USING MICROEMULSION-MODIFIED DIATOMITE FOR REMOVING SULFUR FROM COMMERCIAL DIESEL

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ABSTRACT

Diatomite or diatomaceous earth is a sedimentary rock composed mainly of diatom siliceous skeletons with high porosity that is often used in adsorption processes. This work investigates the enhancement of diatomite properties using microemulsion systems in the removal of sulfur from commercial diesel. Nonionic surfactants containing microemulsions were used to modify its surface. The adsorbents were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray fluorescence (XRF), thermogravimetry (TG), and N₂ adsorption-desorption. A 2³ full factorial design was performed to assess the influence of salt concentration on adsorption capacities in the microemulsion aqueous phase (from 20 to 1500 mg/kg). The experiments were carried out at batch temperature (25 to 60 °C) and using a commercial diesel fuel with sulfur concentration from 300 to 1100 mg/kg. Sulfur adsorption capacity increased from 0.436 mg/g to 1.23 mg/g with the optimization of the microemulsion system and with the salt addition. The microemulsion-modified diatomite was able to remove up to 26.53% sulfur from commercial diesel.

KEYWORDS

commercial diesel; diatomite; microemulsion; desulfurization; adsorption

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1. INTRODUCTION

With environmental requirements becoming increasingly stricter, the market demand for cleaner fuels is growing (Fallah & Azizian, 2012). Sulfur is one of the main contaminants of fossil fuels and, when present in high amounts, it affects both the environment and human health (Hussain & Tatarchuk, 2013). To meet climate change commitments, there is a need to develop new methods that are more efficient and economically feasible for promoting sulfur removal. From this standpoint, the development of advanced desulfurization technologies is essential to produce near zero diesel fuels (Bu et al., 2011).

Diatomite or diatomaceous earth represents an economically viable alternative in adsorption processes because the material is abundant and has characteristics that make the process economically viable. It has a high mesoporosity and/or macroporosity, low thermal conductivity, good acid resistance and hydrophobic character, among many others unique physical and chemical characteristics (Yu et al., 2015). As a result, diatomaceous earth is used widely in the removal of pollutants, such as heavy metals and micro pollutants, from water (Al-Degs et al., 2001; Chu et al., 2012; Dantas et al., 2001b; Khraisheh et al., 2004; Osmanlioglu, 2007). It is a promising material for use in filtration operations and to eliminate radioactivity from liquid waste (Osmanlioglu, 2007; Yusan et al., 2012). Diatomite, in its raw form, has an ordinary capacity for adsorbing organic molecules (Aivalioti et al., 2010). The reduced adsorption affinity for organics is due to impurities and the presence of a silanol group in its structure (Jiang et al., 2016; Yu et al., 2015). Thus, to improve diatomite adsorption capacity, researchers seek to develop methods to modify the diatomite surface. Surfactant agents have been used for this purpose (Al-Ghouti & Al-Degs, 2011; Dantas et al., 2001b; Sprynskyy et al., 2010).

Microemulsions are thermodynamically stable systems containing a mixture of two immiscible liquids stabilized by surfactants with or without the aid of a cosurfactant, such as a short-chain alcohol (Dantas et al., 2001b). Its application in the modification of adsorbents surface, including diatomite surface (Al-Ghouti & Al-Degs, 2011; Dantas et al., 2001a; Khraisheh & Al-Ghouti, 2005; Li et al., 2009), has been demonstrated as an

efficient process to improve the adsorption of organic and inorganic pollutants (Al-Ghouti et al., 2013; Dantas et al., 2001b). Literature reports that microemulsion clusters can be adsorbed in the porous structure of diatomite, enhancing its adsorption capacity for specific molecules (Al-Ghouti & Al-Degs, 2011).

To remove sulfur from fossil fuels, many researches work on developing effective, applicable, and low-cost technologies. Studies using the adsorption process (Al-Ghouti et al., 2010; Muzic et al., 2010; Nejad et al., 2013; Song et al., 2013; Subhan et al., 2012; Teymouri et al., 2013; Wang et al., 2011), oxidative/extractive desulfurization (Chen et al., 2016ab; Julião et al., 2015; Nawaf et al., 2015), and biodesulfurization (Bordoloi et al., 2014; Guchhait et al., 2005; Paixão et al., 2016) have presented effective results.

Muzic et al. (2010) removed sulfur from diesel in batch adsorption experiments using commercial activated carbon (Norit SXRO PLUS) and 13X zeolite. The experiments were carried out using a 2³ factorial design to evaluate the influence of contact time, adsorbent mass, and temperature. They observed that adsorbent mass and contact time presented the greatest effects, with the best results being achieved using Norit SXRO PLUS activated carbon (0.1742 mg/g).

Wang et al. (2011) studied the effect of the addition of five surfactant solutions (two anionic, one cationic, and two non-ionic) during the synthesis of pillared clays (Ti-PILCs) from Na-montmorillonite. Zinc nitrate solution was used to obtain zinc-supported adsorbents (Zn/Ti-PILCs), which were used as desulfurization adsorbents. The adsorption was evaluated in finite batch using a synthetic diesel fuel at a concentration of 10 mmol/L. Clay modified with CTAB (Cetyl trimethyl ammonium bromide) presented the highest percentage of sulfur removal (94.4%). By optimizing the surfactant concentration, it was possible to obtain a 96.3% removal of DBT (dibenzothiophene).

In this context, this study reports the use of novel microemulsion-modified diatomites as adsorbents for desulfurization of commercial diesel fuel. Sulfur adsorption capacity was evaluated considering the effects of temperature, salt concentration in the aqueous phase of the

microemulsion, and the concentration of sulfur in diesel fuel.

2. MATERIALS AND METHODS

2.1 Materials

The diatomite (Maraxanguape, RN - Brazil) was acquired in its raw form. It was calcined at 850 °C and grinded in a hammer mill. Nonylphenol ethoxylate with 9.5 mols of ethylene oxide (RNX95), purchased from Oxiteno (Brazil), was used as a non-ionic surfactant. CaCl_2 , BaCl_2 , butan-1-ol, and n-hexane were purchased from Vetec, Brazil. Commercial diesel fuels were obtained from two Petrobras refineries: one from Clara Camarão Refinery (Guamaré, RN - Brazil), and the second one from LUBNOR (Fortaleza, CE - Brazil). Table 1 shows its physical properties. These diesel fuels were employed in their original concentrations and mixed with each other to obtain various sulfur concentrations. All reagents were used with no further purification.

2.2 Methods

2.2.1 Microemulsion systems

The microemulsion area inside the pseudoternary phase diagram was obtained using the titrating methodology (Dantas et al., 2014). In 15-mL borosilicate glass test tubes various proportions of oil phase (n-hexane) and cosurfactant/surfactant phase (butan-1-ol/RNX95 = 1.0) were weighed. After, these mixtures were titrated with the aqueous phase (distilled water) until passing from a clear (microemulsion) to a cloudy system (two-phase system). Three different

microemulsion structures inside the microemulsion area (oil-in-water, water-in-oil, and bicontinuous) were used for adsorbent modification. Microemulsion systems were characterized considering: surface tension at 25°C (Sensadyne, QC-6000 analyzer), apparent viscosity at 25°C and 2000 s^{-1} shear rate (Brookfield, R/S Rheometer), and droplet diameter/polydispersity at 25°C (Instrutécnica, ZetaPlus potencial zeta analyzer).

2.2.2 Modification of adsorbent surface by using microemulsions

The diatomite was mixed with RNX95 microemulsions, with various amounts of aqueous phases, using a mechanical stirrer (Tecnal, TE-139) until complete homogenization. A 3:1 ratio between the microemulsion (mL) and diatomite (g) was set based on the volume required to soak the adsorbent completely. BaCl_2 and CaCl_2 solutions (20 to 1500 mg/kg) were used to investigate the effect of salt concentration on the removal of sulfur. The microemulsion-wet diatomites were dried on a Biomatic stove at 60°C, for 24 hours.

2.2.3 Adsorbent characterization

The X-ray fluorescence (XRF) was performed on a Shimadzu-1800 XRF spectrometer. The X-ray diffraction (XRD) patterns were obtained on a Shimadzu XRD-7000 Diffractometer equipped with Cu K α radiation at 40 kV and 30 mA in the range of 5 to 80°, at 2°/min. SEM images were recorded using a scanning electron microscope (Hitachi, TM 3000). Nitrogen adsorption-desorption measurements were performed on a Micromeritics ASAP 2020 adsorption analyzer at -195.20°C using adsorbent samples degassed at 180°C for 11 hours prior to the experiments. Thermogravimetric curves were obtained on a TA Instruments

Table 1. Characteristics of the commercial diesel fuels used.

Property	Value	
	Clara Camarão Refinery	LUBNOR
Cetane number	52.5	-
Kinematic viscosity at 40 °C ($\text{mm}^2 \text{s}^{-1}$)	3.470	2.789
Specific mass at 20 °C (kg m^{-3})	834.4	827.9
Flash point (°C)	38	69
Total sulfur content (mg kg^{-1})	1233.0	7.2

Table 2. Real and coded values for the factors used in the 2³ factorial design.

Operating variables	-1	0	1
X ₁ , temperature (°C)	25.0	42.5	60.0
X ₂ , salt concentration (mg/kg)	20.0	760.0	1500.0
X ₃ , sulfur concentration (mg/kg)	300.0	700.0	1100.0

DSC/TGA Simultaneous Thermal Analyzer using an alumina crucible as sample container, at a synthetic air atmosphere, working under a 50 mL/min of purge gas flow rate, and a temperature ramp from 25°C to 1200°C at a 10°C/min heating rate.

2.2.4 Sulfur analysis

The total sulfur in diesel fuel samples were determined before and after adsorption experiments using a sulfur analyzer (Antek Instruments, Model 9000 NS), as per the ASTM D2622 method.

2.2.5 Batch adsorption experiments

The adsorption experiments were carried out in 125-mL Erlenmeyer flasks using a thermostatic Dubnoff-type batch (Tecnal, 053 model) with constant stirring (1200 rpm). The ratio between adsorbent (g) and diesel (mL) was fixed at 1:5. The effects of salt concentration in the microemulsion aqueous phase (20 to 1500 mg/kg), batch temperature (25 to 60 °C), and diesel fuel sulfur concentration (300 to 1100 mg/kg) in the adsorption process were evaluated. Based on [Dantas et al. \(2014\)](#) the contact time was set for 18 hours and, after that, a simple filtration was performed using a qualitative filter paper (Qualy Ø 9 cm) and a 50-mL glass funnel. The sulfur content was determined in the liquid phase. The adsorption capacity (q) and the percentage of sulfur removal were calculated using Eqs. (1) and (2), respectively.

$$q = \frac{V(C_0 - C_f)}{m} \quad (1)$$

$$\text{Sulfur removal (\%)} = \frac{(C_0 - C_f)}{C_f} \times 100 \quad (2)$$

Where C_0 and C_f are the concentrations of sulfur in diesel fuel before and after adsorption (mg.mL⁻¹), V is the volume of diesel fuel (mL), and m is the adsorbent mass (g).

2.2.6 Statistical study

Statistical analysis was performed using a 2³ full factorial design. According to this experimental design, eight experiments, with a central point made in triplicate, were carried out. The three factors used were: batch temperature, salt concentration in the aqueous phase of the microemulsion, and concentration of sulfur in diesel. Factor levels with their real and coded values are shown in Table 2. The experiments were performed in random order and in duplicate. As a result, the average between them was used, except for the central point. Statistical evaluation was performed by using the STATISTICA 7.0 software.

3. RESULTS AND DISCUSSIONS

3.1 Pseudoternary phase diagram

Figure 1 shows the pseudoternary phase diagram with the microemulsion area. Inside this area, for adsorbent modification, three compositions were selected based on the micellar structure present in each system ($\mu 1R$, $\mu 2R$, and $\mu 3R$) (Table 3).

3.2 Microemulsion systems characterization

The physical characterization of the microemulsion systems was carried out by the analysis of: surface tension, apparent viscosity, droplet diameter, and polydispersity. The results are shown in Table 4.

As one can observe, when comparing systems $\mu 1R$ (O/W) with $\mu 3R$ (W/O), the decrease in apparent viscosity is explained by the presence of the highest percentage of n-hexane (0.30 cP, at 25°C) and the lowest percentage of surfactant.

Figure 1. Pseudoternary phase diagram with the microemulsion area and micellar structures (Dantas et al. 2014).

Considering surface tension measurements, the continuous phase influenced the results, considering that the $\mu 3R$ has less surfactant than $\mu 1R$. Moreover, the surface tension of $\mu 3R$ systems was also lower. System $\mu 1R$ (O/W), with water as continuous phase (72.8 mN/m, at 25°C), had a higher surface tension than system $\mu 3R$ (W/O), which had n-hexane as continuous phase (17.9 mN/m, at 25°C). Figure 2 shows the diameter distribution for these systems.

Regarding the diameter distribution, it is possible to observe the polydispersity index of the systems in Figure 2, which is represented by the width of the curves. As one can observe, $\mu 1R$ and $\mu 3R$ have similar polydispersity indexes with the presence of spherical micelles. For $\mu 2R$, the polydispersity index was lower due to the presence of lamellar structures formed by the existence of water and oil in equal proportions (Figure 3).

Table 3. Composition of the selected microemulsion systems.

System	Microemulsion structure	butan-1-ol/RNX 95 (%)	distilled water (%)	n-hexane (%)
$\mu 1R$	oil-in-water (O/W)	60	35	5
$\mu 2R$	bicontinuous	40	30	30
$\mu 3R$	water-in-oil (W/O)	35	2	63

Table 4. Physical characterization of microemulsion systems (25°C).

	Microemulsion structure	Apparent viscosity (cP)	Surface tension (mN/m)	Droplet diameter (nm)
$\mu 1R$	O/W	9.5	26.2	180.2
$\mu 2R$	Bicontinuous	6.0	20.4	174.0
$\mu 3R$	W/O	3.0	17.4	194.1

Figure 2. Diameter distribution for $\mu 1R$, $\mu 2R$, and $\mu 3R$.

Figure 3. Schematic illustration of a bicontinuous microemulsion.

Observing the data of droplet size, systems $\mu 1R$ and $\mu 3R$ have similar values. For system $\mu 3R$, with reverse micelles, the value was slightly larger due to the higher amount of an oil phase, which swelled the micelles, as also observed by [Silva et al. \(2011\)](#). The bicontinuous structure ($\mu 2R$) showed a smaller droplet size because the water and oil phases were present as microphases, with surfactant molecules adsorbed at the oil/water interfaces.

3.3 Adsorbent characterization

The adsorbent characterization used both raw and $\mu 1R$ -modified diatomite. The characterization

was made only with $\mu 1R$ -modified diatomite because during the experimental procedure, as detailed in the following sections, its enhanced ability for sulfur removal was proved. Distilled water (DRA) and BaCl_2 (1500 mg/kg) solution (DRB) represented the aqueous phase of the microemulsion system. The DRB was characterized for presenting the best result for adsorption capacity, and the DRA was tested to compare changes arising from aqueous phase.

An analysis of the morphological aspects of the adsorbent (Figure 4) shows the presence of many fragments of diatomaceous materials, structures with appearance of fossilized skeletons, mostly

Figure 4. Micrographs from raw diatomite, DRA, and DRB adsorbents.

Figure 5. XRD patterns of raw diatomite, DRA, and DRB adsorbents.

tubular, with a broad size distribution. There are also many circular holes called pores (Souza et al., 2003). DRA and DRB present unchanged pores maintaining the original structures. Adsorption and filtration properties are conferred by the pores of the beehive-type arrangement.

As noted in Figure 5, XRD patterns of raw diatomite, DRA, and DRB adsorbents show three significant peaks between 20-30° in the 2θ range, which are characteristic of diatomaceous materials with higher amounts of amorphous silica (SiO_2) and less of kaolinite ($2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$). This result was confirmed by the XRF analysis, which found for raw diatomite, in larger quantities, 95.1% Si, 3.1% Al,

and 1.3% Ca. In smaller concentrations, one could find 0.8% Fe, 0.56% K, 0.22% Mg, and 0.1% Ti. One can observe that the intensity of the peak at approximately 22° of 2θ increased due to microemulsion incorporation in the diatomite structure. However, the diatomite structure was preserved.

For raw diatomite, according to Figure 6, the TG curve presents a total mass loss of about 1.75%, with only one large drop at 195.7°C. This endothermic peak can be associated to the loss of coordinated water from cations and kaolinite dehydration. For modified adsorbents, DRA and DRB, the total mass loss was 58% at 220°C,

Figure 6. TG and DTA curves for raw diatomite, DRA, and DRB adsorbents.

approximately, associated with surfactant loss, since the flash point of RNX95 is 220°C. The observed endothermic peak at 410°C is attributed to the dehydroxylation of the silicate lattice leading to the formation of metakaolinite. There was no significant difference in the curves with different

aqueous phases probably due to low salt concentration (Souza et al., 2002).

Figure 7 shows that the N_2 physical adsorption isotherm is of type IV (Matthias et al., 2015). The modification of diatomite decreased the surface area because the pores were filled up with the microemulsion. Between the aqueous phases, one could observe that with the addition of salt the area decreased due to a higher occupancy caused by the presence of metal cations. The H3 type hysteresis is observed in all curves, but is considered significant only for the raw diatomite resulting in a mesopore structure of about 17 nm (Matthias et al., 2015).

3.4 Sulfur adsorption experiments

3.4.1 Adsorption capacity of raw and modified diatomite

To assess the effectiveness of diatomite surface modification (1:3 diatomite: modifying agent) a test was performed using raw diatomite or

Figure 7. Adsorption-desorption N_2 isotherms for raw diatomite, DRA, and DRB adsorbents.

Table 5. Sulfur adsorption capacities for raw and modified diatomite (40g diatomite, 200 mL diesel fuel, 60°C, 18 hours).

Type	q (mg/g)
μ 1R	0.36
μ 2R	0.31
μ 3R	0.19
Raw diatomite	0.01

modified with the microemulsion systems. Table 5 shows the obtained results for sulfur adsorption capacity.

As observed in Table 5, the raw diatomite has no ability for sulfur removal. The μ 1R has the highest sulfur adsorption capacity. This system has the highest percentage of active material (butan-1-ol/RNX95), confirming that the surfactant is the main responsible for sulfur removal from diesel fuel. The lower sulfur adsorption capacity was obtained for μ 3R. As the continuous phase of this system is n-hexane and diatomite is a hydrophilic material, this may have hampered the contact of the surfactant molecules with the adsorbent surface during its modification. This can be confirmed by comparing it with μ 1R, that has water as continuous phase and presented higher sulfur adsorption ability.

To evaluate the influence of salt presence in sulfur adsorption, two salts (CaCl_2 and BaCl_2) in two different concentrations (20 mg/kg and 1500 mg/kg) were used. These experiments were made by changing the aqueous phase of μ 1R. The results obtained are listed in Table 6.

As shown in Table 6, the presence of salt

improved the adsorption capacity as well as sulfur removal. The best results were reached when using 1500 mg/kg of salt, but low salt concentrations were sufficient to enhance adsorption ability.

Pieterse et al. (2011) achieved an adsorption capacity of 0.26 mg/g using commercial diesel with 6 mg/kg of sulfur and a nickel-based adsorbent. The experiment was conducted at 200°C, under 500 rpm constant stirring, for 72 hours, using 230 g of diesel and 6 g of adsorbent. Sentorun-Shalaby et al. (2011) used a commercial diesel with 14.5 mg/kg of sulfur and a silica-alumina based adsorbent modified with nickel. The result obtained for adsorption capacity was 0.41 mg/g. Sun et al. (2015) achieved 21.2% of sulfur removal as the highest value using commercial diesel and NaY zeolites. One can observe that the adsorption capacities by using this new adsorbent are in the same magnitude order of the ones obtained by these authors.

3.4.2 Kinetic study

Figure 8 shows sulfur adsorption capacity as a function of contact time using μ 1R-modified diatomite. One can observe that the adsorption equilibrium occurs early, within only 30 minutes, reaching the maximum adsorption capacity.

For the kinetic study, the Lagergren pseudo-first order (Eq. (3)) and the Ho and McKay pseudo-second order (Eq. (4)) models were tested. In these Equations, q_t is the adsorption capacity at time t (mg/g); t is the time (min); q_e is the adsorption capacity at equilibrium (mg/g); k_1 is the pseudo-first order equilibrium rate constant (min^{-1}); and k_2 is the pseudo-second order equilibrium rate constant (g/mg min) (Kong et al., 2016).

Table 6. Influence of salt type and concentration in sulfur adsorption capacity and sulfur removal (40g diatomite, 200 mL diesel fuel, 60°C, 18 hours).

Aqueous phase	Salt concentration (mg/kg)	q (mg/g)	Sulfur removal (%)
Distilled water	-	0.36	11.69
CaCl_2 aqueous solution	20	1.14	25.23
	1500	1.20	26.00
BaCl_2 aqueous solution	20	1.08	24.49
	1500	1.23	26.53

Figure 8. Sulfur adsorption capacity as a function of contact time using μ 1R modified diatomite (40 g diatomite, 200 mL diesel fuel, 60°C).

$$q_t = q_{e1}(1 - e^{-k_1 t}) \quad (3)$$

adsorption behavior on μ 1R-modified diatomite.

$$q_t = \frac{t}{\left(\frac{1}{k_2 q_{e2}^2} + \frac{t}{q_{e2}}\right)} \quad (4)$$

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (5)$$

$$q_e = K_F C_e^{\frac{1}{n}} \quad (6)$$

Table 7 shows the constants calculated using the Levenberg-Marquardt mathematical method. The highest value of correlation coefficient (R^2) was obtained for the pseudo-second order model indicating that the adsorption data conformed well to the Ho and McKay kinetics model. This means that the adsorption rate is chemically controlled (chemisorption).

3.4.3 Adsorption isotherms

Langmuir (Eq. (5)) and Freundlich (Eq. (6)) isotherms models were used to study sulfur

Where C_e is the equilibrium concentration (mg/L); q_e is the adsorption capacity (mg/g); K_L is the Lagmuir constant; K_F is the Freundlich constant; n is the intensity of adsorption; and Q_m is the maximum adsorption capacity (mg/g) (Kong et al., 2016). The values of Langmuir and Freundlich constants are listed in Table 8. These values were obtained using the isotherms shown in Figure 9. As can be observed in Figure 9, the experimental data were better fitted to the Langmuir model ($R^2 = 0.99$). Based on the discussion above, it is possible to

Table 7. Kinetic constants for sulfur removal using μ 1R modified diatomite.

Pseudo-first-order				
k_1 (min ⁻¹)	Standard Error	$q_{e1,cal}$ (mg/g)	Standard Error	R^2
0.97	0.19	0.80	0.03	0.95
Pseudo-second-order				
k_2 (g/mg min)	Standard Error	$q_{e2,cal}$ (mg/g)	Standard Error	R^2
1.65	0.25	0.73	0.10	0.98

Figure 9. Langmuir and Freundlich isotherms for sulfur adsorption by μ 1R modified diatomite (40 g diatomite, 200 mL diesel fuel, 30 min, 60°C).

conclude that adsorption occurs as monolayers, a hypothesis that was also confirmed by the studies of several authors on sulfur adsorption (Chen et al., 2016a; Jiang et al., 2010; Shalaby et al., 2009).

3.5 Statistical analysis

To investigate the influence of different parameters on sulfur adsorption capacity by μ 1R-modified diatomite, a 2^3 full factorial design was applied along with the mathematical description to optimize the process and get the highest adsorption capacity, q (mg/g). The experiments were performed using BaCl_2 solution as aqueous

phase. The results of the experiments are listed in Table 9.

The highest value observed for the adsorption capacity was 1.23 mg/g when sulfur, salt concentration, and temperature were at high levels. It is possible to observe that, for the lower sulfur concentrations, there is a higher number of remaining refractory compounds that are more difficult to be removed from diesel.

Effects of individual parameters and their interactions on adsorption capacity are presented in Figure 10. With the Pareto chart data, one can

Table 8. Freundlich and Langmuir adsorption parameters.

Freundlich				
K_F	Standard Error	n	Standard Error	R^2
0.61	0.03	1.16	0.09	0.98
Langmuir				
K_L	Standard Error	Q_m	Standard Error	R^2
0.51	0.20	1.68	0.51	0.99

Table 9. Average results for the experimental runs according to the 2^3 full factorial design.

Run	X_1^*	X_2^{**}	X_3^{***}	q_{exp} (mg/g)	Run	X_1	X_2	X_3	q_{exp} (mg/g)
1	-1	-1	-1	0.24	7	-1	1	1	0.38
2	1	-1	-1	0.23	8	1	1	1	1.23
3	-1	1	-1	0.26	9	0	0	0	0.45
4	1	1	-1	0.37	10	0	0	0	0.41
5	-1	-1	1	0.48	11	0	0	0	0.43
6	1	-1	1	1.08

Figure 10. Pareto chart for individual parameter effects and their interactions.

conclude that salt concentration is not an important variable at the studied conditions while sulfur concentration is the most important one. Temperature is an important variable as well as the interaction between sulfur concentration and temperature, and between temperature and salt concentration.

Multiple regression analysis of experimental data, obtained by the STATISTICA 7.0 software, resulted in Eq. (7), which describes the dependence of the adsorption capacity, q (mg/g). The following parameters were studied: temperature, (T), sulfur concentration, [S], and salt concentration, [BaCl_2]. By using this model, it is possible to describe how the adsorbent will behave by changing the

parameter values within the range studied.

$$q = 0.50 + 0.19(T) + 0.26[S] + 0.04(T)[\text{BaCl}_2] + 0.17(T)[S] \quad (7)$$

The validation of the model and coefficient was carried out with the variance analysis (ANOVA), and the results are presented in Table 10. The F values calculated by regression residuals were higher than the F -table values, indicating that the model is statistically significant and the coefficients are not predictive. The value for R^2 was 0.9768. This means that the model explains 98% of the variability of the response data around its mean.

Table 10. ANOVA results – validation of model and coefficients.

Source of variation	Sum of Squares	Degrees of Freedom	Mean Square	F-value calculated	F-table value
Regression	1.09	7	0.16	18.09	8.887
Residual	0.03	3	8.6×10^{-3}		
Lack of fit	0.02	1	0.02	56.39	18.51
Pure Error	9.0×10^{-4}	2	4.0×10^{-4}		
Total Error	1.12	10			

4. CONCLUSIONS

A nonionic surfactant was used in microemulsion systems for diatomite surface modification. The new adsorbents were used for sulfur removal from commercial diesel. The main conclusions of this work are:

- The raw diatomite is not capable of removing sulfur from diesel, but this removal is possible by adding a microemulsion as modifying agent;
- Finite bath adsorption studies show that the adsorption process occurs quickly, reaching its maximum value in 30 minutes;
- The salt addition positively affects sulfur adsorption capacity, without harming the pores and the diatomite structure;
- The use of a 2³ full factorial design allows one to optimize sulfur removal from commercial diesel. The best condition is achieved at 60°C, 1500 mg/kg BaCl₂ concentration, and 1100 mg/kg sulfur concentration, reaching 1.23mg/g of sulfur adsorption capacity and 26.53% of removal.

Finally, the use of microemulsion-modified diatomite represents a low-cost, efficient alternative to the adsorption of sulfur from commercial diesel with high sulfur contents.

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