

SEQUESTRATION OF CATECHOL AND PENTACHLOROPHENOL BY MECHANOCHEMICALLY TREATED KAOLINITE

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Abstract—The pollution of soils by organic contaminants, such as phenols, is a serious problem because of the high toxicity and persistence in the environment. Mechanochemical treatments (MTs) of polluted soils with minerals, such as clays and oxides, which have surfaces that exhibit catalytic properties, have been suggested to be a new useful strategy to promote both organic and inorganic pollutant degradation. Nevertheless, much still remains to be studied about the capability of clays to promote pollutant removal by means of the mechanochemical activation of the mineral surfaces. This work investigates the efficiency of the mineral kaolinite in promoting the sequestration of catechol (CAT) and pentachlorophenol (PCP) by MT. A well crystallized kaolinite (KGa-1b) was milled for prolonged times with different amounts of organic molecules so as to obtain two different clay:organic compound ratios. Prolonged grinding and a higher clay mineral:organic compound ratio were found to be more effective in promoting a stronger removal than simple contact. After 1 h of mechanochemical treatment, the PCP and CAT removal percentages were 32% and 20%, respectively. Additionally, a 7-day undisturbed incubation of the milled mixtures produced a trend for increased CAT removal (up to 40%). The interaction mechanism between kaolinite and each organic compound (*i.e.* CAT and PCP) after a MT was inferred by integrating information from spectroscopic, diffractometric, and chromatographic analyses. X-ray diffraction and Fourier-transform infrared data suggested a strong interaction between CAT and KGa-1b. This interaction mechanism likely occurs through the formation of an inner-sphere complex by H-bonding between the organic molecules and the oxygens of the kaolinite tetrahedral sheet. On the other hand, a weak interaction (*i.e.* van der Waals type) can occur between the KGa-1b O-planes and the PCP molecules, which likely bind to the external surfaces of KGa-1b.

Key Words—Catechol, Kaolinite, Mechanochemical Treatment, Pentachlorophenol.

INTRODUCTION

Contamination is one of the eight threats of soil degradation processes identified by the European Commission in the document “Towards a Thematic Strategy for Soil Protection” (European Commission, 2002). The pollution of soils by organic contaminants, such as phenols, is a serious problem because of the high toxicity and hazard. The decontamination techniques currently used to remediate polluted soils from organic compounds are time consuming and expensive (Gan *et al.*, 2009; Reddy *et al.*, 2011; Shi, 2009). Pentachlorophenol (PCP, C₆Cl₅OH) is a toxic fungicide used in wood preserving processes (Alexander, 2000; Escher *et al.*, 1996), and catechol (CAT, C₆H₄(OH)₂) is a molecule commonly found in soils (constituent of plant polyphenols) and can be an intermediate of microbial metabolism of some xenobiotics (Martin *et al.*, 1979). Phenols and substituted phenols are easily sorbed onto soil components, especially clay minerals, because the

compounds possess high surface areas and peculiar basic/acidic properties that depend on composition. For this reason, clay minerals can be used as pollutant adsorbents for environmental remediation purposes. Furthermore, such minerals also have good potential as adsorbing agents for cleaning wastewater due to the low cost (Bezzar and Ghomari, 2013; Gianotti *et al.*, 2008).

In recent years, new strategies have been investigated to remediate organic xenobiotic-polluted soils. In particular, mechanochemical treatments of polluted soils with mineral reactants that exhibit active surfaces, such as clays and oxides, have been proven to be a new useful strategy to promote both organic and inorganic pollutant removal (Di Leo *et al.*, 2012, 2013; Montinaro *et al.*, 2007; Napola *et al.*, 2006; Pizzigallo *et al.*, 2011; see also reviews by Nasser and Mingelgrin, 2012 and Ancona *et al.*, 2014). This methodology consists of grinding different solid-phase substrates (toxic compounds and catalytic surfaces) inside a high-energy ball mill in order to transform the contaminant into a less toxic substance by means of mechanochemical reactions. The enhancement of surface reactivity following the grinding process is mainly due to the supply of energy required to break the bonds in the solid medium by

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mechanical means, thus exposing fresh surfaces to the substrate molecules. The mechanochemical treatment of clay minerals, such as kaolinite, induced modifications to the surface and colloidal properties of the mineral (Pardo *et al.*, 2009; Vágvölgyi *et al.*, 2008) by rupture of the OH, AlOH, AlOSi, and SiO bonds, and also induced the formation of new and more catalytically efficient sites in the tetrahedral and octahedral sheets (Yariv and Lapides, 2000). The significantly modified properties of kaolinite by mechanochemical activation (Frost *et al.*, 2001, 2002) indeed determine its applicability in the remediation of contaminated systems (Yariv, 2002a). Although a number of papers dealing with milling and/or the interaction of kaolinite with organic molecules are available at present (Gardolinski and Lagaly, 2005; Zhang *et al.*, 2009; Makó *et al.*, 2009, 2013; Cheng *et al.*, 2012), little work has been done on the MT of KGa-1b with organic toxic compounds, such as catechol and pentachlorophenol. Besides, many studies (*e.g.* Boyd *et al.*, 1988) have looked at the removal of phenols by organo-clays but less have explored the mechanochemical interactions with clay minerals. X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR) studies coupled with the removal percentages can allow an understanding of the interaction mechanisms between mechanochemical activated KGa-1b surfaces and these organic compounds and, consequently, explore the unknown capability that such clays, activated by a high energy milling procedure, can perform in soil remediation practices.

The aim of this work was to assess the efficiency of kaolinite (KGa-1b) in enhancing the removal of PCP and CAT molecules by means of mechanochemical treatments. To this purpose, a well-crystallized kaolinite (KGa-1b) was milled for prolonged times with different amounts of organic molecules. The possible MT-induced interaction mechanism between the kaolinite and each organic compound (*i.e.* PCP or CAT) was inferred by integrating information from spectroscopic, diffractometric, and chromatographic analyses.

EXPERIMENTAL SECTION

Materials

The phyllosilicate employed in the experiments was a naturally occurring, well-crystallized kaolinite (KGa-1b), obtained from the Source Clays Repository of The Clay Minerals Society, from Washington County, Georgia, USA. The purity of the KGa-1b was tested using powder XRD. The CAT and PCP were purchased from the Aldrich Chemical Company (Milwaukee, USA, 99% of purity) and used without any further purification.

Mechanochemical treatments

The KGa-1b aliquots were mixed with CAT or PCP adopting two ratios of clay mineral/organic compound interaction and then milled in a high-energy planetary

ball mill (Pulverisette-7, Frisch, Oberstein, Germany). The reactor consisted of two zirconia pots with seven zirconia balls (10 mm diameter) and each was operated at high energy (700 rpm) for different milling times (four 15 min milling steps followed by a 15 min break time, for a total grinding period of 1 h). Aliquots (50 mg) of the solid mixtures were collected after each milling step. At the end of MT (a total of 60 min grinding), the four kaolinite/organic compound mixtures were left in rest mode (undisturbed incubation) for periods ranging from 24 h to 7 days in capped porcelain cups at 30°C.

The mechanochemical interactions were carried out according to the following experimental designs: (i) KGa-1b + PCP or CAT, the solid pollutant was added to the clay in a 10:1 clay/PCP or CAT ratio (5 g of KGa-1b + 500 mg of PCP or CAT); (ii) KGa-1b + PCP or CAT; the solid pollutant was added to the clay in a 3:1 clay/PCP or CAT ratio (4.2 g of KGa-1b + 1.4 g of PCP or CAT). For comparison, simple contact interactions (same KGa-1b/PCP or CAT ratios) were made without MTs, by stirring with a spatula until the mixture was uniform. The same periods (24 h to 7 days) used in the mechanochemical treatments were used for undisturbed incubation experiments.

Liquid phase analyses

Monitoring of PCP or CAT removal after the treatments (both mechanochemical and simple contact) was achieved by chromatographic analyses of liquid extracts. After each milling step and incubation time, two aliquots of the milled mixtures (50 mg) were extracted with 4 mL of an acetone/hexane mixture (1:1 v/v) by sonication for 6 min with VCX 500 Vibra-cell (Sonics, Newtown, Connecticut, USA), thus obtaining a total extraction energy of 1200 J. Afterwards, the extracts were centrifuged at 4°C for 10 min using a centrifugal force equal to $2880 \times g$ and filtered through 0.2 μm regenerated cellulose filters. The extracts were evaporated to dryness in a rotary evaporator and the residues were dissolved in a suitable solvent (distilled water for CAT and methanol for PCP) before analyses using liquid chromatography. Standard solutions of CAT and PCP were used as controls and the amount of organic compound removed by kaolinite (expressed as percentage) was calculated as the difference between the CAT or PCP measured in the control test and the sample extracted (by sonication) from the mixture. All the experiments were conducted in triplicate.

The HPLC analyses were performed with a Perkin Elmer LC Model 410 apparatus (Monza, Italy) operating at a flow rate of 1 mL min^{-1} , a $3.9 \text{ mm} \times 150 \text{ mm}$ C-18 column, and a diode-array detector (Perkin Elmer, Series 200) set at 220 and 280 nm for PCP and CAT, respectively. The mobile phase, used in an isocratic elution, consisted of a mixture of acidified water (0.05% phosphoric acid) and acetonitrile at a ratio of 70/30 (v/v) for the PCP and 20/80 (v/v) for the CAT.

Solid phase analyses

The XRD patterns of randomly oriented, untreated kaolinite and the kaolinite/PCP or CAT mixtures that were milled for 60 min were collected on a Rigaku Miniflex diffractometer (Japan) with a CuK_α radiation source and a sample spinner. The operational conditions were 40 kV, 30 mA, $0.02^\circ/\text{step}$ scan, $0.5^\circ/\Delta 2\theta/\text{min}$, and were scanned from $2^\circ 2\theta$ to $32^\circ 2\theta$. FTIR spectroscopic analysis was undertaken using a Nicolet 5 PC FT infrared spectrometer (Thermo Scientific, Waltham, Massachusetts, USA) and FTIR spectra between 400 and 4000 cm^{-1} were obtained. The nominal resolution was 4 cm^{-1} and the final spectra were an average of 128 scans. The samples were prepared as KBr pellets using 2 mg of sample to 200 mg of KBr. In order to better discriminate between the MT-induced modifications with or without PCP or CAT in kaolinite, great care was devoted to the analysis of the OH stretching region of the FTIR spectra of KGa-1b samples that were not milled, milled, and milled with CAT or PCP. According to Farmer and Russell (1964), vibrations occurring at 3697, 3669, and 3652 cm^{-1} arise from vibrations of hydroxyl groups of the gibbsite-like sheet [herein designated, inner-surface $\nu(\text{OH})$] and those occurring at 3620 cm^{-1} from vibrations of hydroxyl groups on the side of the tetrahedral sheet [herein designated, inner $\nu(\text{OH})$].

The $\nu(\text{OH})$ region of the FTIR spectra were deconvoluted using curve fitting performed by PeakFit software (Jandel Scientific) in order to highlight the possible changes in the relative intensities of inner-surface and inner OH stretching bands. These changes were quantified through the calculation of the % absorbance ratio

$$\frac{\text{inner - surface } \nu(\text{OH}) (3695, 3670, 3650\text{ cm}^{-1})}{\text{inner } \nu(\text{OH}) (3620\text{ cm}^{-1})}$$

The ratio is of the summed total absorbance of the inner-surface OH groups (at 3695, 3670, and 3650 cm^{-1}) to the absorbance by the inner OH groups at 3620 cm^{-1} .

To support the assessment of kaolinite framework modifications induced by prolonged milling, the percentage changes in absorbance ($P\%$ values) were calculated relative to the absorbance of the Si–O stretching band at 1033 cm^{-1} (labeled “F band”). The choice of this band as a reference standard is justified by the persistence of this band even after prolonged grinding (Yariv, 1975). The equation adopted to calculate $P\%$ is the one derived from previous works (Miller and Oulton, 1970). The $P\%$ values for bands at 1009 (G Band) and 1102 (P Band) cm^{-1} were calculated for the milled kaolinite and the milled kaolinite/organic compound mixtures according to Yariv and Lapidés (2000). For the solid phase analyses, the 3:1 ratio spectroscopic results were used because these are the most representative of the

interactions that occur between PCP or CAT and kaolinite.

RESULTS AND DISCUSSION

Liquid phase analyses

The chromatographic analyses revealed that kaolinite was more efficient in promoting pollutant removal with mechanochemical interactions (for both kaolinite/PCP or CAT ratios adopted) than with simple contact between clay mineral/pollutant.

The interaction between kaolinite and organic compounds by simple contact (no ball milling) showed lower pollutant removal percentages compared to the mechanochemical treatments. The CAT removal was less than 3% after 60 min of simple contact and reached ~5% removal after 4 days of incubation. Moreover, less than 2% of PCP was removed after 60 min of simple contact and ~4% after 4 days of incubation. After 7 days of simple contact, however, the removal percentages of both organic compounds decreased and were equal to 3% and 2% for CAT and PCP, respectively. This suggests that little or no sequestration of pollutants occurs if kaolinite interacts with PCP or CAT by simple contact.

The 20% CAT and 32% PCP removal percentages (Figure 1) obtained after 1 h milling with the highest amount of KGa-1b (10:1 clay/PCP or CAT ratio) suggested a fairly acceptable sequestration of both PCP and CAT. The MTs were followed by different incubation periods (from 24 h up to 7 days) and the longest incubation produced a trend of increased CAT removal (up to ~30%). On the other hand, up to ~40% PCP was removed within 48 h of incubation following MT and then PCP started to desorb and reached a minimum removal of 26% after a 7-day incubation. For the 3:1 ratio, minor CAT removal was achieved with up to 12% removal and a maximum value of 20% removal after 7 days of incubation. For PCP removal, the trend was consistent with up to 11% removal within 60 min grinding and increased up to 18% removal during the 7 days of incubation that followed (Figure 1).

The observations suggest that the amount of clay in solid mixtures influenced both the extent of CAT and PCP sequestration as well as the adsorption trends. Specifically, both CAT and PCP sorption onto kaolinite was enhanced after mechanochemical treatments and sorption continues even after the treatment (*i.e.* during incubation) although with different trends. The CAT was removed during the 7-day incubation while PCP removal increased for the first 48 h of incubation and then decreased until the end of the 7-day incubation.

Solid phase analyses

X-Ray diffraction. The XRD patterns of KGa-1b samples mechanically treated (1 h) showed changes in the kaolinite structure after the grinding process (Figures 2a and 2b). The milling caused the diminution

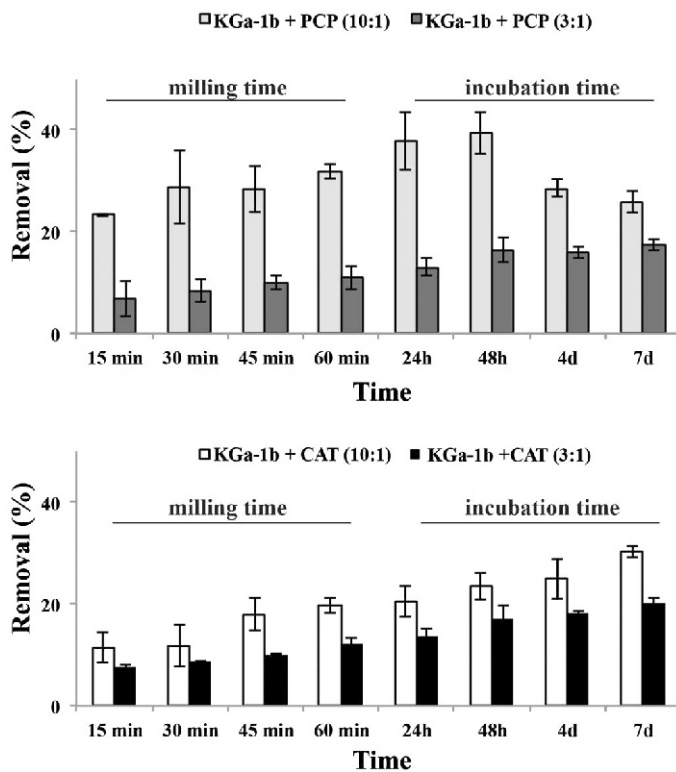


Figure 1. Removal percentages of PCP and CAT after mechanochemical interactions with KGa-1b (clay mineral/PCP or CAT ratios: 10:1 and 3:1) at different milling and incubation times. Error bars represent standard deviation (modified after Ancona *et al.*, 2014).

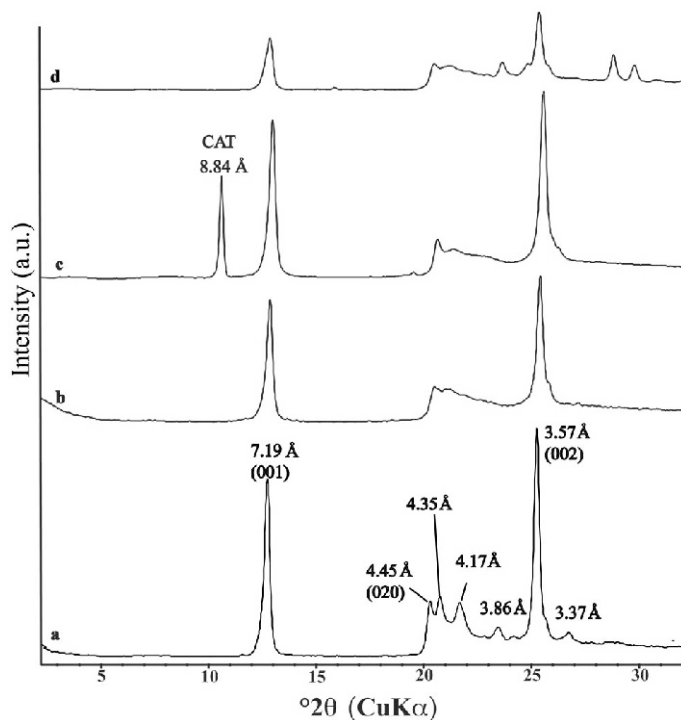


Figure 2. XRD patterns of: (a) KGa-1b not milled, (b) KGa-1b milled for 60 min, (c) KGa-1b + CAT milled for 60 min (3:1 ratio), and (d) KGa-1b + PCP milled for 60 min (3:1 ratio).

of the $d_{(001)}$ intensity and the disappearance of reflections in the $20\text{--}24^\circ 2\theta$ range even after only a 60-min grinding. This was evidence of delamination and that MT is indeed responsible for the rupture of the H bonding between adjacent kaolinite layers, which induced the loss of periodicity along the c axis (Frost *et al.*, 2001). The weakening of reflections between 19 and $25^\circ 2\theta$ in the XRD patterns (Figure 2), which were replaced by a broad peak, showed an increase in structural disorder (Aglietti *et al.*, 1986; Valášková *et al.*, 2011) as well as in the rupture of some kaolinite micelles along a and b planes. The fracture of the layers along planes other than the 001 plane (amorphization) changed the nature and increased the number of exposed functional groups (AlOH, SiOH, AlO^- , SiO^- , and Al-O-Si), and thus brought about an ion-exchange capacity increase (Yariv and Lapidés, 2000).

When grinding kaolinite (for 1 h) with CAT (3:1 ratio), the XRD pattern exhibited a smaller reduction of both basal (001 and 002) and 020 reflections than what was observed in a ground kaolinite sample XRD pattern (Figures 2c and 2b, respectively). This suggests that grinding kaolinite with CAT reduces the extent of the delamination/amorphization process. In contrast, the reduced basal reflections in the XRD pattern (Figure 2d) of the KGa-PCP mixture likely indicate that the delamination/amorphization processes may occur to a greater extent when PCP is milled with kaolinite.

FTIR spectroscopy

Changes in diagnostic vibrations of PCP and CAT. The 60-min-ground kaolinite+CAT IR spectrum evidenced extensive modification in the CAT structure from a consideration of the theoretically assigned CAT spectral bands (Ramírez and López Navarette, 1993). This is especially evident in the $\nu\text{R}+\delta(\text{OH})$ vibrations of the aromatic ring and C–OH bending as well as in stretching vibrations (Figure 3). The 1621 and 1598 cm^{-1} ring vibrations for pure CAT disappeared, whereas the 1514 and 1469 cm^{-1} bands collapsed to a single broad band at 1502 cm^{-1} . The aromatic ring vibration changes can be attributed to the occurrence of a weak π electron interaction with the oxygen planes of the silicate layer (Yariv, 2002b). In addition to this, the narrow band (C–O bending vibration) at 1365 cm^{-1} became broader and was reduced in relative intensity. The disappearance of the C–OH bending vibration at 1281 cm^{-1} , coupled with the collapse of the two bands at 1256 and 1238 cm^{-1} in a single band at 1260 cm^{-1} , suggests that interactions between CAT and the oxygen planes occur by hydrogen bonding through the OH groups (Yariv, 2002a, 2002b). Even if a darkening of the KGa-1b/CAT mixture milled for 60 min was observed, which possibly indicates an oxidative reaction took place during the mechanochemical interactions among these

substrates. No bands ascribable to by-products were observed in the FTIR spectrum. This is probably due to the fact that any by-products were below the detection limit of the technique. Further investigations, such as gas-chromatographic analyses, however, should be carried out to identify these products and evaluate the occurrence of any possible PCP and CAT degradation products.

Similar to what was observed for CAT, the $\nu\text{R}+\delta(\text{OH})$ aromatic ring vibrations and the C–OH bending and stretching vibrations were reduced in intensity after PCP was ground with kaolinite for 60 min (Figure 3). These results suggest that the interaction induces aromatic ring perturbation. Additionally, considering the vibrations which characterized the PCP spectrum (Czarnik-Matusiewicz *et al.*, 1999) within the 60-min-milled KGa-1b-PCP spectrum (Figure 3), a shift of the $\nu\text{R}+\delta(\text{C-O})$ band from 1305 to 1310 cm^{-1} was also observed as well as an increase in the width, thus indicating that the OH group was also involved in bonding. The kaolinite O-plane interactions with the non-polar PCP, therefore, were of the van der

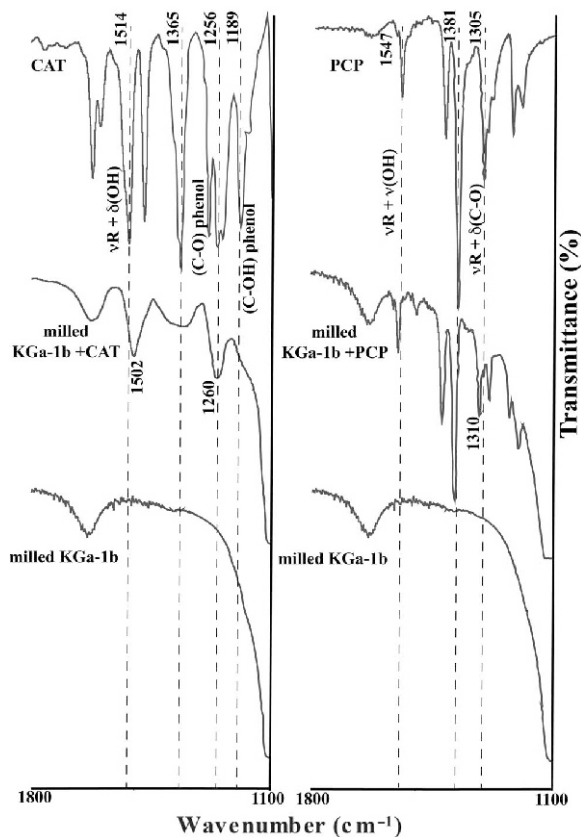


Figure 3. The $1800\text{--}1100\text{ cm}^{-1}$ FTIR spectrum of: (left bottom) KGa-1b milled for 60 min, (left middle) KGa-1b milled with CAT (3:1 ratio), (left top) CAT, (right bottom) KGa-1b milled, (right middle) KGa-1b milled with PCP (3:1 ratio), (right top) PCP.

Waals type as evidenced in previous studies related to organic compound/clay interactions (Yariv, 2002a).

Changes in the OH stretching of kaolinite. Analyses of the OH stretching region of FTIR spectra for KGa-1b samples that were not milled, milled, and milled with CAT or PCP were carried out in order to evaluate possible modifications induced in the kaolinite by MT (Figure 4).

The deconvolution of the $\nu(\text{OH})$ region of the milled KGa-1b spectrum (Figure 5b) evidenced changes in the relative intensities of both inner-surface OH stretching and inner OH stretching bands. These were quantified by calculating the % absorbance ratio (Table 1). Specifically, the increased intensity of the inner-surface OH bands (3695, 3650 cm^{-1}) indicated no evidence of delamination because grinding KGa-1b for 60 min without PCP or CAT doesn't reduce the number of inner surface hydroxyls faster than that of the inner hydroxyls, as alleged by Kameda *et al.*, (2004). On this basis, the increased % absorbance ratio (from 4.26 to 4.55; Table 1) after milling KGa-1b likely indicates that

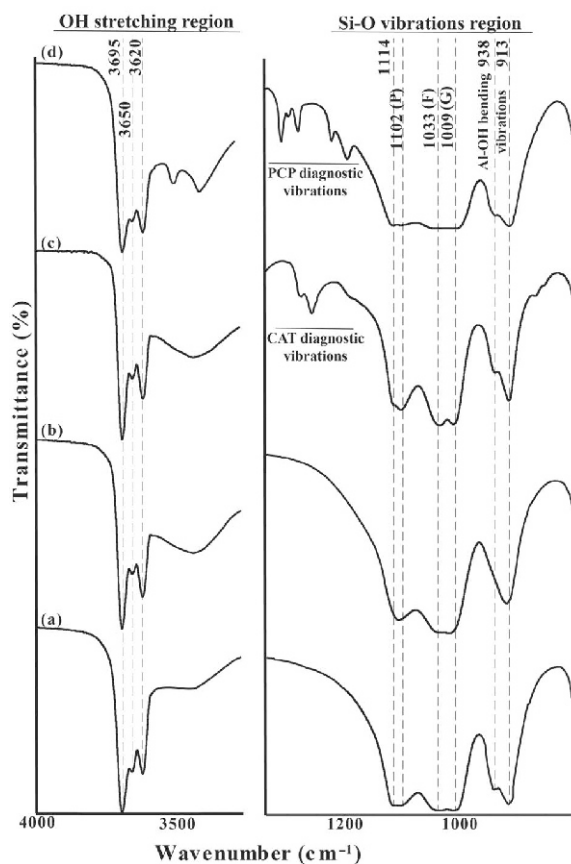


Figure 4. The OH stretching and Si–O vibration regions of FTIR spectra: (a) KGa-1b not milled, (b) KGa-1b milled for 60 min, (c) KGa-1b + CAT milled for 60 min (3:1 ratio), and (d) KGa-1b + PCP milled for 60 min (3:1 ratio).

Table 1. Absolute FTIR % absorbance values calculated using curve fitting data performed with PeakFit software (Jandel Scientific) and $P(\%)$ values calculated for the G and P bands using the equation derived by Yariv and Lapidés (2000).

Sample	Inner surface		Inner		Absorbance ratio (Inner surface bands/Inner band) (%)	P value G Band		P value P Band	
	$\nu(\text{OH})$ 3695 cm^{-1} (%)	$\nu(\text{OH})$ 3670 cm^{-1} (%)	$\nu(\text{OH})$ 3650 cm^{-1} (%)	$\nu(\text{OH})$ 3620 cm^{-1} (%)		$\nu(\text{Si-O})$ 1009 cm^{-1} (%)	$\nu(\text{Si-O})$ 1102 cm^{-1} (%)	$\nu(\text{Si-O})$ 1009 cm^{-1} (%)	$\nu(\text{Si-O})$ 1102 cm^{-1} (%)
KGa-1b	47.79	11.42	21.53	19.23	4.26	50.3	50.3	34	
KGa-1b milled	50.36	5.04	26.84	17.76	4.55	13.25	13.25	54.92	
KG-1b + CAT (3:1)	42.27	13.78	22.16	21.79	3.54	-77.48	-77.48	-90.43	
KGa-1b + PCP (3:1)	44.31	8.28	25.92	21.49	3.54				

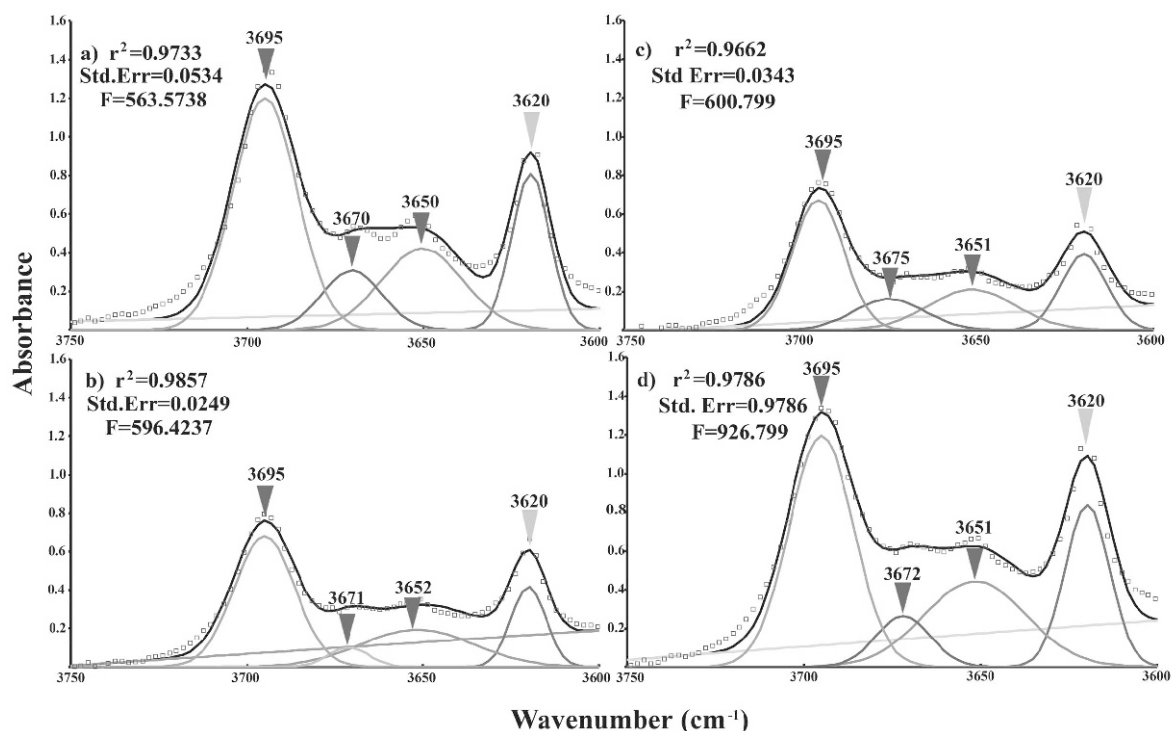


Figure 5. Deconvolution of the 3750–3600 cm^{-1} IR spectrum region showing the characteristic bands for kaolinite relative to OH stretching vibration: (a) KGa-1b not milled, (b) KGa-1b milled for 60 min, (c) KGa-1b + CAT milled for 60 min (3:1 ratio), and (d) KGa-1b + PCP milled for 60 min (3:1 ratio).

protons moved away from the inner hydroxyls. The 3620 cm^{-1} stretching band indeed showed a reduced intensity as grinding proceeded (Figure 5b).

The vOH region of the kaolinite+CAT IR spectrum (Figures 4c and 5c) exhibited changes in OH band relative intensities with respect to the untreated kaolinite as well as to the mechanically treated kaolinite without organic molecules. According to the changes in % absorbance ratio (for 4.26 to 3.54; Table 1), CAT can protonate broken-bond OH groups because CAT interacting with kaolinite preferably acts as a proton donor (Yariv, 2002a, 2002b), thus accounting for the increased absorbance of the band relative to the inner OH at 3620 cm^{-1} (Figure 5c).

The IR spectrum of the kaolinite mechanically treated with PCP has OH region bands with an absorbance variation. The two OH stretching vibrations characteristic of PCP (3514 and 3415 cm^{-1}) were also visible in the spectrum (Figure 4d). The deconvolution of the 3750–3600 cm^{-1} IR region (Figure 5d) highlighted a greater decrease in the inner-surface OH band (3695 cm^{-1} and 3670 cm^{-1}) intensities. Similar to what was observed for CAT, the large reduction of the PCP % absorbance ratio (from 4.26 to 3.54, Table 1) was a consequence of delamination. In the case of PCP, however, this process appeared to have been more intense than for CAT. Additionally, the increased intensity of the band relative to the inner OH at 3620 cm^{-1} (Figure 5d) also indicated protonation of the oxygen surface.

Changes of the Si-O vibration region in kaolinite. In order to better understand kaolinite surface transformations after MT, with or without CAT or PCP, the low-wavenumber region of the IR spectrum was also investigated. The collapse of $\nu(\text{Si-O})$ bands at 1114 and 1102 cm^{-1} in the spectrum of the milled kaolinite (Figure 4b) to a single broad band as well as the disappearance of the 938 cm^{-1} band (relative to Al–OH bending vibration) are compatible with an increase in structural defects and a partial reduction of kaolinite crystallinity, which is in agreement with the XRD results (Figure 2b). As for O–H vibrations, the reduction of Si–O bands perpendicular to the mineral layers (*i.e.* the 001 plane) indicated that a structural deterioration mainly occurs in the direction of the *c* axis. In general, changes in the $\nu(\text{Si-O})$ bands assigned by Franco *et al.* (2004) to out-of-plane vibrations (1114 and 1102 cm^{-1}) and to in-plane vibrations (1033 and 1009 cm^{-1}) suggest distortion in the tetrahedral and octahedral sheets of kaolinite (Vizcayno *et al.*, 2010), as also indicated by the loss of XRD reflections in the 20–24°2 θ range (Figure 2b). The percent changes in absorbance (*P%* values) for bands at 1009 (G Band) and 1102 (P Band) cm^{-1} calculated for the milled kaolinite and the milled kaolinite-PCP or CAT mixtures relative to the absorbance of the Si–O stretching band at 1033 cm^{-1} (F band, Figure 4) were reported in Table 1. The 1102 and 1114 cm^{-1} bands and 1033 cm^{-1} band (F Band) increased in intensity as kaolinite was milled with

CAT (Figure 4c). The $P\%$ values of the P Band at 1102 cm^{-1} increased in the milled KGa as well as in the milled KGa+CAT mixture (Table 1). Such an increase in $\nu(\text{Si-O})$ vibration intensity as a consequence of the grinding procedure indicates that hydroxyls were removed and, therefore, the surface became more similar to an alumina or siloxane surface as evidenced in a previous work (Frost *et al.*, 2001). The main process that leads the inner surface hydroxyls to move away is delamination (Kameda *et al.*, 2004). This process, therefore, likely became even more intense when grinding kaolinite with CAT, although deterioration of the kaolinite layer structure also occurred. The intensification of the 1009 cm^{-1} band (in-plane $\nu(\text{Si-O})$ vibration; $P = 50\%$) resulted from shifting oxygen and silicon atoms from the ideal position in the tetrahedral sheets after delamination of the clay was induced by prolonged milling. This delamination also occurred after grinding with CAT, although the process seemed to be less intense (G Band $P\%$ of 13%).

The IR spectrum of KGa-1b milled with PCP showed a relevant modification in the Si-O region (Figure 4d) with respect to the non-milled clay. In particular, both the bands at 1114 and 1102 cm^{-1} (out-of-plane vibrations) and the bands at 1033 and 1009 cm^{-1} (in-plane vibrations) were strongly affected by the formation of amorphous material during grinding (Franco *et al.*, 2004). The conclusion is, therefore, that when kaolinite was mechanically treated with PCP molecules these bands greatly decreased and tended to disappear. The percentage changes in absorbance ($P\%$ values, Table 1) determined for the 1009 and 1102 bands, respectively, for in-plane and out-of-plane $\nu(\text{Si-O})$ vibrations diminished considerably and became negative with greater amounts of PCP. This implied that prototropy (*i.e.* two forms that differ only in the position of a proton) became quite evident before the kaolinite layer structure deteriorated. The MT, therefore, favored a van der Waals-type interaction between the PCP molecules and the activated KGa-1b surfaces generated by the delamination process (Yariv, 2002a, 2002b). These molecules likely adsorb onto the delaminated surfaces by lying flat against the surfaces, which can explain the significant reduction of the $d001$ reflection observed in the KGa-1b+PCP XRD pattern (Figure 2d). In fact, the normal reduction of the basal reflection intensity due to delamination was reinforced as a consequence of the formation of PCP coatings onto the planar surfaces of kaolinite (perpendicular to c direction).

Surface interaction mechanisms activated by mechanochemical treatments

A comprehensive picture of the two most reliable mechanisms for CAT and PCP sequestration by kaolinite surfaces activated by MT was obtained by integrating data from solid phase (X-ray diffraction and IR spectro-

scopy) and liquid phase analyses. Moreover, the specific kaolinite sites on which CAT and PCP preferentially sorbed were identified. Two different surface reaction mechanisms have been hypothesized for CAT and PCP sorption (Figure 6).

Following the mechanochemical treatment, CAT was sorbed onto KGa-1b likely as a consequence of an oxidative reaction. An inner-sphere surface complex was assumed to form by H-bonding between the hydroxyl group of the organic molecules and the oxygens from the kaolinite tetrahedral/octahedral (TO) sheets (Figure 6). The preferable adsorption sites, for such a polar organic molecule, were the broken-bonds of the KGa-1b surface that were activated by milling (Yariv, 2002a, 2002b). Aluminum ions exposed at the edges of a 1:1 layer or in the interlayers acted as Lewis acids, which catalyzed the oxidation reactions. A partial deprotonation of phenols increased the electron density on the benzene ring, reduced stabilization through the π interaction with the oxygen planes of the clay, and promoted electron transfer according to Wang and Huang (1989).

For PCP, the hydrophobic exterior oxygen plane was the preferable site for the adsorption of this organic molecule on kaolinite crystals (Yariv, 2002a). The presence of a phenolic group supports proton donation to kaolinite surfaces after MTs.

The interactions between the O-planes and PCP were of the van der Waals type. The PCP molecules were likely adsorbed onto the highly delaminated surfaces and lay flat against the surfaces. The weak bond interaction (van der Waals) can justify desorption of the organic molecules after 7 days of incubation, as observed using chromatography results.

CONCLUSIONS

The results obtained in the present study support the initial idea that high-energy milling is crucial in activating kaolinite surfaces, thus promoting the removal of organic compounds, such as PCP and CAT, that does not occur in simple contact interactions or in brief milling treatments achieved manually with a mortar and pestle (Yariv and Lapides, 2000). These results differed from intercalation processes studied in previous works (Zhang *et al.*, 2009; Makó *et al.*, 2009, 2013; Cheng *et al.*, 2012). A removal greater than that obtainable with simple contact was achieved for both pollutants by using a planetary ball mill. For larger amounts of kaolinite and after a 60-min milling, more PCP than CAT was removed (32% vs. 20%).

A likely mechanism for the reaction between organic molecules, such as PCP and CAT, and kaolinite in mechanochemical interactions was proposed and examined in this work. This can increase the knowledge needed to assess kaolinite efficiency in sequestering and possibly degrading organic pollutants. As a consequence, a key step is to evaluate the potential exploita-

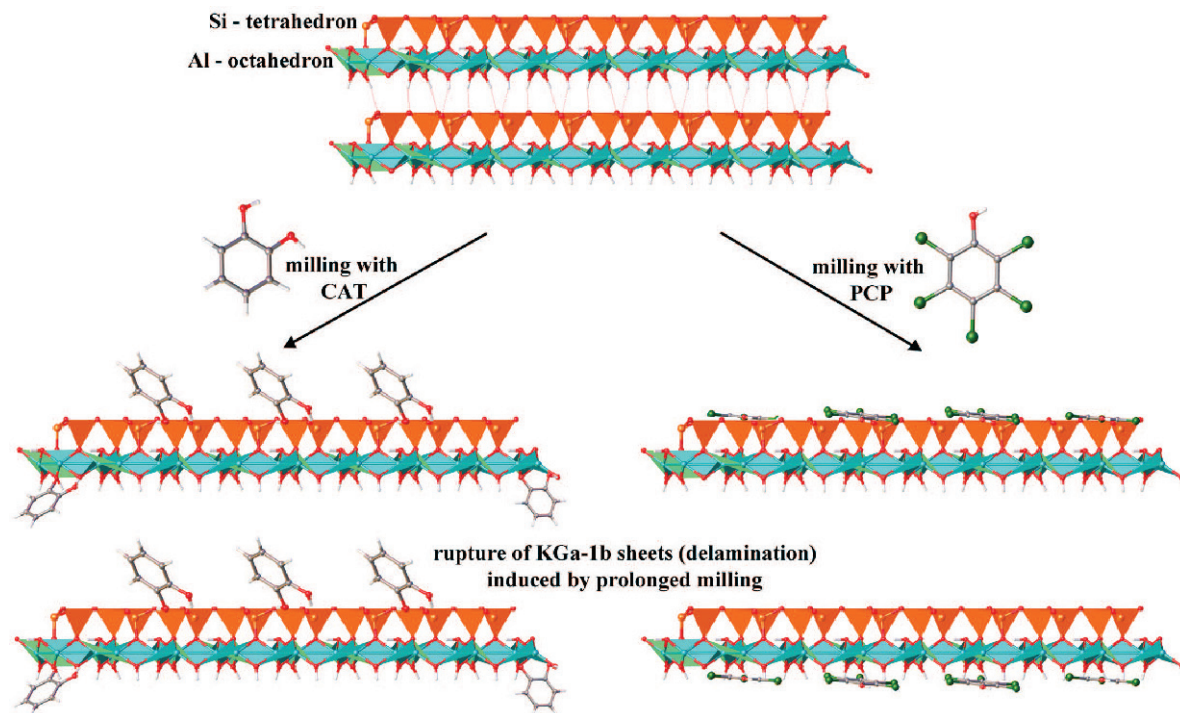


Figure 6. Surface reaction mechanisms of CAT (left) and PCP (right) molecules at kaolinite surfaces after mechanochemical interactions. The number of organic molecules in the sketch and the spatial arrangement are illustrative (modified after Ancona *et al.*, 2014).

tion of kaolinite as an activated natural inorganic substrate in innovative remediation strategies of organic polluted soils based on a mechanochemical approach. Further investigations are in progress to improve the capability of kaolinite to sequester organic compounds using MT and to identify by-products that result from the degradation of organic compounds adsorbed to clay mineral surfaces triggered by mechanochemical treatments.

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