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Novel application for Palygorskite clay mineral: A kinetic and thermodynamic assessment of diesel fuel desulfurization

Anne B. F. Câmara[1], Heloise O. M. A. Moura[1], Enrique Rodriguez-Castellón[2], and Luciene S. de Carvalho[1]

[1] Instituto de Química, Universidade Federal do Rio Grande do Norte, Grupo de Pesquisa em Tecnologias Energéticas, 59078-900, Natal, Brasil.

email:luciene.santos@ufrn.br; anne.beatrizfc@gmauil.com

[2] Dpto. de Química Inorgánica, Cristalografía y Mineralogí, Universidad de Málaga, 29071, Spain [1]

Resumo/Abstract (Helvética, tam. 12)

RESUMO - Paligorsquita (Pal), um argilomineral de baixo custo, foi investigado neste estudo como um novo material para dessulfurização adsortiva de diesel comercial. A amostra foi caracterizada por análises de FRX, XPS e DRX. A atividade química da superfície da Pal foi crucial para a adsorção eficiente, devido a interação adsorbato/adsorvente via complexação-π, principalmente com espécies de Fe. Os resultados cinéticos e de equilíbrio de adsorção mostraram alta correlação com o modelo cinético de pseudo-segunda ordem para o adsorvente ($R^2 > 0,99$), sugerindo um processo de quimissorção como etapa determinante. A capacidade máxima de adsorção calculada a partir da isoterma de Langmuir ($R^2 > 0,97$) foi de 6,25 mg.g^{-1} para Pal natural a 318 K. O adsorvente Pal apresentou potencial significativo na adsorção de compostos sulfurados, destacando-se por ser um argilomineral abundante na natureza, ambientalmente amigável e com grande possibilidade de aplicação em processos de adsorção e catálise.

Palavras-chave: Paligorsquita, Dessulfurização adsortiva, complexação- π, Termodinâmica de adsorção, Cinética de adsorção.

ABSTRACT - Palygorskite (Pal) is a low-cost clay mineral material, was investigated in this study as a novel material for adsorptive desulfurization of commercial diesel. This clay mineral was characterized by XRF, XPS and XRD. The specific surface chemistry activity of Pal were crucial to efficient adsorption, proposing that an interaction between adsorbate/adsorbent involves π-complexation mainly with Fe species. The kinetic and equilibrium adsoprtion results showed high correlation to the pseudo-second order kinetic model for the adsorbent ($R^2 > 0.99$), suggesting a chemisorption process as the determining step. Maximum adsorption capacity calculated from the Langmuir isotherm ($R^2 > 0.97$) was 6.25 mg.g^{-1} for raw-Pal at 318 K. The adsorbent Pal displayed good potential in the adsorption of sulfur compounds in real diesel fuel. Palygorskite stands out for being an abundant clay mineral in nature, environmentally safe, and with high possibility of its applications in adsorption and catalysis processes.

Keywords: Palygorskite, Adsorptive desulfurization, π-complexation, Adsorption thermodynamics, Adsorption kinetic.

Introduction

Palygorskite (Pal) is a hydrated magnesium aluminum silicate present in nature with a fibrous morphology which presents a unique structure and specific surface properties such as low surface charge, high porosity, ion-exchange capability, active surface groups and high specific surface area (SSA) (1), thereby conferring important adsorptive and catalytic (2) properties to Pal. Sulfur compounds are the most undesirable and notorious contaminants present in fossil fuels, mainly in petroleum, and a large portion of these compounds are aggregated to diesel oil during the refining process. These compounds are converted to sulfate oxides (SOX) and sulfate particulates in diesel combustion, which are harmful to human health, while the presence of SOX is a key precursor to acid rain (3). Environmental regulations have been introduced in many countries to reduce the sulfur content of diesel to ultra-low levels (10-15 ppm) with the intention to decrease these problems. This paper proposes a study based on possible interactions between organic-sulfur compounds existing in diesel fuel, and different Fe species observed by the XPS spectrum of palygorskite. An investigation of sulfur compounds removal, such as thiophene and its derivatives, was performed using a cheap raw material, which enables reducing industrial costs when associated with the HDS process, which is more expensive. Among the use of this clay mineral for several applications, its use in sulfur adsorption in diesel fuel is a novel approach and has not been reported earlier. This work was performed with kinetic, thermodynamic and equilibrium adsorption studies for studying the applicability of readily-available clay mineral to remove this contaminant which causes industrial and environmental damage.

Experimental

The samples of palygorskite clay mineral were obtained from deposits located in Guadalupe in the state of Piauí/Brazil and provided by the Mineral Technology Center (CETEM/RJ). The sample was characterized by X-ray fluorescence (XRF), X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD). The quantification of sulfur compounds in the samples was carried out using the fluorescence in the ultraviolet region (UVF) spectrometry technique with an Antek Multitek Total Hs Sulfur Analyzer, following the procedure established by ASTM D-5453 Standard.

The S-compound adsorption rate was studied at different time intervals. In the kinetic studies, 8 mL of model diesel (500 mg.g^{-1} of dibenzothiophene diluted in decane) and 0.3 g from the adsorbents were placed into glass vials. The bottles were agitated at 150 rpm and ambient temperature (298 K) using an isothermal bath shaker table SL180/DT (Solab) until reaching the adsorption equilibrium. This step in the experiments was repeated for different time periods. The remaining dibenzothiophene (DBT) concentration in the solutions was measured with UVF, and the adsorption capacity of the adsorbents was calculated by pseudo-first order and pseudo-second order kinetic models.

The adsorption isotherms were obtained in a finite bath system using six points corresponding to concentrations between 25 and 500 mg.g^{-1} in sulfur compounds present in real diesel samples, being carried out in duplicate. The points were prepared from a sample dilution with high sulfur content, denominated diesel S1800 (1764.14 mg.g^{-1}), and with a low sulfur system denominated diesel S10 (3.56mg.g^{-1}). Bottles of 250 mL were used with 0.3 g of palygorskite and 8.0 mL of diluted diesel. The system was left under stirring at 150 rpm on a shaker apparatus for 3 hours. After this step, the solutions were centrifuged for 15 minutes at 1000 rpm. The supernatant liquid was collected and analyzed for remaining sulfur content. The adsorbed sulfur content was obtained by subtracting the total content from the remainder after the process. The adsorption equilibrium was studied with the use of the Langmuir and Freundlich, isotherm models.

The effect of temperature in S-compound adsorption was studied by varying temperature from 298 to 308 and 318 K. The obtained thermodynamic parameters describe the variation or the transformation of a system. The standard free energy (ΔG°), standard enthalpy change (ΔH°) and standard entropy change (ΔS°) were obtained to investigation the adsorption mechanism.

Results and Discussion

Adsorbents characterization

The chemical composition of the palygorskite samples (Table 1) shows that this clay mineral is mainly constituted by MgO, Al_2O_3, Fe_2O_3 and SiO_2.

In addition to the chemical composition obtained by XRF (Table 1), X-ray photoelectron spectroscopy (XPS) was a very important technique to provide information about the surface chemical composition and the species identifications of the adsorbents. The binding energies measured by XPS are depicted in Fig. 1a. The XPS of raw-Pal indicated the presence of O, Si, Mg, Fe and Al elements and their valence state. Iron (Fe) species stands out from other metals in this clay mineral for desulfurization since the Fe^{3+} ions and the thiophenic aromatic rings could generate a strong interaction denominated π-complexation. The Fe XPS deconvolution (Fig. 1b) shows the presence of Fe(0), Fe(III) and FeOOH in 709.1 eV, 712.4 eV and 715 eV, respectively. The FeOOH peak is referent to the binding between Fe^{2+} ions and the OH- present in silanol groups in the adsorbent structure. Furthermore, the estimated composition of Pal surface obtained by XPS is depicted in Table 2, presenting the same elements observed by XRF.

Table 1. Chemical composition of Pal.

Composition (%)	Pal
SiO_2	58.99
Al_2O_3	15.70
Fe_2O_3	12.45
MgO	4.70
K_2O	2.10
TiO_2	1.18
Others	1.24

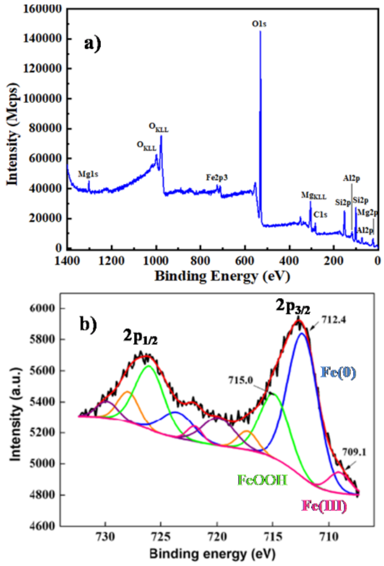

Figura 1. XPS data for Pal clay mineral.

The X-ray diffraction pattern from Pal is depicted in Fig. 2. Crystallographic cards provided by the Inorganic Crystal Structure Database (ICSD) were used to identify the phases present in this material. The Pal diffractogram shows reflections that are typically indexed for palygorskite and quartz, which is consistent with the crystallographic cards Nos. 01-082-1873 and 01-085-0794, respectively (Fig. 2).

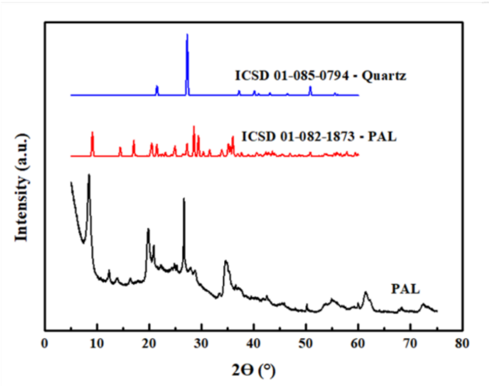

Figura 2. XRD data for Pal clay mineral.

Table 2. Surface composition of Pal obtained by XPS.

Composition (atomic percent)	Pal
C1s	9.03
O1s	61.92
Mg2p	4.01
Al2p	4.73
Si2p	18.67
Fe2P3	1.64

Adsorption kinetics

Pseudo-first order and pseudo-second order, kinetic models were used in this study to test the experimental data in order to evaluate the controlling mechanism of the sorption process. These models can be expressed in a linear form, respectively, as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (1)$$

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \qquad (2)$$

where q_e and q_t are the amounts of sulfur compounds adsorbed (mg g^{-1}) on the adsorbent at equilibrium and at time *t*, respectively, and k_1 is the rate constant of adsorption (L min^{-1}) and k_2 is the pseudo-second order rate constant (g mg^{-1} min^{-1}).

According to the results depicted in Table 3, the experimental data were better adjusted to the pseudo-second order for the adsorbent, since the determination coefficient for these models was near 1 (R^2 = 0.99). In addition, the differences between experimental and calculated q_e values were lower than those obtained from other models (4). The good fit to this kinetic equation indicated that the rate determining step is chemisorption, involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate.

Table 3. Parameters for the fitting to pseudo-first order and pseudo-second order, of model diesel adsorption on Pal.

Parameters	Pal
$q_{max\ exp}$	1.94
Pseudo-first order model:	
q_e(mg g^{-1})	0.56
k_1	0.16
R^2	0.87
Pseudo-second order model:	
q_e(mg g^{-1})	1.95
k_2	0.12
H	0.02
R^2	0.99

Adsorption equilibrium

The Langmuir and Freundlich, equations were used to fit the adsorption experimental results and provide insights on the adsorption mechanism, specific surface properties and adsorbent affinity through the equation parameters. The S-compound adsorptions are more fitted to Langmuir, which suggests a monolayer adsorption onto the adsorbent's surface with a finite number of adsorption sites, assuming there is no transference of the adsorbate onto the surface plane and that uniform energies exist on the surface. The Langmuir monolayer adsorption capacity (Qm) increased from 1.63 to 6.25 mg.g^{-1} as temperature increased from 198 K to 318 K, indicating that the adsorption is endothermic. The better adjustments to this mathematical model suggest a chemisorption process proving what was shown by kinetic models. The Freundlich isotherm models indicate a favorable adsorption process in heterogeneous systems or multilayer adsorption and presents a fit to Pal, with R^2>0.915. The values in the range of n< 1 highlight that the adsorption of S-compounds was a chemical process and indicated the favorability of this adsorption (3). Pal is fitted to kinetic and equilibrium models, which indicates that this material presents a chemisorption process at 298 K. This could happen because of the presence of some metals in the clay mineral structure, suggesting a strong interaction (of the π-complexation type) between the Fe species and the aromatic rings of sulfur compounds in diesel.

Adsorption thermodynamics

Pal thermodynamic assessment in the temperature range of 198 to 318 K is shown in Table 4. The positive value for ΔH° indicates an endothermic process, with a combined chemical and physical process. This is related to the fact that chemisorption process involves a surface reaction, with the rupture and creation of chemical bonds, while physical adsorption involves a surface condensation of the adsorbate. The positive value for ΔS° and ΔG° indicated that a random increase in the solid/solution interface system occurs during the adsorption process. This happens since the unadsorbed molecules become more disordered due to the extra space to move about after a fraction of them was adsorbed, thus increasing the systems' entropy. Furthermore, a positive value of ΔS° suggests that the adsorption process involves a dissociative mechanism, reflecting the affinity of the adsorbent to the adsorbate (5). The decreasing ΔG° values show adsorption being favored at higher temperature. These data suggest that this adsorption process is between the physisorption and chemisorption process, with a dominance of the chemical process.

Table 4. Thermodynamics parameters for the sulfur compounds adsorption on Pal surface.

T (K)	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J K^{-1} mol^{-1})
298	6.02	44.73	42.35
308	4.00		47.52
318	1.84		52.843

Proposed adsorption mechanism

S-compound adsorption onto the Pal surface was evaluated to determine the adsorption mechanism between the adsorbent-adsorbate interactions. Fig. 3 shows several coordination configurations that could be formed between S-compounds and Pal structure Active sites such as Lewis acids, electronic defect centers and van der Waals interactions can participate in the adsorptive process (3). In addition, the presence of Fe species in the clay mineral structure could form a bond with the aromatic rings of DBT. This result indicated that the interaction between adsorbate/adsorbent involves π-complexation. Furthermore, equilibrium studies have shown that S-compounds followed the Langmuir isotherm, indicating a monolayer adsorption onto the adsorbent's surface with a finite number of adsorption sites. Adsorption kinetics followed a pseudo-second order model involving the formation of valence forces through sharing or exchanging electrons between adsorbent and adsorbate. Thermodynamic parameters showed that adsorption is favored at higher temperatures and suggested a combination between physisorption and chemisorption processes. Based on this, the proposed adsorption mechanism in this study suggests the occurrence of combination processes (chemical and physical process), with the domination of chemisorption involving the formation of strong chemical bonds based on π-complexation of S-compounds onto the Pal surface.

Conclusions

Palygorskite appears in this work as a promising adsorbent in diesel fuel desulfurization due to its specific characteristics such as the chemical composition and textural properties, which was proven by different characterizations. The adsorption data was fitted to the pseudo-second order kinetic and the Langmuir isotherm model, describing that the adsorption of S-compounds in diesel fuel onto the adsorbent layer is determined by a chemisorption process. Pal is a low-cost material that exhibited some advantages, since it is environmentally friendly and abundant in nature.

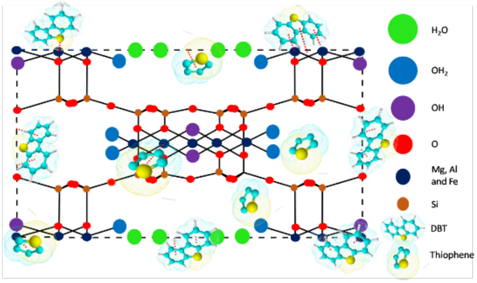

Fig. 3. Proposed mechanism for S-compounds adsorption onto Pal surface.

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