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Adsorption of two phenoxyacid compounds on a clay surface: a theoretical study

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Abstract Using density functional theory methods, we studied the adsorption of (4-chloro-2-methylphenoxy)acetic acid (MCPA) and 2-(4-chlorophenoxy)-2-methylpropanoic acid, therapeutically used under the name of clofibric acid (CA), two commonly detected water pollutants, both in neutral and ionized form on a model surface of muscovite. We report the geometries of the adsorbed species and discuss their interaction with the surface. It was found that the ionized adsorbates interact more strongly with the surface than do their neutral forms particularly for MCPA when compared with CA, which points to the same direction of previous experimental findings. Changes on the electron density due to adsorption has been studied by means of Bader charges analysis and it was found that electronic density is transferred from the anions to the surface and less significantly from the surface to the neutral molecules on adsorption.

Keywords Clay minerals · Clofibric acid · MCPA · Muscovite · DFT

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1 Introduction

An ever-increasing variety of organic xenobiotic compounds have, over the last decades, been showing up in analyses of numerous environmental monitoring studies worldwide, especially in water samples (both of surface and ground waters) (Kuster et al. 2008; Barceló and Petrovic 2008; Farré et al. 2008; Kasprzyk-Hordern et al. 2009; Kümmerer 2011; Buchanan et al. 2011; Verlicchi et al. 2012; Lapworth et al. 2012; Matamoros et al. 2012). Naturally, this raises concerns about the quality of the water resources and the impact on ecosystems and on drinking water supplies.

Among these emerging pollutants are pesticides (such as MCPA, 2,4-D, Mecoprop or Atrazine (Gavrilescu 2005; Silva et al. 2006; Buchanan et al. 2011; Hu et al. 2012; Matamoros et al. 2012)), which have been a long time concern, and more recently an increasing attention is being given to the alarming number of pharmaceuticals and their metabolites (such as ibuprofen, diclofenac, carbamazepine and clofibric acid (CA) (Fent et al. 2006; Aga 2008; Kümmerer 2009; Miège et al. 2009; Bell et al. 2011; Verlicchi et al. 2012; Lapworth et al. 2012; Matamoros et al. 2012)) with an impact on the environment and on public health that has not been entirely clarified up to now.

Conventional wastewater treatment processes are generally not effective in removing micropollutants as they have been designed to treat bulk pollutants (Fent et al. 2006; Aga 2008; Miège et al. 2009; Verlicchi et al. 2012). Some advanced technologies have been evaluated such as advanced oxidative processes, activated carbon adsorption, membrane filtration and membrane bioreactors (Fent et al. 2006; Esplugas et al. 2007; Radjenovic et al. 2007; Rosal et al. 2010; Verlicchi et al. 2012; Kit Chan et al. 2012). However, despite the high removal efficiencies attained by many of these processes, they are not widely used mainly due to the high operational costs they involve (Fent et al. 2006). In recent years, inexpensive widely available materials have been investigated for the selection of efficient adsorbents that can make adsorption processes an attractive wastewater treatment alternative at reasonable costs. Among some of the adsorbents studied, clay-based materials have received some attention (Akcay and Yurdakoc 2000; Dordio et al. 2007; Dordio et al. 2009; Srivastava et al. 2009; Iglesias et al. 2010; Park et al. 2011) due to their interesting properties such as the high cation exchange capacity, swelling properties and high specific surface areas (although admittedly not as large as other materials such as activated carbons or zeolites). In particular for the treatment of wastewaters, these materials can overcome the limitations of biological processes, as used in conventional wastewater treatment, which are ineffective in the case of non-biodegradable pollutants (as many xenobiotic compounds are).

A better understanding of the interactions of certain organic molecules with clay minerals may thus allow a more judicious selection of materials for water/wastewater treatment filters that present significant enhancements in the removal of organic xenobiotics. From other perspectives, such knowledge may also help making better predictions of the environmental fate of many organic pollutants (since clay minerals are an important component of most types of soils and, therefore, can influence processes such as the leaching of pollutants) or be used for other applications such as the custom design of adsorbents for controlled sorption, sensing and separation of guest molecules.

The herbicide (4-chloro-2-methylphenoxy)acetic acid (MCPA) and the metabolite of cholesterol-lowering fibrate drugs, CA, are two commonly detected water pollutants (Ferrari et al. 2003; Tixier et al. 2003; Silva et al. 2006; Kuster et al. 2008; Verlicchi et al. 2012; Lapworth et al. 2012; Matamoros et al. 2012). They both belong to the same chemical family of phenoxyalkanoic acids, with a very similar chemical structure (see structures in Fig. 1). The group of phenoxyalkanoic acids and derivatives comprises a broad spectrum of herbicides used extensively in agriculture. Their behavior in soils (solubility, adsorption–desorption, chemical resistance, and biodegradation) is governed by their chemical structures whose essential features are a carboxylic acid group and a chlorinated aromatic ring. Adsorption to clay minerals, occurs through the polar carboxyl group (which is usually ionized under normal environmental conditions, as the pKa of these compounds is typically within the range of 3–4) but a weaker dispersion type of interactions with the polarizable electronic density of the aromatic ring may also have a non-negligible contribution.

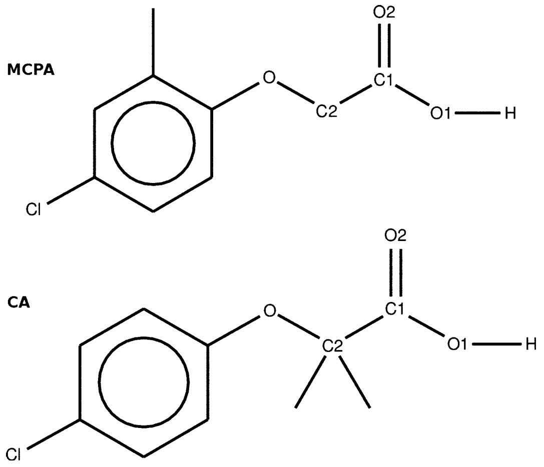

Fig. 1 The structures of (4-chloro-2-methylphenoxy)acetic acid (MCPA) and 2-(4-chlorophenoxy)-2-methylpropanoic acid (CA) molecules

It is commonly considered that the behavior of most compounds in the phenoxyalkanoic acids family shares some similarity. Some of its members (e.g. MCPA or another phenoxyacetic acid herbicide, 2,4-D) are frequently used as model molecules to study the interaction of herbicides with soils. However, previous experimental studies have shown that two very similar molecules, MCPA and CA, have a distinct adsorptive behavior on certain clay materials (Dordio et al. 2007), with MCPA being more extensively adsorbed by light expanded clay aggregates than CA is. The minor differences in the chemical structures of these two organic molecules may, in fact, play a crucial role in their adsorptive behavior. As in many other chemical problems, the elucidation of details at a molecular level by theoretical calculations (molecular simulations or electronic structure calculations) may provide a clarification that is not possible with the experimental data alone.

In this work, electronic structure calculations based on the density functional theory (DFT) are presented on the interaction of MCPA and CA molecules and respective anions with a model surface of the muscovite mineral. The structures and the changes on the electron density due to adsorption of the two molecules are compared in order to highlight the differences that can help explain the two distinct adsorption behaviors as observed experimentally.

2 Computational details

DFT calculations were performed using the VASP code (Kresse and Hafner 1993) within the PBE implementation of the Generalized Gradient Approach exchange–correlation functional (Perdew et al. 1996) on a suitable periodic slab model of the mica surfaces. The valence electron density has been expanded in a plane wave basis set with a cutoff of 450 eV and the interaction of the core electrons with the valence states represented through the projected augmented wave method of Blöchl (1994) as implemented in VASP (Kresse and Joubert 1999).

The surface was modeled as a 2M1-muscovite mica with structure of 2:1 layered dioctahedral hydroxyl-aluminosilicate with the formula unit of $KAl_2(Al,Si_3)O_{10}(OH)_2$. This model has been previously used in ab initio calculations (Odelius et al. 1997) and molecular dynamics simulations (Leng and Cummings 2006). In this structure, one mica layer contains one octahedral aluminium ions layer sandwiched by two tetrahedral silicon layers. In the silicon tetrahedral sheet, silicon is substituted by aluminium in a 1:3 ratio, leaving a net negative surface charge compensated by alkaline metal ions. In this structure two K^+ ions were added to each of the surfaces (top and bottom). For the study of the anions adsorption, an additional H was added to an oxygen on the surface.

During the calculations, the internal surface atoms were kept fixed at the bulk positions while the atoms in the top layer were allowed to relax, including the K^+ ions. Due to the large size of the adsorbed molecules a 2×1 supercell defined by $a = 10.384$ Å, $b = 9.015$ Å and $c = 30.000$ Å lattice parameters was used. The vacuum thickness assured by this box is sufficiently large to avoid any noticeable interaction between the repeated slabs and is large enough to obtain meaningful results by considering the Γ point of the reciprocal space only.

Adsorption energies were calculated by

$$E_{Ads} = E_{Surf-Adsor} - (E_{Surf} + E_{Adsor}) \qquad (1)$$

where $E_{Surf-Adsor}$ is the energy of the surface plus adsorbate optimized system, E_{Surf} is the energy of the optimized surface and E_{Adsor} the energy of the optimized molecule/ion in the gas phase. The energy of the isolated molecules and ions has been calculated using the same size unit cell and energy cuttoff as employed for the adsorbed systems.

3 Results and discussion

In order to validate the present computational approach, the molecular structure of MCPA and CA molecules and anions optimized in the gas phase was compared with available experimental data and literature results of calculations employing basis set DFT approach. Selected bond lengths are shown in Table 1 and the calculated results employing the present periodic PBE approach are in good agreement with the experimental results and with the results of Monicka and James (2011) that used a localized basis set and a different exchange–correlation potentials. The present calculated bond lengths differ by less than 1 % from those obtained experimentally for both the MCPA and CA compounds, except for the bond connecting the hydroxyl oxygen with the carbon, for which the deviation is a little more significant. This small disagreement is not surprising since the experimental structures were obtained from a solid state sample where the hydroxyl is involved in forming hydrogen bonds (Sieron et al. 2011).

Both the adsorbate molecules and the adsorbent surface are structurally quite complex. The rotational freedom of the adsorbates gives rise to a large number of local minima that makes the location of all of them unfeasible. We then had to choose to locate the adsorbates in what were considered to be the most relevant initial configurations. The adsorbate molecules were placed in two different orientations relative to the surface: an extended conformation, oriented perpendicularly to the surface, with the carboxylic acid/carboxylate group over the surface cations, as this functional group is widely considered to have the strongest interaction with clays surfaces and thus play a major role in the adsorption; and another conformation with the aromatic ring laying approximately parallel to the surface, as this conformation has been pointed out as potentially relevant due to the weak but potentially significant dispersive interactions of the surface with the electronic density in the aromatic ring.

Starting from these initial configurations, the system was then permitted to relax, including the upper layer of atoms of the surface and the top cations, until an equilibrium structure was obtained. Resulting structures of the adsorbed systems are depicted in Figs. 2 and 3.

Table 1 Selected bond lengths of CA and MCPA in neutral an ionized form

	O1–H	O1–C1	O2–C1	C1–C2	C–Cl
CA					
Current work	0.98	1.37	1.22	1.54	1.74
B3LYP/6-31G(d)[a]	0.98	1.36	1.21	1.54	1.76
X-ray[b]		1.28	1.23	1.52	1.75
MCPA					
Current work	0.98	1.35	1.22	1.53	1.74
X-ray[c]		1.31	1.22		1.75
CA^-					
Current work		1.27	1.26	1.59	1.75
$MCPA^-$					
Current work		1.26	1.26	1.56	1.76

Also included for comparison with the current calculations the bond lengths in the carboxylic acid group for the isolated molecules as obtained experimentally or in other theoretical calculations. All distances in Ångstrom (Å)

[a] Monicka and James (2011)

[b] Kennard et al. (1982)

[c] Sieron et al. (2011)

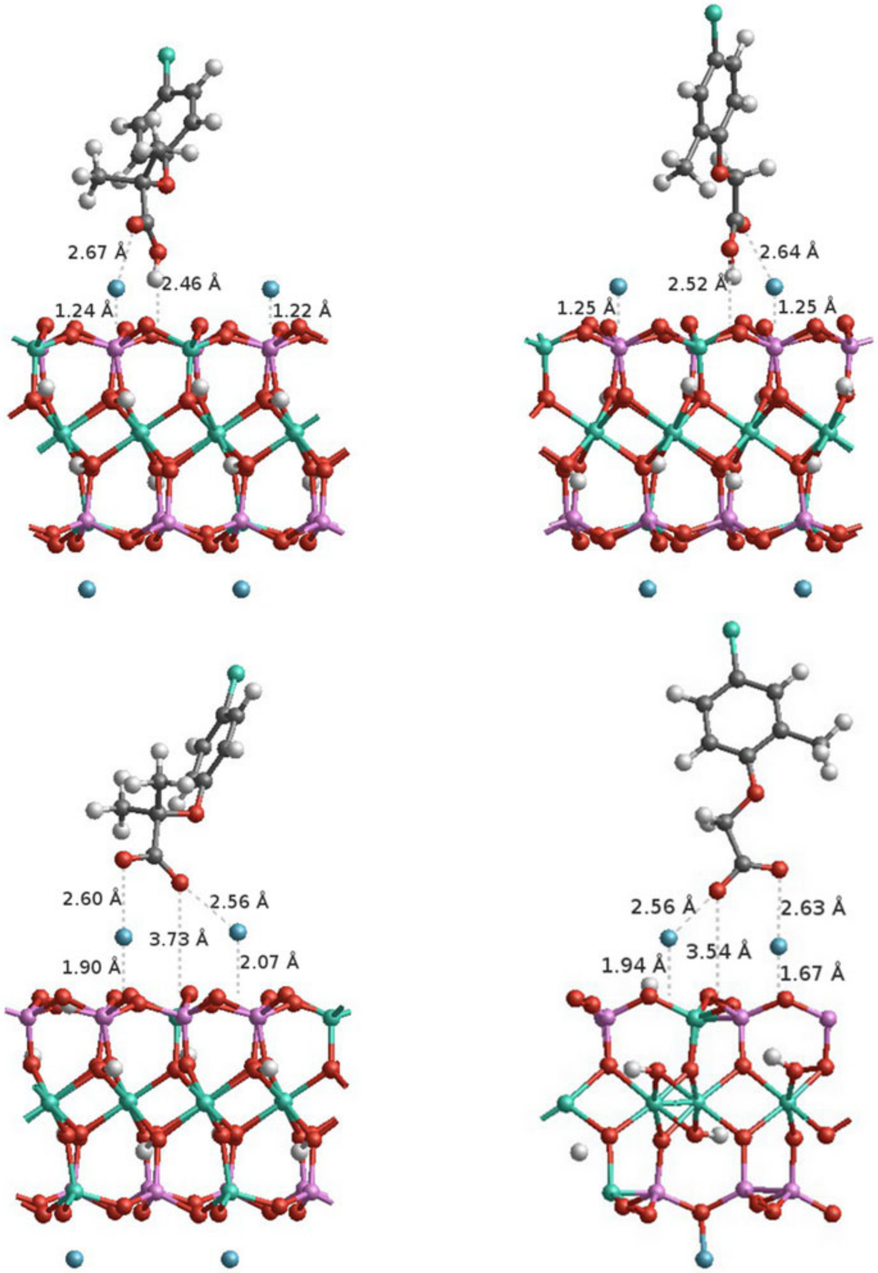

Fig. 2 Structure and selected atom distances of the adsorbed CA and MCPA (*top*) and respective anions (*bottom*) in the upright configuration

Table 2 presents the main features of the optimized geometries, namely the distances between the atoms which are involved in the linkage between the adsorbates and the surface. It can be observed that under the influence of the adsorbate molecules over the surfaces, the K^+ ions are displaced from the positions they occupy in the clean surfaces. In the case of the anions, they are dislocated some distance away from the surface, attracted by the negative charges of the adsorbate. The neutral forms of the compounds, on the contrary, cause the K^+ ions to come even closer to the surface than they are in the clean surfaces. K^+ is pulled further away from the surface by the anionic form of CA than by the anion $MCPA^-$. In the case of the neutral adsorbates, the extent to which K^+ is pushed closer to the surface does not differ much between the two molecules. The differences encountered for these effects between the upright conformations and those parallel to the surface are only slight.

It can also be observed that in $MCPA^-$ the carboxylate oxygen closer to the surface is closest than it is in the case of CA^-. Furthermore, for any of the anions, that oxygen is closer to the surface in the case of the parallel conformations than it is in the case of the upright ones. In the neutral compounds, the protonated oxygen of the carboxylic acid

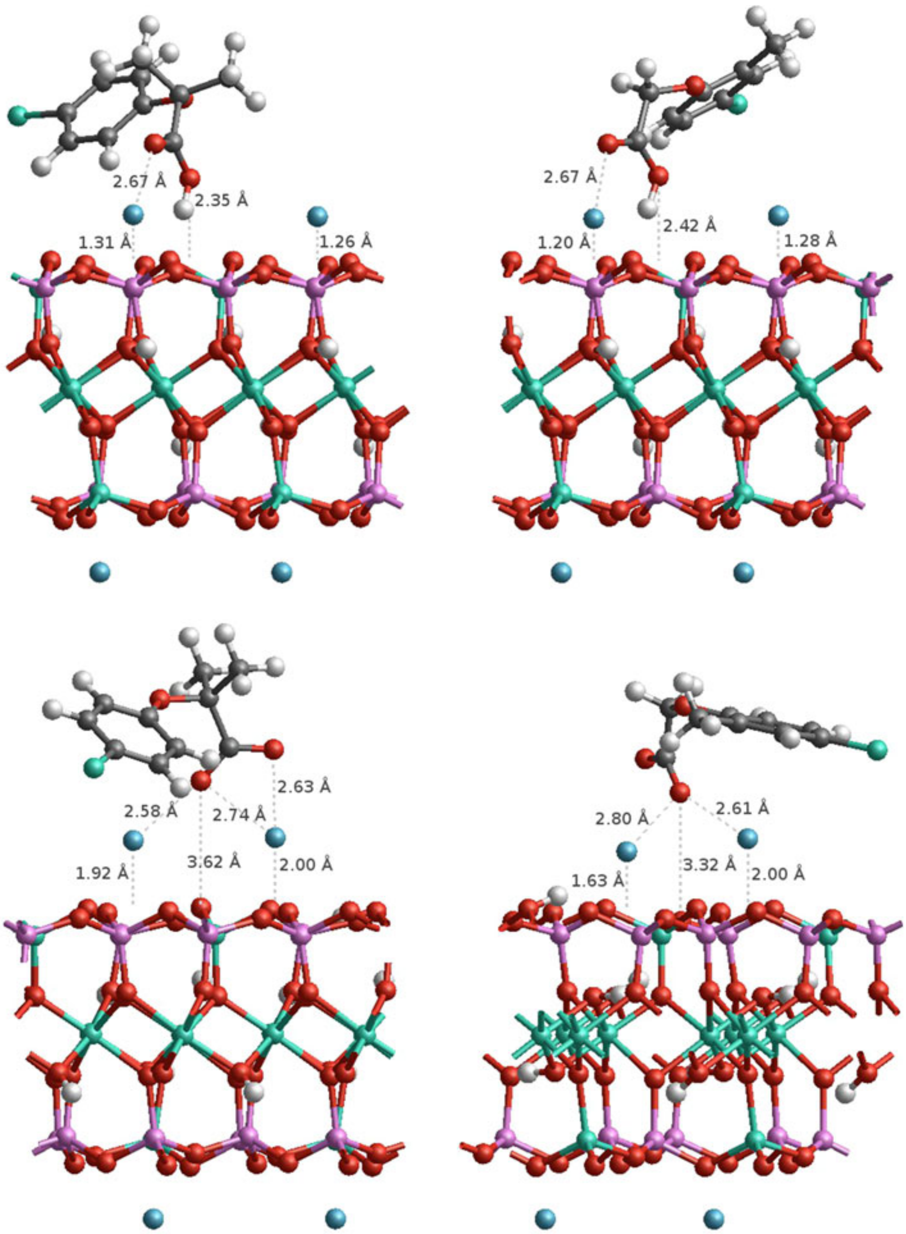

Fig. 3 Structure and selected atom distances of the adsorbed CA and MCPA (*top*) and respective anions (*bottom*) in the parallel configuration

group (which forms a hydrogen bond with a surface oxygen) is always nearer to the surface than in the anions case, but in these forms MCPA's oxygen is farther from the surface than CA's.

The K^+ cations may assist binding of the adsorbates to the surface by formation of bridges between oxygens from the two parts. For the anions, one of the anions' oxygens tends to occupy a location between the two K^+ cations but is closer to one of them and at a slightly longer distance from the other. In the case of the neutral compounds, the unprotonated (carbonyl) oxygen is closer to one of the two K^+ cations (but not as much as in the case of the anionic forms), forming a bridge which complements the hydrogen bond formed by the other oxygen. Distances between oxygens of the adsorbates and the K^+ cations tend to be somewhat longer in the parallel conformations and also slightly longer for MCPA in comparison with CA.

Comparing the O–H bond length between the adsorbed and isolated MCPA or CA one can observe that the O–H bond is longer in the case of the adsorbed molecules, reflecting the interaction with the surface and the hydrogen bond that is formed with a surface oxygen. Conversely, the bond between the hydroxyl oxygen and the carbon atom is shortened while the carbonyl double bond is slightly increased reflecting the electronic reorganization that occurs upon adsorption. Interestingly, this bond length now agrees very well with the X-ray data for crystalline MCPA where a formation of hydrogen bond occurs. For the anions

Table 2 Selected calculated atom distances of the adsorbed neutral and ionized CA and MCPA systems

	K_1–surf	K_2–surf	O1–H	O1–C1	O2–C1	O–surf	O–K_1	O–K_2
Clean surface	1.50	1.50						
Hydroxilated clean surface	1.42	1.47						
Upright								
CA	1.24	1.22	1.02	1.32	1.24	2.46	2.67	
MCPA	1.25	1.25	1.03	1.31	1.24	2.52	2.64	
CA^-	1.90	2.07		1.27	1.27	3.73	2.56	2.60
$MCPA^-$	1.94	1.67		1.28	1.26	3.54	2.56	2.63
Parallel								
CA	1.31	1.26	1.03	1.32	1.24	2.35	2.67	
MCPA	1.20	1.28	1.03	1.32	1.24	2.42	2.67	
CA^-	1.92	2.00		1.28	1.26	3.62	2.58	2.74
$MCPA^-$	1.63	2.00		1.27	1.27	3.32	2.61	2.80

The surface position was defined as the z coordinate of the outmost surface oxygen. All distances in Ångstrom (Å)

Table 3 Adsorption energies of MCPA and CA, both in neutral and ionized forms, as obtained by the PBE calculations

	MCPA	$MCPA^-$	CA	CA^-
Upright	−0.71	−1.11	−0.61	−0.65
Parallel	−0.81	−1.30	−0.88	−0.92

Energies are given in eV

Table 4 Bader charges on the free and adsorbed form of MCPA and CA, both in neutral and ionized forms

	MCPA	$MCPA^-$	CA	CA^-
Upright	−0.05	−0.90	−0.04	−0.88
Parallel	−0.04	−0.89	−0.04	−0.88

a very small increase of the O–C bond lengths can be observed by comparing the adsorbed and isolated molecules' geometries.

Table 3 summarizes the calculated adsorption energies. It is clear that the ionized adsorbates interact more strongly with the surface than do their neutral forms. Also, the comparison between the two compounds shows a stronger interaction with the surface for MCPA than for CA, particularly in the ionized form. This observation points to the same direction of previous experimental findings where MCPA exhibited a more extensive adsorption to clay materials than CA (Dordio et al. 2007). In accordance with other studies on other clay surfaces (Tunega et al. 2004), the adsorption energies are more negative for the conformations where the aromatic rings lye parallel with the surface enhancing the interaction with it.

Further characterization of the adsorbate–substrate interaction was made by analyzing the atomic charges obtained from the "atoms in molecules" (AIM) topological analysis of Bader (Tang and Sanville 2009).

The Bader charges of the free and adsorbed molecules and anions can be calculated by summing over the partial Bader charges of the corresponding atoms. Calculated in this way, these charges allow an estimation of the charge transfer that occurs between the molecules/ions and the surface upon adsorption.

From inspection of Table 4 the first point to note is that, while for the ions there is electronic density transferred to the surface, in the case of the neutral molecules electronic density transfer occurs towards the molecule moiety. The charge transfer is in all cases much bigger in the anions adsorption, where ∼0.1 electrons are transferred to the surface, than when the neutral molecules adsorb, in which case ∼0.04 electrons are transferred from the surface to the adsorbate. The charge transfer from the anions to the surface is slightly larger in the case of CA^- than in $MCPA^-$ in the both conformations (upright and parallel to the surface) and for both anions slightly bigger for the conformations parallel to the surface. This loss of charge by the anions is concomitant with the slight lengthening of the C–O bonds observed in the adsorbed anions. The small charge transferred in the adsorption of the neutral molecules, as well as the direction of the transfer, is typical of an hydrogen bond, where a surface oxygen donates some charge to the H–O fragment of the adsorbate (van der Vaart and Merz 2002).

A more complete picture of the interaction between the neutral molecule or the anion with the surface can be obtained from analysis of the electron density difference defined as

$$\Delta\rho(\mathbf{r}) = \rho_{Surf-Adsor}(\mathbf{r}) - \rho_{Surf}(\mathbf{r}) - \rho_{Adsor}(\mathbf{r}) \qquad (2)$$

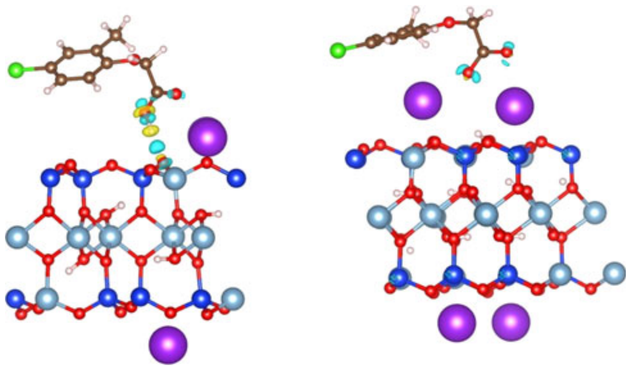

Fig. 4 Electron density difference between the adsorbed MCPA (*left*) and MCPA anion (*right*) and the separated systems. The *yellow* and *light blue* regions correspond to electron accumulation and depletion, respectively. The isosurface values are +0.0015 and −0.0015 e/Å^3 (Color figure online)

where $\rho_{Surf-Adsor}(\mathbf{r})$ is the electronic density of the adsorbate covered surface and $\rho_{Surf}(\mathbf{r})$ and $\rho_{Adsor}(\mathbf{r})$ are the densities of the surface and the adsorbate respectively. This difference illustrates the reorganization of the electronic density that results from adsorption. Electron density difference plots are depicted in Fig. 4 for the MCPA and MCPA$^-$ adsorption case. For the adsorption of the anionic species, a depletion of electronic density is observed in the electron rich oxygens and shows the origin of the charge that is transferred to the surface. For the neutral molecule a much more complex electronic reorganization is depicted localized in all the carboxyl moiety. Like for the anionic case there is a small reduction of density in the carbonyl oxygen. A reduction of charge is also observed in the region between the hydrogen and oxygen which is consistent with the bond length increase observed. It is clear from the picture that the small charge transfer comes from the surface oxygen that forms the hydrogen bond with the molecule hydroxyl.

4 Conclusions

The adsorption of MCPA and CA both in neutral and ionized form on a model surface of the muscovite mineral has been studied by means of periodic DFT methods. Comparison of the obtained gas phase structures have been made with experimental data showing a good agreement which validates the present approach. Differences in the structure and energetics of the adsorbed species have been found with the ionized adsorbates interacting more strongly with the surface than their neutral forms do. The comparison between the two compounds shows a stronger interaction with the surface for MCPA than for CA, particularly in the ionized form which points to the same direction of previous experimental findings. Details of the interaction with the surface were analyzed by means of Bader charges analysis. It was found that charge transfer is more important in the anions adsorption case, where the electronic density is transferred from the anion to the surface, than when the neutral molecules adsorb, in which case a smaller density transfer occurs in the opposite direction (towards the molecule).

References

Aga, D.S.: Fate of Pharmaceuticals in the Environment and in Water Treatment Systems. CRC Press, Boca Raton (2008)

Akcay, G., Yurdakoc, K.: Removal of various phenoxyalkanoic acid herbicides from water by organo-clays. Acta Hydrochim. Hydrobiol. **28**, 300–304 (2000)

Barceló, D., Petrovic, M.: Emerging Contaminants from Industrial and Municipal Waste: Ocurrence, Analysis and Effects. Springer-Verlag, Berlin (2008)

Bell, K.Y., Wells, M.J.M., Traexler, K.A., Pellegrin, M.L., Morse, A., Bandy, J.: Emerging pollutants. Water Environ. Res. **83**, 1906–1984 (2011)

Blöchl, P.E.: Projector augmented-wave method. Phys. Rev. B **50**, 17953–17979 (1994)

Buchanan, I., Liang, H.C., Liu, Z.K., Razaviarani, V.: Pesticides and herbicides. Water Environ. Res. **83**, 1549–1597 (2011)

Dordio, A.V., Candeias, A.J.E., Pinto, A.P., da Costa, C.T., Carvalho, A.J.P.: Preliminary media screening for application in the removal of clofibric acid, carbamazepine and ibuprofen by SSF-constructed wetlands. Ecol. Eng. **35**, 290–302 (2009)

Dordio, A.V., Teimao, J., Ramalho, I., Palace Carvalho, A.J., Estêvão Candeias, A.J.: Selection of a support matrix for the removal of some phenoxyacetic compounds in constructed wetlands systems. Sci. Total Environ. **380**, 237–246 (2007)

Esplugas, S., Bila, D.M., Krause, L.G., Dezotti, M.: Ozonation and advanced oxidation technologies to remove endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PPCPs) in water effluents. J. Hazard. Mater. **149**, 631–642 (2007)

Farré, M.L., Pérez, S., Kantiani, L., Barceló, D.: Fate and toxicity of emerging pollutants, their metabolites and transformation products in the aquatic environment. TrAC Trends Anal. Chem. **27**, 991–1007 (2008)

Fent, K., Weston, A.A., Caminada, D.: Ecotoxicology of human pharmaceuticals. Aquat. Toxicol. **76**, 122–159 (2006)

Ferrari, B., Paxéus, N., Lo Giudice, R., Pollio, A., Garric, J.: Ecotoxicological impact of pharmaceuticals found in treated wastewaters: study of carbamazepine, clofibric acid, and diclofenac. Ecotoxicol. Environ. Saf. **55**, 359–370 (2003)

Gavrilescu, M.: Fate of pesticides in the environment and its bioremediation. Eng. Life Sci. **5**, 497–526 (2005)

Hu, J., Yang, T., Yin, S., Cao, D.: Dissipation and residue of MCPA (4-chloro-2-ethylphenoxyacetate) in wheat and soil. Environ. Monit. Assess. **184**, 5017–5024 (2012)

Iglesias, A., López, R., Gondar, D., Antelo, J., Fiol, S., Arce, F.: Adsorption of MCPA on goethite and humic acid-coated goethite. Chemosphere **78**, 1403–1408 (2010)

Kasprzyk-Hordern, B., Dinsdale, R.M., Guwy, A.J.: The removal of pharmaceuticals, personal care products, endocrine disruptors and illicit drugs during wastewater treatment and its impact on the quality of receiving waters. Water Res. **43**, 363–380 (2009)

Kennard, C.H.L., Smith, G., White, A.H.: Structural aspects of phenoxyalkanoic acids - the structures of phenoxyacetic acid,

(±)-2-phenoxypropionic acid, (±)-2-(4-chlorophenoxy)propionic acid, 2-methyl-2-phenoxypropionic acid and 2-(4-chlorophenoxy)-2-methylpropionic acid. Acta Crystallogr. Sect. B Struct. Sci. **38**, 868–875 (1982)

Kit Chan, W., Jouët, J., Heng, S., Lun Yeung, K., Schrotter, J.C.: Membrane contactor/separator for an advanced ozone membrane reactor for treatment of recalcitrant organic pollutants in water. J. Solid State Chem. **189**, 96–100 (2012)

Kresse, G., Hafner, J.: Abinitio molecular–dynamics for liquid–metals. Phys. Rev. B **47**, 558–561 (1993)

Kresse, G., Joubert, D.: From ultrasoft pseudopotentials to the projector augmented-wave method. Phys. Rev. B **59**, 1758–1775 (1999)

Kümmerer, K.: Emerging contaminants. In: Wilderer, P. (ed.) Treatise on Water Science, pp. 69–87. Elsevier, Oxford (2011)

Kümmerer, K.: The presence of pharmaceuticals in the environment due to human use—present knowledge and future challenges. J. Environ. Manag. **90**, 2354–2366 (2009)

Kuster, M., López de Alda, M.J., Hernando, M.D., Petrovic, M., Martín-Alonso, J., Barceló, D.: Analysis and occurrence of pharmaceuticals, estrogens, progestogens and polar pesticides in sewage treatment plant effluents, river water and drinking water in the Llobregat river basin (Barcelona, Spain). J. Hydrol. **358**, 112–123 (2008)

Lapworth, D.J., Baran, N., Stuart, M.E., Ward, R.S.: Emerging organic contaminants in groundwater: a review of sources, fate and occurrence. Environ. Pollut. **163**, 287–303 (2012)

Leng, Y.S., Cummings, P.T.: Hydration structure of water confined between mica surfaces. J. Chem. Phys. **124**, 74711 (2006)

Matamoros, V., Arias, C.A., Nguyen, L.X., Salvadó, V., Brix, H.: Occurrence and behavior of emerging contaminants in surface water and a restored wetland. Chemosphere **88**, 1083–1089 (2012)

Miège, C., Choubert, J.M., Ribeiro, L., Eusèbe, M., Coquery, M.: Fate of pharmaceuticals and personal care products in wastewater treatment plants—conception of a database and first results. Environ. Pollut. **157**, 1721–1726 (2009)

Monicka, J.C., James, C.: Vibrational spectra and natural bond orbital analysis of the herbicidal molecule 2(4-chlorophenoxy)-2-methyl propionic acid. Spectrochim. Acta A Mol. Biomol. Spectrosc. **78**, 718–725 (2011)

Odelius, M., Bernasconi, M., Parrinello, M.: Two dimensional ice adsorbed on mica surface. Phys. Rev. Lett. **78**, 2855–2858 (1997)

Park, Y., Ayoko, G.A., Frost, R.L.: Application of organoclays for the adsorption of recalcitrant organic molecules from aqueous media. J. Colloid Interface Sci. **354**, 292–305 (2011)

Perdew, J.P., Burke, K., Ernzerhof, M.: Generalized gradient approximation made simple. Phys. Rev. Lett. **77**, 3865–3868 (1996)

Radjenovic, J., Petrovic, M., Barceló, D.: Advanced mass spectrometric methods applied to the study of fate and removal of pharmaceuticals in wastewater treatment. TrAC Trends Anal. Chem. **26**, 1132–1144 (2007)

Rosal, R., Rodriguez, A., Perdigon-Melon, J.A., Petre, A., Garcia-Calvo, E., Gomez, M.J., Aguera, A., Fernandez-Alba, A.R.: Occurrence of emerging pollutants in urban wastewater and their removal through biological treatment followed by ozonation. Water Res. **44**, 578–588 (2010)

Sieron, L., Kobylecka, J., Turek, A.: Crystal packing and supramolecular motifs in four phenoxyalkanoic acid herbicides: low-temperature redeterminations. Org. Chem. Int. **2011**, (2011). doi: 10.1155/2011/608165

Silva, E., Batista, S., Viana, P., Antunes, P., Serodio, L., Cardoso, A.T., Cerejeira, M.J.: Pesticides and nitrates in groundwater from oriziculture areas of the 'Baixo Sado' region (Portugal). Int. J. Environ. Anal. Chem. **86**, 955–972 (2006)

Srivastava, B., Jhelum, V., Basu, D.D., Patanjali, P.K.: Adsorbents for pesticide uptake from contaminated water: a review. J. Sci. Ind. Res. **68**, 839–850 (2009)

Tang, W., Sanville, E., Henkelman, G.: A grid-based Bader analysis algorithm without lattice bias. J. Phys.-Condes. Matter **21**, 084204 (2009)

Tixier, C., Singer, H.P., Oellers, S., Muller, S.R.: Occurrence and fate of carbamazepine, clofibric acid, diclofenac, ibuprofen, ketoprofen, and naproxen in surface waters. Environ. Sci. Technol. **37**, 1061–1068 (2003)

Tunega, D., Haberkauer, G., Gerzabek, M.H., Lischka, H.: Sorption of phenoxyacetic acid herbicides on the kaolinite mineral surface—an ab initio molecular dynamics simulation. Soil Sci. **169**, 44–54 (2004)

van der Vaart, A., Merz, K.M.: Charge transfer in small hydrogen bonded clusters. J. Chem. Phys. **116**, 7380–7388 (2002)

Verlicchi, P., Al Aukidy, M., Galletti, A., Petrovic, M., Barceló, D.: Hospital effluent: investigation of the concentrations and distribution of pharmaceuticals and environmental risk assessment. Sci. Total Environ. **430**, 109–118 (2012)