Atomic-Scale Understanding Of The Na And Cl Remotion From Seawater Promoted By $\text{Mo}_{1.33}\text{C}(\text{OH})_2$ -Mxene

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Abstract

Drinking water scarcity in arid and semi-arid regions is a reality that may turn into a global healthcare problem in the next few years. The scientific community is always looking for new materials to achieve effective sea and brackish water desalination to reduce water scarcity. Commonly, theoretical and experimental methods make a synergy to better understand and explain the chemical and physical processes in water desalination electrodes. In this way, experimental evidence pointed to $\text{Mo}_{1.33}\text{CT}_z$ MXene as an efficient ion intercalation material, in which both Na cations and Cl anions are removed. However, the atomic-scale understanding of the physico-chemical processes due to the cation and anion interaction with the MXene is still unknown. We report the Na cation and Cl anion interaction with an OH functionalized $\text{Mo}_{1.33}\text{C}$ monolayer through a comprehensive first-principles density functional theory assessment. Results demonstrate that Na atoms attach to Oxygen, whereas Cl atoms bond through hydrogen bonds to the functional groups in the MXene, these bonds have two energy contributions: electrostatic and charge transfer, which increases its adsorption energy. Electrostatic potential isosurface calculations evidenced reactive sites. Oxygen atoms have an affinity for the electropositive Na atoms, whereas hydrogen atoms -of the hydroxyl groups- interact with the electronegative Cl atoms. Bader charge analysis and non-covalent interaction isosurfaces help clarifying the way cations and anions attach to the MXene layer. Our findings explain why OH-functionalized $\text{Mo}_{1.33}\text{C}$ can efficiently remove both anions and cations based on their affinities with the functional groups present in the MXene.

Introduction

Freshwater scarcity is a critical global problem. Global warming and the increased demand for agricultural, domestic, and industrial use are drivers of the lower availability of this resource. Additionally, limitations in the development of circular systems for better use, and pollution ⁽¹⁾ generate freshwater scarcity area also problems, as well. Between the alternatives to obtain clean water, the desalination process is widely considered. Despite the growing number of desalination plants, currently 17000 ⁽²⁾, there are important challenges due to their high costs of operation ⁽³⁾, mainly in energy consumption. The desalination technologies include membrane distillation, electrodialysis, reverse osmosis, ion exchange, thermal based processes, and nanofiltration ^(4, 5).

Nanofiltration is applied to improve the performance in the desalination technologies, allowing operation at low pressures, energy efficiency, and increase in the permeability and selectivity ⁽⁶⁾. Application to improve salt rejection, ion exchange and hydrophobic characteristics have been proved using carbon nanotubes ^(7, 8), TiO_2 nanofilms ⁽⁹⁾, and graphene oxide nanotubes ⁽¹⁰⁾. Recently the use of the two-dimensional MXenes family has been recognized, due to the high capacity to rejection, permeability, and selectivity with potential applications on seawater desalination ^(11, 12).

2D MXenes were discovered in 2011 by Michael Naguib et al. They reported a new 2D material $-\text{Ti}_3\text{C}_2\text{T}_x-$ with a potential wide range of applications ⁽¹³⁾. This paper established the birth of a new family of

versatile 2D materials, MXenes, with applications that span from energy, optical, electronic, environmental, sensors, catalysis, and several other ⁽¹⁴⁾. Conventional MXenes could be achieved upon exfoliating them from their 3D counterpart, the MAX phases. Until today, just some MXenes have been fabricated in the lab. However, it is expected to have a large quantity of these materials since there exist > 70 MAX phases ⁽¹⁵⁾. Conventional MXenes can have seven, five, and three layers, which can be carbides or nitrides. A transition metal layer is always sandwiched by either two nitrogen or carbon monolayers. The versatility of these materials also relies on their facility to be engineered into multiple transition metals MXenes, in which, more than one transition metal can be accommodated in the same monolayer, called o-MXenes ⁽¹⁴⁾. As an example, a $Ti_xTa_{4-x}C_3$ monolayer have been already evaluated as an anode for lithium storage, showing a larger efficiency than its conventional Ti_4C_3 counterpart ⁽¹⁶⁾. Such efficiency is related to the enhanced Li-ion transport generated by the mixed TiTa layer ⁽¹⁷⁾. Although the MXene family is already large enough, other members of the MXene family needs to be mentioned, these are the i-MXenes, that can be also synthesized from their i-MAX phases. There exist 32 i-MAX phases ⁽¹⁸⁾ which will generate a variety of monolayers with random and ordered vacancies. The first i-MAX phase $((Mo_{2/3}Sc_{1/3})_2AlC)$ was synthesized in 2017 ⁽¹⁹⁾ and it was the precursor of the $Mo_{1.33}C$ monolayer which is obtained through selective etching. Such monolayer possesses ordered Sc vacancies. Another example is the $Nb_{1.33}C$ i-MXene in which the vacancies are randomly distributed, and it is obtained from the precursor i-MAX phase $(Nb_{2/3}Sc_{1/3})_2AlC$ ⁽²⁰⁾. The randomly distributed vacancies in this monolayer are generated because in the MAX phase, the Sc and Nb atoms are forming a solid solution. In this way, it can be seen that the precursor i-MAX phase is key for the atomic arrangement of the resultant i-MXene phase ^(19, 20). The i-MXenes may be also as versatile as the conventional or the o-MXenes. They could be also engineered to form randomly or ordered o-like MXenes, if advantage is taken of the intrinsic vacancies in the monolayers. i-MXenes can be used in electronic and optical devices ⁽¹⁴⁾ as well as in energy, catalysis, and environmental applications ^(18, 21).

Due to its high versatility, high surface area, and easy way of modification by adding different functional groups, MXenes point to be key in environmental remediation applications ^(22, 23). From these, desalination of seawater and brackish water is key. However, MXene membrane science is still in an early stage and research is needed to understand and explain the desalination processes, the device performance, and industrial scaling ⁽²⁴⁾. In this way, several research papers have appeared in which MXenes enhance the cation trapping to get efficient desalination membranes. $Ti_3C_2T_x$ have demonstrated high selectivity to metal cations with different charges as well as effectivity larger than the one shown by graphene oxide and some other carbon-based nano materials ⁽²⁵⁾. $Ti_3C_2T_x$ membranes were also engineered with Al^{3+} ions to prevent swelling while retaining a high salt rejection and fast water fluxes, promising scalability ⁽²⁶⁾. $Ti_3C_2T_x$ has also been used as an intercalation material in membranes to enhance the desalination via capacitive deionization ^(27, 28). Also, fabricating surface charged MXene membranes generates a performance during nanofiltration and/or forward osmosis processes ⁽²⁹⁾. Research in desalination processes has been focused to $Ti_3C_2T_x$ MXene. From an atomic perspective, ion

sieving has been analyzed where ions of different charges feel different energy barriers for its diffusion through the membrane, where the MXene interlayer distance contracts or expands upon interaction with such ions ⁽³⁰⁾.

In a recent work, desalination via intercalation was analyzed for the $\text{Mo}_{1.33}\text{CT}_z$ i-MXene/Carbon nanotube electrodes, where cation and anion are efficiently removed in the treatment of seawater and brackish water. Such process was achieved without the need of an exchange membrane, so it is hypothesized that the MXene layer is the one carrying the nanofiltration process by trapping Cl and Na at the same time. The carbon nanotubes in the electrode serve to avoid MXene re-stacking ⁽³¹⁾. Although $\text{Mo}_{1.33}\text{C}$ MXene demonstrates a high efficiency for the trapping of Cl and Na in the experimental setup, no atomic scale understanding of such process exists in the literature.

Considering the previous discussion and the proved importance of the $\text{Mo}_{1.33}\text{C}$ MXene in the Brackish and Seawater water desalination process via cation and anion intercalation ⁽³¹⁾, in this work we have performed a comprehensive atomic scale density functional theory study to understand the Cl and Na interaction process with the $\text{Mo}_{1.33}\text{CT}_z$ monolayer, $T_z=\text{OH}$ groups. We explain the viability of intercalation in terms of the atomic Cl and Na electronegativities. Cl atoms prefer to interact with the hydrogen atoms of the hydroxyl groups whereas the Na atoms form bonds with the oxygen atoms of the functional groups. Our study suggests that functionalizing MXenes with hydroxyl groups will make them viable for Brackish and Seawater water desalination in which both Cl and Na ions are removed.

Method

The atomic scale understanding of the brackish and sea desalination water process was treated through density functional theory calculations, as implemented in the Vienna Ab-initio Package ^(32–35) code. The one-electron wavefunctions were treated with the projector augmented wave method as derived by Kresse and Joubert ⁽³⁶⁾. The electronic states were expanded in a plane wave basis set with an optimized cutoff energy of 400 eV. Non-classical electron-electron interactions (exchange-correlation) were approximated with the generalized gradient approximation using the Perdew-Burke-Ernzerhof functional form ⁽³⁷⁾. i-MXenes are experimentally obtained with several functional groups, when hydroxyl groups are involved, long-range interactions may appear. Therefore, we considered the description of dispersion-corrected van der Waals interactions through the Grimme-D3 functional correction ⁽³⁸⁾. Na and Cl were adsorbed on different i-MXene high symmetry sites. To reach convergence in a system, the following criteria was used: the energy must be lower than 1×10^{-4} eV for two consecutive electronic steps, and the norm of all atomic forces must be smaller than 0.01 eV/Å. To evaluate the electronic states at the reciprocal lattice, the Brillouin zone was sampled using an equally distributed ⁽³⁹⁾ k-points mesh with a volume of $12 \times 12 \times 1$. To obtain the electrostatic potential isosurface and the Bader charges, the most stable adsorption models were converged with a denser k-points mesh of $24 \times 24 \times 1$. The Bader charge analysis code ⁽⁴⁰⁾ was used to obtain the valence charge transfer in the stable models.

Results And Discussion

In this section, we describe the $\text{Mo}_{1.33}\text{CT}_z$ monolayer and explain -at the atomic scale- the desalination process of both Cl and Na from saline and brackish water. The $\text{Mo}_{1.33}\text{C}$ structure is typically functionalized with OH, O, and F atoms. It has been found that the $\text{Mo}_{1.33}\text{CT}_2$, with $T = \text{O}$, is unstable⁽⁴¹⁾. However, $T = \text{OH}$ and $T = \text{F}$ generate stable structures which are consistent with the experimental findings. It was also shown that when there is combination of F and O as functional groups (10:2F, 20:1F), the system also is also stable⁽⁴¹⁾. The species observed experimentally by XPS⁽⁴¹⁾ are 50% F, 25% O and 25% OH suggesting that the O/F ratio is 50/50, but with half of the O atoms in OH form. In this work, we used the stable OH functionalized structure in which the ordered vacancies are occupied by OH functional groups (See Fig. 1a). A similar structure has been reported in previous studies by^(21, 41).

Once the atomic structure for the $\text{Mo}_{1.33}\text{C}(\text{OH})_2$ was defined (structural parameters reported in the supplementary section), we proceeded to calculate its electrostatic potential isosurfaces (electron accumulation is depicted in red, whereas electron depletion is depicted in blue). As expected, since the O atoms are the most electronegative, they have electron accumulation, whereas the H and Mo atoms have electron depletion (see Fig. 1b). Considering their electronegativities, O atoms would be available to bond with electropositive atoms like Na and electropositive atoms in the structure, like H, would bond to electronegative atoms like Cl. In the work by Srimuk et al.⁽³¹⁾, it was demonstrated experimentally that $\text{Mo}_{1.33}\text{CT}_z$ was able to eliminate Na and Cl atoms from brackish and seawater with high salt concentration. However, in their work the role of the functional groups was not clarified. It was hypothesized that O or F atoms may be the ones involved in the trapping. However, considering their electronegativities -very similar to Cl-, they would bond to Na but not to Cl atoms⁽⁴²⁾. Also, Srimuk et al.⁽³¹⁾, did not mention the OH groups, which are 25% of the coverage in the $\text{Mo}_{1.33}\text{CT}_z$ MXene. OH groups are more promising for Cl and Na trapping since they possess both electronegative O and H atoms. Using the information coming from the electrostatic potential isosurface, we tried several adsorption sites for both Cl and Na atoms. Adsorption sites were considered on top of the surface layer and bonded to Mo atoms. To avoid getting trapped in a local minimum, for each site, we started at different perpendicular distances, see Figure S1. For example, site S_1 is the same as S_{1a} but the last one is closer to the Mo layer.

Upon structural optimization of all models, we obtained the adsorption energy for all stable sites, see Table 1. As a general trend, after atomic relaxation of the adatoms at different positions, we observed that all S_{xa} models transform into the S_x ones. Upon adsorbing Cl atoms on all defined sites (see Figure S1), S_1 , S_5 , and S_8 sites end up as S_7 structures in which the Cl atom is forming three hydrogen bonds with the surface H atoms. In contrast, S_6 stabilizes on a bridge-like site formed by two OH groups. S_4 stabilizes as a distorted S_1 site and is not further considered. Finally, the S_3 site turns into the S_2 site, which is the most stable structure. Three main adsorption sites were identified as S_7 , S_6 , and S_2 , the last being more stable than S_7 and S_6 by 0.09 eV and 0.26 eV, respectively. S_7 and S_2 are similar. In both sites, Cl forms three hydrogen bonds with the OH groups, the only difference is that S_2 is located at the Mo

vacancy site. The S_6 site is structurally different because the Cl atom is located at a bridge-like position interacting with a couple of Hydrogen atoms. Since S_6 and S_7 are less stable than the S_2 site, they are not further considered for the analysis. However, the main interaction in all observed models for Cl is through hydrogen bonds. The most stable S_2 site is depicted in Fig. 2a. S_7 and S_6 adsorption sites are shown in Figure S2.

Table 1
Adsorption energies (in eV) of the stable adsorption models for Cl and Na atoms on the $\text{Mo}_{1.33}\text{C}(\text{OH})_2$ MXene.

Adsorption Site (Cl)	Adsorption energy	Adsorption Site (Na)	Adsorption energy
S_2	-2.04	S_2	-0.99
S_6	-1.78	S_3	-1.36
S_7	-1.95	S_4	-1.22
		S_5	-0.82
		S_6	-1.21

Figure 2. (a) The most stable adsorption sites **(a)** and **(b)** for Cl and Na on the $\text{Mo}_{1.33}\text{CT}_z$ i-MXene, where T_z are OH functional groups. **(c)** and **(d)** electrostatic potential isosurfaces showing the electron accumulation (red) and depletion (blue) for both Cl and Na atoms interacting with the MXene. Unit cell in (a) and (b) is highlighted as a dashed blue rectangle.

Figure 2c shows the electrostatic potential isosurface for Cl in the S_2 site, which makes evident the depletion of charge on the hydrogen atoms and the accumulation of charge on the adsorbed Cl atoms and the O functional groups. Notice that there is a local charge redistribution due to the Cl atoms.

With respect to Na adsorption (see Table 1), the same sites were considered (see Figure S1). As expected, different results emerge due to the chemistry of the Na atoms. Since Na atoms are electropositive, the interaction with the monolayer is through the oxygen atoms. The most stable site is S_3 . In this case, the Na atom forms three bonds with the oxygen atoms, whereas the neighbor Hydrogen atoms reorient to preclude interaction with Na, an expected behavior since H and Na are both electropositive (see Fig. 2b). Site S_2 is less stable than site S_3 by 0.37 eV and experiences a slight shifting towards S_5 (see Figure S3). S_4 site stabilizes in a threefold coordination with O atoms, however it is 0.14 eV less stable than the S_3 site. The main difference is that S_4 sits on top of a molybdenum atom (See Figure S3) and the S_3 site is on top of a hollow site. Upon adsorbing the Na atom on S_5 site (Figure S3), we noticed that it forms a double bonded configuration with the O atoms of the OH functional groups. This adsorption site is the less stable, with an energy 0.54 eV higher than S_3 . S_1 and S_7 are not stable, after structural relaxation evolve to S_5 . This happens since these sites try to preclude the direct H-Na interaction generated with their

neighboring OH group. Finally, the S_6 site (Figure S3) stabilizes with the same relative energy than S_4 (they are degenerated in energy). The main difference between S_6 and S_4 is that S_6 sits nearby the Mo vacancy site -occupied by an OH group- whereas S_4 is far from the vacancy site, see Figure S3 for structural details.

The electrostatic potential isosurface of the most stable S_3 site can be seen in Fig. 2d. Notice that in the vicinity of the Na atom, O atoms accumulate less charge due to the interaction with Na. On the other hand, the Na atom shows a strong charge depletion. The electrostatic potential isosurface of the atoms far from the adsorbates is similar to the one depicted in the surface without adsorbates, evidencing a local effect of the adsorbed atoms.

To gain a deeper understanding into the charge transfer between the surface and the adsorbates, we determine the Bader charges through the atoms-in-molecules topological analysis⁽⁴⁰⁾. Figure 3a shows the charge transfer between the Cl atom and the monolayer. A charge density transfer of 0.62e from the monolayer to the Cl atom is seen, despite their weak interaction. It is well known that hydrogen bonds are result of several energy contributions. These are: electrostatic interaction, charge transfer interactions, π -resonance assistance, cooperative effects, Pauli repulsion, dispersion interactions, and secondary electrostatic interactions⁽⁴³⁾. In this case, one part of the hydrogen bond is the charge transfer. However, it seems that there are other contributions of electrostatic character. To prove this, we plotted the non-covalent interaction index which is based on the density and its derivatives (the so-called reduced density gradient). In principle, from density -key in DFT- one can obtain all properties of the physical systems. Then, the reduced density gradient allows to identify non-covalent interactions at low-density (low gradient) regions. They appear as spikes, each related to a different non-covalent interaction⁽⁴⁴⁾. These interactions have different character, they may be attractive (hydrogen bonding) or repulsive (steric hindrance). To distinguish between them, the second eigenvalue of the electron-density matrix Hessian is used⁽⁴⁴⁾. This eigenvalue takes negative values for bonding interactions, like hydrogen bond. In contrast, it takes positive values when interactions are antibonding⁽⁴⁴⁾. Then, the second eigenvalue of the Hessian matrix multiplied by the density (which gives us details of the interaction strength) is a way visualize and understand weak interactions. In Fig. 4, we plotted the non-covalent interaction index isosurfaces considering $s = 0.5$ in a range of $sign(\lambda_2)\rho$ from - 0.05 to 0.05. A red-green-blue color code is used to depict the interaction zones. Red depicts repulsive interactions, green stands for weak van der Waals interactions that could be either repulsive or attractive depending on the sign they appear on, and blue shows the strong bonding interactions. Here we can see that the Cl atom has a strong attractive interaction through hydrogen bonds (blue ellipsoidal isosurfaces in Fig. 4) with three hydrogen atoms from the substrate. This characteristic dispersion interaction together with the charge transfer (0.62e from the monolayer to the Cl atom) and the electrostatic character of the interaction, help explain the large adsorption energy obtained for Cl adsorption (see Table 1). Green isosurfaces evidence O-O weak interactions between the functional groups.

On the other hand, for the Na case, the charge density transfer is now from the adsorbate to the monolayer. The Na atom transfers 0.87e to the monolayer (see Fig. 3b). Although Na atom experiences a chemical interaction with the monolayer, the adsorption energy is lower than the one obtained for Cl adsorption as previously explained in the above paragraphs.

The piece of evidence here presented helps to understand the interaction mechanism that explains the way both Cl and Na are efficiently captured by the i-MXene monolayer. Also, we provide an atomic scale understanding of the Cl and Na elimination from brackish and seawater with high saline content, as previously reported in the literature ⁽³¹⁾.

Conclusions

Experimental evidence has demonstrated that $\text{Mo}_{1.33}\text{CT}_z$ MXene is an efficient electrode to capture Cl and Na atoms from sea and brackish water [Srimuk et al. *ACS Sustainable Chem. Eng.* 2018, 6, 3, 3739–3747]. Understanding, at an atomic scale, the chemical and physical processes that happen in these electrodes is key to tune and improve the water desalination processes. In this paper, we report on the Na cation and Cl anion trapping on the $\text{Mo}_{1.33}\text{C}(\text{OH})_2$ monolayer by first-principles density functional theory calculations. Results show that Na atoms bond to Oxygen atoms, whereas Cl atoms bond through hydrogen bonds to the functional groups in the i-MXene, these bonds have two energy contributions: electrostatic and charge transfer. This fact explains its large adsorption energy observed upon adsorbing it on the i-MXene layer. Electrostatic potential isosurfaces show that Oxygen atoms have an affinity for the electropositive Na atoms, whereas hydrogen atoms -of the hydroxyl groups- interact with the electronegative Cl atoms. Bader charge analysis and non-covalent interaction isosurfaces clarify how cations and anions attach to the MXene layer. Na atoms donate charge to the i-MXene, whereas for Cl atoms, the charge density goes from the substrate to the adsorbate. Our findings explain at the atomic scale how anions and cations are removed from sea and brackish water based on their affinities with the functional groups present in the $\text{Mo}_{1.33}\text{C}(\text{OH})_2$ i-MXene.

Declarations

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Data availability

Authors declare that the main data supporting the findings of this study are contained within the paper. The row data is available from the corresponding author upon reasonable request.

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Figures

Figure 1

(a) Model system of the $\text{Mo}_{1.33}\text{CT}_z$ i-MXene, where T_z are OH functional groups. **(b)** electrostatic potential isosurface showing the electron accumulation (red) and depletion (blue). The unit cell is highlighted as a dashed blue square.

Figure 2

(a) The most stable adsorption sites **(a)** and **(b)** for Cl and Na on the $\text{Mo}_{1.33}\text{CT}_z$ i-MXene, where T_z are OH functional groups. **(c)** and **(d)** electrostatic potential isosurfaces showing the electron accumulation (red) and depletion (blue) for both Cl and Na atoms interacting with the MXene. Unit cell in (a) and (b) is highlighted as a dashed blue rectangle.

Figure 3

(a) Schematic of the charge transfer from the substrate to the Cl atom, and **(b)** atomic model for the charge transfer from the Na atom to the substrate. The charge transfer was obtained through a Bader charge analysis. Violet arrows denote the charge transfer direction.

Figure 4

See image above for figure legend.

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