Surfactant molecules to promote removal of cadmium ions from solid surfaces: A complementary experimental-simulational study

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ABSTRACT

Sodium dodecyl sulfate (SDS) was used to interact with metallic ions to demonstrate the efficiency of surfactant molecules to promote desorption of metals from solid surfaces. Scanning electron and atomic force microscopy were employed to study desorption of cadmium ions from highly oriented pyrolytic graphite (HOPG), as a model to understand the removal of metallic ions from carbon substrates. Contact angle measurements were carried out to investigate the wettability behavior of the surfactant on the contaminated surface. The desorption mechanism from a microscopic level was studied by using molecular dynamic simulations. Density profiles and pair correlation functions were analyzed to determine the cadmium–surface interaction in the presence of surfactant molecules to improve ion detachment. Simulations showed that surfactant molecules moved in between the adsorbed cadmium ions and the graphite surface pushing up the metallic groups to improve metal desorption. The experimental and theoretical results agree with atomic absorption spectroscopy results.

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1. Introduction

Contamination by heavy metals is a matter of utmost concern to the public health not only because human exposure to these elements can lead to adverse health effects and potential death, but also because they are non-degradable, and therefore, they remain for a long time in the environment [1,2]. Because of their high degree of toxicity, arsenic, cadmium, lead and mercury rank among the most harmful metals for public health [3]. In particular, because of the widespread use of cadmium in the production of batteries, alloys, cells and many other recent technological applications, remediation of cadmium pollution is of highest priority due to its harmful effects on living organisms [4]. For instance, this metal has been linked to high cancer risk factors while it targets the cardiovascular, renal, gastrointestinal, neurological, reproductive, and respiratory systems after long-term exposure [5]. Moreover, cadmium poisoning occurs through the intake of contaminated food or water, and the inhalation of polluted air in areas of current and historical industrial contamination [6]. In general, remediation of heavy metals such as cadmium, has been widely studied over the last years [7–12] by using several techniques [13,14]. Among these methods, surfactants have proved to

be a good alternative not only as a based remediation technology for organic contaminated systems, but also heavy metals from solid surfaces [15]. Among all the surfactants, sodium dodecyl sulfate (SDS) has demonstrated its capability to remove metal ions and organic contaminants from wastewater [16]. For instance, SDS and different SDS-surfactant mixtures have been used with the Micellar-Enhanced Ultrafiltration technique (MEUF) for the removal of Cd^{2+} and phenol with good results [17]. However, most of those studies have been conducted in solution, and there are not many attempts to our knowledge, to study the desorption of metallic ions from solid surfaces. So, in order to investigate the presence or absence of contaminants on solid surfaces, different techniques have been employed. In particular, one of the most reliable methods for assessing the degree of cleanliness or contamination of a solid surface is the contact angle technique. It is well known that contact angle measurements can be very useful since they are extremely sensitive to surface roughness, contamination and thermal effects. For instance, it has been observed that the presence of contaminants changes significantly the contact angle value since they reduce or increase the natural wettability of the surface. Moreover, it has been noticed that the contaminant might also change the solution characteristics affecting the spreading kinetics of the droplet [18].

On the other hand, computer simulations have proved to be a reliable alternative to study complex systems, such as the

arrangement of surfactants on solid surfaces [19–21], the adsorption/desorption of different molecules under the presence of surfactants [22–24], and more recently, the retention of organic molecules by using surfactant-modified interfaces [25]. It is worth noticing that molecular simulation techniques provide valuable information at the molecular level not easy to extract from experimental results.

The purpose of this work is to study how surfactant molecules can be used as alternative agents to enhance desorption of metallic ions in order to understand remediation mechanisms from solid surfaces. Although there are many toxic metal ions as contaminants in aqueous solutions or onto solid surfaces, because of its widespread use and severe implications on human health, we will focus on cadmium contamination only.

Additionally, since it is well known that the characteristics of the surface play a major role in the physical and chemical interactions with the adsorbates, properties such as roughness, reactivity and crystalline parameters, among others, can influence the behavior of atoms and molecules in close proximity to the interface. Therefore, in order to avoid the impact of the intrinsic characteristics of the surface for the understanding of the ion removal process with surfactants, we used highly oriented pyrolytic graphite as an ideal surface since it is atomically flat, non reactive and carbon has been used consistently as one of the major components in contaminant removal filters [26,27]. Furthermore, sodium dodecyl sulfate was used as ideal surfactant, because it has proved to be an excellent choice as contaminant removal compound [28].

In order to determine the amount of cadmium removed from an HOPG surface after been treated with different surfactant concentrations, different microscopy techniques were employed. For instance, scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to investigate the morphology of the surfaces before and after metal removal. Elemental mapping and energy dispersive X-ray spectroscopy (EDS) were also conducted to qualitatively analyze the distribution and amount of cadmium on the HOPG substrate before and after the surfactant treatment. Moreover, in order to quantify the amount of metal ions removed from the HOPG surface after surfactant exposure, atomic absorption spectroscopy was employed. In addition, the contact angle technique was used to explore not only the presence of the cadmium sulfate contamination onto a highly oriented pyrolytic graphite surface, but also, as a method to examine a possible metal removal by looking at the dynamic contact angle behavior at different experimental conditions. Finally, to elucidate the experimental findings from an atomistic level, molecular dynamics (MD) simulations were conducted. Such simulations provided relevant insights into the adsorption process of cadmium and its removal from a graphite surface. For this purpose, several computer simulations at different SDS concentrations were carried out, and different structural properties were calculated.

2. Methodology

2.1. Materials and Methods

Reagent grade cadmium sulfate and sodium dodecyl sulfate were obtained from Sigma–Aldrich and were used without further purification. Milli-Q water (18.2 M cm) was employed as solvent for all experiments. Highly oriented pyrolytic graphite (HOPG) substrates were purchased from NT-MDT (ZYH grade, mosaic spread $3.5° \pm 0.2°$).

Cadmium sulfate solutions of 200 ppm were prepared and sonicated for 5 min for optimal dispersion. Then, freshly cleaved HOPG substrate layers were immersed in the previously prepared solution for 5 days [29]. The contaminated substrates were removed

and air-dried at room temperature for 24 h. After that, each substrate was immersed in a different surfactant concentration solution, one at 4 mM (below CMC) and another at 10 mM (above CMC). As a reference, a contaminated substrate was immerse in Milli-Q water. The substrates before and after cadmium contamination and SDS exposure were studied by AFM and SEM for comparison.

Surface morphology, elemental mapping and energy dispersive X-ray spectroscopy (EDS) analysis were conducted in a JEOL JSM-7800 microscope couple to a Oxford X-Max^N instrument. AFM measurements were acquired with a JEOL-JSPM4210 microscope in air by using the tapping mode technique at room temperature. For this study, standard silicon probes from Ted PELLA, Inc., (Redding, CA), with a resonance frequency of 297 kHz were employed. Images were processed with the WSxM 5.0 Software.

Contact angles were obtained with an automated and video-based Pocket Goniometer instrument. The measurements were performed by applying a droplet of solution to a previously contaminated HOPG surface. In this study, four solutions were employed: Milli-Q water, 200 ppm cadmium sulfate, 4 mM SDS and 10 mM SDS. As references, contact angle measurements on clean HOPG substrates were also investigated.

Finally, the atomic absorption spectroscopy measurements were carried out with a Varian Spectr system AA-220 model with an Air/Acetylene Flame Type.

2.2. Computational method

Molecular dynamics simulations were conducted to investigate desorption of cadmium sulfate as contaminant, by using the sodium dodecyl sulfate surfactant as the cleansing agent from a graphite surface. The contaminated surface was prepared with 30 cadmium sulfate molecules initially deposited close to the solid. Then, the surfactant was introduced at three different concentrations: 0.005, 0.01 and 0.012 (15, 30 and 36 SDS molecules) close to the liquid/solid interface with the tail groups pointing towards the solid surface. The concentration in the simulations was measured as the number of cadmium ions divided by the total number of water molecules. The dimensions of the simulation cell were X = Y = 40.249 Å and Z = 170 Å using a liquid–vapor interface at one end of the simulation box.

The force field parameters for the sodium dodecyl sulfate (united atom model) and the graphite surface were taken from previous works [30,19]. The graphite plate was simulated using an atomistic model constructed with four layers (2706 atoms) [20] where all the atoms were frozen to form a rigid wall. As the solvent, 3000 water molecules built with the Simple Point Charge (SPC) model were used [31]. For the cadmium sulfate molecules, the GAUSSIAN software was employed to obtain the SO_4 molecular charge distribution by using the natural bond orbital (NBO) base. The Lennard Jones parameters were taken from literature [32]. In Table 1, the Lennard Jones parameters and charges used in the simulations are shown.

The force field employed was used to calculate hydration, and our results agreed with previous computer simulations works [33] and other experimental values [34].

All simulations were conducted in a NVT ensemble using a Nosé-Hoover thermostat with a temperature of T = 298 K and a relaxation time of 0.1 ps [35]. Calculations were run in the DL-POLY package [36] with a timestep of 0.002 ps and the bond lengths were constrained using the SHAKE algorithm with a 10^{-4} tolerance. The short range interactions were calculated using the Lennard Jones potential with a cut-off radius of 10 Å and the Lorentz-Berthelot rules for the unlike interactions [37]. The electrostatic interactions were handle with the particle mesh Ewald

Table 1
Lennard Jones parameters and charges.

Atom	Molecule	ϵ (kcal/mol)	σ (Å)	q (e)
C	Graphite	0.05564	3.4000	0.0000
S	CdSO$_4$	0.25000	3.5500	2.1682
O	CdSO$_4$	0.20000	3.1500	−0.8556
Cd	CdSO$_4$	0.00597	2.7000	1.4798
S	SDS	0.25000	3.5500	1.2840
O (SO$_3$)	SDS	0.20000	3.1500	−0.6540
O (ester)	SDS	0.17000	3.0000	−0.4590
CH$_2$ attached to O	SDS	0.11800	3.9050	0.1370
CH$_2$	SDS	0.11800	3.9050	0.0000
CH$_3$	SDS	0.11800	3.9050	0.0000
Na	SDS	0.11500	2.2750	1.0000
OW	Water	0.15539	3.1659	−0.8200
HW	Water	0.00000	1.7818	0.4100

method [38,39]. All systems were run up to 20 ns where the last 2 ns were used for data analysis.

3. Results

3.1. Experimental results

SEM images obtained for the clean and contaminated HOPG surface can be seen in Fig. 1. All images in this Figure were obtained with secondary electrons since it was observed that this acquisition mode produced a better surface definition and image contrast of the metal ions. Fig. 1a, shows a clean HOPG surface before any contamination or removal process. The energy dispersive X-ray spectroscopy map (not shown here) shows a pure carbon substrate as expected, without any contaminant previous to the immersion process in agreement with the EDS plot.

In Fig. 1b, the presence of the cadmium salt is clear after immersion. Here, the surface coverage is not uniform and aggregates of different sizes are randomly scatter on the HOPG surface. From the contrast characteristics of the image, a contaminant film with different thicknesses and irregular areas can be observed along the surface. In addition, contaminant accumulation was consistently detected along HOPG defects.

In Figs. 1c and d, the HOPG surface after being contaminated and immerse in two different surfactant concentration solutions of SDS, below and above the CMC (4 mM and 10 mM, respectively), is shown. Here, the presence of surfactant aggregates with no defined form can be seen. The difference in thickness related to the concentration can be noticed in the aspect of the films. For instance, the micrograph of the 10 mM SDS solution (Fig. 1d) shows what seems to be a thicker film in contrast with the 4 mM SDS concentration, as expected. In both concentrations, it seems that the cadmium aggregates were covered by the SDS film.

In Fig. 2, the elemental analysis of the previously shown SEM images is plotted. As it was mentioned previously, the clean graphite substrate (Fig. 2a) shows only the presence of carbon. In Fig. 2b, the elemental analysis exhibits the presence of cadmium due to the contamination process and carbon from the substrate. The other two plots (Figs. 2c and d) show clear peaks that correspond to the sulfur, oxygen, sodium and carbon elements which
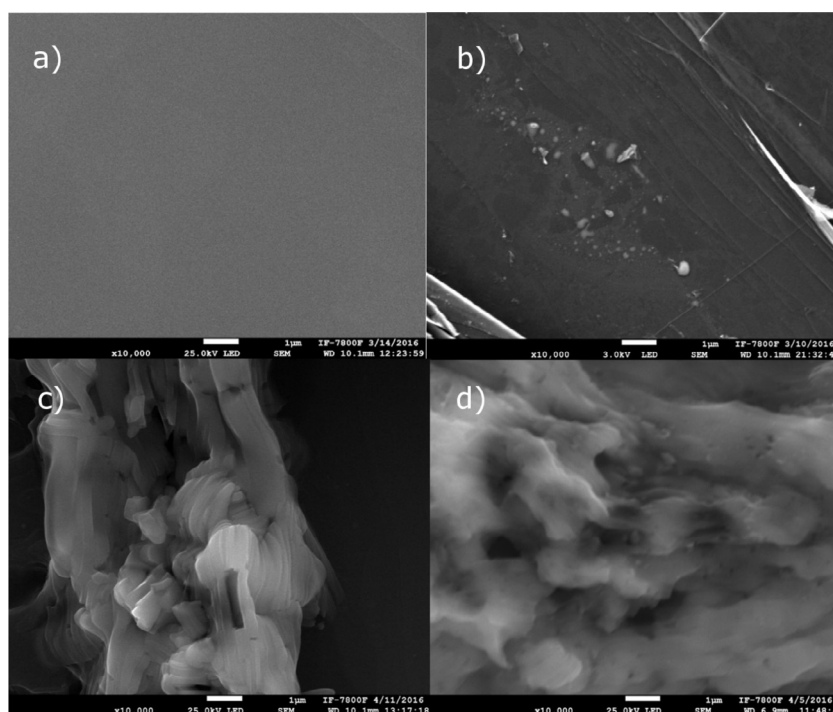

Fig. 1. SEM micrographs of (a) Clean HOPG surface, (b) HOPG surface contaminated with cadmium, (c) cadmium contaminated HOPG surface after 4 mM SDS immersion, and (d) Cadmium contaminated HOPG surface after 10 mM SDS immersion.
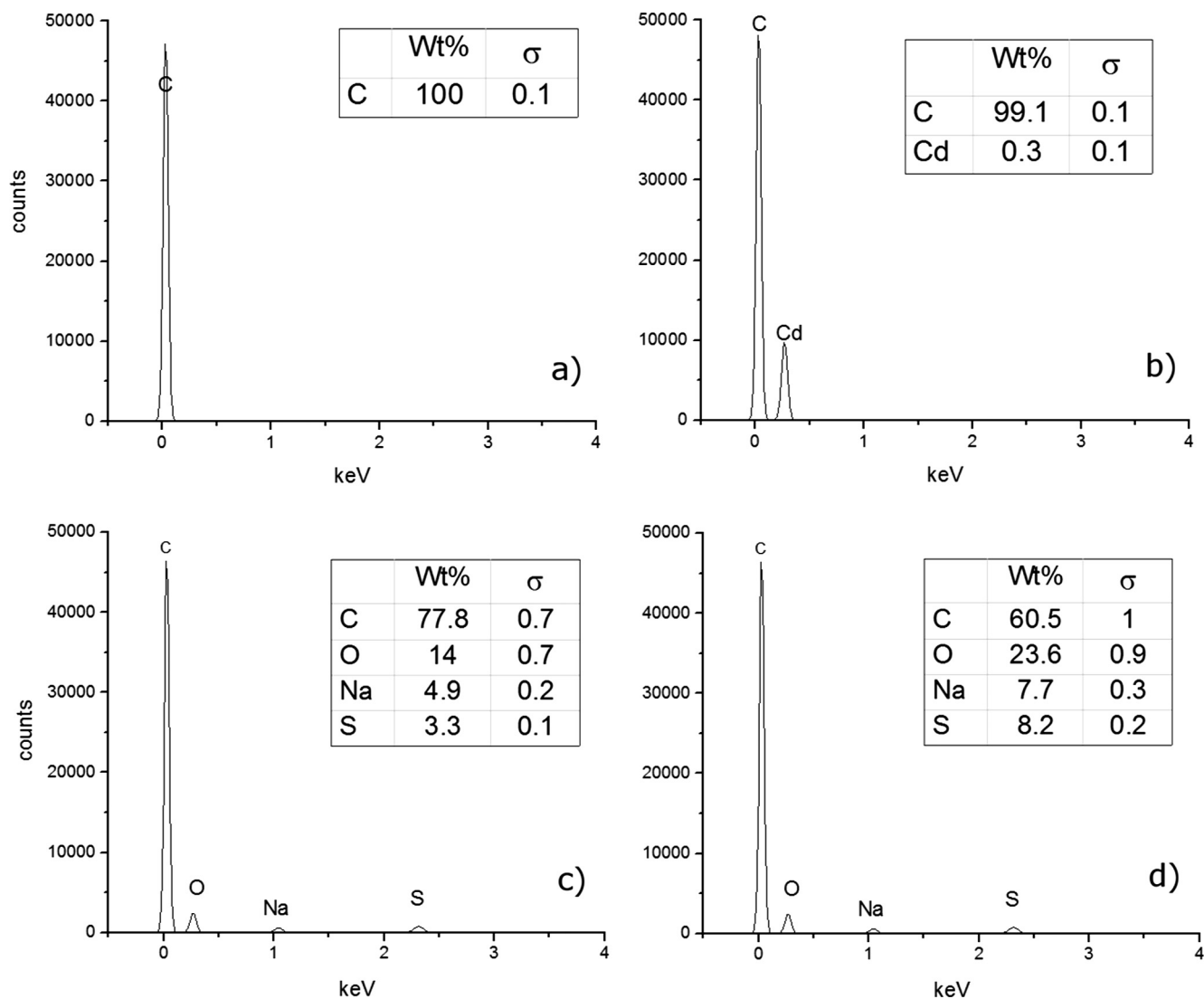
Fig. 2. EDS analysis plots of (a) clean HOPG surface, (b) cadmium contaminated HOPG, (c) Cadmium contaminated HOPG after 4 mM SDS immersion, and (d) cadmium contaminated HOPG surface after 10 mM SDS immersion.

are found in the SDS surfactant molecules. Here, the presence of cadmium is not detected which means that either it was removed by the surfactant or the concentration was too low for the EDS to be detected. There might be various reasons for this results. As we observed from different cadmium contaminated SEM images, the cadmium salt absorption is not evenly distributed on the HOPG. From the micrographs, we can distinguish 3-dimensional aggregates, a film-like deposit and salt-free regions on the graphite surface. Local EDS analysis on each of these features showed that only the 3-dimensional small cadmium aggregates contribute to the semi-quantitative detection, since the film-like deposit is too thin to surpass the EDS detection limit. In addition, after SDS exposure, we noticed that all the surface is covered with SDS molecules. Since SDS exhibits high affinity not only with the metal but also with the graphite surface, it forms SDS + cadmium and pure SDS regions making difficult to identify cadmium contaminated areas during the EDS scan. Therefore, in order to determine if the cadmium was removed from the HOPG surface, atomic absorption measurements were also conducted. In these experiments, the quantification of how much cadmium was released from the HOPG surface was analyzed for three different cases; water, 4 mM SDS

and 10 mM SDS. In the first case, only 0.45% of the metal ions were found in solution suggesting that most of the cadmium remained adsorbed on the graphite surface. For the contaminated graphite surface exposed to the 4 mM SDS concentration, the percentage of metallic ions in solution was 0.14%, indicating that cadmium remain trapped on the surface with the SDS aggregates, in agreement with the simulation results (see next section). Finally, for the highest concentration of SDS (10 mM), the amount of cadmium detected in the aqueous solution was 14.84%, which is the largest concentration of metal released from the HOPG surface of all three cases.

Previous experiments using the Micellar-Enhanced Ultrafiltration technique (MEUF) showed that SDS is a good choice of surfactant to remove metallic ions from aqueous solutions, since the SDS polar head groups absorb the metallic ions while keeping them from moving into the aqueous phase. In our case, since the SDS molecules move towards the graphite surface because of their affinity and the interaction of the metal ions with the polar groups, the cadmium ions get trapped at the interface limiting its release to the aqueous solution at low SDS concentration in agreement with those previous works [15,16]. On the other hand, at high SDS

concentration, although a similar phenomenon is observed another aspect must be considered. Because the amount of SDS molecules in the system is larger, they are not only attracted to the graphite surface, but also, they additionally move in between the metal and the HOPG in larger quantities detaching the cadmium ions from the surface, and therefore, allowing their release to the aqueous solution. This phenomenon explains the larger amount of cadmium ions found in the aqueous medium in the atomic adsorption analysis.

A closer inspection of the surface was performed with AFM as seen in Fig. 3. Image 3(a) shows an atomically flat HOPG surface with a very low surface roughness as expected for a clean graphite. In contrast, in Fig. 3(b), the presence of aggregates due to the salt absorption can be confirmed all over the HOPG surface reaching up to 367.68 nm in height. In Fig. 3(c) and (d) the presence of the SDS surfactant is observed. Since the largest height at these interfaces is lower than the maximum height in the cadmium contaminated HOPG surface, it is clear that a thick layer of surfactant is covering the contaminated HOPG surface in agreement with the SEM micrographs. From these images, we can also notice that at higher surfactant concentration, the exposed layer is more uniform indicating a closer packing arrangement of the molecules in the film.

After the morphological analysis, clean and cadmium contaminated HOPG surfaces were exposed to droplets of ultrapure water, a 200 ppm $CdSO_4$ solution and both SDS concentrations, in order to investigate the hydrophobic character of the interfaces and their wetting behavior after being exposed to SDS solutions.

In Fig. 4, the time dependent change of the contact angles for all solutions onto clean HOPG surfaces is shown. In this image, water and cadmium solutions exhibit constant contact angles over time. In addition, the contact angle values showed hydrophobic nature in both cases being the water the most hydrophobic with an average value of 66°, while the cadmium solution showed a slightly lower value of 62°, which was expected due to the presence of the salt. Here, it is worth mentioning that the contact angle of water onto
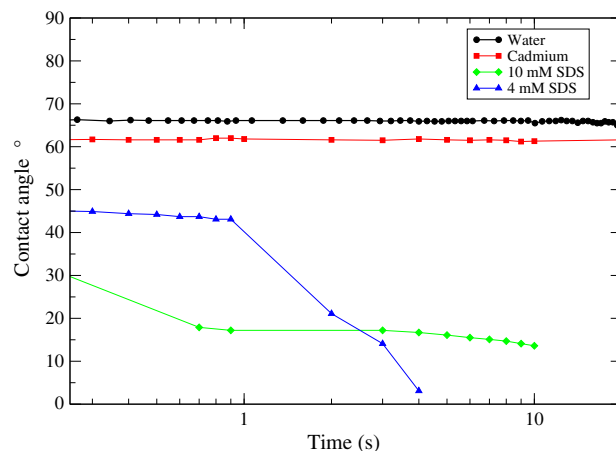

Fig. 4. Contact angle measurements of water, cadmium sulfate, 4 mM SDS and 10 mM SDS on a clean HOPG surface.

HOPG is not as high as 90–95°degrees already been reported in literature, possible due to defects and the high mosaic spread of the graphite employed in this work [29].

On the other hand, the contact angle of the surfactant solutions onto clean HOPG show different transitions from partial wetting to nearly complete spreading over time. In both cases, more than one regime can be easily identified.

Here, the 4 mM surfactant solution showed an initial contact angle of 45°. During the first second, the contact angle decreased to 44°. Later, the spreading accelerated and it dropped to 3° degrees over the next 3 s. On the other hand, the 10 mM surfactant solution showed an initial contact angle of 30° but it dropped to 17° within the first second. After that, the contact angle showed a slow decrease reaching 13° at 10 s.

In both cases, the spreading behavior showed that as the drop thins, spreading accelerates towards the lowest apparent contact
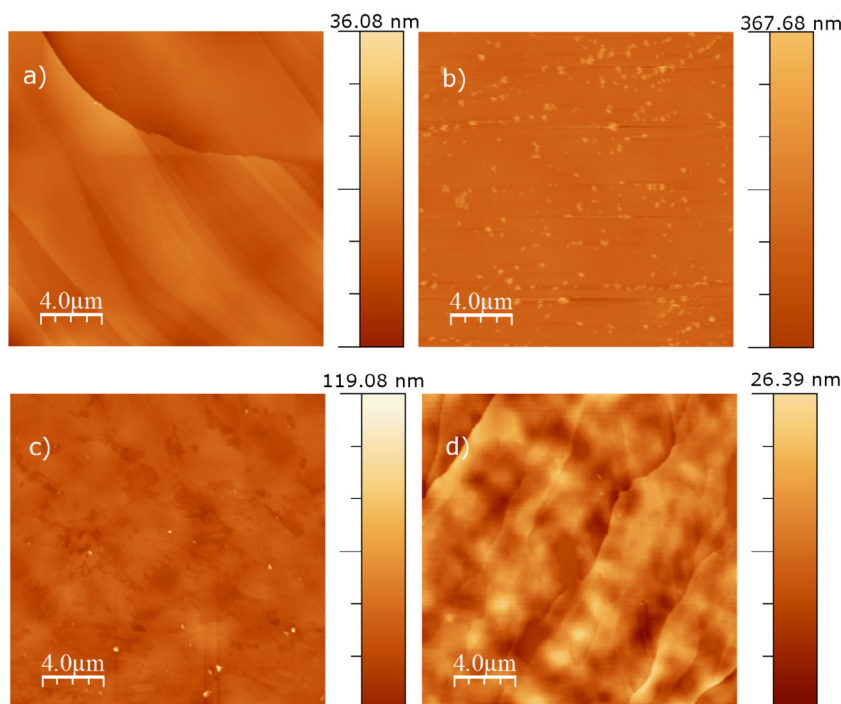

Fig. 3. AFM images of the (a) Clean HOPG surface, (b) HOPG surface with cadmium, (c) cadmium contaminated HOPG surface after 4 mM SDS immersion, and (d) cadmium contaminated HOPG surface after 10 mM SDS immersion.

angles in agreement with other reports [40]. So, in this case, the contact angles followed the expected pattern dictated by surfactant adsorption. In other words, staying rather high at low surfactant concentration and then decreasing when adsorption rises as the surfaces becomes more hydrophilic.

In Fig. 5, the time dependent contact angles obtained on the cadmium contaminated HOPG surfaces by using water (added for comparison), 4 mM and 10 mM SDS solutions are shown. As we can see from these plots, the initial contact angle for the water droplet was 52° and it remained very stable for the time of the experiment, even though the wetness of the salt by the water was expected to change the contact angle over time. It is worth noticing that this value is lower than the water contact angle onto clean HOPG as expected, which suggests a decrease in the hydrophobic nature of the surface due to the presence of the salt. On the other hand, the 4 mM surfactant droplet exhibited a nearly constant angle of 47° for the first 10 s, and then a rapid decrease to zero over the next 30 s.

Finally, the initial contact angle for the 10 mM solution was 52° and then it showed a smooth decrease during the next 10 s until it reach 41°. After that, a rapid contact angle decrease occurred within the next 10 s.

From these plots various conclusions can be drawn. Water droplets showed a constant behavior while SDS solutions exhibited time dependent characteristics. For the clean HOPG surface, the interaction with the SDS solutions showed a maximum spreading within the first 10 s, while it took longer at the contaminated interface. Moreover, the contact angle values are higher on the clean surface, as expected, due to the hydrophobic nature of the carbon substrate. The different spreading regimes observed with the SDS solutions can be attributed to two different mechanisms. First, the water droplet changes its salt concentration (although in a very small amount) during the wetting process, decreasing its contact angle over time. Second, it is well known that SDS molecules exhibit high affinity for the graphite surface and they get easily absorbed increasing the substrate coverage over time. So, the graphite surface reduces its hydrophobic nature due to the presence of the adsorbed SDS molecules, and consequently, the contact angle decreases.

On the other hand, at higher surfactant concentration, the contact angle decreases more rapidly in comparison with the lowest SDS solution. This phenomenon can be understood by considering that at higher SDS concentration, more SDS molecules get absorbed on the HOPG surface at a higher rate, hence, changing the
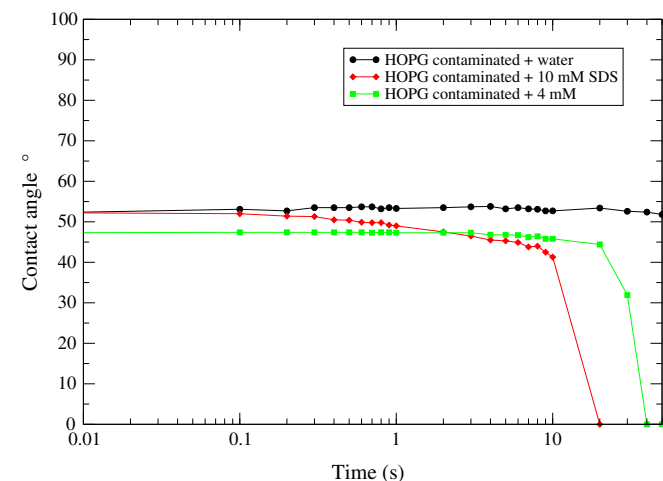
hydrophobic nature of the surface more quickly. In addition, the different stages in the plots exhibit transitions from partial wetting to complete spreading in agreement with other reports [41].

In order to provide some insights of the cadmium–surfactant interaction at the molecular level, computer simulations studies were performed.

3.2. Simulational results

The first simulations were conducted in order to study the adsorption of cadmium ions at the graphite surface. Initially, a uniform distribution of cadmium sulfates were placed close to a graphite plate and the system was run until a cluster of cadmium ions were formed onto the surface. In Fig. 6a, the formation of a single aggregate of cadmium ions on the graphite surface without any particular structure can be observed. In fact, the aggregate just cover a limited area of the surface with a 3-dimensional growth in agreement with SEM observations. In Fig. 7a the density profile of the cadmium ions is shown. Here, it can be seen that all of the ions were deposited on the graphite substrate.

The next simulations were carried out to investigate the cadmium desorption from the graphite surface after being exposed to three different SDS concentrations.

All simulations were run by using the cadmium cluster aggregate from the previous simulation (Fig. 6a) as initial configuration. Then, the SDS molecules were added to the system. The concentration in this case was determined by the number of SDS molecules divided by the number of water molecules. Due to the computational size of the systems, the concentrations employed in the simulations were above the experimental concentration values
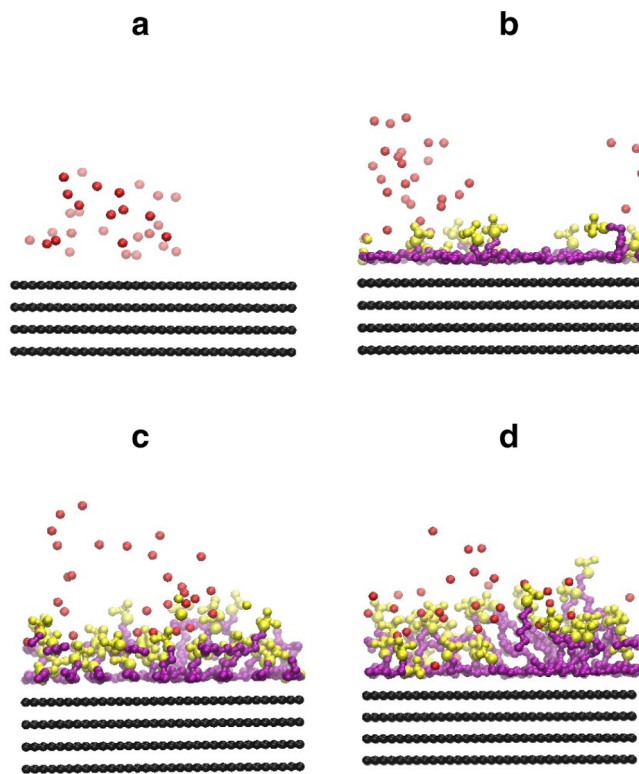

Fig. 6. Snapshots of the last configurations of the cadmium ions at four different SDS concentrations onto graphite. (a) 0.000, (b) 0.005, (c) 0.010 and (d) 0.012. Cadmium ions are red, polar SDS headgroups are yellow, SDS tails are purple and graphite atoms are black. For clarity, the rest of the molecules, such as water, are not shown in the figures. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
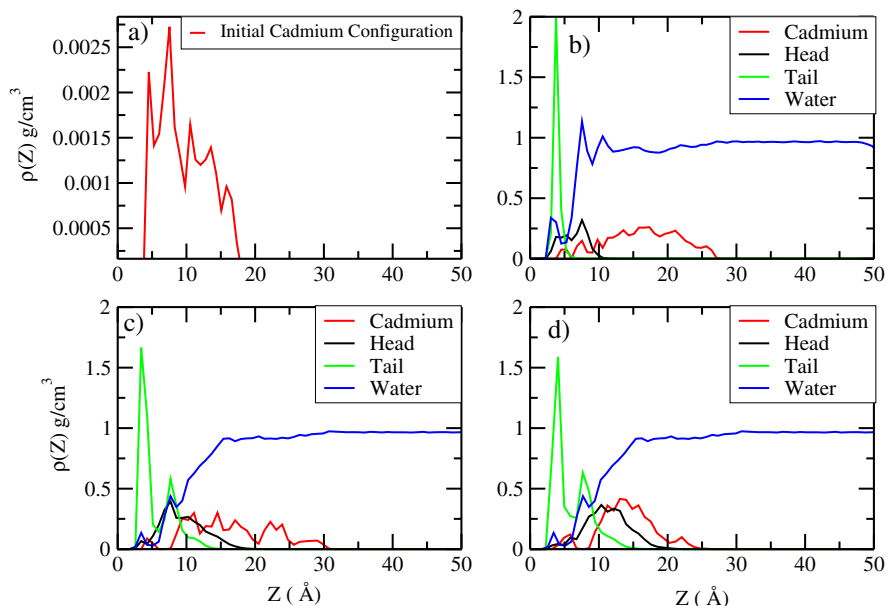

Fig. 5. Contact angles onto cadmium contaminated HOPG where water, 4 mM and 10 mM SDS solutions were employed.

Fig. 7. Z-density profiles for the systems at different SDS concentrations. (a) 0 SDS, (b) 0.005 SDS, (c) 0.01 SDS, (d) 0.012 SDS.

(> 0.2 M). Fig. 6(b–d) exhibit snapshots of the final configurations for each of the surfactant concentrations.

For the lowest SDS concentration (Fig. 6b), the formation of a well defined adsorbed SDS layer is observed. Then, as the SDS concentration increases, a second or more SDS layers are formed (Figs. 6c and d). In order to determine the location of the different molecules in the packing arrangement, density profiles along the normal to the surface (Z-direction) were plotted (Fig. 7). From the cadmium profiles, the peaks of the cadmium positions become higher and broader for all SDS concentrations (Fig. 7b–d) than those without surfactants, i.e., it seems that the presence of SDS molecules cause the cadmium ions to reorganize. However, some ions still remain attached to the graphite surface. Moreover, at high surfactant concentration, the cadmium profiles exhibit a region of zero molecules after the first cadmium peak very close to the graphite interface. In addition, the gap of zero cadmium ions is slightly

larger for the highest SDS concentration. Those results suggest that SDS pushed up the cadmium atoms away from the surface. An estimation of the desorbed metallic ions from the surface was calculated by considering the amount of cadmium ions at a distance lower than 10 Å in the presence of SDS, with respect to the number of cadmiums at the same distance without any surfactant. The percentages of desorbed ions were 74%, 70% and 73% for the SDS concentration of 0.005, 0.01 and 0.012, respectively.

At low surfactant concentration, all the SDS molecules were well adsorbed on the graphite surface as indicated by the first high peaks of the tail groups. Moreover, as it was expected, the surfactants were adsorbed on the surface by their hydrocarbon chains, which agree with the snapshot in Fig. 6. As the surfactant concentration increased, the formation of a second SDS tail layer was observed in agreement with the second peak in the density profile plots. In fact, the second layer seems to promote the pushing up of
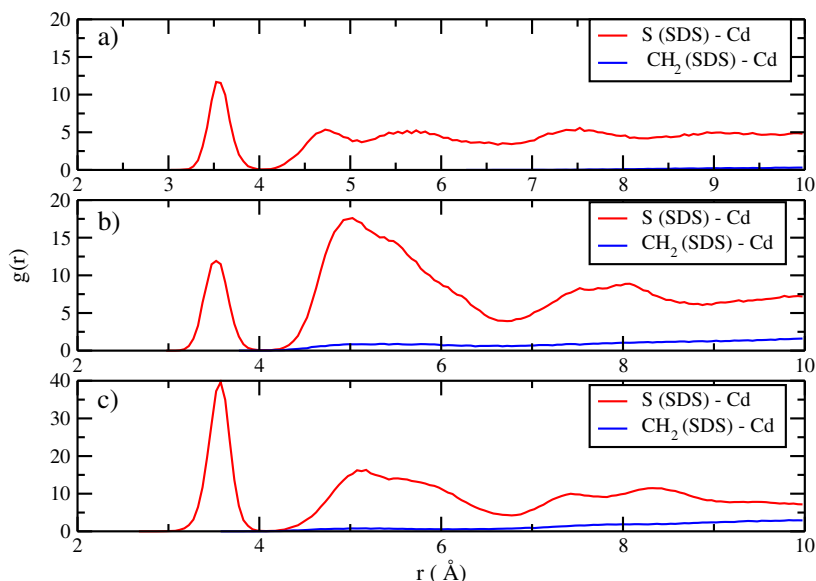

Fig. 8. Pair distribution functions at three different SDS concentrations. (a) 0.001 SDS, (b) 0.01 SDS, (c) 0.012 SDS. Red lines represent the g(r) of the SDS head - cadmium groups, and blue lines correspond to the SDS tails - cadmium groups.

more cadmium ions away the solid surface. It was also interesting to note that at low SDS concentration a rough water interface was formed near the surface as illustrated by the peaks in the density profiles, suggesting that water exhibit some structure near the solid interface. However, that water profile became smoother as the SDS concentration increased. On the other hand, from the density profiles we could noticed that cadmium ions were close to the SDS head groups. However, even when the ions were pushed away from the surface, they remain close to the surfactant molecules as an aggregate. Since more surfactant layers accommodate at the HOPG surface after moving away the cadmium ions at high concentration, a reduction of the hydrophobic nature of the surface can be inferred which explains the decrease in the contact angle value at high SDS concentration in agreement with the experimental results.

On the other hand, by analyzing the density profiles, we can notice that although most of the cadmium ions were close to the SDS head groups, some ions moved above the surfactant profile. This result suggests that the presence of the SDS not only promotes the detachment of the metallic ions from the surface, but also, it promotes the transfer of some ions to the aqueous solution at high SDS concentration in agreement with atomic absorption spectroscopy results.

In addition, pair distribution functions $(g(r))$ were calculated to investigate the surfactant–cadmium interaction in the removal process as seen in Fig. 8. For these calculations, the SDS headgroups were represented by the sulfur atom. The results showed a stronger interaction between cadmium and the SDS headgroups in comparison with the cadmium and SDS tails. This result suggest that the positive metallic ions were strongly attracted to the negative SDS head groups, as expected. In addition, from these plots we can notice that the strongest head-Cd interaction (first peak) is located at 3.5 Å for all concentrations. Moreover, for the low SDS concentration we observed that most of the cadmium ions were close to the SDS headgroups as suggested by the first peak in the distribution function (Fig. 8a). As the surfactant concentration increased, the number of cadmium ions attracted by the SDS headgroups also increased (Figs. 8b and c) as indicated by the height of the first peak in the $g(r)$ plot. In particular, for the highest SDS concentration, the first peak increased considerably in comparison with the other two concentrations.

In addition, at high SDS concentrations the metallic ions were re-distributed around the SDS headgroups as indicated by the different shapes of the pair distribution functions. In fact, the second nearest neighbor peak also increased significantly, suggesting that more cadmium ions were closer to the SDS heads. It is worth noticing that the increment in the $g(r)$ second peak coincided with the formation of the second adsorbed SDS layer from the surface as shown in Fig. 6.

3.3. Conclusions

In the present work, experimental and computational studies were conducted to study how surfactant molecules can promote the desorption of cadmium ions from a graphite surface. The amphiphilic properties of the SDS surfactants are responsible for modifying the surface–cadmium interaction. In particular, due to the affinity of the hydrophobic surfactant tails with the carbons of the HOPG, the SDS tails move closer to the surface by pushing up the metallic ions from the graphite interface. This assumption is supported by the formation of layers in the density profiles from the computational results. Moreover, these results might also explain the change in the contact angle behavior observed in the present experiments. For instance, the surfactants not only get absorbed on the HOPG because of their high affinity, but also penetrate in between the cadmium and the surface lowering the orig-

inal hydrophobic nature of the graphite, and as a consequence, the contact angle value. Although we noticed some metal desorption from the surface at high SDS concentration, we did not observed a complete cadmium removal probably due to the SDS headgroup–cadmium interaction, which keep attached the metallic ions to the SDS polar groups. Moreover, the results indicated the presence of few cadmium ions around the negative SDS headgroups which were anchored to the solid surface. In this case, it is possible that no-ionic or positive charge surfactants repelled more efficiently the positive cadmium ions promoting its surface removal. However, these experiments and simulations are currently under study in our group to elucidate this phenomena. Nevertheless, from the present investigation we showed the mechanism of how surfactant molecules enhance desorption of metallic ions from solid substrates. These results provide some insights about the use of amphiphilic molecules as removing agents of metallic ions from solid surfaces.

4. Conflict of interest

No conflict of interest.

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