

Article

Application of SDS-Coated Polystyrene Nanoparticles as Advanced Collectors for Selective Coal Flotation: A Combined Experimental and Theoretical Study

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Abstract: Semicrystalline polystyrene spheroidal nanoparticles (50–100 nm) were obtained via microemulsion polymerization. They were evaluated as coal collectors in a low-rank carbonaceous mineral containing 2% organic carbon. The recovery of coal using nanoparticles as collectors was 88.2%, in contrast to 53.2%, 46.4%, and 44.8% achieved using an amine-type compound, kerosene, and diesel, respectively. X-ray photoelectron spectroscopy (XPS) and zeta potential measurements confirmed the polystyrene–mineral surface chemical interaction. A Box–Behnken experimental design for flotation optimization was applied, and the results showed that the coal recovery increased up to 99.5% when the dosage of the collector was increased. A contact angle study and density functional theory calculations, together with XPS results, allowed us to postulate an interaction mechanism in which polystyrene nanoparticles adsorb onto the coal surface through hydrophobic interactions, rendering the oxidized surface hydrophobic and the coal buoyant by adhering to the gas bubbles.

Keywords: SDS-polystyrene nanoparticles; oxidized coal; surface characterization; coal flotation; Box–Behnken; DFT



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1. Introduction

Coal is often associated with beneficial minerals such as iron, copper, zinc, and lead sulfides. In these cases, froth flotation separation may be affected, because reagent consumption increases due to the high surface area of the coal particles, which causes the adsorption of ions and molecules. In addition, the coal decreases the grade of the concentrate. These problems can be solved by using pre-flotation stages to separate the coal [1,2]. However, the surface of the coal in this type of ore is oxidized [3], and its flotation is a problem in the industry. Common hydrophobic collectors do not work effectively for oxidized coal [4,5]. This is because surface oxidation is characterized by the presence of hydrophilic groups such as the following: $-C=O$, $-OH$, and $-COOH$, among others. These groups interact with water molecules through hydrogen bonds, resulting in surface hydration, which makes flotation very difficult and hydrophobic reagents inefficient.

In these carbonaceous minerals, pre-flotation has the ambitious goal of separating the coal with the minimum contribution of non-carbonaceous material. For this, the

collector must be highly selective, and this characteristic is another limitation of common reagents. Therefore, better collectors have been sought for the separation of coal in this type of mineral. Authors report that the floatability of low-rank coal can be improved by using a mixture of chemicals, namely collectors and oils; however, consuming these in large quantities results in higher economic costs and, at the same time, an environmental impact on water [6]. Nanostructured reagents may be an alternative because their high surface area/volume ratio translates into high efficiency due to their ability to maximize hydrophobic properties with low surface coverage, which implies less use of materials or substances and much better results.

There are some other reports about the use of nanoparticles for coal flotation. An et al. [7] applied polystyrene nanoparticles for coal flotation fines, recovering above 80%. Liao et al. [8] demonstrated that the chemical modification of the nanoparticles may improve the collecting properties. However, the high selectivity of the nanoparticles is not required in these cases, because real coals always have a significative hydrophobicity, and this facilitates the flotation. The true challenge for a coal collector is a mineral with a high amount of non-carbonaceous hydrophilic material, because this is where conventional collectors fail [9]. The flotation of carbonaceous minerals using nanoparticles has been minimally reported. Consequently, the role of physicochemical factors is not known over selectivity and floatability in these cases. Although it is important to find an efficient method for the separation of coal collectors, it is also necessary to know how this process takes place at a microscopic level. Even after carrying out an extensive search for information, no research reports have been found where the interaction mechanism of nanoparticles with the coal surface was analyzed. Such analysis and knowledge are essential before the technology is scalable. This information can be useful for future studies to improve and understand any coal flotation process where nanometric reagents are used.

This study contributes experimental insights into the flotation behavior of polymeric nanoparticles as coal collectors in carbonaceous minerals and the role of physicochemical factors in the floatability, as well as the generation of knowledge about the interaction between the nanostructured collector and the surface of the carbonaceous material.

2. Materials and Methods

2.1. Mineral Sample

The low-rank carbonaceous mineral was obtained from the Sabinas Unit in the State of Coahuila, Mexico. A carbonaceous mineral (CM) from Mexico was used for the investigation. Table 1 shows its physicochemical properties. These and others have been reported by Vilasó et al. in a previous work [9]. The main phases identified in the carbonaceous sample correspond to quartz (SiO_2 , 59.2%), orthoclase ($\text{K}_{0.94}\text{Na}_{0.06}(\text{AlSi}_3\text{O}_8)$, 17.9%), calcite (CaCO_3 , see Table 1), pyrite (FeS_2 , 2.0%), and sphalerite ($\text{Zn}_{0.73}\text{Fe}_{0.27}\text{S}$, 0.5%). This is a low-rank carbonaceous mineral that is considered an oxidized carbon due to its large number of oxygenated functional groups.

Table 1. Physicochemical properties of the carbonaceous mineral used for coal flotation using a polystyrene nanoparticle collector (NPs PS) [9].

Physicochemical Properties	Value $\pm$ SD
pH	8.1 ± 0.1
Carbonates (%)	20 ± 0.4
TOC (%)	2.0 ± 0.03
Acidic groups (mEq/g)	0.28 ± 0.1
Basic groups (mEq/g)	2.1 ± 0.6

SD: standard deviation and TOC: Total Organic Carbon.

2.2. Synthesis of Polystyrene Nanoparticles

Polystyrene nanoparticles were synthesized via microemulsion polymerization. For the synthesis, 90 mL of sodium dodecyl sulfate (SDS) (1 g SDS/90 mL of water) was added to a 250 mL three-necked flask equipped with a reflux condenser, stirrer, and nitrogen inlet. The temperature was raised to 80 °C; at this point, 10 mL of 1.5% potassium persulfate (KPS) was added to the flask. Under stirring at 200 rpm, the mixture of 1.5 g of styrene and 0.1 g of 1-butanol was slowly added into the system by dropping for 30 min, and stirring continued for up to 1 h. Subsequently, 3.5 g of styrene was added to the flask and the reaction continued for 1 h. Finally, the temperature was raised to 85 °C for another hour before cooling the reactor at room temperature. The nanoparticles were purified via dialysis for 7 days [10].

2.3. Nanoparticle Characterization

X-ray diffraction (XRD) was used to investigate the crystallinity of the nanoparticles. The pattern was obtained in the 2θ range from 4° to 90°, employing a Bruker D8-Advance X-Ray Diffractometer (30 kV, $\text{CuK}\alpha 1$ $\lambda = 1.5406$ Å).

The size and shape of the nanoparticles were studied using a JEOL JEM-1230 (120 kV) Transmission Electron Microscope (TEM). Free software ImageJ (ImageJ v1.53t) was used to measure nanoparticle size and distribution.

The interaction of the nanoparticles with the functional groups on the coal surface was studied with a JEOL JPS-9030 X-ray Photoelectron Spectrometer (XPS). The instrument used an Al $\text{K}\alpha$ X-ray source, with a step energy of 150 eV and step sizes of 1.00 eV.

The Electric Conductivity Four-Point probe is a method used to measure the resistance of carbonaceous material (CM), carbonaceous material with polystyrene nanoparticles deposited (CM-NPs PS), and carbonaceous material with SDS surfactant (CM-SDS). Electric conductivity is measured across four contacts (points), usually equidistant, with a current (I) flow in the outer points, and the voltage across the sample (V) is measured at the internal points at the same time. According to Ohm's law, resistivity (ρ) can be calculated using the following Equation (1):

$$\rho = \frac{2\pi d * V}{I} \quad (1)$$

In such a way that the electrical conductivity (σ) of the material is given by Equation (2):

$$\sigma = \frac{I}{V * 2\pi d} \quad (2)$$

where d is the distance between points (cm), V is the voltage measured between the internal points, and I is the current intensity applied to the external points (nA) [11].

To perform the electrical conductivity measurement, a Keithley Model 2450 SourceMeter® source/meter unit was used, where currents were established to obtain a voltage drop proportional to the electrical conductivity of the sample. The samples were placed at the base of the four-point device, which was adjusted in such a way that contact was ensured between them, and currents of 1 nA were applied. For the calculations, the distance between the tips was 0.207 cm, and for the sample, $a = d = 1.2$ cm was considered.

2.4. Coal Flotation Experiments

The feasibility of using polystyrene nanoparticles as coal collectors in carbonaceous mineral flotation was evaluated in a Hallimond tube, manufactured in Mexico by a manufacturer in the University's manufacturing laboratory. The particle size of the carbonaceous mineral used was $-74 + 37$ μm . For the microflotation tests, 0.5 g of the mineral was wetted for 3 min in the flotation cell, and then 100 μL of the collector was added (0.01 g

of nanoparticles per g of mineral: 0.01 g/g). Conditioning was carried out for 3 min at 200 rpm, the cell was filled with water, and flotation was performed for 2 min under the same agitation. A nitrogen flow rate of 159 mL/min was used for microflotation [12]. The concentrate was filtered and dried for quantification. The results were compared with the ones obtained using an amine-type collector (0.01 g/g), kerosene (0.16 g/g), and diesel (0.16 g/g).

The total Mineral Recovery (RM) (Equation (3)) and Coal Recovery (RC) (Equation (4)) were evaluated for the microflotations. The RM value indicates the amount of concentrate, whereas the RC value indicates the coal grade concerning the feed.

$$RM (\%) = \frac{m_{\text{concentrate}}}{m_{\text{CM}}} \cdot 100 \quad (3)$$

$$RC (\%) = \frac{TOC_{\text{concentrate}} \cdot m_{\text{concentrate}}}{TOC_{\text{CM}} \cdot m_{\text{CM}}} \cdot 100 \quad (4)$$

where m is the mass (g) and TOC is the Total Organic Carbon (%). The concentration index (CI) (Equation (5)) was calculated to indicate the selectivity and concentration efficiency of the flotation.

$$CI (\%) = RC - RM \quad (5)$$

2.5. Total Organic Carbon Quantification

For the quantification of Total Organic Carbon, a sample of the mineral was first weighed in a crucible, and then carbonates were removed by adding 4 mol/L HCl in excess and waiting for 4 h. The sample was then dried at 70 °C for 16 h and washed with deionized water until no chloride was detected using a 1% AgNO₃ solution. The solid was dried at 105 °C for 24 h and then ignited at 1100 °C for 4 h. The TOC was calculated by dividing the loss on ignition by the conversion factor 1.724 [13].

2.6. Zeta Potential Study

The zeta potential was measured with a Zetasizer Nano ZS90 instrument (instrument manufactured by Malvern Panalytical Ltd, Malvern, UK). before and after conditioning the mineral with the polystyrene collector. The mineral sample was suspended in water and the mixture was decanted to remove the largest particles. The experimental sample was taken from the fine suspended portion. The pH was adjusted from 2 to 13 and measurements were performed 5 min later.

2.7. Study of Physicochemical Variables on Coal Flotation and Optimization

The study of the effect of physicochemical variables and the optimization of the coal flotation using the nanoparticles was conducted using a Box–Behnken experimental design [14–16]. The experimental factors evaluated were the following: pH, flotation time, and collector dosage. The response variables were RM and RC. The acceptance criterion for the significance of the factors was a p-value less than the significance level ($\alpha = 0.05$, 95% confidence). For the lack of fit test, the acceptance criterion was a p-value greater than the significance level ($\alpha = 0.05$, 95% confidence).

2.8. Contact Angle Measurements

The sessile drop method was used to measure the liquid–solid contact angle using a Ramé–Hart instrument. A solid CM sample was prepared in epoxy resin for the measurements. After solidification, the test tube was polished up to uncover the surface of the carbonaceous mineral. The contact angle was measured for 1% SDS and polystyrene nanoparticles dispersed in 1% SDS. Water was used as the reference liquid, for which the

contact angle was measured on a graphite surface as a hydrophobic model and on the carbonaceous mineral.

2.9. Computational Details

Carbonaceous materials are considered macrostructures formed mainly by aromatic clusters. For graphite, these aromatic clusters are parallel graphene layers, and for char, the structure is randomly connected by graphene clusters consisting of 3–7 benzene rings [17]. For the present study, the carbonaceous model used is represented by a finite cluster of a single graphene layer, where the edges terminate in hydrogen atoms, except for the top edge, where a single atom of oxygen was placed to simulate an oxidized carbonaceous surface (CM) (see Figure 1).

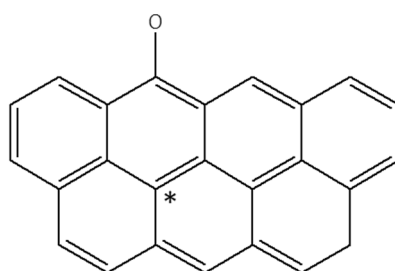


Figure 1. The carbonaceous model used for DFT calculations. The marked carbon atom (*) is the one used for the simulations of the interactions on the basal plane.

All geometries were optimized to evaluate the interactions of the oxidized carbonaceous model with the different compounds that participate in the flotation of coal as water and polystyrene. For the structure optimization and calculations of energies, the density functional theory (DFT) at B3YLP using the 6-31G(d) basis set was used. Additionally, for the simulations, water was considered as a solvent in a polarizable continuum model (PCM). Calculations of all the interaction energies presented later were carried out considering the difference between the total energy of interaction for the pair at a reference distance of separation (D) and the total energy of the pair when D trends to infinite. All structures were constructed using the GaussView 05 program, and DFT calculations were carried out using the Gaussian 09 program [18].

3. Results and Discussion

3.1. Polystyrene Nanoparticle Characterization

Figure 2 shows the XRD pattern of polystyrene nanoparticles. The peaks at 6.5° , the doublet between 20 and 21° , and a less intense peak at 28° are characteristic of SDS surfactant, as reported by Yu et al. [19]. From this, it can be inferred that the polystyrene nanoparticles were coated with it, thanks to which the particle size can be controlled. In this case, there are characteristic signals of the polystyrene that overlap with the peaks of the surfactant. The identification is in correspondence with the main peaks previously reported, one at 9.51° and another at 18.88° . Additionally, at $2\theta \approx 20^\circ$ and 45° , peaks appear with a significant amorphous contribution that has also been reported [20]. Nanoparticle crystallinity is observed with an amorphous contribution due to polystyrene, which has been described as a semi-crystalline polymer, i.e., it has crystalline and amorphous sections [20].

Although no studies have been reported on the influence of the nanoparticle structure on flotation, it is important to mention that there should not be a significant difference in the flotation results when using amorphous or crystalline polystyrene nanoparticles, since if SDS is present in both, the charge distribution is the same and dispersion in water is maintained. The fact that it is amorphous means that its chains do not follow a defined

organization, and this could make the polymer more flexible and fit better on the coal surface because they deform more in contact with it. In contrast, a crystalline structure indicates that the chains are more rigid and the structure is more ordered, and therefore the surface is less permeable, even with fewer free hanging chains, thus maintaining the rigid spherical shape of the particles. It is important to highlight that the T_g of polystyrene is $100\text{ }^{\circ}\text{C}$, and therefore it is in a glassy state and is rigid in both its amorphous and crystalline or semi-crystalline forms at room temperature, which was the temperature at which the flotation studies were carried out. Properties such as hydrophobicity through the contact angle have not been found to be affected by this difference in the molecular structure of the nanoparticles. The nanoparticles evaluated in the works of An et al. [7] and Liao et al. [8] were amorphous and demonstrated the excellent performance of floating coal. Having polystyrene nanoparticles with both contributions, where the highest is observed for the amorphous form, may be advantageous for applications in flotation studies of a low-rank coal.

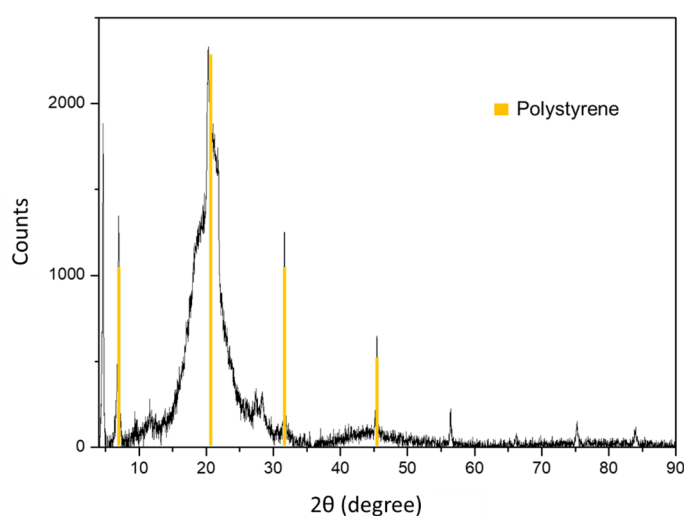


Figure 2. X-ray diffraction pattern for the polystyrene nanoparticles obtained via microemulsion polymerization.

Al Najjar et al. [21] reported polystyrene nanoparticle synthesis via the emulsion polymerization method, where the surfactant plays an important role, because it forms a micelle inside the solution, and the monomer diffuses within them (A) to generate the corresponding polymerization (B) once the initiator (KPS) has been added. Finally, the nanoparticles are formed, and at the same time, they are coated with the surfactant (C). So, it is logical to expect a characteristic signal of the surfactant (Figure 3). However, this could be counterproductive for application as a depressant in carbon flotation, which will be explained later.

The presence of polystyrene nanoparticles was confirmed using TEM micrographs (Figure 4a,b). The shape of the particles was spherical, and they appeared to be covered with a ring or halo that may be associated with SDS surfactant (Figure 4a,b). The sizes were predominantly between 50 and 100 nm (Figure 4c). This size is related to the size of the micelles formed in the solution at the synthesis stage (A, Figure 3), as well as to the concentration of surfactant used. Al Najjar et al. [21] reported the 71 nm size of the nanoparticles when a surfactant is used in 1%, and a similar value was obtained in this investigation.

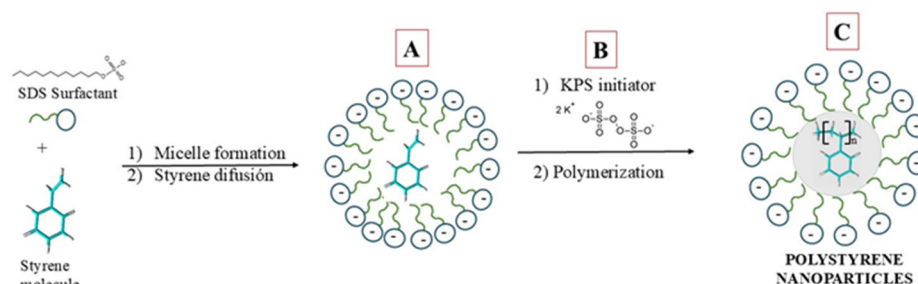


Figure 3. Polystyrene nanoparticle synthesis, (A) micelles formation in the solution in the first stage, (B) Second stage, addition of the compounds KPS and polymerization process and (C) third stage of the synthesis polystyrene nanoparticles formation.

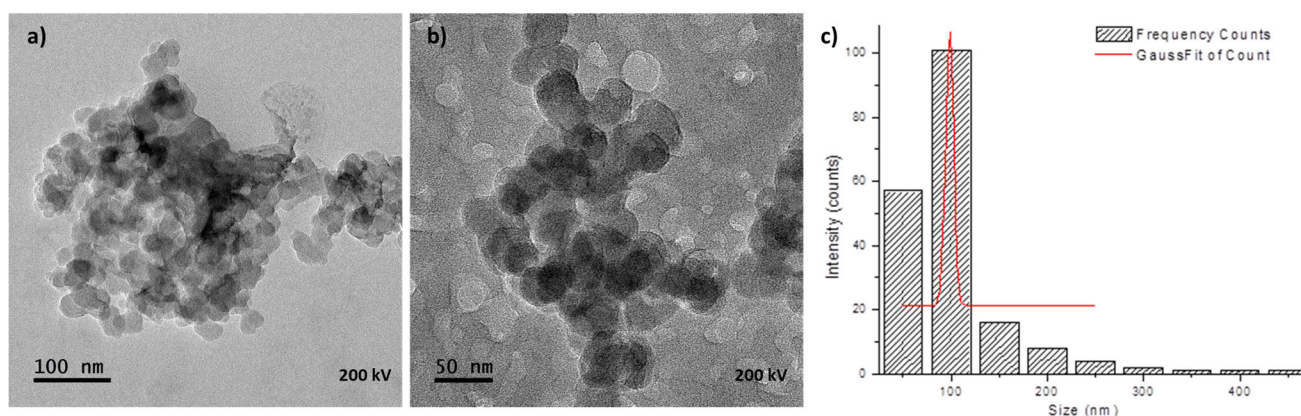


Figure 4. (a) Transmission electron micrographs at 100 nm, (b) 50 nm, and size distribution histogram of nanoparticles (c).

The electrical conductivity of the different materials obtained using the four-point method is presented in Table 2. The highest electrical conductivity is observed for the CM-SDS (1%) material (3.57×10^{-6} S/cm) concerning CM (1.46×10^{-6} S/cm), because SDS is an anionic surfactant. It remains in excess in the solution, increasing the charge carriers because it is completely dissociated, as well as the conductivity. When the nanoparticles adhered to the surface of the CM (CM-NPs PS), the conductivity decreased (2.7×10^{-7} S/cm). The SDS surfactant was redistributed on their surface, orienting the sulfate groups ($-\text{OSO}_3^-$) towards the aqueous medium and the hydrophobic tails towards the surface of the polymeric nanoparticles. In addition, when nanoparticles were on the carbon surface, the concentration of free SDS in the solution decreased. This is the reason why the conductivity value of the CM-NPs PS system drops more than in CM, since in the latter, there are only surface charges related to the polar functional groups present [22,23]. Therefore, when the CM is combined with NPs PS, its electrical conductivity decreases, which suggests that there is an interaction between the combination of materials presented.

Table 2. Electrical conductivity of materials used in flotation test.

Materials	σ (S/cm)
CM	1.46×10^{-6}
CM-NPs PS	2.7×10^{-7}
CM-SDS (1%)	3.57×10^{-6}

This demonstrates once again that SDS is coating the nanoparticles, and can be used in flotation experiments.

3.2. Coal Flotation Experiments

Figure 5 shows the flotation results using the polystyrene nanoparticle suspension as the coal collector. The RC is higher when using the nanometric reagent (88.2%) than when using kerosene (46.4%), diesel (44.8%), or natural flotation (NF-CM) (48.3%). Amines are commonly used for the flotation of oxidized coal [24], and note that here, an amine-type collector was also ineffective (53.2%) compared to nanoparticles. Some authors have noted that amine-type compounds are not universal as collectors for coal [24,25], and flotation here is one of those cases where these collectors fail. This makes it difficult to separate the coal using conventional flotation reagents.

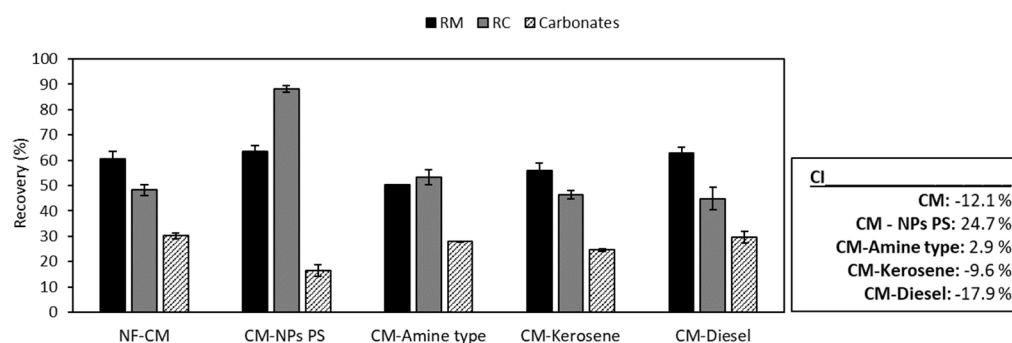


Figure 5. Results of coal flotation in the carbonaceous mineral (CM) using the polystyrene nanoparticles (NPs PS), amine, and hydrophobic reagents as collectors.

The RM is similar for all collectors and natural flotation (NF-CM: 60.4%; CM-NPs PS: 63.5%; CM-kerosene: 56%; CM-diesel: 62.8%). When amine is used, the non-carbonaceous material appears to be depressed (RM for CM-amine: 50.3%); however, the RC was not significantly higher than the RM, and this means that coal selectivity was not achieved. The carbonates in the concentration show a similar trend; only when the nanoparticle collector was used did the carbonates decrease, which may be related to a better concentration process. All this is corroborated by the CI values. The CI is 24.7% for flotation with nanoparticles, a value clearly higher than that obtained in natural flotation, as well as using amine, kerosene, and diesel. In general, the analysis of all these results indicates that the nanometric collector is the only reagent that allows for the separation of coal from this mineral with high selectivity.

It has been proven that when mixtures of cationic/anionic collectors are used, the flotation results improve. In this case, this could be due to the same reason: since the nanoparticles are coated with a layer of SDS (anionic) surfactant, the system that adheres to carbon is more complex and could generate a denser hydrophobic layer on the CM surface, repelling any interaction with water molecules and thus decreasing hydrophilicity. Thus, the synergistic action between SDS and polystyrene nanoparticles results in higher RC and RM values, even when surfactant mixtures are used (Li et al. [26]). These authors reported the flotation of low-rank coal using a mixture of surfactants—CTAB/SDS in different proportions—and the result obtained was 68.71%, which is lower than the value reported using the PSNps-SDS system (88.2%).

Figure 6 shows the plot of the zeta potential as a function of pH for the CM before and after conditioning with the nanoparticles. At pH 7, the value is negative, indicating that the CM surface charged negatively due to the sulfate group ($-\text{OSO}_3^-$) that is oriented outwards from the micelle, that is, towards the aqueous. The negative charge increases up to pH 12, from which the same behavior as before conditioning is observed. When the pH decreases, there is a high concentration of H^+ ; in this sense, Wolowicz and Staszak [27] reported the presence of energetically favorable interactions between H^+ and the polar

head of SDS surfactant micelles, via the replacement of Na^+ with H^+ , protonating the polar head of the SDS. This is probably the reason why the zeta potential decreases under these acidic conditions of the solution. Moreover, there is no isoelectric point in the whole pH range. These results confirm the modification of the surface after conditioning [28,29]. The plot of the zeta potential for CM-NPs PS is lower than that of CM because when the nanoparticles adhere to the carbon, the surface negative charge density increases, increasing the electrostatic repulsion on the surface; unlike the CM, this has oxygenated groups whose dissociation depends on the pH of the medium, so the value of the zeta potential is moderate.

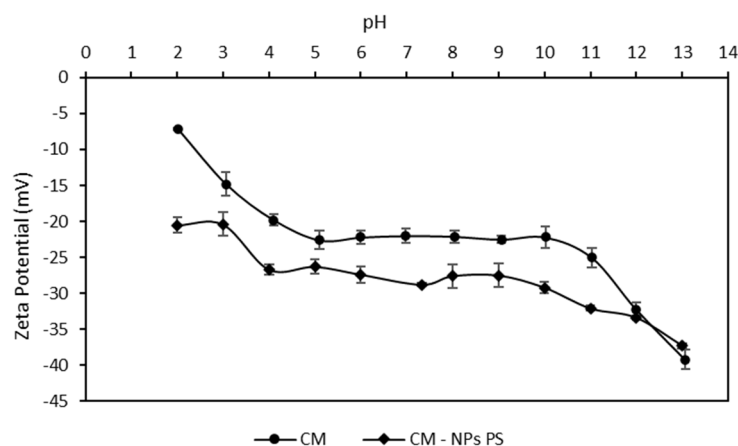


Figure 6. Zeta potential as a function of pH for the carbonaceous mineral (CM) before and after being conditioned with the polystyrene nanoparticle collector (NPs PS).

3.3. Effect of Physicochemical Variables on Coal Flotation and Optimal Conditions

The Box–Behnken design for the optimization of coal flotation in the CM using the polystyrene nanoparticle collector is shown in Table 3.

Table 3. Box–Behnken experimental design for the optimization of coal flotation in a carbonaceous mineral using the polystyrene nanoparticles as collectors.

Experiment	pH	t (Min)	NPs PS (μL)	RM (%)	RC (%)
1	7	3	1000	74.2	100
2	7	2	550	75.1	89.2
3	4	3	550	80.8	100
4	10	2	1000	65.3	95.6
5	10	2	100	73.7	73.3
6	7	2	550	72.0	88.5
7	4	2	100	63.3	62.6
8	10	3	550	73.4	100
9	7	1	100	52.3	59.2
10	4	2	1000	69.6	100.0
11	7	2	550	70.0	89.8
12	4	1	550	53.8	67.4
13	7	2	550	69.8	89.0
14	7	3	100	71.2	100
15	10	1	550	57.7	63.9
16	7	2	550	69.3	89.9
17	7	1	1000	65.8	89.8
18	7	2	550	75.1	80.7

t: time of flotation, NPs PS: volume of collector, RM: total recovery of mineral, and RC: recovery of coal.

The analysis of variance (ANOVA) for the RM is shown in Table 4. Only the flotation time has a statistically significant effect, since its *p*-value is less than 0.05 (α). Furthermore, this factor also presents a quadratic effect ($BB < 0.05$). The pH and the collector dose have a significant synergistic effect ($AC < 0.05$). This indicates that the pH and dose jointly influence the RM, which could be associated with some modification of the nanoparticle dose. At very high dose values, the system viscosity tends to increase, generating floating particles without carbon (which increases ash) and forming bridges between particles (flocculation), which can affect the stability of the nanoparticles and decrease the recovery percentages. An important aspect when using the correct dosage of nanoparticles is that they also act as physical carriers or nuclei for the flotation of fine coal particles, as there are sufficient nuclei for the fine coal to adhere and float efficiently [30]. A dosage of 500 μL is necessary, considering the negative charge of the nanoparticles and the negative charge of the floating coal particles. This is necessary because the greatest or predominant interaction will occur through hydrophobic interactions.

At low pH values below 5 and approaching 2, the anionic surfactant (SDS) begins to lose solubility and micellar capacity [31] as the following reaction occurs:

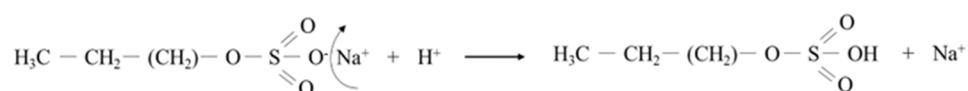


Table 4. Analysis of variance for the total recovery of mineral (RM) in the optimization of coal flotation in the carbonaceous mineral using the polystyrene nanoparticles as collectors.

Source	Sum of Squares	DF	Mean Square	F Stat	<i>p</i> -Value
A: pH	0.845	1	0.845	0.12	0.7433
B: Time	612.5	1	612.5	86.83	0.0002
C: NPs PS	25.92	1	25.92	3.67	0.1134
AA	12.3037	1	12.3037	1.74	0.2438
AB	31.9225	1	31.9225	4.53	0.0867
AC	54.0225	1	54.0225	7.66	0.0395
BB	62.3219	1	62.3219	8.84	0.0311
BC	27.5625	1	27.5625	3.91	0.1050
CC	21.6837	1	21.6837	3.07	0.1399
Lack of fit	84.41	3	28.1367	3.99	0.0853
Error	35.2683	5	7.05367		
Total	987.0	17			

DF: degrees of freedom and NPs PS: volume of polystyrene nanoparticles (collector).

If the results are analyzed solely concerning the pH, it is observed that this variable does not have a significant influence on the RM, because the nanoparticles do not vary with pH. In other words, they do not agglutinate, since when SDS adsorbs to the surface of the nanoparticles, they manage to remain dispersed in water because an electrostatic repulsion is generated between nanoparticles due to the negative charge that covers them. Although stability studies were not performed at different pH values, it can be stated that they did not agglomerate, since the sulfate group of SDS is considered a strong acid and completely dissociates over a wide pH range [32].

Equation (6) shows the model generated for the RM. The coefficient of determination (R^2) is 0.8787, so it explains 87.87% of the variability in the response. The mean value of the residues is 2.18889, with a standard deviation of 2.65587, indicating low dispersion

between the experimental and calculated results. The lack of fit test confirms that the model is predictive of the RM.

$$\begin{aligned} \text{RM}_{\text{CM-NPsPS}} (\%) = & -6.24434 + 6.10093 \cdot \text{pH} + 33.6667 \cdot \text{Time} + 0.0468313 \cdot \text{NPsPS} - 0.186574 \cdot \text{pH}^2 - \\ & 0.941667 \cdot \text{pH} \cdot \text{Time} - 0.00272222 \cdot \text{pH} \cdot \text{NPsPS} - 3.77917 \cdot \text{Time}^2 - 0.00583333 \cdot \text{Time} \cdot \text{NPsPS} - \\ & 0.0000110082 \cdot \text{NPsPS}^2 \end{aligned} \quad (6)$$

Table 5 shows the ANOVA for the RC. Collector dosage and flotation time have a statistically significant effect (p -value < 0.05). Furthermore, both factors have a synergistic effect ($BC < 0.05$). The pH has a second-order effect, since the p -value of the AA interaction is also less than 0.05.

Table 5. Analysis of variance for the recovery of coal (RC) in the optimization of coal flotation in the carbonaceous mineral using the polystyrene nanoparticles as collectors.

Source	Sum of Squares	DF	Mean Square	F Stat	p -Value
A: pH	0.98	1	0.98	0.08	0.7910
B: Time	1791.01	1	1791.01	142.84	0.0001
C: NPs PS	1019.26	1	1019.26	81.29	0.0003
AA	96.3927	1	96.3927	7.69	0.0392
AB	3.0625	1	3.0625	0.24	0.6421
AC	57.0025	1	57.0025	4.55	0.0862
BB	0.460909	1	0.460909	0.04	0.8555
BC	234.09	1	234.09	18.67	0.0076
CC	0.33	1	0.33	0.03	0.8775
Lack of fit	157.017	3	52.3392	4.17	0.0790
Error	62.695	5	12.539		
Total	3426.69	17			

DF: degrees of freedom and NPs PS: volume of polystyrene nanoparticles (collector).

Equation (7) shows the model generated for RC. R^2 is 0.9359, indicating that the model explains 93.59% of the variability in the data series. The mean of the residuals is 2.90278, with a standard deviation of 3.54105. The model is validated by the lack of fit tests.

$$\begin{aligned} \text{RC}_{\text{CM-NPsPS}} (\%) = & -9.3696 + 8.38241 \cdot \text{pH} + 23.5708 \cdot \text{Time} + 0.0801512 \cdot \text{NPsPS} - 0.522222 \cdot \text{pH}^2 + \\ & 0.291667 \cdot \text{pH} \cdot \text{Time} - 0.0027963 \cdot \text{pH} \cdot \text{NPsPS} - 0.325 \cdot \text{Time}^2 - 0.017 \cdot \text{Time} \cdot \text{NPsPS} - 0.00000135802 \cdot \text{NPsPS}^2 \end{aligned} \quad (7)$$

Figure 7 shows the main effects of coal flotation using the polystyrene nanoparticle collector. There is an optimum point at pH 7 for both variables, but it is more accentuated for the RC. In the case of time, direct dependence is observed for the RM, with a tendency to be constant from about 2.8 min onwards—this is because all the minerals have already floated at that time. For the RC, a linear dependence on time is observed, which may be related to the fact that coal is not the main flotation component, as the faster flotation components reach a plateau in a short period [33,34]. In the case of collector dosage, for the RM, there is an optimum point that tends almost to be a plateau, while for the RC, the behavior is linear. A possible explanation for this lies in the following hypothesis: at a low collector dosage, there are many active sites in the coal for a few nanoparticles that come into contact with it. The gangue (quartz, calcite, pyrite, and sphalerite phases, identified in the phase composition of mineral coal) is no longer affected by dosing due to the hydrophobic nature of the collector, but when the coal sites are saturated, the amount of concentrate does not increase because flotation stopped, resulting in the observed plateau for the RM. Coal particles have a high surface area and porosity [35–37], which would explain why it can adsorb more nanoparticles than gangue minerals; moreover, given the

hydrophobic nature of the coal surface, it is likely to have a higher capacity to adsorb polymers. This hypothesis is also supported by what was observed for the time when coal did not appear to be the main component of flotation.

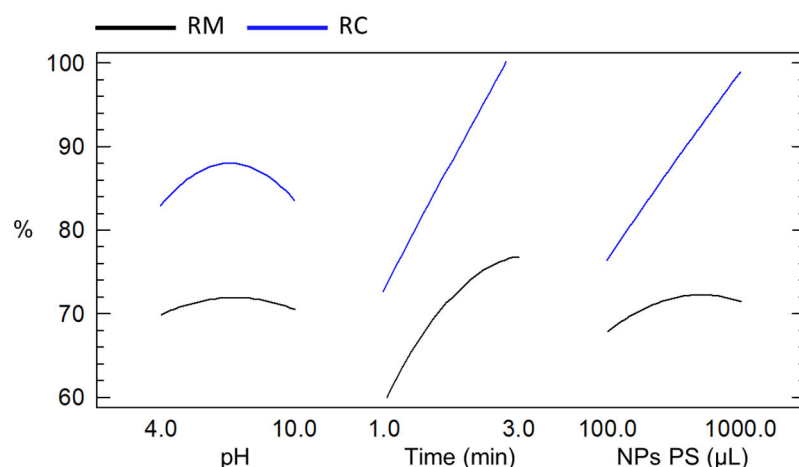


Figure 7. Main effects graph for the optimization of coal flotation in the carbonaceous mineral (CM) using the polystyrene nanoparticle collector (NPs PS).

Figure 8 shows the response surfaces for the joint optimization of the RM and RC. The desirability is aimed at minimizing the RM and maximizing the RC, which leads to the concentration of the coal. The RM of 72.3% and RC of 99.5% are achieved under optimal conditions. These results are superior to those obtained in non-optimized conditions: RM = 63.5% and RC = 88.2%. The CI increases from 24.7 to 27.2%.

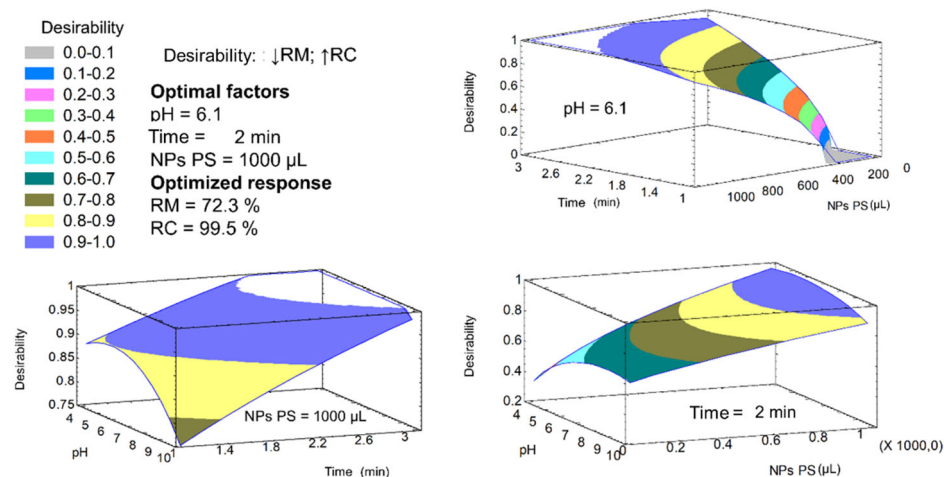


Figure 8. Box–Behnken response surfaces and optimal conditions for the optimization of the coal flotation in the carbonaceous mineral (CM) using the polystyrene nanoparticle collector (NPs PS).

3.4. Study of the CM–Polystyrene Nanoparticles Interaction

3.4.1. X-Ray Photoelectron Spectroscopy (XPS)

Figure 9a shows the full spectrum of the three materials: CM, PS NPs, and CM-PS NPs, in which the elemental composition and characteristic peaks of each chemical element are identified. In the case of CM, it is observed that there is a majority percentage of oxygen, logically associated with a large number of oxygenated surface groups, characteristic of this type of low-rank coal [38]. Other peaks such as aluminum, silicon, and calcium identified correspond with the phase composition reported by Vilasó et al. [9] for the CM sample. In the case of the nanoparticles, the main chemical element identified is carbon. The small

percentage of sulfur is due precisely to the fact that these nanoparticles were coated with the SDS surfactant, as previously mentioned. When these nanoparticles adhere to carbon, it is observed that both the carbon and oxygen contents change, reaching a nearly 50:50 ratio, confirming the incorporation of the nanoparticles into the carbonaceous material.

The deconvolution of the spectrum of C1s (FWHM de 1.0 ± 0.1) is shown in Figure 9b for CM. The binding energy identified was associated with oxygenated functional group aliphatic carbon chains and aromatic rings in the low-rank coal, which are shown in Figure 9b.

The behavior in the deconvolutions for O1s (FWHM de 1.4 ± 0.1) in the carbonaceous material shows peaks at 531.56, 532.72, 533.89, 534.96, and 536.09 eV, associated mainly with the bonds between carbon and silicon, according to the elemental composition in the survey spectrum of CM. These are as follows: Si-O-H, C-O-H, C-O-C, C=O, and Si-O-Si, respectively [39,40] (Figure 9c).

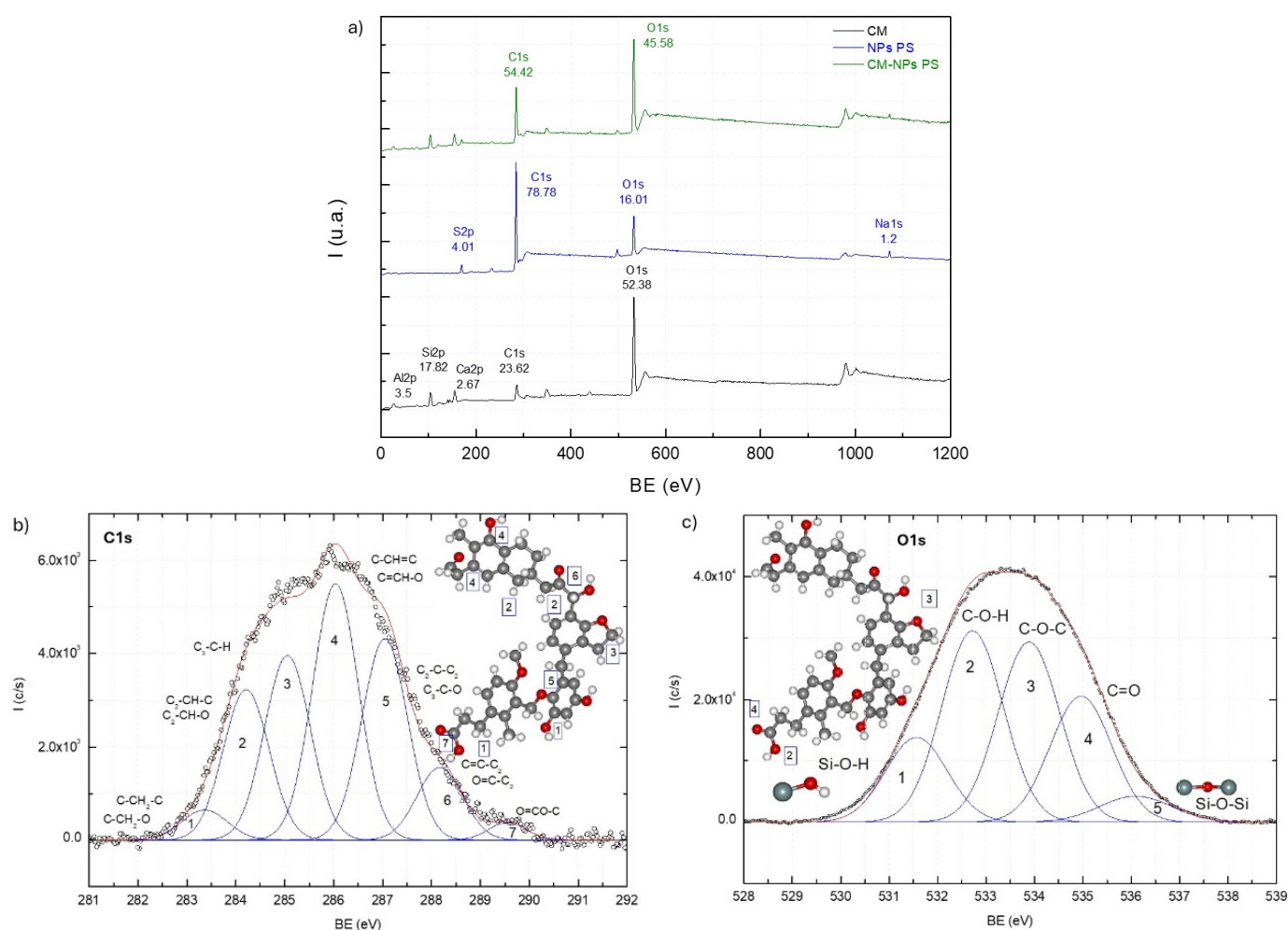


Figure 9. Cont.

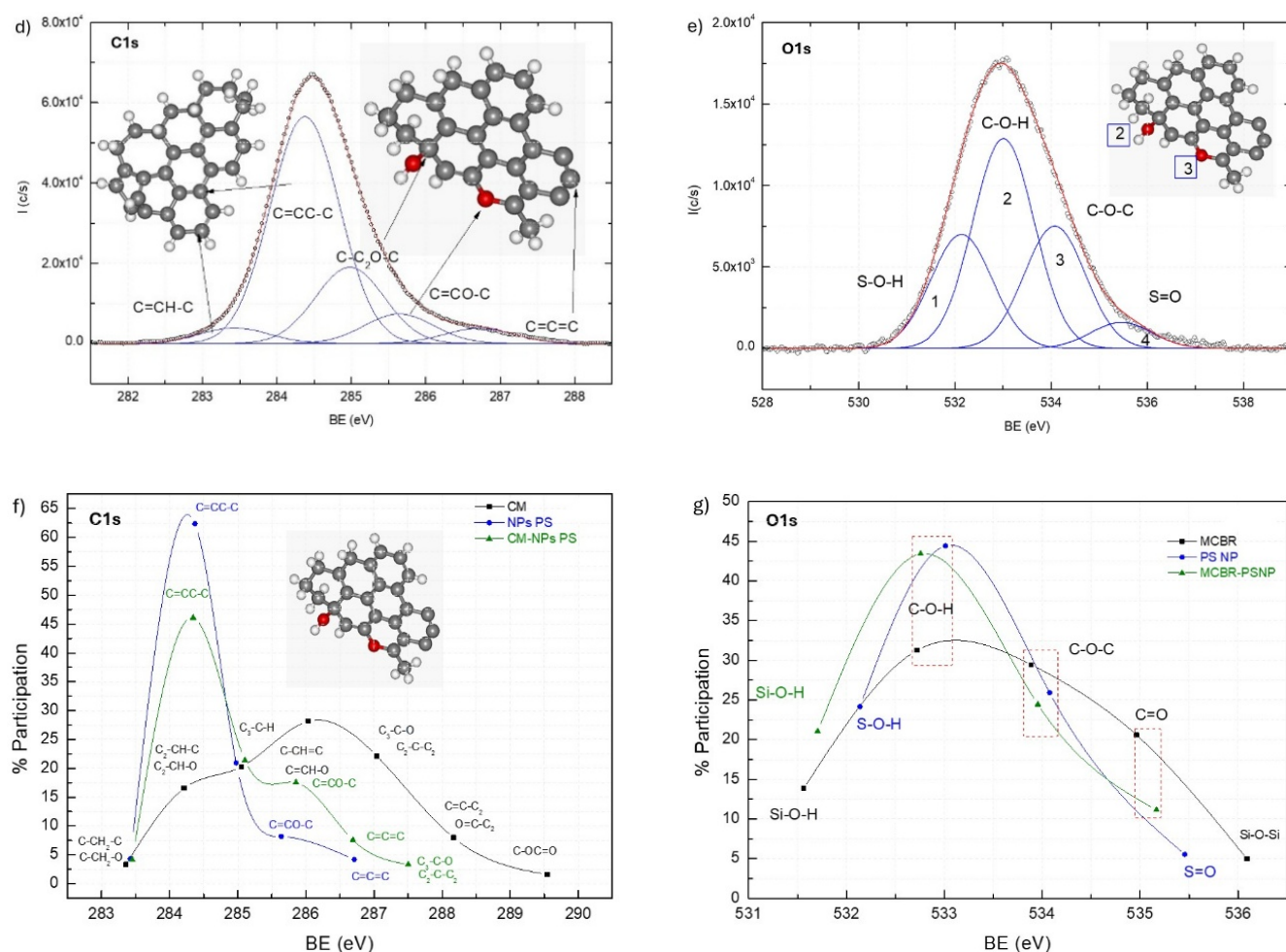


Figure 9. XPS wide energy spectrum of (a) survey of carbonaceous mineral (CM), polystyrene nanoparticles (NPs PS), and carbonaceous materials modified with nanoparticles (CM-NPs PS), (b) C1s peaks for (c) CM, (d) NPs PS, and (e) CM-NPs PS. O1s peaks for (c) CM, (f) CM-NPs PS and (g) comparison for O1s for MCBR, PS NP and MCBR-PS NP.

For polystyrene nanoparticles, the deconvolution of the spectrum of C1s (FWHM 1.0 ± 0.1) is shown in Figure 9d. The main interactions between C, O, and H were associated with C=CH-C, C=C₂-C, C-C₂O-C, C=CO-C, and C=C in 283.43, 284.37, 284.98, 285.64, and 286.71 eV, respectively [41,42] (interaction between C and O is attributed to the bond between the C of the surfactant and the O of the sulfate group in the polar head of the same, confirming again that the nanoparticles were coated with SDS). Clearly, the idea presented above is confirmed by analyzing the deconvolution spectrum of O1s for the nanoparticles, where oxygenated groups associated mainly with the polar head of the surfactant were identified (Figure 9e) at 532.14, 533.01, 534.08, and 535.46 eV.

When the polystyrene nanoparticles are deposited on the CM surface, the deconvoluted spectrum for C1s and O1s shows the same peaks but with a shift, which can be associated with the presence of polystyrene nanoparticles that change the chemical environment of the surface (Figure 9f,g). Figure 9f displays the high-resolution C 1s XPS spectra of three different samples: carbonaceous mineral (CM), polystyrene nanoparticles (NPs PS), and their composite (CM-NPs PS). The composite (green curve) presented intermediate features between both materials. It retained a significant aromatic carbon signal while also showing notable contributions from oxidized groups, suggesting interfacial interactions and possible chemical modification upon nanoparticle incorporation.

Figure 9g shows the CM-NPs PS O1s spectra of the comparison, showing an intermediate profile between the individual components and reflecting the coexistence of oxygen species from both MCBR and PS NP. This suggests possible interfacial interaction or chemical modification upon blending, leading to the redistribution or enrichment of specific oxygen functionalities. The red dashed boxes in the figure denote the key regions where notable spectral shifts or intensity changes occur among the samples. These changes emphasize the impact of polystyrene nanoparticle incorporation on the oxygen surface chemistry of low-rank coal, potentially influencing its physicochemical properties and reactivity.

3.4.2. Contact Angle

For this case, two materials were used as references: carbon with a hydrophobic surface (graphite, CS) and low-rank carbon, whose surface contains oxygenated functional groups (CM) and therefore exhibits a certain degree of hydrophilicity. In both cases, their interaction with water was analyzed (Figure 10a–d).

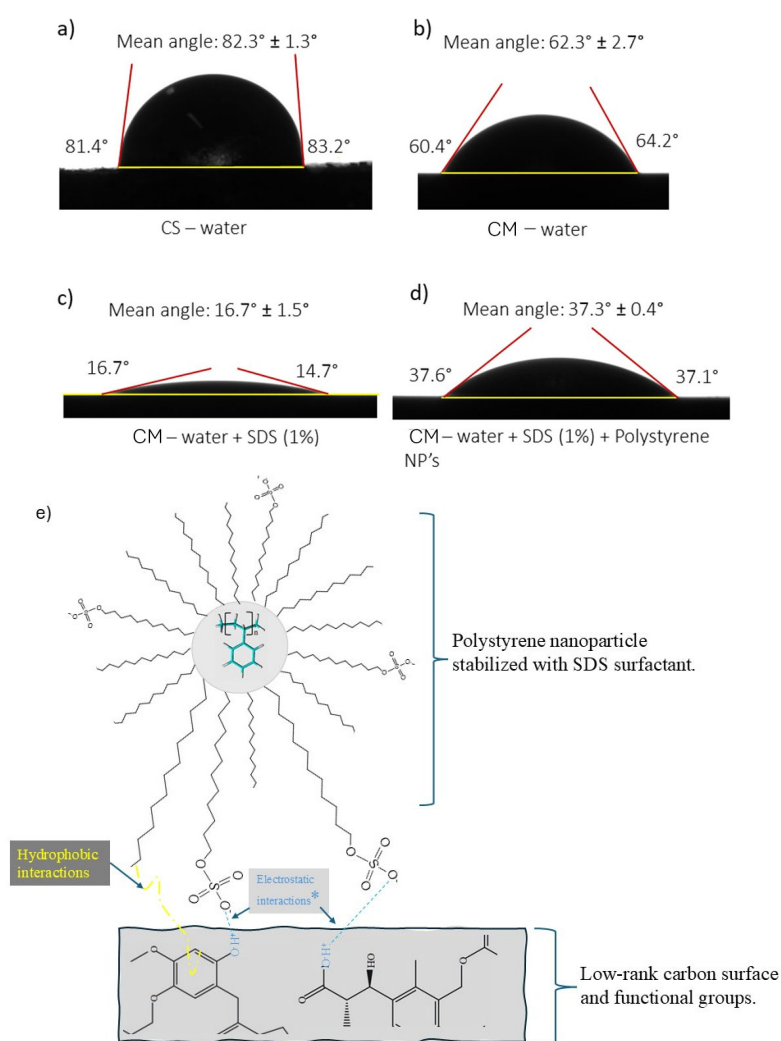


Figure 10. Contact angle results for different cases of interaction: (a) carbonaceous surface (clean) with water, (b) oxidized carbonaceous surfaces with water, (c) oxidized carbonaceous surface with a solution of water–surfactant, (d) oxidized carbonaceous surface with the dispersion of polystyrene nanoparticles, and (e) mechanism of interaction between CM and PS Nps. * This interaction only occurs when the pH of the flotation medium is acidic, and it might be thought that some functional groups would become protonated. At a neutral pH, the prevailing interactions are purely hydrophobic, through pi–pi interactions, for example.

As was expected, for the interaction between CS and water, the higher contact angle was measured ($82.3^\circ \pm 1.3^\circ$), demonstrating the hydrophobic nature of the CS surface. However, when oxygen groups are present on the carbonaceous surface (CM), the contact angle decreases to a value of $62.3^\circ \pm 2.7^\circ$, a typical hydrophilic behavior due to the apparition of hydrogen bonds between the oxygen groups of the surface and hydrogen atoms of the water molecules.

For the main purpose of this work, in the flotation of low-rank coal (CM) with polystyrene nanoparticles (CM-NPs PS), it is mandatory to examine the effect of the surfactant (SDS) used in the synthesis of the polystyrene nanoparticles, since undoubtedly, its presence in the floatation process affects the surface tension of the system. In other words, its presence induces the wettability (depression) of all solids present in the flotation cell affecting the recovery. This behavior can be observed in Figure 10c, where the contact angle value of the CM with water in the presence of 1% of SDS decreases to a value of $16.7^\circ \pm 1.3^\circ$, which is a completely hydrophilic behavior.

When the nanoparticles adhered to the carbon in a 1% SDS solution (CM-NPs PS-water), the contact angle was $37.3^\circ \pm 0.4^\circ$, showing an intermediate behavior between the values obtained for CM–water and CM–water + SDS (1%).

Although the contact angle is less than 90° , it can be stated that when polystyrene nanoparticles adhere to the coal surface, hydrophobicity increases, although it might be thought that the presence of SDS in the flotation of the carbonaceous mineral poses a serious disadvantage to the use of polystyrene nanoparticles to induce hydrophobicity. However, the experimental flotation results showed a 99.5% recovery of the coal; therefore, it can be considered that the polystyrene nanoparticles effectively induce the hydrophobicity of the oxidized coal particles in the flotation process (Figure 10e). It has been reported that when the surface of low-range carbons is modified with surfactant mixtures, the contact angle values vary, as obtained in this study, depending on the ratio of the surfactant content. Despite these values, the recovery percentages reached 78% [6]. It is important to consider that the nanoparticle suspension is dialyzed before being used in flotation, which implies a reduction in the SDS concentration in the collector. In addition, when the mineral is conditioned for flotation, fresh water is added, which further reduces the SDS concentration. All this makes the effect of surfactant molecules at the solid–liquid interface negligible, and hence, the repulsion forces between water molecules and polystyrene nanoparticles dominate, providing hydrophobicity to the CM and facilitating attachment with the air bubbles. It is inferred that this dilution did not cause a very low SDS concentration, because if it had, the nanoparticles would have been destabilized, and this would have affected the flotation results, which was not the case.

3.4.3. DFT Analysis

The energy of the interaction of the oxidized carbonaceous surface with different structures that participate in the flotation as polystyrene, SDS, and water was obtained using the models shown in Figure 11, considering a standard pair separation of $D = 1 \text{ \AA}$. The orientation of the interaction (parallel or vertical) leads to small differences in the calculated interaction energy (ΔE_{inter}). Figure 11a shows the interaction between a water molecule and CM, where the result of $\Delta E_{\text{inter}} = -93.5 \text{ kcal/mol}$ is completely in agreement with the result of the contact angle measurement in Figure 10b. The negative value of energy indicates that attraction at the interface exists, leading to a certain level of wettability of the CM due to the apparition of van der Waals forces. In the same manner, the results in Figure 11b–d agree with the results of the contact angle in Figure 10, where the interaction of the polystyrene with CM was higher ($\Delta E_{\text{inter}} = -769.1 \text{ kcal/mol}$) than the interaction of SDS with CM ($\Delta E_{\text{inter}} = -457.1 \text{ kcal/mol}$), indicating that effectively, the polystyrene nanoparticles were

adsorbed by the CM. This could be related to the fact that the hydrophobic forces appearing between CM and polystyrene are greater than those appearing in the interaction of the hydrophobic carbon chain of SDS and CM. It is important to consider that at this point, the concentration of SDS is smaller than the concentration of polystyrene nanoparticles. However, the energy of interaction for the OCS-SDS is still big, indicating that some of the molecules of SDS were also adsorbed by the CM.

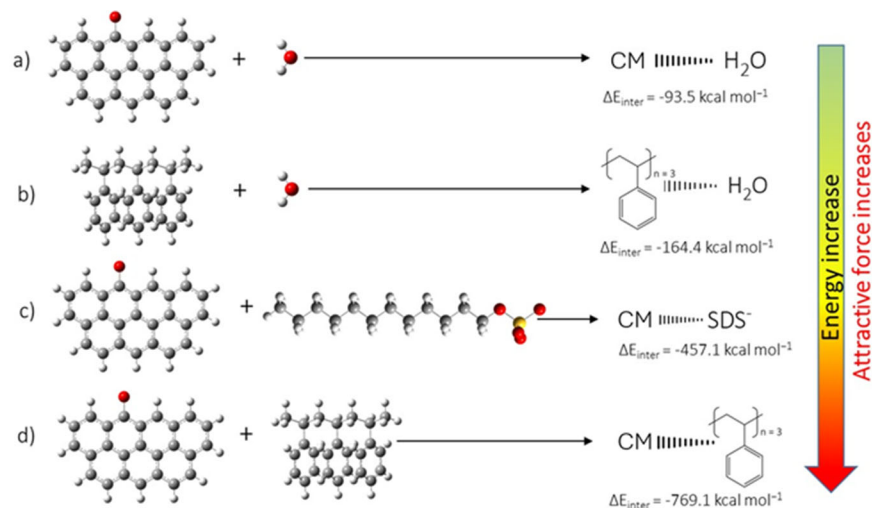


Figure 11. Interaction energies obtained via DFT calculations for oxidized carbonaceous surfaces with different structures that participated in the adsorption of polystyrene nanoparticles at distance $D = 1 \text{ \AA}$ according to Figure 11b. (a) Interaction of CM and a water molecule, (b) polystyrene and a water molecule, (c) CM and SDS, and (d) CM and polystyrene.

From Figure 11, there seems to be a contradiction of the results of the interactions of CM- H_2O and CM-polystyrene. According to the previous description of the results in Figure 10d, a strong repulsion between polystyrene and water molecules should appear. However, according to the DFT results, the interaction of water-polystyrene was higher than that calculated for water-CM. This means that there is wettability at the polystyrene-water interface. However, when the size of the molecules that participated in the interaction is modified, it leads to a difference in the energy calculations. For example, Figure 12a shows the variation in interaction energies when the distance of separation is changed for water clusters of different sizes (1, 3, and 5). It can be noted that as the size of the water cluster increases, keeping the same distance of separation, the ΔE_{inter} decreases significantly. This means that as the amount of water increases, the attractive forces decrease in the CM-water interface, being practically imperceptible under bulk conditions. On the other hand, Figure 12b shows that when the size of the polystyrene molecule increases ($n = 1, 2, 3$), an opposite effect is observed—the value of ΔE_{inter} increases as the size of the polystyrene molecule increases. This fact means that as the polystyrene chain increases, the hydrophobic interaction increases accordingly. Therefore, for the results in Figure 12, a decrease in the interaction energy with the polystyrene nanoparticles is expected as the number of water molecules increases, leading to the apparition of strong repulsion forces.

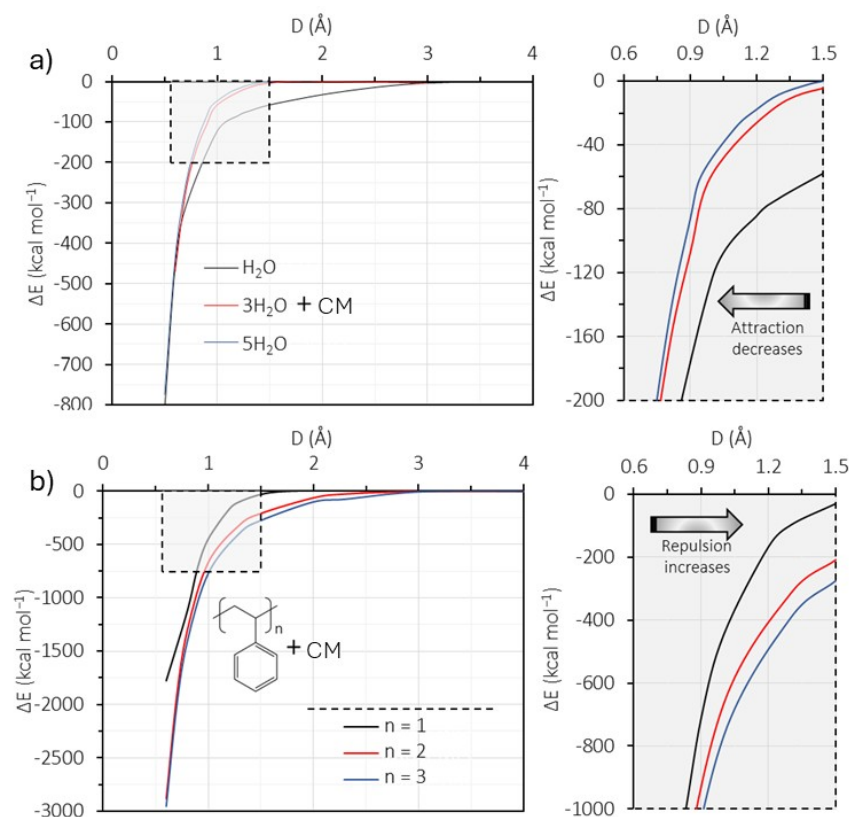


Figure 12. Effect of the separation distance (D) on the interaction energy with CM. (a) For water clusters of different sizes and (b) for polystyrene chains of different sizes.

Note that the DFT study is only focused on a small section of the curves of interaction potential (Figure 12). It has been previously stated that calculations of van der Waals interactions via DFT can be difficult, and that the results cannot be entirely reliable. This is mainly associated with long-range van der Waals interactions [43]. Although there are many approaches to take into account the van der Waals energy, such as the development of new functionals (vdW-DFT functional) or empirical corrections, the computation could be very demanding, or the lack of experimental data could limit the application [44–46]. For this reason, the DFT results obtained in this study were considered only as an approximation of the observed behavior in the flotation and contact angle experiments, and it was not considered necessary to obtain data at a more accurate level of theory.

3.4.4. Mechanism of Interaction—Polystyrene Nanoparticles–Oxidized Coal Surface

Figure 13 shows a schematic of how polystyrene acts to make the oxidized surface coal particle more hydrophobic. Polystyrene is a hydrophobic polymer due to it not presenting oxygenated or nitrogenous polar groups, but the polymer interacts through the sulfate group of the polar head of the surfactant that coats the nanoparticles, establishing electrostatic interactions. Another type of interaction that is believed to be generated in the system are the hydrophobic interactions between the non-polar chains of the nanoparticles and aromatic groups of carbon [47,48]. The chemical reactivity of aliphatic chains and aromatic rings is very limited, so a mechanism through electrostatic interactions is more feasible. By sticking to the surface, the polymeric molecules create a kind of high-volume hydrophobic layer, and this, possibly coupled with some steric blocking of the hydrophilic groups of the coal by the polymeric chains, results in a coal surface less able to interact with water molecules, i.e., more hydrophobic. This, considering that hydrophobic forces are of a longer range than hydration forces [47,48], facilitates the froth flotation process of the

oxidized coal. This mechanism has been proposed based on the results obtained using XPS (Figure 9). This proposed mechanism is also in agreement with the observations obtained in the XRD results, contact angle experiments, and the data of interaction energy obtained via the DFT analyses.

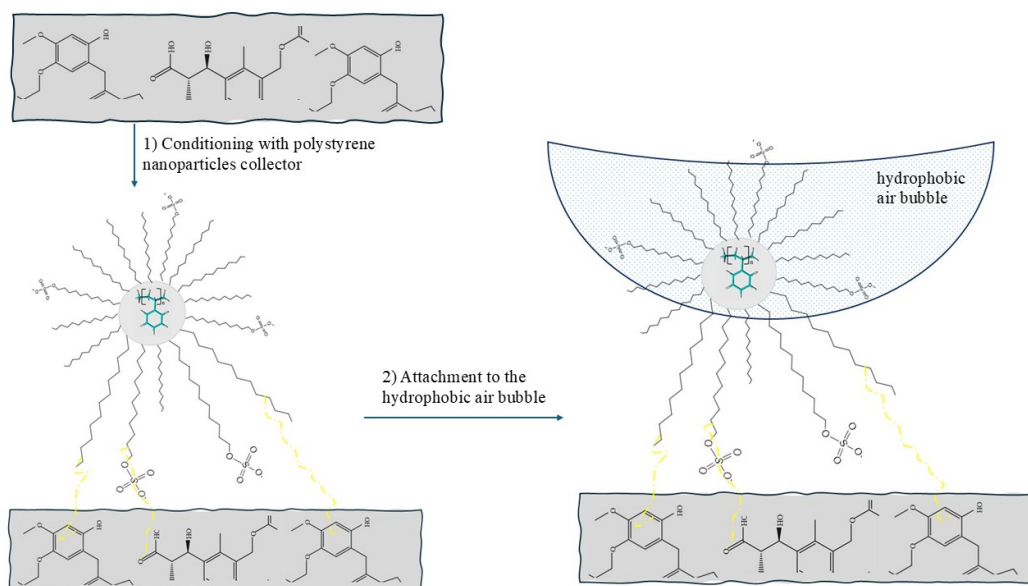


Figure 13. Schematic of the interaction mechanism by which polystyrene nanoparticles increase the hydrophobicity of the oxidized surface of a coal particle.

4. Conclusions

Polystyrene nanoparticles can act as selective collectors for coal flotation in carbonaceous minerals where a high amount of hydrophilic material is present. The results showed that the interaction of the nanoparticles with the oxidized coal surface is via hydrophobic interactions between the non-polar polymeric chain and the hydrophobic organic sections of the surface. Although the presence of sodium dodecyl sulfate induces a certain wettability of the carbonaceous surface, the effect can be considered negligible or insignificant, since the surfactant suffers a great change in concentration during the conditioning step.

One of the principal findings of the flotation study is that the coal yield in the concentrate increases as the collector dosage increases, reaching a recovery of up to 99.5% of carbonaceous material. The coal content in the concentrate is affected by the time–dosage synergy and strongly affected by the flotation time.

Author Contributions: D.M.Á.-M.: investigation and validation; A.B.-F.: conceptualization and writing—original draft; H.P.T.J.: writing—review and editing; M.G.T.: formal analysis and writing—original draft. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available upon request from the corresponding author because the research is still ongoing and being tested in industrial applications.

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Conflicts of Interest: The authors declare no conflicts of interest.

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