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RESEARCH ARTICLE

Montmorillonite Nanoclay Interaction with 2-Aminophenol and 2-Nitrophenol

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ABSTRACT:
The interaction of 2-aminophenol and 2-nitrophenol compounds with the structural iron of montmorillonite nanoclay was studied using Mössbauer spectroscopy in order to determine what effects have the groups of withdrawing and donating electrons on the phenol ring and how they affect the nanoclay structural iron. 100 mg of the organic compound was dissolved in 50 ml distilled water in 100 ml volumetric flask. 1 gm of the montmorillonite nanoclay was added to this solution. The mixture was stirred for 24 hours in order to reach equilibrium, then filtered. It was found that the structural iron (III) of the montmorillonite nanoclay sample can be reduced to iron (II). The reduction process depends on the substituent on the phenolic ring. At high pH, reduction takes place if the phenolic ring has electron donating substituent like NH_2, while no reduction occurs if the phenolic ring has electron withdrawing substituent like NO_2. The process involves electron transfer from the hydroxyl group on the compound substituted with donating group, to the active site at the iron atoms within the montmorillonite lattice. This site is considered to be Lewis acid.

KEYWORDS: Mössbauer spectroscopy, nanoclay, montmorillonite, phenolic ring, donating substituent, withdrawing substituent.

INTRODUCTION:
Montmorillonite is an important type of the three-layer nanoclay minerals. The structure consists of three layers, one octahedral sheet sandwiched between two tetrahedral sheets[1].

Nonoclays particles have the ability to host different types of materials such as drugs and other chemicals[2]. In the pharmaceutical field, nanoclay played a very important role as a drug carrier[3].

The adsorption of phenols on original and surfactant-modified nanoclays was investigated by several researchers. It has found that the adsorbed phenols are modified to a different degree and the adsorption process follows a pseudo-second-order reaction. The process involves chemical and physical interaction and the maximum adsorption found to be at pH 7 and > 7.

The equilibrium isotherm agrees with Freundlich and Langmuir equations[4,5,6,7,8,9,10]. The mechanism proposed for such reactions is a free radical mechanism[11,12].

The adsorption of dihydroxybenzene (catechol) compound and its derivatives on clays was studied[13,14]. It was suggested that these compounds are chemically adsorbed onto the clays. The adsorption of hydroquinone on clay was shown not to be affected by pH and temperature. The adsorption equilibrium followed Langmuir and Dubinin–Radushkevich models[15].

The adsorption of phenol and 4-nitrophenol on montmorillonite was studied. It was shown that the adsorption process involves the ability of the phenol to act as a donor or acceptor of a proton from interlayer water[16]. Organo-clays were used to remove p-nitrophenol, phenol and aniline of organic pollutants[17]. Thermal decomposition behavior of clay-phenolic nanocomposite prepared by in-situ polymerization was also studied[18]. A clay catalyst montmorillonite and kaolinite were used to degrade three phenolic compounds: hydroquinone, resorcinol and catechol. It was found that the modified montmorillonites have very interesting catalytic structural and textural properties and

more effective for the catalytic phenolic compound degradation[19].

The structural iron of montmorillonite can be reduced after the reaction with benzidine[20]. Studies on the adsorption of catechol, substituted catechol and some other hydroxyls containing organic compounds on montmorillonite clay have shown that the structural iron of montmorillonite can be reduced. The reduction process is pH dependent and also depends on the ring substituent and conjugation. At high pH, reduction takes place if the catecholic ring has electron donating substituent, while no reduction occurs if the catecholic ring has electron withdrawing substituent[21].

Mossbauer spectroscopy has been for decades a suitable tool for identifying iron transformation of clays, and many studies have been conducted concern this subject[22,23,24,25,26]. It was found that the reduction process using organic compounds is pH dependent. At high pH, the reduction process involves electron transfer from the organic compounds to the active site at the iron atoms within the montmorillonite lattice. This site behaves as an electron acceptor. Reduction occurs when the compound approaches the Pyramidal edges of the montmorill onite lattice, and the electron then transfers to the lattice by a hopping mechanism[21,22].

The present study concern the possibility of reducing the structural iron of the montmorillonite nanoclay by phenolic ring substituted with donating and withdrawing electrons groups.

MATERIAL AND METHODS:

The nanoclay sample was Wyoming montmorillonite, obtained from Podmore and Sons Ltd. Chemicals, 2-aminophenol and 2-nitrophenol were obtained from Sigma-Aldrich company. Mössbauer spectra were recorded on a Canberra Multichannel Analyzer using ^{57}Co as a source. The spectra were recorded at 77° K.

Preparation of The Samples:

100 mg of the organic compound was dissolved in 50 ml distilled water in 100 ml volumetric flask. The mixture was warmed up and stirred for 15 minutes until the organic compound dissolved completely. 1 gm of the montmorillonite nanoclay was added to this solution. The pH was adjusted using NaOH (0.1N) and HCl (0.1N). The mixture was stirred for 24 hours in order to reach equilibrium, then filtered through Whatman filter paper and washed with distilled water and air dried.

RESULTS AND DISCUSSION:

The Mössbauer spectrum of the original montmorillonite nanoclay sample is shown in (Fig. 1), and the spectrum of the sample treated with water at pH 10 is shown in (Fig. 2). The spectrum of the original sample consists of two sites, one for Fe^{3+} and the other for Fe^{2+}. The isomer shifts are 0.43 mm s^{-1} for Fe^{3+} and 1.25 mm s^{-1} for Fe^{2+}, the quadrupole splittings are 0.65 mm s^{-1} for Fe^{3+} and 3.03 mm s^{-1} for Fe^{2+}, and the absorption areas are 51 for Fe^{3+} and 49 for Fe^{2+}. The Fe^{2+}/Fe^{3+} ratio is around 1 as shown in (Table 1) of the Mössbauer parameters.

The sample treated with water at pH 10 shows no noticeable change in the spectrum parameters, indicating that the change in the pH has no effect on the sample.
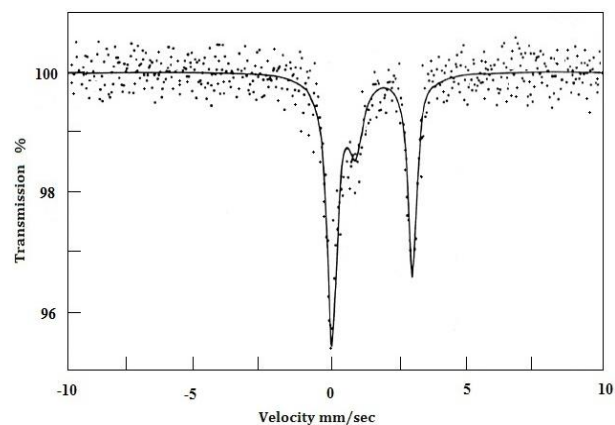

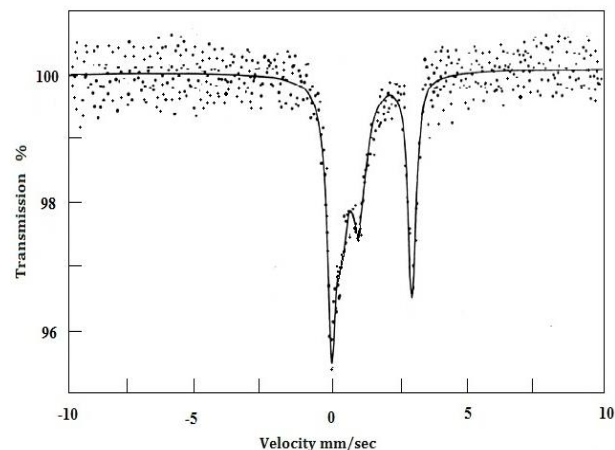**Fig. 1: Mössbauer spectra at 77° K of the original montmorillonite sample**

Fig. 2: Mössbauer spectra at 77° K of the original montmorillonite treated with water at pH 10

Table 1: The ^{57}Fe Mössbauer parameter at 77º K

Samples	δ mm s^{-1}	Δ mm s^{-1}	Absorption Area%	Fe^{2+}/Fe^{3+} Ratio
Original montmorillonite	0.43	0.65	51	1
	1.25	3.03	49	
Montmorillonite-water pH 10	0.41	0.69	55	1
	1.27	3.02	45	
Montmorillonite-2-nitrophenol pH 10	0.42	0.68	48	1
	1.25	3.04	52	
Montmorillonite-2-aminophenol pH 10	0.41	0.70	29	2.5
	1.26	3.02	71	

(Fig. 3 and 4) show the spectra of the nanoclay sample reacted with 2-nitrophenol and 2-aminophenol respectively at pH 10.

No reduction for the structural Fe^{3+} of the montmorillonite sample is observed in the sample reacted with 2-nitrophenol at pH 10 (Figure 3). The Fe^{2+}/Fe^{3+} ratio remains the same as with the original sample.

The reduction of Fe^{3+} in the montmorillonite sample reacted with 2-aminophenol is clear (Figure 4). The absorption area of iron became 29 for Fe^{3+} and 71 for Fe^{2+}. The Fe^{2+}/Fe^{3+} ratio considerably enhanced and became 2.5.

Substituents that are able to withdraw electrons, such as 2-nitro, have a tendency to pull back electron density from the phenol ring. The electrons can be considered to reside on the substituent, leaving the molecule unfit to exchange electrons to the active sites on montmorillonite nanoclay. Electron donating substituent, such as 2-amino, enhance electron exchange from the ring to the montmorillonite nanoclay.
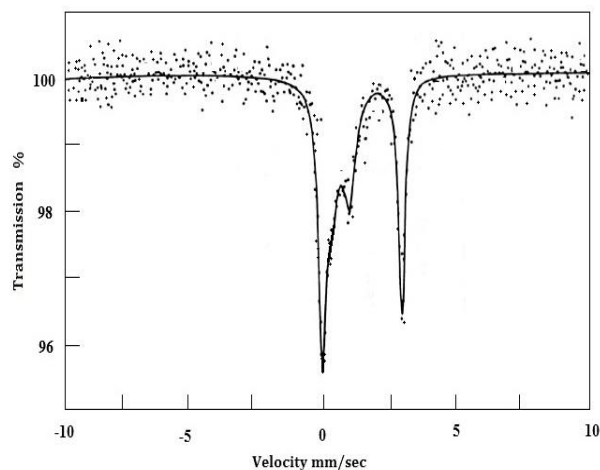

Fig. 3: Mössbauer spectra at 77º K of the original montmorillonite reacted with 2-nitrophenol at pH 10
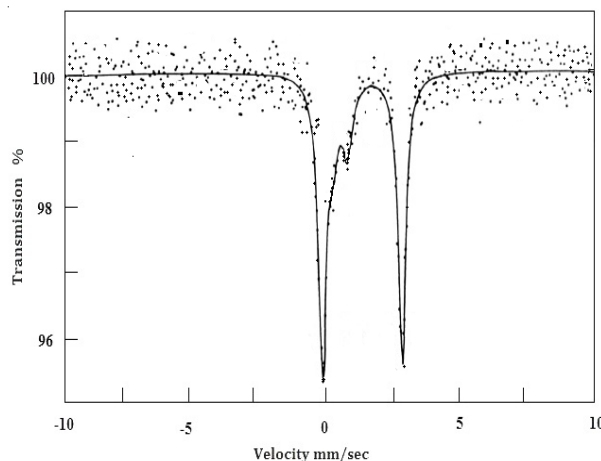

Fig. 4: Mössbauer spectra at 77º K of the original montmorillonite reacted with 2-aminophenol at pH 10

The nature of acidity of phenols is due to the resonance stabilization of phenoxide ion and the existence of any substituent on aromatic ring which can stabilize the phenoxide ion will increase phenol acidity. While the existence of any substituent which causes destabilization of the phenoxide ion by increasing the negative charge will decrease the acidic nature of phenol. If an electron withdrawing group is present on benzene ring in phenol, it increases the acidity and the presence of electron releasing group decrease the acidity. For example, if a nitro group (-NO$_2$) (I) is present, that will increase the acidity of phenol. So the nitrophenol will be more acidic than phenol because the nitro group is able to add negative mesomeric effect and negative inductive effect, and acts as an electron withdrawing group.

Electron donating group like amino (-NH$_2$) (II) decreases the acidity of phenol. As this effect increases the electron density on the hydroxyl group and results in low acidity of phenol.
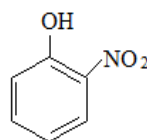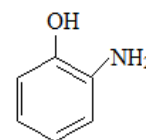
When phenolic molecules with an electron-donating group like 2-aminophenol are brought together with the montmorillonite in solution at a pH high enough to dissociate the proton of the hydroxyl group, electron transfer occurs from the phenolic compound to the active sites on the montmorillonite. These are aluminum exposed at the edges and/or transition metal cations in the higher valence state at the planar surface. The latter site is the one of our interest.

These two site act as electron acceptors (Lewis acids), and when an initial reduction occurs at the surface, it can propagate into the planar sites in the silicate lattice within the octahedral layer.

The phenolic molecules may approach the pyramidal edges of the montmorillonite, and the diffusion of electrons occurs within the octahedral layers since the phenolic compounds are expected to be negatively charged at high pH.

Using a phenolic compound with electron withdrawing group like 2-nitrophenol, no reduction is taking place.

CONCLUSION:

When montmorillonite nanoclay reacts at pH 10 with a phenolic compound containing electron withdrawing group like 2-nitrophenol no change in the iron environment takes place. A clear reduction of the structural iron appeared when the reaction of the montmorillonite was carried out with a phenolic compound containing electron donating group like 2-aminophenol. Mössbauer spectroscopy showed a clear enhancement of the iron(II) ratio of montmorillonite on the expense of iron(III) ratio for the clay sample reacted with 2-aminophenol.

The interaction process involves electron pushing from the hydroxyl on the organic compound having a donating group such as NH_2, to the active site at the iron atoms inside the montmorillonite nanostructure.

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