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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.

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

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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 $3.5^\circ \pm 0.2^\circ$).

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