UNIVERSIDADE FEDERAL DE MINAS GERAIS
Escola de Engenharia

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Pós-Graduação em Engenharia Metalúrgica e de Minas

Tese de Doutorado

“MATERIAIS HÍBRIDOS NANOESTRUTURADOS SINTETIZADOS A PARTIR DA FUNCIONALIZAÇÃO DE ESMECTITAS PARA IMOBILIZAÇÃO DE ESPÉCIES INORGÂNICAS E ORGÂNICAS”

Autora: Angela de Mello Ferreira Guimarães
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Tese de Doutorado apresentada ao Curso de Pós-Graduação em Engenharia Metalúrgica e de Minas da Universidade Federal de Minas Gerais

Área de concentração: Ciência e Engenharia de Materiais
Orientador:Prof. Wander Luiz Vasconcelos
Co-orientadora: Profª Virgínia Sampaio Teixeira Ciminelli

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“O que quer que você seja capaz de fazer, ou imagina ser capaz, comece. Ousadia contém gênio, poder e magia.”

Goethe

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e ao meu filho Alexandre

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Dedico este trabalho ao meu filho, Alexandre
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RESUMO

Este trabalho teve como objetivo a síntese de materiais híbridos nanoestruturados a partir da funcionalização de argilas smectitas com os grupos funcionais sulfidrila (SH) e amino (NH_2) para aplicação em processos de adsorção. Foram utilizadas amostras de montmorilonita e de argila sintética, denominada laponita. Dentre as amostras de montmorilonita, foi utilizada uma *in natura* da região de Campina Grande, PB e outra americana comercial (cloisite-Na). As rotas de modificação propostas basearam-se na reação química entre as hidroxilas superficiais das argilas e os grupos hidrolisáveis dos silanos (3-mercaptopropil)trimetoxissilano e (3-aminopropil)trietoxissilano na presença de tolueno ou solução alcoólica sob refluxo. O presente trabalho demonstrou que as rotas de modificação propostas foram eficientes para imobilizar as moléculas de silano na estrutura das argilas, sendo que o grau de funcionalização variou com o tipo da argila, pré-tratamento ácido, o tipo de agente modificador e o tipo de solvente utilizado. Os resultados de caracterização indicaram que a estrutura original da argila não foi alterada após funcionalização. A funcionalização modificou a natureza da argila de altamente hidrofílica para hidrofóbica e organofílica. A quantidade de grupos mercaptopropil imobilizados foi de 1,76 mmol/g, 1,45 mmol/g e 1,2 mmol/g para as amostras de montmorilonita brasileira, Cloisite e Laponita, respectivamente. Para o grupo aminopropil, foram determinados valores de 2,0 mmol/g (Cloisite) e 1,5 mmol/g (Laponita). Tanto a área superficial quanto o volume de poros foram significativamente reduzidos após a funcionalização. O acesso aos grupos funcionais imobilizados (SH) foi convenientemente determinado através do método de Volhard, sendo que valores na faixa de 60% - 75% foram obtidos para as amostras de montmorilonita e de 100% para a amostra de laponita. Valores de acessibildade similares a estes foram obtidos para os grupos NH_2 imobilizados. As amostras de montmorilonita funcionalizadas com SH apresentaram capacidade de adsorção média para os Cd(II) e de Ag(I) superior comparada à argila natural (160% e 1100% maiores). Este resultado sugere que para as argilas funcionalizadas predominou o mecanismo de complexação dos íons metálicos pelos grupos SH (adsorção específica), enquanto que para a argila natural predomina o mecanismo de troca catiônica (inespecífico). Os ensaios de adsorção demontraram uma maior afinidade da argila laponita modificada com grupos SH pela espécie As(III) do que As(V). A maior adsorção (22,3 mg/g) e melhor seletividade foram obtidas em condições de pH em que predomina a espécie trivalente neutra (H_3AsO_3). O processo de modificação proposto permitiu a obtenção de material adsorvente com seletividade e especificidade controlada através da escolha adequada do grupo funcional do silano e com grande potencial para ser aplicado em processos de separação e pré-concentração.

ABSTRACT

The present work was aimed at synthesizing nanostructured hybrid materials derived from the functionalization of smectite clays with ligands containing thiol (-SH) and amino (-NH_2) groups for application in adsorption processes. Two montmorillonite samples (a commercial American clay-Cloisite-Na and an *in nature* Brazilian clay from Campina Grande, PB) and one synthetic, commercial clay (Laponite) were investigated. The modification routes were based on the grafting reaction between hydroxyl groups present on clay surface and the hydrolyzable alkoxy group of the (3-mercaptopropyl)trimethoxysilane or (3-aminopropyl) triethoxysilane in dry toluene or alcohol solution under reflux. The present work showed that the proposed modification routes were effective for the grafting of the thiol and amino groups in the clay structure. The functionalization degree varied according to the clay sample, acid pre-treatment, modifier type and dispersing media. A detailed characterization of the materials indicated that the functionalization does not modify the original structure of the clays but altered their original hydrophilic nature to hydrophobic**.** The smectite clays showed an immobilization capacity comparable to those reported for silica gel. The immobilization capacities of the mercaptopropyl groups were calculated as 1.76 mmol/g, 1.45 mmol/g and 1.2 mmol/g for the Brazilian clay, Cloisite and Laponite, respectively. With aminopropyl, the immobilization capacities were determined as 2.0 mmol/g and 1.5 mmol/g for the Cloisite and Laponite samples, respectively. The specific surface areas and pore volumes of all clay samples decreased significantly upon grafting. The accessibility to the reactive SH groups was successfully determined by using the Volhard method. It ranged from 60% to 75%, depending on the organic content, for the SH-montmorillonite samples and to 100% for the SH-laponite sample. Similar values of accessibility were observed with the amino-modified clays. The thiol-functionalized montmorillonite samples showed average binding capacities 160% and 1100% higher, respectively, with respect to Cd(II) and Ag(I) to those obtained with the ungrafted material. These results support a mechanism of adsorption involving primarily ion complexation by the thiol groups (specific) instead of cation exchange (unspecific). Adsorption experiments have demonstrated the selectivity of a thiol-modified synthetic clay by As(III) species. The highest loading capacity (22.3 mg/g) and speciation has occurred at pH 4-5, where the trivalent species are present in its neutral form (H_3AsO_3). The proposed modification processes are suggested for the preparation of novel adsorbent materials with controlled selectivity and specificity and therefore with good potential for separation and pre-concentration purposes.

CAPÍTULO 1

INTRODUÇÃO E OBJETIVOS DA TESE

1.1 Argilas e argilominerais

As argilas de uma maneira geral são definidas como materiais de ocorrência natural, de textura terrosa e granulação fina que apresentam plasticidade variável quando misturadas com água. Para o mineralogista, argila designa um mineral ou mistura de minerais em que predominam os chamados argilominerais que são silicatos hidroxilados hidratados de alumínio e ou magnésio. Os argilominerais são constituídos por partículas de tamanho médio inferior a 2 µm e de estrutura cristalina lamelar ou fibrosa. Originaram-se da ação do intemperismo e de ações hidrotermais sobre rochas ígneas ou metamórficas que eram fases estáveis sob condições redutoras, de altas pressões e altas temperaturas nas regiões mais profundas da crosta terrestre. As argilas ainda podem conter outros materiais e minerais, tais como matéria orgânica, sais solúveis, partículas de quartzo, calcita, feldspato, dolomita e outros minerais residuais cristalinos ou amorfos (Olphen, 1977; Santos, 1989).

A estrutura cristalina dos argilominerais é, em geral, constituída por camadas tetraédricas de silício e octaédricas de alumínio. Diferentes elementos, além do silício e alumínio podem ocupar os sítios tetraédricos e octaédricos dando origem a um grande número de diferentes argilominerais. Os vértices dos grupos tetraédricos e octaédricos são compostos por átomos ou íons oxigênio e por hidroxila, que estão ao redor de pequenos cátions. Estes são principalmente Si^{4+} e Al^{3+}, ocasionalmente Fe^{3+} e Fe^{2+}, nos grupos tetraédricos e Al^{3+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, Ti^{4+}, ocasionalmente Cr^{3+}, Mn^{2+}, Zn^{2+}, Li^{+}, nos grupos octaédricos, geralmente com um certo grau de substituição isomórfica. Essas substituições isomórficas são responsáveis pelo excesso de carga elétrica negativa na superfície das camadas. Todas as posições da camada octaédrica podem ser preenchidas (formas trioctaédricas) ou somente dois terços delas podem estar preenchidas (formas dioctaédricas). Os grupos do mesmo tipo estão unidos entre si hexagonalmente formando planos de tetraedros e octaedros conforme está mostrado na Figura 1.1 (Mitchell, 1976; Kingery, 1976).

1.1.1 Classificação dos argilominerais

Os argilominerais lamelares são denominados de filossilicatos (do grego *phyllos* significa folha). Estas lamelas podem ser formadas pela combinação de uma lâmina tetraédrica e uma octaédrica (1:1) ou pela combinação de duas lâminas tetraédricas e uma octaédrica (2:1). A Figura 1.2 mostra as estruturas de argilominerais pertencentes às famílias 1:1 e 2:1.

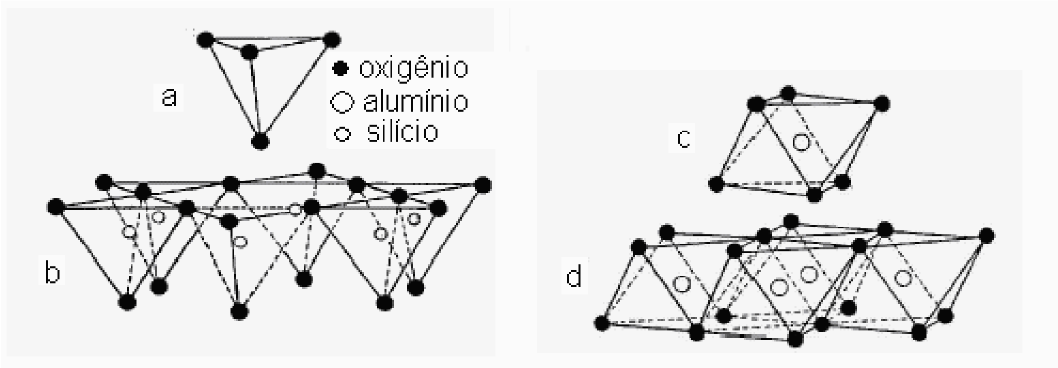
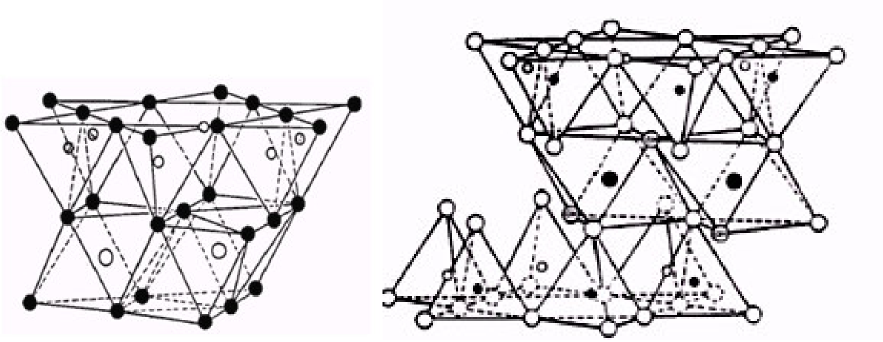


Figura 1.1 - Unidades estruturais dos argilominerais: a: grupo tetraédrico; b: lâmina tetraédrica; c: grupo octaédrico; d: lâmina octaédrica (Kingery, 1976, Mitchell, 1976).



(a) (b)

Figura 1.2 - Modelo esquemático da camada estrutural básica de uma argila: (a)1:1 e (b) 2:1 (Grim, 1953).

A estrutura lamelar apresenta-se como unidades sobrepostas com periodicidade definida e estruturadas normalmente por ligações covalentes, ligações de hidrogênio, e com diversas morfologias características dependendo da sua gênese. As ligações das camadas entre si são mais fracas. Essas ligações fracas são responsáveis pela fácil clivagem paralela aos planos basais, de onde resulta a morfologia da maioria das partículas dos argilominerais. A Figura 1.3 mostra a morfologia de uma argila lamelar do grupo das esmectita obtida por microscopia eletrônica de varredura (MEV). Além do MEV, técnicas como difração de raios X, análise térmica diferencial e gravimétrica, microscopia eletrônica de transmissão e de varredura, análise química e ressonância magnética nuclear do estado sólido permitem a identificação e classificação dos diversos argilominerais.

Atualmente, os argilominerais são agrupados em oito grupos sistemáticos, apresentados na Tabela 1.1. As espécies do grupo da caulinita e da esmectita são as mais abundantes. A estrutura lamelar é apresentada pela maioria dos argilominerais e as subdivisões são feitas em função de suas propriedades estruturais tais como: o tipo de empacotamento (1:1 ou 2:1), a carga da célula unitária, o tipo de cátions interlamelares, distância interplanar basal na forma anidra e hidratada, grau de substituição na camada octaédrica, possibilidade das camadas basais se expandirem pela introdução de moléculas polares e tipo de arranjo cristalográfico ao longo dos eixos.

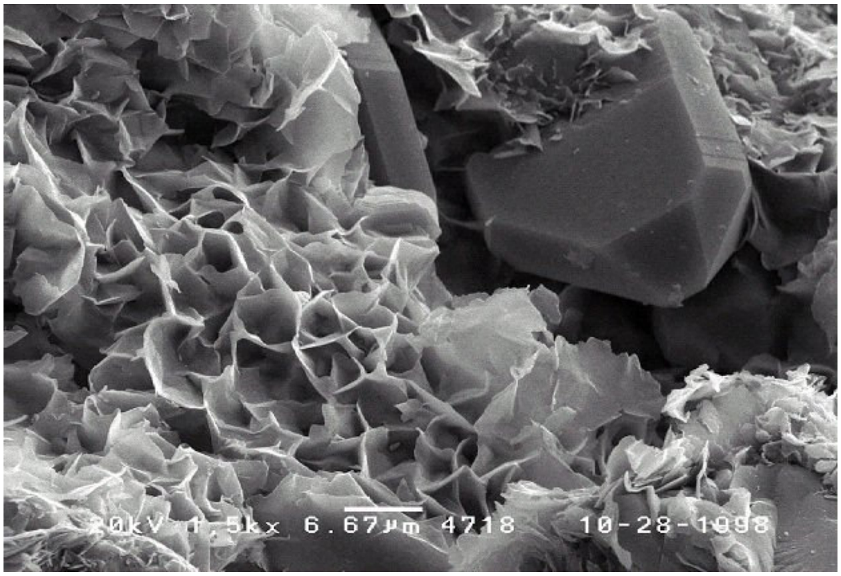


Figura 1.3 - Fotomicrografia de uma argila esmectita obtida por microscopia eletrônica de varredura mostrando sua morfologia (hppt:/www.webmineral.com).

Tabela I.1: Classificação geral dos argilominerais
(Bailey *et al.*,1971, citado por Santos (1989)

Classe Geral	Família	Grupo	Camada octaédrica	Argilomineral
Estrutura Lamelar	Difórmicos 1:1	Caulinita	Dioctaédrica	Nacrita , Caulinita Haloisita
		Serpentina	Trioctaédrica	Antigorita, Crisotila Amesita, Cronstedita
	Trifórmicos 2:1	Esmectita	Dioctaédrica	Beidelita, Nontronita **Montmorilonita**
			Trioctaédrica	Saponita, Hectorita
		Vermiculita	Dioctaédrica Trioctaédrica	Vermiculita Vermiculita
		Mica	Dioctaédrica	Muscovita-Ilita, Flogopita
			Trioctaédrica	Biotita-Lediquita Lepidolita
		Talco-Pirofilita	Dioctaédrica Trioctaédrica	Pirofilita Talco
		Clorita	Dioctaédrica Trioctaédrica	Dombassita, Clinocloro, Chamosita
Estrutura Fibrosa	2:1	Paligorsquita Sepiolita	Trioctaédrica Trioctaédrica	Paligorsquita Sepiolita

1.1.2 Grupo das esmectitas

O grupo das esmectitas pertence à família 2:1 e compreende os minerais argilosos: montmorilonita, nontronita, beidelita, saponita, hectorita e sauconita. A Tabela I.2 apresenta alguns exemplos de fórmulas estruturais ideais de alguns filossilicatos de arranjo 2:1. Os colchetes representam sítios octaédricos, os parênteses representam os sítios tetraédricos e as chaves denotam cátions interlamelares (normalmente, K^+, Ca^{2+}, Na^+) e suas águas de hidratação.

A Figura 1.4 mostra a estrutura típica de uma esmectita, aqui representada por uma montmorilonita que possui 20 átomos de oxigênio e 4 grupos OH por célula unitária, contendo ainda 8 sítios tetraédricos e 6 sítios octaédricos. A distribuição de carga teórica, sem substituição isomórfica, da célula unitária deste argilomineral é mostrado na Tabela I.3. Através desta figura, observa-se as duas lâminas tetraédricas e uma lâmina central octaédrica, unidas entre si por átomos de oxigênio comuns às dua folhas, formando uma camada 2:1. As lâminas crescem na direção **a** e **b**, e são empilhadas ao longo de **c.** Neste caso, íons de cálcio e sódio representam os cátions interlamelares compensadores de carga (Grim, 1953).

As esmectitas são capazes de acomodar moléculas de água ou outras moléculas polares na região interlamelar causando variação do espaçamento basal desde valor mínimo de 0,96nm, correspondendo à argila seca, até 1,8 nm, quando moléculas de água e poliálcoois, por exemplo, são adsorvidas.

Tabela I.2: Fórmulas estruturais ideais de alguns filossilicatos (Santos, 1989).

Arranjo das camadas/grupo	Argilomineral
2:1 Esmectita	Hectorita $\{M_{x/n}^{+n}\ yH_2O\}[Mg_{6-x}Li_x](Si_8)O_{20}(OH,F)_4$ Montmorilonita $\{M_{x/n}^{+n}\ yH_2O\}[Al_{4-x}Mg_x](Si_8)O_{20}(OH)_4$ Nontronita $\{M_{x/n}^{+n}\ yH_2O\}[Fe_4](Si_{8-x}Al_x)O_{20}(OH)_4$

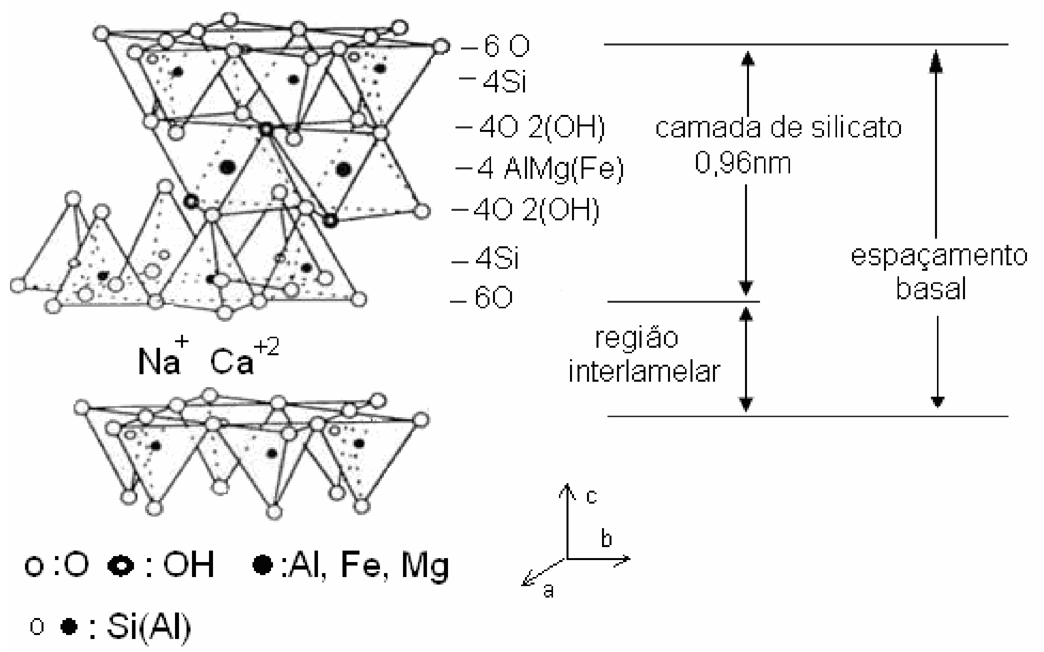


Figura 1.4 - Estrutura da montmorilonita (célula unitária) (Grim, 1953, Mitchell, 1976).

Tabela I.3: Distribuição de cargas da montmorilonita (célula unitária), sem substituição isomórfica (Grim, 1953)

Espécie	Carga	Localização
6 O^{2-}	-12	folha tetraédrica
$4Si^{4+}$	+16	
4 O^{2-} + $2OH^-$	-10	Íons comuns a ambas folhas
$4Al^{3+}$	+12	folha octaédrica
4 O^{2-} + $2OH^-$	-10	Íons comuns a ambas folhas
$4Si^{4+}$	+16	folha tetraédrica
6 O^{2-}	-12	

Os argilominerais deste grupo exibem extensas substituições isomórficas tanto nas folhas tetraédricas quanto nas octaédricas. Grande parte destas substituições ocorrem com cátions de mesma valência não originando cargas negativas superficiais. As substituições pelos cátions de menor valência originam o aparecimento de cargas, notadamente as substituições tetraédricas do Si^{4+} por Al^{3+} e as substituições octaédricas de Al^{3+} e Fe^{3+} por Mg^{2+} e Fe^{2+}. Estas substituições resultam em uma carga superficial média de 0,2 a 0,6 por unidade $O_{10}(OH)_2$. Em função destas substituições é que surge uma variedade de argilominerais pertencentes à família das esmectitas, conforme mostrado na Tabela I.1. Devido à substituição isomórfica em porcentagem moderada de silício por alumínio nas posições tetraédricas surge a beidelita, a substituição octaédrica pode ser de magnésio (montmorilonita), ferro (nontronita), lítio (hectorita) e outros, isoladamente ou em combinação (Mitchell, 1976; Santos, 1989).

1.1.3 Capacidade de troca catiônica e área superficial específica

A capacidade de troca catiônica (CTC) da argila é a quantidade de íons, particularmente cátions, que esta pode adsorver e trocar (Brindley, 1984). É uma das propriedades mais importantes, que resulta do desequilíbrio das cargas elétricas na estrutura cristalina devido às substituições isomórficas e às ligações químicas quebradas nas arestas das partículas. Para neutralizar estas cargas, existem cátions trocáveis, que estão fixos eletrostaticamente ao longo das faces e entre as camadas estruturais. Nas bentonitas as cargas são neutralizadas pelos cátions Na^{+},' Ca^{2+} e Mg^{2+}, acompanhados de suas águas de hidratação. A afinidade dos materiais trocadores de íons está relacionada com a carga e o tamanho dos íons em solução. O poder de troca de um cátion será maior, quanto maior for a sua valência e menor a sua hidratação. A força com que um íon é atraído é proporcional à sua carga iônica (Grim, 1953; Santos,1989).

Vários métodos de medidas da CTC têm sido descritos na literatura, cada qual utilizando diferentes procedimentos (Kahr *et al.*, 1995; Auboiroux e*t al.*, 1996; Bergaya *et al.*, 1997; Ruiz *et al.,* 1997). Entretanto, um método muito utilizado para a determinação da CTC de aluminossilicatos envolve a saturação do material com o íon amônio através do tratamento da argila em solução de acetato de amônio em pH 7 e posterior análise quantitativa dos íons (Na^{+}, Ca^{2+}, K^{+} , Fe^{2+} e Fe^{3+}) deslocados (Lange *et al*. 1973; Embrapa, 1997).

As esmectitas, por exibirem extensas substituições isomórficas tanto nas folhas tetraédricas quanto nas folhas octaédricas, possuem elevada capacidade de troca catiônica. A Tabela I.4 mostra valores de capacidade de troca catiônica (CTC) de alguns aluminossilicatos determinada pelo método direto de saturação com cátion amônio (Santos, 1989).

A matéria orgânica que normalmente está presente nas argilas também possui capacidade de troca catiônica (Bergaya *et al.,*1997).

A elevada área superficial dos argilominerais se deve ao pequeno tamanho de partícula e a presença de poros. A Tabela I.4 também apresenta os valores da área superficial específica de alguns argilominerais. Como pode ser observado, a montmorilonita é um argilomineral que apresenta elevada área superficial e elevada capacidade de troca catiônica e por isso é um dos minerais mais estudados e utilizados em diversas áreas. Segundo um estudo realizado por Pinnavaia *et al.* (1984) a distribuição de poros das argilas pode ser bastante afetada pela forma como o material é seco e desidratado. Eles observaram que a secagem por liofilização ("freeze drying") resulta em uma estrutura menos ordenada com micro e macroporos (Figura1.5(a)), enquanto que a secagem ao ar ou em estufa propicia a formação de agregados mais ordenados, com empilhamento organizado "cara a cara", com menor tamanho de poros (Figura 1.5(b)).

Tabela I.4: Capacidade de troca catiônica (Santos, 1989)[a]

mineral	CTC (meq/ 100g da argila)	Área superficial específica (m^2g^{-1})
caulinita	3-15	15 -50
haloisita $4H_2O$	10-40	60
ilita	10-40	50 -100
montmorilonita	80-150	75 -150
vermiculita	100-150	100 - 150

1.1.4 A bentonita

A bentonita é uma rocha que contém algum ou vários argilominerais do grupo da esmectita, com a montmorilonita como argilomineral predominante. Considera-se como bentonita as argilas formadas a partir de rochas ou cinza vulcânicas que sofreram transformações por milhões de anos gerando partículas cristalinas menores que 2 μm. O nome bentonita tem sua origem na descoberta de uma grande reserva desta argila, em 1898, no Fort Benton, em Wyoming (EUA), onde foi pela primeira vez caracterizada como um tipo especial de argila. A bentonita de Wyoming é naturalmente sódica e de grande emprego industrial. O principal argilomineral das bentonitas, a montmorilonita tem este nome devido à sua descoberta em Montmorillon, no sul da França (Santos, 1989).

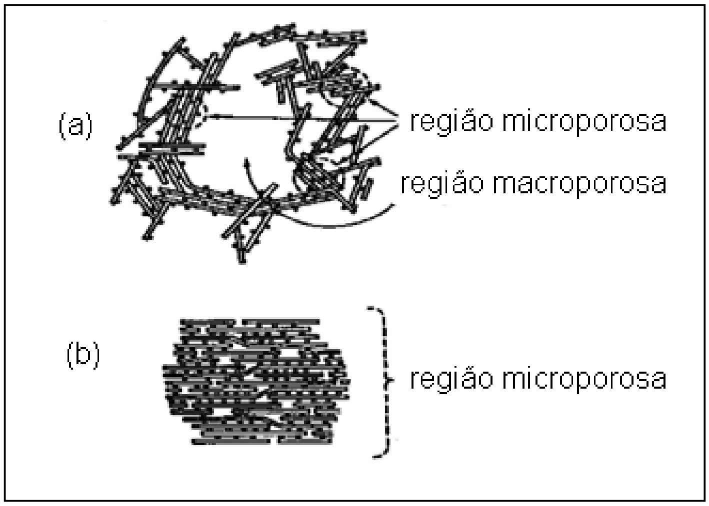


Figura 1.5 - Tipos de arranjo das lamelas dos filossilicatos. (a) argila seca por liofilização; (b) argila seca ao ar ou estufa (Pinnavaia *et al.*, 1984).

A bentonita pode ser cálcica ou sódica e pode ter seu volume aumentado de até 20 (vinte) vezes em relação ao volume da argila seca quando em contato com a água, gerando uma substância gelatinosa e muito viscosa. A bentonita sódica apresenta expansão mais notável. A capacidade de hidratação dessa argila é muito superior a de outras argilas por causa natureza dos cátions interlamelares e das ligações químicas interrompidas nas bordas dos cristais. (Luz e Oliveira, 2005).

No Brasil, as reservas medidas de bentonita, conhecidas até 2004, totalizaram cerca de 47 milhões de toneladas, segundo o Departamento Nacional de Produção Mineral do Ministério das Minas e Energia. No Estado da Paraíba, municípios de Boa Vista e Cubati, estão concentradas 28% das reservas nacionais. São Paulo, nos municípios de Taubaté e Tremembé, responde por cerca de 25%, o estado do Paraná com 37 % e o Espírito Santo com 10%. Estimativas feitas, ainda no início da década de noventa, pelo Bureau of Mines dos Estados Unidos, avaliaram em cerca de 1,36 bilhão de toneladas as reservas de bentonita no mundo, com os EUA participando com mais da metade deste total, a ex-URSS com aproximadamente 17% e o restante distribuído na América Latina e Europa (Trindade, 2001).

A bentonita da Paraíba é policatiônica com predominância do cálcio e é ativada com carbonato de sódio para ser utilizada industrialmente. Na forma sódica, esta argila forma gel coloidal estável e quimicamente ativo, permitindo uma utilização muito diversificada. Existem alguns trabalhos de pesquisa com foco na geologia e na avaliação do potencial tecnológico desta argila (Rodrigues, 2003; Folleto *et al.,* 2001; Valenzuela Diaz e Santos, 2001; José *et al.,* 2002). Alguns estudos apontam para uma porcentagem entre 55%-70% de argilominerais esmectíticos policatiônicos, os quais puderam ser facilmente tranformados em esmectitas sódicas através do tratamento adequado com carbonato de sódio. As propriedades dessa argila na forma sódica foram comparáveis à bentonita naturalmente sódica norte-americana (Volclay) para uso em fundição, pelotização de minério, descoramento de óleos e perfuração de poços (Hanna, 2003).

Em função de suas propriedades físicas e químicas peculiares, esta argila possui hoje diversas aplicações dentre as quais pode-se destacar os usos como aglomerante na preparação dos moldes de areia para fundição, na pelotização de minério; como plastificante em argamassas, na impermeabilização de aterros, como fluido tixotrópico para perfuração de poços e grânulos higiênicos para animais domésticos ("pet litter") (Luz e Oliveira, 2005).

1.1.5 Bentonita como adsorvente natural

Vários estudos vêem sendo feito no sentido de se avaliar o potencial da bentonita como adsorvente natural para íons de metálicos e também para compostos orgânicos. A montmorilonita, assim como as esmectitas em geral, possui dois tipos de sítios ligantes nas partículas. O primeiro se refere às cargas fixas ou permanentes que são originadas pela substituição isomórfica dos íons trivalentes (Al^{3+} e Fe^{3+}) da camada octaédrica pelos íons divalentes (Fe^{2+}, Mg^{2+}). Estes sítios ligantes formados pelas cargas negativas superficial são dominantes neste tipo de argila e são menos sensíveis ao pH do meio. A adsorção por troca catiônica é o mecanismo predominante nas argilas esmectitas naturais devido à sua alta densidade de carga negativa superficial. O segundo tipo é constituído pelos grupos silanol (Si-OH) e aluminol (Al-OH) presentes nas bordas e também na superfície dos cristais (Lu *et al.*, 2001). Em pH básico, parte dos grupos silanol e aluminol podem ser desprotonados para ($Si\text{-}O^-$) e ($Al\text{-}O^-$). Desta maneira, os sítios formados pelos grupos (Si-OH), (Al-OH), ($Si\text{-}O^-$) e ($Al\text{-}O^-$) podem coexistir na superfície das partículas de argila e promover a complexação de íons metálicos e moléculas orgânicas. Em pH ácido ocorre a protonação destes grupos formando a espécie $AlOH_2^+$, gerando cargas positivas nas bordas dos cristais. Desta forma, a variação do pH do meio exerce grande influência no comportamento de uma suspensão de argila e também na sua capacidade de adsorção de determinadas espécies (Santos, 1989). Historicamente, sabe-se que a adsorção em argilas esmectitas ocorre, predominantemente, pelo mecanismo de troca catiônica, que se dá pela formação de complexo tipo "esfera externa", facilmente reversível. No entanto, estudos têm mostrado que a adsorção pela complexação dos cátions metálicos através dos grupos OH nas bordas dos cristais ("esfera interna") pode ser bastante significativo dependendo das condições do sistema (Strawn *et al.*,1999).

Muitos pesquisadores têm estudado a viabilidade do emprego das bentonitas no tratamento de efluentes devido a sua propriedade de troca catiônica. Vários trabalhos envolvendo o uso de bentonita como adsorvente para metais (chumbo, zinco, cádmio, cobre e mercúrio) podem ser encontrados na literatura (Brigatti *et al.*, 2004; Abollino *et al*, 2003; Aguiar and Novaes, 2002; Santos et al., 2002; Cerqueira e Aguiar, 2000; Auboiroux *et al.*, 1996; Brigatti *et al.*, 1995; Viraghavan e Kapoor, 1994). Trabalhos envolvendo a adsorção de poluentes orgânicos como fenol (Banat *et al.*, 2000) e pesticidas (Bojemueller, 2001) são menos numerosos. Esses estudos mostraram que, no seu estado natural, a bentonita apresenta baixa capacidade de acumulação para alguns íons metálicos e também baixa seletividade.

A partir dos últimos anos, no entanto, estudos mais aprofundados das propriedades das bentonitas modificadas vêm despertando interesses crescentes para sua utilização como materiais sorventes alternativos. Estudos mais recentes têm mostrado que a capacidade de acumulação das bentonitas pode ser melhorada através da sua modificação via intercalação de compostos orgânicos ou inorgânicos específicos tornando-as materiais mais seletivos e com boa capacidade de acumulação (Volzone, 2004; De Leon, 2001).

1.1.6 Modificação estrutural de argilominerais 2:1

Dentre os argilominerais de estrutura 2:1, as esmectitas apresentam um conjunto de características estruturais que as tornam atraentes para o desenvolvimento de catalisadores e material adsorvente tais como área superficial elevada, capacidade de troca catiônica, baixo custo e abundância na natureza. Dentre as esmectitas, a montmorilonita é um dos argilominerais mais pesquisados para obtenção de materiais híbridos devido à facilidade de intercalação e sua natureza expansível. Além disso, a montmorilonita possui sítios ativos devido à presença das hidroxilas estruturais (ácido de Lewis e Brönsted) e cátions interlamelares facilmente trocáveis (Herrera, *et al.*, 2006). Outros filossilicatos, como a caulinita, devido às ligações de hidrogênio entre as suas lamelas típicas dos filossilicatos do tipo 1:1, são pouco expansíveis e são capazes de intercalar diretamente um número limitado de pequenas moléculas como formamida, hidrazina e dimetilsulfóxido (DMSO) (Frost e Kristof, 2004; Gonçalves, 2002). O termo intercalação refere-se à inserção reversível de íons, de sais e de moléculas neutras, orgânicas ou inorgânicas em compostos com estrutura lamelar aumentando do espaçamento interlamelar com a manutenção da estrutura dos mesmos (Santos, 1992). A inserção de moléculas no interior das lamelas através da intercalação permite manipular a reatividade desses materiais para diferentes aplicações.

As formas mais comuns de modificar argilominerais são i) pilarização com diferentes oligômeros metálicos, ii) adsorção de cátions orgânicos por troca catiônica e iii) imobilização de molécula com grupos funcionais pela formação de ligação covalente nas bordas dos cristais e/ou região interlamelar (funcionalização) (Bergaya e Lagaly, 2001). Desse modo, uma grande diversidade de reações e, portanto, novos materiais podem ser explorados.

A pilarização de argilas refere-se à inserção de grandes cátions (cátions complexos ou polioxicátions) nos espaços interplanares. Os cátions intercalados agem como "pilares" entre as camadas consecutivas do argilomineral. A argila pilarizada apresenta área superficial e volume de poros maiores que do que a argila natural e tem sido bastante estudada na área de catálise. Várias pesquisas relacionadas à pilarização de argilas bentoníticas através soluções intercalantes de diferentes cátions, como alumínio, gálio, zircônio, háfnio e ferro foram realizadas com o objetivo de se obter catalisadores mais ácidos e mais estáveis termicamente (Oliveira, 2003; Salermo *et al.* 2002; Luna e Schuchardt, 1999; Pinnavaia *et al.*, 1984). O emprego de argilas intercaladas com soluções aquosas de cátions metálicos não é recente. Em 1940, intercalou-se uma bentonita americana com soluções de $FeCl_3$ e $NiCl_2$ visando a obtenção de um catalisador heterogêneo (Santos, 1989).

As demais formas de modificação baseadas na adsorção de cátions orgânicos por troca catiônica e na imobilização de molécula com grupos funcionais pela formação de ligação covalente (funcionalização) serão discutidas nos itens a seguir. Devido à complexidade do assunto, além da grande extensão do tema, o enfoque aqui será limitado às reações que visam à obtenção de compostos híbridos orgânico-inorgânicos através da imobilização de silanos em filossilicatos. Será apresentada também uma noção geral das argilas organofílicas e suas aplicações mais importantes.

1.1.7 Argilas organofílicas

O caráter hidrofílico dos minerais argilosos pode ser alterado para hidrofóbico e, consequentemente, organofílico se os cátions inorgânicos trocáveis forem substituídos por cátions orgânicos, como os cátions quaternários de amônio (Tjong, 2006; Kozak e Domka, 2004; Valenzuela Diaz, 1999), aminas (Lagaly, 1986), polímeros (Dau e Lagaly, 1998). Os cátions quaternários de amônio utilizados na intercalação possuem radicais constituídos de cadeias carbônica longas (n>10) e podem se acomodar na região interlamelar de diferentes formas resultando em lamelas mais ou menos afastatadas como mostra a Figura 1.6.

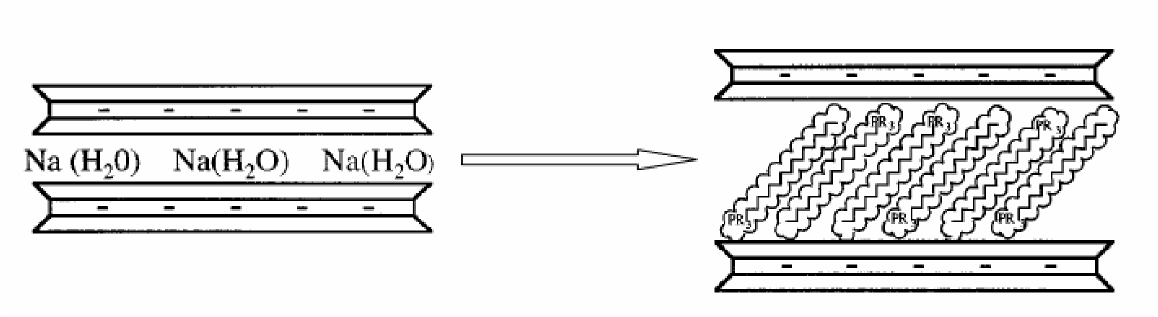


Figura 1.6 - Intercalação de moléculas orgânicas (tensoativo) no espaço interlamelar (Ijdo e Pinnavaia, 1998).

O grande interesse na atualidade é desenvolver argilas organofílicas para obtenção de nanocompósitos polímero/argila. Varias pesquisas têm demonstrado que os nanocompósitos argila/polímero exibem em geral propriedades atraentes do ponto de vista óptico, elétrico, de barreira e redução da flamabilidade. Nesses nanocompósitos, a fase dispersa (argila) deve estar presente sob a forma desfolhada e compatível com a matriz polimérica. Para aperfeiçoar a dispersão de argilas em polímeros, esta deve ser organofílica e possuir espaçamento interplanar basal (d_{001}) elevado para facilitar sua interação com a matriz polimérica e a separação das lamelas (Tjong, 2006; Araújo *et al.*, 2004).

A introdução de aminoácidos na estrutura das argila tem sido apontada, por alguns pesquisadores, como uma maneira alternativa para imobilizar íons metálicos e outros adsorvatos através da formação de complexos estáveis (Brigatti *et al.*,1999, Benincasa *et al.,*2000). A obtenção de argilas pilarizadas com aminoácidos para aplicação em processos de catálise têm sido estudada com resultados animadores (Fudala *et al.* (1999); Kollár *et al.(*2003).

Muitas argilas organofílicas, devido à sua afinidade por compostos orgânicos, têm demonstrado ótima eficiência na remoção de vários contaminantes orgânicos neutros da água e também indicadas para revestimentos de reservatórios de disposição de resíduos e tratamentos de efluentes (Araújo *et al.,* 2004). Diversos pesquisadores realizaram estudos nesta linha de aplicação, ou seja, para a remoção de hidrocarbonetos (Ramos Vianna *et al.*, 2004; Jaynes e Boyd, 1991), pesticidas (Bojemueller e Lagaly, 2001) e pentaclorofenol (Boyd *et al.*, 1988). As argilas organofílicas são atualmente muito utilizadas em vários seguimentos industriais como fabricação de tintas, adesivos, polímeros e cosméticos (Souza, *et al.*, 2004; Santos, 1992).

1.1.8 Funcionalização de argilas com organossilanos

Nas reações denominadas de funcionalização, a molécula é ligada quimicamente à lamela estabelecendo novas funções ao composto. O processo de funcionalização de argilas se difere do processo de obtenção das argilas organofílicas, exposto anteriormente, que se baseia na inserção de moléculas orgânicas pelo mecanismo da troca catiônica, que é reversível. Nas reações de funcionalização ocorre a formação de ligações químicas de forte caráter covalente entre superfície da argila e as moléculas do composto modificador. A imobilização destas moléculas pode ser restritas à superfície do cristal (o espaçamento basal se mantém inalterado) ou pode ocorrer na região interlamelar, neste caso com expansão do espaçamento basal (d_{001}). O composto resultante pode ser definido como material híbrido ou mais especificamente, material inorgânico lamelar modificado (Wypych e Satyanarayana, 2004).

O objetivo principal da modificação química de superfície inorgânica é associar as propriedades da matriz, no caso a argila, com àquelas do agente modificador imobilizado covalentemente na superfície. Assim, o material final, denominado de composto híbrido inorgânico-orgânico, apresentará características da matriz inorgânica, como resistência mecânica, térmica, química, porosidade e da parte orgânica incorporada, que pode conter grupos funcionais específicos de acordo com a aplicação desejada.

Recentemente, uma variedade de superfícies modificadas graças ao uso de silanos (também denominado pela literatura como agentes sililantes) passou a despertar interesse para aplicações na área de catálise, cromatografia, adsorção e eletroquímica (Fonseca e Airoldi, 2003). Dentre essas superfícies, a sílica gel tem-se destacado, sendo sua química de modificação bastante explorada (Walcarius *et al.*, 2004; Bois *et al.*, 2003; Pavan *et al*, 2003; Mori *et al*, 2001; Mahmoud *et al*, 2000; Brown *et al*, 2000; Mercier e Pinnavaia, 1998; Feng *et al*, 1997). A partir de 1995, a utilização de filossilicatos como matrizes hospedeiras para modificação química através da organofuncionalização apareceu como como uma alternativa para o desenvolvimento de novos materiais adsorventes.

Os silanos são denominados agentes de acoplamento e possuem atualmente múltiplas aplicações industriais dentre as quais podemos citar: (i) modificação superficial de cargas (sílica, argilas) para polímeros, (ii) promotores de adesão e agente hidrofóbico em tintas, (iii) agente de reticulação em resinas, (iv) revestimentos híbridos funcionais em cimentos de uso odontológico, e (v) obtenção de sílica e filmes finos de alta pureza (www. Gelest.com). Os compostos que contém ao menos uma ligação C-Si é chamado de organossilanos. Os organossilanos normalmente utilizados apresentam estrutura do tipo R-SiX_3, onde R é o grupo funcional orgânico e X é o grupo hidrolisável, normalmente, metoxi (-OCH_3) ou etoxi (-OC_2H_5). O grupo funcional R contém um grupo reativo R' ligado a um grupo espaçador, geralmente o propil, da seguinte maneira: R'-$(CH_2)_3$-SiX_3. Estes grupos reativos (R') pode ser o vinil (-HC=CH2), amino (-NH_2), mercapto (-SH) dentre outros (Sayilkan *et al.*, 2004; Fonseca e Airoldi, 2003).

O processo de organofuncionalização consiste na imobilização de moléculas de organossilano modificado com grupos funcionais específicos. A introdução deste composto ocorre pela interação entre o radical alcoxi (-OCH_3 ou -OCH_2CH_3) e as hidroxilas superficiais da argila formando ligação química de forte caráter covalente (Sayilkan *et al.*, 2004). Esse processo pode ser conduzido em ambiente anidro ou em meio aquoso. A Figura 1.7 representa esquematicamente os mecanismos possíveis de imobilização de silanos em substratos hidroxilados. A Figura 1.7(a) mostra a funcionalização de argilominerais via condensação direta com silanol ou aluminol presentes na superfície da argila na ausência de água. Neste caso, o processo exige o uso de compostos silanos e solventes puros, como também a eliminaçao, por aquecimento, do excesso de água adsorvida na superfície da argila que são hidrofílicas. Normalmente, os ensaios são conduzidos na presença de solventes orgânicos como o metanol (Syilkan *et al* , 2004), tolueno ou xileno desidratados (Mercier e Detellier, 1995; Celis *et al.*, 2000; Alkan *et al.,* 2005). Na presença de água (Figura 1.7(b)) os silanos são primeiramente hidrolisados e na sequência interagem com o substrato por ligação de hidrogênio. A reação de condensação ocorre durante o processo de cura a 120 ℃ quando a ligação química finalmente se completa. Dependendo das condições utilizadas pode haver a formação de oligômeros siloxanos e um extensivo grau de ligações cruzadas resultando na silanização em múltiplas camadas e, consequentemente, em produtos pouco reprodutíveis.

Nesse trabalho de tese foi dada ênfase à funcionalização da montmorilonita e a hectorita sintética (laponita) com mercaptopropilsilano em meio anidro, na presença de tolueno desidratado. Na literatura há poucos trabalhos citados envolvendo a funcionalização de filossilicatos com grupo funcional mercapto (SH) envolvendo silanos. Aqui, o grupo funcional SH foi imobilizado através de uma rota simples e direta utilizando-se o composto (3-mercaptopropil)trimetoxissilano e reação de condensação direta de forma similar às rotas utilizadas por Walcarius (2004) e Mercier e Pinnavaia (1998) para funcionalização de sílica gel e sílica mesoporosa. Na funcionalização de argilas com o grupo funcional mercapto, podemos ressaltar o trabalho de Mercier e Detelier (1995).

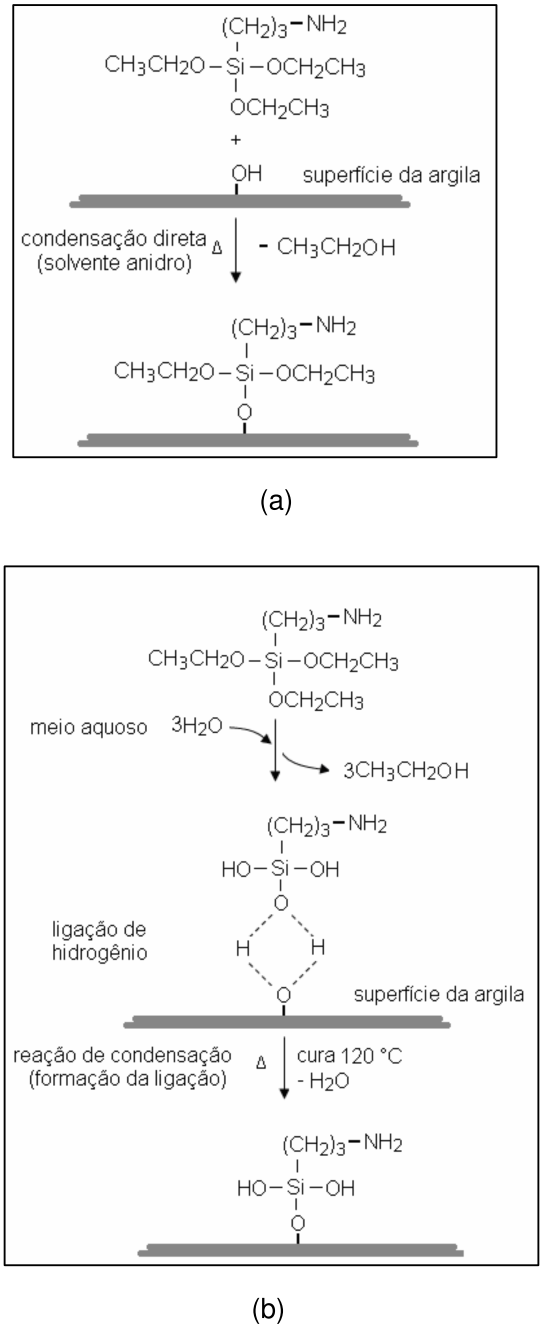


Figure 1.7 - Representação esquemática para mecanismo de imobilização de moléculas de aminopropilsilano na superfície da argila. (a) Reação em meio anidro: condensação direta; (b) Reação em meio aquoso: pré-hidrólise, ligação de hidrogênio e condensação a 120 °C.

Esses pesquisadores funcionalizaram montmorilonita com mercaptossilano através de uma rota indireta: primeiro um composto clorossilano foi imobilizado e posteriormente modificado com NaSH. Nesse trabalho, os autores relataram que apenas 10% dos grupos SH imobilizados formaram complexos com cátions metálicos (Hg^{2+}). Celis e colaboradores (2000) funcionalizaram a argila sepiolita (argila fibrosa) com o mesmo modificador, sendo que, neste caso, 70% dos grupos funcionais imobilizados estavam acessíveis à complexação de espécies metálicas. Um outro trabalho foi publicado por Fonseca e Airoldi (2002b), onde um filossilicato de magnésio e cobre foi sintetizado pelo processo sol-gel e modificado com mercaptosilano através da co-condensação. Os autores relataram bons resultados para adsorção de íons Cu^{2+}, mas a acessibilidade aos grupos funcionais não foi discutida.

O maior desafio atualmente no processo de funcionalização é obter compostos híbridos orgânico-inorgânico com um bom número de grupos funcionais imobilizados e com porosidade suficiente para que estes grupos estejam livres e acessíveis para interagir com o adsorvato. Nesse sentido, este trabalho de tese buscou estudar pré-tratamentos para argila natural a fim de aumentar sua área superficial e também aumentar a densidade de hidroxilas superficiais. Além disso, rotas alternativas foram estudadas através da imobilização com diferentes tipos de silano, no caso mercaptopropilsilano e aminopropilsilano. No caso deste último, rotas anidra e na presença de umidade foram avaliadas. Estudos detalhados das alterações microestruturais dos materiais foram obtidos através de várias técnicas de caracterização como DRX, BET, FTIR, Raman, TG dentre outras. Além da argila natural foi avaliada também argila sintética de elevada área superficial buscando obter materiais híbridos mais porosos e quimicamente mais puros para aplicações mais específicas. A ênfase neste trabalho foi dada para obtenção de argilas funcionalizadas com os grupos funcionais sulfidrila (-SH) e amino ($-NH_2$) visando sua aplicação em processos de adsorção de íons metálicos em meio aquoso. O potencial deste material para adsorção de biomoléculas também é discutido.

1.1.9 Aplicações potenciais para argilas funcionalizadas

Argilas e sílicas funcionalizadas com os grupos reativos sulfidrila (-SH) e amino ($-NH_2$) têm sido estudas para remoção seletiva de alguns metais pesados com bons resultados (Bois *et al.*, 2003; Abolino *et al.,* 2003; Fonseca e Airoldi, 2000b, Mercier e Pinnavaia, 1998; Celis *et al.*, 2000). Sabe-se que metais tais como mercúrio, cádmio, chumbo, cobre e arsênio forma complexos estáveis com os grupos SH e NH_2, portanto, materiais funcionalizados com estes grupos são promissores como adsorvente em processos de pré-concentração e de separação destas espécies em águas e efluentes. Publicações mais recentes têm mostrado o crescente interesse no estudo de eletrodos quimicamente modificados à base de pasta de carbono e argila funcionalizada para pré-concentração e determinação de metais (Ag^+, Hg^{2+}, Cd^{2+}) por voltametria de pulso diferencial (eletroanálise) (Dias Filho *et al.,* 2006; Dias Filho *et al*., 2005, Tonle *et al*., 2004).

Além da adsorção de metais, argilas naturais e sintéticas modificadas têm sido estudas para várias aplicações com resultados animadores tais como (i) modificação de eletrodos para biosensores (Mousty, 2004), (ii) imobilização de enzimas (Tietjen e Wetzel, 2003) (iii) imobilização de catalisadores (Kuzniarska-Biernacka *et al*., 2005), (iv) remoção de bimoleculas indesejáveis em extratos (Bruce, 2006), (v) nanocompósito argila/polímero (Herrera, *et al*., 2006), (vi) imobilização de fármacos (Park et al., 2004) e (vii) adsorção de compostos orgânicos tóxicos (Sayilcan *et al*., 2004).

1.2 Relevância do projeto

Os minerais argilosos formam um grupo de matrizes comumente chamadas de hospedeiras que favorecem a química de intercalação. Nesse aspecto, devido à natureza expansível das esmectitas, como a montmorilonita, por exemplo, estas argilas são bastante estudadas e utilizadas para intercalação de sais quartenários de amônio, aminas alifáticas, aromáticas e mais recentemente para a intercalação de polímeros (Fonseca, 2000). Grande parte dos esforços dos pesquisadores na última década têm se voltado para obtenção de argilas organofílicas visando sua aplicação em sistemas nanoestruturados polímero/argila.

Os trabalhos envolvento funcionalização de argilas esmectitas com silanos são mais raros, principalmente funcionalização com sulfidrila (SH), cuja a aplicação é mais específica. Nessa linha, podemos ressaltar o trabalho de Mercier e Detelier (1995). Esses pesquisadores funcionalizaram montmorilonita com mercaptosilano através de uma rota indireta; primeiro um composto clorossilano foi imobilizado e posteriormente modificado com NaSH. Nesse trabalho, os autores relataram que apenas 10% dos grupos SH imobilizados formaram complexos com cátions metálicos (Hg^{2+}). Este trabalho de tese propõe a utilização de uma rota simples e direta, normalmente utilizada para funcionalizar géis de sílica, para a funcionalização de argilas. Este processo consiste, basicamente, em imobilizar o grupo funcional SH através da reação de condensação direta na ausência de água utilizando-se o composto (3-mercaptopropil)trimetoxissilano como agente modificador. A rota de modificação aqui utilizada é similar às rotas utilizadas por Walcarius (2004) e Mercier e Pinnavaia (1998) para funcionalização de sílica gel e sílica mesoporosa. O presente trabalho de tese propõe a utilização de argilomineral lamelar como matrizes por ser um material barato, disponível em vários lugares do mundo e apresentar características estruturais que justificam esta iniciativa. A grande desvantagem da argila em relação aos géis de sílica é a baixa densidade de hidroxilas superficiais. Para contornar esse problema o método original foi modificado sendo que as argilas foram submetidas a pré-tratamento com ácido para ativação. Dessa forma, a argila passaria, após sua funcionalização, de um adsorvente inespecífico (adsorção por troca catiônica) para um adsorvente mais seletivo e específico capaz de formar complexos com determinados adsorvatos.

No caso específico da funcionalização com grupo funcional amino, os trabalhos publicados já são mais numerosos, mas tem sido relatados problemas como falta de homogeneidade e baixo grau de intercalação. O foco da maioria dos trabalhos publicados envolvendo funcionalização de argilominerais com o grupo funcional amino tem sido a avaliação do potencial de diferentes tipos de argilas como matrizes hospedeiras para os silanos. A maior escassez de informação está no efeito do solvente utilizado na microestrutura do material funcionalizado. Nessa linha de investigação, destaca-se um trabalho recente de Shanmugharaj *et al.* (2006). Esses pesquisadores observaram que solventes de maior energia superficial, como a água, resultaram em melhores resultados de intercalação. Os solventes utilizados por estes pesquisadores (água pura, tetrahidrofurano, tolueno e etilenoglicol), exceto o tolueno, são pouco utilizados de uma maneira geral em processos de funcionalização de silicatos. Como o tolueno e o álcool etílico são solventes mais comuns em processos de modificação de sílica optou-se por investigá-los em sistemas com argila. Neste trabalho de tese, procurou-se elucidar o efeito do tipo de solvente e da matriz inorgânica na microestrutura do material híbrido obtido. Para isto, duas argilas foram modificadas com o composto (3-aminopropil)trietoxissilano na presença de tolueno anidro e também solução alcoólica hidratada a 95%. A partir dos dados de caracterização foi proposto um modelo estrutural do material híbrido obtido por estas duas rotas.

Embora o Brasil seja um importante produtor de bentonita, raros são os trabalhos de pesquisa na área de adsorção e catálise que utilizam a argila nacional. A grande maioria das publicações nacionais e internacionais nesta área utilizam as bentonitas americanas, sobretudo as argilas bentoníticas de Wyoming (USA), e as argentinas naturalmente sódicas. Ambas argilas estão muito bem caracterizadas e suas propriedades bem conhecidas. As bentonitas brasileiras são policatiônicas e possuem diferenças significativas na sua composição comparada com as americanas e argentinas. Segundo o estudo feito por Ciminelli (2002) no CGEE (Centro de Gestão e Estudos Estratégicos) de Brasília, as bentonitas estão entre os seis minerais industriais brasileiros (juntamente com o caulim, talco, agalmatolito, barita e vermiculita) com maior potencial de agregação de valor. Este estudo enfatiza a necessidade de investimentos para ampliação de conhecimento tecnológico, desenvolvimento de novas aplicações e otimização de aproveitamento das reservas brasileiras. Campina Grande, no estado da Paraíba, é a principal região produtora de bentonita (165.000 t/ano) no país e o conhecimento sobre as argilas desta região ainda são muito modestos. O que existe hoje são alguns trabalhos voltados para a caracterização e a avaliação do seu potencial tecnológico nas áreas de produção de agentes tixotrópicos para perfuração de poços de petróleo, aglomerantes para moldes de fundição, agentes ligantes para pelotização de minério de ferro e agentes descolorantes de óleos vegetais, que são as áreas de maior aplicação desta argila no Brasil. Neste contexto, o presente trabalho propõe dar uma contribuição para (i) o conhecimento da composição mineralógica e das propriedades adsortivas da bentonita da região de Campina Grande na Paraíba, (ii) avaliação de seu potencial para obtenção de materiais híbridos orgânico-inorgânicos e (iii) análise do desempenho do material obtido como adsorvente para algumas espécies de metais pesados. Dessa forma, o presente trabalho busca agregar valor à bentonita nacional a partir da sua modificação estrutural e desenvolvimento de uma aplicação totalmente inovadora para este material.

Com relação às possibilidades de aplicação das argilas funcionalizadas, é importante ressaltar que estas são muito amplas, passando pela cromatografia, suporte para catalisador, construção de eletrodos modificados para eletroanálises, biosensores, adsorção de enzimas etc. Neste trabalho, optou-se por avaliar o potencial do material desenvolvido como adsorvente de metais de elevada toxicidade e desta forma, propor aplicações como agente de pré concentração de elementos traço e especiação.

Estudos têm mostrado que a bentonita apresenta boa capacidade de adsorção para alguns metais pesados quando comparada à outras argilas como a caulita, por exemplo. Porém, sabe-se que o mecanismo natural adsorção desta argila é por troca catiônica que é facilmente reversível e não seletivo. Além disso, essas argilas, no seu estado natural, apresentam baixa capacidade de carregamento e pouca afinidade por elementos que se apresentam na forma aniônica ou neutra em meio aquoso. Estudos já mostraram que elementos de elevada toxicidade como mercúrio, cádmio, arsênio, chumbo dentre outros, apresentam grande afinidade pelo grupo sulfidrila e amino e são capazes de formar complexos estáveis com estes grupos funcionais. Diante do exposto, propõe-se neste trabalho, a funcionalização da bentonita nacional com grupos funcionais reativos capazes de formar complexos estáveis com alguns metais como alternativa para melhorar a seletividades e a capacidade de carregamento desta argila.

Ainda tratando de metais tóxicos, vale mencionar que não foram encontrados na literatura trabalhos relacionados à adsorção de arsênio em argilas funcionalizadas. A grande maioria dos trabalhos abordam a adsorção do arsênio em goetita, hidróxido de ferro e solos argilosos (Ladeira, 1999; Dixit *et al*., 2003; Fendorf *et al*., 1997; Goldberg, 1986). Sabe-se que a adsorção do arsênio em argilominerais tais como caulinita e montmorilonita no estado natural não têm sido muito animadores (Golberg *et al*., 2002; Saada *et al*., 2003) em relação aos resultados que envolvem a adsorção em óxidos de Fe e Al. Talvez pelo fato do As(V) apresentar-se na forma aniônica ($H_2AsO_4^-$, $HAsO_4^{2-}$) em pH>2 e o As(III) como espécie neutra (H_3AsO_3) em pH<9, ambos com pouca afinidade pelas argilas naturais que possuem uma carga residual negativa devido às substituições isomórficas. Neste trabalho de pesquisa foi proposto o uso de argila modificada com SH para adsorção seletiva da espécie As(III) baseado no resultado de trabalhos anteriores que mostram a grande afinidade desta espécie pela sulfidrila (Teixeira *et al.*, 2004). A forma trivalente do As é dez vezes mais tóxica que a espécie pentavalente e ainda apresenta uma mobilidade no meio ambiente significativamente maior, sendo, portanto, potencialmente mais perigosa. Do ponto de vista ambiental, este trabalho de tese propõe, pela primeira vez, a utilização de argila modificada com grupo sulfidrila para a separação do arsênio trivalente em sistemas aquosos que exijam a caracterização e pré-concentração desta espécie.

1.3 Objetivos da tese

Os principais objetivos deste trabalho de tese são (i) estudar a funcionalização da montmorilonita e de uma hectorita sintética (laponita) através da imobilização de organossilanos com grupos funcionais sulfidrila (SH) e amino (NH_2) visando obter um novo material híbrido nanoestruturado; (ii) realizar a caracterização microestrutural detalhada do material obtido e (iii) avaliar o potencial do material obtido como adsorvente para os íons Cd^{2+}, As(III) e As(V).

Visando atingir aos objetivos gerais propostos, foram desenvolvidas as seguintes etapas:

- Purificação da bentonita brasileira oriunda da região de campina Grande, Paraíba;

- Pré-tratamento das argilas através da ativação ácida;

- Funcionalização das amostras de argila utilizando-se os silanos (3-mercaptopropil) trimetoxissilano e (3-aminopropil)trietoxissilano através de rotas diretas em solventes orgânicos;

- Caracterização detalhada das argilas antes e após modificação estrutural através das técnicas: difratometria de raios-X (DRX), área superficial específica (método BET), microscopia eletrônica de varredura (MEV/EDS), termogravimetria (TG), espectroscopia na região do infravermelho (FTIR), espectroscopia Raman e análise elementar;

- Avaliação da acessibilidade aos grupos funcionais imobilizados na argila através do protocolo baseado no método de Volhard no caso do grupo SH e por titulação potenciométrica no caso do grupo amino.

- Proposição de um modelo estrutural para as moléculas de silano imobilizadas na estrutura das argilas com base nos resultados da caracterização;

- Avaliação do desempenho das argilas na sua forma natural e modificada como material adsorvente para $Cd^{2+,}$, As(III) e As(V) através de ensaios de adsorção em meio aquoso em diferentes condições de pH.

1.4 Organização da tese

A estrutura desta tese segue uma divisão por capítulos de 1 a 5, sendo que cada capítulo corresponde a um manuscito a ser submetido à publicação, com exceção do capitulo 1 e capítulo 5. O capítulo 1 apresenta a introdução ao tema bem como uma revisão da literatura. São ainda destacados a relevância e os objetivos do trabalho.

O capítulo 2 trata da funcionalização com o composto mercaptopropilsilano da montmorilonita brasileira e americana para fins de comparação. São apresentados os resultados da caracterização detalhada das argilas antes e após a modificação. É também apresentado o protocolo desenvolvido com base no método de Volhard para avaliar a capacidade de carregamento da argila bem como a acessibilidade aos grupos imobilizados. Ao final, o material é avaliado para a adsorção dos íons Cd^{2+} em diferentes condições de pH.

Capítulo 3 descreve a funcionalização da laponita com o grupo mercaptopropil visando obter um material híbrido mais poroso, uma vez que esta argila apresenta elevada área superficial específica (326 m^2/g). Além disso, foi avaliada a seletividade da argila funcionalizada em relação às espécies As(III) e As(V). Neste trabalho, ênfase foi dada às técnicas FTIR e Raman para avaliação das alterações estruturais da argila após funcionalização e adsorção do arsênio. A laponita funcionalizada apresentou bons espectros no Raman o que nos permitiu obter várias informações adicionais sobre os grupos imobilizados e sobre o envolvimento dos grupos SH na adsorção do As(III). A espectroscopia Raman não foi utilizada nos demais capítulos pelo fato das amostras de montmorilonita ter apresentado elevada luminescência.

O capítulo 4 trata da funcionalização de duas argilas, uma natural, a montmorilonita e outra sintética, a laponita, com aminopropilsilano. O foco principal deste capítulo é avaliar a influência do solvente e também a natureza da argila na microestrutura do material híbrido obtido. Os resultados da caracterização detalhada das argilas funcionalizadas possibilitaram a proposição de modelos para a imobilização das moléculas de silano na estrutura das duas argilas.

No capítulo 5 são apresentadas as considerações finais e as conclusões do trabalho. São apresentadas ainda as contribuições inéditas do trabalho, a lista de publicações, bem como as sugestões para trabalhos futuros.

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CAPÍTULO 2

SYNTHESIS OF THIOL-FUNCTIONALIZED HYBRID MATERIALS FROM SMECTITE-TYPE CLAYS FOR HEAVY METAL UPTAKE

Abstract

The properties of functionalized clays derived from the reaction of two natural smectite clays, one from Campina Grande, Brazil, and the other, a purified smectite supplied from Southern Clays, were investigated. The samples were modified by acid treatment followed by intercalation with organic ligands containing thiol (-SH) group through the covalent grafting with interlayer and surface silanol groups. The modification of bentonites from different procedence was carried out under anhydrous conditions with (3-mercaptopropyl) trimethoxysilane. Functional group immobilization efficiency was demonstrated by comparing the physico-chemical characteristics of the clays before and after reaction with the organosilane. The X-ray powder diffraction patterns of the modified montmorillonite samples indicated that their original structure had been preserved. The BET results indicated decreased porosity depending on the amount of functional group attached to the aluminosilicate structure. Organic loading, calculated through TG analysis, was of 1.76 mmol/g for the Brazilian clay and 1.45 mmol/g for the cloisite sample. TG analysis demonstrated also that the functionalization process altered the original hydrophilic nature of the clay to hydrophobic**.** The accessibility to the reactive centers was successfully determined by using the Volhard method ranging from 60 – 70% depending on the organic group content. The DRIFT spectra and elemental analyses (EDS) demonstrated the presence of organic chains and thiol groups in the modified clays. The adsorption capacities of untreated and functionalized bentonite were found to be 17 mg Cd/g of adsorbent (0.15mmol/g) and 44 mg Cd/g of adsorbent (0.41mmol/g), respectively. We concluded that the adsorption capacity of natural bentonite can be enhanced by surface modification using organo-functional silane coupling agents. This new material may well be an alternative for separation and pre-concentration purposes.

Keywords: montmorillonite, (3-mercaptopropyl)trimethoxysilane; functionalization, cadmium, adsorption.

2.1 INTRODUCTION

Many efforts have recently been devoted to the design and preparation of inorganic-organic nanomaterials because of their potential application in novel functional materials. The intercalation of organic species within the spaces between interlayers of inorganic layered crystals provides nanostructures consisting of alternating layers of inorganic and organic compound. The intercalation reactions occur by insertion of mobile guest species (neutral, molecules, or ions) into the accessible crystallographic-defined vacant sites located between the layers (interlayer spacing) of the layered host structure (Wypych, 2004). The most commonly used procedure to modify 2:1 clay minerals is by ion exchange with organic cations such as alkyl ammonium compounds containing different lengths of the alkyl chain (Dau and Lagaly, 1998).

Silane coupling agents, used widely for the modification of silica surfaces, have also been employed more recently for interlayer modification of layered silicates (He *et al*, 2005; Prado *et al.*, 2005; Walcarius *et al.*, 2004; Celis *et al.*, 2000). Modification with organosilane involve grafting reactions that occur by establishing covalent bonds between the reactive groups of the layer, normally hydroxyl groups, and silane molecules, which ensure high chemical structural, and thermal stability for the compound. These reactions can be restricted to the crystal surface (the basal spacing remains unchanged) or to the layer surface, in which case an interlayer expansion occurs. The resulting material can be defined as a hybrid material or, more specifically, a surface–modified inorganic layered material (Wypych, 2004). Some recent works have shown that it is possible to create specific chemical activity through the selection of an adequate functional group, such as amino, thiol, vinyl, long carbon chain. and many others. Functionalized clays may provide specific sites for the adsorption of specific adsorvates (Okutomo *et al.,*1999). Some of these modified clays possess attractive features for various applications, such as the sorption of organic and inorganic pollutants (Sayilkan *et al.,* 2004; Mercier and Pinnavaia, 1998); the manufacture of polymer/layered silicate nanocomposites (Herrera *et al.*, 2006) as well as of modified electrodes (Tonle *et al.,* 2004), of supports for catalysts (Kuzniarska-Biernacka *et al.,* 2005), and of sensor and biosensors (Mousty, 2004); supports of drugs or enzymes (Park and Kwon, 2004); and preconcentration agents for heavy metal determination (Dias Filho *et al.*, 2006).

The functionalization mechanism of organosilane on amorphous silica and alumina surfaces is reasonably well-elucidated (Pavan *et al.* 2003; Bois et al, 2003; Mansur *et al.*, 2000; Mercier and Pinnavaia, 1998b). Other works have investigated the preparation of sorbents by covalent attachment of organic molecules to synthetic layered materials obtained by the sol-gel process (Fonseca *et al.*, 1999; Mori and Pinnavaia, 2001). More recently, chemical modification of natural clays, mainly of the smectite-type, especially by reactions those involving the interlayer surface have been investigated. The mineral clays of the smectite group present a set of structural characteristics that make them attractive to the development of catalysts, adsorbents, supports of drugs or enzymes, and intercalation complexes (Bruce, 2006, Liu *et al*., 2004; Sezer *et al,* 2003; Sayilkan *et al*, 2004; Pinnavaia *et al,* 1984; Occelli *et al*, 1987). Bentonite, a clay composed predominantly of montmorillonite, has been commonly studied as a sorbent for heavy metal removal from soil and water due to its characteristics of high cation exchange capacity, high specific surface areas associated with their small particle size, low cost, and frequent occurrence in most soils (Abolino *et al.*, 2003; Brigatti *et al.*, 2004). The smectite-type clays present adequate characteristics of expandability but low hydroxyl density. Hydroxyl groups are known to exist on the edges of a clay particle. Acid activation is used to increase the hydroxyl concentration on clay surfaces, thereby its adsorbent and catalytic properties (Valenzuela Díaz and Santos, 2001). This increase results from the creation of structural defects in the Si-O tetrahedral sheet and also by exchanging non-bonding metal ions such as sodium, potassium, and calcium with H^+. These additional acid sites are susceptible to grafting via a hydrolysis reaction similar to that of silica (He, *et al.,* 2005).

The properties of nanocomposite materials depend on their nanostructures, in particular on the structures of the interfaces and on the characteristic of the clay (Okutomo *et al.,* 1999). Most of the works concerned with the development of organic-inorganic hybrid compounds used American bentonite samples, whose properties and characteristics are well described (Mercier and Detellier, 1995; Celis *et al*., 2000; Madejová, 2003). The Brazilian bentonite from Campina Grande is polycationic clay. The material is usually activated by the addition of soda ash prior to application as a bonding material in the preparation of molding sand for metal casting, cat litter, the pelletizing of ore fines, the drilling mud, and in civil engineering. There is no publication that the authors are aware of describing the functionalization of a Brazilian bentonite with organosilanes. The present work investigates the possibility of utilizing this smectite clay for the preparation of a organic-inorganic hybrid material. In addition to adding value to this raw material through new applications, this work is also intended to contribute to a better understanding of the properties of this clay.

The modification process used here is based on the strategy commonly used for silica gel functionalization. It consists of a direct condensation reaction between (3-mercaptopropyl) trimethoxysilane and the hydroxyl groups available in the clay structure. The strategy of functionalization used here differs from that proposed by Mercier and Detellier (1995) which involved the immobilization of (3-chloropropyl)trimethoxysilane followed by treatment with NaSH. A detailed material characterization was provided by chemical analysis, diffuse reflectance infrared Fourier transform spectroscopy (DRIFT), X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive spectrometry (MEV/EDS), N_2 adsorption/desorption experiments (BET method), and thermogravimetric analysis (TG). The sorption capacity as well as the accessibility to the binding sites were evaluated using a modified protocol of the Volhard silver nitrate method developed here for this purpose.

2.2 EXPERIMENTAL

2.2.1 Materials

Two montmorillonite samples were used in this study. The first was, a naturally polycationic Brazilian bentonite with a predominance of calcium as interlayer cation (sample BCa) from Campina Grande, Paraíba, Brazil. The sample was purified by sedimentation in aqueous suspension, containing 2% of solids, for four h; the supernatant was centrifuged and freeze-dried. The purified fraction showed a size distribution of 10% < 0.7μm, 50% < 2.6μm, and 90% < 7.5 μm (water dispersed particle sizes) obtained by laser granulometer (Cilas, model 1064). The cation exchange capacity (CEC) of 80 meq/100g clay was measured by ammonium acetate (Volzone *et al.*, 2001). The specific gravity was 2.60 $g.cm^{-3}$ and X-ray diffraction indicateds d_{001} =1.47nm. The second sample was a well-known, natural sodic and purified montmorillonite supplied by the Southern Clay Products, Inc, named Cloisite-Na (sample CNa) with a size distribution of 10% < 2 μm, 50% < 6μm, and 90% < 13 μm (typical dry particle sizes), a CEC of 92.6 meq/100g clay, a specific gravity of 2.86 $g.cm^{-3}$, and d_{001} =1.17 nm, according to supplier information. This clay was used without further purification.

The BCa chemical composition is summarized in Table II.1. It is possible to observe that the acid activation treatment was efficient in exchanging the interlayer cations (Ca, Na, and K) by H^+ ions without causing significant aluminum leaching from the clay structure.

Table II.1: Chemical analysis of acid activated and raw bentonite samples (wt %).

Clay sample	SiO_2	Al_2O_3	FeO	Fe_2O_3	MgO	CaO	TiO_2	Na_2O	K_2O	L.O.I	R
BCa)	55.43	15.45	0.28	9.56	0.93	0.40	0.92	0.15	0.23	16.64	3.58
(BH)	55.17	14.75	0.25	9.40	0.67	0.00	1.12	0.02	0.09	17.78	3.74

R= SiO_2/Al_2O_3 ratio; L.O.I = loss on ignition 950 °C; BCa - natural bentonite purified by sedimentation method; BH - acid activated purified bentonite

2.2.2 Reagents

The organosilane grafting agent, the (3-mercaptopropyl)trimethoxysilane (MPTMS) ($Si(OCH_3)_3C_3H_6SH$), 98% pure, was purchased from Sigma-Aldrich and used without further purification. Toluene (99.8%) was also provided by Sigma-Aldrich. Reagent grade chemicals NaOH (>98%, pellets) and HCl (~37%) from Merck were used for acid treatment and pH adjustments during the adsorption experiments. The solutions of $AgNO_3$, KSCN, and $Fe(NH_4)(SO_4)_2$ used in the measurement of binding capacity were prepared with reagent grade chemicals (Merck). All solutions were prepared with high-purity water (18 $M\Omega.cm^{-1}$) obtained from a MilliQ water purification system.

2.2.3 Characterization methods

The X-ray diffraction patterns of modified and unmodified clay samples were obtained with a Philips model PW1710 diffractometer, fitted with a Cu tube (λ=1.5418 Å, 40 kV and 20 mA, step size 0.06° 2θ, 5 s/step). Thermogravimetric curves were obtained in a TGA model TGA50 Shimadzu under N_2 environment, (20 mL/min), with a temperature ramp of 10 ℃/min between 30 ºC and 800 ºC. DRIFT analyses were performed at room temperature, in the spectral range of 400 - 4000cm^{-1}, using a FT/IR- spectrophotometer, model SPECTRUM-1000, Perkin Elmer (64 scans of accumulation, resolution of 4cm^{-1}). The samples were mixed with KBr powder in 5 wt.% and a pure KBr spectrum was used as a reference. The morphological and semi-quantitative analysis of the samples was carried out in a scanning electron microscopy (Jeol instrument model JSM-6360LV) operating at 25 kV and with a Noran energy-dispersive spectrometer (ZAF corrections coupled). These results were used to assess the relative percentage ratios for Si, Al, S, and Ag. The isotherms of adsorption-desorption of N_2 were obtained at 77 K (liquid nitrogen). Before the adsorption experiments, the samples were outgassed under vacuum overnight at 60 ℃. The specific surface area was obtained by a multipoint BET method. The volume of pores was estimated from the t-method and the pore size distribution was assessed by the BJH method using an Autosorb equipment from QUANTACHROME instruments.

2.2.4 Modification process

Prior to the grafting process, 1g of the calcic or sodic bentonite **(BCa,CNa)** samples were acid activated with 100 cm^3 of 0.15 $mol.dm^{-3}$ HCl solution. A dilute HCl solution was used to avoid the dissolution of the octahedric sheet and the collapse of the structure. This suspension was maintained under agitation overnight, rinsed in deionized water until a neutral pH was achieved, then centrifuged and freeze-dried (Mercier e Detellier, 1995). The resulting samples were designated as **BH** and **CH.** In a next step, approximately 1g of each clay, in natural and acid activated forms, previously dried at 140 ºC for 2 h, was dispersed in 50 cm^3 of 0.2 mol dm^{-3} MPTMS in dry toluene. The resulting mixture was refluxed and agitated for 24 h within an inert atmosphere of N_2 to avoid the oxidation of the SH groups. The obtained solid was sequentially washed three times with toluene to remove the non-bonded silane, ethyl alcohol; filtered; and dried for 2 h at 120 ºC in an inert nitrogen atmosphere. The functionalized samples were denominated as **BCASH, BHSH, CNASH,** and **CHSH**. The modification method is similar to that described by Walcarius *et al* (2004) for the functionalization of silica gel.

2.2.5 Binding capacity of the mercaptyl functional groups

In the present investigation, the amount of the immobilized and accessible thiol groups was successfully determined according to a protocol based on the Volhard silver nitrate method (Dominguez *et al.,* 2002). This protocol was, for the first time, applied to a thiol-modified inorganic substrate. The determination is based on the thiol groups' chemical affinity toward silver. Following the protocol, 25 cm^3 of 0.01mol.dm^{-3} silver nitrate solution were added to flasks containing 100 mg of dry modified clay (reaction (2.1)). The flasks were covered to avoid exposure to light and stirred in a shaker for 12 h prior to testing. The remaining silver nitrate was titrated with a standardized 0.01 mol.dm^{-3} potassium thiocyanate (KSCN), using iron ammonium sulfate hexahydrate as an indicator (reaction (2.2)). The endpoint was detected when an excess of the thiocyanate anion, together with the iron compound, formed a red colored complex (reaction 2.3). The binding capacity of the mercaptyl functional group was expressed in mmol/g of clay. In all cases, the tests were carried out in three replicates to determine the reproducibility and standard deviation of the experiment. The results were compared with those obtained using unmodified clay, used here as a reference. Another flask containing a pure solution was submitted to the same procedure in order to assess eventual precipitation. This methodology was used as a protocol to quantify the accessible SH groups grafted in clay structure. The sequence of reactions is described below:

Adsorption step:

$$\underset{\text{(modified clay)}}{\sim RSH_{(S)}} + Ag^+_{(aq)} \longrightarrow \sim RSAg_{(s)} + H^+_{(aq)} \qquad (2.1)$$

Titration step:

$$Ag^+_{(aq)} + SCN^-_{(aq)} \longrightarrow AgSCN_{(S)} \qquad (2.2)$$

End point:

$$6SCN^-_{(aq)} + Fe^{3+}_{(aq)} \longrightarrow \underset{\text{(Red complex)}}{Fe(SCN)_6^{3-}{}_{(aq)}} \qquad (2.3)$$

2.2.6 Cadmium adsorption

The cadmium adsorption onto natural and modified clay was measured as a function of time in batch experiments to determine the equilibrium time. For the cadmium immobilization experiments, 100 mg of modified clay (500 mg of natural clay) was shaken with 50 cm^3 of 45 $mg.dm^{-3}$ of Cd^{2+} solution in erlenmeyer flasks (250 cm^3), at 25 ℃ and 150 rpm, using a controlled environment incubator shaker (New Brunswick) for 6 h. The remaining cadmium in the solution was analyzed by atomic absorption spectrometry (Perkim Elmer Analyst A300). The experiments were carried out in a pH range of 3 to 6.

2.3 RESULTS AND DISCUSSION

2.3.1 Functionalization process

The functionalization of the clay samples involves a direct condensation reaction between the terminal (OH) groups from the silicate surface and the alkoxy group of the silane. It is assumed that the silylation of a silicate is favored over the polysiloxane formation if the reaction is carried out in a dry environment. Figure 2.1 shows a schematic illustration of the functionalization process used here. The silane coupling agents are a family of organosilicon monomers with the general structure of SiX_3LR. In this work, we chose the (3-mercaptopropyl)trimethoxysilane (MPTMS) with the chemical formula $Si(OCH_3)_3C_3H_6SH$. The reactive group (R) is the mercapto (–SH) and the hydrolyzable alkoxy group (X) is the methoxy ($-OCH_3$), which releases methanol during the coupling reactions.

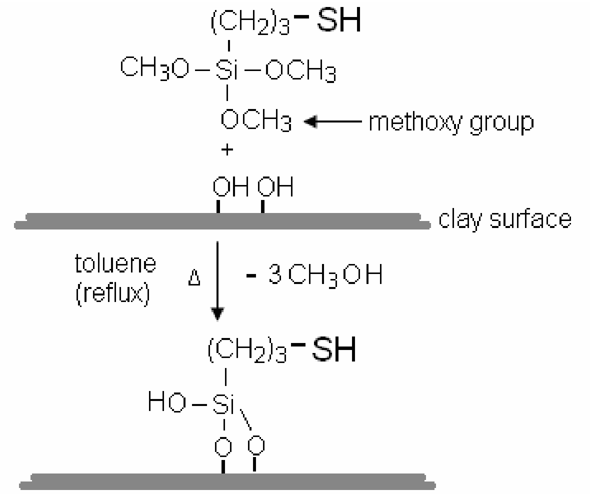

Figure 2.1 - Schematic illustration of the direct hydrolysis and condensation reaction.

As shown in Figure 2.1, a propylene group ($(CH_2)_3$) works as a linker (L) of the reactive group (SH) with silicon. The mercapto functional group was selected due to its great affinity to some highly toxic heavy metals (Hg, Cd and As) and many other adsorvates

2.3.2 DRIFT Analysis

Infrared spectroscopy is very sensitive to modifications of the clay mineral structure upon functionalization. Changes following the modification process can be observed in all frequency ranges of the FTIR spectra. As all the organoclays obtained in this study showed similar features, only the spectra of the sample with higher organosilane content (BHSH, CHSH) are reported.

The DRIFT spectra of both unmodified (BH, CH) and modified (BHSH, CHSH) clay samples are presented in Figure 2.2. The spectra of the acid activated samples (CH/BH) shows a strong band at 3620 cm^{-1} related to the stretching vibration of the structural hydroxyls group (AlAlOH, AlMgOH), typical of montmorillonite (Farmer, 1974). These clay samples exhibit two bands due to the presence of physisorbed water, namely the ν(H-O-H) stretching frequency at approximately 3400 cm^{-1} and the corresponding deformation band (δ(O-H)) at 1620 cm^{-1} (Park and Kwon, 2004). In the low energy region, the spectrum shows one broad band in the range of 1000 - 1200 cm^{-1} with a maximum peak at 1035 cm^{-1} assigned to Si-O and Si-O-Si stretching vibrations, and another band at 916 cm^{-1} assigned to AlAlOH bending vibration (Farmer, 1974).

In the organoclay spectra (CHSH/BHSH), one may observe aliphatic CH stretching vibrations in the 3000–2800 cm^{-1} region. The aliphatic CH_2 groups give rise to a doublet at 2924 cm^{-1} and 2850 cm^{-1}, which is assigned to asymmetric and symmetric stretching, respectively. The corresponding deformation modes of these groups are observed between 1400 cm^{-1} and 1460 cm^{-1}. The CH_2 wagging bands in propyl chains are spread over the range of 1200–1400 cm^{-1} and CH_2 wagging bands are intensified as CH_2–Si at about 1238 cm^{-1}. The characteristic stretching band of the SH group in thiol-functionalized clays is located at 2540 cm^{-1}. This assignment is consistent with previous reports (Shanmugharaj *et al.*, 2006, Bois *et al.*, 2003; Fonseca *et al.*, 2000; Coates, 2000). All of these vibrations confirm the presence of the $–CH_2-CH_2-CH_2-SH$ bonded to the clay structure. The formation of disulfides (S-S bridge) was not evidenced here (600-620 cm^{-1}). The hydrolysis of the methoxy group seems to have been completed since the band assigned to the unhydrolyzed methoxy (νO-CH_3, at 2850 - 2815 cm^{-1}) group was not observed.

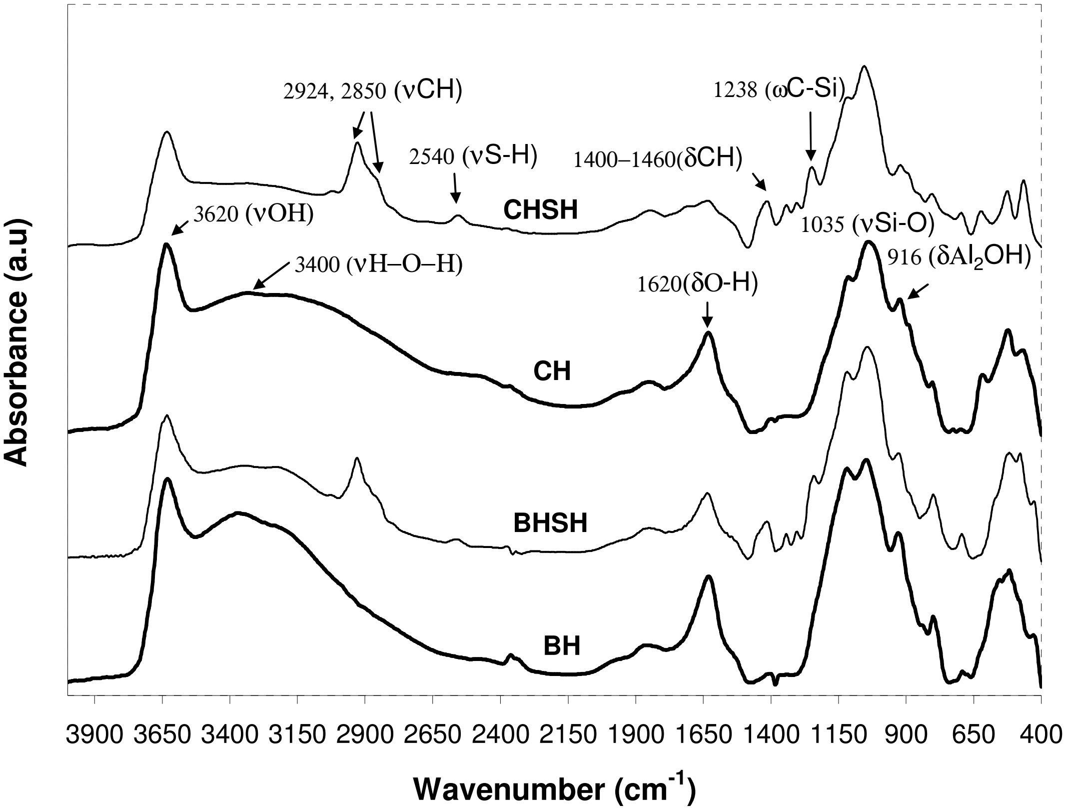

Figure 2.2 - DRIFT spectra of acid activated and functionalized samples.

Figure 2.3a shows the variation of the O-H stretching band at 3620 cm^{-1} of the modified samples with respect to the raw samples. After grafting, there was an important decrease in the intensity of this band in both samples. The corresponding bending vibration band (δAlAlOH) at 916 cm^{-1} follows the same trend (Figure 2.3b). The reduction of the intensity of these two bands confirm the previous hypothesis that the grafting occurs by a condensation reaction of hydroxyl groups of clay surface with the hydrolysable methoxy group of the MPTMS molecule (Figure 2.1). In an attempt to quantify this alteration, we have calculated the peak ratio of ν(OH) at 3620 cm^{-1} and νSi-O at 1035 cm^{-1} (Table II.2). The band at 1035 cm^{-1} was chosen because it remained constant after grafting (Figure 2.3b). Table II.2 shows a decrease in the (νOH/νSiO) band ratio after grafting, this appearing more pronounced in the CHSH sample. The results confirm that the structural hydroxyl group was indeed involved in the grafting process. After functionalization, one may also observe the broadening of the band centered at 3400 cm^{-1} (Figure 2.3a) and the decrease in the corresponding bending vibrations at 1620 cm^{-1} (Figure 2.3c). These results indicate drastic reduction of the adsorbed water content, with a consequent increase in the sample's hydrophobicity. This may in turn suggest an intercalation of MPTMS molecules in the interlayer region with the expulsion of the adsorbed water.

TableII.2: The peak ratio of ν(OH) at 3620 cm^{-1} and νSi-O-Si at 1035 cm^{-1}

Sample	Peak ratio (νOH/νSiO)
CH	0.978
CHSH02	0.653
BH	0.921
BHSH02	0.722

After the spectra normalization, the peak height was obtained by Spectrum BX FT-IR version 3.02.00 – Perkin Elmer

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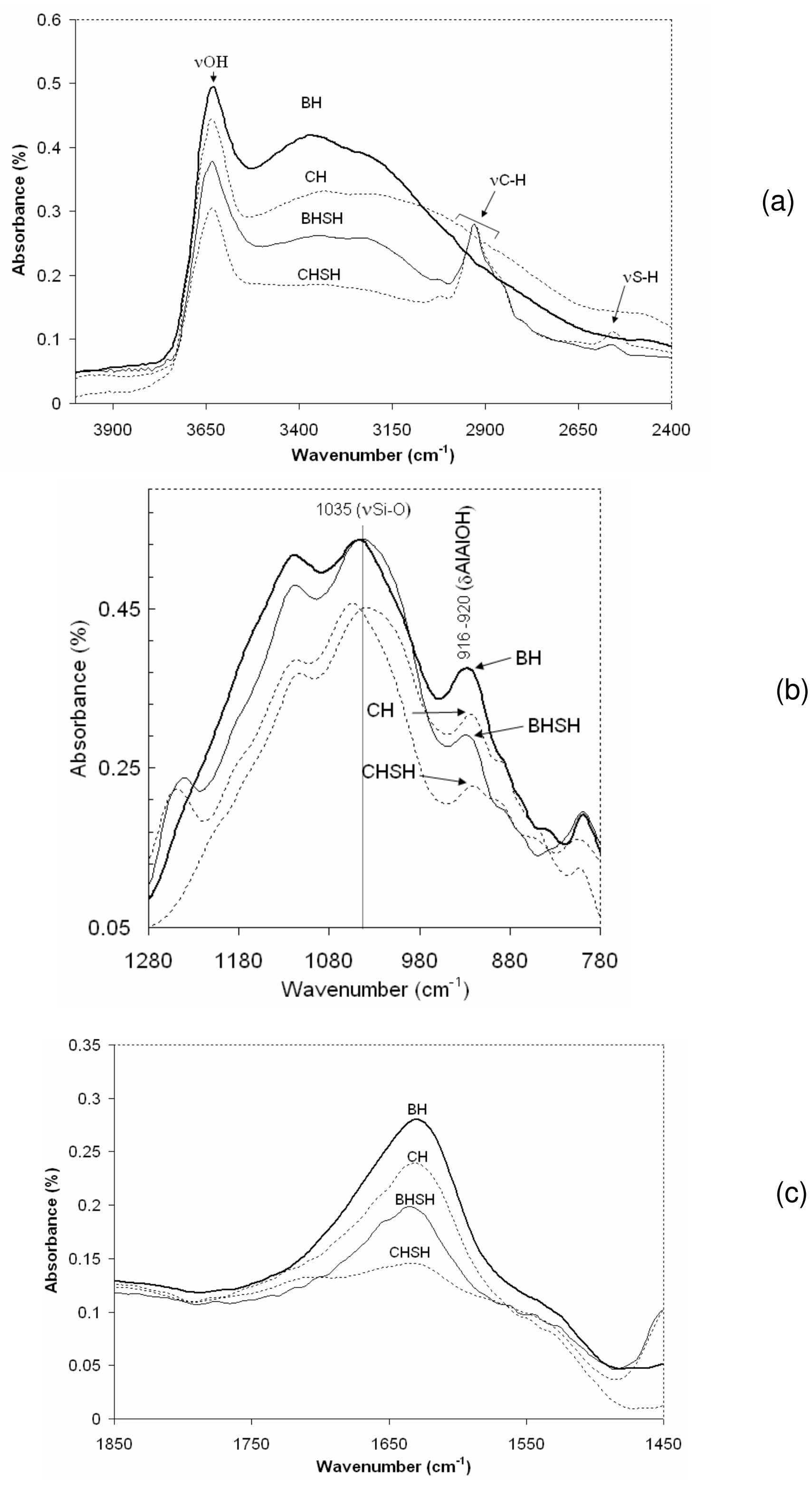
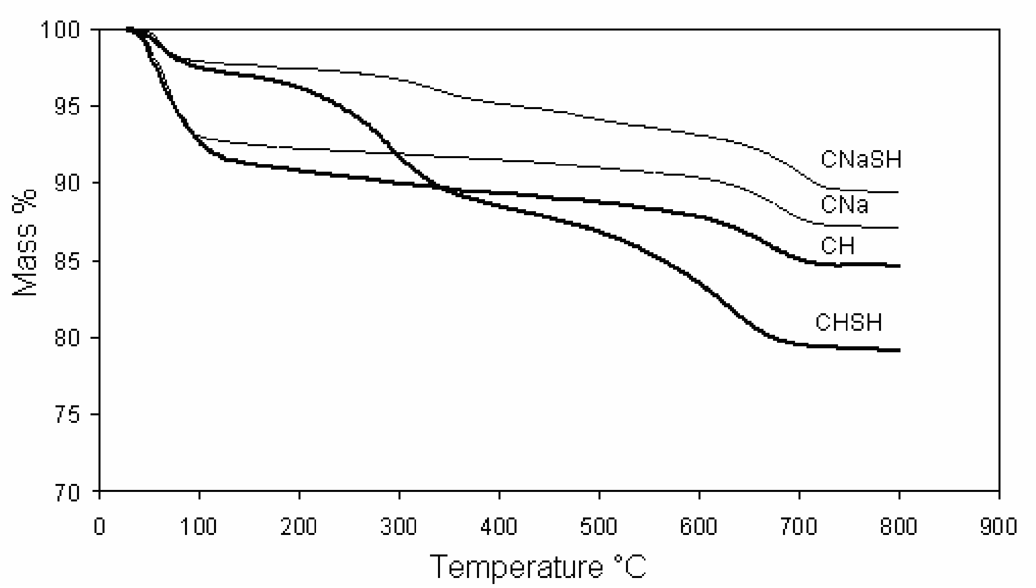


Figure 2.3 -DRIFT spectra of acid activated and functionalized samples.(a) 4000 -2400 cm^{-1}, (b) 1280 -780 cm^{-1}, and (C) 1850 -1450 cm^{-1}.

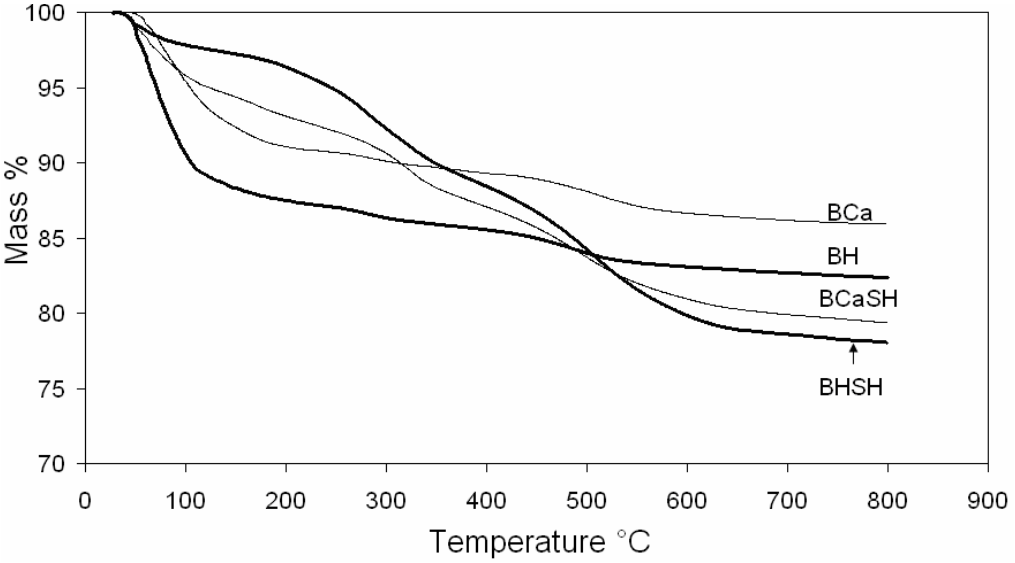
2.3.3 Thermogravimetry

Figure 2.4 presents the results of thermogravimetry. Each sample was heated from 30 ºC to 800 ºC. The unmodified CNa/CH samples (Figure 2.4a) and BCa/CH (Figure 2.4b) show two important events of mass loss. The first, within the temperature range of 30 °C to 200 °C, is due to a release of adsorbed water whereas the other, at temperature > 500°C is due to the dehydroxilation of the silicate sheets. It is interesting to note that the dehydroxylation event that happens at 667 °C (CH) and at 495 °C (BH) suggest that the reference sample presents higher thermal stability than the Brazilian sample. In contrast to the original clays, the functionalized samples present additional mass loss in the temperature range of 200 °C to 800 °C assigned to the decomposition of organic compounds. At 500 °C, there is the co-occurrence of the decomposition of the chemically bound silane and the dehydroxylation of the clay. The organic content was calculated by subtracting the mass loss assigned to hydroxyl groupd in the 200 °C – 800 °C interval.

The profile of mass loss shown in Figure 2.4 also shows the influence of acid activation on the grafting yield. It becomes evident that the acid activated samples (BHSH, CHSH) exhibit larger amounts of the immobilized Mercaptopropyl group. The good immobilization capacity of both clays is demonstrated by mass losses of 13.2% (1.76 mmol/g) and 10.9% (1.45 mmol/g) for the BHSH and CHSH samples, respectively, over a temperature range of 200 °C to 800 °C). Without acid pre-treatment, BCaSH and CNaSH exhibited low immobilization capacity 8.6% (1.15 mmol/g) and 2.8% (0.37 mmol/g), respectively. The acid activation step has improved the organic content in 50% and 290% for the Brazilian and the reference clay, respectively. These results support the hypothesis that acid activation creates more active sites for immobilization. The organic content of modified Brazilian clay were 21% and 207% higher than the values presented by the reference clay in acid activated and natural forms, respectively, despite the higher purity and, consequently, the higher montmorillonite content of the latter. It is interesting to note that the Brazilian clay, even in its natural form, exhibited good silane immobilization capacity. Our hypothesis to explain this result is the relatively high number of structural defects that produce susceptible sites to grafting. Previous literature has shown that the high grade of isomorphous substitution in octahedral sites (Fe and Mg for Al) can distort the structure and lead to the reduction of the crystalline order and structural imperfections (Stucki *et al.*, 2002). Since the Brazilian samples have high Fe content (as Fe_2O_3 + FeO ~10%, Table II.1), it can be concluded that these impurities can create active sites for grafting and thus constitute an advantage of the BCa over the CNa sample.



(a)



(b)

Figure 2.4 - TG curves for (a) natural and modified cloisite sample and (b) natural and modified Brazilian bentonite samples.

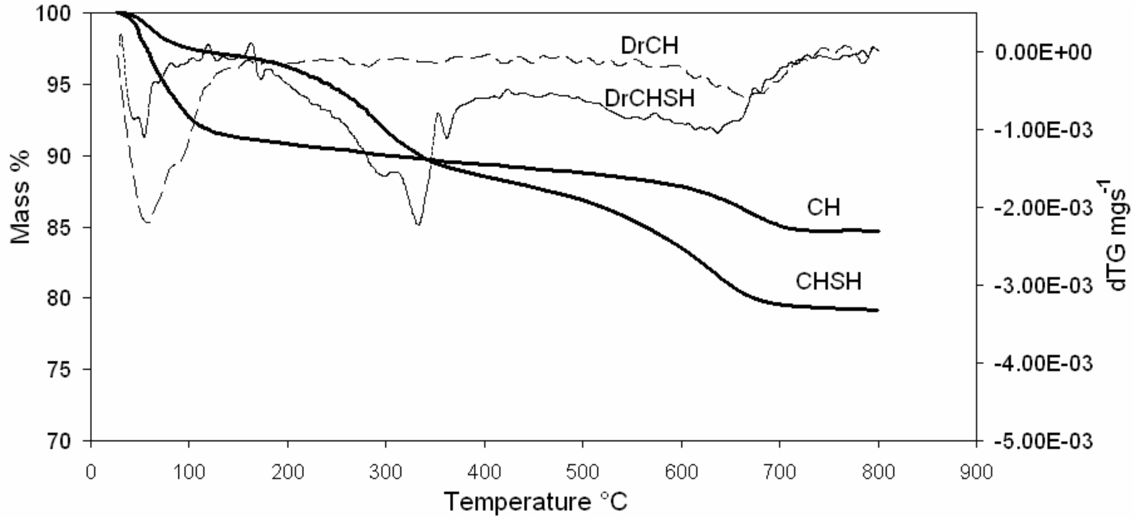
The relatively high specific surface area of the BCa sample is another point that favors the relatively higher immobilization capacity of the untreated BCa sample (Table II-3).

Figure 2.5 depicts mass loss and the peak of the first derivative. Similar curves were obtained for all samples and results were summarized in appendix II. All of the functionalized samples present additional mass loss in the temperature range of 200 ℃ to 400 ℃ followed by a more gradual loss between 400 ℃ and 600 ℃. Both of these events can be assigned to the loss of the grafted silane molecule. The first event was assigned to a more weakly bonded silane molecule (DTG peak around 285 ºC). The second was assigned to strong bonded molecules on the external surface and at the edge of crystals (DTG peak at approximately 330 ºC) whereas the last (DTG peak around 550 ℃) was assigned to strongly bonded molecules in the interlayer space. We assume that at higher temperatures (>500 ºC) there would be a mixed mass loss due to organic decomposition and clay sheet dehydroxylation, which is typical of organoclays.

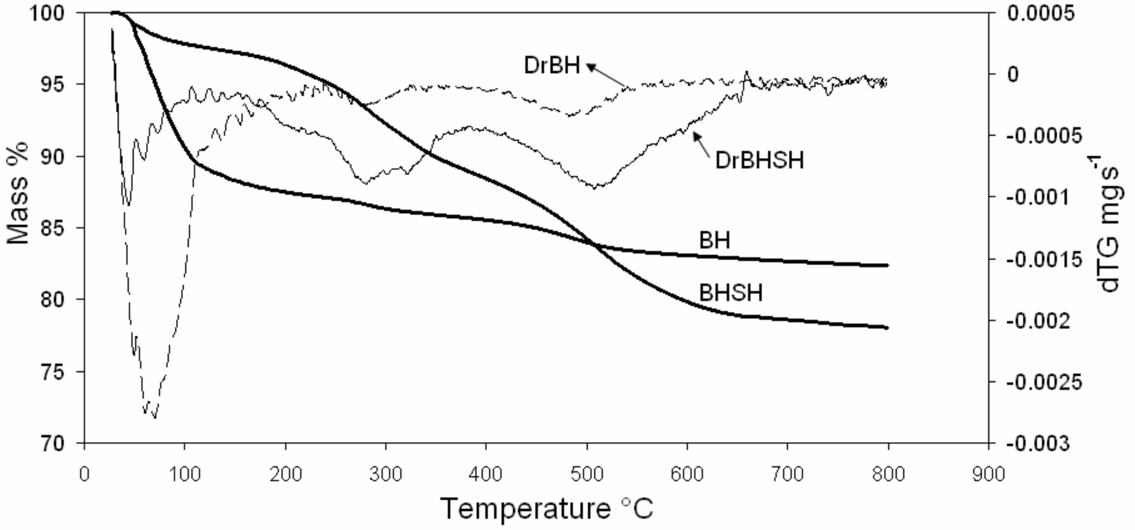
In both clays, the functionalization promotes an increase in hydrophobicity with the amount of functional group attached to the structure. One can observe a decrease in the adsorbed water from 9.2% to 2.90% for CH/CHSH samples and from 12.5% to 3.7% for BH/BHSH samples in the 30 ℃ – 200 ℃ range (Figure 2.5). Another evidence of hydrophobicity is that, unlike the hydrophilic natural bentonite, the functionalized clay was hardly suspended in water.

2.3.4 XRD analysis

Figure 2.6 shows the X-ray diffraction patterns of the Brazilian samples before and after funcionalization. The crystallographic structure of this clay is preserved even after the functionalization as no significant changes were observed in the characteristic basal spacing (d_{001}:~14.5 Å to 15.6 Å) after Functionalization. Normally, the intercalation of molecules in the interlayer region of a clay mineral causes significant changes in the interlayer distance (He *et al.*, 2005; Park and Kwon, 2004). TG analysis showed an important decrease of the amount of water in the interlayer region: from 12.5% to 3.7% in BH/BHSH samples in the 30℃ – 200℃ range (Figure 2.5). Normally, the decrease of water content in the interlayer region is followed by a significant decrease in d_{001} space to values of approximately 9.6 Å (Olphen, 1977; Mitchell, 1976). Taken into account that such reduction did not happen, our hypothesis is that there was a replacement of water molecules by organossilane in the interlayer region of the clay. In order to verify this hypothesis, samples of Brazilian clay were submitted to a thermal treatment at 130 ℃ for 24 h followed by DRX analyses. The results are shown in Figure 2.7.



(a)



(b)

Figure 2.5 - TG and DTG curves for the cloisite (a) and Brazilian (b) clay before and after functionalization.

After the heat treatment, the unfunctionalyzed samples (BCa and BH) showed an important decrease in the basal spacing (d_{001}) and broadness of the basal diffractions, typical of pure montmorillonite. This occurs due to a decrease in layer periodicity, which is related to the progressive loss of H_2O molecules in the interlayer region (Celis et al., 2000). It should be noted that the nearly collapsed structure of the BH sample (the d_{001} peak) almost disappeared. Conversely, the basal spacing of the functionalized samples remains practically the same. This provides further evidence of intercalation taking place in the interlayer galleries as organic molecules may act as a pillar between the clay sheets. The broadness of the (001) peak can be attributed to some stacking disorder of the functionalized sample or to the fact that some crystals remain ungrafted due to the unhomogeneity of the grafting process. The broadness of the (001) peak following a smectite-type clay modification has also been reported in previous literature (Liu et al., 2004; Celis et al., 2000).

Figure 2.8 shows the XRD pattern of cloisite samples. In this case, there was a clear increase in the average interlayer spacing (12 Å to 15.0 Å) after functionalization, which was ascribed to intercalation of organosilane in the interlamelar region. Further evidence of intercalation is the small adsorbed water content in interlayer region, as discussed before (Figure 2.5). In addition, there was a clear existence of a nearly collapsed d_{001}= 10.0 Å in the sample without acid activation (CNaSH). This result suggests that adsorbed water leaves the interlayer region and the intercalation does not occur. In this case the silylation is restricted to the edge of the clay particles.

By subtracting the thickness of the montmorillonte sheet (9.6 Å) from the observed d_{001} spacing (15.0 Å for the reference and 15.6 Å for the Brazilian sample), one may obtain a gallery height of 5.4 – 6 Å between the montmorillonite layers. This difference corresponds to the height of the mercaptopropyl group in the interlayer region, estimated at ~5 Å (Fonseca and Airoldi, 2000). In summary, the DRX patterns have shown that all the samples submitted to acid activation process followed by modification with MPTS were intercalated. The Brazilian bentonite was also intercalated in its natural form with calcium as the interlayer cations.

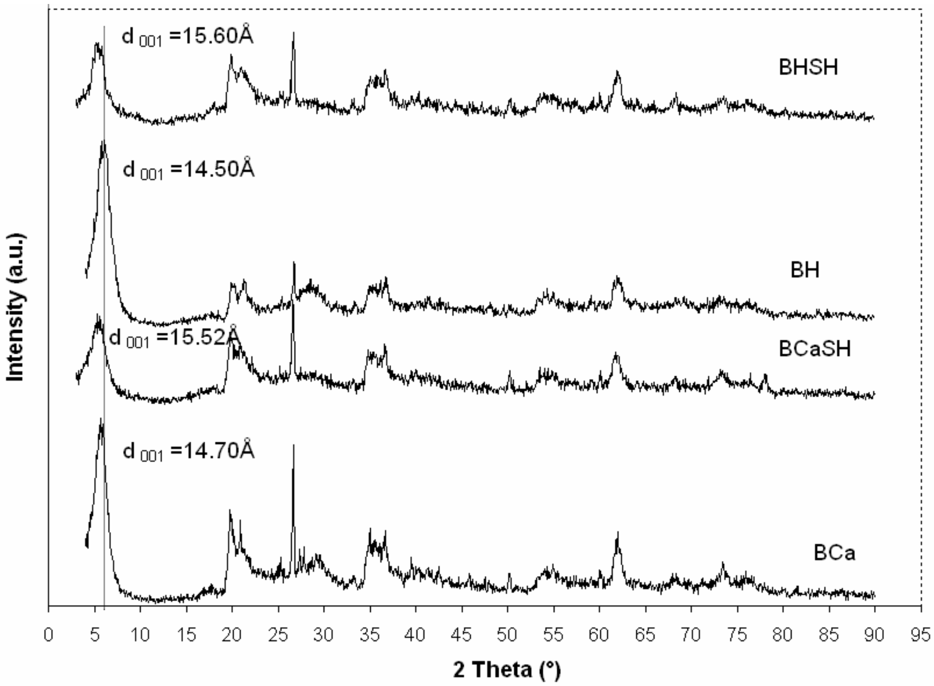
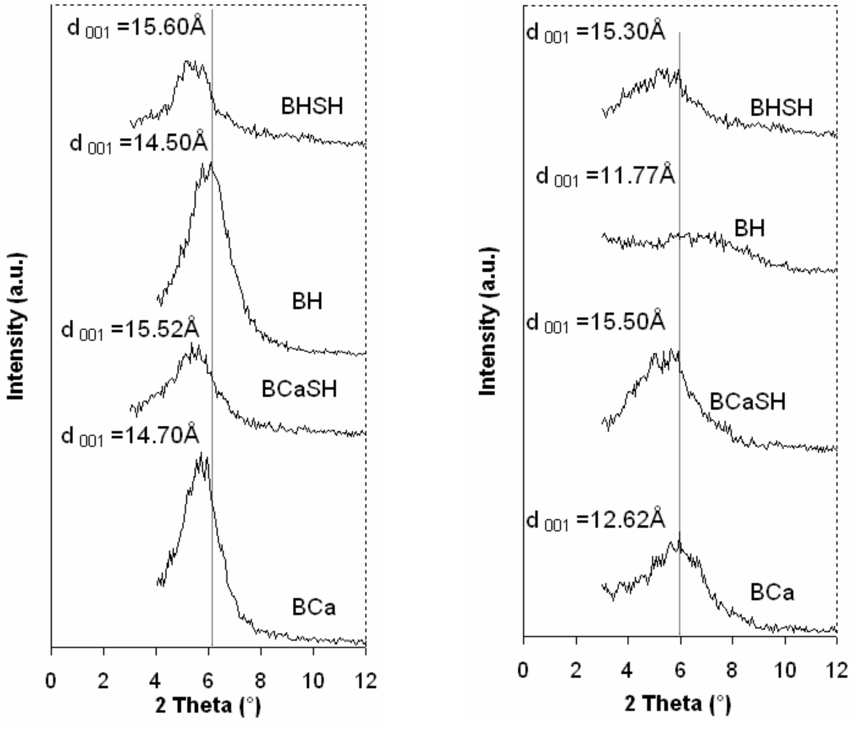


Figura 2.6 - DRX pattern of the Brazilian samples before and after functionalization.



(a) (b)

Figura 2.7 - DRX pattern Brazilian samples (a) room temperature, (b) after having been heated at 130 °C for 24 h.

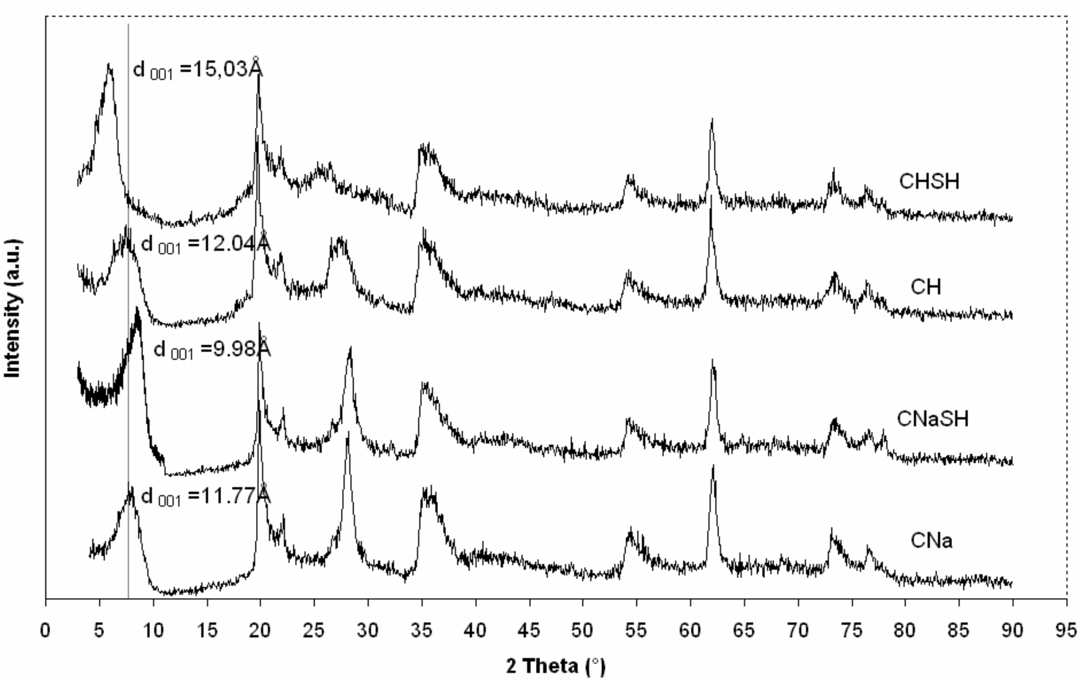


Figura 2.8 - DRX pattern of the Cloisite samples before and after functionalization.

2.3.5 Porosity analysis

Figure 2.9 depicts typical nitrogen adsorption-desorption and pore size distribution for cloisite and Brazilian bentonite samples before and after modification. Table II.3 summarizes the results. The isotherms for the raw samples (BCa and CNa) are characteristic of type IV. The hysteresis curves are associated with slit-shaped pores, or the space between parallel plates, indicating a mesoporous structure with a contribution of micropores (Lowell and Shields, 1991). The most dominant pores are found in the 2-10 nm range for both clays. These results are in agreement with the adsorption data previously reported for similar layered silicates (Okutomo *et al.*, 1999; Maes *et al.*, 1997). Significant changes in nitrogen adsorption-desorption were observed upon acid treatment and grafting with organosilanes. The results indicated that both the specific surface area and pore volumes were increased after acid activation and drastically decreased after functionalization. The micropore contributions were suppressed and mesopores decreased after functionalization.

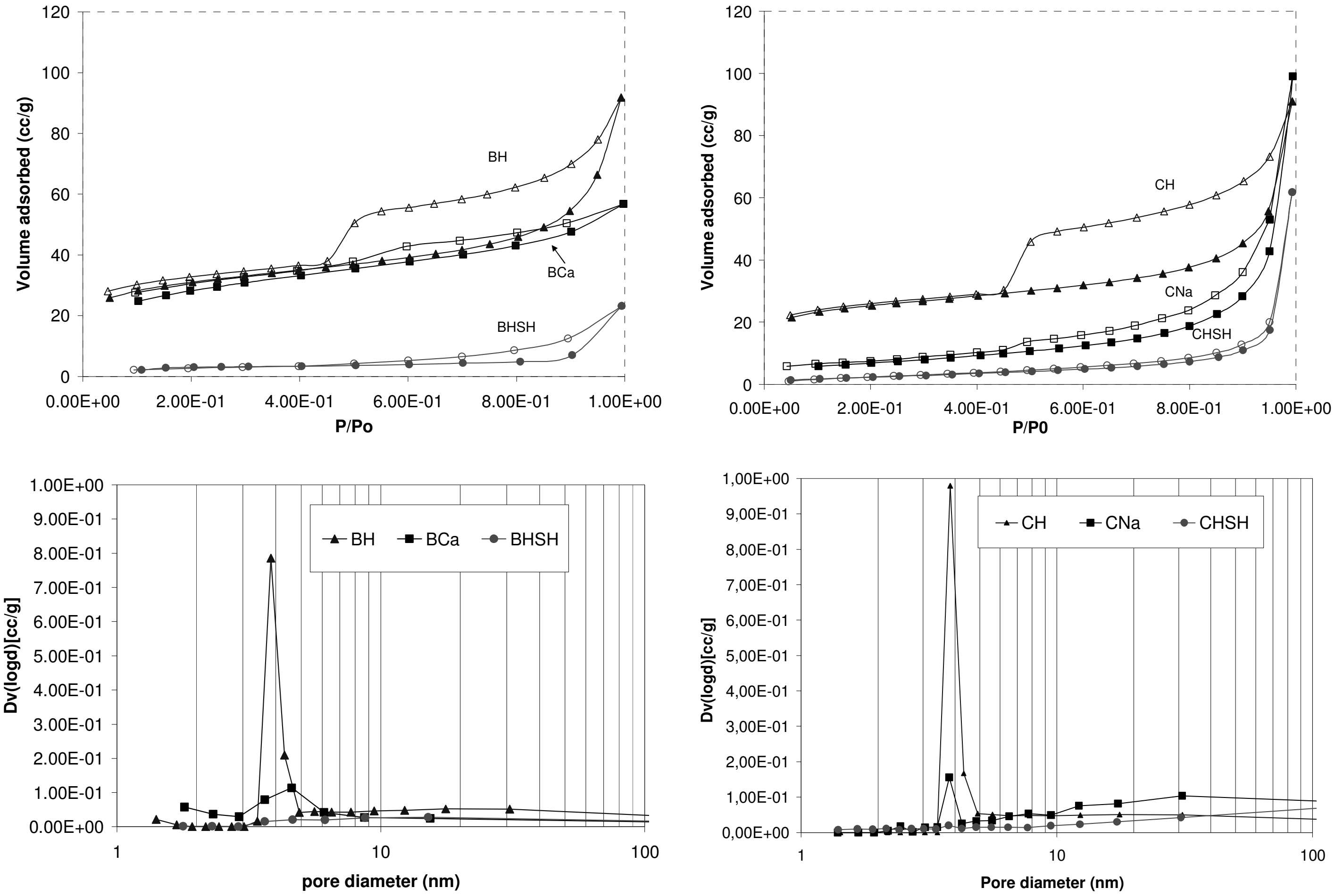
Distinct differences in the shape of the isotherms for BCa and CNa samples were observed (Table II.3). Even in its natural form, Brazilian bentonite shows a higher porosity and surface area (82 m^2/g) than the CNa sample (25 m^2/g). This fact can partly explain the better organosilane immobilization by the BCaSH sample. The acid activation improves the grafting efficiency by increasing the specific surface area and the density of superficial hydroxyl groups. The specific surface area increases from 82 m^2/g to 93 m^2/g in the Brazilian clay and from 25 m^2/g to 80 m^2/g in the cloisite sample.

The funcionalized samples of CHSH and BHSH present similar isotherm shape and specific surface area (~10 m^2/g). The increase of the average pore diameter is due to the reduction of microporous contribution. Some pore space may have been occupied or blocked by the grafting agent. Similar findings were reported by Mercier and Pinnavaia (1998) in the functionalization of porous clay heterostructure and by Walcarius *et al* (2002) with amorphous silica gels grafted with amine and thiol groups.

Table II.3: Effect of the functionalization on the porosity of the clay samples

Sample	S_{BET} (m^2/g)	S_{micro} (cm^3/g)	V_{micro} (cm^3/g)	V_P (cm^3/g)	$D_{p(average)}$ (Å)
BCa	82	22	0.0124	0.080	39
BH	93	23	0.0126	0.089	38
BHSH	11	0	0	0.036	135
CNa	25	1	0.005	0.054	126
CH	80	38	0.0207	0.141	71
CHSH	10	0	0	0.095	393

Surface Area (S_{BET}), Micro Pore Surface Area (S_{micro}), Average Pore Diameter (D_P), Total Pore Volume (V_p), t-Method Micro Pore Volume (V_{micro}), BJH Method Adsorption Pore Diameter.



(a) (b)

Figure 2.9 - (a) N_2 adsorption/desorption isotherms (solid symbols: sorption and empty; desorption) and porous size distribution of Brazilian bentonite.(a) and the reference sample (b) .

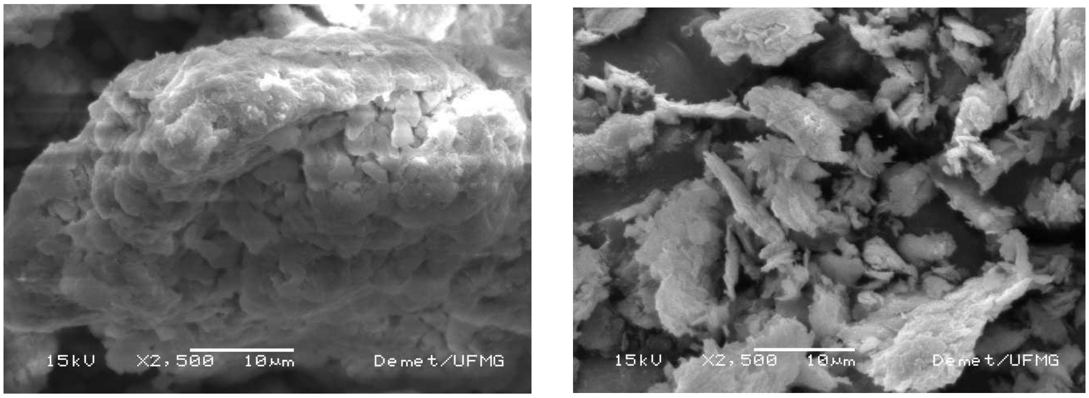
2.3.6 SEM analysis

Figure 2.10a and Figure 2.10c show SEM micrographs of the natural clay samples. One may observe particles formed by large agglomerates of irregular shapes. The strong tendency toward aggregation and the compact aspect of the material can also be observed. Figures 2.10b and 2.10c display the SEM micrographs of the functionalized clay. In these cases, the particles are apparently smaller in size and are constituted of disordered, thin sheet particle aggregates. One can conclude that functionalization promotes the formation of disordered and less cohesive aggregates, probably due to a reduction of the edge-to-edge and face-to-face interactions. Unlike the hydrophilic CNa and BCa samples, which formed large size aggregates after drying, the functionalized samples were hardly dispersed in water (hydrophobic) and easily kept as a powder after drying. This change constitutes an important advantage considering commercial applications.

2.3.7 Binding capacity of the mercaptyl functional groups

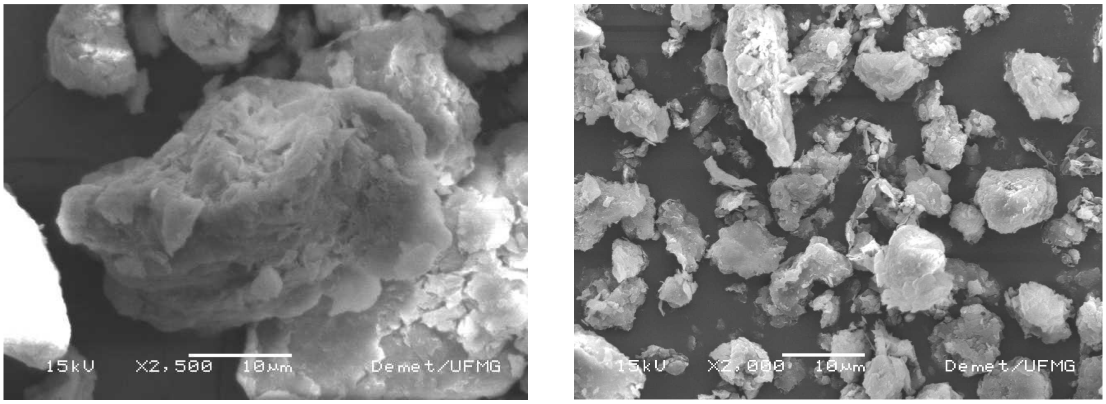
Following functionalization, the binding capacity with respect to silver ions was measured according to a protocol based on the Volhard method. It is important to emphasize that this protocol is, for the first time, applied to functionalized inorganic substrate. Table II.4 shows that the unmodified clay samples (BCa, BH, CNa and CH) adsorb silver ions in negligible amounts (0 - 0.08 mmol/g). Even though the original samples show a very low affinity for silver ions, some ion immobilization may have occurred due to a cation exchange mechanism. The functionalized samples demonstrate high affinity towards Ag^+. The binding capacity of the samples with the highest organic content (BHSH and CHSH) was very similar (~1 mmol/g of clay).

The results of Table II.4 suggest that the mechanism of adsorption involves primarily silver ion complexation by the thiol groups instead of cation exchange. The reduction of the SH stretching band in the DRIFT spectra of the modified clay (Figure2.11) demonstrates that the mechanism of adsorption involves silver ion complexation by the thiol group. It is important to emphasize that the thiol groups immobilized in clay structures are very stable and no pre-treatment step was necessary before uptake experiments. The samples that presented larger organic content also presented larger silver uptake (Table II.4), thus meaning that the Volhard method was capable and sensitive enough to classify the samples regarding their binding capacity. More importantly, it provides the possibility of inferring the amount of immobilized organic in a fast and simple way.



(a) CNa

(b) CHSH



(c) BCa

(d) BHSH

Figure 2.10 - MEV micrographs of clay samples

Table II.4: The binding capacity (Volhard method) and amount of ligand grafted.

Clay samples 1	Binding capacity (mmol/g)	Ligand (mmol/g)*	Ag/S Molar ratio**	Clay Samples 2	Binding capacity (mmol/g)	Ligand (mmol/g)*	Ag/S Molar ratio
BCa	0.08 ± 0.05	-	-	CNa	0.08 ± 0.03	-	-
BH	0.06 ± 0.03	-	-	CH	0	-	-
BCaSH	0.85 ± 0.10	1.15	0.75	CNASH	0.34 ± 0.10	0.38	0.90
BHSH	1.03 ± 0.15	1.76	0.60	CHSH	1.05 ± 0.14	1.45	0.70

(*) Calculated from TGA analysis in the 200℃ - 800℃ range, subtracting the mass loss assigned to the hydroxyl group in the 200 ℃ -800℃ interval; (**) Calculated from the ratio of binding capacity and ligand content.

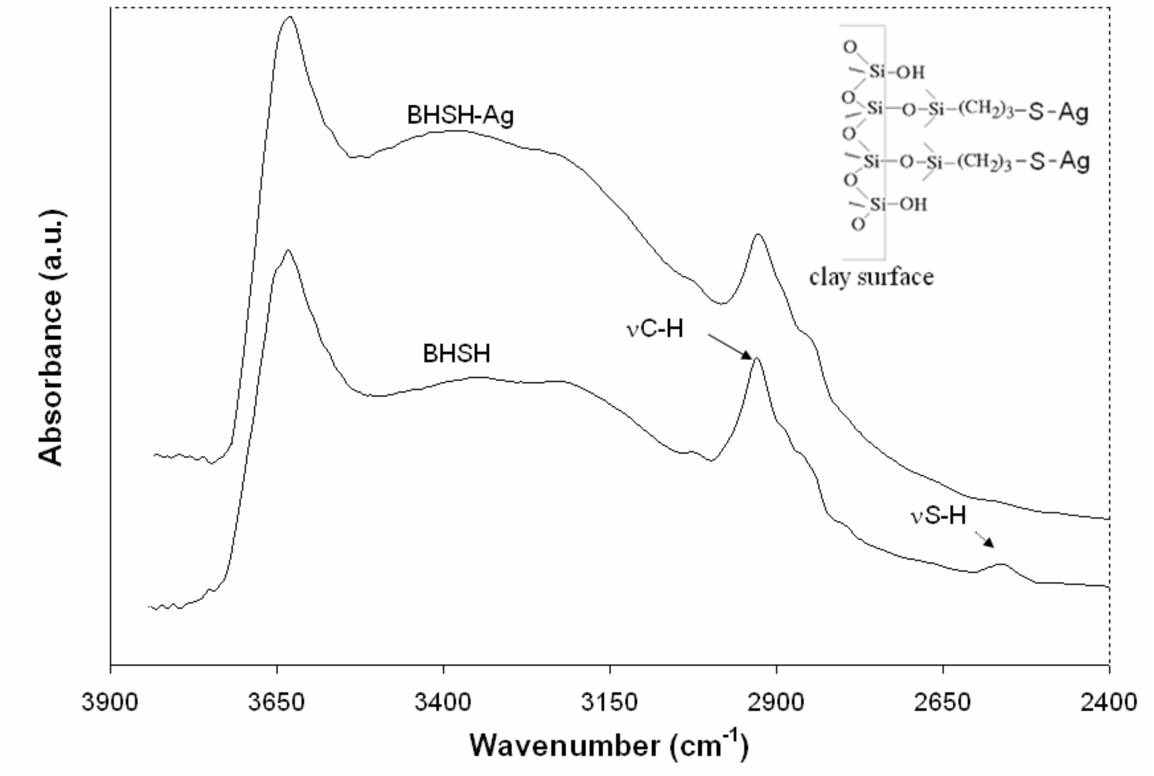


Figure 2.11 - DRIFT spectra of BHSH samples before and after silver ion adsorption.

The accessibility to the grafted functional group was inferred by the molar ratio Ag/S (Table II.4). It is possible to observe that accessibility varies from 60% to 75% and from 70% to 90% for the Brazilian and the cloisite samples, respectively. Higher organic content results in smaller accessibility. Mercier and Detellier (1995) reported loadings corresponding to less than 10% of the total number of thiol groups in the adsorbent. These authors attributed the relatively low loading to the blockade of pore space by intercalated molecules. An improvement of the previous result was later reported by Mercier and Pinnavaia (1998) who prepared porous functionalyzed clay through a sophisticated route, in which heterostructures were obtained by self assembly of framework silica within the galleries of fluorohectorite. The authors found that 67% of the thiol groups were accessible for Hg(II) ions trapping. This result is similar to that reported by Celis *et al.* (2000) for MPTS-sepiolite. The amount of ligand grafted in the BHSH and CHSH samples are comparable to the values obtained by Walcarius *et al.* (2002). These authors have reported a grafting efficiency of 1.0–1.5 mmol of mercaptopropyl per gram of amorphous silica gels of chromatographic grade using a modification route which is very similar to that used in the present work. According to these authors, the accessibilities varied from 57% to 95% with respect to Hg(II) species using different types of gels, dependent mainly on pore diameter. Results from other works are summarized in Table II.5. The present work describes the preparation of material from low cost clay. This new material shows a binding capacity comparable to the functionalized silica, which therefore indicates its positive potential as an adsorbent.

2.3.8 Elemental analysis

Elemental semi-quantitative analyses provided by EDS were also used to quantify the percentage of immobilized thiol groups effectively involved in a silver ion complexation and to assess the stability of the functionalized clay. The results are summarized in Table II.6. The percentage of the Si/Al atomic ratio of the pair of samples BCa/BH and CNa/CH was slightly varied, thus indicating that no release of Al from the clay lattice occurred after acid treatment. The increase in the atomic percentage of the Si/Al ratio in the functionalized sample is related to the incorporation of the organosilane molecule. The improvement in the amount of organosilane molecule immobilizations by acid activation can be observed by the Si/Al, S/Si ratios. These results corroborate those of Table II.4. It is important to notice that the S/Si and S/Al ratios of all functionalized samples are practically the same after Ag^+ adsorption. This indicates that the SH groups were not leached from the structure during the adsorption process and provide strong evidence of the good stability of the obtained material. According to the Ag/S atomic ratio obtained from the EDS analysis (Table II.6), 51% to 65% of accessibility for BHSH-Ag and CHSH-Ag, respectively, was found.

Table II.5: Thiol functionalized materials

Material	Thiol content (mmol/g)	Accessibility (%)	Modifier	Reference
SWY-1montmorillonite	3.2	< 10 (Hg(II))	CPTMS + NaSH.XH$_2$O	Mercier and Detelier, 1995
Heterostructure: fluorohectorite/silica	1.10	67 (Hg(II))	MPTMS	Mercier and Pinnavaia, 1998
Sepiolite	0.83	67 (Hg(II))	MPTMS	Celis *et al.*, 2000
Silica gel	1.0 – 1.5	57 - 95 (Hg(II))	MPTMS	Walcarius *et al.,* 2002
Mesoporous silica molecular sieves	0.57 – 1.5	61 - 100 (Hg(II))	MPTMS	Pinnavaia and Mercier, 1998
Silica – sol gel (co-condensation)	2.1	40 (Cu(II))	MPTMS	Bois *et al.,* 2003
Brazillian montmorillonite	1.15 – 1.76	60 - 75 (Ag$^+$)	MPTMS	Present work

MPTMS- 3- mercaptopropyltrimethoxysilane, CPTMS - 3-choropropyltrimethoxysilane; Metals in ( ) correspond to de metal ions used in adsorption experiments.

The high accessibility for the sample CNaSH-Ag (Ag/S ~1) is due to the small amount of organosilane immobilization. These results are in agreement with those obtained through TG analysis and the Volhard Method (Table II.4).

Finally, it can conclude that the binding capacity increases with the amount of silane molecules immobilized in clay structures while the accessibility decreases. This effect can be attributed to the blockade of pore space by the intercalated molecules. Pore congestion resulting from the high density of mercaptopropyl in the clay structure contributes to a decrease in the accessibility of reactants to the binding sites resulting in decreased adsorption efficiency.

TableII.6: EDS Semi-quantitative analysis for clays samples

	Atomic % ratio			
Samples	**Si/Al**	**S/Al**	**S/Si-**	**Ag/S**
BCa	3.12			
BH	3.14		-	
BCaSH	3.50	0.66	0.19	-
BCaSH–Ag	3.57	0.68	0.18	0.65
BHSH	3.72	0.78	0.21	-
BHSH–Ag	3.81	0.78	0.21	0.51
CNa	2.70			
CH	2.74			
CNaSH	2.81	0.12	0.074	
CNaSH-Ag	2.79	0.14	0.065	1.01
CHSH	3.40	1.16	0.34	
CHSH-Ag	3.41	1.12	0.33	0.65

BCaSH – Ag, BHSH – Ag, CNaSH-Ag, CHSH-Ag indicate the functionalized clay after silver adsorption.

2.3.9 Adsorption of cadmium

Adsorption experiments have been performed to highlight the possible use of grafted clays for heavy metal removal from dilute solutions. Cadmium was selected as a case study due to its high toxicity to animals and humans. The stability area of the ion Cd(II) is shown in Figure2.12. At 25 °C with a metal concentration of 0.01 mol dm^{-3}, the soluble cadmium cation remains stable over a wide pH range (pH 0-8). At pH >8 the metal precipitates as $Cd(OH)_2$. The adsorption experiments were carried out in a pH range of 3.5 to 6 and a concentration of 45 mg/L (4.0×10^{-4} mol dm^{-3}), appropriate conditions to avoid the hydroxide precipitation.

Figure 2.13 shows the effect of pH on the adsorption of cadmium ions by the natural and modified clay samples. The inset demonstrates that Cd^{2+} uptake by both clay samples is a fast reaction as equilibrium is reached within two h for the functionalized clay and within approximately 30 minutes for the natural clay. The presence of thiol groups in the clay structure improved the adsorption capacity. The maximum uptake capacity was 44 mg/g (0.41 mmol/g) and 17 mg/g (0.15 mmol/g) for the functionalized and natural clay, respectively, at pH 6 (160% higher). A thiol-functionalized silica prepared through co-condensation of tetraethoxysilane and MPTMS adsorbed 22.4 mg/g of cadmium (Bois *et al.*, 2003). Mercier and Detellier (1995) reported loadings corresponding to 31 mg/g of cadmium ions by functionalized montmorillonite (SWY-1 type) with (3-chloropropyl)methoxysilane and subsequent treatment with $NaSH.XH_2O$. According to these authors, the thiol functionalized material was a more effetive adsorbent for Hg(II) and Pb(II) and less effective towards Cd(II) and Zn(II).

For both clay samples, the amount of cadmium adsorbed increases with the increase of pH. However, while the adsorption in natural clay presented a slight pH-dependence, the adsorption in the modified clays showed a strong pH-dependence in the 3.5 – 6 pH interval. These differences can be explained by the mechanisms involved in the two cases. The main mechanism of adsorption in the raw clay is by a cation exchange, which is little affected by pH under condition of low ionic strength (Strawn *et al.,* 1999). For the functionalized clay, a proposed mechanism involves the complexation of the ion Cd (II) by the thiol (-SH) group and the release of H^+ ions to solution as shown in the equation (2.4):

$$Cd^{2+} + 2R\text{-}SH \longrightarrow R\text{-}S\text{-}Cd\text{-}S\text{-}R + 2H^+ \qquad (2.4)$$

Evidence for the mechanism described above is includes the reduction of pH values during cadmium uptake observed for all the tests using the modified clay. The affinity of the SH-modified clay towards Cd^{2+} ions can be explained by the Lewis acid–base theory. The Cd(II) is a soft Lewis acid, thus it should bind strongly to thiol groups, which is a soft Lewis base. The formation of CdS bonds is expected to significantly improve the stability of the pollutant inside the silicate layer (Merrifield et al., 2004). Therefore, this new material may be an alternative for the separation and pre-concentration of metals with affinity by thiol groups such as Ag, Hg, Au, Cd, Pb, Cu, and Zn.

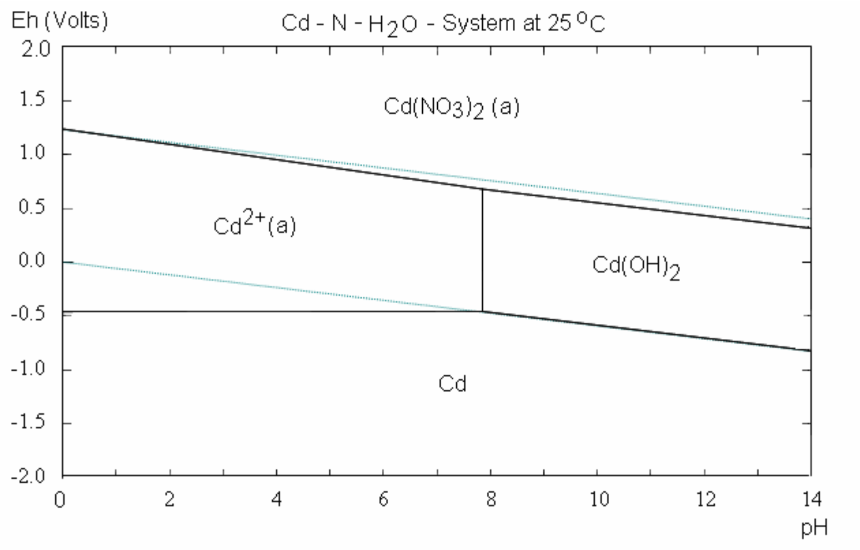


Figura 2.12 - Stability diagram of cadmium ion in aqueous media. Region of stability and stability boundaries for Cd-N-H_2O system Cd(II)/NO_3^- ion at 10^{-2} mol/L, 25 ℃. Obtained by HSC-Chemistry version 4.0.

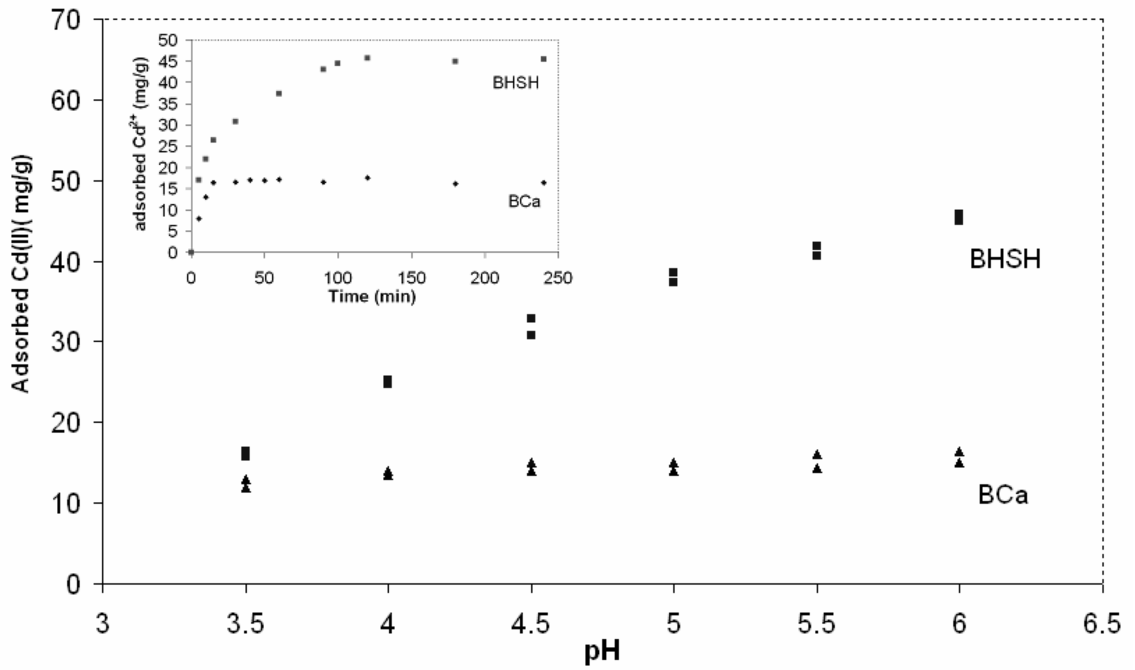


Figure 2.13 - Effect of the initial pH on the cadmium ions adsorption by natural- BCa (▲) and modified bentonite-BHSH (■). Conditions: 100 mg of dried clay, 50 cm^3 of Cd^{2+} solution at an initial concentration of 45 mg/L, over 6 h, at 25 ºC, 150 rpm. Inset shows kinetics study at pH 6.

2.4 CONCLUSIONS

The present study showed that a thiol-functionalized clay can be prepared in a simple and reproducible manner. The route was shown to be an effective means through which to prepare functional inorganic-organic nanostructured materials. The grafting the Brazilian bentonite clay with (3-mercaptopropyl)trimethoxysilane was found to be quite efficient and comparable to the well-known cloisite sample. Organic loading of 1.76 mmol/g and 1.45 mmol/g of clay have been achieved for the Brazilian and cloisite samples, respectively. This work emphasizes the crucial role played by the acid pre-treatment. The highest mercapto group content was ascribed to the acid activated sample. The functionalized clays displayed good binding capacity properties for Ag+ species (~1 mmol/g) in comparison to those obtained using ungrafted raw materials (~0.1 mmol/g). The accessibility to the reactive centers varied from 60% to 75% for the functionalized Brazilian bentonite depending on the organic content. As expected, both the specific surface areas and pore volumes decreased significantly upon grafting. Analyses by XRD and TG also showed that silylation changes the basal spacing and drastically reduces adsorbed water. These results indicate that intercalation occurred in the interlayer galleries as well as on the external surface of the clay particles. The DRIFT results confirmed the presence of thiol groups and organic compounds in the modified clay. The DRIFT results also provide evidence about the mechanism involved in the grafting process according to the differences in OH stretching band intensities. Regarding cadmium ion uptake, it was observed that the functionalization improved the affinity of the clay towards this metal ion. At pH 6, adsoprtion capacities of 17 mg Cd/g (0.15mmol/g) and 44 mg Cd/g (0.41mmol/g) were determined for the natural (BCa) and functionalized (BHSH) bentonites, respectively. The protocol developed based on the Volhard method proved to be a quick and efficient method for the binding capacity determination of a thiol functionalized substrate. Finally, the present work shows that the adsorption capacity of natural clays can be enhanced by surface modification using organo-functional silane coupling agents. This chemical modification may be a useful tool for the preparation of new adsorbents with high binding capacity and selectivity towards some metal ions, therefore with good potential for separation and pre-concentration purposes.

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CAPÍTULO 3

TAYLOR-MADE HYBRID MATERIAL FOR AS(III) SPECIATION AND IMMOBILIZATION

Abstract

This work describes the functionalization process of laponite through the grafting of (3-mercaptopropyl)trimethoxysilane (MPTMS). Laponite is a synthetic smectite clay with a surface area of 326 m^2/g. Infrared spectroscopy and elemental analyses confirmed the presence of organic chains and thiol groups in the modified clay. The immobilized and available thiol group reached a total of 1.16 meq/g of clay, with approximately 100% of this group accessible for Ag^+ trapping. Adsorption experiments demonstrated the strong affinity of thiol modified clay to As(III). The highest loading capacity (22.3 mg/g), as well as maximum arsenic speciation, occurred at pH5, where the trivalent species are present in their neutral form, H_3AsO_3. The involvement of thiol groups in As(III) adsorption was clearly indicated by the vibrational modes of As-S bonds combined with the reduction of the S-H band intensity evidenced by Raman spectra. DRIFT and Raman techniques were successfully used to assess the clay's structural changes, following chemical modification and upon As(III) adsorption. The results obtained in the present work showed that the thiol functionalized clay is a novel effective sorbent for selective As(III) immobilization.

Keywords: laponite, mercaptosilane, arsenic adsorption, Raman spectroscopy, Infrared spectroscopy

3.1 INTRODUCTION

Organosilanes have been employed for modifications of layered silicates, with natural smectites being the most commonly tested clays in functionalization processes (Frost and Mendelovici, 2006; He *et al.*, 2005; Park and Kwon, 2004; Mercier and Detellier, 1995). Organoclays produced from synthetic clay have also been studied for various applications. These include (i) the preparation of modified electrodes for electrochemical applications and (bio) sensors (Moust, 2004; Coche-Guérente *et al.*, 1998), (ii) the immobilization of several enzymes (Tietjen and Wetzel, 2003), (iii) the immobilization of catalysts (Kuzniarska-Biernacka *et al.*, 2005), (iv) the immobilization of antifungal compounds (Park *et al.*, 2004), and (v) the preparation of polymer/laponite nanocomposites (Herrera *et al.*, 2006).

In chapter 2, the functionalization of a natural smectite clay with mercaptosilane as a modifier is discussed. It was demonstrated that the accessibility to the reactive centers ranges from 60% to 75% depending on the organic group content. In the present chapter, a synthetic clay named laponite was functionalized using the same route used in chapter 2. This work was aimed at obtaining a more porous hybrid material with high accessibility to active sites, in addition to elucidating the effect of clay minerals on the microstructure of the grafting products. Moreover, some applications (biomolecule adsortion, chromatography, medicine immobilization) request inorganic matrices with a high grade of purity; in these cases, synthetic clays are more appropriate than natural clays.

Surface modification is a key step concerning the application of clays in biotechnology. One of the main obstacles hindering these applications is the interaction of organic molecules with the acid and hydrophilic clay surface, which in turn may cause the denaturation of enzymes (Tietjen and Wetzel, 2003). This limitation can be overcome by passivating the acid surface sites and creating a more organophilic clay matrix with different functionalities. In appendix 1, the authors proposed the surface modification of synthetic clay aimed at biomolecule adsorption (Guimarães *et al,* 2007). The characterization results showed that the grafting of mercaptosilane converted the high hydrophilic surface of laponite to a more hydrophobic and organophilic surface**.**

Laponite is a synthetic smectite clay and has a layered structure of a dioctahedral phyllosilicate that closely resembles the natural clay mineral hectorite in both structure and composition (Figure 3.1). It can be described by the chemical formula of $Na_{0.7}$ [$(Mg_{5.5}\ Li_{0.3})$ $Si_8\ O_{20}\ (OH)_4$] (Prado *et al.* 2005).

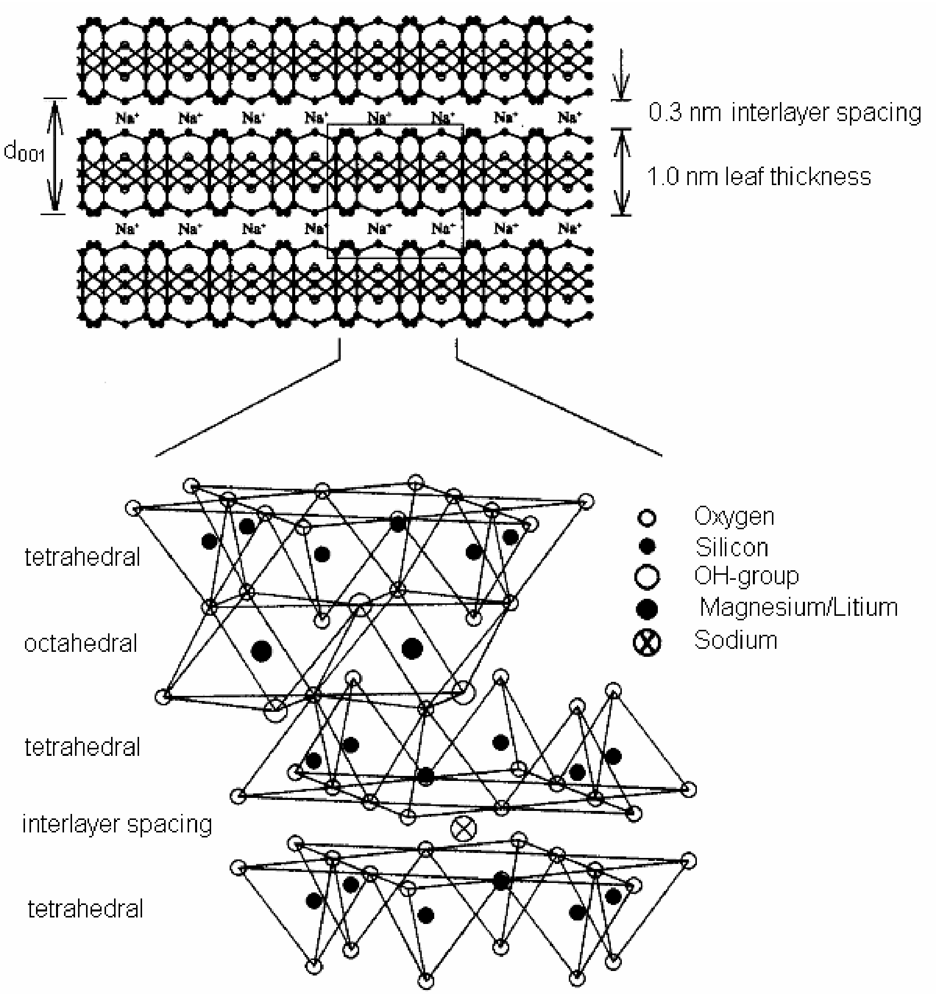


Figure 3.1 – Schematic representation of the laponite structure. The area in the box is depicted magnified in the lower plot. There are sodium atoms in the basal spacing and the Magnesium in octahedral sites. The d_{001} correspont to the basal spacing reflection measured by X ray diffraction (Koon, 1998).

This clay is made up of regular crystallites of a small size and specific surface area of approximately 326 m^2/g. Each single-particle is a crystalline disc with an average radius of 20 nm and a thickness of 1.0 nm.

It is possible to observe that each mineral leaf is generated by a combination of tetrahedral and octahedral sheets (Figure 3.1). The stacking of tetrahedral and octahedral sheets leads to the formation of the 2:1 layer silicates. The tetrahedral sheet of laponite is composed of corner-linked tetrahedrons, with Si^{4+} as the central ions. The basal oxygen of a tetrahedron is shared by the neighboring tetrahedron, forming a hexagonal pattern. Thus, the crystal lattice of 2:1 phyllosilicate consists of 1 nm thin layers, with an octahedral sheet containing magnesium as the central atom sandwiched between two tetrahedral silica sheets. Replacement of Mg^{2+} by Li^+ in the octahedral sheet produces negatively charged layers. This negative charge is balanced by the sodium ions (Na^+) in the interlayer space. The gallery height of this clay depends on the degree of hydration of the interlayer cations. The cation exchange capacity (CEC), expressed as meq/100 g clay is used to characterize the degree of isomorphous substitution (Mg^{2+} by Li^+) in the octahedral sites (Koon, 1998; Tjong, 2006).

In this work a detailed material characterization was provided by chemical analysis (EDS), thermogravimetry (TG), and X-ray diffraction (XRD). Emphasis was given to the diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) and Raman spectroscopy. Infrared (IR) spectroscopy has been for decades a frequently used method to investigate the structure, bonding, and chemical properties of clay minerals (Madejová, 2003; Farmer, 1974). This technique is also the most widely used to characterize organoclays as it permits the identification of the functional groups immobilized onto the clay structure (Frost and Mendelovici, 2006; He *et al.*, 2004; Madejová, 2003; Akyuz *et al.*, 2000). However, for clays modified with mercaptosilane, there is a restriction. Unlike the oxygen–containing compound, the equivalent C-S and S-H stretching vibrations tend to give rise to very weak absorptions in the infrared spectrum. Conversely, the C-S and S-H bonds are highly polarizable, and hence produce stronger spectral activity in the Raman spectrum than the infrared spectrum (Coates, 2000). Raman spectroscopy has been extensively used for the investigation of protein backbone conformations, disulfide bond conformations, and the local microenvironment of certain functional groups (Tu, 2003; Qian and Krimm, 1992). There are few reports in the literature on Raman spectra of clays due to high fluorescent backgrounds, which is normally associated with conventional dispersive Raman spectroscopy (Frost and Rintoul, 1996). Most published studies are devoted to the investigations of the OH stretching modes of limited mineral groups (Wang *et al.* 2002). However, previous studies have assured that Raman spectroscopy is particularly useful in the investigation of clay-organic interaction (Frost and Mendelovici, 2006; Akyuz *et al.*, 2000). Based on these considerations, we decided to use the Raman spectroscopy as a characterization tool for clay functionalized with thiol group. This technique was not used in chapter 2 due to the high fluorescence backgrounds presented by the thiol modified montmorillonite.

In this work, adsorption experiments have been performed to highlight the possible use of grafted clays for arsenic species from dilute solutions. Arsenic was selected as a case study due to its very high toxicity as well as to its affinity to SH groups in specific conditions. The modified clays reported in previous publication (Guimarães *et al.,* 2007) and chapter 2 of this thesis have demonstrated the good adsorptive properties of the thiol modified clay towards cadmium and silver ions. In the present study, the aim was to test the ability of functionalized clay with respect to arsenic species that present a more complex speciation in an aqueous system.

Teixeira and Ciminelli (2005) have demonstrated the accentuated affinity of thiol groups toward As(III). These authors have also demonstrated that a cysteine-rich biomass was highly selective for arsenic removal in its trivalent form and is also appropriate for the treatment of arsenic-containing solutions. The thiol reduced group tends to be the active groups involved in arsenic biosorption. Thus, on can expect to find similar effects from thiol modified clays. In addition, as far as we know, neither the As(III) adsorption on thiol functionalized clays nor Raman spectroscopy of this system have ever been reported.

Arsenic is a toxic trace element occurring in natural waters in a variety of forms, including soluble and particulate and organically bound, but are mainly found in inorganic forms. The trivalent As(III) and pentavalent As(V) species are derived from the arsenious (H_3AsO_3) and arsenic (H_3AsO_4) acids, respectively. Within the pH range of 2 to 10, the predominant species are the negatively charged pentavalent species ($H_2AsO_4^-$, $HAsO_4^{2-}$) and the neutral trivalent (H_3AsO_3) molecule. The trivalent arsenous acid (H_3AsO_3) species is of great environmental concern because of its high mobility in soils due to its weak bind to soil sediments. As(III) species are considered 10 times more toxic than arsenate (As(V)) species, and this toxicity is mostly explained by the irreversible complexation with thiol groups present in active biomolecules, such as enzymes (Nies,1999). In many parts of the world, surface and groundwater is polluted with arsenic. This pollution may have been caused by human activities (mining, pesticides, etc.) but the most common source of arsenic is geogenic. Epidemiological studies have demonstrated a significant increase in the risks of lung, skin, liver, and other cancers associated with high levels of arsenic in drinking water (Lenoble *et al.*, 2002).

Based on the previous considerations, this work with aimed to obtain a more porous hybrid material containing thiol groups than that obtained in chapter2, with high accessibility to the active sites that can be used as sorbents. The sorption studies were focused on the investigation of the sorption capacity as well as the selectivity of developed sorbent with respect to As(III) and As(V) under different conditions of pH. Emphasis was given to the identification of vibrational modes of the species on the functionalized clay structure before and after As(III) adsorption by Raman and Infrared spectroscopy. An additional aim was to obtain a practical new system based on functionalized clay with good selectivity with respect to As(III) for removal and preconcentration purposes.

3.2 EXPERIMENTAL

3.2.1 Materials

The laponite sample used in the experiments was supplied by Rockwood Specialties Inc. and can be identified by the chemical formula $Na_{0.7}$ [(Si_8 $Mg_{5.5}$ $Li_{0.3}$) $O_{20}(OH)_4$]. According to the supplier, the material has a specific density of 2.53 g/cm^3 and a cation exchange capacity (CEC) of 50 to 60 meq/100g clay. When fully dispersed in water, the particles appear disc-shaped. The nano-sized crystals have approximately 20 nm in diameter, and 1nm in thickness. The organosilane grafting agent, the (3-mercaptopropyl)trimethoxysilane (MPTMS) ($Si(OCH_3)_3C_3H_6SH$), 98% pure, was purchased from Sigma-Aldrich and used without further purification. Toluene (99.8%) was also provided by Sigma-Aldrich.

3.2.2 Characterization methods

The X-ray diffraction patterns of modified and unmodified clay samples were obtained with a Philips model PW1710 diffractometer, fitted with a Cu tube (λ=1.5418 Å, 40 kV and 20 mA, step size 0.06° 2θ, 5 s/step). Thermogravimetric curves were obtained in a TGA model TGA50 Shimadzu under in an N_2 environment, (20 mL/min), with temperature ramp of 10°C/min between 30 ºC and 1000 ºC. The specific surface area was obtained using the BET method – Multiplepoint. The volume of pores was estimated using the t-method, while the pores size distribution was evaluated by the BJH method using an Autosorb equipment of QUANTACHROME instruments.

DRIFT analyses were performed using a FT/IR-spectrophotometer, model SPECTRUM-1000, Perkin Elmer (32 scans of accumulation; resolution of 4 cm^{-1}). The IR measurements were taken at room temperature, in the spectral range of 400-4000cm^{-1}. The samples were mixed with KBr powder in 5 wt.% and a pure KBr spectrum was used as a reference.

Raman spectra were obtained through a Jobin Yvon/Horiba LABRAM-HR 800 spectrograph equiped with a He-Ne laser (633 nm, 20 mW). The Raman signal was collected by a microscope Olympus BHX provided with objectives (50 X 0.75 and 100 X 0.90) in a back scattering configuration. The entrance slits to the spectrograph were 100 µm with a correspondent resolution of 2.0 cm^{-1}. The utilized holographic grating was of 600 g/mm. Depending on the sample background fluorescence, the acquisition time ranged from 10 to 120s. To reduce the signal/noise ratio, the spectra were acquired 20 times. Collected Raman spectra were analyzed and optimized with Labspec 1.1 and Origin 5.0.

3.2.3 Modification process

Prior to the grafting process, 1 g of laponite (LNa), previously dried at 140 ºC for 4 h, was dispersed in 50 cm^3 of 0.2 mol dm^{-3} MPTMS in dry toluene. The resulting mixture was refluxed and agitated for 24 h within an inert atmosphere of N_2 to avoid the oxidation of the SH group. The obtained solid was sequentially washed with toluene and absolute ethyl alcohol, filtered, and dried for 2 h at 120 ºC in an inert nitrogen atmosphere. The functionalized sample was denominated LNaSH. The method adopted here is similar to that described in chapter 2 and in a previous publication (Guimarães *et al.,* 2007). Guimarães *et al.* (2007) observed that laponite is less resistant to acid treatment (0.01 mol dm^{-3} HCl) compared to the natural smectite and some dissolution of this clay has occurred with a consequent release of Mg^{2+} from the clay lattice. Based on this finding, laponite modification was carried out in a sodic form (with no pretreatment) to preserve the integrity of the clay structure.

3.2.4 Adsortion experiments

The adsorption experiments were carried out at pH3, pH5, and pH10 in sealed Erlenmeyers flasks of 250 cm^3 capacity containing 50 mg or 100 mg of clay, and 50 cm^3 of A(III) or A(V) solutions with initial concentrations of 40, 100, 150, and 200 mg/dm^3. The solutions were prepared through the dissolution of disodium hydrogen arsenate heptahydrate ($Na_2HAsO_4.7\,H_2O$ PA; 99% purity, Fluka) and sodium (meta)arsenite ($NaAsO_2$ of 99.0% purity, Fluka) in deionized MilliQ water. The pH was adjusted with 0.1 mol dm^{-3} NaOH or HCl solutions prepared with analytical grade reagents and a deionized Milli-Qwater (18 MΩcm). The suspension was maintained under agitation at 150 rpm in a shaker with a controlled atmosphere (New Brunswick Scientific) at 25 °C for 24 h to reach the equilibrium. After agitation, the suspension was filtered, and the solution was analyzed for the remaining arsenic through atomic absorption spectrometry (model ANALYST A300, Perkin-Elmer).

3.3 RESULTS AND DISCUSSION

3.3.1 Physical characteristics of clay

Table III.1 highlights the effects of the functionalization on the physical characteristics of the clay. Both the specific surface (from 326 m^2/g to 32 m^2/g) and pore volumes (from 0.254 cm^3/g to 0.033 cm^3/g) were significantly decreased after functionalization (Figure 3.2). The pore diameter increased from 31 Å to 69 Å as the micropore contribution was suppressed after modification.

These results suggest that the functionalized sample had its access to internal porosity partially blocked by the grafted molecule. A similar result was obtained for montmorillonite (chapter 2), but a more porous hybrid material was obtained from laponite (32 m^2/g) in comparison to that from montmorillonite (10 m^2/g).

Figure 3.3 shows the mass loss in a range of 30–900 °C before and after modification. Table III.2 summarizes the mass loss and the DTG peak values. In contrast to the original clay, which does not show any important mass loss in the temperature range of 200 °C to 700 °C, the functionalized sample exhibits a sharp DTG peak at 337 ºC, and a smaller and broader peak can be observed at 549 ºC. This feature was mainly ascribed to the degradation and removal of organic compounds. At higher temperatures (>750 ºC), the dehydroxylation of the clay sheets takes place.

Table III.1: Main physical characteristics of the clay samples before and after modification with mercaptosilane.

Clay samples	Basal spacing d_{001} (Å)	S_{BET} (m^2/g)^a	Pore Volume (cm^3/g)	Pore diameter (Å)	Ligand content (mmol/g)^a	Binding Capacity (Ag^+ adsorption)^b (mmol/g)	Ag/S Molar ratio^c
LNa	12.50	326	0.254	31	-	0.15	-
LNaSH	15.50	32	0.033	69	1.2	1.16	0.97

(a) calculated from TG analysis in 200-700°C range in mmol/g of clay. (b)Volhard Method reported by Guimarães *et al.* (2007), (c) Calculated from the ratio of binding capacity and ligand content.

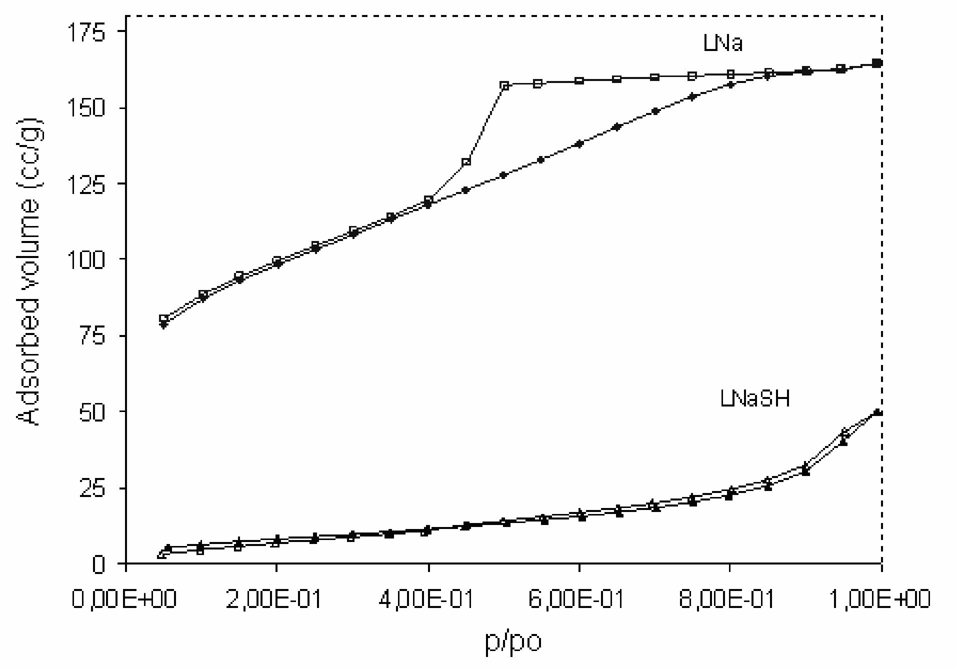


Figure 3.2 - N_2 adsorption/desorption isotherms of laponite samples

The increase of hydrophobicity following functionalization is indicated by the decrease of adsorbed water from 14.5% to 4% for the LNa and LNaSH samples, respectively, in a 30 - 200 ℃ interval. Taking into account the mass loss in the range of 200-700 ºC, one can calculate 1.2 mmol of mercaptopropyl groups per gram of grafted clay (Table III.1). Following functionalization, the concentration of the immobilized thiol groups in the clay was measured according to the Volhard method (Guimarães *et al.*, 2007). The total binding capacity was determined as 1.16 mmol/g and 0.15 mmol/g for the functionalized and the original clay (LNa), respectively (Table III.1). The unmodified sample exhibits some ion immobilization capacity that may be related to a cation exchange mechanism even though the original sample shows a very low affinity toward silver ions. This indicates that the mechanism of adsorption primarily involves silver ion complexation by the thiol groups instead of cation exchanges. Comparing the ligand content (1.2 mmol/g) determined by TG analysis with the binding capacity (1.16 mmol/g) one can assume that practically 100% of the SH group is accessible for Ag^+ trapping (Ag/S = 0.97, Table III.1). This result represents an improvement as compared to that obtained in the functionalization of montmorillonite (BHSH and BCaSH samples, chapter 2) in which the effect produced by functional group blockage limits the access of species to 60–75% of the complexing sites.

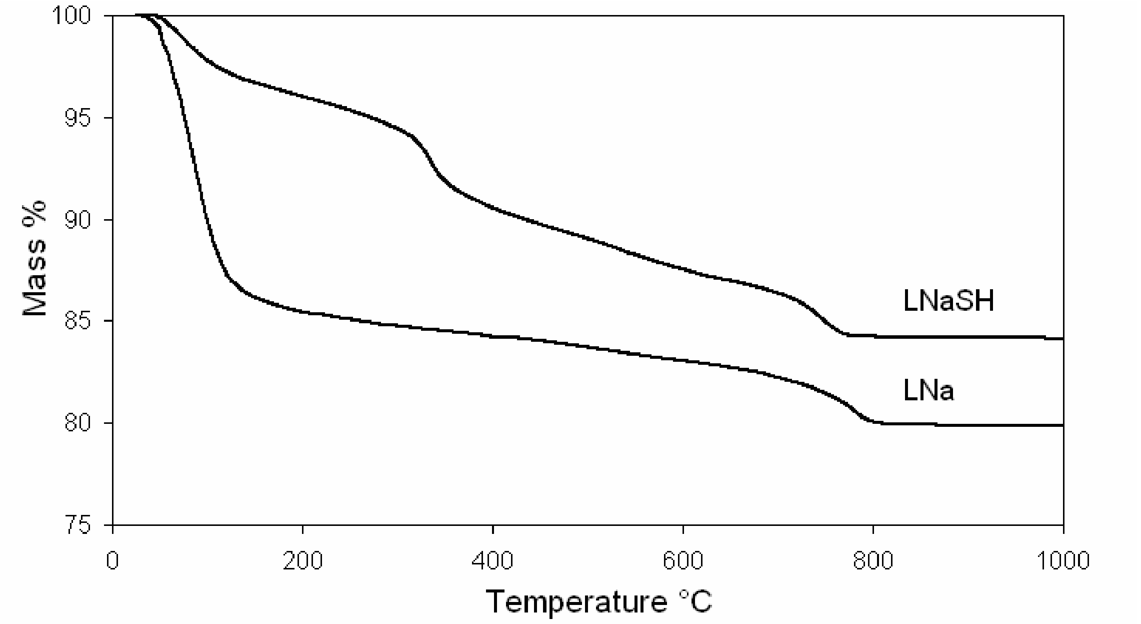


Figure 3.3 - TG curves for laponite before and after functionalization.

Table III.2: Mass loss, Δm (%), range of temperature, ΔT (℃), and assignment of mass loss for laponite samples before and after modification with mercaptopropyl group

Clay	ΔT/ºC	Δm/%	DTG peak/ºC	Assignment (Δm/%)
LNa	30 -200	14.5	90	adsorbed water
	200-800	3.2	785	hydroxyl
LNaSH	30 -200	4	75	adsorbed water
	200-700	9.64 (1.2)	337, 549	organic compound
	700-800	2.1	748	hydroxyl

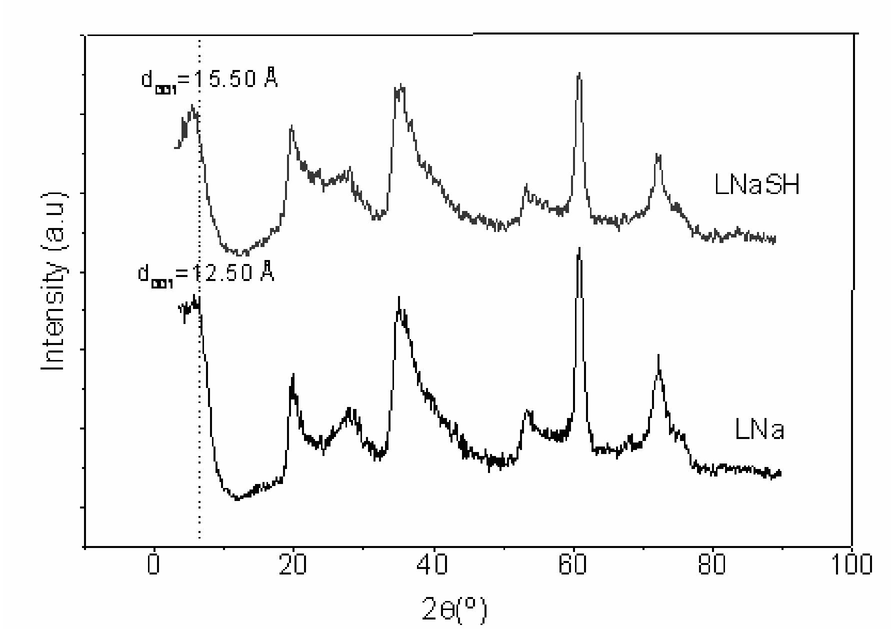
in ( ) values of mmol/g

As illustrated in Figure 3.4, the XRD patterns for all the laponite samples are quite similar. A comparison of the overall patterns indicates that the original structure was preserved after modification. The main d-spacing parameters of all samples are indicated. An approximate value of 12.5 Å was estimated for the interlayer distance in the LNa sample despite the broadness of the d_{001} peak. Other authors report similar broadening, which was attributed to the very low dimensions and low crystallinity of the laponite crystals (Kuzniarska-Biernacka *et al.,* 2005; Park *et al.,* 2004). By comparing the interlayer distance (d_{001}) of laponite before and after modification, the increase of basal spacing from 12.5 Å to 15.5 Å can be observed. This increase is consistent with the intercalation of the mercaptopropyl molecule, which indicates that silylation may take place at the surface of the particles as well as within the interlayer galleries.

3.3.2 DRIFT and Raman spectra

The DRIFT spectra of the clay samples are presented in Figure 3.5. The DRIFT spectrum of the unmodified laponite (LNa) sample exhibits strong bands assigned to structural hydroxyl group stretching vibrations at 3680-3715 cm^{-1} intervals. The ν(O-H) stretching frequency at 3450 cm^{-1} is due to physisorbed water with the corresponding deformation band (δ(O-H)) at 1621 cm^{-1} (Farmer, 1974; Kuzniarska-Biernacka *et al*., 2005; Madejová, 2003). In the low energy region, the spectrum shows one broad band within a range of 1000–1200 cm^{-1} with a maximum peak at 1010 cm^{-1} assigned to Si-O and Si-O-Si stretching vibrations as well as two other bands at 650 cm^{-1} and 480 cm^{-1} assigned to the MgOH bending vibration and the Mg-O vibration, respectively (Farmer, 1974; Madejová, 2003). Figure 3.6 shows the Raman spectra of the samples. The laponite (LNa) exhibits peaks in four spectral regions: (i) 3800-3000cm^{-1}, stretching mode of OH or water in the phyllosilicate structures, (ii) 1200-800cm^{-1} (weak peaks), stretching mode of the Si-O in SiO_4 tetrahedra, (iii) 700-670cm^{-1} (strong peak), also a stretching mode of the Si-O in SiO_4 tetrahedra, and (iv) <600cm^{-1} vibrational modes of the cations in octahedral sites and in interlayer spacing. These vibrational modes are typical of phyllosilicates (Wang *et al*.,2002).

For comparative purposes, the bands' positioning and their assignments obtained by Raman and DRIFT are summarized in Table III.2. An important difference between the spectrum of the raw laponite obtained by Raman (Figure 3.6) and DRIFT (Figure 3.5) can be observed. This leads to the conclusion that Raman spectroscopy is not as sensitive as infrared spectroscopy to the presence of water (Prost and Rintoul, 1996).



Sample	d-spacing/ Å (Bragg angle/degree)				
LNa	12.5 (7.0)	4.5 (19.6)	3.2 (28.1)	2.5 (35.1)	1.5 (60.8)
LNaSH	15.5 (5.6)	4.5 (19.6)	3.2 (28.1)	2.5 (35.1)	1.5 (60.8)

Figure 3.4 - XRD patterns of sodium (LNa) and functionalized (LNaSH) laponite. The inset shows the precise peak indexation.

Table III.2: Assignment of the observed vibration mode of organoclays Coates (2000),

Band assignments	FTIR band (cm^{-1})	Raman band (cm^{-1})
νOH -structural	3680, 3715	3688, 3714
νSi-O	1000 - 1200	1000 – 1200 and 680
ν_sCH_2, ν_aCH_2	2852 , 2924	2887, 2926
δCH_2	1400 -1430	1406-1450
νSH	2562	2570
ν(S-S) dissufides*	Not observed	506
ν(C-S)	Not observed	651
ν(As-S)**	Not observed	350 - 450

δ and ν indicate bending and stretching bands, respectively. “a” and “s “ indicate asymmetric and symmetric stretching. Qian and Krimm (1992) * and Brodsky,(1983)**.

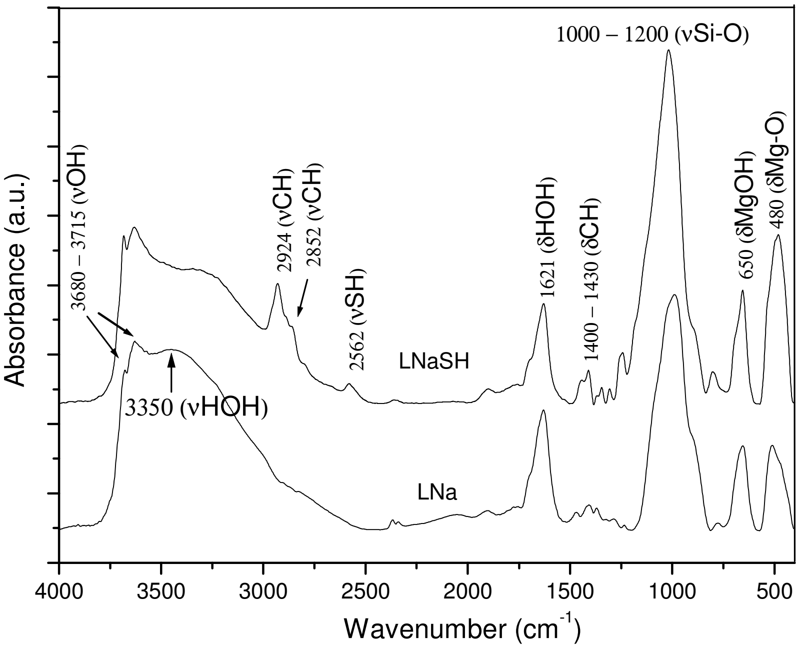


Figure 3.5 - FTIR spectra of laponite before and after functionalization with thiol groups.

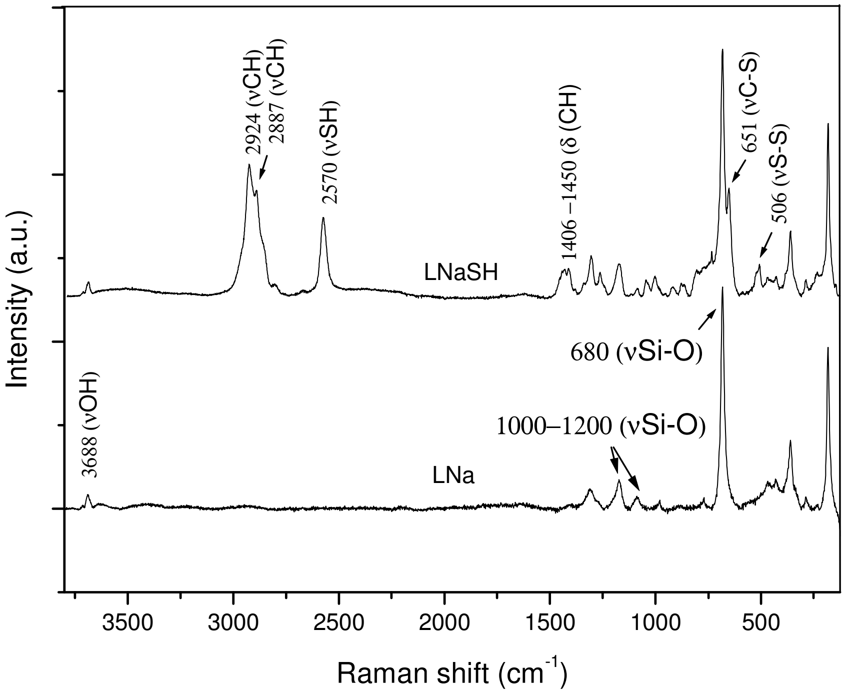


Figure 3.6 - Raman spectra of laponite before and after functionalization with thiol groups.

Thus, the band assigned to physisorbed water (around 3350 cm^{-1}) and its corresponding deformation vibration band (around 1620 cm^{-1}) is not evident in the spectra of Figure 3.6. Conversely, the DRIFT spectrum exhibits strong bands assigned to structural hydroxyl stretching vibrations (3680 - 3715 cm^{-1}) and Si-O and Si-O-Si stretching vibrations (1000-1200 cm^{-1}). In Raman spectrum, these bands are very weak, but an additional band appears at 680 cm^{-1}, which is assigned to the stretching mode of SiO_4 tetrahedra, as this FTIR is inactive (Wang *et al*., 2002, Frost and Rintoul,1996).

After functionalization, important changes in the DRIFT spectra can be observed (Figure 3.5). The LNaSH spectrum shows the characteristic SH stretching vibration at 2562 cm^{-1}. Aliphatic CH_2 groups give rise to a doublet at 2924 and 2852 cm^{-1}, which is assigned to asymmetric and symmetric stretching, respectively. The corresponding deformation modes of these groups are observed between 1400 and 1430 cm^{-1} (Coates, 2000), thus indicating that the organic molecules were effectively grafted to the clay structure.

Through the Raman spectrum of LNaSH samples (Figure 3.6), it is also possible to observe the bands corresponding to the CH asymmetric and symmetric stretching modes at 2924 cm^{-1} and 2887 cm^{-1} as well as the band correspondent to SH stretching vibration at 2570 cm^{-1}. The presence of these vibrations once again confirms the presence of the $–CH_2\text{-}CH_2\text{-}CH_2\text{-}SH$ bonded to the clay structure. Our work demonstrates that the vibration modes of immobilized molecules are more resolved and prominent in the Raman spectra. The formation of disulfides (S-S), not evidenced at DRIFT spectra, was observed by Raman at 506 cm^{-1}. The C-S band at 651 cm^{-1} is also better defined in the Raman spectrum. The intensity of the S-S band is very weak compared to the SH stretching band (Figure 3.6), therefore, one may conclude that only a few SH groups were oxidized to the S-S bridges. Unlike the oxygen–containing compound, the equivalent C-S and S-H stretching vibrations tend to give rise to very weak absorptions in infrared spectra. The C-S and S-H bonds are highly polarizable, and hence produce stronger spectral activity in the Raman spectrum (Coates, 2000).

Based on the aforementioned observations, a grafting mechanism involving the direct reaction of a hydrolizable silane group with hydroxyl groups present at broken edges and on the surface (derived from the structural defects in Si–O silicate) is proposed as shown in Figure 3.7

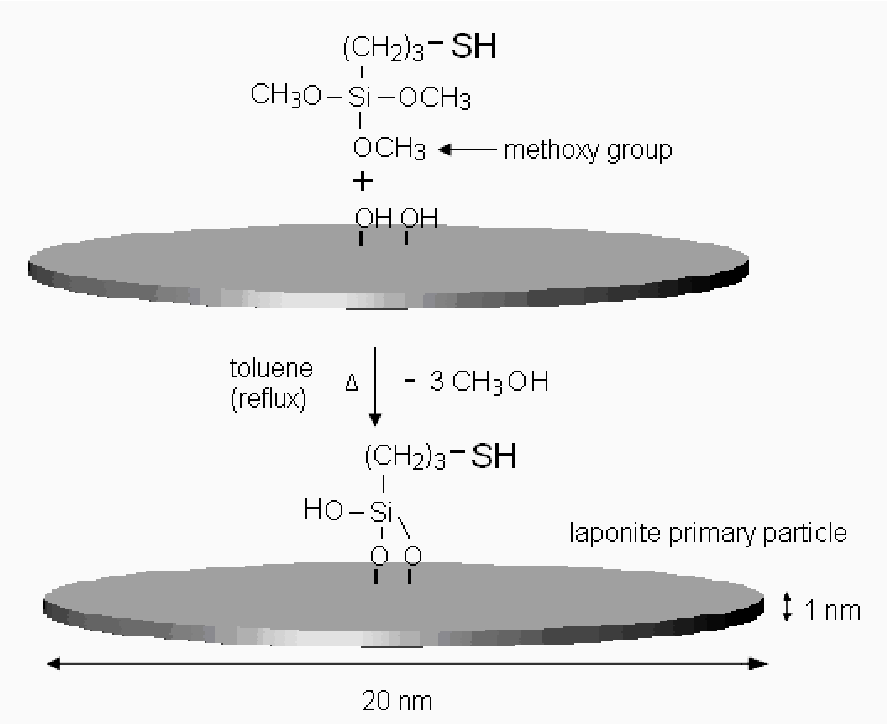
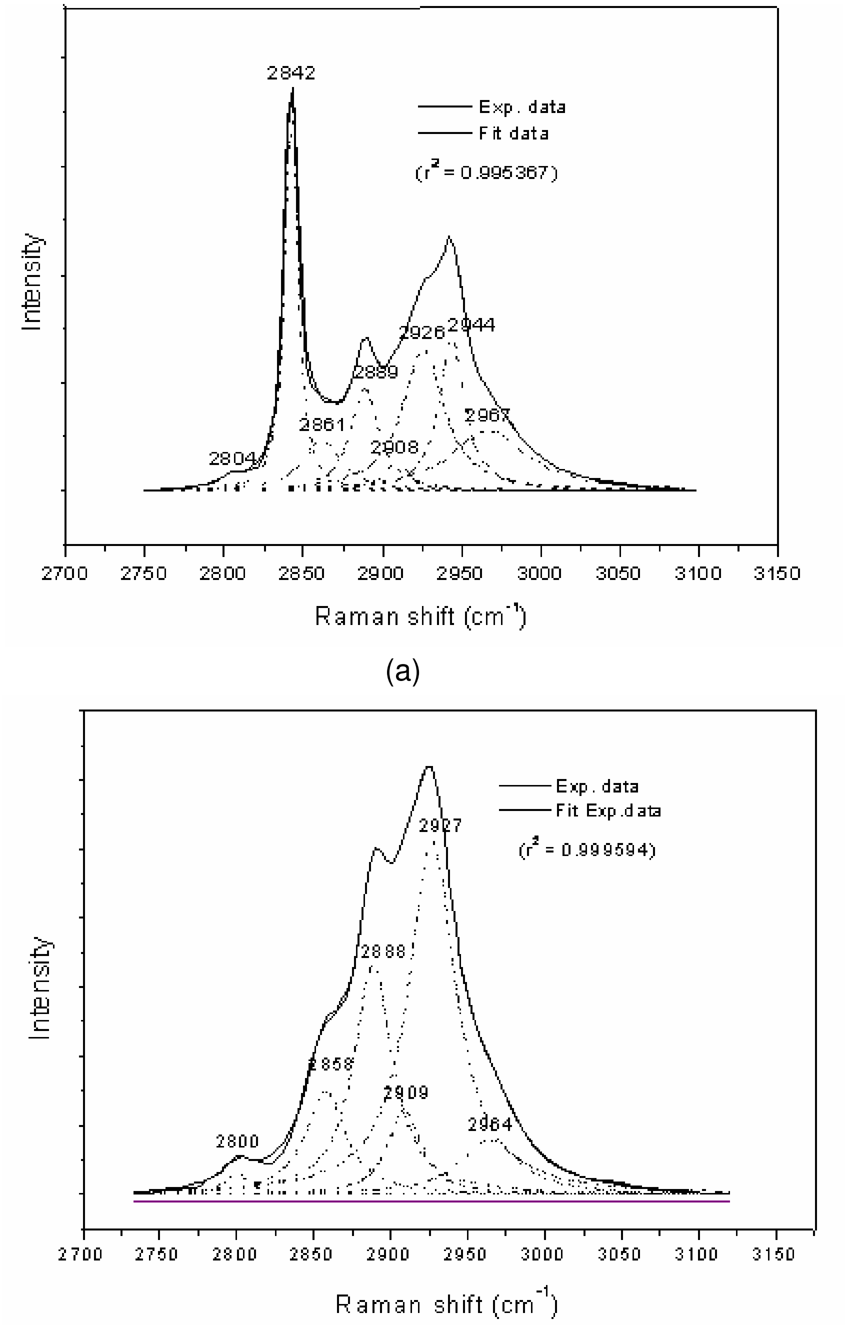


Figure 3.7 - Schematic representation for immobilization mechanism of the silane molecule on a clay surface.

This modification was carried out under anhydrous conditions; the hydroxyl groups react directly with methoxy group of silanes. The deconvolution of Raman spectra peaks within the 2700–3150 cm^{-1} range was carried out to confirm the mechanism depicted in Figure 3.7. Figure 3.8 shows the Raman spectra of the pure modifier (MPTMS) (Figure 3.8(a)) and of the modified clay (Figure 3.8 (b)). It is possible to observe a sharp and intense peak at 2842 cm^{-1} and a band at 2944 cm^{-1} assigned to the methoxy group (Figure 3.8(a)). These vibration modes disappeared after the immobilization of mercaptosilane in clay structure (Figure 3.8(b)). These results suggest that all or most of the methoxy groups of the silane were involved in the condensation reaction with clay surface hydroxyl groups. The other six deconvoluted peaks observed in Figure 3.8(a) and Figure 3.8(b) from 2800 to 2967 cm^{-1} were assigned to three pairs of asymmetric and symmetric stretching vibration modes from three aliphatic CH_2 groups from the mercaptopropyl group ($-CH_2-CH_2-CH_2-SH$) present in MPTMS molecule. The three CH_2 groups possess different vibration energies due to the differences in their neighbors.



(a)

(b)

Figure 3.8 - Deconvoluted Raman spectra peaks at 2700 – 3150 cm^{-1} range of (a) the pure modifier (MPTMS) and (b) the modified clay. Band fitting was carried out using a Lorentz lineshape analysis.

3.3.3 Selective Arsenic adsorption onto thiol-functionalized clay

Comparative results of As(III) and As(V) loading onto the functionalized clay at four different pH values are summarized in Table III.3. During the adsorption experiments, the pH value was monitored and adjusted when necessary. The results demonstrated the large affinity of thiol-modified clays toward As(III). For all pH values, the As(III) uptake was greater than those obtained using As(V). The highest load capacity and speciation occurred successfully at pH5 with 13.6 mg/g and 0.7 mg/g of As(III) and As(V) uptakes, respectively. This finding is important as this pH value is more consistent with conditions often found in natural water. Taking into account that the pKa_1 for H_3AsO_3 is 9.2, one may conclude that As(III) in its neutral form is adsorbed preferentially by SH-clay. At pH8 and pH10, the As(III), as a negatively charged species, presents lower affinity toward the thiol groups, and different adsorption complexes are produced (Teixeira, 2004). The thiol modified clay presented good selectivity towards As(III) neutral species. The loading capacity of the unfunctionalized clay (LNa) with respect to As(III) and As(V) was negligible (< 0.5mg/g).

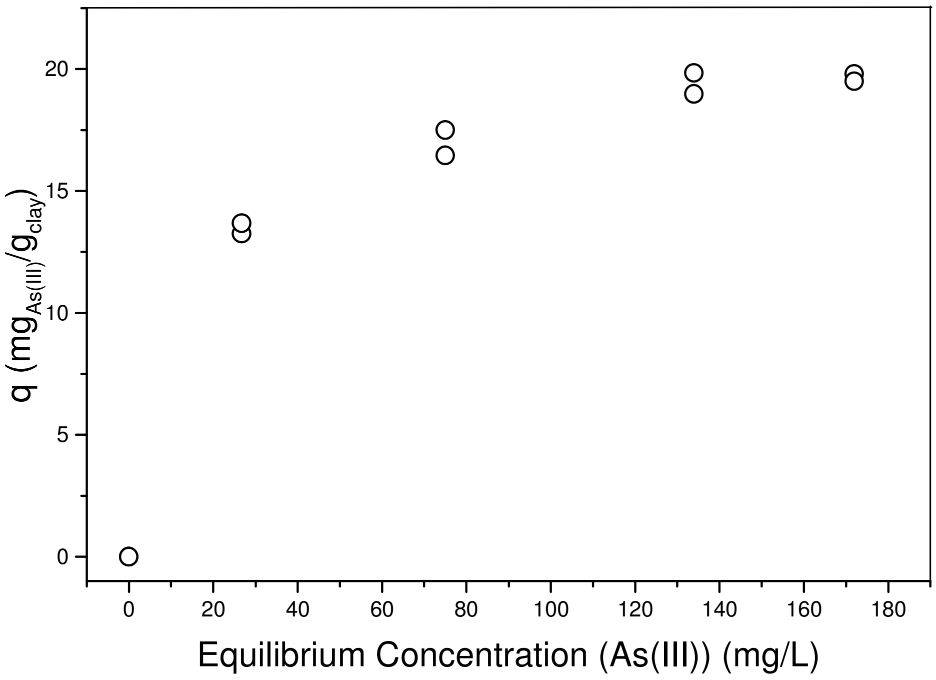
Table III.3: As(III) and A(V) adsorption on functionalized clay
(As initial conc. = 40 mg/L; time: 24 h; 25 °C)

Sample	Adsorvate	pH	As adsorbed (mg/g)
LNaSH	As(III)	3	13.4
	As(III)	5	13.6
	As(III)	8	6.0
	As(III)	10	5.9
LNaSH	As(V)	3	3.6
	As(V)	5	0.7
	As(V)	8	2.3
	As(V)	10	3.0

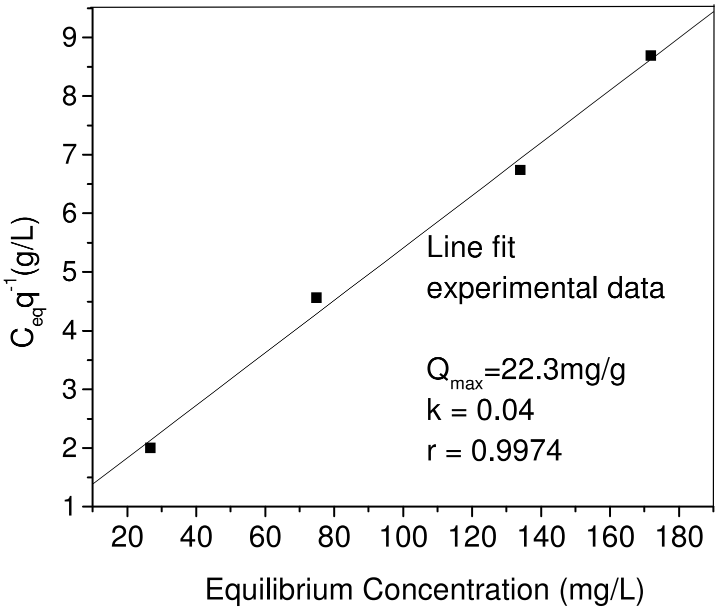
The isotherm curve was obtained in order to determine the maximum loading capacity (Q_{max}) of the functionalized clay with respect to As(III) (Figure 3.9(a)). To obtain the adsorption parameters (Q_{max}, k), the experimental data were adjusted to a linear expression of Langmuir equation (Figure 3.9(b)):

$$C_{eq}q^{-1} = kQ_{max}^{-1} + C_{eq}Q_{max}^{-1} \qquad (3.1)$$

where C_{eq} represents the As equilibrium concentration in the aqueous phase, Q_{max} represents the maximum loading capacity, and k represents a coefficient related to the affinity adsorbent-adsorbate.



(a)



(b)

Figure 3.9 (a) Isotherm of As(III) adsorption onto functionalized clay. Conditions: 100 mg of clay, 50 mL of As(III) solution at initial concentrations of 40, 100, 150, and 200 mg/L; pH 4.0 - 5.0, 25 °C, 24 h under agitation at 150 rpm. (b) Linearized experimental data (scatter) adjusted to Langmuir equation (line).

The linearized experimental curve is shown in Figure 3.9(b), while the straight line indicates the line fit determined by the Langmuir equation. The obtained parameters were Q_{max} = 22.3mg/g (0.30 mmol/g) within a pH range of 4 to 5. This value corresponds to 26% of that obtained with Ag^+ ions (1.16 mol/g, Table III.1). Recent XANES and EXAFS studies of the As(III) with the cysteine rich biomass showed that As(III) is adsorbed in its trivalent form and each arsenic atom is bound to three sulphur atoms (Teixeira and Ciminelli, 2005). Then, a similar process can be expected to occur with the functionalized clay. While As(III) coordinate to three atoms of sulfur, the silver ions are bound to only one. Therefore, silver uptake is expected to be three times larger than arsenic uptake. The obtained results corroborate with this hypothesis.

A similar As(III) adsorption study was carried out on functionalized montmorillonite (characterized in chapter 2). A loading capacity of 6 mg/g was obtained, which corresponds to much lower uptake than that observed with the LNaSH. This was an unexpected result considering that the functionalized montmorillonite presented a good loading capacity and affinity towards some metals ions (Cd^{2+}, Ag^+) as well as a high ligand content (1.76 mmol/g) (Table II.4, chapter 2). Possible reasons leading to this conclusion include: the lower surface area of functionalized montmorillonite (10 m^2/g) in relation to the functionalized laponite (32 m^2/g) and the relatively higher hydrophobicity of the SH-montmorillonite sample. The reason for the low uptake of arsenic by SH-montmorillonite requires further and more in-depth investigation.

Conventional adsorbents for arsenic species, such as the alumina, (Yalcin and Le, 2001), or modified silica and resins with strong anion exchange capacity (Duarte, 2006) are considered efficient for As(V) species but are not suitable for seletive As(III) adsorption. Thus, thiol modified clay developed in the present study is a promissing option for the retention of arsenic in the trivalent form.

Lenoble *et al.* (2002) reported on arsenic adsorption onto clay pillared with titanium(IV) and iron(III). These authors found similar maximal capacities for both matrices, 3 mg/g for As(V) and 13 mg/g for As(III) at $4<pH<9$. Teixeira and Ciminelli (2005) have demonstrated that a cysteine-rich biomass, residue from the poultry industry, is appropriate for the treatment of arsenic-containing solutions. These authors reported a loading capacity of 13.0 mg/g and 10.1 mg/g for As(III) at pH2 and pH5 respectively. Previous work with commercial resins containing chelating thiol as a functional group have demonstrated a loading capacity with respect to As(III) of 32.6 mg/g at pH5. These authors reported the necessity of a regeneration step prior to adsorption to reactivate the thiol group, which was spontaneosly oxidized to S-S bridges (Duarte, 2006). It is important to emphasize that the thiol groups (SH) immobilized into the clay structure proved to be very stable and no pretreatment step was necessary before performing the uptake experiments. The lifetime of the thiol modified clay while in stock was estimated by measuring the silver ions uptake capacity by the Volhard Method described by Guimarães *et al.* (2007). It was observed that one year after the synthesis, the uptake capacity decreased approximately 10% from its initial value. This decrease is most likely due to the oxidation of thiol to disulfide when in the presence of air and moisture in a polyethylene bottle. As no pretreatment is necessary, this material is promising in new system development for inorganic arsenic speciation field work purposes.

The As(III) loaded samples were also examined by Raman spectroscopy (Figure 3.10), so as to assess the changes in the clay structure after As(III) uptake. The involvement of thiol groups in As(III) adsorption was clearly indicated by the vibrational modes of As-S bonds combined with the reduction of the SH band intensity evidenced by a difference in the LNaSH-As(III)/LNaSH spectrum. The As-S frequency is the most important feature in the LNaSH-As(III) Raman spectrum as this band is not present in the mofified clay spectrum (LNaSH). The region between 350 cm^{-1} and 450 cm^{-1} is usually assigned to the vibrational modes of the As-S group (Brodsky, 1983; Bell *et al.* 1997). This result also demonstrates that the thiol groups immobilized in the clay structure are free to form complexes with the adsorvate species.

By analyzing the spectra shown in Figure 3.10, one can also observe a small variation in the intensity of the CH stretching band, which is confirmed by the spectrum difference. This result suggests that a small number of mercaptopropyl groups, which were weakly bonded into clay structure, were leached out during adsorption. Nevertheless, most of these groups remained bonded after adsorption, which also indicates the stability of the obtained material. Based on the SH band intensity after adsorption, it was observed that only a fraction of the thiol groups are involved in As(III) ion complexation. This was an expected result, once the adsorption experiments were carried out far from the saturation condition. In addition, the S-S bridge (at 506 cm^{-1}) seems not to have interacted with the As(III) since this band was maintained the same after the As(III) adsorption step.

Finally, the features of the modified clay, prior to and after the adsorption of the As(III) discussed herein based on the Raman spectra, clearly indicated that As(III) adsorption involves a complexation with the thiol groups available in the modified clay. The major advantage of Raman spectroscopy in this specific case rests on the ability of this technique to make it possible to analyze the changes in vibrational modes of the As-S, S-S, and SH groups. Another advantage of this technique is that measurements can be taken without any sample preparation.

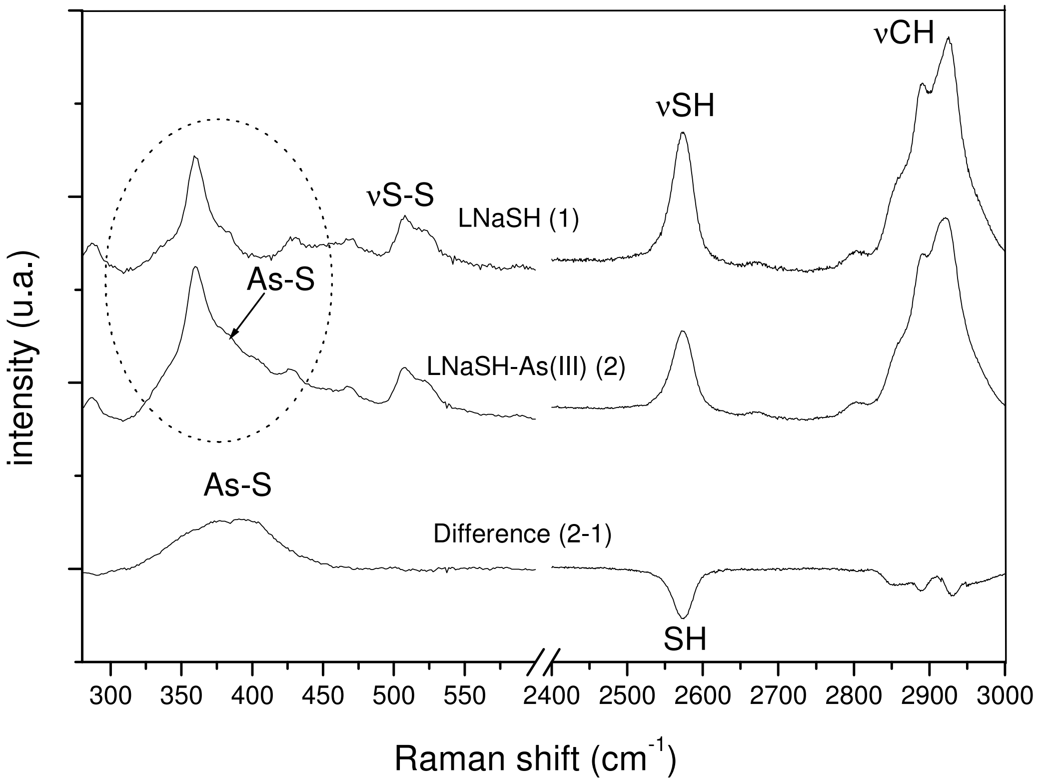


Figure 3.10 - Raman spectra for functionalized laponite before (1) and after (2) As(III) adsorption at pH 5.0 and As(III) solution at initial concentration of 40.0 mg/L. The difference As(III) - modified clay/modified clay spectra is also shown.

3.4 CONCLUSIONS

Laponite, a synthetic silicate, was successfully functionalized through a simple direct reflux using organosilanes. The samples were modified in their as-received sodium form. The XRD results showed that the modification process did not significantly affect the crystallographic structure of the clay and presented an increase in basal spacing (from 12.5 Å to 15.5 Å). Therefore, it can be assumed that the silylation process took place at the surface of the particles as well as within the interlayer galleries. Both the specific surface (from 326 m^2/g to 32 m^2/g) and pore volumes (from 0.254 cm^3/g to 0.033 cm^3/g) were significantly decreased after functionalization. Binding capacity measurements showed that the functionalized laponite present practically 100% of SH group accessible for Ag^+ trapping.

Raman spectroscopy has shown to be a useful tool for the characterization of thiol modified clay. The C-S and S-H bonds are highly polarizable and thus produce stronger activity in the Raman spectrum compared to that obtained with infrared. The involvement of thiol groups in As(III) adsorption was clearly indicated by the vibrational modes of As-S bonds combined with the reduction of the S-H band intensity. The adsorption experiments have demonstrated the strong affinity of a thiol modified clay toward As(III). For all pH values tested, the As(III) uptake was higher than those obtained for As(V). The performance of modified clay is pH dependent. The highest loading capacity, as well as maximum speciation, occurred successfully at pH5, where the trivalent species are present in its neutral form, (H_3AsO_3). The As(III) uptake onto thiol modified laponite was of 22.3 mg/g (0.30 mmol/g) at pH 4–5. It is also important to emphasize that the thiol groups immobilized into the clay structure proved to be very stable and no pretreatment step was necessary before performing uptake experiments. Finally, the results obtained in the present work have shown that thiol functionalized clay can be used as a new effective sorbent for selective arsenic immobilization. It therefore represents a good alternative for removal and preconcentration for field and laboratory purposes.

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CAPÍTULO 4

THE EFFECT OF MATRIX AND FUNCTIONALIZATION ROUTE ON THE MICROSTRUCTURE OF NANOCLAY GRAFTED WITH AMINOPROPYLSILANE

Abstract

The functionalization of montmorillonite clay has been performed by different routes using (3-aminopropyl)triethoxysilane (APTES) in the presence of two solvent media. The organically modified clays are derived from two kinds of 2:1 type layered silicates: a naturally purified montmorillonite and a synthetic smectite. A sample of a natural montmorillonite was modified by acid treatment, followed by intercalation organic ligands, and the synthetic sample was modified in sodic form. The XRD patterns clearly indicate that aminosilane was successfully intercalated in acid activated montmorillonite in both routes used and that this clay has more adequate characteristics of expandability for the functionalization process. The synthetic clay showed a different behavior as only the samples modified in alcohol-aqueous solutions were intercalated. The free space between the two sheets after functionalization was approximately 9 Å for montmorillonite and 7.5 Å for laponite. Qualitative evidence of the presence of aminosilane attached to the clay platelets has been identified using Fourier transform infrared spectroscopy (FTIR). The amount of grafted aminosilane, calculated through thermogravimetric analyses, was of 8% for laponite and 12% for montmorillonite. By titration of functionalized clays with 0.01mol/L HCl solution, it was determined that 63% and 100% of the NH_2 group are accessible in modified montmorillonite and laponite, respectively. Our study demonstrates that the modification media influences the density of the intercalated molecules in the interlayer space. As regards the alcohol-aqueous media, a material with higher surface area and pore volume can be obtained, due to preferential grafting in the clay interlayer space.

Keywords: montmorillonite; laponite; aminopropyltriethoxysilane; functionalization

4.1 INTRODUCTION

Layered silicate exhibits many interesting structural features, such as active sites due the presence of structural hydroxyl groups, Lewis and Brønsted acidity, and exchangeable interlayer cations (Herrera, *et al.*, 2006). The 2:1 type layered silicates present a "sandwiched" structure; i.e., one Al(Mg)–$O_4(OH)_2$ octahedral sheet bound to two Si–O tetrahedral sheets, as shown in Figure 4.1. The smectites present a 2:1 structure and, among the mineral clays of this group, montmorillonite and hectorite have been the most commonly used clays to investigate the functionalization processes due to their availability and adequate characteristics of expandability (Prado *et al.*, 2005; He *at al.*, 2005; Szabó *et al.,* 1998). The most common ways of modifying 2:1 clay minerals include (i) ion exchange with inorganic cations and cationic complexes, (ii) ion exchange with organic cations, (iii) binding of inorganic and organic anions, mainly at the edges, (iv) grafting of organic compounds, (v) pillaring by different types of polyhydroxo metal cations, and (vi) physical treatments, such as lyophilisation and ultrasound (Bergaya and Lagaly, 2001).

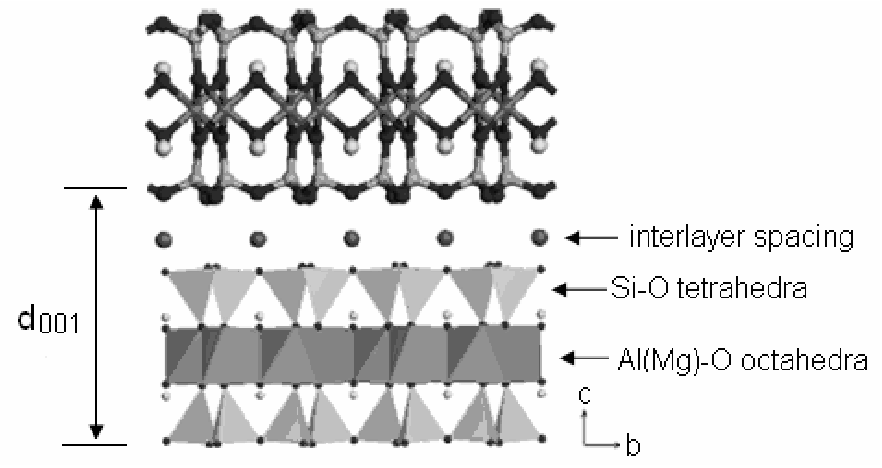


Figure 4.1 - Idealized structure of 2:1 type layered silicate. (Top: stick and ball style; bottom: polyhedron style.) (He *et al,*.2005).

Among the many modification techniques available, the adsorption of alkyl ammonium cations in the interlayer swelling clay mineral has been extensively studied for a wide range of nanostructured materials (Kozak and Domka, 2004; Dau and Lagaly, 1998). Much effort has been focused on the elaboration of polymer/layered silicate nanocomposites using natural or synthetic clay minerals modified with polymer using alkylamines in a preswelling step (Zheng *et al.,* 2004). Recently, polymer nanocomposites reinforced with lower volume fraction of nanoceramics, and carbon nanotubes have attracted steadily growing interest due to their peculiar and fascinating properties. The incorporation of nanoceramics (such as layered silicate clays arranged on the nanometer scale with a high aspect ratio and an very large surface area) into polymers improves their mechanical performances, increases thermal stability, and lowers gas/vapor permeability (Herrera *et al.,* 2006,Tjong, 2006).

Recently, organosilanes with the amine group have been used for the modification of layered silicates (He *et al*. 2005; Park and Kwon, 2004). The intercalation and grafting of aminosilane convert the hydrophilic surface into an organophilic surface. In addition, the attached amine groups on the clay surface can offer reactive sites for chemical bonds with epoxy and other polymers (Park and Kwon, 2004). For this reason, amine-modified clay is a promissing material for the polymer/layered silicate nanocomposite synthesis. Besides clay-polymer nanosystems, many other new applications have also been ascribed to clay minerals modified with amineorganosilane, such as supports for catalysts (Kuzniarska-Biernacka *et al.,* 2005), sorbents for organic pollutants (Sayilkan *et al.,* 2004), and the manufacture of modified electrodes for (bio)electrochemical applications (Tonle *et al*., 2004, Coche-Guérente and Labbe, 1998).

The intercalation reactions occur by insertion of mobile guest species (neutral, molecules, or ions) into the accessible crystallographic defined vacant sites located between the layers (interlayer spacing) in the layered host structure (Wypych, 2004). Modification with organosilane involves grafting reactions which occur by establishing covalent bonds between the reactive groups of the layer, normally hydroxyl groups and silane molecules, which in turn ensures high chemical, structural, and thermal stability for the compound. These reactions can be restricted to the crystal surface (the basal spacing remains unchanged) or to the layer surface, in which case an interlayer expansion would occur. The resulting material can be defined as hybrid materials, or more specifically, surface–modified inorganic layered materials (Wypych, 2004).

Despite numerous investigations regarding the influence of clay and silane types on functionalized clay characteristics, few reports are available on the influence of modification media on the resulting modified layered material. The influence of solvents (destilled water, toluene, and ethylene glicol tetrahydrofuran) on the grafting process of pure sodium montmorillonite clay was recently reported by Shanmugharaj *et al.* (2006), but the accessibility to the active sites was not discussed. Therefore, there is a need to devise methods to increase the loading capacity of the clays while maintaining the mesoporous framework structure.

In chapter 2 and 3 we discussed the functionalization of the natural and synthetic smectite clay with mercaptosilane as a modifier. It was demonstrated that the natural and synthetic clay samples were successfully functionalized through a simple reflux with organosilanes in a toluene media. The characterization results showed that, for both clays, the specific surface (S_{BET}) and pore volumes were significantly decreased after functionalization. However, the modification of laponite resulted in a more porous hybrid material with higher accessibility to the reactive centers. In the present study, however, a different organosilane containing amine as a functional group will be used. The amine group was selected due to its wide range of applications, as aforementioned.

In this work, we investigated the chemical functionalization of two different smectites: natural (montmorillonite) and synthetic (laponite). The clays were modified with (3-aminopropyl) triethoxysilane in the presence of different solvents. The aim of this work is to assess the effect of different solvents on the microstructure of the grafting products applied to the two different clay materials. The functionalized clays have been characterized by various techniques, such as Diffuse reflectance Fourier transform infrared spectroscopy (DRIFT), thermogravimetric analysis (TGA), X-ray diffraction (XRD), and specific surface area measurement (BET method).

4.2 EXPERIMENTAL

4.2.1 Materials

Two smectite clay samples were used. One was a well-known natural sodic and purified montmorillonite supplied by Southern Clay Produts, Inc, denominated Cloisite-Na (**sample CNa**). According to supplier information, this material presents a particle size distribution of 10% < 2 μm, 50% < 6 μm, and 90% < 13 μm (dry particle sizes); a cation exchange capacity (CEC) of 92.6 meq/100g clay; a specific gravity of 2.86 g/cm^3; and an X-ray diffraction (d_{001})

of 11.7 Å. This clay was used without purification. The second sample was a synthetic smectite, denominated laponite (**sample LNa**), which closely resembles the natural clay mineral hectorite in both structure and composition and can be described by the chemical formula of $Na_{0.7}$ $[(Si_8\ Mg_{5.5}\ Li_{0.3})\ O_{20}(OH)_4]$. The laponite sample used in the experiments was supplied by Rockwood Specialties Inc. According to the supplier, the material presents a specific density of 2.53 g/cm^3 and a CEC of 50 to 60 meq/100g clay. When fully dispersed in water, the particles display disc-shaped, nano-sized crystals of approximately 20 nm in diameter and 1 nm in thickness.

The organosilane grafting agent, the (3-aminopropyl)triethoxysilane (APTES) ($Si(OCH_2CH_3)_3C_3H_6NH_2$; MM=221.37 g/mol), 98% pure, was purchased from Sigma-Aldrich and used without further purification. Toluene (99.8%) and absolute ethyl alcohol were also provided by Sigma-Aldrich. NaOH (>98%, pellets) and HCl (~37%) from Merck were used for acid treatment of the clay and pH adjustments during adsorption experiments. All solutions were prepared with high-purity water (18 MΩ.cm^{-1}) obtained from a MilliQ water purification system.

4.2.2 Characterization methods

The X-ray diffraction patterns of the modified and unmodified clay samples were obtained with a Philips model PW1710 diffractometer, fitted with a Cu tube (λ=1.5418 Å, 40 kV and 20 mA, step size 0.06° 2θ, 5 s/step). Thermogravimetric curves were obtained in a TGA model TGA50 Shimadzu in an N_2 environment, (20 mL/min), with a temperature ramp of 10 °C/min between 30 ºC and 1000 ºC. DRIFT analyses were performed using an FTIR-spectrophotometer, model SPECTRUM1000, Perkin Elmer (64 scans of accumulation; resolution of 4 cm^{-1}). The IR measurements were taken at room temperature, within the spectral range of 400-4000 cm^{-1}. The samples were mixed with KBr powder in 5 wt. % and a pure KBr spectrum was used as a reference. The isotherms of adsorption-desorption of N_2 were obtained at 77 K. Before the adsorption experiments, the samples were outgassed under vacuum overnight at 60 °C. The specific surface area was obtained by multipoint BET method. The porous volumes were estimated using the t-method while the pore size distribution was assessed by the BJH method, using QUANTACHROME instruments, model Autosorb.

The amount of amine ligands was also determined by acid–base titration, to monitor their accessibility to a solution-phase reagent (*i.e.* protons in this case), according to a previously published procedure applied to silica gels grafted with the same ligands (Walcarius *et al.*, 2002).

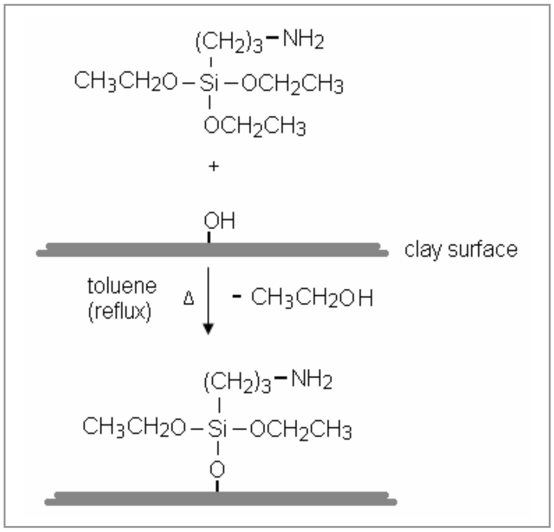
4.2.4 Modification process

Prior to the grafting process, approximately 1g of the montmorillonite, sample **CNa,** was acid activated with 100 cm^3 of 0.15 mol dm^{-3} HCl solution under agitation at 25 ºC overnight. A low HCl concentration solution (0.15 mol dm^{-3}) was used to avoid the dissolution of the octahedral sheet and the collapse of the structure. The resulting sample, **CH**, was washed in deionized water until a neutral pH was achieved, then centrifuged and freeze-dried (Mercier & Detellier, 1995). The acid activation was used to remove the sodium ions from the interlayer region and to create more active sites for the subsequent funcionalization process. The synthetic sample, **LNa**, was not submitted to the acid activation process to avoid the octahedral sheet dissolution with a consequent release of Mg^{2+} from the clay lattice.

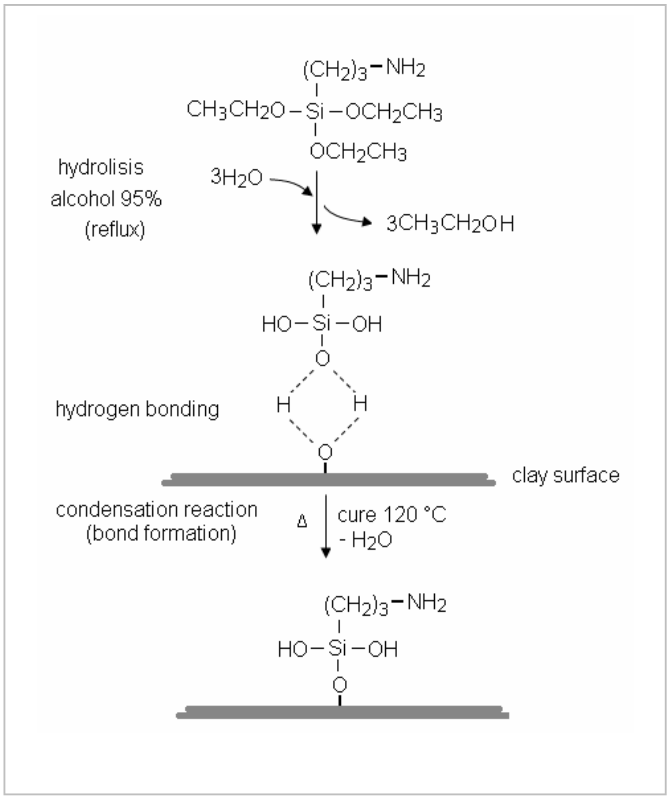
In chapter 2, it was demonstrated that silane interacts with structural hydroxyl groups of clay and thus forms chemical bonds at the interface. For the clays, broken edges and structural defects in Si–O silicate edges, normally generated through acid activation, are also active sites for grafting reactions. In dry environments, the grafting reaction involves a direct nucleophilic displacement of the silane as shown in Figure 4.2a (Kanan *et al*, 2002). Another possibility would be to subject the silane to hydrolysis of the ethoxy group attached to the silicon prior to the surface treatment with aqueous alcohol solutions (prehydrolysis). Following hydrolysis, a reactive silanol group is formed, which can form hydrogen bonds with OH groups on the clay surface. Finally, during drying or curing, the condensation reaction occurs, forming siloxane links on the clay surface coupled with a concomitant loss of water, Figure 4.2b (Sayilkan *et al*, 2004).

Clay modification was then conducted according to anhydrous and alcohol-aqueous solution routes.

In the anhydrous route, approximately 1g of clay in a natural and acid activated form, previously dried at 140 ºC for 4 h, was dispersed in 50 cm^3 dry toluene containing 2% (3-aminopropyl)triethoxysilane (APTES). The resulting mixture was refluxed and agitated for 8 h. The obtained solid was sequentially washed three times with toluene to remove the non-bonded silane and followed by absolute ethyl alcohol; filtered; and dried for 2 h at 120 ºC. The functionalized samples were denominated as **CNaNHT, CHNHT, LNaNHT.**



(a)



(b)

Figure 4.2 – Schematic representation for immobilization mechanism of silane on clay surfaces. (a) Anhydrous route with direct hydrolysis and (b) Alcohol-aqueous solution with prehydrolysis, followed by hydrogen bond and condensation reaction.

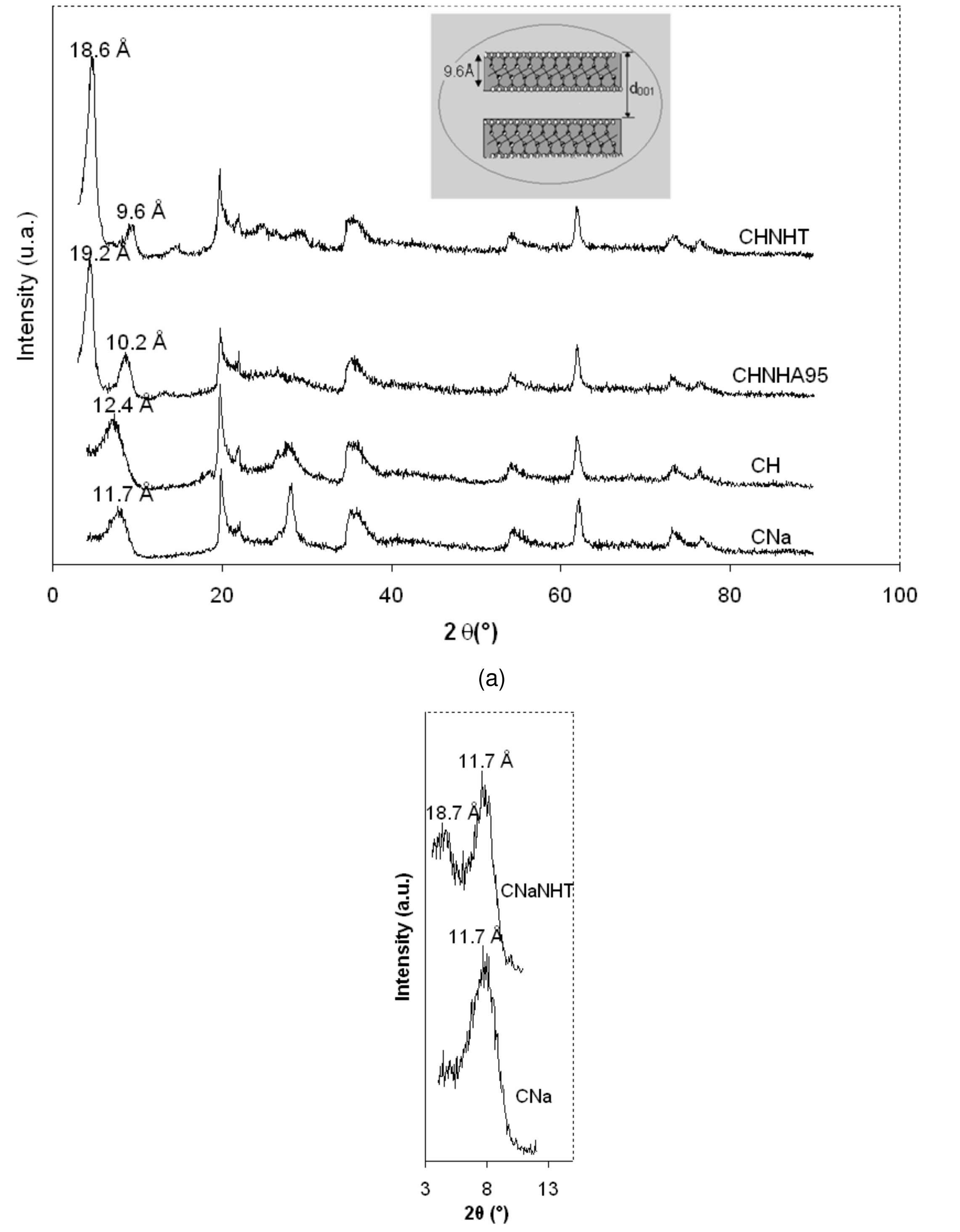
In the alcohol-aqueous solution route, APTES was added to 25 cm^3 of 95% ethanol (to yield a 2% final concentration) and stirred for 2 h. This solution was sequentially mixed to 1 g of clay previously dispersed in 25 cm^3 of 95% ethanol. The resulting mixture was refluxed and agitated for 8 h. The obtained solid was sequentially washed three times with a 95% ethanol solution to remove the non-bonded silane, filtered, and dried for 2 h at 120 ºC. The functionalized sample was denominated as **CNaNHA95, CHNHA95, and LNaNHA95.**

4.3 RESULTS AND DISCUSSION

4.3.1 XRD analysis

Figure 4.3 and Figure 4.4 show the X-ray powder diffraction pattern of the basal spacing reflexation of the samples. Since the characteristic reflections are present, the crystallographic structure of both silicates is preserved even after functionalization. A significant increase of the interlayer spacing of montmorillonite (Figure 4.3a) was observed after modification. The basal spacing increases from 12.4 Å to 18.6 Å and to 19.2 Å in dry toluene and alcohol-aqueous solutions, respectively. These results show that aminosilane was successfully intercalated in acid activated montmorillonite in both routes used. The same was observed with the laponite sample modified in an alcohol-aqueous solution (Figure 4.4). The *d*-spacing value is strongly dependent on the amount of intercalated silanes; therefore, one can conclude that the sample processed in an alcohol-aqueous solution shows the highest intercalation degree, which induces the highest *d*-spacing value. A reflection of the 9.6 Å and 10.2 Å in CHNHT and CHNHA95 diffraction pattern could also be observed (Figure 4.3a). This indicates the existence of non-intercalated crystals. Shanmugharaj *et al.* (2006) presented similar results. The intensity and sharpness of all diffraction patterns presented by the functionalized acid activated montmorillonite samples (Figure 4.3a) are a good indication of the homogeneity of the intercalated sample and the regular stacking of the sheets.

Different results were obtained by He *at al.* (2005) who observed a broad (001) reflection after functionalization of the montmorillonite sample with an 95% alcohol–water solution. For comparative purposes, a sample of Na-montmorillonite was submitted to the same modification process in dry toluene but without performing the acid activation step (CNaNHT sample). The XRD pattern of this sample is shown in Figure 4.3.b. It is possible to observe two peaks related to (001) reflection of 18.7 Å and 11.7 Å. This finding suggests that many crystals remaining ungrafted. The broadness of the (001) peak of the CNaNHT sample can be attributed to the partially stacked disorder of the functionalized sample as well as to the absence of homogeneity in the intercalation process. The DRX pattern analysis indicates that the acid activated montmorillonite samples were more successfully intercalated.



(a)

(b)

Figure 4.3 - XRD of montmorillonite samples. The d_{001} alues are evidenced. (a) acid activated montmorillonite (CH) modified in dry toluene (CHNHT) and 95% ethanol (CHNHA95); (b) natural montmorillonite (CNa) modified in dry toluene (CNaNHT).

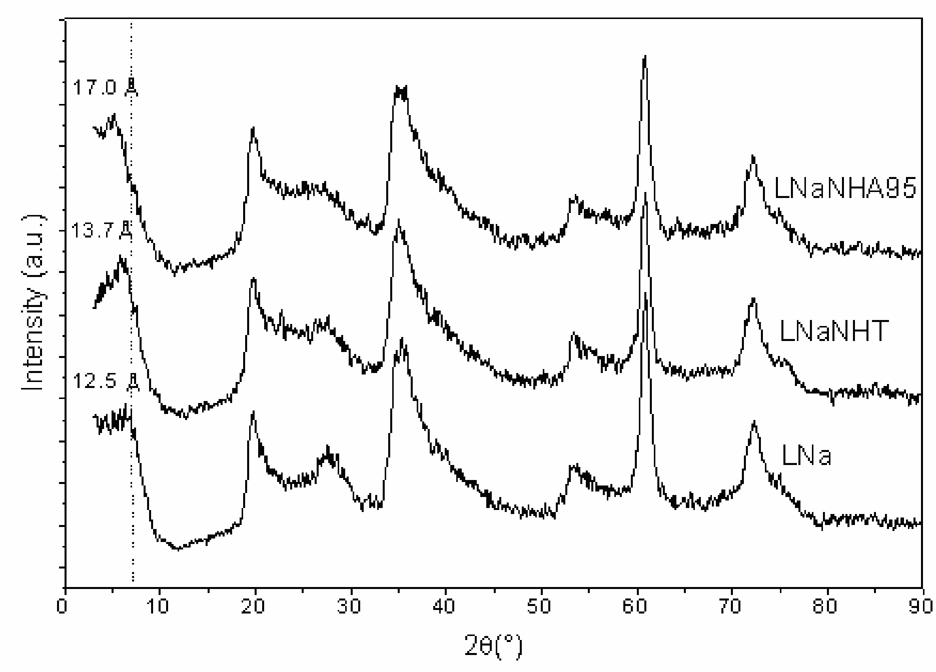


Figure 4.4 - XRD of laponite samples modified in dry toluene and 95% ethanol.

The synthetic clay presented a different behavior as only the samples modified in alcohol-aqueous solutions were successfully intercalated. For the LNaNHT sample, modified in dry toluene, the intercalation did not occurred and no important changes in the interlayer distance were noticed (d_{001} varying from 12.5 Å to 13.7 Å, Figure 4.4).

This result suggests that the aminosilane immobilization took place only at the surface of the particles and not within the interlayer galleries. Similar results were reported by to Prado *et al.* (2005), who studied the modification of a synthetic clay with organosiloxanes containing imidazole groups.

The Figure 4.4 shows that the LNaNHA95 sample, modified in an 95% alcohol-aqueous solution, was successfully intercalated with a significant increase in the interlayer space from 12.50 Å (LNa) to 17.01 Å (LNaNHA95). This value is greater than that observed by He *at al* (2005), who observed a basal spacing of 14.5 Å for a synthetic fluorohectorite modified with aminesilane in a mixture of 75% ethanol-aqueous solution.

The expansion observed for the synthetic clay samples was smaller than that observed for the acid activated montmorillonite. This suggests that the montmorillonite has more adequate characteristics of expandability for the functionalization process. In addition, the alcohol-aqueous media seems to be more appropriate for the intercalation process, as a higher expansion was observed in this media. Since the grafting reaction conditions for CH and LNa were identical, their different gallery heights reflect the role of the clays on the gallery structure of the resultant products.

Taking into account the thickness of the phyllosilicate sheet of 9.6 Å, the free space between two sheets increases from 2.8 Å (which corresponds to the presence of the water molecule) to between 9 Å and 9.6 Å for montmorillonite and to 7.5 Å for laponite. According He *et al.* (2005), the height of the aminopropyl group is approximately 0.4 nm. This value is in accordance with the presence of a double layer of aminopropyl molecules in the interlayer space for both clays.

In summary, it was found that the nature of the clay materials, as well as the type of solvent, do indeed have an important effect on the intercalation degree. The montmorillonite presents more adequate characteristics of expandability for the functionalization process. The clay expansion observed with aminosilane intercalation is greater than that observed with organosilane containing thiol group, discussed in chapter 2. These results suggest that the intercalation degree also depends on the organosilane type.

4.3.2 FTIR analysis

DRIFT spectra of the modified and unmodified clays are presented in Figure 4.5 and Figure 4.6. Significant changes following the modification process can be observed in all frequency ranges of the FTIR spectra. The main band assignments of diffuse reflectance spectra of the raw and functionalized clays are summarized in Table IV.1. DRIFT spectra of both amine-functionalized clays show the doublet at 3350 cm^{-1} and 3290 cm^{-1} due to asymmetric and symmetric stretching of the NH_2 group. The NH_2 deformation occurs at 1580 cm^{-1} and 1540 cm^{-1}. Aliphatic CH_2 groups give rise to a doublet at approximately 2950 cm^{-1} and 2850 cm^{-1}, which is assigned to asymmetric and symmetric stretchings, respectively. The corresponding deformation modes of these groups are observed between 1430 cm^{-1} and 1480 cm^{-1}. The CH_2 wagging bands in propyl chains are spread within the range of 1290 to 1325 cm^{-1}. This assignment is consistent with previous reports (Shanmugharaj *et al.,* 2006, Bois *et al.*, 2003; Fonseca *et al*, 2000, and Coates, 2000). The presence of these vibrations confirms the presence of the $–CH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2$ bonded to the clay structure.

The hydrolysis of the ethoxy group appears to be completed since the CH_3 vibration, normally present as a shoulder at approximately 2970 cm^{-1} (Ahenach *at al.*, 2000), was not observed.

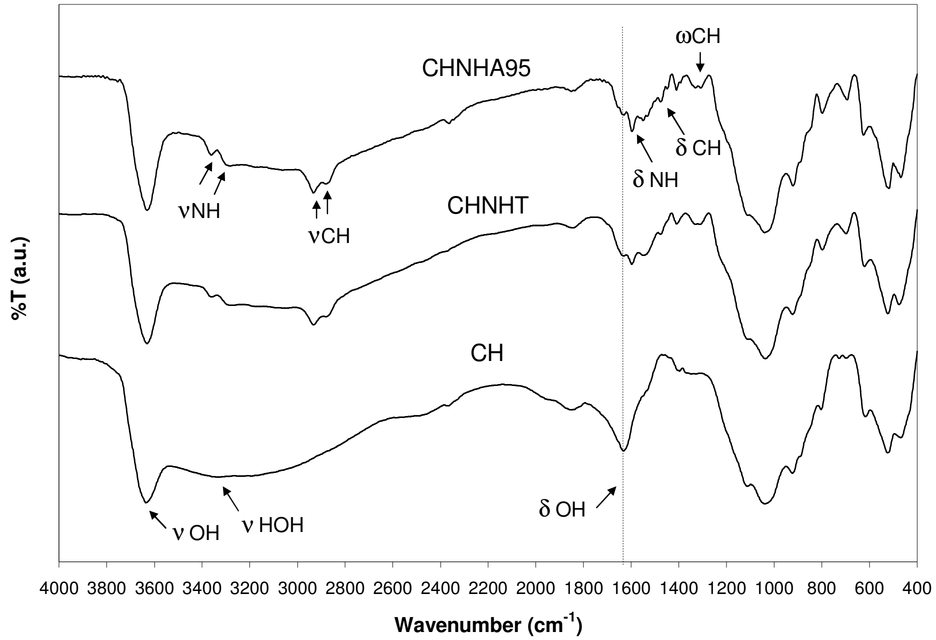


Figure 4.5 - FTIR spectra of acid activated and functionalized montmorillonite samples.

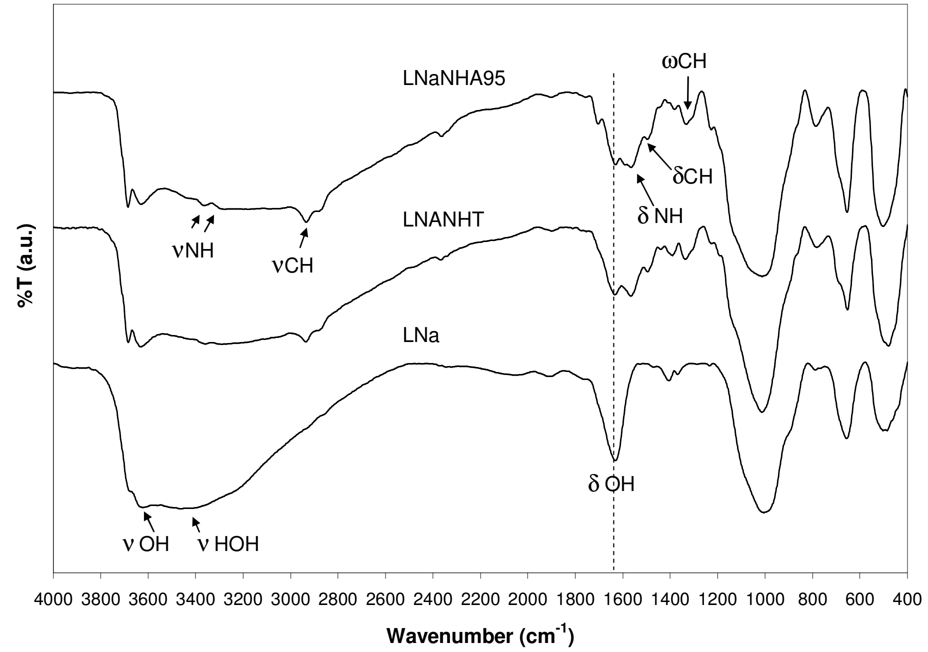


Figure 4.6 - FTIR spectra of acid activated and functionalized laponite clay samples.

Table IV.1: Assignment of the observed wavenumbers in FTIR spectra of organoclays. (Coates, 2000; Ahenach *at al.*, 2000; Famer *et al.,* 1974; Bois *et al.,* 2003)

Band assignments	Wavenumbers (cm^{-1})
Structural νOH	3620 - 3700
$\nu OH_{\text{adsorbed water}}$	3350 - 3450
$\delta OH_{\text{adsorved water}}$	1620 - 1640
$\nu Si\text{-}O$	960 - 1200
ωCH_2	1290 -1325
δCH_2	1430-1480
δNH_2	1540 -1580
$\nu_s CH_2$	2845 - 2860
$\nu_a CH_2$	2925 - 2965
ν O-CH_2CH_3, (unhydrolyzed ethoxy group)	2970
$\nu_s NH_2$	3290
$\nu_a NH_2$	3350

δ, ω, and ν indicate scissorin, wagging, and stretching bands, respectively. “a” and “s “ indicate asymmetric and symmetric stretching.

The broad peak within the range of 1200 cm^{-1} to 960 cm^{-1}, with the peak maximum at 1035 cm^{-1}, is due to the Si–O stretching of silicates present in the clay. The structural O-H stretching bands occur within the range of 3620 cm^{-1} to 3670 cm^{-1} for montmorilonite (AlAlOH, AlMgOH) and within 3628 cm^{-1} to 3700 cm^{-1} for laponite (MgMglOH, MgLiOH) samples (Famer, 1974). Both clays present an intense reduction of the broad band centered around 3400 cm^{-1} and the corresponding bending vibrations peak at 1630 cm^{-1} assigned to adsorbed water after modification process. This fact confirms the increased hydrophobicity of the functionalized samples and corroborates the previous conclusion that the aminosilane molecules were intercalated in the interlayer region, thus expelling the adsorbed water molecule.

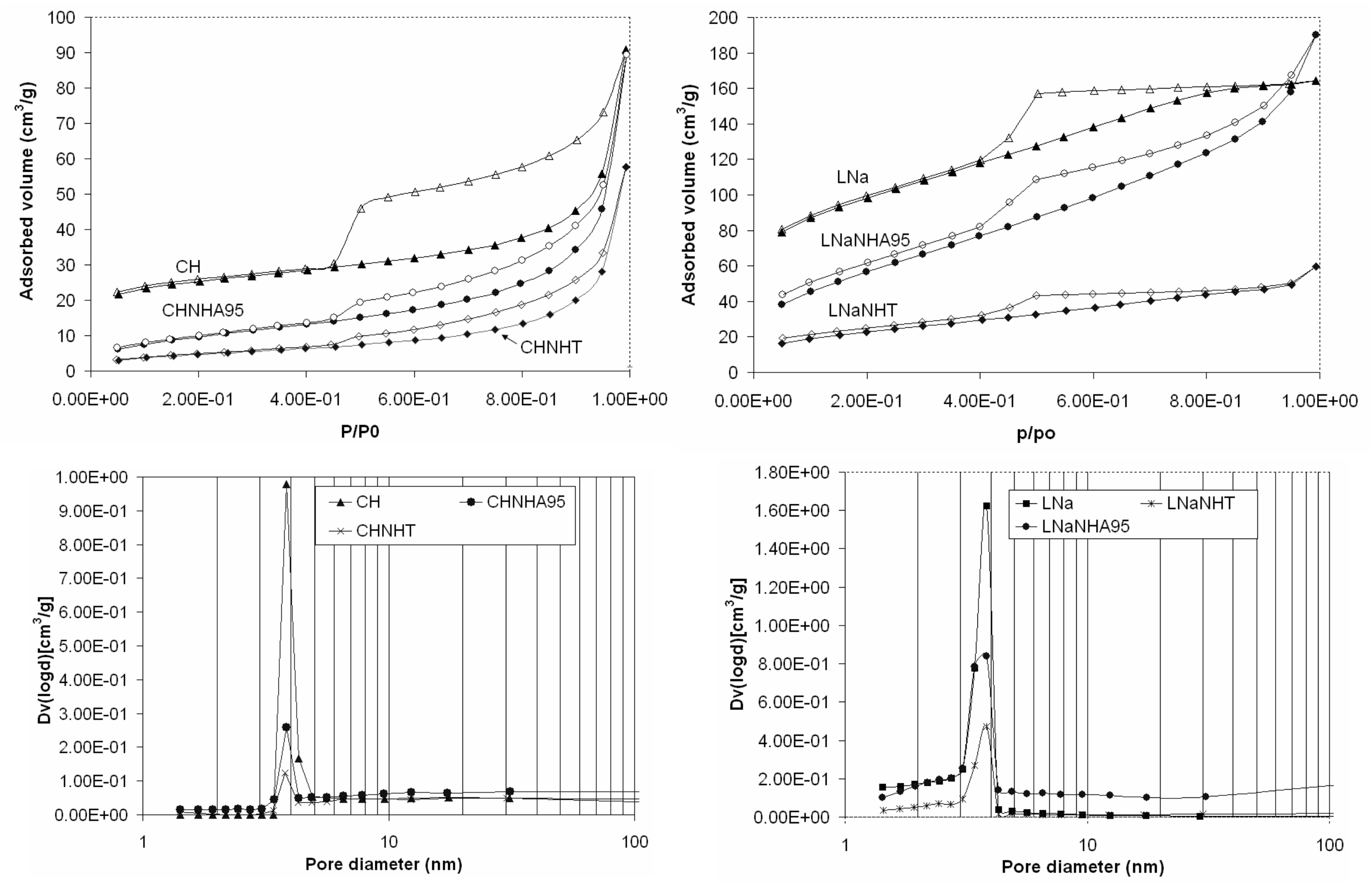
4.3.3 Textural analysis

Figure 4.7 depicts the nitrogen adsorption-desorption for raw and modified montmorillonite and laponite samples. Table IV.2 summarizes the results. The most dominant pores are found in the 2-100 nm range for montmorillonite and < 4 nm, predominantly, for laponite. Only after modification in alcohol-aqueous media the synthetic clay develop pores in the 2-100 nm range. The synthetic clay (LNa) presents a higher specific surface area (326 m^2/g) and microporous contribution than does the Na-montmorillonite sample (25 m^2/g). The latter has its surface area increased to 80 m^2/g after acid activation (sample CH), as depicted in Table IV.2. These results are in accordance with the adsorption data previously reported for similar layered silicates (Okutomo *et al.*, 1999; Maes *et al.*, 1997). We believe that the acid activation may improve the grafting efficiency by increasing the specific surface area as well as increase the density of superficial hydroxyl groups. All the samples follow the same trend, as illustrated by the curves in Figure 4.7. Significant reduction of surface area upon grafting with aminopropylsilane can also be observed. Both the specific surface and pore volumes were decreased after functionalization, these being less pronounced in the sample processed in alcohol-aqueous media. In all cases, the micropore contribution was also suppressed. The specific surface area of montmorillonite decreased from 80 m²⁄g (CH) to 37 m²⁄g (CHNHA95) and to 18 m²⁄g (CHNHT). A similar situation was observed with the laponite samples, where the surface area decreased from 326 m²⁄g (LNa) to 215 m²⁄g (LNaNHA95) and to 82 m²⁄g (LNaNHT). These results suggest that the sample functionalized in anidrous media (toluene) have the access to internal porosity blocked by the molecule grafted onto the border of the clay stacks. In the case of samples processed in alcohol-aqueous media, the majority of silane immobilization has occurred in the interlayer region, resulting in a material in which the internal porosity is more accessible. The d_{001} spacing also supports this hypothesis (Figure 4.3 and 4.4) since CHNHA95 shows higher d_{001} spacing (19.2 Å) than does CHNHT (18.8 Å). Laponite samples follow the same trend, as shown by LNaNHA95 (17.0 Å) and LNaNHT (13.7 Å). These results suggest that, in alcohol-aqueous media, the silane can reach the galleries between the clay platelets more easily, thus resulting in successful intercalation. The interaction between the (3-aminopropyl)triethoxysilane and the edge clay platelets is less significant, and, consequently, the internal porosity tends to be less blocked. These results are in accordance with findings from Shanmugharaj *et al.* (2006), who found that the intercalation of trifunctional silane in smectite tended to be more successful in aqueous media than in ethylene glycol.

Table IV.2: Textural characteristics of the clay samples.

Sample	S_{BET} (m^2/g)	S_{micro} (cm^3/g)	V_{micro} (cm^3/g)	V_P (cm^3/g)	D_p (Å)
CNa	25	1	0.005	0.054	125
CH	80	36	0,0207	0.141	71
CHNHA95	37	0	0	0.138	149
CHNHT	18	0	0	0.089	200
LNa	326	81	0.0445	0.254	31
LNaNHA95	215	0	0	0.219	78
LNANHT	82	0	0	0.092	45

Specific surface area (S_{BET}), micro pore surface area (S_{micro}),
micro pore volume (V_{micro}), total pore volume (V_p), and average pore diameter (D_P).



(a) (b)

Figure 4.7 - Montmorillonite samples: N$_2$ adsorption/desorption isotherms (solid symbols represent adsorption and empty ones) and pore size distribution of montmorillonite (a) and laponite samples (b).

According to Szabó *et al.* (1998), the terminal amino groups are protonated in aqueous solutions as follows:

$$(OCH_2CH_3)_3Si\text{-}(CH_2)_3NH_2 + H_2O \rightleftarrows (OCH_2CH_3)_3Si\text{-}(CH_2)_3NH_3^+ + OH^- \qquad (4.1)$$

Our hypothesis is that the insertion of the protonated APTES may also occur through an ion exchange reaction. The amino group induces a basic character to the silane, making it more compatible with the acid sites of the clay. The acid sites of clay surface present a high affinity toward the alkylamino even though the alkylamino groups are a weak basic group. The acid–base affinity of the guest-host pairs may have led to the adsorption in the interlayer space. Both factors shift the equilibrium of the reaction (4.1) to the right and the intercalation proceeds. During the drying step, the condensation reactions occur and siloxane linkages are form. We believe that the intercalated APTES molecules are hydrolyzed *in situ* by the water present in the interlayer region since the polymerized silane molecule can not be intercalated due to the large size of the polymers.

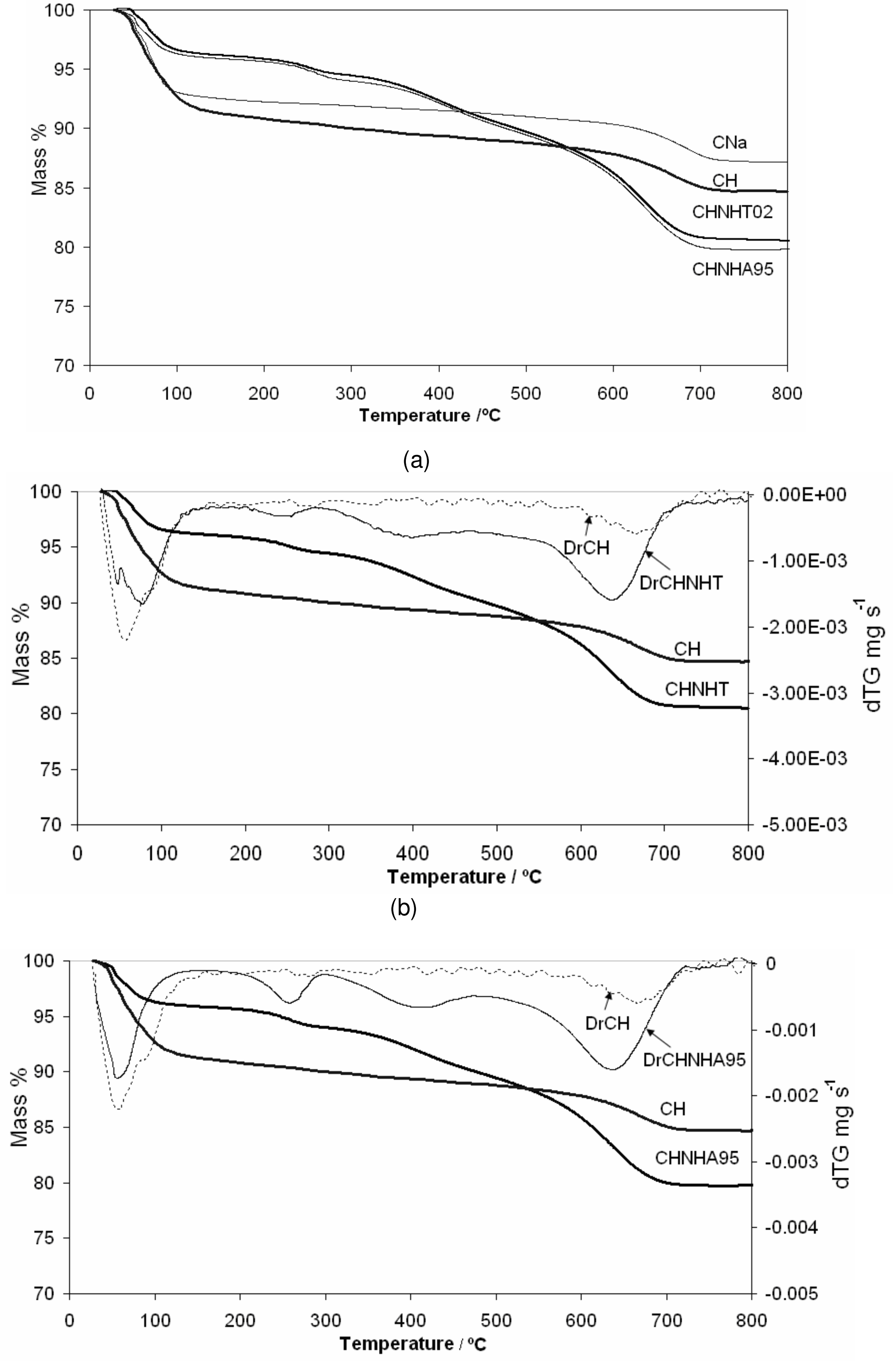
Currently, several works are concerned with detailed studies on the accessibility to the active chemical functions in organic-inorganic hybrid materials. A number of efforts are focusing on improving their applications in both catalysis and metal ion uptake by producing new materials with increased accessibility. The present study found that the porosity and the specific surface area of the hybrid material can be controlled by the dispersing media as well as by the clay type used in the modification process.

4.3.4 Thermogravimetry

Figure 4.8 and Figure 4.9 present the TG and DTG curves of all studied samples. It is possible to observe that the montmorillonite samples functionalized through different routes presented similar mass loss (Figure 4.8), whereas the laponite samples presented different profiles depending on the dispersing media (Figure 4.9). The mass loss of the functionalized clays is greater than that of the original clay. The initial degradation of both unmodified and silane-functionalized clay below 200 °C is attributed to the loss of physically adsorbed water molecules. In this region, relatively small mass loss for the functionalized clay can be observed, indicating hydrophobicity introduced by APTES intercalation. Higher hydrophobic character of the functionalized montmorillonite, in comparison with the functionalized laponite, can also be observed. The major mass loss above 650 °C is due to the dehydroxylation of aluminosilicate.

Regarding the functionalized samples, all of them exhibit, between 200 ℃ and 650 ℃, additional mass loss when compared to the original clay. Three steps can be distinguished. For both functionalized clays, the DTG peak, at approximately 260 ℃, is attributed to mass loss of physisorbed silane molecule, while the broader peak, at approximately 400 ℃, is attributed to the degradation and removal of the chemically bounded silane. The peak at approximately 650 ℃ (for NH_2-montmorillonite) and 550 ℃ (for NH_2-laponite) represents the removal of the grafted and intercalated silane. In case of montmorillonite, the latter peak is more intense due to the co-occurrence of the decomposition of chemically bound silane and the dehydroxylation of the clay. Similar observations were reported by Park and Kwon (2004).

Taking in account the mass loss within the range of 300 ºC to 650 ºC, the amount of grafted silane molecule was calculated as 11.6% (2.00 mmol/g) and 11.7% (2.02 mmol/g) of organic content for CHNHT and CHNHA95, respectively, and 7.14% (1.23 mmol/g) and 8.14% (1.51mmol/g) for LNaNHT and LNaNHA95, respectively. In spite of the higher specific surface area of laponite (Table IV.2), this clay grafted 30-40% less than the montmorillonite. The unexpected better grafting yield of montmorillonite can be attributed to the higher density of binding sites and its expandability properties. It is interesting to notice that the differences in the temperature of dehydroxylation, at 794 ℃ (LNaNHA95) and at 752 ℃ (LNaNHT), suggests different changes in the structure after the grafting process, depending on the dispersion media (Figure 4.9b / Figure 4.9c).

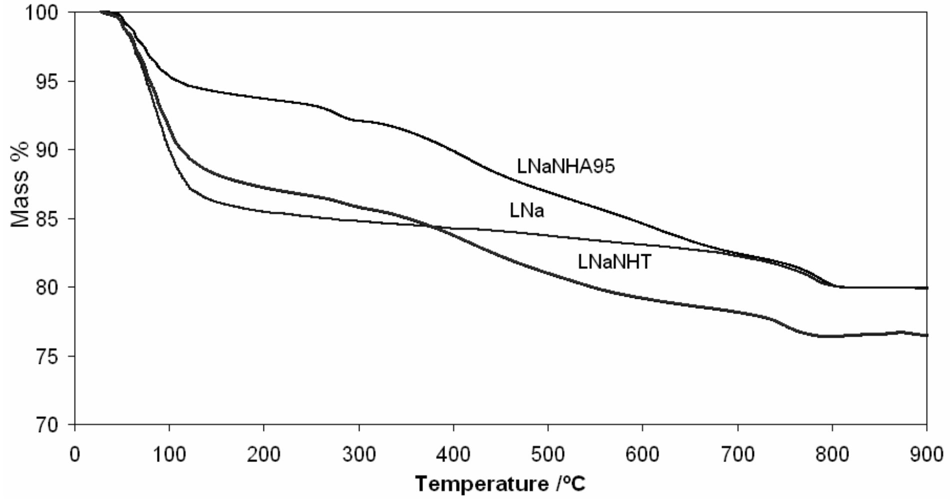


(a)

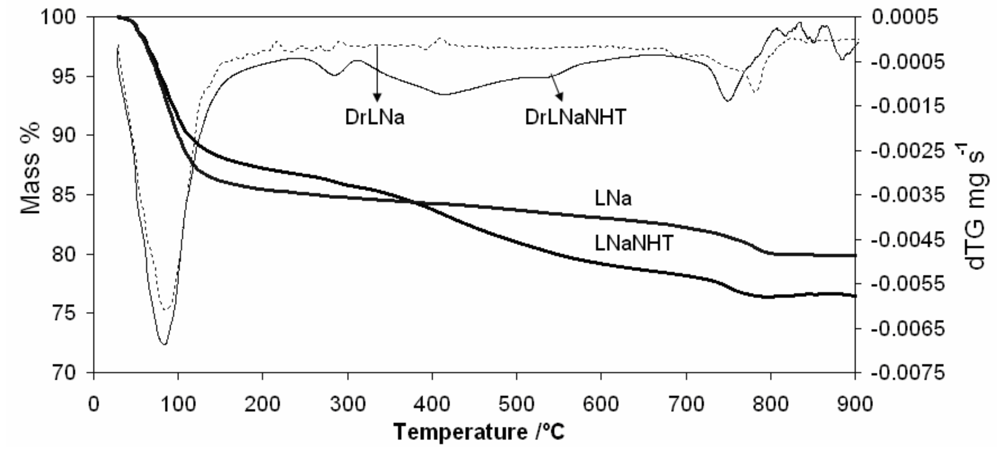
(b)

(c)

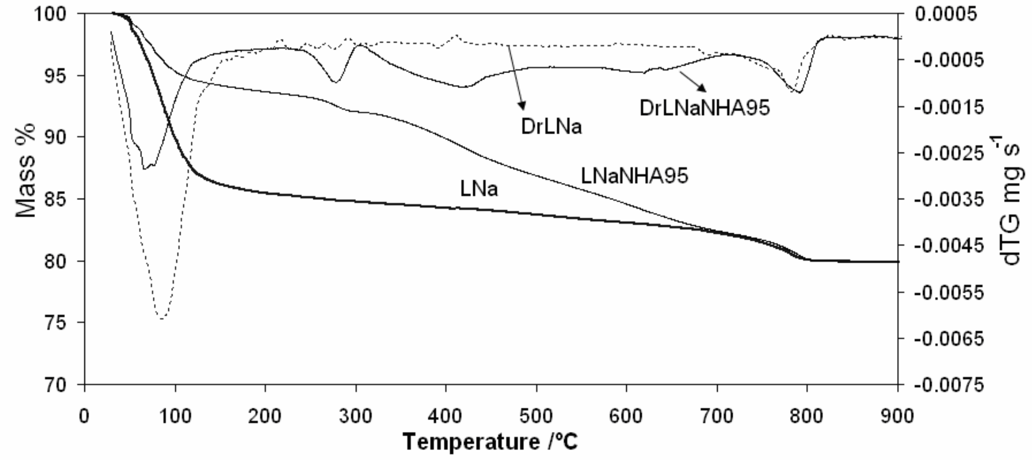
Figure 4.8 -TG and DTG curves of montmorillonite before and after functionalization.



(a)



(b)



(c)

Figure 4.9 - TG and DTG curves of laponite before and after functionalization.

4.3.5 Titration of amino groups

The amino group content was determined by the titration of the functionalized clays with an HCl solution of 0.01 mol dm^{-3}. Figure 4.10 shows the titration curve of the functionalized clay (CHNHA95 and LNaNHA95) dispersed in deionized water. These curves were obtained by adding the acid slowly enough to ensure quantitative protonation of all NH_2 groups. A similar curve profile was obtained for both functionalized clays. The two-step titration exhibits two equivalent points. For the CHNHA95 sample, the first, Eq_1 (pH 7.5; V_{HCl} = 8.50 cm^3), can be assigned to the protonation of "free" amine, while the second, Eq_2 (pH 5.0; V_{HCl} =12.8 cm^3), can be assigned to that of the zwitterion-like species ($-RNH_3^{+}\ ^{-}OSi-$), as illustrated in Figure 4.11. For the LNaNHA95 sample, the two equivalent points were Eq_1 (pH 7.5; V_{HCl} = 10.70 cm^3) and Eq_2 (pH 5.0; V_{HCl} =15.7 cm^3).

Coche-Guerente *et al.* (1998) and Walcarius *et al.* (2002) demonstrated that aminopropyl-siloxane immobilized on synthetic clay and silica gels exhibit zwitterionic functions on their surface. According these authors, these functions result from the deprotonation of silanol groups, inducing the protonation of adjacent amino groups (Figure 4.11). A similar process can be expected to occur to the functionalized clays studied herein. The two titration steps are in accordance with the existence of the two acid-basic species. The experimental equivalent volume of 12.8 cm^3 to CHNHA95 and 15.7 cm^3 to LNaNHA95 corresponds to the volume of hydrochloric acid necessary to neutralize the total amount of the grafted amino group. This result has shown that the ratio -RNH2/-NH3^{+} $^{-}$OSi- is close to 67:33 of the total acido-basic functions of both functionalized clays. This result is similar to that reported by Walcarius *et al*. (2002) who found that the ratio $-RNH_2/-NH_3^{+}\ ^{-}OSi-$ is close to 60:40 for silica gels grafted with aminosilane. Based on the equivalent volume, we calculated that 1.28 mmol and 1.57 mmol of amino group per gram of CHNHA95 and LNaNHA95, respectively, were accessible to the protons ions.

Comparing this value to the ligand content in mmol/g determined by the TG analysis (Table IV.3), one can conclude that 63% and 100% of NH_2 groups from CHNHA95 and LNaNHA95, respectively, are accessible to acid reactions. The higher accessibility of LNaNHA95 can be attributed to the larger surface area and pore volume presented by this sample.

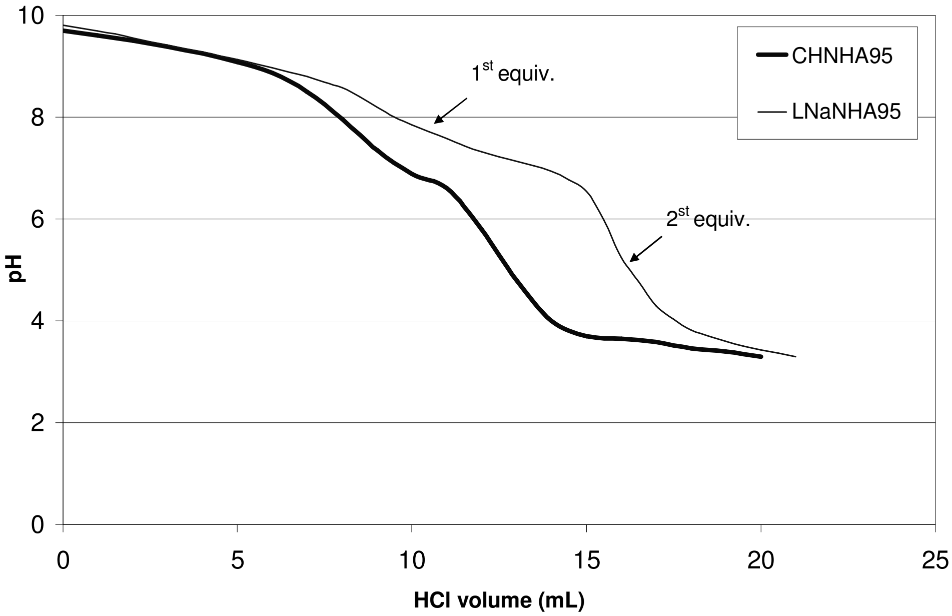


Figure 4.10 - Titration curve for suspension (100 mg of CHNHA95 in 50 ml DI water) by 0.01 mol dm^{-3} of HCl.

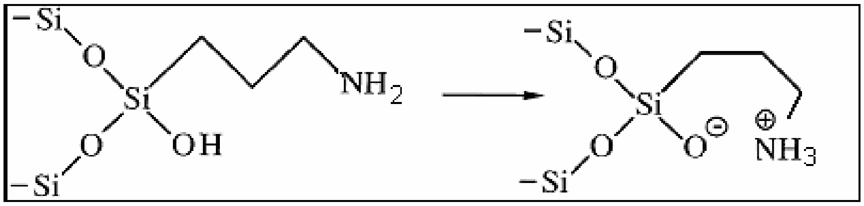


Figure 4.11 - The zwitterionic function of siloxane species.

For final considerations, all main characteristics of the clay samples before and after functionalization with aminosilane are summarized in Table IV.3. The results indicate the organic content of the functionalized montmorillonite samples are 30% to 40% higher than functionalized laponite samples when both were modified under the same conditions. This result was unexpected as laponite has a significantly higher specific surface area (326 m^2/g) than montmorillonite (80 m^2/g). The montmorillonite samples were successfully intercalated in both tested routes, illustrated by the fact that there was a clear increase in the average basal spacing (d_{001}) from 12.4 Å to 18.6 Å and 19.2 Å for CHNHT and CHNHA95 samples, respectively. The laponite sample was intercalated only in alcohol-aqueous media, with basal spacing varying from 12.5 Å to 17.1 Å. The interlayer expansion and organic content of montmorillonite is greater than those observed in laponite samples. These results suggest that montmorillonite sample has more active sites available for binding, combined with more adequate characteristics of expandability for the functionalization process, than does laponite sample. It was also observed that the media has a significant effect on the textural characteristic of the resultant material products. Modification in alcohol-aqueous media resulted in hybrid material with relatively higher surface areas and pore volumes due to preferential grafting in the clay interlayer space, as evidenced by the expansion of the basal spacing (d_{001}).

Table IV.3: Main characteristics of the clay samples before and after modification with aminosilane.

Clay samples	Ligand content % and (mmol/g of clay)*	d_{001} (Å)	S_{BET} (m^2/g)	Pore Volume (cm^3/g)
CNa	-	11.7	25	0.054
CH	-	12.4	80	0.141
CHNHT	11.6 (2.00)	18.6	18	0.089
CHNHA95	11.7 (2.02)	19.2	37	0.138
LNa	-	12.5	326	0.254
LNANHT	7.1 (1.23)	13.7	82	0.092
LNANHA95	8.7 (1.51)	17.1	215	0.419

* values in ( ) were calculated using the TG analysis in the 300 °C to 650 °C range in mmol/g of clay.

4.4 PROPOSED MODEL FOR AMINOSILANE IMMOBILIZATION

Based on the aforementioned results, we propose a model for the immobilization of aminopropylsilane in the clay structure (Figure 4.12 and Figure 4.13). The modification media has shown an influence on the density of the intercalated molecules in the interlayer space. In the case of alcohol-aqueous media, a material with a relatively higher surface area and pore volume is obtained due to the preferential grafting in the clay interlayer space. The surface area of montmorillonite decreases from 80 m^2/g (CH) to 37 m^2/g (CHNHA95) and to 18 m^2/g (CHNHT). A similar situation was observed with laponite samples where the surface area decreases from 326 m^2/g (LNa) to 215 m^2/g (LNaNHA95) and to 82 m^2/g (LNaNHT). In a dry toluene environment, the silane molecules react preferentially on the broken edge of the clay layer rather than on the interlayer surface, especially in a synthetic clay, thus the access to internal porosity is blocked by the grafted molecule. The d_{001} spacing also supports this hypothesis. In addition to the adequate characteristics of expandability, the preferential grafting in the clay interlayer space of the acid activated montmorillonite may be explained by the fact that the amino group induces some basic character to the silane, making it more compatible with acid sites present in the interlayer region of this clay. The acid–base affinity of the guest-host pairs may have led to adsorption in the interlayer space. In addition, in aqueous solutions, the terminal amino groups are protonated. Thus the insertion of the protonated APTES may also occur through an ion exchange mechanism since the clay surface is negatively charged (in this case both clays are sucessfully intercalated). After intercalation, the condensation reactions occur during the drying step and siloxane linkages are formed. In dry enviromments, the protonation of the amine does not occur, and the intercalation is less intense.

Taking into account the thickness of the phyllosilicate sheet of 9.6 Å, the free space between two sheets increases from 2.8 Å (which corresponds to the presence of the water molecule) to between 9 Å and 9.6 Å for montmorillonite and to 7.5 Å for laponite. This value demonstrates the presence of a double layer of the aminopropyl molecule (lengh of ~0.4 nm) in the interlayer space.

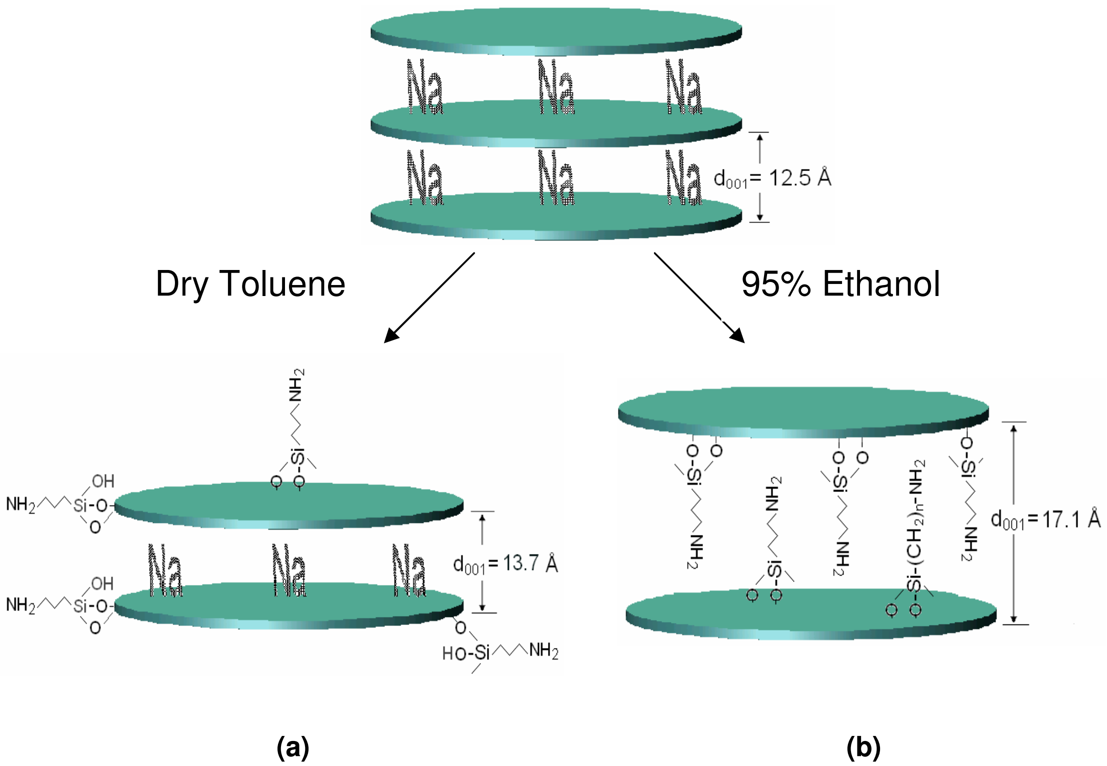


Figure 4.12 - The hypothetical diagram for the intercalation and grafting of aminopropylsilane into laponite samples using (a) dry toluene and (b) 95% ethanol as dispersing media.

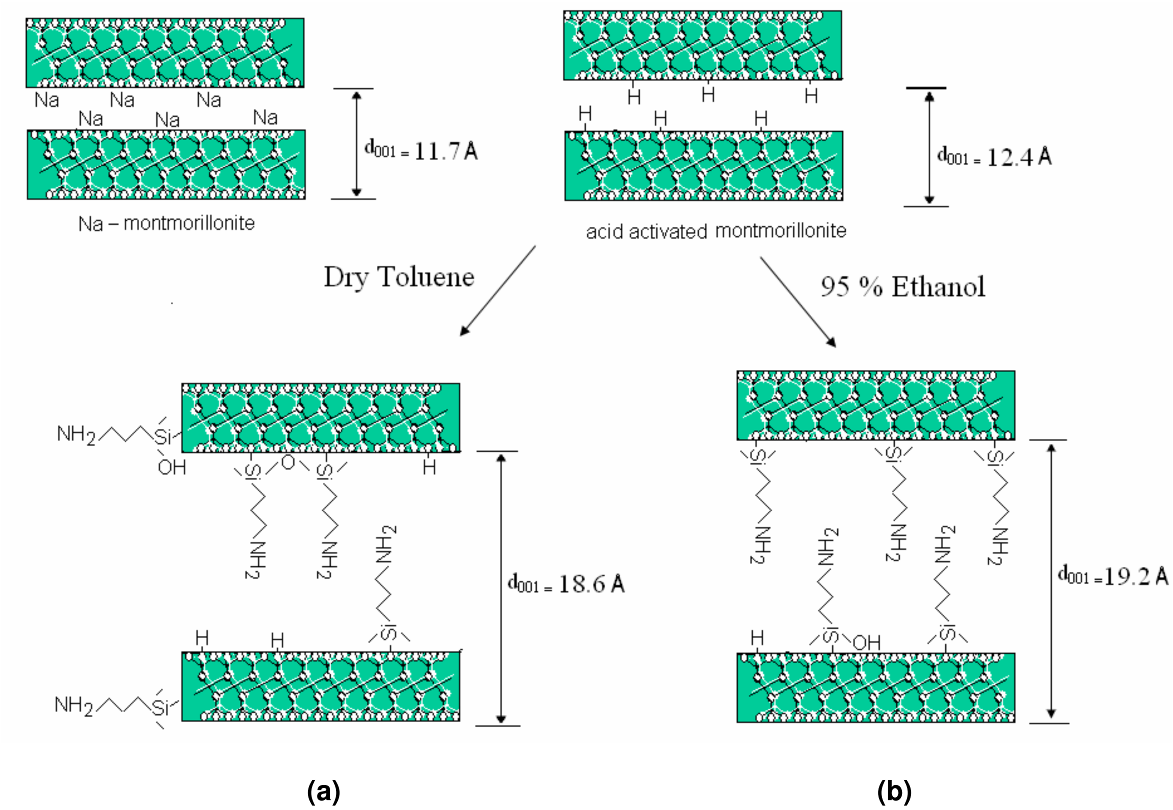


Figure 4.13 - The hypothetical diagram for the intercalation and grafting of aminopropylsilane into montmorillonite samples using (a) dry toluene and (b) 95% ethanol as dispersing media.

4.5 CONCLUSIONS

Montmorillonite, a natural layered silicate, and laponite, a synthetic silicate, have been conveniently functionalized with amine-organosilane. It was observed that the nature of the clay materials, as well as the type of solvent, have important effects on the intercalation degree. The XRD patterns clearly indicate that aminosilane was successfully intercalated in acid activated montmorillonite in both routes used. In addition, these patterns indicate that this clay presents more adequate characteristics of expandability for the functionalization process. The synthetic clay showed a different behavior as only the samples modified in alcohol-aqueous solution were intercalated. The free space between the two sheets was approximately 9 Å for montmorillonite and 7.5 Å for laponite after functionalization. These values demonstrate the presence of a double layer of aminopropyl molecule in the interlayer space for both clays. Qualitative evidence of the presence of aminosilane attached to the clay platelets has been provided using diffuse reflectance infrared Fourier transform spectroscopy (DRIFT). The BET results showed that the specific surface and pore volumes were decreased after functionalization, these being less pronounced in the sample processed in alcohol-aqueous media. The results indicate that the organic content of the functionalized montmorillonite samples are 30% to 40% higher than functionalized laponite samples when both are modified under the same conditions. This result suggests that montmorillonite samples have more active sites available for binding, combined with a greater expandability for functionalization, than do laponite samples,. However, the titration results indicated that 63% and 100% of NH_2 group are accessible to H^+ ions in modified montmorillonite and laponite, respectively. The higher accessibility of LNaNHA95 can be attributed to the larger surface area and pore volume presented by this sample. In addition, the clays showed two titration steps that are in accordance with the existence of the two acid-basic species with the ratio $-RNH_2/-NH_3^+\ ^-OSi-$, which is close to a ratio of 67:33 for both functionalized clays. Our study has demonstrated that the modification media influences the density of the intercalated molecules in the interlayer space. In the case of the alcohol-aqueous media, a material with a higher surface area and pore volume is obtained due to preferential grafting in the clay interlayer space.

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CAPÍTULO 5

CONSIDERAÇÕES FINAIS

5.1 CONCLUSÕES

A síntese de materiais híbridos nanoestruturados para aplicação na imobilização de espécies inorgânicas e orgânicas foi obtida a partir da funcionalização de smectitas. O trabalho demonstrou que as rotas de modificação propostas foram eficientes para imobilizar as moléculas de silano na estrutura das argilas sendo que o grau de funcionalização variou com o tipo da argila utilizada, o tipo de agente modificador e o tipo de solvente utilizado. A técnica utilizada permitiu a obtenção de material adsorvente com seletividade e especificidade controlada através da escolha adequada do grupo funcional do silano.

Os principais resultados obtidos a partir da modificação de duas amostras de montmorilonita (uma brasileira e uma americana comercializada como *Cloisite-Na*) e de uma argila sintética (laponita) com mercaptosilano (sob refluxo com tolueno como solvente) foram apresentados nos capítulos 2 e 3 e são resumidos a seguir:

i. A montmorilonita brasileira, tanto na forma *in natura* como ácido ativada, mostrou-se adequada para a imobilização de moléculas de mercaptosilano. A amostra de montmorilonita brasileira apresentou um grau de funcionalização superior ao do produto comercial *Cloisite*-Na: 1,76 mmol/g e 1,45 mmol/g, respectivamente. A argila laponita apresentou capacidade de imobilização de silano menor que as amostras de montmorilonita (1,2 mmol/g), apesar da sua área superficial (326 m^2/g) ser superior à das amostras de montmorilonita ácido ativada (aproximadamente 85 m^2/g).

ii. A estrutura original das amostras de argilas foi preservada após a funcionalização. O espaçamento interlamelar expandiu (12 Å para 15 Å) após a modificação, indicando a intercalação. A redução significativa do volume de poros e da área superficial (montmorilonita: ~85 m^2/g para 10 m^2/g; laponita: 326 m^2/g para 32 m^2/g) somada à baixa expansão basal sugere que a imobilização do silano se deu preferencialmente na superfície externa e também na bordas dos cristais de argila.

iii. A funcionalização modificou a natureza da argila de hidrofílica para hidrofóbica. Esta modificação é evidenciada pela redução da quantidade de água adsorvida (~ de 12 % para 3 % na análise térmica) bem como das bandas características da água (3400 cm^{-1} e 1600 cm^{-1}) nos espectros de infravermelho.

iv. O mecanismo de imobilização das moléculas de silano envolve uma reação de condensação entre os grupos hidrolisáveis do silano (metoxi) e as hidroxilas presentes na superfície da argila. Esta reação é evidenciada pela redução da intensidade da banda característica dos grupos OH (νOH ~3600 cm^{-1} e δAlAlOH ~916 cm^{-1}) e pela presença dos grupos funcionais imobilizados (νCH ~2800 - 3000 cm^{-1},νSH ~2560 cm^{-1}) nos espectros obtidos por infravermelho (DRIFT).

v. O acesso aos grupos funcionais imobilizados, medido pela adsorção de íons prata (método Volhard), foi de 60% - 75 % para as amostras de montmorilonita, dependendo da quantidade de grupos imobilizados, e de 100% para a amostra de laponita.

vi. A capacidade de adsorção dos íons Cd(II) e de Ag(I) pelas amostras de montmorilonita foi consideravelmente melhorada com a funcionalização. A adsorção de íons Cd(II) aumentou de 17 para 44 mg/g (aumento de 160%). Para os íons Ag(I) houve um aumento médio de 9 mg/g para 111 mg/g (aumento de ~1100 %). Nas argilas funcionalizadas predomina o mecanismo de complexação dos íons metálicos pelos grupos SH (adsorção específica) enquanto na argila *in natura* predomina o mecanismo de troca catiônica (inespecífico).

vii. Os ensaios de adsorção das espécies de As(III) e As(V) mostraram que a argila laponita funcionalizada com grupos SH é eficiente e seletiva na remoção do arsênio em sua forma trivalente. A maior adsorção e melhor seletividade foram obtidas em condições de pH em que predomina a espécie trivalente neutra (H_3AsO_3). O carregamento máximo para As(III) foi de 22,3 mg /g em pH 4-5.

viii. A reação da espécie As(III) com os grupos SH foi comprovada pela espectroscopia Raman através do surgimento dos modos de vibração da ligação As-S (350-450 cm^{-1}) combinado com a redução da intensidade da banda do grupo SH (2570 cm^{-1}).

ix. Os grupos SH imobilizados mostraram-se estáveis na estrutura da argila não exigindo nenhum tratamento prévio aos ensaios de adsorção. Após um ano da síntese a redução da capacidade de imobilização foi de 10 %.

x. A argila funcionalizada forma aglomerados menores comparados aos obtidos com o material *in natura*. Ao contrário do observado com a bentonita natural, a argila organofuncionalizada é facilmente filtrada, não forma suspensão estável e gelatinosa em meio aquoso, seca rapidamente ao ar e mantém-se na forma de pó após a secagem. Estas características constituem uma grande vantagem para sua aplicação em processos de separação.

Amostras de montmorilonita e laponita foram funcionalizadas com aminopropilsilano através de duas rotas, uma utilizando solvente anidro (tolueno) e outra utilizando solução etanol-água a 95 %. Com base nos resultados obtidos (capitulo 4) concluiu-se que:

i. A montmorilonita apresentou alto grau de intercalação pelas moléculas de aminossilano em ambas as rotas de modificação utilizadas (d_{001}: 12 Å para 19 Å). A amostra de laponita apresentou intercalação expressiva somente quando funcionalizada em solução alcoólica a 95%.

ii. Em meio alcoólico, a laponita sódica apresentou menor capacidade de imobilização (1,5 mmol/g) que a montmorilonita ácido ativada (2 mmol/g) apesar da maior área superficial da primeira (326 m^2/g) em relação à segunda (80 m^2/g).

iii. A titulação potenciométrica com ácido clorídrico indicou que 63 e 100 % dos grupos amino das amostras de montmorillonita e laponita, respectivamente, são acessíveis aos íons H^+. A maior acessibilidade da amostra de laponita funcionalizada se deve a sua maior área superficial (215m^2/g) comparada à apresentada pela montmorilonita (37 m^2/g) após funcionalização.

iv. O tipo de solvente utilizado no processo de modificação influenciou o mecanismo de intercalação. As amostras funcionalizadas em álcool a 95% apresentaram maior expansão basal (d_{001}): 12 Å para 19 Å (montmorilonita) e de 12.5 Å para 17 Å (laponita), maior área superficial e maior volume de poros devido à imobilização preferencial na região interlamelar. A expansão das argilas devido à intercalação correspondeu a um espaço livre entre as lamelas de aproximadamente 9 Å, está coerente com a presença de uma dupla camada de moléculas de aminopropil (4 Å cada). A menor expansão obtida em ambiente anidro (tolueno) indica que a imobilização se deu preferencialmente na superfície externa das partículas e nas bordas dos cristais.

5.2 CONTRIBUIÇÕES ORIGINAIS DESTE TRABALHO

- Demontração do potencial da bentonita de origem brasileira para ser utilizada como matriz inorgânica para imobilização de organossilano com funcionalidades específicas.

- síntese de material adsorvente com boa capacidade de acumulação para metais em meio aquoso (Cd e Ag) a partir da funcionalização de três diferentes argilas esmectitas através da reação de condensação direta entre moléculas do composto (3-mercaptopropil)trimetoxissilano e a superfície da argila devidamente preparada.

- Obtenção de adsorvente específico para As(III) capaz de adsorvê-los seletivamente em pH neutro ou ácido com bom potencial para se aplicado em processos de separação e concentração. É a primeira vez que se propõe o emprego de argila funcionalizada para imobilização seletiva do As(III) através de um processo simples e direto sem a necessidade de pré-condicionamento (necessário para resinas quelantes comerciais) para ativação dos grupos SH.

- Identificação do mecanismo da adsorção do As(III) na argila SH-modificada através da técnica da espectroscpia Raman que possibilitou distinguir os modos vibracionais As-S na estrutura da argila.

- Demonstração do efeito do pré-tratamento ácido no grau funcionalização e na homogeneidade da intercalação da argila utilizando organossilanos como agentes de modificação. As amostras ácido ativadas, de um modo geral, apresentaram maior expansão basal e imobilizaram maior número de moléculas de silano, 50% maior para a argila brasileira e 290% maior para argila de referência. Além de aumentar a área superficial específica da argila, a ativação gera sítios ácidos adicionais para imobilização das moléculas de silano.
- Demonstração da influência do tipo de solvente na microestrutura do material híbrido obtido a partir da funcionalização de argila com o grupo funcional aminopropil. Argilas funcionalizadas em solução alcoólica a 95% resultaram em sólidos com maior quantidade de organossilano imobilizado e também maior área superficial e volume de poros.

- O protocolo desenvolvido baseado no método de Volhard se mostrou como uma metodologia rápida e com boa repetibilidade para quantificar os SH imobilizados e acessíveis em substratos inorgânicos funcionalizados.

5.3 SUGESTÕES PARA TRABALHOS FUTUROS

- Utilização da técnica ressonância magnética nuclear (RMN) para melhor avaliação do mecanismo de imobilização das moléculas de silano na superfície da argila.

- Estudo da adsorção dos íons Hg(II) nas argilas modificadas com grupos amino e mercaptopil em diferentes condições de pH e concentração da solução.

- Estudo da adsorção dos íons Cd(II), Hg(II), As(III) e As(V) na presença de íons competitivos.

- Estudos da adsorção de enzimas utilizando as argilas funcionalizadas e também avaliação da atividade das enzimas imobilizadas através de reações específicas.

- Avaliação do desempenho das argilas funcionalizadas para obtenção de eletrodos modificados para pré-concentração e determinação qualitativa e quantitativa de metais traço (Hg, Cd, etc) através da técnica voltametria cíclica (eletroanálise).

- Avaliação da estabilidade das argilas modificadas em diferentes condições de pH e tempo, bem como a possibilidade de regeneração e reutilização das mesmas em processos de adsorção.

5.4 TRABALHOS GERADOS A PARTIR DESTE TRABALHO DE TESE

Trabalhos publicados em periódicos

Guimarães, A.M.F., Ciminelli, V.S.T., Vasconcelos, W. L. (2007). Surface Modification of Synthetic Clay Aimed at Biomolecule Adsorption: Syntesis and Characterization. Journal of Materials Research, v.10, p.37-41.

Guimarães, A. M. F., Ciminelli, V.S.T., Vasconcelos, W. L. (2007). Synthesis of thiol-functionalized hybrid materials from smectite-type clays for heavy metal uptake. (a ser submetido para Journal Applied Clay Science).

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Guimarães, A.M.F.,Ciminelli, V.S.T.,Vasconcelos, W.L. (2006). Surface modification of synthetic clay for biomolecules adsorption: synthesis and characterization. In: 4º Congresso Latino Americano de Órgãos Artificiais e Biomateriais, 2006, Caxambu. 4º Congresso Latino Americano de Órgãos Artificiais e Biomateriais, 2006. v. 1. p. 1-9.

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APPENDIX 1

SURFACE MODIFICATION OF SYNTHETIC CLAY AIMED AT BIOMOLECULE ADSORPTION: SYNTHESIS AND CHARACTERIZATION

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Abstract

This work describes the process for functionalization of laponite through the grafting of 3-mercaptopropyltrimethoxysilane (MPTS). Laponite is synthetic smectite clay with surface area of 330 m^2/g. The samples, prior to and after functionalization, were characterized by chemical analyses, thermogravimetric analysis (TGA), X-ray diffraction (XRD), diffuse reflectance infrared Fourier transform spectroscopy (DRIFT), scanning electron microscopy and energy dispersive spectrometry (MEV/EDS). Infrared spectroscopy and elemental analyses confirmed the presence of organic chains and thiol groups in the modified clay. The immobilized and available thiol group, measured according to the Volhard method, totaled 1.4 meq/g of clay, with approximately 90% accessible for Ag^+ trapping. These results represent an improvement as compared to other works concerning the functionalization of smectite-type clays in which the effect produced by functional group blockage limits the access of species to less than 10% of the complexing sites.

Keywords: *Laponite, Functionalization, Biomolecule Adsorption*

1 INTRODUCTION

Mineral clays of the smectite group present a set of structural characteristics that make them attractive for the development of catalysts, sorbents, supports for drug or enzymes, and intercalation of organic molecules (He *et al.,* 2005; Patil *et al.,* 2005; Kuzniarska-Biernacka *et al*., 2005 Celis *et al*., 2000; Coche-Guuérente *et al*., 1998). Organosilanes are widely used for the modification of silica surfaces. The silylation mechanism for the attachment of organosilane to amorphous silica and alumina surfaces has been commonly reported 2006, Walcarius *et al*.,2004; Bois *et al.,* 2003; Mansur *et al*., 2000). Recently, organosilanes have been employed for the modification of layered silicates, with smectites and vermiculites being the most commonly clays used to investigate the functionalization processes (Herrera *et al*., 2006), Sayilkan *et al*., 2004; Park et al., 2004; Mercier and Pinnavaia, 1998; Mercier and Detelier, 1995). Among the smectites, montmorillonite has been the most common choice, mostly due to its availability and adequate characteristics of expandability (Park and Kwon, 2004). More recently, the functionalization of other clays, such as the synthetic laponite, has been also studied for various applications. These include (i) the preparation of modified electrodes for electrochemical applications and (bio) sensors (Moust, 2004, Coche-Guérente *et al*., 1998; Tonle *et al*., 2004), (ii) the immobilization of several enzymes within clay matrices (Tietjen and Wetzel, 2003), (iii) the immobilization of catalysts (Kuzniarska-Biernacka *et al*., 2005) and (iv) the removal of undesirable bimolecules from extractors and slurry (Bruce, 2006).

Laponite is a layered hydrous magnesium silicate, hydrothermally synthesized from mixing silicate, lithium, and magnesium salts in the presence of mineralizing agents. This clay is normally used as a rheology modifier for a wide range of industrial and consumer products and to produce electrically conductive, antistatic, and barrier thin coatings. Laponite is an entirely synthetic smectite clay, which closely resembles the natural clay mineral hectorite in both structure and composition, and has a specific surface area of 350 m^2/g. Laponite can be described by the chemical formula of $Na_{0.7}$ $[(Si_8\ Mg_{5.5}\ Li\ _{0.3})\ O_{20}(OH)_4]$ and is made up of small disc-like particles. Each single-particle is a crystalline disc with an average radius of 20 nm and a thickness of 1.0 nm. Only in dilute suspension, the charged platelets become dispersed as individual units. In a dry form, these units are usually agglomerated into larger clusters. The silanol groups located at the edges of the laponite sheets may be used to covalently attach themselves to organic compounds. The lamellar spacing of laponite may be expanded to incorporate intercalants (Prado *et al*., 2005).

Surface modification is a key step concerning the application of clays in biotechnology. One of the main obstacles hindering these applications is the interaction of organic molecules with the acid and hydrophilic clay surface, which in turn may cause the denaturation of enzymes (Tietjen and Wetzel, 2003). This limitation can be overcome by passivating the acid surface sites and creating a more organophilic clay matrix with different functionalities. The clay surface may be modified through reactions with various functional groups, such as thiol, amine, or long carbon chains. The present study was aimed to developing clay-based materials that can be used as sorbents for biomolecules. This work focused on the functionalization of a synthetic clay with thiol groups through the grafting of 3-mercaptopropyltrimethoxysilane (MPTS). A detailed material characterization was provided by chemical analysis; diffuse reflectance infrared Fourier transform spectroscopy-DRIFT, X-ray diffraction-XRD, scanning electron microscopy and energy dispersive spectrometry – MEV/EDS. The sorption capacity of the mercaptyl functional groups in the clay was evaluated using the Volhard silver nitrate method.

2 EXPERIMENTAL

2.1 Materials

The laponite sample used in the experiments was supplied by Rockwood Specialties Inc. and is identified by the chemical formula $Na_{0.7}$ $[(Si_8\ Mg_{5.5}\ Li\ _{0.3})\ O_{20}(OH)_4]$. According to the supplier, the material has a specific density of 2.53 and cation exchange capacity (CEC) of 50 to 60 meq/100g clay. When fully dispersed in water, the particles display disc-shaped, nano-sized crystals of approximately 20nm in diameter and 1nm in thickness. The organosilane-grafting agent, the 3-mercaptopropyltrimethoxysilane (MPTMS) ($Si(OCH_3)_3C_3H_6SH$), 98% pure, was purchased from Sigma-Aldrich and used without further purification. Toluene (99.8%) was also provided by Sigma-Aldrich. The solutions of $AgNO_3$, KSCN, and $Fe(NH_4)(SO_4)_2$ used in the adsorption experiments were prepared with reagent grade chemicals (Merck). All solutions were prepared with high-purity water (18 $M\Omega.cm^{-1}$) obtained from a MilliQ water purification system.

2.2 Modification process

Prior to the grafting process, 1 g of the sodic laponite (LNa) was acid activated with 100 mL of 0.1mol/L HCl solution. This suspension was maintained under agitation for a short period to avoid the octahedral sheet dissolution. The resulting sample was denominated LH. The acid activation was used to remove the sodium ions from the interlamelar region. In a next step, 1 g of acid activated laponite, previously dried at 150 ºC for 4 h, was dispersed in 50 cm^3 of 0.1 mol/L MPTMS in dry toluene. The resulting mixture was refluxed and agitated for 24 h within an inert atmosphere of N_2 to avoid the oxidation of the group SH. The obtained solid was sequentially washed with toluene, absolute ethyl alcohol, and MilliQ water, filtered and dried for 2 h at 120 ºC in an inert nitrogen atmosphere. The functionalized sample was denominated LHSH. This method is similar to that described by Walcarius *et al.*(2004) for the functionalization of silica gel.

2.3 Characterization methods

The X-ray diffraction patterns of modified and unmodified clay samples were obtained with a Philips model PW1710 diffractometer, fitted with a Cu tube (λ=1.5418 Å, 40 kV and 20 mA, step size 0.06°2θ, 5 s/step). DRIFT analyses were performed using a FT/IR- spectrophotometer, model SPECTRUM-1000, Perkin Elmer (32 scans of accumulation; resolution of 4 cm^{-1}). The IR measurements were taken at room temperature, in the spectral range of 400-4000 cm^{-1}. The samples were mixed with KBr powder in 5 wt.% and a pure KBr spectrum was used as reference. Thermogravimetric curves were obtained in a TGA model TGA50 Shimadzu under in N_2 environment, (20 mL/min), with temperature ramp of 10 °C/min between 30ºC - 1000 ºC. The morphological and semi-quantitative analyses of the samples was carried out in a Scanning Electron Microscopy (Jeol instrument model JSM-6360LV, operating at 25 kV and with a Noran energy-dispersive spectrometer (ZAF corrections coupled).

2.4 Binding capacity of the mercaptyl functional groups

In the present investigation, the amount of the immobilized and accessible thiol groups was successfully determined according to a protocol based on the Volhard silver nitrate method developed by the authors (Domingues *et al.*, 2002). The determination is based on the chemical affinity of silver by the thiol groups. Following the protocol, 25 mL of 0.01 mol/L silver nitrate solution were added to flasks containing 100 mg of dry modified clay. The flasks were covered to avoid exposure to light and stirred in a shaker for 6 h prior to testing. The remaining silver nitrate was titrated with standardized 0.01 mol/L potassium thiocyanate (KSCN) using iron ammonium sulfate hexahydrate as an indicator. The endpoint was detected when an excess of thiocyanate anion formed a red colored complex with the iron compound. The binding capacity of the mercaptyl functional group was expressed in meq/g of clay. In all cases the tests were carried out in triplicate and the results compared with those obtained using a sample of unmodified clay as a reference. Another flask containing pure solution was submitted to the same process in order to evaluate eventual precipitation. This methodology was used as protocol to quantify the accessible SH groups. The sequence of reactions is described below:

Adsorption step:

$$\underset{\text{(modified clay)}}{\sim RSH_{(S)}} + AgNO_{3(aq)} \longrightarrow \sim RSAg_{(s)} + HNO_{3(aq)} \qquad (1)$$

Titration step:

$$AgNO_{3(aq)} + KSCN_{(aq)} \longrightarrow AgSCN_{(S)} + KNO_{3(aq)} \qquad (2)$$

End point:

$$6SCN^{-}_{(aq)} + Fe^{3+}_{(aq)} \longrightarrow \underset{\text{(Red complex)}}{Fe(SCN)_6^{3-}}{}_{(aq)} \qquad (3)$$

3 RESULTS AND DISCUSSION

3.1 Functionalization process

The silylation of silicates involves a direct condensation reaction between the terminal (OH) groups from the silicate surface and the species derived from the hydrolysis of the alkoxysilanes. It is believed that the silylation of silicate is favored over the polysiloxane formation if the reaction is conducted in a dry environment. Figure 1 depicts a schematic illustration of the functionalization process followed by biomolecule adsorption. The silane coupling agents are a family of organosilicon monomers with the general structure of R–SiX_3. X is the hydrolyzable alkoxy group, typically methoxy (-OCH_3) or ethoxy (-OC_2H_5), which releases methanol and ethanol during the coupling reactions. R is an organo-functional group attached to silicon. Some recent works have shown that it is possible to create specific chemical activity through the selection of an adequate functional group, in a way that the functionalized clay will provide specific sites for the adsorption of specific enzymes (Patil *et al.*, 2005). In the present work, the mercapto group was selected as functional group due to its great affinity to many biomolecules.

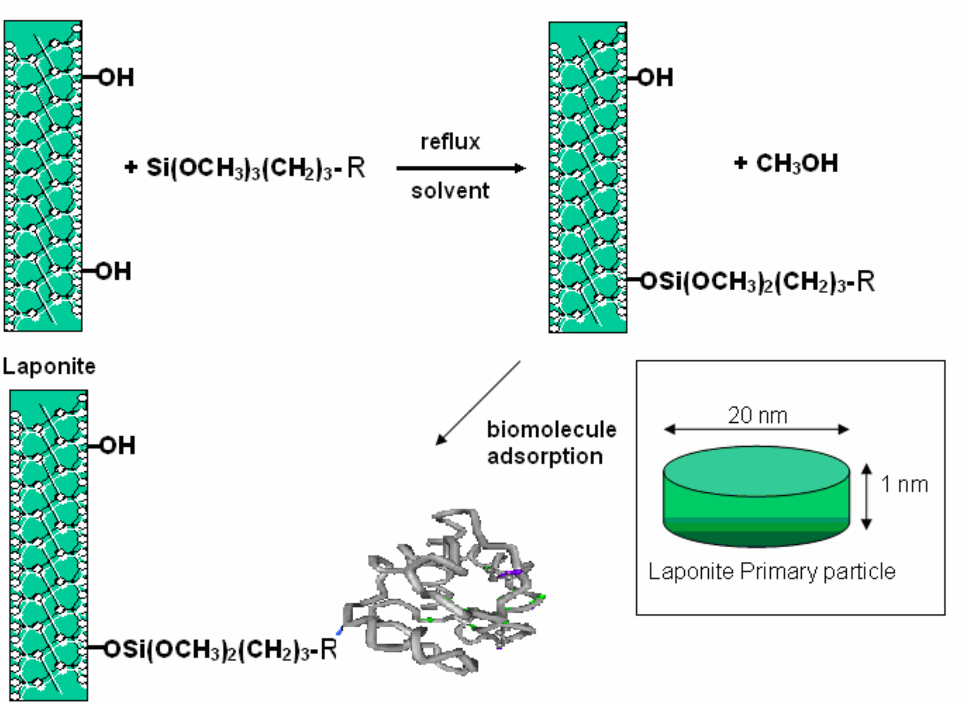


Figure 1 - Schematic illustration of the direct hydrolysis and condensation reaction followed by biomolecule adsorption. The inset shows a schematic representation of the size and morphology of the individual clay platelets (the "primary particles").

Following functionalization, the concentration of the immobilized thiol groups in the clay was measured according to the Volhard method. The total binding capacity was determined as 1.4 meq/g and 0.15 meq/g for the functionalized and the original clay (LNa), respectively. This value is comparable to the values obtained by Dominguez *et al.*, (2002) in a synthesis of mercaptyl fibers (1.7 meq/g). It indicates that the mechanism of adsorption involves primarily silver ion complexation by the thiol groups instead of cation exchange. The unmodified sample exhibits some ion immobilization capacity that may be related to a cation exchange mechanism, even though the original sample shows a very low affinity for silver ions. The average CEC indicated by the supplier is of 0.55 meq/g.

Elemental semi-quantitative analyses provided by EDS are summarized in Table1. The atomic % ratio, Si/Mg, increases from 1.9 to 2.4 after acid treatment, thus indicating that clay dissolution has occurred to some extent with a consequent release of Mg^{2+} from the clay lattice. We believe that this reaction may increase the density of Mg-OH and Si-OH groups on clay surface and thereby improve the organosilane immobilization, since this immobilization involves a reaction with the silicate's OH groups. The increase of the atomic % ratio, Si/Mg, in the LHSH-Ag sample is related to the incorporation of the organosilane molecule. The atomic % ratio, Ag/S, in this sample suggests that almost all of the mercaptyl groups (~90%) were accessible to silver binding. This presents a positive result, once Mercier and Detellier (1995) who reported that the intercalation of mercaptopropyl groups in the galleries of smectite-type clay led to loadings corresponding to less than 10% of the total number of thiol groups in the adsorbent. An improvement of the previous result was later reported by Mercier and Pinnavaia (1998) who prepared an MPTS-fluorohectorite and found that 67% of the thiol groups were accessible for Hg(II) ions. This result is similar to those reported by Celis *et al.* (2000) for MPTS-sepiolite. These authors attributed the relatively low loading to the blockade of pore space by intercalated molecules.

Table 1: EDS Semi-quantitative analyses for the clays samples

	Atomic % ratio		
Samples	**Si/Mg**	**S/Mg**	**Ag/S**
LNa	1.9	-	-
LH	2.4	-	-
LHSH + Ag	3.5	0.8	0.9

LHSH + Ag indicates the functionalized Laponite after silver adsorption.

3.2 Sample characterization

The DRIFT spectra of modified and unmodified clay are presented in Figure 2. Changes following the modification process can be observed in all frequency range of the FTIR spectra. The spectrum of the sodium laponite (LNa) exhibits a broad shoulder at around 3700-3400 cm^{-1}, in a range of frequencies usually assigned to surface hydroxyl groups and adsorbed water. The poorly resolved shoulder consists of the overlapping of two components: Si-OH (at ~3628 cm^{-1}) and Mg-OH (at 3680 - 3700 cm^{-1}) stretching vibrations and the ν(O-H) stretching frequency at 3350 cm^{-1} due to physisorbed water (Kuzniarska-Biernacka *et al.,* 2005). The δ(O-H) deformation band at 1621 cm^{-1} is yet another indication of the presence of water (Park *et al*., 2004). In the low energy region, the spectrum shows one broad band with a maximum peak at 1010 cm^{-1} assigned to Si-O and Si-O-Si stretching vibrations, one band around 660cm^{-1} due to Mg-OH bending vibration, and one band at 488 cm^{-1} assigned to Mg-O vibration (Madejová, 2003). After acid activation, some changes in the FTIR spectra can be observed. In the high-energy range, the band intensity at 3700-3400 cm^{-1} and at 1620 cm^{-1} increase, thus suggesting that the LH sample is more hydrophilic than the LNa. It is possible to observe a broadening of the band assigned to the Si-O and Si-O-Si stretching vibrations, an indication that acid activation may have promoted some structural modification. After functionalization, the LHSH sample shows the characteristic SH stretching vibration at 2562 cm^{-1} and CH stretching vibration at 2800-3000 cm^{-1}, thus indicating that the organic molecules were effectively grafted to the surface silanol groups (Coates, 2000). The relatively lower intensity of the band centered at 3350 cm^{-1} and the δ(O-H) deformation band at 1620 cm^{-1} indicates a reduction of the adsorbed water content, with a consequent increase of the hydrophobicity of the LHSH sample.

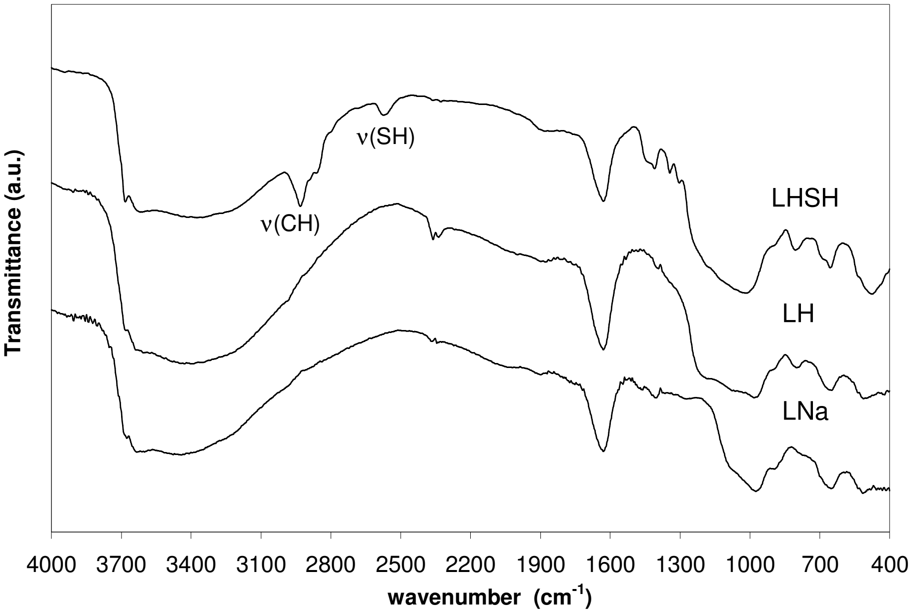


Figure 2 - DRIFT spectra of sodium (LNa), acid activated (LH) and functionalized (LHSH) laponite samples.

Figure 3 presents the mass loss and the peak of the first derivative in order to illustrate the most significant events regarding mass loss events. In contrast to the original clay, which that does not show any important mass loss in the temperature range of 200 ℃ to 600 ℃, the functionalized sample exhibits a sharp DTG peak at 280 – 330 ºC. This feature was mainly ascribed to the loss of the mercaptopropyl group. A smaller and broader peak is also observed at temperatures of 650 ºC. This typical behavior of organoclays (Mercier and Detelier, 1995) can be used as an indication of how much organic has been loaded onto the clay particles. At higher temperature (~780ºC), the dehydroxylation of the clay sheets takes place. The increase of hydrophobicity following functionalization is indicated by the decrease of adsorbed water from 14.5% to 5.1% for the LH and LHSH samples, respectively, at 30–200 ℃. Taking into account the mass loss in the range 200 to 700 ºC, one may calculate 1.7mmol of mercaptopropyl groups per gram of grafted clay. Comparing this value to the binding capacity (1.4 meq/g) determined by the Volhard Method we assume that 82% of SH group are actually accessible to complexation of Ag^+ ions. This finding is in good agreement with accessibility of 90 % inferred by the atomic Ag/S ratio determined by EDS analysis (Table 1).

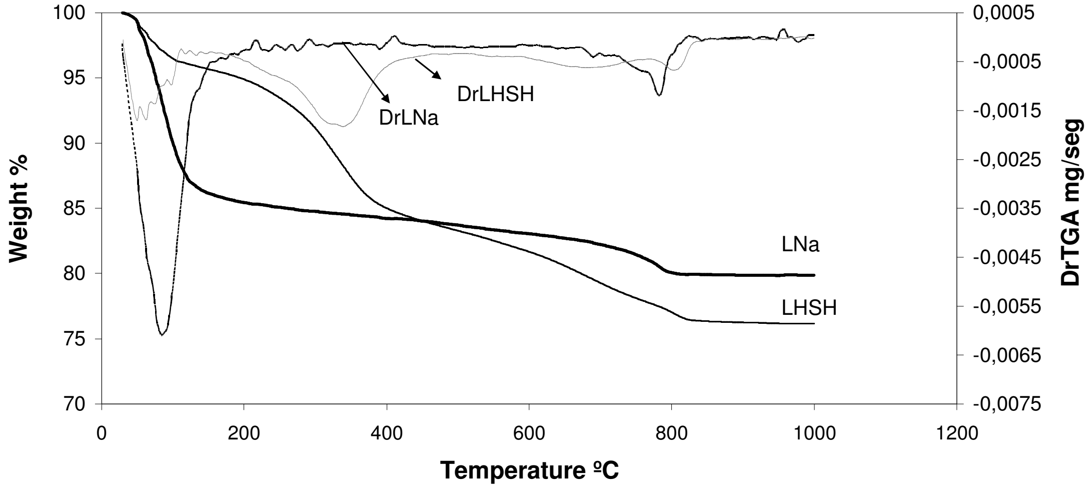
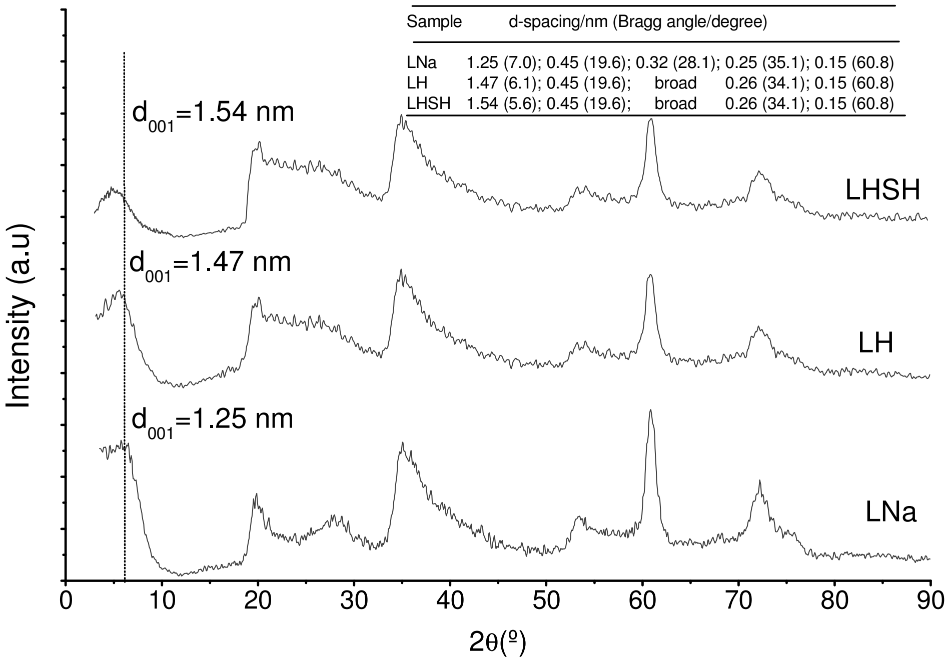


Figure 3 - TG and DTG curves of laponite samples.

For comparative purposes, a sample of laponite-Na was submitted to the same modification process but without acid activation. A value of 0.83 mmol of mercaptopropyl groups per gram of grafted clay was determined by TG analysis, 104 % less than the previous of 1.7 mmol/g. Therefore, the acid pretreatment showed a significant influence on improving the grafting process without collapse of the structure. It is interesting to notice that the differences in the temperature of dehydroxylation (at 780 °C in LNa sample and at 808 °C in LHSH) suggests changes in the structure after the grafting process.

As illustrated in Fig. 4, the XRD patterns for all the laponite samples are quite similar, with only the reflection at 2θ ~28° showing some loss of definition. A comparison of the overall patterns indicates that the original structure was preserved after modification. The main d- spacing parameters of all samples are indicated. An approximate value of 1.25 nm was estimated for the interlayer distance in the LNa sample, despite the broadness of the d_{001} peak. Other authors report similar findings, which were attributed to the very low dimensions and low crystallinity of the laponite crystals (Kuzniarska-Biernacka *et al.,* 2005; Park *et al.,* 2004). Acid activation led to an increase in the interlayer spacing (1.25 nm to 1.47 nm), most likely due to water adsorption. The increased hydrophilic feature of the LH sample with respect to the starting laponite was previously indicated by the DRIFT spectra. No significant differences were observed in the basal spacing of the LH and LHSH samples (from 1.47 nm to 1.54nm). Normally, the intercalation of molecules in interlayer region of clay mineral cause significant changes in the interlayer distance (Park *et al.,* 2004). In spite of this, it was observed by TG analysis an important decreasing in amount of adsorbed water. Usually the decrease of water content causes a significant decreasing in d_{001} spacing (Mercier and Detelier, 1995). Taken into account that such reduction has not happened, our hypothesis is that there was replacement of some water molecule to organosilane in interlayer region of the clay. It indicates that silylation may take place at the surface of the particles and also within the interlayer galleries. Prado *et al.* (2005) and Park *et al.*(2004) have reported similar results. It was possible to observe that the peak d_{001} becomes broader and less intense following functionalization, thus indicating that this process may have caused some degree of disorder of the crystallites.



Sample	d-spacing/nm (Bragg angle/degree)
LNa	1.25 (7.0); 0.45 (19.6); 0.32 (28.1); 0.25 (35.1); 0.15 (60.8)
LH	1.47 (6.1); 0.45 (19.6); broad 0.26 (34.1); 0.15 (60.8)
LHSH	1.54 (5.6); 0.45 (19.6); broad 0.26 (34.1); 0.15 (60.8)

Figure 4 - XRD patterns of sodium (LNa), acid activated (LH) and functionalized (LHSH) laponite. The inset shows the precise peak indexation.

Figure 5a shows a SEM micrograph of the Na-laponite sample. One may observe particles formed by agglomerates of irregular shapes and flat surfaces. The strong tendency toward aggregation and the compact aspect of the material can be observed. The images 5b and 5c display the SEM micrographs of the functionalized clay. In this case, the particles are apparently smaller in size than the previous sample and are composed of disordered thin sheet particles aggregates (Fig. 5c). One can conclude that functionalization promotes the formation of disordered and less cohesive aggregates, probably due to a reduction of the edge-to-edge and face-to face interactions. Unlike the hydrophilic laponite (LNa), which formed large size aggregates after drying, the LHSH sample was hardly dispersed in water (hydrophobic) and easily kept as a loose powder after drying. This change constitutes an important advantage considering the product application in commercial units.

4 CONCLUSIONS

Laponite, a synthetic silicate, was functionalized through a straightforward reflux with organosilanes, in a route that seems attractive for the preparation of a selective sorbent for biomolecules. Analyses by XRD showed that the silylation process did not significantly affect the crystallographic structure of the clay as no important changes were observed in the basal spacing after functionalization. Analyses by XRD and TG analysis showed that the silylation drastically reduced adsorbed water without causing basal spacing contraction, suggesting that intercalation may have occurred also in the interlayer region. The DRIFT results confirmed the presence of thiol groups and organic compounds on the modified clay. The Volhard method indicated a binding capacity of 1.4 meq/g of clay with approximately 90% accessible for Ag^+ trapping. This method showed to be a fast and efficient methodology for binding capacity determination to be applied to thiol functionalized substrates.

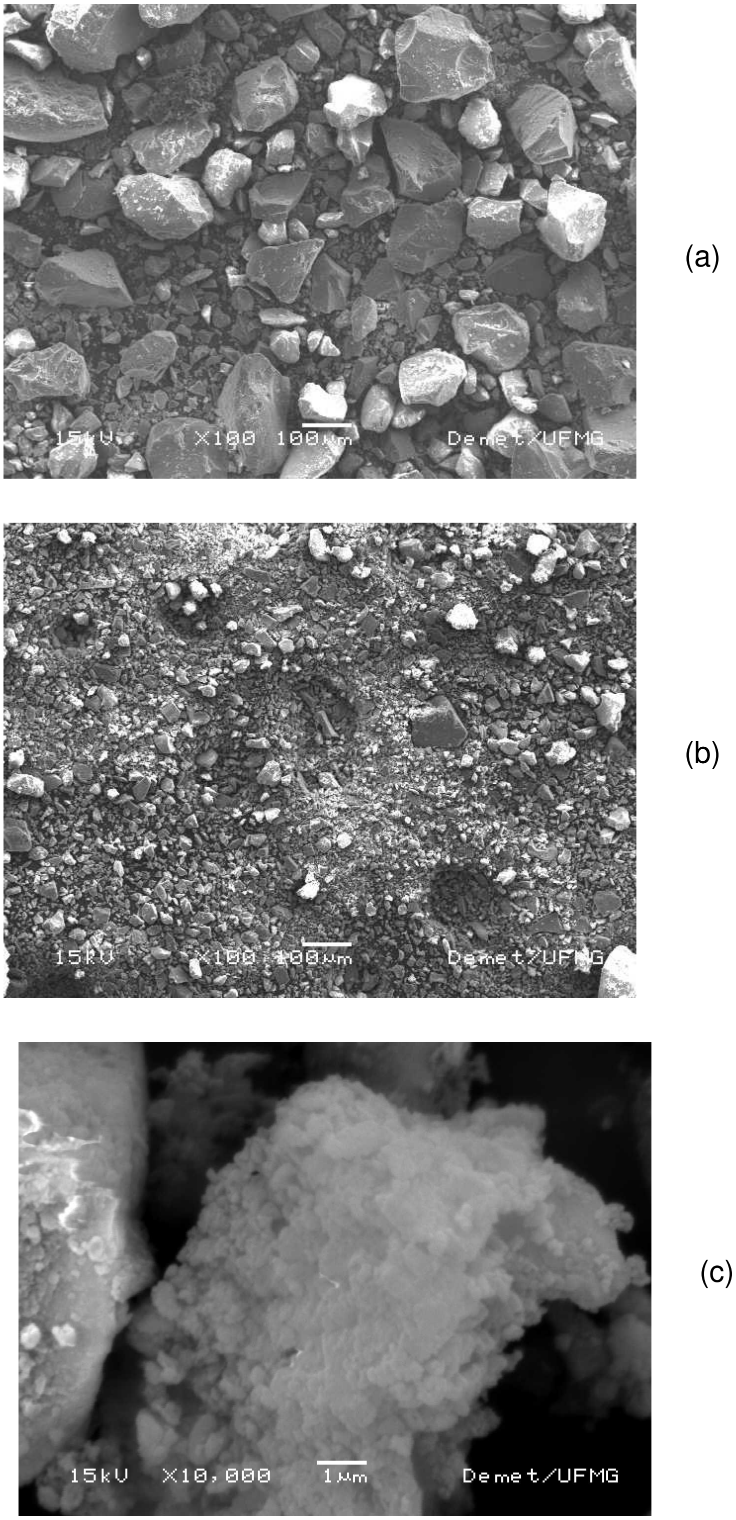


Figure 5 - SEM micrographs of (a) sodium laponite (100x), (b) functionalized laponite (100x) and (c) functionalyzed laponite (10000x).

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APPENDIX 2

TABLES OF DRIFT SPECTRA AND TG ANALYSIS OF CHAPTER 2

Table A2.1: Assignment of the observed wavenumbers in DRIFT spectra of organoclays – chapter 2
Coates (2000) and Famer (1974)

Band assignments[a]	Wavenumbers (cm^{-1})
νOH (AlAlOH, AlMgOH)	3620
$\nu OH_{\text{adsorbed water}}$	3400 -3450 -
$\delta OH_{\text{adsorved water}}$	1600 -1640
νSi-Oi	1000- 1100
$\nu_s CH_2,\ \nu_a CH_2$	2800 - 2980
νSi- (CH_2)	1220 - 1250
δCH_2	1400-1460
ωCH_2	1200 - 1400
$\nu O\text{-}CH_3$ methoxy group	2850 - 2815
νSH	2540 - 2560
ν(S-S) dissufides	620 -600
ν(C-S)	700 -685

δ ω, and ν indicate scissorin, wagging and stretching bands, respectively. “a” and “s “ indicate asymmetric and symmetric stretching.

Table A2.2: Mass loss, Δm (%), range of temperature, ΔT (℃), and assignment of mass loss for closite samples in natural form and modified with mercaptopropyl group

Clay	ΔT/ºC	Δm/%	DTG peak/ºC	Assignment (Δm/%)
CNa	30-200	7.7	51 and 77	adsorbed water
	200-800	5.1	690	OH
	Σ	12.9		
CH	30-200	9.2	57 and 89	adsorbed water
	200-800	6.1	667	OH
	Σ	15.3		
CHSH	30-200	2.9	50, 58 and 75	adsorbed water
	200-400	7.6	302 , 338	organic compound
	400-800	9.4	644	organic and residual OH
	Σ	19.9		
CNaSH	30-200	2.6	57	adsorbed water
	200-400	2.2	280, 337	organic compound
	400-800	5.8	705	organic and residual OH
	Σ	10.6		

Table A2.3: Mass loss, Δm (%), range of temperature, ΔT (℃), and assignment of mass loss for Brazillian bentonite in natural form and modified with mercaptopropyl group

Clay	ΔT/ºc	Δm/%	DTG peak/ºC	Assignment (Δm/%)
BCa	30 -200	8.9	72, 92 and (159)	adsorbed water
	200-800	5.1	(290) and 520	OH
	∑	14.1		
BH	30 -200	12.5	50, 62and 71	adsorbed water
	200-800	5.1	(284) and 495	OH
	∑	17.7		
BHSH	30-200	3.7	45, 60 and 74	adsorbed water
	200-400	7.9	286 and 332	organic compound
	400-800	10.4	516	organic and residual OH
	∑	22.0		
BCaSH	30-200	6.9	47, 61and 75	H_2O and residual alcohol
	200-400	4.9	294 and 337	organic compound
	400-800	8.8	499	organic and residual OH
	∑	20.7		

Values in ( ) represent a shouder

APPENDIX 3

TABLES OF TG ANALYSIS OF CHAPTER 4

Table A 4.1: Mass loss, Δm (%), range of temperature, ΔT (℃), and assignment of mass loss for closite and laponite samples in natural form and modified with aminopropyl group.

Clay	ΔT/ºC	Δm/%	DTG peak/ºC	Assignment (Δm/%)
CNa	30-200	7.74	51 and 77	adsorbed water
	200-800	5.133	690	structural OH
	∑	12.87		
CH	30-200	9.18	57 and 89	adsorbed water
	200-800	6.13	667	structural OH
	∑	15.31		
CHNHT	30-200	4.17	77	adsorbed water
	200-300	1.38	(257)	physisorbed organic
	300-650	11.6	407, 640	organic compound
	650 -800	2.24	-	structural OH
	∑	19.38		
CHNHA95	30-200	4.37	66	adsorbed water
	200-300	1.63	(262)	physisobed organic
	300-650	11.7	414, 639	grafted organic
	650-800	2.53		structural OH
	∑	20.23		
LNa	30-200	14.56	90	adsorbed water
	200-800	5.44	786	structural OH
	∑	20.00		
LNaNHT	30-200	12.7	86	adsorbed water
	200-300	1.45	292	physisorbed organic
	300-650	7.14	426, (547)	grafted organic
	650-800	2.23	752	structural OH
	∑	23.60		
LNaNHA95	30-200	6.33	75	adsorbed water
	200-300	1.64	282	physisorbed organic
	300-650	8.14	427, (546)	grafted organic
	650-800	2.72	794	structural OH
	∑	18.83		

Values in ( ) broad peak