam was synthesized by the mixture and stirring of the system A (polyol, water, glycerol, pentane, silicon and DMCHA) with system B (isocyanate). After the polymerization reaction and expansion, there was a 48 h cure time. The Table 1 shows the amount of reagents used in the synthesis of the foam. The NCO(isocyanate)/OH(polyol) ratio employed in this study was 1.1. The contents of the formulation additives were those that allowed the production of the foam with better dimensional stability.

p-PUF was characterized by thermogravimetry (Thermobalance Shimadzu DTG60, heating rate of 10  $^{\circ}\text{C min}^{-1}$ , nitrogen flow of 100  $\text{mL min}^{-1}$  in alumina crucible) and

**Table 1** Quantity of reagents used in the synthesis of the foam, in parts per hundred parts of polyol (php)

Water	Polyol	Glycerol	Silicon	DMCHA	Pentane	p-MDI
3.3	100	22.2	2.2	1.1	22.2	110

Differential scanning calorimetry (DSC 60, Shimadzu, Standard ASTM D3418, aluminium crucible and nitrogen flow of 50 mL min<sup>-1</sup>) and by Fourier transform infrared spectroscopy FTIR (Perkin Elmer RX FTIR System, scanning 4000 to 500 cm<sup>-1</sup>, KBr tablet method, resolution of 4 cm<sup>-1</sup> and 32 scans).

To determinate apparent density of the foam the standard ASTM D 1622–08 was used.

## Demulsification Tests

p-PUF was used as sorbent in the demulsification process through the measure of the turbidity removal from metal-working fluid. Static batch method was the sorption technique used in this study. The nephelometric method was used to the turbidity measurement with the Digimed turbidimeter, model DM-TU.

The emulsion (MWF) was prepared by the dissolution of oil in distillate water in different concentrations (0.1–3.0%, in volume). The demulsification tests were realized by the addition of the p-PUF (16 g L<sup>-1</sup>) on the MWF and stirring in shaker at 170 rpm for 24 h. All procedures were realized at room temperature.

The influence of the pH on the demulsification was analyzed through the turbidity measurement in pH 3, pH 4, pH 6, pH 8 and pH 10 with MWF concentration of 0.1% and – 0.7 mm fraction of p-PUF. For the pH correction it was used NaOH, 1 mol L<sup>-1</sup> or H<sub>2</sub>SO<sub>4</sub>, 10% in volume.

The point of zero charge (pH<sub>PZC</sub>) of an adsorbent is a parameter that determinates the pH in which the total charge of the material is zero. The determination of pH<sub>PZC</sub> was based on the procedure described on the literature [28, 29]: 0.15 g of pulverized foam was added to an erlenmeyer containing 50 mL of NaCl 0.01 mol L<sup>-1</sup>, the pH of the solutions was adjusted to the values of 2 and 12 with HCl or NaOH both at 0.1 mol L<sup>-1</sup> (initial pH). The mixture was stirred at 200 rpm for 48 h at room temperature and after this time, the pH was measured again (final pH). The value of the pH<sub>PZC</sub> is the value where initial pH is equal to final pH. To support the explanation about the demulsification process the p-PUF was also analyzed by FTIR after contact with H<sub>2</sub>SO<sub>4</sub> 0.1 mol L<sup>-1</sup>. For the software Origin was used and the deconvolution studies the

second derivative of the spectra was used and the correlation coefficients of the fitting process were more than 0.99.

The influence of the size of the foam particles in the demulsification was evaluated by the gravimetric method using two different granulometries: p-PUF pulverized in a mill (– 0.7 mm fraction) and p-PUF chopped (– 4 + 2 mm fraction) and different MWF concentrations (0.1; 0.5; 1.0; 1.5; 2.0; 2.5 and 3.0%). The oil sorption was determined by Eq. (1) [30]:

$$S = \frac{m_f - m_i}{m_i} \quad (1)$$

where S is the oil sorption capacity (mg g<sup>-1</sup>); m<sub>f</sub> is the mass of foam saturated with oil and m<sub>i</sub> is the mass of the foam (g).

The percentage of demulsification in different concentrations was calculated by Eq. (2) [30]:

$$R = \frac{W_o}{W_a} \times 100 \quad (2)$$

where R is the percentage of demulsification; W<sub>o</sub> is the oil withheld in the foam (g); W<sub>a</sub> is the oil initial weight (g).

Adsorption isotherm studies were carried out to analyse the sorption process and predict the maximum amount of oil that can be adsorbed by the foam. The kinetics study was constructed by analysing the relation between the amount of oil adsorbed and the equilibrium concentration of oil using the Langmuir and Freundlich models [31]. All tests were performed at room temperature; p-PUF 16 g L<sup>-1</sup>, 24 h stirring, 170 rpm, pH 4. Isotherms expressions used in this study are presented in the Table 2.

The best-fit equilibrium isotherm model for the oil adsorption from MWF was identified through the isotherms parameters and the maximum value of the coefficient of determination and minimum value of Marquardt's Percent Standard Deviation (MPSD) which is seen as a suitable model error function in most adsorption studies (Eq. 3) [32].

$$\text{MPSD} = 100 \sqrt{\frac{1}{n-p} \sum_{i=1}^n \left( \frac{q_{e,\text{exp}} - q_{e,\text{cal}}}{q_{e,\text{exp}}} \right)^2} \quad (3)$$

where q<sub>e</sub> = Quantity of solute adsorbed (mg g<sup>-1</sup>) at equilibrium; n = the number of experimental points; p = the number of parameters of the equation.

**Table 2** Types of isotherm and linear expressions used in this study

Type of isotherm	Linear expression	Parameters
Langmuir	$\frac{C_e}{q_e} = \frac{1}{K_L + Q_m} + \frac{C_e}{Q_m}$	q <sub>e</sub> = Quantity of solute adsorbed (mg g <sup>-1</sup> ) at equilibrium
Separation factor	$R_L = \frac{1}{1 + K_L C_0}$	C <sub>e</sub> = Concentration at equilibrium (mg L <sup>-1</sup> )
Freundlich	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	Q <sub>m</sub> = Maximum adsorption capacity (mg g <sup>-1</sup> )
		K <sub>L</sub> = Constant of the Langmuir isotherm (L g <sup>-1</sup> )
		C <sub>0</sub> = Initial adsorbate concentration (mg L <sup>-1</sup> )
		R <sub>L</sub> = Separation factor
		K <sub>F</sub> = Freundlich isotherm constant (mg g <sup>-1</sup> (mg L <sup>-1</sup> ) <sup>-1/n</sup> )

For the reutilization tests, p-PUF was washed with neutral commercial detergent and dried at 50 °C for 48 h at a stove. It was used MWF concentration of 0.1% and – 0.7 mm fraction of the foam. All procedures were realized in triplicate.

## Results and Discussion

### Characterization of p-PUF

The synthesis of polyurethane happens by reactions of polycondensation between diisocyanates and polyol groups, originating urethane group (–OCONH–). On polyurethane foams synthesized with polymeric MDI and polyol with functionality above three, the resultant polymer has a reticulated three-dimensional structure and with high amounts of urethane groups, which can lead to the formation of rigid segments in the structure of the material.

Polyurethanes can form hydrogen bonds of different magnitude between the –NH and –C=O groups, within the hard-hard (urethane-urethane) segment or hard-soft (urethane-ester) segment [33]. Beyond the carbonic chains deriving from the polyol (polyester polyol from castor oil) polyurethane foams have high amount of urethane groups which are reactive groups. In this context, it would be expected that both soft and hard segment of the foam contribute to the capacity of demulsification and separation of oil/water in MWF. p-PUF has density of  $28 \pm 2 \text{ kg m}^{-3}$  and this value is related to the expansion of the polymer, promoted by the expansion agents (water and pentane), which also were employed in order to adjust the dimensional stability and formulation stoichiometry.

The thermogravimetric analysis showed the thermal decomposition occurred into two stages that is characteristics of the polyurethane foams. The first staged happened with a loss of mass between 200 and 350 °C due the decomposition of urethane groups and the second stage, between 400 and 600 °C is related to the breakage of C–C bonds and other substances remained from the first stage of thermal degradation [30]. The thermogravimetric curve can be seen in Fig. 1.

The FTIR analysis confirmed the success of the polymer synthesis and the corresponding band assignments are summarized in Table 3.

The infrared absorption analysis shows a broadband with a more intense peak centered at  $3315 \text{ cm}^{-1}$ , attributed to N–H stretching bonded from urethane group. The bands between 2925 and  $2850 \text{ cm}^{-1}$  are assigned to CH stretching of aliphatic carbons. The band at  $2270 \text{ cm}^{-1}$  is due to N=C=O stretching from excess isocyanate (ratio NCO/OH 1.1). The band at  $1715 \text{ cm}^{-1}$  is from C=O stretching and the band in  $1600 \text{ cm}^{-1}$  region is due to N–C stretching (urethane group). The region between 1630 and  $1520 \text{ cm}^{-1}$  is

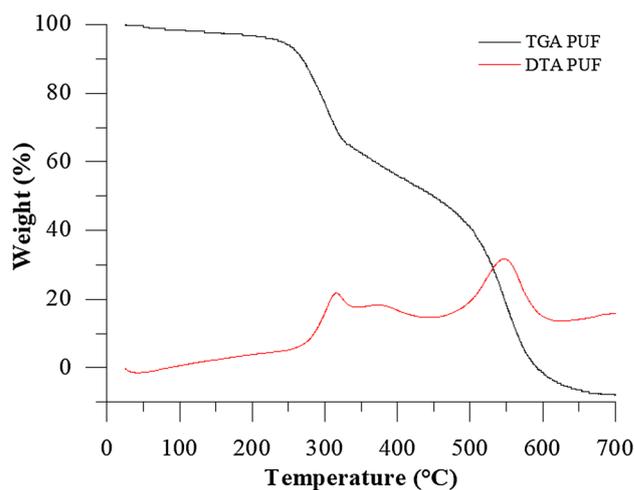


Fig. 1 Thermogravimetric curve of the p-PUF

Table 3 FTIR spectroscopy bands identified for p-PUF

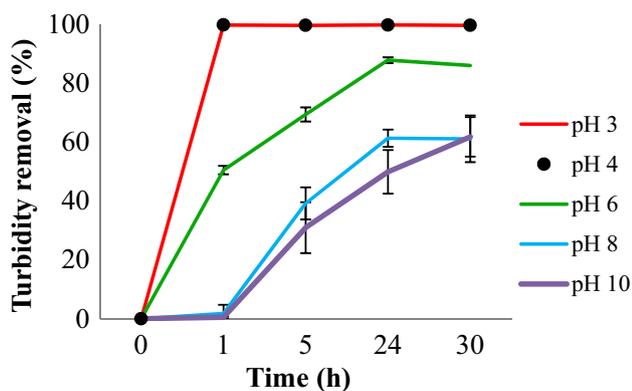
Wavenumber [ $\text{cm}^{-1}$ ]	Absorption bands
3700–3200	$\nu$ N–H
2926–2854	$\nu$ C–H ( $\text{CH}_2$ e $\text{CH}_3$ ) aliphatics
2280	$\nu$ N=C=O stretching
1770–1630	$\nu$ C=O (urethane/ester/urea)
1630–1520	$\delta$ N–H and $\nu$ C–N (urethane/urea)
1400	$\nu$ C–C aromatic
1220–1100	$\delta$ C–O e C–O–C (urethane/urea/ester)
814–508	$\delta$ C–H (aromatic groups)

due to N–H deformation and C–N stretching. Between 1220 and  $1100 \text{ cm}^{-1}$ , bands can be attributed to C–O and C–O–C deformation. The bands between 810 and  $610 \text{ cm}^{-1}$  are due to deformations of the aromatic CH bonds [30, 34].

### The Influence of pH on the Demulsification Process

The influence of the pH in the demulsification process of the oil/water system by p-PUF can be seen in Fig. 2. For pH values lower than 4, it was observed a turbidity removal higher than 99% in only 1 h of stirring. The higher turbidity removal at the pH values of 3 and 4 can be attributed to a higher protonation of p-PUF surface which should occur in the urethane groups.

The adsorption studies in a wide pH range are justified due the sorption processes are strongly pH dependent. The pH can affect the surface charge of the sorbent and the determination of the Point of Zero Charge ( $\text{pH}_{\text{PZC}}$ ), which is the pH value when the electrical charge density in the surface of the material is zero, is an important parameter for predicting the behavior of the adsorption in relation to pH [28, 35, 36]. The  $\text{pH}_{\text{PZC}}$  value found for p-PUF was 6.9. This



**Fig. 2** pH influence in relation with stirring time on the demulsification process by foam (p-PUF  $16 \text{ g L}^{-1}$  and  $-0.7 \text{ mm}$  fraction, room temperature, MWF  $0.1\%$ ,  $170 \text{ rpm}$ )

value means that at pH above 6.9, the surface of p-PUF is negatively charged and at pH below the 6.9 p-PUF surface is positively charged.

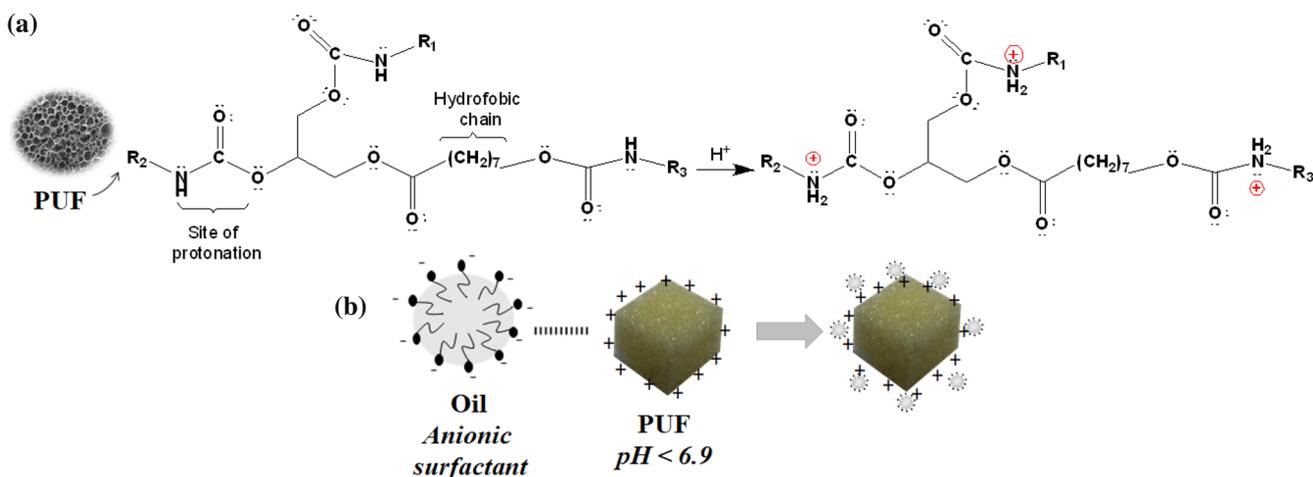
The Fig. 3a suggests the protonation that could occur in the polyurethane foam structure in pH values lower than  $\text{pH}_{\text{PZC}}$  value. For values of  $\text{pH} < \text{pH}_{\text{PZC}}$  the net charge in surface of the adsorbent is positive [37, 38].

These results corroborate with a possible predominance of electrostatic interactions between surface positive charges of p-PUF and the negative charges in groups present on the oil as suggested in Fig. 3b.

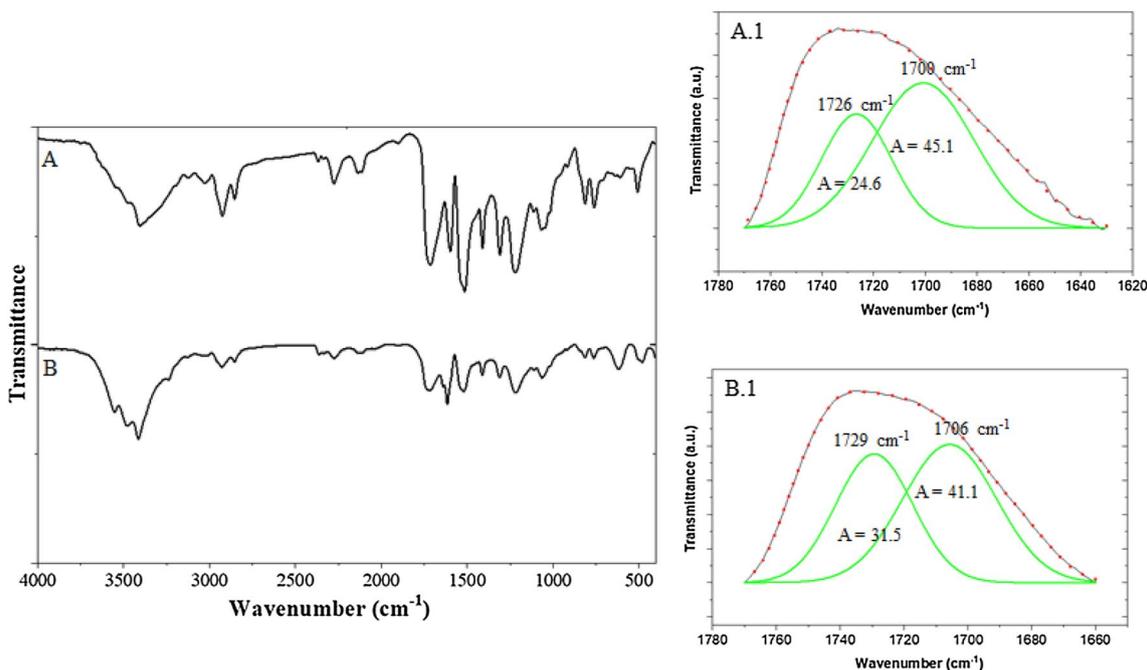
For pH 6, the process of demulsification by the removal of turbidity reaches equilibrium after 24 h of contact and with maximum turbidity removal of 86%, which can be assigned to the reduction of positive surface charge of p-PUF, since this pH value is close to that found for  $\text{pH}_{\text{PZC}}$ . The turbidity removal in pH 8 reaches equilibrium in 24 h, as observed in

the study with pH 6. In pH 10, the results suggest that the demulsification process does not reach equilibrium in less than 30 h of stirring of the system. These results suggest that the demulsification process conducted in an environment with pH value above the  $\text{pH}_{\text{PZC}}$  the turbidity removal would be approximately 60%. Although it is expected to reduce the protonation of the polymer surface in pH above the  $\text{pH}_{\text{PZC}}$ , the sorption of the pollutant can also be favored by hydrophobic interactions such as Van der Waals forces between carbonic chains of the foam (deriving from the polyol) and the lipophilic chain of the oil from MWF.

Polyurethane foams are interesting sorbent materials especially due the presence of functional groups such as urethane, amide, ester, ether and urea in its structure. As previously mentioned polyurethane foams are capable to have hard and soft hydrogen bond interaction. Especially for sorption studies, two spectral regions are more interesting:  $-\text{NH}$  and  $-\text{C}=\text{O}$ . The regions between  $3700\text{--}3200 \text{ cm}^{-1}$  and  $1770\text{--}1630 \text{ cm}^{-1}$  are due free  $-\text{NH}$  and hydrogen bonded  $-\text{NH}$ , free and hydrogen bonded  $-\text{C}=\text{O}$ ,  $[-\text{NH}-\text{O}=\text{C}-]$ , respectively. Some authors describe the Hydrogen Bonding Index (R) as a ratio between the area corresponding to hydrogen bonded carbonyl and free carbonyl area ( $R = A_{\text{hbc}}/A_{\text{fc}}$ ). Figure 4 illustrates the FTIR spectra of the foam used in this study before and after the contact with the solution of  $\text{H}_2\text{SO}_4$   $0.1 \text{ mol L}^{-1}$ . The deconvolution of  $-\text{C}=\text{O}$  stretching regions shows the R value as 1.84 for p-PUF before its contact with  $\text{H}^+$ . After contact with  $\text{H}^+$  the R value decreased to 1.30. This result suggests more significant phase separation between hard and soft segment and it would indicate greater availability of the reactive groups to participate in the sorption processes [33, 39, 40] and it can be related to the best definition of the absorption band peaks between 3700 and



**Fig. 3** Suggestion of protonation mechanism of urethane groups in acid media (a), illustration of the sorption process by electrostatic interaction (b)

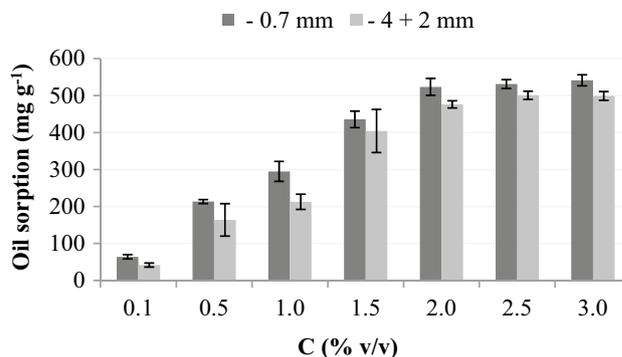


**Fig. 4** FTIR spectrum, p-PUF (A) and carbonyl stretching deconvolution (A.1) before contact with the H<sub>2</sub>SO<sub>4</sub> 0.1 mol L<sup>-1</sup> (B) and carbonyl stretching deconvolution (B.1) after contact with the H<sub>2</sub>SO<sub>4</sub> 0.1 mol L<sup>-1</sup>

3200 cm<sup>-1</sup> as a result of electronic repulsions between N–H protonated. This result is in line with that observed in the pH influence on the demulsification of MWF which showed higher oil sorption by p-PUF in lower values of pH.

### Influence of Particle Size on the Demulsification Process

The influence of the foam particle size in oil adsorption in different concentrations of MWF is shown in Fig. 5. It was observed that smaller granulometry (– 0.7 mm) of p-PUF have removed a bigger amount of oil from water if compared to a bigger granulometry (– 4 + 2 mm). The bigger contact surface between the smaller particles may have provided a higher contact between the foam and the oils drops emulsified during stirring of the system, causing a higher oil removal by the foam in every concentration studied. Besides, it can also be observed the influence of the concentration of the emulsion on the oil adsorption by the foam. The higher the concentration of the emulsion, the higher amount of adsorbed oil by the foam. On the highest concentration of MWF studied (3%) there was a 541 mg g<sup>-1</sup> adsorption by the foam of the lowest granulometry (– 0.7 mm) and of 501 mg g<sup>-1</sup> by the foam with the highest granulometry (– 4 + 2 mm), i.e., it has been

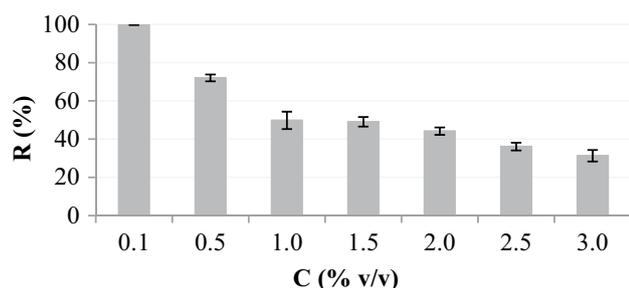


**Fig. 5** p-PUF particle size influence on the oil adsorption in different concentrations of MWF (p-PUF 16 g L<sup>-1</sup>, room temperature, 24 h stirring, 170 rpm, pH 4)

achieved an improvement of 7% on demulsification process by the foam of lowest granulometry.

### Percentage of Demulsification

The Fig. 6 shows the percentage of oil removal by p-PUF. The figure evidenced that with increasing of oil concentration in the emulsion, the oil sorption percentage decreases. This behavior was already expected due to saturation of the foam surface with the adsorbed oil. Nevertheless, p-PUF showed a good demulsification capacity, with an oil removal capacity exceeding 99% for MWF concentration



**Fig. 6** Oil sorption percentage obtained for p-PUF in different MWF concentrations (p-PUF  $16 \text{ g L}^{-1}$ ,  $-0.7 \text{ mm}$  fraction, room temperature and  $170 \text{ rpm}$ ,  $\text{pH } 4$ )

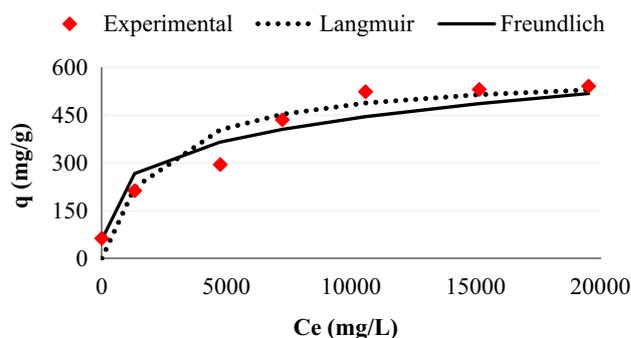
**Table 4** Estimated parameters for the oil adsorption from MWF by foam using Langmuir and Freundlich models

Isotherm model	Parameters				
Langmuir	KL	Qm	RL	R <sup>2</sup>	MPSD
	0.0005	588	0.6904	0.9604	4.0
Freundlich	q <sub>e</sub>	n	K <sub>F</sub>	R <sup>2</sup>	MPSD
	519	4.19	46.5	0.9603	1.5

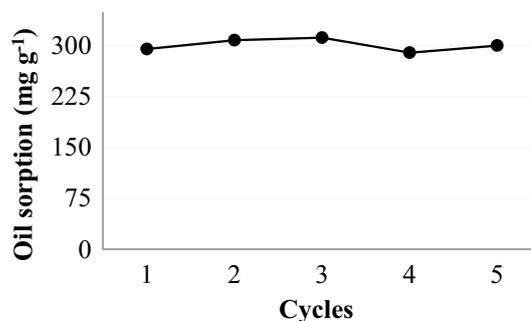
of  $0.1\%$  and maximum oil adsorption of  $541 \text{ mg g}^{-1}$  for MWF concentration of  $3\%$  and p-PUF concentration of only  $16 \text{ g L}^{-1}$ .

## Adsorption Isotherms

Through the adsorption isotherms is possible to describe how the solute is related to the adsorbent. According to the calculated adsorption parameters shown in Table 4 and Fig. 7 both models fit to the experimental data. Freundlich model has a better fit to experimental data predicting an adsorption value of  $519 \text{ mg}$  of oil per gram of foam at equilibrium and a lowest value of error than Langmuir model. In addition the magnitude of the constants  $n$  and  $k_F$  gives an indication of the adsorption favorability. In this study  $n=4.19$  and  $K_F=46.5$  and these values represent favorable adsorption conditions and a high affinity between adsorbate and adsorbent. The Freundlich model is widely used because of its simplicity to describe adsorption on membrane surfaces and because it is not just applicable to monolayers and homogeneous surfaces [41–43]. Freundlich isotherm could have fit better in this study than Langmuir because is more fitting for non-uniform adsorption process. As was showed in the Fig. 3 the sorption process between oil from MWF and foam happens by hydrophobic and electrostatic interaction with the oil (anionic surfactant) and Freundlich model describes processes on surface adsorption sites that are energetically heterogeneous [44].



**Fig. 7** Comparison between the adsorption isotherms (Langmuir and Freundlich) and experimental data



**Fig. 8** Oil adsorption capacity for p-PUF during five cycles (p-PUF  $16 \text{ g L}^{-1}$ ,  $-0.7 \text{ mm}$  fraction, room temperature, MWF of  $1\% \text{ v/v}$ ,  $170 \text{ rpm}$ ,  $\text{pH } 4$ )

## Reuse of the Foam

The Fig. 8 shows the oil sorption capacity by p-PUF during 5-cycles. In between each cycle, no organic solvent or thermal treatment was applied for cleaning the foam. p-PUF was only washed with neutral detergent and dried at  $50 \text{ }^\circ\text{C}$  for  $48 \text{ h}$  in laboratory oven. It is clear the good performance of the p-PUF, which is foam with a facile and low cost synthesis and without either surface modification or use of fillers, and because was not observed any loss of the oil sorption capacity during the five cycles. This result was very interesting. The reuse of adsorbent materials in addition to saving raw material generates less residues and reduces the cost of producing new materials.

## Conclusion

This study evidences the demulsification capacity of the p-PUF by its ability to remove the turbidity from the oil/water system. The granulometric fraction of  $-0.7 \text{ mm}$  of the foam presents a better oil adsorption capacity ( $541 \text{ mg g}^{-1}$ ) when compared to the granulometry of  $-4+2 \text{ mm}$

(501 mg g<sup>-1</sup>). The pHP<sub>ZC</sub> value showed that for pH values below 6.9 positive charges are predominant at p-PUF surface. The pH value has a strong influence on the demulsification process, where 99.9% of turbidity removal was reached in pH values below 4 with only 1 h of stirring. In this context the FTIR deconvolution spectra elucidated that the acid media could improve the availability of the reactive groups to participate in the sorption processes. The obtained results suggest that the oil adsorption by p-PUF happens because of hydrophobic interactions between the carbonic chains of the foam and the lipophilic chains of the oil and by electrostatic interactions between surface positive charges of the p-PUF and the negative charges in groups present in the oil. Freundlich model showed a good agreement to the experimental data and predicted an adsorption value of 519 mg g<sup>-1</sup> at the equilibrium and a MDSP of 1.5. The recyclability results have showed that the developed adsorbent can be used for at least five cycles without loss on oil adsorption capacity and this showed that p-PUF is a suitable candidate for industrial process.

**Acknowledgements** The authors thank PRPq/UFGM, CAPES, FAPEMIG and CNPQ for financial assistance, the Projeto Manuelzão and Grutam (UFGM) for technical contributions as well as the businesses Polyuretane Indústria e Comércio LTDA and Evonik Industries.

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