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THERMO-XRD ANALYSIS OF THE ADSORPTION OF CONGO-RED BY MONTMORILLONITE SATURATED WITH DIFFERENT CATIONS

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Abstract

The adsorption of the organic anionic dye Congo red (CR) by montmorillonite saturated with Na^+, Cs^+, Mg^{2+}, Cu^{2+}, Al^{3+} and Fe^{3+} was investigated by XRD of unwashed and washed samples after equilibration at 40% humidity and after heating at 360 and at 420°C. The clay was treated with different amounts of CR, most of which was adsorbed. Clay samples, untreated with CR, after heating showed collapsed interlayer space. Unwashed and washed samples, which contained CR, before heating were characterized by three peaks or shoulders, labeled A (at 0.96–0.99 nm, collapsed interlayers), B (at 1.24–1.36 nm) and C (at 2.10–2.50 nm). Peak B represents adsorbed monolayers of water and dye anions inside the interlayer spaces. Peak C represents interlayer spaces with different orientations of the adsorbed water and organic matter. Diffractograms of samples with small amounts of dye were similar to those without dye showing peak B whereas diffractograms of most samples with high amounts of dye showed an additional peak C. Heated unwashed and washed samples were also characterized by three peaks or shoulders, labeled A' (at 0.96 nm), B' (at 1.10–1.33 nm) and C' (at 1.61–2.10 nm), representing collapsed interlayers, and interlayers with charcoal composed of monolayers or multilayers of carbon. When the samples were heated from 360 to 420°C some of the charcoal monolayers underwent rearrangement to multilayers. In the case of Cu the charcoal decomposed and oxidized. The present results show that most of the adsorbed dye was located inside the interlayer space.

Keywords: basal spacings, charcoal, congo-red, montmorillonite, X-ray diffraction

Introduction

The adsorption of organic cationic dyes by smectite minerals has been investigated for many years. The adsorption process takes place by the mechanism of cation exchange and is followed by secondary short range interactions, such as hydrogen bond formation between proton donor sites inside the interlayer space and basic sites on the dye cation, π interactions between the cation and the oxygen plane of the clay or dimerization and formation of higher associations of the dye cations inside the interparticle space of flocs. The major methods used in the study of the adsorption of cationic dyes were cation ex-

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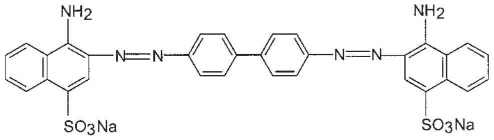
change, infrared spectroscopy, visible spectroscopy, DTA and X-ray. These studies contributed much to the understanding of the mechanism of adsorption of aromatic cations in general [1–7].

There is very little information on the adsorption of organic anions by smectite minerals. The broken-bonds surfaces under certain pH values may react as sites for anion-exchange and organic anions can be adsorbed onto these surfaces [8]. The interlayer space has a negative potential and therefore it is expected that anionic species will not be adsorbed into this space. In the presence of polyvalent metallic cations, benzoate and glyphosate anions were adsorbed with short-range interactions between the organic anion and the metallic cation [9, 10]. Pyrocatechol and some of its derivatives were adsorbed from aqueous solutions by Fe-smectite. From that study it was concluded that the anionic species penetrated into the interlayer space only if they were able to create stable coordination complexes with the metallic cations with a net positive charge [11, 12].

The purpose of the present investigation is to study the adsorption of an anionic dye onto montmorillonite by thermo-XRD-analysis. In this technique the sample is heated to different temperatures and is diffracted by X-rays. From the different diffractograms one gets information about changes due to temperature. In the case of montmorillonite, if there is no organic matter in the interlayer space, at about 300°C interlayer water is evolved and a basal spacing of about 0.95 nm is obtained which is characteristic for collapsed interlayers. If organic matter is present in the interlayer before the thermal treatment, it is converted to charcoal [13, 14] and basal spacings higher than 1.1 nm are obtained [15]. Simultaneous DTA-EGA study of cationic dyes adsorbed by Laponite and montmorillonite showed that the oxidation of the dye in air atmosphere started slightly above 200°C with the evolution of H_2O and CO_2 and the formation of charcoal inside the interlayer space [16–18]. The basal spacings that are obtained after the thermal treatment at temperatures above 300°C are those of the clay complex with the interlayer charcoal [15]. Depending on the clay mineral and on the type of interaction between the clay and the organic compound, the oxidation of charcoal is completed above 600°C. The formation of a charcoal layer inside the interlayer space may occur only if the precursor dye was located in that site.



Scheme 1 Congo Red (CR)

Congo-red (CR, Scheme 1) was chosen for this purpose because preliminary experiments showed that in spite of being an anionic dye, it is adsorbed by smectite minerals in considerable amounts. This dye is a bisazo-dye prepared by coupling tetrazotised benzidine with two molecules of 1-naphthylamine-4-sulphonic acid [20]. CR is used in aqueous solutions as an acid-base indicator. It is red in alkaline solutions and blue in acid solutions. The sodium salt dyes cotton a full red. It was the first synthetic dye produced in 1885 that was capable of dying cotton directly. In the present investigation we are going to determine whether the adsorbed anion is located inside the interlayer space or on the broken–bonds at the edges of the clay platelets.

Experimental

Materials

Montmorillonite (Wyoming bentonite) from Upton, Wyoming [21] was purchased from Wards National Science Establishment. Almost monoionic montmorillonites saturated with Na^+, Cs^+, Mg^{2+}, Cu^{2+}, Al^{3+} and Fe^{3+} were prepared as follows: a portion of 10 g Wyoming bentonite was dispersed in 800 mL water and stirred for two days. The stable clay suspension was separated from the sedimented quartz and feldspar and 200 mL of 0.2 M aqueous solution of the respective chloride salt was added and the suspension was stirred. After two days the clay was washed several times by distilled water until it was free of chloride (examined by $AgNO_3$ solution). Monoionic montmorillonites obtained by this treatment contained small amounts of Na^+, Ca^{2+} and Mg^{2+} in addition to the principal exchangeable cation [22, 23].

Methods

Preparation of CR-montmorillonite complexes

Each monoionic montmorillonite was treated with 1.25, 22.0 and 87.0 mmol CR per 100 g clay. In the first treatment 1.0 mL of $7.5\cdot10^{-4}$ M CR aqueous solution was added into 5 mL of aqueous clay suspension (1.2 mass%). In the second and third treatments 1.0 and 4.0 mL, respectively, of $1.3\cdot10^{-2}$ M CR aqueous solution were added into the 5 mL of the clay suspensions. Each system was treated for 10 min in ultrasound bath before and after adding the dye.

Determination of adsorbed dye

After 24 h the suspensions were centrifuged for 30 min (8.000 rpm) and the supernatants were separated from the sedimented clays. After dilution with water the spectra of the supernatants were recorded in the range 350–900 nm. The curve-fitted spectrum of an aqueous solution of CR shows a major peak maximum at 497 nm and two small peaks at 440 and 540 nm. The total peak area in the different supernatants was obtained by the curve fitting function in ‘Grams 32’ (Galactic) software. Mixed Lorentzian–Gaussian peak-shapes were used. The CR contents in the different supernatants were determined and the amounts of CR adsorbed by the different samples were calculated.

Washing of CR-montmorillonite complexes of samples treated with 87 mmol dye per 100 g clay

The separated clay sample was washed four times by adding up to 10 mL distilled water. The mixture was shaken thoroughly and the water was separated by centrifugation. The dye in the supernatant was determined by spectrophotometric analysis and the loading of the clay by CR after washing was calculated.

X-ray study of CR-montmorillonite complexes of samples treated with 1.25, 22 and 87 mmol dye per 100 g clay

X-ray patterns of samples with a preferred orientation were recorded at room temperature by a Philips Automatic Diffractometer (PW 1710) with a Cu tube anode. Oriented samples were obtained by sedimenting unwashed and washed CR-clay samples from aqueous suspensions on glass slides. Air-dry samples were equilibrated for five days in a desiccator under an atmosphere of hydrated $Mg(NO_3)_2$. Diffractograms were recorded before and after thermal treatments at 360 and at 420°C for 3 or 5 h.

Results and discussion

Adsorption capacities of the different montmorillonites and the effect of washing on the loading

Supernatants of samples treated with 1.25 mmol CR per 100 g clay were colorless, indicating that in these systems the dye was completely adsorbed by the clay. Supernatants of samples treated with 22.0 mmol CR per 100 g clay were pale-red, indicating that in these systems the dye was almost completely adsorbed by the clay. The loadings of Na-, Cs-, Mg-, Cu- Al- and Fe-montmorillonite were 21.3, 21.8, 21.9, 21.9, 21.8 and 21.8 mmol CR per 100 g, respectively.

Table 1 Adsorption of CR by monoionic montmorillonites treated with 87 mmol CR per 100 g clay and the amounts of CR which remained adsorbed by the clay after washings

Exchangeable cation	Adsorbed dye in mmol CR per 100 g montmorillonite		
	unwashed	washed twice	washed four times
Na^+	83.4	80.1	80.0
Cs^+	70.8	66.2	66.1
Mg^{2+}	84.6	81.0	80.5
Cu^{2+}	86.1	85.8	85.7
Al^{3+}	68.5	63.9	63.8
Fe^{3+}	50.6	45.9	45.5

The amounts of adsorbed dye by samples treated with 87.0 mmol CR per 100 g clay before and after two and four washings were calculated and are listed in Table 1. Preliminary results showed that the adsorption capacity depends on the clay concentration (paper in preparation). It should therefore be taken into account that the results of Table 1 are significant only for the present clay concentration. It appears that the loading depends on the dispersability of the clay. Al- and Fe-montmorillonite are highly flocculated and they show the smallest loadings. The table also shows that the desorption due to washing is significant only in the first two washings. These results indicate that the rest of the dye is strongly adsorbed by the different montmorillonites.

X-ray diffractions

Oriented specimens of Na-, Cs-, Mg-, Al-, Cu-, and Fe-montmorillonite samples unloaded and loaded with 1.25, 22 and 87 mmol CR per 100 g clay were examined by X-ray diffraction after equilibrating at 40% humidity and after heating at 360 and at 420°C. The basal spacings were determined and are summarized in Table 2. The samples gave either non-integral or integral high orders of reflection. Integral series are signed in the table by an asteric. The integral order of reflections indicates homogeneous spacing with a high order whereas non-integral reflections indicate poor order of packing of the layers. Basal spacings determined from non-integral reflections should be considered only as trends. Random interstratifications of layers with different *c*-spacings should not give X-ray diffraction.

Monoionic montmorillonites

The basal spacings of the different air-dried monoionic montmorillonites saturated with monovalent and polyvalent exchangeable cations are 1.25 and 1.50 nm, respectively (Table 2). Some representative diffractograms are depicted in Fig. 1 (curves A). These basal spacings indicate the presence of water mono- and bilayers, respectively, in the interlayer space [24, 25]. Cu-montmorillonite is an exception among the montmorillonites saturated with polyvalent exchangeable cations by having a basal spacing of 1.25 nm.

The thermal treatment of the different monoionic montmorillonites at 360 or 420°C resulted in dehydration as indicated from the decrease of the basal spacing to 0.96 nm. Some representative diffractograms are depicted in Fig. 1 (curves C). In the case of Na-, Mg-, Al- or Cu-montmorillonite the 0.96 nm was the major peak already after three h at 360°C. Cs-montmorillonite required 5 h at 360°C in order to sharpen the 0.99 nm peak. Fe-montmorillonite became completely dehydrated only at 420°C. A peak at 0.96 nm indicates the presence of collapsed interlayer spaces.

Unwashed CR-montmorillonite complexes

The X-ray diffractograms of montmorillonites treated with 1.25 mmol CR per 100 g clay were similar to those of the unloaded montmorillonites. Na-, Cs- and Cu-clay showed a relatively sharp peak at 1.25 nm whereas Mg-, Al- and Fe-clay showed a peak at 1.45–1.50 nm (Table 2), characterizing water mono- and bilayers in the interlayers. The organic anions can be embedded between the water molecules or on the external surfaces. Representative diffractograms are depicted in Fig. 1 (curves B and D).

Table 2 Basal spacings (in nm) of untreated and thermal treated CR- montmorillonite complexes before and after heating at 360 and 420°C

Cation	Saturation mmol CR/ 100 g clay	Temperature/ 25°C	Temperature/ 360°C (3 h)	Temperature/ 360°C (5 h)	Temperature/ 420°C (3 h)
Na^{+}	0	1.25 *s	0.96 *s	0.96 *s	0.96 *s
	1.25	1.25 *s	2.10 sh, 0.96 *s		0.96 *s
	22	1.25 *$^{+}$s	1.98 sh, 1.22 sh, 0.96 *s		0.96 *$^{+}$s
	87	2.20 sh, 1.31 s, 0.99 sh	1.99 s, 1.21 vs		1.84 vs, 1.11 s
Cs^{+}	0	1.24 s	1.18 s	0.99 s	0.99 s
	1.25	1.24 *$^{+}$s	1.18 $^{+}$s		2.10 sh, 1.10 s
	22	2.05 sh, 1.24 s	1.18 $^{+}$s		1.18 $^{+}$s
	87	2.10 sh, 1.31 s, 0.99 sh	2.10 sh, 1.10 s		2.10 s, 1.10 s
Mg^{2+}	0	1.45 s	0.96 *s		1.14 s
	1.25	1.45 s	0.96 *$^{+}$s		0.96 *$^{+}$s
	22	1.26 $^{+}$s	1.82 sh, 0.96 s		1.82 sh, 0.96 s
	87	1.33 s, 0.99 m	1.73 w, 1.33 s, 1.17 vs		1.73 s, 1.17 s
Cu^{2+}	0	1.24 *s	0.96 *s		0.96 *s
	1.25	1.24 *s	0.96 *s		0.96 *$^{+}$s
	22	1.24 *$^{+}$s	0.96 *$^{+}$s		0.96 *$^{+}$s
	87	2.10 sh, 1.31 s, 0.99 sh	1.73 s, 1.16 sh, 0.99 sh		1.73 s, 1.16 s, 0.99 sh
Al^{3+}	0	1.50 s	0.96 *s		0.96 *s
	1.25	1.50 s	1.00 $^{+}$s		0.96 $^{+}$s
	22	2.10 sh, 1.25 s	1.80 sh, 1.25 s		1.68 s, 1.10 s
	87	2.50 m, 1.36 s, 0.93 w	2.18 m, 1.25 s		1.96 vs, 1.13 m
Fe^{3+}	0	1.45 s	1.25 sh, 0.96 s	0.96^{+}s	0.96 *s
	1.25	1.45 s	1.00 s		0.96 *$^{+}$s
	22	1.25 *$^{+}$s	1.61 sh, 0.96 *s		1.61 sh, 0.96 *$^{+}$s
	87	2.32 m, 1.34 s, 0.94 w	2.02 m, 1.15 sh		1.83 s, 1.10 sh

$^{+}$ – with an extension of the diffraction line towards longer basal spacings;
* – integral set of lines; *s* – strong line; *sh* – shoulder; *m* – medium; *w* – weak; *vs* - very strong line

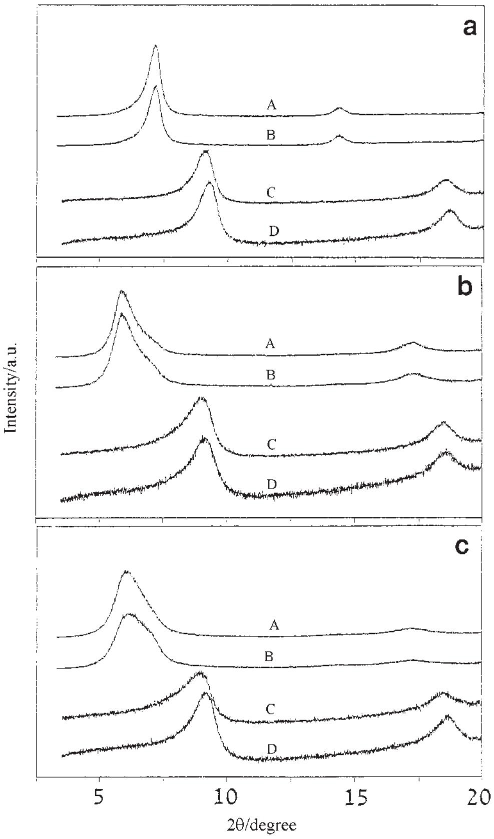


Fig. 1 X-ray diffractograms of Cu, Al and Fe-montmorillonite (a, b and c, respectively). Curves A and C untreated monoionic montmorillonites and curves B and D montmorillonites treated with 1.25 mmol CR per 100 g clay. Curves A and B unheated samples and curves C and D samples heated at 420°C

X-ray diffractograms of Na- and Cs- montmorillonite treated with 22 and 87 mmol CR per 100 g clay are depicted in Fig. 2. CR complexes of Cu-montmorillonite show similarities with those of the monovalent ion montmorillonites (Figs 3A and C). The diffractograms of these three samples treated with 22 mmol CR per 100 g clay showed a relatively sharp peak at 1.25 nm and an extension of the diffraction line towards longer basal spacings. The three clays treated with 87 mmol CR showed a very broad diffraction line of overlapping peaks in the range 0.85–2.50 nm with a shoulder at 0.99, a maximum at 1.31 and another shoulder at 2.10–2.20 nm. These peaks or shoulders are labeled A, B and C, respectively.

Mg- and Fe-montmorillonite treated with 22 mmol CR per 100 g clay showed a broad peak B at 1.25 nm and an extension towards higher basal spacings. These basal spacings differ from those determined for the monoionic clay samples not treated with CR. Al-montmorillonite treated with 22 mmol CR per 100 g clay showed a

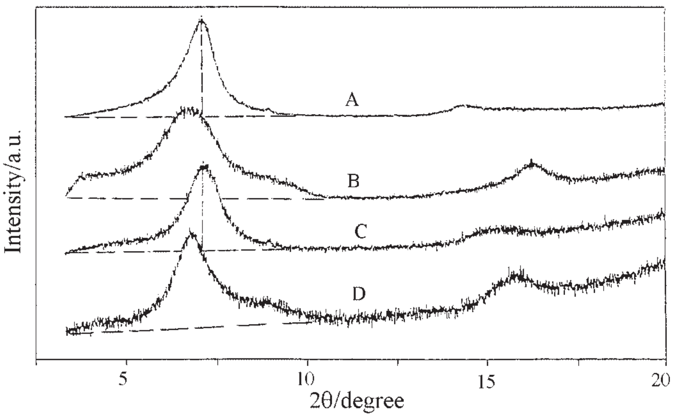


Fig. 2 X-ray diffractograms of A – Na-montmorillonite treated with 22 mmol dye per 100 g clay; B – Na-montmorillonite treated with 87 mmol dye per 100 g clay; C – Cs-montmorillonite treated with 22 mmol dye per 100 g clay; D – Cs-montmorillonite treated with 87 mmol dye per 100 g clay (perpendiculars and extrapolated base-lines are drawn in the figure to demonstrate the asymmetry of peak B and its extension to shorter or longer spacings, respectively)

broad diffraction line in the range 0.82–2.50 with a maximum at 1.25 and an intense shoulder at 2.10 nm (peaks B and C, respectively). Mg-montmorillonite treated with 87 mmol showed an intense asymmetric broad peak at 1.33 nm and a medium size peak at 0.99 nm (peaks B and A, respectively). Al- and Fe-montmorillonite treated with 87 mmol CR per 100 g clay showed three peaks A, B and C (Table 2). The diffractogram of the latter sample is depicted in Fig. 4A.

Peak A represents collapsed interlayers. Peak B at 1.24–1.36 nm represents adsorbed monolayers in the interlayer spaces, composed of water molecules with dye anions. With such a basal spacing the dye anions must be located parallel or almost parallel to the silicate layers probably embedded in the water monolayers. Peak C at 2.10–2.50 nm and the extension of the diffraction line of peak B towards spacings above 1.6 nm represent interlayer spaces with different orientations of the adsorbed water and organic matter. Peak B was the strongest one in all diffractograms of samples treated with CR and peak A was the weakest indicating that in these samples most of the clay contained monolayers inside the interlayer spaces.

With 87 mmol dye per 100 g clay the diffractograms show a very broad diffraction line of overlapping peaks and do not show integral high orders of reflections. This is an indication for lack of homogeneity of the interlayer spaces. Some of the interlayers contain monolayers, others contain bi-, tri- or tetra-layers of adsorbed water together with dye. In this case the dye anions may be randomly oriented (parallel, perpendicular or tilted) relative to the silicate layers.

It should be noted that before the CR treatment of Mg-, Al- and Fe-clay, or after the treatment with small amounts of dye (1.25 mmol CR per 100 g clay), the basal spacings were 1.45–1.50 nm. Comparing these spacings with those obtained with 22 mmol dye per 100 g clay (1.25 nm) suggests that in the adsorption process water was replaced by the dye. It appears that in the presence of exchangeable di- or polyvalent cations water favors the formation of bilayers whereas CR favors mono- or polylayers.

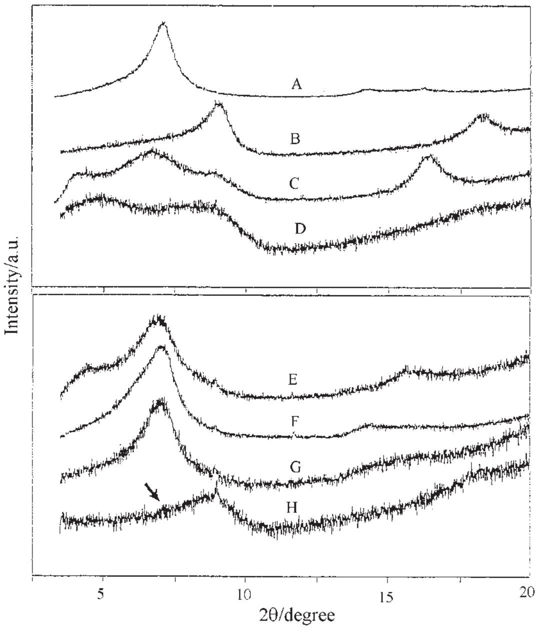


Fig. 3 X-ray diffractograms of A – Cu-montmorillonite treated with 22 mmol CR per 100 g clay; B – sample A heated at 420°C; C – Cu-montmorillonite treated with 87 mmol CR per 100 g clay; D – sample C heated at 420°C; E – sample C after the separation of the supernatant; F – sample E washed twice; G – sample E washed four times; H – sample G heated at 420°C (the arrow in curve H shows the location of peak B)

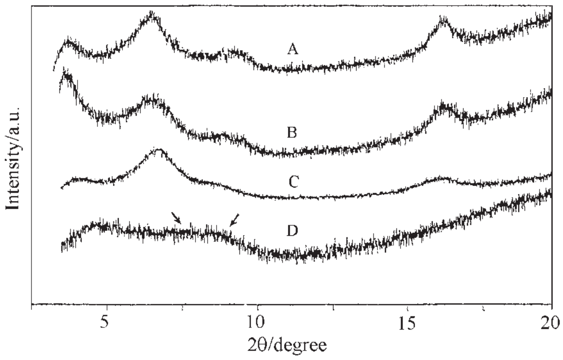


Fig. 4 X-ray diffractograms of Fe-montmorillonite treated with 87 mmol CR per 100 g clay A – unwashed; B – after the separation of the supernatant; C – after two washings; D – after four washings and heating at 420°C (the two arrows in curve D show the locations of peaks A and B)

Thermal treatment of unwashed CR-montmorillonite complexes

Heating Na-, Mg-, Al-, Cu- and Fe-montmorillonite treated with 1.25 mmol CR per 100 g clay at 360 and at 420°C gave diffractograms with peak A at 0.96 nm, very similar to those of non-loaded collapsed montmorillonites (Fig. 1, curves C and D). This observation is typical for the case that the adsorbed organic anions were not present inside these interlayers before the thermal treatment. Since the amount of adsorbed dye in these samples is very small, it is not clear whether the adsorbed dye was present in few interlayers or it was adsorbed on the external surfaces of the clay. Heating Cs-montmorillonite treated with 1.25 mmol CR per 100 g clay gave different results. Peak B’ at 1.10–1.18 nm with an extension to longer spacings indicated that the adsorbed CR was located inside the interlayer space. Peak A did not appear.

Na-montmorillonite treated with 22 mmol dye per 100 g clay after heating at 360°C gave a broad asymmetric peak with a maximum at 0.96 and shoulders at 1.22 and 1.98 nm (peaks A’, B’ and C’ respectively). At 420°C the shoulders merged and became an extension of the principal peak towards longer spacings. Mg-, Cu- and Fe-montmorillonite treated with 22 mmol CR per 100 g clay after heating gave a very broad asymmetric diffraction line of overlapping peaks with a sharp maximum at 0.96 nm (peak A’), an extension towards longer basal spacings (corresponds to peaks B’) and a shoulder C’ (1.61–1.82 nm). The diffractogram of Cu-montmorillonite is shown in Fig. 3B. Al-montmorillonite treated with the same amount of CR, after heating at 360°C, gave a broad peak B’ with a maximum at 1.25 and a shoulder which became a distinct peak at 1.68 nm (peak C’) after heating to 420°C (Fig. 5A). Cs-montmorillonite treated with 22 mmol CR per 100 g clay at 360 and 420°C gave peak B’ at 1.18 nm with an extension to longer spacings.

These changes in the diffractograms after the thermal treatment are attributed to dehydration and collapse of some interlayers (peak A’) and to the partial oxidation of the organic anion and the formation of charcoal inside the other interlayers (peaks B’ and C’). The two latter maxima characterize interlayers with carbon monolayers and multilayers, respectively. A spacing of 1.1–1.2 nm enables the occurrence of carbon monolayers and that in the range above 1.6 nm enables the occurrence of multilayer carbon assemblages inside the interlayer space.

Na-montmorillonite treated with 87 mmol dye per 100 g clay after heating to 360°C showed a broad diffraction line in the range 0.83–2.50 nm with two maxima at 1.21 (peak B’, very strong) and 1.99 nm (peak C’, weaker). After heating at 420°C both maxima shifted to lower spacings (Table 2). Peak C’ became the most intense and peak B’ became weaker. Cs-montmorillonite treated with 87 mmol dye per 100 g clay gave at 360°C an asymmetric peak at 1.10 with a shoulder at 2.10 nm, which became a distinct peak at 420°C. The thermal behavior of Mg-, Al- and Fe-montmorillonite treated with 87 mmol CR per 100 g clay was similar to that of Na-clay. After heating at 360°C peaks B’ and C’ were observed. After heating at 420°C peak C’ shifted to shorter spacings and became very sharp and intense. Peak B’ also shifted to shorter spacings (Table 2) but its intensity decreased. Diffractograms of CR treated Al-montmorillonite heated at 360 and at 420°C are de-

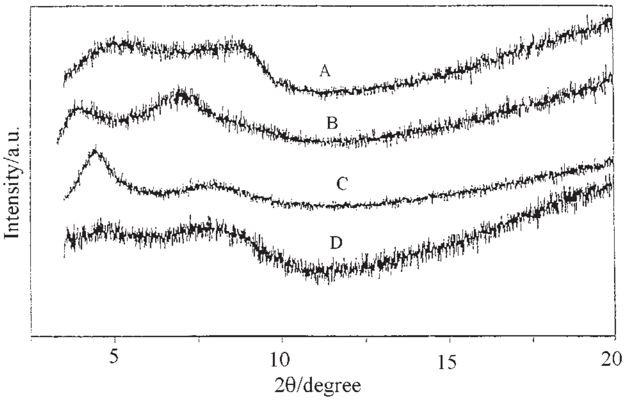


Fig. 5 X-ray diffractograms of Al-montmorillonite A – treated with 22 mmol CR per 100 g clay and heated at 420°C; B – treated with 87 mmol CR per 100 g clay and heated at 360°C; C – sample B heated at 420°C; D – treated with 87 mmol CR per 100 g clay, washed four times and heated at 420°C

picted in Figs 5B and C, respectively. It should be noted that peak C was not observed before heating the CR complex of Mg-montmorillonite.

Peak A was clearly detected in the diffractograms of montmorillonites treated with 87 mmol CR per 100 g clay recorded before the thermal treatment but peak A' was not observed after heating these samples. It is possible that the excess CR, which was adsorbed on the external surface penetrated into empty interlayer spaces during the thermal treatment and thereby prevented their collapse. Peak B' was the principal peak at 360°C whereas peak C' became more intense at 420°C. The change in the shape of these diffractograms by heating from 360 to 420°C suggests rearrangement of carbon assemblages that form the charcoal inside the interlayers.

It seems that the charcoal which is formed in the interlayer space is composed of small carbon assemblages. Due to the steric hindrance of the interlayer space in the 1.1–1.2 nm spacings the assemblages are almost monolayers and are oriented parallel to the clay layer. When the interlayer space is higher than 1.6 nm the carbon assemblages may be randomly orientated. It is also possible that the thermal condensation of layered assemblages results in three dimensional species.

The changes in the basal spacings observed when Cu-montmorillonite treated with 87 mmol CR per 100 g clay was heated from room temperature to 360 and 420°C differed from those of the other clays. The broad peak in the range 0.78–2.47 nm showed a maximum at 1.73 nm (peak C') and shoulders at 1.16 and 0.99 nm (shoulders B' and A', respectively) (Fig. 3D). At 420°C shoulder B' became a distinct peak and peak C' decreased. This observation suggests that during the thermal treatment the multilayer carbon assemblages decomposed.

From the present XRD results of the heated samples treated with 22 and 87 mmol CR per 100 g clay it is obvious that most of the adsorbed dye was located inside the interlayer space in all the monoionic montmorillonites.

Table 3 The locations of peaks A, B and C in the diffractograms of the montmorillonites treated with 87 mmol CR per 100 g clay, before and after the separation of the supernatants and after washings, and the intensities of peaks A and C relative to that of peak B. Data are given for unheated samples (r.t.) and for samples heated at 420°C before the separation of the supernatants and after four washings

Exchangeable cation and thermal treatment	Dye content/ mmol 100 g^{-1} clay	Number of washings	Basal spacings/nm			Intensity ratio	
			peak A (or A')	peak B (or B')	peak C (or C')	$\frac{\text{peak A}}{\text{peak B}}$	$\frac{\text{peak C}}{\text{peak B}}$
Na$^+$, r.t.	87.0	0	0.99	1.31	2.20	0.60	0.45
	83.4	0	0.99	1.33	2.15	0.53	0.76
	80.1	2	0.99	1.31	2.10	0.43	0.46
	80.0	4	0.99	1.31	2.25	0.36	0.26
Na$^+$, 420°C	87.0	0	–	1.11	1.84	–	0.98
	80.0	4	0.99	1.13	1.80	1.15	1.07
Cs$^+$, r.t.	87.0	0	0.99	1.31	2.10	0.26	0.09
	70.8	0	0.99	1.29	2.10	0.19	0.19
	66.2	2	0.99	1.30	–	0.13	–
	66.1	4	0.99	1.29	–	0.11	–
Cs$^+$, 420°C	87.0	0	–	1.10	2.10	–	0.33
	66.1	4	0.99	1.10	–	0.66	–
Mg^{2+}, r.t.	87.0	0	0.99	1.33	–	0.57	–
	84.6	0	0.99	1.31	2.15	0.54	0.60
	81.0	2	0.99	1.33	2.30	0.45	0.36
	80.5	4	0.99	1.30	2.20	0.36	0.32
Mg^{2+}, 420°C	87.0	0	–	1.16	1.73	–	1.33
	80.5	4	0.99	1.14	1.78	1.07	1.18
Cu^{2+}, r.t.	87.0	0	0.99	1.31	2.10	0.64	0.68
	86.1	0	0.99	1.29	1.96	0.26	0.55
	85.8	2	–	1.26	–	–	–
	85.7	4	–	1.27	–	–	–
Cu^{2+}, 420°C	87.0	0	0.99	1.10	1.79	1.05	0.81
	85.7	4	0.99	1.26	–	4.00	–
Al^{3+}, r.t.	87.0	0	0.93	1.36	2.50	0.34	0.50
	68.5	0	0.94	1.36	2.50	0.30	0.60
	63.9	2	1.02	1.33	2.10	0.29	0.36
	63.8	4	1.03	1.33	2.23	0.27	0.16
Al^{3+}, 420°C	87.0	0	–	1.13	1.96	0.50	1.33
	80.5	4	0.99	1.13	1.87	0.85	1.18
Fe^{3+}, r.t.	87.0	0	0.94	1.34	2.32	0.45	0.60
	50.6	0	0.99	1.34	2.38	0.44	1.03
	45.9	2	1.00	1.30	2.20	0.38	0.31
	45.5	4	0.99	1.30	2.26	0.33	0.30
Fe^{3+}, 420°C	87.0	0	–	1.10	1.83	–	1.65
	45.5	4	0.99	1.13	1.96	0.82	1.18

Washing of CR-montmorillonite complexes

The effect of washings on the X-ray diffractograms of Fe-montmorillonite loaded with 87 mmol CR per 100 g clay may represent this effect on the other CR-montmorillonites (Fig. 4). As was stated in the previous section about unwashed samples of montmorillonites treated with 87 mmol CR per 100 g clay, most samples showed a very broad diffraction line of three overlapping peaks. The diffractograms recorded after washings also showed the broad overlapping three peaks but their locations and relative intensities might be different. The locations of peaks A, B and C in the diffractograms of the different samples treated with 87 mmol CR per 100 g clay, before and after the separation of the supernatant and after two and four washings, are collected in Table 3. By extrapolating a base-line and measuring the height of each peak, the intensities of peaks A and C relative to that of peak B were calculated and are also shown in this table. Because of the overlapping of the peaks, all these ratios must be considered only as trends. From the table it appears that in the diffractograms of most montmorillonites peak C increased after the separation of the supernatants and decreased with the number of washings whereas peak A gradually decreased from the first treatment. In the case of Al- and Fe- montmorillonite the relative intensity of peak C did not change after the second washing. Peak C disappeared after the second washing in the diffractograms of Cs-montmorillonite.

These results suggest the presence of collapsed interlayers. Since the loading of the clay was carried out in aqueous suspensions, it appears that the collapse was due to CR anions located at the edges of the platelets, bonded to the broken-bonds of the clay. The bound anions act as valves, allowing water molecules to diffuse outside the interlayer space but do not allow them to return into the interlayer space. As a result of the separation of the supernatant some of the external adsorbed anions were washed out and the collapsed interlays swelled.

The increase in the intensity of peak C relative to peak B indicates that during the separation of the excess dye water was adsorbed into some of the interlayers, which initially contained water monolayers. With washing some dye was washed out from the expanded interlayers and more interlayers with a basal spacing of about 1.3 nm were obtained.

The behavior of Cu-montmorillonite upon washing differed from that of the other samples (Figs 3E, F and G). In the presence of the supernatant, the X-ray diffractogram showed peaks A, B and C at 0.99, 1.31 and 2.10 nm respectively. The relative intensities of peaks A and C became weak after the separation of the supernatant and they disappeared after the second washing.

Thermal treatment of washed CR-montmorillonite complexes

After four washings the samples were heated at 420°C and examined by X-ray diffraction. All the diffractograms were non-integral. Except for Cu-montmorillonite, all the samples showed the presence of three peaks A’, B’ and C’ (Figs 4D and 5D). Peak A’ which characterizes collapsed interlayers, was not observed in the thermal treated unwashed samples. The appearance of collapsed interlayers after the thermal treatment of the washed samples indicates that during washing some anionic species were washed out from the interlayers, being replaced by water molecules. The three peaks were very broad indicating that the products lack homogeneity. There was a strong overlapping of peaks A' and B'. The basal spacings according to the maxima of the different peaks are collected in Table 3. After the thermal treatments the charcoal with the monolayer or the multilayer carbon show basal spacings shorter than the hydrated phases.

The intensities of peaks A' and C' relative to the intensity of peak B' were calculated and are also listed in Table 3. For comparison, the table also contains the intensities of peak C' relative to the intensity of peak B' in the diffractograms of the unwashed samples heated at 420°C. Because of the overlapping of the peaks, all these ratios must be considered only as trends. The table shows that in most cases the relative intensities of peak C' in the unwashed samples are slightly higher than those in the washed samples. The table also shows that the relative intensities of peaks A and C in the washed samples before heating at 420°C are smaller than those obtained after heating. This is obvious due to the fact that the thermal treatment is accompanied by dehydration of the interlayer space and by thermal condensation of the organic matter during charcoal formation into three dimensional species.

Cu-montmorillonite showed the presence of a very intense peak A at 0.99 nm. A very weak peak B' was observed at 1.31 nm (Fig. 3H). The intensity of peak A' relative to that of peak B' is equal to 4.0 (Table 3). The thermal collapse of Cu-montmorillonite in spite of the initial high loading of the sample may suggest that the organic matter was decomposed or oxidized during the thermal treatment and that the Cu^{2+} cation reacted as a catalyst in this reaction.

Conclusions

The dye CR was adsorbed by Na-, Cs-, Mg-, Cu-, Al- and Fe-montmorillonite in considerable amounts in spite of being anionic. X-ray diffractions of samples with preferred orientation with no organic matter and of samples treated with CR were heated up to 420°C showed that the former collapsed completely and the latter expanded up to 2.10 nm. The significant difference in the behavior of these clays suggests that the organic dye was adsorbed into the interlayer space of the clay.

From basal-spacing determinations of the CR-montmorillonite complexes three types of interlayer spaces were identified, collapsed interlayers and interlayers with monolayers or multilayers of water molecules together with CR anions. When heated at 360 and at 420°C the CR-montmorillonite complexes were dehydrated and the organic matter inside the interlayer space was converted into charcoal. From basal-spacing determinations three types of interlayer spaces were identified, collapsed interlayers and interlayers with charcoal composed of monolayer or multilayer carbon assemblages. The rise in temperature supports the rearrangement of the monolayer carbon charcoal into multilayer carbon charcoal and it seems to result of thermal condensation of small charcoal monolayered assemblages.

In the presence of exchangeable Cu the opposite phenomenon occurred and it appears that Cu catalyses the decomposition and oxidation of the organic matter. This is probably associated with the ability of Cu to form two types of π complexes with aromatic compounds [26–30]. In these complexes cationic radicals may be formed and they may either polymerize or decompose [31, 32].

It should be noted that the adsorption of the anionic CR onto the negatively charged montmorillonite is not taking place by the mechanism of ion exchange. The adsorption mechanism of CR by montmorillonite is now under investigation by visible spectroscopy methods.

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