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SPECTROCHEMICAL INVESTIGATION ON THE ABILITY OF HYDROXYBENZENE COMPOUNDS TO REDUCE STRUCTURAL IRON OF MONTMORILLONITE

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The oxidation state of the structural iron of montmorillonite MMT plays an important role in determining its properties. Many chemical species have the ability to oxidize or reduce this iron, including hydroxybenzene compounds HB. The ability of six compounds containing hydroxyl groups such as 2,3-dihydroxypyridine, 2,3-dihydroxybenzoic acid, 2,3-dihydroxybenzaldehyde, 2,5-dihydroxy-p-benzoquinone, 4,5-dihydroxynaphthalene,2,7-disulfonic acid, and 5-hydroxy,1,4-naphthoquinone to reduce the structural iron of MMT has been studied. Most of these species are considered good iron reducing agents in solution. Mossbauer evidence of the MMT samples reacted with these compounds indicated that all of the above compounds have the ability to reduce structural iron except 2,5-dihydroxy-p-benzoquinone. The MMT sample was added to the solution of the HB compound and stirred for 24 hours to achieve equilibrium, before being filtered, washed, and air-dried. Mossbauer spectroscopy, infrared, X-ray powder diffraction, electron spin resonance, and total surface area determination were used to monitor the reactions.

Keywords: montmorillonite, hydroxybenzenes, iron, Mossbauer, oxidize, reduce.

1. Introduction

MMT is a three-layer clay mineral belonging to the smectite group that is widely distributed and used. The structure consists of three layers, two tetrahedral sheets and one octahedral sheet [1]. MMT contains iron in both Fe(II) and Fe(III) oxidation states [2, 3]. The oxidation states of iron in clay structure affect its physicochemical characteristics such as surface area and cation exchange capacity [4-6]. The reduction of the structural iron(III) of clay minerals can be conducted either microbially or chemically using chemical reducing agents [7, 8]. It was found that bacterial reduction of clay iron changes its properties [9, 10]. The bioreduction rate of structural Fe(III) in clays can be successfully stimulated by humic acid [11]. The adsorption of phenol, substituted phenols, and their derivatives, as well as their effect on clay minerals has been established in several investigations [12-16]. Catechol and its derivatives have been used to reduce the

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structural Fe(III) in MMT. The reduction process was found to be pH-dependent and depends on the ring substituents as well. Electron-donating substituents on the ring reduce the iron at high pH, while electron-withdrawing substituents cause no reduction [17]. In another experiment, it was found that phenolic compounds containing an electron donating substituent have the ability to reduce Fe(III) structural iron [18]. The reduction process of clay can be carried out using a mixture of citrate-bicarbonate-dithionite. The clay sample reduced by this method was used to reduce Hg(II) to Hg(0) [19]. The ability of selectively adsorbed iron(II) to reductively transform 2-nitrophenol was found to be similar to goethite in synthetic polyhydroxy-Fe pillared MMT [20]. Fe(II) reduces a considerable amount of Fe(III) in a low-Fe MMT, according to a Mossbauer spectroscopy study. Through a pH range of 4.0-7.5, the reduction rate ranges from 12 to 78%. Electron transport through the basal plane is thought to be responsible for substantial reduction [21]. In the presence of four different compounds, the oxidant generation after oxygenation of reduced nontronite was investigated. Phosphate, tripolyphosphate, nitrilotriacetic acid, and diamine tetraacetic acid were the compounds. The oxidant yields are increased by all compounds, although the mechanisms vary depending on the compound type [22]. An investigation was carried out on the mechanism of selenium sorption on MMT clay under reducing conditions. The element was dissolved as Se (-II) ions. It was found by X-ray that the Se oxidation state was (0), which suggests oxidation on MMT [23]. Fe-bearing clay minerals, on the other hand, were employed to reduce hexavalent chromium. Different environmental conditions have an impact on the process [24-28].

The aim of the current research is to determine the susceptibility of two groups of HB compounds to reduce structural Fe(III) of MMT. These compounds belong to different classes of chemical compounds and contain different functional groups attached to the benzene ring of the compound. Some compounds also contain fused aromatic rings.

2. Materials and methods

2.1. Materials

The sample of MMT is a Wyoming type obtained from Podmore and Sons Ltd. All of the compounds used throughout this research were of analytical grade obtained from the company of Sigma-Aldrich. Mossbauer spectra were obtained on Canberra Multichannel Analyzer at 77 ^{o}K. The source used was obtained from the Radiochemical Centre, Amersham, it was a 25 mCi cobalt-57 in a rhodium matrix. The infrared spectra were recorded on a Perkin Elmer 1330 spectrophotometer. X-ray diffraction patterns were recorded on a Philips diffractometer using CuKα radiation. The ESR spectra were recorded on a Varian El04A X-band spectrometer. The total surface area of the samples was measured using ethylene glycol mono-ethyl ether (EGME). The pH was monitored using a Philips (PW-91109) digital pH meter.

2.2. Samples preparation

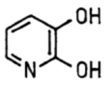
100 mg of the HB compound was added to 50 ml distilled water in a 100 ml flask. 1g of the MMT clay sample was added to the mixture. The pH was adjusted to 10.5 and monitored periodically using 0.1 N NaOH and 0.1 N HCl. The slurries were stirred for 24 hours to reach equilibrium, then filtered, washed, and air-dried.

3. Results and discussions

Transition metal coordination chemistry in ion exchange forms of minerals and adsorbed molecules containing donor atoms is frequently analogous to that of the naked metal ion in a homogenous solution. At the same time, it can be affected by the unique environment of the clay surface [29]. The importance of the interaction of HBs with MMT lies in being able to donate electrons to the Fe(III) of the clay. Such compounds donate an electron to the Fe(III) if their affinity for it is less than that of the Fe(III). The affinity differs from one compound to another and depends in part on the degree of conjugation of the aromatic ring [17]. When HB molecules are brought together with MMT clay in a solution with a pH high enough to dissociate one or two protons, electron transfer from the HB component to the MMT active sites occurs. These active sites can act as electron acceptors. Any initial reduction takes place at the surface, it can propagate into the planar sites by electron hopping or diffusion [30]. Because the HB compounds are expected to be negatively charged at 10.5 pH, they may approach the pyramidal edges of the MMT, and electron transport occurs within the octahedral layers. There will be a charge imbalance after the reduction process, which can be maintained by protonation of the nearby OH group. The protons come from dissociated water molecules in the interlayer space. Proton tunneling allows these protons to enter the structure. The OH^- ions that form in the spaces can pick up H^+ from the solution [31].

3.1. Selection of HB compounds

Two groups of HB compounds were selected for this study, the first group consisting of three compounds, the first is a pyridine containing two hydroxyl groups (2,3-dihydroxypyridine I), a second is a carboxylic acid with two hydroxyl groups (2,3-dihydroxybenzoic acid II), and the third is an aldehyde with two hydroxyl groups (2,3-dihydroxybenzaldehyde III). These compounds are considered good agents to reduce iron in solutions [32, 33].



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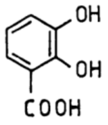

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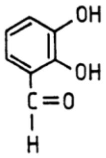

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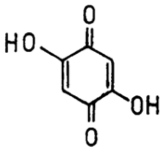
The second group also consists of three compounds, one with a fully quininoid ring containing the hydroxy groups (2,5-dihydroxy-p-benzoquinone I), a second with two fused aromatic rings (4,5-dihydroxynaphthalene,2,7-disulfonic acid II), and the third possessing a fused quininoidal and aromatic rings (5-hydroxy,l,4-naphthoquinone III).



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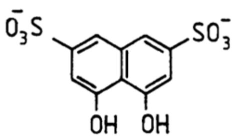

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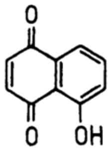

III

The two latter compounds were found to be capable of reducing the Fe(III) in solution [34].

3.2. Mossbauer spectroscopy

Fig. 1 shows the Mossbauer spectra of the original MMT sample and the sample stirred with water at pH 10.5 for 24 hours, and the parameters are listed in Table 1. As it appears from the spectra, the ratio of Fe(II) to Fe(III) is almost equal. There is no change in the parameters of the samples treated with water at pH 10.5 for 24 hours from that of the untreated sample.

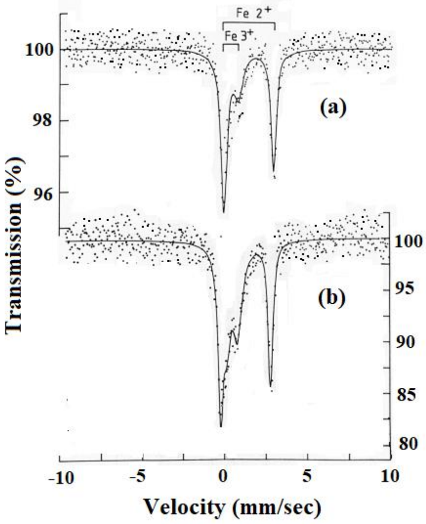

Fig. 1. The ^{57}Fe Mossbauer spectra at 77 °K of (a) original MMT sample (b) the sample treated with water at pH 10.5

Table 1

The ^{57}Fe Mossbauer parameters at 77 ºK of the original MMT sample and the sample treated with water at pH 10.5. Data were collected on the dried solids.

Sample	δ mms^{-1}	Δ mms^{-1}	Γ mms^{-1}	Absorption area %	Fe^{2+}/Fe^{3+} ratio
Original MMT	0.43(2) 1.25(1)	0.65(2) 3.03(1)	0.30(2) 0.14(1)	51(3) 49(3)	1(2)
Original MMT treated with water at pH 10.5	0.43(1) 1.27(1)	0.64(2) 3.06(2)	0.31(2) 0.16(1)	53(2) 47(3)	0.9(2)

The Mossbauer spectra of the MMT samples reacted with the first group HB compounds are shown in Fig. 2 and the parameters are given in Table 2. In all three samples, there is an enhancement of Fe(II) content, indicating that reduction has occurred. 2,3-dihydroxybenzoic acid showed more reducing power, then 2,3-dihydroxybenzaldehyde and 2,3-dihydroxypyridine.

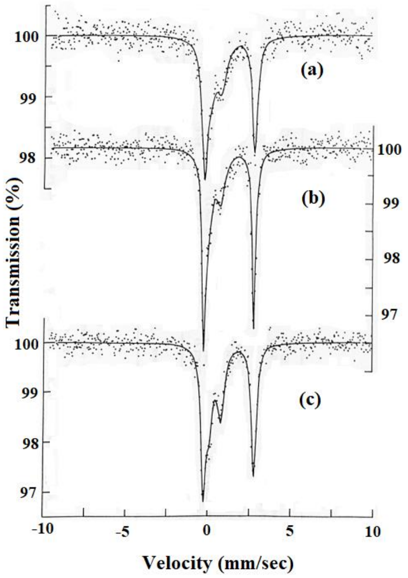

Fig. 2. Mossbauer spectra at 77 ºK of MMT reacted for 24 hours at pH 10.5 with (2,3-dihydroxypyridine, (b) 2,3-dihydroxybenzoic acid, (c) 2,3-dihydroxybenzaldehyde

Table 2

The ^{57}Fe Mossbauer parameters at 77 °K of the MMT samples reacted with the HB compounds at pH 10.5 in aqueous solution. Data were collected on the dried solids.

Sample	δ mms^{-1}	Δ mms^{-1}	Γ mms^{-1}	Absorption area %	Fe^{2+}/Fe^{3+} ratio
MMT-2,3-dihydroxypyridine	0.42(3) 1.26(1)	0.67(4) 3.07(1)	0.38(4) 0.20(1)	43(6) 57(3)	1.4(3)
MMT-2,3-dihydroxybenzoic acid	0.42(2) 1.26(1)	0.64(3) 3.04(1)	0.30(3) 0.15(1)	34(4) 66(3)	2(3)
MMT-2,3-dihydroxybenzaldehyde	0.42(1) 1.25(1)	0.65(1) 3.04(1)	0.24(1) 0.18(1)	40(3) 60(2)	1.5(2)

In the second group of HB compounds, we observed that the MMT sample reacted with 2,5-dihydroxy-p-benzoquinone shows no clear reduction. The Fe^{2+}/Fe^{3+} ratio was 1.2(2), which does not differ much from the original MMT sample. In this compound, the ring system is fully quininoid and no electron density is available for the reduction. The sample reacted with 4,5-dihydroxynaphthalene,2,7-disulfonic acid shows a little enhancement of Fe(II) content. The electron density is not restricted by the two fused aromatic rings, allowing some electron transport to the MMT. In 5-hydroxy-l,4- naphthoquinone, the quininoidal ring is conjugated, leaving some electron density available for electron transfer. Fe^{2+}/Fe^{3+} has a higher ratio of 1.7(3) than the other two compounds. The non-quininoidal ring is shown to behave as an electron donor. Mossbauer spectra of the MMT samples reacted with these compounds are shown in Fig. 3 and the parameters are listed in Table 3.

Table 3

The ^{57}Fe Mossbauer parameters at 77 °K of the MMT samples reacted with the HB compounds at pH 10.5 in aqueous solution. Data were collected on the dried solids

Sample	δ mms^{-1}	Δ mms^{-1}	Γ mms^{-1}	Absorption area %	Fe^{2+}/Fe^{3+} ratio
MMT-2,5-dihydroxy-p-benzoquinone	0.55(2) 1.37(1)	0.70(1) 3.07(1)	0.30(2) 0.20(1)	45(4) 55(3)	1.2(2)
MMT-4,5-dihydroxynaphthalene, 2,7-disulfonic acid	0.43(2) 1.24(1)	0.74(2) 3.07(1)	0.34(2) 0.12(2)	41(4) 59(2)	1.4(2)
MMT-5-hydroxy,l,4-naphthoquinone	0.40(3) 1.25(1)	0.65(5) 3.06(1)	0.38(5) 0.17(1)	37(6) 63(3)	1.7(3)

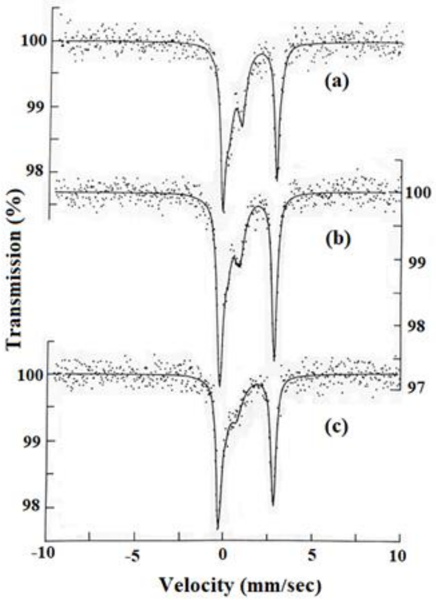

Fig. 3. Mossbauer spectra at 77 ºK of MMT reacted for 24 hours at pH 10.5 with (a) 2,5-dihydroxy-p-tenzoquinane, (b) 4,5-di-hydroxynaphthalene,2,7-disulfonic acid, (c) 5-hydroxy,1,4-naphthoquinone

3.3. *Infrared spectroscopy*

The Si-O stretching and OH bending are the two main bands of MMT in the IR region (Table 4). The positions of these bands are at 800 cm^{-1} for Fe^{3+}-OH-Fe^{3+}, 850 cm^{-1} for Al-OH-Mg, 880 cm^{-1} for Fe^{3+}-OH-Al, 917 cm^{-1} for Al-OH-Al, and 1040 cm^{-1} for Si-O [35, 36]. The adsorbed compounds on the MMT produce bands in the IR spectrum as well, but we will focus on the effect of these compounds on the prominent MMT bands. The sharpness and location of the OH bending modes of the sample reacted with various HB compounds varied from one compound to another. The Si-O stretching band at 1040 cm^{-1} disappeared in most of the samples, and the Fe^{3+}-OH-Al band at 880 cm^{-1} either disappeared or appeared as a shoulder in most of the samples. In the reduced samples, the disappearance of the latter band is evident. It was reported that the disappearance of this band is due to protonation of the adjacent OH group [31, 37]. The Fe^{3+}-OH-Fe^{3+} bending band at 800 cm^{-1} in the reacted MMT sample has been shifted to 795 cm^{-1}. This shift has been observed in a number of different samples. The Al-OH-Mg bending band is also shifted from 850 cm^{-1} to a lower value.

Table 4

Selected features of the infra-red spectra (cm^{-1}) of the MMT sample reacted with the HB compounds.

Sample	pH	Si-O	Al-OH-Al	Fe^{3+}-OH-Al	Al-OH-Mg	Fe^{3+}-OH-Fe^{3+}
MMT	-	1050 sh	917 w	880 w	850 m	800 s
MMT-2,3-dihydroxypyridine	10.5	-	912 m	-	845 s	800 s
MMT-2,3-dihydroxybenzoic acid	=	-	-	-	840 m	790 m
MMT-2,3-dihydroxybenzaldehyde	=	-	913 m	890 sh	845 s	795 s
MMT-2,5-dihydroxy-p-benzoquinone	=	-	915 w	890 sh	840 m	795 m
MMT-4,5-dihydroxynaphthalene,-2,7-disulfonic acid	=	-	915 w	890 sh	845 m	800 m
MMT- 5-hydroxy,1,4-naphthoquinone	=	1030 sh	915 s	-	845 m	795 s

sh = shoulder, w = weak, m = medium, s = strong

3.4. *X-ray powder diffraction*

The air-dried MMT sample showed a 13 Å basal spacing increasing to 17 Å on ethylene glycol treatment. All the MMT samples that reacted with the HB compounds at pH 10.5 did not show the 13 Å basal spacing, but showed 12.27 Å, possibly due to the presence of Na ions from the sodium hydroxide used for pH adjustment. On treatment with ethylene glycol, again the sample containing the HB compounds did not show the 17 Å basal spacing but showed 16.67 Å, which suggests that the compounds are present on the crystal edges of the MMT (Fig. 4). These then cause blocking of some of the MMT layers and prevent the complete swelling of ethylene glycol. Furthermore, slightly asymmetrical peaks were found in the XRD patterns, indicating a mixed-layer sequence. It was reported that MMT may give a mixed-layer structure on treatment with some organic liquids

[38]. No evidence for the intercalation of these HB compounds into the MMT interlayer.

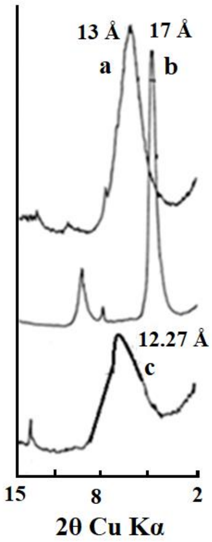

Fig. 4. X-ray powder diffraction patterns of MMT (a) untreated sample, (b) treated with EG, (c) reacted with 2,3-dihydroxybenzoic acid

3.5. Electron spin resonance

Ions such as silicon, aluminum, magnesium, and alkali and alkaline earth metals are the most abundant ions that usually exist in clay minerals and are diamagnetic ions. Paramagnetic ions like Fe^{3+} can be found substituted for silicon, aluminum, or magnesium. The main features of our MMT are g-values of 2.0, 2.2, 3.7, 4.3, and 9.6, which are similar to the result reported by other workers [39]. The ESR features with g-values of 3.7, 4.3, and 9.6 have been attributed to Fe^{3+} in a site with near rhombic symmetry, whereas the other features are associated with Fe^{3+} in a different sort of environment [39]. Apart from the samples reacted with 5-hydroxy,1,4-naphthoquinone, which showed no change in g =2 signal, all the samples (except the 4,5-dihydroxynaphthalene,2,7-disulfonic acid, which has not been examined by ESR), exhibited substantial changes in the main features of the ESR spectra. The g = 2 signal was noticeably enhanced, and the signals with g-values of 2.2 and 9.6 are broader than those found in the untreated MMT sample. The signal with a g-value of 3.7 either disappeared from the spectra or left traces, and that with a g-value of 4.3 was narrower and less intense than in the untreated sample (Fig. 5). These observations are very similar to those reported by other workers [39], for a hydrazine-reduced sample. The reaction of MMT with HB compounds caused a reduction in the intensities of the signals which can be assigned to the structural Fe(III). This result is in good agreement with the Mossbauer data which revealed an incomplete reduction of the structural Fe(III). An enhancement in the g = 2.0 signal was clear, which is due to the formation of a radical. There is a similarity between this signal and those reported by other workers [40], obtained from the reaction of some aromatic molecules with clays. The interactions of HB compounds with MMT result in the formation of a radical in the initial step, which eventually oxidizes to a quinone. According to the ESR data, a portion of these HB compounds remains on the MMT surface in the radical (semiquinone) state. These radicals are responsible for the signals appearing at g = 2.0.

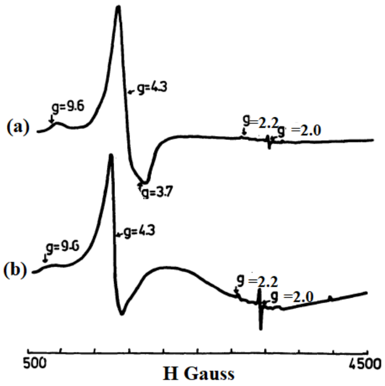

Fig. 5. ESR spectra at room temperature of (a) MMT sample, (b) MMT sample reacted with 2,3-dihydroxybenzaldehyde

3.6. Total surface area determination

The total surface area is an important property of clays, which can be determined by the retention of ethylene glycol or ethylene glycol monoethyl ether. MMT clay can accommodate two layers of ethylene glycol monoethyl ether molecules between interlayer spacing. The total surface area of the samples was measured using Dyal and Hendricks [41] value of 810 m^2/g for the total surface area of MMT (Table 5).

The original MMT sample showed a value of 839 m^2/g. This value was reduced by about 200 m^2/g in the samples reacted with the HB compounds. The presence of these compounds on the crystal edges of MMT causes blocking of some layers, preventing complete swelling.

Table 5

The total surface areas of the samples

Samples	pH	Total surface area in m^2/g
MMT	-	839
MMT-2,3-dihydroxypyridine	10.5	639
MMT-2,3-dihydroxybenzoic acid	10.5	629
MMT-2,3-dihydroxybenzaldehyde	10.5	632
MMT-2,5-dihydroxy-p-benzoquinone	10.5	615
MMT-4,5-dihydroxynaphthalene,-2,7-disulfonic acid	10.5	623
MMT- 5-hydroxy,1,4-naphthoquinone	10.5	622

4. Conclusions

HB compounds have been used to reduce the structural Fe(III) in MMT at pH 10.5. The interactions of these compounds with MMT result in the formation of a radical in the first step, which eventually oxidizes to a quinone. A portion of these HB compounds remains on the MMT surface in the radical (semiquinone) state. When HB molecules reacted with MMT in a solution with a pH high enough to dissociate one or two protons, electron transfer from the HB component to the MMT active sites occurs. These active sites can act as electron acceptors. Any initial reduction takes place at the surface, it can propagate into the planar sites by electron hopping or diffusion. All the six compounds used have been found to be able to reduce Fe(III) except 2,5-dihydroxy-p-benzoquinone. According to the Mossbauer data, the 2,3-dihydroxybenzoic acid compound appears to be the most effective in the reduction process.

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